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Syntheses of Methyl Methacrylate–Stearyl Methacrylate Graft Copolymers and Characterization by Inverse Gas Chromatography

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ABSTRACT: Graft copolymers of well-defined structure and composition were prepared by radical copolymerization of methyl methacrylate and poly(stearyl methacrylate) macromonomers. The latter was prepared by polymerization of stearyl methacrylate (SMA) in the presence of thioglycolic acid as a transfer agent, followed by reaction with glycidyl methacrylate. The copolymerization involving the methacrylate monomer and macromonomer was azeotropic with $r_1 \approx r_2 \approx 1$, allowing a quantitative conversion to a graft copolymer of the desired composition. The gas chromatograph retention diagram of *n*-dodecane on the graft copolymers revealed that a microscopic phase inversion occurs around 20–30 wt % SMA, above which the poly(SMA) segments constitute a continuous phase. The random copolymers and the homopolymer blends showed different diagrams which were expected for a single-phase polymer with a lower T_g and for a completely phase-separated mixture, respectively.

Graft copolymers have found many important applications in the polymer industry. We have a particular interest in their use for surface modification purposes. Generally, the surface structure and properties of polymers are known to be of considerable importance in determining their applications for uses as coatings, adhesives, and dispersants and also for biomedical use of current interest. Among many surface modification techniques including chemical, UV, and plasma treatments, graft copolymers appear to be most promising in obtaining a structure–property relationship to obtain a design of a controlled surface structure for any particular use. This is expected because graft copolymers of controlled structure and composition can be relatively easily prepared in favorable cases and also because they offer possibilities for providing a wide range of properties depending on the amphipathic nature of the segments (polar–nonpolar, soft–hard, and hydrophilic–lyophilic), their surface activity, and also their ability to compatibilize polymer blends.

The present paper describes the preparation of stearyl methacrylate (SMA)–methyl methacrylate (MMA) graft copolymers as a simple model in approaching the above mentioned goal. The comb-type graft copolymers of well-controlled architecture and composition were prepared by radical copolymerization, using macromonomers according to the method described by Walbridge and Waite.[1] The surface properties and the morphology were characterized by use of the inverse gas chromatography[2] which has been successfully applied in the characterization of the surface of hydrophilized polyethylene[3] and the surface and bulk properties of styrene–tetrahydrofuran block copolymers[4] and random copolymers containing *p*-dodecylstyrene or fluorinated methacrylate.[5]

Experimental Section

Materials. Commercial MMA, glycidyl methacrylate, and thioglycolic acid were distilled under vacuum. SMA and azobis(isobutyronitrile) (AIBN) were recrystallized from ethanol and methanol, respectively. Benzene and xylene were distilled over sodium. Chloroform, used as a coating solvent for gas chromatography, was dried over calcium chloride and distilled. Methanol, ethanol, hydroquinone, *N*,*N*-dimethyllaurylamine, *n*-dodecane, and Chromosorb G (AW-DMCS treated, 60–80 mesh) were used as supplied commercially.

Graft Copolymers. SMA, AIBN, and thioglycolic acid (TGA) were weighed into an ampule and degassed and sealed under vacuum. Polymerization at 60 °C gave a prepolymer having a carboxyl group terminal at the one end. The polymer was precipitated into ethanol, purified twice by reprecipitation from benzene into methanol or ethanol, then dried under vacuum. The carboxyl-group content was determined by titrating the polymer in tetrahydrofuran with 0.1 N aqueous potassium hydroxide, using phenolphthalein as an indicator.

The carboxyl group of the prepolymer was reacted with glycidyl methacrylate (50 mol % excess) at 140 °C in xylene with small amounts of hydroquinone and *N*,*N*-dimethyllaurylamine to yield the macromonomer having a methacryl group at one end. After the reaction had gone on for 4 h it was complete as confirmed by there being no titratable carboxyl group. The polymer was recovered by precipitation into methanol and reprecipitated from benzene into methanol.

The poly(SMA) (PSMA) macromonomer thus obtained was copolymerized with MMA in benzene with AIBN at 60 °C to give the comb-type graft copolymers with PSMA branches. The copolymerization was conducted in an ampule which was degassed by three freeze–thaw cycles and sealed under vacuum. The reaction was continued for 4 to 6 days to give a quantitative con-

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version to the copolymer without contamination of the unreacted PSMA macromonomer. The graft copolymers were recovered by precipitation into ethanol, reprecipitated twice from benzene into methanol, and freeze-dried from benzene.

