Studies on Transition Phenomena of Block Copolymers by Inverse Gas Chromatography

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ABSTRACT: Melt and glass transition phenomena of various block copolymers were investigated by inverse gas chromatography. Linear triblock copolymers of poly(ethylene oxide) (PEO) and poly(methyl methacrylate) (PMMA) having relatively high molecular weight showed transitions at 64 and 82 °C. An intramolecular plasticizing effect caused the two transition temperatures to deviate somewhat from the transition temperatures of the original homopolymers. The transition phenomena of two kinds of PEO-grafted block copolymers of PEO and PMMA were different from each other, which was ascribed to the difference in matrix block copolymers, i.e., diblock and triblock copolymers. Two transitions were observed at 32 and 70 °C in a linear triblock copolymer of poly(tetramethylene oxide) (PTMO) and PMMA. The lower glass transition temperature of the PMMA segment in this copolymer in comparison with that in the copolymer of PEO and PMMA indicated a stronger intramolecular plasticizing effect associated with PTMO than with PEO. The effect of thermal treatment on the surface structure of the block copolymer was inferred from the difference in the retention diagrams of the first and second measurements on the same column.

Introduction

Melt and glass transition phenomena in polymers can be detected by inverse gas chromatography (IGC), which has been developed by Guillet and co-workers.[1-5] Recently, attempts have been made to characterize multicomponent polymer systems such as random or block copolymers by means of IGC.[6-10] Ito et al. studied the IGC of diblock copolymers of polystyrene (PS) and poly(tetramethylene oxide) (PTMO) and discussed the effect of thermal hysteresis on these copolymers.[6]

In previous studies, application of IGC to the morphology of hydrophilic–hydrophobic polymer systems was discussed.[11,12] In the surface structure of a polymer blend of poly(ethylene oxide) (PEO) and PS supported on Chromosorb, the inversion of sea and island phases occurred at about 50 wt% of PEO,[11] while such phase inversion was not observed in the polymer blend of poly(acrylic acid) and PS.[12]

We have also previously studied synthesis and characterization of triblock copolymers of PEO and poly(methyl methacrylate) (PMMA)[13-15] and of PTMO and PMMA.[16] In certain cases a grafted block copolymer was obtained in addition to a linear block copolymer. Although compatibility of a polymer blend of PEO and PMMA has been discussed,[17] the physical properties of such block copolymers have not yet been investigated.

Here we study thermal transitions (melt and glass transitions) of block copolymers previously prepared by the IGC technique.

Experimental Section

Materials. Polymer samples used in this study are listed in Table I. Details of the preparation of these polymers have been described in previous papers.[13-16] Polymers A, B, and C are linear triblock copolymers of PMMA–PEO–PMMA, prepared by anionic polymerization of methyl methacrylate (MMA) initiated with the dilithium salt of PEO diisobutyrate (PEDB-Li_2; M_n (PEDB) = 2700).[15] Polymer D is a PEO homopolymer (M_n = 3600). Polymer E is a radically prepared PMMA homopolymer (M_n = 70 400). Polymers F and G were prepared by anionic polymerization of MMA initiated with the disodium salt of PEO (PEO-Na_2; M_n (PEO) = 3600) in the presence of dicyclohexyl-18-crown-6.[13,14] Comparing the molecular weight of the copolymer with the composition of the MMA monomer unit against the PEO unit in the copolymer, polymers F and G were considered to be PEO-grafted block copolymers of PEO and PMMA. A transesterification reaction between the disodium salt of PEO and the methoxy group in MMA occurred during the polymerization. Polymer H is a linear triblock copolymer of PMMA–PTMO–PMMA, prepared by anionic polymerization of MMA initiated with the disodium salt of PTMO (PTMO-Na_2; M_n(PTMO) = 1100).[16]

Columns. The columns prepared in this study are summarized in Table II. A calculated amount of polymer was dissolved in benzene (2.5 w/v %), and a known amount of Chromosorb P AW-DMCS 60–80 mesh (Johns-Manville Co.) was immersed in the solution. Benzene and Chromosorb P AW-DMCS were suitable for obtaining a distinct Z-shaped retention diagram (RD) at the glass-transition temperature (T_g) of PMMA.[18] The benzene was allowed to evaporate at 50 °C by gentle and continuous stirring of the solution followed by drying at ambient temperature under reduced pressure. The polymer loading (wt %) was calculated from the weight increase of the Chromosorb. A weighed amount of the polymer-loaded Chromosorb was tightly packed into a 1.5 m × 3 mm i.d. stainless steel column. The column was dried for 5 h at ambient temperature under a constant stream of helium.

