

Inverse Gas Chromatography on Graft and Random Copolymers of Styrene and 2-Hydroxyethyl Methacrylate

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(Received January 31, 1983)

ABSTRACT: Inverse gas chromatography (IGC) was applied to amphiphilic graft copolymers of poly(2-hydroxyethyl methacrylate) (PHEMA) with polystyrene (PSt) branches using various probes at 160°C. Retention of tetradecane or amylbenzene, which selectively interacts only with PSt phase, suggested that a microphase inversion occurs around 20–30 wt% PSt, below which PSt segments constitute a discontinuous phase (islands). Rather nonselective probes such as dimethylformamide and 2-(2-methoxyethoxy)ethanol showed a retention which exceeds that expected from a simple additive relation, suggesting a considerable contribution of their interaction with the interface of the microphase-separated domains. In contrast, random copolymers showed a retention behavior as expected for a statistical distribution of the monomer units. General discussion is given on IGC as a means of characterizing binary polymer systems.

KEY WORDS Inverse Gas Chromatography / Amphiphilic Graft Copolymer / 2-Hydroxyethyl Methacrylate / Styrene / Microphase Separation / Morphology / Selective and Nonselective Probes /

Inverse gas chromatography (IGC) has been developed by Guillet and others^{1,2} as a simple and convenient method for evaluating various properties of polymers such as melting point (T_m), glass-transition point (T_g), crystallinity, interaction parameter, and solubility parameter. In principle, it relies on the interaction of an appropriate volatile compound as a probe with a target polymer as a stationary phase in conventional gas chromatography. Since any change in polymer phase would be reflected in the retention behavior of a probe, IGC also appears to be useful as a method for examining a multi-phase structure in block or graft copolymers and in polymer blends, in addition to being a simple method of evaluating their interaction with the probe. Galin and Rupprecht³ investigated the retention of decane on polystyrene (PSt)–polydimethylsiloxane (PDMS) block copolymers to estimate the domain size of PSt. Ward *et al.*⁴ similarly evaluated the morphology of PDMS–bisphenol A polycarbonate block copolymers and

blends. Decane as a probe was assumed in these cases to interact independently with the PDMS matrix and surface (interface) of PSt- or polycarbonate domains at a temperature below their T_g . Suzuki *et al.*⁵ studied the surface morphology of PSt–poly(ethylene oxide) blend by following the retention behavior of octane in comparison with scanning electron-microscope observation.

We also examined a retention of dodecane on PSt–polytetrahydrofuran (PTHF) block copolymers⁶ and on poly(methyl methacrylate) (PMMA)–poly(stearyl methacrylate) (PSMA) graft copolymers⁷ to show that PTHF or PSMA segments, which have a lower T_m and a lower surface-energy, tend to make a continuous phase as compared to PSt or PMMA segments, respectively. In general, the IGC method may be expected to give more clear-cut and interesting information on the morphology of these multi-phase polymer systems by analyzing the retention behavior of several probes which may interact selectively with a par-

ticular component. To this end, the present paper describes the application of various probes to IGC on amphiphilic graft and random copolymers of styrene (St) and 2-hydroxyethyl methacrylate (HEMA). The graft copolymers were found by ^1H NMR and contact-angle measurements to have a distinct tendency to form micellar domains in contrast with a single-phase structure of random copolymers.⁸ The morphology of the same graft or block copolymer systems were examined by means of transmission electron-microscopy (TEM) by Yamashita *et al.*⁹ and Okano *et al.*¹⁰

EXPERIMENTAL

Materials

Graft copolymers, random copolymers, and homopolymers were prepared, purified, and characterized as reported before.⁸ Table I shows the polymers used and their column data. Acid- and silane-treated diatomaceous earth, Uniport HP of Gasukuro Kogyo Co., Ltd., 60–80 mesh with a nominal specific surface area $1\text{ m}^2\text{ g}^{-1}$, was used as an inert support for polymers. Methane and probes for IGC were used as supplied commercially.

