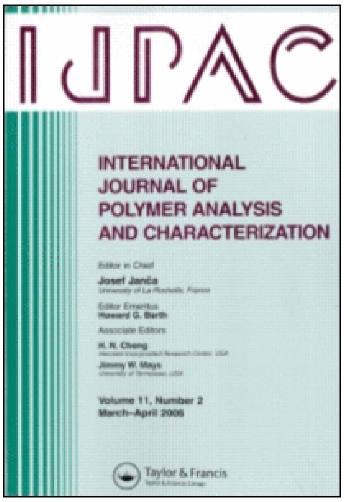

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Study of Degradation on Deuteration of a Diblock Copolymer of Polystyrene and Poly(ethylene-*alt*-propylene)*

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This paper reports a method of selectively deuterating the aromatic ring in a diblock copolymer of polystyrene and poly(ethylene-*alt*-propylene). The molecular weight distribution and molecular weight of the copolymer were determined by size exclusion chromatography and the extent of deuteration by ^{1}H nuclear magnetic resonance spectroscopy. High levels of deuteration were sought with minimal changes in molecular weight distribution. A range of deuteration experiments were performed, some of which produced significant changes in molecular weight of the diblock copolymer. Changes in molecular weight are discussed with reference to groups in the copolymer chain.

Keywords: Diblock copolymer; Deuteration; Size exclusion chromatography

INTRODUCTION

Small angle neutron scattering experiments (SANS) on polymeric systems frequently rely on labeling some parts of the system with deuterium to provide contrast between molecules or parts of molecules. The scattering of neutrons by deuterium nuclei is quite different to that of hydrogen, but the chemical effect of the substitution

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is often minimal. When deuterated and hydrogenous molecules are to be mixed, a matched set of deuterated and hydrogenated chains is most helpful for the interpretation of SANS patterns.[1,2] Furthermore deuterated polymers are also of great use in the NMR studies of chain dynamics.[3,4]

For studies involving phase separation of polymeric systems, an inability to match exactly the deuterated and nondeuterated chains may present difficulties in the interpretation of scattering data. For diblock copolymers, for example, characterization parameters will be monomer composition, individual block lengths, and overall molecular weight. A mismatch in block lengths may result in segregation of the deuterated chains from nondeuterated when the polymeric system is in a phase separation situation. Consequently, there is a requirement to develop methods for preparing matched sets of chains. Three procedures may be considered. Firstly, saturation of a common parent polymer with deuterium to obtain neutron scattering contrast. This will be restricted to polymers of a specific type, e.g., hydrogenated and deuterated polybutadienes. Secondly, synthesis of otherwise identical polymers from nondeuterated and deuterated monomers. This is extremely demanding on experimental technique in particular for a block copolymer. Finally, chemical exchange of deuterium to form a deuterated or partially deuterated polymer from a hydrogenated polymer. This represents an ideal choice for producing matched pairs as long as the deuteration conditions do not significantly alter the chain structure.

Previously, an exchange method for selectively and rapidly deuterating aromatic compounds was reported.[5] This method was later extended to the deuteration of polystyrene,[6] but was found to decrease molecular weight and increase broadening in high molecular weight samples, possibly due to a chain scission process induced by the catalyst used for the exchange reaction. Our preliminary studies of this methodology have involved performing exchange reactions with benzene-d_6 and the aromatic protons in a diblock copolymer of polystyrene (PS) and poly(ethylene-*alt*-propylene), referred to as SEP, catalyzed by ethylaluminium dichloride with a trace of water. SANS studies of micelles formed by these diblock copolymers indicated that the reduced size and increased polydispersity of PS(D) cores compared with PS(H) cores in micelles might be due to changes in copolymer molecular weight introduced during the deuterium exchange.[7]

The aim of this work was to investigate the deuteration of SEP diblock copolymer with a range of experimental conditions and characterize the products by size exclusion chromatography (SEC) and ^{1}H nuclear magnetic resonance spectroscopy (NMR). Whilst an objective was to identify deuteration conditions to produce high levels of deuteration without major changes in molecular weight distribution, it was judged important to understand what factors, relating to the chain structure of the diblock copolymer, might be responsible for changes in molecular weight during deuterium exchange.

