FULLERENE END-CAPPED POLYSTYRENE

OF NARROW POLYDISPERSITY

By

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PREFACE

In the production of ordinary plastics, monomer (the single starting unit, usually a small molecule) is converted to polymer (several connected monomer units or a larger molecule) by linking monomers together in a process called chain-growth polymerization. This produces high molecular weight polymers with broad molecular weight distributions via three steps - initiation (the beginning stages of chain growth), propagation (where links of the polymer chain are added to increase its length), and termination (where chain growth stops). One type of polymerization makes use of free radicals. Free radicals are molecules that have in their network of atoms and pairs of electrons associated with those atoms, a single electron. The unpaired or free electron makes this site reactive with the electrons of other molecules as it attempts to gain a pairing. In the process of pairing the radical electron with an electron of another molecule a bond between the two molecules is formed, and a new free radical appears elsewhere on the new molecule. Free radical reactions are especially useful for polymerizations because of the persistent active site of the radical.

Using a free-radical polymerization method, we were able to produce polystyrene that chemically incorporated C_{60}. However, the polymers formed in the presence of C_{60} had highly branched structures and showed a dramatic decrease in the length of their polymer chains. An alternative method for producing polystyrene was employed - living polymerization. These polymerizations avoid a termination step so that chain ends remain active even after all the monomer has been polymerized.

Living polystyrene was prepared by a stable free-radical living polymerization mechanism. The presence of a radical on the end of the polymer chain end allowed for reaction with C_{60}. These end-capping reactions gave products that were analyzed with size exclusion chromatography (a separation method which distinquishes molecules by their size) equipped with UV, refractive index, and viscosity detectors. The number of polystyrene chains added to the C_{60} in these product mixtures was mainly 0, 1 or 2. Using molar ratios of 1, 2 and 4 polymer chains per mole of C_{60} during the reaction produced nearly identical

results. Increased polymer content in the reaction mixture does not effect the resulting products. The products were affected when residual monomer was present during the end-capping reactions and when the reaction solutions were cleansed of by-products produced by end-capping reactions. More of the resulting product had two polymer chains attached to C_{60} in these latter scenarios.

Our goal was to create a plastic film that contained C_{60} for use in protective optical devices. With the C_{60} bonded to the end of a polymer chain, the new material could be processed like any plastic. The optical properties of C_{60}, combined with the utility of polystyrene results in a material with the best qualities of both of these substances.

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I wish to express my sincere appreciation to Dr. Rockley for giving me a desire to know more about chemistry, Dr. Holt for her guidance and motivation during my undergraduate studies, and for being my undergraduate advisor. I'd like to thank Dr. Berlin for his encouragement and confidence in me and for serving on my committee, and finally Dr. Ford for leading me in this pursuit of knowing more about the field that I chose and for teaching me how to traverse that path.

I also want to thank my parents for their encouragement, love, and support throughout my life and especially during my education. Finally, I would like to thank the Department of Chemistry for their financial support through this process.

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CHAPTER I

INTRODUCTION

Background. In 1990, gram sized quantities of C_{60}[1] became available, and research dealing with this new form of carbon exploded. Because of its unusual potential optical, electrical, physical, and chemical properties, [60]fullerene (a systematic name for **1**) was expected to become a useful material in many applications and had a certain and promising future as a new material for research.

1

The optical properties were what peaked the interest of our research group. Since C_{60} shows nonlinear absorbance of intense amounts of laser radiation over a wide range of wavelengths,[2] it would be a superior material for use as a protective device for optical sensors or human eyes. Its ability to absorb from 532 to 660 nm would make it more versatile than most other nonlinear optical materials. A protective device containing this material would most likely be made with clear glass or a plastic. However, C_{60} is not very soluble in any monomer or polymer, and so materials produced by mixing it with polymers contain crystals or aggregates of the C_{60} that scatter light. We discovered this phenomenon when emulsion polymerization techniques were used to prepare a polystyrene in the presence of C_{60}. Our first successful attempt to chemically incorporate the fullerene into the polymer occurred when radical polymerization techniques were used in solution.[3] Meanwhile, other researchers were also achieveing chemical incorporation of C_{60} into polymers by various means. These results have been compiled in a review article[4] and the *Polymer Data Handbook.*[5]

Free radical polymerization of styrene is well understood which makes the process a good candidate for study when new variables are introduced. The introduction of C_{60} into this reaction caused several changes in the products. The radical initiator azobisisobutyronitrile (AIBN) (2) reacted with the C_{60} as well as with monomer to produce polymer chains. It was even suspected that clusters of C_{60} were forming.[6] Thus, C_{60} was very reactive with carbon radicals.[7]

$$\underset{NC}{\nearrow}\!\!-N\!\!=\!\!N\!\!-\!\!\underset{CN}{\searrow}$$
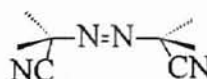
2

At that time, little was known about the chemistry of radical reactions with C_{60}. In order to understand this chemistry better, we reduced the complexity of the system by removing the monomer. With only AIBN and C_{60} in the reaction, it was suspected that the products from that reaction would be simpler, and if they could be characterized, we would be closer to understanding the radical mechanism of incorporation of C_{60} into polymers.

Further study of the reaction between AIBN and C_{60} produced more mixtures of substituted fullerenes. These C_{60}-derivatives were susceptible to air oxidation, and reactions in which air present in the gas space above the reaction was compared to reactions done under argon[6]. LSIMS analysis of the product mixtures showed a series of peaks spaced 24 mass units apart from as low as m/z 528 (C_{44}) to as much as m/z 2424 (C_{202}). Increasing amounts of oxygen increased the number of peaks in otherwise identical reactions. Finally, three isomers of disubstituted C_{60}, accounting for approximately 18% of the sample after three chromatographic separations, were isolated from product mixtures resulting from reactions of C_{60} with AIBN performed under an inert atmosphere. Structure identification of these isomers has allowed us to determine where AIBN radicals attach to a C_{60} molecule.[6,8] The incoming radical adds at one side of a double bond of a benzene ring on the molecule, and the newly formed C_{60} radical stays localized on that benzene ring in two of the addition scenarios. A second radical then adds at either the 2-position or most often with radical reactions at the 4-position. The product is a disubstituted C_{60} derivative. The other alternative is a 1,16- addition.[9] Refer to Scheme 1 in text.
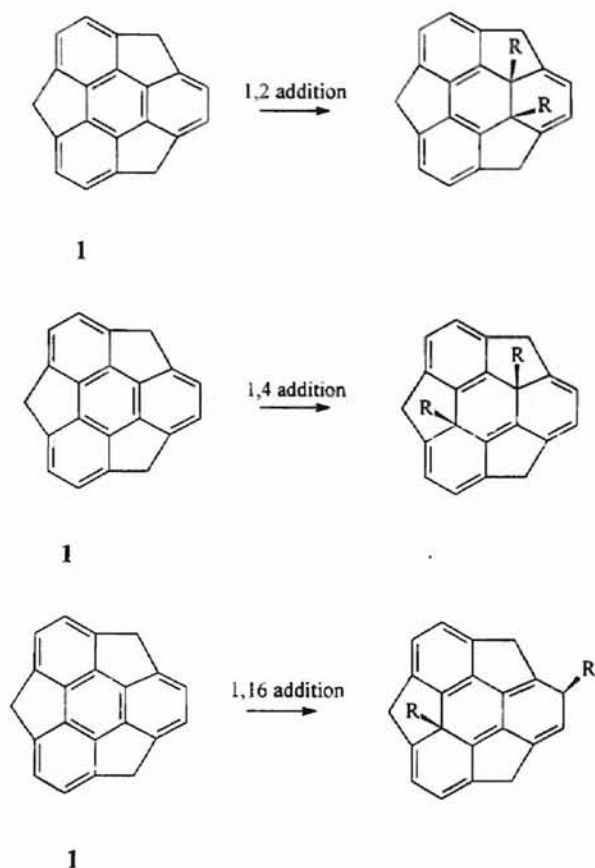
Scheme 1. Addition of radicals to C_{60} (These structures illustrate only a portion of the C_{60})

Low and high conversion polymerizations of methyl methacrylate and styrene initiated with AIBN in o-DCB solutions of C_{60} revealed that all of the C_{60} was incorporated after low conversion of monomer.[6] The low conversion polystyrene and C_{60} were insoluble in tetrahydrofuran - a good solvent for polystyrene and PMMA - which suggested the formation of polyC_{60}.[5] High molecular weight polystyrene was formed and contained as many as 10-100 C_{60} units per molecule while the high molecular weight PMMA contained one C_{60} per polymer molecule.[10]

We not only wanted to create a durable plastic material that contained the C_{60} but also to understand the chemistry that incorporated the fullerene into the polymer. A well characterized product would enable us to do this. However, the previous approach was not sufficient. At this point we began investigating the possibility of using living polymerization techniques because C_{60} and living polystyrene would give a polymer of more certain structure.

LIVING POLYMERIZATION

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Introduction. While conventional radical chain polymerizations proceed through initiation, propagation, and termination steps, "living" polymerizations differ by avoiding the termination step. These special polymerizations were so named because the polymer chains that form remain active even when the monomer supply is depleted. When more monomer is added, polymerization resumes without increasing the number of polymer chains.[11] There are several benefits associated with living polymerizations, including narrow molecular weight distribution, molecular weight control, synthesis of block copolymers, and introduction of specific end-groups. Living polymerization allows for a more sophisticated approach to polymer product design than conventional radical polymerization.

Some of the more well known living polymerizations proceed via anionic and cationic propagating sites. Anionic methods have been used to make the narrow polydispersity and specific molecular weight polystyrene standards used for calibrating size exclusion liquid chromatography equipment. This method is useful not only for styrene but for a variety of different monomers. However, the experimental conditions are rigorous. End capping reactions are sensitive to techniques, solvent, and counter ion and require temperatures of -70 °C to achieve reproducible results.[11] Cationic living polymerization also requires very low temperature and is even more complex due to numerous side reactions that occur. The living polymers are light sensitive and require additives to effect reversible termination.[11] These demanding reaction conditions were what eliminated anionic and cationic living polymerization techniques as possible methods for us to produce living polystyrene. A C_{60} end-capped polystyrene was made with anionically produced polystyrene[12-14] and will receive further discussion later.

Living radical polymerization. Although the challenge of controlling structural features, such as polydispersity, molecular weight, chain ends, and macromolecular architecture, had been met by the other types of living polymerizations, the procedures were synthetically demanding as well as being

incompatible with many functional groups and monomers. Free-radical living polymerizations are the most recent breakthrough in the pursuit of structural design control through living polymerizations and overcome many of the problems associated with the other techniques. First the initiating or propagating center is more robust than in the other techniques.[15] The polymers are produced under very mild conditions, much like any radical polymerization, and do not require a number of complex experimental steps. Finally, using an active radical propagating center would insure reaction of the polymer with C_{60} in an end-capping reaction. It is well known that C_{60} is very reactive with radicals.[3,7,16,17] The following is a detailed explanation of the reactions and mechanism of the polymerization of styrene under "living" radical conditions, followed by an overall reaction scheme for the product compounds described in this thesis.

Mechanism of formation of benzoyloxy end-grouped polystyrene. Before a commercial initiator became available, an initiator was synthesized prior to each polymerization by combining benzoyl peroxide (BPO) (3), styrene (4), and TEMPO (5). The reaction proceeds by homolytic cleavage of the BPO to form two benzoyloxy radicals. A radical reacts with a styrene unit in an initiation step. Then TEMPO reversibly bonds to the styryl radical to give initiator (6)[18]. See Scheme 2.

3   4   5

$95\,^{\circ}C$ | 5 hours

6
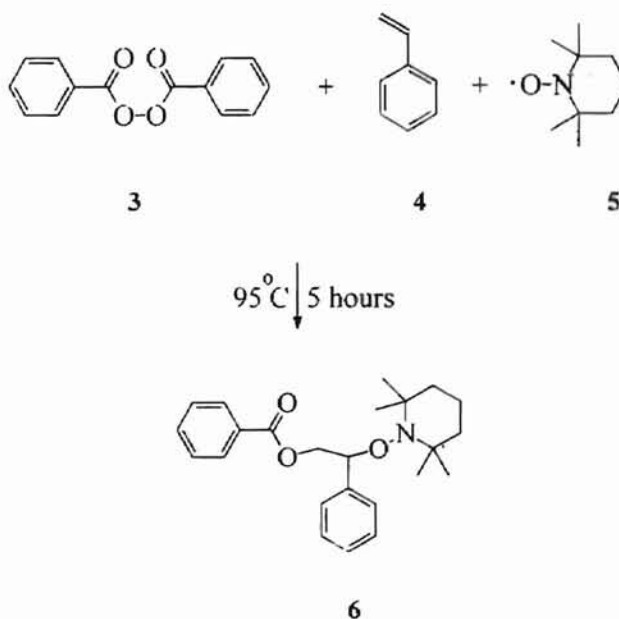
Scheme 2. Prepolymerization synthesis of initiator.

Nitroxyl radicals, such as TEMPO, have extremely low rates of reaction with oxygen centered radicals, such as a benzoyloxy radical, but have nearly diffusion controlled rates of reaction with carbon

centered radicals, such as a styryl radical.[18] Significantly, TEMPO radical does not initiate the growth of any polymer chains. Prolonged exposure of the newly formed initiator to air, light, and moisture results in no detectable decomposition and demonstrates the stable nature of the aminoxy group. At elevated temperatures, however, these molecules are thermally unstable and dissociate in an equilibrium process to give TEMPO and a styryl radical (7). See Scheme 3.

6	**7**	**5**
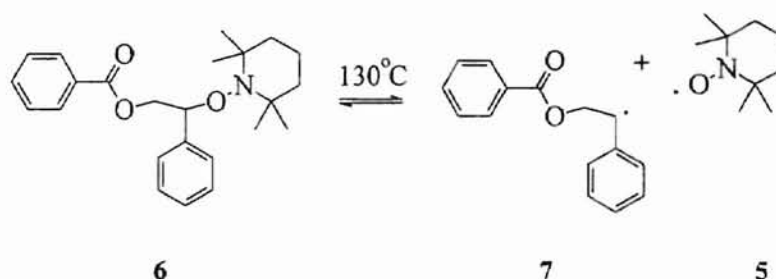
Scheme 3. Reversible Alkoxyamine Bond Breaking.

Mechanism of autopolymerization of polystyrene.[19] Thermal initiation of styrene polymerization proceeds by a Diels-Alder reaction to give the Mayo adduct (8). Hydrogen atom transfer to another molecule of styrene allows this adduct to achieve greater aromaticity by forming the aromatic radical (9) and the radical derived from styrene (10). In the presence of TEMPO these radicals are trapped as compounds 11 and 12 and the autopolymerization that would occur becomes a nitroxide controlled living polymerization.[20] The TEMPO terminated compound (11) is available commercially as an initiator[21] for producing living polystyrene and is addressed later. Scheme 4 illustrates the TEMPO mediated self-initiation process.
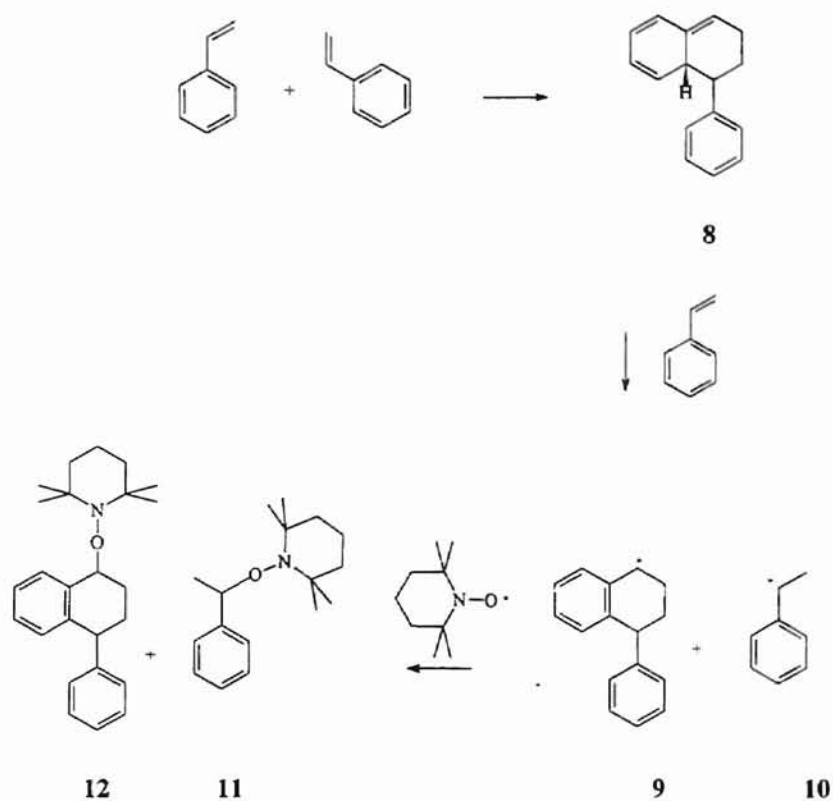
Scheme 4. Thermal initiation of styrene.

The living nature of these nitroxide mediated processes is a direct result of the thermally labile alkoxyamine C-ON bond between the mediating nitroxide free-radical TEMPO and the propagating chain end. To summarize, the previous reactions result in a dormant, or inactive, intermediate which is homolytically unstable and undergoes thermal fragmentation to give the stable nitroxide and the monomeric radical.

In the presence of excess monomer, the monomeric radicals (**7, 9 and 10**) initiate single growing polymer chains. Chain extension with a limited number of monomer units yields polymeric radicals and thus the degree of polymerization increases. Recombination of a polymer radical with TEMPO renders the polymer chain dormant again (**13**) as shown in Scheme 5.

7   5

13 (B-PS-T)
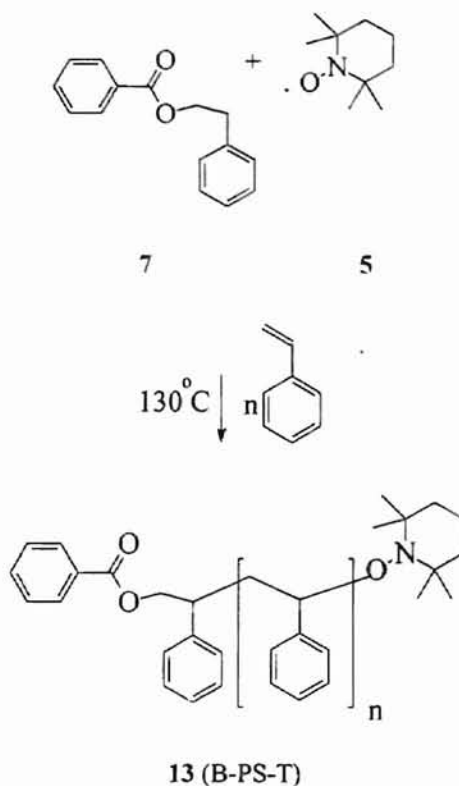
Scheme 5. Polymerization with benzoyloxy ended initiator.

The presence of the TEMPO counter-radical suppresses deactivation or termination reactions. It is the presence of a substantial amount of dormant chain ends in the polymerization mixture which is believed to be responsible for the living nature of this unique process and the observed low polydispersities. This low concentration of active chain ends in an equilibrium with the dormant chain ends make this system "living". This is why the molecular weight distribution is narrow, and why the molecular weight is directly proportional to percent conversion.

Overall reaction scheme. Scheme 6 is representative of polymerizations initiated with the commercial initiator **11** described in the Experimental Section. The alkoxyamine bond of the initiator cleaves reversibly at 130 °C to give free TEMPO and a polystyryl radical, which, in the presence of excess styrene, begins the growth of a polymer chain. No solvent is needed as the initiator is soluble in styrene.
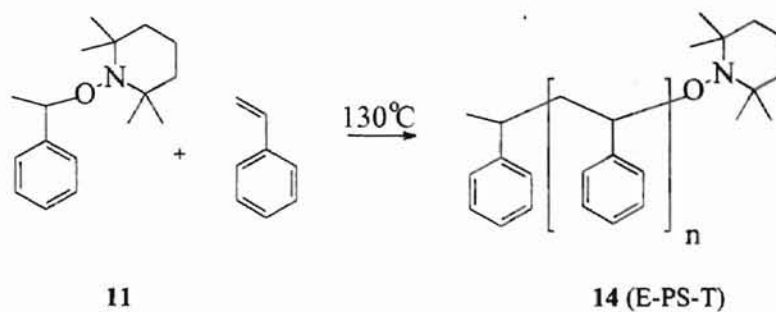
Scheme 6. Polymerization with commercial initiator.

The polymer that forms is isolated from monomer. More detail is given in the Experimental Section. End-capping reactions follow. The TEMPO-ended polymer and C_{60} are dissolved in *o*-dichlorobenzene and heated to 130 °C as depicted in Scheme 7.
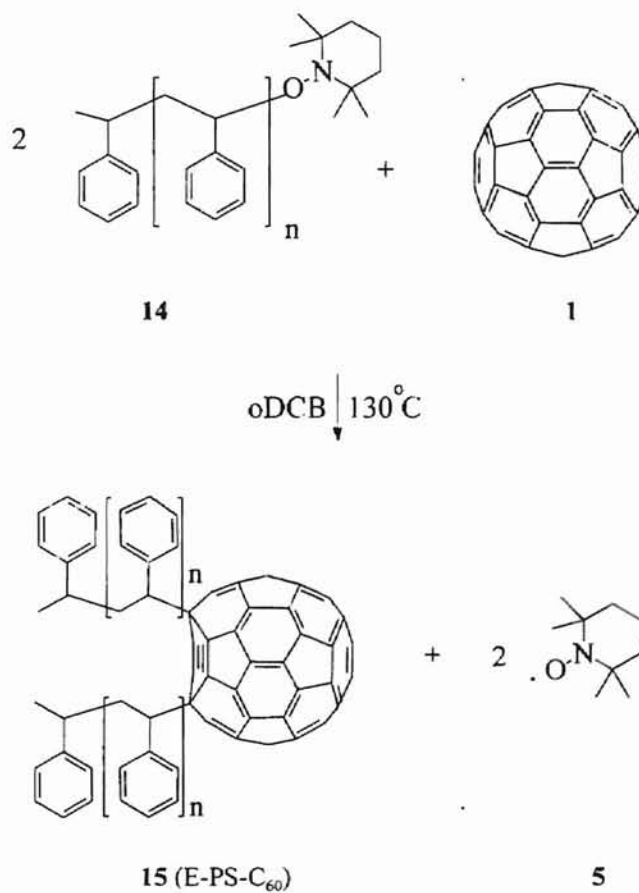
Scheme 7. End-capping with C_{60}.

The products are isolated from o-dichlorobenzene. The remaining solid is dissolved with tetrahydrofuran which dissolves polymer products but leaves unreacted C_{60} as a solid which is filtered away from the solvent. The dried polymer is brown and contains mostly C_{60}-polymer derivatives (15). The Experimental contains specific details of the reactions.

Using a similar reaction scheme with C_{60} in excess over LPS, the Fukuda group reported the sole product of this reaction to be the bis-adduct 15 based on characterization by ^{1}H NMR and UV-vis data.[22] The reactions reported here differ from theirs most significantly in that excess LPS was used instead of excess C_{60}, and products containing one, two, and three polystyrene chains were identified.

Living polystyrene that was produced with these techniques is reported in this thesis as are the end-capped C_{60}-derivatives made from it. The different polystyrenes can be distinguished from one another by their end groups. For example, the Hawker initiator (6, page 5) produced polystyrene with a benzoyloxy group on one end and a TEMPO group on the other. Thermal initiation in the presence of TEMPO gives polystyrene with a mixture of endgroups that arise from the Mayo dimer mechanism (9 and 10) and TEMPO on the reactive end of every polymer chain. The commercial initiator 11 yields polystyrene with a phenylethane and TEMPO endgroup pair. Samples are represented by these endgroups with B-PS-T (benzoyloxy-polystyrene-TEMPO) being made in a process such as that of Scheme 5. The M-PS-T (Mayoadduct-polystyrene-TEMPO) represents the autopolymerization of Scheme 4. Finally, E-PS-T (phenylethane-polystyrene-TEMPO) is the product of the commercial initiator in Scheme 6, and the end-capped products appear as B-PS-C_{60}, M-PS-C_{60}, and E-PS-C_{60}, respectively.

CHAPTER II

EXPERIMENTAL

Materials. A sample of C_{60} in greater than 99.5% purity was obtained from MER Corporation. The *o*-dichlorobenzene, tetrahydrofuran (THF), hexanes, and methanol were used as received. Styrene monomer was distilled under vacuum and passed through an alumina plug prior to use. Benzoyl peroxide (Aldrich) and TEMPO (Aldrich) were used as received. The d_8-styrene (Aldrich, 98+% D content) was passed through alumina and analyzed by ^{1}H NMR before use, with referencing to the residual *cis* vinyl proton whose signal appeared at 5.21 ppm in styrene (Figure 1). The methylene signals at 5.21 and 5.78 ppm have about twice the area per mole of hydrogen when compared to the aromatic (7.2-7.6 ppm) and methine (6.65 ppm) signals. The commercial initiator **11**, 1-phenyl-1-(2,2,6,6-tetramethyl-1-piperidinyloxy)-ethane, was obtained from Binrad Industries, Inc. and used as recieved.

