

ABA Triblock Copolymers with Two Crystallizable Blocks

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SYNOPSIS

Triblock copolymers of the ABA type were synthesized in which the A block is poly(ethylene oxide) (PEO), having molecular weight of 1000 or 2000, and the B block is poly(dimethylsiloxane) (PDMS), having molecular weight of about 8000 or 10,000. When the triblock copolymer was cooled from the melt, the PEO block crystallized at around room temperature. Upon further cooling to liquid nitrogen temperature and reheating, the crystallization of the PDMS middle block took place at around -90°C . The melting temperatures and degrees of crystallinity of the PEO blocks in the copolymers were depressed from their respective pure state values. On the other hand, the melting points of the PDMS middle blocks in the copolymers were the same as the pure state values; furthermore, the degrees of crystallinity were unexpectedly much higher. © 1993 John Wiley & Sons, Inc.

I. INTRODUCTION

We have reported in a separate paper¹ the synthesis of a triblock copolymer of the ABA type in which the A block is poly(ethylene oxide) (PEO) with an average molecular weight of 5000 and the B block is poly(dimethylsiloxane) (PDMS) with an average molecular weight of 9000. When the triblock copolymer was cooled from the liquid state, the PEO block crystallized at around 40°C . Upon quenching to liquid nitrogen temperature and reheating, glass transition, crystallization, and melting of the PDMS middle block were seen in calorimetric measurements at -117 , -74 , and -42°C , respectively. The degree of crystallinity of the PDMS block was estimated from the heat of fusion to be about 27%. That the PDMS segments were able to crystallize after PEO had already crystallized was surprising because the PDMS prepolymer did not crystallize in the pure state when subjected to the same thermal history. To ascertain that the difference in the degrees of crystallinity of the PDMS in the copolymer and in the pure state is not an artifact due to the synthetic procedure employed, we have now used a

different route for the synthesis of the triblock copolymer. The results are reported in this paper.

II. EXPERIMENTAL

1. Materials

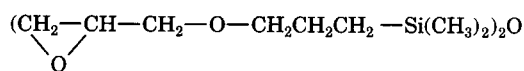
Tetramethyldisiloxane and octamethylcyclotetrasiloxane (D_4) were purchased from Petrarch Co. Allyl glycidyl ether and poly(ethylene glycol) were obtained from Aldrich Co. and poly(acrylic acid) from Polyscience Co.

2. Epoxy-terminated Disiloxane

Tetramethyldisiloxane was added slowly to a solution of allyl glycidyl ether in toluene at 110 – 120°C over a period of 3 h. Chloroplatinic acid was used as the catalyst. The reaction product, 1,1,3,3-tetraethyl-1,3-bis[3-(2,3-epoxypropoxy)propyl]-disiloxane, was collected by distillation at 185 – $195^{\circ}\text{C}/2$ – 3 Torr. The epoxy equivalent of the disiloxane was determined by titration to be 186 (theoretical value 181). The FTIR spectra of the compound showed no absorption at 2115 cm^{-1} due to SiH stretching or at 1563 cm^{-1} due to the $\text{C}=\text{C}$ of the starting materials; the epoxy group was identified by absorptions at 850 and 920 cm^{-1} . ^{13}C -NMR spec-

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tra indicated seven different carbons and the chemical shifts are consistent with the structure



as shown in Figure 1.

3. Epoxy-terminated Siloxane Oligomer

The epoxy-terminated disiloxane was mixed with D_4 and 0.5% (w/w) of tetramethylammonium silanolate as catalyst. The reaction took place at 80°C for 24 h; after completion of the reaction, temperature was raised to 145–150°C for 3 h to decompose the catalyst. The unreacted D_4 compound and the residues of the decomposed catalyst were extracted by methanol. Vacuum distillation at 80–100°C removed low molecular weight compounds. The remaining transparent liquid was the desired siloxane prepolymer. The molecular weight of the oligomer was controlled by the ratio of D_4 to disiloxane used. The two oligomers used in the synthesis of triblock

copolymers had molecular weights (calculated from epoxy equivalents) of 7810 and 10,320; they were designated as S8 and S10. The yields of the reactions were about 82%.