Methods

Polymers were dissolved in tetrahydrofuran (or methanol for PHEMA homopolymer) and coated on the inert support, Uniport HP, by slowly evaporating the solvent with gentle stirring, and finally dried under vacuum. The polymer loading was determined by the calcination method. The polymer-coated supports were packed into a copper column (4 mm i.d., 80–100 cm length) and conditioned at 60°C . The column data were given in Table I.

Retention data were collected on a Yanaco gas chromatograph G-180 equipped with a flame ionization detector. A probe in less than $0.1\ \mu\text{l}$ was injected simultaneously with methane as a noninteracting marker, and the net retention time t_R was determined from the peak-to-peak distance from the probe to methane. t_R thus determined was independent of the probe size injected. Retention volume V_R^0 and specific retention volume V_g^0 , corrected to 0°C , were calculated from t_R as follows.^{1,2}

$$V_g^0 = \frac{V_R^0}{w} = \frac{f \cdot t_R}{w} \frac{273}{T_r} \frac{p_o - p_w}{p_o} \frac{(p_i/p_o)^2 - 1}{(p_i/p_o)^3 - 1} \quad (1)$$

where w is a polymer loading weight, f , the flow rate of the carrier gas (helium) measured by a soap-bubble flow meter at an ambient temperature T_r ; p_i and p_o are the column inlet and outlet pressures, respectively, which were measured by a mercury manometer, and p_w is a water-vapor pressure at T_r . The flow rate f was kept constant at 15 ml/min. The column temperature T was changed in the ranges $150\text{--}170^\circ\text{C}$ and $50\text{--}70^\circ\text{C}$, which are well above and below the T_g 's of the homopolymers, around 100°C for PSt¹¹ and 120°C for PHEMA.¹² A linear regression line was obtained between $\ln V_g^0$ and $1/T$, as given in Figure 1 as an example. V_g^0 at 60 and 160°C were read on this line within a precision of 1 ml g^{-1} , and the interaction enthalpy ΔH between the probe and the polymer was calculated from their slope, which should be effectively equal to $(\Delta H_v - \Delta H)/R$,^{1,2,13,14} where ΔH_v is a heat of vaporization of the probe, which was in turn obtained from a literature source^{15,16} or estimated from the vapor-pressure data. The 95% confidence limit of ΔH was in a range of ± 1 to $\pm 2\text{ kcal mol}^{-1}$ at 160°C .

THEORETICAL CONSIDERATION

In general, the gas chromatographic retention of a probe by a polymer is due to two mechanisms, absorption into the polymer bulk phase and adsorption onto the polymer surface, so that^{1,2,13}

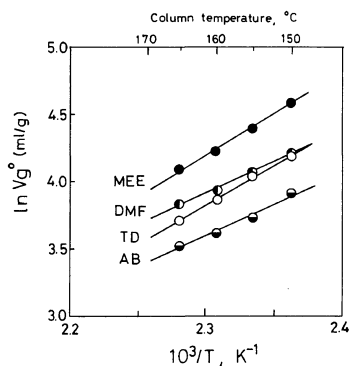


Figure 1. Retention diagram of 2-(2-methoxyethoxy)ethanol (MEE), tetradecane (TD), dimethylformamide (DMF), and amylbenzene (AB) on a graft copolymer, G-2.

$$V_r^0 = K_b w + K_{a,s} A_s \quad (2)$$

or

$$V_g^0 = V_R^0/w = K_b + K_{a,s} A_s/w \quad (3)$$

where K_b is the partition coefficient of a probe between polymer bulk and gas phase, $K_{a,s}$, that between polymer surface and gas phase, w , the polymer loading weight and A_s , the surface area of the polymer. In the case of a predominant bulk absorption mechanism, V_g^0 can be put equal to K_b which can be expressed approximately by the glc theory as follows.^{1,2,13,17}

$$V_g^0 = K_b = \frac{273R}{\gamma_1^\infty p_1^0 M_2} = \frac{273R}{(a_1/\omega_1)^\infty p_1^0 M_1} \quad (4)$$

where γ_1^∞ and $(a_1/\omega_1)^\infty$ are the mole-fraction and weight-fraction activity coefficients, respectively, of the probe at infinite dilution, p_1^0 is a saturated-vapor pressure of the probe at the column temperature, and M_1 and M_2 are the molecular weights of the probe and the polymer, respectively. The absorption mechanism into the bulk polymer phase should be predominant for amorphous polymers at a sufficiently higher temperature than T_g and with a sufficiently high polymer loading.¹⁸