The poly(MMA) (PMMA) macromonomers were similarly prepared and copolymerized with SMA to give the graft copolymers with PMMA branches. The copolymerization was stopped at relatively low conversions in order to examine the relative reactivity of the macromonomer and the monomer. In this case, the unreacted PMMA macromonomer could be selectively removed by reprecipitation from benzene into ethanol or methanol.

Random Copolymers and Homopolymers. Random copolymers were prepared in low conversions (9–22 wt %) by copolymerization of SMA and MMA in benzene with AIBN in a similar manner as that described above and purified twice by reprecipitation from benzene into methanol. PSMA and PMMA homopolymers were similarly prepared by radical polymerization in bulk in the presence of a small amount of TGA to keep the molecular weight from getting too high. The molecular weights ($\bar{M}_n$) were estimated by gel permeation chromatography to be 4.6×10^4 and 2.9×10^4, respectively.

Vapor Pressure Osmometry. Molecular weights of prepolymers and macromonomers were measured with a VPO apparatus (Hitachi Perkin-Elmer Type 115) in benzene at 40 °C.

Gel Permeation Chromatography. GPC (Toyo Soda HLC 801) with two columns, G2000 (2.5×10^2 Å, 1 m) and G4000 (1×10^4 Å, 1 m), was used to roughly estimate the molecular weights of graft copolymers and homopolymers. Chloroform was used as the eluent at a flow rate of 1 mL/min. Calibration was performed with standard polystyrene samples.

Gas Chromatography. Retention data of *n*-dodecane on polymers were collected with a Hitachi gas chromatograph K-53 equipped with FID (flame ionization detector), in a similar manner to that described before.[4] Polymers were coated on the inert support, Chromosorb G (AW-DMCS treated, 60–80 mesh), from the chloroform solutions first by slowly evaporating the solvent under a slightly reduced pressure using a rotary evaporator and then completely dried to a constant weight under vacuum at room temperature. The polymer loading was usually near 6 wt %, determined by the calcination method corrected for the weight loss of Chromosorb G.[6] The polymer-coated supports were packed into a U-shaped stainless steel column (3 mm o.d., 1 m in length) and conditioned in the gas chromatograph oven under helium at 160 °C for about 5 h. The columns were then allowed to cool to room temperature and stand for at least 2 days before the measurements of the retention data were taken. Weight loss of the polymers during heating at 160–180 °C for 5 h was found to be negligible by thermogravimetric analyses (Shimadzu DT-20B, TG-20). It was also found that the retention data were almost independent of the thermal history of the column after preconditioning.

The specific retention volume (V_g in mL/g, corrected to 0 °C) was calculated by the following equation,[7] including the corrections for a pressure drop across the column and water vapor pressure in a soap bubble flow meter

$$V_g = \frac{ft}{w}\,\frac{273}{T_r}\,\frac{p_0 - p_w}{p_0}\,\frac{3}{2}\,\frac{(p_i/p_0)^2 - 1}{(p_i/p_0)^3 - 1}$$

where w is a polymer loading weight (g), t is a retention time (min), f is the flow rate (mL/min) of the carrier gas (helium) which was measured at an ambient temperature T_r (K), p_i is the pressure at the column inlet which was measured with a mercury manometer, p_0 is the pressure at the column outlet which was taken as approximately equal to the atmospheric pressure, and p_w is a water-vapor pressure at T_r. The flow rate (f) was kept constant at 15 mL/min. The solute size injected was usually 0.1 μL. The net retention time (t) from the methane peak as a standard was determined at the point of interaction of the base line with the tangent with the greatest slope for the front side profile of the *n*-dodecane peak because the peaks observed with various solute size had a common front side profile so that the V_g obtained by this method was thought to be approximately equal to that obtained from the peak maximum at infinitely small solute size, i.e., that to be obtained at a supposedly ideal condition.