EXPERIMENTAL

Materials

The SEP diblock copolymers were supplied by Shell (London, UK) who provided values of PS content of 38% and 34% for SEP1 and SEP2 respectively. Fisher Scientific (Loughborough, UK) supplied tetrahydrofuran (SEC grade) and the polystyrene standards were supplied by Polymer Laboratories (Church Stretton, UK). All other chemicals and reagents were supplied by Aldrich Chemical Company (Gillingham, UK). Ethylaluminium dichloride was supplied as a 1.0 M solution in hexane. All chemicals were used as supplied unless otherwise stated.

Deuteration of Aromatic Ring of an Anionically Prepared Polystyrene

Polystyrene (0.1 g) was added to a solution of benzene-d_6 (1 mL) and cyclohexane (2 mL) contained in a round-bottom flask (25 mL) that had previously been dried in a vacuum oven at 120°C overnight and subsequently cooled in a desiccator. As traces of water acted as a cocatalyst in the reaction, rigorously dry conditions were not applied. A rubber septum was used to seal the flask and a nitrogen inlet was added. The solution of polymer was stirred with a magnetic stirrer for 15 min to aid dissolution. Ethylaluminium dichloride in hexane was then added and the solution stirred for 1 h. The reaction was quenched with water (2 mL) and methanol was added to precipitate the polymer. The reaction mixture was filtered and the polymer dried under vacuum at 60°C overnight. The polymer was then purified by dissolution in toluene and re-precipitation in methanol.

Deuteration of the Aromatic Ring of an SEP Diblock Copolymer

The SEP copolymer (0.1g) was added to a solution of benzene (d_6, 1 mL) and cyclohexane (2 mL) contained in a round-bottom flask (25 mL) that had previously been dried at 120°C overnight and cooled in a desiccator. A rubber septum was used to seal the flask and a nitrogen inlet was added. The solution of polymer was stirred with a magnetic stirrer for 15 min to aid dissolution. Ethylaluminium dichloride in hexane was then added and the solution stirred for 30 min. The reaction was quenched with water (2 mL) and methanol was added to precipitate the polymer. The reaction mixture was filtered and the polymer dried under vacuum at 60°C overnight. The polymer was then purified by dissolution in toluene and reprecipitation in methanol. A second method was also used to deuterate the SEP copolymer. The method followed the same procedure as outlined above except only benzene-d_6 (2 mL) was used as solvent, and to aid dissolution the polymer was stirred for 45 min.

Spectroscopic Characterization

The level of deuteration in each copolymer or polystyrene was determined from a ^{1}H NMR spectrum obtained on a 400 MHz Bruker instrument. The polymer (20 mg) was dissolved in $CDCl_3$ (1 mL) in a 5-mm NMR tube and the spectrum recorded between 0–8 ppm. The ratio of the aromatic portion of the spectrum (6.6–7.3 ppm) and the aliphatic portion (0.7–1.3 ppm) was used to determine the percentage of deuterium incorporation.

Chromatographic Characterisation (SEC)

A system was established comprising 2 × PLgel Mixed-B (10 µm) columns (300 × 7.5 mm), (Polymer Laboratories, Church Stretton, UK). Injections were made using a Rheodyne 7125 injection valve fitted with a 100 µL loop and THF at a flow rate of 1 mL/min was used as the eluent. A differential refractometer (Knauer) was used as detector and Caliber software (Polymer Laboratories, Church Stretton, UK) was used to determine number-average and weight-average molecular weights, M_n and M_w, and peak molecular weight M_p for an injected sample. The column set was calibrated by dissolving narrow polystyrene standards in the molecular weight range 1700–1290000 in THF at a concentration of 0.1%. A linear calibration was then fitted to the retention results. Polymers and copolymers were dissolved in THF at a concentration of 0.1% and injected onto the column set described above. A baseline was fitted to a chromatogram with the aid of the Caliber software.