Gas Chromatography. Gas chromatograms were recorded on a Yanaco G 1800 equipped with a thermal conductivity detector, with helium as a carrier gas, *n*-nonane as a solute, and air as a noninteracting marker. In all measurements the flow rate and injection temperature were fixed at 20 mL/min and 100 °C, respectively. The net retention volume, V_n (mL), from the air peak to the front side of the solute peak was measured. The specific retention volume, V_g (mL/g), was obtained by the equation $V_g = V_n/w$, where w is a polymer loading weight (g).[11,19] Series of measurements were carried out at increasing column temperature, T (K). The retention diagrams were obtained by plotting log V_g against $10^3/T$. Several days after a measurement made on a freshly packed column (the first measurement), successive measurements on the same column (the second measurement) were carried out in order to investigate the effect of thermal treatment on the phase structure of a copolymer.

Results and Discussion

Linear Triblock Copolymer of PEO and PMMA. Figure 1 shows the RDs of columns no. 1–3 prepared by the use of linear triblock copolymers of PEO and PMMA (polymers A–C) together with the RDs of PEO homopolymer (polymer D) and PMMA homopolymer (polymer E). The temperature at which upward deviation from the straight line portion of the RD is observed corresponds to the transition temperature of the polymer.[5] It should be noted that the transition temperature of the polymer is not estimated from the minimum point of the RD. From Figure 1, the melting temperature (T_m) of PEO homo-

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Table I
Polymer Specifications

polymer	type[a]	initiator	10^{-3}MW[b] M_w	10^{-3}MW[b] M_n	SD(PMMA)[c] mm	SD(PMMA)[c] mr + rm	SD(PMMA)[c] rr	PMMA content,[d] wt %	ref
A	PEO-*b*-PMMA (li)	PEDB-Li_2	76.8	27.8	0.04	0.38	0.58	90.6	15
B	PEO-*b*-PMMA (li)	PEDB-Li_2	69.0	33.0	0.04	0.38	0.58	92.1	15
C	PEO-*b*-PMMA (li)	PEDB-Li_2	17.0	9.5	0.00	0.40	0.60	72.6	15
D	PEO		3.7	3.6					
E	PMMA		98.3	70.4	0.06	0.35	0.59		
F	PEO-*b*-PMMA (gr)	PEO-Na_2	30.4	8.9	0.10	0.44	0.46	82.7	14
G	PEO-*b*-PMMA (gr)	PEO-Na_2	25.6	4.5	0.10	0.43	0.47	70.5	14
H	PTMO-*b*-PMMA (li)	PTMO-Na_2	24.8	10.8	0.14	0.48	0.38	89.8	16

[a] li = linear; gr = grafted. [b] Estimated from the GPC traces calibrated with standard polystyrenes. [c] Stereosequence distributions of PMMA part. Observed values from ^{13}C NMR spectra. [d] Content of PMMA in the copolymer obtained by ^1H NMR spectra.

Table II
Column Specifications[a]

column no.	polymer	polymer loading,[b] wt %	w,[c] g
1	A	9.9	0.496
2	B	10.0	0.517
3	C	11.8	0.583
4	D	10.0	0.512
5	E	9.1	0.453
6	F	11.8	0.612
7	G	13.8	0.712
8	H	13.1	0.727

[a] Support: Chromosorb P AW-DMCS 60-80 mesh. [b] Polymer (g)/[polymer (g) + Chromosorb (g)] × 100. [c] Weight of polymer packed in a column.

polymer and the T_g of PMMA homopolymer were about 55 and 115 °C, respectively. Since the microstructures of the PMMA part in the copolymers were almost identical with those of the PMMA homopolymer, the T_g of the PMMA block in the copolymers should be near 115 °C.

