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THE SYNTHESIS AND CHARACTERIZATION OF CHLORINATED
POLYETHYLENE-G-STYRENE AND ITS APPLICATION AS A BLEND
MODIFIER

The University of Oklahoma

PH.D.

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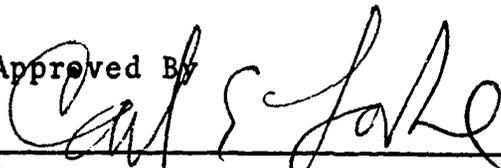
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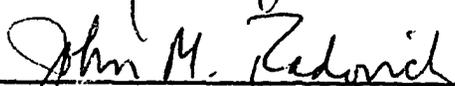
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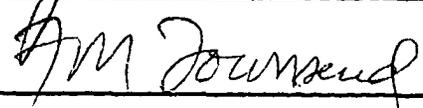
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Approved By









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My mother, who brought me up and made me what I am with her endless love, deserves all the joy and pride.

The encouragement, help and understanding of my wife, Si Lian, provided a constant source of strength which has made this work possible.

ABSTRACT

Chlorinated polyethylene-g-styrene copolymers have been synthesized by chemical and radiation initiation methods. With the use of a pre-initiation technique, graft efficiency as high as 0.84 has been achieved from the chemical-initiated graft copolymerization. The chemical-initiated grafting was found to be significantly affected by the degree of swelling, initiation time and temperature, and concentration of initiator and monomer. High initiation temperatures or long initiation times may result in crosslinking in the CPE films. The radiation-induced grafting was carried out using a mutual-irradiation method and graft efficiency was found to be around 0.40. No crosslinking was observed with the dose level used in this study.

The graft products were purified by solvent extraction followed by selective precipitation to remove the styrene homopolymer and unreacted chlorinated polyethylene. Solubility behavior of CPE and polystyrene in various solvents was studied and the solubility parameter was estimated from the solubility result. The compositions of the separated fractions were determined by infrared spectroscopy (IR) so

that the degree of grafting and graft efficiency could be evaluated.

The graft copolymers and CPE were characterized by IR and laser-Raman spectroscopy, differential scanning calorimetry and dilute solution viscosity measurement.

The graft copolymers were melt blended with incompatible polyblends such as polyvinyl chloride-polystyrene blend and low density polyethylene-polyvinyl chloride-polystyrene blend in an attempt to improve the interface adhesion between incompatible phases. Evidences of interaction between the graft copolymer and the homopolymers were obtained from photomicrographs and dynamic mechanical results of the graft modified polyblends. Impact strength of the polyvinyl chloride-polystyrene blend increased by 48 to 75%, with the addition of CPE-g-styrene copolymers. The fact the addition of the graft copolymer reduced the domain size substantially indicates the modification effect due to graft copolymer.

TABLE OF CONTENTS

	<u>Page</u>
ACKNOWLEDGMENTS.	iii
ABSTRACT	iv
LIST OF TABLES	x
LIST OF FIGURES.	xii
<u>CHAPTER</u>	
I. INTRODUCTION	1
II. BACKGROUND	5
Graft Copolymers.	5
Graft Synthesis	7
Free Radical Mechanism	
Ionic Mechanism.	13
Chlorinated Polyethylene.	14
Stabilization of Chlorine-Containing Polymers	15
Purification.	17
Characterization.	21
Quantitative Analysis by IR.	22
Morphology and Thermal Behaviors	25
Differential Scanning Calorimetry.	27
Dilute Solution Viscosity.	29
Dynamic Mechanical Behavior.	31

TABLE OF CONTENTS (Continued)

<u>CHAPTER</u>	<u>Page</u>
II. BACKGROUND (Continued)	
Compatibility.	35
Literature Works - CPE Graft Copolymers. . .	37
III. EXPERIMENTAL.	39
Graft Synthesis.	39
Chemical Polymerization	39
Irradiation Polymerization.	43
Purification	44
Solubility Studies for Removal of Styrene Homopolymer	44
Removal of Unreacted CPE.	47
Pressure Filtration	48
Characterization	52
Infrared Analysis	52
Laser-Raman Spectroscopy.	53
Dilute Solution Viscosity	55
Microscopy.	57
Dynamic Mechanical Testing.	57
Differential Scanning Calorimetry	60
Impact Strength	63
Blending and Molding	65
Grinding	67
Materials.	68

TABLE OF CONTENTS (Continued)

<u>CHAPTER</u>	<u>Page</u>
IV. RESULTS AND DISCUSSION.	71
Preliminary Study.	72
Swelling Test	72
Solubility Study.	75
Isolation of Styrene Homopolymer.	84
Isolation of Unreacted CPE.	87
Composition Determination by IR	89
Graft Synthesis and Purification	94
Extraction.	99
Methanol-Precipitation.	104
Determination of Graft Efficiency and Degree of Grafting.	107
Effect of Reaction Conditions.	111
Radiation Grafting	111
Effect of Radiation Dose.	113
Effect of the Presence of Oxygen	123
Chemical Grafting	115
Effect of the Type and Amount of Initiator	115
Effect of Swelling Time	118
Effect of Initiation Time	120
Effect of Reaction Temperature.	123
Effect of Polymerization Time	124

TABLE OF CONTENTS (Continued)

<u>CHAPTER</u>	<u>Page</u>
IV. RESULTS AND DISCUSSION (Continued)	
Effect of Methanol Concentration in The Monomer Solution.	126
Effect of Type of CPE on Grafting	128
Evaluation of The Chemical Initiating Graft Copolymerization.	129
Characterization	133
IR and Laser-Raman Spectroscopy	133
Dilute Solution Viscosity	143
Differential Scanning Calorimetry	148
Microscopy.	154
Dynamic Mechanical Properties	159
Impact Strength	167
V. CONCLUSIONS	169
LITERATURE CITED.	177

LIST OF TABLES

<u>TABLE</u>	<u>Page</u>
2- 1. Dispersibility of PVA-Styrene Graft Copolymer in various solvents.	20
4- 1. Solubility of CPE and Polystyrene in Various Solvents at Room Temperature	76
4- 2. Solubility Parameters of Polyethylene, Polyvinyl Chloride and Polystyrene	81
4- 3. Three-Dimensional Solubility Parameters of CPE and Solvents	82
4- 4. Separation Result of Product C-9	86
4- 5. Definition of The Notations of Reaction Variables.	95
4- 6. Reaction Conditions of Graft Copolymerizations and their yields	97
4- 7. Reproducibility of Synthesis	98
4- 8. Results of The First Stage Separation.	100
4- 9. Results of The Second Stage Separation	105
4-10. G. E. I. and Degree of Grafting obtained from IR Analysis.	110
4-11. Effect of Type and Amount of Initiator	116
4-12. Effect of Swelling Time.	118
4-13. Effect of Swelling on Crosslinked Films.	119
4-14. Effect of Reaction Temperature	123
4-15. Effect of Polymerization Time.	124
4-16. Effect of The Type of CPE Backbone	128

LIST OF TABLES (Continued)

<u>TABLE</u>		<u>Page</u>
4-17.	Change in Chlorine Content of CPE 2552 During Processing.	131
4-18.	Dilute Solution Viscosities of Graft Copolymers and Homopolymers.	144
4-19.	Impact Strength Data of Unmodified and Graft-Modified PVC-PS Blends.	167

LIST OF FIGURES

<u>FIGURE</u>	<u>Page</u>
2- 1. A Typical Graft Copolymer.	6
2- 2. Interface Modification By Graft Copolymer.	6
2- 3. DSC-2 Block Diagram.	28
2- 4. A Typical DSC Thermogram Showing various Types of Physical Change.	28
3- 1. Fractionation Scheme Used for Purification	50
3- 2. Base-Line Determination in IR Composition Analysis	51
3- 3. Fabrication of Pressure Filter	55
3- 4. Cannon-Fenske Viscometer	57
3- 5. Photograph and Block Diagram of Rheovibron Dynamic Viscoelastometer	60
3- 6. Breaking Operation and Dimensions of A Izod Type Specimen	66
4- 1. Degree of Swelling and Weight Loss of CPE 2552 in Benzene-Methanol Mixture.	73
4- 2. Solubility of CPE 3614 and PS in Cyclohexane- Acetone Mixture.	78
4- 3. Solubility of CPE 2552 in Cyclohexane-Acetone Mixture.	79
4- 4. IR Spectra of Extracted CPE 2552 - Polystyrene Mixture.	85
4- 5. Solubility of CPE 2552-Polystyrene Blends in 18/82 Cyclohexane-Acetone Mixture.	88
4- 6. Calibration Curve for CPE 2552-Polystyrene Mixture	91

LIST OF FIGURES (Continued)

<u>FIGURE</u>	<u>Page</u>
4- 7. Calibration Curve for CPE 3614-Polystyrene Mixture	92
4- 8. Spectrum of Graft Product C-9 After Three Consecutive Extractions.	102
4- 9. Spectra of Extracted CPE-PS Mixture and Extracted Graft Copolymer.	103
4-10. Effect of Initiation Time on G. E. I. and Degree of Grafting	121
4-11. Effect of Methanol Content in Monomer Solution	127
4-12. Spectra of CPE 2552 and CPE 3614	134
4-13. Spectrum of CPE 2552, 340-1640 Wave Number	136
4-14. Spectrum of Polystyrene and CPE 2552, Low Frequency Region	137
4-15. Spectra of CPE-g-Polystyrene Copolymers.	138
4-16. Laser-Raman Spectrum of CPE 2552	140
4-17. Laser-Raman Spectra of CPE 2552 and CPE-g- Polystyrene Copolymer.	142
4-18. Thermograms of CPE 4814 and CPE 2552	149
4-19. Thermograms of CPE 2552-g-Styrene and CPE 4814-g-Styrene	150
4-20. Thermograms of Unmodified and Modified PVC-PS Blends	153
4-21. Thermograms of Unmodified and Modified PE-PVS-PS Blends	155
4-22. Photomicrographs of Unmodified and Modified PVS-PS Blends.	156
4-23. Photomicrographs of Unmodified and Modified PE-PVC-PS Blends	158
4-24. Dynamic Mechanical Behavior of CPE 2552.	160
4-25. Dynamic Mechanical Behavior of Graft-Modified PVC-PS Blends.	161

LIST OF FIGURES (Continued)

<u>FIGURE</u>		<u>Page</u>
4-26.	Dynamic Mechanical Behavior of Graft-Modified PE-PVC-PS Blends.	162

THE SYNTHESIS AND CHARACTERIZATION OF
CHLORINATED POLYETHYLENE-g-STYRENE
AND ITS APPLICATION AS
A BLEND MODIFIER

CHAPTER I

INTRODUCTION

Despite the fact that most commercial polymers at this time are homopolymers, applications that demand combination of properties not attainable with simple homopolymers are being developed to a continually increasing degree. In an effort to satisfy this need, a lot of work has been done on utilizing combinations of existing polymers as blends or copolymers. Synthesis of graft copolymers is one such way to develop new material with predicted and desired properties by utilizing combination of existing polymers. Most graft copolymers are characteristic in their facility for blending with their parent homopolymers. This feature of graft copolymers has broadened their application to include being employed as "compatibilizing agents" in incompatible polymer blends.

As is well known, most polymer blends are incompatible due to the thermodynamic restriction imposed by their large chain length. The incompatibility of the polymers in a blend leads to poor adhesion between phases which implies poor mechanical properties. Techniques for modification of those incompatible blends has drawn great attention in past decades. This is one reason why development of graft copolymers has become an increasingly noticed task. A study has been done on utilizing graft copolymers to modify the properties of blends involving polyethylene, polyvinyl chloride and polystyrene(1,2). In this study, a gamma-irradiation initiated polyethylene-g-styrene copolymer was found to be a good modifier for polyethylene-polystyrene blends. However, the improvement was not so pronounced as to make the blend strong enough for construction use. The reason for this may be that the graft material used was not well purified which means the graft copolymer accounted for only a small fraction of the blend. In addition, no modification on PVC-containing blends was expected from such a graft copolymer. This result led to the consideration of utilizing other graft copolymers which will be purified to modify blends involving PE, PVC, and PS. This is the impetus to conduct this proposed project.

A graft copolymer involving chlorinated polyethylene may possess three-block like structure since the chlorinated polyethylene itself, as will be discussed more fully below,

can be manufactured in such a way that it has block-copolymer like structures. When blending this three-block like copolymer into incompatible blends, each segment in the graft copolymer is expected to have high affinity toward its homopolymer counterpart and therefore enhance the interfacial adhesion among phases. This is the reason why we expect the CPE-g-Styrene copolymer to be a suitable modifier for blends involving PE, PVC, and PS.

Very few investigators have worked on the synthesis of this graft copolymer, and virtually no work on the characterization and purification has been reported in the literature so far. Therefore, the reaction mechanisms of the synthesis as well as the characterization of the graft copolymer produced have become significant in this study. Since the graft product has to be purified before being fully characterized, great effort has also been anticipated in the development of a separation process for the graft product. The graft copolymer has then been utilized to modify the polyethylene, polyvinyl chloride and polystyrene blends, with its effectiveness in modification investigated through mechanical testings, thermal analysis, and morphological study.

Ultimately, this graft material will be utilized in an attempt to help ease the problem of waste-plastics disposal. As polyethylene, polyvinyl chloride and polystyrene are largely used they are the plastics most prevalent in the solid

waste stream. It is highly desired that these plastics be separated from the solid waste and reused. However, even though the plastics could be removed from the solid waste without technical problem, it would be very difficult to separate them into the generic forms of plastics. This difficulty may be avoided if these plastics can be reused in the form of blends. Since blends made from polyethylene, polyvinyl chloride and polystyrene show very poor mechanical properties(3), the modification using the graft copolymer developed in this work would be required. It is the hope of the author that the information obtained in this study will be helpful in the process development of this graft copolymer, if its engineering application is proved practical.

This work consists of three parts:

(1) preparation and characterization of the graft copolymer.

(2) evaluation of the effect of reaction variables on the graft efficiency and graft composition.

(3) study of the modification mechanism by examining the morphology and mechanical properties.

CHAPTER II

BACKGROUND

This chapter briefly reviews the practices, theories, techniques, and literatures that are related to this work. Discussion will be made under the titles of graft copolymers, graft synthesis, chlorinated polyethylene, purification, characterization, compatibility of polyblends, and literature works.

2.1. Graft Copolymers

A graft copolymer consists of a polymer backbone on which a second polymer is attached as a branch (Figure 2-1). It may be looked upon as a chemically linked pair of homopolymers. This type of polymer hybrid is a single chemical species that displays properties characteristic of each of the components. Two-phase or multiphase morphology is commonly observed in this type of material.

The attachment of a graft changes the properties of the backbone polymer to a certain extent. Changes in crystallinity, transition temperatures, thermal stability, gas permeability, solution viscosity and mechanical properties such

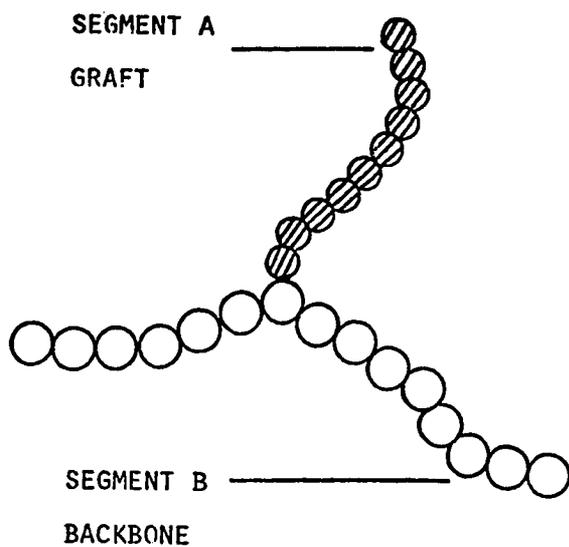


FIGURE 2-1: A TYPICAL GRAFT COPOLYMER

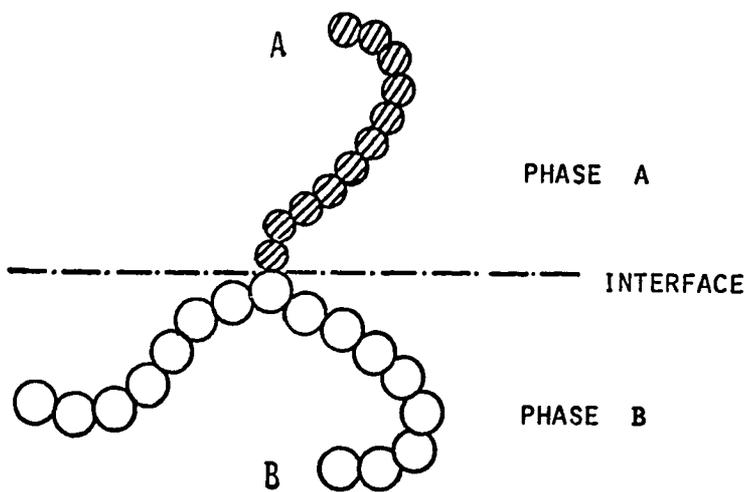


FIGURE 2-2: INTERFACE MODIFICATION BY GRAFT COPOLYMER

as tensile strength, impact strength, have been reported and discussed by a number of authors. (4-11) Some of the grafting effects have provided the basis for commercial polymers. Certain types of impact polystyrene and ABS are examples of commercial application of graft copolymers. (12)

Graft copolymers also have applications other than in bulk form. Surface modification by grafting has been widely studied and has been widely used in the fiber field. (13) Its ability to improve surface adhesion of two incompatible polymer phases have been well known and this feature provided the basis for this research.

When a graft copolymer is melt blended into a polyblend of its parent polymers, each segment in the copolymer tends to interact with its homopolymer counterpart, and functions as a bridge across the two separate phases of homopolymers. The covalent bond at the grafting site provides the force to hold two phases together (Figure 2-2). With better adhesion between two separate phases, better mechanical performance of the polymer blend is expected.

2.2 Graft Synthesis

A graft copolymer can be synthesized by either of two ways: (14) 1) by polymerizing the branch monomers in the presence of a preformed polymer backbone on which active sites have been created, which is termed "graft from" mechanism;

2) by the attack of a growing polymer to another polymer along the chain and thereby attaches a branch to a preformed trunk, which is termed "graft onto" mechanism.

Since the highest graft efficiency obtained so far was reported in synthesis using "graft from" mechanism, our attention will focus on the "graft from" techniques.

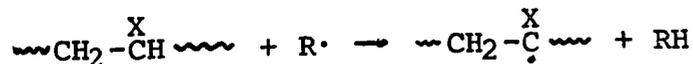
The type of graft copolymerization can also be classified by 1) free radical mechanism, 2) ionic mechanism, 3) coordination mechanism, 4) miscellaneous ring opening and coupling reaction. Since synthesis of a stereoregular polymer is not our interest and the functional groups required for ring opening or coupling reaction is not available in our backbone-branch system, only free radical and ionic mechanism are discussed here.

2.2.1. Free Radical Mechanism

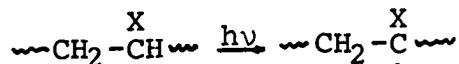
The free radical technique has been commonly used for synthesis of graft copolymers in both the literature work and commercial production (15), and has been employed in this study. The free radical mechanism involves the generation of free radicals as the active sites on the polymer backbone. Monomer molecules then react with the backbone polymer at the active sites and the polymerization is thus initiated. The mechanism of free radical grafting on a halogen containing polymer backbone is illustrated below.

Initiation:

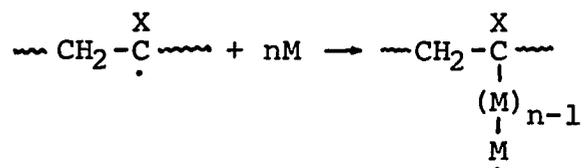
(by chain transfer)



(by radiation)



Propagation:



Termination is achieved usually by chain transfer to solvent followed by drying or by drying at reduced pressure.

In most free radical copolymerizations, initiation is achieved with either chemical method such as peroxide initiation, photolytic method or high energy irradiation techniques such as gamma-ray irradiation. Among these initiation techniques for creation of free radicals, high energy irradiation may be the one most commonly used for graft synthesis in literature work.

2.2.1.1. Radiation Induced Grafting

The mechanism of the free radical generation process is discussed below.

When electromagnetic radiation passes through matter its intensity decreases, primarily as a result of scattering and energy absorption by some of the irradiated molecules. There are three major processes in which electromagnetic radiation may interact with the irradiated substance:

- 1) the photoelectric effect.
- 2) Compton Scattering.
- 3) production of electron pairs.

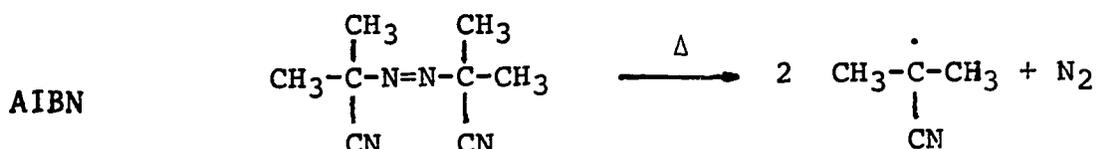
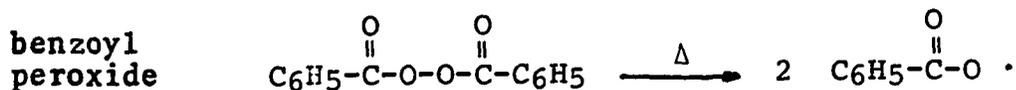
For gamma rays from cobalt 60 source, which is used in this work to produce graft, the predominant effect in organic materials is Compton's scattering. (16) In the Compton scattering process, a fraction of the incident radiation energy is absorbed by an orbital electron, causes the electron to be ejected from its orbital or to become excited, and a low-energy photon is scattered as a result of the collision. The Compton effect thus creates either ions or excited molecules which are very reactive. They either react with other materials present in the system or decompose into radicals and atoms. The free radicals produced in this process may be used to initiate graft copolymerization. Initiation can be carried out by either direct irradiation or pre-irradiation. Direct irradiation methods have been used in several works to produce polystyrene graft on vinyl polymer backbones (1,5, 17-25). The advantage of this technique is its simplicity while disadvantages are simultaneous homopolymerization and the possible

radiation damage of the exposed backbone polymer. The effectiveness of direct irradiation for initiating the graft copolymerization may be determined by the G-values (the number of free radicals formed per 100 eV absorbed per gram) of the backbone polymer and the monomer. Only a favorable combination of G-values, i.e. $G_{\text{backbone}} \gg G_{\text{monomer}}$, may result in a significant concentration of graft copolymer in the reaction product. For those backbone-monomer systems that do not possess favorable G-values, pre-irradiation techniques may be desired. In this technique, free radicals usually generated by irradiation of the polymer backbone at temperature below its glass transition point and then the monomer is introduced after initiation has been completed. In doing so, homopolymerization may be minimized as the monomer is not directly irradiated. However, even in a system which has very favorable G-values or in a pre-irradiation initiated polymerization, the formation of homopolymer is inevitable due to chain transfer to monomer. Determining factors of the efficiency of a graft copolymerization using irradiation techniques will be the ease of monomer diffusion into the polymer, irradiation medium, and the dose rate (26).

2.2.1.2. Chemical Initiated Grafting

Free radicals can also be created chemically from thermal decomposition of a free radical initiator such as peroxides or

2,2'Azo-bis-isobutyronitrile(AIBN). The free radical generation due to decomposition of peroxide and AIBN is as illustrated below.



The initiation and propagation are achieved by chain transfer process as described in the section "Free Radical Mechanism". High graft efficiency has not been reported so far in graft synthesis using this initiation mechanism. However, this might be the simplest way to synthesize a graft copolymer without using any special equipment. In addition, there is still a possibility to obtain better graft efficiency from a chemical initiated reaction by properly selecting the reaction conditions. A combination of low conversion (27), adequate polymerization temperature and monomer concentration may favor the formation of graft. The pre-initiation technique which has initiation and polymerization achieved in separate reactors should help to eliminate homopolymerization due to initiation of the monomer by the initiator free radicals present in the solution.

2.2.2. Ionic Mechanism

Despite all the convenience associated with free radical initiated copolymerization, graft copolymers prepared by this techniques are highly contaminated by homopolymers due to either chain transfer to monomer or direct initiation of monomer, or because not every backbone macromolecult enters into reaction. Better control of structure and less homopolymer contamination may be achieved by ionic mechanism.

Theoretically, the highest graft efficiency may be obtainable via the anionic mechanism due to the much lower propensity for spontaneous termination in anionic systems. Anionic grafting has been reviewed in several articles (28,29) and has been carried out in a number of works with either "graft from" (30,31) or "graft onto" techniques (32,33). Synthesis of essentially pure graft copolymer with organolithium-compound initiation has been reported for certain backbone-branch system (30). However, initiation of a halogenated vinyl polymer is commonly complicated by side reactions (30,34) and the efficiency of this graft copolymerization has not been evaluated.

Because of the difficulty in controlling the initiation which may lead to large amount of homopolymer along with graft copolymer and the backbone degradation often associated with the initiation, application of cationic techniques received little attention until recent years. Kennedy and co-workers

conducted a series of studies on cationic graft copolymerization in past five years and found that cationic co-initiator based on certain alkylaluminum compounds is useful for the efficient synthesis of graft copolymers, especially for that involves halogen containing polymer backbones (35-38). By proper selection of the reaction conditions, graft efficiency up to 100% have been reportedly achieved without significant degradation of backbone polymer (21).

So far, the knowledge in ionic graft synthesis is still limited. The ionic polymerization is extremely sensitive to the presence of impurity so that great care must be taken when conducting the laboratory work. Nevertheless, its much higher graft efficiency makes it a prospective way to prepare graft copolymers.

2.3. Chlorinated Polyethylene

Chlorinated polyethylene is produced by randomly chemical substitution of chlorine for hydrogen on the polyethylene chain. The material used in this study is prepared by slurry phase chlorination of high density polyethylene. This process gives a unique material with physical properties unlike those of polyvinyl chloride and high density polyethylene, but with certain similarity to both. This material is rather flexible like HDPE while showing some characteristics of polyvinyl chloride such as the flame resistance. The random distribution

of chlorine in the HDPE chain gives it a block copolymer-like structure with some blocks similar to HDPE and the others similar to polyvinyl chloride or polydichloroethylene. Upon mixing with polyethylene and polyvinyl chloride, those block-like segments contribute some interfacial adhesion between these two incompatible phases. The properties of chlorinated polyethylene are mainly determined by product variables such as chlorine content, melt viscosity and molecular weight (39). In this study, the chlorine content of CPE receives the most attention since it affects the crystallinity of the polymer and determines the relative concentration of PE-like block and PVC-block in the final graft product. Previous work showed that the chlorine content of CPE does play an important role in the modification of PE-PVC blends (40,41). CPE with higher chlorine content will have higher affinity toward PVC whereas a low-chlorine CPE will adhere better with PE. Thus, with different types of commercial CPE available, to find suitable modifiers for blends having varied PE-PVC composition will be possible.

Chlorinated polyethylene, a chlorine containing polymer, is susceptible to thermal degradation and needs to be stabilized during processing.

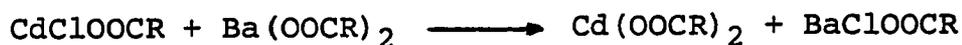
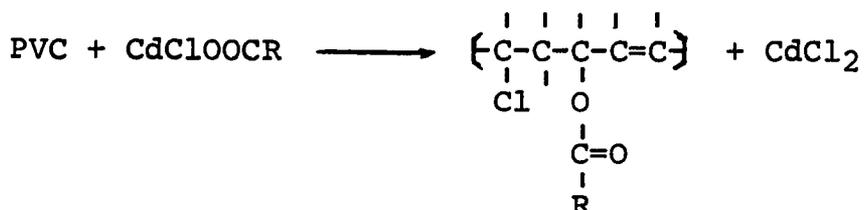
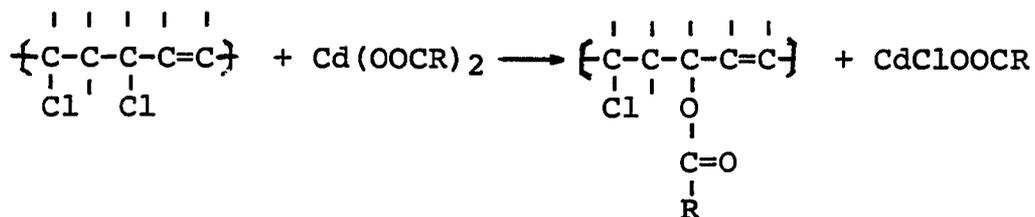
2.3.1. Stabilization of Chlorine-Containing Polymers

This study involves the processing of two chlorine-containing polymers, polyvinyl chloride and chlorinated

polyethylene. Polyvinyl chloride is famous for its rapid degradation at processing temperatures due to the labile chloride structures formed during polymerization. Chlorinated polyethylene, with randomly distributed chlorine atoms in it, is also susceptible to heat degradation. Color change of CPE has been observed in the molding work. A temperature of about 120°C, heating period of two to three minutes and exertion of pressure for several seconds would cause the originally white CPE film to turn to yellow. The degradation mechanism of CPE is considered similar to that of PVC, and protection of the polymer by adding stabilizer is necessary.

It has been proposed that the degradation of PVC is due to the presence of labile chloride which is highly susceptible to dehalogenation (42). Once dehalogenation is initiated, the chlorides are detached consecutively and form HCl and polyene structures. Therefore, a stabilization work should involve the elimination of labile chloride in the polymer so that dehalogenation can be halted.

The stabilization of chlorine containing polymers usually involves the use of metal salts of organic acids. Metals such as barium, cadmium, tin and zinc have been found effective. Secondary stabilizers such as epoxy plasticizers are also recommended to be used in combination with the metal salts. The mechanism of stabilization has been suggested as follows.



The ester structure formed in the first two reactions is much more stable than the labile chloride and dehalogenation can thus be halted. The barium soap is used to regenerate the cadmium soap as described in the last two steps. The epoxy plasticizers react to form an ether at the site of the labile chloride.

Locke (43) found that a combination of Ba/Cd metal salt and epoxidized soybean oil at a level of 3 phr each gave the best protection to CPE.

2.4. Purification

Since the graft copolymers obtained from reaction are usually contaminated by homopolymers, purification is required

to yield pure or nearly pure graft product before the graft copolymer can be characterized. Fractionation by solubility is the most commonly used techniques for purification. What we expect to see in a separation of graft product mixture is a fractionation due to chemical inhomogeneity of components in the mixture in stead of their molecular weight. Although solubility is determined by molecular weight as well as the chemical structure of the molecules, fractionation according to chemical structure will dominate if the chemical inhomogeneity is so pronounced as in a mixture of different chemical species (44). For the purpose of separation of a colymer mixture, any of the well-known preparative fractionation methods such as solvent extraction, column elution, chromatographic fractionation etc., can be utilized.

Gel permeation chromatography (GPC) should be a potential tool for separation of graft products since the separation in GPC is carried out according to the molecular size which may be significantly influenced by adding a graft on the backbone macromolecule (45). This technique has recently been used to determine the graft sites of a graft copolymer (46). It also was employed in combination with UV analysis to determine the graft efficiency of copolymerization (37).

However, in an effort to recover most graft copolymer in one fraction, selective extraction should be the best way if a solvent system with high selectivity can be found.

Many of the previous works on separation of graft product involve only simple extraction of the reaction products that, in most cases, were in solid film form. It has been shown that this kind of extraction was insufficient to isolate all the homopolymer (47).

Purification work in this study involved the use of a extraction-precipitation two-stage process. Much effort was made in the search of a selective solvent system during the development of this process. A highly selective solvent system is the most important ingredient of a successful extraction.

Since in the same molecule a graft copolymer has two segments different in their solubility behavior, it is possible that the graft copolymer is dispersed into the extracting solvent and results in micelle formation. The dispersion of graft copolymer results in the turbidity of the extracting solvent and sometimes leads to difficulty in separation. Y. Ikada and his college studied the dispersion behavior of several purified PVAc-styrene graft copolymer in various selective solvents at room temperature (48). They prepared two different types of samples from the same graft copolymer; one was recovered from THF, which is a good solvent for polystyrene, by pouring it into water, a good solvent for PVAc but nonsolvent for polystyrene. The other sample was recovered from benzene solution which was poured

into n-hexane. The former sample, to be referred to as A, is likely to have such a microstructure that the PVAc chains are extended and polystyrene chains collapsed, whereas the other sample, say B, has the inverse structure. Solubility behaviors of these two samples are summarized in Table 2-1, the relation between the solubilities of the homopolymers and the solution behavior of the graft copolymer can be clearly seen.

Table 2-1: Dispersibility of PVAc-styrene Grafts in Various Solvents from Dried Samples at Room Temperature (48)

Solvent	PVAc ^a	PS ^b	Graft	
			A	B
Methanol	soluble	insoluble	ND	ND
Cyclohexane ^c	insoluble	$T_{\theta} = 34^{\circ}\text{C}$	ND	ND
Acetone	soluble	swollen	D	D
EAA ^d	soluble	$T_{\theta} = 108.5^{\circ}\text{C}$	D	D
n-Octyl Acetate	$T_p = 83^{\circ}\text{C}^e$	soluble	ND	D

D: Dispersed; ND: Not Dispersed; a: $\bar{M}_n = 1.14 \times 10^5$; b: $\bar{M}_n = 2.11 \times 10^5$; c: at 50°C ; d: Ethyl Acetoacetate; e: Initial Cloudy Point.

It is obvious from the table that dispersion can be avoided if the solvent is a good solvent for one segment but a very bad one for the other, as the case for methanol and cyclohexane. In other words, the dispersion of graft copolymer, which may cause the graft copoly molecules to elute during separation will not happen if a highly selective solvent is used.

2.5. Characterization

The purification and characterization work is important in this study since it enables us to estimate how much graft copolymer has been produced, to better understand the structure and morphology of the graft material, and therefore to better understand the mechanism of modification in graft-modified blends.

Various techniques such as IR, Raman spectrophotometry, NMR, differential thermal analysis, dynamic mechanical study, optical microscopy, and GPC have been utilized to characterize the structure and/or composition of the graft copolymers. IR has been commonly used for determination of the composition of graft copolymers. It is also possible to detect the difference in structures between a graft copolymer and its corresponding mixture of homopolymers by IR spectroscopy (49). Raman spectroscopy has become important in polymer characterization since the introduction of Laser source. Raman scattering depends on change in the induced dipole moments of a molecule during a normal vibration whereas infrared absorption depends on the permanent dipole moments. As a result, these two processes are governed by different selection rules depending on the symmetry of the molecule. Since a given mode of molecular vibration may appear in either infrared or Raman spectra or both, a knowledge of both spectra will help to determine the structure of polymer. In this study, it is hoped that

significant change which is characteristic of the graft will be observed in IR or Laser-Raman spectra.

IR utilized to determine the composition of fraction obtained in separation procedures in this research. Theoretical background and some practices of using IR for determination of the composition of a binary polymer mixture are discussed below.

2.5.1. Quantitative Analysis By IR

The relationships dominating the quantitative use of IR spectra are expressed in the Beer-Lambert Law which defined an absorption coefficient in terms of concentration and thickness of the specimen. The Beer-Lambert Law can be written in the following form:

$$A = \log_{10} \frac{I_0}{I} = Ecl \quad (2-1)$$

where A= absorbance

I_0 and I are intensities of radiation effectively entering and leaving the sample, respectively.

E= coefficient of absorption

C= concentration of absorbing material in sample.

l= path length of radiation within sample.

The absorbance A is measurable from the spectrum but to find the concentration c in a sample, which is related to the number of absorbing molecules along the path, requires E and l to be known.