Scheme I

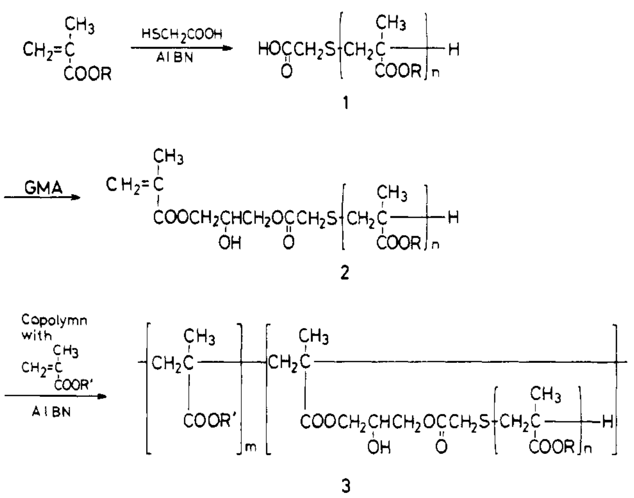

Table I
Preparation of PSMA Prepolymer and Macromonomer

	run no.	
	1	2
prepolymer[a]		
$[TGA]_0/[SMA]_0$, mol/mol	0.20	0.42
polymerization time, h	1.0	1.5
conversion, %	55	67
$\bar{M}_n$ by VPO	4320	2380
$\bar{M}_n$ by end-group titration[b]	4000	2200
degree of polymerization, *n*, by end group titration[b]	11.8	6.5
transfer constant,[c] C_s	0.33	0.26
macromonomer		
$\bar{M}_n$ by VPO	4460	2480

[a] Polymerization in bulk, AIBN 1 mol % to monomer, 60 °C. [b] Assuming one carboxyl terminal per polymer. [c] $C_s = \log(1 - \alpha[M]_0/n[S]_0)/\log(1 - \alpha)$, where S and M denote the transfer agent and the monomer, respectively, α is a fractional conversion of monomer to polymer, and n is the degree of polymerization of the polymer.

Results and Discussion

Preparation of Graft Copolymers. Among a number of preparation methods of graft copolymers, the copolymerization using the appropriate macromonomer[1] appears to be the most generally applicable method for obtaining well-defined graft copolymers. In the present case, the method is based on the polymerization of SMA in the presence of TGA as a transfer agent to give PSMA prepolymer **1** having one terminal carboxyl group, which was then reacted with glycidyl methacrylate (GMA) to give the PSMA macromonomer **2** having the methacryl group terminal. Copolymerization with MMA produces the graft copolymers with PSMA branches **3**, where R = $C_{18}H_{37}$ and R′ = CH_3 (Scheme I). Table I gives the results of the preparation of two prepolymers with the molecular weights (VPO) of 4300 and 2400 which were in good agreement with those calculated from the end group analyses, assuming one carboxyl group per polymer. The chain transfer constant (C_s) was estimated to be around 0.30 ± 0.04 by using the observed conversion and degree of polymerization (*n*, from the end-group titration) and the feed ratio of SMA to TGA. The C_s value obtained is close to the reported range (0.51–0.31 at 50 and 70 °C) for MMA.[8] These findings clearly support the idea that the carboxyl-terminated prepolymer of a desired molecular weight can be readily prepared by controlling the feed ratio of the monomer to the transfer agent and also suggest that the

Table II
Preparation of Graft Copolymers[a]

	feed			graft copolymers			
				% of C			
$\overline{M}_n$ of PSMA branch	wt % of SMA	mol % of SMA	mol % of PSMA	obsd	calcd[b]	$\overline{M}_n \times 10^4$ GPC[c]	no. of PSMA branches[d]
4460	9.1	2.9	0.22	61.0	61.5	6.58	1.3
4460	20.0	6.9	0.56	63.1	63.3	4.29	1.9
4460	30.0	11.2	0.95	65.0	64.9	4.51	3.0
4460	49.5	22.5	2.2	68.2	68.1	7.26	8.1
4460	69.0	39.7	4.8	71.4	71.3	11.8	18.3
2480	10.0	3.2	0.45	60.9	61.5	6.66	2.7
2480	20.1	6.9	1.0	63.4	63.0	6.01	4.9
2480	30.0	11.2	1.7	64.4	64.5	6.99	8.5
2480	49.4	22.4	3.8	68.3	67.4	7.19	14.3
2480	69.7	40.5	8.5	70.3	70.5	9.77	27.5

[a] Copolymerization of the PSMA macromonomer with MMA in benzene, AIBN 2 mol %, 60 °C, 4-6 days, quantitative yields. [b] Percent of C assuming the same polymer composition as in the feed. [c] $\overline{M}_n$ calculated from GPC by the use of polystyrene calibration. [d] Calculated based on the composition and the molecular weights of the graft copolymer and the PSMA branch.