Measurements. Size exclusion chromatography was performed with a Hewlett-Packard series 1100 chromatograph equipped with a diode array UV-vis detector and with one or three 30 cm PLgel 10 μm mixed-B columns (Polymer Laboratories, Amherst, MA) thermostated at 25 °C or 40 °C. The eluent was THF and chromatograms were obtained at a flow rate of 1 mL min^{-1}. Samples containing 5 mg mL^{-1} of polymer in THF, were filtered through a 0.2 μm micropore membrane and injected in 20 μL aliquots. The chromatograms were analyzed using a first-order polynomial and the GPC macro of the HP Chemstation calibrated with polystyrene standards of 800, 2000, 9000, 17500, and 100000 MW. Linear polystyrene equivalent molecular weights of the samples were measured via UV detection at 218, 260, 300, and 330 nm.

NMR spectra were aquired on a Varian Gemini spectrometer that operates at 300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR. The signals were referenced to TMS using CDCl$_3$ as solvent unless otherwise stated.
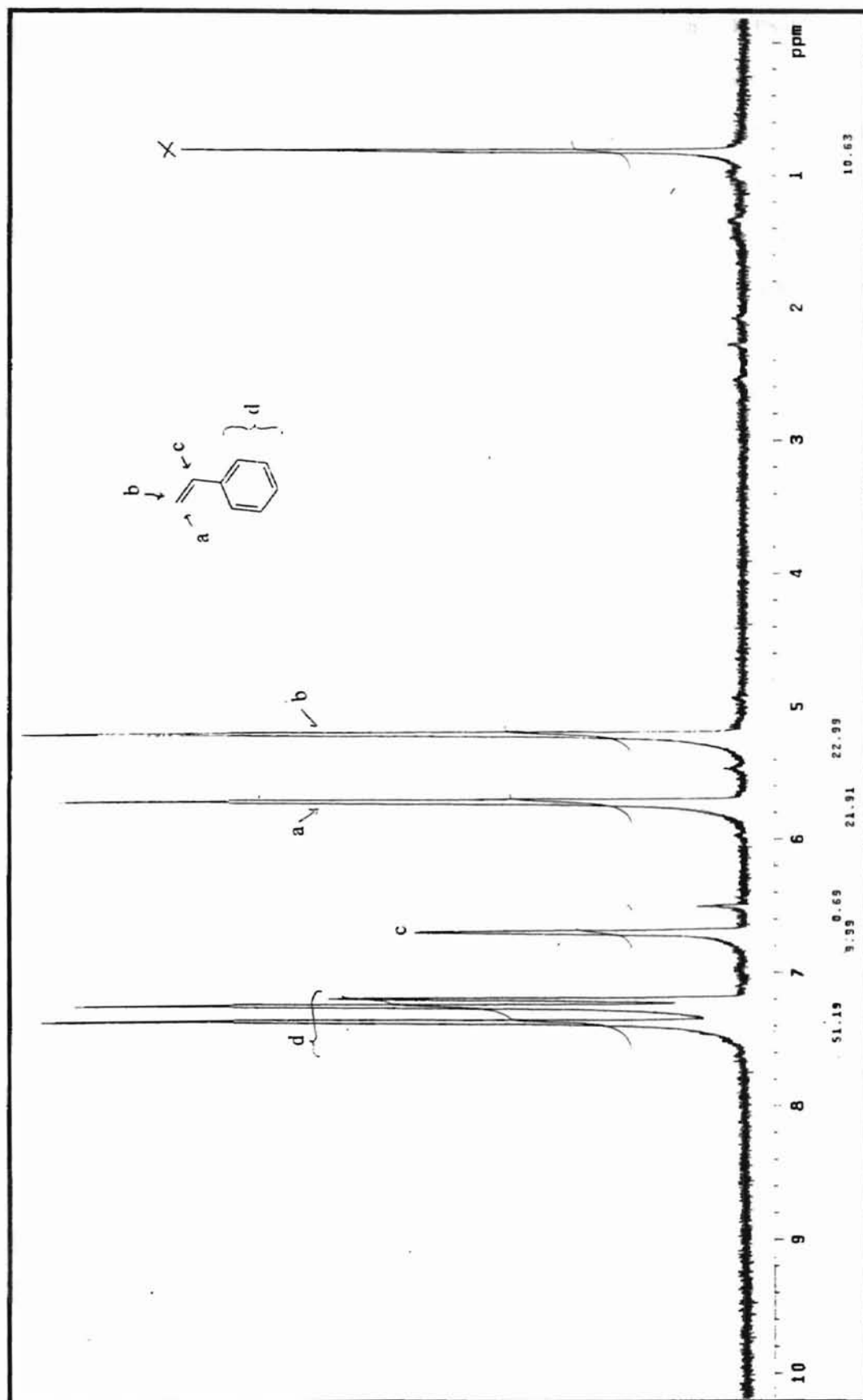
Figure 1. ¹H NMR spectrum of deuterated styrene.

ω-**Benzoyloxy-1-(2,2,6,6-tetramethylpiperidine-1-oxy)polystyrene (B-PS-T).** A 1:100:1.2 molar mixture of 968 mg of BPO (4 mmol), 41.6 g of distilled styrene (0.4 mol), and 748.8 mg of TEMPO (4.8 mmol) was mixed together, divided between two thick-walled glass tubes and freeze-thaw degassed three times under vacuum. A small portion of the solution was transferred to a 5 mm NMR tube and sealed at atmospheric pressure, and the larger tubes were sealed under vacuum. The three were heated in an oven at 95 °C for 5 hours. The tubes were moved to a 130 °C oven for 13.5 h. One of the larger tubes was opened, and the solution was pipetted dropwise into methanol, and then centrifuged. The methanol was decanted, and the polymer was redissolved in minimal dichloromethane. Precipitations were done three times into methanol, once into hexane, and then once again into methanol. Minimal methylene chloride was used to dilute or dissolve the polymer between precipitations. The other tube was stored in the freezer at 0 °C. The final product **13** was about 15 g of the vacuum dried white-tan precipitate (B-PS-T). Assuming half of the sample was treated with isolation techniques, 69% of that half of the styrene was recovered as polymer.

ω-**Benzoyloxy-1-(2,2,6,6-tetramethylpiperidine-1-oxy)polystyrene/styrene (B-PS/S-T).** B-PS/S-T indicates benzoyloxy-polystyrene-TEMPO containing styrene monomer. A 1.2:100:1.2 or 1:100:1.2 molar mixture of 112.8 mg of benzoyl peroxide (0.466 mmol) or 96.8 mg of BPO (0.40 mmol), 4.16 g of distilled styrene (40 mmol), and 74.8 mg of TEMPO (0.479 mmol) was prepared as described above and similarly heated for 10 hours. These samples - B'-PS/S-T and B-PS/S-T, respectively - were used without isolation from monomer for end capping experiments ((1,2 and 4)B'-PS/S)-C_{60} and ((2 and 2')B-PS/S)-C_{60}.

2-Benzoyloxy-1-phenyl-1-(2,2,6,6-tetramethyl-1-piperidinyl-oxy) ethane (6) (B*-PS-T). A solution containing 3.138 g of benzoyl peroxide (12.9 mmol), 125.6 mL of distilled styrene (1.09 mol), and 4.46 g of TEMPO (28.5 mmol) was heated for 20 hours at 80 °C under nitrogen and rotary evaporated down to about 7 mL of a viscous brown liquid. Refer to Scheme 2 of the Introduction. This solution was separated by column chromatography using 118 g of 60-200 mesh silica gel and 13% dichloromethane and 87% hexane to give about 20 fractions. All fractions from the column were examined via ¹H NMR analysis which showed that the solution contained 77 mg of compound **6**. The 77 mg of this initiator was

used to polymerize 3 mL of styrene. The initiator and the styrene were transferred to a thick-walled glass tube, freeze thaw degassed three times, sealed under vacuum, and heated for 72 h at 130 °C to give 1.694 g of TEMPO-terminated polystyrene **12** refered to as B*-PS-T (pure(*)benzoyloxy-polystyrene-TEMPO).

TEMPO-terminated polystyrene by thermal initiation (M-PS-T). A 51.2 mg aliquot of TEMPO (0.32 mmol) in 3.0 mL of styrene (26.2 mmol) was freeze thaw degassed and sealed under vacuum in a heavy walled glass tube. The tube was placed in a 130 °C oven for 24 h. The samples of TEMPO-terminated polystyrene were separated from monomer by pipetting the solution dropwise into approximately 300 mL of hexane, followed by centrifuging, and decanting. The polymer was redissolved in minimal dichloromethane and precipitated again into hexane and twice into methanol using minimal dichloromethane to dissolve the polymer. The final product was 1.035 g of the vacuum-dried white-tan precipitate (M-PS-T).

1-Phenylethyl-polystyrene-TEMPO (E-PS-T, E-dPS/S-T, and E-dPS-T). This reaction was initiated with 103.2 mg of 1-phenyl-1-(2,2,6,6-tetramethyl-1-piperidinyloxy)ethane (0.398 mmol) (Binrad Industries, Inc.). Deuterated styrene (8 mmol), 896 mg, or styrene (832 mg) was added to the initiator in a heavy-walled, glass tube. The sample was degassed and transferred to an NMR tube which was then sealed and finally placed in an oven (130 °C) for 30 h to reach about 50% conversion. The polymer was isolated from monomer by pipetting it dropwise into methanol in the case of samples E-PS-T and E-dPS-T while sample E-dPS/S-T was not isolated from monomer. A white powdery solid precipitate (high MW polymer, used in later experiments) was recovered from the Whatman number four filter paper, and the supernatant was evaporated down to a white powder residue (low MW polymer). The two components were heated gently and dried under vacuum for several hours. See Results section for respective yields.

Chain extension test. [23] A solution of 100 mg (10 weight percent, or 1 mole equivalent) of sample B-PS-T was stirred together with 900 mg of styrene (90 weight percent, or 605 mole equivalents). This solution was freeze/thaw degassed three times, sealed under vacuum, and heated at 130 °C for 24 hours. Cooling to room temperature left a solid cylinder of polystyrene. The solid polymer product was analyzed with SEC.

End-capping reactions. Unless otherwise stated, C_{60} and the polymer were dissolved in *o*-dichlorobenzene with the aid of mechanical stirring. Various molar ratios were used and heating times were varied. See Results for specific details and Scheme 7 of the Introduction for a representation of the reaction.

The reaction mixtures were freeze thaw degassed three times under vacuum and sealed under vacuum in a thick-walled glass tube. After reaction, the polymers were isolated by two precipitations into hexane, the first of which usually left a pale purple hexane solution, and two precipitations into methanol, followed by vacuum drying to constant weight.

All of the previously mentioned reactions followed this general scheme with two exceptions, [2'(B-PS/S)-C_{60} and 2'(B-PS)-C_{60}], which were isolated by two precipitations into methanol only. After drying they were redissolved into *o*-DCB and transferred back into a sealing tube where they were freeze thaw degassed three times and then sealed under vacuum. The sealed tubes were then returned to the 130 °C oven for an additional 24 hours. Isolation of the resulting polymer was carried out as described before by two precipitations into hexane and two into methanol. See Results section for yields.

End-capped 1000 MW living polystyrene (LPS). A mixture of 100 mg of C_{60} (0.138 mmol) and 100 mg (0.138 mmol - assuming $P_n = 720$) of LPS (E-PS-T or E-dPS-T) was dissolved in 20 mL of *o*-DCB with stirring. The solution was transferred to a thick-walled glass tube, freeze thaw degassed three times and sealed under vacuum. These mixtures were heated in a drying oven at 130°C for three days. The tubes were removed from the oven and opened, and the work-up procedure was immediately followed. First, the oDCB was rotary evaporated to as close to dryness as could be achieved with the aid of a 99 °C water bath, 0°C water condenser, and a vacuum pump. THF was added to the black material caked onto the walls of the flask to dissolve the polymer. A fine, black powdery substance - presumably unreacted C_{60} - was filtered away from the clear brown supernatant using Whatman number four filter paper. The THF was rotary evaporated away from the supernatant leaving a dark brown coating in the flask. Using minimal dichloromethane, the remaining polymer was dissolved in the flask and pippetted dropwise into stirring methanol. The precipitate was collected by filtration, and the supernatant was allowed to evaporate leaving the methanol soluble components of the reaction. These components were dried at 45 °C in a vacuum

desiccator for several hours. See the Results section for yields of 2(E-PS)-C$_{60}$, 2(E-dPS/S)-C$_{60}$ and 2(E-dPS)-C$_{60}$.

TEMPO trapping reactions. As an example, an approximate 2:1:2 molar mixture B-PS-T (502 mg - 0.068 mmol - P_n = 6400), 24.8 mg of C$_{60}$ (0.034 mmol), and 7.02 mg of acetic anhydride (AA, 0.068 mmol), were dissolved in 7 mL of oDCB with stirring. The solution was transferred to a thick-walled glass tube, freeze thaw degassed three times, sealed under vacuum and then heated for 24 hours at 130 °C. The product 1AA was isolated by precipitating twice into hexanes and twice into methanol followed by vacuum drying.

RESULTS

Living polystyrene with benzoyloxy and TEMPO endgroups. The preparation and separation of the benzoyloxy ended initiator (**6**) was first described by Hawker.[18] The molar ratios (1:85:2.2) described in the reference were slightly changed to 1:85:2.8. The viscous brown liquid that was separated by column chromatography produced a number of fractions which had to be concentrated, tested with thin-layer chromatography, and combined where appropriate. ^{1}H NMR analysis of one of the fractions (Figure 2) showed it to be the purified "Hawker initiator". The ^{1}H NMR spectrum of this compound shows a broad signal between 0.5 and 1.8 ppm resulting from the piperidinyl methylene protons and four sharp peaks rising out of the signal characteristic of the four diastereotopic methyl groups of the TEMPO moiety. Also of interest are the three aliphatic protons of the styrene group that appear between 4.50 and 5.20 ppm. Hawker explains this downfield signal as a result of the deshielding effect of the nearby oxygen atoms.[18] The signals from the four methyl groups, as well as the three single proton signals change as polymerization occurs. Other small signals in the spectrum at 4.2, 4.3, and 6.2 ppm are not from the desired compound and most likely result from some small conjugated impurity. The procedure produced 77 mg of this initiator which was eventually used to polymerize three mL of styrene. One third of the
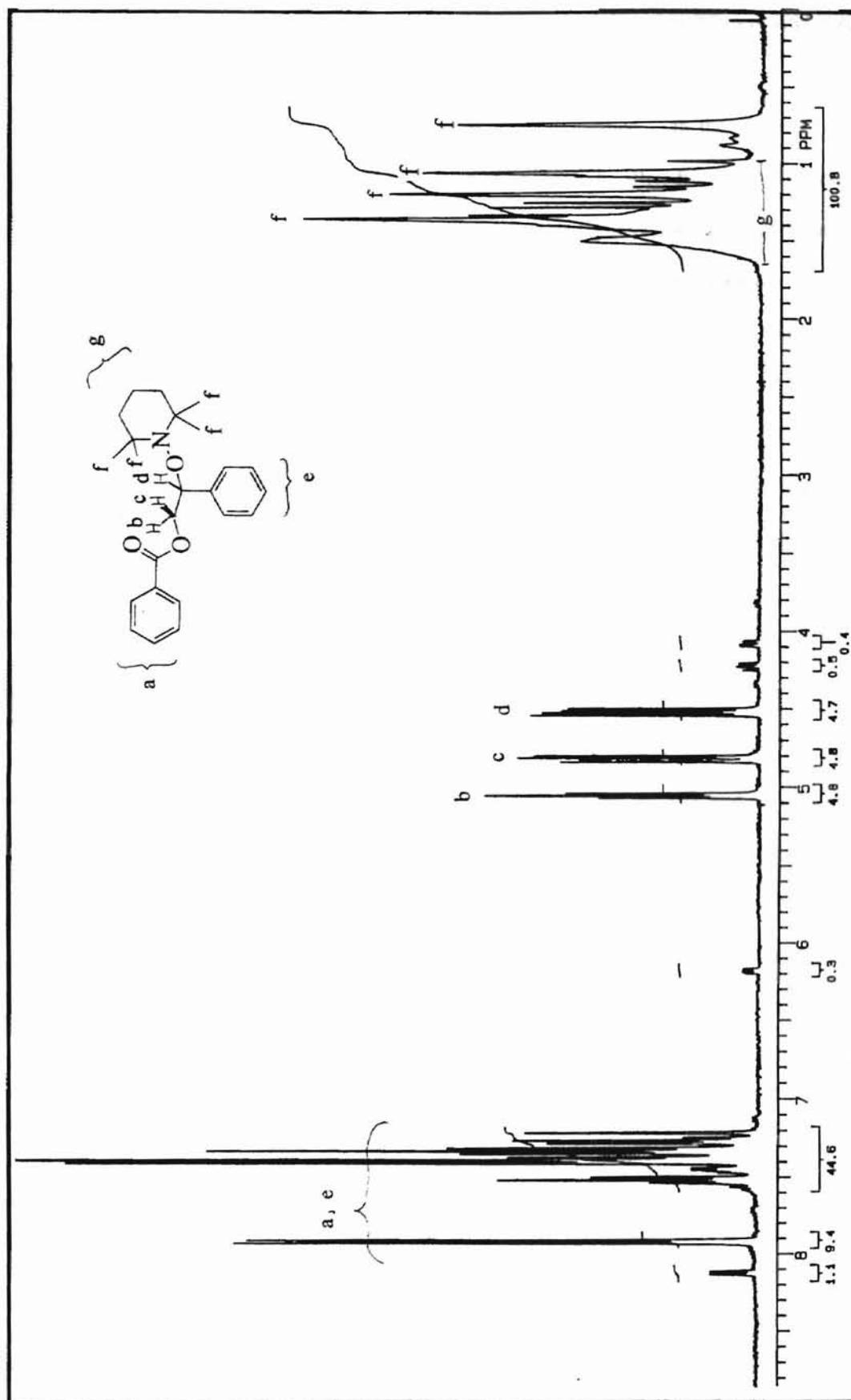
Figure 2. ^{1}H NMR spectrum of the Hawker initator.

crude sample **6** was set aside for analysis. The product yield of the other 2/3 was 1.69 g of TEMPO-terminated polystyrene (B*-PS-T) with P_n(polystyrene equivalent molecular weight) = 11,300.

(B'-PS/S-T) and (B-PS/S-T). This synthesis was modified from the procedure described by Yoshida and Yasushi[24] which used MTEMPO instead of TEMPO. It differs from that of Hawker in that the initiator is not purified. We believed that by lowering the temperature of the end-functionalization reaction, the remaining monomer would not polymerize during the end-capping procedure. The progress of the polymerization was followed with a sample in an NMR tube. Conversion of about 52% occurred after 10 hours (determined by ^{1}H NMR integrations of the aromatic and alkene signals). This sample was used for end-capping reactions ((1,2 and 4)B-PS/S)-C_{60} and ((2 and 2')B-PS'/S)-C_{60}.

(B-PS-T). A larger scale production of the previous sample was accomplished in this polymerization. However, monomer was removed by repeated precipitations of the polymer into methanol and hexane as described in the Experimental. After 13.5 hours, about 76% conversion had been reached. The yield was approximated since only half of the sample was isolated from monomer while the other half was stored at 0 °C. The SEC showed P_n = 6400 and P_w = 9900. This TEMPO-terminated polystyrene sample was used to test and improve other aspects of the reaction between it and C_{60}. Further reactions involving this sample can be found in the sections on the chain extention test, end capping reactions, and TEMPO trapping reactions.

Living polystyrene without initiator (M-PS-T). Since the isolated yield of the Hawker initiator was very low, we tried an alternate method for producing TEMPO-terminated polystyrene where no formal initiator was used. Styrene undergoes thermal self-initiation starting with a Diels-Alder reaction. The mechanism of this reaction was proposed in the late 1960's[25] and confirmed in 1983.[19] It produces what has been termed the "Mayo Dimer." In the presence of excess TEMPO, styrene polymerization is inhibited at first because the TEMPO traps polystyryl radicals. Once the TEMPO has been consumed, the polymerization proceeds at normal TEMPO-mediated rates.[15] In this reaction, 3.0 mL of styrene and 51.2 mg of TEMPO achieved 48 % conversion after 24 hours. See Figure 3. The samples of this living polystyrene were isolated from monomer and produced 1.035 g of product. This sample was used for end-capping reactions (0.5,1,2 and 4)(M-PS)/C_{60}.
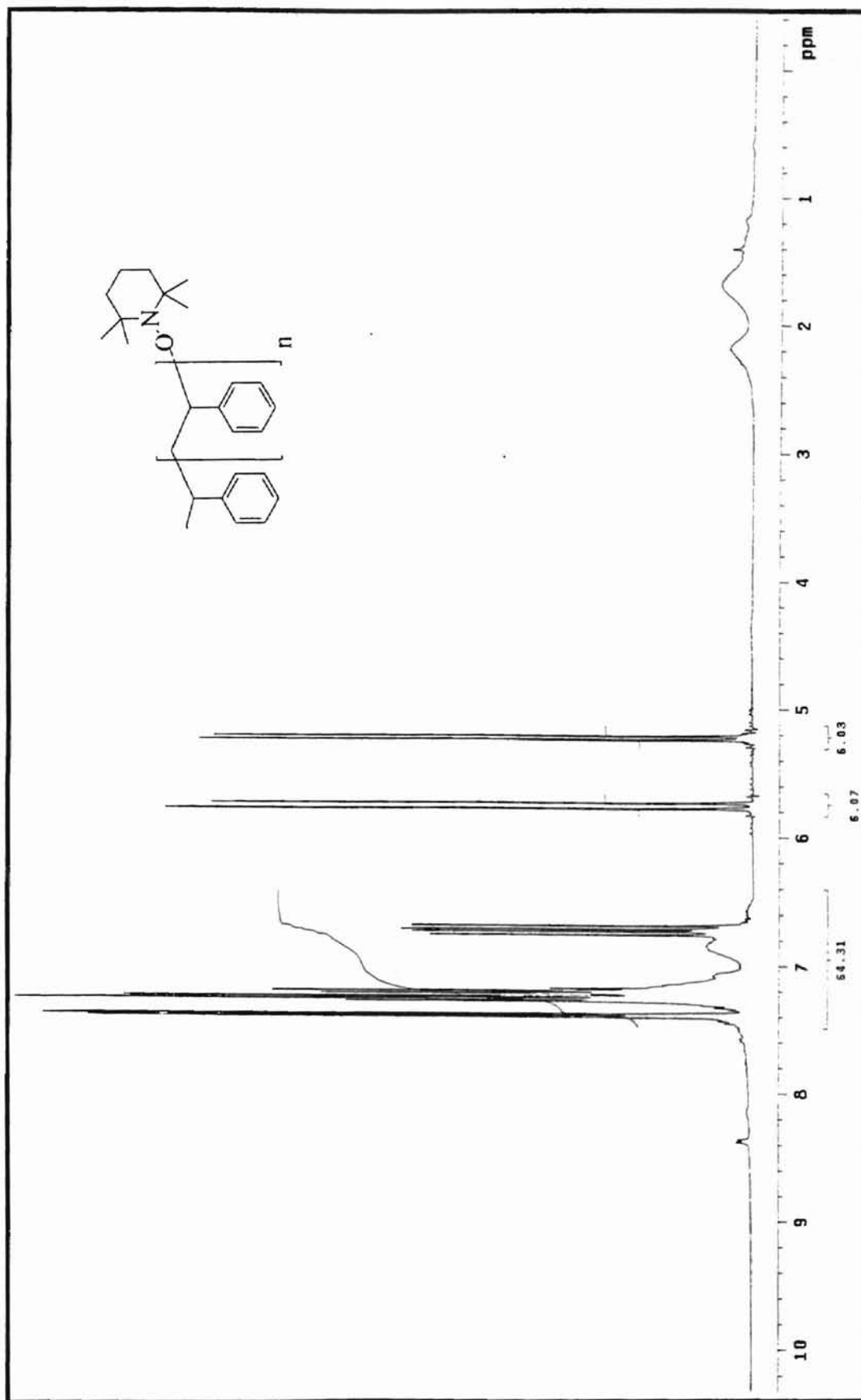
Figure 3. ^{1}H NMR spectrum of M-PS-T.

Table 1. Preparations of TEMPO-terminated polystyrene.

Sample	BPO mg (mmol)	Styrene g (mmol)	TEMPO mg (mmol)	Recovery	P_w	P_n
6	3138	114.17	4460	77 mg	N/A	N/A
B*-PS-T	0.0	2.73	0.0	1.69 g		11,300
B'-PS/S-T	112.8 (0.47)	4.16 (40)	74.8 (0.40)	1.640 g[a]	8,700	7,100
B-PS/S-T	96.8 (0.40)	4.16 (40)	74.8 (0.40)	1.97 g	6,000	3,900
B-PS-T	968 (4.0)	41.6 (400)	748.8 (4.0)	15 g	9,900	6,400
M-PS-T	0.0	2.73	51.2	1.035 g[a]	9,000	7,400

[a] Theoretical value based on calculations from starting materials and % conversion calculated from integration of aromatic and alkene signals in the ^{1}H NMR spectrum.

Living polystyrene with 1-phenylethyl end groups (E-PS-T, E-dPS/S-T, and E-dPS-T). The Hawker initiator and other similar molecules proved to be the most viable initiating systems for free-radical living polymerizations of styrene. In these reactions, 103.2 mg of 1-phenyl-1-(2,2,6,6-tetramethyl-1-piperidinyloxy)ethane (11, Figure 4), a commercially available initiator and offspring of the Hawker initiator was used with 896 mg of deuterated styrene (E-dPS/S-T and E-dPS-T) or 832 mg of protonated regular styrene (E-PS-T) to achieve 1000 molecular weight (14, see page 9).

The quantities used in these reactions fit into an NMR tube and so one was used as the reaction vessel. ^{1}H NMR spectrum was taken of the initiator dissolved in the deuterated monomer, with no added solvent, the sample after 30 hours of heating and diluted with CDCl$_3$, and the methanol insoluble portion after isolation from monomer (Figure 5 A,B and C, respectively). Several results were obtained from these spectra. Confirmation of 50% conversion of the styrene, 98.7% deuteration of the enriched styrene, and negligible contribution of polymer signals to the aliphatic region were calculated from the integration values.