When Beer-Lambert Law is applied to determine the relative concentration of two components present in one sample, this requirement can be relaxed by the use of internal standard. If the sample is uniform, the length of path affects the absorbances of two peaks, each characteristic of one of the two components, in the sample proportion and does not have to be considered in the calculation (50). The relative concentration of the two components is therefore related to the absorbance of the two characteristic peaks in the following way.

$$\frac{A_1}{A_2} = \frac{E_1 C_1}{E_2 C_2} \quad (2-2)$$

but $C_1 + C_2 = C_0$ (a constant for certain sample)

Equation 2-2 can then be rewritten as

$$\frac{A_1}{A_2} = \frac{E_1}{E_2} \frac{C_1}{C_0 - C_1} \quad (2-3)$$

The relationship between A_1/A_2 and C_1/C_2 may be found by careful calibration. In the calibration work, A_1/A_2 values of samples with varied compositions or C_1/C_2 values are measured and A_1/A_2 is plotted against the C_1/C_2 to obtain a calibration curve. If the absorption coefficient ratio $\frac{E_1}{E_2}$ is not affected by the composition change of the environment, A_1/A_2 should have a linear relation with C_1/C_2 and the calibration curve should therefore be linear. However, if the absorption coefficients are composition dependent or the calibration curve is constructed based on weight fraction instead molar concentration ratio,

curvature is expected. In this study, the calibration curves were constructed by plotting $\frac{A_1}{\Sigma A}$ against the weight fraction and will be shown in Chap. IV.

The accuracy of quantitative analysis using IR mainly depends on the uniformity of the sample, the accuracy in the measurement of intensities as well as the performance of the spectrometer. Since the absorbance is the logarithm of the ratio I_0/I , it varies drastically when this ratio is either very large or very small hence the reliability of the absorbance in these cases is relatively low. It is recommended that both I_0 and I be kept in a region of 30-70% of maximum intensity. Base-line determination is also essential in accurate quantitative analysis. The selection of a base line for one peak is usually complicated by interference due to the presence of other peak(s) in the neighborhood. There are many different ways to select a base line for determination of peak intensity and each one may have advantage over the others in particular case. A "tangent line" method is usually adopted for its simplicity and generally better reproducibility, if the interference is not very significant. Differential thermal analysis and dynamic mechanical study will also be useful to characterize the copolymer. By investigating the transition behavior of the graft copolymer, some clues about the structure may be obtained. With careful calibration, differential thermal analysis can also be used for

determination of the composition of graft products. Dilute solution viscosity of graft copolymers, and CPE has been measured. Since the geometric shape of a graft copolymer is complicated, it was difficult to determine the average molecular weight from the viscosity data. However, since the dilute solution viscosity is related to the size of the polymer molecule, it yielded some information about the degree of grafting. Above mentioned techniques will be discussed to some detail in the following sections.

2.5.2. Morphology and Thermal Behaviors

Solid polymers may exist in a crystalline state, semi-crystalline state, or an amorphous state according to the chemical structure, the steric regularity and thermal history of the material. As the temperature changes, changes in polymer structure take place. Melting, glass transition, and some secondary transitions are the most often observed structural change phenomena. Melting is the most significant morphological change associated with a crystalline polymer and this change occurs at a temperature characteristic of the polymer, its melting point T_m . For an amorphous polymer, the glass transition is the major morphological change which transforms the polymeric material from glassy state into a rubbery state. The temperature at which glass transition occurs is termed the glass transition temperature, T_g . A

semicrystalline polymer may exhibit both transitions.

Melting occurs in a crystalline polymer at so high a temperature that the thermal vibration of the molecules is vigorous enough to overcome the energy which holds the crystal lattice together. This transition is usually observed over wide range because the melting point is molecular-weight dependent and most polymers have a broad molecular-weight distribution. Conventionally, the melting point is defined as the temperature at which all the solid material becomes liquid. However, in the manual of DSC the melting point is defined as the temperature at which the melting transition is first observed. In order to be in accordance with the DSC manual, the melting point is defined as the temperature at which the transition is first detected in this work. The melting point is also dependent on the crystallinity of the polymer. A polymer with relative low crystallinity and low molecular weight is expected to melt at lower temperature.

Glass transition temperature is the temperature at which main-chain movement begins. This transition is accompanied by a step change in the heat capacity and specific free volume of the polymer, which can be easily detected.

Melting, glass transition and some secondary transitions are measurable by thermal analysis. Differential thermal analysis may yield information on the melting point, glass transition temperature, specific heat, crystallinity,

molecular weight distribution, and morphological change due to additives and is useful in characterization and evaluation of polymers and polymer blends. Differential Thermal Analysis and Differential Scanning Calorimetry are the two most widely used techniques for thermal analysis at this time. Differential Scanning Calorimetry is used in this work for study of the thermal behavior, and will be discussed in more detail.

2.5.3. Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) is a technique of non-equilibrium calorimetry in which the heat flow into or from a sample and reference is measured as a function of time or temperature. This is different from differential thermal analysis (DTA) where the temperature difference between a sample and reference is measured as certain function of time and temperature (51). In the DSC equipment, the heat flow is measured while keeping the sample and reference thermally balanced by changing the current passing through the heaters under the two sample holders. Figure 2-3 shows a block diagram of a differential scanning calorimetry apparatus.

The temperature of the sample and reference holder is monitored by the average temperature control circuit which keeps the temperature of the holder changing at a constant rate according to a time-temperature program. A differential

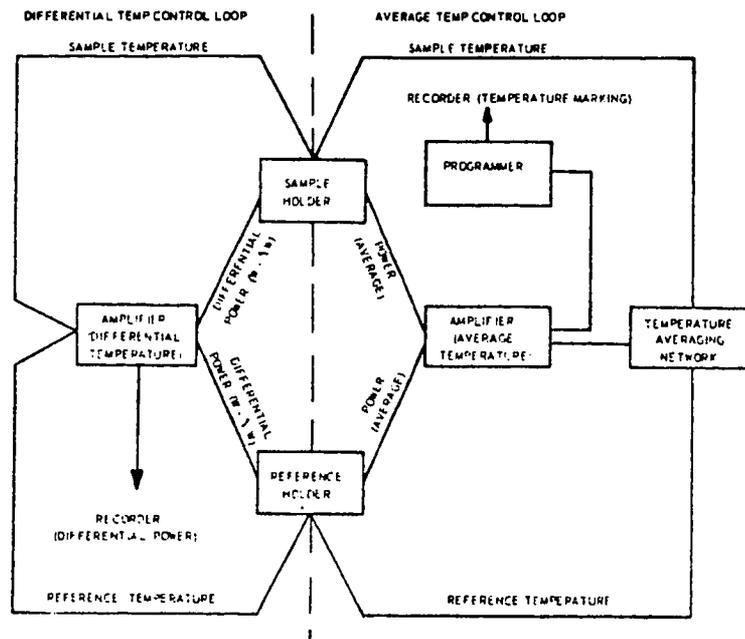


FIGURE 2-3: MODEL DSC-2 BLOCK DIAGRAM (52)

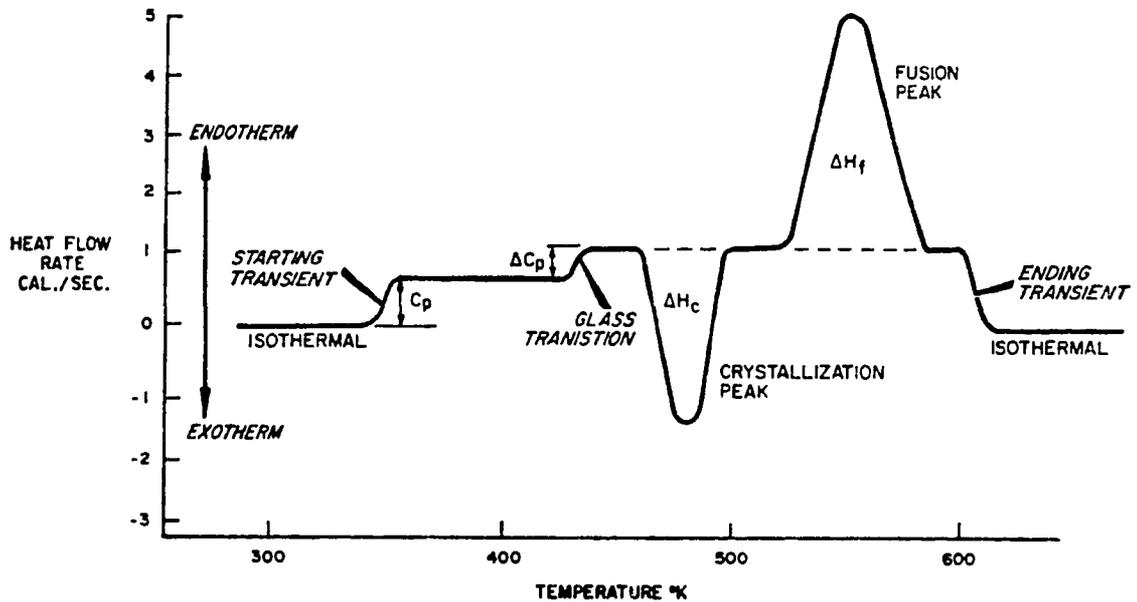


FIGURE 2-4: A TYPICAL THERMOGRAM SHOWING VARIOUS TYPES OF PHYSICAL CHANGE

control circuit monitors the temperature of the sample and reference and maintains the holder at equal temperatures. Changes in the temperature of the sample holder due to physical transitions of the sample are sensed by the differential control circuit which responds by adjusting the power to the heaters to maintain thermal balance between the two holders. A signal proportional to the power difference is sent to the recorder.

Figure 2-4 shows a typical chart record, the chart abscissa indicates the transition temperature and the peak area represents the total energy transfer to or from the sample. For example, the area under the peak due to melting can be translated to heat of fusion by careful calibration.

DSC has found various applications in polymer research, especially polymer characterization. Informations obtainable from DSC are on 1) thermal properties, such as specific heat; 2) heat of fusion; 3) transition temperatures; 4) composition of polymer blends and copolymers; 5) distinguishing folded chain from extended chain morphology; 6) thermal stability; 7) crystallinity; 8) degree of crosslinking of thermoset resins; 9) crystallization rate; 10) heat of reaction, etc. In this study, DSC is used to characterize the graft copolymer, to detect the morphological change in polymer blends due to the addition of a graft copolymer, and to some extent, to help determine the composition and structure of the graft copolymers.

2.5.4. Dilute-Solution Viscosity

Dilute-solution viscosity, or the intrinsic viscosity, has long been known as a measure of the average molecular weight for a simple polymer in a given solvent system. Actually, the viscous drag created by the presence of random-coil polymers in a flowing solvent is a measure of the size, not the mass, of the polymer molecules. Measurement of the dilute-solution viscosity of polymer solution provides one of the easiest ways to obtain information about the molecular structure of the polymer sample.

The intrinsic viscosity, η , can be defined by the following equations.

$$\begin{aligned} [\eta] &\equiv (\eta_{sp}/c)_{c=0} \\ \eta_{sp} &= \eta_r - 1 = \frac{\eta - \eta_0}{\eta_0} = \frac{t - t_0}{t_0} \end{aligned} \quad (2-4)$$

Where c is the concentration of the solution in g/dl, η and η_0 are the viscosities of polymer solution and the pure solvent, respectively; t and t_0 are efflux time of the solution and the pure solvent, respectively. The intrinsic viscosity can be obtained by extrapolating $\frac{\eta_{sp}}{c}$ to $c=0$. However, empirical equations have been developed to estimate the intrinsic viscosity by the viscosity measured at fixed concentration (55). Viscosity at a fix concentration, 0.2 or 0.5 g/dl, is sometimes taken as an easily obtained approximation to the intrinsic viscosity.

Glass capillary viscometers, such as Cannon-Fenske viscometer and Ubbelohde viscometer, are usually used to measure the viscosity of polymer solution. These viscometers are so designed that the relative viscosity, η_r , can be approximated by the ratio of the efflux time for the solution, t , t_0 that of the solvent t_0 . Viscosities of the solution and solvent are related to the corresponding efflux time by

$$\eta = ct_d - Ed/t^2; \quad \eta_0 = ct_0d_0 - Ed_0/t_0^2 \quad (2-5)$$

where d is density and C, E are constants for the particular viscometer used (56). For dilute solutions d and d_0 are nearly equal, and the viscometers are designed so that, for efflux time greater than 100 sec, the second terms are negligible.

The intrinsic viscosity is usually related to the molecular parameters by the Mark-Houwink relation.

$$[\eta] = k\bar{M}_v^a; \quad \bar{M}_v = \left[\frac{\sum M_i^{a+1/2} N_i}{\sum M_i N_i} \right]^{1/a} \quad (2-6)$$

K and a are constants dependent on the solvent-solute system, and the temperature and \bar{M}_v is the viscosity average molecular weight. For linear polymers, the Mark-Houwink relation can be used to determine \bar{M}_v , if K and a are known. However, for more complex polymers such as graft copolymers, this method is invalid. The exponent a is related to the average degree of extension of the solute chain molecules (57) therefore will vary with the number and length of the graft. Thus, two graft copolymers of the same molecular weight may have different

intrinsic viscosities since the a value changes with the structure of the graft copolymer. However, since the exponent a is related to the degree of extension of the polymer chain molecules, it may be utilized as a measure of grafting provided a good estimate of the molecular weight is available.

2.5.5. Dynamic Mechanical Behavior

The viscoelastic nature of polymers is unique in the field of material properties. Dynamic mechanical testings are carried out to study the time-dependent mechanical properties of polymers, which in limiting cases can behave either as elastic solids or as viscous liquid. A knowledge of the viscoelastic behavior of polymers and its relation to molecular structure is essential to the understanding of processing and end-use properties.

Dynamic mechanical testings usually involve measurement of the stress response in a material subjected to a periodic strain, generally a sinusoidal one. If the sinusoidal strain is applied to a specimen at a frequency ω and with a small amplitude, the stress also varies sinusoidally but is out of phase with the strain by a phase angle δ . Thus

$$\gamma = \gamma_0 \sin \omega t \quad (2-7)$$

$$\sigma = \sigma_0 \sin(\omega t + \delta) \quad (2-8)$$

where γ_0 and σ_0 are the peak strain and peak stress, respectively.

The phase delay in the stress response is a result of the viscous nature of the polymer. For an elastic solid, the stress responds to a sinusoidal strain according to the following equation

$$\sigma = E\gamma \quad (2-9)$$

where E is the modulus, which is effectively a constant for perfect elastic solids. Thus the stress σ can be described by equation 2-10 which shows that the stress and strain are in phase.

$$\sigma = E \gamma_0 \sin \omega t \quad (2-10)$$

A viscous Newtonian fluid behaves differently, following the Newton's law

$$\sigma = \mu \dot{\gamma} \quad (2-11)$$

where μ = viscosity, $\dot{\gamma} = \frac{d\gamma}{dt}$

The stress σ therefore becomes

$$\sigma = \mu \gamma_0 \omega \cos \omega t \quad (2-12)$$

The stress now leads the strain by 90° since $\cos \theta = \sin (\theta + 90^\circ)$.

Polymeric materials exhibit both elastic and viscous nature and their behaviors are generally between the perfect elastic solid and Newtonian viscous fluid. Therefore, the stress is out of phase with the strain, by a phase angle $\theta < 90^\circ$.

The peak stress σ_0 in equation (2-8) can be resolved into a component $\sigma_0 \cos \delta$ which is in phase with the strain and is related to the stored elastic energy, and a component

$\sigma_0 \sin \delta$ which is 90° out of phase with the strain and is related to the viscous loss of energy (53). The ratio of the two components, $\tan \delta$, is named the dissipation factor and is an indicator of the relative importance of the viscous as compared to the elastic aspects of the behavior of the polymer. Storage modulus and loss modulus are defined:

$$E' \equiv \left(\frac{\sigma_0}{\gamma_0} \right) \cos \delta \quad (2-13)$$

and
$$E'' \equiv \left(\frac{\sigma_0}{\gamma_0} \right) \sin \delta \quad (2-14)$$

whose ratio is the dissipation factor.

E' and E'' are the two components of the complex modulus E^* :

$$E^* = E' + E'' \quad (2-15)$$

and
$$|E^*| = \sqrt{E'^2 + E''^2} \quad (2-16)$$

Dynamic Mechanical testings are used to determine the complex modulus, which is a combination of E' and E'' . E'' and $\tan \delta$ provide a measure of the energy dissipated as heat of the polymer when deformed. The storage modulus E' , for small loss, is the usual Young's modulus. Dynamic mechanical testing has a great advantage over the other rheological testings as it yields information on the elastic modulus in addition to the viscosity.

The storage modulus E' , loss modulus E'' , and the dissipation factor have been found to undergo characteristic changes when physical transitions of a polymer occur. For example, when glass transition occurs, E' undergoes a two or three decade decreases while E'' and $\tan \delta$ go through maxima.

Secondary transitions are generally accompanied by a relative small decrease in E' , and a small peak in E'' and $\tan\delta$ curves. E' becomes very small when melting has taken place since the polymer solid has become viscous fluid. The value of $\tan\delta$ becomes large at this point because the viscous nature has become much more pronounced.

Peaks of glass transition and secondary transitions on $\tan\delta$ curve can be interpreted in terms of molecular mobility (54). Immobile segments in the structure can store more energy than those which can move more freely. When the testing temperature passes through the transition range, some of the "frozen" segments become free to move and the stored excess energy is dissipated into heat. The dissipation of stored energy into heat is reflected in the form of an increased $\tan\delta$. The $\tan\delta$ begins to increase as the testing temperature is near the transition temperature and reaches a maximum at the transition temperature. $\tan\delta$ then decreases since the freeing of the molecules tends to cease. The energy-dissipation process thus goes through a minimum until the sample temperature approaches another transition. This change in the molecular mobility was thus shown as small peaks on the $\tan\delta$ curve. The loss modulus E'' curve has a shape similar to that of $\tan\delta$.

An incompatible polymer blend usually shows the characteristic transitions of both components on E' and $\tan\delta$ curve.

Changes in the shape of the curves are often considered as a sign of structural change of the blend. This feature is useful in the understanding of the modification mechanism in blend-modification work.

2.6. Compatibility of Polymer Blends

The term "compatibility" in the polymer blend study has the similar meaning as the miscibility for a mixture of liquids. The question whether two or more polymers in a physical blend are compatible or not may be answered in terms of different criteria and, sometimes, it is difficult to find a definite answer. In this study, the major concern of compatibility is on the mutual interaction between different polymer molecules, which ultimately determines the mechanical performance of the polymer blend.

The necessary condition for two polymers to be compatible upon mixing is that the free energy change of mixing, ΔG_{mix} , has to be negative (58). At constant temperature,

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \quad (2-17)$$

The state of blends is considered more probable than the state of separate phases when ΔG is negative and the polymers in the blend are considered compatible. This is possible when the heat of mixing is negative, or the entropy increase is large. For simple molecules such as molecules of simple liquid, the degree of randomness increases greatly during

mixing and the liquid mixture will be compatible if the solubility parameters of the components are close. However, the entropy increase in blending two high polymers is usually small due to the large chain length. As the mixing of polymers is generally an endothermic process, to have a negative ΔG is highly unlikely. Therefore, except for polymer pairs which have very strong interaction force, most polymers are incompatible. (59)

Fettes (60) stated that two incompatible polymers, when mechanically blended tend to form separate phases. Usually a phase of one polymer is dispersed in the continuous phase of the other and the larger is the phase domain, the lower is the probability to have interaction at molecular level. Low compatibility can lead to poorer mechanical properties for the blend than either of the individual components as found by Paul (3) for melt blends of polyethylene, polystyrene and polyvinyl chloride. Although phase separation of polymers in a blend does not necessarily mean poor mechanical properties, as in the case of high impact resins (61), good interphase adhesion is essential for satisfactory mechanical performance. For most incompatible blends, modification by a blend modifier is needed in order to obtain acceptable properties.

Graft copolymers and block copolymers have been found effective in achieving better interphase adhesion in previous

works. The modification of the PE, PVC, PS containing blends by the CPE-styrene graft copolymer will be discussed in more detail later.

Several techniques have been employed to determine compatibility of polymer mixtures, but not all of them predict the same result (62). The compatibility, and the modification ability of the graft copolymer are studied by thermal analysis, microscopy and dynamic mechanical testing in this work.

2.7. Literature Works - CPE Graft Copolymers

Some work, mostly patents, has been reported in the literature on utilizing CPE as backbone material for synthesis of graft copolymers (63-73). Varied types of monomer such as acrylonitrile, methyl methacrylate, acrylates, diallyl phthalate, allyl chloride, vinyl acetate, vinyl chloride, and styrene were grafted on the CPE backbones by free-radical initiation. Initiators used in these works were peroxides and AIBN. Neither purification nor characterization work has been discussed in the literature.

Some of the graft copolymers were employed as modifiers in PVC-based impact resistant compounds. Takahashi et al. utilized a graft copolymer of CPE with pendant polystyrene chain on it to modify the impact resistance of PVC and reported a greatly improved impact strength of their new compound (64). Yokoyama et al. grafted allyl compounds such as allyl chloride on the CPE and used this material to modify

the impact strength of PVC (66). Nish et al. conducted a graft copolymerization to produce PMMA or polyacrylate graft on CPE and blended this graft copolymer with PVC. Both the impact strength and tensile strength of this blend were found to be superior to that of an ungrafted CPE-PVC blend (67).

Graft copolymers based on CPE were also used as blend modifiers. Nakamura et al. prepared a CPE-g-PMMA copolymer and blended it with LDPE and acrylic monomers. The introduction of this material gave a compatible blend whereas the blends without the graft copolymer were incompatible (72). A graft copolymer involving CPE, styrene and acrylonitrile was also utilized as the base compound of fire-resistant foamed materials (73).

Since most of these work were patent work and were done in Japan, very little detail regarding efficiency of copolymerization and graft structure was disclosed. However, success in preparation and application of these graft copolymers encourages further effort on graft synthesis involving CPE.

CHAPTER III

EXPERIMENTAL

3.1. Graft Synthesis

3.1.1. Chemical Polymerization

Synthesis was made using pre-initiation technique. The CPE backbone was first initiated in a 1000 ml resin flask and was then transferred to another flask where the polymerization took place. The CPE used in this study was supplied by Dow Chemical Company and was in Crumb form when received. In order that the initiated CPE backbone may be conveniently transferred, the CPE pellet was processed into films with a hydraulic press. In each synthesis, six pieces of CPE films were suspended from a glass supporter and were immersed into the initiation solution. The weight and thickness of these films were measured. The initiation solution was a mixture of benzene and methanol with the initiator dissolved in it. The CPE films were swollen in the initiation solution for a period of time to allow the initiator to diffuse into the films. The initiation flask was in a polyethylene glycol

bath of which the temperature was controlled with a Haake E51 model regulator. After the films had been swollen at room temperature for a desired time, a condenser was installed and nitrogen bubbled through the initiation solution for twenty minutes to purge the air.

The solution was then heated up to and maintained at the desired temperature at which the initiator would decompose and the initiation began. The initiation lasted for a period of 4 to 12 hours during that nitrogen continued to bubble at a slow rate. As soon as the initiation was accomplished, the initiated films were transferred into the polymerization flask, which contained a mixture of styrene monomer and methanol, and the polymerization proceeded. The solvent in initiation solution was evaporated and the amount of CPE dissolved in the solution weighed. Nitrogen still bubbled for the first twenty minutes. The polymerization was generally terminated by evaporating the remaining monomer at reduced pressure. The dried reaction products were weighed and then pressed into films for further study.

Synthesis were made under varied reaction conditions. Several reaction parameters were varied in such a way that effect of each parameter on the graft yield and efficiency could be evaluated. Benzyl peroxide was used as the initiator in all the synthesis but one, in which AIBN was used.

3.1.1.1. Purification of Monomer

The styrene monomer was purified before use to remove the impurities, mainly the inhibitor. The monomer was washed with 4% sodium hydroxide solution for six times in a separatory funnel. Each time a caustic solution of a volume one sixth to that of the monomer was used. The separatory funnel was shaken vigorously to allow good contact between monomer and the caustic solution. The mixture would then settled into two layers and the bottom portion, which is the aqueous solution, was removed. The monomer was then washed again for six times with distilled water. The acidity of the washed monomer was checked with a litmus paper to ensure complete removal of caustic. The monomer was settled again in a beaker and then transferred into a cylinder for volume determination, with the bottom portion discarded. The clear monomer liquid was stored over calcium chloride in a refrigerator.

3.1.1.2. Film Preparation

All polymer sheets used in this study were molded by a Carver 2101 C-type hydraulic press equipped with heated plates. The polymer, positioned between two Teflon plates, was preheated at 275 F for three minutes and then pressed to 20000psi. The pressure was immediately released and the film formed was removed and allowed to cool down. Excess heat and pressure would cause severe degradation since CPE is susceptible to heat degradation, like polyvinyl chloride.

3.1.1.3. Determination of the Composition of Initiation Solution

In the initiation step, solvent was used to swell the CPE films. The swelling facilitated the diffusion of initiator into the films and therefore would achieve more homogeneous grafting (24). However, the solvent should not be too strong otherwise a large amount of CPE would be dissolved and lost in the initiation step. Benzene, a relatively good solvent for CPE, was the swelling agent while methanol, a nonsolvent, was introduced to prevent dissolution of the films. The composition of the mixture was determined by the degree of swelling and CPE dissolution that were measured experimentally. To determine the degree of swelling and dissolution, a simulation test was done on the CPE films. A piece of CPE film was immersed in a mixture of benzene and methanol, which was at the temperature of initiation, for a length of time which the initiation would last. The film was removed from the solvent mixture after swelling and was immediately wiped dry. It was then suspended from a metal wire and was allowed to dry in the atmosphere. The film was weighed every ten minutes in the first thirty minutes and was later weighed every thirty minutes. The per cent degree of swelling was defined as the per cent weight increase due to the swelling and this value decreased as the film dried up. The amount of CPE dissolved was determined by weighing the film after it had been dried for more than one week. If the weight of film remained

constant upon further drying, the film was considered solvent free and its weight would give the amount of CPE dissolved.

3.1.2. Irradiation Polymerization

The irradiation grafting of styrene to CPE was carried out using the direct irradiation method. The CPE 2552 pellets as received from the manufacturer were mixed thoroughly in a beaker with purified styrene monomer through which nitrogen had been bubbled for 15 minutes. The mixing process, which gave a very viscous slurry, enabled the CPE pellets to be well swollen. The mixed slurry was then transferred to a 41 mm x 7 inch tall glass tube with a syringe-like glass ware. The glass tube was immersed in a dry-ice bath until the styrene was frozen and then was evacuated with a mechanical pump to about 50 torr. The tube was sealed with a torch while evacuated thus maintained the vacuum in the tube. Three tubes for irradiation were prepared with two of them sealed under vacuum while the other one sealed under atmosphere. The sealed tubes were then stored in a refrigerator. During irradiation, the tubes were placed in beakers located at the center of an aluminum canister. The canister was sealed by a lid held in place against an o-ring with bolts. The canister was lowered to the center of the gamma-ray source, which consisted a number of Cobalt-60 elements, held in a doughnut shaped holder at bottom of a water pool. The intensity of

the radiation was about 7968 rads per hour based on the 5.2 years half-life of Cobalt-60 and the dose rate of 70000 rads per hour determined in July 1968. The samples were exposed to the radiation for 2 or 3 days and total dose levels of 0.4 and 0.6 megarads were achieved. The samples were removed from the radiation source and were exposed to room temperature for two days. The tubes were then broken, the polymer heated in an oven at 60°C under vacuum to remove the residual monomer. The yield of polystyrene in the radiation product was determined by weighing the dried polymer and comparing to pure CPE pellets. The products were later pressed into films and ground to fine powders for further analysis.

3.2. Purification

In order to better characterize the graft copolymers, the reaction products must be purified using one of the separation techniques cited in the Background Chapter. Preliminary studies on solubility of CPE, polystyrene and their physical mixture in various solvent systems were done and the solvent extraction technique was employed to separate the homopolymers from the graft. Details are given below.

3.2.1. Solubility Studies for Removal of Styrene Homopolymer

The selective extraction method was employed to separate the reaction product mainly because this method is preparative and simple to apply. Since a large quantity of purified

graft copolymer was required for characterization and modification of blends in this work, it was desired to obtain the purified graft in as small number of fractions as possible. If a selective solvent system could be found, selective extraction should be the method most suitable for this purpose. It was important to find solvents with high selectivity when selective extraction method was to be used.

A number of solvent systems were tested for their selectivity. The literature values of solubility parameter δ of polystyrene have an average of 9.0 (74) but δ of CPE is not available in literatures. It was postulated that δ of CPE might be somewhere between that of polyethylene and polyvinyl chloride. However, since PE has an average δ value of 8.05 and polyvinyl chloride 9.75, it seems that δ of CPE would be quite close to that of polystyrene. The author was not able to find any solvent system from the literature which would apparently have high selectivity for the polystyrene - CPE system, since the solubility parameter of CPE was unknown. The solvent system used in this separation work was selected according to the result of solubility studies done in this laboratory.

Benzene, toluene, cyclohexanol, carbon tetrachloride, cyclohexane, and acetone were chosen for the preliminary trial. Half gram of polymeric pellets was added to 100 ml of solvent to be tested and the solution was left at room temperature

for about ten hours before the solution was heated up with stirring to about 60°C. The solution was allowed to cool down gradually to room temperature and to set for one to seven days depending on the system.

The polymer which remained as a solid was separated from the solution by pressure filtration, and was then dried in an oven and weighed. For the solvents which showed very poor selectivity, the solubilities were described only qualitatively, as complete soluble, mostly soluble, partially soluble, or non-soluble.

The polystyrene used as control in the solubility study was synthesized in this laboratory with the reaction conditions similar to the graft copolymerization so that the sample used would have solubility comparable to the styrene homopolymer found in the graft product. According to the result of the solubility study, which will be discussed in the next chapter, a 18:82 cyclohexane-acetone mixture was selected as the solvent system for the extraction. The next problem in design of the extraction process was to decide how many extractions would be enough to completely remove the styrene homopolymer.

A graft copolymer was extracted consecutively and the amount of material extracted in each extraction was measured and analysed. A simulation test was also done on a CPE-polystyrene mixture having the same composition of the graft

product and the IR spectra of the extracted fractions were studied. The solubilities of CPE-polystyrene mixtures were also measured and revealed some information on the removal of styrene homopolymer. It was found that only one single extraction would be sufficient to isolate all the styrene homopolymer as will be discussed later in Chapter IV.

3.2.2. Removal of Unreacted CPE

Another solvent system was needed to separate the unreacted CPE from the graft copolymer. However, such a solvent system had never been found as any solvent found to dissolve CPE would also dissolve polystyrene and the graft. In this work, removal of unreacted CPE was achieved by precipitation of the unreacted CPE out of the solution of graft product. Approximately 0.5 g of polystyrene-free graft product was dissolved in 180 ml of hot toluene and the solution was transferred to four 50-ml centrifuge tubes. Three drops of methanol were added to each tube to precipitate the less soluble portion, which should be CPE-rich, and the samples were centrifuged with a Model CL International Clinical Centrifuge. It was desired that only small amount, which is barely enough for composition analysis, be precipitated. The precipitated fraction was then characterized by IR. If the precipitated fraction was shown to be pure CPE, further precipitation would be carried out until it was determined to

contain some polystyrene. The amount of unreacted CPE was estimated by summing up the weight of all the precipitated fractions, but the last one.

The whole picture of the separation process is shown in Figure 3-1. The compositions of the separated fractions were later determined by IR spectroscopy and DSC.

3.2.3. Pressure Filtration

The fractionated samples were separated into two fractions by either pressure filtration or centrifuging. Pressure filtration was employed in the first stage of purification to separate the soluble polystyrene homopolymer from the reaction product while centrifuging was used mainly to remove the unreacted CPE from the polystyrene-free graft product.

A small-size pressure filter with a capacity of treating 300 ml of solution, was employed in the purification of samples for characterization and composition analysis. Figure 3-2 describes the mechanism of the pressure filter. The pressure of the nitrogen line was the driving force for the viscous polymer solution to pass through the filter. The pressure required to achieve separation in a reasonable amount of time varied from 3 psig to 100 psig depending on the type and amount of polymer dissolved in the solution. Several filter systems were tested but a Whitman #1-glass fiber-Whitman #50 sandwich-type filter system was found to be the better

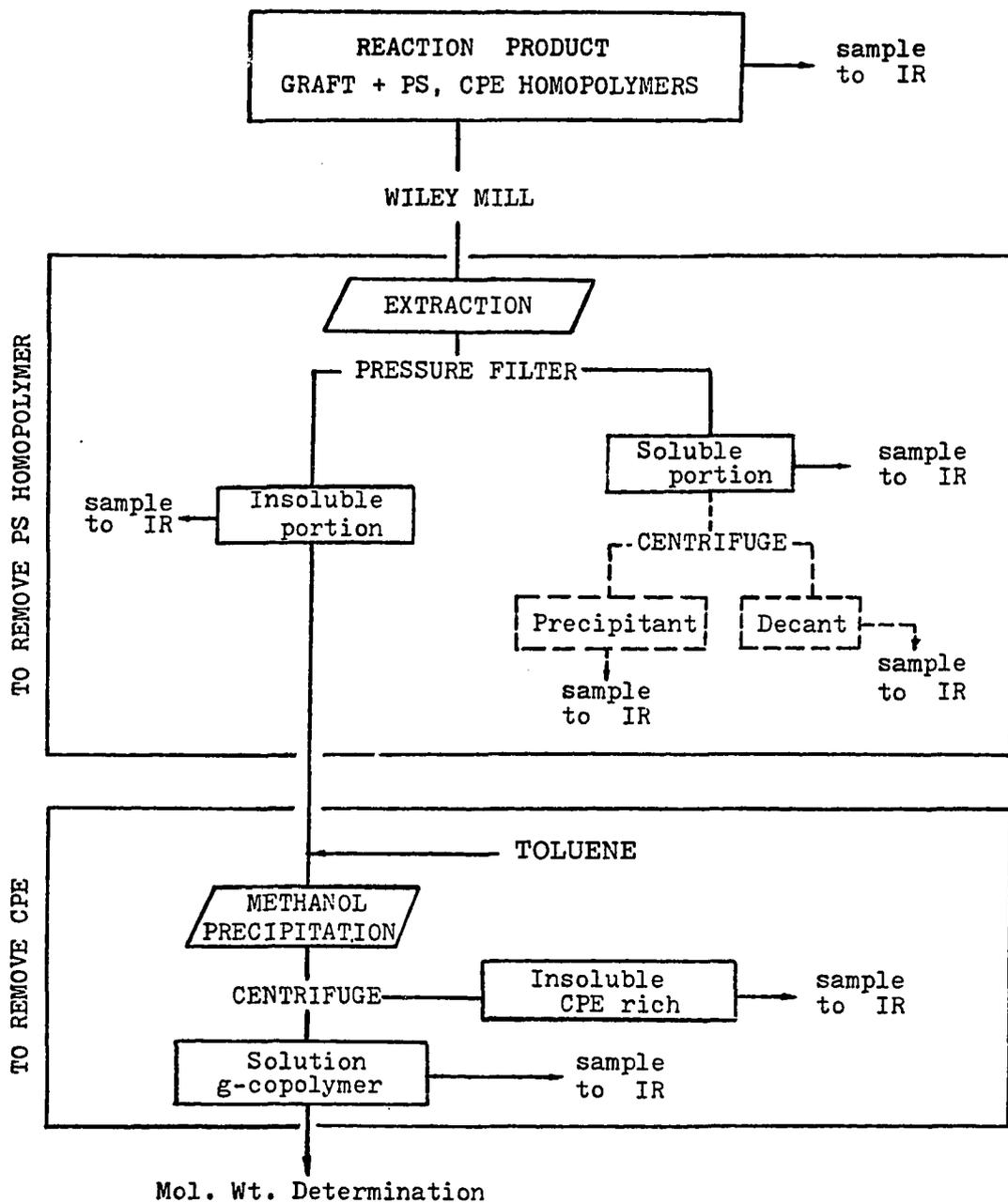


FIGURE 3-1: FRACTIONATION SCHEME USED FOR PURIFICATION

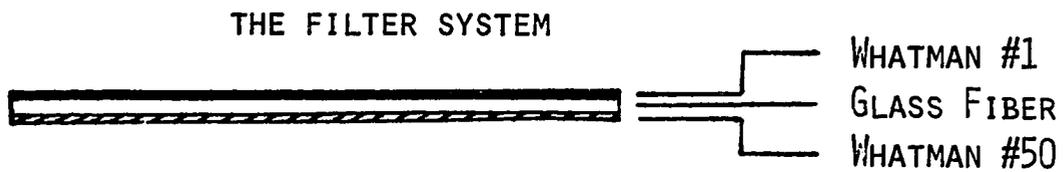
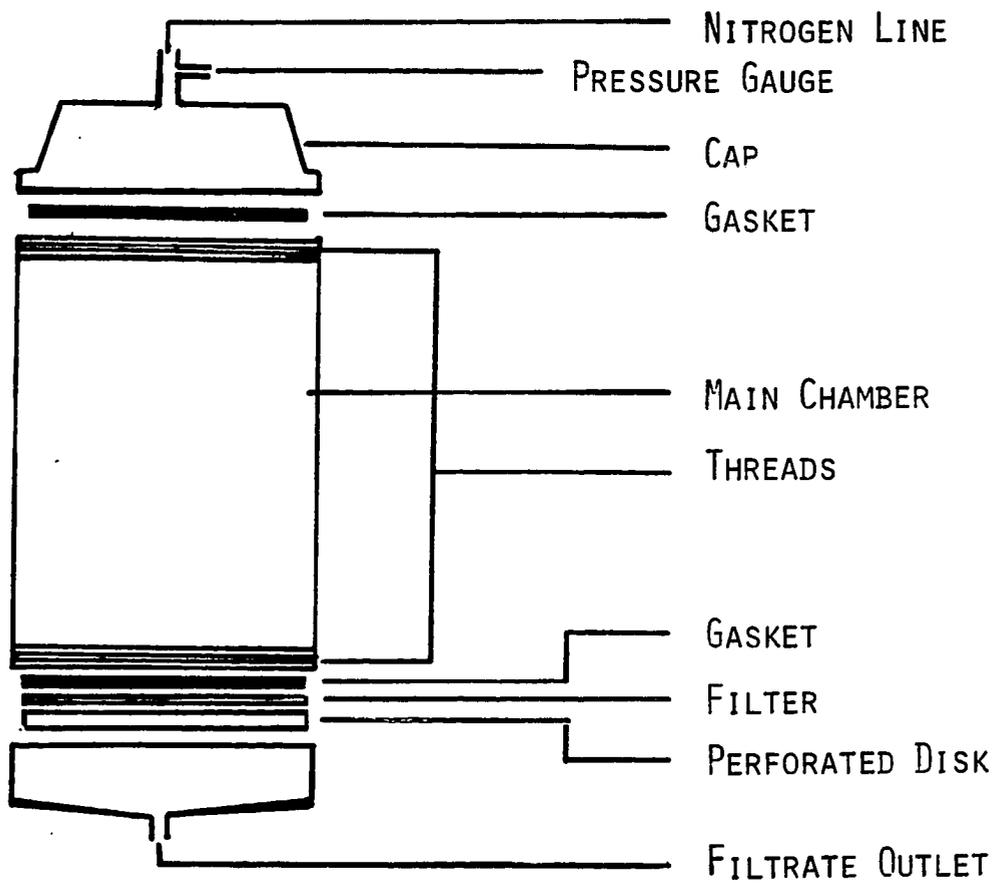


FIGURE 3-2: FABRICATION OF PRESSURE FILTER

system. The glass fiber-Whitman #50 combination was able to filter particles smaller than 2 μ m at relatively slow rate while the Whitman #1 filter paper served as the pre-filter to prevent the fine-pore filter from being clogged and to facilitate faster separation. The glass fiber filter used in this work was a GELMAN TYPE A/E filter. The perforated aluminum disk holder supported the filter to avoid a rupture of filter paper under high pressure. A ring-type gasket made of nitrile or DuPont Viton rubber was essential in achieving good sealing.