4. Triblock Copolymers

The siloxane oligomers containing terminal epoxy groups were reacted with $\text{HO}(\text{---CH}_2\text{CH}_2\text{O})_n\text{H}$ at 80°C in toluene under acidic conditions for 3 h. Two PEO oligomers having nominal average molecular weights of 1000 and 2000 were used. They are designated as E1 and E2, respectively. The molar ratio of PEO to siloxane was 1.5 in the reaction mixture. At the end of the reaction, the excess PEO was extracted by methanol and the unreacted siloxane oligomer removed by refluxing with hexane. The triblock copolymers were designated by the numerals following S and E; for example, S8E1 indicates the molecular weight of the middle block as ~8000 and that of the PEO end blocks as 1000. The yields of the reactions were 70% for S8E1, 61% for S8E2, 81% for S10E1, and 79% for S10E2. The ratio of methyl-to-methylene groups in the copolymer was

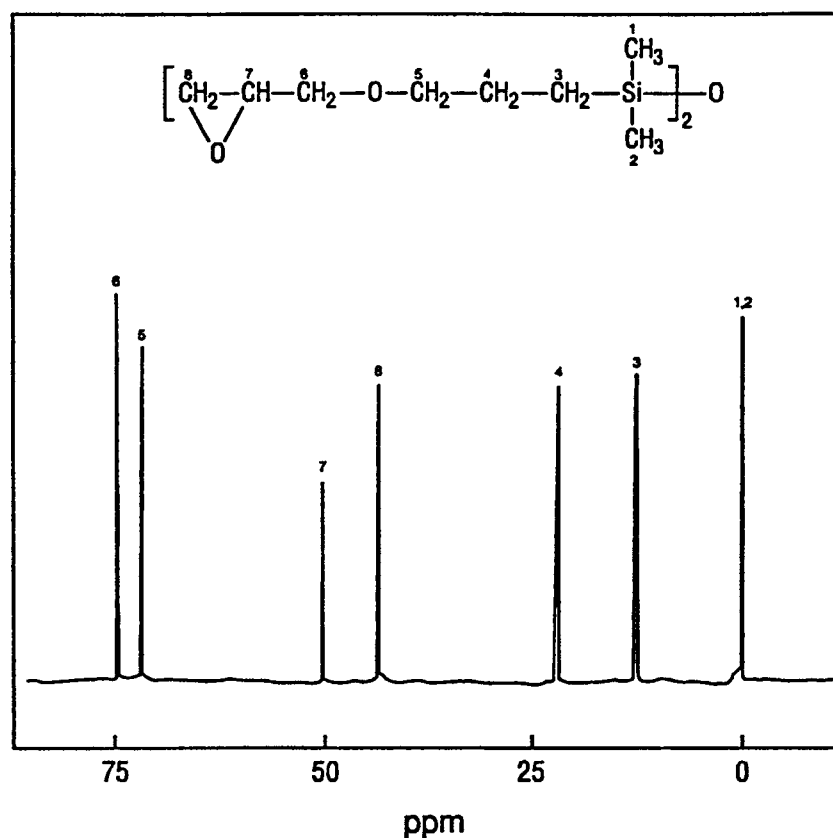


Figure 1 NMR spectra of epoxy-terminated disiloxane.

determined by ^{13}C -NMR. The ratio was 2.16 for S8E1, which is to be compared with the calculated value of 2.33. Since the nominal molecular weight of PEO was used in the calculation, the agreement between the experimental and calculated values was deemed acceptable.

5. Differential Scanning Calorimetry

Thermal analysis of the polymers was carried out with the use of a DuPont instrument, Model 9900. A heating rate of $15^\circ\text{C}/\text{min}$ was used throughout. After the first thermal scan, the sample was quenched to liquid nitrogen temperature and the experiment was repeated. The midpoint of the specific heat jump in the glass-to-liquid transition was taken as the glass transition temperature, T_g , and the peak temperature of the melting endotherm as the melting point, T_m . In comparing the results of the first and second runs, we found that there was little difference in the T_g , T_c , and T_m values. However, the heat of fusion values differed significantly in several cases; the ΔH values obtained from the second runs were used in the calculation of the degrees of crystallinity.

III. RESULTS AND DISCUSSION

1. Thermal Analysis of the Component Blocks

The two ethylene oxide oligomers show prominent melting endotherms. The melting temperatures increase with increasing molecular weights of PEO, namely, 40°C for E1 and 57°C for E2. The corresponding degree of crystallinity also increases from

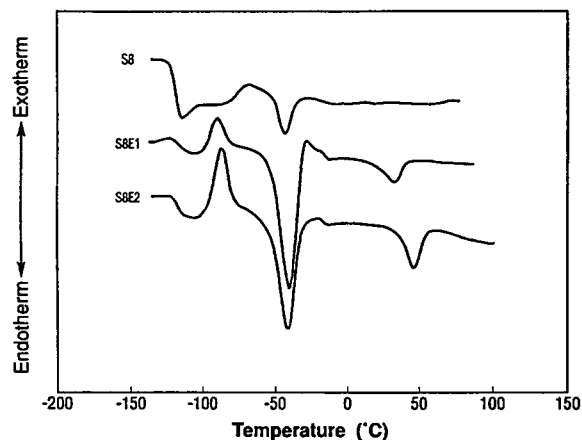


Figure 2 Thermograms of S8, S8E1, and S8E2.

