STRUCTURES AND PROPERTIES OF POLYMERS FORMED IN MICROEMULSIONS

By

SPENCE COLMAN PILCHER

Bachelor of Science

Northeastern State University

Tahlequah, Oklahoma

1994

Submitted to the Faculty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of
the requirements for
the Degree of
DOCTOR OF PHILOSOPHY
December, 2000

STRUCTURES AND PROPERTIES OF POLYMERS

FORMED IN MICROEMULSIONS

Thesis approved:

Warren T. Ford

Thesis Advisor

K. D. Berlin

Mark S.

Alfred Carlozzi

Dean of the Graduate College

PREFACE

A microemulsion is a dispersion of an oil in water stabilized by a surfactant. A surfactant (soap) is a molecule that contains a water-soluble section and a water-insoluble portion. The surfactant molecules are able to disperse the oil in water by orienting their water-insoluble part into the oil phase and the water-soluble portion into the aqueous phase, forming spherical or ellipsoidal clusters referred to as micelles.

A polymer is a large molecule formed by the repetitive combination of many smaller molecules called monomers. A polymer containing 10 000 of the connected monomer molecules generally has an average end-to-end distance of >50 nm. A sphere enclosing all of the polymer and its segments must be even larger. Formation of a polymer chain in a microemulsion leads to small spheres (<30 nm in diameter) containing a high molecular weight polymer (>10 000 connected monomer molecules). Thus, the polymers formed in microemulsions are conformationally restricted. If the forming chain end during polymerization is also restricted, a change in the orientation of the substituents on the polymer backbone could be seen. Altering the structure of a polymer will change how the polymer behaves. In this study, the structures of the polymers formed in microemulsions did not differ from the analogous polymers prepared in solution. However, the microemulsion-prepared samples had larger molecular weights and higher temperatures at which the polymer goes from a glassy state to a rubbery state.

ACKNOWLEDGMENTS

I would like to offer my sincere gratitude to Dr. Warren Ford for his guidance, motivation, and, most of all, for his patience. I would like to thank Dr. Bruce Ackerson, Dr. K. Darrell Berlin, Dr. Martin High, and Dr. Mario Rivera for their encouragement and for serving on my committee. I would like to thank the Chemistry Department for their financial support. I would like to acknowledge Dr. Ackerson and the students in his lab for performing light scattering data for my project, Dr. Allen Apblett for allowing me to use his DSC after the instrument in our lab malfunctioned, and Dr. Nicholas Matterer for allowing me to use his peak-fitting program. I am also grateful for all the undergraduates, graduate students, and post-docs with whom I have worked in the lab during my time at OSU. I would especially like to thank Dr. Richard Bunce, Dr. Donald Thompson, Shawn Childress, Yiyan Chen, Ken Hampton, Jason Kreider, and Paul Miller for their friendship and advice. I would also like to thank Dr. Keith Osterhout for talking me into becoming a chemistry major. It's been quite an adventure, and I thank you all.

I would like to offer my love and appreciation to my parents, Tommy and Janice Pilcher, for their unconditional love and support. I would also like to thank Granny for the home-cooked meals on my trips back home and my Aunt Phyllis for always bragging on me. I would also like to express my gratitude to my fiancée, Brianna Conness, for loving me and putting up with me during these stressful times. Most importantly, I would like to thank God for always being there for me when I needed Him.

TABLE OF CONTENTS

Chapter Page

I. INTRODUCTION 1

- Definition of a Microemulsion 4
- Uses of Microemulsions. 6
- Polymerization in Microemulsions. 7
- Mechanism of Polymerization. 10
- Formation of Single Chains 14

Polymerization in Confined Spaces 16
- Polymer Properties. 16
- Polymerization in One Dimension. 18
- Polymerization in Vesicles. 19
- Polymerization in Zeolites 20
- Properties of Single Chains 21

Objective of the Research 23
References 26

II. STRUCTURES AND PROPERTIES OF POLY(METHYL METHACRYLATE) FORMED IN MICROEMULSIONS 29

Abstract 29
Introduction 30
Experimental 32
- Materials. 32
- Polymerizations 32
- Particle Size Measurements 33
- Precipitation of Polymer Samples 34
- Molecular Weight Analyses 34
- Glass Transition Temperatures 34
- Tacticity Measurements. 34

Results 36
- Stability of Latexes 41
- Particle Sizes 42
- Molecular Weights 47
- Number of Macromolecules per Latex Particle 49
- Tacticity of PMMA 51
- Glass Transition Temperatures 54

Discussion 58

Mechanism of Particle Formation 58
Initial conditions 58
Initiation 58
Particle size and molecular weight 59
Termination of the chain reaction 59
Product mixture 60
Tacticity of PMMA 60
Glass Transition Temperatures 63
Conclusions 68
References 69

III. STRUCTURES AND PROPERTIES OF POLY(PHENYL METHACRYLATE) AND POLY(1-NAPHTHYL METHACRYLATE) PREPARED IN MICROEMULSIONS 72

Abstract 72
Introduction 73
Experimental 79
Materials 79
Solution Polymerization of PhMA and 1-NM 79
Polymerization in Microemulsions 80
Particle Size Analyses 82
Determination of Phase Boundaries 83
Isolation of Polymer and Removal of Surfactant 83
Conversion to Polymethacrylic Acid 84
Methylation of Polymethacrylic Acid by Diazomethane 84
Tacticity Analyses 85
Glass Transition Temperatures 85
Molecular Weight Analyses 86
Results 87
Phase Boundaries 87
Particle Sizes 88
Molecular Weights 92
Number of Macromolecules per Latex Particle 95
Tacticity 95
Glass Transition Temperatures 101
Discussion 104
Polymerization of PhMA and 1-NM 104
Particle Sizes 104
Molecular Weights 105
Number of Polymer Chains per Latex Particle 107
Tacticity 108
Glass Transition Temperature 113
Conclusions 115
References 116

IV. FREE RADICAL POLYMERIZATION OF α-METHYL STYRENE IN MINIEMULSIONS 118

- Abstract 118
- Introduction 119
  - Polymerization in Miniemulsions. 119
  - Free Radical Polymerization of AMS. 119
- Experimental 126
  - Materials. 126
  - Polymerization in Miniemulsions 126
  - Isolation of Polymer and Removal of Surfactant 127
  - Tacticity Analyses. 127
  - Molecular Weight Analyses 128
  - Peak Fitting 128
  - Attempted Depolymerization of PAMS 128
- Results 130
  - Percent Conversion 130
  - Molecular Weights 132
  - Surfactant Content of Polymer Samples 141
  - Precipitation of PAMS into Methanol 144
  - Tacticity 146
- Discussion 148
  - High Molecular Weight PAMS 148
  - Bimodal Distribution of PAMS Samples 149
  - Kinetics for Polymerization of AMS 153
  - Tacticity of PAMS 153
- Conclusions 155
- References 156

V. OUTLOOK AND CONCLUDING REMARKS 158

- References 161

LIST OF TABLES

Chapter II

Table .... Page

1. Compositions of Microemulsions Based on Literature Procedures 37
2. Particle Sizes and Molecular Weights of PMMA Produced in Microemulsions Based on Literature Procedures 38
3. Particle Sizes and Molecular Weights of PMMA Produced at 60 °C at Various Surfactant to Monomer Weight Ratios 39
4. Particle Sizes and Molecular Weights of PMMA Produced at 35 °C at Various Surfactant to Monomer Weight Ratios 40
5. Tacticities and Glass Transition Temperatures. 53

Chapter III

Table .... Page

1. Comparison of PMMA and PPhMA 75
2. The Tacticity of PPhMA Depends on Polymerization Temperature 75
3. Comparison of P-1-NM to PMMA. 77
4. The Tacticity of P-1-NM Depends on the Polymerization Solvent 77
5. Compositions of Various Microemulsions That Led to the Formation of Stable Latex Particles 81
6. Particle Sizes and Molecular Weights of PPhMA Formed in Microemulsions and Compared to a Solution Polymerized Sample 89
7. Particle Sizes and Molecular Weights of P-1-NM Formed in Microemulsions and Compared to a Solution Polymerized Sample 89
8. Repeated Measurements of the Molecular Weights Obtained for a Sample of PPhMA and P-1-NM. 92

9. Molecular Weights of Two PPhMA Samples and the Corresponding Derived PMMA Samples. ..94

10. Tacticities and T_g's of PPhMA 100

11. Tacticities and T_g's of P-1-NM.. 100

12. Molecular Weight Comparison of P-1-NM Before and After Reprecipitation 114

Chapter IV

Table Page

1. Ceiling Temperatures of Various Monomers in Bulk 123

2. Polymer Yields of PAMS after 120 Hours 129

3. The Results of the Chromatograms Analyzed as the Sum of Two Gaussian Peaks 138

4. Molecular Weights from Attempted Depolymerization of PAMS 139

5. Percent Surfactant Contained in PAMS Samples 143

6. Tacticities of PAMS Samples 147

LIST OF FIGURES

Chapter I

Figure .... Page

1. Graphical illustrations of: a) a representative surfactant molecule, b) a typical anionic surfactant, c) a typical cationic surfactant, and d) a typical nonionic surfactant 2

2. A sodium dodecyl sulfate (SDS) micelle showing the hydrocarbon chains packing into the interior of the micelle and the hydrophilic head groups oriented into the aqueous phase.. ..3

3. Sample bottles containing an opaque emulsion, a polymerized microemulsion, and a transparent microemulsion, respectively 5

4. The partial phase diagram of microemulsions formed with MMA, H_2O, and either STAC or TTAB. The unshaded areas represent the stable unpolymerized microemulsions at 30 °C and the shaded areas symbolize the stable microemulsions after polymerization at 60 °C for 24 h 9

5. The three intervals of emulsion polymerization. 11

6. (a) Polymer Initiation – micelles swollen with monomer are initiated by radicals diffusing in from the aqueous phase. (b) Particle Nucleation – growth of particles containing polymer chains results from monomer transport from unpolymerized microdroplets. (c) Completion of Polymerization – latex particles larger than the primary microdroplets coexist with a large surplus of empty micelles.. 13

7. A portion of a PMMA chain showing the stereocenters associated with the macromolecule and illustrating the configurational sequences as *racemo* or *meso*. Also shown are the relative diad and triad units 18

8. Representation of a unilamellar vesicle 20

9. Representation of an aluminosilicate mesoporous zeolite (Al-MCM-41) 21

10. The polymer chain formed in a microemulsion is conformationally restricted.. 24

Chapter II

Figure .... Page

1. Particle sizes decrease with increasing surfactant to monomer weight ratio 44

2. TEM of PMMA prepared with CTAB/KPS at $S = 0.1$ 45

3. TEM of PMMA prepared with CTAB-KPS at $S = 3.0$ 46

4. SEC chromatograms from PMMA prepared in the following microemulsions: (a) STAC-AIBN $S = 1.0$, (b) STAC-AIBN $S = 2.0$, (c) STAC-AIBN $S = 3.0$ 48

5. Particle size distributions as weight fraction vs. particle diameter from TEM measurements (x symbols) and from SEC molecular weights (square symbols) converted to particle diameter assuming $d = 1.20$ g cm^{-3} for samples (a) STAC-KPS, $S = 3$, $n_p = 1.0$, and (b) CTAB-KPS, $S = 3$, $n_p = 1.0$. Each graph is normalized so that the two distributions have equal areas.. 50

6. ^{1}H NMR spectrum of PMMA (CTAB-KPS at $S = 3$)................................ ..52

7. DSC thermogram of Plexiglas®.. ..55

8. DSC thermogram of PMMA prepared from a bulk polymerization............. ..56

9. DSC thermogram of PMMA prepared in a microemulsion (Triton $S = 2$)... ..57

10. Tacticities of PMMA formed by radical chain polymerization as a function of temperature during polymerization 62

11. The T_g's of high molecular weight PMMA as a function of the tacticity..... ..64

Chapter III

Figure .... Page

1. The weight percent of PhMA required to turn the dispersion from a transparent solution to a turbid solution at 60 °C 87

2. TEM for PhMA polymerized using STAC/V-50 at 70 °C (Sample 1)......... ..91

3. TEM of the P-1-NM latexes formed using STAC/V-50 at 70 °C (Sample 7) 91

4. SEC chromatogram of PPhMA (Sample 2). ..93

5. Overlaid SEC chromatograms illustrating the broad molecular weight distribution obtained for P-1-NM (Sample 7 and solution-prepared P-1-NM) ..93

6. ^{1}H NMR spectrum of PPhMA prepared using Triton surfactants (Sample 1).. ..97

7. ^{1}H NMR spectrum of the derived PMMA obtained from PPhMA (Sample 1).. ..98

8. ^{1}H NMR spectrum of P-1-NM prepared with CTAB/V-50 (Sample 8).. 100

9. The naphthalene rings can interact with the methacrylic double bond of the monomer 108

10. A monomer unit can add to a propagating radical chain either *racemo* or *meso* 109

Chapter IV

Figure .... Page

1. SEC chromatograms used in the determination of the molecular weights of the following samples: (a) PAMS formed at 3 °C, (b) PAMS formed at 10 °C, and (c) PAMS formed at 15 °C 133

1. SEC chromatograms used in the determination of the molecular weights of the following samples: (d) PAMS formed at 20 °C, (e) PAMS formed at 25 °C, and (f) PAMS formed at 30 °C 134

1. SEC chromatograms used in the determination of the molecular weights of the following samples: (g) PAMS formed at 35 °C, (h) PAMS formed at 40 °C, and (i) PAMS formed at 45 °C 135

2. The chromatograms analyzed as the sum of two Gaussian peaks for the following samples: (a) PAMS@25°C, (b) PAMS@40°C, and (c) PAMS@45°C 137

3. SEC chromatograms from attempted depolymerization of PAMS corresponding to (a) formed at 8 °C for 144 hours, (b) heated to 50 °C for 36 hours, and (c) cooled to 40 °C for 48 hours 140

4. ^{1}H NMR spectrum of PAMS formed at 10 °C used for tacticity analysis 142

5. SEC chromatograms for the repeated polymerization of AMS at 30 °C: (a) unprecipitated PAMS/surfactant mixture, (b) precipitated PAMS sample, and (c) PAMS/Triton N-150 mixture (16 wt.% surfactant/polymer) patterned after surfactant content obtained from ^{1}H NMR analysis 145

6. The syndiotactic content of PAMS decreases with increasing polymerization temperature 147

7. PAMS chains can terminate by chain transfer to monomer or chain transfer to surfactant 150

LIST OF SCHEMES

Chapter IV

Scheme .... Page
1. Steps in Free Radical Polymerization 120

CHAPTER I

INTRODUCTION

As we all know, oil and water do not mix. However, when surface-active agents (i.e. surfactants), commonly known as soaps and detergents, are used, a stable dispersion of oil and water can be obtained. A surfactant molecule (Figure 1) consists of two different regions, a hydrophobic (water-insoluble) and a hydrophilic (water-soluble) portion. The water-soluble head group may be anionic, cationic, or nonionic (Figure 1). Surfactant molecules can organize in such a manner to form spherical or ellipsoidal clusters referred to as micelles (Figure 2) with the hydrophilic head group oriented into the aqueous phase and the hydrophobic portion oriented into the oil region of the mixture.[1] The formation of micelles and their properties are responsible for the cleansing action observed with soaps and foams. Grease and dirt are dissolved into the oil-like interior of the micelles. The dirt is then washed away with water, not because it dissolves in water but because it dissolves in the micelles that are dispersed in the water.

Each micelle is composed of 50 to 100 individual molecules and is approximately spherical because a sphere encloses the maximum volume of material for a given surface and disrupts the water structure the least. Two micelles tend to repel one another (due to like charges of ionic surfactants) and remain dispersed in the aqueous phase instead of clustering together to form larger aggregates. The colloidal suspension of one immiscible liquid in another is known as an emulsion. For example, whole milk is an emulsion of fat in water with casein as the surfactant. Mayonnaise is an emulsion of oil in vinegar with egg yolk (lecithin) as the surfactant.

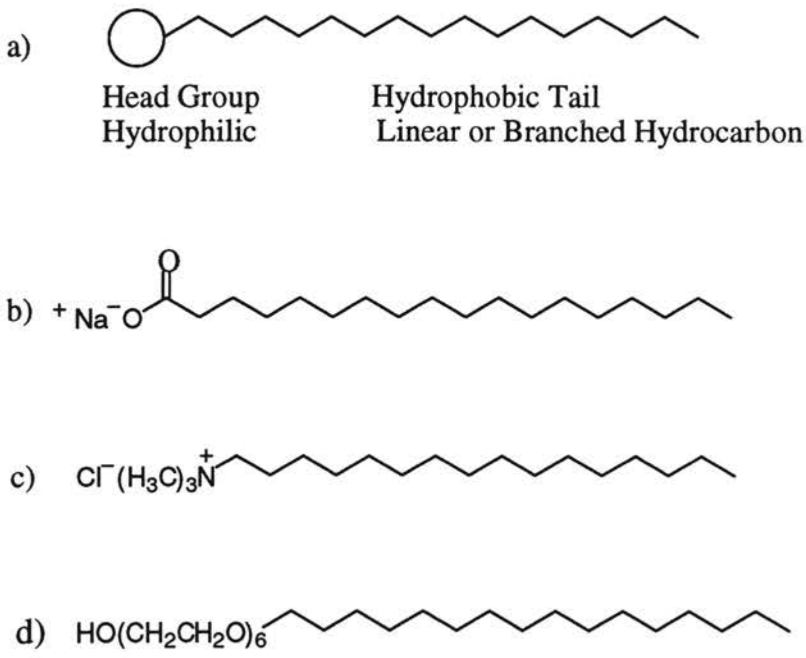


Figure 1. Graphical illustrations of: a) a representative surfactant molecule, b) a typical anionic surfactant, c) a typical cationic surfactant, and d) a typical nonionic surfactant.

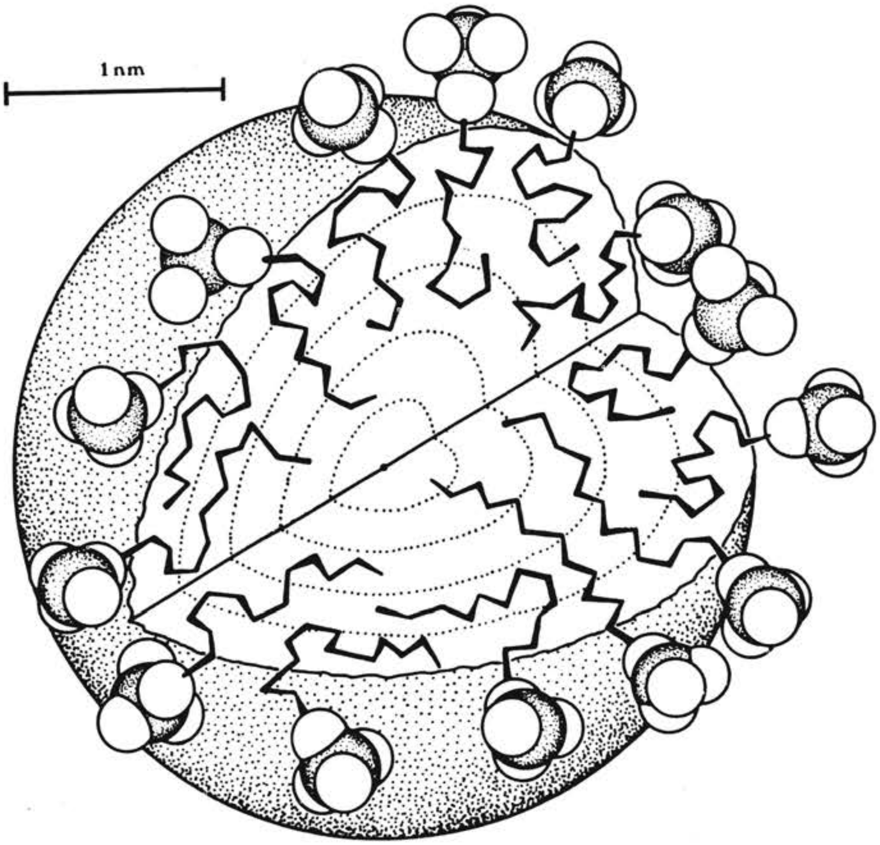


Figure 2. A sodium dodecyl sulfate (SDS) micelle showing the hydrocarbon chains packing into the interior of the micelle and the hydrophilic head groups oriented into the aqueous phase. (Reproduced from Israelachvili, J. N. *Intermolecular and Surface Forces*; Academic Press: San Diego, 1992, pp 372)

Definition of a Microemulsion. Emulsions and microemulsions both consist of colloidal dispersions of two immiscible liquids (oil and water) stabilized by one or more surfactants. However, many differences between these two systems are observed. Emulsions are opaque and thermodynamically unstable systems of droplets of oil in water (0.1-10 μm in diameter).[2,3] The formation of an emulsion is a non-spontaneous process that requires an input of energy through vigorous stirring. The stability of an emulsion is kinetic in origin, and the oil droplets obtained tend to grow continuously with time. Microemulsions are transparent and thermodynamically stable dispersions of smaller droplets of oil in water (~10 nm in diameter).[2,3] These differences are the consequence of the amount of surfactant needed to stabilize the system. The overall surface coverage of all the small droplets obtained from a microemulsion requires much more surfactant than what is needed for an emulsion. Microemulsions are often found containing surfactant to oil ratios as high as 2 to 1 or greater.

In 1943, Schulman and Hoar were first to describe these transparent systems which formed spontaneously from the mixture of two immiscible liquids (oil and water) with a surfactant or a mixture of surfactants.[4] The notation, "microemulsion", for these systems was introduced in 1959 by Schulman, Stoeckenius, and Prince.[5] The visual differences between a microemulsion, a polymerized microemulsion, and an emulsion are illustrated in Figure 3. The emulsion exists as a cloudy suspension due to larger droplets that strongly diffract light, whereas a microemulsion is optically transparent due to the smaller droplet size. Microlatexes obtained from a polymerized microemulsion (which will be discussed in detail later) have a bluish tint and are less transparent than the original microemulsion due to an increase in particle size and also the higher refractive index of the polymer when compared to the monomer.[2,3]

Figure 3. Sample bottles containing an opaque emulsion, a polymerized microemulsion, and a transparent microemulsion, respectively.

Uses of Microemulsions. Microemulsions have many practical applications and have been used for enhanced oil recovery.[6,7] Approximately 30% of the oil in a reservoir can be extracted through the initial recovery and flooding with water. Another 20% can be obtained using enhanced oil recovery. Due to the very low interfacial tensions and good wetting properties of these systems, flooding of the reservoir with surfactants, microemulsions, or microemulsion-polymer systems is used.[6,7]

Microemulsions are used for liquid-liquid extraction of metals from ores with low metal contents and can also be used to extract organic pollutants from soil through the oil fraction of the microemulsion.[7] Many washing processes use microemulsions in addition to conventional detergents. The removal of contaminants from solid surfaces is dramatically improved through the extremely low interfacial tensions provided by a microemulsion. Microemulsions have also found uses in pharmaceutical and cosmetic applications.[7] They have been used as lubricants, cutting oils, and in textile finishing.[7]

The primary use of microemulsions in this work falls under the category of chemical reactions using these systems as their reaction medium. There are a wide variety of organic reactions that can occur in a microemulsion.[7] Many times water-soluble inorganic reagents need to be reacted with water-insoluble organic compounds. Phase transfer catalysis is the most widely used method to perform such a reaction. The reaction takes place by migration of one of the reactants from the aqueous phase into the organic phase as induced by a phase transfer catalyst, commonly a quaternary ammonium salt or a crown ether. For example, consider the following reaction (1):

$$C_8H_{17}Cl + NaCN \longrightarrow C_8H_{17}CN + NaBr \qquad (1)$$

Sodium cyanide does not dissolve in octyl chloride. The two reactants contact each other only at the surface of the solid sodium cyanide, and the rate of the reaction is too slow to be of synthetic value. Dissolving the sodium cyanide in water is of little help, since octyl chloride is not soluble in water, and the reaction can only occur at the interface of the two phases. Adding a small amount of a quaternary ammonium salt causes the desired product to be formed rapidly by transferring the ^-CN anion from the aqueous phase, where it cannot contact the substrate, to the organic phase.[8] Phase transfer catalysis is successful for two reasons. It provides a means to introduce a reactive anion into a medium that contains the reactive substrate. More importantly, this anion is introduced in a weakly solvated and thus highly reactive state.

When using a microemulsion for these types of reactions, the aqueous phase in which the reactant is dissolved is transported into the organic phase. Instead of an individual molecule being transported and reacting, the reaction takes place at the oil-water interface. The reactants may be slightly less reactive using a microemulsion, but this is compensated by the much larger interface at which the reaction occurs.[7]

Polymerization in Microemulsions. Another type of chemical reaction that can take place in a microemulsion is free-radical polymerization. If the microemulsion droplets contain a monomer, polymerization can lead to the production of ultrafine microlatex particles (15-40 nm in diameter) that are often one order of magnitude smaller than those produced by conventional emulsion polymerization (50-300 nm).[3,9,10] The microlatex particles frequently contain as little as one macromolecule per particle[11-15] which will be discussed later in more detail.

Polymerization reactions in microemulsions were first shown by Stoffer and Bone who polymerized methyl methacrylate (MMA) using sodium dodecyl sulfate (SDS)[16] and by Atik and Thomas when they polymerized styrene in an oil-in-water (o/w) microemulsion and obtained narrowly distributed latex particles with diameters on the order of 30-35 nm.[17] These systems, however, were based on the use of pentanol or hexanol, respectively, as the cosurfactant, and it was found that the stability of the microemulsion is limited by the solubility of the polymer in the cosurfactant.[18] Kaler and coworkers were the first to demonstrate that the polymerization of styrene in a microemulsion could be performed with a single surfactant.[19]

Several polymerization procedures have been reported that produce stable latex particles with a narrow size distribution. Gan and coworkers produced PMMA particles with an ultrahigh molecular weight ($M_W = 7.0 \times 10^6$) with a diameter of 42 nm using stearyltrimethylammonium chloride (STAC).[20] Use of a surfactant with a shorter hydrophobic chain length such as tetradecyltrimethylammonium bromide (TTAB) produced larger particles (~100 nm in diameter) that coagulated with time. Thus the stability of PMMA latexes increases with increasing hydrophobic chain length of the cationic surfactant used. Figure 4 displays the stable polymerized and unpolymerized regions of microemulsions formed with either TTAB or STAC.[20] The stable polymerized microemulsion region (shaded area) using TTAB is smaller than the unpolymerized microemulsion region. Latex particles formed with TTAB tend to coagulate at 60° C. However, the stable regions of a microemulsion formed with STAC are approximately the same for the polymerized (60° C) and unpolymerized regions (30° C). The latex particles are therefore stable against coagulation at 60° C.[20]

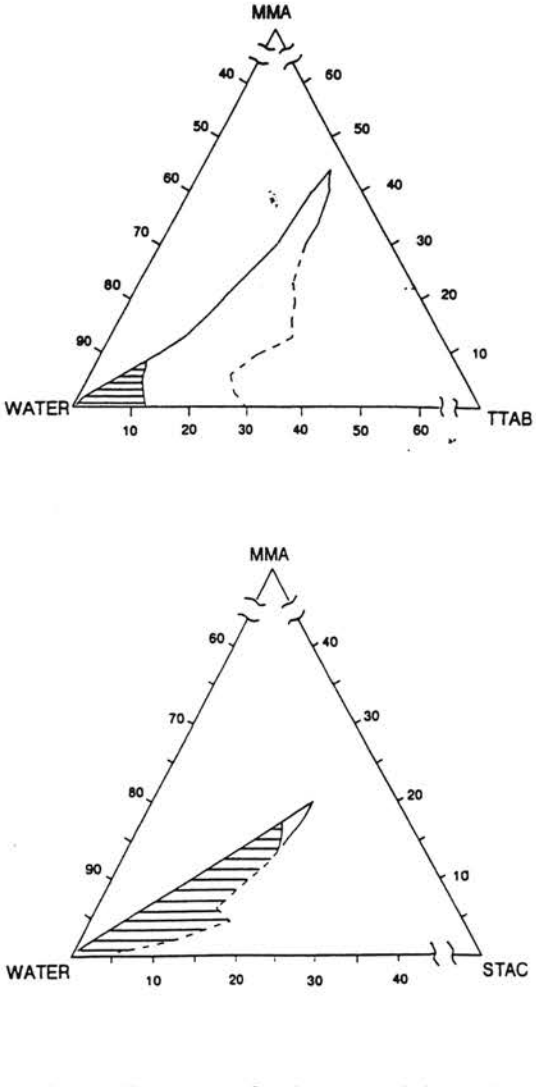


Figure 4. The partial phase diagram of microemulsions formed with MMA, H_2O, and either STAC or TTAB. The unshaded areas represent the stable unpolymerized microemulsions at 30 °C, and the shaded areas symbolize the stable microemulsions after polymerization at 60 °C for 24 h. (Reproduced from Gan et. al. *J. Polym. Sci. Part A: Polym. Chem.* **1995**, *33*, 1161)

Antonietti and coworkers have reported many procedures for producing small, crosslinked latex particles with a narrow size distribution and have shown that the droplet size of microemulsions can be thermodynamically controlled by the amount and character of the surfactant.[21-24] Crosslinked polystyrene latexes with radii between 9 and 17 nm were obtained using cetyltrimethylammonium bromide (CTAB) or dodecyltrimethylammonium bromide (DTAB) as the surfactant for the formation of the microemulsion.[22] Smaller particle sizes were typically observed because crosslinked polymer particles do not swell with as much monomer. Methyl methacrylate was also polymerized yielding latex particles with radii as small as 15.5 nm. Small latex particles were produced using nontoxic, natural surfactants (a mixture of lecithin and sodium cholate) which could be useful for biomedical applications.[23] The use of a metallosurfactant, such as a tetradecyldiethanolamine-copper complex, produced small microlatexes (r_h=10.0 nm) at a relatively low surfactant to monomer weight ratio (S = 0.5).[24]

Mechanism of Polymerization. Unlike free-radical polymerization performed in solution, emulsion and microemulsion polymerization lead to high molecular weight polymers at fast reaction rates due to a reduced rate of bimolecular termination of polymer radicals. Microemulsion and emulsion polymerization have many similarites but also some important differences in their primary mechanistic components. Emulsion polymerization can be divided into three intervals, namely Interval I, the particle formation stage, and, Intervals II and III, the particle growth stages (Figure 5).[2,3] At the start of an emulsion polymerization there are three primary components: monomer,

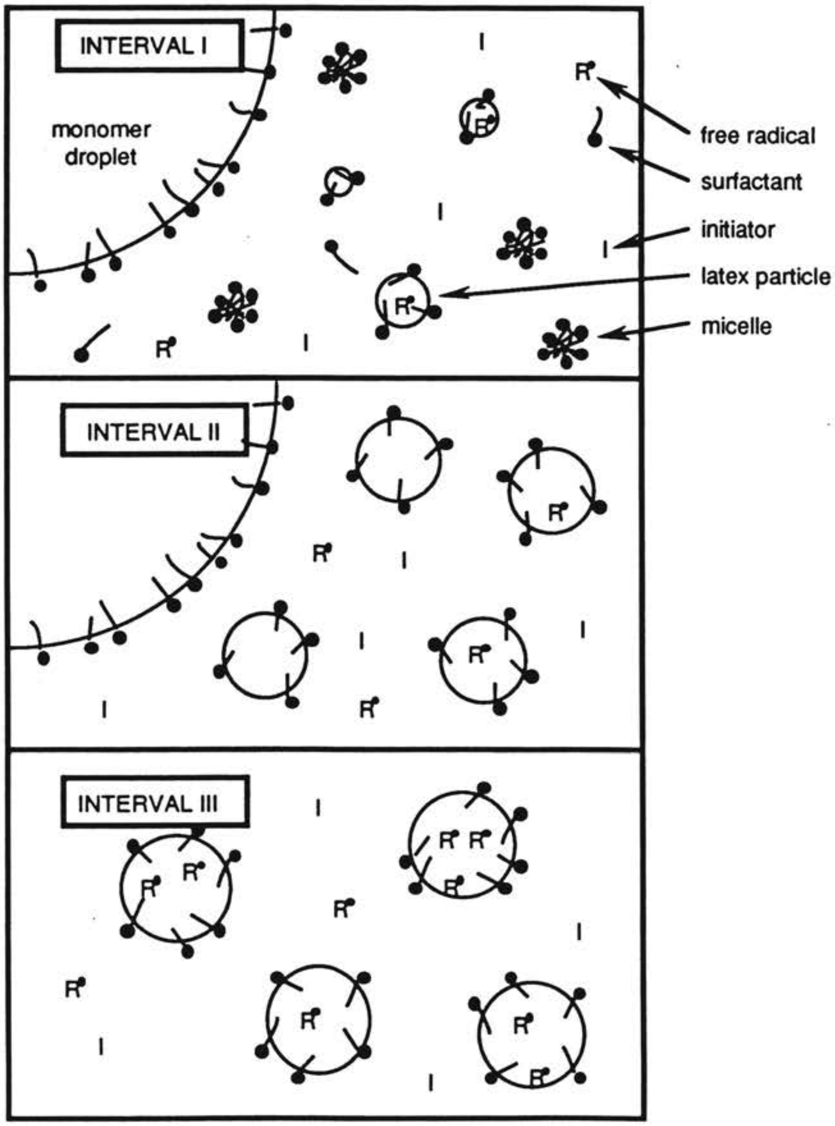


Figure 5. The three intervals of emulsion polymerization. (Reproduced from Gilbert, R. G. *Emulsion Polymerization*; Academic Press: London, 1995, p. 53)

surfactant, and water. During Interval I, surfactant molecules aggregate together to form empty micelles and micelles with their hydrophobic cores swollen with monomer. However, the bulk of the monomer exists in large monomer droplets. Upon addition of an initiator into the aqueous phase, radicals form and begin polymerization. Despite the larger size of the monomer droplets, radicals primarily tend to enter micelles because the micelles have much larger total surface area. Interval I corresponds to the particle nucleation where particles can grow by recruiting monomer from the monomer droplets. These particles are stabilized by absorbing surfactant from neighboring micelles. The depletion of empty micelles marks the end of Interval I, and the number of particles remains constant for the rest of the polymerization. Interval II embodies the bulk of the polymerization process. Particles continue to grow by diffusion of monomer through the aqueous phase from the monomer droplets. If a radical enters a particle that already contains a growing polymer chain, termination will occur rapidly. However, another radical can then enter the particle and start a new chain. Therefore, single latex particles in emulsion polymerization contain numerous polymer chains. Interval III takes place when all of the monomer in the monomer droplets has been consumed, and only the monomer in the particles is left to be polymerized.[2,3]

The initial solution in a typical microemulsion polymerization consists of micelles swollen with monomer suspended in the aqueous phase.[25] The monomer swollen micelles are then initiated through a radical diffusing in through the aqueous phase (Figure 6a). Polymer chains continue to propagate by recruiting monomer from unpolymerized monomer-swollen micelles, either by coalescence of micelles and the

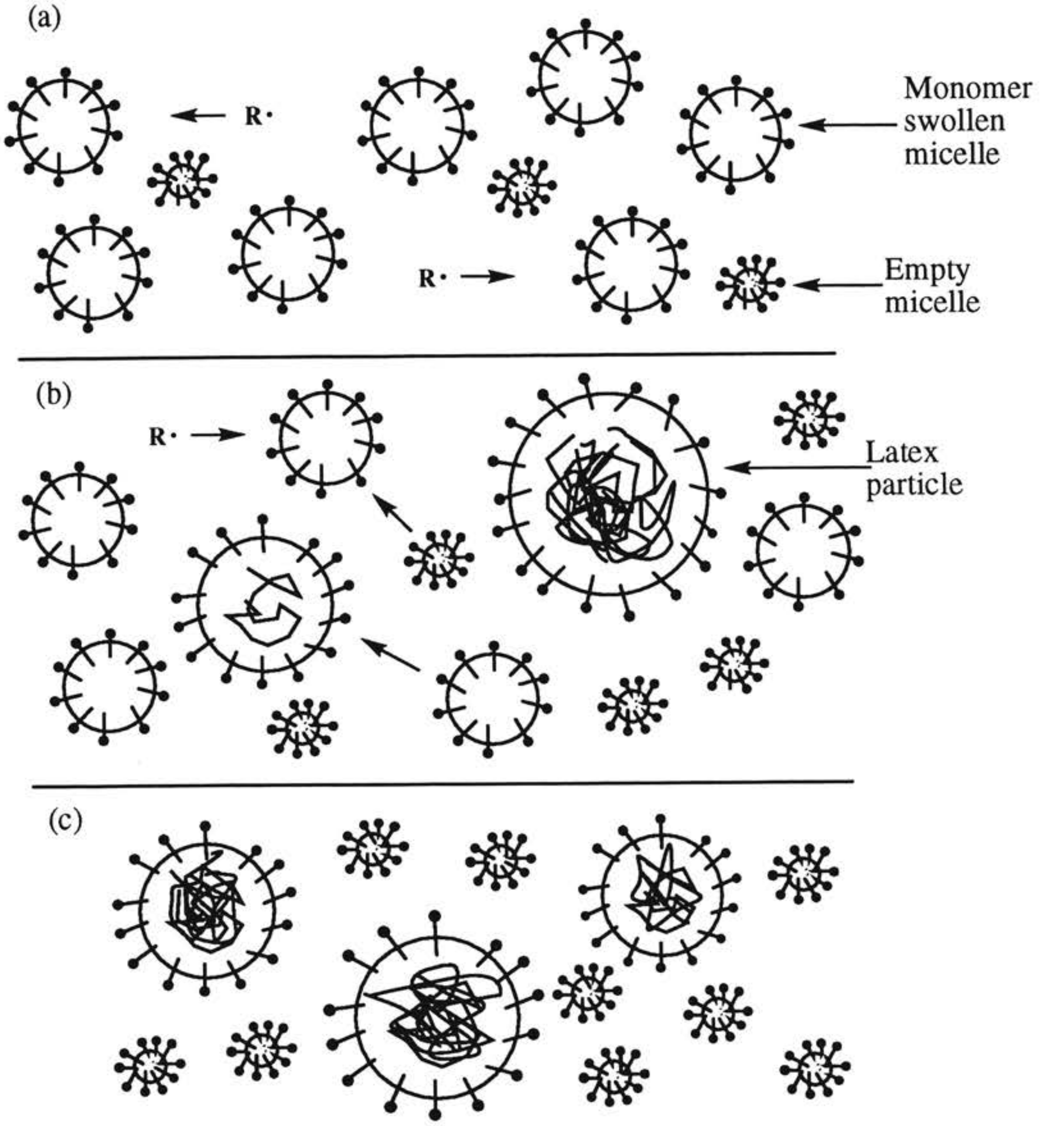


Figure 6. (a) Polymer Initiation - micelles swollen with monomer are initiated by radicals diffusing in from the aqueous phase. (b) Particle Nucleation - growth of particles containing polymer chains results from monomer transport from unpolymerized microdroplets. (c) Completion of Polymerization - latex particles larger than the primary microdroplet coexist with a large surplus of empty micelles.

polymerizing particle or by diffusion of monomer through the aqueous phase.[12,19,25,26] At this point, the number of monomer-swollen micelles greatly outnumbers the number of radical species in the solution. The probability of a radical entering a droplet that already contains a radical species is low. Thus termination of the polymer chain is reduced, and many latex particles consist of only one or two polymer chains. The polymerization is predominantly terminated by chain transfer to monomer, even though chain transfer to surfactant is also possible (Figure 6b). The particle size and average molecular weight remain constant thoughout the polymerization, indicating a continuous nucleation mechanism.[11] Surplus surfactant molecules are used in the formation of latex particles larger than the initial microdroplet but many are left over and form empty micelles. After polymerization is complete, latex particles larger than the initial microdroplets along with a surplus of empty micelles are left in solution[25] (Figure 6c). The existence of two populations with vastly different sizes has been shown by small angle neutron scattering (SANS)[27] as well as through ultracentrifugation experiments.[26]

Formation of Single Chains. During microemulsion polymerization, particles containing a growing polymer chain compete with uninitiated microdroplets in capturing radicals. The greater number of monomer swollen micelles when compared to particles containing a growing polymer chain provides a much larger surface area and a high probability of a radical entering an uninitated microdroplet and not a particle that already contains a growing polymer chain. The average time required for a particle with a growing polymer chain to capture a second radical and terminate the growing chain is greater than that of chain transfer to monomer. Thus chain transfer to monomer is the dominant mechanism for termination of the polymer chain. The radicals generated by chain transfer to monomer tend to diffuse out of the polymer particle. Moreover, due to the large number of small particles, it is highly probable that the particles will be void of radicals or possess one radical at a time. Thus microemulsion polymerization results in latex particles that contain very few polymer chains of high molecular weight.[11-35] The number of polymer chains per 20-30 nm diamter particle is much less than what is commonly observed in emulsion polymerization which typically results in 50-300 diameter latex particles with numerous polymer chains.[2,3]

The number of polymer chains per latex particle, n_p, can be calculated using the average particle size and the average molecular weight. Although some of the polymerizations performed in microemulsions lead to polymer particles with two or more polymer chains,[28-31] many of these polymerizations can often lead to latex particles containing a single polymer chain. Gan and coworkers produced small polystyrene latexes (~40 nm) with a high weight average molecular weight (~6 x 10^6 g/mole) containing an average of two polymer chains per latex particle.[34] The authors also obtained small PMMA latexes of high molecular weight polymer that contained between one and two polymer chains per latex particle.[20,35] Kaler and coworkers produced small polystyrene latexes using DTAB with diameters of approximately 20 nm (M_w = ~2 x 10^6 g/mole) containing an average of a single polymer chain per latex particle.[27] Latex particles containing a single chain provide support for the aforementioned mechanism of continuous particle nucleation.