In the RD of the first measurement of column no. 1, deviations from linearity were observed at about 64 and 82 °C. This seems to correspond to two transitions of the respective segments in the block copolymer. If PEO and PMMA segments were completely compatible, such distinct transitions would not be observed. Therefore, the segments were not miscible with each other and two different transitions, due to each segment, were observed. The transitions at 64 and 82 °C are attributable to the melt transition of the PEO segment and the glass transition of the PMMA segment, respectively. However, these two transition temperatures deviated somewhat from the transition temperatures of the corresponding original homopolymers, as shown in Figure 1. This is accounted for by the intramolecular plasticizing effect of the PEO center block, which reduced the T_g of the PMMA block by about 33 °C. On the other hand, the T_m of the PEO block increased about 9 °C, due to strong fixing of both PEO ends to rigid PMMA blocks. These indicate that the block copolymers used here may be expected to have a new characteristic feature as well as the physical properties of the original PEO and PMMA. Only slight deviation from linearity in the RD of the PMMA block at about 64 °C, compared with the RD of PEO homopolymer, may partly be due to the small content of PEO in the block copolymer (9.4 wt % PEO).

Since polymer B was essentially similar to polymer A, the RD of polymer B (column no. 2) showed the same behavior as that of polymer A. In contrast, in the RD of polymer C (column no. 3), a Z-shaped curve was hardly observable, and only a slight change in the slope was observed around 64 °C. The transition of the PMMA segment from glass to rubber state was not observed. Since the microstructure of the PMMA part in polymer C was almost the same as that in polymer A or B, the disappearance of the Z-shaped curve observed around 82 °C could not be ascribed to the difference in their microstructures. This phenomenon is presumably ascribed to the lower molecular weight of polymer C (M_n = 9500). In such a low molecular weight triblock copolymer, the molecular weight of one PMMA block is about 3400. Usually glass transition phenomenon of a polymer having such a low molecular weight is not readily observable. Ito et al. reported that a Z-shaped curve at the T_g of PS disappeared in the RD of a diblock copolymer of PTMO and PS containing a small amount of PS.[6]

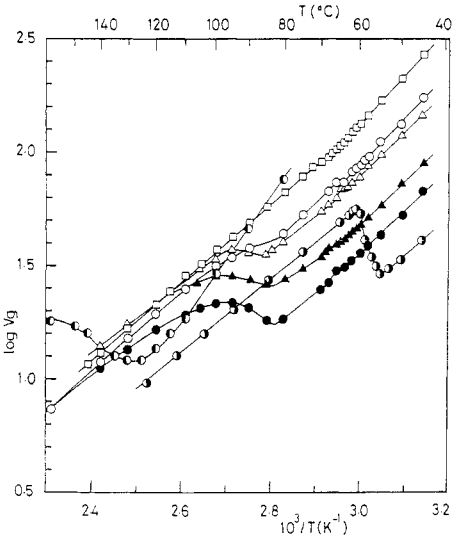

Figure 1. Retention diagrams of PEO, PMMA, and linear triblock copolymers of PEO and PMMA: (○) column no. 1 (polymer A, first measurement); (●) no. 1 (A, second): (△) no. 2 (B, first); (▲) no. 2 (B, second); (□) no. 3 (C, first); (◑) no. 4 (D, first); (◐) no. 5 (E, first).

Information from the Second Measurement. In the RDs of the second measurements of columns no. 1 and 2, the transition phenomena were essentially the same as those observed in the respective first measurements. However, the Z-shaped curves around 82 °C were more clearly observed in the second measurements than in the first measurements. In contrast the RDs at around 64 °C did not change greatly. The reason may be that these copolymers were mainly composed of PMMA segments, and the surface structures of the copolymers on Chromosorb changed with thermal treatment. In general, the retention of a solute is caused exclusively by surface adsorption below the T_g of a polymer, and above this, the

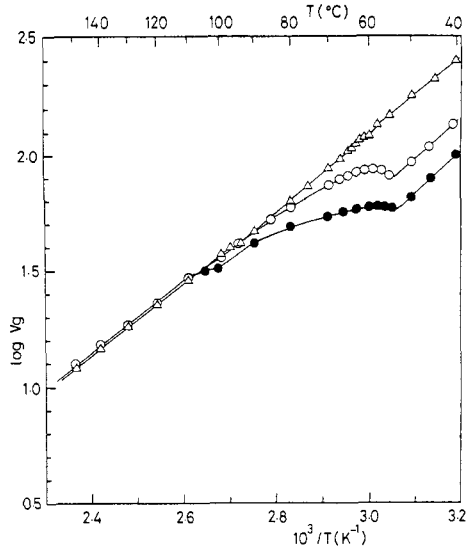

Figure 2. Retention diagrams of PEO grafted block copolymers of PEO and PMMA: (○) column no. 6 (polymer F, first measurement); (●) no. 6 (F, second); (△) no. 7 (G, first).