Now consider a retention of a probe, denoted by a subscript 1, through the bulk absorption into a two-component polymer system, denoted by subscripts 2 and 3. Independent retention by the two components should be given by

$$V_R^0 = K_{b,2} w_2 + K_{b,3} w_3 \quad (5)$$

or

$$V_g^0 = K_{b,2} \omega + K_{b,3} (1 - \omega) \quad (6)$$

where $K_{b,2}$ and $K_{b,3}$ are partition coefficients for the components 2 and 3, respectively, with w_2 and w_3 being their weights, and ω is the weight-fraction of the component 2, *i.e.*, $\omega = w_2/w$ or $1 - \omega = w_3/w$, and $w = w_2 + w_3$.

When $K_{b,2}$ and $K_{b,3}$ take the same values as those for the corresponding homopolymers, then a simple additive relation^{19,20} should follow, *i.e.*,

$$V_g^0 = V_{g,2}^0 \omega + V_{g,3}^0 (1 - \omega) \quad (7)$$

where $V_{g,2}^0$ and $V_{g,3}^0$ are the specific retention volumes for the corresponding homopolymers. This relation may first appear to hold with the bi-phase polymer systems such as polymer blends and

block or graft copolymers. However, block or graft copolymers should generally have a very high interface area as a result of microphase separation so that adsorption onto this interface may contribute to the retention. Therefore, we propose as a general expression,

$$V_R^0 = K_{b,2} w_2 + K_{b,3} w_3 + K_{a,i} A_i \quad (8)$$

or

$$V_g^0 = V_{g,2}^0 \omega + V_{g,3}^0 (1 - \omega) + K_{a,i} A_i/w \quad (9)$$

where $K_{a,i}$ is the partition coefficient for adsorption onto the interface between the components 2 and 3 whose area is A_i . When a probe is completely selective for one of the components, say 2, such that $K_{b,3} = K_{a,i} = 0$, then eq 9 reduces to

$$V_g^0 = V_{g,2}^0 \omega \quad (10)$$

In that case including a contribution of the interface adsorption, such that $K_{b,3} = 0$ but $K_{a,i} \neq 0$,

$$V_g^0 = V_{g,2}^0 \omega + K_{a,i} A_i/w \quad (11)$$

Equation 11 was applied to estimate the domain size for block copolymers PDMS (component 2)–PSt (3),³ and PDMS (2)–polycarbonate (3)⁴ by assuming that, below T_g of the component 3, $K_{b,3}$ should be reasonably negligible but $K_{a,i}$ should assume a definite value just as $K_{a,s}$ for the corresponding homopolymer of component 3. A similar situation was noted for the retention of dodecane on PSMA (2)–PMMA (3) graft copolymers.⁷

In the case of random copolymers, it may be reasonable to consider that $K_{b,2}$ and $K_{b,3}$ in eq 5 and 6 are not always equal to $V_{g,2}^0$ and $V_{g,3}^0$, respectively, but may be rather functions of the composition since the interaction should change depending on the statistical distribution of the two monomer units. In fact, V_g^0 data reported for random copolymers^{19,21} are not always additive as was also found in the present work.