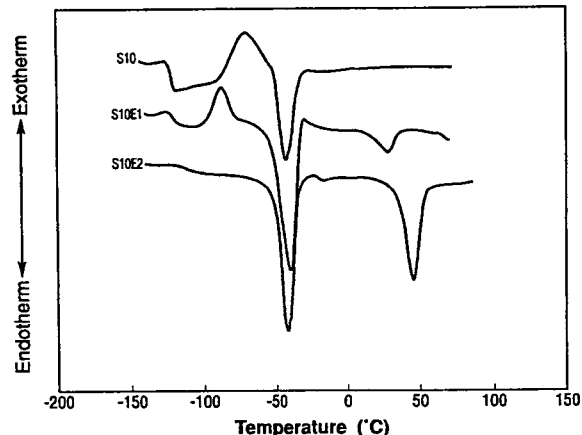


Figure 3 Thermograms of S10, S10E1, and S10E2.

59 to 80%. (In the above calculation, 205 J/g was used as the heat of fusion of completely crystalline PEO.²) The glass transition temperatures of the PEO samples, reported in the literature as -70 to -80°C , were not observed unequivocally, probably because the crystallinities of the specimens are high.

The thermogram of S8 is shown in Figure 2. The glass transition is located at -114°C ; an exotherm due to crystallization is seen at -70°C (T_c) and is followed by melting at -45°C (T_m). The heat of fusion is small, only 2.1 J/g . Comparison to the heat of fusion of 63.4 J/g ³ for completely crystalline poly(dimethylsiloxane) indicates that the quenched S8 is 3.4% crystalline. The low degree of crystallinity found here agrees with the result reported in the previous study for an oligomer of comparable molecular weight.¹

The S10 sample shows similar thermal events (Fig. 3). The observed T_g , T_c , and T_m are located at -121 , -71 , and -42°C , respectively. The degree of crystallinity, however, is much higher than that of S8; a value of 23% is calculated from the heat of fusion of 14.2 J/g . These results are summarized in Table I.

2. Thermograms of Triblock Copolymers

The thermograms of the two S8 copolymers are shown in Figure 2. The quantities of interest, T_g , T_c , T_m , and ΔH_m , for both the siloxane and the PEO blocks are listed in Table I. The results can be summarized as follows: (a) The incorporation of the siloxane oligomer in the block polymers does not change its T_g but shifts T_c to much lower temperatures in the copolymers. (Crystallization of the siloxane block was undetectable for S8E2 in the second

Table I Calorimetric Data of Triblock Copolymers (Second Run)

	S8	S10	E1	E2	S8E1	S8E2	S10E1	S10E2
$T_g(s)$ ($^{\circ}\text{C}$)	-114	-121			-119	-114	-120	-116
$T_c(s)$ ($^{\circ}\text{C}$)	-70	-71			-91	—	-87	—
$T_m(s)$ ($^{\circ}\text{C}$)	-45	-42			-41	-42	-39	-42
$\Delta H(s)$ (J/g)	2.1	14.2			27.2	21.2	27.5	22.8
$X_c(s)$ (%)	3.4	23			55	52	53	51
$T_m(E)$ ($^{\circ}\text{C}$)			39	57	31	52	32	53
$\Delta H(E)$ (J/g)			121.9	164.0	4.2	9.3	3.7	16.0
$X_c(E)$ (%)			59	80	10	13	11	28

ΔH is expressed as J/g polymer sample.

run.) (b) The melting temperature of the siloxane middle block was the same as that of the oligomer in the pure state. (c) The degree of crystallinity of the siloxane middle block increased dramatically in the copolymer. (d) The melting points of the PEO end block were depressed from the corresponding values for the oligomers in the free state. (e) In complete contrast with the siloxane middle block, the PEO oligomers had much lower degrees of crystallinity when incorporated as end blocks in the copolymers.