A 20-molar excess of styrene-to-initiator allowed polymers that reached 50 % conversion to have a molecular weight of about 1000. The low molecular weights allow end-group analysis with less interference from aliphatic polymer signals. The spectrum of initiator dissolved in deuterated styrene (Figure 5A) provided a quantitative measure of possible polymer contribution to the aliphatic region where
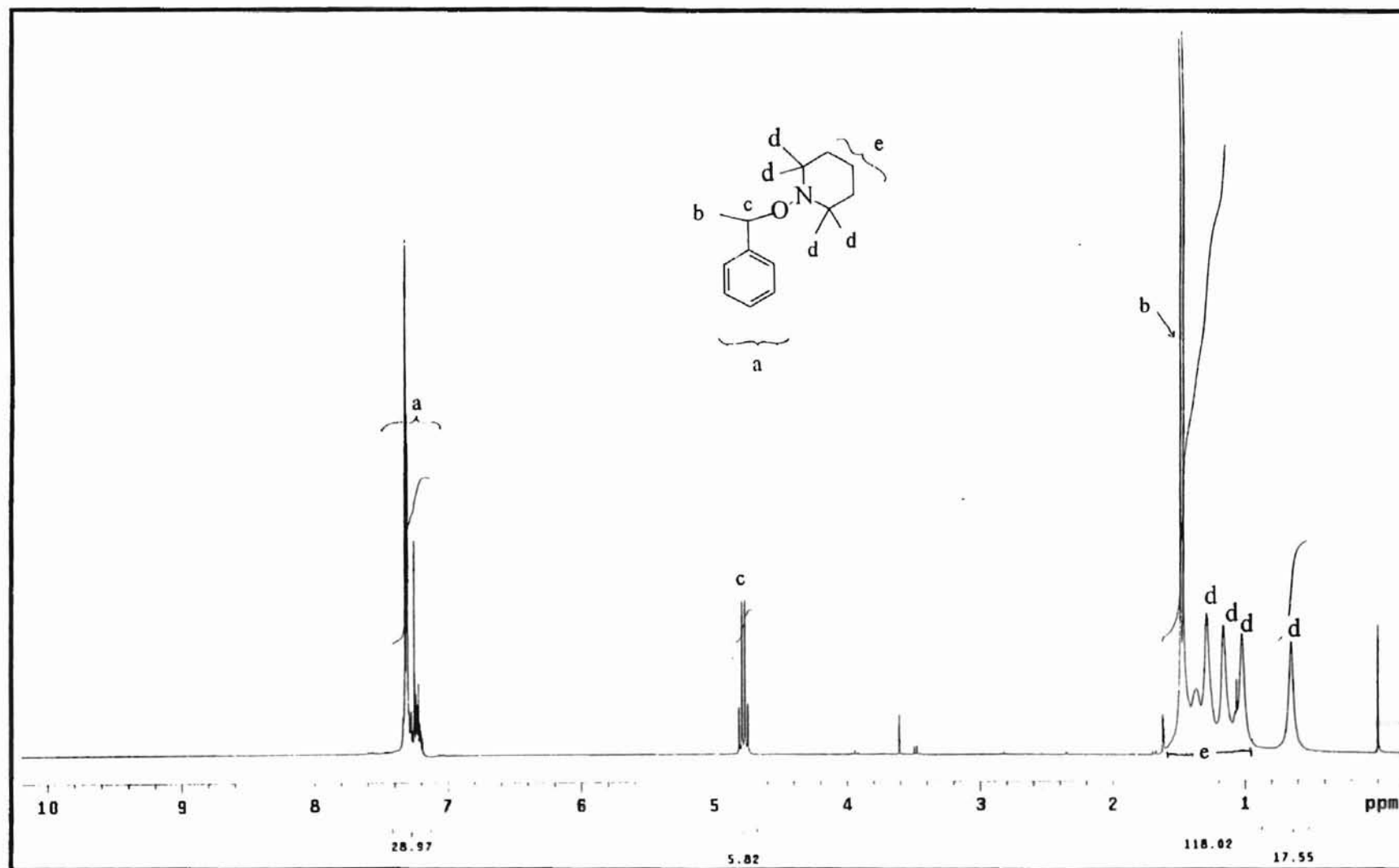
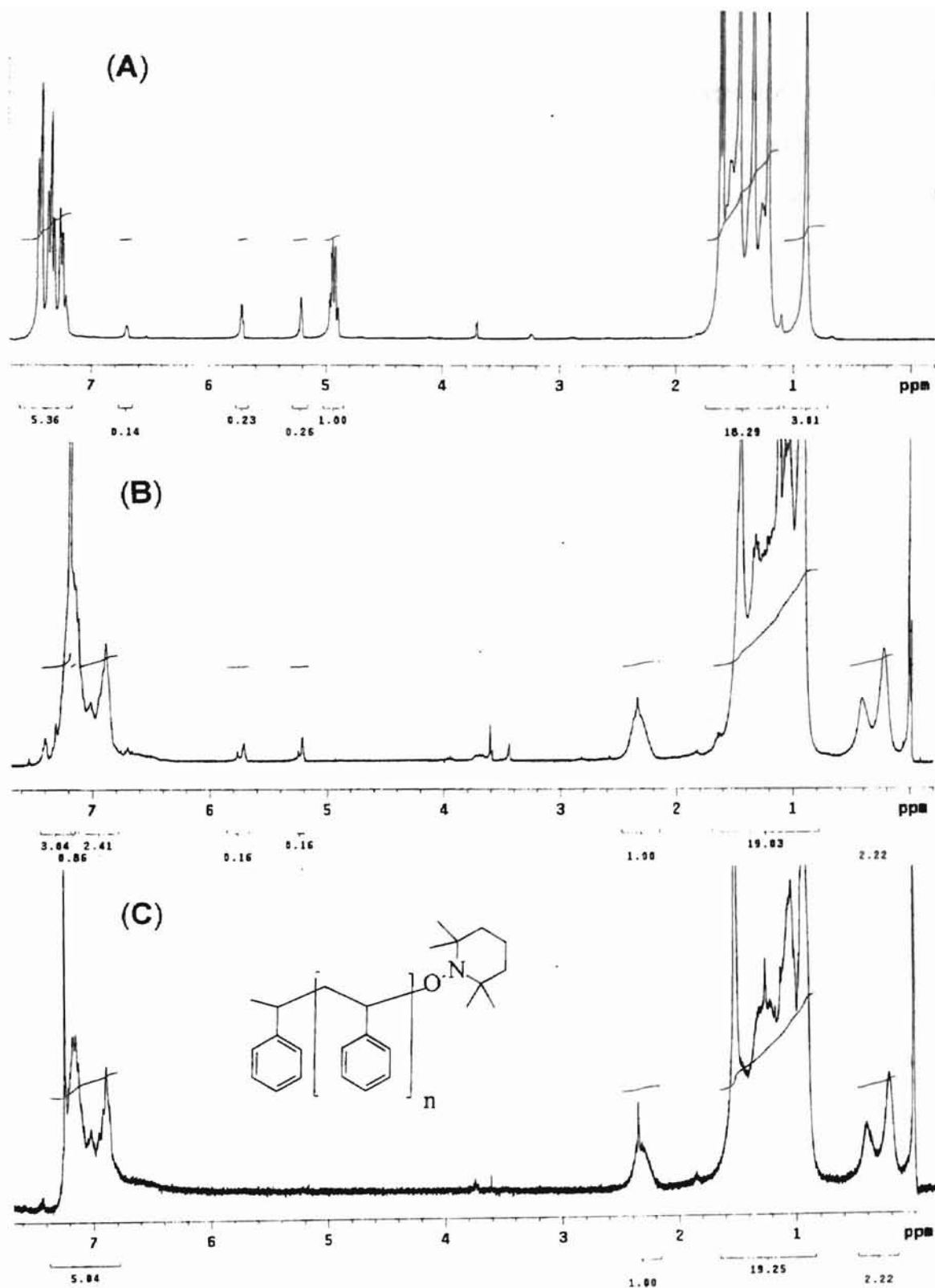Figure 4. ^{1}H NMR spectrum of commercial initiator in CDCl$_3$.

Figure 5. ^{1}H NMR spectra of initiator in deuterated styrene (**A**),
after 30 hours at 130 ^{o}C (**B**), and methanol insoluble
component (**C**).

only TEMPO signals should be. The spectrum 5A is normalized to the 4.99 ppm signal of the phenethyl end group. The four non-equivalent methyl groups of the TEMPO end-group are clearly visible at 0.95, 1.24, 1.40, 1.56 ppm in Figure 5A. The methyl group on the 1-phenylethyl end of the initiator is the doublet at 1.72 ppm coupled to the single methine proton quartet at 4.99 ppm. Signals from single protons on monomer are also visible at 5.21, 5.78 and 6.70 ppm. Polymer aliphatic protons, which came from methylene and methine monomer protons, can not contribute more than about 2% of the signal in the aliphatic region of Figure 5B after 50% conversion if the TEMPO end group is retained completely in the polymer. Isolation of polymer from monomer produced in each case two samples - methanol soluble and methanol insoluble components (Figure 5C). SEC analyses of these polymers are reported in Table 2.

Table 2. Living polystyrene made with commercial initiator.

Sample	Initiator	Styrene	MeOH insol.	SEC P_n @ 260 nm	MeOH sol.	SEC P_a @ 260 nm
E-PS-T	103.6 mg	832 mg	481.3 mg	790	31.6 mg	520
E-dPS/S-T	103.6 mg	896 mg	115.0 mg	730	*	*
E-dPS-T	103.6 mg	896 mg	615.8 mg	1200	91.7 mg	790

* not isolated into methanol.

Measurement of molecular weights by size exclusion chromatography (SEC). Molecular weights of polymer samples are statistical averages.[26] The *number average molecular weight* (M_n) is based on the number of polymer molecules in a sample and is determined by measuring colligative properties such as vapor pressure lowering, freezing point depression, boiling point elevation, and osmotic pressure. M_n is defined by the following equation.

$$\overline{M_n} = \frac{\sum N_x M_x}{\sum N_x} \qquad (1)$$

The summations encompass all the different lengths of polymer molecules, and N_x is the number of moles whose molecular weight is M_x. The *weight average molecular weight* (M_w) is determined by the angular and concentration dependence of scattered light intensity and is defined as follows.

$$\overline{M_w} = \sum w_x M_x \qquad (2)$$

Where w_x is the weight-fraction of molecules whose weight is M_x. Since the optical absorbance of a homopolymer sample is directly proportional to its weight, the value, w_x, can be calculated by the following equation.

$$w_x = \frac{Abs_x}{\sum Abs_x} \qquad (3)$$

Polymers are further described by the distribution of the molecular weight or polydispersity, M_w/M_n where the closer this ratio is to unity the more monodisperse the polymer sample. Polymer molecular weights are measured with SEC equipment and this is reflected in the data by reporting P_n and P_w - the polystyrene standard equivalent molecular weight - instead of M_n and M_w.

SEC interpretation. Size exclusion chromatography is routinely performed with refractive index and ultraviolet detectors to determine the molecular weight averages. The instrument is calibrated with standards of narrow polydispersity polystyrene. Typically four or five standards are used to generate a calibration curve. From the calibration, the software interpolates absolute molecular weight at every retention time of the chromatogram. Absorbance is directly proportional to concentration, and this quantity is used to calculate N_x, $N_x = Abs_x/M_x$. Greater absorbance means a greater abundance of material at that retention time or more polymer chains at a specific molecular weight. Figure 6 is an example of a typical chromatogram. The sample has P_n = 6400, P_w = 9900, and P_d (polydispersity) = 1.4. This particular polymer was created with living polymerization techniques.
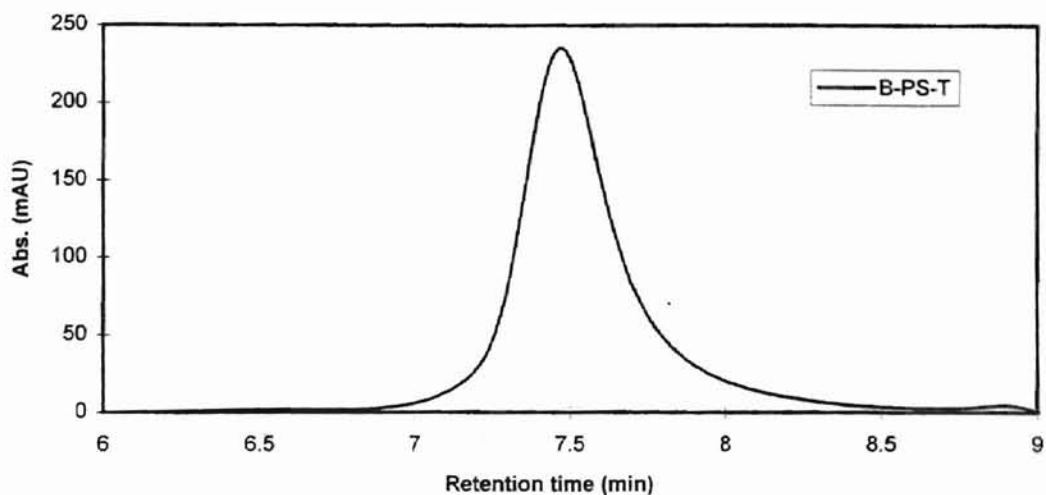
Figure 6. SEC profile of a straight chain (Pn = 6400) polystyrene from one mixed B column.

Interpreting chromatograms of polymers is not always so straight-forward. The SEC technique separates by hydrodynamic volume. Branched or star-shaped architectures have different masses of chains per hydrodynamic volume from linear random coil polymers such as in the polystyrene standards. These variations in form affect the physical properties and cause special considerations when measuring molecular weights. The data included in the end-capping reactions section also needs special consideration because the products are mixtures of various numbered substitutions of linear polystyrene chains onto a C_{60} molecule which is evident by the shoulders and overlapping peaks in these chromatograms. Although different columns and column combinations were tried, baseline separation of the samples was not achieved. The result is illustrated in Figure 7.
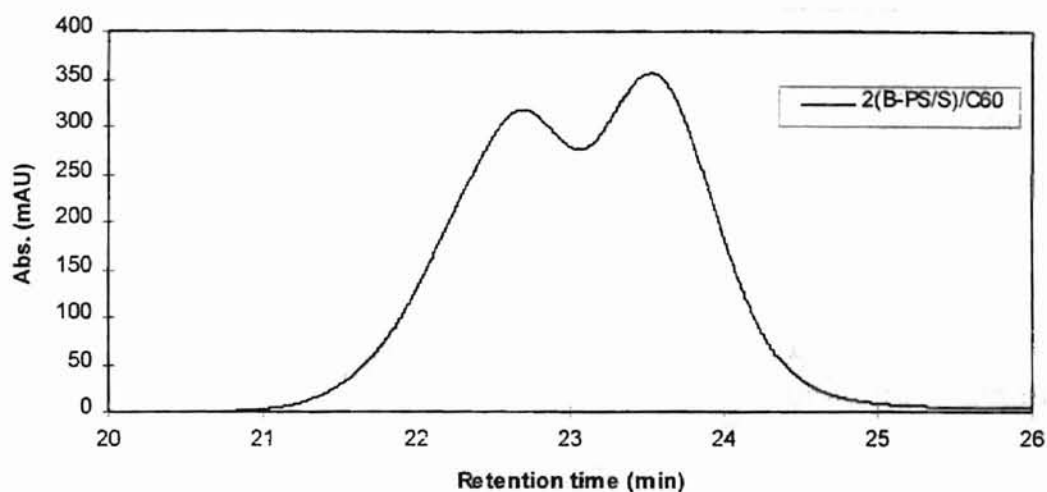
Figure 7. An example of a SEC profile of two overlapping peaks from three mixed B columns.

The molecular weights of components with overlapping peaks cannot be calculated accurately. To extract the maximum amount of accurate data from these chromatograms, the latter were simulated as the sum of two gaussian peaks using a program called Tablecurve. This peak fitting program requires the user to specify the dimensions of the Gaussian peaks which are height, center and width. Once the simulated data closely matches the actual data, further calculations can be done to determine the contribution of the peaks to the total area. This procedure was performed on the chromatogram shown in Figure 7, and the results are represented pictorially in Figure 8.
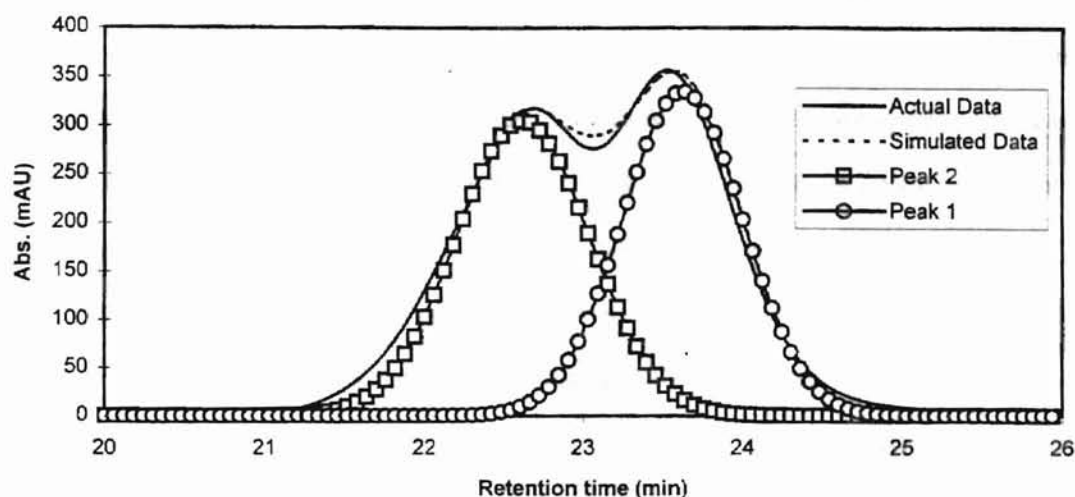
Figure 8. Simulation of the chromatogram of Figure 7.

In this example, peak 2 (P(2)) and peak 1(P(1)) are Gaussian peaks with height, center and width of 306, 22.62, and 0.42 for P(2) and 335, 23.62, and 0.38 for P(1). Using the simulated data in an Excel speadsheet, the molecular weights of the components were calculated using equations 1-3 ($P_n(2)$ = 14000 and $P_n(1)$ = 6000). P_w's were 16000 and 6600 for P(2) and P(1) respectively. The polydispersities ($P_d(2)$ = 1.14 and $P_d(1)$ = 1.10) is lower than the starting polymer simply because the actual chromatograms are not truly Gaussian. The contributions of P(2) and P(1) to the total area are 50 and 49.7% respectively. Table 7, which appears in the Appendix contains the fitted equations and integrated values of the peaks.

The molecular weights corresponding to the retention time values at the peak tops closely approximate the P_n and P_w values calculated from the simulations. These relative molecular weights are called P_t. $P_t(2)$ = 15000 and $P_t(1)$ = 6300 for the chromatogram of Figure 8. These values are not averages, rather they are the molecular weights of the most abundant fractions of the polymer. It will be referred to as P_t and reported instead of P_n and P_w when peak-overlapping occurs since the P_t value is within experimental error of the fitted data.

Finally, the two components of the end-capped polymers - polystyrene and C_{60} adducts- have different absorption spectra. We assume that polystyrene and C_{60}-derivatives absorb at 260 nm

proportionally to the weight of the sample regardless of the fullerene content. The assumption is reasonable is the weight fraction of fullerene is very small or if the absorbance per weight of fullerene equals the absorbance per weight of polystyrene. Comparison of the chromatograms at both of these wavelengths reveals relative amounts of fullerene in the high and low molecular weight components of the sample. Moreover, at 330 nm, peaks overlap and data must be simulated to report area contributions and P_t molecular weights. Using the area contributions from simulated data, we are able to calculate the percent of unreacted LPS that remains in the sample after isolation procedures.

Chain extension test. As described by Fukuda *et a.l,*[23] 10 weight percent of the TEMPO-terminated polystyrene (B-PS-T) was stirred together with 90 weight percent styrene at 130 °C for 24 hours. The product was a solid polymer (CET, P_n = 109100) whose SEC is shown in Figure 9 overlaid with the SEC of the starting polymer (B-PS-T, P_n = 6400). The chromatogram shows some residual area at the same retention time as the starting polymer. This residual area is 9.8% of the total area of the CET chromatogram. The original B-PS-T sample contained 62.5 mole% unreactive or dead polymer.
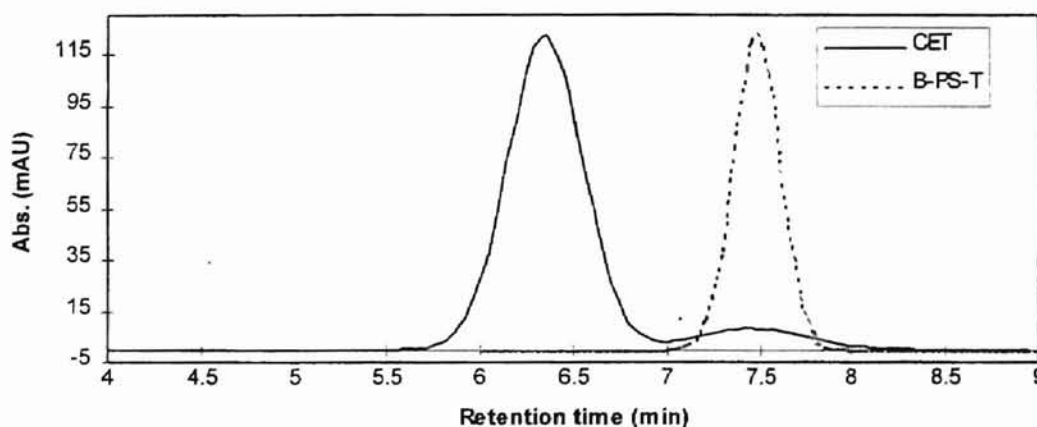
Figure 9. SEC overlay of B-PS-T (—) and chain extention test (—)product.

End-capping reactions. The following Table 3 contains information on all reactions where LPS samples were reacted with C_{60}. Further sections include comparisons between results from different batches of TEMPO-terminated polystyrene to insure that end-capped samples having different endgroups could be compared. Samples reacted in the presence of residual monomer were useful indicators of what

these reactions do when a radical trap is present. Those data are compared to similar samples where polymer was isolated from monomer. We investigated the possibility that increasing amounts of LPS would initiate more reactions to occur with C_{60} by use of molar ratios of approximately 1, 2 and 4 LPS to 1 C_{60}. The reheat method - where samples are heated for a time, isolated from solvent, then redissolved and heated again - was investigated to determine the effect of removing residual TEMPO. We tried different temperatures and reaction times and compared results from sonicating solutions versus stirring them. Table 3 reports the reaction conditions and amounts of products isolated.

Table 3. Experimental Conditions for End-capping Reactions.

Entry	Sample	Molar Ratio[a]	time hours	temp. °C	LPS (mg)	C_{60} mg	oDCB ml	Recovery mg
1	2(B*-PS)/C_{60}	2.18:1	96	80	250	7.3	1	107.5
2	2'(B*-PS)/C_{60}	2.18:1	72	130	250	7.3	1	117.9
3	1(B'-PS/S)/C_{60}	1.06:1	24	80	860	61.9	7	317.5
4	2(B'-PS/S)/C_{60}	2.13:1	24	80	860	30.9	6	292.9
5	4(B'-PS/S)/C_{60}	4.25:1	24	80	860	15.5	5	375.5
6	2(B-PS/S)/C_{60}	2.27:1	24	100	1040	37.4	6	152
7	2'(B-PS/S)/C_{60}	2.27:1	24	100	1040	37.4	6	103.5
8	2(B-PS)/C_{60}	2.14:1	24	100	502	24.8	6	237.1
9	2'(B-PS)/C_{60}	2.14:1	24	100	502	24.8	6	2.7[c]
10	1A(B-PS)/C_{60}[b]	1.07:1	15	130	502	49.6	7	225.7
11	2A(B-PS)/C_{60}[b]	2.14:1	15	130	502	24.8	7	301.5
12	4A(B-PS)/C_{60}[b]	4.29:1	15	130	502	12.4	7	256.5
13	1B(B-PS)/C_{60}[b]	1.07:1	120	100	502	49.6	7	232.1
14	2B(B-PS)/C_{60}[b]	2.14:1	120	100	502	24.8	7	248.5
15	4B(B-PS)/C_{60}[b]	4.29:1	120	100	502	12.4	6	261.1
16	1C(B-PS)/C_{60}	1.07:1	168	130	502	49.6	6	211.0

| 17	2C(B-PS)/C$_{60}$	2.14:1	168	130	502	24.8	6	251.3
18	4C(B-PS)/C$_{60}$	4.29:1	168	130	502	12.4	6	222.3
19	1D(B-PS)/C$_{60}$	1.07:1	24	130	502	49.6	6	79.2[c]
20	2D(B-PS)/C$_{60}$	2.14:1	24	130	502	24.8	6	16.5[c]
21	4D(B-PS)/C$_{60}$	4.29:1	24	130	502	12.4	6	37.4[c]
22	0.5(M-PS)/C$_{60}$	0.5:1	24	130	258.9	106.1	9	151.2
23	1(M-PS)/C$_{60}$	1:1	24	130	258.9	53.1	9	197.2
24	2(M-PS)/C$_{60}$	2.01:1	24	130	258.9	26.5	6	180.2
25	4(M-PS)/C$_{60}$	4:1	24	130	258.9	13.3	4	200.4

[a]The molar ratio of living polystyrene to C$_{60}$.
[b]Sonicated to dissolve C$_{60}$.
[c]Less recovery because only a portion of the sample was isolated.