Since a large quantity of purified graft copolymer was needed in the modification work (at least 15 grams were needed in order to prepare a blend with a graft concentration of 25%), a large-scale filtration was carried out. The structure of the large pressure filter was similar to that of the small one, except that the large one was sealed with bolts. The main compartment and the cap were made of carbon steel, with the inside surface nickel plated, while the perforated disk and the bottom parts were machined from an aluminum cylinder. This filter was capable of treating one gallon of solution at one time. The graft product was first extracted with one half of the solvent and, after separation, was again extracted with the other half of fresh solvent to ensure complete removal of polystyrene homopolymer. The

concentration of all the polymer solutions separated was 200 ml of solvent for each gram of polymer.

The use of pressure filtration as the means for separation should have eliminated the co-precipitation of styrene homopolymer, which would occur if the centrifuging technique was employed.

3.3. Characterization

The graft products were characterized by IR spectroscopy, Differential scanning calorimetry, microscope photography, and Rheovibron dynamic mechanical testings, and dilute-solution viscosity, as described below.

3.3.1. Infrared Analysis

IR spectra of the graft products were obtained using a Beckman Model IR 12 spectrophotometer. Characteristic absorptions were detected from the film transmission spectra with a range from 300 cm^{-1} to 1660 cm^{-1} . Generally the spectra were run using the following format: scanning rate -- 8 cm^{-1} per minute, integral time -- 2 seconds, slit width -- 2x standard, energy gain -- 1.2-2.8% of maximum. The film samples were prepared by casting from solutions. Approximately 0.5 gram of the material to be tested was dissolved, with heating and agitation, in 60 ml of toluene. The solution was slowly poured onto a glass plate, flowing down along a stainless steel guide rod and was then dried in a vacuum oven

to remove the water and then stored in a decicator.

Spectroscopic works were done on pure CPE, polystyrene, and physical mixture and these spectra were compared with that of graft products to detect the possible sign of structural change due to grafting.

IR spectroscopy was also used to determine the compositions of the graft products . Peaks at 614 cm^{-1} and 1605 cm^{-1} were chosen as the characteristic peaks of CPE and polystyrene respectively. Calibration curves were constructed using the internal standard approach and the peak height was used as the measure of the intensity (Fig. 3-3). With the calibration curves, the composition of the graft products were obtained by measuring the relative intensity,

$$\frac{A_{1605}}{A_{1605} + A_{614}} .$$

3.3.2. Laser-Raman Spectroscopy

Laser-Raman spectroscopy was also employed in the characterization of the graft copolymer. The spectroscopic work was carried out using a Spex Ramalog-5 spectrometer equipped with a spectrophysics 2 Watt Argon Ion Laser. Spectroscopic work was done using the following format:

Laser beam wave length 4880 \AA

power 100 ma

Integral time 2 sec.

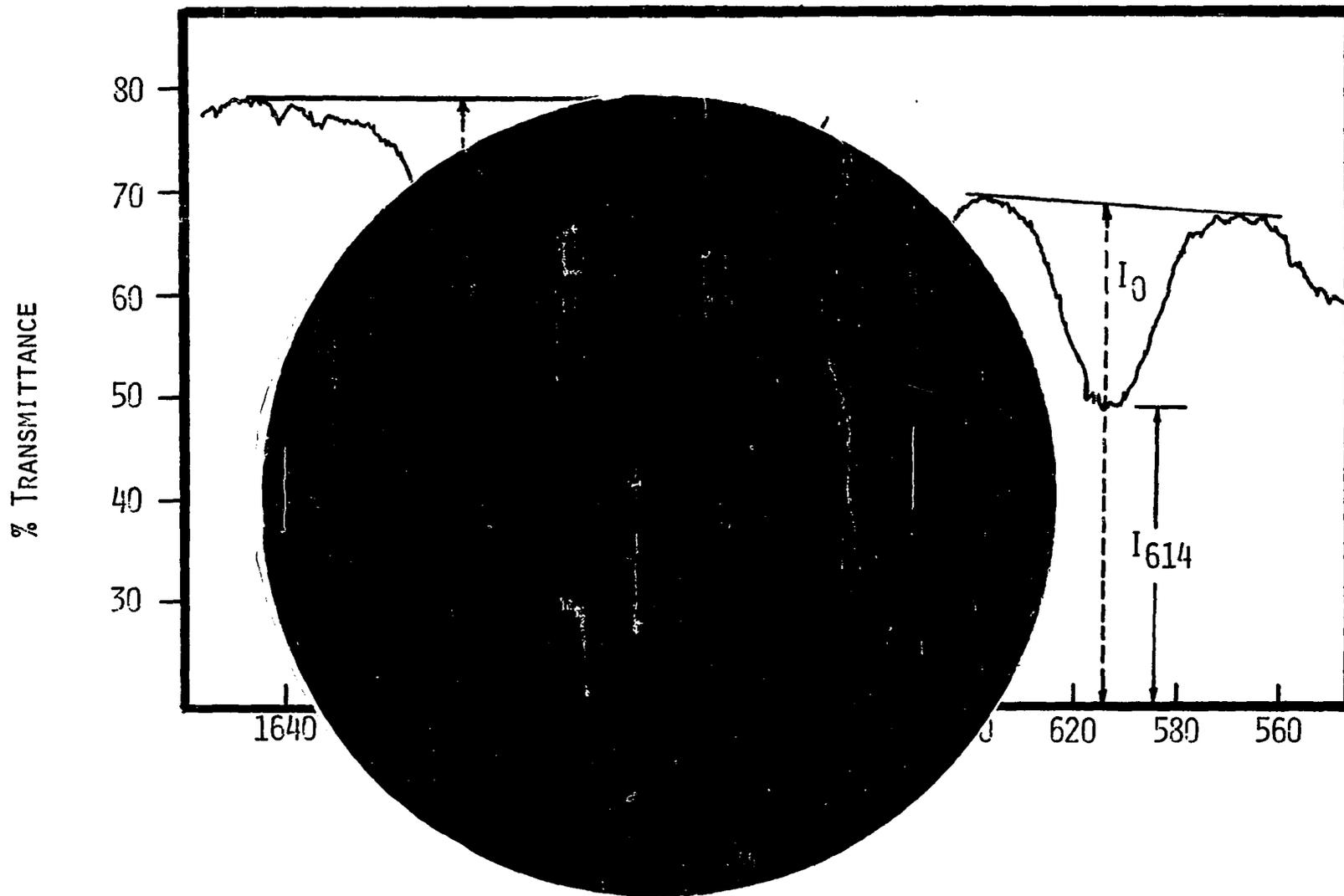


FIGURE 3-3: BASE LINE DETERMINATION IN IR COMPOSITION ANALYSIS

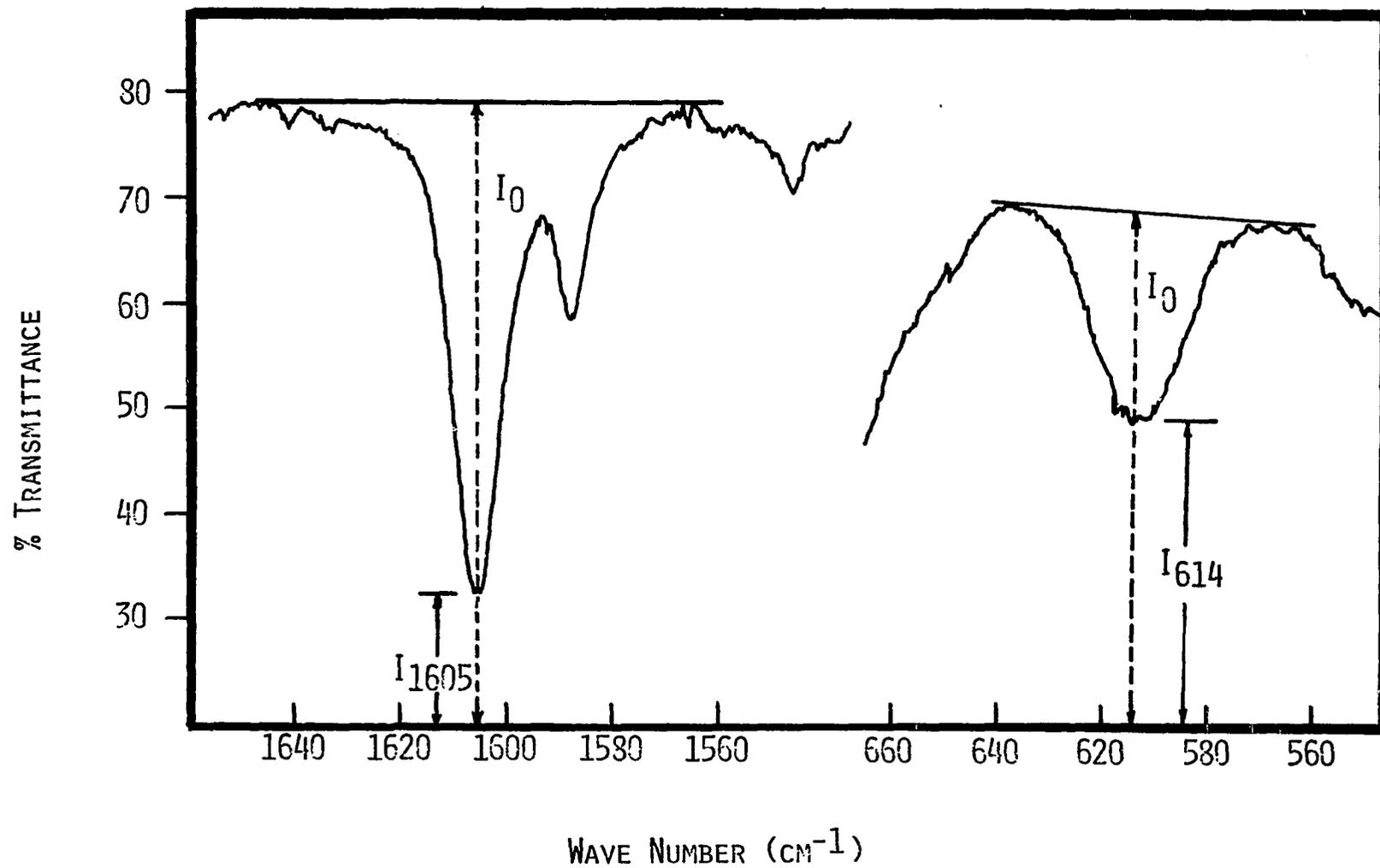


FIGURE 3-3: BASE LINE DETERMINATION IN IR COMPOSITION ANALYSIS

Slits $400 \mu \times 400 \mu \times 400 \mu \times 2$

Anti-stoke scanning @ $30 \text{ cm}^{-1}/\text{minute}$.

The author did not operate the laser-Raman spectrometer himself. All the Raman work was performed by Dr. R. E. Frech, professor in Chemistry at the University of Oklahoma.

3.3.3. Dilute Solution Viscosity

Viscosity of dilute polymer solution, which is a measure of the molecular size, was measured with the use of a Canon-Fenske Capillary Viscometer (Figure 3-4). Solution viscosities of CPE, initiated CPE, CPE-PS mixture and purified graft copolymers were measured (since CPE 2552 is partially crystalline, the solution has to be heated up in order that CPE containing sample may completely dissolve). The experiment was performed at a temperature of $100 \pm 0.5^\circ\text{C}$ in a polyethylene glycol bath with temperature controlled by a Haake E51 Regulator.

Toluene was used as the solvent and a concentration of 0.5 g per 100 c.c. solution was used in this work. The solution was prepared by dissolving the polymer in toluene within a stoppered volumetric flask with heat and agitation and was then immersed in the constant temperature bath for about 15 minutes. Ten ml of solution was transferred with a pippotte to the main liquid reservoir of the viscometer. Suction was applied to the open end to bring the liquid level

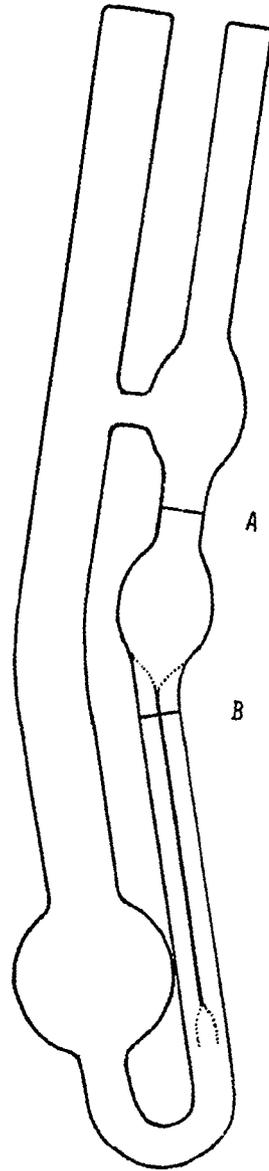


FIGURE 3-4: CANNON-FENSKE VISCOMETER

above point A. The liquid was allowed to drain down the capillary and the time required for the meniscus to move from point A to point B was recorded. The efflux time was determined for several times, until at least three nearly-constant values were recorded. The average efflux times were used to calculate the specific viscosities according to equation (2-12) in the Background section. The empirical equation of Schulz and Sing (75) shown below was applied to find the intrinsic viscosity.

$$[\eta] = \frac{\eta_{sp}/c}{1 + 0.28\eta_{sp}}$$

3.3.4. Microscopy

Optical microscopy was carried out using a Leitz-Wetzler microscope. A photographic stage was set up to record the micgrographs. A magnification rate of 2500:3 was adopted for all the photographic work. Samples of plastics blends and graft-modified plastic blends were sectioned with a mocrotome set at 5 microns. The sectioned samples were placed on slides, covered with 4% formalin aqueous solution and a cover glass.

3.3.5. Dynamic Mechanical Testing

The dynamic mechanical properties of the polymers were studied using the Rheovibron Model DDV-II Direct Reading Dynamic Viscoelastometer made by Toyo Measuring Instruments (76).

The basic operating units and their relationship are schematically illustrated in Figure 3-5. The sample is oscillated in tension by force vibrations caused by the driver. The driver can be operated sinusoidally at four different frequencies, 3.5, 11, 35 and 110 Hertz. A frequency of 110 Herz was applied in this work. The sample was clamped between strain gauges and subjected to a small sinusoidal tensile strain at the fixed frequency. The stress was regulated by a feed screw mechanism. The amplitude of the sinusoidal deformation and the stress was measured and converted to electrical signals by unbonded type strain gauges. The signals from the two strain gauges were added as vectors by an electrical circuit which then read out this sum as $\tan \delta$ directly. Dynamic force was also read off directly and was used to calculate the dynamic complex modulus.

The dynamic complex modulus, elastic modulus and loss modulus could be calculated using the equations below:

$$E^* = 2.0 \times 10^9 \times 1/(AxD) \times L/S$$

$$E' = |E^*| \cos \delta$$

$$E'' = |E^*| \sin \delta$$

where L is the sample length in cm, S the sample section area in cm^2 , D the dynamic force dial when measuring $\tan \delta$ and A a correction factor for the $\tan \delta$ range used.

The elastic modulus, loss modulus, $\tan \delta$ of the sample were measured at varied temperatures. An Imass

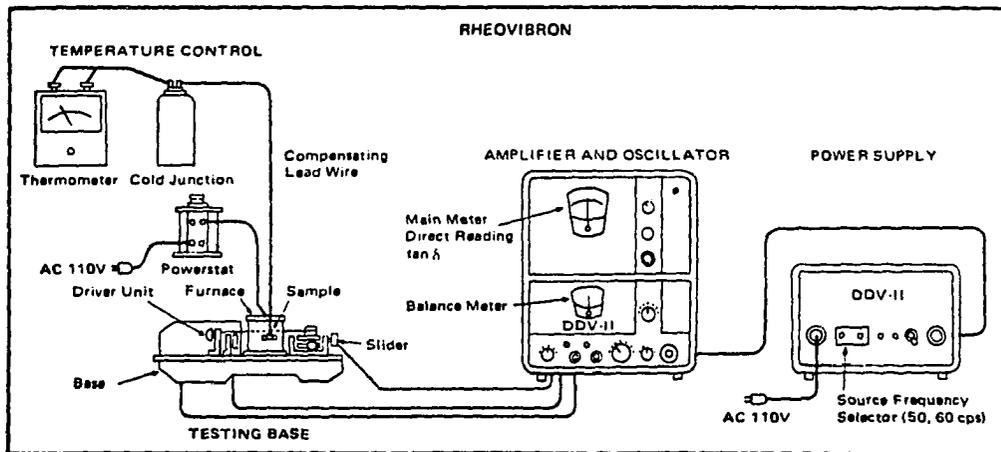
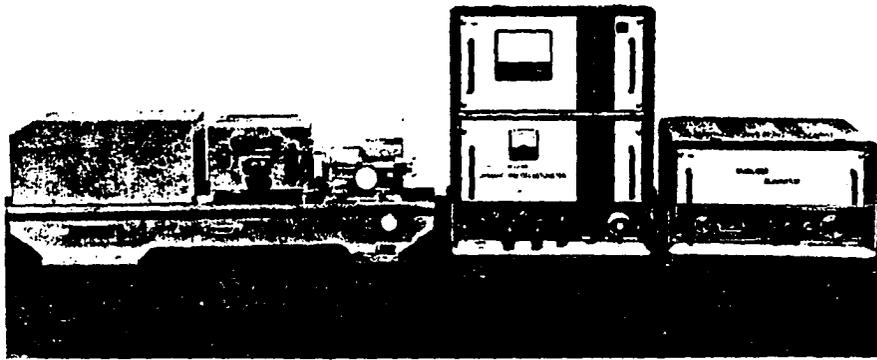


FIGURE 3-5: PHOTOGRAPH (ABOVE) AND BLOCK DIAGRAM OF RHEOVIBRON DYNAMIC VISCOELASTOMETER (56)

Temperature Chamber was used to control the sample temperature over the range of -150°C to 200°C . This chamber consists of a massive copper block in which two heaters were installed, and a shallow copper tray sitting atop the block. Liquid nitrogen was added to achieve the cooling. Precooled nitrogen gas was purged through the chamber to maintain a dry atmosphere during the subambient experiments. The ends of the chamber were covered with cones made of stiff paper to allow the dry gas to flow along the pullrods and prevent atmospheric moisture from condensing in the chamber.

Samples in the form of thin films were prepared by compression molding and were about 0.4 to 1.0 mm thick. The films were annealed for about three minutes between glass slides. Samples that were 1.3 to 2.5 mm wide and 1.5 to 2.6 mm long were cut off the annealed films.

The chamber was cooled to -150°C and then was heated up at rates of 1 to 2°C per minute. The temperature of the chamber was measured with a temperature indicating millivoltmeter by changing polarity at the input terminals. The dynamic force dial D , $\tan \delta$, sample length increment, amplitude factor and sample section area were recorded at 3 to 6°C intervals.

3.3.6. Differential Scanning Calorimetry

The thermal behaviors were studied using Perkin-Elmer

DSC-2. The temperature range studied was -120°C to 180°C . Polymer samples tested were placed in an aluminum sample pans and were covered with thin aluminum disks. The sample pans were then sealed with a crimper supplied by Perkin-Elmer Company. The sample pan was placed in one holder and an empty pan was placed in the other holder as reference. Liquid nitrogen was used to accomplish cooling. The sample holders were cooled down to and maintained at the lower-limit temperature until thermal equilibrium was reached.

The samples were then heated up to 180°C at a scanning rate of 20°C per minute. The signal level for full scale ordinate deflection of the recorder pen was set to correspond to a power difference of 1 millicalorie per second. The peaks and structures observed in the DSC spectra indicated the differences in power supplied to the sample holders when physical transitions such as melting and glass transition occurred. To avoid condensation of moisture in the whole atmosphere, the whole sample holder was covered with a dry box in which vacuum was established before dry nitrogen was introduced to fill the box. It was necessary to purge the helium through the sample holder enclosure when liquid nitrogen was used as the coolant. Other inert gases such as nitrogen, argon, etc., have condensation temperatures close to that of the coolant, and the increased density of those gases might lead to undesired convection which would result in non-reproducible baselines.

Since the scanning range studied was quite wide (-120 to 200°C), to optimize the base line was a difficult task. With the high sensitivity required for this study, it was impossible to obtain a straight base line over the entire scanning range. Correction was made to eliminate the effect of the curvature of the base line. For each DSG spectrum, the response due to the base line was subtracted from the total response observed digitally, and a new spectrum was plotted according to the new track.

Thermal data were taken for chlorinated polyethylene 2252 and 4814 and graft copolymers with CPE 2552 and 4814 as backbones. In order to detect the effect of graft modification on the thermal behavior of the blends, polyvinyl chloride-polystyrene, LDPE-PVC-polystyrene blend and blends modified with CPE-polystyrene graft were also studied.

Temperature calibration was made using indium and cyclohexane as the references. The indium, with a melting point of 429.8°K, was adopted to calibrate the high temperature range, while cyclohexane, crystallizes at 186.1°K, was used for the subambient range. The setting of the temperature calibration range control required for temperature calibration was determined by the following equation (52):

$$\Delta R = R^2 \left(\frac{\Delta T_{\text{IND}} - \Delta T_{\text{ACT}}}{\Delta T_{\text{ACT}}} \right) \times 1000$$

where ΔR = number of division change required to TEMP
Calibration Control

R = setting of temperature control

ΔT_{IND} = difference between measured transition
temperatures

ΔT_{ACT} = difference between the actual reference
transition temperatures.

The TEMP CALIB RANGE control setting R was adjusted by the amount ΔR calculated according to the above equation, until $\Delta T_{IND} = \Delta T_{ACT} \pm 0.5^{\circ}\text{K}$. The cyclohexane and indium transition points were again measured individually and the TEMP CALIB ZERO control was adjusted until the indicated temperatures were within $\pm 0.2^{\circ}\text{K}$ of the actual value.

All samples evaluated by DSC were obtained from films prepared by compression molding. The disk-shape samples were cut off the films with a cork bore. Sample weights ranged from 9 to 17 mg.

3.4. Impact Strength Test

Impact resistance of PVC-PS blend and graft modified PVC-PS blends were measured using a TMI Model 52004 Impact Tester which is a free swing pendulum type tester. The pendulum is equipped with an impact hammer and a vise for holding the specimen. A 5-ft-pound hammer was used in the testing of these plastics blends. The test procedure was in accordance

with the ASTM standard test D 256-73, method A, which is a Izod type test.

The specimen was held as a vertical cantilever beam and was broken by a single swing of the pendulum with the line of initial contact at a fixed distance from the specimen clamp and from the center line of a notch and on the same face as the notch. Figure 3-6 illustrate the breaking operation and the dimensions of a Izod type test specimen. The samples were molded by the use of a three-piece aluminum mold at 170°C. The width of the test section was measured for each sample with a micrometer to 0.001 inch. The energy absorbed in breaking the sample was read from the energy scale. Calibration was made to correct for the energy lost by the pendulum to friction in the pendulum bearing and to windage. This was done by observing the location of the pointer after free swings of the pendulum. Correction was also made for the energy loss due to friction and inertia in the movement of the pointer. The calibration procedure is described in detail in ASTM Standard D 256-73. Three free-swing tests were performed and the average value was used for calibration.

Due to lack of material, only one specimen was tested for each plastics blend and the values of impact strength obtained was considered only an estimate of the true values.

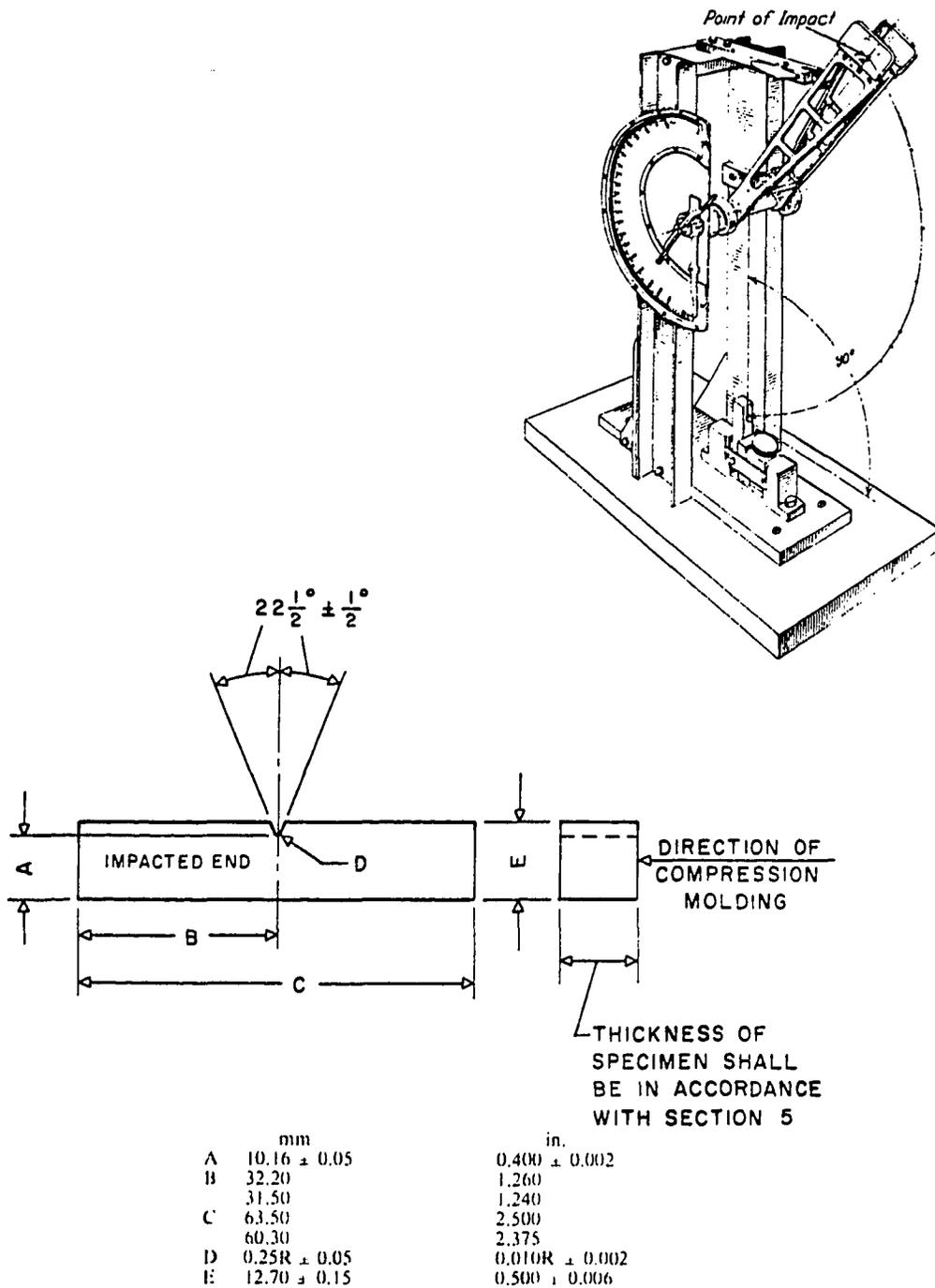


FIGURE 3-6: BREAKING OPERATION AND DIMENSIONS OF A IZOD TYPE SPECIMEN.

3.5. Blending and Molding

The blending work for all the polymer-blend samples were done in a Brabender Plasticorder type PL V150 equipped with a GP-100 adjustable speed drive which was connected to a laboratory mixing head type REE-6. The mixing head was equipped with roller type mixing blades as described in the literature (77) and in ASTM Standard D-2538-69 for the fusion rate test of polyvinyl chloride. The mixing head was heated electrically with temperature controlled by a Brabender Model 2003 Control Console. The plasticorder includes a prong type brake and a recording system to monitor the torque which is an indication of the melt viscosity of the blend. The Brabender provides a means to melt mix the sample while simultaneously giving information concerning the viscosity of the blend. Approximately 50 grams of polymer was used in each blending work.

The blend was prepared by dry mixing whereas all the rest samples, which were chlorine containing, were mixed with liquid stabilizer, Plastoflex E 50, added. In addition to the liquid stabilizer, BC-26, a powerform stabilizer, was also used to provide better protection for chlorine containing samples against degradation. Three phr of each of these stabilizers, based on the amount of the chlorine containing component in the blend, was added. All the blending was carried out at 170°C and a motor speed of 20 rpm. The mixing

head was preheated to the desired temperature and the motor speed set before the solid sample was gradually added into the mixing chamber.

The solid samples were usually fluffy and would overflow the mixing chamber until they began to melt and flow. The liquid stabilizer, when used, was then added. The mixing time was five minutes which was sufficient to yield melt blends appeared well-mixed. A ram closure was equipped to force the solid outside the chamber to back in.

At the end of the blending, the motor speed was lowered to about 5 rpm and the mixing chamber was removed away from the still rotating blades. Some of the blended material was recovered easily, but the rest remained adhering to the blades and the wall of mixing chamber. The portion remaining on the blades and in the chamber was scrapped with a copper spatula to form a large lump. It was then recovered and later molded into a sheet.

The mixing chamber and blades were then cleaned with a spatula. The residual polymer was cleaned by blending high impact polystyrene or low density, high melt index polyethylene.

All polymer sheets used in this study were molded using a Carver 2101 C-type hydraulic press equipped with heated plates. This press has a capacity of exerting 25,000 psi pressure on the six inch square plates. The polymer, positioned between two Teflon sheets, was preheated at desired

temperature for three minutes. The Teflon sheets served as releasing agent in this work. The plates were forced against and exerted a slight pressure on the polymer. At this point, the temperature of the plates would drop due to cooling by the sample. After the plate temperature returned to the desired value, pressure was slowly increased to allow the polymer melt to flow until 15,000 psi was reached. The pressure was released, the Teflon sheets removed, and allowed to cool at room temperature. The molding temperature was 130°C when preparing CPE sheets, and 170°C when molding plastics blends into sheets.

A three-piece aluminum mold was used to prepare samples for impact test. The samples prepared by this mold had dimensions conforming to that specified by ASTM, in which details on sample preparation are described.

3.6. Grinding

For the sake that better sampling and easier extraction could be achieved, all the samples of reaction products were ground into powder form before extraction was carried out. All the grinding work was done using a Wiley Mill equipped with 20 - 100 mesh stainless screens. All the reaction products recovered were molded into sheets, which were later sliced into strips approximately 1/8 inch in width. Since polyethylene and chlorinated polyethylene were pretty

flexible, all the polyethylene or CPE containing samples were too tough to be easily crushed. These samples were dipped in liquid nitrogen and became brittle enough to be broken down. The frozen strips were fed into the hopper of the mill, pressed by a wood cover against the rotating fly-wheel type blades, and got crushed into fine particles. Those particles which were fine enough to pass the 40-mesh screen were collected in a glass bottle.

3.7. Materials

All polymer samples were kindly supplied by several manufacturers and are described below.

Chlorinated polyethylene

<u>Designation</u>	<u>Sp. Gr.</u>	<u>C12 content W*%</u>	<u>% Crystallinity</u>	
			<u>X-ray</u>	<u>DSC</u>
CPE 2552	1.10	25	25	15
CPE 3614	1.16	36	2	0
CPE 4814	1.25	48	2	0

The chlorinated polyethylenes were made by Dow Chemical Company.

Low Density Polyethylene

<u>Designation</u>	<u>Sp. Gr.</u>	<u>Melt Index</u>	<u>Manufacturer</u>
DFDA 440	0.917	1.8	Union Carbide

Polyvinyl Chloride

<u>Designation</u>	<u>PVC Content Wt%</u>	<u>Inherent Viscosity</u>	<u>Manufacturer</u>
QSAH-7	100	0.76 0.2 gm/100ml cyclo- hexanone @ 30°C	Union Carbide

Polystyrene

Designation

Manufacturer

CX 2892

Cosden Oil & Chemical

Styrene monomer used in the synthesis work was manufactured and supplied by Cosden Oil & Chemical Company. This monomer contained an inhibitor to prevent polymerization during storage.

Benzoyl peroxide, used as initiator in the graft synthesis, was made by Pennwalt and was designated as LUCIDOL-98.