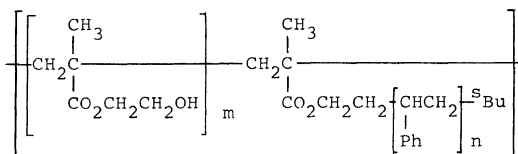
RESULTS AND DISCUSSION

The specific retention volumes V_g^0 were collected with the columns given in Table I at a column temperature around 160°C and with a polymer loading of *ca.* 10 wt%. Under these conditions, it is reasonable to assume that V_g^0 should represent the retention by absorption into the polymer bulk phase, with little contribution from surface ad-

Table I. Polymer and column data

| Code | HEMA wt% | $M_n \times 10^{-4}$ GPC ^b | M_w/M_n GPC ^b | Number of PSt- branches | IGC column | | |
|------------------------------|-------------|------------------------------------------|-------------------------------|-------------------------------|------------|---------|---------|
| | | | | | Polymer | Support | Loading |
| | | | | | g | g | wt% |
| PSt | 0 | 6.15 | 1.69 | — | 0.447 | 3.730 | 10.7 |
| PHEMA | 100 | c | — | — | 0.435 | 3.707 | 10.5 |
| Random copolymer | | | | | | | |
| R-1 | 24 | 5.15 | 1.36 | — | 0.471 | 3.973 | 10.6 |
| R-5 | 47 | — | — | — | 0.491 | 4.053 | 10.8 |
| R-2 | 54 | 5.04 | 1.46 | — | 0.464 | 3.911 | 10.6 |
| R-3 | 70 | — | — | — | 0.470 | 3.838 | 10.9 |
| R-4 | 81 | 7.57 | 1.28 | — | 0.399 | 4.034 | 9.0 |
| Graft copolymer ^a | | | | | | | |
| G-1 | 28 | 2.88 | 2.33 | 5.5 | 0.331 | 2.979 | 10.0 |
| G-2 | 56 | 2.49 | 2.77 | 3.1 | 0.339 | 2.950 | 10.3 |
| G-3 | 70 | 2.67 | 1.74 | 2.3 | 0.344 | 2.874 | 10.7 |
| G-4 | 85 | 2.70 | 2.74 | 1.2 | 0.336 | 2.929 | 10.8 |

^a Prepared by radical copolymerization of HEMA with PSt-macromonomer ($M_n=4020$, $M_w/M_n=1.03$ by GPC):



^b Gel-permeation chromatography calibrated with standard PSt.

^c $[\eta]=0.43$ in methanol at 25°C.

Table II. Probe data

| Probe ^a | ΔH_v^b kcal mol ⁻¹ | Solubility at 160°C of | | V_g^{0b} ml g ⁻¹ | | ΔH^b kcal mol ⁻¹ | |
|--------------------|------------------------------------------|------------------------------|-------|----------------------------------|-------|----------------------------------------|---------|
| | | PSt | PHEMA | PSt | PHEMA | PSt | PHEMA |
| | | TD | 13.9 | No | No | 106.6 | 2.0 |
| MEE | 12.4 | No | Yes | 37.2 | 70.2 | 4.6±2.4 | 4.5±1.8 |
| AB | 11.5 | Yes | No | 76.9 | 0 | 1.1±1.0 | — |
| DMF | 9.3 | Yes | Yes | 20.5 | 61.1 | 0.9±1.6 | 0.7±0.4 |

^a TD, tetradecane; MEE, 2-(2-methoxyethoxy)ethanol; AB, amylbenzene; DMF, dimethylformamide.

^b Values at 160°C.

sorption, *i.e.*, the second term in eq 2 and 3 being negligible. Braun and Guillet¹⁸ showed for PSt coated on Chromosorb G that the surface area A_s , independent of the polymer loading above 0.02 wt%, has almost a constant value of 0.11 m² per 1 g of the support, as compared with the nominal

specific area of 0.6–1.3 m² g⁻¹ for that support, and that V_g^0 , at a sufficiently higher temperature than T_g , is also essentially independent of the loading above *ca.* 1 wt%. We also estimated the surface area of PHEMA supported on Uniport HP according to the same procedure with decane at

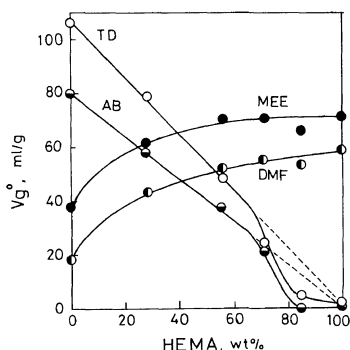


Figure 2. Specific retention volume V_g^0 of various probes on graft copolymers at 160°C.