RESULTS AND DISCUSSION

Two SEP diblock copolymers were characterized by SEC and ^1H NMR. SEP1 had an M_n (based on a PS calibration) of 137000 and showed resonances in the NMR spectrum at 0.84, 1.07 and 6.8 ppm (Fig. 1a). By comparison of the integral of the peak at 0.84 ppm due to the methyl group of the ethylene–propylene unit and the peak at 6.8 ppm due to the aromatic protons, it is possible to calculate the weight fraction of styrene as 0.34. This weight fraction is the ratio of the number-average molecular weights for PS block and diblock copolymer, and so M_{ps} is 47000. Similarly, for SEP2 the M_n was 190000 based on a PS calibration and NMR peaks were observed at 0.84, 1.08 and 6.8 ppm (Fig. 1b). The styrene content was calculated as a weight fraction of 0.3 and hence M_{ps} for the PS block would be 57000. The SEC data are based on a PS calibration, but it can be predicted that calibrations for polyethylene and polypropylene are positioned below a PS calibration.[8] Therefore, values of M_n obtained for a diblock copolymer are too high, and values of M_{ps} for the PS block will be an overestimate.

Our initial deuteration experiments followed the original procedure of Willenberg[6] for the deuteration of PS. The deuteration of SEP1 was performed using benzene-d_6 as solvent and the effect of adding increasing amounts of $EtAlCl_2$ was studied (Tab. I). The same procedure was also used to deuterate the higher molecular weight SEP2 copolymer and the results are shown in Table II. A typical SEC

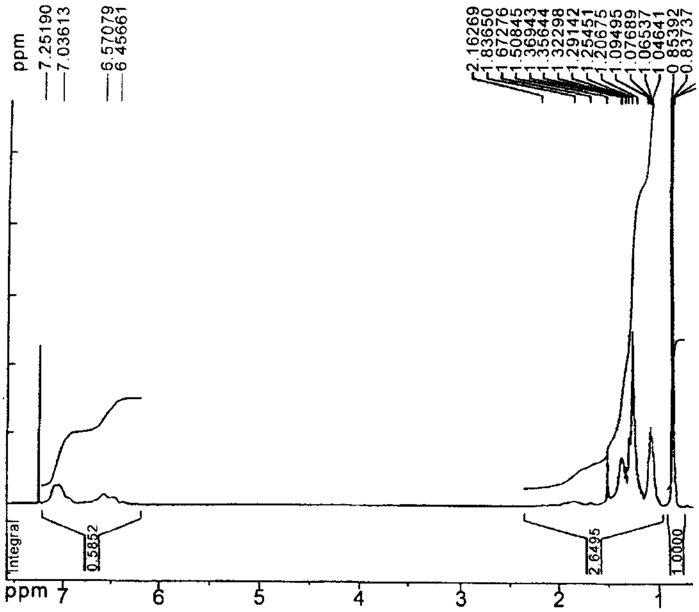

FIGURE 1a ^{1}H NMR spectrum of SEP1 copolymer.

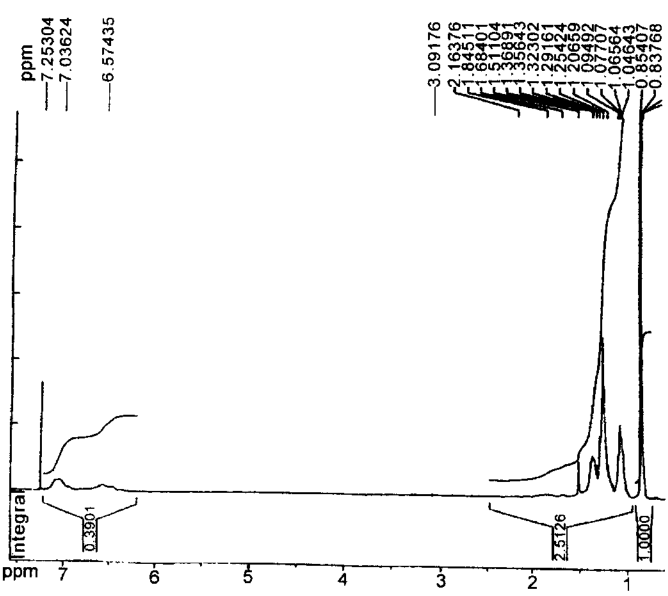

FIGURE 1b ^{1}H NMR spectrum of SEP2 copolymer.