Samples of commercial stabilizers were obtained from Cincinnati Milacron Chemicals and are described below:

Designation

Content

Appearance

BC-26

Barium/Cadmium

White powder

E50

Epoxidized soybean oil

Yellowish liquid

CHAPTER IV

RESULTS AND DISCUSSION

Results of work on the preliminary study, synthesis, purification, characterization and blend modification are presented and discussed in this chapter.

4.1. Preliminary Study

Before graft synthesis and purification were performed some preliminary work was done to help set up the reaction conditions and the separation process for purification of the reaction product. This work included swelling test of the CPE films and the solubility study of the polymers.

4.1.1. Swelling Test

Swelling tests were carried out to determine the proper composition of initiation solution in which the chlorinated polyethylene films would swell significantly but would not dissolve. The result of the swelling test for the benzene-methanol system is shown schematically in Figure 4-1.

The degree of swelling, previously defined in Chapter III as the % weight increment due to the absorption of solvent,

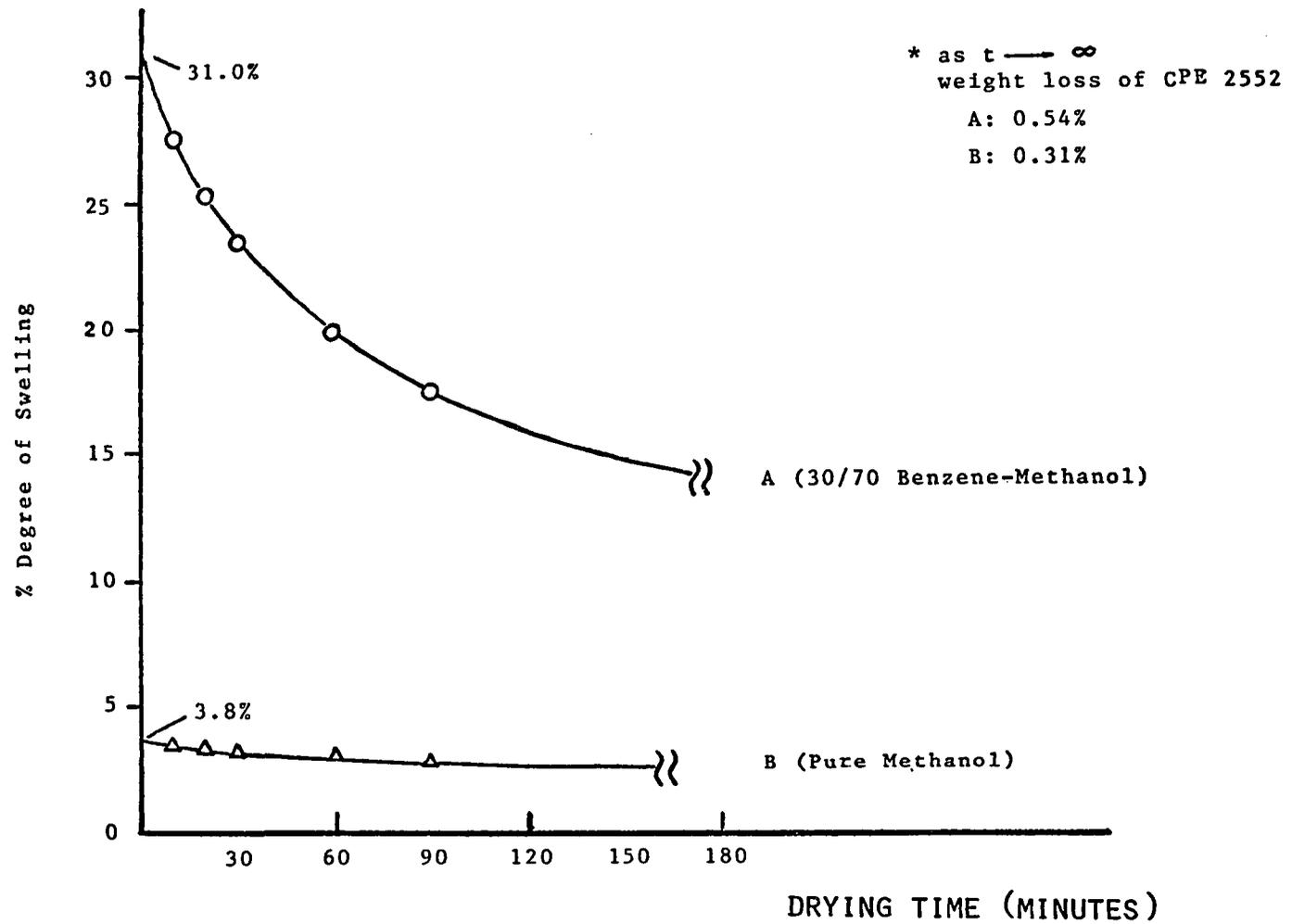


FIGURE 4-1: DEGREE OF SWELLING AND WEIGHT LOSS OF CPE2552 IN BENZENE-METHANOL MIXTURE

was plotted against the drying time. As the film dried up, the degree of swelling decreased. The weight of the film decreased quite a bit at the beginning of the drying period, but the rate of decrease slowed down, and finally leveled off when the solution had been dried for over a week.

The weight percentage of the solvent absorbed in the film after 8 hours of immersion, which should represent the degree of swelling of the films at the end of the initiation step, was obtained by extrapolating the values of degree of swelling measured after varied drying periods back to zero drying time. The amount of polymer dissolved during the initiation step was obtained by measuring the weight of the film which had been dried for over a week and comparing it with the original weight of the film. It was found that a 30:70 benzene-methanol mixture would be the better solvent for the CPE 2552. It yielded a relatively high degree of swelling (31%) comparing to that of pure methanol (3.8%) while the difference in the amount of CPE dissolved was not significant (0.54% to 0.31%). A mixture with benzene concentration higher than 30% would cause the film to collapse. CPE 3614 needed a mixture with lower solvating power, as it would collapse in solvent mixtures with benzene concentration higher than 10%. Therefore, a 10% Benzene mixture was adopted as the initiation solvent for graft synthesis with CPE 3614 as the backbone.

The reason CPE 3614 was more soluble in the solvent was its high chlorine content structure. The presence of chlorine in the polyethylene-like long chain interfered with the crystalline structure and hence destroyed the crystallinity of the polymer. It is also understood that polymers with higher crystallinity are generally less soluble because extra energy is required to overcome the crystallization energy barrier before they can be dissolved. Comparing to CPE 2552 (25% chlorine, 25% residual crystallinity), CPE 3614 has higher chlorine content (36%), hence lower residual crystallinity (0 - 2%) and is more soluble than CPE 2552 in the solvents.

As expected, the degree of swelling was later proved an important factor in achieving a high-yield graft copolymerization. With the use of the solvent system selected in this study, the average amount of CPE backbone dissolved in the initiation solution was later found to be around 3.4%, which was reasonable compared to the result of previous work (78).

4.1.2. Solubility Study

Solubilities of chlorinated polyethylene and polystyrene in various solvent systems form the basis for the design of a selective extraction process to remove polystyrene homopolymer from the reaction product, as mentioned in Chapter III. The solubility study was carried out on

several selected solvent systems and the general solubility behaviors of CPE 2552, 3614, 4814 and polystyrene in those solvents are listed in Table 4-1.

TABLE 4-1: Solubility of CPE and Polystyrene in Various Solvents at Room Temperature.

	<u>CPE 2556</u>	<u>CPE 3614</u>	<u>CPE 4814</u>	<u>PS</u>
Benzene	MS	MS	S	S
Toluene	MS	S	S	S
Cyclohexane	PS	PS	PS	MS
Acetone	SS	SS	SS	MS
CCL ₄	PS	PS	--	MS
Cyclohexanol*	SS	SS	--	S
Cyclohexane/Acetone 18:82	SS	SS	PS	S

S: Soluble

PS: Partial Soluble

MS: Most Soluble

(% soluble > 80)

SS: Slightly Soluble

(% soluble < 20)

* @ 90°C. The temperature of the filter system was controlled with a thermo-electric temperature monitor.

Both benzene and toluene were too strong to yield any selectivity as they completely dissolve CPE 4814 and polystyrene, while dissolving most of CPE 3614 and CPE 2552. Neither cyclohexane nor acetone alone could dissolve polystyrene completely at room temperatures and would not be

efficient to completely remove polystyrene homopolymer from the product. CCl_4 dissolved partially both CPE and polystyrene and it showed little selectivity over these polymers.

Cyclohexanol showed the highest selectivity at elevated temperature ($\approx 90^\circ\text{C}$) but would not dissolve either CPE or polystyrene at room temperature. At 90°C , polystyrene was completely dissolved whereas only 1.3% of CPE 3614 was dissolved. However, this solvent system had several disadvantages:

- (1) the separation required high temperature operation. Although the pressure filter could be kept at 90°C with a temperature monitor, it took quite long for the filter temperature to stabilize. Therefore, the experiment was inconvenient to conduct;
- (2) the low vapor pressure of cyclohexanol (normal B. P. $\approx 162^\circ\text{C}$) made drying difficult;
- (3) such a high temperature operation caused the CPE to degrade.

A mixture of cyclohexane and acetone showed the best over-all performance. This solvent mixture completely dissolved polystyrene but dissolved only less than 13% of CPE at room temperature. The composition of the mixture was determined according to the solubility diagrams (Figure 4-2,3). Figure 4-2 and 4-3 clearly showed for both CPE 3614 and 2552 that the maximum separation efficiency would be achieved with

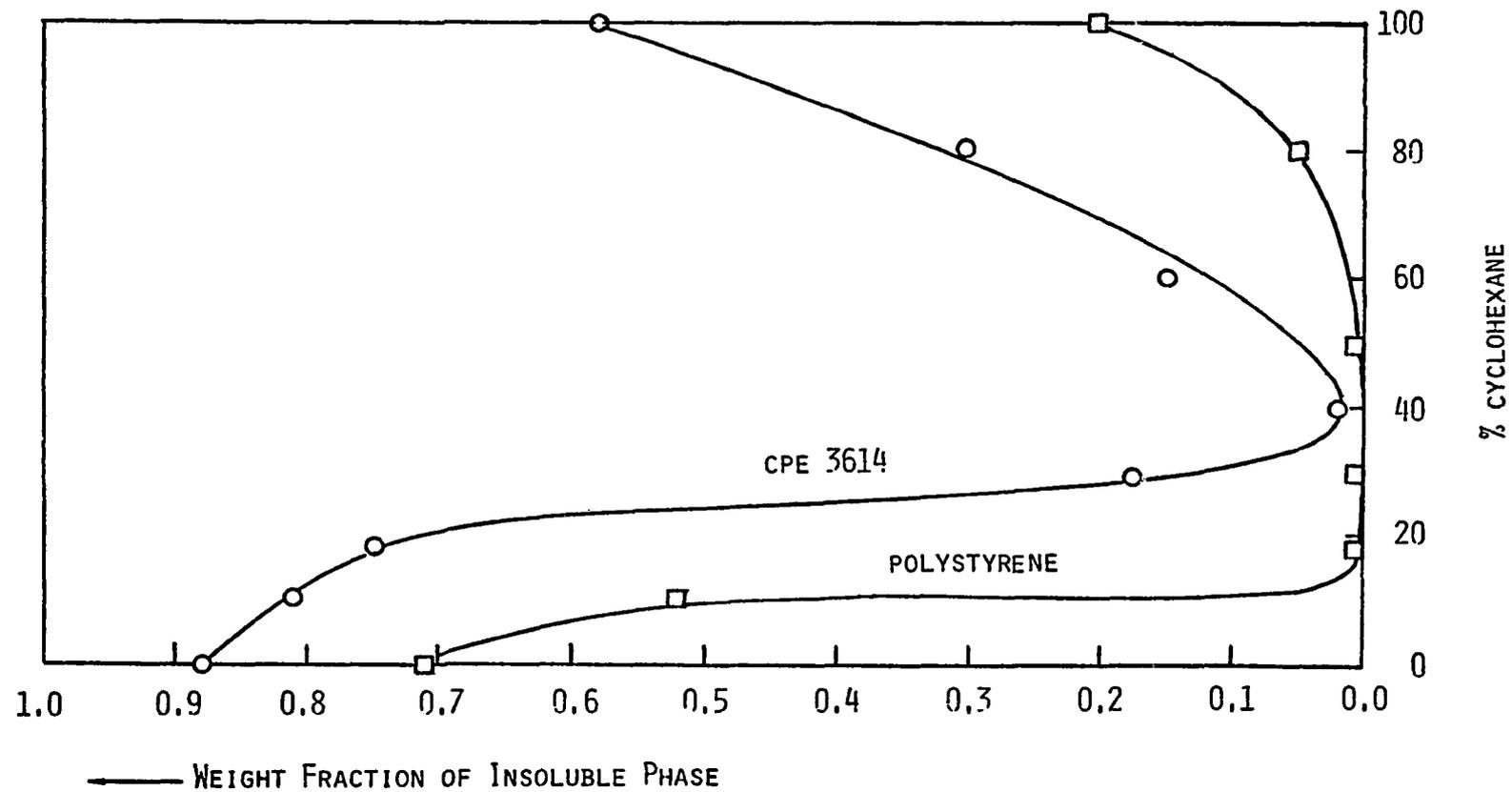


FIGURE 4-2: SOLUBILITY OF CPE3614 AND POLYSTYRENE IN CYCLOHEXANE-ACETONE MIXTURE

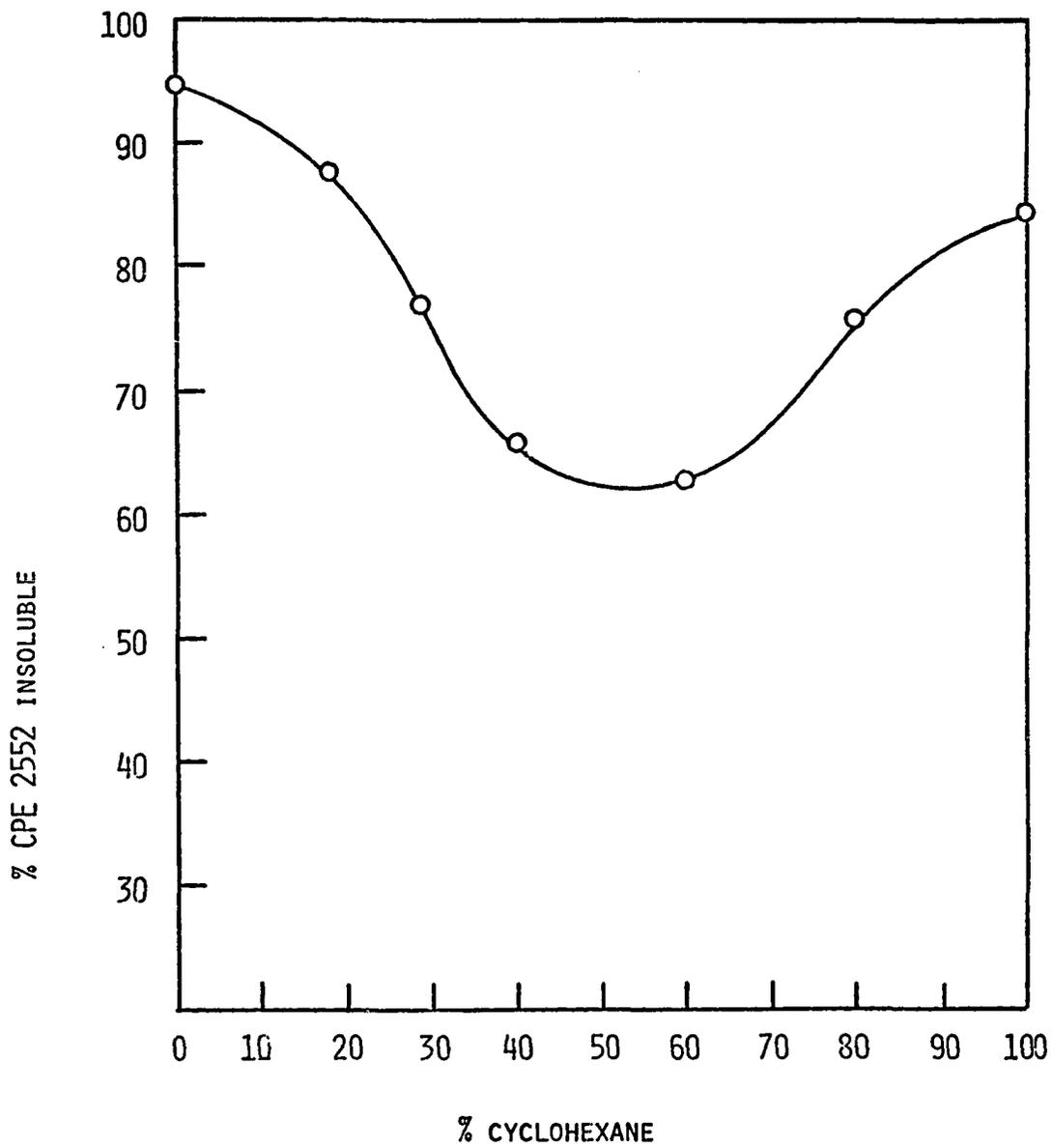


FIGURE 4-3: SOLUBILITY OF CPE2552 IN CYCLOHEXANE-ACETONE MIXTURE

the use of an 18% cyclohexane mixture.

It was also noticed that the solubility of CPE 3614 showed a maximum at a cyclohexane concentration of 40%. This fact suggested that the solubility parameter of CPE 3614 might be approximated by properly combining the solubility parameters of acetone and cyclohexane.

Kumar and Prausnitz (79) discussed the multidimensional nature of the solubility parameter, and predicted the solubility parameters of solvent mixtures. In their calculation, the parameter of each dimension was considered nearly additive, e.g., for the fractional polarity dimension,

$$\delta_{p,mixture} \approx \sum_i \phi_i \delta_{pi} \quad (4-1)$$

volume fraction and the polarity parameter of the i^{th} component in the mixture. Hansen (80) proposed a three-dimensional approach for the solubility parameters which suggested that the solubility parameter is a vector sum of contributions due to dispersion, polarity, and hydrogen bonding components and the following relation exists:

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (4-2)$$

where δ_d , δ_p , δ_h are the dispersion, polarity, and hydrogen bonding parameter respectively. With the use of Hansen's approach, the solubility parameter of the cyclohexane-acetone mixture could be estimated by the equation

$$\delta_{1-2}^2 = (\sum_i \phi_i \delta_{di})^2 + (\sum_i \phi_i \delta_{pi})^2 + (\sum_i \phi_i \delta_{hi})^2 \quad (4-3)$$

which gives $\delta_{1-2} = 8.64$;

where δ_{1-2} is the solubility parameter of the mixture; component 1 = cyclohexane; component 2 = acetone; values of δ_d , δ_p , δ_h for each pure solvent are (74)

$$\delta_{d1} = 8.18, \quad \delta_{p1} = 0, \quad \delta_{h1} = 0$$

$$\delta_{d2} = 7.58, \quad \delta_{p2} = 5.1, \quad \delta_{h2} = 3.4$$

It was also noticed that the above calculated δ value was close to that of toluene ($\delta \approx 8.91$), which had shown the strongest solvating power for CPE in the solubility study. According to the above discussion, the solubility parameter of an amorphous chlorinated polyethylene is estimated to fall between 8.3 and 9.0. This value lies between that of polyethylene and polyvinyl chloride (see Table 4-2), and is pretty close to the δ value of polystyrene.

Table 4-2 Solubility parameters of polyethylene, polyvinyl chloride and polystyrene (74)

	<u>average value</u>	<u>range</u>
polyethylene	8.05	7.70 – 8.79
polyvinyl chloride	9.75	9.40 – 10.80
polystyrene	9.01	8.60 – 9.70

The fact that the solubility parameters of polystyrene and CPE is so close explained why it was so difficult to find a solvent system with high selectivity for this polymer pair.

CPE 2552 showed a maximum solubility in 54% cyclohexane mixture (Figure 4-3) and an estimated solubility parameter of

about 8.39. This value is more different from the δ value of polystyrene than CPE 3614 therefore a higher separation efficiency than with CPE 3614 is expected. As a result of lower chlorine content, CPE 2552 behaves more like polyethylene than CPE 3614, exhibiting higher residual crystallinity and smaller solubility parameter.

The relations among the structure of CPE, solubility parameters, and the solubility behavior can be further discussed by examining the table below.

Table 4-3 Three-Dimensional Solubility Parameters of CPE and Solvents (74).

	Solvating Power	δ	δ_d	δ_p	δ_h
CPE 3614*	--	8.64	7.82	3.06	2.04
CPE 2552*	--	8.39	7.90	2.35	1.56
toluene	high ↓	8.91	8.82	0.70	1.00
benzene		9.05	8.95	0.50	1.00
cyclohexane		8.18	8.18	0	0
acetone		9.77	7.58	5.10	3.40
cyclohexanol		low ↓	10.95	8.50	2.0
methanol	14.28		7.42	6.0	10.9

* Values of δ_d , δ_p and δ_h of CPE 3614 and CPE 2552 were estimated from that of the solvent mixtures which were calculated from equation 4-3 .

Generally, the solubility of CPE in a solvent increases with smaller $\Delta\delta$ value, which is the difference between δ_{CPE} and δ solvent. The situation for benzene and cyclohexane is a little vague as benzene showed a better solvating power than cyclohexane while possessing a slightly larger $\Delta\delta$ value for CPE 2552. This phenomenon may be explained in terms of three-dimensional solubility parameters. The three-dimensional solubility parameter approach requires small enough difference in each of the three components parameters in order to have a polymer soluble in a solvent. That means it is the summation of $|\Delta\delta_d|$, $|\Delta\delta_p|$, and $|\Delta\delta_h|$, not $\Delta\delta$ that determine the solubility of polymer in solvent. With this criteria, the higher solubility of CPE 2552 in benzene than cyclohexane is reasonable. Cyclohexane is more compatible with CPE 2552 in the sense of dispersion behavior, but this effect is masked by the larger polar and hydrogen bonding force between benzene and CPE 2552. It is also possible that the slightly smaller $\Delta\delta$ value for cyclohexane that appears in Table 4-3 was due to the δ values adopted, which may be subjected to some error as the solubility parameter of CPE was determined from the value of the solvent mixture whereas the δ value of the solvents cited in the Table was obtained by other methods.

The presence of chlorine atoms in CPE might result in some polar and hydrogen bonding forces and affect the solubility of CPE in solvents of different polar nature. Thus CPE 2552,

having lower chlorine content than CPE 3614, possesses lower δ_p and δ_h and should be more soluble in less polar or hydrogen bonding dominated solvent if the crystallinity effect is disregarded.

4.1.3. Isolation of Styrene Homopolymer

It was also necessary to know the number of extractions required to completely remove the styrene homopolymer once the solvent system had been decided. In order to know how many extractions would be enough to remove all the polystyrene monomer, a graft product was subjected to consecutive extractions. The results of extractions are given in Table 4-4. About 49.7% of the mass was extracted in the first extraction while amount extracted in the second and third extraction was only 2.6 and 0.07%. It was observed that what was extracted in the second and third extractions was a viscous, waxy material instead of solid polymer. This suggested that the excess extraction removed some low molecular weight polymer instead of polystyrene homopolymer. A simulated extraction was also made on a physical mixture of CPE and polystyrene, and the insoluble phase after the first extraction was characterized by IR spectroscopy (Fig. 4-4). No peak characteristic of polystyrene appeared in the spectrum. This indicated one single extraction should be efficient to remove the polystyrene homopolymer. Another evidence of efficient removal of

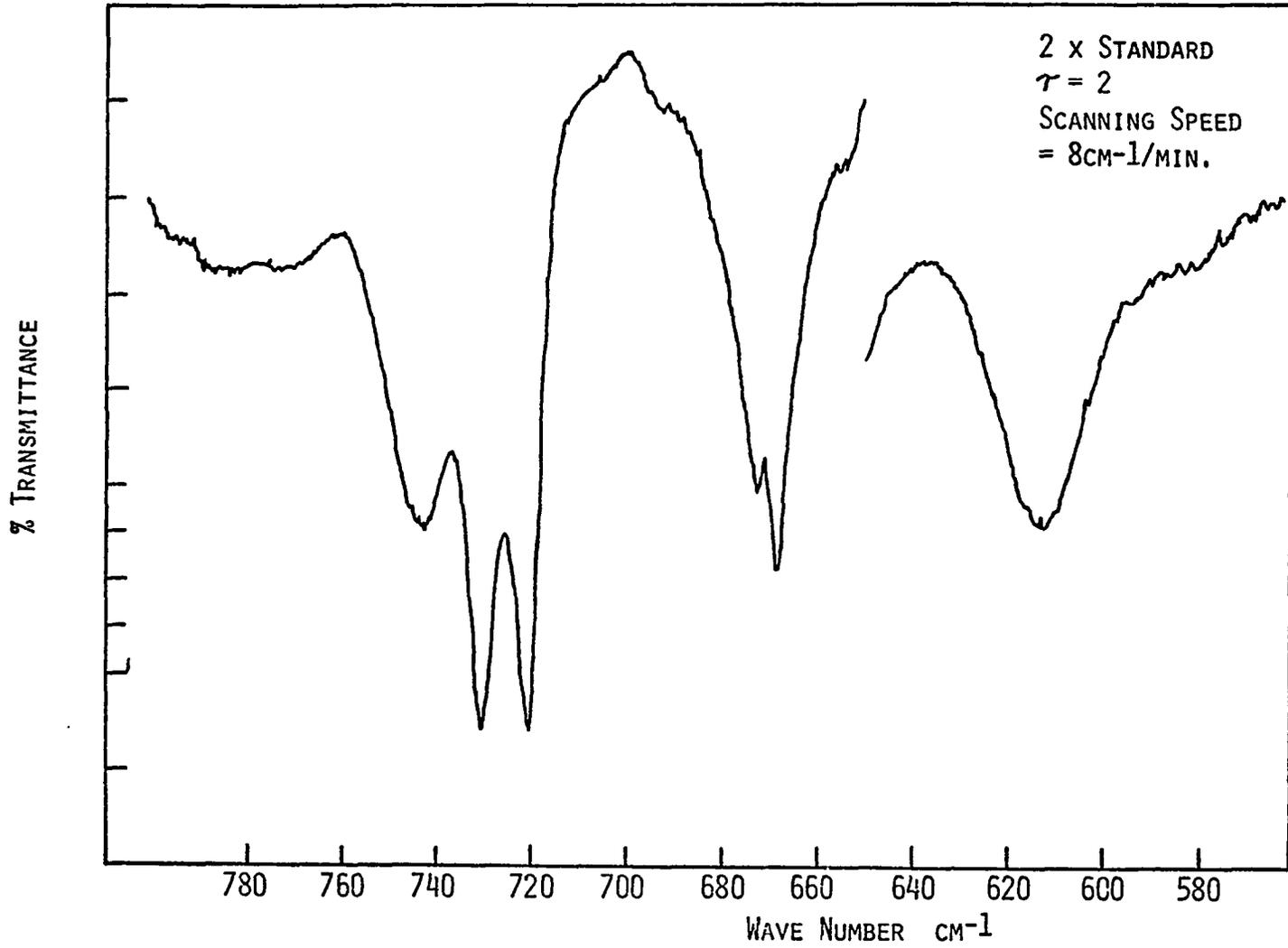


FIGURE 4-4: IR SPECTRUM OF EXTRACTED CPE2552-POLYSTYRENE MIXTURE

Table 4-4: Separation Result of Product C-9.

	<u>Separation*</u>
First Extraction % insoluble	50.3
Second Extraction % insoluble	97.4
Third Extraction % insoluble	99.3

*Extraction solvent: 18-82 cyclohexane-acetone mixture; Ex-
traction procedure: powder sample was swollen in solvent
mixture at room temperature for 1 day, then the solution was
boiled for 1 hour. Solution was allowed to cool down gradually.
Setting time - 1 day. Filter used: Whatman Quantitative filter
paper #50, hardened.

polystyrene homopolymer came from the solubility of CPE 2552-polystyrene mixtures in the 18/82 cyclohexane-acetone solvent. (Fig. 4-5). After extraction, the weight fraction of the mixture that remained undissolved showed a linear relation with the composition of the mixture and the straight line passed through the point corresponding to the solubility of pure CPE 2552. This observation suggested that the solubility behavior of each component in the mixture did not change due to the presence of the other component. It could hence be inferred that the styrene homopolymer would be completely soluble as it behaved in single component solubility study. Otherwise, the solubility curve of the mixtures would not be linear and would not pass through the point representing the solubility of pure CPE 2552. With the above supporting evidence, it was determined that only one single extraction would be carried out in the separation of styrene homopolymer.

4.1.4. Isolation of Unreacted CPE

In order to obtain the pure graft, unreacted CPE had to be removed from the styrene homopolymer-free product. It was considered that the isolation of unreacted CPE should be achieved by selective precipitation instead of selective extraction, because 1) it was extremely difficult to find a solvent to dissolve CPE without dissolution of the graft copolymer, 2) the solution had to be heated up to a rather high

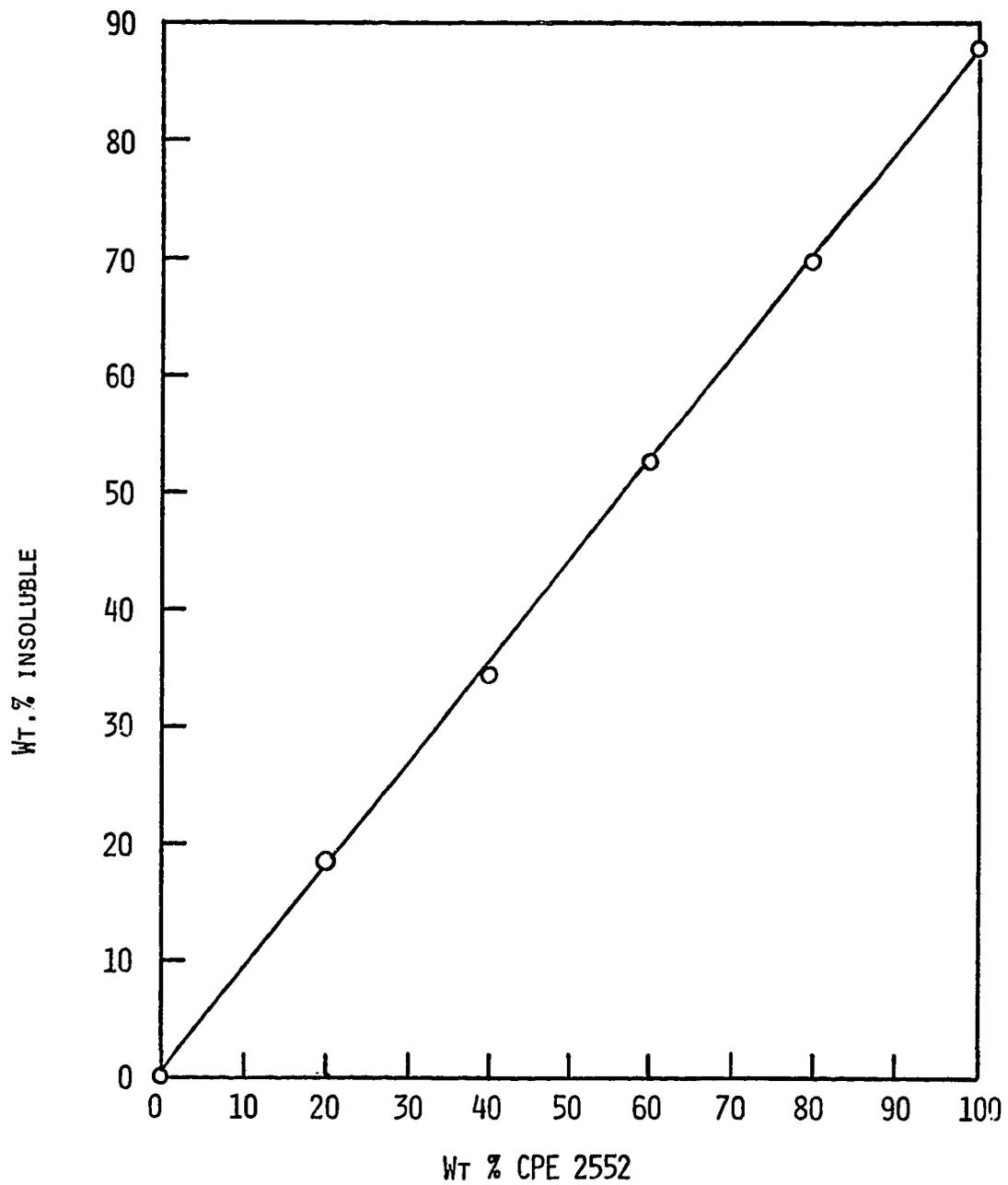


FIGURE 4-5: SOLUBILITY OF CPE2552-POLYSTYRENE MIXTURES IN 18/82 CYCLOHEXANE-ACETONE MIXTURE

temperature in order to dissolve the CPE having residual crystallinity and thermal degradation of CPE would thus be more severe. As for the selective precipitation, it was necessary to be able to precipitate ungrafted CPE without precipitating out the graft copolymer if this technique was to be used. It was assumed that CPE had a lower solubility than the graft based on the fact polystyrene was much more soluble than CPE in good solvents such as benzene and toluene.

A simple test was carried out to study the solution behaviors of both the CPE and polystyrene homopolymer in the selective precipitation procedure. The polystyrene homopolymer completely dissolved in the toluene and remained after four drops (approximately 0.1 ml) of methanol was added. No phase separation was observed after the solution was centrifuged. CPE 2552 was also dissolved in hot toluene and was precipitated with the addition of methanol. After setting for two days at room temperature a good amount of precipitation was observed. The solubility behavior of CPE and polystyrene would not reflect the solubility behavior of graft copolymer during precipitation. They, however, did represent the two extreme conditions which might exist in the precipitation process.

4.1.5. Composition Determination by IR

Compositions of all the fractions obtained in the

separation procedure were determined using infrared technique. IR spectra of CPE - polystyrene mixtures of varied composition were obtained and calibration curves for CPE 2552 - polystyrene and CPE 3614 - polystyrene mixtures were constructed using the "internal-standard" (44) method (Fig. 4-6,7).

The peak at 614 cm^{-1} has been assigned as the C-Cl stretching mode (81) and the 1605 cm^{-1} peak as the aromatic C=C mode. They are characteristic of CPE and polystyrene respectively. According to Lambert-Beer's Law, the relation between the relative absorbance of these peaks and the molar composition is linear, if the absorption behavior of these modes are not affected by the variation in the environment. The curvatures observed in Fig. 4-5 and 4-6 are results of the fact that the charts were based on weight fraction, instead of mole fractions, as well as the environment effect. Since the "internal-standard" technique was employed, the thickness of the film should not affect the relative intensity of the characteristic peaks. However, it was found that the thickness of the film did affect the shape of the absorption peaks and made it more difficult to interpret the spectra and to measure the peak intensity accurately. All the films were prepared to have a thickness close to $30\text{ }\mu\text{m}$.