Polymerization in Confined Spaces

Polymer Properties. Polymeric materials are selected on the basis of their processing and performance properties. The properties associated with a given polymer are primarily dependent upon the three-dimensional structure of the polymer. The properties of polymers can also vary even when the polymers have the same primary structure. A linear polymer will have differing properties from a branched polymer of the same type. Still yet, there are other factors regulating the properties of a polymer sample. For example, properties are also dependent upon the molecular weight of the sample and the configuration of the substituents on the polymer backbone.[37] Changing any of these parameters will affect how the polymer behaves. Such polymerization variables generate great interest in the preparation and properties of different polymeric materials. Could designing a unique macromolecular architecture lead to a polymer with advanced chemical and physical properties? Could controlling the stereochemistry of the polymer backbone lead to a material with better mechanical properties? The answer is "YES", and that is why scientists are eagerly pursuing the synthesis of new polymers possessing different behaviors than traditional linear polymers.

During polymerization, there are many different modes of propagation possible that could lead to differences in the geometric and configurational arrangements of the atoms in the repeat unit. There exists the possibility of head-to-tail and head-to-head placements of the repeat units, although head-to-tail linkages can predominantly be expected.[2] For head-to-tail attachment of a monomer with two different substituents on a carbon, two configurational sequences can be expected. The polymers are chiral because every other carbon atom in the polymer chain is a stereocenter. However, the stereoisomers of the repeat unit do not display any optical activity because the polymer chain residues attached to the chiral carbon are essentially identical. The substituents on two neighboring chiral carbon atoms could be on opposite sides of the polymer chain and display opposite chiralities and thus be *racemo* or on the same side of the polymer chain with the same chiralities and be *meso* (Figure 7). Each two neighboring repeat units can therefore characterize the tacticity of the polymer chain in terms of diad units (*m* or *r*). The portion of the polymer chain shown in Figure 7 contains two *m* diads and two *r* diads. The stereochemistry of the backbone can also be classified in terms of each three respective repeat units in the polymer chain by triad units. The segment of the PMMA molecule shown in Figure 7 would then have one *rr* triad termed syndiotactic, one *mm* triad (isotactic), and one *mr* triad that represents a random sequence called atactic. The polymer chain could be classified further. For example, the segment of the polymer chain contains a *rrm* and a *rmm* tetrad unit. The molecule also possesses a *rrmm* pentad sequence. Only triad units will be discussed within this text.

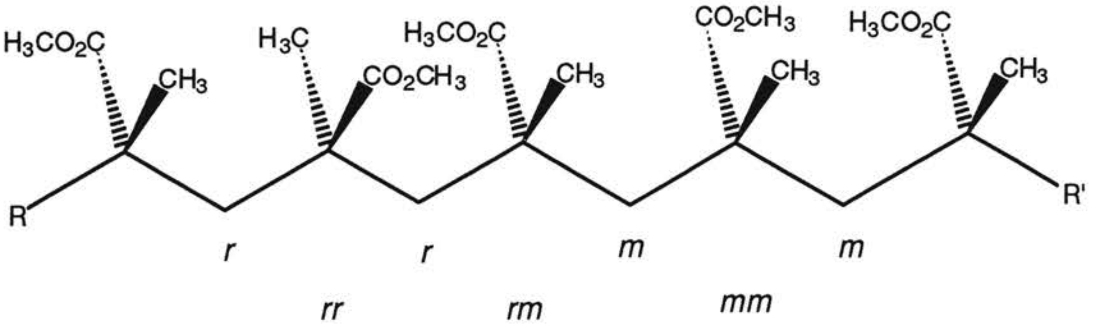


Figure 7. A portion of a PMMA chain showing the stereocenters associated with the macromolecule and illustrating the configurational sequences as *racemo* or *meso*. Also shown are the relative diad and triad units.

The isomeric forms of the repeat units in the chain and their distribution along the chain are very significant. Subtle changes in the polymer backbone can have a large effect on the polymer's performance and use properties. Syndiotactic PMMA has a much higher glass transition temperature than isotactic PMMA. The T_g for a 70% syndiotactic PMMA sample is 120 °C whereas the T_g for a 95% isotactic sample is only 41.5 °C.[38]

Polymerization in One Dimension. Spatial confinement of monomers in one dimension during polymerization can markedly alter the regio and stereochemical structures of the product polymer.[39] In clathrate crystals such as urea and thiourea,[40-41] cyclotriphosphazines,[42] and deoxycholic acid,[43] narrow channels permit only end-to-end contact of diene monomers. Gamma irradiation of 1,3-butadiene in thiourea canal complexes at -78°C gives all *trans*-1,4 polybutadienes.[40] In channels of chiral deoxycholic acid, 1-chloro-1,3-butadiene gave an optically active polymer.[43] Vinyl monomers give enhanced tacticity, up to 87% in isotactic triad units for polyacrylonitrile,[44] >80% syndiotactic poly(vinyl chloride),[41] and syndiotactic poly(methacrylic acid).[42]

Polymerization in Vesicles. Surfactants bearing one aliphatic chain aggregate to form a micelle in water.[45] When the amphiphilic molecule possesses two long aliphatic chains, the molecules aggregate to form bilayer membranes. These membranes, can be sonicated to form closed spherical or ellipsoidal structures called vesicles (Figure 8).[45] The vesicle forming surfactants can be functionalized with polymerizable groups to obtain a stable polymerized vesicle. Polymerized vesicles have found a variety of potential uses, including biomembranes as the media for biomimetic reactions, carriers of drugs, and devices for photochemical energy conversion.[45] Poly(methacrylic acid) derived from polymerization of dioctadecyldimethylammonium methacrylate (DODAM) vesicles has resulted in a polymer that was 75.4% syndiotactic, 22.3% atactic, and 2.3% isotactic.[46] Most of the research in this area focuses on polymerization *of* vesicles. Polymerization of styrene *in* vesicles has also been achieved, and resulted in particles with unique parachute type morphologies, although no attention was paid to stereochemistry.[47]

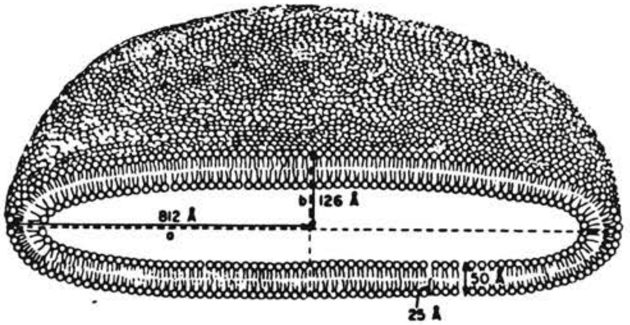


Figure 8. Representation of a unilamellar vesicle. (Reproduced from Paleos, C. M. *Polymerization in Organized Media*; Gordon and Breach Science Publishers: Philadelphia, 1992, p 284)

Polymerization in Zeolites. Zeolites are crystalline, porous metal oxides whose structure contains many well-defined pores and channels.[48] Free radical polymerization of methyl methacrylate within the pores (27 Å) of a mesoporous zeolite, MCM-41 (Figure 9)[49], gave a high molecular weight polymer with a tacticity similar to a polymer obtained under a non-constraining environment (67% *rr*, 32% *mr*, 1% *mm*).[50] Thus, the nanosized channels of MCM-41 were large enough not to affect the stereochemistry of the polymer backbone. Polymerization of methyl methacrylate has been performed in zeolites with pores ranging from 5 to 35 Å. However, the microstructures of the formed polymer were not analyzed.[48] Polymerizations in narrower channels of microporous zeolites do not give high molecular weight polymers.[51] A polymerization of methyl methacrylate in a zeolite with a 5.1 x 5.5 Å pore size was incomplete, possibly due to the lack of penetration of the initiator into the pores or an increased strain of the polymer chain within the channels which suppressed polymerization.[48] Methyl methacrylate adsorbed onto the surface of a zeolite and polymerized prefers an isotactic placement.[52] Conceivably, polymerization in a microemulsion would provide small confined dimensions for polymerization and still give a high molecular weight polymer.

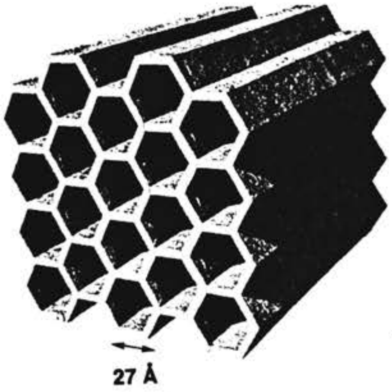


Figure 9. Representation of an aluminosilicate mesoporous zeolite (Al-MCM-41). (Reproduced from Kageyama et. al. *Macromolecules* **1998**, *31*, 4069)

Properties of Single Chains. Polymerizations in microemulsions often lead to latex particles that contain a single, high molecular weight, polymer chain. Space-filling considerations show that the chain cannot adopt its random coil conformation and must be highly compact and conformationally restricted inside the latex particle. Infrared spectroscopy has been used to show that single chain polystyrene differs slightly from a multichain sample. Analysis of bands found in the difference spectra in the 500-600 cm^{-1} region suggest that single chain polystyrene has a higher conformational temperature than a multi-chain sample.[53] DSC measurements have also displayed an exothermic transition near the T_g for the single chain polystyrene during the first scan, that was not observable for a multichain sample prepared in bulk.[53] This exothermic transition disappeared on subsequent scans and was also removed after annealing the sample at 100 °C. After the first DSC scan, the glass transition temperature of the single chain polystyrene was similar in behavior to the analogous multichain polystyrene sample but was 9 °C higher.[53] The T_g of the standard polystyrene sample was 96 °C compared to the second scan of the single chain sample that displayed a glass transition temperature of 105 °C. Commercial samples of polystyrene show a great variation in T_g that can be as high as 104 °C, although the commercial samples may contain additives.[53] Single chain polystyrene is also more resistant to electron radiation.[54] Polymerization of other monomers in a microemulsion could lead to single chain polymers with properties that differ from an analogous polymer prepared by standard means.

Objective of the Research

The stereochemistry of the propagating chain end of a polymer controls the tacticity of a polymer. The configuration of a polymer is determined from the addition of a monomer molecule to the propagating terminal active center in free radical polymerization. For restricted volume to affect the tacticity of the polymer, the transition state energies of the propagation steps leading to the various sequences of repeating units must differ from those of normal solution polymerization. To fit into a smaller volume, the polymer chain must have more gauche conformations overall than in unperturbed dimensions, and more gauche conformations are needed near the surface of the particle to turn the path of its random walk back into the latex particle. One molecule of polystyrene having a molecular weight of 1 x 10^6 g/mol and a density of 1.04 g/cm^3 occupies a sphere that has a diameter of 14.5 nm. In a theta solvent or in the bulk amorphous phase, the unperturbed root-mean-square end-to-end distance of that polystyrene molecule is 64 nm,[55] and the spheres that would enclose all of its chain segments in most conformations are even larger. Therefore, the polystyrene formed in a microemulsion is conformationally restricted, and the polymerization itself must occur with conformational restrictions (Figure 10).

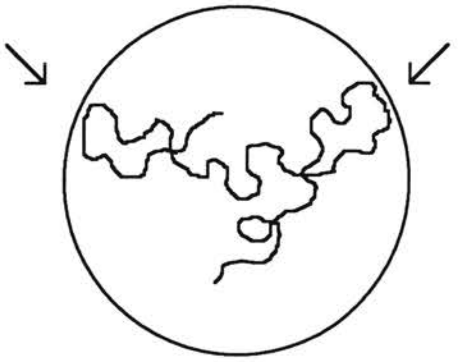


Figure 10. The polymer chain formed in a microemulsion is conformationally restricted.

The confinement of a monomer in the small spherical volumes produced by microemulsions could thus influence the microstructure of the polymer formed therein. Altering the configuration of the polymer chain would likely influence how the polymer behaves thus creating a polymer with different properties than those commonly observed. Unlike polymerizations that occur in one- and two-dimensional confined spaces, the polymers formed in microemulsions could be produced in quantities large enough for commerce.

The composition of the microemulsion and the sizes of the particles produced by the polymerization of various monomers in microemulsions were investigated to see how the microstructure of the polymer was affected. The protons of the α-methyl carbon of PMMA resolve into three signals of different chemical shifts in the proton NMR spectra, corresponding to the three triad sequences. The fraction of each triad sequence in the polymer is directly proportional to the relative areas of these peaks, making changes in the tacticity of PMMA easily measured by high resolution NMR spectroscopy.[56] The tacticity is known to depend greatly on the environment and temperature of the propagating chain. If the microstructure of a polymer formed in a microemulsion is different from that of the model polymer, the change could lead to enhanced or depressed properties of the polymer.

References

1. Israelachvili, J. N. *Intermolecular and Surface Forces*; Academic Press: San Diego, 1992, pp 372.

2. El-Aasser, M. S.; Sudol, E.D. *Emulsion Polymerization and Emulsion Polymers*; Lovell, P. A.; El-Aasser, M. S., Eds. Wiley: New York, 1997, pp 38-55.

3. Gilbert, R. G. *Emulsion Polymerization*; Ottewill, R. H.; Rowell, R. L., Eds. Academic Press: London, 1995, pp 1-73.

4. Schulman, J. H.; Hoar, T. P. *Nature* **1943**, *152*, 102.

5. Schulman, J. H.; Stoeckenius, W.; Prince, L. M. *J. Phys. Chem.* **1959**, *63*, 1677.

6. Sharma, M. K.; Shah, D. O. *Macro- and Microemulsions in Enhanced Oil Recovery*; ACS Symposium Series; American Chemical Society: Washington D.C., 1985, Vol. 272.

7. Schwuger, M.-J.; Stickdorn, K. *Chem. Rev.* **1995**, *95*, 849.

8. McIntosh, J. M. *J. Chem. Ed.* **1978**, *55*, 235.

9. Mendizabal, E.; Rodriquez-Ruvalcaba, R.; Rabelero, V.; Puig, J. E.; Velazquez, R.; Castano, V. *J. Polym. Mater.* **1995**, *30*, 167.

10. Rodriquez-Guadarrama, L. A.; Mendizabal, E.; Puig, J. E.; Kaler, E. W. *J. Appl. Polym. Sci.* **1993**, *48*, 775.

11. Escalante, I. I.; Rodriquez-Guadarrama, L. A.; Mendizabal, E.; Puig, J. E.; Lopez, R. G.; Katime, I. *J. Appl. Polym. Sci.* **1996**, *62*, 1313.

12. Full, A. P.; Puig, J. E.; Gron, L. U.; Kaler, E. W.; Minter, J. R.; Mourey, T. H.; Texter, J. *Macromolecules* **1992**, *25*, 5157.

13. Guo, J. S.; Sudol, E. D., Vanderhoff, J. W.; El-Aasser, M. S. *J. Polym. Sci. Part A: Polym. Chem.* **1992**, *30*, 691.

14. Candau, F.; Leong, Y. S.; Fitch, R. M. *J. Polym. Sci.: Polym. Chem. Ed.* **1985**, *23*, 193.

15. Pilcher, S. C.; Ford, W. T. *Macromolecules* **1998**, *31*, 3454.

16. Stoffer, J. O.; Bone, T. *J. Polym. Sci.: Polym. Chem. Ed.* **1980**, *18*, 2641.

17. Atik, S.; Thomas, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 4515.

18. Gan, L. M.; Chew, C. H.; Friberg, S. E. *J. Macromol. Chem.* **1983**, *A19*, 739.

19. Kaler, E. W.; Pérez-Luna, V. H.; Puig, L. E.; Castaño, V. M.; Rodriquez, B. E.; Murthy, A. K. *Langmuir* **1990**, *6*, 1040.

20. Gan, L. M.; Lee, K. C.; Chew, C. H.; Tok, E. S.; Ng, S. C. *J. Polym. Sci. Part A: Polym. Chem.* **1995**, *33*, 1161.

21. Antonietti, M.; Lohmann, S.; Van Niel, C. *Macromolecules* **1992**, *25*, 1139.

22. Antonietti, M.; Bremser, W.; Müschenborn, D.; Rosenauer, C. *Macromolecules* **1991**, *24*, 6636.

23. Antonietti, M.; Basten, R.; Gröhn, F. *Langmuir* **1994**, *10*, 2488.

24. Antonietti, M; Nestl, T. *Macromol. Rapid Commun.* **1994**, *15*, 111.

25. Candau, F. *Polymerization in Organized Media*; Paleos, C. M. Ed. Gordon and Breach Science Publishers: Philadelphia, 1992, pp 215-282.

26. Candau, F.; Leong, Y. S.; Pouyet, G.; Candau, S. J. *J. Colloid Interface Sci.* **1984**, *101*, 167.

27. Full, A. P.; Kaler, E. W.; Arellano, J.; Puig, J. E. *Macromolecules* **1996**, *29*, 2764.

28. Guo, J. S.; El-Aasser, M. S.; Vanderhoff, V. M. *J. Polym. Sci., Polym. Chem.* **1989**, *27*, 691.

29. Gan, L. M.; Chew, C. H.; Lye, I.; Imae, T. *Polym. Bull.* **1991**, *25*, 193.

30. Bléger, F.; Murthy, A. K.; Pla, F.; Kaler, E. W. *Macromolecules* **1994**, *27*, 2559.

31. Lusvardi, K. M.; Schubert, K.-V.; Kaler, E. W.; *Ber. Bunsenges. Phys. Chem.* **1996**, *100*, 373.

32. Carver, M. T.; Dreyer, U.; Knoesel, R.; Candau, F. *J. Phys. Chem.* **1989**, *93*, 4867.

33. Larpent, C.; Tadros, T. F. *Coll. Poly. Sci.* **1991**, *269*, 1171.

34. Gan, L. M.; Chew, C. H.; Lee, K. C.; Ng, S. C. *Polymer* **1994**, *35*, 2659.

35. Gan, L. M.; Lee, K. C.; Chew, C. H.; Ng, S. C. *Langmuir* **1995**, *11*, 449.

36. Grulke, E. A. *Polymer Process Engineering* PTR Prentice Hall: New Jersey 1994.

37. Cowie, J. M. G. *Polymers: Chemistry and Physics of Modern Materials* Blackie Academic and Professional: New York, 1991.

38. Wittmann, J. C.; Kovacs, A. J. *J. Polym. Sci. Part C* **1969**, *16*, 4443.

39. Farina, M.; Giuseppe, D. S. *Encyclopedia of Polymer Science and Engineering* John Wiley & Sons, Inc.: New York 1988, *12*, 486.

40. Brown, J. F.; White, D. M. *J. Am. Chem. Soc.* **1960**, *82*, 5671.

41. White, D. M. *J. Am. Chem. Soc.* **1960**, *82*, 5678.

42. Allcock, H. R.; Silverberg, E. N.; Dudley, G. K. *Macromolecules* **1994**, *27*, 1033.

43. Tsutsumi, H.; Okanishi, K.; Miyata, M.; Takemoto, K. *J. Polym. Sci. Part A: Polym. Chem.* **1990**, *28*, 1527.

44. Minagawa, M.; Yamada, H.; Yamaguchi, K.; Yoshii, F. *Macromolecules* **1992**, *25*, 503.

45. Paleos, C. M. *Polymerization in Organized Media*; Paleos, C. M. Ed. Gordon and Breach Science Publishers: Philadelphia, 1992, pp 283-326.

46. Fukuda, H.; Diem, T.; Stefely, J.; Kezdy, F. J.; Regen, S. L. *J. Am. Chem. Soc.* **1986**, *108*, 2321.

47. Jung, M.; Hubert, D. H. W.; Bomans, P. H. H.; Frederik, P. M.; Meuldijk, J.; van Herk, A. M.; Fischer, H.; German, A. L. *Langmuir* **1997**, *13*, 6877.

48. Moller, K.; Bein, T.; Fischer, R. X. *Chem. Mater.* **1998**, *10*, 1841.

49. Kageyama, K.; Ogino, S.; Aida, T.; Tatsumi, T.; *Macromolecules* **1998**, *31*, 4069.

50. Ng, S. M.; Ogino, S.; Aida, T.; Koyano, K. A.; Tatsumi T.; *Macromol. Rapid. Commun.* **1997**, *18*, 991.

51. Miyata, M.; Noma, F.; Osaki, Y.; Takemoto, K.; Kamachi, M. *J. Polym. Sci., Part C: Polym. Lett.* **1986**, *24*, 457.

52. Quaegebeur, J. P.; Seguchi, T.; Bail, H. L.; Chachaty, C. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 2703.

53. Qian, R.; Wu, L.; Shen, D.; Napper, D. H.; Mann, R. A.; Sangster, D. F. *Macromolecules* **1993**, *26*, 2950.

54. Bu, H.; Cao, J.; Zhang, Z.; Zhang, Z.; Festag, R.; Joy, D.; Kwon, Y. K.; Wunderlich, B. *J. Polym. Sci.: Part B Polym. Physics* **1998**, *36*, 105.

55. Brandrup, J.; Immergut, E. H. *Polymer Handbook, Third Ed.*, Wiley: New York, 1989, pp VII/1-VII/60.

56. Tonelli, A. E. *NMR Spectroscopy and Polymer Microstructure: The Conformational Connection*; VCH Publishers: New York, 1989.

CHAPTER II

STRUCTURES AND PROPERTIES OF POLY(METHYL METHACRYLATE) LATEXES FORMED IN MICROEMULSIONS

Abstract

Polymerizations of methyl methacrylate (MMA) in ternary oil-in-water microemulsions using the cationic surfactants stearyltrimethylammonium chloride (STAC), cetyltrimethylammonium bromide (CTAB), or a mixture of nonionic nonylphenoxy poly(ethylene glycol) surfactants produce latex particles having mean diameters of 15-40 nm. The small particle sizes and high molecular weights ($M_w = 2.5\text{-}7 \times 10^6$) indicate that most samples consist mainly of particles containing one macromolecule. The particle size varied little when the surfactant to monomer weight ratio is ≥ 1. Polymerizations using STAC at 35 °C produce smaller particles than at 60 °C. Radical polymerization of MMA in microemulsions produced predominantly syndiotactic PMMA containing 58-61% *rr* triads at 60 °C and 63-65% *rr* triads at 35 °C. The high molecular weight PMMA samples have a T_g = 125-126 °C.

Introduction

Polymerization of nonpolar monomers in oil-in-water microemulsions produces latex particles <50 nm in diameter, compared with >100 nm from conventional emulsion polymerizations.[1-4] The initial microemulsion is a thermodynamically stable mixture of monomer, surfactant, and water in which the amount of surfactant often exceeds the amount of monomer, and the monomer is swollen into surfactant micelles. The first polymerizations in microemulsions employed an aliphatic alcohol as a cosurfactant.[5-10] Recently, attention has been focused on the kinetics and mechanisms of polymerizations in three-component microemulsions,[11-24] but little attention has been paid to the structures and the properties of the polymers. Therefore, the tacticities and the glass transition temperatures of poly(methyl methacrylate) (PMMA) formed in ternary microemulsions were analyzed.

Polymerizations in one dimension by confinement of vinyl monomers in the narrow channels of clathrate crystals of urea, thiourea, cyclotriphosphazines, and deoxycholic acid, give more highly isotactic or more highly syndiotactic polymers than polymerizations in solution or in bulk.[25-31] Polymerization reactions confined to two dimensions in lipid bilayers and in monolayer films have also been studied but no attention has been paid to tacticity.[32-34] The confinement of a monomer in the small volume of a microemulsion might influence the microstructure of the polymer formed therein. Unlike polymers formed in one- and two-dimensional confined spaces, the polymers formed in these small spheres might be produced in quantities large enough for commerce.

Some of the smaller latexes formed in microemulsions contain an average of little more than one macromolecule per particle. Due to the ultrahigh molecular weight of the polymer, the polymer chain must be strongly collapsed in order to accommodate the small particle dimensions (~30 nm in diameter) encountered in a microemulsion. The polymer chain must have more gauche conformations than in its unperturbed state, especially near the surface of the particle, so that the path of its random walk turns back into the particle. The polymer formed in a microemulsion is conformationally restricted. If the propagating chain end is also restricted during polymerization, the tacticity of the polymer may be altered.

The particle sizes, molecular weights, tacticities, and glass transition temperatures of PMMA formed in microemulsions were analyzed. MMA was chosen as the monomer because changes in tacticity are easily determined by NMR spectroscopy,[36,37] and the tacticity of PMMA is known to depend strongly on the temperature of radical polymerization.[38-40]

Polymerizations of MMA were first carried out in microemulsions already known to produce 18-30 nm diameter particles containing only a few macromolecules by using methods patterned after previously reported procedures.[12,22] In other experiments the initiator, temperature, and amounts of surfactant in the microemulsion were experimental variables. Molecular weights of the polymers were measured by size exclusion chromatography (SEC) and were used to calculate the number of polymer chains per particle. Tacticities of the PMMA samples were then correlated with the composition of the starting microemulsion, the size of the product particles, which was measured by transmission electron microscopy (TEM), and the glass transition temperatures of the polymers.

Experimental

Materials. Stearyltrimethylammonium chloride (STAC, >97%), cetyltrimethylammonium bromide (CTAB, >98%), dodecyltrimethylammonium bromide (DTAB, >99%) from TCI, sodium dodecylbenzenesulfonate (DBS) from Polysciences Inc., Triton N-150 from Union Carbide, and Triton N-57 from Aldrich were used as received. Methyl methacrylate (MMA) from Aldrich was vacuum distilled. Potassium persulfate (KPS) from Sigma, ascorbic acid from Aldrich, and a 30% hydrogen peroxide solution from Fisher were used as received. 2,2'-Azobisisobutyronitrile (AIBN) from Aldrich was recrystallized from ethanol. Water was deionized and had resistivity >1 Mohm-cm after exposure to air.

Polymerizations. The general procedure is illustrated by the polymerization of MMA using STAC at a surfactant to monomer weight ratio (S) of $S = 2$ with KPS as the initiator. To 3.0 g of STAC in a three-necked, 50 mL, round-bottomed flask equipped with a condenser, a mechanical stirrer, and a nitrogen inlet was added 29.0 mL of deionized water. The air in the flask was replaced by a stream of nitrogen, and the mixture was kept under nitrogen until the polymerization was finished. The flask was placed in a 60 °C oil bath, and the mixture was stirred for 1 h until it became homogeneous. MMA (1.50 g) was added, and the solution was stirred for 30 min to form a transparent microemulsion. A solution of 15.0 mg of KPS (1 wt. % relative to monomer) in 1.0 mL of deionized water was added, and the solution was stirred for 4 h in an oil bath at 60 °C to produce a transparent solution with a bluish tint. The sample had no odor, indicating that no monomer remained.

The polymerizations using the Triton surfactants and a trace of DBS at differing surfactant to monomer ratios were performed by first mixing the surfactants and water. MMA was added and stirred for 30 min. For redox initiation, the ascorbic acid was dissolved in 1 mL of deionized water, and the hydrogen peroxide was added to this solution immediately before addition to the microemulsion. In the experiments using an oil soluble initiator, AIBN (0.5 wt. % with respect to monomer) was dissolved into the MMA before the microemulsion was heated to 60 °C.

Particle Size Measurements. An aliquot of the latex was diluted 15:1 with deionized water and sonicated for one hour. A drop of this sample was placed on a Formvar-coated Cu grid for 1 min, the excess latex was removed by touching a piece of filter paper to the drop, and the grid was dried in air for 1 min. A drop of 1% uranyl acetate solution was placed on the grid for 1 min to stain the sample, the excess solution was removed with filter paper, and the grid was dried in air. Transmission electron microscopy (TEM) was performed using a JEOL 100-CS2 instrument with 100 μA filament current, 80 kV accelerating voltage, and the electron beam normal to the sample plane. Diameters of at least 50 randomly chosen particles were measured directly from the micrograph negatives using an optical microscope with a calibrated stage. No size standards were used, and reported sizes were calculated from the nominal instrument magnification. The number and weight average diameters were calculated using equations 1 and 2 where D_i is the diameter of a particle and n is the number of particles measured.

$$D_n = \Sigma D_i / n \qquad (1)$$

$$D_w = \Sigma D_i^4 / \Sigma D_i^3 \qquad (2)$$

Particle sizes were also measured by dynamic light scattering (DLS). The signal from the scattered light of an Argon ion laser (Spectra-Physics 2020-05) was collected from latex samples diluted 20:1 at a scattering angle of 90° and analyzed using an ALV-5000 digital correlator.

Precipitation of Polymer Samples. To 20 mL of methanol contained in a 30 mL beaker, 5 mL of the latex dispersion was added and mixed, and the mixture was allowed to stand overnight. The precipitated polymer was vacuum filtered, washed successively with methanol and water, and dried in a vacuum desiccator for 24 h at 60 °C. No surfactant peaks were detected in the ^{1}H NMR spectra of $CDCl_3$ solutions of the polymers.

Molecular Weight Analyses. Molecular weights were measured by size exclusion chromatography (SEC) using a series of 10^6 Å, 10^5 Å, and 10^4 Å 10 μm PLgel columns from Polymer Laboratories at a flow rate of 1.0 mL/min at 40 °C using a Hewlett-Packard (HP) series 1100 chromatograph. The sample size injected was 20 μL of a 1.0 mg/mL solution in THF. The measurements were calibrated with polystyrene standards having molecular weights of 6 000 000, 900 000, and 233 000 in one solution and 1 800 000, 390 000, and 100 000 in a second solution. Molecular weights were calculated using the HP Chemstation software and a GPC Macro supplied by HP.

Glass Transition Temperatures. The T_g values were measured using a Perkin-Elmer Model DSC-2 differential scanning calorimeter and 10.0 mg samples at a scan rate of 10 K/min from 300 to 450 K followed by rapid cooling. The instrument was calibrated with naphthalene (mp = 353.4 K) and indium (mp = 429.8 K). Since the T_g from the first measurement of each sample often was higher than that from subsequent measurements, T_g is reported as the average of measurements 2-4 using the midpoint method. The T_m values of the standards were reproducible to better than 0.2 K. The T_g of independent samples from one polymerization was reproducible to ±1 K.

Tacticity Measurements. ^{1}H NMR analyses were performed at 400 MHz using $CDCl_3$ solutions at room temperature. The tacticities of the samples were measured from the integrated areas of the syndiotactic (*rr*), isotactic (*mm*), and atactic (*mr*) triad signals.[37] ^{1}H NMR analyses of a few samples were performed at 110 °C in deuterated *o*-dichlorobenzene to improve the resolution of the spectra. The tacticities measured at 110 °C were identical with those measured at room temperature. Only results from room temperature spectra are reported. The tacticity analyses of the PMMA produced using STAC and redox initiation were perfomed at 300 MHz.