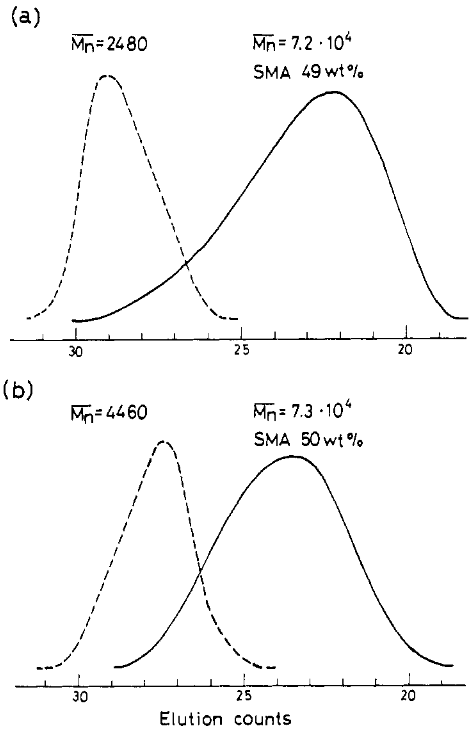

Figure 1. Gel permeation chromatograms of graft copolymers as compared with PSMA macromonomers: (—) graft copolymers; (---) PSMA macromonomers.

PSMA radicals have simlar reactivities toward TGA as compared to PMMA radicals. The terminal carboxyl group could be completely reacted with GMA at 140 °C in xylene to give the macromonomer 2 whose molecular weight was naturally a little higher than that of the prepolymer, as given in Table I.

The PSMA macromonomers thus obtained were copolymerized with MMA to quantitative conversions to the graft copolymers 3, using AIBN at 60 °C for 4–6 days. As given in Figure 1, gel permeation chromatograms of the graft copolymers obtained show that the peaks due to the macromonomers are essentially absent.

Furthermore, in order to expect copolymers of homogeneous composition to be independent of the conversion, the copolymerization should be preferably azeotropic. This was in fact observed in low conversion copolymerizations of SMA with MMA or PMMA macromonomer. In the latter system, the unreacted PMMA macromonomer could be removed by a reprecipitation procedure. The results given in Figure 2 clearly show that the azeotropic random copolymerization prevails over a whole range of compositions for these systems, supporting strongly the same behavior for the copolymerization of the PSMA macromonomer with MMA, since the same methacrylate radicals and (macro)monomers participate in the propagation reactions, the difference being only in the side groups which are remote from the reaction center. Thus, all the monomer reactivity ratios for the copolymerizations involving MMA, SMA, and their macromonomers can be set to be very close to unity, $r_1 \approx r_2 \approx 1$.

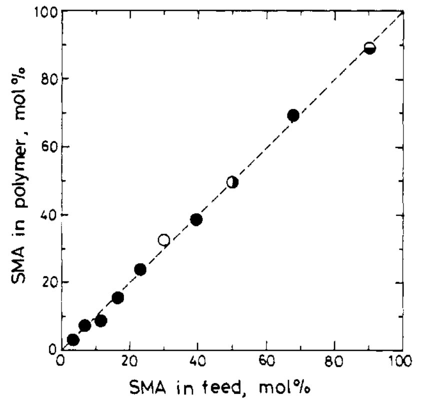

Figure 2. Copolymer composition data for copolymerization of SMA with: (●) MMA, 9–22 wt % conversions; (○) PMMA macromonomer ($\overline{M}_n$ = 1650), 39 wt % conversion; (◑) PMMA macromonomer ($\overline{M}_n$ = 4080), 61 wt % conversion; (◒) PMMA macromonomer ($\overline{M}_n$ = 4080), 35 wt % conversion.

Therefore, the copolymer composition and its distribution, or the frequency and the distribution of the branches in the present case, should be those expected directly from the feed composition. Table II summarizes the characterizations of the graft copolymers used in the present study. The number-average molecular weights were estimated from gel permeation chromatograms. The number of PSMA branches estimated from these molecular weights ranged from 1–28 per molecule, depending on the composition and the molecular weight of the PSMA branch, which was taken as being equal to that of the macromonomer used.