When we interpret these chromatograms, we are mostly interested in comparing different procedures to see what effect, if any, the experimental conditions made on the final product compositions since all of the reactions produce similar products. By comparing peak areas of the 330 nm and the 260 nm chromatograms, we can determine which reaction conditions produced the largest weiht fraction of substituted C$_{60}$. Another consideration is that an unreacted polymer molecule and a C$_{60}$ molecule with one chain grafted to it have almost the same hydrodynamic volume and differ in molecular weight by only 720 units. Therefore, their average molecular weights, are for all practical purposes indistinguishable. The only time we can be sure from a 260 nm chromatogram that more polymer has reacted is when a detected product has double or triple the molecular weight of the starting polymer. We also look at chromatograms that were detected at 330 nm, where only the C$_{60}$ components of a product molecule absorb.

As an example, let's consider 2(B*-PS)/C$_{60}$, entry 1 from Table 3 and Figure 10. The starting TEMPO-terminated polystyrene (B*-PS-T) had P_n= 11300. It was prepared in a 0.02 molar LPS, 0.01 molar C$_{60}$ solution of oDCB. After the reaction and isolation that were described previously, SEC of the polymer product at 260 nm showed a bimodal chromatogram with peak maxima at 18.15 and 16.9 minutes. The maximum of the peak at 18.15 minutes ($P_t(1)$) corresponded to 15,700 MW and the maximum of the
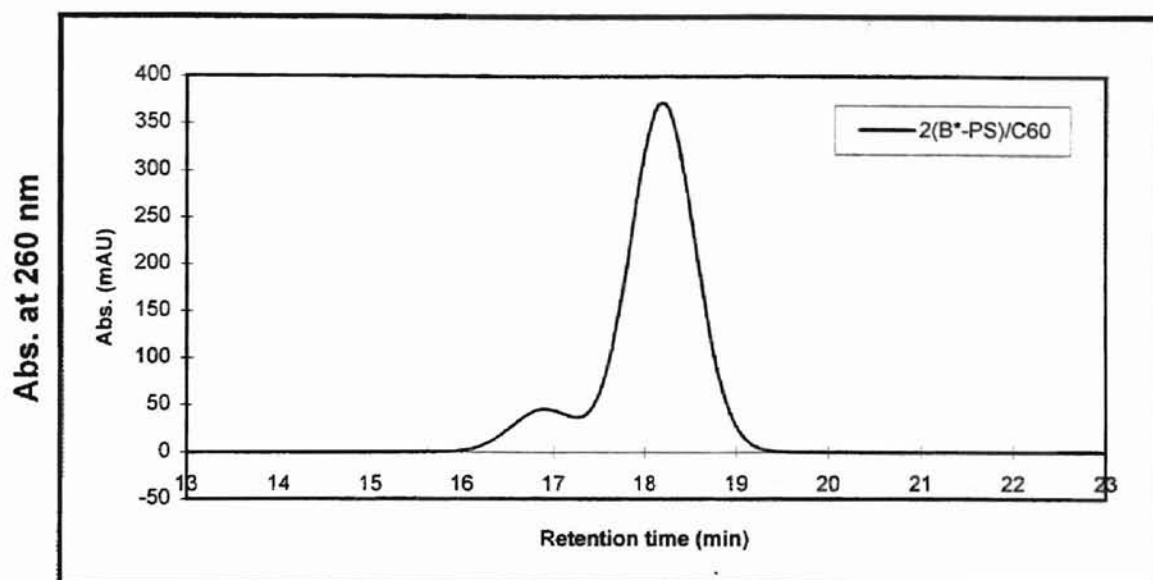
Sample	$2(B^*\text{-}PS)C_{60}$
% Area from P(2)	10.2
% Area from P(1)	89.9
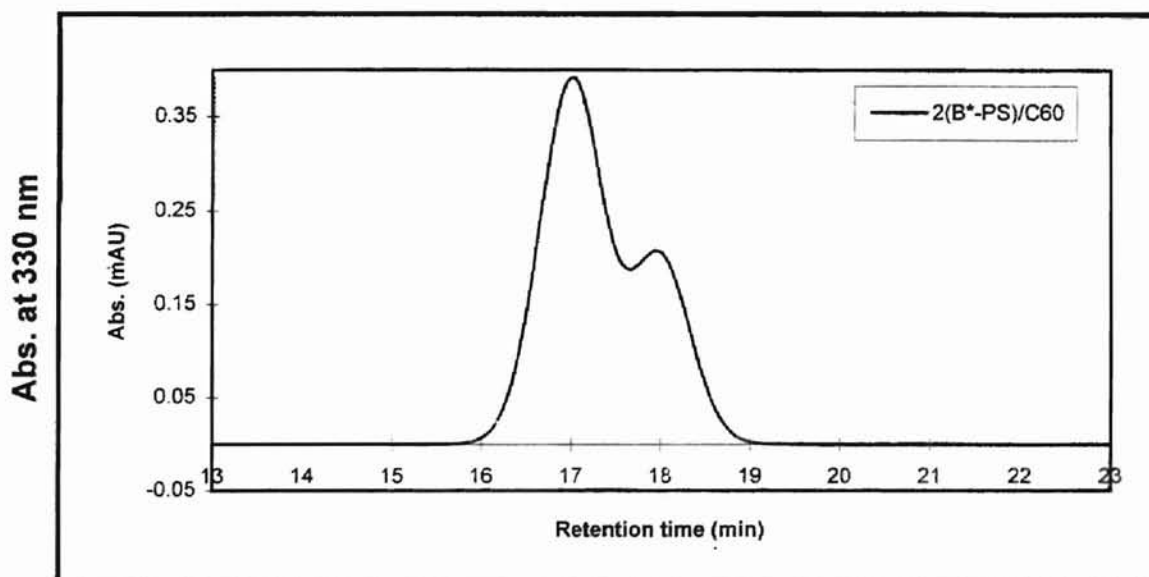
Sample	$2(B^*\text{-}PS)C_{60}$
% Area from P(2)	66.5
% Area from P(1)	33.5

Figure 10. SEC of samples 2 (B-PS)/C_{60}.

In this SEC profile, peak 2 at 16.9 min. has a molecular weight that is twice that of peak 1 at 18.15 min. 2(B*-PS)/C_{60} was heated to 80 °C for 96 hours (Table 3, entry 1).

peak at 16.9 minutes ($P_t(2)$) corresponded to 32,800 MW. As mentioned before, P(1) probably contains singly substituted C_{60} ((B-PS)-C_{60}-H) as well as some unreacted polymer chains (B-PS-T) while P(2) contains disubstituted C_{60} (2(B-PS)C_{60}) or a polyfullerene/polystyrene ((B-PS)$_2$(C_{60})$_x$) where x is the number fullerenes. When the same SEC is examined at 330 nm, we learn more about the C_{60} content of the sample. The two peak tops now have retention times of 17.99 (P(1)) and 16.98 (P(2)) minutes. These retention times correspond to P_t MW's of 17,700 and 32,600, respectively. Their relative areas, however, are now 2 to 1 in favor of the high molecular weight material. This would appear to be the result of viewing the sample so that only C_{60} products appear and more of those products existing as disubstituted C_{60}'s. Another alternative is that the extinction coefficient of the C_{60} products changes with each reaction that occurs on the fullerene, and the result is that the disubstituted products absorb stronger than the monosubstituted ones at 330 nm. All P_t molecular weight data are reported in Table 4.

Table 4. Molecular Weights Determined from Simulated SEC Chomatograms at 260 and 330 nm.

Entry	Sample	260 nm			330 nm			Figure #
		$P_t(3)$	$P_t(2)$	$P_t(1)$	$P_t(3)$	$P_t(2)$	$P_t(1)$	
	B*-PS-T			11,300				
1	2(B*-PS)/C_{60}		34,700	15,400		33,000	17,100	11
2	2'(B*-PS)/C_{60}		32,300	15,400		32,900	16,100	11
	B'-PS/S-T			8,700				
3	1(B'-PS/S)/C_{60}		19,000	8,000		18,000	7,500	12
4	2(B'-PS/S)/C_{60}		19,500	8,000		17,700	7,600	12
5	4(B'-PS/S)/C_{60}		19,500	8,000		19,000	7,500	12
	B-PS/S-T			6,300				
6	2(B-PS/S)/C_{60}		15,000	6,300		15,300	6,100	13
7	2'(B-PS/S)/C_{60}		15,000	6,600		15,000	6,100	13
	B-PS-T			6400				

|							
8	2(B-PS)/C_{60}		29,300	12,300		28,500	11,700	14
9	2'(B-PS)/C_{60}		29,000	12,300		26,900	11,500	14
10	1A(B-PS)/C_{60}[b]		27,000	11,700		27,000	12,000	15
11	2A(B-PS)/C_{60}[b]		27,000	11,700		27,000	12,000	15
12	4A(B-PS)/C_{60}[b]		27,000	11,700		27,000	11,700	15
13	1B(B-PS)/C_{60}[b]		28,500	11,700		28,500	11,700	16
14	2B(B-PS)/C_{60}[b]		28,500	11,700		27,900	11,400	16
15	4B(B-PS)/C_{60}[b]		31,700	12,100		28,500	11,700	16
16	1C(B-PS)/C_{60}		28,500	12,000	.	27,800	11,700	17
17	2C(B-PS)/C_{60}	62,900	31,700	12,000	42,600	30,900	11,900	17
18	4C(B-PS)/C_{60}		30.600	11,400		30,500	12,800	17
19	1D(B-PS)/C_{60}		16,500	6,600		15,600	6,500	18
20	2D(B-PS)/C_{60}		15,600	6,600		14,800	6,500	18
21	4D(B-PS)/C_{60}		17,600	6,700		15,800	6,600	18
	M-PS-T			9,200				
22	0.5(M-PS)/C_{60}		14,000	6,700		14,800	7,300	19
23	1(M-PS)/C_{60}		14,800	7,000		14,800	7,000	19
24	2(M-PS)/C_{60}		14,800	6,900		14,800	6,900	19
25	4(M-PS)/C_{60}		16,100	6,400		14,000	N/A	19

In accordance with the first paragraph of this section, the following topics examine the effects of the experimental parameters on the PS-C_{60} products.

Isolation procedures. The reaction mixtures were removed from the 130 °C oven and then subjected to the work-up or isolation procedure described in the Experimental. Samples 1,2 and 4(D)(B-PS)/C_{60} were analyzed with SEC prior to isolation (solid line) and after isolation from solvent (dotted line, Figures 20, 21 and 22). These Figures are displayed differently because they are the actual experimental
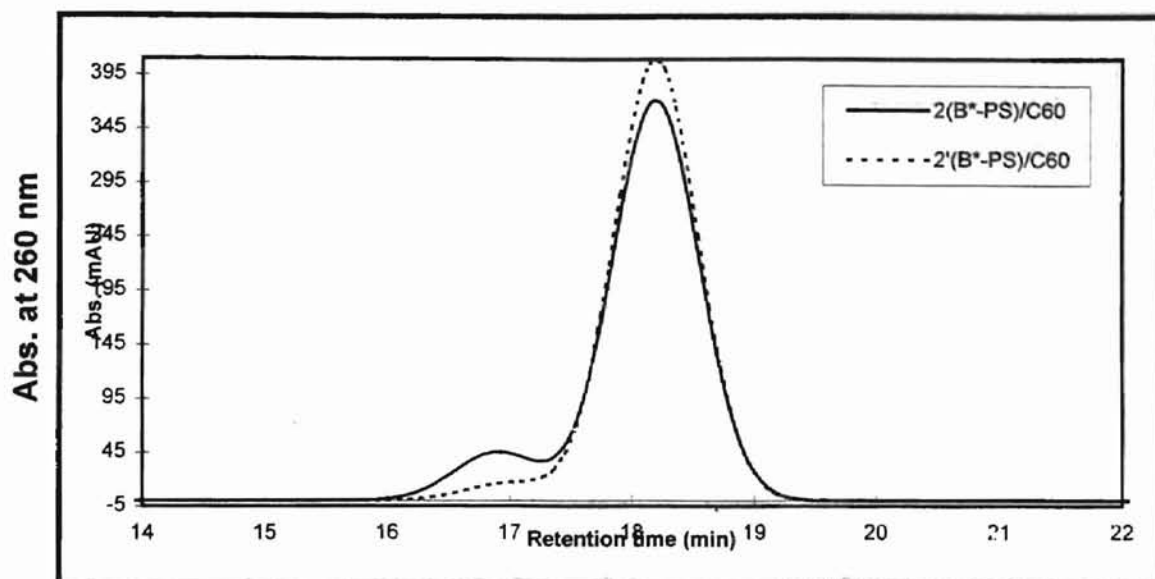
Sample	2(B*-PS)/C$_{60}$	2'(B*-PS)/C$_{60}$
% Area from P(2)	10.2	4.2
% Area from P(1)	89.9	96
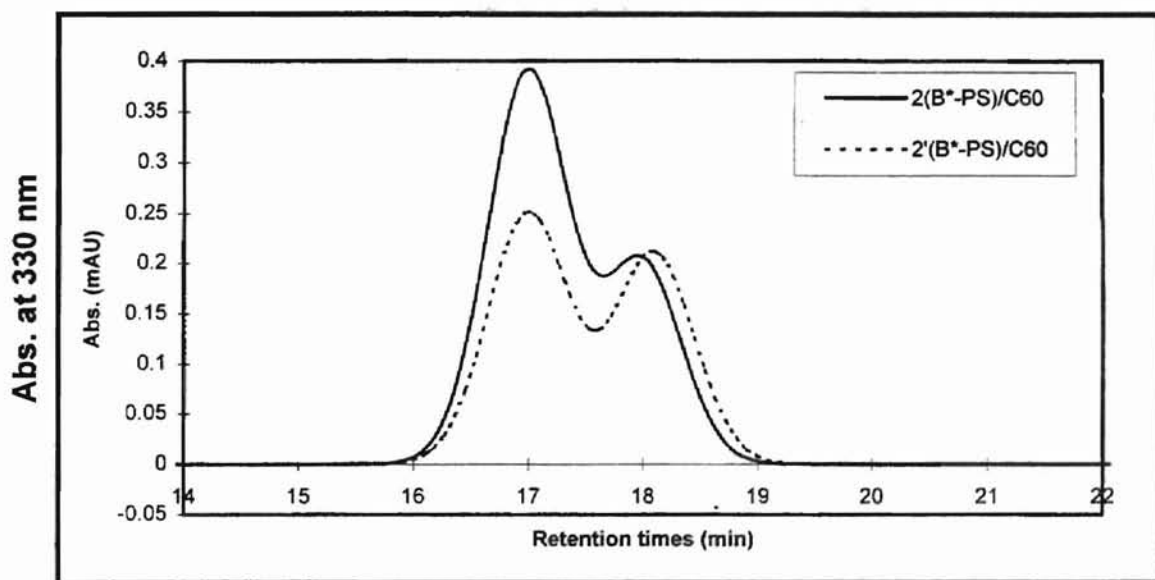
Sample	2(B*-PS)/C$_{60}$	2'(B*-PS)/C$_{60}$
% Area from P(2)	66.7	54.4
% Area from P(1)	33.5	46

Figure 11. SEC of samples 2 and 2'(B*-PS)/C$_{60}$.

Sample 2(B*-PS)/C$_{60}$ was heated to 80 °C for 96 hours. Sample 2'(B*-PS)/C$_{60}$ was heated to 130 °C for 72 hours (Table 3, entries 1 and 2).
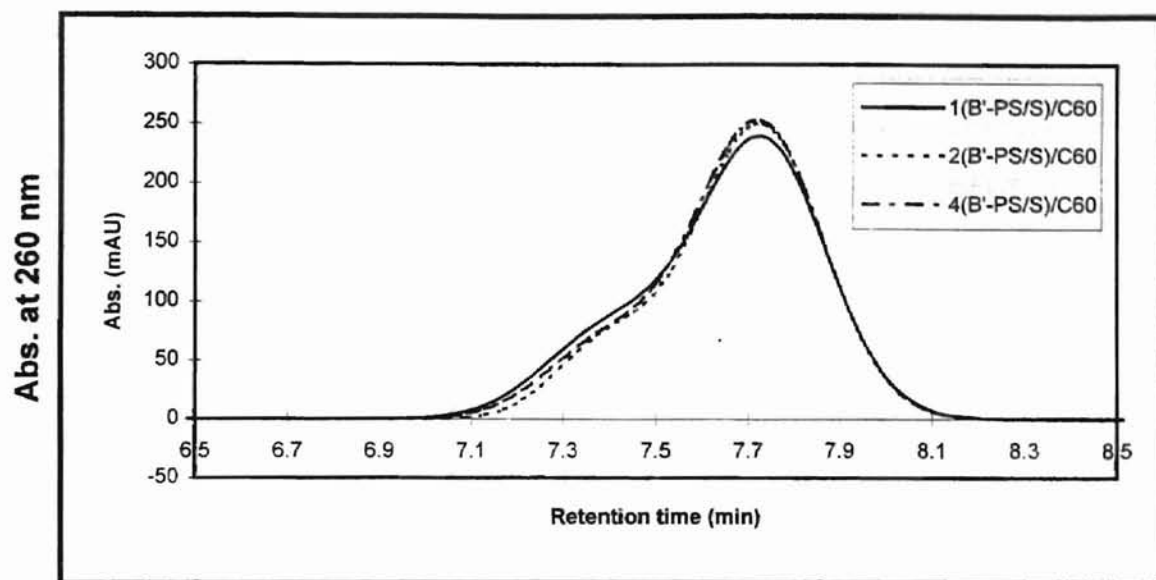
Sample	1(B'-PS/S)/C$_{60}$	2(B'-PS/S)/C$_{60}$	4(B'-PS/S)/C$_{60}$
% Area from P(2)	24.5	18.9	18.9
% Area from P(1)	76	80.9	81.1
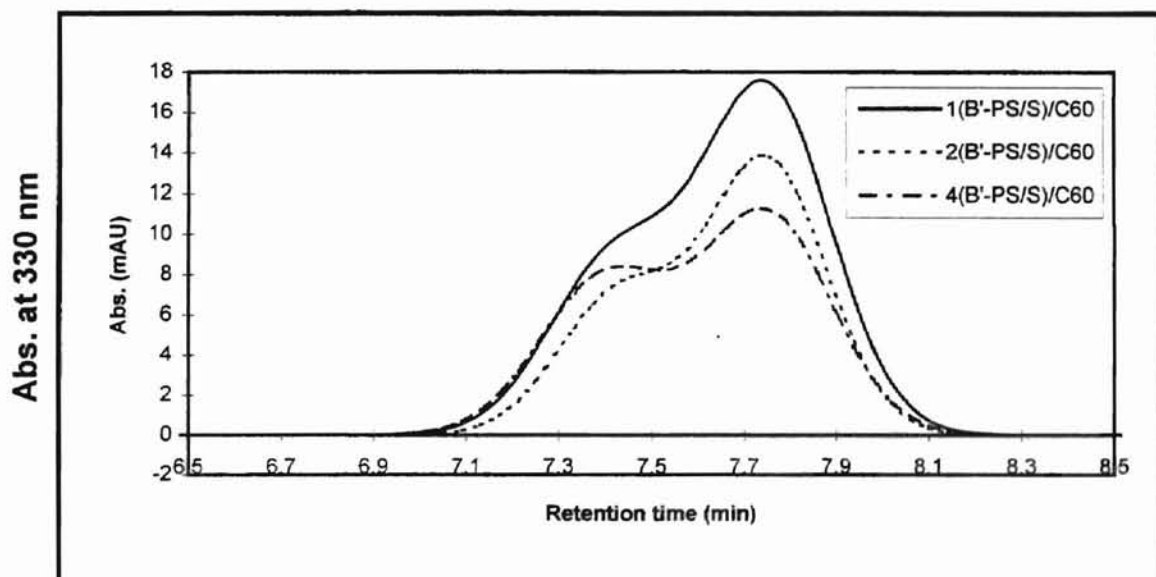
Sample	1(B'-PS/S)/C$_{60}$	2(B'-PS/S)/C$_{60}$	4(B'-PS/S)/C$_{60}$
% Area from P(2)	33.2	32.3	42.2
% Area from P(1)	66.7	63	58.3

Figure 12. SEC of samples 1,2 and 4(B'-PS/S)/C$_{60}$.

Molar ratios of 1, 2 and 4 polymer chains, in the presence of residual styrene, per C$_{60}$ were heated to 80 °C for 24 hours during end-capping reactions (Table 3, entries 3, 4 and 5).
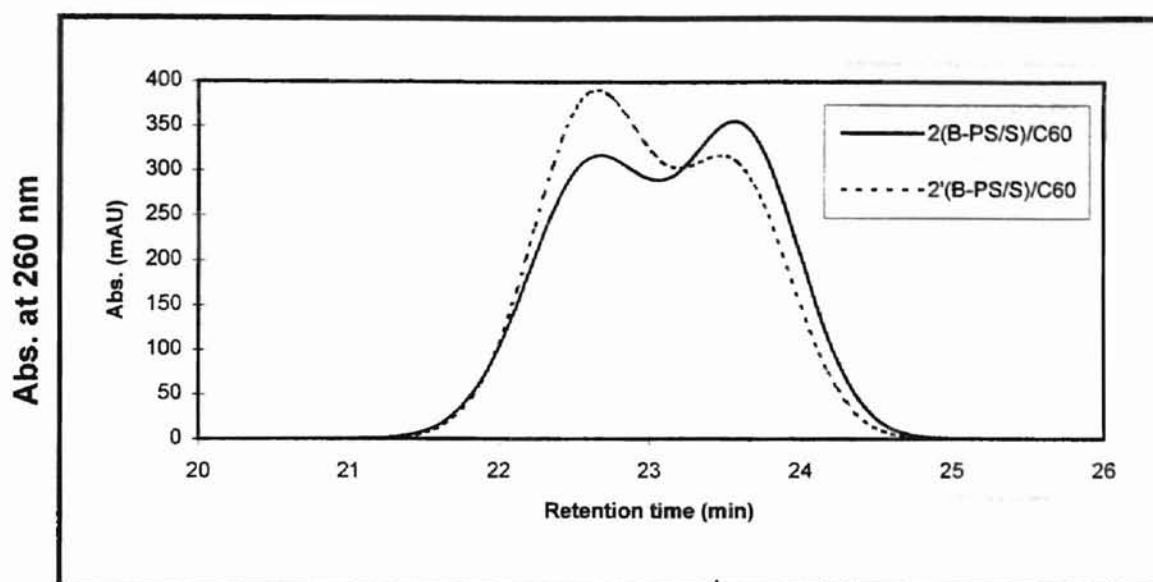
Sample	2(B-PS/S)/C_{60}	2'(B-PS/S)/C_{60}
% Area from P(2)	50	57.6
% Area from P(1)	49.7	42.4
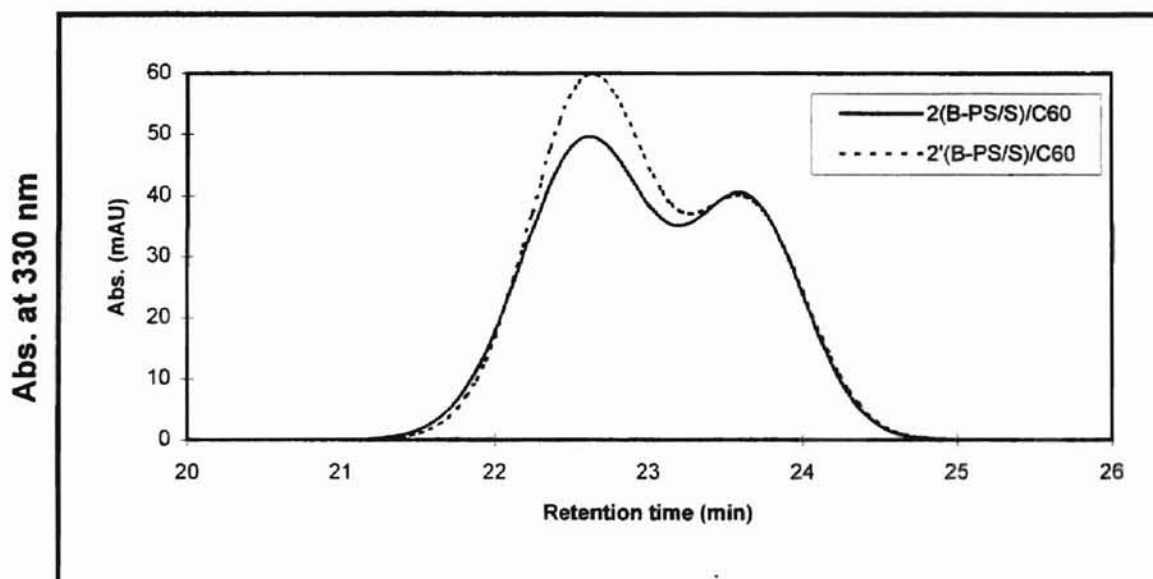
Sample	2(B-PS/S)/C_{60}	2'(B-PS/S)/C_{60}
% Area from P(2)	60.3	62.4
% Area from P(1)	39.8	37.8

Figure 13. SEC of samples 2 and 2'(B-PS/S)/C_{60}.