Results

Procedures for polymerization of methyl methacrylate (MMA) in microemulsions were modified from those already known to produce small latex particles. Typical compositions and characterization of these samples are given in Tables 1 and 2, respectively. Gan and coworkers[22] produced PMMA in ternary microemulsions using the cationic surfactants stearyltrimethylammonium chloride (STAC), cetyltrimethylammonium bromide (CTAB), and dodecyltrimethylammonium bromide (DTAB) with either a water-soluble or an oil-soluble initiator. It was found that the longer the hydrophobic chain length of the surfactant, the smaller and more stable the latex particles. The results in Table 3 show smaller particles produced using CTAB (C_{14}) than STAC (C_{18}) cationic surfactants. Kaler and coworkers also produced small latexes from styrene and from several different methacrylic esters using cationic surfactants.[15,16,19,20,23,24] Larpent and Tadros[12] utilized mixtures of nonionic surfactants (Triton N-150 and Triton N-57, nonylphenoxy poly(ethylene glycols) having averages of fifteen and five ethylene oxide units, respectively), to form microemulsions of MMA and of styrene in water, and produced small latex particles at varied surfactant to monomer ratios using ascorbic acid/hydrogen peroxide as a redox initiator. Results from polymerizations using mixtures of these nonionic surfactants are reported in Table 4.

Table 1. Compositions of Microemulsions Based On Literature Procedures

Surfactant	Amount, g	Water, mL	MMA, g	Initiator	Amount, mg
STAC	2.8	30	2.5	ascorbic acid 30% H_2O_2	30 370
Triton N-150 Triton N-57 DBS	4.64 0.54 0.012	28	2.73	ascorbic acid 30% H_2O_2	28 400
STAC	2.8	30	2.54	KPS	2
CTAC	2.5	26	2.14	KPS	1.5
CTAB	3.2	31	3.2	AIBN	1.5

Table 2. Particle Sizes and Molecular Weights of PMMA Produced in Microemulsions Based on Literature Procedures[a]

Sample Description	D_n, nm	D_w, nm	D_z[c], nm	$M_w \times 10^{-6}$	M_w/M_n	n_p[e]
STAC-Redox[b]	15	17	21	0.156	2.2	6.5
Triton-Redox[b]	27	30	36	3.0	2.0	2.4
STAC-KPS[c]	26	32	49	4.4	1.8	2.2
CTAC-KPS[c]	26	34	49	2.9	2.2	4.1
CTAB-AIBN[c]	28	37	44	1.4	2.2	11

[a] See Table 1. [b] 35 °C. [c] 60 °C. [c] Measured using dynamic light scattering. [e] Average number of polymer chains per latex particle calculated from D_w, M_w, and PMMA density of 1.20 g cm^{-3}.

Table 3. Particle Sizes and Molecular Weights of PMMA Produced at 60 °C at Various Surfactant to Monomer Weight Ratios[a]

Sample Description	D_n, nm	D_w, nm	D_z[b], nm	M_w x 10^{-6}	M_w/M_n	n_p[c]
STAC-KPS						
S = 0.01	70	80	98	5.5	1.5	32
S = 0.1	24	31	44	7.0	2.1	1.3
S = 0.5	25	28	39	6.5	1.4	1.0
S = 1	26	27	41	4.4	1.2	1.3
S = 2	22	26	38	5.0	1.6	1.0
S = 3	21	26	42	5.8	1.7	1.0
STAC-AIBN						
S = 0.1	39	62	69	5.0	3.9	16
S = 0.5	35	41	56	5.9	1.6	3.7
S = 1	24	28	42	5.4	1.6	1.2
S = 2	22	26	40	4.5	1.5	1.1
S = 3	27	31	45	5.4	1.6	1.6
CTAB-KPS						
S = 0.1	55	63	51	4.9	1.5	17
S = 0.5	21	28	45	6.5	2.5	1.0
S = 1	20	25	38	4.2	2.0	1.0
S = 2	19	23	38	2.7	1.7	1.2
S = 3	18	21	38	2.5	1.4	1.0

[a] Microemulsions contained 30 mL of water, 1.5 g of MMA, and 1 wt % of KPS or 0.5 wt % of AIBN. [b] Measured using dynamic light scattering. [c] Average number of polymer chains per latex particle calculated from D_w, M_w, and PMMA density of 1.2 g cm^{-3}.

Table 4. Particle Sizes and Molecular Weights of PMMA Produced at 35°C at Various Surfactant to Monomer Weight Ratios

Sample Description	D_n, nm	D_w, nm	D_z[a], nm	M_w x 10^{-6}	M_w/M_n	n_p[b]
Triton N-150 Triton N-57 DBS						
S = 1	37	45	64	4.0	1.9	7.3
S = 2	34	41	58	2.7	1.8	8.1
S = 3	29	33	52	3.0	1.4	3.6
STAC-Redox						
S = 0.01	44	63	72	0.075	2.8	1100
S = 0.1	36	44	54	0.090	1.8	300
S = 0.5	22	28	38	0.035	2.0	180
S = 1	19	24	32	0.041	2.1	92
S = 2	11	18	29	0.036	4.1	39

[a] Measured using dynamic light scattering. [b] Average number of polymer chains per latex particle calculated from D_w, M_w, and PMMA density of 1.20 g cm^{-3}.

All microemulsion compositions having a surfactant to monomer weight ratio $S \geq 1$ lie within the single phase regions of previously published phase diagrams for the ternary surfactant/MMA/water mixtures.[12,16,22] Polymerizations were performed with both water-soluble and oil-soluble thermal initiators at 60 °C and with a redox initiation system of hydrogen peroxide and ascorbic acid at 35 °C. Prior to polymerization the samples containing surfactant to monomer weight ratios of $S \geq 1$ were transparent at the reaction temperature, and as polymerization proceeded, the mixtures became turbid or developed a bluish tint indicating the presence of colloidal particles. In contrast, samples containing cationic surfactants at $S \leq 0.1$ were turbid initially and remained so during polymerization. In one case, using STAC/monomer = 0.1 and potassium persulfate as initiator, the initial mixture was turbid and but cleared to give a dispersion with a bluish tint after polymerization.

Stability of Latexes. Of the cationic surfactants, STAC produced the most stable latexes. PMMA particles from DTAB microemulsions (not reported in the tables) precipitated immediately after polymerization was complete. Although Full and coworkers[23] obtained stable polystyrene latexes in microemulsions prepared with salt solutions and mixtures of dodecyltrimethylammonium bromide and didocedyldimethylammonium bromide, stable microemulsions using only dodecyltrimethylammonium bromide and the same amount of MMA were not obtained as with the longer chain cationic surfactants. The latexes produced using CTAB aggregated slightly after standing for about one month. The latexes produced using STAC at $S \geq 1$ showed no visible signs of coagulation for up to six months. Thus particle stability increases with the increasing hydrophobic chain length of the surfactant.

Latexes prepared at $S \geq 1$ were more stable than those produced at $S = 0.1$ and $S = 0.5$, even when the particle sizes were similar, such as the samples reported in Table 3. Slight coagulation was observed in samples from STAC-KPS at $S = 0.1$ and $S = 0.5$ after one week. Using the cationic surfactants STAC and CTAB, the initial microemulsions of MMA in water were optically transparent at 60 °C and $S \geq 0.5$. However, the solutions with $S = 0.1$ were slightly cloudy, and the $S = 0.01$ dispersion was opaque throughout the preparation of particles. This would seem to imply that to obtain a transparent microemulsion, one needs to perform the polymerization at surfactant to monomer ratios greater than or equal to 0.5.

Polymerizations using the mixture of nonionic surfactants were carried out at 35 °C with ascorbic acid/hydrogen peroxide as the initiator. The mixtures of MMA and Triton surfactants did not form stable microemulsions at 60 °C. The latexes obtained with the nonionic surfactants at 35 °C and $S \geq 1$ showed no sign of coagulation over six months, but the particles obtained at $S = 0.1$ and 0.5 were unstable and individual particles could not be distinguished from coagulum by TEM. However, the samples prepared at higher surfactant to monomer ratios at 35 °C were extremely stable. One sample prepared with the Triton surfactant mixture (Table 1) showed no coagulation after four years.

Particle Sizes. The sizes measured by transmission electron microscopy (TEM) and by dynamic light scattering (DLS) generally agreed well. Sizes from DLS were slightly larger than the sizes from TEM as expected, since DLS measures a diffusion coefficient due to the particle and the hydrated counterions in the electrical double layer. The diffusion coefficient is used to calculate a *z*-average diameter from the Stokes-Einstein equation, whereas the number average and weight average diameters are reported from the TEM measurements. Aggregated particles were excluded from the measurements of the electron micrograph negatives, and only particles in good focus were included. The sizes obtained from light scattering would include larger aggregates in the final average particle size.

The dependence of particle sizes on surfactant to monomer weight ratios is reported in Table 3 and Figure 1. At $S = 0.01$, a ratio typical of normal emulsion polymerizations, the particles were larger than those formed with more surfactant, but quite small for an emulsion polymerization due to the small amount of monomer (5 wt %) and perhaps to the C_{18} surfactant. TEM images of the latex particles formed using CTAB at $S = 0.1$ and $S = 3$ are in Figures 2 and 3. The particle sizes were found to decrease with increasing surfactant to monomer ratio but did not differ significantly when the surfactant to monomer ratio was greater than or equal to 0.5. Although the average size of the particles obtained with STAC-KPS and $S = 0.1$ did not correlate with results from other S ratios, the experiment was duplicated with no significant change in particle size.

Sizes of the PMMA particles produced in microemulsions using STAC and the oil-soluble initiator, AIBN, are reported in Table 3 and Figure 1. Again, at $S < 1$, particle sizes decreased with increasing S, and at $S \geq 1$ the particle sizes did not vary significantly. The sizes of the latex particles prepared using the nonionic surfactants reported in Table 4 decreased with increasing surfactant to monomer weight ratios at $S \geq 1$, but the particles were larger than those produced using cationic surfactants, even though the polymerizations were performed at 35 °C. Using STAC, the particles produced at 35 °C were smaller than those produced at 60 °C. Particle sizes decrease with polymerization temperature only when the same surfactant is employed in the polymerization.

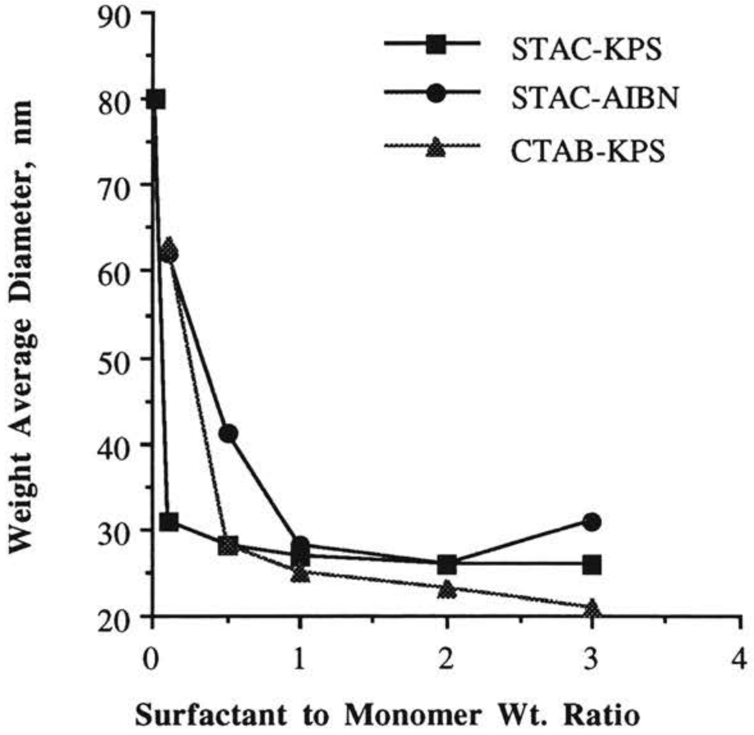


Figure 1. Particle sizes decrease with increasing surfactant to monomer weight ratio.

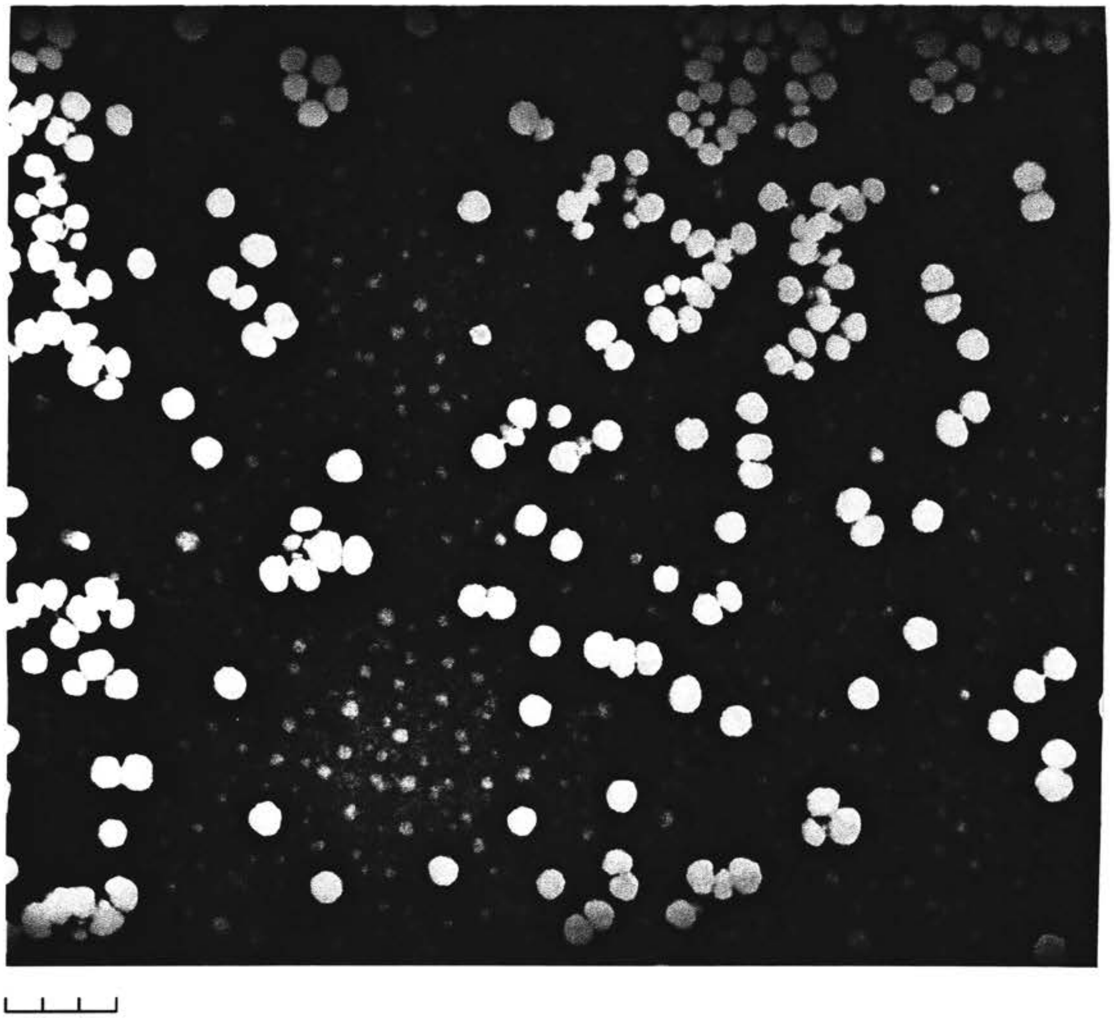


Figure 2. Transmission electron micrograph of the sample CTAB-KPS $S = 0.1$.

Figure 3. Transmission electron micrograph of the sample CTAB-KPS $S = 3.0$.

Molecular Weights. The molecular weights were measured by size exclusion chromatography (SEC) relative to polystyrene standards. Figure 4 displays sample chromatograms used for the molecular weight analyses. The PMMA samples prepared in microemulsions have M_w = 3-6 x 10^6 using cationic surfactants and thermal initiators, or using nonionic surfactants and a redox initiator. These M_w values are typical of PMMA and polystyrene prepared in microemulsions.[22,24] Some of the molecular weight distributions were difficult to measure because of tailing of the chromatographic peak, which would affect M_n more than M_w. It is also possible that the molecular weight distributions are narrower than measured, if the chromatograms are broadened by shear degradation of the high molecular weight PMMA in the SEC columns. Much lower molecular weights were obtained using STAC with hydrogen peroxide/ascorbic as redox initiator, which can be attributed to chain transfer to Cl_2 produced from chloride ion and hydrogen peroxide.[41]

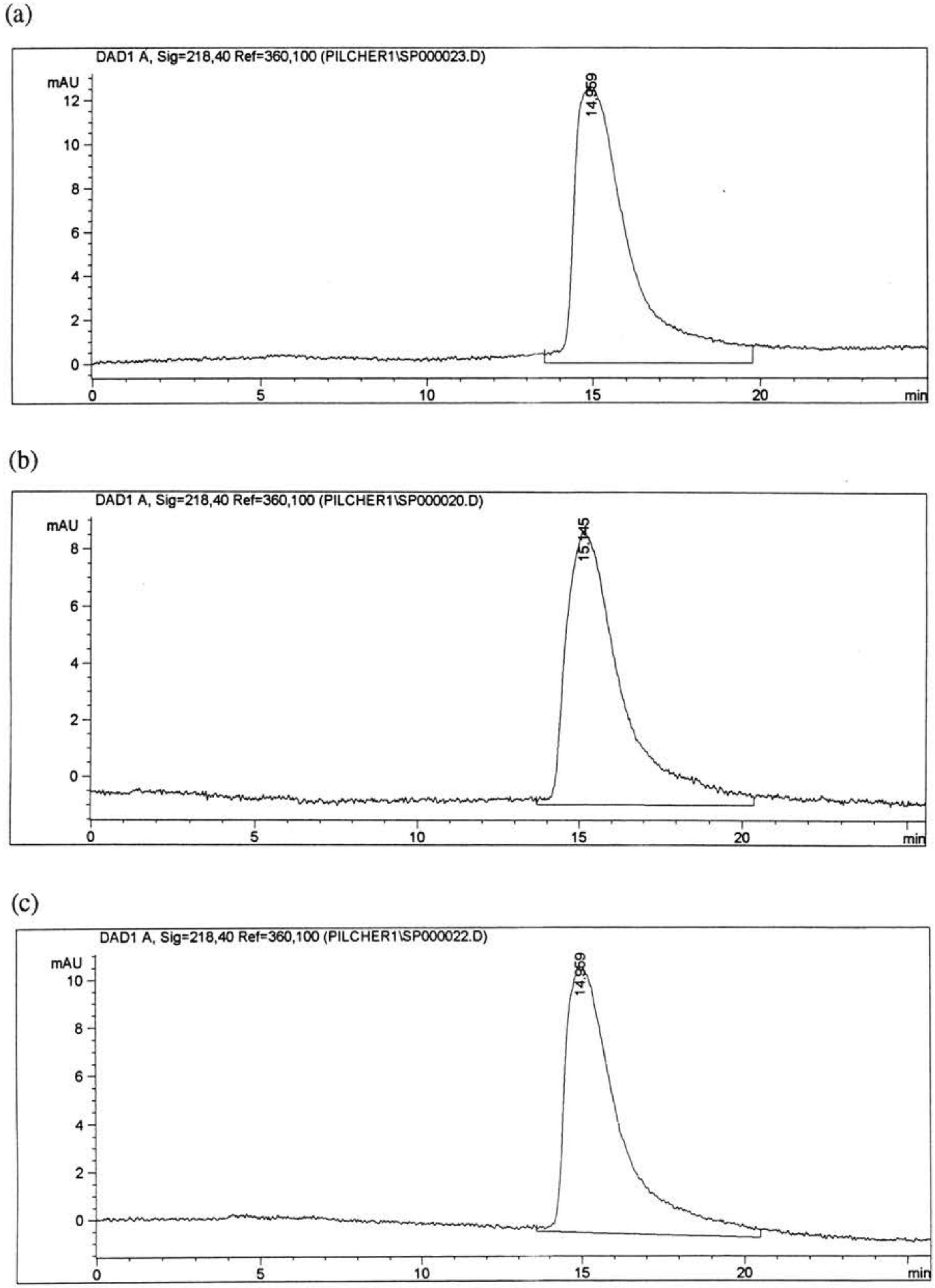


Figure 4. SEC chromatograms from PMMA prepared in the following microemulsions: (a) STAC/AIBN *S* = 1, (b) STAC/AIBN *S* = 2, (c) STAC/AIBN *S* = 3.

Number of Macromolecules per Latex Particle. The number of macromolecules per particle, n_p, was calculated for each PMMA sample from the weight average mass of a particle according to eq 3.

$$n_p = M_p N_A / M_w \quad (3)$$

$$M_p = V_p d \quad (4)$$

where M_p = mass of a particle, $N_A = 6.02 \times 10^{23}$ mol^{-1}, M_w = weight average molecular weight, V_p = volume occupied by a particle calculated from D_w and corrected for a volume of surfactant assumed to be a monolayer, d = density of particle measured by pycnometry to be 1.18 g cm^{-3}, and 100% conversion of monomer to polymer was assumed. Full and coworkers[23] used the number-average radius and weight-average molecular weights in their similar calculations and, in some cases, obtained $n_p < 1$, which is physically impossible. Gan and coworkers[22] used the z-average radius from dynamic light scattering and M_w for their calculations of n_p. The results reported in Table 3 show $n_p < 2$ for most of the latexes produced using cationic surfactants and $S \geq 1$. Lesser S ratios gave larger particles and $n_p > 2$, and the combination of STAC with hydrogen peroxide/ascorbic acid gave much larger n_p values due to lower molecular weights (Table 4).

The particle sizes and molecular weight distributions of two samples having n_p values of 1.2 and 1.0 are superimposed in Figure 5. In the limit of exactly one macromolecule per particle, the size distributions measured by TEM and the molecular weight distributions should be identical, and they are to a first approximation for these samples.

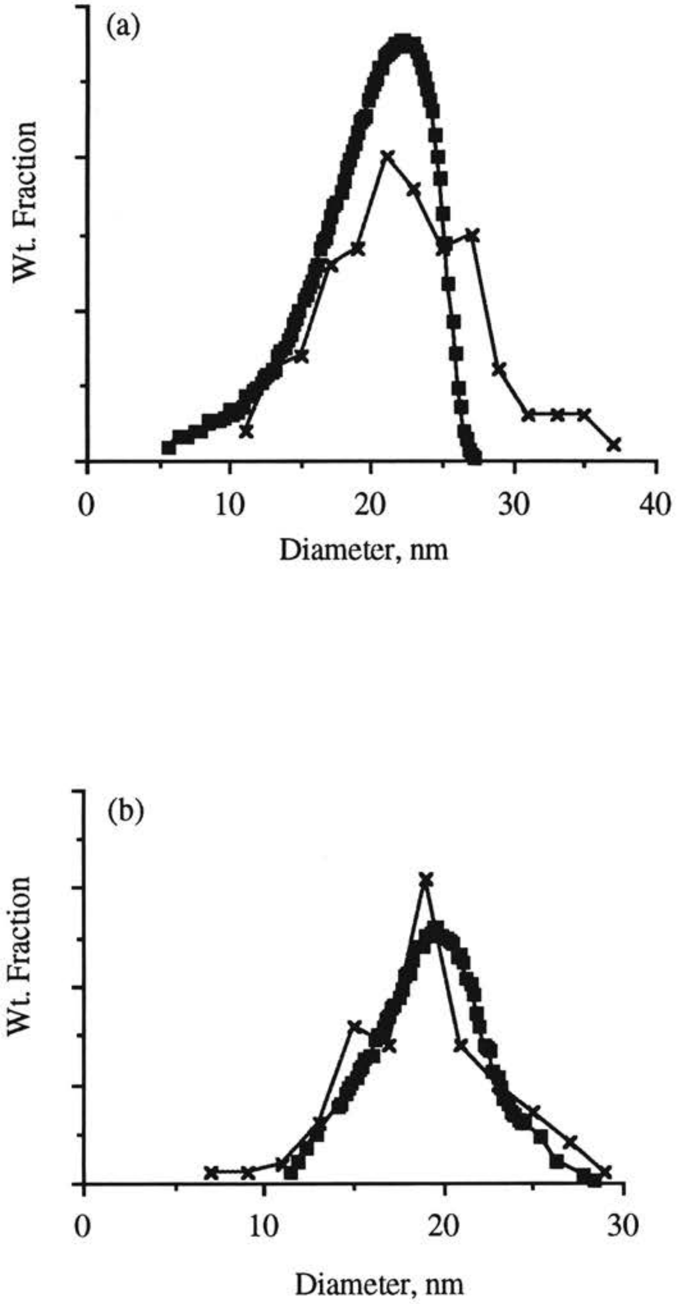


Figure 5. Particle size distributions as weight fraction vs. particle diameter from TEM measurements (x symbols) and from SEC molecular weights (square symbols) converted to particle diameter assuming $d = 1.20$ g cm^{-3} for samples (a) STAC-KPS, $S = 3$, $n_p = 1.0$, and (b) CTAB-KPS, $S = 3$, $n_p = 1.0$. Each graph is normalized so that the two distributions have equal areas.

Tacticity of PMMA. The chemical shift of the α–methyl protons on the backbone of poly(methyl methacrylate) is dependent upon the configuration of the polymer. From the differing chemical shifts, one can measure the integration region of each peak and determine the microstructure of the polymer. The tacticities of the PMMA samples were analyzed to the triad level from ^{1}H NMR spectra of $CDCl_3$ solutions by measuring the integrated areas of the syndiotactic, isotactic, and atactic triads (*rr*, *mm*, and *mr* shown on the sample spectrum in Figure 6). The tacticity results are reported along with the glass transition temperatures in Table 5. (Error limits are ± 0.01 for tacticities and ± 1 °C for T_g). The samples prepared in microemulsions are more highly syndiotactic (58-65% *rr*) than commercial PMMA (~43% *rr*). Surprisingly, however, the tacticity did not vary with the surfactant to monomer ratio, indicating that the microstructure of the polymer is not dependent upon the size of the initial microdroplet. Even the PMMA produced in a normal emulsion ($S = 0.01$) was determined to be ~60% syndiotactic. The tacticity was dependent on the polymerization temperature. The percent of syndiotactic triads increased with decreasing polymerization temperature, from 58-60% *rr* at 60 °C to 63-65% *rr* at 35 °C.

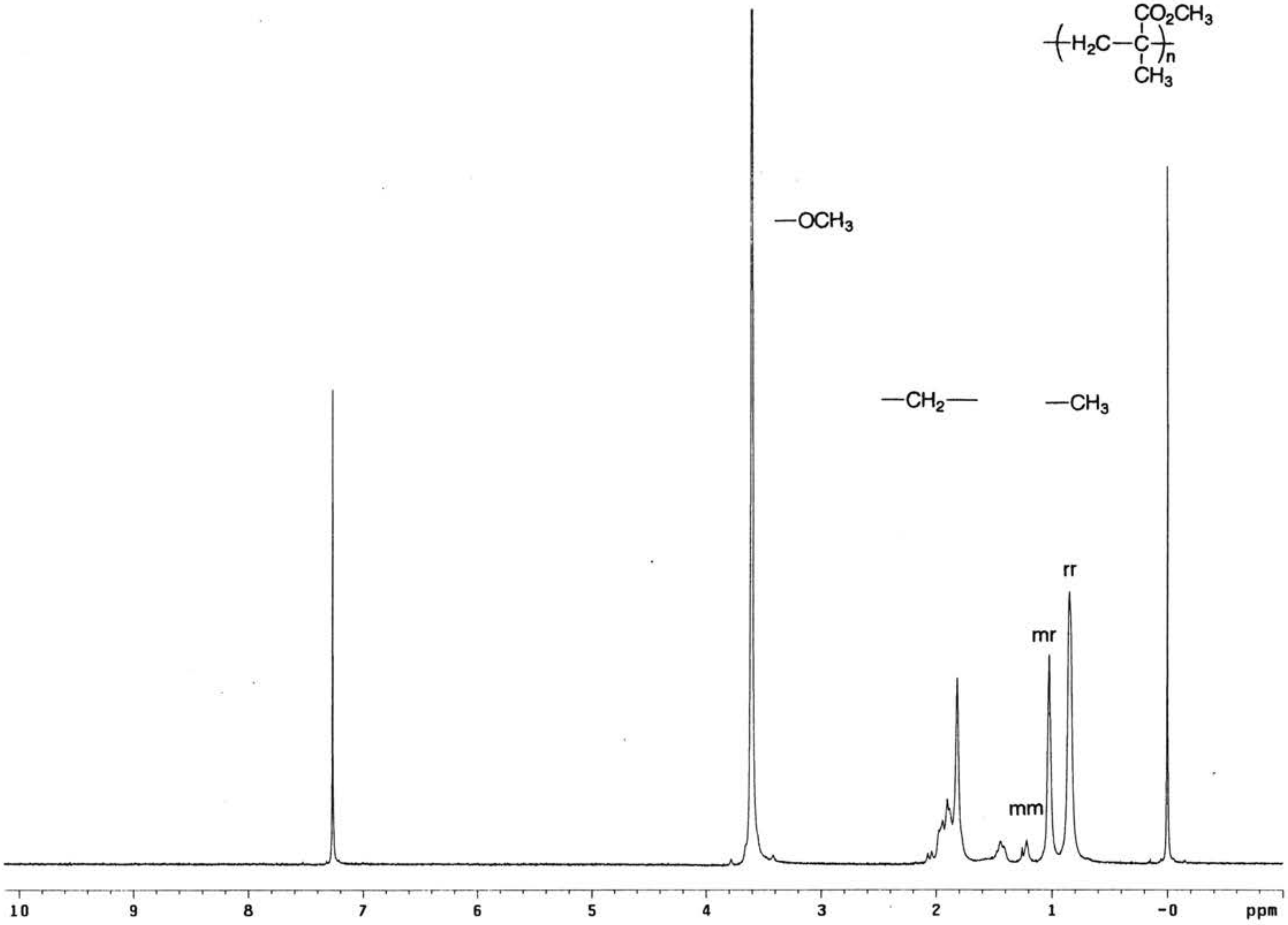


Figure 6. ^{1}H NMR spectrum of PMMA (CTAB-KPS at *S* = 3).

Table 5. Tacticities and Glass Transition Temperatures[a]

Sample[b]	*rr*	*mr*	*mm*	T_g, °C
Plexiglas®	0.43	0.40	0.17	105
STAC-Redox	0.58	0.30	0.12	114
Tritons-Redox	0.66	0.31	0.03	123
STAC-KPS				
S = 0.01	0.60	0.35	0.05	122
S = 0.1	0.60	0.35	0.05	126
S = 0.5	0.59	0.34	0.07	-
S = 1	0.59	0.35	0.06	125
S = 2	0.59	0.35	0.06	-
S = 3	0.59	0.35	0.06	126
STAC-AIBN				
S = 0.1	0.61	0.32	0.07	-
S = 0.5	0.61	0.35	0.04	126
S = 1	0.60	0.35	0.05	126
S = 2	0.58	0.34	0.08	-
S = 3	0.60	0.35	0.05	125
CTAB-KPS				
S = 0.1	0.61	0.33	0.06	-
S = 0.5	0.61	0.34	0.05	125
S = 1	0.61	0.34	0.05	125
S = 2	0.60	0.35	0.05	-
S = 3	0.59	0.35	0.06	126
STAC-Redox				
S = 0.01	0.65	0.32	0.03	125
S = 0.1	0.66	0.31	0.03	124
S = 0.5	0.64	0.32	0.04	122
S = 1	0.64	0.32	0.04	122
S = 2	0.63	0.32	0.05	121
Triton-Redox				
S = 1	0.64	0.32	0.04	125
S = 2	0.64	0.32	0.04	126
S = 3	0.63	0.32	0.05	126

Glass Transition Temperatures. Table 5 reports the T_g values. Samples prepared in microemulsions at either 60 °C or 35 °C have T_g = 125-126 °C. The glass transition temperature of a PMMA sample is dependent on the tacticity of the polymer sample. This explains why the polymers prepared at 35 °C that were ~65% syndiotactic would have a higher T_g, but it does not explain the higher T_g's of the PMMA prepared at higher temperatures with a lower syndiotactic content.

The lower molecular weight samples obtained using STAC and hydrogen peroxide/ascorbic acid had slightly lower T_g's (~122 °C), but none are close to the T_g = 105 °C of the commercial PMMA, which was 43% *rr*. A bulk polymerized sample of PMMA prepared using photoinitiation with 2,2-dimethoxy-2-phenylacetophenone was found to have a T_g = 117 °C. Sample thermograms are shown in Figures 7, 8, and 9.

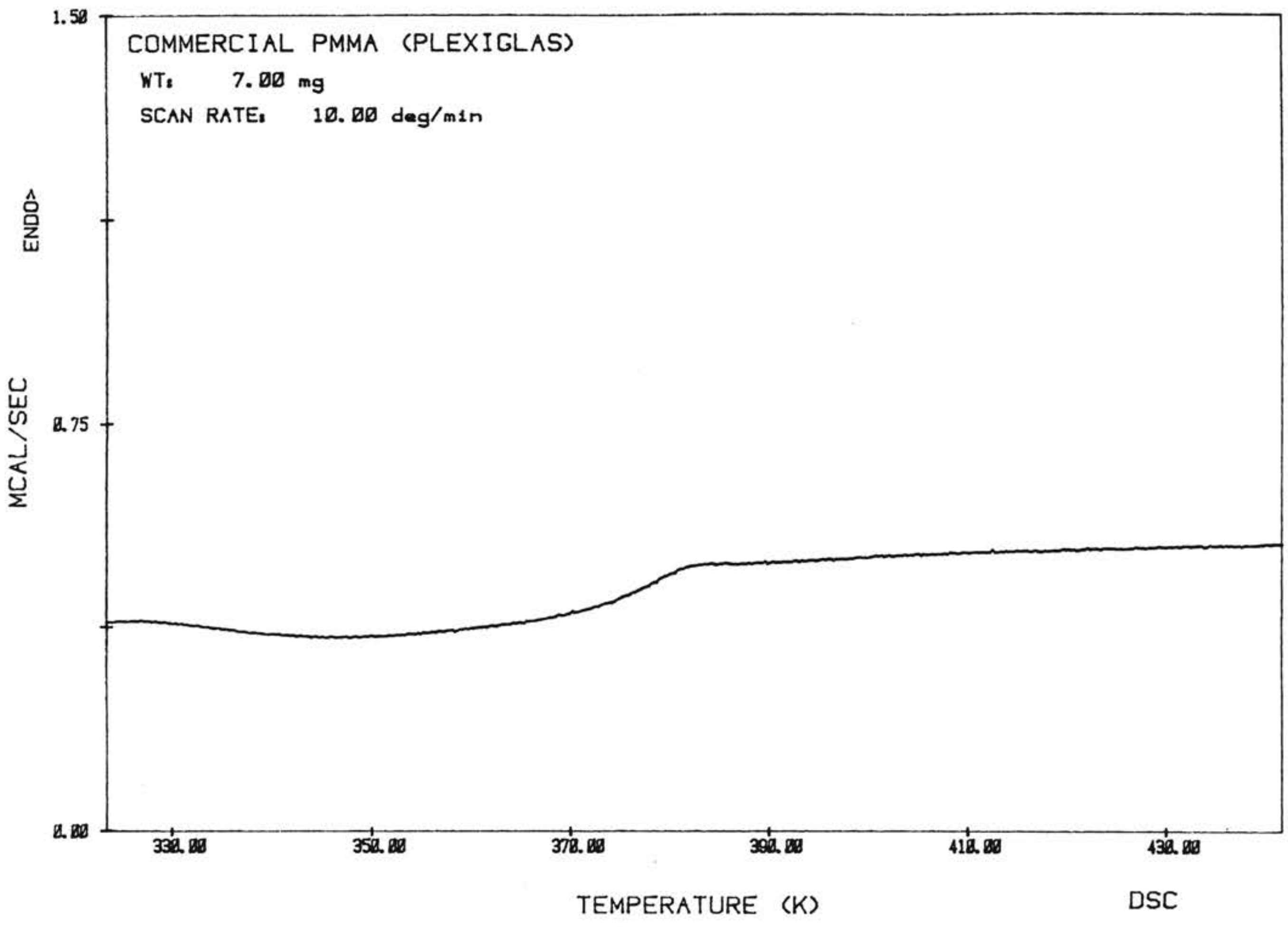


Figure 7. DSC thermogram of Plexiglas®.