The intensity of the 614 cm^{-1} peak was relatively low compared to that of the 1605 cm^{-1} peak. When a mixture or graft product with high polystyrene concentration was analyzed

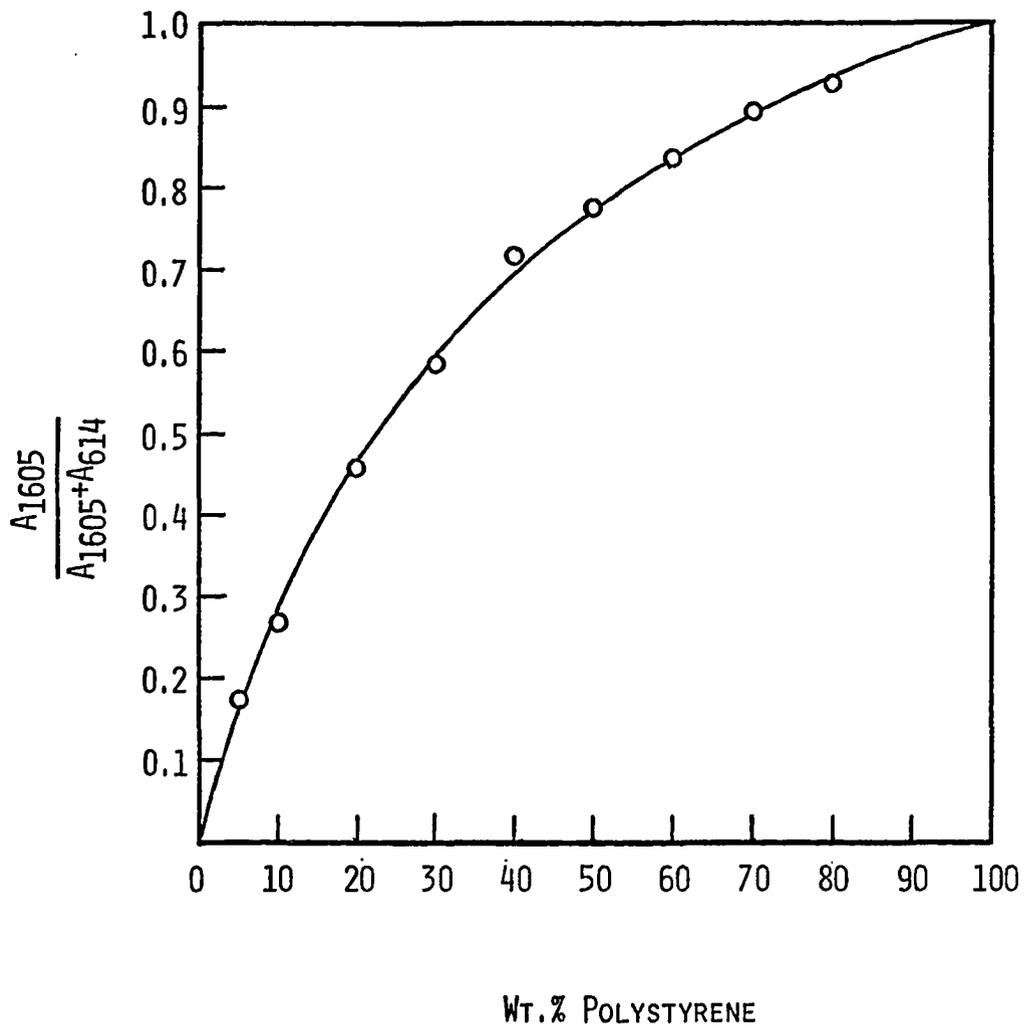


FIGURE 4-6: CALIBRATION CURVE FOR CPE2552-POLYSTYRENE MIXTURE

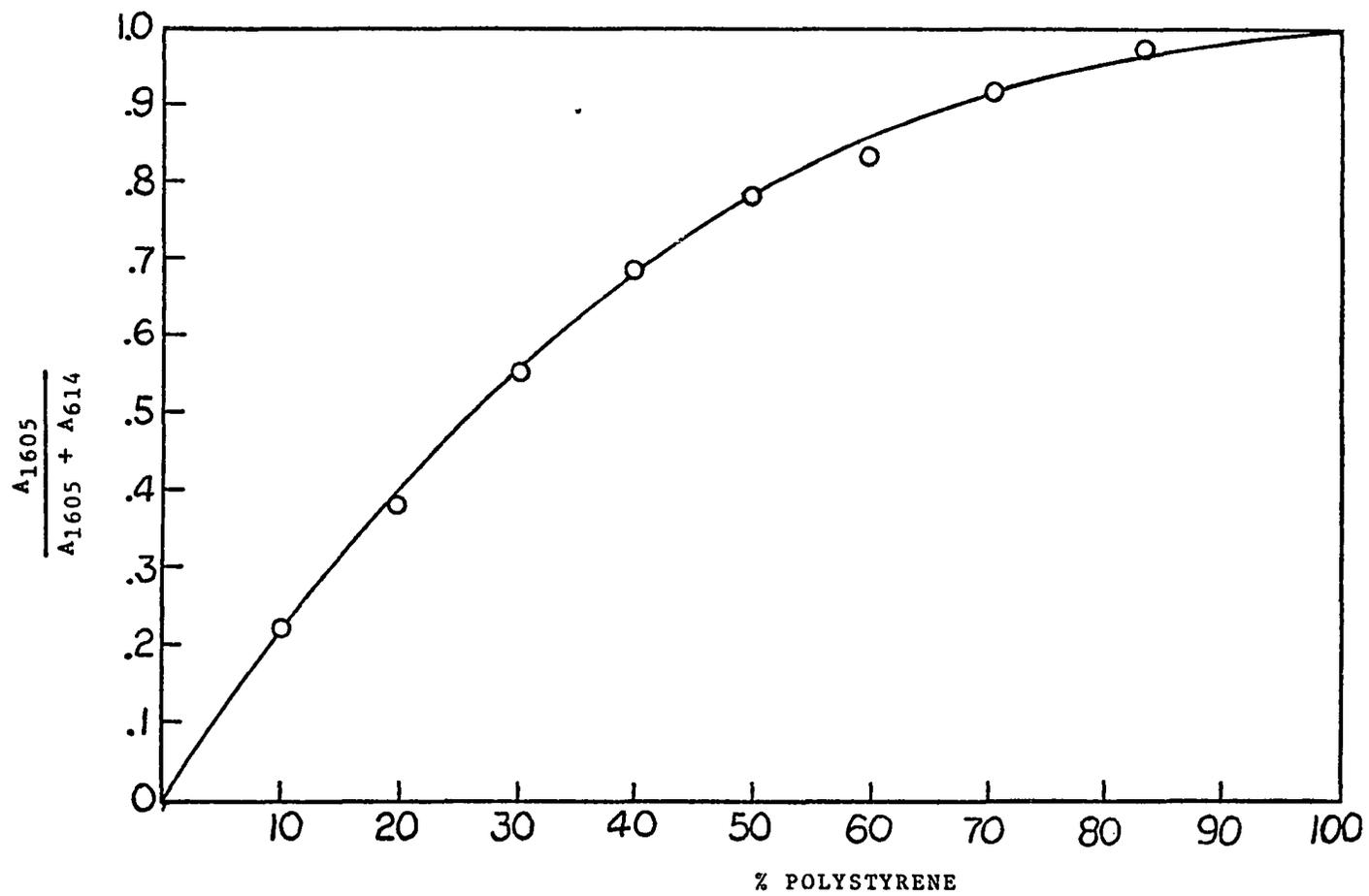


FIGURE 4-7: CALIBRATION CURVE FOR CPE3614-POLYSTYRENE MIXTURE

the 614 cm^{-1} peak was usually too weak to be measured accurately. Besides, there is a very weak peak due to styrene at the wave number of 625 cm^{-1} . This peak was usually too weak to be seen, but it became observable when the CPE concentration was low ($<10\%$). In this case, this peak interfered with the 614 cm^{-1} peak and made the determination of 614 cm^{-1} peak intensity even difficult. This feature had caused the difficulty in composition determination of the extracted fraction, which was styrene homopolymer-rich.

When these calibration curves were used to determine the composition of the graft copolymer, it was assumed that the bulk absorption behavior of the molecular vibrational modes would not change significantly after grafting. Molecular vibrations near the grafting sites might have been affected by the attached long chain, but the effect would be insignificant as the concentration of the grafting sites was very low, compared with the number of monomeric units in a high polymer. This assumption is supported by NMR study of a graft copolymer. It was found that the resonance curves and the relaxation times of the styrene in the graft were the same as that of the pure styrene (7). Thus, after the intensities of characteristic peaks were measured, the composition could be directly read off the calibration chart.

The experimental error anticipated in the construction of the IR calibration curves was assessed by repeating the

determining procedures for three of the data points on the curve. Percentage deviation of 0.6%, 0.6% and 0.1% were found for these three data points, which showed an average deviation of 0.43%. The reproducibility of these procedures was considered satisfactory.

4.2 Graft Synthesis and Purification

Graft copolymerizations via chemical initiator were carried out under varied reaction conditions. Several reaction variables were considered important, and their effect on the grafting were studied. These reaction variables were type of the initiator and its dose, initiation time, type of backbone polymer, reaction temperatures, reaction time, monomer concentration, and swelling time. A set of notations are defined to represent the reaction conditions and are listed in Table 4-5. Synthesis was also made using irradiation technique. The irradiation-induced graft copolymerization was carried out under three different conditions. Two samples were copolymerized under vacuum, with an irradiation and copolymerized with the presence of air and a dose of 0.4

The results of the graft copolymerizations were analyzed in terms of the yield, graft efficiency and % degree of grafting. These terms are defined in this work as follows:

Table 4-5: Definition of the Notations of Reaction Variables.

	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
A initiator dose (phr)	Bz ₂ O ₂ 2	Bz ₂ O ₂ 1	Bz ₂ O ₂ 3	AIBN 2
B initiation time (hr)	8	4	12	6
C chlorine % in CPE	25	36	48	-
D reaction temperature °C	60	40	70	-
E reaction time (hr)	28	16	48	-
F monomer-MeOH ratio	70/30	100/0	50/50	80/20
G swelling time (hr)	12	0	36	-

$$\text{yield} = \frac{\text{weight of styrene polymerized}}{\text{weight of CPE used in reaction}} \times 100\%$$

$$\text{Graft Efficiency (G.E.)} = \frac{\text{weight of polystyrene in graft}}{\text{weight of styrene polymerized}}$$

$$\% \text{ Degree of Grafting} = \frac{\text{weight of polystyrene in graft}}{\text{weight of CPE used in reaction}} \times 100\%$$

The % degree of grafting is simply the product of the yield and the graft efficiency.

Yield is an indication of the amount of styrene polymerized in the reaction, and this quantity includes both styrene in the graft and the undesired styrene homopolymer. It reflects the conversion achieved in the copolymerization but does not directly relate to the amount of graft produced. A copolymerization may give a very high yield while only small amount of graft copolymer is produced.

Graft Efficiency, which is the ratio of the amount of desired graft copolymer produced to the undesired by-product, the homopolymer, is an important factor in evaluation of a graft synthesis. A high graft efficiency, which means low degree of contamination in the product, can minimize the purification effort required.

The degree of grafting indicates the concentration of the polystyrene graft in the graft copolymer and is a measure of the amount of graft produced. This quantity is directly related to the structure of the graft hence, is the most important parameter in the structure-properties study of graft copolymers.

Yield can be obtained from gravimetric data with simple calculation.

However, the true graft efficiency or the degree of grafting can not be evaluated unless the graft copolymer is completely purified and recovered, and its composition precisely analyzed. The graft efficiency and degree of grafting were calculated in this work according to the result of separations and composition analysis.

Table 4-6 lists the reaction conditions for twenty five selected graft synthesis and the yields of those reactions.

Some synthesis experiemnts were repeated and the results are given below.

Table 4-7: Reproducibility of Synthesis

Reaction Conditions	Yield %		G.E.I.		Degree of Grafting	
	#1	#2	#1	#2	#1	#2
(A) $A_1B_1C_1D_1E_1F_1G_1$	112	98	0.193	0.228	22.2	20.9
(B) $A_1B_3C_1D_1E_1F_1G_1$	27	14	0.175	0.156	3.1	2.7

In test (A), a yield of 105 ± 7 , G.E.I. of 0.211 ± 0.017 , degree of grafting of 21.6 ± 0.7 were obtained. Test (B) showed a yield of 20.5 ± 6.5 , G.E.I. of 0.166 ± 0.01 and degree of grafting 2.9 ± 0.2 . The main source of the experimental error probably was the produre of evaporating the residual monomer. Since the evaporation was carried out at about 60°C , post-polymerization might have happened during the evaporating period.

Table 4-6: Reaction Conditions of Graft Copolymerizations and Their Yields.

		Yield (Gravimetric)	Yield (IR)
^a C-9	A2 B1 C1 D1 E1 F1 G1	87	-
C-10	A3 B1 C2 D1 E1 F2 G1	461	-
C-11	A1 B1 C1 D1 E3 F1 G1	163	150.0
C-16	A1 B3 C1 D1 E1 F1 G1	27	15
C-20	A1 B3 C1 D1 E1 F1 G1	14	14
C-21	A1 B2 C1 D1 E1 F1 G1	97	70
C-22	A1 B1 C1 D2 E1 F1 G1	52	43
C-23	A1 B1 C1 D1 E1 F1 G2	67	53
C-24	A1 B1 C1 D1 E1 F2 G1	333	331
C-25	A1 B1 C1 D1 E1 F1 G1	112	104
C-26	A4 B1 C1 D1 E1 F1 G1	67	54
C-27	A1 B1 C1 D1 E1 F4 G1	115	113
C-31	A3 B1 C1 D1 E1 F1 G1	169	163
C-32	A1 B1 C1 D3 E1 F1 G1	69	52
C-33	A2 B3 C1 D1 E1 F1 G3	20	20
C-34	A1 B4 C1 D1 E1 F1 G3	250	250
C-37	A1 B1 C1 D1 E1 F1 G1	98	89
C-38	A1 B1 C1 D1 E3 F1 G1	174	163
C-39	A1 B3 C1 D1 E1 F1 G3	95	87
C-40	A1 B4 C1 D1 E1 F1 G1	360	270
C-42	A1 B4 C1 D1 E1 F1 G3	136	133
^b R-1	0.4 Mrad, vacuum	113	-
R-2	0.4 Mrad, atmosphere	88	-
R-3	0.6 Mrad, vacuum	125	-

^aC: Chemical initiated

^bR: Radiation initiated

4.2.1. Extraction - The First Stage of Separation

The purification work was carried out to separate the homopolymers from the graft copolymer. The graft products were first extracted with the cyclohexane-acetone solvent mixture and then went through the methanol-precipitation procedure as discussed in Chap. III.

In the first stage of separation, essentially all the styrene homopolymer was removed from the reaction product according to the result of preliminary study. The result of the extraction works on selected graft samples is presented in Table 4-8. However, it was also observed that some of the solutions obtained in the extraction process appeared milky and the IR spectra of these soluble-phase fractions showed tiny, but detectable peak at the wave number of 614 cm^{-1} . This observation was an indication of the presence of graft copolymer in the soluble phase, which meant some graft copolymer was dissolved along with the styrene homopolymer. This problem was inherent since the solubility of chlorinated polyethylene and polystyrene was so close that complete selective extraction seemed impossible.

It has been discussed that unless the solvent used for extraction is highly selective over the two polymer sequences (good solvent for one chain but a very bad solvent for the other), the graft copolymer is likely to be dispersed into the extracting solvent, resulting in micelle formation (48).

Table 4-8: Results of the First Stage Separation

	<u>Wt. Fraction extracted</u>	<u>Wt. Fraction PS in Insoluble Phase*</u>
C-9	0.497	0.145
C-11	0.537	0.120
C-16	0.230	0.030
C-20	0.250	0.026
C-21	0.435	0.148
C-22	0.325	0.090
C-23	0.401	0.100
C-24	0.247	0.670
C-25	0.460	0.182
C-26	0.461	0.050
C-27	0.370	0.234
C-31	0.390	0.330
C-32	0.375	0.115
C-33	0.238	0.045
C-34	0.097	0.660
C-37	0.417	0.173
C-38	0.502	0.335
C-39	0.452	0.160
C-40	0.523	0.440
C-42	0.303	0.229
R-1	0.380	0.318
R-2	0.390	0.290
R-3	0.340	0.360

*Determined by IR.

However, the best solvent found in the solubility study was not highly selective over the CPE and polystyrene (cyclohexane-acetone mixture completely dissolved polystyrene but also dissolved 12.4% of CPE), therefore, the dispersion of graft copolymer was sometimes inevitable. Consecutive extraction using a relative weak solvent acetone was considered the alternative way to remove the styrene homopolymer, but this effort was also found fruitless. Three consecutive extractions with acetone did not completely dissolve the styrene homopolymer at room temperature.

This defect had led to some difficulty in the evaluation of graft efficiency and degree of grafting.

Since the extraction process has been proved efficient to completely remove the styrene homopolymer, any polystyrene remained in the extracted reaction product should be in the graft. Figure 4-8 shows the spectrum of a CPE 2552-g styrene copolymer which has been extracted by the 18% cyclohexane solvent for three times. The presence of a strong peak at 700 cm^{-1} , which is characteristic of styrene, is a proof of grafting. Figure 4-9 showed spectra of extracted CPE 2552 graft product and a extracted CPE-P5 mixture. The 1605 cm^{-1} peak, which is due to $\text{c}=\text{c}$ stretching in benzene ring, is not seen in the spectrum of the extracted mixture, but is observed in that of the extracted graft product. The fact that a 1605 cm^{-1} peak is an indication of grafting provided the basis for

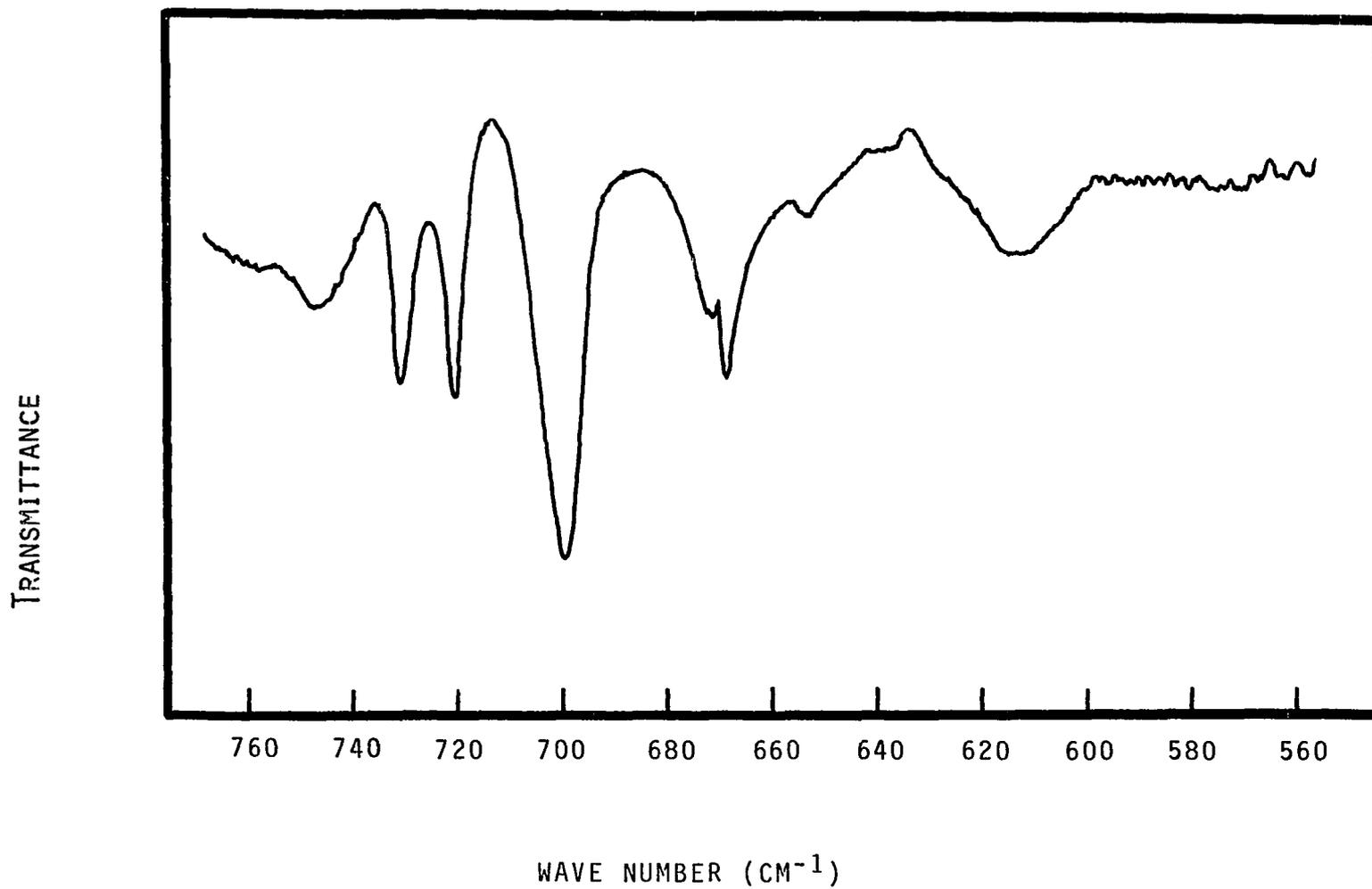


FIGURE 4-8: SPECTRUM OF GRAFT PRODUCT C-9 AFTER THREE CONSECUTIVE EXTRACTIONS

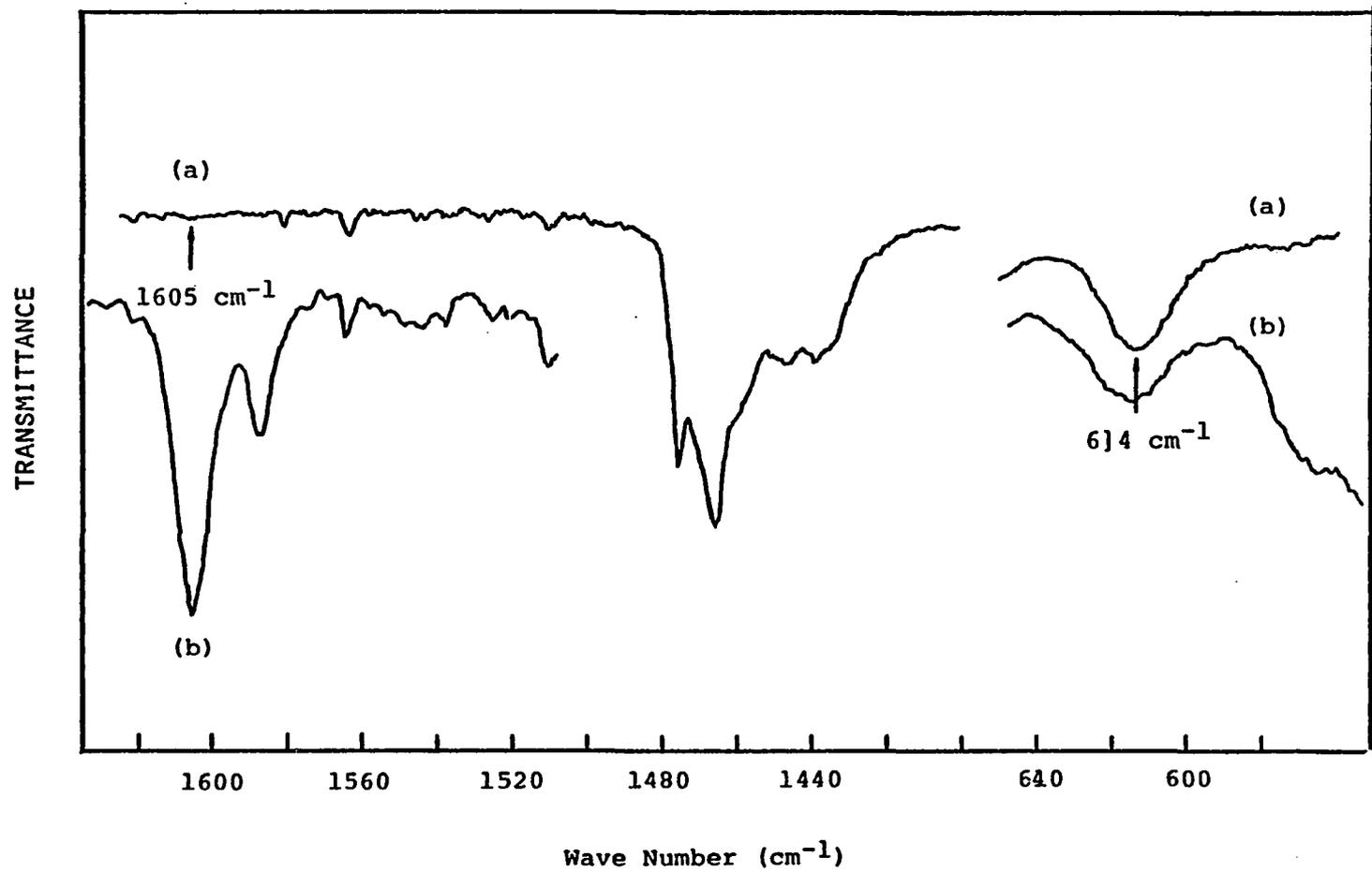


FIGURE 4-9: A SPECTRA OF EXTRACTED CPE-PS MIXTURE (a) AND EXTRACTED GRAFT COPOLYMER (b)

the determination of degree of graft by IR.

One extraction experiment was repeated for four times so that the experimental error associated with the extraction and pressure filtration procedure could be estimated. One graft copolymer product, C-9, was extracted in 18% cyclohexane solvent and then separated by pressure filtration for four times. The weight fraction of the insoluble phases were found to be 0.508, 0.517, 0.503 and 0.492, respectively. These data have an average of 0.505 and root-mean-square-deviation (RMSD) of 0.010.

4.2.2. Methanol Precipitation of Graft Product - The Second Stage Separation

Methanol precipitation was carried out on a number of graft products and result of selected samples are presented in Table 4-9. It was found that the solubility behavior of the styrene homopolymer-free graft product varied with the reaction conditions and was greatly affected by the presence of crosslinking. Thus, it was inadequate to calculate the graft efficiency and degree of grafting using the result of the second stage separation as the amount precipitated did not always indicate the amount of unreacted CPE present.

Several samples which were found to be crosslinked during reaction gave large amount of precipitation. The crosslinks existing in the graft copolymer made the polymer

Table 4-9: Results of the Second Stage Separation

<u>Sample No.</u>	<u>Wt. fraction Precipitated</u>	<u>Wt. fraction of PS^a in precipitated phase</u>	<u>Remark</u>
C-11	0.10	0.040	
C-20	0.62	-	initiation time 12 hours
C-21	0.20	0.020	
C-25	0.14	0.090	
C-31	0.18	0.035	
C-32	0.40	0.040	init. temp. 70°C
C-33	0.30	0.057	init. time 12 hrs.
C-34 ^b	0.20	0.203	high degree of grafting
C-39	0.90	0.145	init. time 12 hrs.
C-40	0.18	0.055	
R-1	0.03	0.250	0.4 vacuum
R-2	0.05	0.270	0.4 air
R-3	0.05	0.330	0.6 vacuum

a. determined by IR.

b. cloudy.

insoluble in the solvent and resulted in the mass precipitation. One sample which had been determined to have high degree of grafting also yield relatively large amount of precipitation, but the polystyrene content in the precipitated fraction was also high. It was also observed that the toluene solution became turbid after addition of methanol and remained a bit cloudy after centrifuging. This phenomenon suggested that the reaction efficiency of this graft copolymerization was so high that the extracted product was nearly pure graft. When methanol was added, fractionation of the graft copolymer also occurred according to the concentration of polystyrene in the copolymer molecules. The trace amount of unreacted CPE precipitated was then emulsified by the graft copolymer and the solution became cloudy. Under this condition, separation of unreacted CPE from the graft copolymer was impossible and, a relatively high polystyrene content in the precipitated fraction was therefore obtained. All the other samples of chemical initiated graft products showed an average precipitation of 10% and an average polystyrene content of 4.8% in the precipitated fractions. This observation indicated that the average amount of unreacted CPE might be less than 10% of the original CPE involved in the reaction.

A relatively small amount of precipitation was seen for the radiation-induced graft samples and the polystyrene content in these precipitated materials was relatively higher

than the chemical initiated copolymerization samples. This fact might indicate that the number of active sites created in the irradiated samples was higher than that of the chemical initiated samples and the number of unreacted CPE molecules was therefore substantially lower in the irradiated samples.

4.2.3 Determination of Graft Efficiency and Degree of Grafting

Many of the previous works on separation of styrene homopolymer from the polyolefin-styrene graft copolymers involved only a simple acetone-extraction of the reaction product which, in most cases, is in the form of solid film. The values of degree of grafting obtained from such extractions were referred as apparent graftings and could be considerably different from the true values. The true grafting to apparent grafting ratio was found to range from 0.02 - 0.57 (47). The separation process described in Chap. III was proved by solubility studies to be efficient to remove the styrene homopolymer, and should also be able to isolate most of the unreacted CPE from the graft. This process can therefore be considered successful if to obtain a graft copolymer with high purity is the only major concern. However, the degrees of grafting obtained from the results of these separations would be somewhat lower than that of the true values due to the elution loss of graft copolymer in the extraction process

and possibly the incomplete removal of unreacted CPE. Since there was inherent error associated with the graft efficiency obtained according to the separation results in this work, this quantity was considered only a graft efficiency index. Further discussion on the effect of reaction variables are in terms of this index. The calculations of yield, graft efficiency index, and degree of grafting are shown below.

$$\text{Yield} = \frac{\text{weight of styrene polymerized}}{\text{weight of CPE used in the reaction}} \times 100\%$$

$$= 100\% \times \left(\frac{\text{wt. of dried reaction product}}{\text{wt. of CPE used} - \text{wt. of CPE lost in initiation}} - 1 \right)$$

The yield can also be obtained from the composition of reaction product determined by IR spectroscopy.

$$\text{Yield} = \frac{\text{wt. fraction of polystyrene}}{\text{wt. fraction of CPE}} \times 100\%$$

The graft efficiency index (G.E.I.) and the degree of grafting were calculated based on the compositions of purified graft copolymers determined by IR and the result of separations. G.E.I. is an estimate of the graft efficiency which has been defined as the ratio of weight of polystyrene in graft to weight of styrene polymerized, and is calculated as follows.

$$\text{G.E.I.} = A(D/C) \quad \text{from extraction result}$$

$$= BD(1-E)/C \quad \text{from two-stage separation result}$$

Degree of grafting

$$\% \text{ Degree of Grafting} = \frac{\text{weight of polystyrene in graft}}{\text{weight of CPE used in reaction}} \times 100\%$$

$$= \frac{A}{1-A} \times 100\% \quad \text{from extraction result}$$

$$= \frac{B}{1-B} \times 100\% \quad \text{from two-stage separation result}$$

where A = weight fraction of polystyrene in the insoluble phase of first-stage separation (extraction), determined by IR.

B = weight fraction of polystyrene in the soluble phase of the second separation (precipitation), determined by IR.

C = weight fraction of polystyrene in the reaction product (from IR)

D = weight fraction of insoluble phase in the first stage separation.

E = weight fraction of insoluble phase in the second stage separation.

The calculated yield, graft efficiency index, and degree of grafting of selected copolymerizations are listed in Table 4-10. It should be noticed that both the graft efficiency index and the degree of grafting reported here are somewhat lower than their true values.

The graft efficiency and degree of grafting could also be calculated using only the separation data, if no graft copolymer were "dissolved" away in the extraction, or if somehow, the amount of the graft copolymer eluted could be known. Nevertheless, some graft copolymer did elute away during the extraction, and it was difficult to measure the amount eluted

TABLE 4-10
G.E.I. AND DEGREE OF GRAFTING OBTAINED FROM IR ANALYSIS

Synthesis Number	Reaction Conditions	G.E.I.		Degree of Grafting, %	
C - 9	A ₂ B ₁ C ₁ D ₁ E ₁ F ₁ G ₁	0.161 ^a	-	17.0 ^a	-
C - 16	A ₁ B ₃ C ₁ D ₁ E ₁ F ₁ G ₁	0.175	-	3.1	-
C - 20	A ₁ B ₃ C ₁ D ₁ E ₁ F ₁ G ₁	0.156	0.108 ^b	3.7	4.9 ^b
C - 21	A ₁ B ₂ C ₁ D ₁ E ₁ F ₁ G ₁	0.204	0.200	17.4	22.0
C - 22	A ₁ B ₁ C ₁ D ₂ E ₁ F ₁ G ₁	0.203	0.185	10.0	19.2
C - 23	A ₁ B ₁ C ₁ D ₁ E ₁ F ₁ G ₂	0.174	0.169	11.1	11.7
C - 24	A ₁ B ₁ C ₁ D ₁ E ₁ F ₂ G ₁	0.657	-	203.0	-
C - 25	A ₁ B ₁ C ₁ D ₁ E ₁ F ₁ G ₁	0.193	0.157	22.2	21.8
C - 26	A ₄ B ₁ C ₁ D ₁ E ₁ F ₁ G ₁	0.075	0.101	5.3	7.5
C - 27	A ₁ B ₁ C ₁ D ₁ E ₁ F ₄ G ₁	0.278	0.304	30.6	71.5
C - 31	A ₃ B ₁ C ₁ D ₁ E ₁ F ₁ G ₁	0.320	0.318	49.3	66.7
C - 32	A ₁ B ₁ C ₁ D ₃ E ₁ F ₁ G ₁	0.215	0.190	13.0	20.5
C - 33	A ₂ B ₃ C ₁ D ₁ E ₁ F ₁ G ₃	0.205	0.181	4.7	6.0
C - 34	A ₁ B ₄ C ₁ D ₁ E ₁ F ₁ G ₃	0.835	0.739	194.1	270.4
C - 37	A ₁ B ₁ C ₁ D ₁ E ₁ F ₁ G ₁	0.228	0.223	20.9	29.0
C - 38	A ₁ B ₁ C ₁ D ₁ E ₃ F ₁ G ₁	0.180	0.168	32.0	49.9
C - 39	A ₁ B ₃ C ₁ D ₁ E ₁ F ₁ G ₃	0.189	0.064	19.1	96.1
C - 40	A ₁ B ₄ C ₁ D ₁ E ₁ F ₁ G ₃	0.288	0.347	78.6	185.7
C - 41	A ₁ B ₄ C ₁ D ₁ E ₁ F ₁ G ₁	0.121	0.143	15.7	20.5
C - 42	A ₁ B ₄ C ₁ D ₁ E ₁ F ₁ G ₁	0.319	0.379	29.7	51.5
R - 1	0.4 Mrad, Vacuum	0.371	0.362	46.6	47.1
R - 2	0.4 Mrad, Air	0.378	0.359	40.9	40.9
R - 3	0.6 Mrad, Vacuum	0.427	0.412	56.3	57.5

a: data in this column were obtained from the result of one-stage separation.

b: data in this column were obtained from the result of two-stage separation

within good accuracy. The CPE concentration in the extracted phase was usually so low that it was very difficult to identify on the IR spectra, and the polystyrene content determined from the spectra would be associated with larger error. With this measurement error involved and without knowing the composition of the graft which dissolved away in extraction, any calculation of graft efficiency based only on the gravimetric data would be unreliable.

In later discussion of the effects of reaction variables, graft efficiency index and degree of grafting calculated according to the composition of the extracted product, which are relatively reliable, will be used.

4.3. Effects of Reaction Conditions - Radiation Grafting

4.3.1. Effect of Radiation Dose

Two graft copolymer samples, R-1 and R-3, were prepared by irradiation under vacuum using doses of 0.4 and 0.6 Mrad, respectively. The yields, graft efficiency indices, and degrees of grafting of these samples have been shown in Table 4-6 and 4-10. Sample R-3 showed higher yield, graft efficiency and degree of grafting than R-1. No crosslinking phenomenon has been observed as both these samples completely dissolved in hot toluene.

The higher graft efficiency and higher degree of grafting of R-3 indicated that the longer exposure to radiation

had created more available free radicals for initiation of grafting than for homopolymerization of styrene. This implied a higher G-value for CPE than styrene. It has been reported that the G-value for styrene monomer is approximately 0.69 and that for polyethylene approximately 6.0 to 8.0 (16). These G-values for styrene and polyethylene suggest that the simultaneous homopolymerization of styrene should be highly unlikely in direct-irradiation grafting of polyethylene-g-styrene copolymer. Polyvinyl chloride also has a relative high G-value, 10-15, compared with styrene (26). Since CPE used in this synthesis was prepared by random chlorination of high density polyethylene and has lower chlorine content than PVC, it seems likely that CPE has a G-value in between that of HDPE and PVC. If so, the grafting should be the predominant reaction during irradiation, and the higher graft efficiency obtained from higher-dose radiation grafting is expected.

However, it should be noticed that the G-values reported for styrene, polyethylene and PVC were determined independently and may not predict the actual number of free radicals produced in the backbone polymer when irradiated with the presence of styrene monomer, due to the possible "protective effect" of styrene.