TABLE I Molecular weight and deuteration data for SEP1 copolymers using benzene-d_6 as solvent

Sample	$EtAlCl_2$ *added* (μL)	M_p	M_w	M_n	M_w/M_n	% *Deuteration*
SEP1		146000	147000	137000	1.07	–
DP50	50	139000	142000	130000	1.09	> 98
DP100	100	137000	141000	129000	1.09	> 98
DP200	200	135000	141000	129000	1.09	> 98

TABLE II Molecular weight and deuteration data for SEP2 copolymers using benzene-d_6 as solvent

Sample	$EtAlCl_2$ *added* (μL)	M_p	M_w	M_n	M_w/M_n	% *Deuteration*
SEP2	–	201000	205000	190000	1.08	–
dps50	50	211000	216000	194000	1.11	> 98
dps100	100	215000	222000	199000	1.11	> 98
dps200	200	210000	213000	193000	1.10	> 98

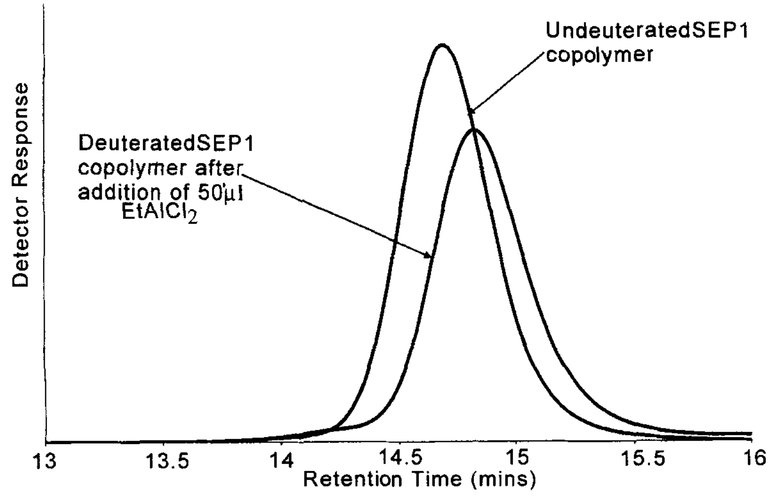

FIGURE 2 SEC of deuterated/nondeuterated SEP1 copolymer using benzene-d_6 as solvent.

profile is shown in Figure 2 for a deuterated SEP1 copolymer and an undeuterated SEP1 copolymer. The chromatograms have the same profile with no shoulders or tailing; however, the peak for the deuterated product is displaced towards lower molecular weight. The results in both Tables I and II show high levels of deuteration with minimal peak broadening. The data for SEP2 copolymer follow the expected pattern of slightly increased molecular weight, as hydrogen is being exchanged for deuterium. However the data for SEP1 copolymer show a decrease in molecular weight which was unexpected, possibly due to some degradation reaction.

To investigate the effect of reducing the concentration of benzene-d_6, cyclohexane was used as cosolvent. As the work of Willenberg[6] was carried out in benzene-d_6 alone, it was decided to carry out a series of experiments using an anionically prepared PS sample of comparable molecular weight to the PS block in the SEP1 copolymer ($M_n \sim 30000$). These results are presented in Table III showing high levels of deuteration. It is noticeable that the change in polydispersity as the concentration of $EtAlCl_2$ is raised is higher in Table III than in Table I. A minor trend of decreasing M_n at increasing concentrations of $EtAlCl_2$ is also observed, possibly as a consequence of degradation. Results for the deuteration of the SEP1 copolymer employing the cyclohexane–benzene-d_6 solvent system are shown in Table IV.

TABLE III Molecular weight and deuteration data for PS30000 samples using a benzene-d_6 and cyclohexane solvent system

Sample	*$EtAlCl_2$ added (μL)*	M_p	M_w	M_n	M_w/M_n	*% Deuteration*
PS30000		30600	30700	28300	1.08	
DP16	50	30500	30500	28000	1.09	93
DP17	100	31000	31200	28000	1.11	93
DP18	150	30200	31100	27800	1.12	93
DP19	200	30500	30300	26600	1.14	92
DP21	300	30900	30300	27000	1.12	93
DP22	400	31700	31900	28000	1.14	92

TABLE IV Molecular weight and deuteration data for SEP1 copolymer using a benzene-d_6 and cyclohexane solvent system