These samples represent a control (2(B-PS/S)/C_{60}) and a sample that underwent the isolation and reheat method (2'(B-PS/S)/C_{60}) described in the Results. The starting polymer was not isolated from monomer (Table 3, entries 6 and 7).
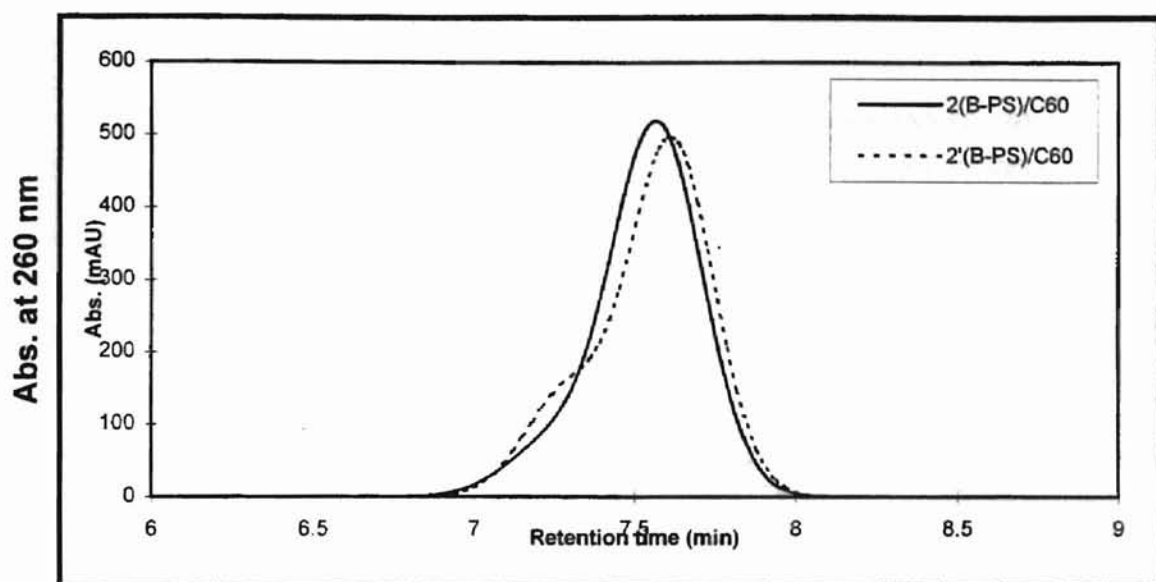
Sample	2(B-PS)C_{60}	'(B-PS)/C_{60}
% Area from P(2)	12	22.6
% Area from P(1)	88.3	77.6
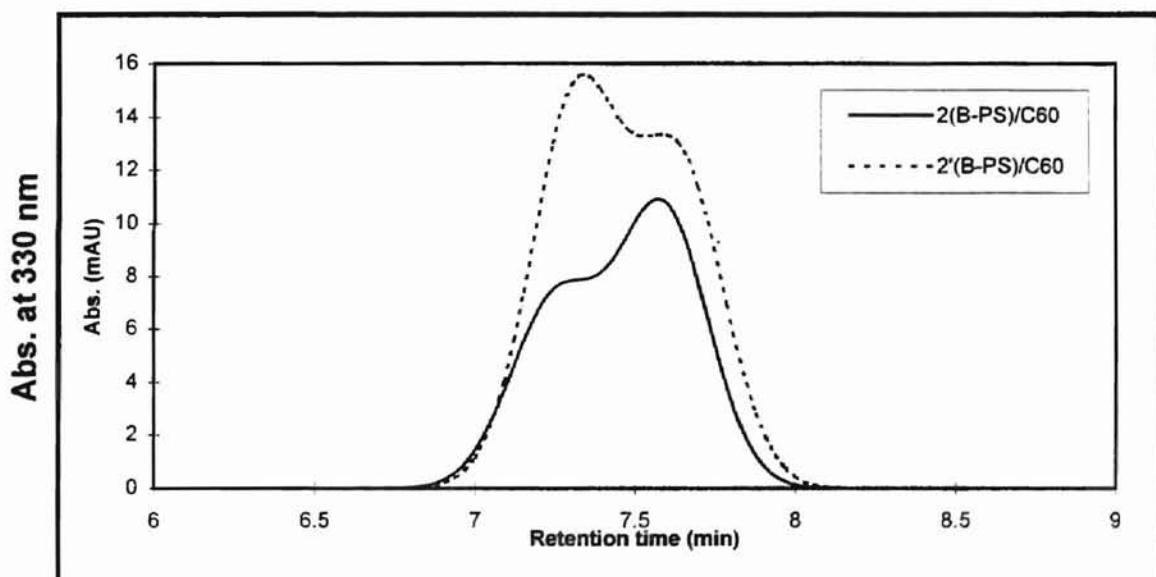
Sample	2(B-PS)C_{60}	'(B-PS)/C_{60}
% Area from P(2)	40.2	54.7
% Area from P(1)	59.7	44.9

Figure 14. SEC of samples 2 and 2'(B-PS)/C_{60}.

These samples reprsent a control (2(B-PS)/C_{60}) and isolation and reheat sample (2'(B-PS)/C_{60}). End-capping reactions occured at 100 °C for 24 hours (Table 3, entries 8 and 9).
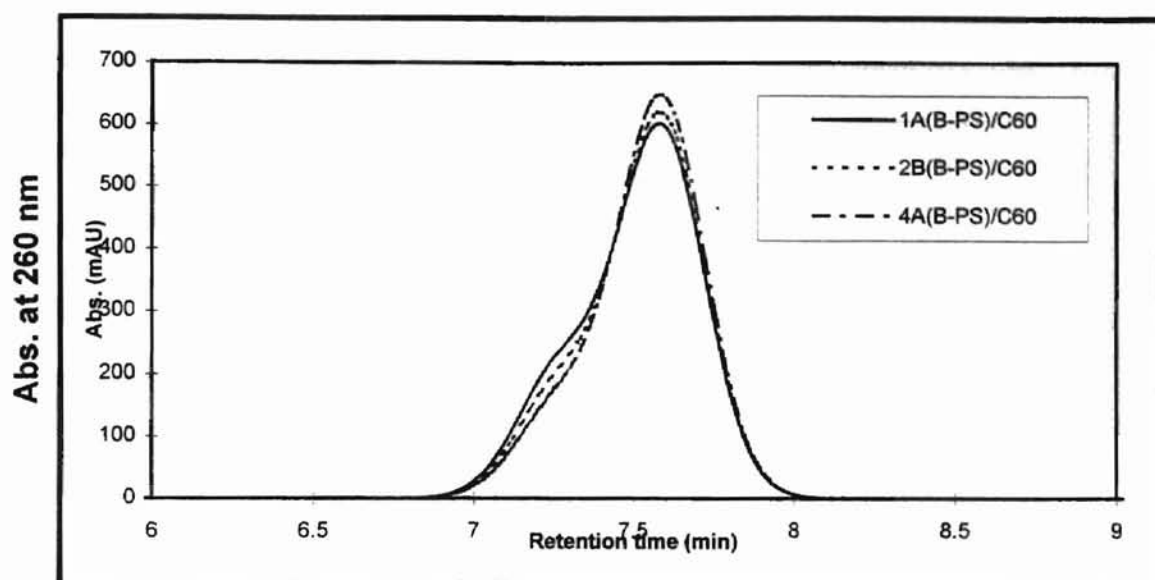
Sample	1A(B-PS)/C_{60}	2A(B-PS)/C_{60}	4A(B-PS)/C_{60}
% Area from P(2)	25.7	22.2	19
% Area from P(1)	74.7	77.1	81.1
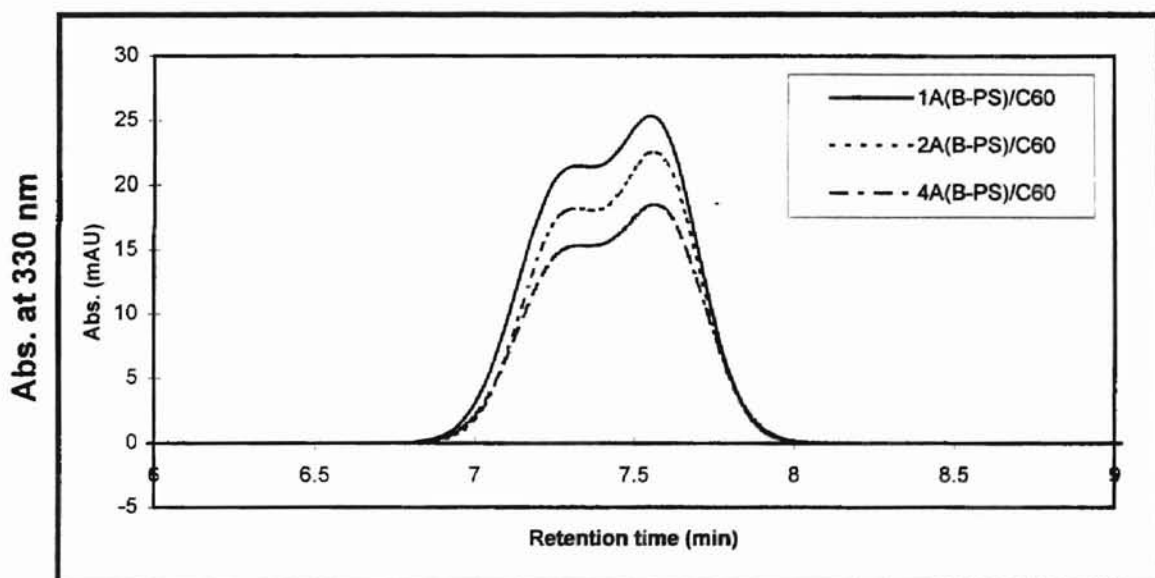
Sample	1A(B-PS)/C_{60}	2A(B-PS)/C_{60}	4A(B-PS)/C_{60}
% Area from P(2)	45.8	43.5	45.7
% Area from P(1)	54.3	56.7	55

Figure 15. SEC of samples 1,2 and 4(A)(B-PS)/C_{60}.

Molar ratios of 1, 2 and 4 polymer chains per C_{60} were heated to 130 °C for 15 hours (Table 3, entries 10-12).
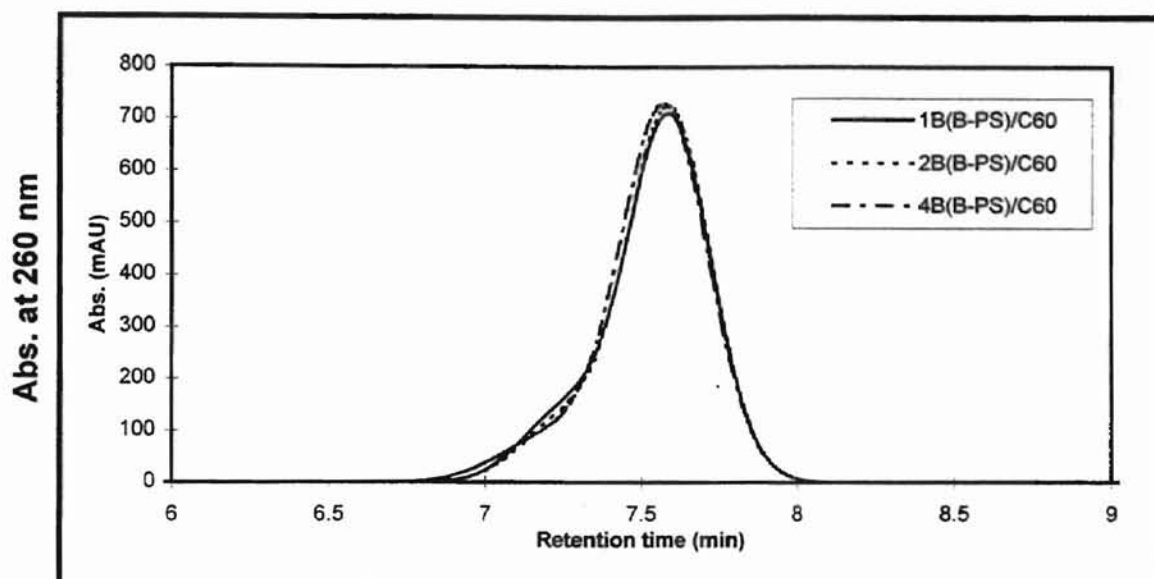
Sample	1B(B-PS)/C$_{60}$	2B(B-PS)/C$_{60}$	4B(B-PS)/C$_{60}$
% Area from P(2)	15.4	13.7	10.8
% Area from P(1)	83.6	85.8	89.5
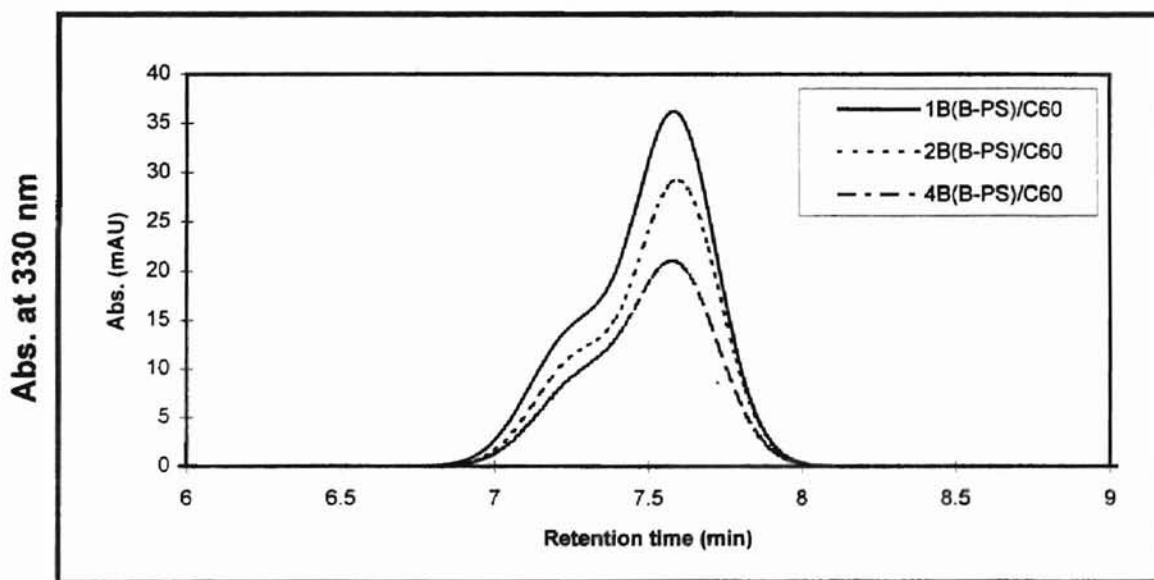
Sample	1B(B-PS)/C$_{60}$	2B(B-PS)/C$_{60}$	4B(B-PS)/C$_{60}$
% Area from P(2)	27.9	26.4	28.6
% Area from P(1)	72.7	73.6	71.6

Figure 16. SEC of samples 1,2 and 4(B)(B-PS)/C$_{60}$.

Molar ratios of 1, 2 and 4 polymer chains per C$_{60}$ were heated to 100 $^{\circ}$C for 120 hours (Table 3, entries 13-15).

Sample	1C(B-PS)/C_{60}	2C(B-PS)/C_{60}	4C(B-PS)/C_{60}
% Area from P(2)	27.6	33.8	30.4
% Area from P(1)	74.4	66.1	69.5

Sample	1C(B-PS)/C_{60}	2C(B-PS)/C_{60}	4C(B-PS)/C_{60}
% Area from P(2)	44.7	65.9	64.7
% Area from P(1)	55.2	34.3	35.3

Figure 17. SEC of samples 1,2 and 4(C)(B-PS)/C_{60}.

Molar ratios of 1, 2 and 4 polymer chains per C_{60} were heated to 130 °C for 168 hours (Table 3, entries 16-18).

Sample	1D(B-PS)/C_{60}	2D(B-PS)/C_{60}	4D(B-PS)/C_{60}
% Area from P(2)	32.4	19.9	17.3
% Area from P(1)	66.8	79.7	83.3
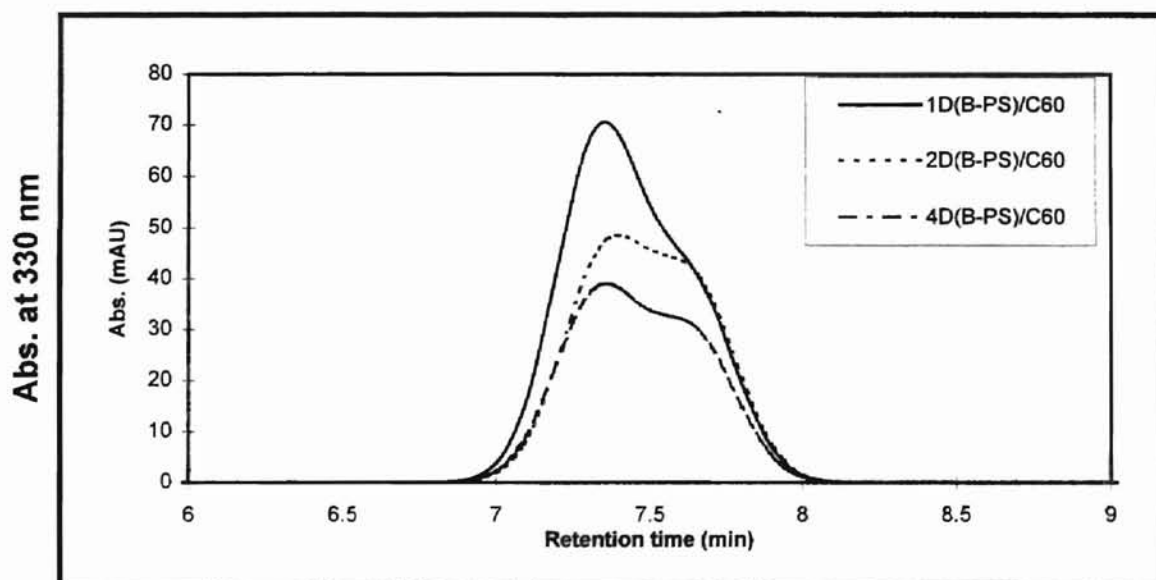
Sample	1D(B-PS)/C_{60}	2D(B-PS)/C_{60}	4D(B-PS)/C_{60}
% Area from P(2)	65.6	54	57
% Area from P(1)	35	46.4	43.3

Figure 18. SEC of samples 1,2 and 4(D)(B-PS)/C_{60}.

Molar ratios of 1, 2 and 4 polymer chains per C_{60} were heated to 130 °C for 24 hours (Table 3, entries 19-21).
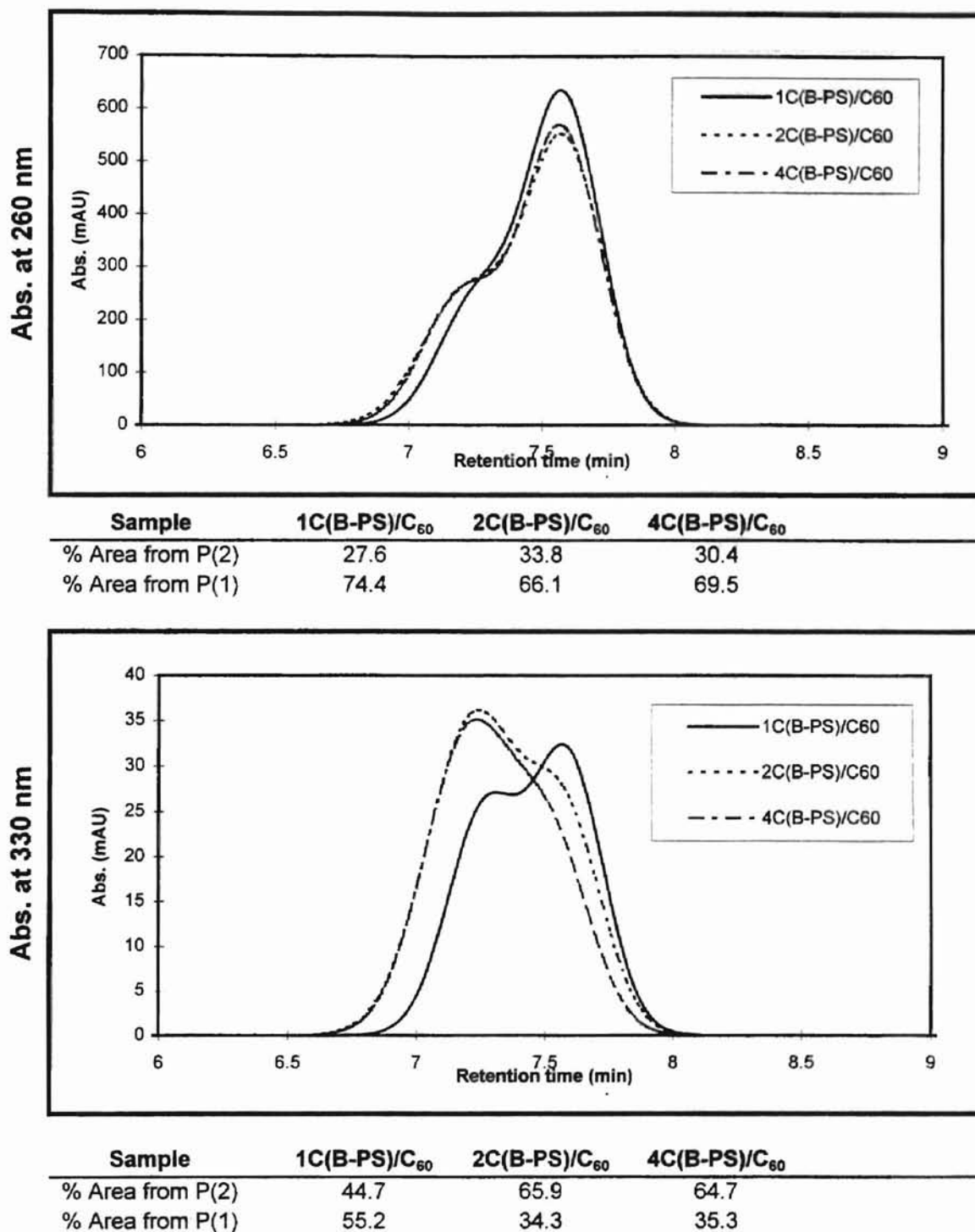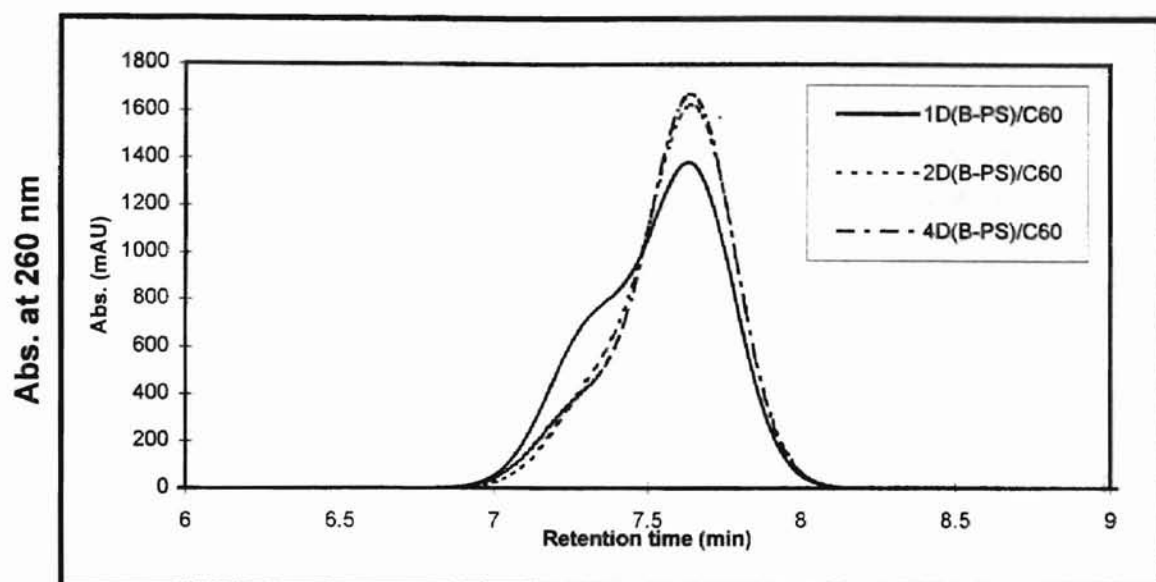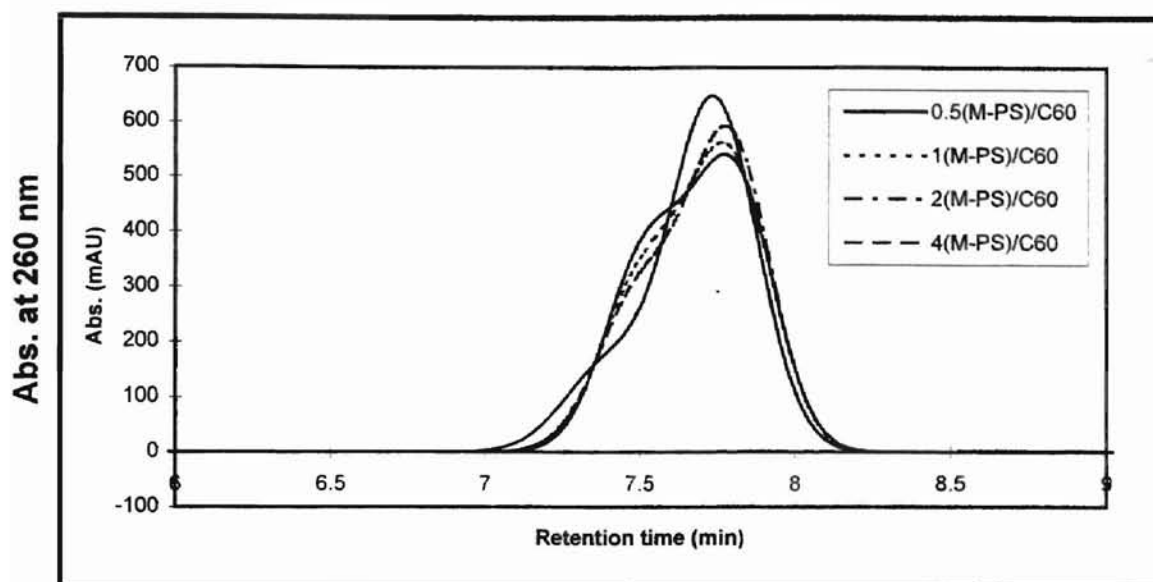
Sample	0.5(M-PS)/C_{60}	1(M-PS)/C_{60}	2(M-PS)/C_{60}	4(M-PS)/C_{60}
% Area from P(2)	41.1	34.7	34.5	20.6
% Area from P(1)	59.3	65.5	66	79.1
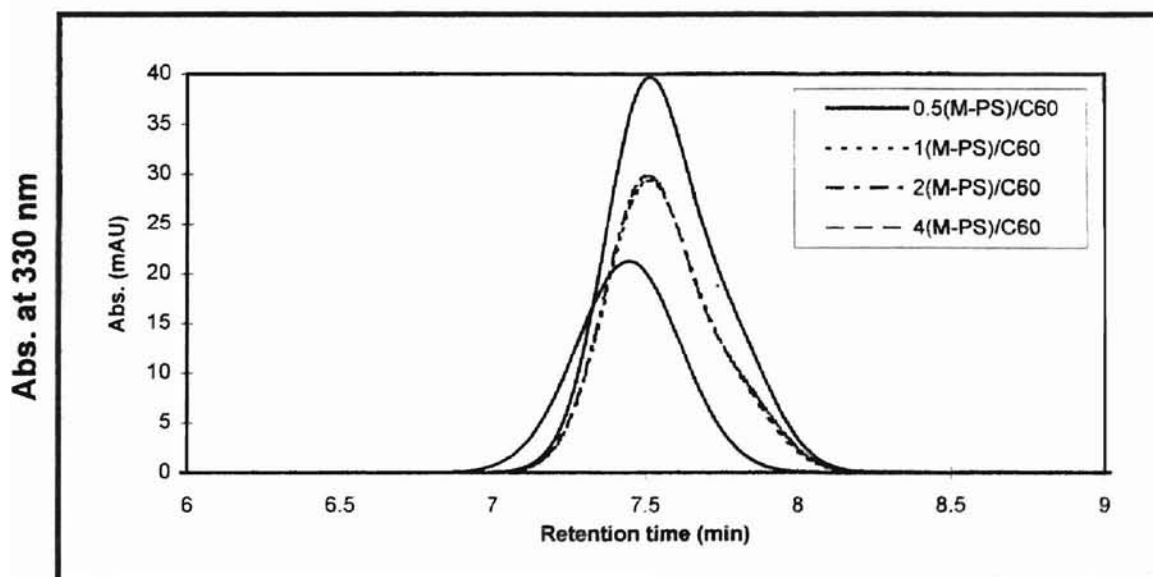
Sample	0.5(M-PS)/C_{60}	1(M-PS)/C_{60}	2(M-PS)/C_{60}	4(M-PS)/C_{60}
% Area from P(2)	73.8	78.5	78	100
% Area from P(1)	26.2	22.2	21.4	0

Figure 19. SEC of samples 0.5, 1, 2 and 4(M-PS)/C_{60}.