Locke (1) prepared polyethylene-g-styrene copolymer using the same direct-irradiation technique and observed

crosslinking when a dose higher than 2 Mrad was applied. The fact that no crosslinking was observed in the CPE-g-styrene samples exposed to doses up to 0.6 Mrad suggests that the G-value of CPE should not be much larger than polyethylene. A G-value smaller than 20 is expected for CPE 2552.

4.3.2. Effect of the Presence of Oxygen

Oxygen in air, an effective free radical scavenger, will react with the free radicals to form peroxides during irradiation and therefore reduce the number of free radicals available for grafting initiation (26). These peroxides may decompose thermally to produce free radicals for initiation if the irradiated sample is later heated up to the decomposition temperature of the peroxide. One graft sample, R-2, was prepared by irradiation under ambient atmosphere at a dose of 0.4 Mrad. The yield, graft, efficiency and degree of grafting of this sample can be compared with that of R-1, prepared under the same conditions except in the absence of oxygen. Sample R-2 showed a lower yield, lower degree of grafting, but a comparable graft efficiency (Table 4-4,8). The reason for the lower yield and degree of grafting may be that some of the peroxides formed during irradiation have not been effective in the initiation of grafting. Generally, the rate of grafting is affected by several factors: 1) the number of active sites available; 2) the concentration of monomer

in the CPE crumb; 3) rate of termination. The second and third factor relate to the ease of diffusion of monomers and propagating active polymeric chains, and is affected by the morphology and the viscosity of the swelling CPE crumbs. In this radiation grafting work, the type of CPE used and the CPE : styrene ratio is the same for all the radiation samples. Styrene monomer had been well mixed with the CPE crumbs before being sealed in the reaction tubes so that the degree of swelling of the CPE crumbs could be considered invariant for all the radiation samples. Thus, the morphology, the viscosity of the CPE crumbs, and the monomer concentration should make no difference in the grafting rates of the different samples. The only determining factor was the first one, which is related to the initiation mechanism.

Free radicals can survive longer in a highly crystalline polymeric material because the free radicals are less mobile in the crystalline region. Therefore the chance for two free radicals to recombine and become deactivated is smaller. Free radical initiation is thus the main initiation mechanism for the grafting of crystalline polymers at room temperature such as HDPE. If so, the degree of grafting of the produced-under-vacuum sample, R-1, should be much higher than that of R-2. However, the crystallinity of CPE 2552 is substantially lower than HDPE and the larger amorphous area makes the peroxide initiation more important. In the

amorphous region, the deactivation of free radicals is more probable and the initiation efficiency is lower than in crystalline region. Nevertheless, if some of the free radicals which may become deactivated can react with oxygen in air to form peroxides, which may initiate the grafting upon heating, the ability to initiate of those free radicals is preserved. This accounted for the fact that the degree of grafting of the sample prepared by irradiation under vacuum was not much higher than that by irradiation - under atmosphere - as would happen to polyethylene-g-styrene copolymers.

The peroxides formed in the sample R-2 might have not all been consumed for initiation during the heat-drying period. Besides, the monomer concentration was decreasing during drying of the product and the growth of the graft chains were limited. This probably was the reason for the lower yield and degree of grafting obtained from sample R-2.

4.4 Effect of Reaction Conditions - Chemical Grafting

4.4.1 Effect of the Type and Amount of Initiator

Two initiators, benzoyl peroxide and AIBN, were used in the chemical initiated copolymerizations. The result of four synthesis, carried out under identical conditions except the use of different initiators, is listed in Table 4-11.

Table 4-11: Effect of Type and Amount of Initiator

Initiator	Benzoyl Peroxide	Benzoyl Peroxide	Benzoyl Peroxide	AIBN
<u>Amount, phr</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>2</u>
Yield, %	87	112	169	67
G.E.I.	0.16	0.19	0.32	0.08
Degree of Grafting, %	17.0	22.2	49.3	5.3

The yield and degree of grafting increases as the concentration of benzoyl peroxide increases.

As expected, higher concentration of benzoyl peroxide in the initiation solution provided greater driving force for the diffusion of benzoyl peroxide into the swollen CPE films and facilitated the creation of free radicals in the backbone matrix. This increase in the number of free radicals inside the film should result in higher grafting rate and yield, unless crosslinking has taken place.

Notice that the graft efficiency index also increased with increasing amount of initiator. This phenomenon is not fully understood at this point, but may be explained in terms of the fraction of the free radicals involved in activating the backbone polymer. After initiation of the CPE films, some of the free radicals produced and remained in the films reacted with the backbone molecules by chain transfer mechanism to form active sites on the backbone molecules which led to the grafting of styrene to the CPE backbone. But a portion

of the free radicals inside or on the surface of the films might have not been involved in the initiation of the grafting. They might have become inactive or have led to the homopolymerization of styrene after the initiated films were immersed in the monomer. The number of these radicals which were not involved in the grafting would not be proportional to the total number of free radicals in the CPE films, unless the distribution of free radicals inside the films and on the surface of the films were the same. It seems more likely that the free radicals on or near the surface of the films would be easier to become inactive in grafting since they were exposed to the environment. During the transferring of the films from initiation reactor to the polymerization reactor, the surface of the films was exposed to the atmosphere, though temporarily, and some of the radicals on the surface might have reacted with oxygen to form peroxides on the surface of the films. Besides, some of the unreacted radicals on or near the surface might have been "dissolved" away into the monomer solution and led to homopolymerization. If a large number of initiator molecules have diffused into the films and created free radicals for initiation, the effect of the unreacted free radicals on or near the surface would be relatively insignificant. But this effect would cause significant decrease in the number fraction of the grafting-active radicals if the total number of free radicals in the

films was small. In this case, the graft efficiency of the synthesis using higher concentration of initiator should be higher. With the same dose, AIBN showed a much lower initiating ability than benzoyl peroxide as can be seen from the degrees of grafting and graft efficiency indice listed in Table 4-11. The inability of AIBN to initiate graft copolymerization was attributed to the inferior capacity of the resonance stabilized 2-cyano-2-propyl radicals, $(\text{CH}_3)_2\dot{\text{C}}(\text{CN})$, relative to benzoyl, $\text{C}_6\text{H}_5\text{COO}\cdot$, to engage in hydrogen abstraction reactions (13,26). This should be the main reason for the low graft efficiency and low degree of grafting obtained from AIBN-initiated graft product.

4.4.2. Effect of Swelling Time

Some of the CPE films had been swollen in the initiation solution at room temperature before the solution was heated up. The pre-swelling has proved to be important in initiation of grafting, as can be seen from the data listed below.

Table 4-12: Effect of Swelling Time

<u>Swelling Time,</u> <u>hours</u>	<u>0</u>	<u>12</u>	<u>36</u>
Yield, %	67	112	250
G.E.I.	0.174	0.193	0.835
Degree of Grafting, %	11.1	22.2	194.1

It is easily seen that the yield, degree of grafting, and graft efficiency all increases with the increasing swelling time. The synthesis in which pre-swelling was not performed gave very low yield and graft efficiency while the one using highly swollen films gave very high yield and graft efficiency. The effect of the pre-swelling is on the degree of swelling of the films, which affects the diffusion of initiator and the monomer solution into the films. A high degree of swelling facilitates the diffusion of initiator and monomer into the films and helps to achieve more homogeneous grafting. The synthesis without pre-swelling probably had a large fraction of free radicals present near the surface of the films which was not involved in the grafting reaction and led to poor graft efficiency as discussed in the previous section.

The effect of pre-swelling was also observed in copolymerizations involving crosslinking. In several of the graft copolymerizations crosslinking was observed due to the high temperature or long time of initiation as will be discussed later. Even with the presence of crosslinks in the initiated films, the reaction which involving longer period of pre-swelling still showed substantially higher yield and degree of grafting (Table 4-13).

Table 4-13: Effect of Swelling on Crosslinked Films*

<u>Swelling Time, hours</u>	<u>12</u>	<u>36</u>
Yield %	14	95
G.E.I.	0.156	0.189
Degree of Grafting, %	3.7	19.1

*both samples were prepared using a initiation time of 12 hours and had crosslinking observed.

The crosslinking reaction consumed the active sites available for grafting reaction and led to relative poor yield and degree of grafting. The films subjected to longer pre-swelling contained more peroxide molecules and had higher number of free radicals formed during initiation. The higher concentration of free radicals or the higher number of active molecular chains would facilitate the crosslinking reaction, but due to the larger total number of radicals present the number of remaining radicals available for grafting might still be higher. This might be the reason why the more-swollen CPE films gave better yield and degree of grafting.

4.4.3 Effect of Initiation Time

The effect of varying initiation time on the degree of grafting and graft efficiency is illustrated in Figure 4-10. The degree of grafting and yield increases with increasing initiation time until an initiation time of six hours has been reached. As initiation time continues to increase, both yield and degree of grafting decline. It is relatively easy to explain the increase in degree of grafting when a longer period of initiation was carried out. The longer initiation time should have helped to achieve more complete decomposition of initiators and to allow more backbone molecules to be

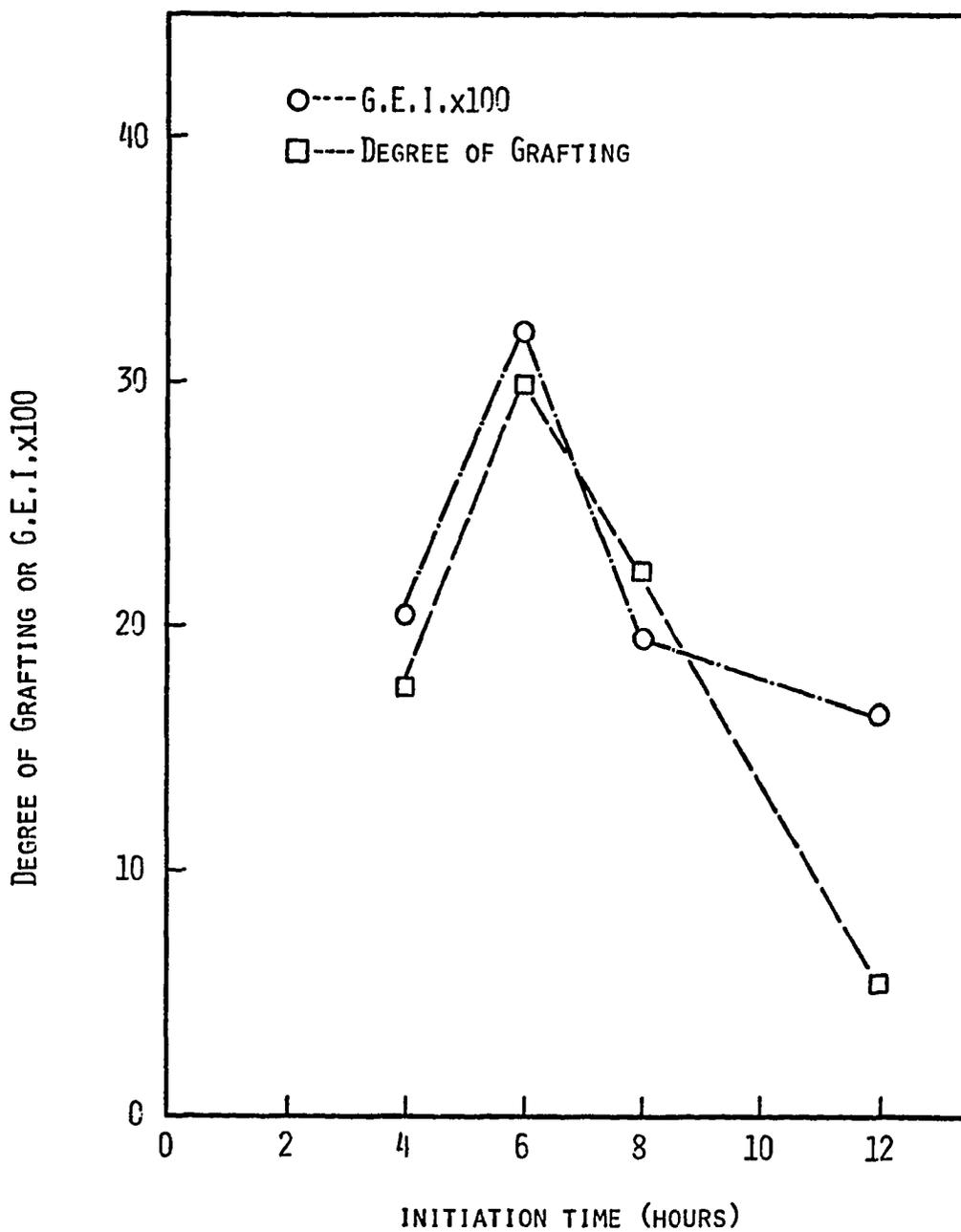


FIGURE 4-10: EFFECT OF INITIATION TIME ON G.E.I. AND DEGREE OF GRAFTING

activated, therefore to increase the grafting rate. The slight drop in degree of grafting as initiation time increased from six to eight hours and the very low degree of grafting when using an initiation time of twelve hours were unexpected and were later determined to be the result of crosslinking. As initiation time became longer and longer, the active sites created continually increased.

When the concentration of active sites was very high, the crosslinking reaction became significant. The crosslinking reaction destroyed active sites which would have led to further grafting and therefore reduced the yield of graft copolymer.

Crosslinking was observed in several synthesis using an initiation time of twelve hours and all these synthesis were associated with poor yield and degree of grafting. The crosslinking was detected by examining the solubility behavior of the graft products. All these products prepared through twelve hours of initiation were not completely soluble in good solvent such as toluene, even the solution was heated up with agitation to boil. Small particles suspending in the solution were always observed for these products. This observation accounted for the very low yield and degree of grafting obtained.

It seems that an inversion exists between the initiation time of six and eight hours. When the initiation period

was shorter than six hours the increasing initiation time enhanced the grafting rate but the crosslinking effect became dominant as the initiation time further increased.

The fact that the graft efficiency had the same trend as the degree of grafting might also be related to the number of fraction of free radicals involved in grafting as discussed in Section 4.4.1. The crosslinking reaction taking place inside the films lowered the number of free radicals available for grafting while those which did not tend to initiate the grafting probably were less affected by the crosslinking.

4.4.4. Effect of Reaction Temperature

The effect of reaction temperature on grafting is a combination of the effects on initiation and on the polymerization. Generally, the higher temperature tends to enhance the rate constant of both initiation and propagation reactions and monotonically increasing grafting rate is expected. However, the result obtained from graft copolymerizations under three different reaction temperatures again showed a maximum in the degree of grafting and yield. (Table 4-14).

Table 4-14: Effect of Reaction Temperature

<u>Reaction Temperature, °c</u>	<u>40</u>	<u>60</u>	<u>70</u>
Yield, %	52	112	69
G.E.I.	0.203	0.193	0.215
Degree of Grafting, %	10.0	22.2	13.0

The degree of grafting and yield showed a maximum at a reaction temperature of 60°C while no significant difference in graft efficiency was observed. The reason for this observation on degree of grafting is similar to that for the effect of initiation time on grafting. Higher temperature and longer initiation time both would increase the grafting rate and both could lead to crosslinking of activated molecules. The temperature of reaction usually tends to enhance the crosslinking rate exponentially and a temperature rise from 60° to 70° could be very significant in the rate of formation of crosslinks. The degree of grafting data suggested that crosslinking might have taken place during initiation at the reaction temperature of 70° . This statement was confirmed by the solubility experiment as undissolvable particles in hot toluene solution was observed.

4.4.5. Effect of Polymerization Time

Only two different polymerization time periods were studied in this work and the result of these reactions is shown below.

Table 4-15: Effect of Polymerization Time

<u>Polymerization Time, hours</u>	<u>28</u>	<u>48</u>
Yield, %	112	169
G.E.I.	0.193	0.180
Degree of Grafting	22.2	32.0

Longer polymerization time, 48 hours, resulted in higher yield and degree of grafting because higher conversion and degree of polymerization were achieved. However, the prolonged polymerization seemed not beneficial to the graft efficiency as a slight decrease in the graft efficiency index was observed when the polymerization time increased to 48 hours. The difference was not significant enough to make any conclusion on the effect of polymerization time on the graft efficiency.

Kennedy (35, 36) and Riess (27) both reported low graft efficiency from synthesis associated with high conversion. This phenomenon was explained as a result of increasing relative importance of chain transfer to monomer to the rate of graft initiation and chain growth of graft. At the initial stage of their polymerization works, new initiating sites were being created along the backbone with time, and therefore the grafting rate kept increasing as time elapsed. However, as the conversion became higher, the potential active sites had been gradually used and the increase in grafting rate declined. Up to certain degree of polymerization, chain transfer to monomer became relatively important and the graft efficiency began to decrease. This explanation may not be adequate for the CPE-g-styrene copolymerization in this study since, unlike their polymerization procedure in which initiation and propagation took place in the same reactor, the

initiation of CPE was accomplished in a separate reactor. In this copolymerization, the polymerization time or the conversion is not expected to have significant effect on the graft efficiency.

4.4.6. Effect of Methanol Concentration in the Monomer Solution

The presence of methanol in the monomer solution has been reported to have significant effect on the grafting rate by several authors (17-19). The presence of methanol was considered to have limited the mobility of growing graft chains and led to the "Trommsdorf Effect" in the synthesis of polyethylene-g-styrene copolymer. However, this phenomenon was not observed in this work. Graft copolymerizations using monomer solutions of varied methanol content indicated a monotonically increasing degree of grafting with lower methanol content (Figure 4-11). The fact that no Trommsdorf Effect was observed might be due to the more amorphous nature of CPE than polyethylene. It might be possible that the much more amorphous CPE films had been so swelled that even the presence of methanol would not affect the viscosity of the bulk film significantly. Both Machi (7) and Odian (9) have found that the methanol content of the sorbed solution inside PE films was quite low (< 8%) even when the methanol concentration of the outside monomer solution was as high as 90%.

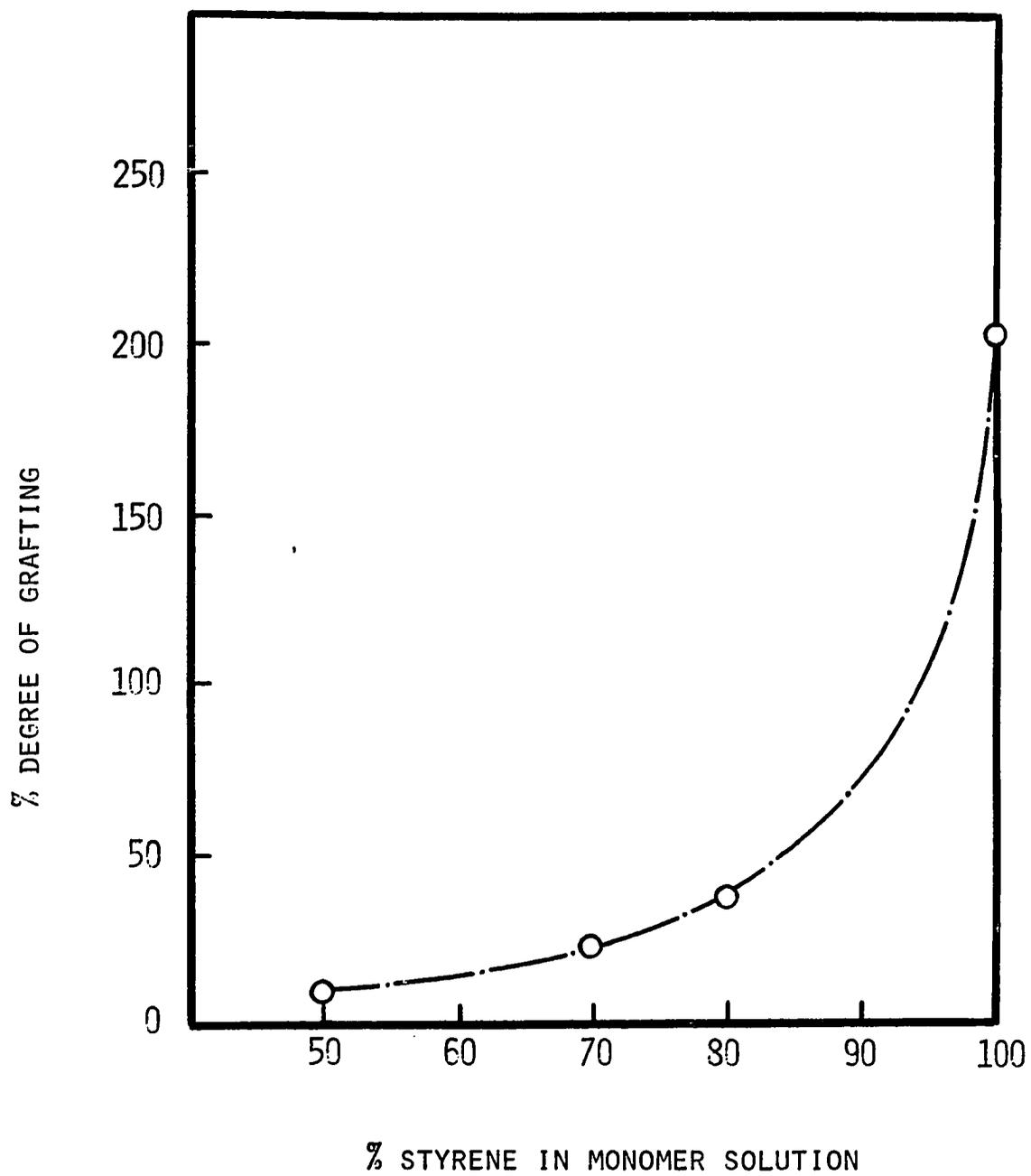


FIGURE 4-11: EFFECT OF METHANOL CONTENT IN MONOMER SOLUTION

If the solubility of styrene-methanol mixture in CPE is not very different from that in polyethylene, which is likely, the methanol content in the swollen CPE films is also expected to be low. If so, the amount of methanol absorbed should not be able to cause significant increase of the viscosity of the reaction media, the films, by diluting the styrene concentration. Thus, the effect of the presence of methanol was to dilute the styrene, which would lead to lower grafting rate and lower degree of grafting.

4.4.7. Effect of Type of CPE on Grafting

Graft copolymerization using different types of CPE were carried out by Angaji (83). CPE films with 25%, 36% and 48% of chlorine content were used as the backbone material. The results of his work is summarized below.

Table 4-16: Effect of the Type of CPE Backbone*

<u>CPE Type</u>	<u>2552</u>	<u>3614</u>	<u>4814</u>
Yield %	82	138	324
G.E.I.	0.436	0.349	0.537
Degree of Grafting	43.8	64.7	195.6

*Above data were estimated from the fractionation result obtained by Angaji.

It appears that the increasing chlorine content in the CPE backbone would facilitate the grafting substantially. This observation seems reasonable because CPE with higher chlorine

content has lower crystallinity and is easier to swell. This nature would have benefit the diffusion of initiator in the initiation step and the diffusion of monomer in the propagation step, therefore have led to higher yield and degree of grafting.

4.4.8. Evaluation of the Chemical Initiated Graft Copolymerization

The above discussion suggests that under different reaction conditions, the amount of graft produced by chemical initiated graft copolymerization may vary substantially. With adequate arrangement of the reaction variables, high graft efficiency and high degree of grafting can be achieved. A combination of suitable initiation time and temperature, a well swollen backbone material, and high initiator concentration may result in high degree of grafting ($\approx 195\%$) and high graft efficiency (0.84). This high graft efficiency was obtained from a copolymerization which was carried out under the following reaction conditions: preswelling time -- 36 hours; initiator - 3 phr of benzoyl peroxide; initiation time and temperature - 6 hours at 60° ; monomer to methanol ratio - 70:30; polymerization time - 28 hours. The high graft efficiency achieved by chemical-initiation may be attributed to the pre-initiation technique, which eliminated simultaneous initiation of homopolymerization. With the use of this

technique and proper reaction conditions, the highest graft efficiency achievable from chemical grafting is substantially higher than that from radiation-induced grafting (0.37 - 0.43), within the range of this study.

Neither dehydrochlorination nor decomposition has been found significant in the initiation of CPE backbone, as will be discussed in the following sections. Crosslinking during initiation can be avoided by properly selecting the initiation conditions.

4.4.9 Check for Dehydrochlorination by IR

IR spectroscopy was also employed to determine whether dehydrochlorination of CPE had occurred during chemical grafting reaction and processing. CPE 2552 samples experienced various treatments such as heating, extraction, molding and grinding were compared with the CPE sample as received in terms of chlorine content. IR spectra of samples containing 70% CPE and 30% PS were taken and the relative intensity of the 614 cm^{-1} band and 1605 cm^{-1} band measured. The chlorine content of these samples was determined from the calibration curve and are presented in Table 4-17. The three standard mixtures containing 70% untreated CPE were determined to have an average CPE content of 68.7% by IR. The sample 2552 B, which had been extracted in benzene-methanol mixture at 60° for eight hours, was determined to have 68% of CPE by

TABLE 4-17

CHANGE IN CHLORINE CONTENT OF CPE 2552 DURING PROCESSING

CPE in the CPE-PS Mixture	Description	A_{1605}	CPE %
		$A_{614} + A_{1605}$	
2552 - 1	CPE 2552 as received	0.5956	69.5
2552 - 2	"	0.6175	68.0
2552 - 3	"	0.6091	68.5
2552 EC	CPE 2552 extracted by cyclohexane-acetone mixture	0.6523	65.0
2552 EPC	CPE 2552 molded and ground into powder form + cyclohexane-acetone extraction (insoluble phase)	0.6763	63.0
2552 B	CPE 2552 extracted by benzene-methanol mixture	0.6174	68.0
2552 EP	CPE 2552 molded and ground into powder form + cyclohexane-acetone extraction (both insoluble and soluble phase)	0.6292	67.0

IR which is only slightly lower than that of the control. This result indicates that the dehydrochlorination in the chemical initiation was not significant. The sample 2552 EP, which had been molded into films, ground into powders and later extracted by cyclohexane-acetone solvent mixture, was determined to contain 67% of CPE. Since this value is only 1.7% lower than that of the control, the decrease in the concentration of C-Cl group due to above treatment seems not very severe. Sample 2552 EP and sample 2552 EPC, which were made of the insoluble phases of extracted CPE 2552 and powdered/extracted CPE 2552, showed somewhat lower CPE content, 65% and 63% respectively. These lower values of CPE content seem to be due to the fractionation of CPE in the extraction process. CPE molecules containing more C-Cl group were easier to be extracted by the cyclohexane-acetone mixture and led to a relatively low CPE content in the insoluble phase. The reason for the three standard 70% CPE 2552 mixtures to show only 68.7% of CPE 2552 from IR quantitative analysis might be dehydrochlorination during casting the films for IR analysis from hot toluene solution. The compositions determined by IR analysis for these three standard mixtures gave an estimate of the possible experimental error associated with the mixture preparing and composition determination procedure, These data showed an average of 31.3, RMSD of 0.34, and a range of 1.5.

4.5. Characterization

IR and Laser-Raman spectroscopy, dilute solution viscosity measurement, and DSC were employed to characterize the structure and composition of the CPE-g-styrene copolymer.

4.5.1. IR and Laser-Raman Spectroscopy

Both IR and Laser-Raman spectroscopy have been employed to characterize the structure of the graft copolymers. Spectra of CPE homopolymers and styrene homopolymer were also obtained and were compared with that of the graft copolymer. Figure 4-12 shows a portion of the spectra of CPE 3614 and CPE 2552 which have been used as the backbone polymer in the graft copolymerization. The doublet structure observed for CPE 2552 at $730\text{-}720\text{ cm}^{-1}$ region is the well-known crystal splitting caused by the in-phase $(\text{CH}_2)_n$ rock vibration (84), and is an indication of the residual crystallinity of CPE 2552. CPE 3614 showed only one in-phase CH_2 chain rock band at 724 cm^{-1} instead of two bands at 720 cm^{-1} and is considered totally amorphous. This observation was in accordance with the reported crystallinity of CPE 3614, 0-2 percent. A splitting was also observed for CPE 2552 in the neighborhood of 1470 cm^{-1} , which is the region of CH_2 bending band. Both CPE 2552 and 3614 did not show an absorption band at 1605 cm^{-1} , where polystyrene showed a benzene-ring stretching band. This was why the 1605 cm^{-1} band was selected as the characteristic band of polystyrene in the quantitative analysis.

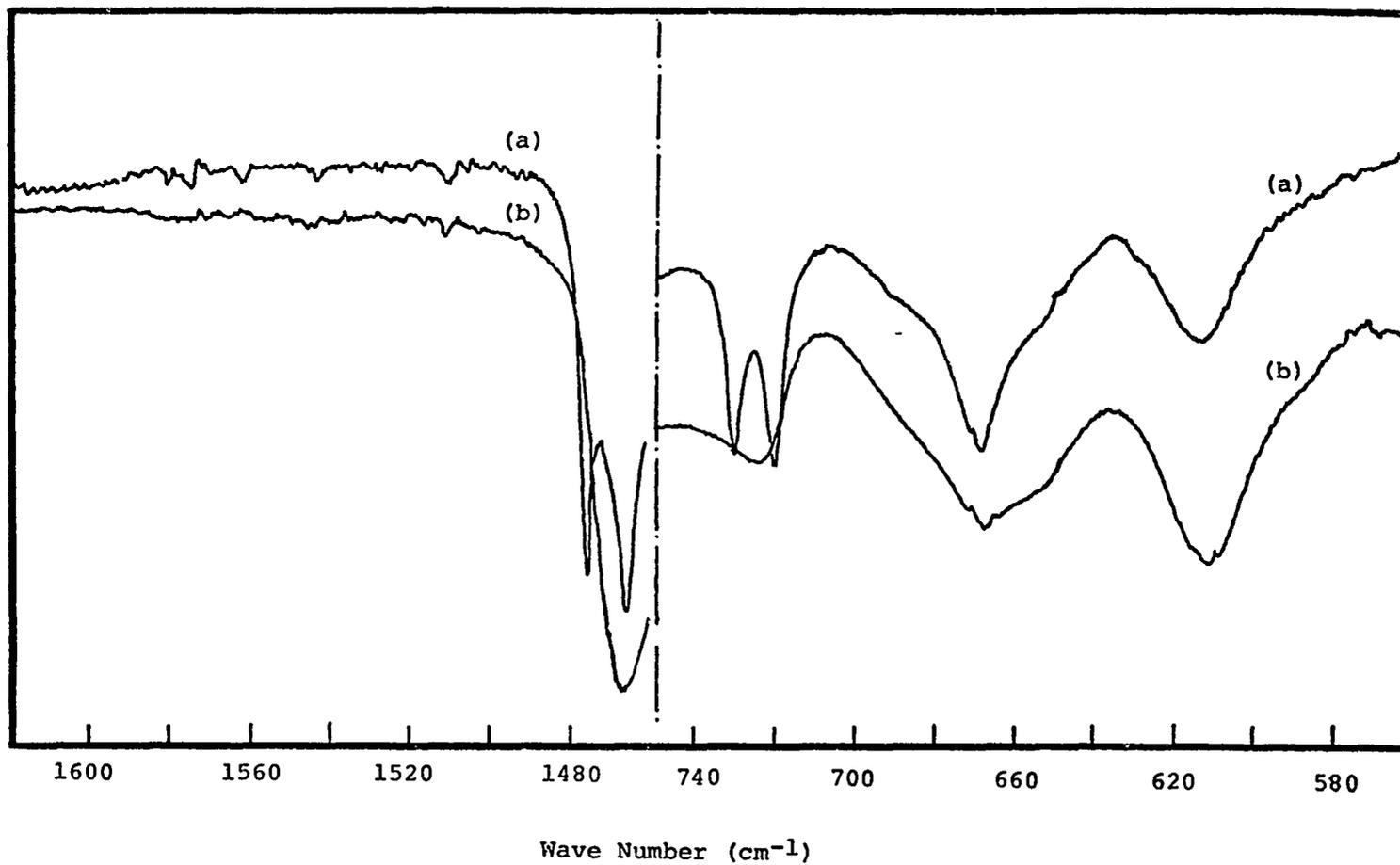


FIGURE 4-12: SPECTRA OF CPE 2552 (a) AND CPE 3614 (b)

Figure 4-13 shows the spectrum of CPE 2552 from 340 cm^{-1} to 1640 cm^{-1} . Since the spectrum was obtained using a 2 x standard slit width and a relatively slow scanning rate, 20 cm^{-1} per minute, the fine structure in the region of 340-420 cm^{-1} was resolved. It was the low frequency region which received the most attention in the study of the structure of the graft copolymer since the frequency of the vibrational mode associated with a grafting site was expected to be low due to the attachment of a heavy graft at the grafting site. Figure 4-14 gives details of the low-frequency absorptions of CPE 2552 and polystyrene. It was hoped that evidence of structural changes due to grafting could be detected by IR. However, no conclusions could be inferred from the spectra of the CPE-g-styrene copolymers in this study.

Curve (a) in Figure 4-15 is a portion of a typical spectrum of CPE 2552-g-styrene copolymer. It appears to be merely a superposition of the spectra of CPE 2552 and polystyrene. A graft copolymer of higher degree of grafting only changes the relative intensity of the characteristic peaks (Figure 4-15(b)). It is possible that the intensity of any band characteristic of the grafting site, if such a band exists, is simply too weak to be observed with the present signal-to-noise ratio. The reason for the weakness of the band intensity may be the low concentration of the grafting site in the molecule of graft copolymer. Battaerd and

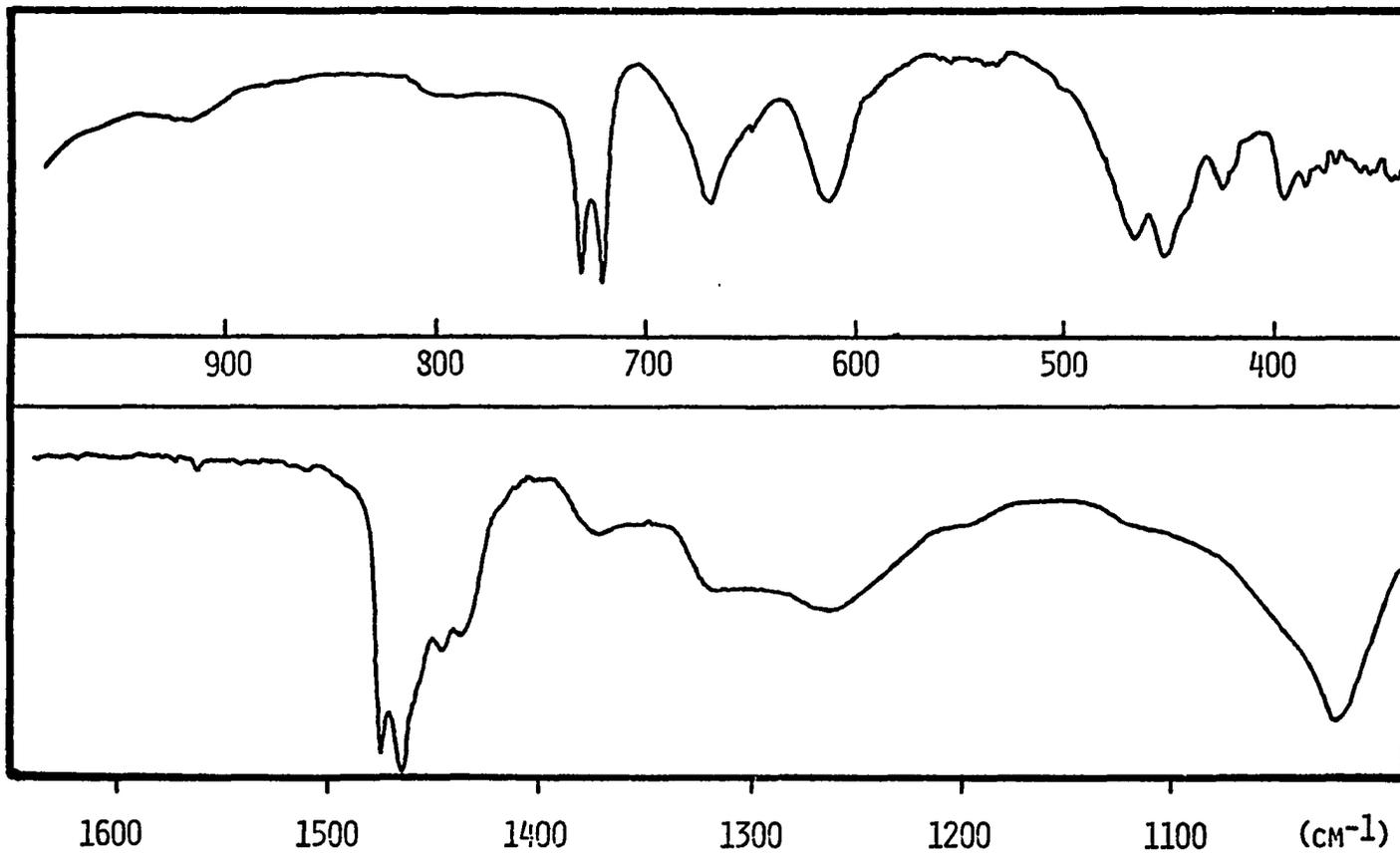


FIGURE 4-13: SPECTRUM OF CPE 2552 (SCANNING SPEED: 20 CM⁻¹/MIN., SLIT WIDTH: 2 X STANDARD, PERIOD : 2 SEC.)