60°C, and found A_s to have a similar value, 0.14 m² per 1 g of the support. This corresponds to a polymer-coating thickness of about 10⁴ Å for the columns in Table I. There data support the negligible contribution of either polymer surface or support surface to V_g^0 obtained.

Probes which interact selectively with either PSt or PHEMA segments as in Table II were chosen based on the solubility of each homopolymer in the probe and on the value of their V_g^0 , the latter being clearly a more direct measure of the interaction of a given probe with respective polymers. Thus tetradecane (TD) and amylbenzene (AB) are almost completely selective for PSt, while 2-(2-methoxyethoxy)ethanol (MEE) and dimethylformamide (DMF) are rather nonselective in that they prefer PHEMA to a small extent but also interact considerably with PSt.

Figure 2 shows the results of V_g^0 for graft copolymers as a function of composition. Most interesting was the directly proportional relation observed between V_g^0 for TD or AB and the PSt content above ca. 30 wt%. This is expected in terms of eq 10, in which the components 2 and 3 represent PSt and PHEMA segments, respectively, because the interaction of these probes with PHEMA should be negligible so that $K_{b,3} = K_{a,i} = 0$, just as was found in the case of the PHEMA homopolymer. Thus these probes interact only with the PSt segments which constitute a continuous phase (sea or lamella) in this range of composition. Below 20–30 wt% PSt, however, V_g^0 is nearly zero, indicating little interaction even with PSt segments. This can be clearly understood by a microphase inversion to discontinuous

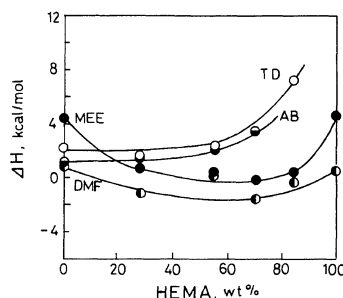


Figure 3. Interaction enthalpy ΔH of various probes with graft copolymers at 160°C.

PSt domains (islands), because the probes could then interact only with a very small proportion of PSt domains which may be present on the top surface⁸ in PHEMA matrix. The microphase separation in this manner has been reported with TEM observation for the same graft⁹ and block copolymer systems.¹⁰ The interaction enthalpy of a probe with polymer ΔH , given in Figure 3, also supports the above conclusion. Thus ΔH is almost constant and equal to that of the PSt homopolymer above ca. 30 wt% PSt, while it sharply increases with decreasing PSt content below 30 wt% PSt.

MEE and DMF are rather nonselective probes which interact comparatively with PSt and PHEMA segments. Their V_g^0 is somewhat convex upwards, corresponding to eq 9 instead of a simple additive relation eq 7. Thus the authors' view is that this upward deviation should be due to a contribution of the adsorption onto the interface whose area A_i should be much higher, as a consequence of microphase separation, as compared to a simple surface area A_s of the polymer. For example, A_i/w comes to even 300 m² per 1 g of the polymer for spheres of 100 Å size, a typical order of magnitude for such microphase separation, as compared to A_s of 0.14 m² per 1 g of the support. Furthermore the interaction of these probes with the polymer at the interface appears to be cooperative by the contribution of both monomer units so that $K_{a,i}$ may well be higher compared to $K_{a,s}$ for adsorption onto the surface of the respective homopolymers. This is expected because a much higher cooperative interaction was observed for the retention of these probes on random copolymers, as given in Figure 4, although the interaction is through bulk retention, K_b , in this case. The interaction en-

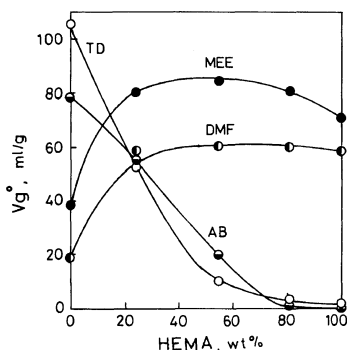


Figure 4. Specific retention volume V_g^0 of various probes on random copolymers at 160°C.