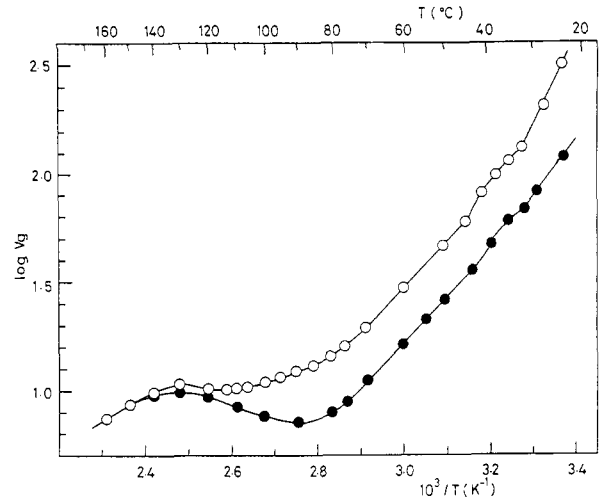

Figure 3. Retention diagrams of a linear triblock copolymer of PTMO and PMMA, column no. 8 (polymer H): (○) first measurement; (●) second measurement.

penetration of the solute into the bulk of the polymer (bulk sorption) begins in the amorphous domain.[5] Consequently, when the RD of the second measurement with that of the first measurement are compared, below 82 °C the decrease in the values of log V_g at the same column temperatures corresponds to a decrease in the amount of surface adsorption, indicating a decrease in the surface area of the copolymer on Chromosorb after thermal treatment.

The RD of the second measurement of column no. 3 was almost identical with that of the first measurement. This indicates that the surface structure of polymer C scarcely changed with thermal treatment.

PEO-Grafted Block Copolymer of PEO and PMMA. The RDs of PEO-grafted block copolymers of PEO and PMMA are shown in Figure 2. In the RD of first measurement of polymer F (column no. 6), a distinct Z-shaped curve due to melt transition of the PEO segment was observed at around 55 °C and that due to glass transition of the PMMA segment was just observable at around 100 °C. Compared with the RD of polymer A or B, the essentially different pattern of the RD of polymer A or B, the essentially different pattern of the RD at the melt transition of the PEO segment could be explained by the existence of PEO–grafted diblock copolymer of PEO and PMMA in which one of the PEO chain ends was not fixed to a PMMA segment. In contrast, both chain ends of PEO were fixed to PMMA segments in polymer A or B. The increase in the flexibility of the PEO segment in polymer F resulted in a similar thermal behavior to that of the PEO homopolymer.

In the RD of polymer G (column no. 7) only slight changes in the slope were observed at around 58 and 95 °C. This may be because polymer G mainly consisted of a PEO-grafted triblock copolymer of PEO and PMMA. Fixation of both chain ends of PEO to the PMMA segments would result in a similar thermal behavior of the PEO segment to that in a linear triblock copolymer like polymer A or B. Such structural difference between polymers F and G could only be elucidated by an IGC measurement, and would not be detected by conventional instrumental analyses such as nuclear magnetic resonance spectrometry and gel permeation chromatography.

The less distinct feature around the T_g of the PMMA segment in the RD of polymer G than in that of polymer F may be due to the relatively small PMMA content. Since the molecular weights of the PMMA part of polymers F and G were considerably lower than those of the linear triblock copolymers, it is difficult to discuss the glass-transition phenomenon of the PMMA segment.

The RD of the second measurement of column no. 6 is also depicted in Figure 2. The Z-shaped curve around 100 °C was clearer than that observed in the RD of the first measurement. The second measurement is, therefore, effective for accurate measurement of the transition temperature of a polymer when a clear Z-shaped curve is not observed in the first measurement. The RDs of the second and first measurements of column no. 7 were almost the same as well as in the case of polymer C.

Linear Triblock Copolymer of PTMO and PMMA. In Figure 3 are shown the RDs of the first and second measurements of column no. 8. A slight deviation from linearity and a Z-shaped curve were observed at around 32 and 70 °C, respectively. Since the T_m of the PTMO homopolymer was about 32 °C, the transition at 32 °C is attributed to the melt transition of the PTMO segment and that at 70 °C to the glass transition of the PMMA segment. The melt transition of the PTMO segment in polymer H was observed over a relatively wide temperature range. The T_g of the PMMA segment in this copolymer was 12–13 °C lower than that in polymer A or B. The decrease in the T_g of the PMMA segment must be due to the higher compatibility of PTMO with PMMA than that of PEO, indicating that the intramolecular plasticizing effect of PTMO is stronger than that of PEO. Guillet et al. reported that the T_g of poly(vinyl chloride) observed by IGC decreased with increasing the amount of dioctyl phthalate added as plasticizer.[4]

In a diblock copolymer of PTMO and PS, the Z-shaped curve around the T_g of the PS segment disappeared by thermal treatment, as previously reported.[6] In the case of a linear triblock copolymer of PTMO and PMMA, as can be seen from the RD of second measurement of column no. 8, two different transitions were clearly observed, implying that the phase structure of the copolymer essentially did not change with thermal treatment.