Characterization by Gas Chromatography. Inverse gas chromatography,[2] using a polymer to be studied as the stationary phase, is a convenient and useful method for characterizing the surface and bulk properties of surface-active copolymers.[4,5] Figure 3 shows the retention diagram in which the logarithm of the specific retention

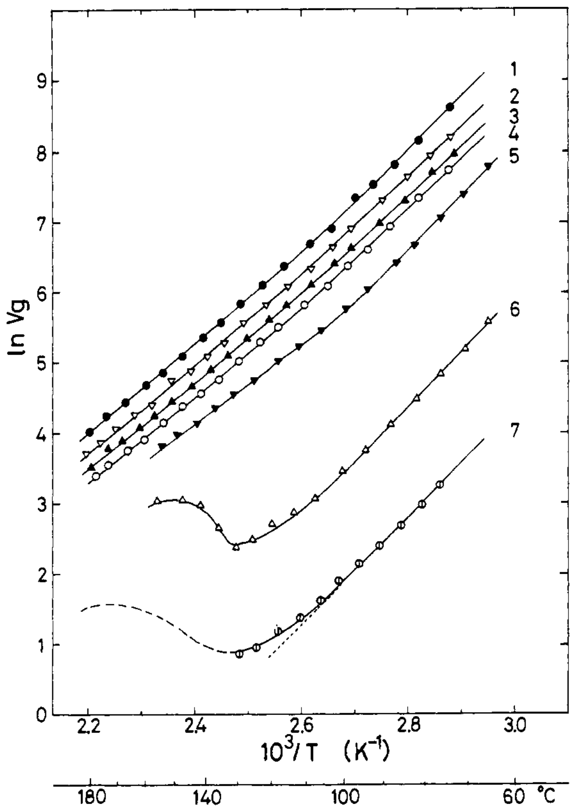

Figure 3. Retention diagrams of *n*-dodecane on graft copolymers with PSMA branches ($\bar{M}_n$ = 4460). SMA contents in wt %: (1) 100 (PSMA homopolymer); (2) 69; (3) 50; (4) 30; (5) 20; (6) 9; (7) 0 (PMMA homopolymer).

volume (V_g) is plotted against the reciprocal column temperature. The plot should be linear for a retention mechanism which does not change over the temperature range applied. (Strictly speaking, some curvature of the plot over a wide range of temperature is expected as a result of a small change in the heat of vaporization of the solute with temperature.[9]) The slope should be effectively given by $(\Delta H_v - \Delta H)/R$,[10,11] where ΔH_v is the heat of vaporization of the solute (*n*-dodecane), ΔH is the enthalpy of interaction between the polymer and the solute, and R is the gas constant. In fact, the retention diagram is essentially linear for PSMA homopolymer, which has mp 36–38 °C, so that the retention in the temperature range in Figure 3 should be due to the equilibrium bulk absorption mechanism in which the solute interacts with the whole polymer phase. In contrast, the PMMA homopolymer shows a linear diagram below T_g around 105 °C according to a surface adsorption mechanism, while an upward deviation occurs above T_g, due to a nonequilibrium, diffusion-controlled sorption of the solute into the bulk phase. At a much higher temperature range, another linear region is to be observed due to the bulk equilibrium sorption mechanism, forming a z-shaped diagram as a whole.[5,10]

As compared with homopolymers, graft copolymers show z-shaped to almost linear diagrams, depending on their composition. With 9 wt % SMA, the retention diagram is z shaped, similar to that of the PMMA homopolymer, indicating that the surface adsorption mechanism prevails below the T_g of the PMMA segments. However, above 20 wt % SMA, the diagram is almost linear, indicating that the bulk sorption mechanism is mainly operating for these graft copolymers even below T_g of the PMMA segments. This can be understood by considering the morphology of microphase separation[12] such that the PSMA segments, which should be in the melt phase and have a lower surface energy as compared to the PMMA segments, constitute a continuous phase ("sea"), while the PMMA segments make a discontinuous, dispersed phase ("islands"). This leads to the situation that the polymer surface is essentially covered by PSMA segments and that the solute (*n*-dodecane) could interact preferentially with the molten PSMA segments even below the T_g of the PMMA segments.

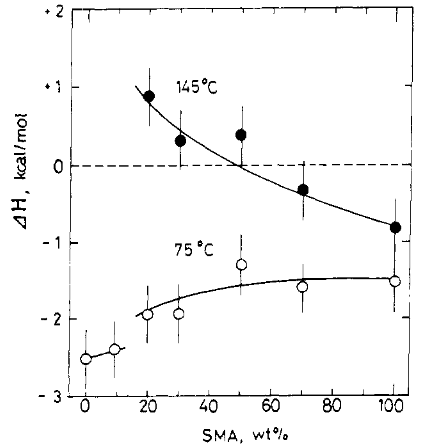

Figure 4. Interaction enthalpy of *n*-dodecane with graft copolymers with PSMA branches ($\bar{M}_n$ = 4460) at 75 and 145 °C.