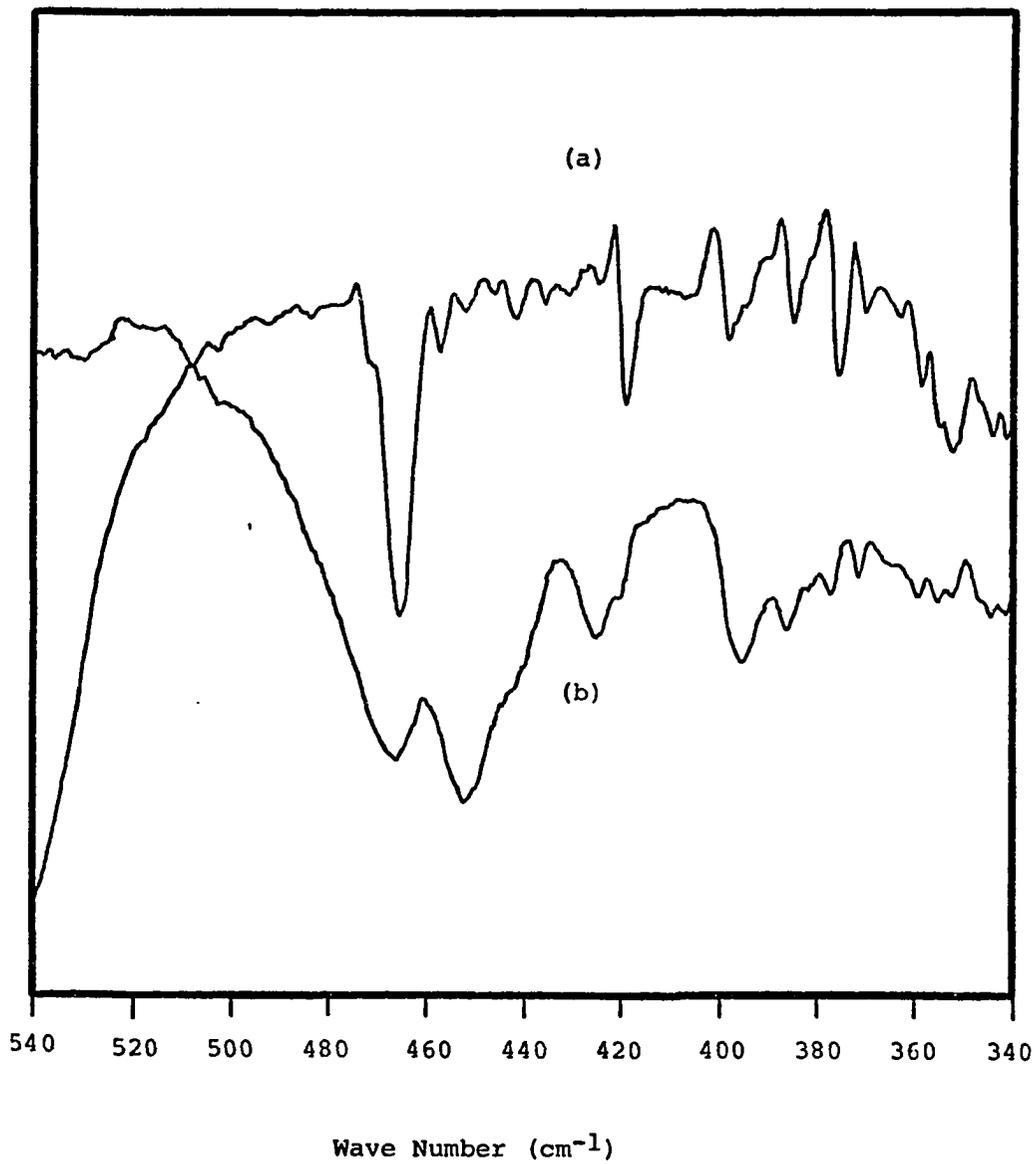


FIGURE 4-14: SPECTRUM OF POLYSTYRENE (a) AND CPE 2552 (b)
LOW FREQUENCY REGION

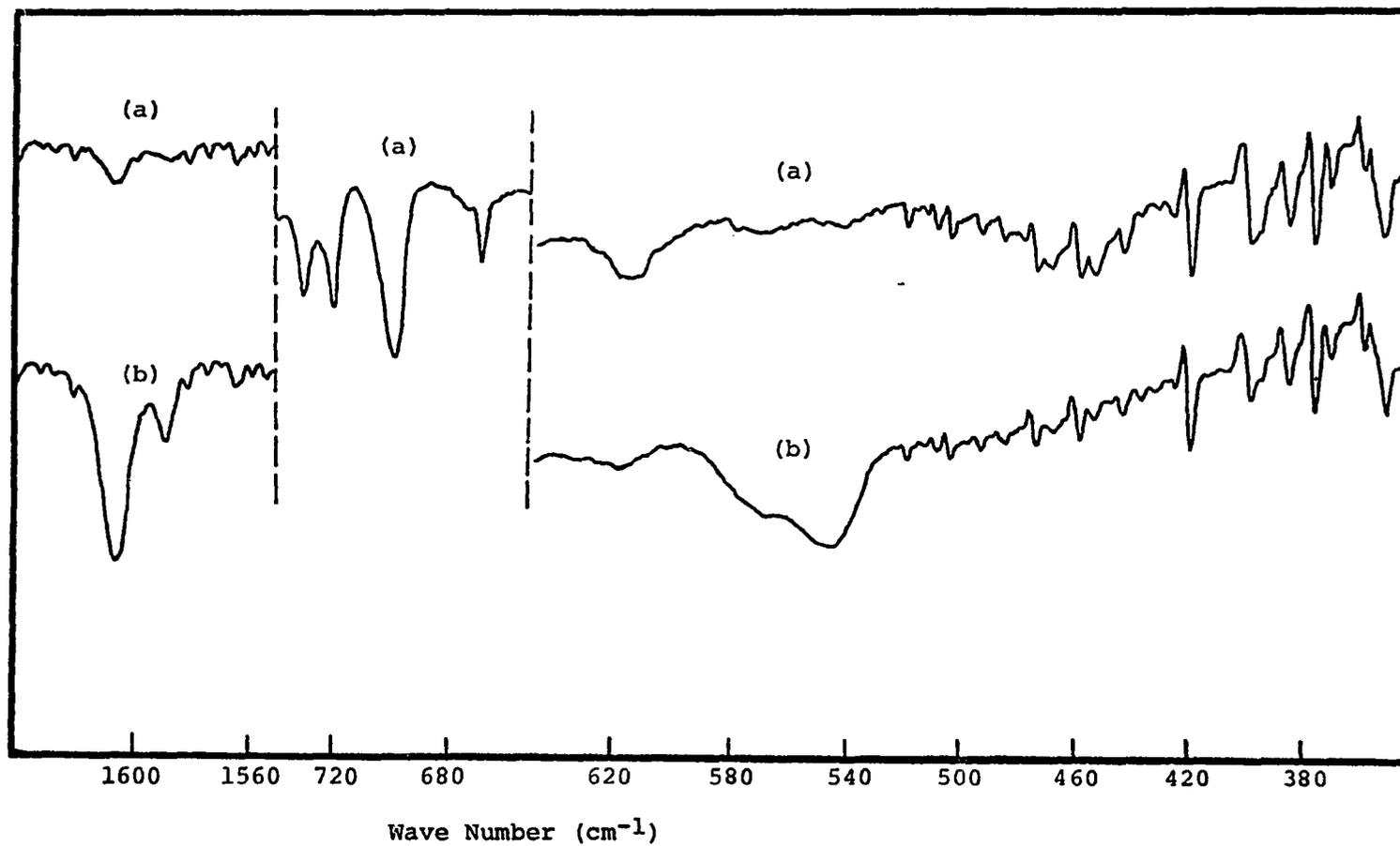


FIGURE 4-15: SPECTRA OF CPE-g-POLYSTYRENE COPOLYMERS (a) DEGREE OF GRAFTING = 18%
(b) DEGREE OF GRAFTING = 52%

Tregear (26) also found out that graft copolymers of the heterogeneous type, with grafted chain of comparable length with the backbone, showed IR spectra which seem to be additive for the homopolymers. However, several other authors did claim to have detected structural change due to grafting by IR (49, 85, 86). Despite the fact that conventional IR transmission spectroscopy was not able to detect signs of grafting of styrene to the CPE backbone, it is still possible to detect the grafting by using other special technique, such as Fourier transform spectroscopy, which can yield a much higher signal-to-noise ratio.

Attempts were also made to detect structural change due to grafting from laser-Raman spectra. This task was difficult due to interference of fluorescence and some problems in preparation of CPE-containing samples. A high-power laser beam could not be used for CPE-containing samples since the laser beam would "burn" the CPE sample. With this limitation, characteristic Raman scattering was very difficult to detect as the background of a CPE spectrum was tremendously high. The tremendously high background observed in "Stokes" Raman spectra was considered to be due to the fluorescence radiation. The fluorescence problem was later solved by observing the anti-Stokes Shifts instead of the Stokes shifts. A very nice Raman spectrum of CPE 2552 was obtained by observation of the anti-Stokes scattering (Figure 4-16). Although

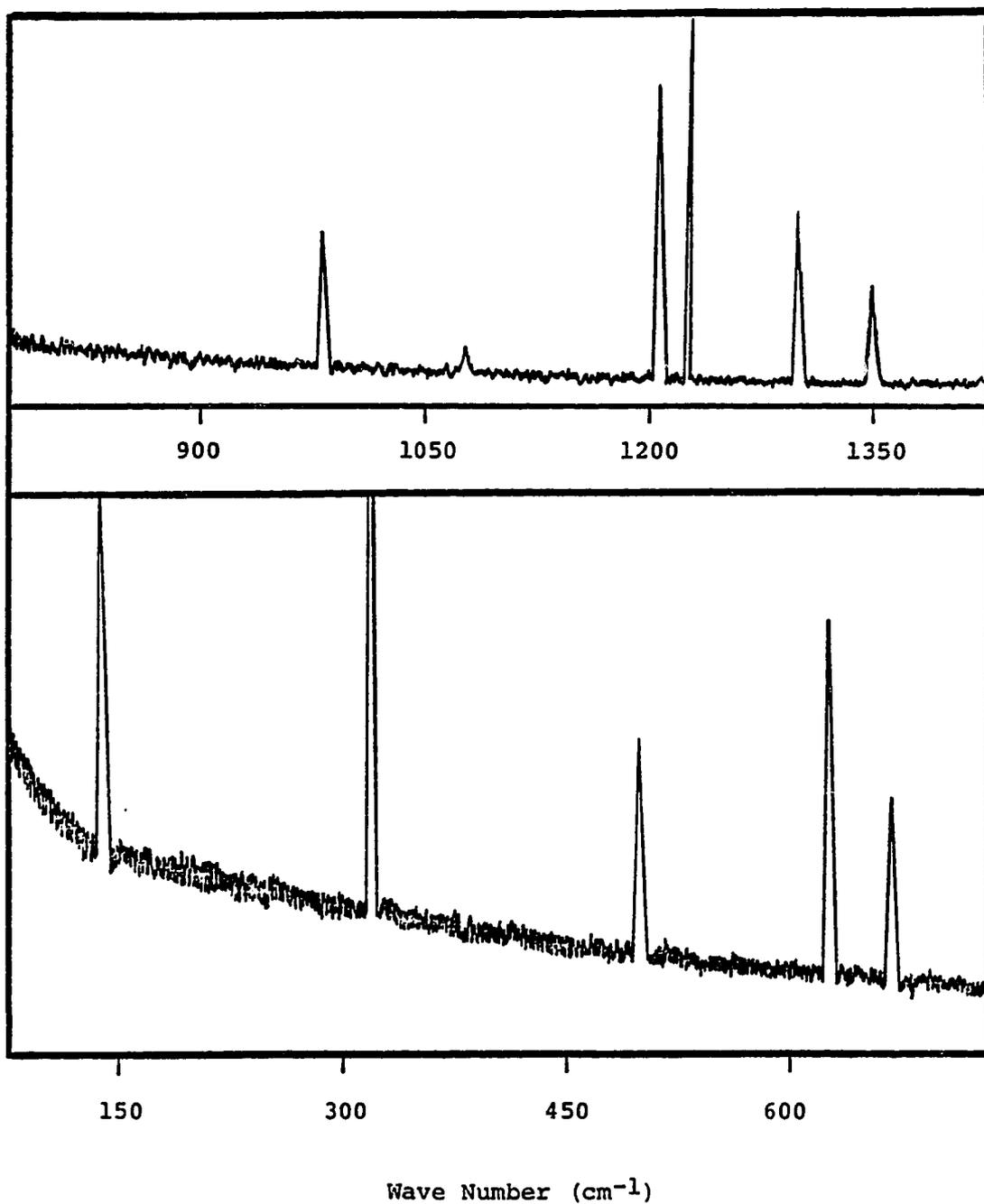


FIGURE 4-16: LASER-RAMAN SPECTRUM OF CPE 2552, ANTI-STOKE LINES,
 (4880 Å BLUE LASER @ 100 MA, 2 K SCALE, 30 CM⁻¹/MIN.
 INTEGRAL TIME 2 SEC., SLITS 400 x400 x400 x2)

anti-Stokes lines usually have smaller intensity than Stokes lines due to lower thermal population of molecules in excited state, the Raman bands were clearly observed in the anti-Stokes spectrum at a 2K scale. At the same 2K scale, the Stokes lines were masked by the fluorescence background even though they might have higher absolute intensity. This observation suggests that the energy of the scattered photons in Stokes scattering may be close to that of the fluorescence radiation, but the photons involved in anti-Stokes scattering possess substantially higher energy than that of the fluorescence, therefore, the anti-Stokes lines are interfered with less fluorescence.

An anti-Stokes Raman spectrum of the low frequency region was obtained for one CPE 2552-g-styrene copolymer (Figure 4-17) and was compared with that of pure CPE 2552. The Raman bands observed in the spectrum of the graft copolymer were all found in the pure CPE spectrum but the band intensity of the graft copolymer was substantially lower. The lower intensity probably was due to the lower concentration of CPE in the copolymer. The fact that no new band was observed in the spectra of the copolymer might be due to the low concentration of grafting site in the copolymer molecule, but it is also possible that the vibrational mode associated with a grafting site was not Raman-active or only weakly Raman active.

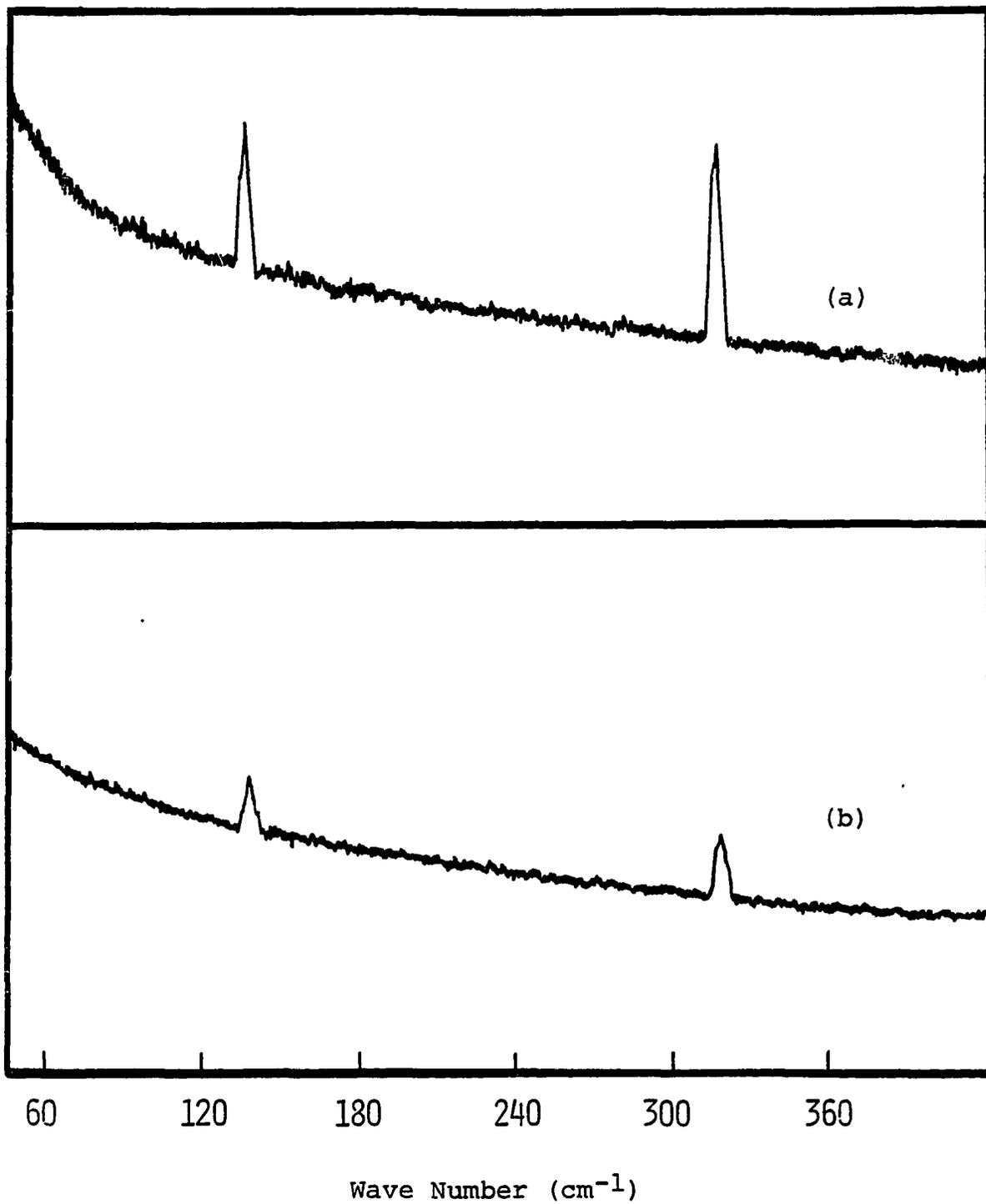


FIGURE 4-17: LASER-RAMAN SPECTRA OF CPE 2552 (a) AND CPE-g-POLYSTYRENE COPOLYMER (b), ANTI-STOKES. (a) 2 K SCALE; (b) 20 K SCALE.

4.5.2. Dilute-Solution Viscosity

Dilute-solution viscosity of CPE, polystyrene and graft copolymers were measured and results are listed in Table 4-18. These results have provided useful informations about the performance of the chemical grafting and the relationship between the dilute solution viscosity and the molecular size.

4.5.2.1. Check for Decomposition of CPE Molecules During Chemical Initiation

Experiment No. 2 and No. 3 compared the intrinsic viscosity of initiated CPE 2552 with that of the CPE 2552 as received. Since for polymers of simple geometric shape the intrinsic viscosity is a measure of the molecular weight, the intrinsic viscosities of initiated and not-initiated CPE will show the effect of initiation on the molecular weight of CPE molecules. If decomposition occurred during initiation, the average molecular weight of CPE should have decreased. However, the CPE sample which had been swelled in benzene-methanol mixture at 60° for eight hours showed a slightly higher intrinsic viscosity, instead showing a decrease in (η) value. This observation suggests that no significant decomposition due to initiation is detectable, at least by dilute solution viscosity measurement. The slight increase in (η) value for the initiated CPE sample may be due to experiment error or slight crosslinking during initiation.

TABLE 4-18

DILUTE SOLUTION VISCOSITIES OF GRAFT COPOLYMERS AND HOMOPOLYMERS

Expt No.	Samples	t (min)	η_{sp}	(η)	degree of grafting %
1	Toluene	1.961	-	-	-
2	CPE 2552	3.047	0.554	0.959	-
3	CPE 2552 initiated	3.130	0.596	1.022	-
4	Polystyrene, synthesized	2.462	0.255	0.476	-
5	Styrene homopolymer, extracted	2.607	0.329	0.602	-
6	CPE 2552-PS mixture (1:1)	2.997	0.528	0.920	-
7	C - 42	3.780	0.928	1.473	(136)*
8	C - 42 CS	4.120	1.101	1.683	52
9	C - 11 CS	3.821	0.948	1.498	18
10	C - 41 CS	3.867	0.972	1.528	21
11	C - 40 CS	4.743	1.419	2.031	186
12	C - 34 CS	5.446	1.777	2.373	208

144

* yield data

4.5.2.2. Molecular Weight of the Extracted Styrene Homopolymer

Intrinsic viscosities of polystyrene synthesized in this laboratory and styrene homopolymer extracted from one graft product were obtained (Expt. No. 4 and 5, Table 4-18). Since the synthesized polystyrene has been used in the solubility study to predict the solubility behavior of styrene homopolymer, it is important to know if the solubility of the synthesized polystyrene is close to that of the homopolymer formed during copolymerization. Since the solubility of polymer is molecular-weight dependent, it is desired to obtain information about the molecular weight of these two homopolymers. Dilute solution viscosity data provide information on molecular weight and can be used to calculate the molecular weight if the Mark-Houwink constants are available. The intrinsic viscosity of the extracted homopolymer was found to be higher (0.602) than that of the synthesized one (0.476). The reason for the higher $[\eta]$ value obtained for the extracted homopolystyrene is not very clear at present. Chen and Friedlander (20) reported that the styrene homopolymer extracted had significantly higher molecular weight than that of the homopolymer formed in the solution bath during polymerization. They attributed this phenomenon to the Trommsdorf Effect taking place in the much more viscous medium, the PE film. However, in this study Trommsdorf effect has been found not to be so pronounced as in the case of grafting styrene

to polyethylene and may not be the main reason for the higher (η) value, obtained for the extracted homopolymer. It is possible that the extracted homopolystyrene sample might still contain small amount of graft copolymer which would have caused the higher intrinsic viscosity. With this reasoning, the difference in intrinsic viscosity may not indicate significant difference between the molecular weight of the homopolystyrene formed during grafting and that prepared in simulating polymerization. This point of view is supported by the fact that excessive extractions by the cyclohexane-acetone solvent mixture, which was designed according to the solubility study using the synthesized polystyrene, extracted only wax-like, low molecular-weight polymeric material instead of significant amount of polystyrene.

4.5.2.3. Relationship between Intrinsic Viscosity and Degree of Grafting

In experiment No. 7 and 8, intrinsic viscosity was determined for a purified graft product, C-42CS, and a not-purified product, C-42. The purified product showed a higher (η) value than the product not purified. This observation is expected since the homopolymer in C-42 would have relatively smaller molecular size than the graft copolymer. The (η) values of CPE polystyrene, and mixture of these homopolymers are all substantially lower than that of the graft

copolymers.

From the results of experiment No. 8 to No. 12, the value of intrinsic viscosity seems to increase with increasing degree of grafting. The relation was not strictly linear as reported for the grafting using anionic technique (31), but was understandable. The intrinsic viscosity, a measure of the drag force exists in the movement of the fluid, is related to the molecular size of the graft copolymer. The molecular size is further related to the geometric shape of the molecule. Thus, graft copolymers with the same degree of grafting may have different molecular sizes as the number of graft chains and the length of the graft chains may not be the same. Since graft copolymerizations initiated by free radical mechanism are generally more difficult to control and the samples were randomly selected, it is probable for the products obtained in this work to possess geometric shape with less regularity. This may be the explanation for not seeing a linear relationship between (η) and degree of grafting.

The measurement of the intrinsic viscosity of polystyrene in toluene has been repeated at different date. The efflux time t varied only from 1.600 to 1.603 minutes, a deviation of 0.18%.

4.5.3. Differential Scanning Calorimetry

Thermograms of CPE homopolymers and CPE-g-styrene graft copolymers were obtained by using a DSC II calorimetry. Figure 18 shows thermograms of CPE 4814 and 2552. CPE 2552 showed a sharp melting peak at 113° with the melting started at about 98° while CPE 4814 showed no melting transition. This observation is consistent with the result of IR spectroscopy and the crystallinities reported by Dow Chemical Company. CPE 4814 showed a significant base-line shift which started at about -10° while CPE 2552 also showed a base-line shift at -29° . These base-line shifts are considered to be the glass transition for CPE 4814 and 2552. That fact that CPE 2552 showed a lower glass transition temperature seems reasonable as CPE 2552 is more like polyethylene than CPE 4814 and is more flexible.

Figure 4-19 shows thermograms of a CPE 2552-g-styrene copolymer and a CPE 4814-g-styrene copolymer. The CPE 2552-g-styrene copolymer also showed a melting transition which started at about 95° and had a peak at about 109° , which is slightly lower than that of CPE 2552. It appears that the grafting of styrene has depressed the onset of melting transition. This might be due to the interference effect of the polystyrene graft on the crystalline portion of CPE 2552. The glass transition of this graft copolymer was too weak to be seen from the thermogram, probably because the CPE

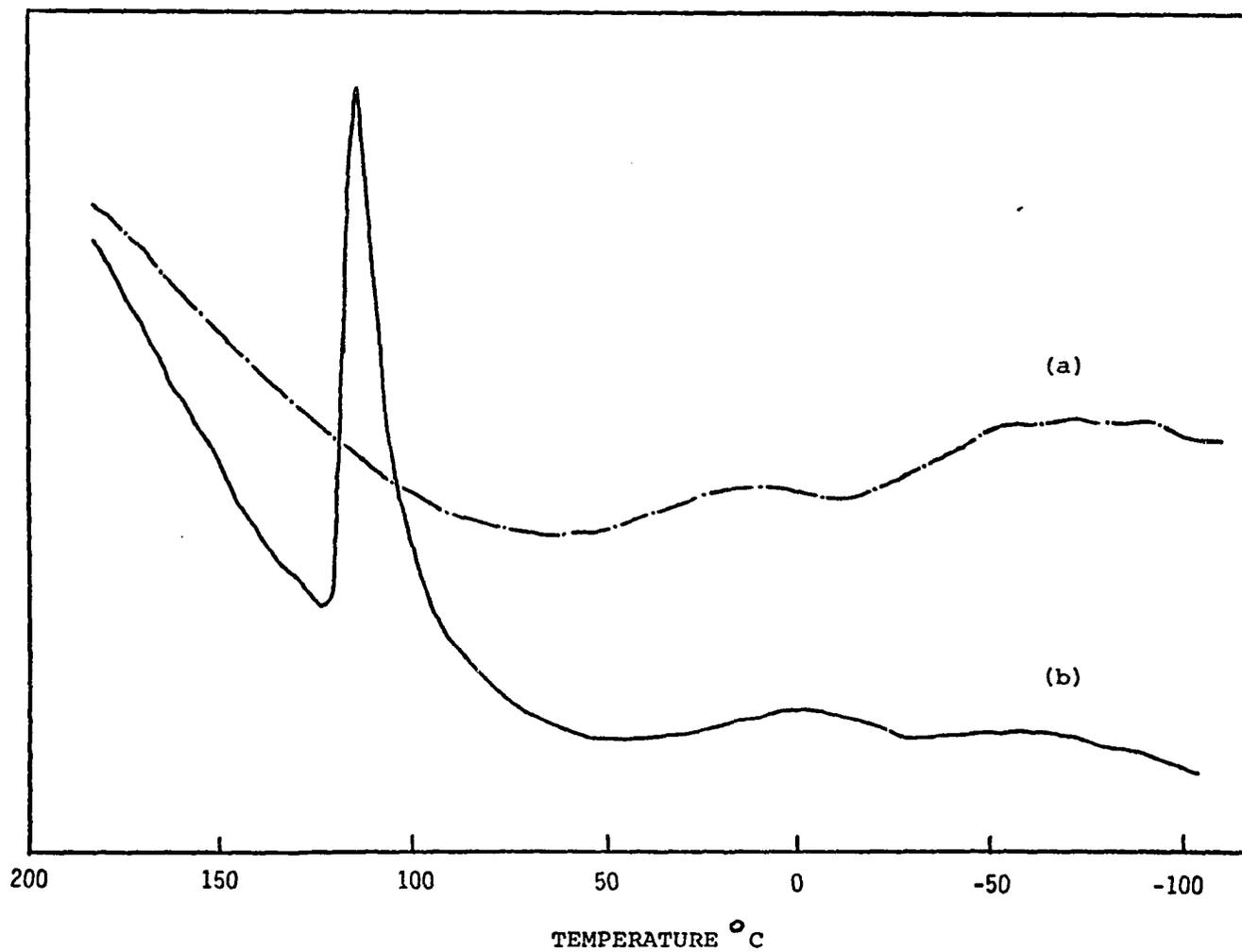


FIGURE 4-18: THERMOGRAMS OF CPE4814 (a) AND CPE2552 (b).

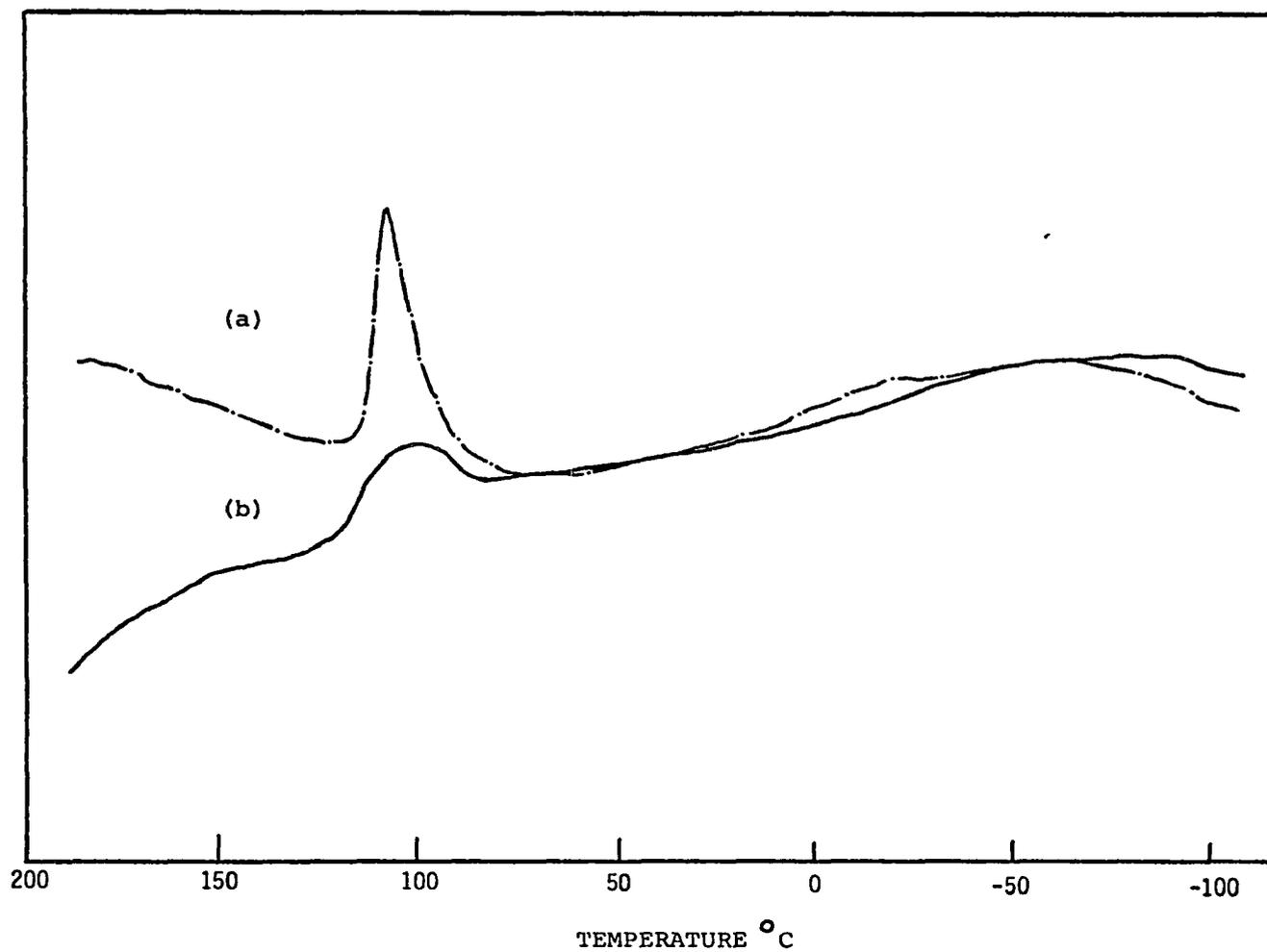


FIGURE 4-19: THERMOGRAMS OF (a) CPE2552-g-STYRENE COPOLYMER
(b) CPE4814-g-STYRENE COPOLYMER

concentration was diluted by the presence of the polystyrene graft. The melting peak was more broad than that of the pure CPE 2552. The broadening of the melting peak might be due to the overlapping of the polystyrene glass transition and the CPE melting in the region of 90° to 100° . The CPE-g-styrene copolymer showed a "hump" in the region of 85 to 105° which did not appear in the thermogram of CPE 4814. This structure may be due to the glass transition of polystyrene. The glass transition of CPE 4814 was not seen in the thermogram of the copolymer probably because the concentration of CPE in the copolymer was too low.

The crystallinities of the graft copolymers were determined from the DSC data by Angaji (83) and were utilized in an effort to determine the degree of grafting of the copolymers. He found that the crystallinity of a graft copolymer was lower than that of a corresponding mixture of homopolymers. He also found that the magnitude of the crystallinity change due to grafting generally increased with increasing degree of grafting. It seems evident that the presence of the styrene long chain branches did destroy a portion of the residual crystallinity of CPE 2552. According to his results, the relationship between the percentage decrease in crystallinity due to grafting and the degree of grafting seems only to be a qualitative one. As discussed before, the degree of grafting depends on the number of grafts present in the

copolymer as well as the chain length of the grafts. The crystallinity of the copolymer probably is also dependent of the graft number and vary graft length, but in a different manner. Unless the graft number and graft length can be determined, it will be difficult to understand the quantitative relation between the crystallinity drop and the degree of grafting of the copolymer.

4.6. Modification of Incompatible Polyblends

The feasibility of utilizing CPE-g-styrene copolymer to modify the physical properties of incompatible polyblends was examined by DSC, microscopy, impact test and dynamic mechanical testings.

4.6.1. Differential Scanning Calorimetry

Figure 20 shows the thermograms of modified and unmodified PVC-PS polyblends. Not much information was obtained from these thermograms, however. The PVC-PS blend showed a "hump" in the region of 75 to 105° and a relative weak structure adjacent to the hump. With the addition of a CPE 4814-g-styrene copolymer, the shape of the curve changed and only one glass transition starting at about 105° was observed. This may be a sign of interaction of the graft copolymer with the homopolymer components but since the transitions were all weak this effect is not very clear.