Sample	*$EtAlCl_2$ added (μL)*	M_p	M_w	M_n	M_w/M_n	*% Deuteration*
SEP1		146000	147000	137000	1.07	
DP10	50	138000	161000	46400	3.47	> 98
DP11	100	139000	160000	47100	3.40	> 98
DP12	200	143000	177000	38700	4.57	> 98

These results for SEP1 copolymer show a marked contrast from the results obtained using benzene-d_6 alone as solvent, with the value of M_w increasing and M_n decreasing considerably even at low levels of addition of $EtAlCl_2$. This is shown in Figure 3 where SEC chromatograms for SEP1 copolymer before and after deuteration are displayed. A shoulder can be observed on the high molecular weight side and there is tailing towards low molecular weights.

Various methods are available for the hydrogenation of polydienes and poly(styrene-*b*-isoprene) to give the SEP copolymer.[9] These include homogeneous methods using metal alkyl and transition metal complexes, and the in-situ production of a diimide via toluene sulfonyl hydrazide. Heterogeneous supported metals such as Ni on calcium carbonate may also be used. The method used to produce the SEP copolymer studied in this investigation is unknown. However, it is known that some of the methods outlined above do give incomplete saturation for polydienes.[9] This would leave some sites of unsaturation on the copolymer for the $EtAlCl_2$ used in the deuteration to participate in side reactions, since the lowering of the benzene-d_6 concentration effectively increases the availability of $EtAlCl_2$. $EtAlCl_2$ has been used to initiate isobutylene polymerizations[10] and could therefore react with any remaining sites of unsaturation. If a carbocation species is generated, then a range of other reactions, such

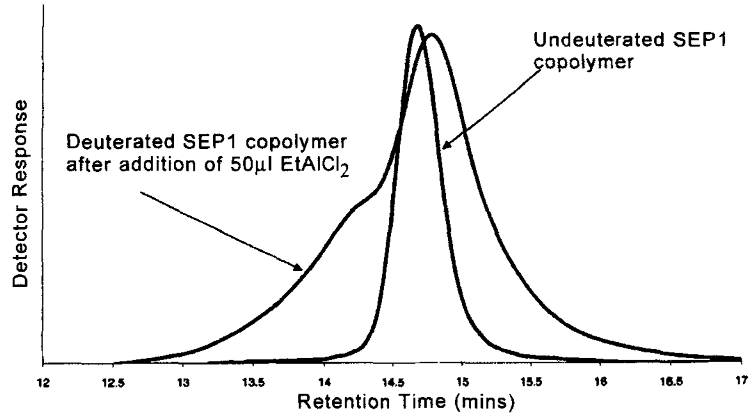

FIGURE 3 SEC of deuterated/nondeuterated SEP1 copolymer using a benzene-d_6 and cyclohexane solvent system.

as transfer, migration, isomerization, might occur,[11] which might lead to a substantially broadened distribution as shown in Figure 3. The in-situ production of a diimide via toluene sulfonyl hydrazide has been shown to fully saturate residual double bonds on a polymer backbone.[9] However, this method has been shown to leave sulfur containing residues on the product. Lenz has presented evidence of sulfur residues after hydrogenation of a statistical copolymer of styrene and butadiene and an ABA poly(styrene-*b*-butadiene) triblock copolymer.[12] Such a sulfur species may provide a site for reaction of $EtAlCl_2$. In summary, it appears that the broad chromatogram in Figure 3 with a consequential increase in M_w and decrease in M_n results from side reactions in the poly(ethylene-*alt*-propylene) block during deuteration of the PS block which, as exemplified by the results in Table III, is less affected.

CONCLUSIONS

Characterization results demonstrate that high levels of deuteration of SEP diblock copolymer with minimum change in molecular weight can be achieved by deuterium exchange of aromatic protons. However, even for the optimum deuteration conditions, a high concentration of benzene-d_6 and a low concentration of $EtAlCl_2$, slight changes in molecular weight and polydispersity are observed. By performing deuteration experiments at a reduced concentration of benzene-d_6, significant changes in molecular weight of SEP are found, which appear to result largely from side reactions in the poly(ethylene-*alt*-propylene) block with much less influence on the PS block.

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