The above consideration is supported by Figure 4, which shows the interaction enthalpy estimated from the slope of the linear region of the retention diagram at 75 and 145 °C, typical for temperatures below and above the T_g of PMMA, respectively. The interaction enthalpy is about 1 kcal/mol exothermic for the PSMA homopolymer, as expected from the fact that the polymer is easily soluble in *n*-dodecane. In contrast, the PMMA homopolymer, which is insoluble in *n*-dodecane, shows a repulsive interaction in bulk at a much higher temperature than T_g (ΔH of +4.4 kcal/mol was reported for *n*-hexadecane by Lavoir and Guillet[10]). The interaction enthalpy of the graft copolymers at 75 °C is almost constant at −1 to −2 kcal/mol, independent of the composition above 20 wt % SMA, supporting the idea that the interaction is mainly due to the continuous PSMA melt phase in bulk. At 145 °C, the interaction enthalpy changed from negative (attractive) to positive (repulsive) with increasing MMA content, as expected because *n*-dodecane is forced to interact also with the PMMA segments in bulk above their T_g.[13] An apparent interaction enthalpy of about −2.5 kcal/mol, which was obtained at 75 °C for PMMA and the graft copolymer with 9 wt % SMA, arises mianly from the surface adsorption and may be attributed to a van der Waals attraction between the solute and the polymer surface. The difference in ΔH between 75 and 145 °C constitutes a part of the reason for the slight inflection which was observed in the retention diagrams for the graft copolymers with 20 wt % and higher SMA contents.

The graft copolymers with PSMA branches of lower molecular weight showed similar retention behavior, as shown in Figure 5, except that the copolymer with 20 wt % SMA still gives a z-shaped diagram. This result suggests some effect of the molecular weight of the branches on their morphology; the PSMA branches of lower molecular weight appear to require a higher composition to make a continuous phase ("sea").

For comparison, the retention diagrams for random copolymers and homopolymer blends were measured and the results are given in Figures 6 and 7, respectively. The random copolymers with 10 and 20 wt % SMA showed z-shaped diagrams indicative of decreasing T_g (around 88

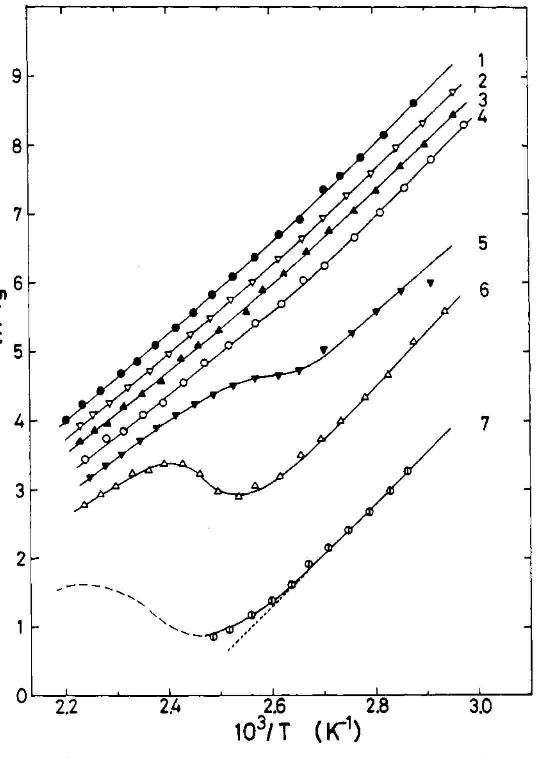

Figure 5. Retention diagrams of *n*-dodecane on graft copolymers with PSMA branches ($\bar{M}_n$ = 2480). SMA contents in wt %: (1) 100 (PSMA homopolymer); (2) 70; (3) 49; (4) 30; (5) 20; (6) 10; (7) 0 (PMMA homopolymer).