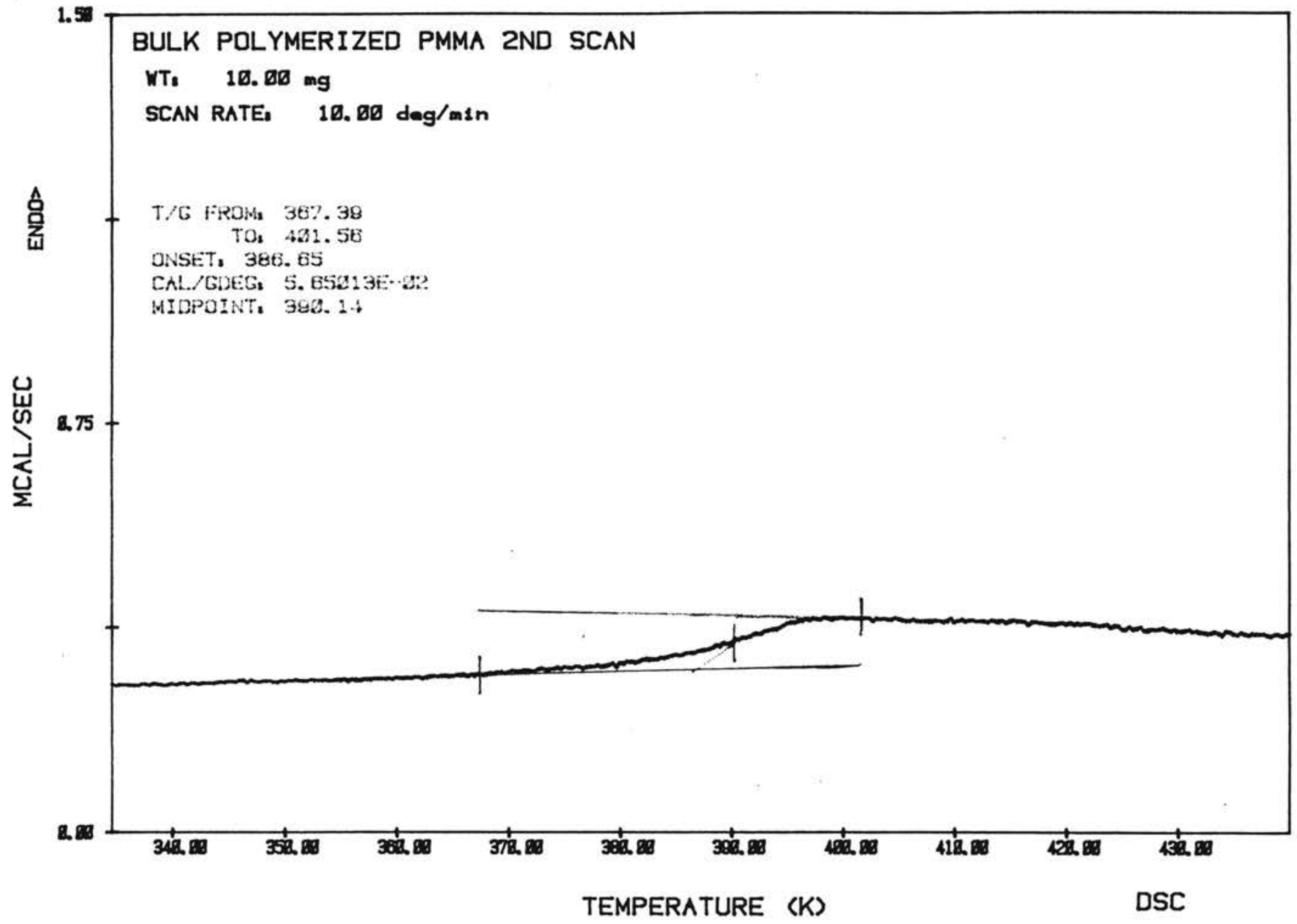


Figure 8. DSC thermogram of PMMA prepared from a bulk polymerization.

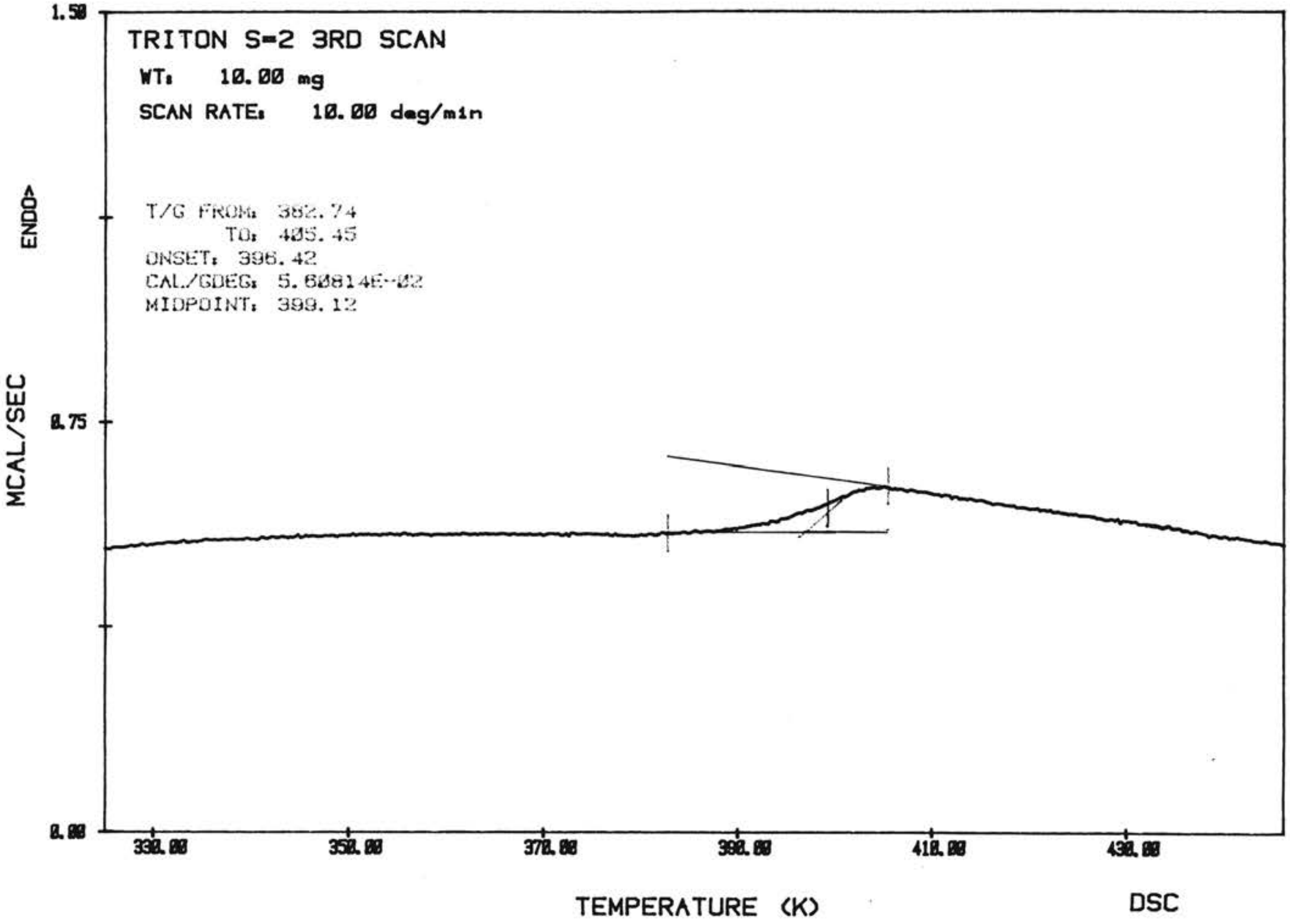


Figure 9. DSC thermogram of PMMA prepared in a microemulsion (Triton *S* = 2).

Discussion

Mechanism of Particle Formation. The present understanding of the mechanisms of polymerization in microemulsions has developed from contributions from several research groups,[10,21,24] and has been elaborated in most detail by Morgan, Lusvardi, and Kaler[24] to explain polymerizations in pseudo-ternary mixtures of hexyl methacrylate, dodecyltrimethylammonium bromide/didocecyldimethylammonium bromide, and water. Their discussion is particularly relevant to my results because it explains formation of particles containing only one polymer chain as follows.

(1) Initial conditions. The starting microemulsions containing $S \geq 1$ consist of monomer-swollen surfactant micelles, which are about 6 nm in diameter according to SANS (small angle neutron scattering) measurements of ternary microemulsions of styrene, cationic surfactant, and water.[20,23] The number of micelles increases with increasing surfactant concentration, and the size of the micelles may decrease slightly with increasing S because of decreasing amount of monomer per micelle.

(2) Initiation. Both water-soluble KPS and oil-soluble AIBN initiate polymerization. The final particle sizes and molecular weights of the PMMA do not depend significantly on the initiator, as shown in Table 2. Radicals generated in the aqueous phase from KPS initiate polymerization of MMA in the water. Oligomeric PMMA radicals are captured by monomer-swollen micelles, where polymerization continues to high molecular weight. Because of the small volume of the polymerizing particle, two radicals in one particle would result in fast termination. AIBN forms a pair of 2-cyano-2-propyl radicals in the organic phase, and can initiate polymerization only when one of the radicals escapes the micelle, leaving behind one radical for polymer chain growth. The escaped radical can then initiate chain growth in the aqueous phase or in another micelle.

(3) Particle size and molecular weight. The product particles are 20-30 nm in diameter, much larger than the ~6 nm diameter of starting micelles,[23] and yet many of them contain only one macromolecule. Growth of more than one polymer molecule in a particle is uncommon because at all times the number of uninitiated monomer-swollen micelles greatly exceeds the number of polymer particles, and, consequently, there is a high probability that a new polymer chain will start in a micelle rather than in a polymer particle. The particle size and molecular weight are independent of the surfactant to monomer ratio at $S \geq 1$, and are controlled by chain transfer to monomer or to surfactant. A 6 nm diameter micelle containing 50 wt % of MMA accounts for 30 000 amu of MMA, whereas the final molecular weight is often $M_w = 4\ 500\ 000$. Therefore, a large amount of monomer must be transported into the particle from uninitiated micelles during growth of a single polymer chain. The time required for growth of PMMA chains of molecular weights 1-10 x 10^6, calculated from the propagation rate constant and local concentration of monomer in the growing particle, is on the order of 10-100 s. The molecular weight and particle size are controlled by chain transfer to monomer or surfactant. To account for one chain per particle, the new monomeric or surfactant radical escapes from the particle into the aqueous phase. The high probability of escape of small radicals from micelles also explains why the oil-soluble initiator AIBN leads to polymers having the same particle size and molecular weight as the polymers from a water-soluble initiator. In the aqueous phase, a small radical originating in the oil or aqueous phase either terminates by reaction with another radical or enters a micelle and initiates a new chain polymerization.

(4) Termination of the chain reaction. If a growing polymer radical traps a small radical from the aqueous phase, or if AIBN produces new radicals in an already growing particle, fast diffusion-controlled termination results. Although termination of PMMA occurs by both combination and disproportionation, both types of termination reactions of a polymer radical and a small radical produce one macromolecule and one small molecule. Most termination of kinetic chains must occur in the aqueous phase. The probability of termination in a polymer particle is low because the probability of a radical from the aqueous phase entering a growing particle, rather than an unitiated micelle, is low.

(5) Product mixture. After polymerization is completed, the mixture consists of 20-30 nm diameter, surfactant-coated PMMA particles and a larger number of much smaller surfactant micelles, as observed using SANS[20,23] for polymerization of styrene in a dodecyltrimethylammonium bromide/water microemulsion.

Tacticity of PMMA. One goal of this investigation was to determine how polymerization in the confined three-dimensional space of a microemulsion affected the tacticity of the polymer chain. PMMA was studied because its tacticity is known to vary greatly with the temperature of radical polymerization. The microstructure of the polymer chain depends on the free energies of activation of the propagation steps for conversion of the radical end of a PMMA chain to new stereocenters. The penpenultimate, as well as the penultimate stereocenter, of a growing PMMA chain in solution influences the configuration of the new stereocenter.[42] In a microemulsion the growing chain end could be located in a monomer/polymer mixture in the core of the particle or at the surface in contact with surfactant and perhaps water as well as monomer. If the solvent were to influence the stereochemistry of propagation, one might expect altered tacticity from polymerization in a microemulsion because the surfactant environment at the surface of a particle is considerably different from the usual bulk monomer/polymer mixture. However, at the diad level, a tacticity of $76 \pm 1\%$ r has been reported to be independent of conversion and independent of solvents ranging from ethanol to benzene.[43] We also note that the conformation of a polymer chain in a microemulsion is more compact than its usual random coil conformation. A random coil of PMMA of molecular weight 1 x 10^6 has an unperturbed root-mean-square end-to-end distance of 55 nm in bulk,[35] compared with a diameter of 13.8 nm of a compact particle of one polymer chain, assuming that the density of the single macromolecule is the same as that of bulk glassy PMMA. The compact size requires more gauche conformations in the polymer chain. More gauche conformations near the end of a growing polymer chain may influence the probability of formation of *meso* and *racemic* diads. Thus there are several reasons why the tacticity of PMMA formed in a microemulsion might differ from that formed in bulk.

The experimental results, however, show that the tacticity of the PMMA at the triad level does not depend on the type or hydrophobic chain length of the surfactant or on the surfactant to monomer ratio over a range of compositions from conventional latexes formed when $S = 0.01$ to microemulsion latexes formed when $S \geq 1$. Possible reasons for this lack of variation of tacticity with the composition of the polymerizing mixture are (1) the primary locus of propagation could be in the bulk of the particle or (2) the tacticity of the chain is not affected by the environment of the particle surface.

Temperature is the one factor that does affect the tacticity of PMMA formed by radical polymerization (Figure 10). The syndiotactic content of the PMMA was higher when polymerized at 35 °C than that of the PMMA prepared at 60 °C. A commercial PMMA sample taken from a sheet of Plexiglas® was found to be 43% *rr*, much less syndiotactic than any of the samples prepared in emulsions and microemulsions. The strong temperature effect on tacticity suggests that the commercial material was formed at high temperature, perhaps on the order of 200 °C.

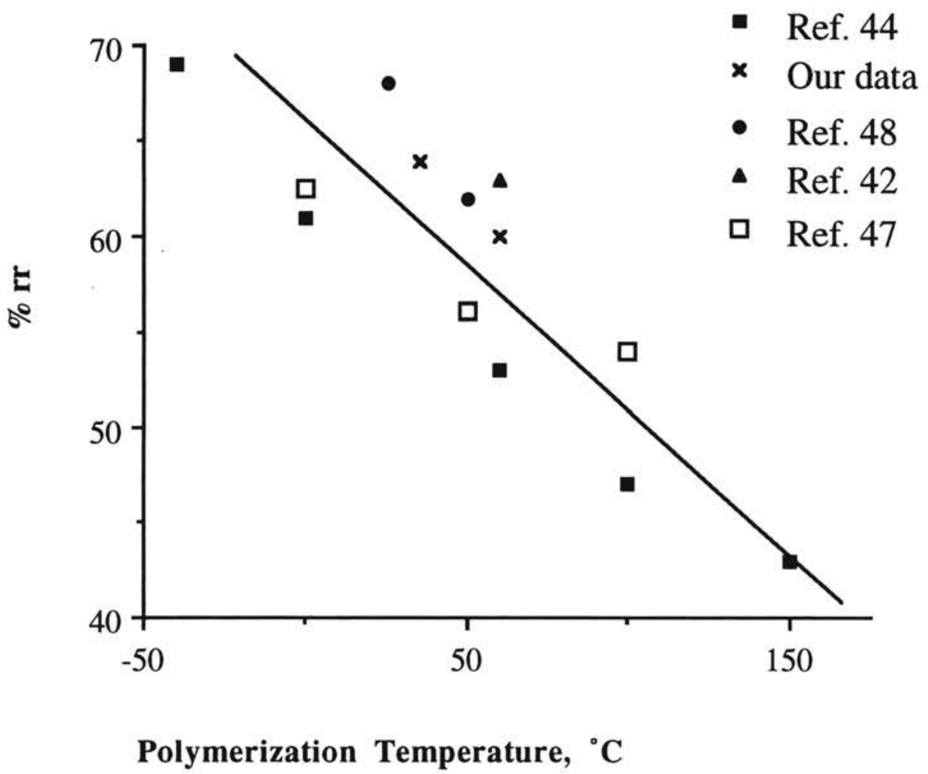


Figure 10. Tacticities of PMMA formed by radical chain polymerization as a function of temperature during polymerization.

Glass Transition Temperatures. The glass transition temperature of PMMA depends on the conformation of the polymer chain. The T_g of PMMA changes from 43 °C for an isotactic sample to 160 °C extrapolated for pure syndiotactic PMMA.[40] Wittman and Kovacs found a T_g = 41 °C for an isotactic sample (95% *mm*) and a T_g = 120 °C for a syndiotactic sample (70% *rr*).[39] The PMMA samples prepared in microemulsions at 60 °C consistently had T_g = 125-126 °C, which is higher than what is commonly seen for 60% *rr* PMMA samples. The measured T_g's are much higher than the standard values of 105-107 °C commonly cited in textbooks and in the *Polymer Handbook.*[50] These differences cannot be due to the high molecular weight of our samples because there should be little effect of molecular weight on T_g when $M > 10^5$.[51] A more careful selection of recent reports of the T_g of PMMA indicate that the usual value for materials from bulk polymerization is about 115 °C.[52] Figure 11 shows T_g vs. tacticity from our results and from various literature reports in which both T_g and tacticity are reported, and the molecular weight is high enough for T_g to be close to its upper limit. Not surprisingly, there is considerable scatter in the correlation of T_g with tacticity when the data come from many sources, but the T_g values of our PMMA samples are higher than usual for 60% *rr* samples.

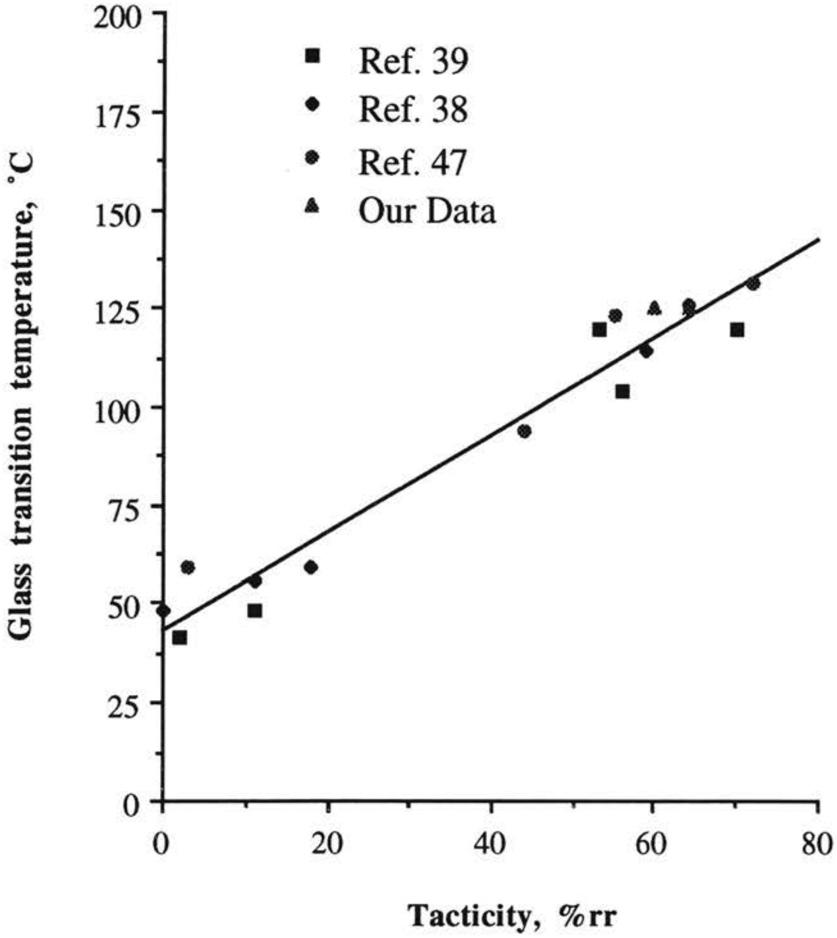


Figure 11. The T_g's of high molecular weight PMMA as a function of the tacticity.

One possible reason for the high T_g observed for the microemulsion prepared polymers is that a single precipitation into methanol removed low molecular weight components that would depress T_g. Dialysis was attempted as an alternative method for purification. The latex solution was dialyzed for two weeks, and then the water was evaporated off. The recovered polymer displayed glass transitions at 116 °C, 120 °C, and 111 °C for the first, second, and third scans, respectively. These results were not in agreement with previous DSC scans where the second and third scans did not differ by more than a degree. The former was due to surfactant still remaining in the sample, which was confirmed by ^1H NMR.

A PMMA sample that was prepared in bulk by photoinitiation at 35 °C ($M_w = 2.2 \times 10^5$ g/mole) was found to have a $T_g = 117$ °C before and a $T_g = 121$ °C after reprecipitation of the polymer from chloroform into hexane. This verifies that methanol removes low molecular weight components that depress T_g. Reprecipitations of two samples which had $T_g = 126$ °C (CTAB, $S = 3$ and STAC/KPS, $S = 2$) from chloroform into hexane (a method that should produce highly entangled chains) gave PMMA with $T_g = 122$ and 123 °C, respectively. Thus the samples first isolated from microemulsions have a T_g value 3-4 °C higher than they do after reprecipitation. It appears that fractionation is not the reason for the higher T_g's observed for the microemulsion prepared samples.

A more interesting possiblity for the difference between the samples formed in microemulsions and all of the other samples is the more compact conformations required by confinement of a $M > 10^6$ PMMA chain in a single particle. Single chain polystyrene prepared in a microemulsion was found to differ spectroscopically and thermally from ordinary polysytrene.[53] Precipitation of the glassy particles of the PMMA microemulsion into methanol at room temperature should not mix the polymer chains appreciably. The T_g values of the PMMA samples are from the second, third, and fourth DSC scans from 25 °C to 175 °C at 10 deg min^{-1}. The samples were cooled rapidly as soon as they reached 175 °C. If the isolated chains of PMMA have higher T_g, the chains must not mix during the series of T_g measurements. Consequently, a sample was annealed at 175 °C in the DSC. The T_g was still 125 °C after 14 hours and decreased only to 124 °C after 72 hours annealing at 175 °C. The sample pan was then opened to reveal the polymer was powdery indicating that the polymer did not flow together. Thus the evidence points to higher T_g of the single chain particles, but not beyond a reasonable doubt.

Another possibility is that the chains are so conformationally restricted and entangled that the chains, in effect, form knotted structures (i.e. the polymer chain ties itself into a knot). A microemulsion prepared PMMA sample (STAC-KPS $S = 2$) was dissolved in THF at room temperature and was analyzed by SEC over a period of ten days. The molecular weight distribution did not change and evidence for "unknotting" of the polymer chain was not obtained. (Note: This experiment was performed by Tom Mourey at Eastman-Kodak Labs).

Puig and coworkers discovered that core-shell polymers of styrene and butyl acrylate prepared in a microemulsion were harder and more rigid than core-shell polymers of similar composition made by emulsion polymerization.[54] They concluded that this behavior was most likely the result of the higher specific-surface area of the microemulsion-prepared polymers. Thus the higher glass transition temperature could be due to the increased surface area obtained by polymerization in a microemulsion.

To determine if any other properties were different, the density of a single-chain microemulsion-prepared sample (STAC-KPS $S = 3$) was measured by pycnometry. The density was found to be 1.196 g/mL which does not vary significantly from that in the Polymer Handbook (1.20 g/mL). Spectroscopic differences in the infrared spectrum were not observed between a single chain PMMA sample (STAC-KPS $S = 3$) and a PMMA sample that was prepared in bulk by photoinitiation.

Commercial samples of PMMA, such as a cell cast sheet, typically have a T_g of about 105 °C. The highest T_g of a commercial PMMA is about 115 °C.[55] An economical process for polymerization of PMMA having T_g around 125 °C, like the PMMA produced in the microemulsions, would be important commercially. The major economic problem with PMMA from microemulsions is the cost to recover a large amount of surfactant after the polymerization is complete.

Conclusions

Polymerizations of MMA in ternary microemulsions containing alkyltrimethylammonium halide surfactants produce 20-30 nm diameter latex particles consisting of one macromolecule when the surfactant to MMA weight ratio is at least one. STAC produced the most stable latexes when compared to other cationic surfactants that were used. The water-soluble potassium persulfate and the oil-soluble AIBN initiators gave the same results, which are consistent with a model in which the molecular weight and size of the single macromolecule particle are controlled by chain transfer to monomer and escape of the monomer radical from the particle. The triad tacticities of the PMMA formed in the microemulsions are 58-61% *rr* at 60 °C and 63-65% *rr* at 35 °C and do not depend on surfactant structure, surfactant to monomer weight ratio, or water-soluble versus oil-soluble initiator. The T_g values of the PMMA formed in both the emulsions and the microemulsions are 125 °C, higher than those of PMMA of the same tacticity produced by bulk or solution polymerizations.

References

1. Gilbert, R. G. *Emulsion Polymerization: A Mechanistic Approach*; Academic Press: London 1995, p 12.

2. Lovell, P. A.; El-Aasser, M. S. *Emulsion Polymerization and Emulsion Polymers*; Wiley: New York 1997, p 723-741.

3. Candau, F. In *Polymerization in Organized Media*; Paleos, C. M., Ed.; Gordon and Breach: Philadelphia, 1992, p 215-282.

4. Antonietti, M.; Basten, R.; Lohmann, S. *Macromol. Chem. Phys.* **1995**, *196*, 441.

5. Stoffer, J. O.; Bone, T. *J. Polym. Sci.: Polym. Chem. Ed.* **1980**, *18*, 2641.

6. Atik, S.; Thomas, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 4515.

7. Kuo, P.-L.; Turro, N. J.; Tseng, C.-M.; El-Aaser, M. S.; Vanderhoff, J. W. *Macromolecules* **1987**, *20*, 1216.

8. Guo, J. S.; El-Aasser, M. S.; Vanderhoff, J. W. *J. Polym. Sci.: Part A: Polym Chem.* **1989**, *27*, 691.

9. Guo, J. S.; Sudol, E. D.; Vanderhoff, J. W.; El-Aasser, M. S. *J. Polym. Sci. Part A: Polym. Chem.* **1992**, *30*, 691.

10. Guo, J. S.; Sudol, E. D.; Vanderhoff, J. W.; El-Aasser, M. S. *J. Polym. Sci. Part A: Polym. Chem.* **1992**, *30*, 703.

11. Kaler, E. W.; Pérez-Luna, V. H.; Puig, L. E.; Castaño, V. M.; Rodriquez, B. E.; Murthy, A. K. *Langmuir* **1990**, *6*, 1040.

12. Larpent, C.; Tadros, T. F. *Coll. Polym. Sci.* **1991**, *269*, 1171.

13. Antonietti, M.; Bremser, W.; Müschenborn, D.; Rosenauer, C. *Macromolecules* **1991**, *24*, 6636.

14. Antonietti, M.; Lohmann, S.; Van Niel, C. *Macromolecules* **1992**, *25*, 1139.

15. Full, A. P.; Puig, J. E.; Gron, L. U.; Kaler, E. W.; Minter, J. R.; Mourey, T. H.; Texter, J. *Macromolecules* **1992**, *25*, 5157.

16. Rodríquez-Guadarrama, L. A.; Mendizábal, E.; Puig, J. E.; Kaler, E. W. *J. Appl. Polym. Sci.* **1993**, *48*, 2559.

17. Antonietti, M.; Basten, R.; Gröhn, F. *Langmuir* **1994**, *10*, 2488.

18. Antonietti, M; Nestl, T. *Macromol. Rapid Commun.* **1994**, *15*, 111.

19. Bleger, F.; Murthy, A. K.; Pla, F.; Kaler, E. W. *Macromolecules* **1994**, *27*, 2559.

20. Full, A. P.; Kaler, E. W. *Langmuir* **1994**, *10*, 2929.

21. Gan, L. M.; Lee, K. C.; Chew, C. H.; Ng, S. C. *Langmuir* **1995**, *11*, 449.

22. Gan, L. M.; Lee, K. C.; Chew, C. H.; Tok, E. S.; Ng, S. C. *J. Polym. Sci. Part A: Polym. Chem.* **1995**, *33*, 1161.

23. Full, A. P.; Kaler, E. W.; Arellano, J.; Puig, J. E. *Macromolecules* **1996**, *29*, 2764.

24. Morgan, J. D.; Lusvardi, K. M.; Kaler, E. W. *Macromolecules* **1997**, *30*, 1897.

25. Blumstein, A. *Adv. Macromol. Chem.* **1970**, *2*, 123.

26. Farina, M.; Giuseppe, D. S. *Encyclopedia of Polymer Science and Engineering;* Wiley: New York **1988**, *12*, 486.

27. Brown, J. F.; White, D. M. *J. Am. Chem. Soc.* **1960**, *82*, 5671.

28. White, D. M. *J. Am. Chem. Soc.* **1960**, *82*, 5678.

29. Allcock, H. R.; Silverberg, E. N.; Dudley, G. K. *Macromolecules* **1994**, *27*, 1033.

30. Tsutsumi, H.; Okanishi, K.; Miyata, M.; Takemoto, K. *J. Polym. Sci. Part A: Polym. Chem.* **1990**, *28*, 1527.

31. Minagawa, M.; Yamada, H.; Yamaguchi, K.; Yoshii, F. *Macromolecules* **1992**, *25*, 503.

32. Shimomura, M. *Progr. Polym. Sci.* **1993**, *18*, 295.

33. O'Haver, J. H.; Harwell, J. H.; O'Rear, E. A.; Snodgrass, L. J.; Waddell, W. H. *Langmuir* **1994**, *10*, 2588.

34. O'Brien, D. F. *Trends Polym. Sci.* **1994**, *2*, 183.

35. Brandrup, J.; Immergut, E. H. *Polymer Handbook, Third Ed.*, Wiley: New York, 1989, p VII/36.

36. Tonelli, A. E. *NMR Spectroscopy and Polymer Microstructure: The Conformational Connection*; VCH Publishers: New York, 1989.

37. Schilling, F. C.; Bovey, F. A.; Bruch, M.; Kozlowski, S. *Macromolecules* **1985**, *18*, 1418.

38. Thompson, E. V. *J. Polym. Sci. Part A-2:* **1966**, *4*, 199.

39. Wittmann, J. C.; Kovacs, A. J. *J. Polym. Sci. Part C* **1969**, *16*, 4443.

40. Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1968**, *1*, 537.

41. Lide, D. R. *CRC Handbook of Chemistry and Physics, 71st Ed.*, CRC Press: Boston, 1990, p 8-17.

42. Moad, G.; Soloman, D. H.; Spurling, T. H.; Johns, S. T.; Willing, R. I. *Aust. J. Chem.* **1986**, *39*, 43.

43. Fox, T. G.; Schnecko, H. W. *Polymer* **1963**, *3*, 575.

44. Otsu, T.; Yamada, B.; Imoto, M. *J. Macromol. Chem.* **1966**, *1*, 61.

45. Jasse, B.; Oultache, A. K.; Mounach, H.; Halary, J. L.; Monnerie, L. *J. Polym. Sci. Part B: Polym. Phys.* **1996**, *34*, 2007.

46. Jenkins, R.; Porter, R. S. *Polymer* **1982**, *23*, 105.

47. Bovey, F. A.; Tiers, G. V. D. *J. Polym. Sci.* **1960**, *44*, 173.

48. Turro, N. J.; Pierola, I. F.; Chung, C.-J. *J. Polym. Sci.: Polym. Chem. Ed.* **1980**, *18*, 2641.

49. Fernandez-Martin, F.; Fernandez-Pierola, I. J. *J. Polym. Sci.: Polym. Physics Ed.* **1981**, *19*, 1353.

50. Brandrup, J.; Immergut, E. H *Polymer Handbook, Third Ed.*, Wiley: New York, 1989, p VI/219.

51. Fox, T. G.; Loshaek, L. *J. Polym. Sci.* **1955**, *15*, 371.

52. Faivre, A.; David, L.; Vassoille, R.; Vigier, G.; Etienne, S.; Geissler, E. *Macromolecules* **1996**, *29*, 8387.

53. Qian, R.; Wu, L.; Shen, D.; Napper, D. H.; Mann, R. A.; Sangster, D. F. *Macromolecules* **1993**, *26*, 2950.

54. Aguiar, A.; Gonzalez-Villegas, S.; Rabelero, M.; Mendizabel, E.; Puig, J. E.; Dominquez, J. M.; Katime, I. *Macromolecules* **1999**, *32*, 6767.

55. Cholod, M., personal communication.

CHAPTER III

STRUCTURES AND PROPERTIES OF POLY(PHENYL METHACRYLATE) AND POLY(1-NAPHTHYL METHACRYLATE) PREPARED IN MICROEMULSIONS

Abstract

Phenyl methacrylate (PhMA) and 1-naphthyl methacrylate (1-NM) were polymerized in various microemulsions using stearyltrimethylammonium chloride (STAC), cetyltrimethylammonium bromide (CTAB), and a mixture of nonionic Triton surfactants to form latexes that were 20-30 nm in diameter as determined by dynamic light scattering (DLS) and transmission electron microscopy (TEM). The tacticity of PPhMA was approximately the same as the tacticity (~55% *rr*) of the PPhMA prepared in solution. Less syndiotactic configurations (~47% *rr*) were obtained for the polymerization of P-1-NM in microemulsions and in a solution of toluene. The weight average molecular weights were 1 x 10^6 and 5 x 10^5 g/mole for PPhMA and P-1-NM prepared in microemulsions, compared with 2.6 x 10^5 and 4 x 10^4 g/mole for the analogous polymers prepared in solutions of toluene. Both solution and microemulsion-prepared PPhMA samples displayed glass transition temperatures of 127 °C as measured by differential scanning calorimetry (DSC). The P-1-NM sample prepared in solution showed a glass transition at 129 °C, but the T_g was increased to 142 °C upon reprecipitation. Each microemulsion-prepared sample displayed glass transition temperatures of 145-146 °C.

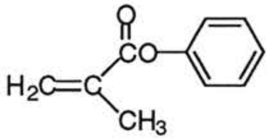
Introduction

A stable microemulsion, prior to polymerization, consists of extremely small droplets (~6 nm) of monomer in water that are larger than micelles but much smaller than the monomer droplets that are obtained in emulsion polymerization.[1] The resulting latex particles obtained from polymerization are often one order of magnitude smaller (10-30 nm in diameter) than those obtained with traditional emulsion polymerization techniques and contain only a few polymer chains.[2-8] Both emulsion and microemulsion polymerizations lead to a high molecular weight polymer and thus long polymer chains. The polymer chains must then be conformationally restricted to fit into the small volumes of the latex particles produced in a microemulsion polymerization.[8] Polymerization of monomers with bulky aromatic substituents in the restricted volume imposed by a microemulsion could lead to a change in the configuration of the polymer.

The stereochemical configuration of a polymer chain controls its physical properties, particularly its thermal properties as well as its mechanical behavior. Crystallinity, melting point, glass transition temperature, and solubility are among the properties that may depend on configuration. Spatial confinement of monomers in one dimension can markedly alter the stereochemistry of the polymer chain produced in the polymerization.[9] Likewise, a polymerization performed in the confined volume commanded by a microemulsion could lead to changes in the properties of the polymer.

The tacticity of poly(methyl methacrylate) prepared in microemulsions was not altered from that of PMMA prepared by free radical polymerization in bulk.[8] A syndiotactic polymer (~60% *rr*) was obtained in all polymerizations at 60 °C, regardless the surfactant to monomer ratio, and the polymer that was produced at 35 °C contained ~65% syndiotactic triads.[8] However, monomers with bulkier substituents may be affected by the confined volume. Methacrylic esters containing aromatic nuclei and other bulky substituents polymerized by free radical polymerization often form stereoregular structures that differ from those of PMMA.[10-27]

The polymers of phenyl methacrylate (**1**) have more random configurations when compared to PMMA due to the aromatic phenyl substituent.[10,11] A comparison of PPhMA and PMMA prepared under the same conditions (AIBN at 60 °C) is shown in Table 1.[11] Phenyl methacrylate (PhMA) should show a greater dependence upon confinement of the monomer than methyl methacrylate because phenyl methacrylate has a bulkier aromatic substituent. Although PPhMA prepared under identical conditions is less syndiotactic than standard PMMA, the syndiotactic content can be increased by lowering the polymerization temperature (Table 2).[12]



1

Table 1. Comparison of PMMA and PPhMA[a]

Polymer	*rr*	*mr*	*mm*
PMMA	0.64	0.32	0.04
PPhMA	0.50	0.41	0.09

[a]Polymers prepared in 1 M solutions of the monomer in benzene at 60 °C using AIBN. Data taken from reference 11.

