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Structural and Thermodynamic Study of Dimethylsiloxane–Ethylene Oxide PDMS–PEO–PDMS Triblock Copolymers

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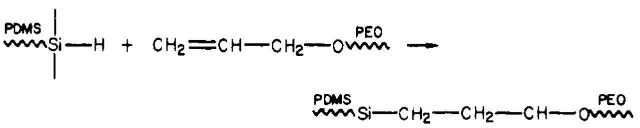
ABSTRACT: Linear triblock dimethylsiloxane–ethylene oxide PDMS–PEO–PDMS copolymers have been synthesized by hydrosilation polycondensation of α,ω-diallylpoly(ethylene oxide) ($\bar{M}_n = 6 \times 10^3$ and 10×10^3) and α,ω-dihydro(polydimethylsiloxane) ($\bar{M}_n = (1\text{–}4.5) \times 10^3$). Studies by dilatometry, differential scanning calorimetry, and X-ray scattering have shown that the copolymers are characterized by a periodic organization in lamellae or hexagonal cylindrical structures according to composition. PEO crystallizes within its own domains, with specific features such as a lower degree of crystallinity, a lower melting point with respect to that of the PEO precursor, and crystallinity independent of thermal conditions. Gas chromatography has allowed a semiquantitative estimation of the $\chi_{\text{PDMS–PEO}}$ interaction parameter and its dependence on temperature and composition. The values in the range 0.4–1.1 are in good agreement with the high incompatibility of the PDMS and PEO chains.

Within the wide field of block copolymers, poly(dimethylsiloxane)–poly(ethylene oxide) block copolymers are of special interest since their chains show a regular alternation of incompatible and highly different blocks: semicrystalline and hydrophilic poly(ethylene oxide) (PEO) on the one hand and liquid and hydrophobic poly(dimethylsiloxane) (PDMS) on the other hand. Although the synthesis and the solution properties of these multiblock or star-branched amphiphilic copolymers of low molecular weight ($\bar{M}_n < 1000$) have been investigated for a long time and are well documented[1,2] because of their technological importance as urethane foam surfactants, the study of their bulk properties seems to have been more or less neglected, except for a single report on their internal pressure.[3] We have thus focused our interest on well-defined PDMS–PEO–PDMS linear triblock copolymers of higher molecular weights ($\bar{M}_n > 8 \times 10^3$) with two complementary aims: the structural analysis of the semicrystalline copolymers by dilatometry, differential scanning calorimetry (DSC), and small-angle X-ray scattering (SAXS), with special emphasis on the specific features of PEO crystallization, and the study by inverse gas chromatography of the thermodynamics of the interactions in the block copolymer–volatile probe ternary systems, with special emphasis on the incompatibility of the PEO and PDMS blocks.

Experimental Section

1. Preparation of the Block Copolymers. The block copolymers were synthesized by condensation of PEO α,ω-diallyl ethers with PDMS bearing SiH end groups, using chloroplatinic acid as catalyst.[1,2] The silyl hydride addition to the double bond leads to a hydrolysis-resistant Si–C linkage between the PDMS and the PEO blocks according to the scheme



$$\overset{\text{PDMS}}{\sim\!\sim}\text{Si}\text{—H} + \text{CH}_2\text{=CH—CH}_2\text{—O}\overset{\text{PEO}}{\sim\!\sim} \longrightarrow \overset{\text{PDMS}}{\sim\!\sim}\text{Si—CH}_2\text{—CH}_2\text{—CH—O}\overset{\text{PEO}}{\sim\!\sim}$$

This feature is of outstanding interest for the hydrolytic stability and hence for the long-term properties of the copolymers.

PEO diallyl ethers were prepared from the parent PEO glycols (previously characterized samples from Hoechst, $\bar{M}_w/\bar{M}_n < 1.1$) according to a Williamson synthesis: reaction of an excess of freshly distilled allyl bromide over the sodium alcoholate[4] in THF solution at 25 °C. Their average functionality was determined by titration of the residual OH groups previously transformed into CO_2H functions by reaction with succinic anhydride according to Inagaki et al.[5] The typical value of $f = 1.85 \pm 0.09$ is in excellent agreement with that obtained by Schnecko et al.[6] for the same reaction carried out in Me_2SO, a nonpolar solvent but very difficult to eliminate quantitatively.