Molar ratios of 0.5, 1, 2 and 4 polymer chains per C_{60} were heated to 130 °C for 24 hours (Table 3, entries 22-25).

Figure 20. SEC overlay of sample 1(B-PS)/C$_{60}$ before (—) and after (---) isolation.

Figure 21. SEC overlay of sample 2(B-PS)/C$_{60}$ before (—) and after (---) isolation.

Figure 22. SEC overlay of sample 4(B-PS)/C$_{60}$ before (—) and after (---) isolation.

data while Figures 10 through 19 show chromatograms simulated from experimental data. In this series of Figures we see that the isolation process removed some of the unreacted LPS.

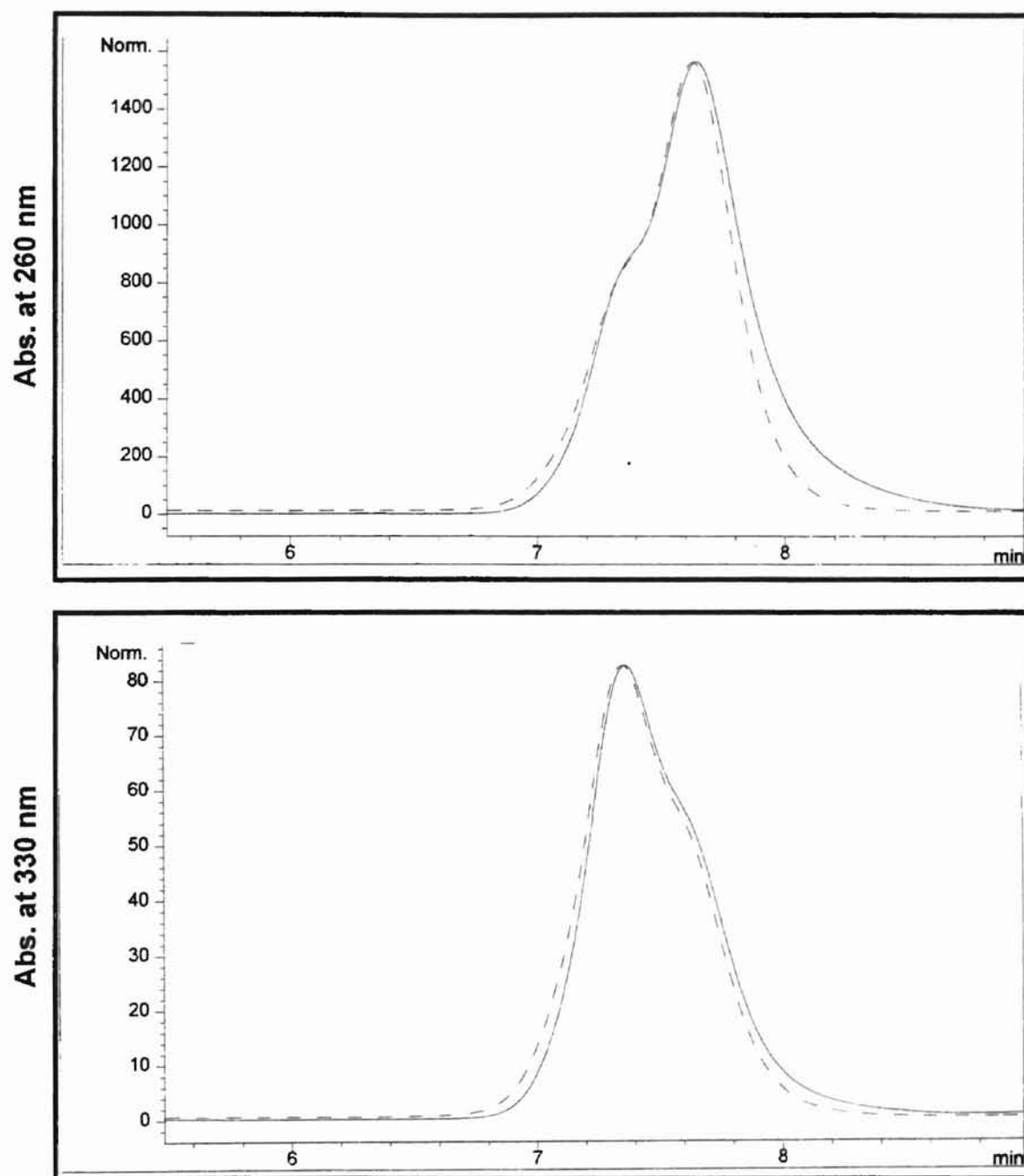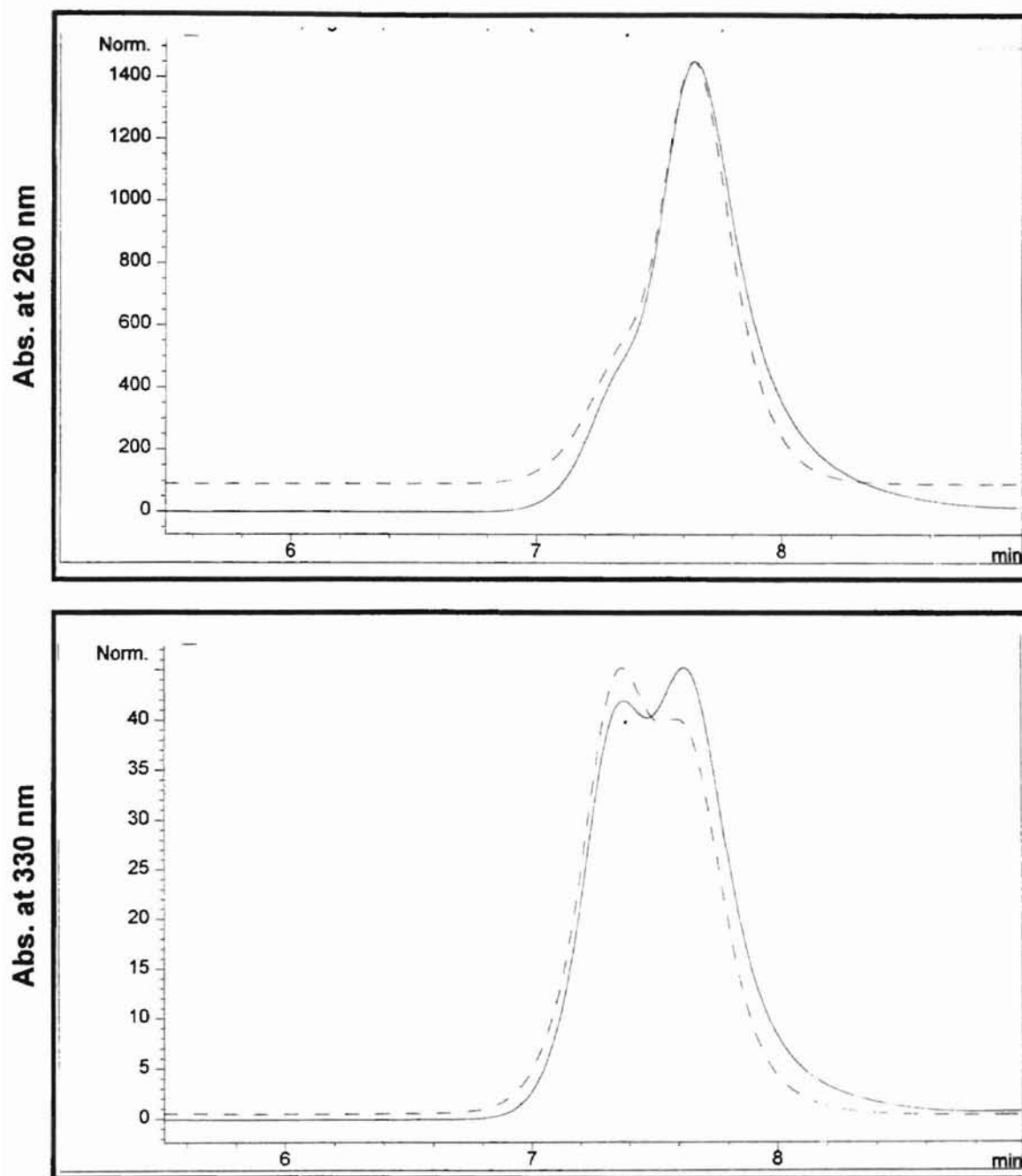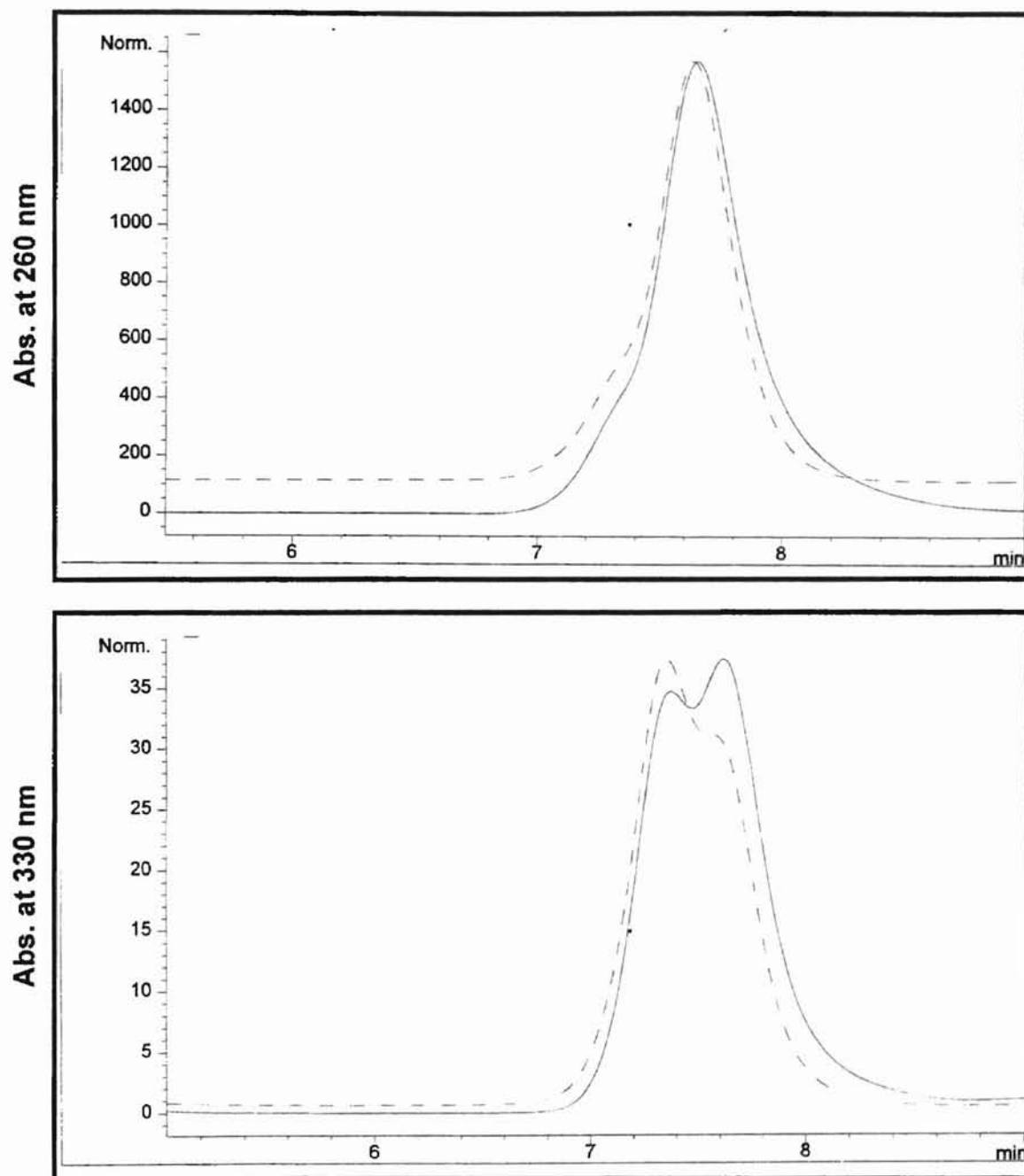**Molar ratios of 1, 2, and 4 LPS per C_{60}.** Several examples test the effect of varying the molar ratios of living polystyrene to C_{60}. For samples (1, 2 and 4)(B'-PS/S)/C_{60} see Figure 23. There is very little difference between these chromatograms at 260 nm. One molar equivalent of polymer appears to give the same fraction of LPS reacted with C_{60} as four molar equivalents of polymer. At 330 nm there is still very little difference between various molar ratios, but there is a small increase in the fraction of the fullerene content in the higher molecular weight peak of the chromatograms. These samples contained residual monomer. Samples (1, 2 and 4)(B-PS)/C_{60} (Figure 24) show similar results. At 260 nm, a leading shoulder appears to be about one quarter the height of the lower MW peak in all three samples. At 330 nm the leading shoulder appears to be about one half the height of the lower MW peak. This result occurs despite the increasing amount of polymer in the reaction mixtures which suggests that the substitutions on C_{60} are limited by some aspect of the reaction. Under these conditions increasing the amount of polymer does not increase much the number of reactions that occur on the C_{60}.

Constant temperature of 130 °C for various times. For samples 2A(B-PS)/C_{60}, 2D(B-PS)/C_{60}, 2'(B*-PS)/C_{60}, and 2C(B-PS)/C_{60} see Figure 25. All samples show at 260 nm a leading shoulder at higher MW. The 330 nm chromatograms are more informative. Sample 2A(B-PS)/C_{60} (15 hours) shows two peak tops of nearly equivalent height or a sample with equal amounts of fullerene in the low and high molecular weight material. Sample 2D(B-PS)/C_{60} (24 hours) shows the high MW peak slightly more abundant than the low MW peak. Sample 2'(B*-PS)/C_{60} (3 days) shows the high MW peak two times more abundant than the low MW peak from area comparisons and it looks nearly twice as tall. Sample 2C(B-PS)/C_{60} (7 days) shows the high MW peak at slightly more than two times the area of the low MW peak. These data suggest that longer reaction times do increase the number of polymer chains that react. It also appears that the number of reactions approach a limit, where increasing intervals of time do not significantly increase the number of polymer chains that attach to C_{60}.

Constant temperature of 100 °C for various times. For samples 2B(B-PS)/C_{60} and 2(B-PS)/C_{60} see Figure 26. These two samples show at 260 nm a leading shoulder at higher MW. At 330 nm, sample
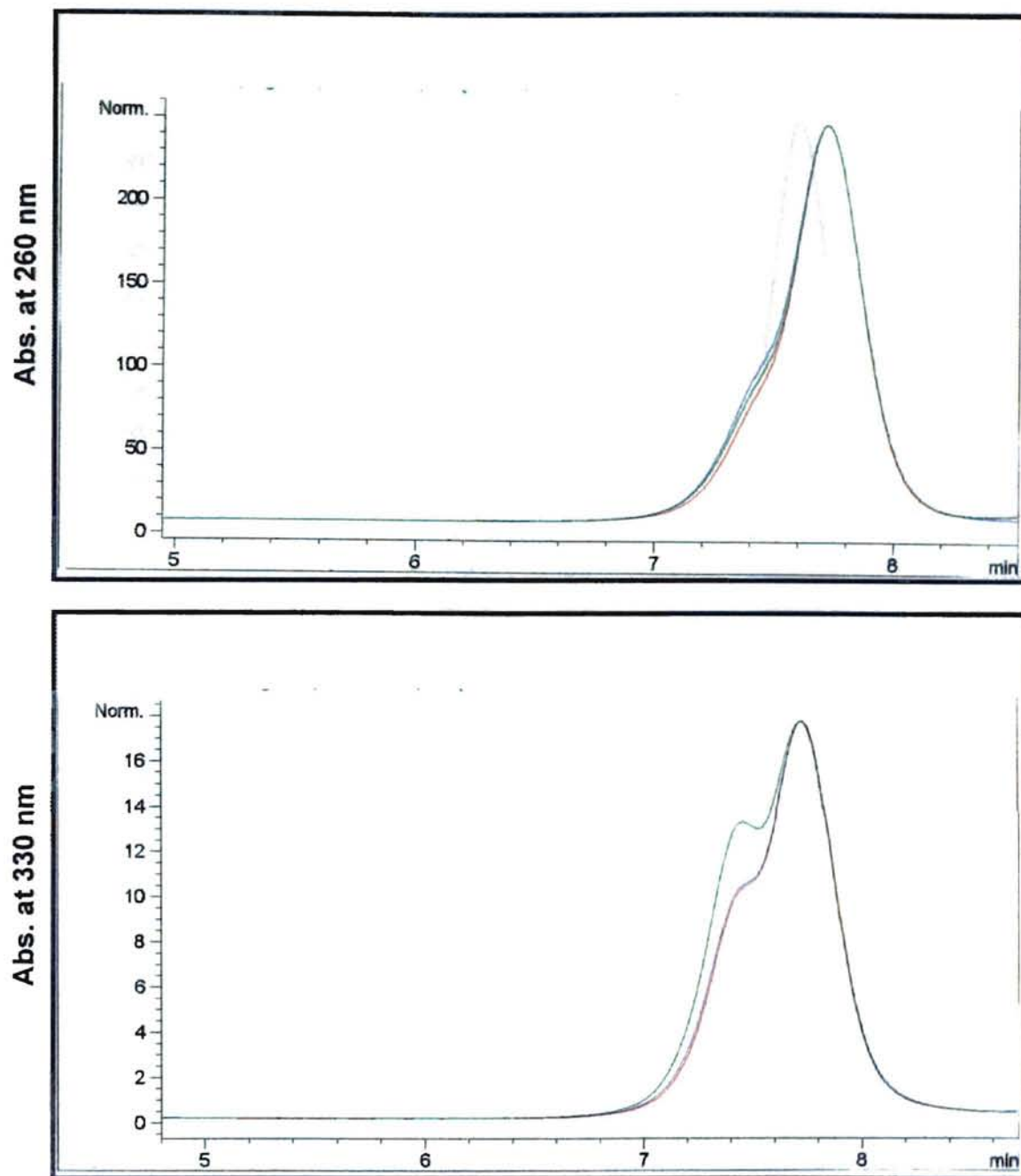
Figure 23. SEC overlay of samples 1(B'-PS/S)/C_{60} (●),
2(B'-PS/S)/C_{60} (●) and 4(B'-PS/S)/C_{60} (●).

Molar ratios of 1, 2 and 4 polymer chains were reacted with 1 molar
equivalent of C_{60}. Little difference is seen at 260 nm, while at 330 nm the 4:1
show slightly more disubstituted C_{60} (Table 3, entries 3-5).
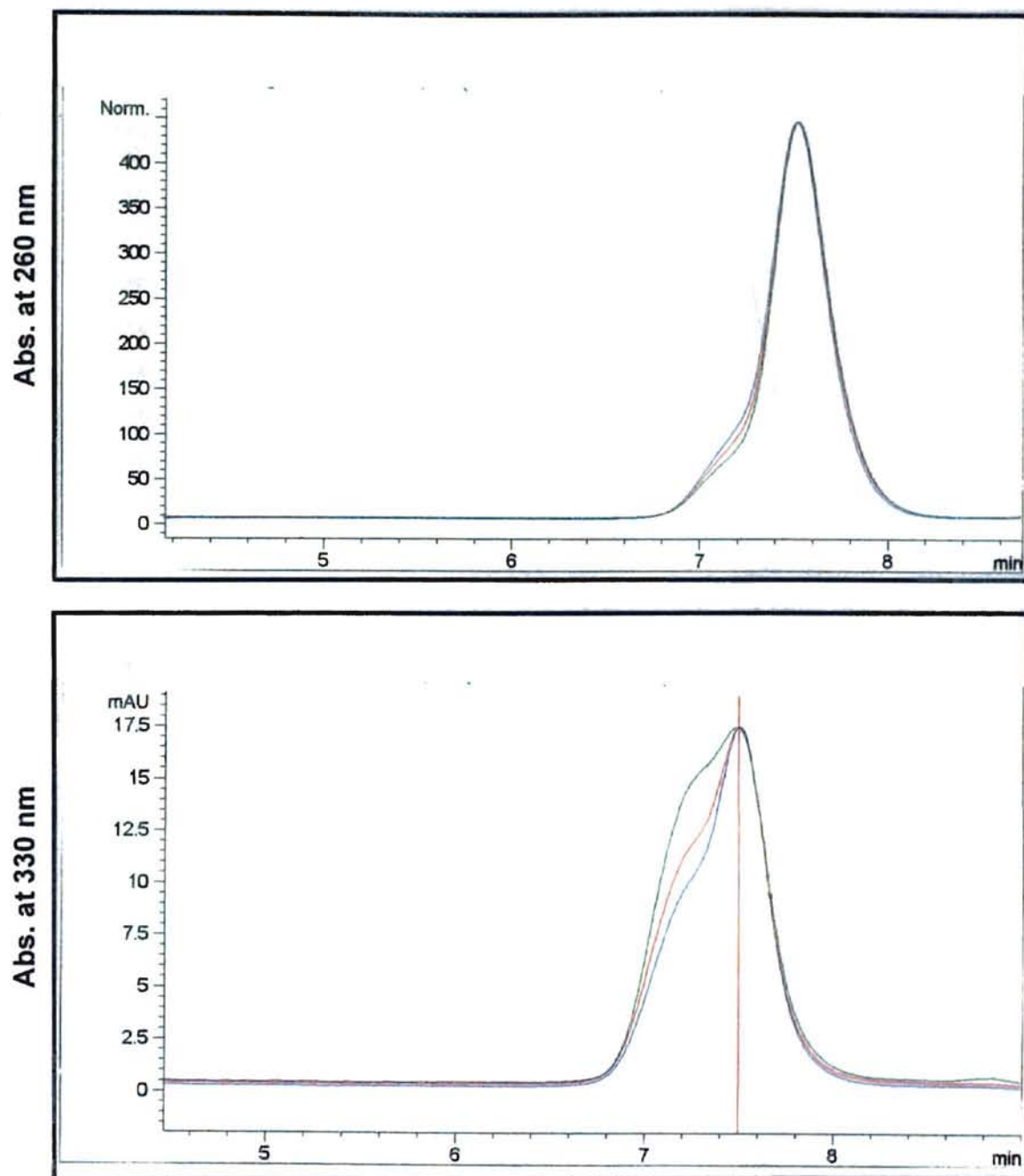
Figure 24.   SEC overlay of samples 1B(B-PS)/C$_{60}$(⬤),
2B(B-PS)/C$_{60}$(⬤) and 4B(B-PS)/C$_{60}$(⬤)