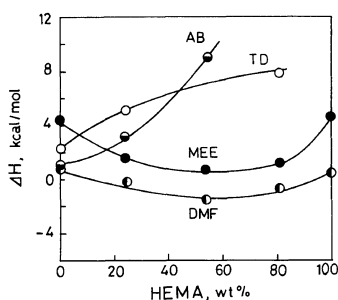


Figure 5. Interaction enthalpy ΔH of various probes with random copolymers at 160°C.

thalpy ΔH for these probes showed a minimum at an intermediate composition, as in Figures 3 and 5, supporting the synergistic cooperation of both monomer units for their retention.

The results of V_g^0 and ΔH for random copolymers in Figures 4 and 5 can be understood in terms of the changes in the partition coefficients $K_{b,2}$ and $K_{b,3}$ in eq 5 or 6, depending on the statistical distribution of the monomer units. PSt-selective probes, TD and AB, for which $K_{b,3}=0$, appear to have a lower $K_{b,2}$ and a higher ΔH than those for PSt homopolymer. In contrast, nonselective probes, MEE and DMF, appear to have a higher $K_{b,2}$ or $K_{b,3}$ and a lower ΔH in random copolymers as compared to the homopolymers, as discussed above.

Retention behavior was similarly examined with various probes at a column temperature of 60°C, which is below the T_g 's of both homopolymers, the results are given in Figures 6 and 7. Decane, a nonsolvent for both homopolymers, should clearly interact with the polymers only through adsorption

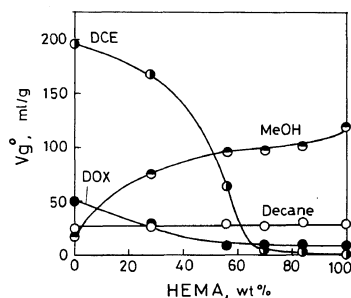


Figure 6. Specific retention volume V_g^0 of methanol (MeOH), decane, 1,2-dichloroethane (DCE), and dioxane (DOX) on graft copolymers at 60°C.

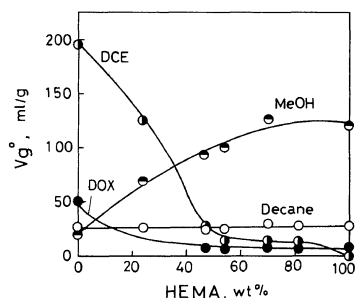


Figure 7. Specific retention volume V_g^0 of various probes on random copolymers at 60°C.

on their top surface, so that its retention appears to be almost insensitive to the composition both in graft and random copolymers. Methanol, a solvent for PHEMA, appears to interact selectively with HEMA units not only by adsorption onto the polymer surface but also by penetration into their bulk. On the other hand, dioxane and 1,2-dichloroethane, solvents for PSt, interact rather selectively with St units. A quantitative discussion, however, is not so simple in this case because factors such as adsorption on the top surface and extent of penetration into bulk must also be considered for evaluation of their interaction at such a temperature below T_g . Nevertheless, the retention data in Figures 6 and 7 are qualitatively consistent with the above conclusion of the polymer morphology drawn from the results at 160°C.

In conclusion, IGC appears to be useful as a practical method for examining the morphology of the multi-phase polymer systems through their interactions with selective and nonselective probes. We proposed eq 9 as a general expression of the

retention including a contribution of the adsorption onto the interface. Several other graft copolymers involving poly(ethylene oxide) segments were also found to obey this general relation, which will be published in the near future.

Acknowledgement. This work was supported in part by a Grant-in-Aid for Scientific Research (No. 56550645) from the Ministry of Education.

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