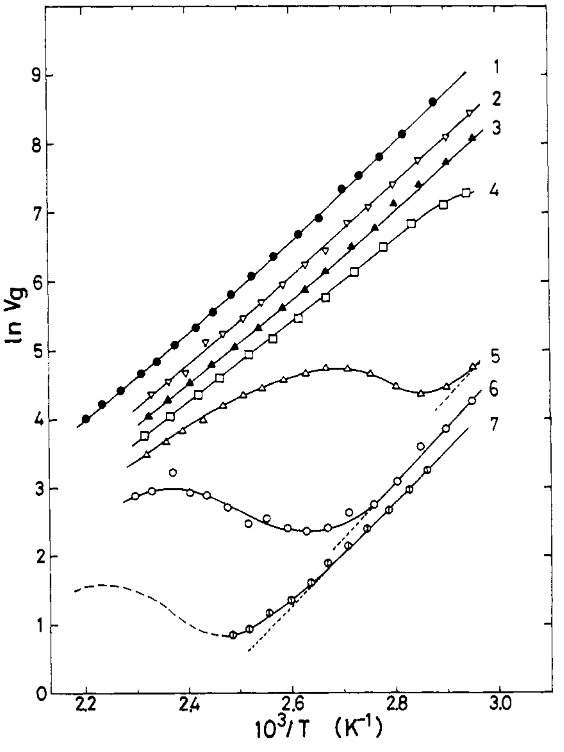

Figure 6. Retention diagrams of *n*-dodecane on random copolymers. SMA contents in wt %: (1) 100 (PSMA homopolymer); (2) 50.4; (3) 40.0; (4) 30.1; (5) 20.2; (6) 9.7; (7) 0 (PMMA homopolymer).

and 65 °C, respectively) with increasing SMA content, and those with 30 and higher SMA percent showed linear diagrams similar to that of the PSMA homopolymer in the temperature range studied (above 65 °C). Thus the random copolymers undoubtedly behave as a homogeneous, single-phase polymer as expected.

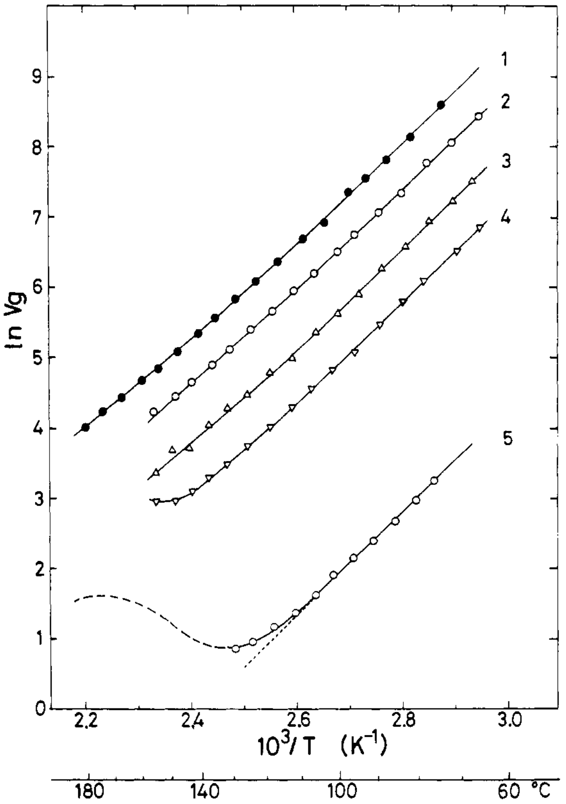

Figure 7. Retention diagrams of *n*-dodecane on homopolymer blends. PSMA contents in wt %: (1) 100 (PSMA homopolymer); (2) 49.7; (3) 20.7; (4) 10.2; (5) 0 (PMMA homopolymer).

In contrast, the homopolymer blends showed almost linear retention diagrams with the same slope, independent of the composition ranging from 10–50 wt % SMA. And surprisingly, the deviation due to the T_g phenomenon was not observed within the temperature range studied (65–160 °C), although some slight deviation appears to begin above 140 °C for the blend of 10 wt % PSMA. These results can be explained by considering a complete phase separation of these incompatible homopolymers. Thus, the molten PSMA phase which should have a lower surface energy covers over the PMMA phase so that *n*-dodecane interacts only with the molten PSMA phase without interacting with the PMMA phase, which has repulsive interaction with *n*-dodecane. This was supported by the fact that the specific retention volume corrected for the SMA content, i.e., $V_g' = 100V_g/\text{wt}$ % SMA, completely coincided with that of the PSMA homopolymer, Figure 8, indicating that the retention is completely due to the interaction with the PSMA phase only.