Molar ratios of 1, 2 and 4 polymer chains were reacted with 1 molar equivalent of
C$_{60}$. Viewed at 260 nm the sample is mostly composed of monosubstitued C$_{60}$ and
unreacted polymer. At 330 nm, the C$_{60}$-derivatives have increased disubstituted
C$_{60}$s with increasing polymer chain molar ratios (Table 3, entries 13-15).
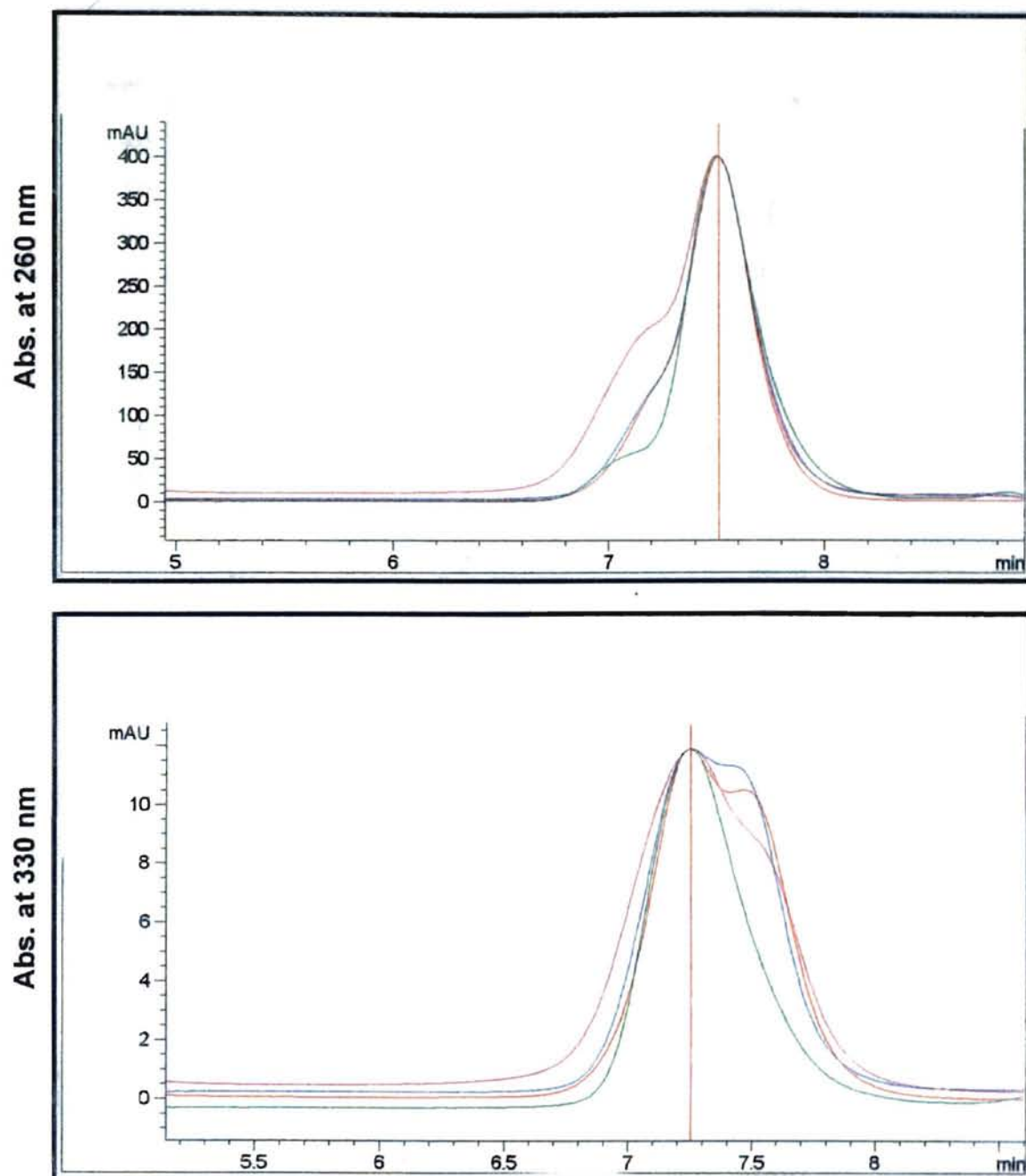
Figure 25. SEC overlay of 2A(B-PS)/C$_{60}$(●), 2D(B-PS)/C$_{60}$(●), 2'(B*-PS)/C$_{60}$(●) and 2C(B-PS)/C$_{60}$(●)

These samples were end-functionalized at 130 °C for 15, 24, 96 and 168 hours, respectively. The longer reaction times produce more higher molecular weight material with the exception of 2'(B*-PS)/C$_{60}$. This may be the result of using a different starting LPS sample (Table 3, entries 11,20, 2 and 17).
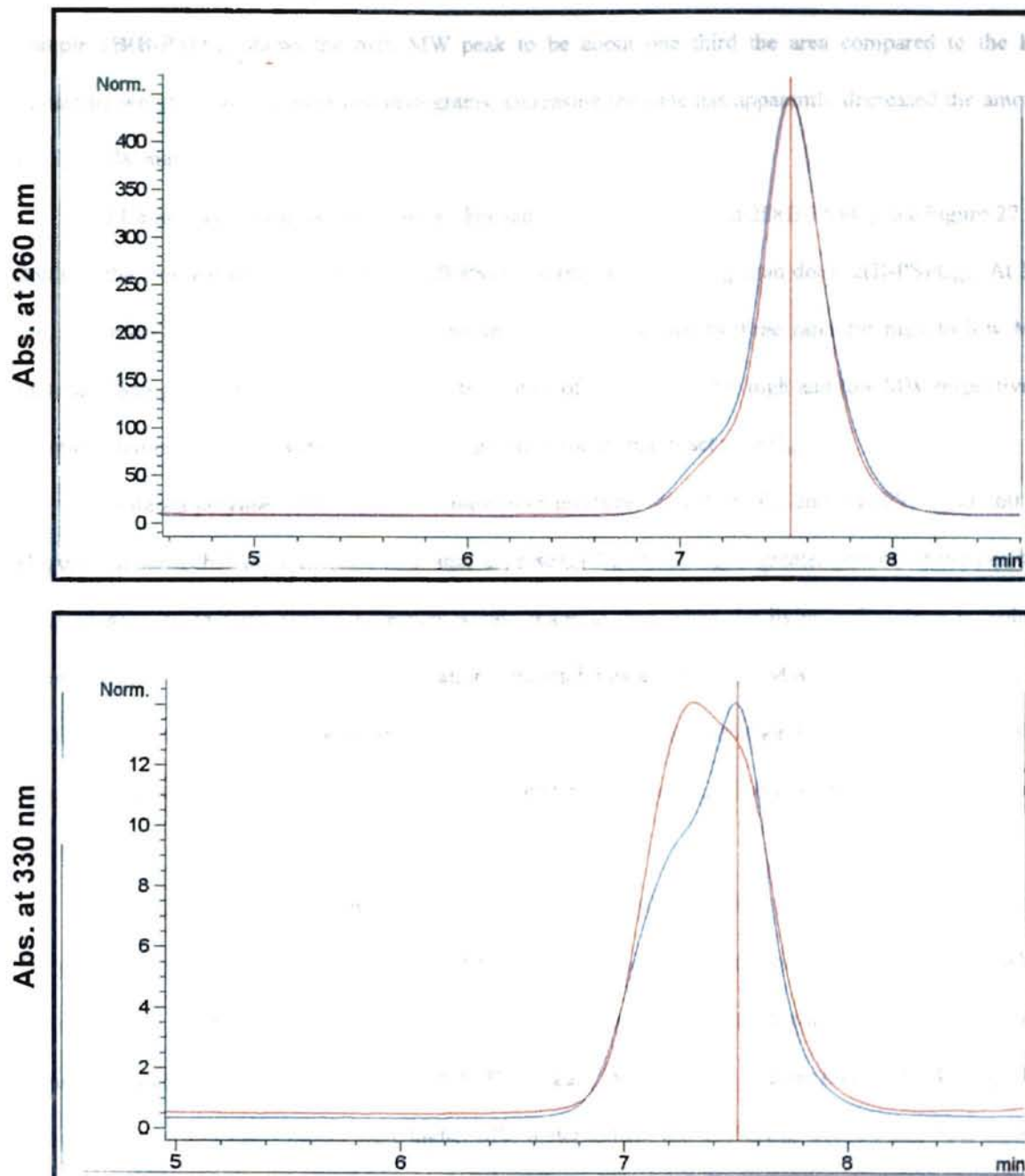
Figure 26. SEC overlay of samples 2B(B-PS)/C$_{60}$(●) and 2(B-PS)/C$_{60}$(●)

These samples were end-capped at 100 °C for 24 and 120 hours. Although the samples appear the same at 260 nm, at 330 nm the shorter reaction time has produced more disubstituted C$_{60}$ (Table 3, entries 14 and 8).

2(B-PS)/C_{60} (24 hours) the high MW peak and low MW peak at about a two to three ratio respectively. Sample 2B(B-PS)/C_{60} shows the high MW peak to be about one third the area compared to the low molecular weight peak. In these chromatograms, increasing the time has apparently decreased the amount of high MW material.

24 hours at various temperatures. For samples 2(B-PS)/C_{60} and 2D(B-PS)/C_{60} see Figure 27. At 260 nm, the chromatograms show that 2D(B-PS)/C_{60} forms more (PS)$_2$$C_{60}$ than does 2(B-PS)/C_{60}. At 330 nm, 2(B-PS)/C_{60} (100 C) the peak areas correspond to about a two to three ratio for high to low MW material. Sample 2D(B-PS)/C_{60} (130 C) has area ratios of three to two for high and low MW respectively. Increased temperatures increase the number of polymer chains that react with C_{60}.

Isolated polymer versus polymer-monomer mixture. 2(B-PS/S)/C_{60} and 2(B-PS)/C_{60} at 260 nm (Figure 28) show that when residual monomer is present (2(B-PS/S)/C_{60}) a greater portion of the polymer solution goes on to form higher molecular weight material than when the living polystyrene is isolated from monomer. At 330 nm more C_{60} containing material appears at higher MW in sample 2(B-PS/S)/C_{60} while in 2(B-PS)/C_{60} more material appears than in the 260 nm chromatogram but the lower MW peak is more abundant. This data suggests that more polymer reacts with C_{60} if monomer is left in the polymer solution.

Isolation and reheat method. For samples (2 and 2')(B-PS/S)/C_{60} and (2 and 2')(B-PS)/C_{60} see Figures 29 and 30. Samples that underwent the reheat method were precipitated into methanol, which removed freed TEMPO and monomer but not C_{60} or polymers. These were dissolved in oDCB and heated again. Comparing 2(B-PS/S)/C_{60} to 2'(B-PS/S)/C_{60} (Figure 29) at 260 nm, we see that 2'(B-PS/S)/C_{60} - the sample that was reheated - shows more higher MW material than 2(B-PS/S)/C_{60}. At 330 nm, both samples show more high molecular weight material however 2'(B-PS/S)/C_{60} increased more than 2(B-PS/S)/C_{60}. When comparing (2 and 2')(B-PS)/C_{60} (Figure 30) we see, at 260 nm 2'(B-PS)/C_{60} - the reheat sample - has higher MW material about one fifth as abundant as the lower MW peak, while 2(B-PS)/C_{60} has higher MW material at one eighth the abundance of the lower MW material. These results show that the limiting aspect of the reaction, where polymer chains are grafted onto C_{60}, is reduced when the sample is isolated from solvent, redissolved, and allowed to heat again. Initially, one might think that the reheat samples simply

Figure 27. SEC overlay of samples 2(B-PS)/C$_{60}$(⬤) and 2D(B-PS)/C$_{60}$(⬤)

These samples were both reacted for 24 hours during end-capping. Sample 2(B-PS)/C$_{60}$ was heated to 100 °C and sample 2D(B-PS)/C$_{60}$ was heated to 130 °C. At 260 nm there is slightly more high molecular weight material, while at 330 nm the product distibution is very similar (Table 3, entries 8 and 20).

Figure 28. SEC overlay of samples 2(B-PS/S)/C_{60}(●) and 2(B-PS)/C_{60}(●)

The first sample was end-capped in the presence of monomer. The second sample acts as a control, where no monomer was present. More high molecular weight material is observed at both wavelengths when there is residual monomer (Table 3, entries 6 and 8).

Figure 29. SEC overlay of samples 2(B-PS/S)/C$_{60}$(●) and
2'(B-PS/S)/C$_{60}$(●)

These samples are a control (2) and its counterpart (2') which after one
heating interval underwent precipitation into methanol to remove freed
TEMPO and monomer but not C$_{60}$ or polymer, then was heated again. The
reheat sample (2') shows more high molecular weight material at both 260
and 330 nm (Table 3, entries 6 and 7).

Figure 30. SEC overlay of samples 2(B-PS)/C$_{60}$(●) and
2'(B-PS)/C$_{60}$(●)

This is another example of a control and its counterpart (2') which after one heating
interval underwent precipitation into methanol to remove freed TEMPO but not C$_{60}$ or
polymer, then was heated again.   There was no residual monomer in these samples.
The reheat sample (2') shows more high molecular weight material at both 260 and
330 nm (Table 3, entries 8 and 9).

were allowed to heat twice as long as their counterparts. However, 2B(B-PS)/C$_{60}$ was prepared under the same conditions as 2(B-PS)/C$_{60}$ and 2'(B-PS)/C$_{60}$ with the exception that it heated undisturbed for 5 days instead of 24 hours (2(B-PS)/C$_{60}$) or 48 hours in the case of 2'(B-PS)/C$_{60}$, and its chromatogram at 260 nm shows at higher MW one eighth the abundance of material that exists at lower MW, an nearly identical result as sample 2(B-PS)/C$_{60}$. A possible reason for this behavior is that as reactions between TEMPO-terminated polystyrene and C$_{60}$ occur, a TEMPO molecule is released into solution. Subsequent reactions of polymer chains compete between an irreversible reaction onto a C$_{60}$ and a reversible reaction with TEMPO that reforms the starting polymer. As polymer reacts with C$_{60}$ free-TEMPO concentrations increase, favoring the recombination reaction over the end-capping reaction. The reheat method not only allows for more time for reactions to occur but more importantly the isolation from solvent step washes away freed TEMPO.

Sonicating versus mixing. For samples 2D(B-PS)/C$_{60}$ and 2A(B-PS)/C$_{60}$ see Figure 31. Sample 2A(B-PS)/C$_{60}$ (sonicated) shows two peak tops of nearly equivalent height at 330 nm or a sample with equal amounts of fullerene in low and high molecular weight material. Sampl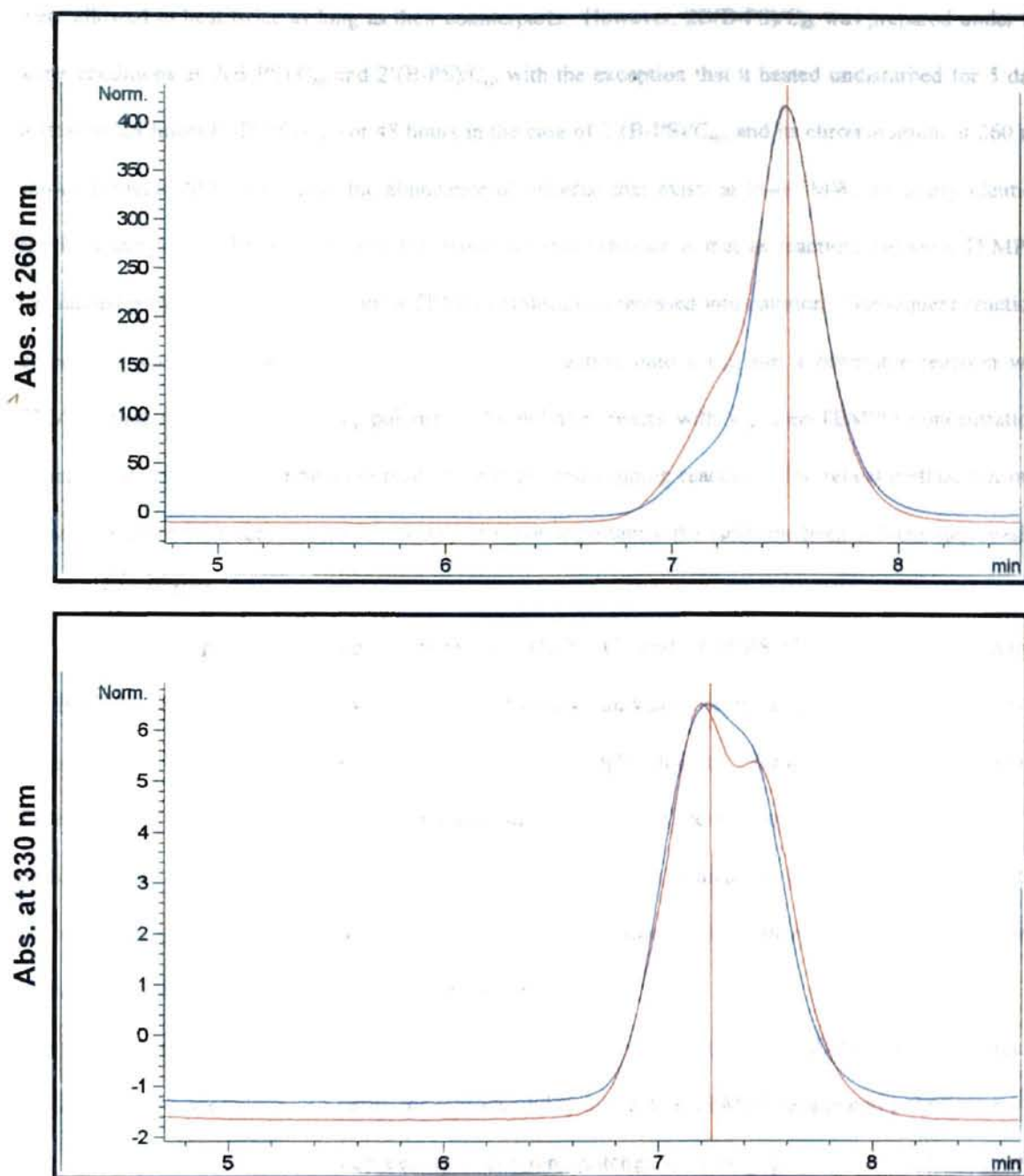e 2D(B-PS)/C$_{60}$ (mixed) shows the high MW peak slightly more abundant than the low MW peak. Sample 2D(B-PS)/C$_{60}$ was also heated longer than sample 2A(B-PS)/C$_{60}$. We suspected that sonication causes side reactions that contribute to irreproducible results and therefore mixed samples unless otherwise noted. These data, however, do not indicate any difference in the two samples.

Method of initiation. For samples (1,2 and 4)(M-PS)/C$_{60}$ vs. (1,2 and 4)D(B-PS)/C$_{60}$ see Figures 32, 33, and 34, respectively. To verify the reproducibility of reactive TEMPO-terminated polystyrene with C$_{60}$, a comparison was made between two different batches of living polystyrene and their end-functionalized products. Samples 1(M-PS)/C$_{60}$ (autopolymerization) and 1D(B-PS)/C$_{60}$ (benzoylperoxide initiated polymerization) have chromatograms at 260 nm that are nearly identical as they should be. These samples were both heated at 130 °C for 24 hours. Samples 2(M-PS)/C$_{60}$ vs. 2D(B-PS)/C$_{60}$ and 4D(B-PS)/C$_{60}$ vs. 4(M-PS)/C$_{60}$ also have similar chromatograms at 260 nm. However, making these same comparisons using the chromatograms at 330 nm, reveals some differences. The D(B-PS) samples show an increase in the amount of high molecular weight material and a bimodal chromatogram.

Figure 31. SEC overlay of samples 2D(B-PS)/C$_{60}$(●) and 2A(B-PS)/C$_{60}$(●)

In the preparation of these samples for end-capping reactions, 2A(B-PS)/C$_{60}$ was sonicated to induce mixing while 2D(B-PS)/C$_{60}$ was mixed with a mechanical stirrer. There is no significant difference in these results (Table 3, entries 20 and 11).

Figure 32.   SEC overlay of samples 1(M-PS)/C$_{60}$(●) and
1D(B-PS)/C$_{60}$(●).

The method of initiation of the starting polymer and its effect on the fullerene
products from end-capping reactions are compared in the next three figures.
Little difference is seen at 260 nm. At 330 nm, the 1(M-PS)/C$_{60}$ sample has
no low molecular weight fullerene material Table 3, entries 23 and 19).

Figure 33. SEC overlay of samples 2(M-PS)/C60(●) and
2D(B-PS)/C60(●).

The self-initiated polymer sample (2(M-PS)/C_{60}) shows at 330 nm, only high
molecular weight fullerene products, while 2D(B-PS)/C_{60} - a benzoyloxy
initiated sample - shows about equal amounts of high and low molecular
weight fullerene material (Table 3, entries 24 and 20).

Figure 34. SEC overlay of samples 4(M-PS)/C$_{60}$(●) and 4D(B-PS)/C$_{60}$(●)

This is another example of the different result achieved when using polymer chains derived from different methods of initiation (Table 3, entries 25 and 21).

Figure 34. SEC overlay of samples 4(M-PS)/C$_{60}$(●) and 4D(B-PS)/C$_{60}$(●)

This is another example of the different result achieved when using polymer chains derived from different methods of initiation (Table 3, entries 25 and 21).

The M-PS samples show a single symmetrical peak at shorter retention time corresponding to all fullerene-containing molecules having two PS chains. Despite this result, there is still value in comparisons between different batches of living polystyrene and the end-capped products formed from them.

In summary, we believed the best results could be obtained if the end-capping reactions were allowed to run for 5 days at 130 °C. Adding extra polymer (4:1) did not significantly change the mass fractions of the two peaks in the SEC. The same fraction of the LPS reacts with C_{60} at every LPS/C_{60} ratio. Residual monomer as well as a reheating method prompted further reactions with C_{60}. One example (2C(B-PS)/C_{60}) showed by SEC with better resolution than ours to have 0, 1, 2 and 3 polymer chains on a C_{60} (Figure 35). Detectable amounts of mono and trisubstituted C_{60} lead us to the question: What is the second group on C_{60} when one polystyrene chain is bound? Fullerene radicals would not be stable as the major reaction product, so the radical from addition of one polymer chain to a fullerene must abstract a hydrogen atom from solvent or polymer or a chlorine atom from oDCB, or combine with another fullerene radical or with TEMPO. The following experiments were designed to address these possibilities.

End-capped 1000 MW LPS. The LPS samples in these reactions had a molecular weight of about 1000 to facilitate detection of end groups by NMR. Recoveries are summarized in Table 5. Peak top MW is included in Table 5, and the 260 nm chromatograms are in Figures 36-38. These Figu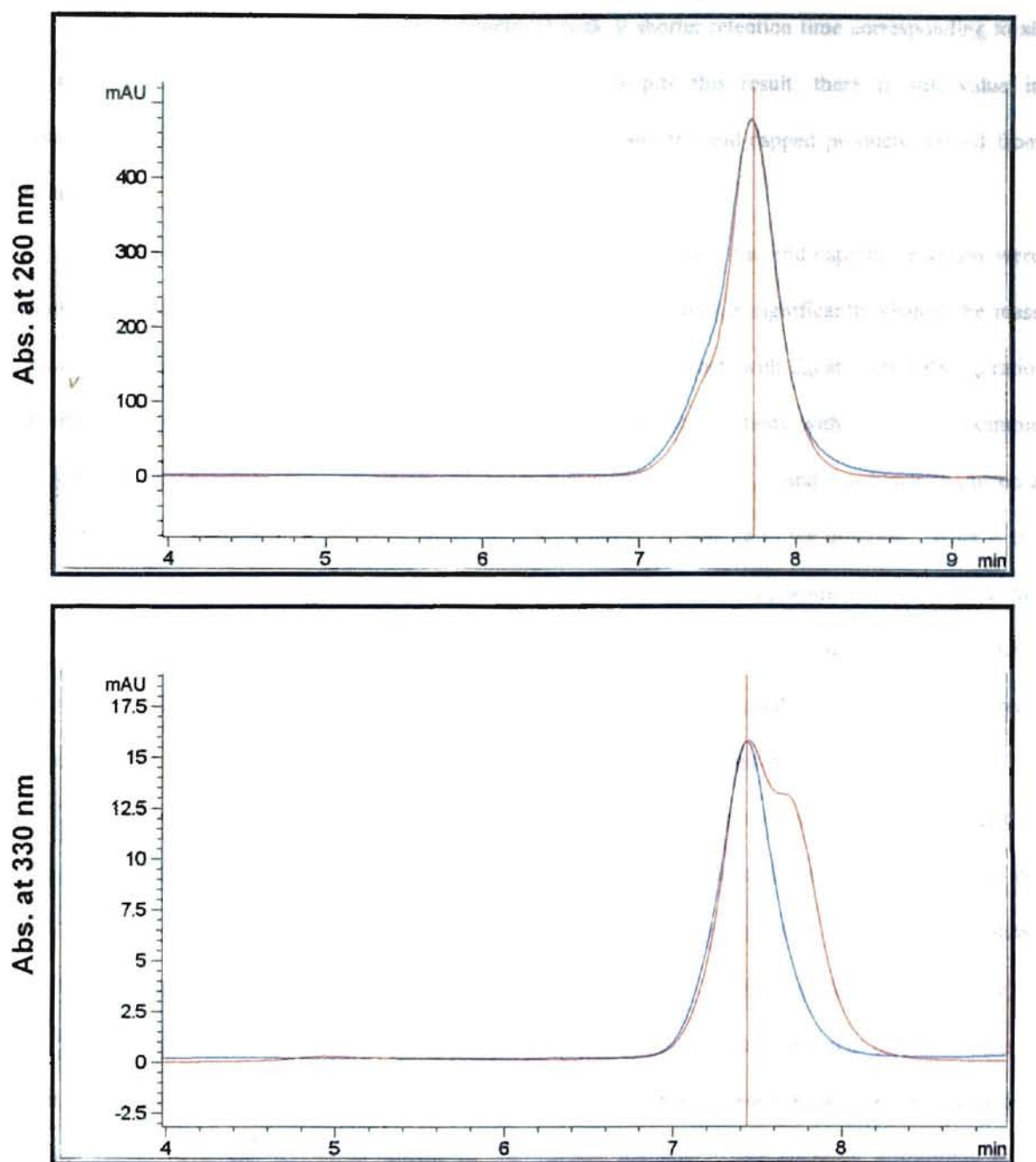res show most significantly, single peaks. At 260 nm absorbance, the methanol insoluble component (solid line) is at shorter retention time (higher molecular weight) and the methanol soluble component (dotted line) is at relatively longer retention time (lower MW). At 330 nm, a single peak appears for the methanol insoluble component at twice the molecular weight of the starting polymer. The isolation procedures have successfully removed the unreacted polymer as is evident by the very low absorbance of the methanol soluble component.