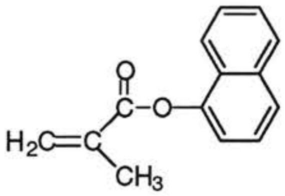
Table 2. The Tacticity of PPhMA Depends on Polymerization Temperature[a]

Temperature, °C	*rr*	*mr*	*mm*
30	0.52	0.39	0.09
50	0.49	0.42	0.09
80	0.46	0.46	0.08
100	0.44	0.47	0.09

[a]Polymerizations were performed in 3 M solutions of the monomer in benzene using AIBN (0.3 mol % monomer). Data are from reference 12.

Like phenyl methacrylate, the bulky aromatic substituent of 1-naphthyl methacrylate (**2**) also affects the kinetics of its radical polymerization[13,14] and the tacticity of the resultant polymer.[10,15] The aromatic substituent of 1-naphthyl methacrylate is responsible for the formation of a polymer with a more random configuration than PMMA polymerized under radical conditions (Table 3).[16]

Propagation may occur in bulk, giving the same tacticity as in bulk polymerization, or at the interface, where neighbors are surfactant molecules, tails, or head groups. If a solvent influences the stereochemistry of propagation, an altered tacticity could be expected because the surfactant environment at the surface of the particle is different from the usual bulk monomer/polymer mixture. The structures of the polymers of 1-naphthyl methacrylate are dependent on the solvent in which the solution polymerization is performed (Table 4).[17] One disadvantage is that 1-NM polymerizes at a lower rate and has a higher activation energy of polymerization than phenyl methacrylate.[13] During the solution polymerization in acetone and acetonitrile, the polymer precipitated out of solution.[17] Radical polymerization of 1-NM results in a polymer that is more atactic than the polymers obtained with 2-naphthyl methacrylate.[17] Thus 1-NM would more likely to be affected by polymerization in a microemulsion. 2-Naphthyl methacrylate is also a solid at room temperature and would be less adept for polymerization in a microemulsion. For these two reasons, only polymerizations with 1-naphthyl methacrylate were performed.



2

Table 3. Comparison of P-1-NM to PMMA[a]

Polymer	rr	mr	mm
PMMA	0.66	0.31	0.03
P-1-NM	0.45	0.45	0.10

[a]Data are from reference 16.

Table 4. The Tacticity of Poly(1-naphthyl methacrylate) Depends on the Polymerization Solvent[a]

Solvent	rr	mr	mm
average[b]	0.46	0.45	0.09
acetone	0.37	0.43	0.20
acetonitrile	0.34	0.43	0.23

[a]Data are from reference 17. [b]Average values from polymerizations carried out in benzene, cyclohexane, and hexane with AIBN at 60 °C.

Changing the configuration of polymethacrylates is very important in polymer syntheses to obtain polymers with different properties. For example, highly syndiotactic PMMA is desirable for industrial materials such as optical fibers and disks due to the increased glass transition temperature. Obtaining poly(1-naphthyl methacrylate) with a different configuration could be beneficial since the fluorescence intensity of the polymer is dependent upon the tacticity.[18] Polymers of 1-NM that contain a greater number of isotactic triads show higher values for the ratios of excimer to monomer fluorescence intensity than those with a smaller isotactic content.[18]

Phenyl methacrylate and 1-naphthyl methacrylate were polymerized in varying microemulsions to determine if both the stereochemistry and properties of the resultant polymers were affected by the confined volume. The particle sizes and molecular weights for each sample were then obtained and correlated with the components of the initial microemulsion. The microstructures and glass transition temperatures of the polymers formed in microemulsions were then compared to analogous polymers prepared in solution.

Experimental

Materials. Stearyltrimethylammonium chloride (STAC, >97%) and cetyltrimethylammonium bromide (CTAB, >98%) from TCI, sodium dodecylbenzenesulfonate (DBS) from Polysciences Inc., Triton N-150 from Union Carbide, and Triton N-57 from Aldrich were used as received. Potassium persulfate (KPS) from Sigma, 2,2'-azobis(2-methylpropionamidine) dihydrochloride (V-50) from Aldrich, ascorbic acid from Aldrich, 30% hydrogen peroxide solution from Fisher, potassium bicarbonate from Fisher, Diazald® (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide) from Aldrich, and *n*-pentane from Fisher were each used as received. 2,2'-Azobisisobutyronitrile (AIBN) from Aldrich was recrystallized from ethanol. Phenyl methacrylate (PhMA) and 1-naphthyl methacrylate (1-NM) from Monomer-Polymer and Dajac Labs were purified by passing the monomer through alumina followed by an additional base extraction with sodium hydroxide using pentane as the solvent to remove any traces of phenol or naphthol that may be present. The purities of the monomers were confirmed by ^{1}H NMR at 300 MHz in $CDCl_3$. Water was deionized and had resisitivity >1 Mohm-cm.

Solution Polymerizations of PhMA and 1-NM. A solution of 27.4 g of toluene, 10.0 g of PhMA, and 30 mg of AIBN contained in a glass tube was degassed by three successive freeze-thaw cycles and sealed off under high vacuum. The sealed tube was then submerged in a 70 °C oil bath for 18 hours. Adding the viscous solution dropwise to a beaker containing vigorously stirred methanol precipitated the polymer. The same method was followed for the solution polymerization of 1-naphthyl methacrylate with 10.0 g of toluene, 2.0 g of 1-NM, and 10.0 mg of AIBN.

Polymerization in Microemulsions. The compositions of the microemulsions that produced stable latex particles are summarized in Table 5. The following is the general procedure for polymerizations performed in microemulsions: To 2.40 g of STAC contained in a three-necked, 50 mL, round-bottomed flask equipped with a condenser, a mechanical stirrer, and a nitrogen inlet was added 29 mL of deionized water. The air in the flask was replaced by a stream of nitrogen, and the mixture was kept under nitrogen until the polymerization was finished. The flask was placed in a 70° C oil bath and the mixture was stirred for approximately one hour until a transparent microemulsion was obtained. PhMA (1.2 g) was added, and the solution was stirred for approximately one hour until a transparent microemulsion was obtained. A solution of 15.0 mg of V-50 dissolved in 1 mL of deionized water was added, and the dispersion was stirred 4 hours in an oil bath at 70°C to complete the polymerization. An odorless and transparent solution with a bluish tint was obtained indicating that the polymerization was complete. In the case of 1-naphthyl methacrylate, the resulting polymer latex solution was an orangish color with a bluish tint. The isolated polymer had a light brownish color that disappeared upon reprecipitation.

Table 5. Compositions of Various Microemulsions That Led to the Formation of Stable Latex Particles[a]

Sample	Amount, Surfactant	Amount, monomer	Amount, Initiator	% Polymer Recovered
1	4.62 g Triton N-150[b] 0.53 g Triton N-57	2.48 g PhMA	30 mg ascorbic acid 0.4 g 30% H_2O_2	93
2	2.44 g STAC[c]	1.24 g PhMA	15.0 mg V-50	85
3	2.45 g CTAB[c]	1.40 g PhMA	15.0 mg V-50	90
4	2.40 g STAC[c]	1.30 g PhMA	9.0 mg AIBN	87
5	2.43 g STAC[c]	0.93 g PhMA	10.0 mg KPS	82
6	2.42 g STAC[c]	1.22 g 1-NM	14.9 mg V-50	71
7	2.41 g STAC[c]	1.20 g 1-NM	15.0 mg V-50	72
8	2.36 g CTAB[c]	1.22 g 1-NM	15.1 mg V-50	87

[a] All mixtures contained 30 mL of water. [b] Polymerization performed at 35 °C. [c] Polymerization performed at 70 °C.

Particle Size Analyses. An aliquot of the latex was diluted 15:1 with deionized water. A drop of this sample was placed on a Formvar-coated Cu grid for 1 min, the excess latex was removed by touching a piece of filter paper to the drop, and the grid was dried in air for 1 min. A drop of 1% uranyl acetate solution was placed on the grid for 1 min to stain the sample, the excess solution was removed with filter paper, and the grid was dried in air. Transmission electron microscopy was performed using a JEOL 100-CS2 instrument with 100 μA filament current, 80 kV accelerating voltage, and the electron beam normal to the sample plane. Diameters of at least 50 randomly-chosen particles were measured directly from the micrograph negatives using an optical microscope with a calibrated stage. No size standards were used, and reported sizes were calculated from the nominal instrument magnification. Sample micrographs are shown in Figures 1 and 2. The number and weight average diameters were calculated using equations 1 and 2 where D_i is the diameter of a particle and n is the number of particles measured.

$$D_n = \Sigma D_i / \Sigma n \tag{1}$$

$$D_w = \Sigma D_i^4 / \Sigma D_i^3 \tag{2}$$

Particle sizes were also measured by dynamic light scattering (DLS). The signal from the scattered light of an Argon ion laser (Spectra-Physics 2020-05) was collected from latex samples diluted 20:1 at a scattering angle of 90° and analyzed using an ALV-5000 digital correlator.

Determination of Phase Boundaries. The following amounts of CTAB were added to test tubes (18 x 150 mm) to give the following surfactant to water concentrations: 0.05 g (1%), 0.10 g (2%), 0.15 g (3%), 0.20 g (4%), 0.26 g (5%), 0.36 g (7%), 0.41 g (8%), and 0.50 g (10%). To each of the test tubes were added 5 mL of deionized water and a small magnetic stirring bar. The top of the test tube was then covered with a piece of durafilm which was held in place with Scotch™ tape. The test tubes (grouped in groups of four with a rubber band) were submerged in a 60 °C water bath that was placed on a Lab-Line™ Multi-Magnestir. A VWR Scientific™ water circulator was used to maintain the temperature of the water bath. A piece of styrofoam was used to hold the test tubes in place and insulate the water bath. A thermometer submerged into the water bath showed a temperature of 59 °C. To the test tubes were added aliquots of 0.05 mL of PhMA via a 100 μL syringe through a small hole created in the durafilm. The phase boundaries were determined visually by the point at which the addition of monomer turned the solution from colorless to slightly turbid. The procedure was repeated using STAC.

Isolation of Polymer and Removal of Surfactant. To precipitate the polymer, 5 mL of the latex particles was added dropwise to 50 mL of vigorously stirred methanol contained in an 100 mL beaker. The mixture was centrifuged, and the supernatant was decanted. Additional methanol was added, and again the supernatant was decanted. This procedure was repeated until the supernatant did not contain any residual surfactant as detected by ^{1}H NMR analyses. The polymer was then isolated by vacuum filtration and dried in a vacuum desiccator at 60°C for 24 hours.

Conversion to Polymethacrylic acid (PMAA). A poly(phenyl methacrylate) solution (0.1 mol/L) in concentrated sulfuric acid was stirred at room temperature for 200-300 hours. The solution was then added dropwise to 50 mL of ice water and set in an oven at 60°C for one hour to precipitate the polymer. The mixture was centrifuged, and the supernatant was decanted. The water-insoluble fraction was redissolved in methanol, and the solution was added dropwise to a beaker of vigorously stirred ether to reprecipitate the PMAA. The polymer was redissolved into a minimal amount of methanol, and the solution was added dropwise to a large excess of ether to ensure the removal of all of the sulfuric acid. The solid was isolated by centrifugation and dried in a vacuum desiccator at 60°C for 24 hours. Typical yields for the hydrolysis of PPhMA and P-1-NM were approximately 85%.

Methylation of PMAA by Diazomethane. A procedure patterned after that of Lombardi[28] was used for the conversion of polymethacrylic acid to poly(methyl methacrylate). To a 25 mL vacuum flask containing a magnetic stirring bar and equipped with a two-hole stopper was added 1.0 g of Diazald® suspended in 6 mL of ethanol. (It is assumed that 1 g of fresh Diazald generates 3 mmole of diazomethane). Nitrogen was passed through the system by a rubber hose that was connected to a piece of glass tubing through the stopper and beneath the liquid layer in the flask. The stopper also contained a septum for the addition of sodium hydroxide. The side arm of the flask was connected by a piece of tubing to a disposable pipet that was submerged in a 15 mL centrifuge tube containing 129 mg of PMAA suspended in chloroform and cooled in a beaker of ice water. As nitrogen was passed through the system, a sodium hydroxide solution (8 M) was added via a syringe until all the polymer had reacted into solution and the yellow color had disappeared from the flask indicating that all of the Diazald® was reacted. The PMMA was collected by precipitation into methanol. The polymer was isolated, redissolved into chloroform, and reprecipitated into methanol. The polymer was dried in a vacuum desiccator for 24 hours at 60°C. Typical yields of the polymer obtained from the methylation procedure were on the order of 50%. Some unreacted PMAA remained on the side of the centrifuge tube after the reaction. The unreacted polymer was responsible for the decreased yield.

Tactiicity Analyses. ^{1}H NMR analyses were performed at 300 MHz using $CDCl_3$ solutions at room temperature. The tacticities of the samples were measured from the integrated ratios of the α-methyl resonance of the sample for the syndiotactic (*rr*), atactic (*mr*), and isotactic triad (*mm*) signals.[12,29]

Glass Transition Temperatures. The T_g values of PPhMA were measured using a Perkin-Elmer Model DSC-2 differential scanning calorimeter and 10.0 mg samples at a scan rate of 10 deg/min from 300 to 450 K followed by rapid cooling. The instrument was calibrated with naphthalene (mp = 353.4 K) and indium (mp = 429.8 K). Since the T_g value from the first measurement of each sample often was higher than that from subsequent measurements, the T_g reported is the average of the second, third, and fourth scans using the midpoint method. The T_g values of the standards were reproducible to better than 0.2 K. The T_g values of independent samples from one polymerization was reproducible to ± 1 K. The T_g's of P-1-NM were measured using a Seiko DSC 6100 instrument at a scan rate of 10 K/min.

Molecular Weight Analyses. Molecular weights were measured by size exclusion chromatography (SEC) using a Mixed B 10 μm PLgel column from Polymer Laboratories at a flow rate of 1.0 mL/min at 40 °C in a Hewlett-Packard (HP) series 1100 chromatograph using UV detection at $\lambda = 218$ nm. The sample size injected was 20 μL of a 1.0 mg/mL solution in THF. The SEC was calibrated with polystyrene standards having molecular weights of 900 000, 390 000, and 17 500 in one solution and 600 000, 100 000, and 9 000 in a second solution. Molecular weights were calculated using the HP Chemstation software and a SEC Macro supplied by HP. Molecular weights of the derived PMMA were also measured and compared to the molecular weights obtained from the original polymer.

Results

Phase Boundaries. The phase boundaries for the surfactant/PPhMA/water mixtures were found to be approximately the same for CTAB and STAC. Test tubes containing surfactant at varying concentrations were examined visually upon the addition of aliquots of PPhMA at 60 °C. Addition of monomer was stopped after the solution became turbid. The results for the phase boundaries for STAC at varying concentrations are shown in Figure 1. All polymerizations were then performed within transparent regions of the microemulsion system, assuming that the phase behavior is the same at 70 °C as the phase boundaries at 60 °C. The polymerizations of 1-NM were also within the phase boundaries as evidenced by the optical transparency of the system. The compositions of the stable polymerized microemulsions that were obtained were summarized earlier in Table 5.

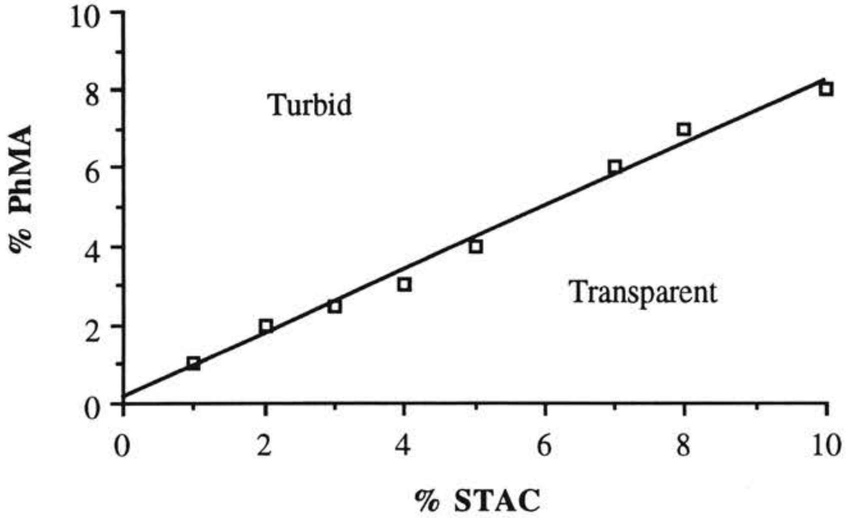


Figure 1. The weight percent of PhMA required to turn the dispersion from a transparent solution to a turbid solution at 60 °C.

Particle Sizes. Particle sizes of the PPhMA and P-1-NM latexes were determined by dynamic light scattering (DLS) and transmission electron microscopy (TEM) and are reported in Tables 6 and 7. Only particles with distinct borders that appeared in good focus were counted in the TEM measurements. Although obvious aggregates of the particles from the measurements were excluded, some aggregates may have been counted. Coagulated particles are counted in the DLS measurements. As a result, the diameters reported in Tables 6 and 7 are upper limits, and there is not always good agreement between the TEM and the DLS results.

All particle sizes of the latexes produced were in the same range as the previous PMMA microemulsions (20-35 nm).[8] The PPhMA latexes prepared with the oil-soluble AIBN as the initiator were slightly larger than the PPhMA latexes prepared with a water soluble initiator (V-50). The P-1-NM latexes had particle sizes in the 20-40 nm range, smaller than the corresponding PPhMA polymer latexes. Sample 6 in Table 7 shows a larger particle size than sample 7 even though identical conditions were used in each polymerization. The difference may be due to the purity of the monomer used in each polymerization. The monomer used in samples 7 and 8 was passed through a longer column of alumina and as a consequence a purer monomer was obtained. The monomer from Aldrich was highly colored. Most of the color was removed by passing the monomer through alumina except the monomer used for sample 6 was still colored.

Table 6. Particle Sizes and Molecular Weights of PPhMA Formed in Microemulsions and Compared to a Solution Polymerized Sample

Sample	D_z, nm[a]	D_n, nm[b]	σ[c]	D_w/D_n	M_w g/mol	M_w/M_n	n_p
1	26	20	5.6	1.2	1.0×10^6	6.0	3.9
2	29	21	5.8	1.2	1.3×10^6	6.8	3.4
3	29	22	5.3	1.1	1.3×10^6	6.6	3.2
4	39	26	6.1	1.2	1.1×10^6	14.1	8.2
5	28	21	6.6	1.3	4.0×10^5	27.0	11.4
Solution	-	-	-	-	2.6×10^5	2.5	-

[a] DLS diameter using average from three scans resulted in particle sizes ± 0.2 nm. [b] Diameter using TEM. [c] Standard deviation for D_n.

Table 7. Particle Sizes of and Molecular Weights of P-1-NM Formed in Microemulsions and Compared to a Solution Polymerized Sample

Sample	D_z, nm[a]	D_n, nm[b]	σ[c]	D_w/D_n	M_w g/mol	M_w/M_n	n_p
6	23	24	12.0	1.6	3.8×10^5	17.1	45.4
7	22	18	6.8	1.4	5.2×10^5	18.5	7.6
8	27	16	5.2	1.2	6.4×10^5	24.3	3.2
Solution	-	-	-	-	4.0×10^4	3.8	-

[a] DLS diameter using average from three scans resulted in particle sizes ±0.2 nm. [b] Diameter using TEM. [c] Standard deviation for D_n.

Theoretically, dynamic light scattering provides larger particles sizes than those obtained with transmission electron microscopy. The light scattering data for the P-1-NM latexes indicated a smaller particle size. In this case, the light scattering results were taken immediately after polymerization, but the electron micrographs were not obtained until two weeks after the polymerization was complete. Thus the particle sizes taken from the electron micrographs included aggregates of the P-1-NM particles, and larger particle sizes were obtained. Sample micrographs for the samples are shown in Figures 2 and 3.

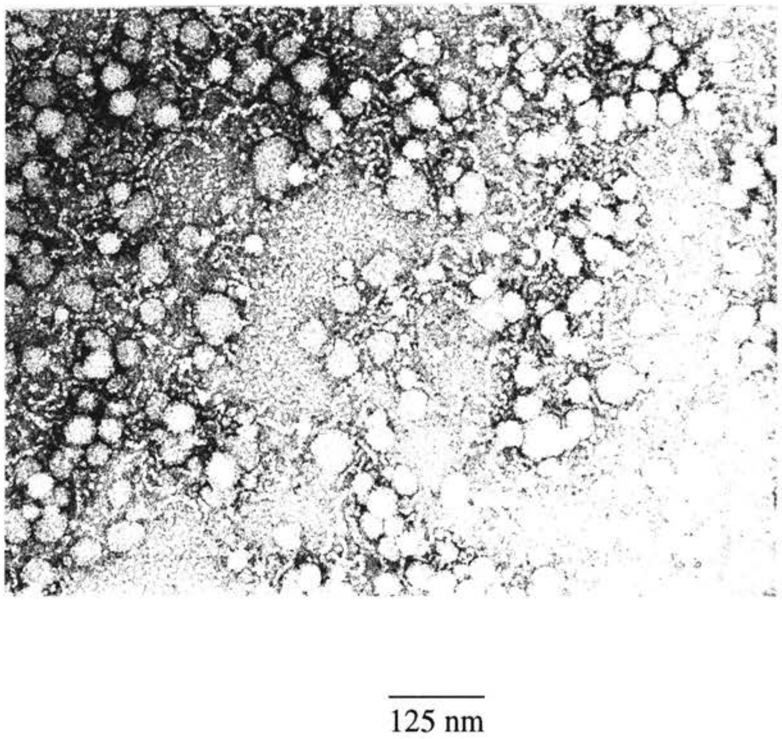


Figure 2. TEM for PhMA polymerized using STAC and V-50 at 70 °C (Sample 1).

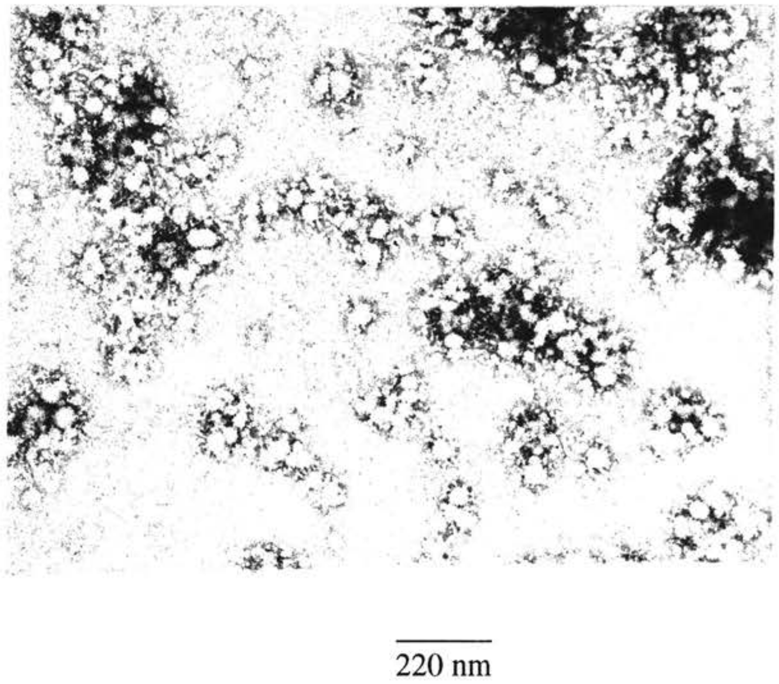


Figure 3. TEM of the P-1-NM latexes formed using STAC/V-50 at 70 °C (Sample 7).

Molecular Weights. Relatively high molecular weights (~1 x 10^6 g/mole) and broad molecular weight distributions were seen for all PPhMA samples and are reported in Table 6. The PPhMA sample prepared from a solution polymerization had a lower molecular weight of 3 x 10^5 g/mole. The P-1-NM samples prepared in microemulsions using V-50 (Table 7) had lower molecular weights (~5 x 10^5 g/mole) and broader molecular weight distributions than the polymers of PhMA prepared with V-50 (~1 x 10^6 g/mole). The P-1-NM samples prepared in microemulsions had a much higher molecular weight than the same polymer formed in solution (~3 x 10^4 g/mole). Sample chromatograms are shown in Figures 4 and 5. Molecular weight ranges are also reported on the x-axis along with the retention times. Repeated measurements are shown in Table 8 to illustrate the reproducibility of the obtained molecular weights. The measurements were taken on different days. The SEC was recalibrated each day with the same range of polystyrene standards. Some error is expected in the reported molecular weights since the instrument was calibrated with polystyrene standards and not corrected with Mark-Houwink constants.

Table 8. Repeated Measurements of the Molecular Weights Obtained for a Sample of PPhMA and P-1-NM

Description	M_w, g/mol	M_w/M_n
PPhMA/STAC/V-50	1.3 x 10^6	6.8
PPhMA/STAC/V-50	1.2 x 10^6	6.5
P-1-NM/STAC/V-50	5.2 x 10^5	18.5
P-1-NM/STAC/V-50	5.5 x 10^5	19.6
P-1-NM/STAC/V-50	5.6 x 10^5	19.2

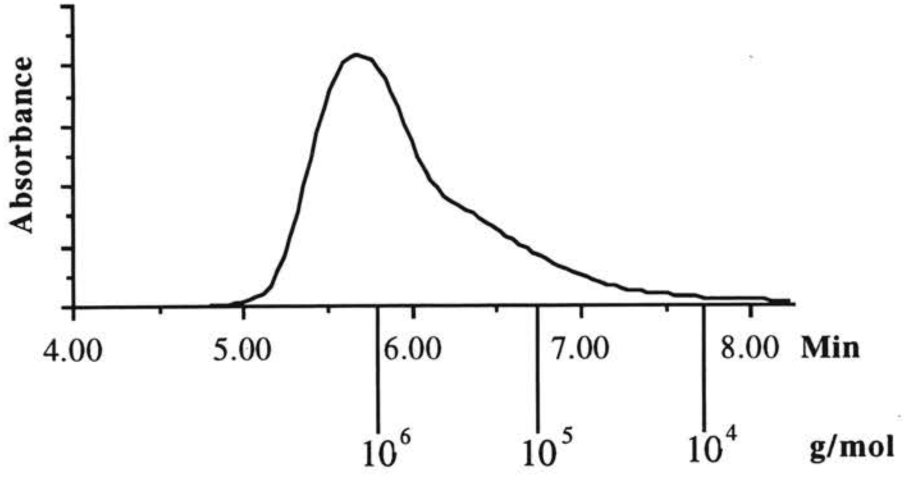


Figure 4. SEC chromatogram of PPhMA (Sample 2).

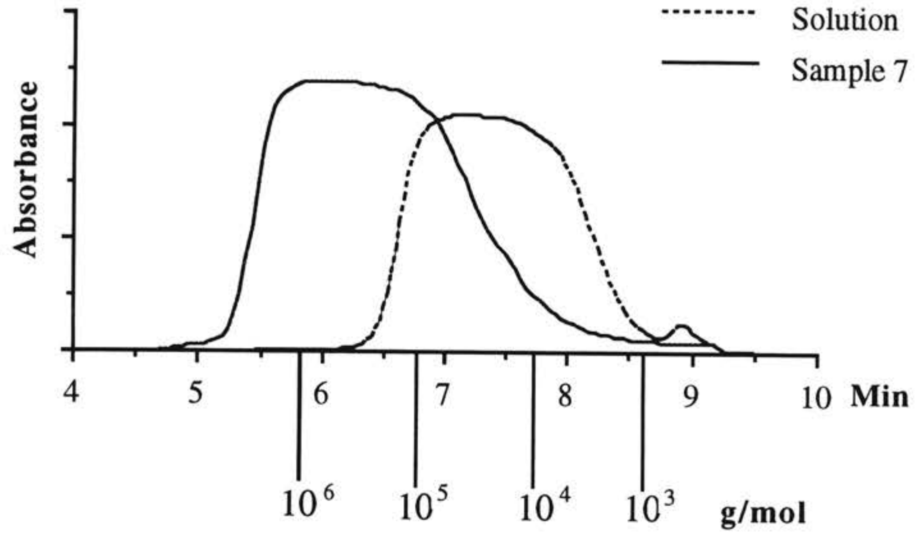


Figure 5. Overlaid SEC chromatograms illustrating the broad molecular weight distribution obtained for P-1-NM (Sample 7 and Solution-Prepared P-1-NM).

A portion of each PPhMA sample was converted to PMMA by hydrolysis in H_2SO_4 to poly(methacrylic acid) followed by esterification with diazomethane. A comparison of two of the PPhMA and the derived PMMA samples are reported in Table 9. Reliable measurements could not be extracted from the SEC analysis of the other derived PMMA samples due to increased baseline noise. PPhMA is expected to have a higher molecular weight due to the increased molar mass of the repeat unit (162 g/mol compared to 100 g/mol for MMA). The PMMA derived from the PPhMA sample prepared with the Triton surfactants (Sample 1) is in good agreement with the original PPhMA sample. The derived PMMA sample had $M_w = 7.7 \times 10^5$ g/mol. Using this molecular weight to calculate the degree of polymerization of the sample, the corresponding molecular weight of PPhMA is 1.2×10^6 g/mol compared to the 1.0×10^6 g/mol result obtained directly on the PPhMA. The slightly higher value is due to a lower molecular weight distribution ($M_w/M_n = 3.2$) obtained for the derived PMMA sample. As

Table 9. Molecular Weights of Two PPhMA Samples and the Corresponding Derived PMMA

Description	M_w, g/mol	M_n, g/mol
PPhMA (Sample 1)	1.0×10^6	1.7×10^5
PMMA[a] (Sample 1)	7.7×10^5	2.4×10^5
PPhMA (Sample 4)	1.1×10^6	7.7×10^4
PMMA[a] (Sample 4)	3.0×10^5	7.3×10^4

[a]Measured relative to polystyrene standards.

illustrated in Figure 4, the SEC chromatogram for the PPhMA is not perfectly Gaussian and contains a tail. This tail corresponds to low molecular weight polymer formed during the polymerization. PMMA is less absorbent in the UV detector used in the analysis and less tail is distinguished from baseline noise in the calculation of the molecular weight. Thus there is greater uncertainty in the molecular weight averages of the PMMA samples.

Number of Macromolecules per Latex Particle. The number of macromolecules per particle, n_p, was calculated for each PPhMA and P-1-NM sample from the weight average mass of a particle according to equations 3 and 4.

$$n_p = M_p N_A / M_w \qquad (3)$$

$$M_p = V_p d \qquad (4)$$

where M_p = mass of a particle, $N_A = 6.02 \times 10^{23}$ mol^{-1}, M_w = weight average molecular weight, V_p = volume occupied by a particle calculated from D_w and corrected for a volume of surfactant assumed to be a monolayer, and d = density of particle measured by pycnometry to be 1.22 g cm^{-3}. A conversion of monomer to polymer of 100% was assumed. The results reported in Tables 6 and 7 show $n_p > 3$ for all the PPhMA and P-1-NM. Larger n_p values were obtained when AIBN or KPS was used to initiate the polymerization.

Tacticity. Spectra of PPhMA can be analyzed in a similar way to the spectra of PMMA (in terms of triad integration).[12] The α-methyl resonance of PPhMA appears as three peaks, which are assigned to the different triads, syndiotactic (*rr*), atactic (*mr*), and isotactic (*mm*) in order of increasing chemical shift.[12] The tacticity of PPhMA can be determined by ^{1}H NMR analysis by integration of the triad region. As a consequence of the effect of the aromatic ring current on the α-methyl protons, the differences in the chemical shifts for the α-methyl resonances are much less than in the spectra of PMMA, and some peak overlap is seen. The tacticity analyses performed on the original polymer led to varying results from sample to sample due to the decreased resolution in the triad region that would affect the integration ratios. To ensure accurate results, PPhMA and P-1-NM samples were converted to PMMA whose spectrum is more highly resolved. Conversion of the polymers to PMMA does not affect the stereochemical integrity of the chemical backbone and leads to more accurate tacticity analyses.[18,24] Figures 6 and 7 illustrate spectra showing the triad region for a sample of PPhMA and for the derived PMMA. As can be determined from these spectra, the integration ratios of the triad regions of the derived PMMA are much more reliable.

The majority of the PPhMA samples (Table 10) polymerized in microemulsions were approximately 55% syndiotactic which is the same result for the polymer produced in solution. The one exception is the microemulsion-produced polymer which had a syndiotactic content of 61% resulting from the polymerization taking place at a lower temperature (35°C). The P-1-NM samples prepared in microemulsions or in solution were more atactic than the PPhMA (Table 11). The triad region of a ^{1}H NMR spectrum of P-1-NM (Figure 8) was unresolvable, and the polymer was thus converted to PMMA for a reasonable tacticity analysis. The atactic results for the P-1-NM were approximately the same for the polymer produced in a microemulsion and the solution-produced polymer. The results agree well with literature values for the radical polymerization of 1-naphthyl methacrylate.[16]

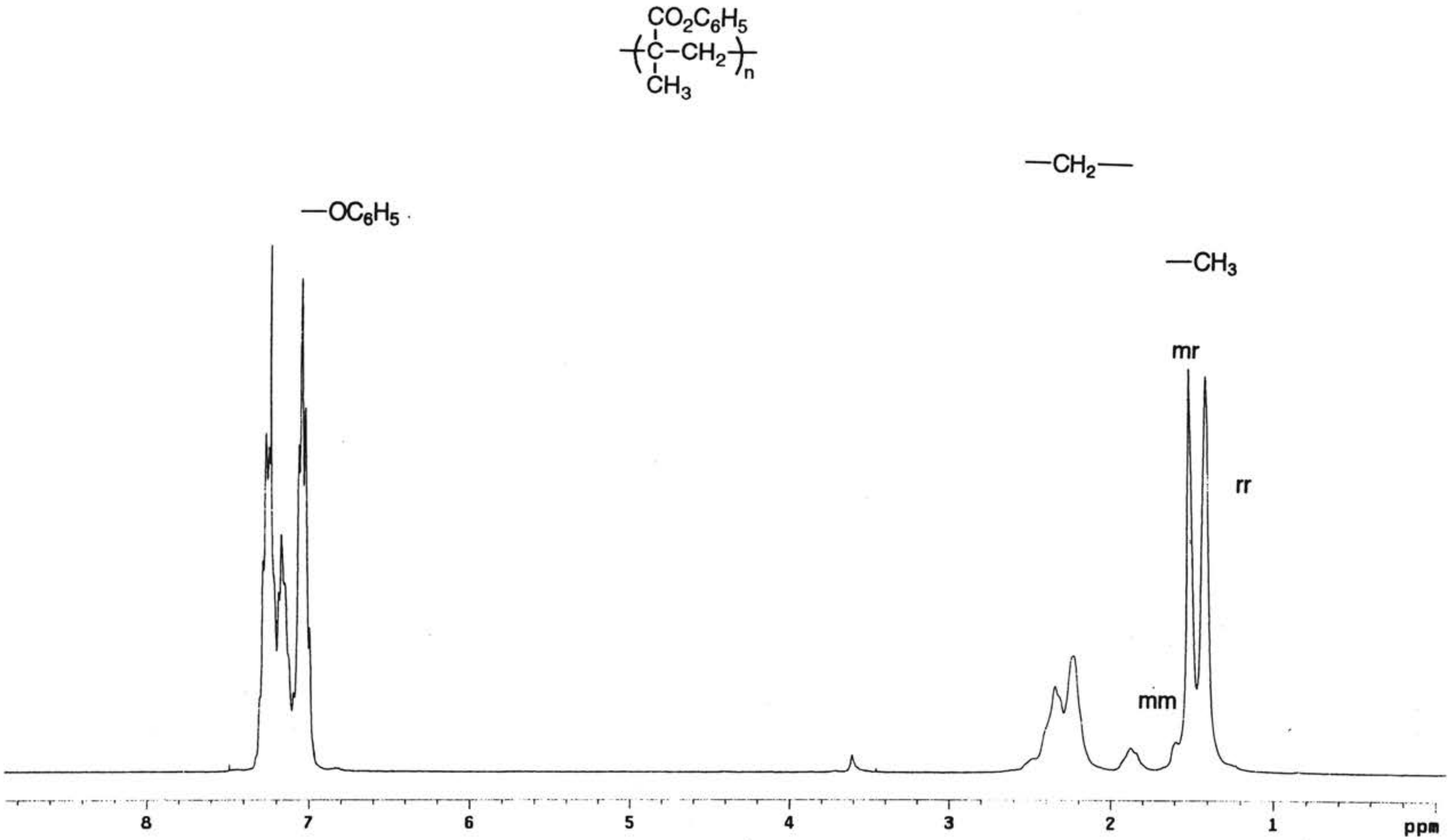


Figure 6. ^{1}H NMR spectrum of PPhMA prepared using Triton surfactants (Sample 1).