In conclusion, IGC measurements of block copolymers offered valuable information on the block copolymers such as melt and glass transition temperatures, compatibility, intramolecular plasticizing effect, and the effect of thermal treatment. This information is not readily obtained by conventional instrumental analyses of block copolymers, e.g., nuclear magnetic resonance spectrometry, infrared

spectrometry, and gel permeation chromatography. IGC will be widely applicable to the studies of multicomponent polymer systems.

Registry No. PMMA-PEO-PMMA, 52864-39-8; PMMA-PTMO-PMMA, 83560-33-2.

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Dynamics and Hydrophobic Binding of Quaternized Laurylpoly(ethylenimine) in Aqueous Solution

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ABSTRACT: A spin-label method was used to investigate the dynamics of quaternized laurylpoly(ethylenimines) (LQPEI) in aqueous solution. The nitroxide radical was covalently attached to the polymer in two different ways; in the first, the radicals were coupled at primary amino groups of LQPEI, whereas in the second a small amount of the radical was attached at cross-linking positions. The ESR spectra of these spin-labeled polymers in aqueous solution consisted of two components having different rotational relaxation times. The fraction of the lower mobility component increased with increase in the lauryl content of the LQPEI. It was concluded that the polymer consists of two types of domains, one a hydrophobic cluster of lower mobility and the other a peripheral region of higher mobility. The hydrophobic binding ability of the polymeric cluster was quantitatively evaluated from static and dynamic fluorescence measurements of the excimer of pyrenebutyric acid bound to LQPEI, and the results were compared with those for micelles of low molecular weight cationic detergents, cetyltrimethylammonium chloride (CTAC), and lauryltrimethylammonium chloride (LTAC). The LQPEI cluster binds the hydrophobic molecule effectively at concentrations one to several orders of magnitude lower than required for similar binding by CTAC or LTAC micelles.

Introduction

Quaternized poly(ethylenimine) with lauryl adducts (LQPEI) has been utilized as an effective catalyst for ester hydrolysis and as a favorable environment for other reactions and interactions.[1,2] The efficacy of this polymer has been attributed to the formation of micelle-like clusters within the polymer framework. The micellar effects observed with the LQPEI were often much more pronounced than those of the low molecular weight cationic detergents. Such behavior may be a result of higher local densities of the hydrophobic groups and the positive charges along the highly branched poly(ethylenimine) chain than are present in conventional detergent micelles.

In this study the static and dynamic structures of LQPEI were investigated by a spin-labeled technique.[3] Since the ESR line shape of a nitroxide radical is very sensitive to its mobility in solution, this label attached to the modified PEI can detect a small change in the mobility of its environment. The technique has been applied to micellar aggregates of low molecular weight detergents.[4] Because the spin-label method provides dynamic information for the polymer cluster, it reflects more directly the environmental differences in this domain than do the static data obtained by ^{19}F NMR[5] and by stationary fluorometry.[6]

The application of the spin-label technique to modified PEI's may be perturbed by the presence of two types of amino groups, primary (about 25%) and secondary (about 50%). These may possess different mobilities, yet react equally with spin-labeling reagents for amino groups. In this study two approaches were attempted to eliminate the complexity. One used regenerated primary amino groups[7] which had been protected during the attachment of lauryl moieties and the subsequent quaternization. After the protecting groups had been removed, a spin-labeling reagent was added. In this way one can attach the spin probe exclusively to primary amino groups of the modified PEI. The second type of approach placed the spin probe at a bridged position in a slightly cross-linked polymer. The latter polymer was prepared by reaction of PEI with a diester derivative of the nitroxide radical, which was used as a cross-linking reagent for the PEI. With the cross-linked polymer, information on skeletal motions of PEI could be obtained.

Excimer formation of aromatic hydrocarbons in micelles

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