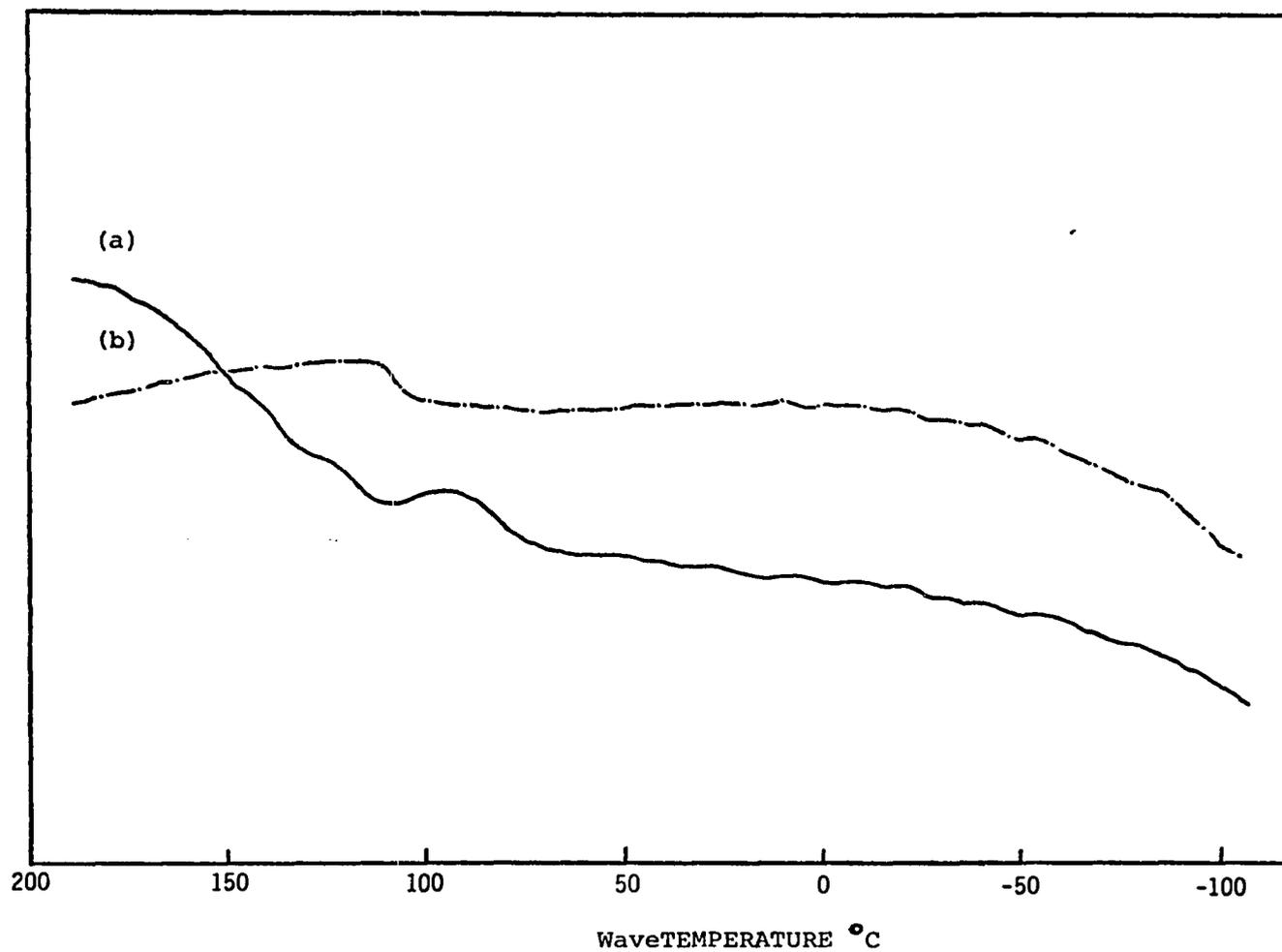


FIGURE 4-20: THERMOGRAMS OF (a) UNMODIFIED PVC-PS BLEND; (b) PVC-PS BLEND MODIFIED BY CPE4814-g-STYRENE COPOLYMER.

Figure 21 shows the thermograms graft copolymer modified PE-PVC-PS polyblend and the unmodified one. The PE-PVC-PS polyblend had a melting peak at 110° which started at about 95° . This peak overlapped with a broad hump starting at about 60° . The polyblend modified with the CPE 2552-g-styrene copolymer showed a thermogram which was nearly an superposition of the graft copolymer and the unmodified blend except the hump became even broad and more flat. The melting peak seems to be a hybrid of the CPE and PE melting peak and was not resolved. The peak temperature was about 109° , only slightly lower than that of the unmodified blend. Since PVC and polystyrene only showed glass transition on the DSC thermogram, which is less intensive than the melting transition, the interaction between the graft copolymer and the homopolymer mixture was not clearly seen. No conclusion may be made on the modification effect of the graft copolymer.

4.6.2. Microscopy

Photomicrographs for unmodified blends and graft copolymer modified blends are shown in Figure 4-22 and 4-23. Figure 4-22 shows the photographs of modified and unmodified PVC-PS blends. The unmodified PVC-PS blend has relatively large domain size compared to those modified blends. It was difficult to identify the component in the continuous and dispersed phase but the average domain size of both phases

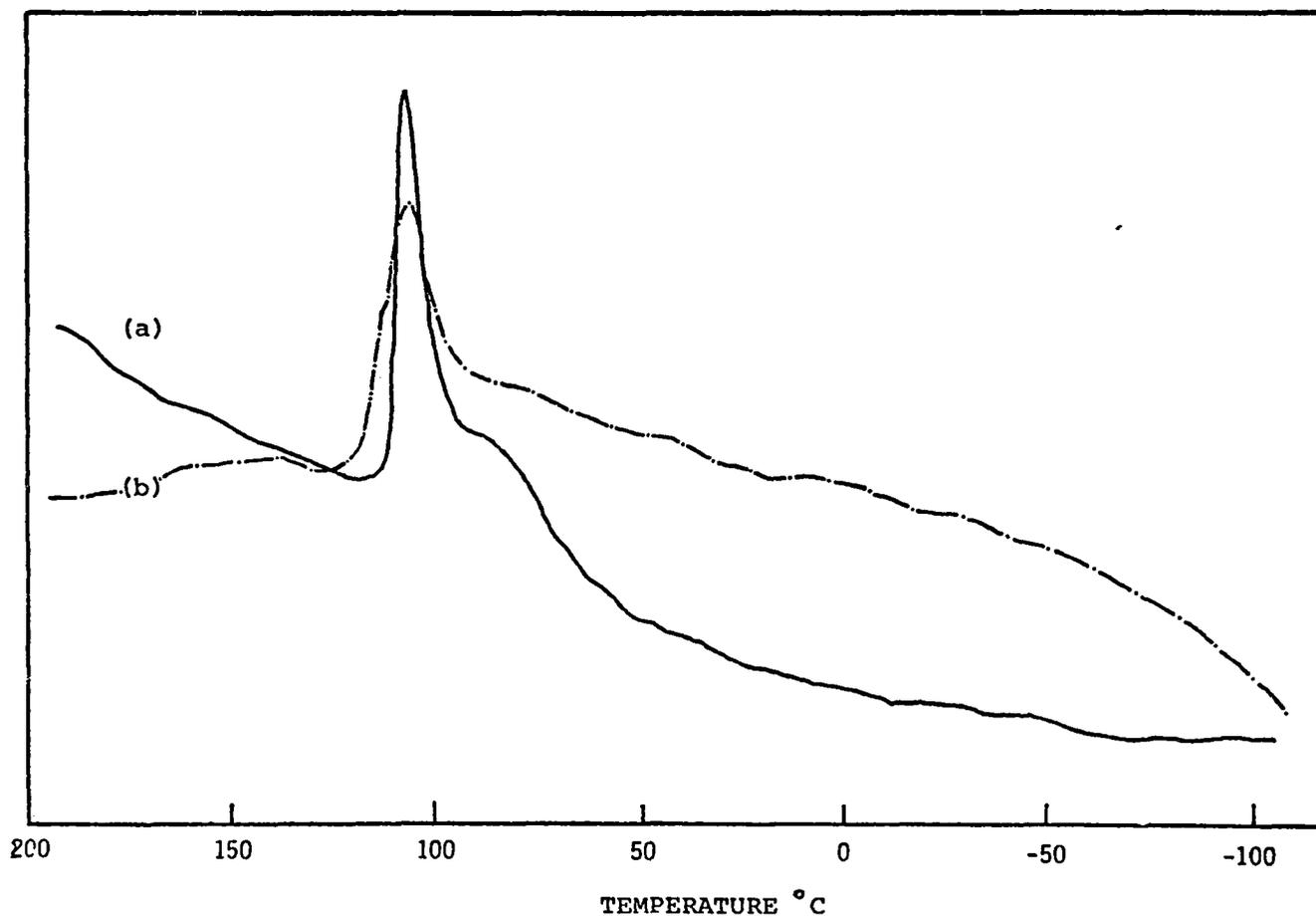
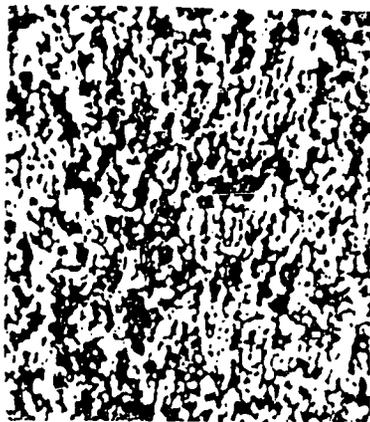


FIGURE 4-21: THERMOGRAMS OF (a) PE-PVC-PS TERBLEND AND (b) PE-PVC-PS BLEND MODIFIED BY CPE2552-g-STYRENE COPOLYMER.



(a)



(b)

— 30μ —

(c)



(d)



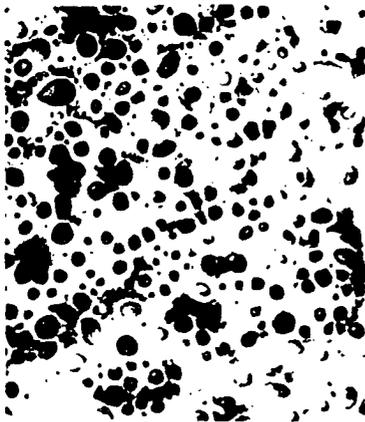
FIGURE 4-22: PHOTOMICROGRAPHS OF UNMODIFIED AND GRAFT MODIFIED PVC-PS BLENDS (a) UNMODIFIED (b) CPE2552-g-STYRENE (c) CPE3614-g-STYRENE (d) CPE4814-g-STYRENE MODIFIED.

became smaller and more uniform with the addition of graft copolymer. The domain boundaries also became less clear with the addition of the graft copolymer. This may be an evidence of the interphase-modification effect of the graft copolymer.

It appears that a graft copolymer with a backbone containing more chlorine ability for the PVC-PS blend. The average domain size of the graft modified blends follows this order: CPE 4814-g-styrene < CPE 3614-g-styrene < CPE 2552-g-styrene. The reason for the higher modification ability of CPE 4814-g-styrene may be its high chlorine content which resulted in higher affinity toward the PVC phase.

In Figure 4-23 are microphotographs of CPE 2552-g-styrene copolymer modified PE-PVC-PS blend. The phase boundaries in the PE-PVC-PS microphotograph was quite clear but became much less clear in the graft modified blends. The domain size of both the dispersed and continuous phases reduced with the addition of graft copolymer. Furthermore, the domain size seems to depend on the degree of grafting of the copolymer, which determines the relative concentration of the three components in the copolymer. When the degree of grafting of the copolymer increased from 22% to 50% the domain sizes dwindled significantly.

This effect was not so significant when the degree of grafting increased to 194%. It seems that phase inversion may have happened as the degree of grafting changed from 50%



(a)



(b)

—30μ—

(c)



(d)



FIGURE 4-23: PHOTOMICROGRAPHS OF UNMODIFIED AND CPE2552 -g-STYRENE COPOLYMER MODIFIED PE-PVC-PS BLENDS (a) UNMODIFIED (b) 22% PS GRAFTED (c) 50% PS GRAFTED (d) 194% PS GRAFTED

to 194%. In all cases, the modification effect of graft copolymer was evident.

4.6.3. Dynamic Mechanical Properties

The results of the dynamic mechanical results for CPE 2552 and graft-modified polymer blends are given in Figures 4-24, 25 and 26 as plots of the storage modulus, E' , loss modulus, E'' , and $\tan \delta$ as functions of temperature. All data were obtained at a test frequency of 110 Hz.

The storage moduli of CPE 2552 at -150° , 25° and 150° were found to be 1.2×10^{10} , 1.2×10^9 , and 5.6×10^8 dynes/cm² respectively. At -150° , which is below the glass transition temperature, the CPE 2552 was in glassy state therefore the modulus was high. At 25° , which is higher than T_g of CPE 2552, the polymer became rubbery and showed a lower storage modulus. At higher temperature, 50° , the modulus dropped even more. The loss modulus and $\tan \delta$ both show a broad transition in the region of -100 to -120° which is probably due to the γ -transition of the polyethylene-like segment in the CPE. The large peaks in the loss modulus and $\tan \delta$ are considered as an indication of glass transition. The loss modulus showed a peak at -12° while the $\tan \delta$ curve peaked up at 21° . The assignment of the glass transition temperature is difficult due to the difference between the peak temperature, obtained from E'' and $\tan \delta$ curve. Both temperatures

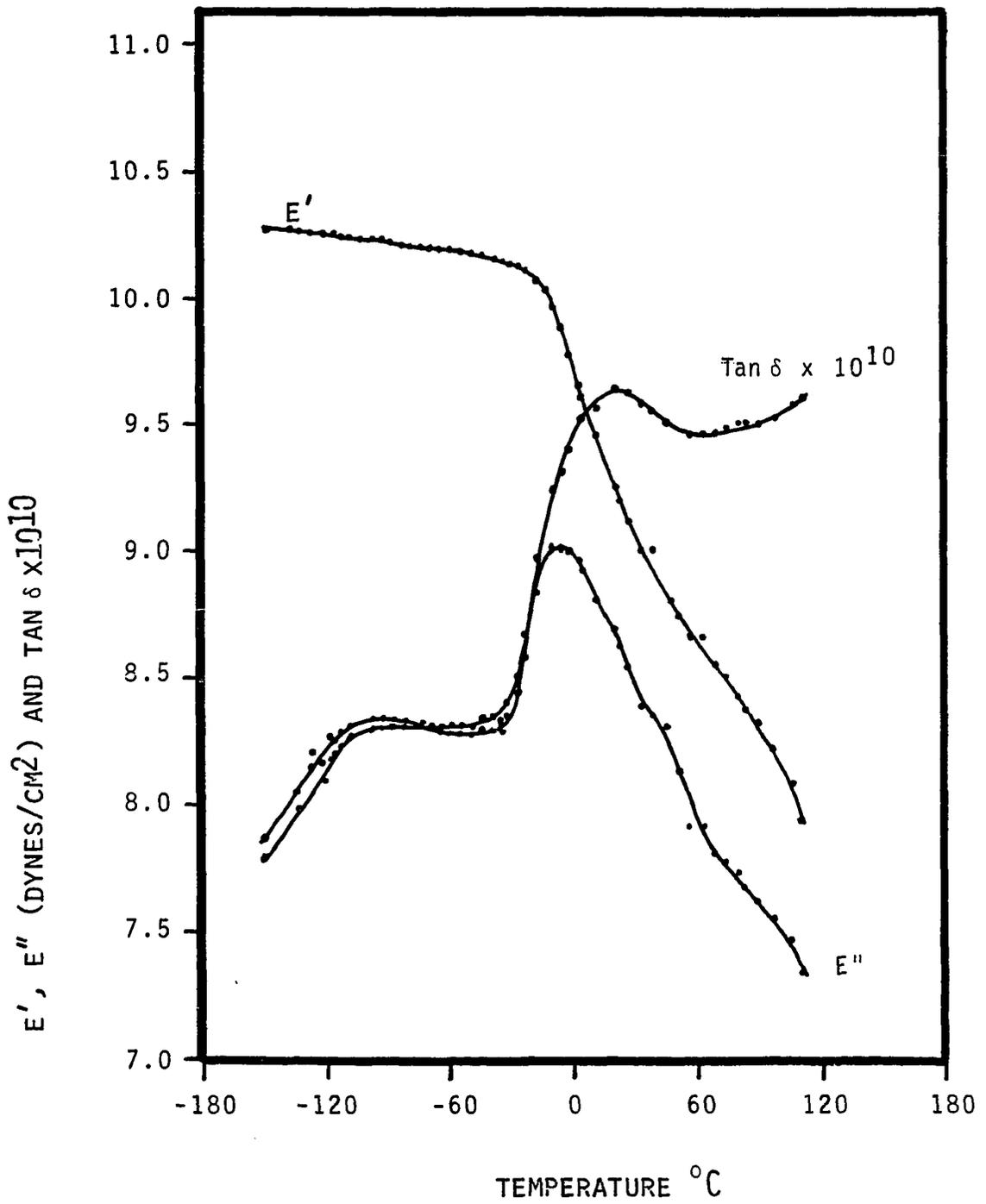


FIGURE 4-24: DYNAMIC MECHANICAL BEHAVIOR OF CPE 2552

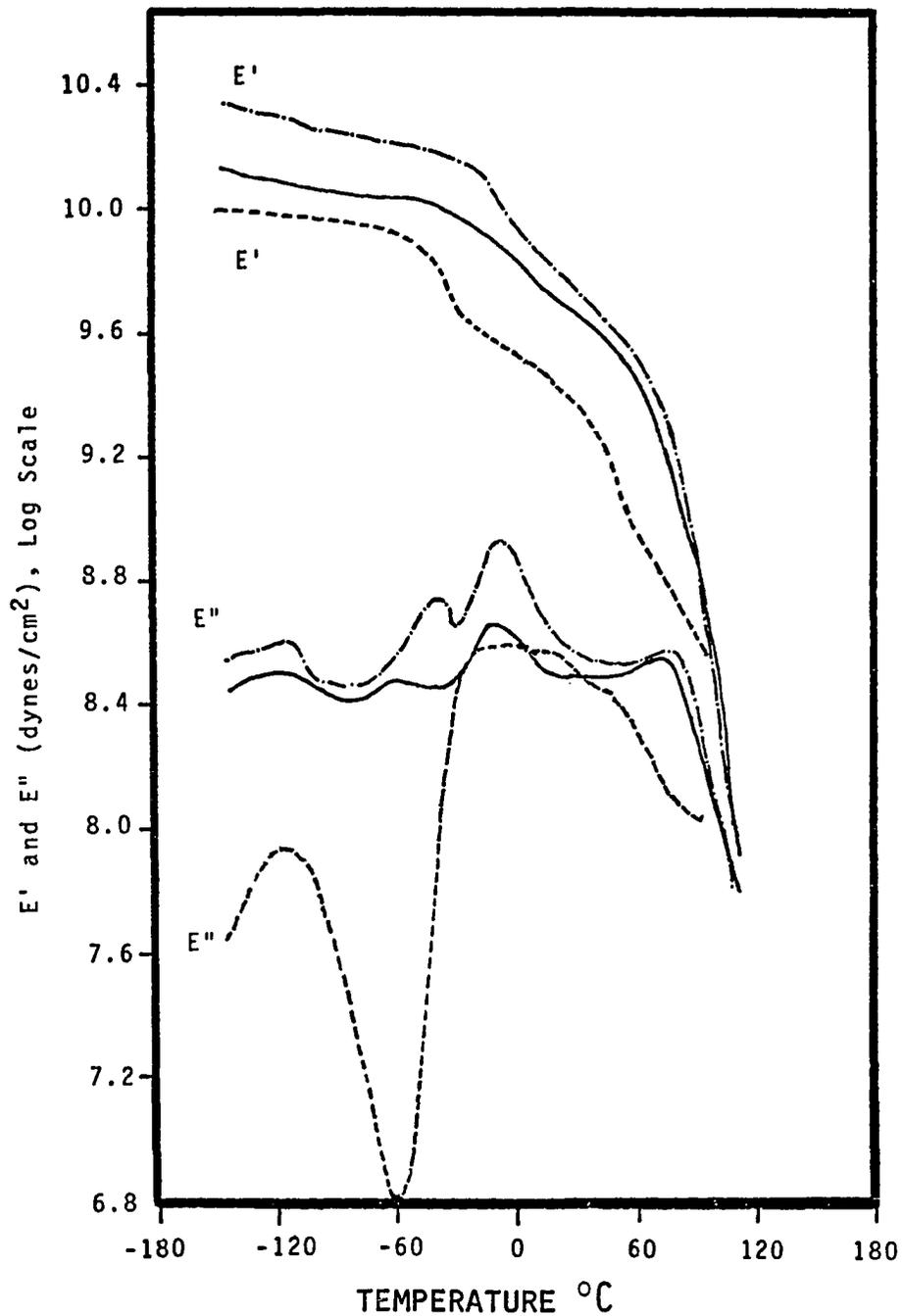


FIGURE 4-26: DYNAMIC MECHANICAL BEHAVIOR OF GRAFT MODIFIED PE-PVC-PS POLYBLENDS.

- PE-PVC-PS UNMODIFIED
- MODIFIED BY CPE2552-g-STYRENE,
DEGREE OF GRAFTING 194%
- · - · - · - MODIFIED BY CPE2552-g-STYRENE,
DEGREE OF GRAFTING 22%

are higher than that obtained from DSC (-29°). This kind of discrepancy is not unusual as great variation in glass transition temperatures obtained using different method of testing has frequently been observed. The characterization of the CPE 2552 dynamical mechanical behavior of CPE 2552 helps us understand the behavior of polyblends modified by graft copolymers containing CPE 2552 as backbone.

Figure 4-25 showed the storage and loss moduli of PVC-PS blend and PVC-PS blends modified by various graft copolymers. At -150° the PVC-PS blend had the lowest storage modulus, approximately 10^{10} dynes/cm², but this value did not decrease with the increasing temperature over a very wide temperature range. Those graft-copolymer-modified blends showed a drop in modulus at relative lower temperature than the PVC-PS blend. This earlier modulus change was due to the presence of CPE in the blends which has a much lower glass transition temperature than either of the homopolymers in the blend. It was observed that the CPE 4814-graft-blend had the modulus change at a higher temperature than the CPE 3614-graft-blend and the CPE 2552-g-graft blend. This seems to be due to the higher glass transition temperature of CPE 4814 than that of CPE 3614 and 2552, which has been confirmed by the DSC result of this study and the dynamic mechanical testing result obtained by Lock (43). Two strong peaks appeared on the loss modulus curve of the PVC-PS blend. A relatively

weak modulus change occurred in the region of $75 - 100^{\circ}$. This is the range where glass transitions of polystyrene and polyvinyl chloride occur. The transitions of the two strong peaks are not understood but the peak at about -45° has also been observed by Locke (43) in the study of polyvinyl chloride. The peaks at about -100° observed from the loss modulus curves of the modified blends were due to the γ -transition of the polyethylene-like portion in the CPE. It is very meaningful to observe only one peak on the E'' curve of each of the modified blends in the region of -60° to 40° where two peaks were observed for the PVC-PS blend. The addition of a graft copolymer have caused significant peak shift which is a sign of interaction between the CPE-g-styrene copolymers and the homopolymers. The peaks at -5° observed from the E'' curve of the modified blends seems to be characteristic of the γ -transition of polyethylene-like portion in CPE. The intensity of these peaks follows this order: CPE 3614-graft blend > CPE 2552-graft blend > CPE 4814-graft blend. Since these peaks are considered to be due to the polyethylene-like segment in CPE it was expected to see a stronger peak from the CPE containing less chlorine. The fact that CPE 2552-graft blend showed a stronger peak than the CPE 4814-graft blend is reasonable but the unexpected high intensity of the peak due to CPE 3614 needs other explanations. The extraordinarily high intensity of the -5°

peak of CPE 3614-graft blend may be explained by its relatively high concentration of CPE due to its relatively low degree of grafting. This CPE 3614-g-styrene copolymer had a degree of grafting of 65%, comparing to 194% for the CPE 2552-g-styrene and 196% for the CPE 4814-g-styrene copolymer.

It was also interesting to see a weak structure at about -45° on the E'' curve of the CPE 2552-graft blend but not on the other two E'' curves. The appearance of this structure seems to indicate that the interaction between the graft copolymer and homopolymer was not sufficient to cause enough peak shift which would allow the peaks to mingle completely. This phenomenon suggests that the modification effect of CPE 2552-g-styrene is weaker than CPE 3614 and CPE 4814 graft copolymers for the PVC-PS system. This is understandable since CPE containing higher chlorine is more like the polyvinyl chloride and therefore has stronger interaction with the PVC phase in the blend. The peaks observed in the region of 60 to 90° seem to be hybrids of the PVC and PS glass transitions.

Figure 26 shows the storage and loss modulus of PE-PVC-PS blend and CPE 2552-g-styrene modified PE-PVC-PS blends. The PE-PVC-PS blend showed a relatively low storage modulus (10^{10} dynes/cm²) at -150° and showed substantial drop in E' at around -50° . The addition of CPE 2552-g-styrene graft copolymer stiffened the blend a bit and led to relatively moderate change in E' at slightly higher temperature. The

presence of low density polyethylene dominated the shape of the E' , E'' and $\tan \delta$ curves of the PE-PVC-PS blend. A sharp peak at -120° , on both E'' and $\tan \delta$ curves, which should be the γ -transition of polyethylene, was observed while the transitions due to PVC and PS were too weak to be noticed. The addition of the graft copolymer led to significant change in the shape of the E'' and $\tan \delta$ curves. The γ -transition was still observed at -120° , but the transitions possibly due to PVC and polystyrene became more pronounced. This phenomenon probably was due to decrease of the concentration of polyethylene in the blend because of dilution. The CPE transition was still observed but had shifted to a lower temperature ($\approx -14^{\circ}$). The intensity of this peak on E'' curve still was dependent on the degree of grafting. The blend modified by graft copolymer C-25, which had a degree of grafting of 22%, showed a higher intensity than the one modified by copolymer C-34, having a degree of grafting of 194%. Since the E'' and $\tan \delta$ curves of the PE-PVC-PS blend were so lacking in structure, to interpret the effect of modification was difficult. No definite conclusion on phase interaction can be made for the case of PE-PVC-PS system. However, the interaction between the graft copolymer and the PVC-PS blend was so pronounced that the ability of this graft copolymer to modify the incompactible polyblend seems certain. The result of the microscopic work together with the observation of

dynamic mechanical behaviors provided evidence of modification effect of the CPE-g-styrene copolymer.

4.6.4. Impact Strength

Table 4-19 lists the impact strength data of PVC-PS blend and graft-modified PVC-PS blends obtained according to ASTM standard method D 256-73.

Table 4-19: Impact Strength Data of Unmodified and Graft-Modified PVC-PS Blends

<u>Blend Composition</u>	<u>Impact Strength 256-73 (ft.-lbs/in.)</u>	<u>Impact Strength per Unit Area (ft.-lbs/in.)</u>
PVC/PS (1:1)	1.32	3.16
CPE 3614-g-styrene/PVC/PS (1:1:1)	1.95	4.75
CPE 2552-g-styrene/PVC/PS (1:1:1)	2.32	5.54

The impact strength of PVC-PS blend was very poor. With the addition of graft copolymer the impact strength increased for 48 to 75%. The blend modified by CPE 2552-g-styrene copolymer showed a higher impact strength than that modified by CPE 3614-g-styrene. This may be due to the more flexible nature of CPE 2552 segment instead of due to higher modification ability of the CPE 2552-g-styrene graft, since CPE 3614-g-styrene copolymer should be more compatible with the PVC phase of the blend.

For lack of material, only one sample for each of the

blends was tested. As the impact strength test is subjected to relatively great error and usually requires at least five samples be tested, the data shown above probably are not the absolute values of impact strength. However, this experiment provided information about the relative impact strength of the graft-modified blends and the unmodified one. The graft copolymers did cause an increase in impact strength but whether this increase was due to the modification effect or simply the contribution of the more flexible CPE component in the graft is not clear at this time. This experiment served as a preliminary study of the modification effect due to graft copolymers.

CHAPTER V

CONCLUSIONS

The major conclusions drawn from the study of synthesis, purification, characterization and blend modification are itemized below.

1) CPE-g-styrene copolymers were synthesized by chemical-initiated grafting and radiation-induced grafting, and the grafting of styrene has been proved by solubility study and IR result.

2) Both the chemical-initiated and the radiation-induced graft copolymerizations gave reaction products containing homopolystyrene and unreacted CPE. The amount of parent homopolymers in the reaction product varies with the reaction conditions. With the use of pre-initiation technique and proper reaction conditions, a graft efficiency as high as 0.84 has been achieved from chemical initiated graft copolymerization.

3) The mutual-radiation method yielded graft products with graft efficiencies relatively lower than that obtainable from the pre-initiated chemical grafting. The grafting was initiated by free-radicals and/or peroxides, but the graft

product obtained under vacuum gave a slightly higher yield and degree of grafting than that irradiated under atmosphere. The reason the synthesis under vacuum did not yield a substantially higher degree of grafting might be the more amorphous nature of the CPE compared to that of high density polyethylene. The yield and degree of grafting increased with the use of a higher dosage. No crosslinking was observed with the dose level used in this study.

4) In chemical initiated graft copolymerizations, the degree of grafting and graft efficiency are significantly affected by the degree of swelling, initiation time and temperature, concentration of the initiator and monomer. The degree of swelling seemed to affect the diffusion of the initiator and the monomer into the CPE films which would have affected the initiation and propagation rate of grafting. The Trommsdorf effect was not observed under the reaction conditions studied in this work. The reason for not seeing this effect, which has been observed by many authors in the grafting of styrene onto polyethylene, was probably the relatively lower crystallinity of CPE which had led to easier swelling and therefore lower viscosity of the reaction media, the CPE films. Higher initiation temperature and longer initiation time increased the rate of grafting unless the initiation time and temperature were beyond certain limits. Beyond the limiting temperature or time of initiation, crosslinking was

observed and the grafting rate declined. The crosslinking destroyed a fraction of the active sites on the backbone molecules and led to low yield and degree of grafting. Higher dosage of initiator and higher monomer concentration were found to benefit the grafting and monotonically increase in degree of grafting was observed. CPE's with varied chlorine content exhibited different degree of swelling due to their different crystallinity. CPE 4814 was most easily to be swelled because of its highest chlorine content and therefore led to a high graft yield when being used as the backbone in grafting.

5) A selective extraction process was employed and found efficient to remove the styrene homopolymer from the graft product. A 18/82 cyclohexane-acetone mixture was found to be the better solvent for the selective extraction. The samples were processed into powder form so that more efficient extraction could be achieved. One single extraction was found sufficient to remove the styrene homopolymer according to the result of solubility study of CPE-PS mixtures and the IR analysis of the extracted graft products. However, since the solubility parameters of CPE and polystyrene are very close, completely selective extraction was almost unachievable and miscelle formations were sometimes observed. A fraction of the graft copolymer was believed to have eluted along with the extracting solution during the pressure filtration.

6) The solubility parameter of CPE 3614 was estimated from the solubility curve for cyclohexane-acetone mixture. The solubility parameter was found to be around 8.6, which is intermediate between that of polyethylene and polyvinyl chloride. The solubility parameter, together with the three-dimensional parameter approach, well predicted the solubility behavior of the polymers in various solvents.

7) A selective precipitation procedure found some success in isolating the unreacted CPE from the graft copolymer. This procedure separated the homopolystyrene-free product into a graft copolymer-rich and a unreacted CPE-rich phase by the difference between the solubility of graft copolymer and the unreacted CPE. This success, however, was limited to only a fraction of the graft products synthesized since the solubility behavior of the graft copolymer was affected by the chain length of the graft and the crosslinking nature of graft copolymer. Some of the precipitant-added solution did not separate into two phases after centrifuging.

8) The IR quantitative analysis using an "internal standard" technique was utilized to determine the composition of purified graft products and was found to have good reproducibility. The composition determined by IR was adopted for calculation of the graft efficiency and graft index. Due to the inherent problem of this polymer system, solubility parameters were too close for the CPE - PS pairs, which led to

certain extent of co-solution and co-precipitation the graft efficiency and degree of grafting obtained may be somewhat lower than the true values.

9) The CPE-g-styrene copolymers were characterized by IR, laser-Raman Spectroscopy, dilute solution viscosity and DSC. The IR spectrum of a graft copolymer was found to be a superposition of the spectra of pure CPE and polystyrene. The laser-Raman spectrum was obtainable only when the Anti-Stokes shifts were measured. No new peak or significant peak shift due to grafting has been observed.

10) No decomposition of the CPE backbone during the initiation has been observed, according to the intrinsic viscosity of the initiated CPE. Also the dehydrochlorination of CPE during initiation, extraction, molding and grinding was found to be not significant according to the measurement of C-Cl group concentration in the CPE-PS mixtures by IR.

11) The intrinsic viscosity of graft copolymers in toluene was found to increase with increasing degree of grafting. The relationship did not appear to be linear but may be further understood if the number of grafts can be accurately measured. The molecular weight of the extracted homopolystyrene was found to be somewhat higher than the polystyrene synthesized under simulated reaction condition. But the difference in molecular weight was not so great as reported for the grafting of polyethylene-g-styrene copolymer. This

observation suggests that the Trommsdorf effect was not pronounced in the grafting of CPE-g-styrene.

12) The melting peaks and some glass transitions of CPE 2552, CPE 4814, CPE-g-styrene copolymers, and polyblends involving polyethylene, polystyrene and polyvinyl chloride were characterized from DSC thermograms. But due to the fact that transitions other than melting were very weak, no definite conclusion could be made on the interaction of graft copolymer with the incompatible polyblends from DSC result.

13) The photomicrographs of incompatible blends and blends modified by graft copolymers showed evidence of interaction between graft copolymer and the homopolymers. The average domain size of the polyblend decreased significantly with the addition of graft copolymer which should be a sign of interaction between the graft and the homopolymers. For polyvinyl chloride-polystyrene blend, a graft copolymer made from a CPE with higher chlorine content showed stronger interaction as the domain size became very fine and more uniform. In a PE-PVC-PS blend, adding a CPE 2552-g-styrene copolymer with a degree of grafting of 50% gave domains of finer sizes than that obtained by adding a graft copolymer with only 22% styrene in graft. But adding a graft copolymer with a degree of grafting of 194% did not cause significant further domain size reduction. A phase conversion seemed to have occurred when increase the degree of grafting from 50 to 194%. This

observation suggests that the overall interaction toward both homopolymer phases is dependent upon the relative concentration of CPE and polystyrene in the graft material when the composition of the homopolymer blend is fixed. A maximum modification effect may be obtained from a graft copolymer with proper number of grafts and graft length.

14) Evidence of modification due to the addition of graft copolymers was also found from the dynamic mechanical results. Upon mixing of a graft copolymer to a PVC-PS blend, the two peaks characteristic of the PVC-PS mixture seemed to have shifted toward each other and have been mixed with the β -transition peak due to the polyethylene-like portion in the CPE. Only one peak showed up on the E'' curve at a temperature region between the two peak temperatures of PVC-PS mixtures. This type of change is an indication of interaction due to the graft and better compatibility among the components in the blend. Storage modulus, transition peaks on loss modulus and $\tan \delta$ curves of CPE 2552 and graft modified PE-PVC-PS blends were also identified and discussed.

15) Impact strength of a PVC-PS blend increased 48% and 75%, respectively, by the addition of graft copolymers made from CPE 3614 and CPE 2552. Whether this increase was due to modification of the graft copolymer or was simply a result of the presence of CPE in the blend is not clear at this point.

16) The result of microscopic work and dynamic mechanical testing showed evidence of the interaction effect due to graft copolymer in the polyblend. This interaction should result in a better interphase adhesion and therefore better mechanical properties. The use of the CPE-g-styrene graft copolymer as a modifier for polyblends involving styrene and PVC or styrene, PVC and PE appears to be possible, and worths further study. In further pursuit of this work, more complete characterization of the graft copolymer as well as mechanical testings such as stress-strain, adhesion and impact strength, will be essential in evaluating the feasibility of engineering application of this graft copolymer.

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