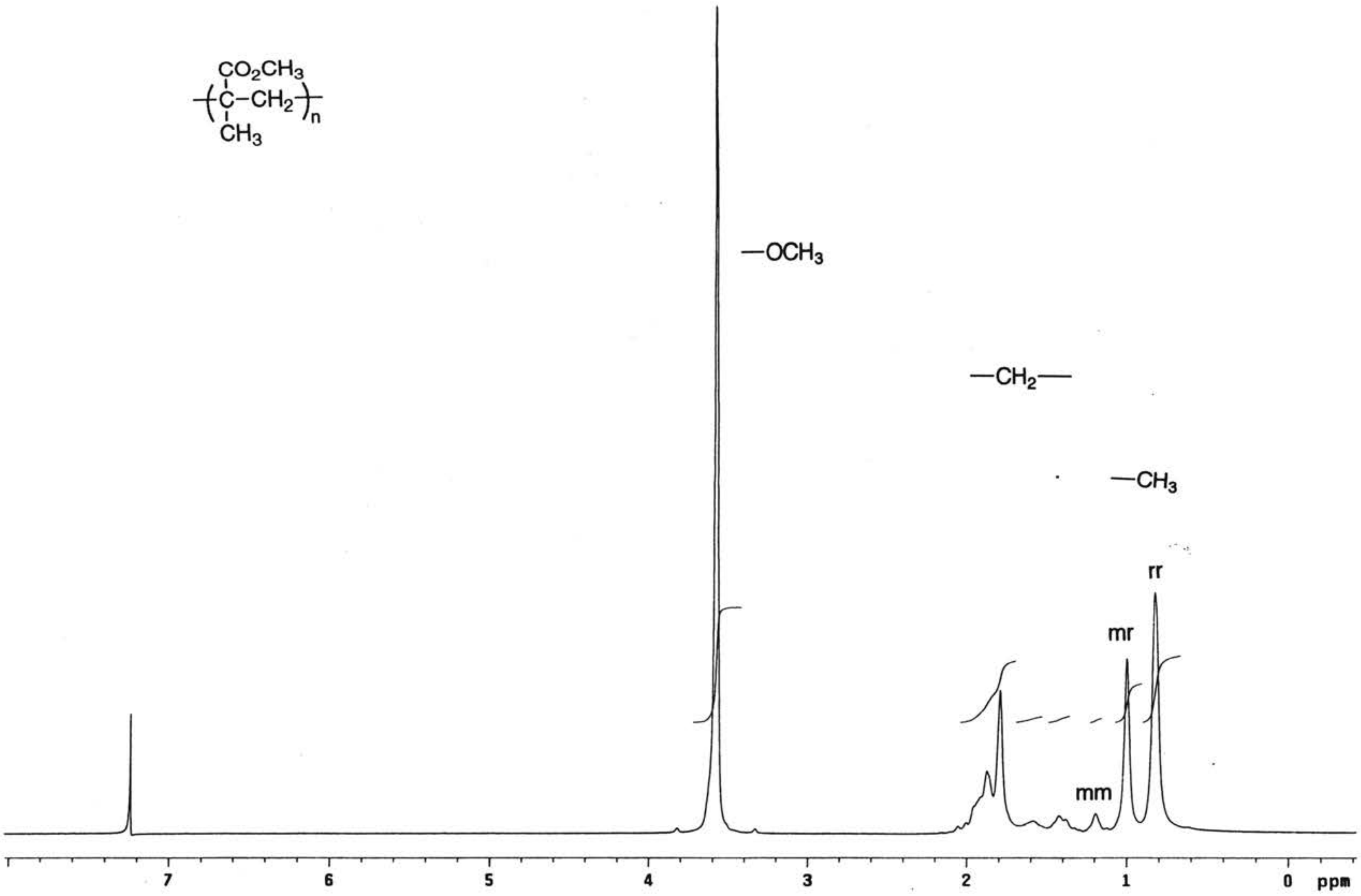


Figure 7. ^{1}H NMR spectrum of the derived PMMA obtained from PPhMA (Sample 1).

Table 10. Tacticities and T_g's of PPhMA[a]

Sample	*rr*	*mr*	*mm*	T_g, °C
1	0.61	0.36	0.03	127
2	0.55	0.38	0.07	127
3	0.54	0.39	0.07	128
4	0.56	0.37	0.07	127
5	0.55	0.38	0.08	127
Solution	0.55	0.40	0.05	127

[a]Error limits are ± 0.01 for tacticities and ± 1 °C for T_g's.

Table 11. Tacticities and T_g's of P-1-NM[a]

Sample	*rr*	*mr*	*mm*	T_g, °C
6	0.46	0.41	0.13	146
7	0.48	0.44	0.08	145
8	0.47	0.44	0.09	147
Solution	0.47	0.42	0.11	129

[a]Error limits are ± 0.01 for tacticities and ± 1°C for T_g's.

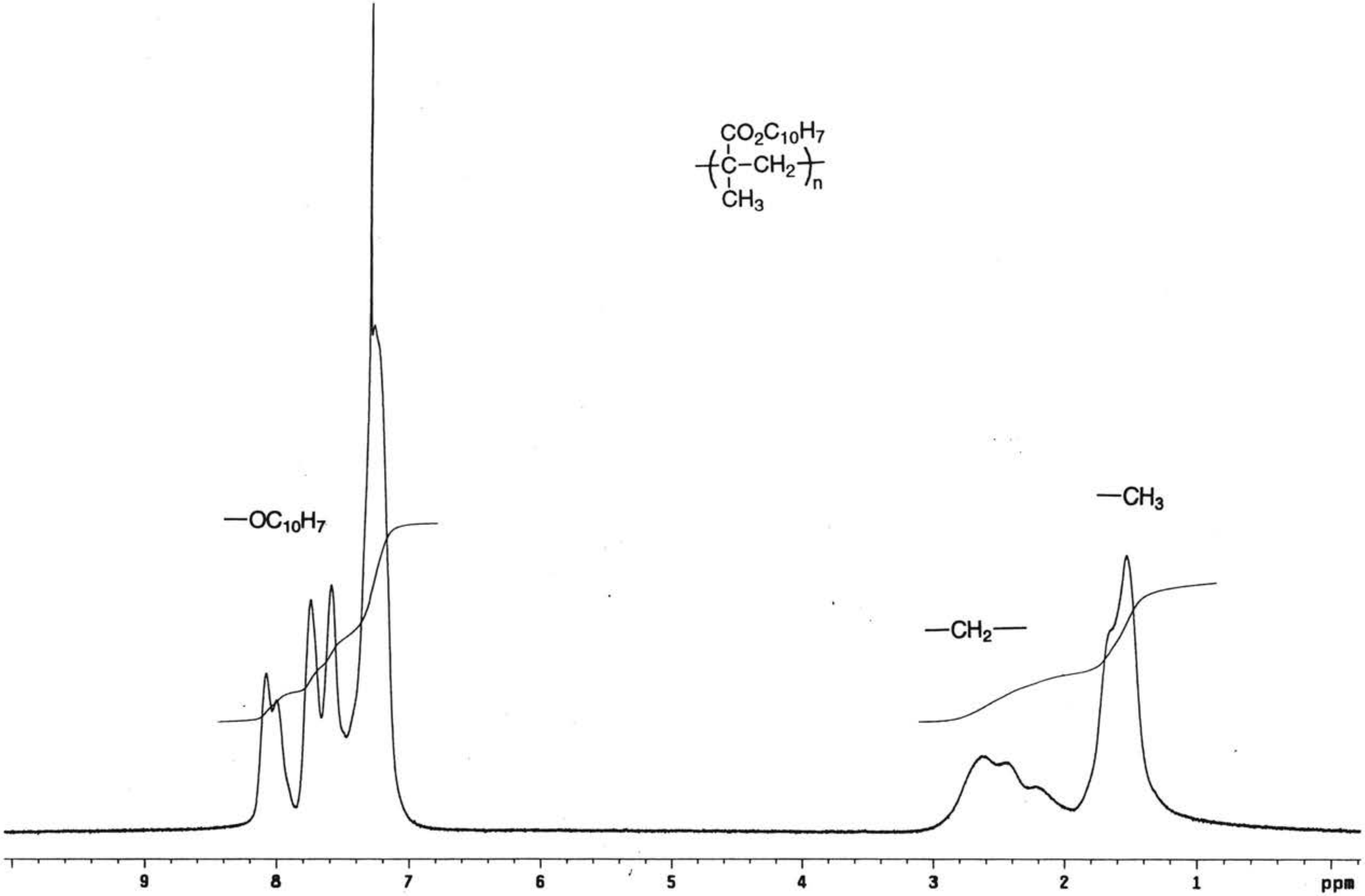


Figure 8. ^{1}H NMR spectrum of P-1-NM prepared with CTAB using V-50 (Sample 8).

Glass Transition Temperatures. Glass transition temperatures of around 127 °C were obtained for all the poly(phenyl methacrylate) samples (Table 10). The PPhMA formed in a microemulsion did not show a difference from that prepared in solution. However, the results obtained are much different than the T_g of 110 °C for a standard sample of commercially available PPhMA[30] or PPhMA samples commonly cited in the literature.[31-33] A bulk polymerized sample displaying a T_g of 110 °C has a high enough molecular weight (M_n = 810 000 g/mole) not to affect the T_g of the sample.[32] The most probable reason for the differences observed is different microstructures (not reported but possibly less syndiotactic) for the samples reported in the literature. T_g's of the derived PMMA were not obtained due to lack of product for analyses.

A more interesting result was obtained with the P-1-NM samples (Table 11). The glass transition temperatures of the P-1-NM formed in microemulsions were approximately 146 °C. The analogous polymer prepared in solution had a much lower T_g (129 °C). This sample does have a lower molecular weight than the other samples which would affect the T_g. The glass transition temperature of a polymer increases with molecular weight up to ~1 x 10^5 after which it usually does not vary.[20] However, the great variation seen for these samples (~17 degrees) appeared to be more than a molecular weight dependency.

A microemulsion-prepared sample with a T_g of 146 °C and the solution-prepared sample were both reprecipitated from chloroform into methanol. The T_g's were then analyzed, and the microemulsion-prepared sample had a T_g of 146 °C whereas the solution-prepared P-1-NM sample had a T_g of 142 °C after reprecipitation. The results of reprecipitation on the molecular weights are shown in Table 12. Dissolving the polymer in chloroform and precipitating into methanol fractionates the sample. Some of the low molecular weight components of the polymer sample remain soluble in the methanol, and a narrower distribution of higher molecular weight polymer is obtained. Removing low molecular weight components increases the number-average molecular weight as can be seen in Table 12. Although the M_n of the solution polymer did increase upon reprecipitation, the change was not significant enough to affect the T_g. Thus the reason for the depressed T_g was due to other components in the mixture. A small amount of solvent can drastically affect the glass transition temperature of a polymer sample. The ^{1}H NMR spectrum of the solution P-1-NM showed that trace amounts of toluene were present in the polymer sample. The chromatogram for the solution-polymerized P-1-NM also had a small peak corresponding to a weight-average molecular weight of 681 g/mole (Figure 5). The peak shape in the chromatogram of the solution-polymerized P-1-NM after reprecipitation remained identical to the peak shape of the chromatogram before reprecipitation. The only change was the removal of the small peak corresponding to a low molecular component of the sample. The small peak corresponds to a small amount of oligomer in the solution-polymerized P-1-NM sample that could also serve to depress the T_g of the sample. This peak was not included into the average of the molecular weight of the P-1-NM prepared in solution. The major factor contributing to the depressed T_g was solvent and/or the oligomeric component that was removed upon reprecipitation into methanol.

Table 12. Molecular Weight Comparison of P-1-NM Before and After Reprecipitation

Description	M_n, g/mol	T_g, °C
μE-prepared sample	2.8×10^4	146
Reprecipitated μE sample	3.1×10^4	146
Solution-prepared sample	0.9×10^4	129
Reprecipitated sln sample	1.0×10^4	142

Discussion

Polymerization of PhMA and 1-NM. As reported in Chapter II, microemulsion polymerizations of methyl methacrylate were performed at 60 °C with KPS but at this temperature, phenyl methacrylate and 1-naphthyl methacrylate did not polymerize. A temperature of 70 °C was needed to polymerize the PhMA and 1-NM using thermal initiation (KPS or V-50). The most probable reason for unsuccessful polymerizations at 60 °C was the presence of an inhibitor during the early stages of polymerization. The monomers are most likely susceptible to hydrolysis, which would produce phenol (or 1-naphthol) inhibiting the polymerization. Evidently, when the temperature is increased to 70 °C, the rate of radical production from V-50 is fast enough to overcome the small amount of inhibitor that may be present and the polymerization can proceed normally. The redox initiation system of hydrogen peroxide/ascorbic acid is efficient enough to start the polymerization at 35 °C.

Particle Sizes. The particles of PPhMA that were initiated with the oil-soluble initiator, AIBN, are slightly larger (D_n = 26 nm) than the particles initiated with a water-soluble initiator, V-50, or with the redox initiation system of ascorbic acid/hydrogen peroxide (D_n = 20-22 nm). Both water-soluble V-50 and oil-soluble AIBN initiate polymerization. Radicals generated in the aqueous phase from V-50 (or ascorbic acid/hydrogen peroxide) initiate polymerization of PhMA in the water phase. Oligomeric PPhMA radicals are captured by monomer-swollen micelles, where polymerization continues to high molecular weight. Because of the small volume of the polymerizing particle, two radicals in one particle would result in fast termination. AIBN forms a pair of 2-cyano-2-propyl radicals in the organic phase, and polymerizes to high molecular weight only when one of the radicals escapes the micelle, leaving behind one radical for polymer chain growth. Since the monomer-swollen micelles are initiated through diffusion of a radical through the aqueous phase, there would be fewer radicals of AIBN diffusing into the aqueous phase due to its limited solubility in water. Since high local concentration of AIBN radicals leads to faster termination, AIBN appears to be a less efficient initiator when compared to V-50 in the microemulsion polymerization of PPhMA.

Molecular Weights. Higher molecular weights were obtained by performing the polymerization in a microemulsion in contrast to the results obtained in a solution polymerization. Unlike free-radical polymerization performed in solution, polymerization in a microemulsion leads to high molecular weight polymers at fast reaction rates due to a reduced rate of bimolecular termination of polymer radicals.

The polymers prepared with V-50 and redox initiation had narrower molecular weight distributions than samples prepared with AIBN or KPS. The polymerization with KPS was in a microemulsion containing less monomer (Table 5) which could affect the molecular weight and distribution. The larger particle sizes and broader molecular weight distribution observed at relatively the same surfactant and monomer concentration using AIBN as the initiator indicates that V-50 and ascorbic acid/H_2O_2 are more efficient initiators. If fewer PPhMA monomer radicals escape the particle after chain transfer and transport of uniniated micelles to growing particles is much slower, AIBN would produce more low molecular weight material in the particle due to termination of the two radicals formed by decomposition of one AIBN molecule. Thus fewer new particles would be initiated because fewer radicals escape the particle. This point is also shown by the larger number of polymer chains per latex particle (Table 6) and the low molecular weight tail in the SEC chromatogram resulting in the large molecular weight distribution.

The P-1-NM samples prepared in microemulsions (Table 7) had lower molecular weights (~5 x 10^5 g/mole) and broader molecular weight distributions than the polymers of PhMA (~1 x 10^6 g/mole) due to the lower rate of propagation of the monomer.[13] The larger aromatic rings of naphthyl methacrylate are stronger electron donors and form more stable intermolecular complexes (Figure 9) when compared to the phenyl rings of phenyl methacrylate. The overall rate constant in benzene at 70 °C for PPhMA has been reported to be 4.44 min^{-1} compared to 1.43 min^{-1} for P-1-NM.[13] Thus naphthyl methacrylate polymerizes at a lower rate and has a higher activation energy than phenyl methacrylate as well as most other methacrylates (E_a = 20 100 kcal/mol for 1-NM and E_a = 19 650 kcal/mol for PhMA).[13,14] The lower polymerizability would account for the lower molecular weight that was obtained under the same conditions.

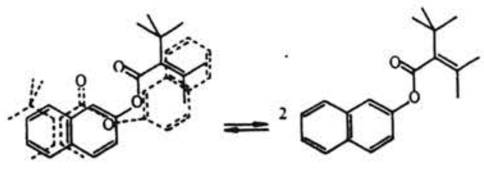


Figure 9. The naphthalene rings can interact with the methacrylic double bond of the monomer (Reproduced from reference 17).

Number of Polymer Chains Per Latex Particle. During polymerization in a microemulsion, particles containing a growing polymer chain compete with uninitiated microdroplets in capturing radicals. The greater number of monomer swollen micelles when compared to particles containing a growing polymer chain provides a much larger surface area and a higher probability of a radical entering an uninitated microdroplet and not a particle that already contains a growing polymer chain. The average time required for a particle with a growing polymer chain to capture a second radical and terminate the growing chain is greater than that of chain transfer to monomer. Thus chain transfer to monomer is the dominant mechanism for termination of the polymer chain. If the radicals generated by chain transfer to monomer diffuse out of the polymer particle, each latex particle will contain a single polymer chain.

The PPhMA and P-1-NM latex particles contained at least three polymer chains per latex particle. The reason for the multiple polymer chains per particle is the lower molecular weight of the polymer. The particle sizes of the PPhMA and P-1-NM are approximately the same as those of the PMMA latexes reported in Chapter II. However, the PPhMA and P-1-NM polymer samples do not have as high of a molecular weight as the PMMA analyzed in Chapter II. In the limits of one macromolecule per latex particle, smaller particle sizes should have been seen with the PPhMA and P-1-NM latexes. This leads to the question of why the PPhMA and P-1-NM latexes contained more than one polymer chain. Coagulation in the later stages of polymerization would lead to particles containing a few polymer chains. Also a long nucleation period could explain the formation of multiple polymer chains in a latex particle. If a particle gained monomer through collision with a monomer-swollen micelle before the monomeric radical generated from chain transfer to monomer could diffuse out of the particle, a new polymer chain could begin forming. In comparison to the results achieved with MMA, the radicals generated from PhMA and 1-NM are most likely less soluble in the aqueous phase and exhibit less of a tendency to diffuse out of the particle before coalescence with another monomer-swollen micelle. This would also explain the formation of a greater number of polymer chains in the PPhMA latex particles initiated by AIBN.

Tacticity. The stereoregulation in the addition of monomers to propagating radicals is influenced by the structure of the substituents. α,α-Disubstituted monomers such as MMA and α-methylstyrene usually give syndiotactic polymers because of the repulsion between the α-methyl group at the chain end and the approaching monomer. The syndiotactic content of a poly(methacrylic ester) decreases from poly(methyl methacrylate) to poly(triethyl methacrylate) in a series of radically-polymerized, saturated polymers. Polymethacrylates containing aromatic substituents have a lower syndiotactic content than the corresponding saturated polymers.[10,11,15,19]

The tacticity of polymethacrylates containing aromatic substituents shows that not only steric repulsion between the substituents but also interactions of the ester group play an important role in radical polymerization for determining the stereochemical configuration of a polymer chain. The polymerization of methacrylic esters with aromatic substituents favors syndiotactic placement less when compared to the polymerization of MMA. The calculated values of the dyad and triad differential enthalpies and entropies of activation reveal that a PPhMA radical favors syndiotactic placement less when compared to PMMA.[12] Figure 10 illustrates the different modes of addition (*meso* and *racemo* placement).

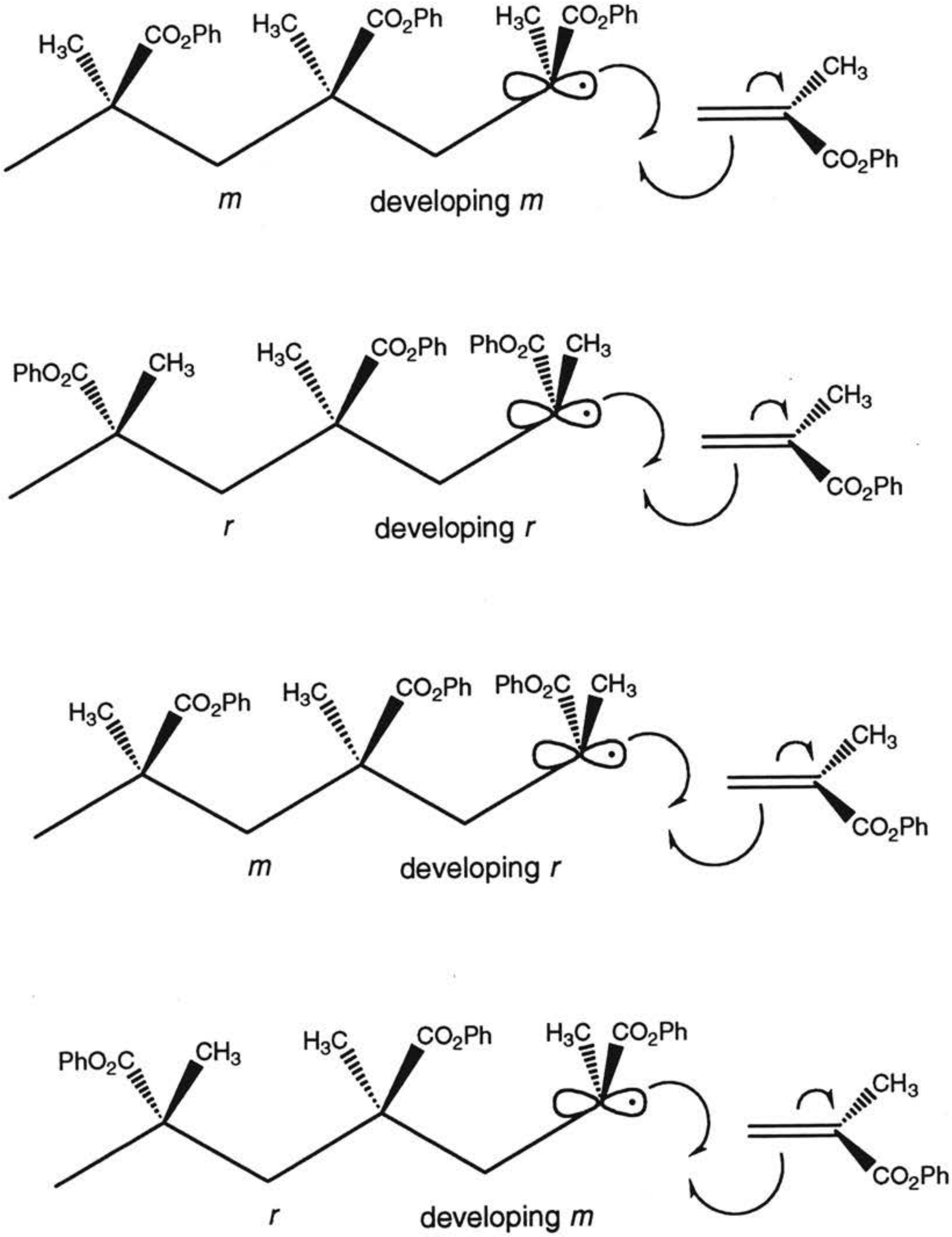


Figure 10. A monomer unit can add to a propagating radical chain either *racemo* or *meso*.

Most methacrylates with radical initiators form polymers with predominantly syndiotactic structures. Thus, methacrylate monomers containing aromatic substituents at the ester position forming less syndiotactic structures is very unusual. The corresponding aliphatic ring substituents have very little effect on the stereoregulation of the polymer backbone.[15] This odd behavior is most likely the consequence of specific interactions of the aromatic rings at the growing chain ends with incoming monomer.[10,12] The tacticity of a polymer is controlled by the relationship of the last-formed stereocenter to the propagating chain end. For polymethacrylates with aromatic substituents, the formation of syndiotactic triads is probably less favored due to specific interactions between the aromatic ring of the penultimate monomeric unit of the growing radical chain and the approaching monomer molecule.[13,17,21,34] The naphthyl rings of 1-NM have even stronger electron donating capabilities than the phenyl rings of PhMA and the effect on the tacticity is more pronounced.[15]

The end to end distance of a PPhMA polymer chain with a molecular weight of 1 x 10^6 g/mol is 67 nm.[35] The end to end distance of a P-2-NM macromolecule with a molecular weight of 5 x 10^5 g/mol is 41 nm and should be approximately the same for a P-1-NM polymer chain.[35] The sphere that would enclose all of the segments of each of these polymers must be even larger. Thus the PPhMA and P-1-NM formed in the small spherical volumes imposed by a microemulsion are conformationally restricted. If the propagating chain end during the polymerization is also restricted, a change in the tacticity could be observed.

The microstructures of PMMA formed in microemulsions remained unaffected compared to the microstructures commonly achieved by free radical polymerizations of the monomer.[8] However, changes in the tacticities of PPhMA and P-1-NM formed in microemulsions are more likely to be detected. The more extended isotactic form of a polymer will not pack as efficiently as the syndiotactic polymer. For example, the end to end distance of isotactic PMMA with a molecular weight of 1 x 10^6 g/mol in acetonitrile is 67.0 nm.[35] The end to end distance of of atactic PMMA with a molecular weight of 1 x 10^6 g/mol in acetonitrile is 55.5 nm, and the end to end distance of a similar syndiotactic PMMA molecule is expected to be even less.[35] PMMA prepared by a radical polymerization is already a highly syndiotactic polymer, and thus it should be able to pack more efficiently than the less stereoregular structures that are formed from PPhMA and P-1-NM. The radius of gyration which can be used to define the average volume occupied by a molecule for PMMA is also smaller ($\sigma = 2.08$) than the corresponding radii of gyration for PPhMA ($\sigma = 2.8$) or for P-1-NM ($\sigma = 3.1$).[35]

However, the microstructures of PPhMA and P-1-NM were not affected by the environment of the particle surface. The most probable reason for the unchanged configuration of the monomers with bulky substituents is that the propagation occurs in the bulk of the particle and not at the surface. Another possible reason is that although there is a restricted volume posing as the media for polymerization, the wall of the micelle is not a rigid hard shell, but it is flexible and capable of moving and expanding. A growing polymer chain at the surface can grow only along the surface or back into the particle. The rate of propagation is much less than the rate of diffusion for small molecules so after each propagation step there is time for surfactant and monomer to reorganize around the radical chain end.

Glass Transition Temperature. The T_g of a polymer is dependent upon the tacticity of the polymer and is lower for an isotactic polymer due to greater segmental mobility than for a syndiotactic one.[22] Thus altering the stereochemistry of a polymer backbone will also affect the glass transition of a polymer. The glass transition temperature of polymethacrylates increases as the flexibility of the polymer chain is decreased. The segmental mobility of a polymer will decrease with an increase in the bulkiness of the ester group regardless of tacticity.[22] Thus, it is not surprising that the T_g of PPhMA (127 °C) is higher than that of ordinary PMMA (105-115 °C), and the glass transition (145 °C) of P-1-NM is higher than either PMMA or PPhMA. However, these results are much different than the T_g = 110 °C commonly cited for PPhMA[30-33] and the literature value of 135 °C for the T_g of P-1-NM formed in solution at 50 °C that resulted in a high molecular weight (200 000 – 330 000 g/mol) polymer.[36]

Reported T_g's for the same polymer often differ greatly because the glass transition occurs over a temperature range and not a single, sharply defined temperature. Thus the observed T_g may vary depending on the method of measurement used and the thermal history of the sample. Although agreement was not seen with the literature samples, PPhMA prepared under identical conditions in solution yielded the same T_g as the polymer prepared in a microemulsion. The T_g of P-1-NM prepared in solution was lower than the P-1-NM obtained in microemulsion polymerizations. The T_g of a polymer sample is dependent upon the molecular weight of the polymer by equation 3 where K is on the order of 10^5. (For PMMA prepared in bulk at 60°C, $K = 0.76 \times 10^5$).[23]

$$T_g(\infty) = T_g(\text{experimental}) + K/M_n \qquad (3)$$

Thus the difference of $T_g = 142$ °C after reprecipitation for the solution-prepared sample and the $T_g = 146$ °C obtained for the microemulsion-prepared samples is the result of differing molecular weights. The solution P-1-NM sample before reprecipitation contained very low molecular weight components (removed by reprecipitation) which greatly depressed the T_g resulting in a value of 129 °C.

Conclusions

This is the first report of polymerizations of PPhMA and P-1-NM in microemulsions. The polymerization must take place at 70 °C with thermal initiators (V-50 or KPS). Performing the polymerization in a microemulsion resulted in higher molecular weight polymer than solution polymerization. The water-soluble V-50 and the redox initiation system of ascorbic acid/hydrogen peroxide are more efficient than AIBN at initiating the polymerization. The P-1-NM had a lower molecular weight than PPhMA due to a lower rate of propagation of the monomer. The results indicate that the tacticity remains unaffected from the polymerization in a microemulsion.

Our PPhMA displayed a much greater glass transition temperature (127°C) than did a commercial sample[30] (110°C), but its T_g was the same as that of the polymer prepared in solution. Initial T_g measurements on P-1-NM showed a great difference between a sample made in a microemulsion (~146 °C) and the corresponding solution-prepared sample (129 °C). Upon reprecipitation, the solution-prepared P-1-NM showed an increase in its T_g (142 °C), indicating that the initial T_g measurement was depressed due to low molecular weight components of the polymer sample. SEC analysis confirmed the presence of an oligomeric component in the solution-polymerized sample.

References

1. Full, A. P.; Kaler, E. W. *Langmuir* **1994**, *10*, 2929.
2. Gilbert, R. G. *Emulsion Polymerization: A Mechanistic Approach*; Academic Press: London 1995, p 12.
3. Lovell, P. A.; El-Aasser, M. S. *Emulsion Polymerization and Emulsion Polymers*; Wiley: New York 1997, p 723-741.
4. Candau, F. *Polymerization in Organized Media*; Paleos, C. M., Ed.; Gordon and Breach: Philadelphia, 1992, p 215-282.
5. Antonietti, M.; Basten, R.; Lohmann, S. *Macromol. Chem. Phys.* **1995**, *196*, 441.
6. Gan, L. M.; Lee, K. C.; Chew, C. H.; Tok, E. S.; Ng, S. C. *J. Polym. Sci. Part A: Polym. Chem.* **1995**, *33*, 1161.
7. Full, A. P.; Kaler, E. W.; Arellano, J.; Puig, J. E. *Macromolecules* **1996**, *29*, 2764.
8. Pilcher, S. C.; Ford, W. T. *Macromolecules* **1998**, *31*, 3454.
9. Farina, M.; Giuseppe, D. S. *Encyclopedia of Polymer Science and Engineering* John Wiley & Sons, Inc., New York 1988, *12*, 486.
10. Niezette, J.; Desreux, V. *Makromol. Chem.* **1971**, *149*, 177.
11. Otsu, T.; Yamada, B.; Sugiyama, S.; Mori, S. *J. Polym. Sci. Polym. Chem Ed.* **1980**, *18*, 2197.
12. Roman, J. S.; Madruga, E. L. *Eur. Polym. J.* **1980**, *17*, 15.
13. Boudevska, H.; Popminchev, V. *Makromol. Chem.* **1971**, *143*, 19.
14. Boudevska, H.; Mintcheva, M. *Eur. Polym. J.* **1974**, *10*, 875.
15. Nishino, J.; Nakahata, H.; Sakaguchi, Y. *Polym. J.* **1971**, *2*, 555.
16. Boudevska, H.; Brutchkov, C.; Kolova, V.; Pham, Q. T. *Eur. Polym. J.* **1978**, *14*, 619.
17. Boudevska, H.; Brutchkov, C. *Makromol. Chem.* **1979**, *180*, 1661.
18. Boudevska, H.; Brutchkov, C.; Astrug, A. *Makromol. Chem.* **1979**, *180*, 1113.
19. Matsuzaki, K; Kanai, T.; Yamawaki, K.; Samre Rung K. P. *Makromol. Chem.* **1973**, *174*, 215.
20. Fox, T. G.; Loshaek, L. *J. Polym. Sci.* **1955**, *15*, 371.
21. Radiotis, T.; Spyros, A.; Dais, P. *Polymer* **1993**, *34*, 1846.
22. Yuki, H.; Hatada, K. *Adv. Polym. Sci.* **1979**, *31*, 1.
23. Yuki, H.; Hatada, K.; Niinomi, T.; Kikuchi, Y. *Polym. J.* **1970**, *1*, 36.
24. Yuki, H.; Hatada, K.; Kikuchi, Y.; Niinomi, T. *J. Polym. Sci. Part B: Polym. Lett.* **1968**, *6*, 753.

25. Hatada, K; Kitayama, T.; Ute, K. *Progr. Polym. Sci.* **1988**, *13*, 189.

26. Okamota, Y.; Ohta, K.; Hatada, K.; Yuki, H. *ACS Symp. Ser.* **1981**, *166*, 353.

27. Yuki, H.; Okamota, Y.; Okamota, I. *J. Am. Chem. Soc.* **1980**, *102*, 6356.

28. Lombardi, P. *Chem. Ind.* **1990**, *21*, 708.

29. Schilling, F. C.; Bovey, F. A.; Bruch, M.; Kozlowski, S. *Macromolecules* **1985**, *18*, 1418.

30. Monomer-Polymer & Dajac Laboratories, Inc. 1675 Bustleton Pike Feasterville, PA 19053 *Catalog No. M911.*

31. Turnhout, J. V. *Polym. J.* **1971**, *2*, 173.

32. Krause, S.; Gormley, J. J.; Roman, N.; Shetter, J. A.; Watanabe, W. H. *J. Polym. Sci: Part A* **1965**, *3*, 3573.

33. Petrovic-Djakov, D. M.; Filipovic, J. M.; Vrhova, L. P.; Velickovic, J. S. *J. Therm. Anal.* **1993**, *40*, 741.

34. Boudevska, H.; Brutchkov, C.; Pham, Q. T. *Eur. Polym. J.* **1980**, *16*, 393.

35. Brandrup, J.; Immergut, E.H.; Grulke, E. A. *Polymer Handbook, Fourth Ed.*, Wiley: New York, 1999, p VII/52-53.

36. Madruga, E. L.; Roman, J. S. *Makromol. Chem., Rapid Commun.* **1986**, *7*, 307.

CHAPTER IV

FREE RADICAL POLYMERIZATION OF α-METHYLSTYRENE IN MINIEMULSIONS

Abstract

Radical polymerizations of α-methylstyrene (AMS) were performed in oil-in-water miniemulsions using a mixture of nonionic nonylphenoxy poly(ethylene glycol) surfactants and initiated with ascorbic acid/hydrogen peroxide at polymerization temperatures ranging from 3 °C to 45 °C. A bimodal distribution of one high molecular weight component (~60 000 g/mol) and a low molecular weight component (~8 000 g/mol) was analyzed by size exclusion chromatography (SEC). The relative amount of the low molecular weight fraction increased with increasing polymerization temperature. The high molecular weight fraction is much higher than previously achieved in radical polymerizations of AMS. An increased percent conversion and higher molecular weights were obtained at temperatures $\leq$ 25 °C when compared to bulk radical polymerizations of AMS. The polymer yields decreased from 66% at 3 °C to 4% at 45 °C. The syndiotactic content of PAMS decreased from 70% *rr* at 3 °C to 58% *rr* at 45 °C.