Figure 35. SEC profile of sample 2C(B-PS)/C$_{60}$ from
T. Mourey.

This sample shows a third peak at three times the molecular weight of the starting
polymer. The smaller chromatogram is that of the starting LPS. Table 3, entry 17.

Retention time	Pw	Pn	Pd
8.188	1900	1200	1.54
8.365	900	600	1.45

Retention time	Pw	Pn	Pd
8.095	2000	1300	1.59

Figure 36. SEC profiles of the methanol insoluble (—) and methanol soluble (---) components of (E-PS)/C_{60}.

Retention time	Pw	Pn	Pd
7.736	13500	8800	1.52
8.272	2000	1600	1.2
8.4	1500	800	1.87

Retention time	Pw	Pn	Pd
7.695	923400	7259	127

Figure 37. SEC profiles of the methanol insoluble
(—) and methanol soluble (---)
components of $(E\text{-}dPS/S)/C_{60}$.

Retention time	Pw	Pn	Pd
8.107	3200	2200	1.43
8.378	1300	1000	1.35

Retention time	Pw	Pn	Pd
8.081	3600	2600	1.35

Figure 38. SEC profiles of the methanol insoluble (—) and methanol soluble (---) components of (E-dPS)/C_{60}.

Table 5. Low Molecular Weight End-capped Reactions.

Sample	LPS (mg)	C_{60} (mg)	methanol insoluble	P_t	methanol soluble	P_t	unreacted C_{60} (mg)
E-PS-C_{60}	100	100	20 mg	1500	48.8 mg	940	76.6
E-dPS/S-C_{60}	200	100	74.9 mg	7400/1800	39.3 mg	1300	NA
E-dPS-C_{60}	100	100	47.2 mg	2800	25.7 mg	1400	84.1

The TEMPO-ended initiators have four diastereotopic methyl groups in the ^{1}H NMR (Figures 2, 4 and 5A). The signals from these four methyl groups change as polymerization occurs (Figure 5B). It seemed possible that these signals could be used to determine if hydrogen from chain transfer or TEMPO was part of the LPS-derivatized product.

A TEMPO group on the end of a polystyrene chain would presumably give a signal with a different chemical shift than a TEMPO group attached to a C_{60}. By using deuterated styrene and making low molecular weight LPS with it, we might be able to see signals from TEMPO end-groups on LPS chains (Figure 39, top) and compare them to TEMPO groups, if present, attached to C_{60}-derivatives (Figure 39, bottom). The spectra are normalized to the 2.3 ppm signal of the phenethyl end-group. The single TEMPO CH$_3$ at 0.4 and 0.25 ppm indicates that about 3.3% of the TEMPO remains as unreacted polymer 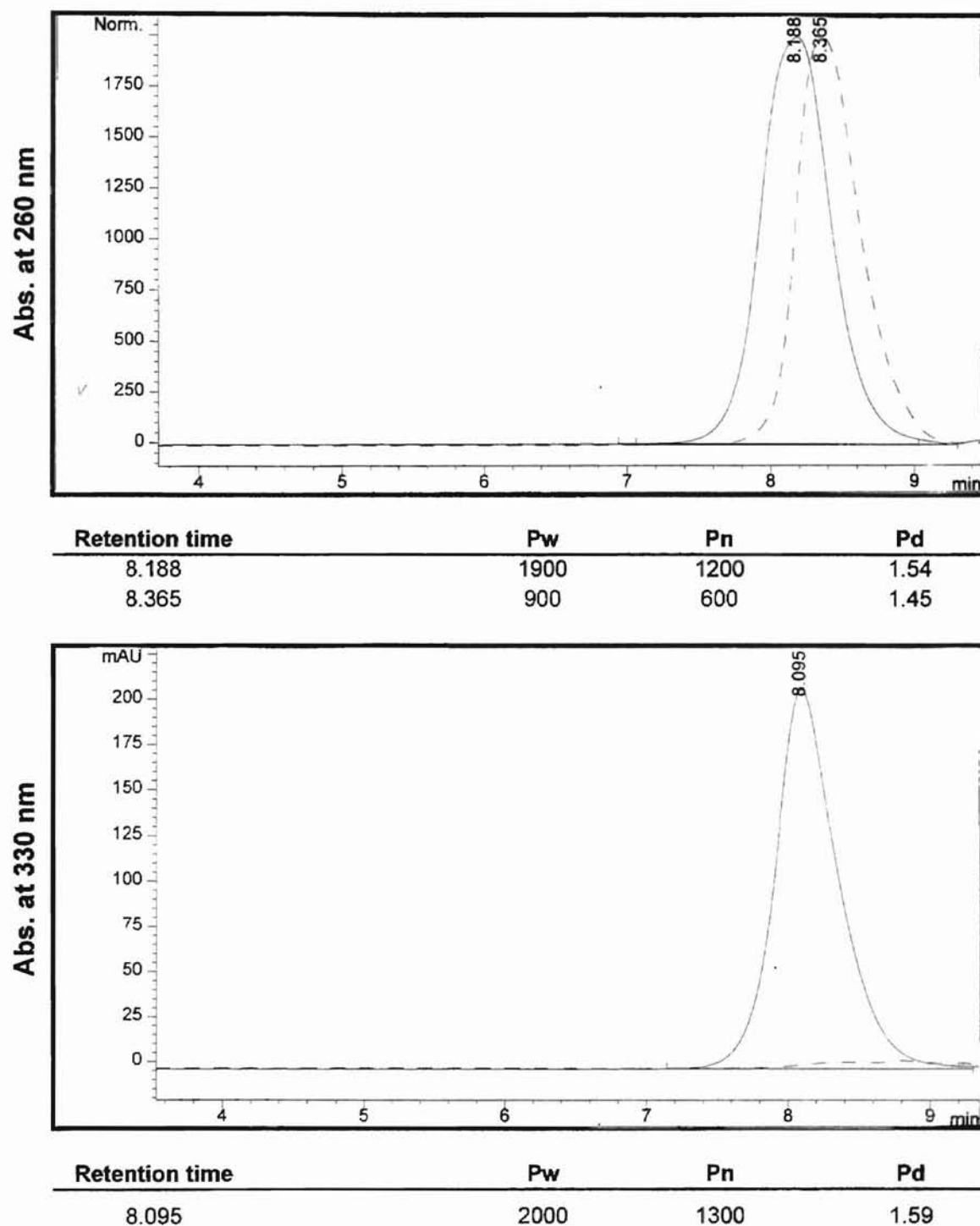that was not separated during the isolation procedure since the chemical shifts of the signals in the aliphatic region have not changed. There is no sign of TEMPO NMR signals at any new positions in the spectrum.

TEMPO trapping reactions. Acetic anhydride (AA) and camphorsulfonic acid (CSA) were investigated as possible TEMPO trapping agents.[27-30] A 2:1 molar ratio of LPS (B-PS-T) and C_{60} was prepared in oDCB and varying amounts of AA were added. These amounts corresponded to 1, 5, and 10 eqvivalents of AA for every 1 equivalent of TEMPO-ended polystyrene. A 1:5 molar ratio was tested with camphor sulphonic acid. The samples were heated at 130 °C for 24 hours.

Figure 39. ^{1}H NMR spectra of E-dPS-T(top) and (E-dPS)-C$_{60}$(bottom).

Table 6. TEMPO Trapping Reactions

Sample	molar ratio[a]	LPS (mg)	C_{60} (mg)	trapping agent (mg)	recovery (mg)
control	2:1	502	24.8	none	356.6
AA(1)	2:1:2	502	24.8	AA - 7.02	316.4
AA(5)	2:1:10	502	24.8	AA - 35.1	
AA(10)	2:1:20	502	24.8	AA - 70.3	335.0
CSA(5)	2:1:10	502	24.8	CSA - 79.7	290.8

[a]The molar ratio of living polystyrene to C_{60} to TEMPO trapping agent.

SEC showed that increasing amounts of AA slightly increased the relative amount of products having 2 PS chains per C_{60}, as can be seen in Figure 40. CSA did not increase the number of reactions on C_{60} (Figure 41).

Figure 40.   SEC overlay of samples for acetic anhydride
experiments, control (●), 1AA (●), 5AA (●)
and 10AA (●).

Figure 41.   SEC overlay of samples for camphor sulfonic
acid experiments, control (   ) and CSA (   ).

DISCUSSION

Many polymer materials have been combined with C_{60} using a variety of techniques.[4,5] Living anionic polystyrene chains have been grafted onto C_{60} to give a product similar to ours.[12-14] The work of Wang *et. al.* and Fukuda *et. al.* is most similar to ours using the stable free radical mechanism to produce living polystyrene and reacting this living polymer with C_{60}.[22,31] Wang *et al* did not recognize that there is unreacted living polystyrene present even after reaction with C_{60}.[31] Fukuda[22] circumvented this problem by fractionating the sample, thereby removing unreacted LPS.[22] We all seem to know what the LPS radical does, but what becomes of the TEMPO? TEMPO is a stable free radical. We believe it does not react with the C_{60} derivative. Its concentration builds up as more LPS radicals react with C_{60}. Eventually the concentration is high enough to stop the end-capping reaction. When the polymer solutions go through the isolation proedure, TEMPO is removed with the solvent.

Improving the end-functionalization reaction. Mathis[12] noticed that multiple additions occur on the fullerene and that there seems to be a limit of six anionically produced 'living' chains that can be grafted onto the molecule. We have also noticed these multiple additions (usually 1,2 and 3), and in our other research with C_{60} and 2-cyano-2-propyl radicals generated from AIBN, six additions to the fullerene resulted from a 5:1 mole ratio of AIBN to C_{60}.[6] This may be the result of the initiator efficiency of about 0.6 and the use of 5 moles of AIBN per mole of C_{60}.
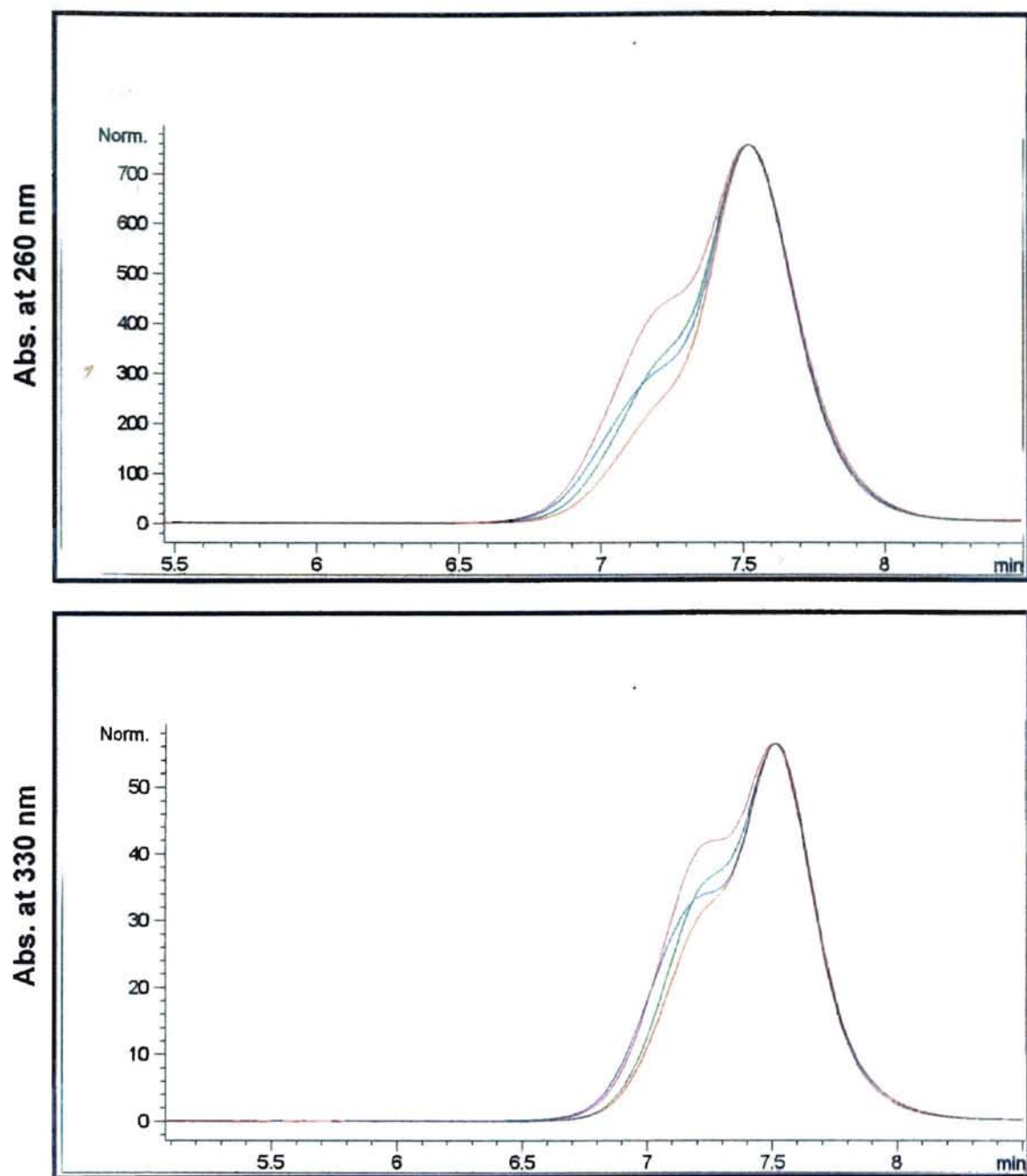
We have made efforts to reduce the amount of unreacted polymer by varying techniques and heating times and temperatures. Specifically, we have tried using higher temperatures and/or longer reactions times. Our preliminary assumption about the reaction mechanism that incorporates C_{60} onto the polymer led us to believe that TEMPO was being released during the end-capping reaction. Thus free TEMPO was building up in the solution resulting in a competitive reaction between C_{60} and TEMPO with 'living' polymer. This led to reactions that were designed to trap or remove the released TEMPO. In these reactions, increasing amounts of acetic anhydride increased the reaction on the C_{60}. We tried adding 1, 5, and 10 moles of acetic anhydride for every mole of TEMPO in an attempt to trap it, and in a different

reaction, we tried isolating the reaction solution into methanol twice (as described in the Experimental) to wash away the freed TEMPO and then heated the solution again. In these reactions, increasing amounts of acetic anhydride increased the reactions on the C_{60}, and reheated samples also increased the amount of high molecular weight material. It seemed that isolation procedures themselves might be affecting our 'living' polymers' liveliness, and so we eliminated the step of isolation from monomer that follows the initial polymerization. In these cases a monomer/polymer solution reacted with C_{60} produced a much higher molecular weight material than an identical sample where no monomer was present. This may also have been the result of residual monomer autopolymerizing which would produce radicals that could act as a trap for the free TEMPO.

Proposed mechanism. In our proposed mechanism, there is the suggestion that although TEMPO itself does not react with C_{60} it may react with a C_{60} radical derivative. To better understand a mechanism we would like to know where the free TEMPO goes. It could be part of the product, meaning it does react with the C_{60} radical derivatives. ^{1}H NMR analysis of deuterated polystyrene before and after reaction with C_{60} were used to test the following mechanism:

$$\text{PS-TEMPO} \quad \text{PS} \bullet + \text{TEMPO} \bullet \qquad (1)$$

$$\text{PS} \bullet + C_{60} \rightarrow \text{PS-}C_{60} \bullet \qquad (2)$$

$$\text{PS-}C_{60} \bullet + \text{XH} \rightarrow \text{PS-}C_{60}\text{-H} + \text{X} \bullet \qquad (3)$$

$$\text{PS-}C_{60} \bullet + \text{PS} \bullet \rightarrow \text{PS-}C_{60}\text{-PS} \qquad (4)$$

$$\text{PS-}C_{60} \bullet + \text{TEMPO} \bullet \quad \text{PS-}C_{60}\text{-TEMPO} \qquad (5)$$

$$\text{PS-}C_{60} \bullet + \text{PS-}C_{60} \bullet \rightarrow \text{PS-}C_{60}\text{-}C_{60}\text{-PS} \qquad (6)$$

$$\text{PS} \bullet + \text{PS} \bullet \rightarrow \text{PS-PS} \qquad (7)$$
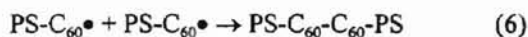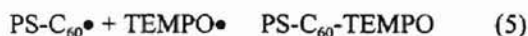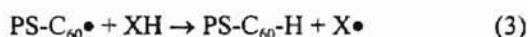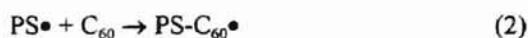
In step 1 the TEMPO-ended polystyrene cleaves reversibly. The PS radical goes on to react with C_{60} in step 2 to form a radical C_{60} derivative. That radical C_{60} derivative can then do one of the following: abstract a hydrogen atom from polymer or solvent (3); react with another PS radical (4); or it can react reversibly with TEMPO (5). There is also the possibility that two radical C_{60} derivatives can combine (6). Finally, termination by combination (7) can occur between two active polymer chains.

The deuterated samples are informative and show signals from unreacted TEMPO end-groups even after allowing long time at 130 °C for reaction with C_{60}. There are no apparent new signals in the NMR spectrum for TEMPO molecules attached to C_{60}. The magnitude of these peaks has changed, however which can mostly be accounted for by the reaction of 2PS• with C_{60} and 2 TEMPOs being removed during the work-up procedure. The residual signal is probably due to unreacted polymer still in the sample.

Fukuda and coworkers[22] showed that using high concentrations of C_{60} and reactions temperatures of 145 °C, disubstituted C_{60} could be obtained and fractionated away from unreacted polymer. We have determined that using excess polymer and temperatures of 130 °C produces mostly mono-and-di and sometimes trisubstituted C_{60}, which we also have fractionated away from at least some of the unreacted polymer.

CONCLUSIONS

In conclusion, living polystyrene has been prepared by a stable free-radical mechanism and has been further reacted with C_{60} in various molar ratios. The reactions of TEMPO-terminated polystyrene chains with C_{60} are limited by a build up of TEMPO in the oDCB solution. This limit was increased by precipitating the polymer to remove free TEMPO and polymerizing further, and by the presence of TEMPO traps such as residual monomer and acetic anhydride. In all of these reactions, the products consisted mainly of one and two chains per fullerene.

Our goals were to obtain optical quality polymer films and a well defined product. Further research should include testing these materials for optical activity. To cast C_{60}-containing polymer films with reasonable film properties, we and others[32] must add large amounts of high molecular weight polystyrene to these fullerene materials. The polymer chains can be lengthened during the production of the living polystyrene. The ability to vary and increase the amount of polymer chains reacted with C_{60} would eliminate the necessity of mixing in additional polymer and allow greater versitility in processing.

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Table 7. Integrated Areas and Height (mAU), Center (retention time in min), and Width at Half-height of Simulated Chromatograms.

| Sample | 260 nm, Peak 2 | | | | 260 nm, Peak 1 | | | | | 330 nm, Peak 2 | | | | 330 nm, Peak 1 | | | | |
	Int. 2	hgt	ctr	wth	Int. 1	hgt	ctr	wth	Int. Sum	Int. 2	hgt	ctr	wth	Int. 1	hgt	ctr	wth	Int. Sum
CET	61.679		6.35	0.2	6.0438				67.19	NA				NA				NA
B-PS-T	NA				75.182				75.182	NA				NA				NA
2(B*-PS)/C60	37.299	45	16.9	0.35	327.97	372	18.2	0.35	366.82	0.3434	0.39	17	0.35	0.1726	0.2	18	0.34	0.51525
2'(B*-PS)/C60	15.538	16.3	17	0.35	349.98	410	18.2	0.34	363.88	0.2203	0.25	17	0.35	0.1848	0.21	18.1	0.35	0.40508
1(B'-PS/S)/C60	26.642	74	7.4	0.14	82.737	235	7.73	0.14	108.76	2.9781	8.7	7.42	0.14	5.9781	17	7.75	0.14	8.9507
2(B'-PS/S)/C60	20.638	61	7.39	0.11	88.077	250	7.72	0.14	105.23	2.2684	6.96	7.43	0.13	4.4068	13.5	7.75	0.13	6.6949
4(B'-PS/S)/C60	20.562	63	7.39	0.13	88.22	251	7.73	0.14	109.18	2.7316	7.77	7.4	0.14	3.8305	10.9	7.75	0.14	6.5819
2(B-PS/S)/C60	321.17	305	22.6	0.42	319.53	335	23.6	0.38	642.34	52.08	49	22.6	0.42	34.416	38	23.7	0.36	86.314
2'(B-PS/S)/C60	370.5	379	22.6	0.39	272.54	292	23.6	0.37	641.84	57.983	59.1	22.6	0.39	35.271	37.9	23.7	0.37	93.178
2(B-PS)/C60	24.818	70	7.24	0.14	182.48	515	7.57	0.14	206.57	2.4818	7	7.25	0.14	3.6861	10.5	7.59	0.14	6.1679
2'(B-PS)/C60	46.744	141	7.29	0.13	160.5	492	7.62	0.13	206.5	5.1299	14.6	7.32	0.14	4.2203	12	7.64	0.14	9.3362
1A(B-PS)/C60	68.907	202	7.27	0.14	200.14	589	7.59	0.14	268.47	6.8814	19.6	7.27	0.14	7.6158	23.3	7.58	0.13	14.477
2A(B-PS)/C60	59.489	175	7.27	0.14	206.57	610	7.59	0.14	267.88	5.4015	16.5	7.27	0.13	7.0438	21.5	7.58	0.13	12.409
4A(B-PS)/C60	50.96	148	7.27	0.14	217.36	640	7.59	0.14	268.36	4.8531	13.8	7.27	0.14	6.0734	17.3	7.59	0.14	10.749
1B(B-PS)/C60	44.161	130	7.25	0.14	238.69	705	7.59	0.14	285.4	4.635	13	7.25	0.14	12.08	35.5	7.59	0.14	16.606
2B(B-PS)/C60	39.147	115	7.25	0.14	244.98	721	7.59	0.14	283.9	3.661	10.4	7.26	0.14	10.141	28.8	7.6	0.14	13.291
4B(B-PS)/C60	30.878	87.4	7.25	0.16	255.62	723	7.58	0.14	288.9	2.8672	8.16	7.25	0.14	7.161	20.4	7.59	0.14	10.085
1C(B-PS)/C60	81.387	230	7.25	0.14	219.34	620	7.58	0.14	294.54	8.6679	24.5	7.26	0.14	10.712	30.5	7.59	0.14	19.38
2C(B-PS)/C60	99.683	247	7.21	0.16	194.85	536	7.58	0.15	295.5	15.763	34.9	7.22	0.18	8.5523	22.7	7.58	0.15	24.11
4C(B-PS)/C60	89.677	244	7.2	0.15	204.86	561	7.57	0.15	293.5	13.997	32.8	7.2	0.17	7.5593	20.1	7.53	0.15	21.568
1D(B-PS)/C60	228.47	650	7.32	0.14	470.8	1340	7.65	0.14	704.38	23.832	67	7.34	0.14	12.737	36	7.34	0.14	36.314
2D(B-PS)/C60	140.39	395	7.34	0.14	561.58	1595	7.65	0.14	700.5	15.268	43.4	7.35	0.14	12.966	36.8	7.65	0.14	28.164
4D(B-PS)/C60	122.15	343	7.29	0.14	587.43	1659	7.64	0.14	707.6	12.74	36.2	7.33	0.14	9.8023	27.8	7.64	0.14	22.542
0.5(M-PS)/C60	115.24	353	7.52	0.13	164.97	500	7.8	0.13	279.6	13.192	37.5	7.5	0.14	4.5367	12.9	7.77	0.14	17.288
1(M-PS)/C60	96.512	296	7.5	0.13	182.22	532	7.79	0.14	277.7	11.667	33.1	7.5	0.14	3.3263	9.47	7.79	0.14	12.288
2(M-PS)/C60	95.985	280	7.5	0.14	183.58	562	7.79	0.13	278.1	9.8905	29	7.5	0.14	2.7226	8	7.79	0.14	12.664
4(M-PS)/C60	52.737	149	7.39	0.14	202.08	641	7.74	0.14	277.4	6.7701	21.2	7.45	0.17	0				9.0678

VITA

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