Here it should be pointed out that V_g' for the graft copolymers with nearly linear retention diagrams (20 wt % and higher SMA contents) was found to be appreciably higher than that of the PSMA homopolymer, indicating some contribution of the PMMA segments for the retention of *n*-dodecane. Since *n*-dodecane cannot permeate the PMMA domains below T_g, the contribution should be ascribed to the surface adsorption mechanism. This can be reasonably understood because the microphase-separated PMMA domains ("islands") are expected to have in total a very large interface ("surface") area that can interact effectively with the solute (adsorption interaction at the interface). Very recently, Galin and Rupprecht used the V_g of polystyrene (PS)–poly(dimethylsiloxane) (PDMS) block copolymers to estimate the surface area of

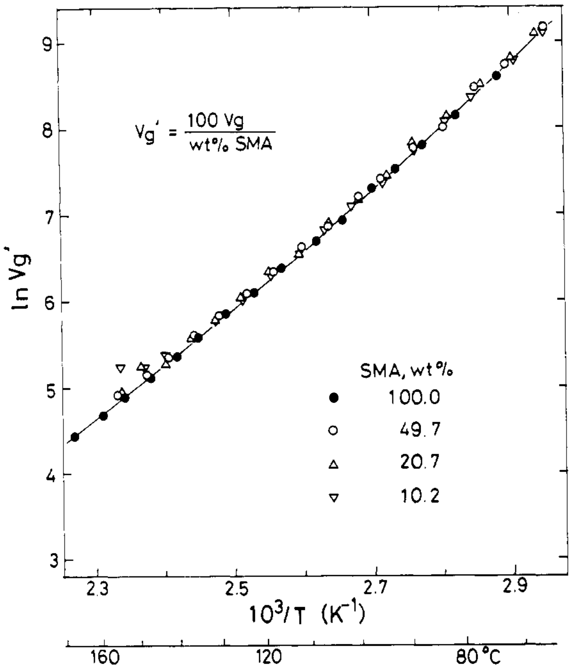

Figure 8. Retention diagrams of *n*-dodecane on homopolymer blends. V_g' represents a specific retention volume corrected per unit weight of SMA involved.

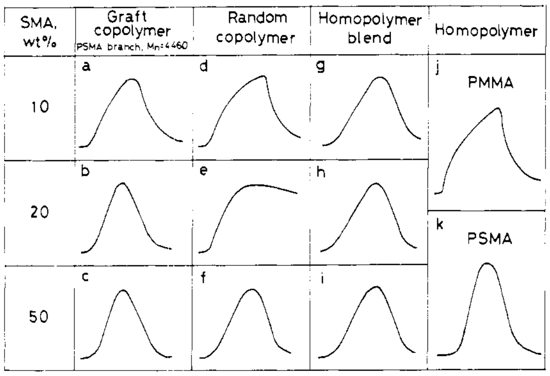

Figure 9. Schematic peak shapes of gas chromatograms of *n*-dodecane on graft and random copolymers, homopolymer blends, and homopolymers at 75 °C.

PS domains surrounded by PDMS matrix at 60 °C.[14]

Finally it is to be noted that the peak shapes in the gas chromatogram are also indicative of the retention mechanism.[15] Figure 9 shows schematically the peak shapes of *n*-dodecane at a column temperature near 75 °C. In the case where the bulk absorption mechanism prevails, almost symmetrical peaks are observed as exemplified by the PSMA homopolymer (k), the graft and random copolymers with high SMA contents (b, c, and f), and the homopolymer blends (g, h, and i). The retention due to the surface adsorption gives rise to an unsymmetrical peak with a steeply descending rear slope, as found for the PMMA homopolymer (j) and the random and graft copolymers with low SMA contents (a and d). A very broad peak accompanied by a very long tailing is typical for the nonequilibrium, diffusion-controlled sorption mechanism, as exemplified by a random copolymer with 20 wt % SMA (e).

In summary, the retention diagrams for graft copolymers, random copolymers, and homopolymer blends are clearly different from each other and could be reasonably understood by considering the possible surface and bulk structure (morphology) of these polymer systems. Since the present synthetic method, as well as the characterization by gas chromatography, appear to have a general applicability, we are continuing the studies with graft copolymers with more hydrophilic or hydrophobic segments which are expected to contribute more definitely to the polymer–surface design.

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(13) In fact, V_g in this region was found to be simply expressed by a linear combination of the bulk retention mechanisms due to PSMA and PMMA phases, as follows, $V_g = xV_{g,PSMA} + (1 - x)V_{g,PMMA}$, where x is a weight fraction of the PSMA phase, and $V_{g,PSMA}$ and $V_{g,PMMA}$ are the retention volumes for pure PSMA and PMMA polymers, respectively. In this respect, the authors appreciate the comments of one of the reviewers, pointing out the above relation.

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