Introduction

Polymerization in Miniemulsions. A miniemulsion polymerization is the intermediate between a microemulsion and an emulsion polymerization.[1,2] The major distinction is the size of the initial droplets of oil in water and the stability of the dispersion. Emulsions have a larger primary droplet size (1-10 μm).[1] The droplets of oil in water in an emulsion tend to coalesce and the stability is limited to a matter of minutes or hours unless the system is well mixed.[2] Microemulsions are thermodynamically stable dispersions (for years or longer) of smaller droplets of oil in water (~10 nm).[1,2] Miniemulsions are the dispersions of oil and water that occur in between microemulsions and emulsions in terms of droplet size (~30 nm) and stability. Miniemulsions may be stable for as little as days and for as long as months.[1,2] The particles produced from polymerization are also different for each system. The latex particles produced in emulsions typically have diameters between 100 and 600 nm.[1] Polymerization in microemulsions generally produce smaller particles (20-60 nm in diameter) and the particles formed in a miniemulsion have an intermediate particle size (60-200 nm).[1] Some overlap in the classification of the different regions exists and distinct boundaries must be approximated.

Free Radical Polymerization of AMS. Free radical polymerization can be viewed as having three steps (Scheme 1). An initiator dissociates into two radicals that can add to monomer units creating additional active centers. During propagation, rapid chain growth takes place by addition of monomer to the active center on the polymer chain, creating a new active center. The last step is termination of the polymer chain.

Scheme 1. Steps in a Free Radical Polymerization

Initiation

$$I \longrightarrow 2R^{\bullet}$$

$$R^{\bullet} + M \longrightarrow R\text{-}M^{\bullet}$$

Propagation

$$M_n^{\bullet} + M \underset{k_{dp}}{\overset{k_p}{\rightleftharpoons}} M_{n+1}^{\bullet}$$

Termination

$$M_n^{\bullet} + M_m^{\bullet} \longrightarrow M_{n+m}$$

Termination can take place by combination of two existing radicals or disproportionation by the abstraction of a hydrogen atom leading to the formation of one saturated and one unsaturated polymer chain. An active site of polymerization can also be deactivated (i.e. terminated) by chain transfer where the radical is transferred to another molecule which starts the growth of another polymer chain.[1]

One step that is not often considered in free radical polymerization is depropagation due to the fact that the propagation reaction is usually much faster than depropagation. Depropagation is the reverse reaction where the polymer chain loses a monomer unit. Under conditions where depolymerization needs to be considered, the propagation reaction must be written as a reversible reaction where k_p is the propagation rate constant and k_{dp} is the rate constant for depropagation. Scheme 1 illustrates the steps in a radical polymerization. In free radical polymerization, there is a competition between the entropic effects and the enthalpic effects.[2,3] The linking together of two small monomer units by the conversion of the π-bond in the monomer to a σ-bond of the polymer chain is an exothermic process and ΔH_p is negative. While the enthalpy change is favorable for polymerization, the change in entropy is not favored (negative ΔS_p) due to the monomer being incorporated into a covalently bonded chain structure. Since both the enthalpy and entropy terms are negative, the sign of the Gibbs energy of propagation is dependent on the temperature. Polymerization will take place only when the temperature is low enough for the enthalpic term in $\Delta G_p = \Delta H_p - T\Delta S_p$ to dominate. As the temperature is increased, depropagation begins to play an important role and ΔG_p becomes less negative. The temperature at which $\Delta G_p = 0$ is called the ceiling temperature, T_c. The ceiling temperature is defined as the temperature at which the rate of propagation is equal to that of depropagation. Polymerization will not proceed at temperatures above the ceiling temperature.[2,3] The overall rate equation for a radical polymerization taking into account depropagation can be written as

$$R_p = k_p[M][R^\bullet] - k_{dp}[R^\bullet] \qquad (1)$$

At the ceiling temperature of the monomer, the rate of propagation is equal to the rate of depropagation and the overall rate of polymerization, R_p, is zero. Thus

$$k_p[M] = k_{dp} \qquad (2)$$

The value of ΔS_p in $\Delta G_p = \Delta H_p - T\Delta S_p$ does not vary greatly among monomers and typically has a value between –100 and –120 J/K mol. Thus the value of ΔG_p for different monomers is principally controlled by ΔH_p, which commonly has values between –30 and –150 kJ/mol.[2,3] Monomers that display significant steric hindrance to propagation have low ΔH_p values and therefore display low ceiling temperatures. Table 1 displays ceiling temperatures of some common monomers.[3] The ceiling temperature of a monomer is dependent upon the monomer concentration (Equation 2) and pressure.[2,3] The addition of solvent to the monomer will increase the configurational entropy of the initial, monomeric state, compared to the final, polymeric state and thus lower the ceiling temperature. Likewise, an increase in pressure will decrease the entropy of the initial monomeric solution and raise the ceiling temperature.[2,3] The rate of increase of T_c with pressure is ~0.17 °C/MPa for α-methylstyrene.[3]

Table 1. Ceiling Temperatures of Various Monomers in Bulk.[3]

Monomer	T_c
Styrene	310 °C
Methyl methacrylate	220 °C
Tetrahydrofuran	80 °C
α-Methylstyrene	61 °C

α-Methylstyrene (AMS) is a unique monomer with a relatively low ceiling temperature of 61 °C due to the steric hindrance associated with the polymer. AMS exhibits very little tendency to polymerize with thermal or free radical initiation. For this reason, polymerizations of this monomer are typically performed using ionic initiators at sub-zero temperatures to obtain increased yields of higher molecular weight polymer. AMS is used in copolymerizations with other monomers such as styrene, divinylbenzene, acrylates, acrylonitrile, and butadiene for the production of commercial polymers.[4] It improves the impact and heat-resistant properties of the polymers.

Poly(α-methylstyrene) (PAMS) possesses far more steric strain than other polymers, and this should be the greatest controlling factor in polymerizations of this monomer. Anionic polymerization leads to a polymer where the tacticity is dependent on the polymerization temperature,[5-7] molecular weight,[5,8] and solvent.[9] In general, the syndiotactic content of the PAMS produced in anionic polymerizations decreases with increasing polymerization temperature, although some variation is observed in this trend.[5-7] Likewise, the syndiotacticity decreases with increasing molecular weight.[5,8] Cationic polymerizations of AMS lead to a highly syndiotactic polymer regardless of the initiator or polymerization temperature.[10-12] In all samples prepared by cationic polymerizations, PAMS prefers syndiotactic placement over isotactic even with polymerization catalysts that normally provide a great deal of stereoregularity with other monomers.[10]

Low conversions, low molecular weights, and long reaction times are typically observed in free radical polymerizations of AMS.[13-15] The chain transfer constant of PAMS to monomer at 50 °C (4.12×10^{-3}) is over two orders of magnitude larger than what is observed for methyl methacrylate (5.15×10^{-5}) or styrene (5.27×10^{-5}).[13] Thus the dominant chain stopping reaction in a bulk polymerization of AMS is chain transfer to monomer. From the high value of the chain transfer to monomer constant, the highest achievable number-average molecular weight in a free radical polymerization of AMS in bulk at 50 °C was calculated to be 8,000 g/mole.[13]

In this chapter, the free radical polymerization of AMS performed in miniemulsions is reported. The tacticity of the polymer backbone was investigated to see if changes occured as the ceiling temperature was approached. The assignments of the triad regions of this polymer have been well established[16] and the microstructure of the polymer was determined by ^{1}H NMR spectroscopy. The percent conversion and molecular weights of each polymer sample were also measured.

Greer and coworkers have previously investigated PAMS formed in an equilibrium polymerization (near the ceiling temperature of the monomer) where the polymerization can be carried out reversibly, and the monomer and polymer can remain in equilibrium.[17-21] Using anionic polymerization techniques, such things as the mass density,[17] heat capacity,[20] and the kinetics of polymerization[21] for PAMS prepared near the polymerization line were examined. However, no attention was paid to the tacticity of the polymer formed at temperatures near the ceiling temperature.

Experimental

Materials. Triton N-150 (nonyl phenol with ~15 ethylene oxide units) from Union Carbide, Triton N-57 (nonyl phenol with ~5 ethylene oxide units) from Aldrich, and sodium dodecylbenzenesulfonate (DBS) from Polysciences were used as received. Ascorbic acid from Aldrich and a 30% hydrogen peroxide solution from Fisher were each used as received. α-Methylstyrene (AMS) from Aldrich was purified by passing the monomer through alumina to remove the inhibitor (*p-tert*-butylcatechol). The purity of the monomer was confirmed by ^{1}H NMR analysis at 300 MHz in $CDCl_3$. Methanol from Pharmco, THF (HPLC-grade) from Aldrich, and $CDCl_3$ from Cambridge were each used as received. Water was deionized and had a resisitivity >1 Mohm-cm after exposure to air.

Polymerization in Miniemulsions. The conditions used for the polymerization were intended to be for a polymerization in a microemulsion. However, the initial transparent mixture of surfactant and water turned cloudy after the addition of AMS. Due to the increased primary droplet size, the polymerization must be classified as a miniemulsion. The following is the general procedure for the polymerization of AMS. To 18.9 g of Triton N-150, 2.7 g of Triton N-57, and 0.1 g of DBS contained in a three-necked, 200 mL, round-bottomed flask equipped with a condenser, a mechanical stirrer, and a nitrogen inlet was added 108 mL of deionized water. As nitrogen was bubbled through the mixture, the flask was placed in a constant temperature bath, and the mixture was stirred overnight to yield a transparent solution. AMS, 11.0 g (0.09 mol), was added, and the turbid solution was stirred for one hour. A solution of 0.132 g (0.75 mmol) of ascorbic acid dissolved in 4 mL of deionized water was added, followed immediately by the addition of 2.0 g (0.03 mol) of 30% H_2O_2. The solution was stirred for 120 hours at a constant temperature to complete the polymerization. The turbidity of each solution remained constant throughout the polymerization. A water bath was used for polymerizations at $\leq$ 25 °C; an oil bath was used for polymerizations at > 25 °C. The temperature was controlled to ± 1 °C.

Isolation of Polymer and Removal of Surfactant. An aliquot of 20 mL of the latex dispersion was saved, and the rest of the latex solution was added to 750 mL of vigorously stirred methanol contained in a 1 L beaker. The mixture was centrifuged, and the supernatant was decanted. Additional methanol (~200 mL) was added, the mixture was centrifuged, and the supernatant was decanted. This procedure was repeated 4-5 times to remove the surfactant. The polymer was air-dried overnight followed by drying in a vacuum desiccator at 35 °C for 48 hours. ^1H NMR analyses showed surfactant was still present in the PAMS samples (2-15 wt.% surfactant to polymer).

Tacticity Analyses. ^1H NMR analyses were performed at 300 MHz at 40 °C. NMR samples were prepared by adding 50 mg of PAMS to 1.5 mL of $CDCl_3$. The tacticities of the samples were measured from the integrated ratios of the syndiotactic (*rr*), atactic (*mr*), and isotactic triad (*mm*) signals.[16] Since the *rr* triad region is located near 0.1 ppm, TMS interfered with the tacticity analyses and could not be used in the NMR solvent. ^1H NMR analyses of solutions of PAMS in chlorobenzene-d_5 resulted in decreased resolution of the spectra.

Molecular Weight Analyses. Molecular weights were measured by size exclusion chromatography (SEC) using a Mixed B 10 μm PLgel column from Polymer Laboratories at a flow rate of 1.0 mL/min at 40 °C using a Hewlett-Packard (HP) series 1100 chromatograph. The sample size injected was 20 μL of a 1.0 mg/mL solution in THF. UV detection was used at $\lambda = 218$ nm. The GPC was calibrated with polystyrene standards having molecular weights of 600 000, 390 000, 100 000, 17 500, 9 000, and 2 000 g/mol. The calibration curves for PAMS and polystyrene in THF at room temperature are identical.[14] Thus PAMS and polystyrene have similar hydrodynamic volumes and the molecular weights do not need to be corrected with Mark-Houwink parameters. Molecular weights were calculated using the HP Chemstation software and a GPC Macro supplied by HP.

Peak Fitting. The data were taken directly from the SEC chromatograms, and each point was transferred into a Microsoft Excel file. The file was then converted to a text document and imported into Augerscan 2 (PC program designed by RBD Enterprises 563 S.W. 13th St. Suite 201 Bend, OR 97702). This program has a peak fitting function where the peak can be analyzed as the sum of two Gaussian distributions.

Attempted Depolymerization of PAMS. A miniemulsion polymerization was performed at 8 °C using the previously reported procedure. After 24 hours, 5 mL of the stirring latex solution was taken from the flask via a disposable pipet and precipitated into methanol and washed by the aforementioned procedure. After 144 hours, an additional 5 mL was taken from the flask and precipitated and washed. Additional initiator (0.132 g of ascorbic acid and 2.0 g of 30% H_2O_2) was added to the latex solution and then heated to 50 °C (above the range of the proposed ceiling temperature) for 36 hours. A 5 mL aliquot was then precipitated and washed with methanol. The solution was cooled to 40 °C for 48 hours, and again 5 mL of the latex solution was precipitated and washed with methanol.

Results

The ceiling temperature of α-methylstyrene is strongly dependent on the initial concentration of the monomer in solution and only weakly dependent on the type of solvent. The ceiling temperature decreases as the concentration of the monomer decreases.[17] Thus diluting the monomer in a miniemulsion will serve to decrease the ceiling temperature of α-methylstyrene (61 °C in bulk). The free radical polymerization of AMS was investigated from a polymerization temperature just above freezing (3 °C since a miniemulsion consists mainly of water) to the polymerization temperature at which polymer was not formed (50 °C). The highest temperature at which polymer was obtained was 45 °C indicating that the ceiling temperature of AMS in these miniemulsions is between 45 °C and 50 °C.

Percent Conversion. The percent yields of the polymer produced decreased with increasing polymerization temperature at temperatures greater than 25 °C. The yields remained constant at lower temperatures (3 °C to 20 °C) indicating that depropagation does not significantly affect the polymerization until temperatures greater than 25 °C. The yield of the polymer sample is directly proportional to the percent conversion of the polymer sample. As the ceiling temperature was approached the percent conversion of monomer to polymer decreased. The dependence of polymer conversion on the polymerization temperature is shown in Table 2. The polymerizations at 30 °C and 40 °C were carried out twice each at different times. The conversions for a polymerization at 8 °C slightly increased with reaction time.

Table 2. Polymer Yields of PAMS after 120 Hours

Polymerization Temperature, °C	% Yield
3	66
8[a]	68
8[b]	75
10	61
15	63
20	64
25	52
30	28
30[c,d]	23
35	16
40[c]	17
40[c]	13
45	4
50	0

[a] Polymerization stopped after 24 hours. [b] Polymerization stopped after 144 hours. [c] Experiment performed twice under identical conditions. [d] Polymerization stopped after 40 hours.

Even though long reaction times were employed in the polymerization of AMS in miniemulsions (~120 hours), this reaction time was much shorter than the reaction time of 215 hours used in previous free radical polymerizations of this monomer.[13] The percent yield of polymer obtained from a polymerization performed in a microemulsion at 8 °C after only 24 hours was 68%. The percent yield for the same polymerization increased to 75% after 144 hours. The small differences between the yields could be due to early consumption of the initiator. The polymerization of AMS in miniemulsions could be performed with much shorter reaction times without a significant loss of the amount of polymer obtained.

In an attempt to depolymerize the polymer, the above polymerization mixture was then heated to a temperature above the ceiling temperature (50 °C). The percent conversion was found to remain constant (76%) after 36 hours at 50 °C and did not change significantly (78%) after cooling to 40 °C for an additional 48 hours. Depropagation does not affect the polymer after it is formed and only plays a significant role during the polymerization of the monomer.

Molecular Weights. The SEC chromatogram of PAMS prepared at 40 °C has a bimodal distribution. The polymerization at 40 °C was repeated, and the same result was obtained. The trend towards a bimodal distribution can be seen at even lower temperatures (see Figure 1). As the polymerization temperature is increased, the amount of the lower molecular weight component increases. A slight shoulder can be seen for the chromatogram for the polymerization performed at 3 °C (Figure 1a). The shoulder becomes more pronounced for the chromatogram for the polymer formed at 20 °C

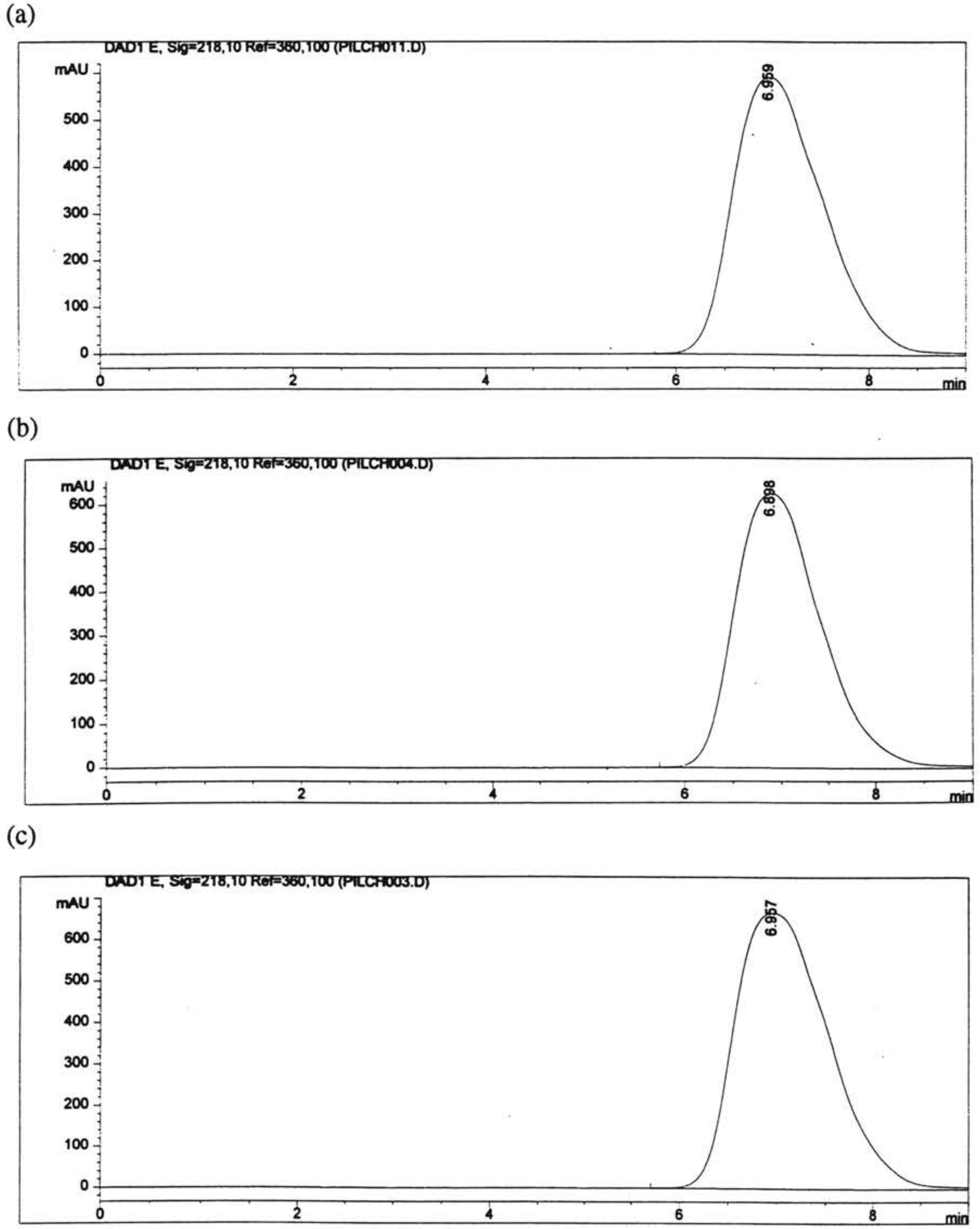


Figure 1. SEC chromatograms used in the determination of the molecular weights of the following samples: (a) PAMS formed at 3 °C, (b) PAMS formed at 10 ° C, and (c) PAMS formed at 15 °C.

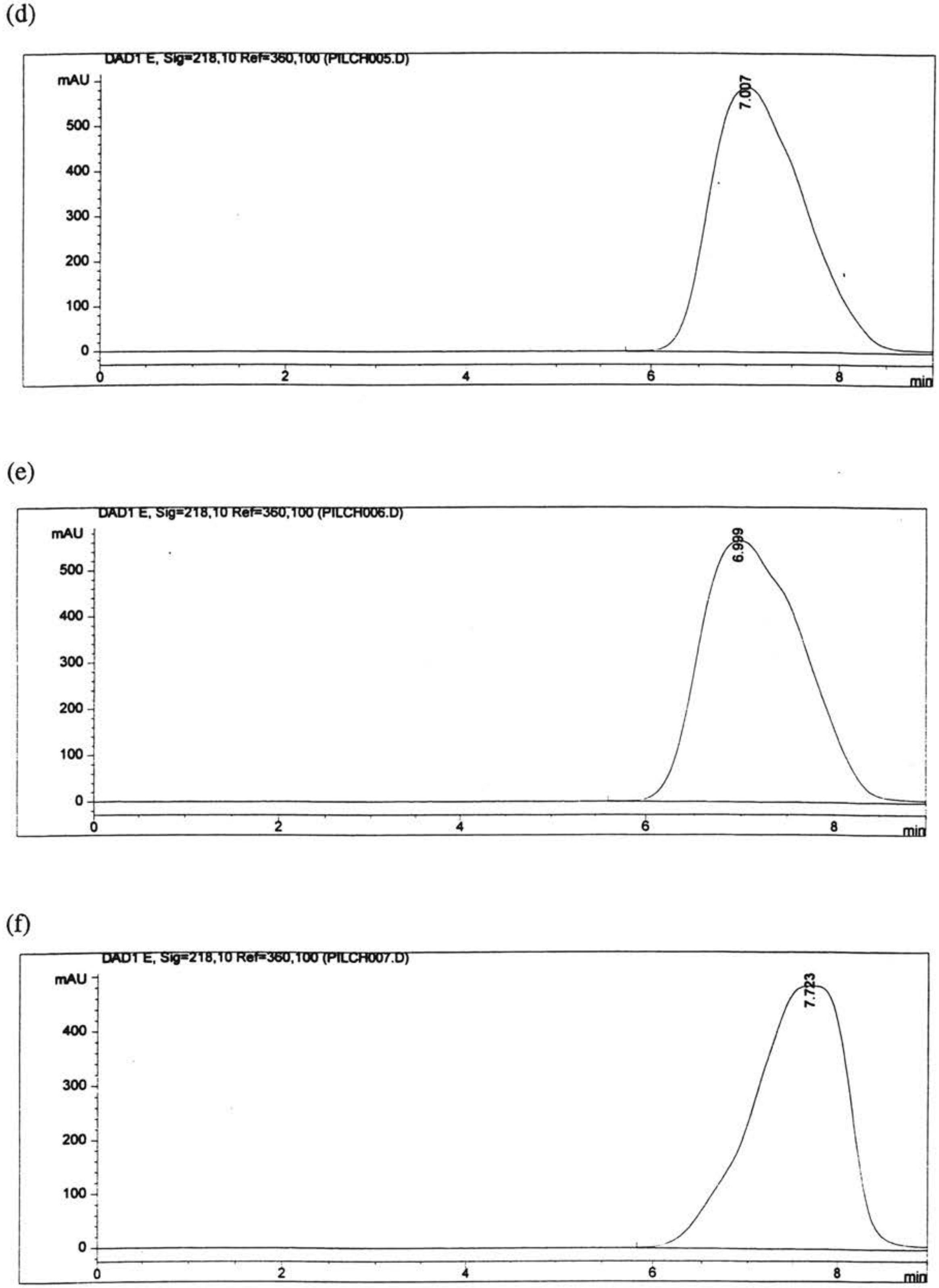


Figure 1. SEC chromatograms used in the determination of the molecular weights of the following samples: (d) PAMS formed at 20 ˚C, (e) PAMS formed at 25 ˚ C, and (f) PAMS formed at 30 ˚C.

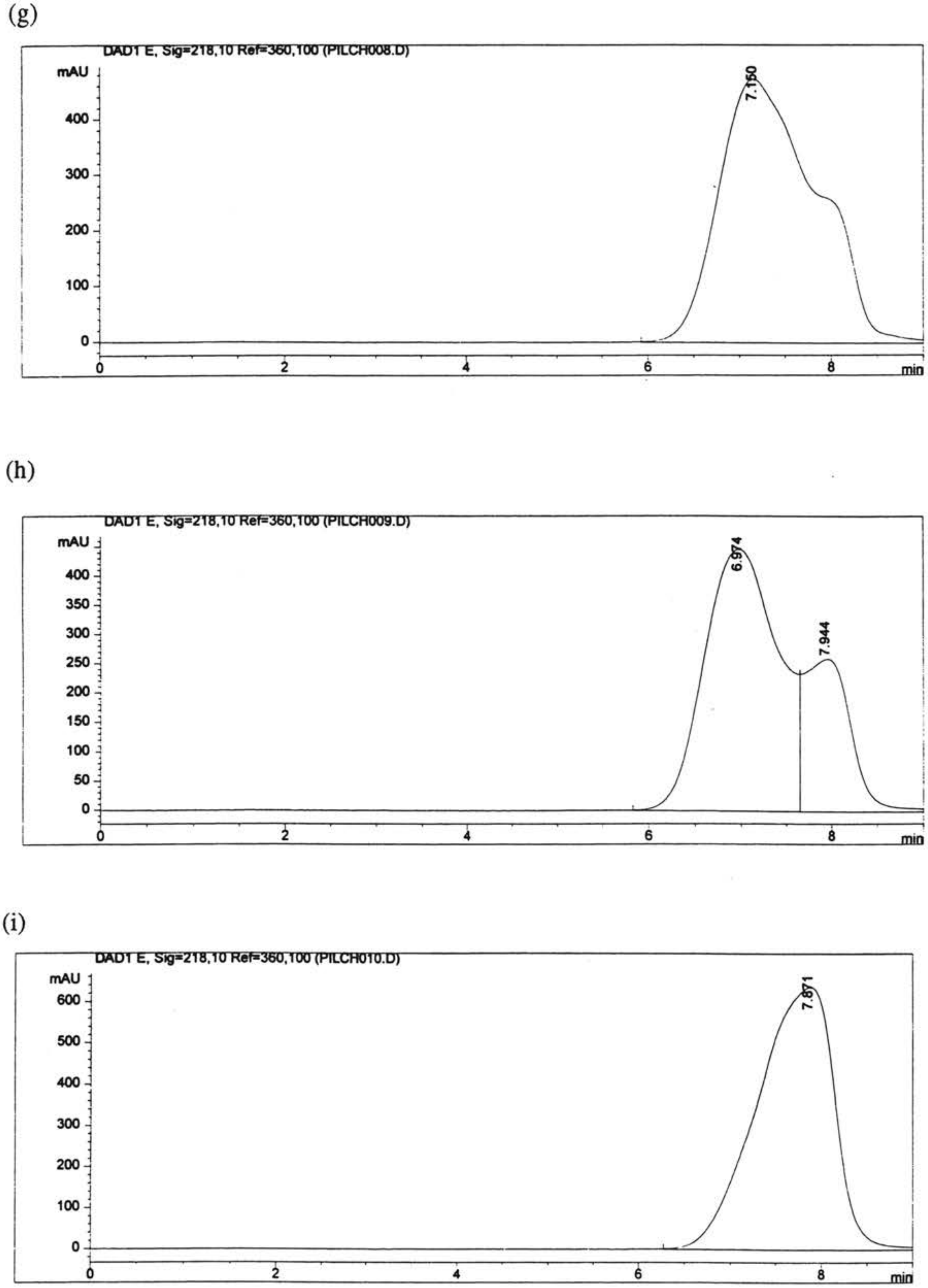


Figure 1. SEC chromatograms used in the determination of the molecular weights of the following samples: (g) PAMS formed at 35 °C, (h) PAMS formed at 40 ° C, and (i) PAMS formed at 45 °C.

(Figure 1d). Finally, the polymer formed at 40 °C (Figure 1h) displays two peak tops. The exception to this trend is the polymerization performed at 30 °C (Figure 1f) that contains a majority of the low molecular weight component. The polymerization at 30 °C was repeated and again a low molecular weight polymer was obtained.

To obtain a more accurate representation of these two molecular weight fractions, the SEC data were taken and fitted as the sum of two Gaussian peaks as shown in Figure 2. Three examples are shown corresponding to the PAMS sample polymerized at 25 °C that consisted mainly of the high molecular weight fraction, a sample with a bimodal distribution (PAMS at 40 °C), and a sample consisting of mainly the high molecular weight component (PAMS at 25 °C). The areas under each peak and the molecular weights at the peak tops are reported in Table 3. The percent area of the low molecular weight fraction increased as the polymerization temperature was increased with the exception of the PAMS obtained at 30 °C. The PAMS formed at 30 °C did show a high molecular weight fraction that fit well with the rest of the data. The polymerization of AMS at 40 °C was repeated, and more of the high molecular weight component was observed in the bimodal distribution.

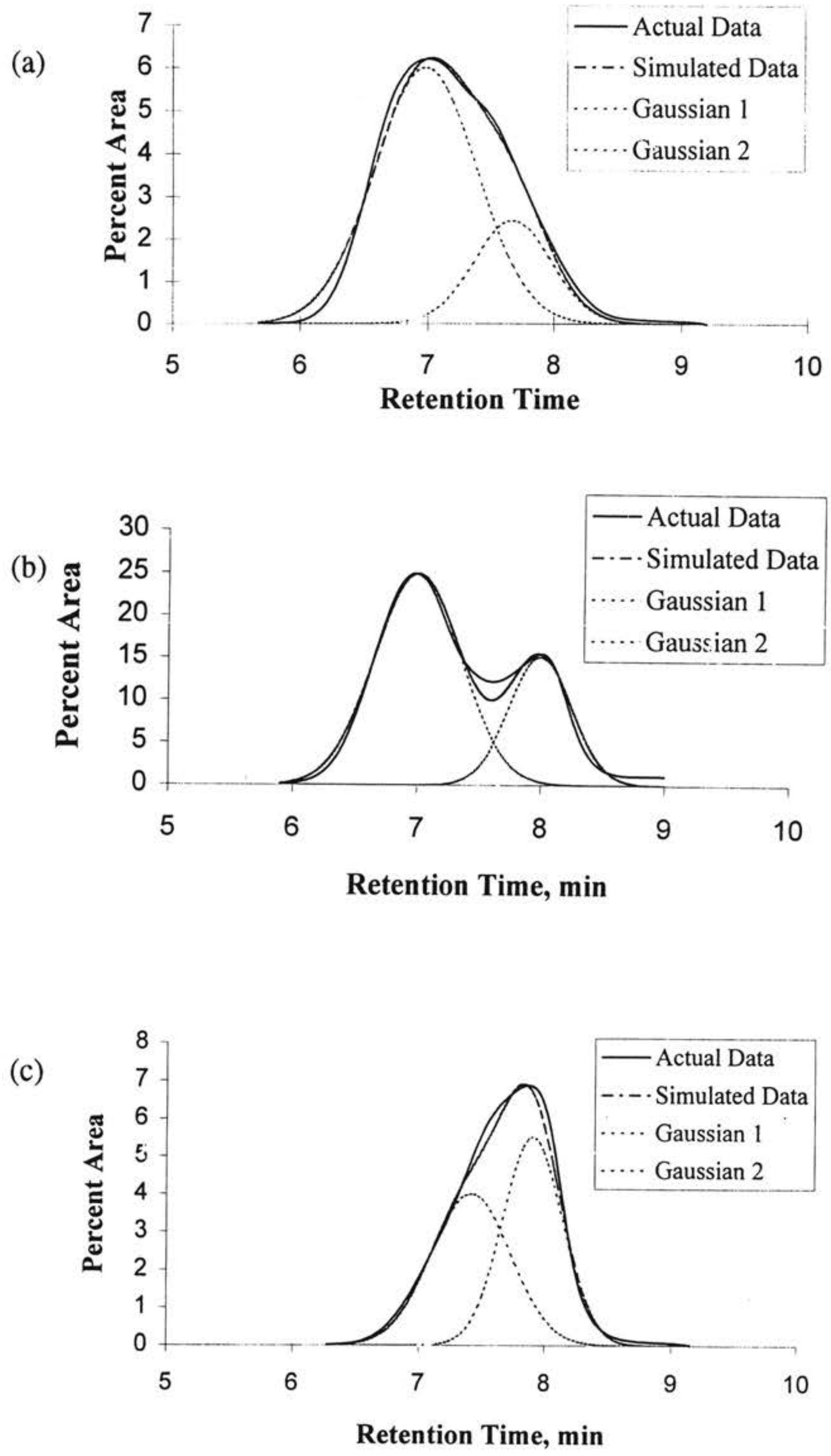


Figure 2. The chromatograms analyzed as the sum of two Gaussian peaks for the following samples: (a) PAMS@25°C, (b) PAMS@40°C, and (c) PAMS@45°C.

Table 3. The Results of the Chromatograms Analyzed as the Sum of Two Gaussian Peaks

Polymerization Temperature, °C	Peak	% Area	M (peak top), g/mol
3	1	82	56 000
	2	18	10 000
10	1	90	64 000
	2	10	9 500
15	1	81	61 000
	2	19	11 600
20	1	81	50 000
	2	19	7 600
25	1	76	52 000
	2	24	9 500
30	1	20	58 000
	2	80	8 100
30[a]	1	51	23 000
	2	49	6 500
35	1	79	33 000
	2	21	4 200
40[b]	1	77	69 000
	2	23	6 200
40[b]	1	65	52 000
	2	35	4 400
45	1	49	18 000
	2	51	5 100

[a]Separate polymerization for 40 hours. [b]Same experimental conditions used for each polymerization.

One possibility for the appearance of two separate distributions is decomposition of the high molecular weight polymer into lower molecular weight components caused by depolymerization at increased temperatures. Depolymerization was attempted by taking a sample of PAMS that was produced at 8 °C, adding more initiator, and heating to 50 °C. The following molecular weights were obtained (Table 4), and the chromatograms are shown in Figure 3.

Table 4. Molecular Weights from the Attempted Depolymerization of PAMS

Description	M_w, g/mole	M_w/M_n
PAMS @ 8 °C (24 hrs)	81 000	2.7
PAMS @ 8 °C (144 hrs)	76 000	2.9
PAMS → 50 °C (36 hrs)	75 000	3.6
PAMS → 40 °C (48 hrs)	75 000	4.3

A small decrease in the molecular weight is observed and two very low molecular weight components can be seen in the chromatograms. This could be due to slight decomposition of the polymer. However, examination of the main peaks shows that the retention times are identical (6.880, 6.884, and 6.882 for each sample, respectively). Thus the low molecular weight small peaks (at tails of chromatograms) are probably from oligomer formation as a consequence of the additional initiator that was added prior to heating. This is confirmed by the increase in the percent yield of the polymer obtained as reported earlier.