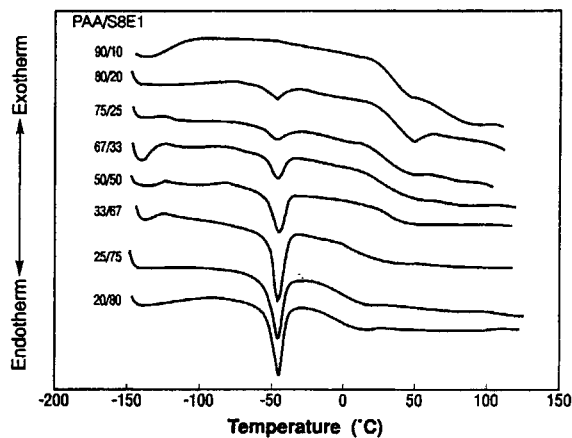
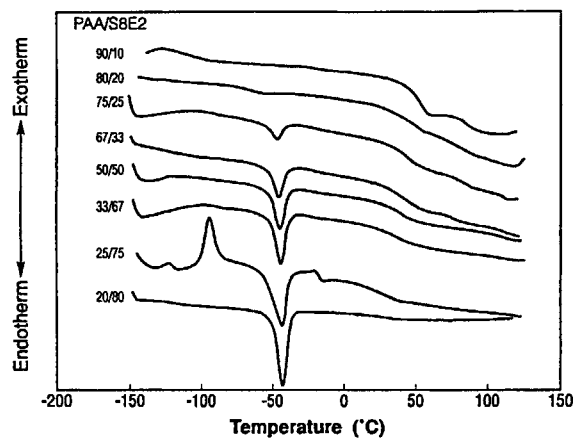
The depression of the melting points of PEO end blocks, relative to the pure state values, and the accompanying decreases in the degrees of crystallinity can be rationalized by the fact that the PEO lamellae, sandwiched between PDMS layers, are likely to be thinner in thickness, less perfect, or distorted. The same phenomena were reported previously for PEO/PS block copolymers^{4,5} and a theoretical analysis was given by Chow.⁶ Our results conformed qualitatively to his predictions.

The high crystallinity of the middle block in the

copolymer, however, is completely unexpected. We had thought that the PDMS units that were linked covalently to PEO would not crystallize readily at low temperatures once the PEO segments had crystallized. Apparently this was not the case, as we had also found previously.

To ascertain whether the prior crystallization of PEO is responsible for the enhancement of crystallization of the middle block by inducing the alignment of segments, we have blended the two S8 block polymers with poly(acrylic acid) (PAA). PAA is known to be miscible with PEO,⁷ and when the amount of PAA in the blend is sufficiently high, PEO no longer crystallizes. The purpose of this set of experiments is to determine whether PEO crystallites are prerequisite for crystallinity enhancement of the PDMS middle block. The results of thermal analysis of PAA-S8E1 and PAA-S8E2 blends are shown in Figures 4 and 5.

It can be seen that the melting endotherm of PEO is absent in the thermograms of all the blends studied. On the other hand, the melting of the PDMS

**Figure 4** Thermograms of blends of PAA with S8E1.**Figure 5** Thermograms of blends of PAA with S8E2.

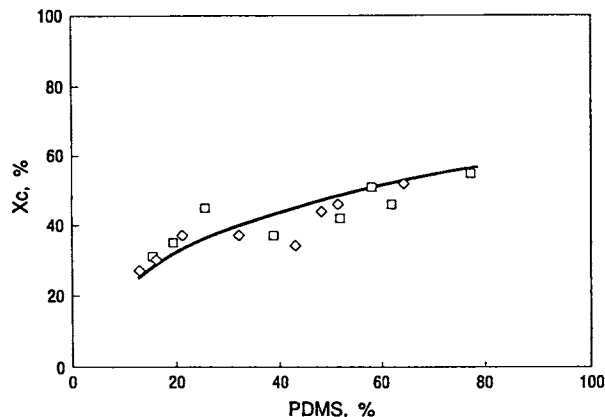


Figure 6 Degrees of crystallinity of the PDMS block in blends of PAA with (□) S8E1 and (◇) S8E2.

middle block is evident when the blend contains 20% or more of the block copolymer. The degree of crystallinity of the siloxane block, $X_c(s)$, in each blend is again higher, by a large margin, than the value in the pure state. Furthermore, there is a trend of increasing crystallinity with increasing amount of siloxane segments in the blend. The trend becomes clear when $X_c(s)$ is plotted against PDMS content. The two sets of data, for the S8E1 and S8E2 blends, can be represented by a single curve, shown in Figure 6, which substantiates the internal consistency of the experimental results. We therefore arrive at the conclusion that the enhancement of crystallization

of the middle block is not contingent upon the prior crystallization of the PEO end blocks. We are not aware of any precedent in the literature. However, a possible reason for the enhanced crystallization of the middle block is the extension of chain segments caused by microphase separated domains in the manner discussed by Mayes and Cruz.⁸

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