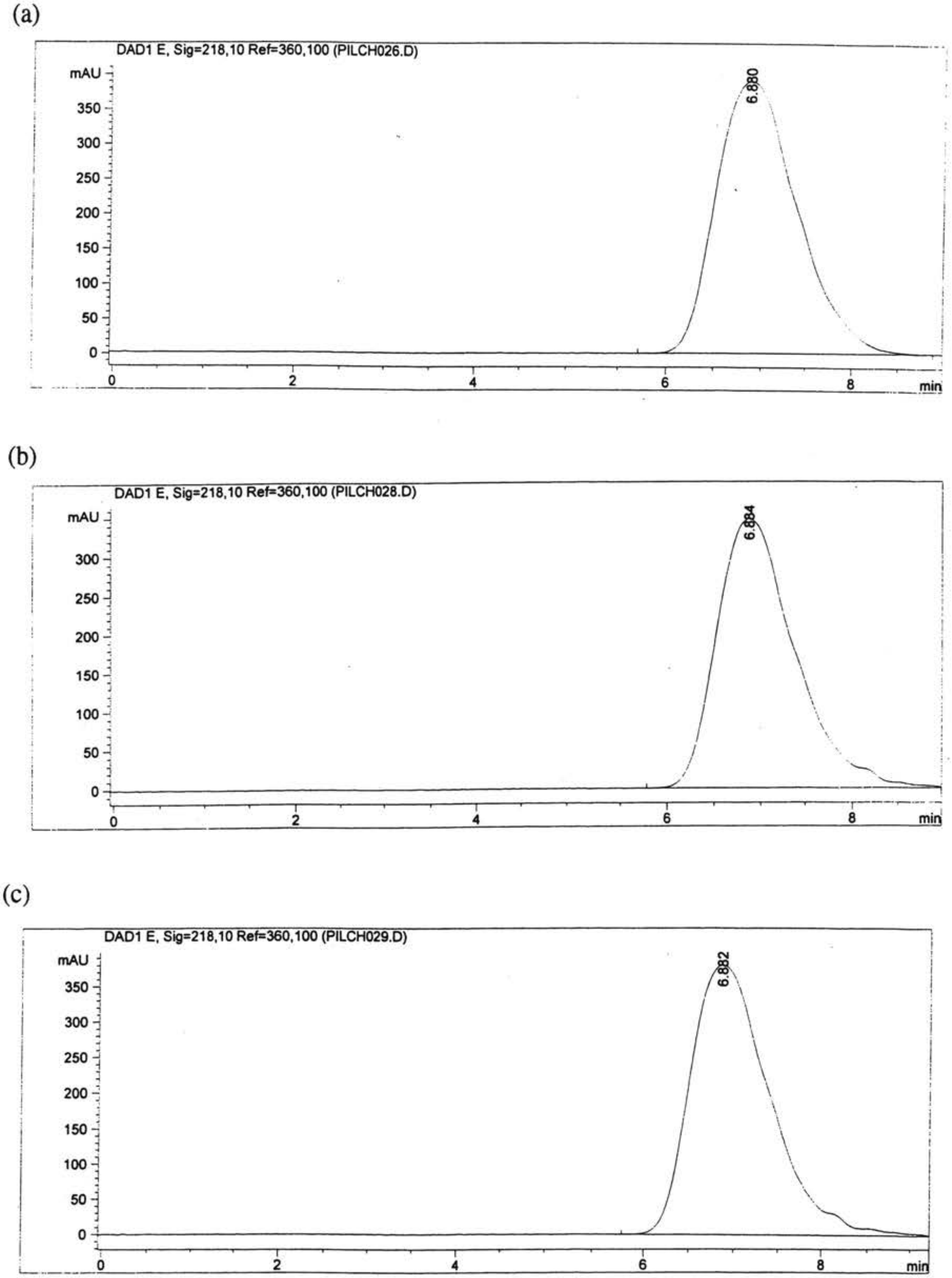


Figure 3. SEC chromatograms from attempted depolymerization of PAMS corresponding to (a) formed at 8 °C for 144 hours, (b) heated to 50 °C for 36 hours, and (c) cooled to 40 °C for 48 hours.

Surfactant Content of Polymer Samples. The peaks appearing between 3.6-4.2 ppm in the ^{1}H NMR spectrum (Figure 4) are from the ethylene oxide units of the Triton surfactants. The surfactant present in the ^{1}H NMR spectra does not affect the integration ratios used to determine tacticity within experimental error (± 1 percent triad unit). The integration ratio of the ethylene oxide of the surfactant was assumed to be equal to 60 H's. The mole percent of surfactant relative to a monomer repeat unit was calculated by comparing this value to the integration ratio of the 10 H's for the AMS repeat unit. The weight percent of surfactant to polymer was calculated by finding the mass ratios of surfactant to polymer. The number of H's for the integration ratio of the α-CH_3 resonance was found by multiplying the degree of polymerization (using M_n) by three. The mass of each component was then calculated by multiplying the mole fraction by the molecular weight of the surfactant or polymer.

The PAMS samples prepared at $\leq$ 25 °C each contained $\leq$ 0.7 mol.% of surfactant relative to a polymer repeat unit. The PAMS samples formed at > 25 °C contained > 1 mol.% of surfactant/polymer repeat unit. Some of the samples were reprecipitated in order to remove more of the surfactant. The PAMS@10°C sample originally contained 0.5 mol.% of surfactant/polymer repeat unit after the initial precipitation and washings. Upon reprecipitation, the percentage decreased to 0.4 mol.%. A second reprecipitation gave a polymer that contained 0.3 mol.% surfactant relative to a polymer repeat unit. This value remained constant after the third reprecipitation. The PAMS@30 °C sample contained 1.8 mol.% of surfactant/repeat unit and 1.7 mol.% of surfactant/repeat unit after reprecipitation. The PAMS formed at 45 °C sample contained 2.5 mol.% of

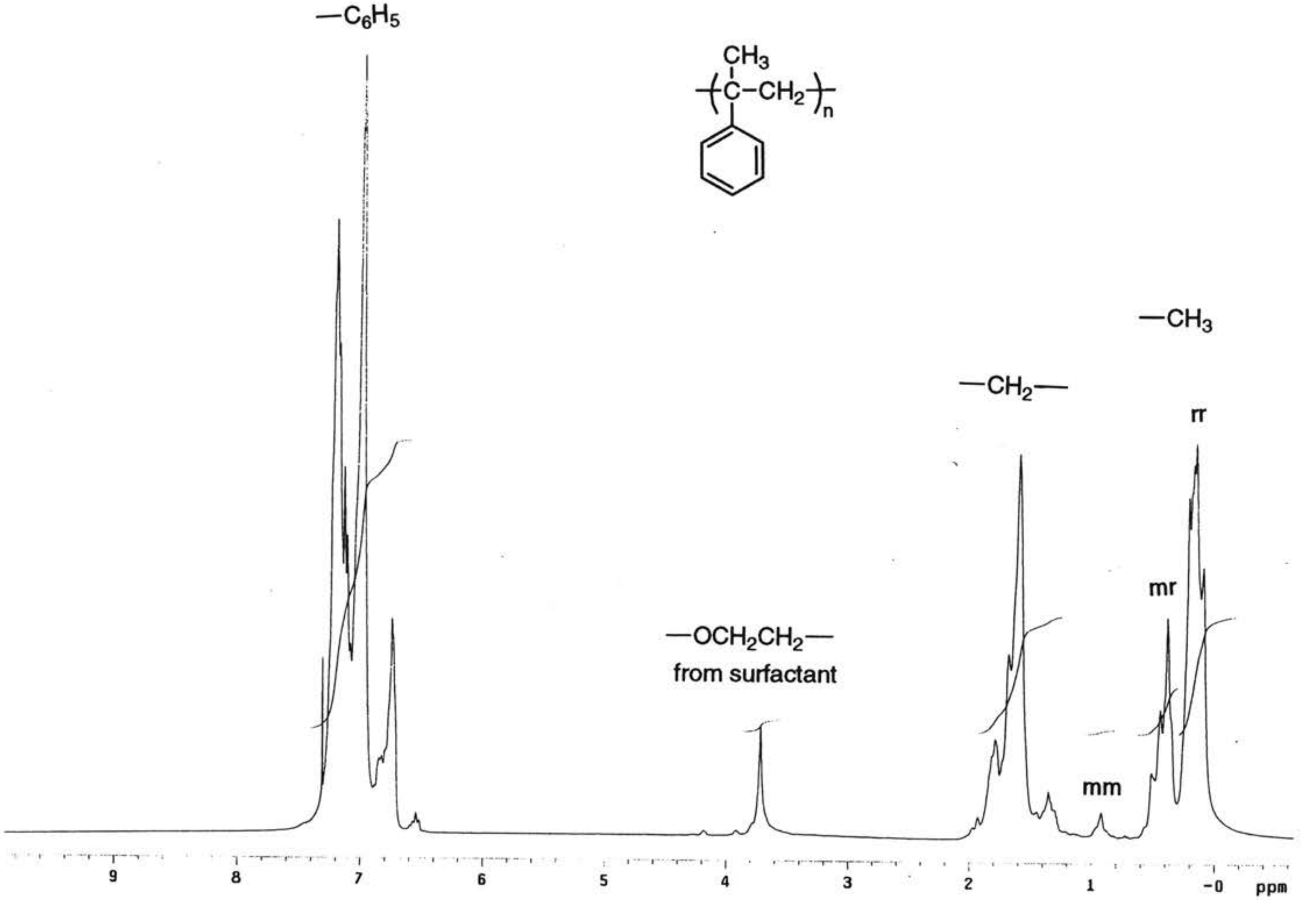


Figure 4. ^{1}H NMR spectrum of PAMS formed at 10 °C used for tacticity analysis.

surfactant/repeat unit and 2.2 mol.% of surfactant/repeat unit after reprecipitation. The tacticities of the samples remained constant (± 0.01) after the reprecipitations. The mole percent of surfactant relative to a polymer repeat unit and the weight percent of surfactant to polymer are reported in Table 5.

Table 5. Percent Surfactant Contained in PAMS Samples

PAMS Polymerization Temperature	Surfactant to Polymer Repeat Unit, mol%	Surfactant to Polymer, wt. %
3	0.6	4.1
10	0.5	3.7
10[a]	0.4	2.6
10[b]	0.3	2.1
10[c]	0.3	2.1
15	0.6	4.4
20	0.7	5.5
25	0.7	5.3
30	1.8	12.0
30[a]	1.7	12.0
30[d]	2.3	15.5
35	1.1	8.1
40	1.3	9.5
40[d]	1.3	9.0
45	2.5	16.0
45[a]	2.2	15.8

[a] Sample was reprecipitated. [b] Sample was reprecipitated twice. [c] Sample was reprecipitated a third time. [d] Polymerization was repeated at same temperature.

Precipitation of PAMS into Methanol. Isolation of polymers into methanol could possibly fractionate the sample by removing low molecular weight components. The water and unreacted monomer were evaporated from an aliquot of the latex PAMS solution prepared at 30 °C. The SEC chromatograms for the PAMS sample before and after precipitation are shown in Figure 5. The broad peak at 7.5 min in Figure 5a is PAMS and the peak at 8.5 min is the Triton N-150 surfactant (the low molecular weight shoulder is from the Triton N-57 surfactant). The same sample was also analyzed by SEC, after the precipitation and washings with methanol and the chromatogram is shown in Figure 5b. The tail of the peak in the chromatogram for the unprecipitated PAMS sample was truncated in the calculation of the molecular weight because of the presence the surfactant peak. This resulted in a lower number-average molecular weight (10 000 g/mol) for the PAMS sample precipitated into methanol, compared to 9 000 g/mol for the unprecipitated PAMS sample. The weight average molecular weight for each sample remained constant (M_w = 19 000 g/mol).

A peak at 8.5 minutes was observed in the SEC analysis of the Triton N-150 surfactant. A distinct peak at 8.5 min was not observed in the SEC chromatograms for any of the PAMS samples that were precipitated into methanol, as illustrated in Figure 5b. The amount of surfactant determined by ^{1}H NMR analysis for the repeated PAMS at 30 °C (15.5 wt.% of surfactant to polymer) was intentionally mixed with the sample and analyzed by SEC. A distinct surfactant peak can definitely be observed in the chromatogram (Figure 5c). Thus the majority of the surfactant remaining in the sample must be a part of the polymer.

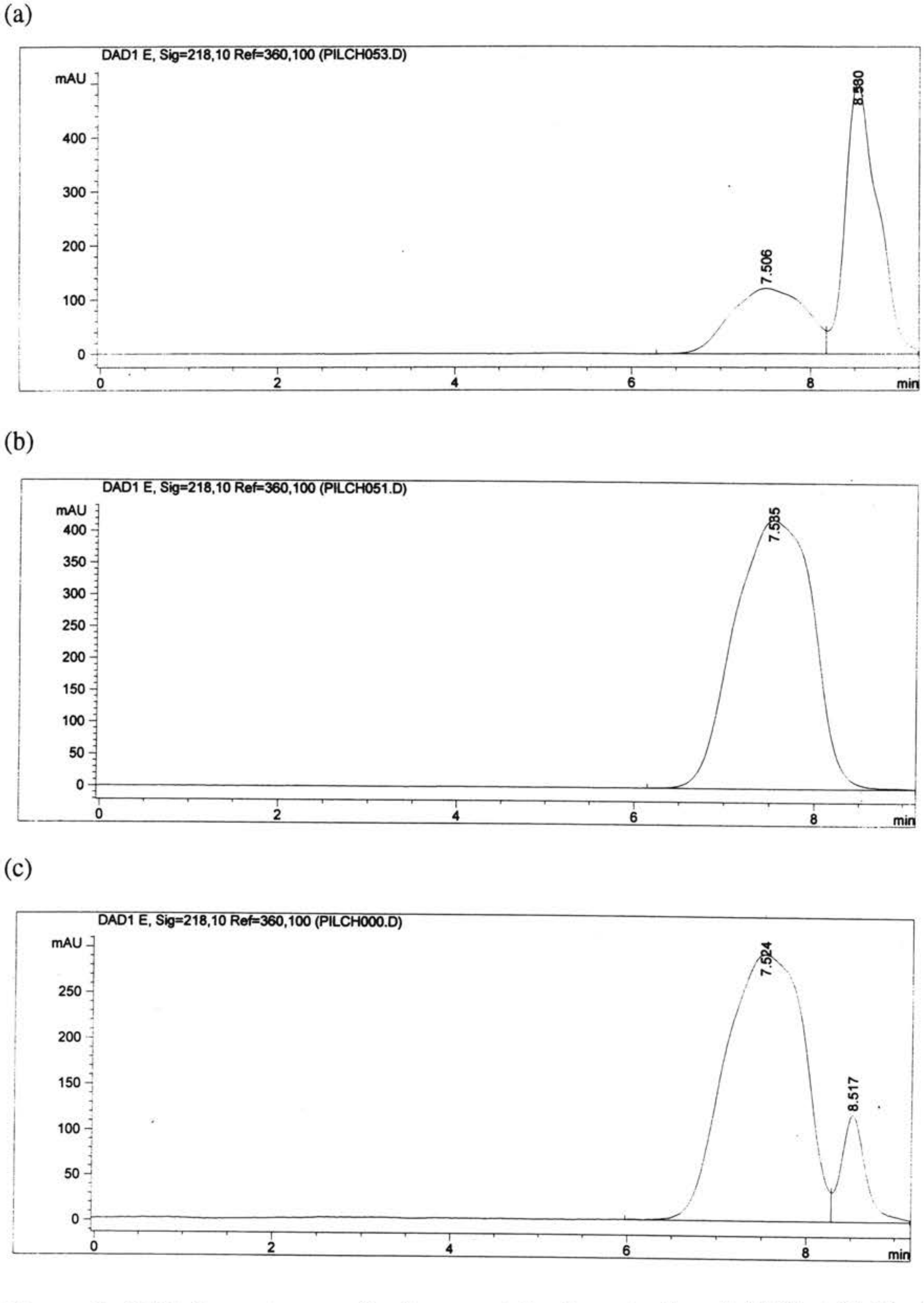


Figure 5. SEC chromatograms for the repeated polymerization of AMS at 30 °C: (a) unprecipitated PAMS/surfactant mixture, (b) precipitated PAMS sample, and (c) PAMS/Triton N-150 mixture (16 wt.% surfactant/polymer) patterned after surfactant content obtained from ^{1}H NMR analysis.

Tacticity. The configuration of the polymer backbone was determined by ^{1}H NMR spectroscopy.[16] The α-methyl resonance of PAMS splits into three multiplets which are assigned to the different triads, syndiotactic (*rr*), atactic (*mr*), and isotactic (*mm*) at 0.15, 0.4, and 0.9 ppm, respectively. A TMS peak interfering with the integration of the *rr* triad thwarted preliminary investigations of the tacticity. Thus, subsequent ^{1}H NMR spectra were recorded in $CDCl_3$ that did not contain any TMS.

The syndiotactic content of PAMS prepared by free radical polymerization decreases with increasing polymerization temperature. PAMS formed at 3 °C contained 70% *rr* triads whereas PAMS prepared at 45 °C had 58% *rr* triads. The syndiotactic content of PAMS formed at 40 °C is approximately the same as the PAMS prepared at 35 °C. The results are shown in Table 6 and the linear dependence is illustrated in Figure 6.

Table 6. Tacticities of PAMS Samples

Polymerization Temperature, ˚C	*rr*	*mr*	*mm*
3	0.70	0.29	0.02
10	0.69	0.29	0.02
15	0.67	0.31	0.03
20	0.66	0.32	0.02
25	0.65	0.33	0.03
30	0.63	0.30	0.07
35	0.61	0.35	0.04
40	0.61	0.35	0.04
45	0.58	0.35	0.08

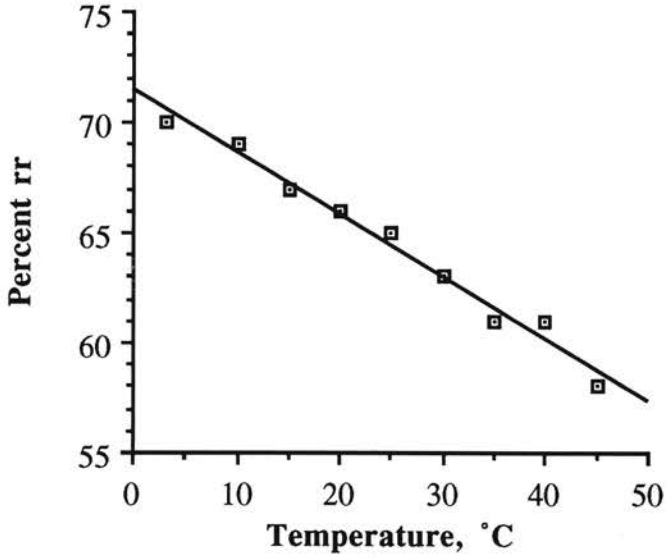


Figure 6. The syndiotactic content of PAMS decreases with increasing polymerization temperature.

Discussion

High Molecular Weight PAMS. The highest reported molecular weight of a PAMS sample obtained from a cationic polymerization is ~40 000 g/mol[11] and molecular weights of only a few thousand are commonly observed[11,22] even at low (sub zero) polymerization temperatures. Thus radical polymerization in a miniemulsion at temperatures above 0 °C produces polymer that has a molecular weight slightly higher than the polymer produced in a cationic polymerization at < 0 °C. PAMS with a molecular weight of ~1×10^6 g/mol can be achieved through an anionic polymerization[4] at –78 °C although molecular weights on the order of 10^4 g/mol are more common for anionic polymerization.[5,7,8]

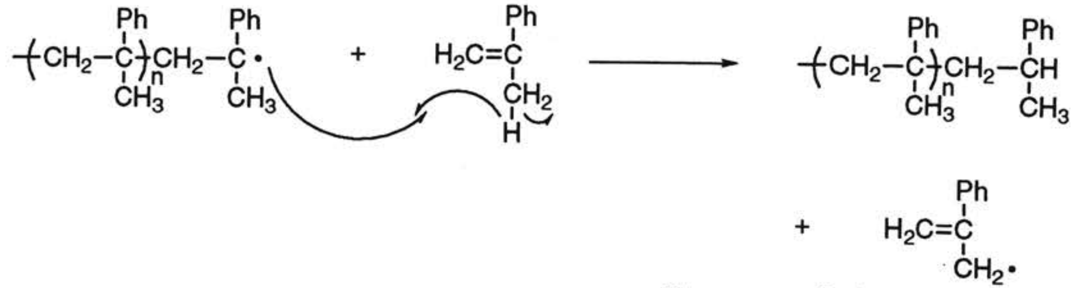
Kukulj and co-workers obtained weight-average molecular weights of ~4 000 g/mol in bulk radical polymerizations of AMS at 50 °C.[13,14] The polymerization of AMS in a miniemulsion at 45 °C resulted in a polymer with a higher weight-average molecular weight (15 000 g/mol). Dilution of AMS decreases the ceiling temperature of the monomer. Thus the PAMS sample prepared at 45 °C should be closer to the ceiling temperature of the polymerization than the bulk polymerizations at 50 °C (T_c = 61 °C). Lowering the miniemulsion polymerization temperature just a few degrees to 40 °C results in a PAMS sample with a much higher weight-average molecular weight (70, 000 g/mol). So there is a definite advantage in performing the free radical polymerization in a miniemulsion over bulk radical polymerization due to the increased conversions and higher molecular weights in shorter reaction times.

Microemulsion, miniemulsions, and emulsions typically give higher molecular weight polymers due to a reduced rate of bimolecular termination. However, neither combination nor disproportionation, but chain transfer to monomer, is the dominant chain-stopping mechanism for AMS[13] (Figure 7). When performing a polymerization in a miniemulsion, the presence of surfactant provides an alternate means for chain transfer (Figure 7). If the polymer chain terminates by abstracting a hydrogen from the surfactant either from an ethylene oxide unit or the hydrocarbon chain, the surfactant molecule can initiate the formation of a new polymer chain. The presence of surfactant in the NMR spectra points to the surfactant either not being completely removed upon precipitation and washings, or to being a part of the polymer chain. The surfactant remained in the sample after multiple reprecipitations suggesting that the surfactant is a part of the polymer chain. SEC analyses did not show a distinct peak for the surfactant, also indicating that the surfactant present in the sample is a part of the polymer.

Bimodal Distribution of PAMS Samples. The appearance of two components in the SEC analyses of PAMS samples is very peculiar. Bimodal distributions have been seen before in cationic polymerizations of AMS due to the nature of the propagating species. Two polymers of differing molecular weights were attributed to the BCl_4^- anion (from the alkyl chloride) and the BCl_3OH^- anion (from H_2O present in polymerization).[22] This does not explain the formation of two different polymeric chains in the radical polymerization of AMS.

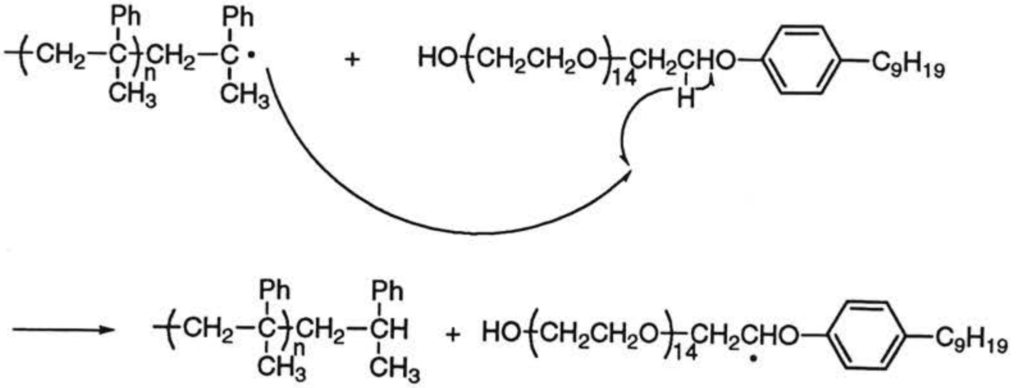
The amount of surfactant present in the ^1H NMR spectra correlates directly to the amount of the low molecular weight component present in the distribution (Table 5). The

Chain Transfer to AMS



Monomer radical can further initiate polymerization

Chain Transfer to Triton N-150



Surfactant radical can initiate further polymerization

Figure 7. PAMS chains can terminate by chain transfer to monomer or chain transfer to surfactant.

highest amounts of surfactant appear in the PAMS samples prepared at 30 °C and 45 °C. Each of these samples contains a higher amount of the low molecular weight component and the surfactant content did not decrease significantly upon reprecipitation. This could be the result of the surfactant being more difficult to remove from the lower yields produced from these polymerizations or increased difficulty in removing surfactant from low molecular weight PAMS. The presence of surfactant seen by ^{1}H NMR analyses and the absence of a surfactant peak in the SEC analyses (Figure 5) indicates that the surfactant is a part of the polymer. The high molecular weight polymer could arise from multiple polymer chains grafted onto a surfactant molecule.

Other possibilities include the high molecular weight polymer being formed as a consequence of chain transfer to polymer. The polymeric radical could then initiate a new polymer chain. If additional chain transfer to the polymer took place, a highly branched structure with a high molecular weight would be obtained. The low molecular weight polymer fraction would then be the portion of the polymer initiated by monomeric, surfactant, or ascorbate radicals. After chain transfer to monomer, the monomeric radical, being in close proximity to the polymer chain due to nature of a microemulsion, could abstract the hydrogen from the end of the polymer chain which would then continue polymerization. Repetition of this process would also produce a high molecular weight polymer.

The most probable reason for the bimodal distribution is the nature of the polymerization media. In a miniemulsion polymerization, two or more nucleation mechanisms could be responsible for polymer chain growth. Nucleation can take place in monomer droplets present in the dispersion, in micelles, or in the aqueous phase (homogeneous nucleation).[2] Radicals generated in the aqueous phase could enter monomer-swollen micelles and initiate polymerization for micellar nucleation.[2] Monomer can diffuse into the growing particles from uninitiated monomer-swollen micelles and monomer droplets. Monomer droplets, stabilized due to the adsorption of surfactant molecules, could also be initiated by radicals formed in the aqueous phase.[2] During homogeneous nucleation, radicals propagate in the aqueous phase by adding monomer present in the aqueous phase until they reach the limit of their solubility in the aqueous phase and precipitate out of solution. The precipitated oligomeric radicals can then form particles by absorbing surfactant molecules. If the particles then absorb additional monomer, further propagation and chain growth can be achieved.[2]

All three nucleation mechanisms could be operating simultaneously. The dominant mechanism for particle formation is primarily dependent upon the surfactant concentration and the monomer solubility in water. Miniemulsions are often prepared with less surfactant to try to eliminate micellar nucleation.[2] However, the miniemulsions prepared in this work contained a surfactant to monomer weight ratio of approximately 2 to 1. The most likely source of a bimodal distribution comes from droplet and micellar nucleation compared to homogeneous nucleation. High molecular weight polymers could form in droplets or monomer-swollen micelles and the low molecular weight fraction of the PAMS samples could be from homogeneous nucleation. The solubility of

AMS in the aqueous phase could prevent any appreciable amount of polymer from forming in the aqueous phase. In this case, a polymer with a higher molecular weight must be formed in either a monomer droplet or a monomer-swollen micelle. The low molecular weight PAMS would then be the product of the other nucleation mechanism.

Kinetics for the Polymerization of AMS. The number-average degree of polymerization of a polymer is

$$\mathrm{DP}_n = R_p/R_t \qquad (3)$$

where R_p is the rate of polymerization and R_t is the overall rate of termination. If the only mode of termination is chain transfer the equation becomes

$$\mathrm{DP}_n = R_p/R_{tr} \qquad (4)$$

If chain transfer occurs only to monomer

$$R_{tr} = k_{tr}\,[\mathrm{M}][\mathrm{R}\bullet] \qquad (5)$$

$$\mathrm{DP}_n = \{k_p[\mathrm{M}] - k_{dp}\}/\,k_{tr}\,[\mathrm{M}] \qquad (6)$$

$$\mathrm{DP}_n = k_p/k_{tr} - k_{dp}/k_{tr}\,[\mathrm{M}] \qquad (7)$$

and the degree of polymerization is inversely dependent upon the rate of chain transfer. Thus the primary effect of chain transfer is decreasing the polymer chain length. The molecular weight of the polymer sample is directly dependent upon the degree of polymerization. As the polymerization temperature is increased, k_{dp} increases more than k_p, and the chain length decreases. This explains why the molecular weight decreases as the polymerization temperature is increased.

Tacticity of PAMS. Due to steric and electronic repulsions between similar substituents, syndiotactic configurations are slightly favored thermodynamically over isotactic placements. As the polymerization temperature is increased, the difference between the rate coefficients for the two modes of propagation decreases, and a more random polymer is formed. In general, reducing the polymerization temperature in free radical polymerizations increases the proportion of syndiotactic placements.[2]

The dependence of tacticity on polymerization temperature in free radical polymerization of AMS is in direct contrast to anionic polymerization techniques. Whereas the syndiotactic content decreases with temperature in radical polymerization, the syndiotactic content increases with temperature in anionic polymerizations of AMS.[5-7] For example, PAMS formed at 30 °C was 59% *rr* and at –49 °C was 40% *rr*. The difference is most likely due to the nature of the propagating species. In anionic polymerizations, a complex formed at the propagating chain end with the initiator and the penultimate residue causes isotactic placement to be more highly favored. A propagating chain end in a radical polymerization does not form such a complex, and the more thermodynamically favored syndiotactic placements are obtained at lower temperatures (see Chapter III, Figure 10). Thus the syndiotactic content of PAMS decreasing with increasing polymerization temperature is not surprising. At higher temperatures, the polymerization becomes less selective, and the syndiotactic content is reduced due to more of the kinetic product being formed.

Conclusions

PAMS formed in miniemulsions led to the formation of a low molecular weight component common for radical polymerizations of AMS and also an uncommonly high molecular weight fraction. Chain transfer to surfactant was responsible for some termination of the polymer chain, due to the presence of surfactant in the polymer. Increased conversion and higher molecular weights are seen when the polymerization is performed at temperatures less than 25 °C. The syndiotactic content of the polymer decreased with increasing polymerization temperature.

The polymerization of AMS in a miniemulsion is beneficial for producing an increased yield of higher molecular weight polymer in shorter reaction times than conventional radical polymerizations of AMS. Future research should include exploring the possibility of forming the high molecular weight polymer with less surfactant to reduce the cost of the removal of surfactant in the commercial production of PAMS. The mechanism for the formation of high molecular weight polymer should also be investigated further.

References

1. Gilbert, R. G. *Emulsion Polymerization*; Ottewill, R. H.; Rowell, R. L., Eds. Academic Press: London, 1995, pp 1-73.

2. El-Aasser, M. S.; Sudol, E. D. *Emulsion Polymerization and Emulsion Polymers*; Lovell, P. A.; El-Aasser, M. S., Eds. Wiley: New York, 1997, pp 38-55.

3. Cowie, J. M. G. *Polymers: Chemistry and Physics of Modern Materials* Blackie Academic and Professional: New York, 1991.

4. www.herdillia.com/htm/alphamethyl.htm lists applications of AMS.

5. Elgert, K.-F.; Seiler, E. *Makromol. Chem.* **1971**, *145*, 95.

6. Wicke, R.; Elgert, K.-F. *Makromol. Chem.* **1977**, *178*, 3075.

7. Kawamura, T.; Uryu, T.; Seki, T.; Matsuzaki, K. *Makromol. Chem.* **1982**, *183*, 1647.

8. Elias, V. H.-G.; Kamat, V. S. *Makromol. Chem.* **1968**, *117*, 61.

9. Salman, R. S.; Al-Jarrah, M. M. F.; Abas, K. *Polym. Degrad. Stab.* **1990**, *28*, 209.

10. Brownstein, S.; Bywater, S.; Worsford, D. J. *Makromol. Chem.* **1961**, *48*, 127.

11. Toman, L.; Pokorny, S.; Spêcvácek, J. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 2217.

12. Kawamura, T.; Uryu, T.; Seki, T.; Matsuzaki, K. *Polym. J.* **1983**, *15*, 107.

13. Kukulj, D.; Davis, T. P.; Gilbert, R. G. *Macromolecules* **1998**, *31*, 994.

14. Kukulj, D.; Heuts, J. P. A.; Davis, T. P. *Macromolecules* **1998**, *31*, 6034.

15. Kukulj, D.; Davis, T. P. *Macromolecules* **1998**, *31*, 5668.

16. Elgert, K.-F.; Seiler, E.; Puschendorf, G.; Ziemann, W.; Cantow, H.-J. *Makromol. Chem.* **1971**, *144*, 73.

17. Zheng, K. M.; Greer, S. C. *Macromolecules* **1992**, *25*, 6128.

18. Andrews, A. P.; Andrews, K. P.; Greer, S. C.; Boué, F.; Pfeuty, P. *Macromolecules* **1994**, *27*, 3902.

19. Das, S. S.; Andrews, A. P.; Greer, S. C. *J. Chem. Phys.* **1995**, *102*, 2951.

20. Zhuang, J.; Andrews, A. P.; Greer, S. C. *J. Chem. Phys.* **1997**, *107*, 4705.

21. Zhuang, J.; Das, S. S.; Nowakowski, M. D.; Greer, S. C. *Physica A* **1997**, *244*, 522.

22. Toman, L.; Pokorny, S.; Spêcvácek, J. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 2229.

CHAPTER V

OUTLOOK AND CONCLUDING REMARKS

Polymerization in microemulsions is useful for the production of small microlatexes (10 nm < D < 40 nm) with many unique properties. Two advantages of using these novel systems are the low viscosity and the optical transparency of the polymer dispersion. The microlatexes are highly stable and a high molecular weight polymer can be obtained in a relatively short time span. These microlatexes could find applications in much the same way as the millions of tons of polymer latexes that are produced each year. These latexes have found uses as coatings, adhesives, paints, additives, and in biomedical research.

Commercially, the main drawbacks of performing polymerizations in microemulsions are the high surfactant concentrations required to form the initial microemulsion ($S \geq 1$) and the low monomer concentrations responsible for a low polymer content (<10 wt.%). Expensive processing would be needed to remove the excess surfactant. Recently, increased polymer content of small microlatexes produced in microemulsions has been achieved.[1-4] Fu and coworkers have developed a modified procedure in which the original microemulsion contains just a small amount of monomer typical of a normal microemulsion polymerization.[1,2] During the polymerization, a continuous feed of monomer is added to the mixture, being careful to avoid the build-up of unreacted monomer droplets. The polymerization continues then by recruiting the additional monomer that has been added to the solution. As a result, nanosize latex particles (<20 nm) with high solids content (10-30 wt.%) were produced using a relatively small amount of a conventional surfactant (<1 wt.%) such as dodecyltrimethylammonium bromide (DTAB).[1,2] Gan and coworkers obtained polystyrene/surfactant ratios as high as 14:1 by continuously supplying styrene to the polymerizing mixture.[3]

Puig and coworkers synthesized core-shell polymers of styrene and butyl acrylate using a continuous feed of monomer to the polymerizing mixture.[4] High-solid content polystyrene latexes (~40 wt.%) with a small particle size (<30 nm) and a high molecular weight (> 2×10^6 g/mol) were obtained prior to the addition of butyl acrylate to form the core-shell polymer. The core-shell polymers were produced using both emulsion and microemulsion procedures. The emulsion-made core-shell polymer exhibited an elastic response at small strains, followed by a flow up to a yield point where necking occurred and rupture took place.[4] This behavior is typical of core-shell polymers. On the other hand, the microemulsion-made core-shell polymers behaved like tough materials. They were much more rigid and displayed a higher yield stress than typical core-shell polymers. The Young modulus was larger, and the overall strength of the microemulsion-made polymer was greater than those of the emulsion-made samples. The authors attributed the improved behavior to the high specific surface area of the microemulsion-made polymers.[4]

Future research could include finding new surfactant systems that function in a more effective way to stabilize the interfaces in a microemulsion. Antonietti and coworkers have used metallosurfactants to produce small cross-linked latexes called microgels.[5] Functionalized microgels have the possibility of being used in applications in much the same way as dendrimers. The microgels would have the advantage of a much easier and cheaper synthesis. Antonietti and coworkers also used a more biocompatible surfactant, lecithin, in the production of microlatexes that could be useful in biomedical applications.[6] Polymerization in microemulsions is a continuously growing field, and the breadth of the application and challenges is broader than what has been discussed within this text. Look for many interesting developments in this field for industry and academic research alike.

References

1. Ming, W.; Jones, F. N.; Fu, S. *Macromol. Chem. Phys.* **1998**, *199*, 1075.
2. Ming, W.; Jones, F. N.; Fu, S. *Polym. Bull.* **1998**, *40*, 749.
3. Xu, X. J.; Chew, C. H.; Siow, K. S.; Wong, M. K.; Gan, L. M. *Langmuir* **1999**, *15*, 8067.
4. Aguiar, A.; Gonzalez-Villegas, S.; Rabelero, M.; Mendizabel, E.; Puig, J. E.; Dominquez, J. M.; Katime, I. *Macromolecules* **1999**, *32*, 6767.
5. Antonietti, M; Nestl, T. *Macromol. Rapid Commun.* **1994**, *15*, 111.
6. Antonietti, M.; Basten, R.; Gröhn, F. *Langmuir* **1994**, *10*, 2488.

VITA

Spence Colman Pilcher

Candidate for the Degree of

Doctor of Philosophy

Thesis: STRUCTURES AND PROPERTIES OF POLYMERS FORMED IN MICROEMULSIONS

Major Field: Chemistry

Biographical:

Personal Data: Born in Siloam Springs, Arkansas, USA, June 12, 1972, the son of Tommy Jr. and Janice Pilcher.

Education: Graduated from Kansas High School, Kansas, Oklahoma, in May, 1990; received Bachelor of Science degree in Chemistry and a Bachelor of Science degree in Mathematics from Northeastern State University, Tahlequah, Oklahoma, in May, 1994; completed requirements for the Doctor of Philosophy degree at Oklahoma State University in December, 2000.

Experience: Raised on a dairy farm in Kansas, Oklahoma, and employed as a farm laborer before graduate school; employed by Oklahoma State University, Department of Chemistry, as a graduate teaching and research assistant, Department of Chemistry, Oklahoma State University, 1994 to present.

Professional Memberships: American Chemical Society, Phi Lambda Upsilon.