The condensation between functionalized PEO and α,ω-dihydropoly(dimethylsiloxane) (obtained from Rhone-Poulenc, $1.82 < f < 2.00$, $\bar{M}_w/\bar{M}_n \sim 1.6$) was performed under an argon atmosphere at 100 °C in xylene solution at a polymer concentration of about 30% w/v in presence of H_2PtCl_6 introduced as a 2% solution in *n*-octyl alcohol ($[H_2PtCl_6]/[SiH] = 0.03$). Formation of PDMS–PEO–PDMS triblock copolymer was favored with a [PDMS]/[PEO] ratio of 3. During the prolonged heating (24 h), the reaction medium progressively goes from a turbid to a clear solution as the condensation proceeds. At the end of the reaction, xylene was removed by rotary evaporation under vacuum, and the excess PDMS homopolymer was separated from the copolymer by selective extraction with hexane. The PEO homopolymer content of the copolymers may be safely considered to be negligible, taking into account the stoichiometric conditions of the synthesis and the prepolymer functionalities. Some diblock chains, however, may be present in the copolymers which were fractionated by precipitation, using $CHCl_3$–Et_2O as the solvent–nonsolvent system.

2. Molecular Characterization of the Copolymers. Notation. The various samples are identified according to their structure and to the approximate molecular weight of the individual blocks: for instance, sample 2-6-2 denotes a PDMS–PEO–PDMS triblock copolymer with a middle PEO block of about 6000 molecular weight ($\bar{M}_n = 6200$) and with a terminal PDMS block of about 2000 molecular weight ($\bar{M}_n = 2100$).

The composition of the block copolymers was determined from elemental analysis with an accuracy of about 2% or from ^1H NMR spectrometry.

Molecular Weights. The $\bar{M}_n$ values of the PDMS precursors and of the block copolymers were obtained by vapor pressure osmometry (Knauer apparatus); measurements were carried out at 37 °C on benzene solutions after calibration with well-defined PEO samples.[7] GPC measurements, performed on toluene solutions at 35 °C (Waters apparatus fitted with Styragel columns of 60–10^6-Å pore size), were disturbed by PEO irreversible adsorption on the columns; they were therefore used only to check for the lack of any PDMS homopolymer in the copolymer samples.

Structural Characterization of the Block Copolymers. Irrespective of the experimental techniques (DSC, dilatometry, or SAXS) the thermal history of all the samples was the same, namely, melting at 80 °C for 15 min before cooling to the selected crystallization temperature, t_c.

Dilatometric measurements, as previously described,[8] allowed the determination of the specific volume at any temperature, the study of the isothermal crystallization at $t = t_c$, and the derivation of the degree of crystallinity τ calculated with respect to the PEO weight fraction. The required specific volumes of PEO and PDMS at a given temperature were taken from literature data.[9,10] The accuracy of the τ values is generally better than 3%.

Table I
Composition of the Copolymers

sample[a]	$\overline{M}_n$ PEO block	$\overline{M}_n$ PDMS block	$\overline{M}_n$ block copolymer	exptl wt fraction of PEO
1-6-1	6200	1000	8500	0.756
2-6-2	6200	1700	9300	0.714
2-6	6200	1700	7100	0.791
5-6-5	6200	4700	11500	0.378
1-10-1	10700	1000	12200	0.840
2-10-2	10700	2100	14500	0.808
2-10	10700	2100	12500	0.852
5-10-5	10700	4500		0.490

[a] Samples 2-6-2 and 2-10-2 are mixtures of di- and triblock copolymers in the weight ratio 0.5:0.5 and 0.75:0.25, respectively. Samples 2-6 and 2-10 are diblock fractions extracted from the preceding mixtures.

On the other hand, the melting point t_m was determined from the variations of the mercury column height in the dilatometer vs. temperature for heating rates of 0.3 °C/min: t_m is arbitrarily measured at the inflection point of the curve $h = f(t)$; the accuracy is estimated to be ±0.5 °C.

For **differential scanning calorimetry** measurements (Perkin-Elmer DSC2 apparatus calibrated with indium standard), the sample (3–5 mg) was crystallized from the melt at $t_c = 25$ or 40 °C with a cooling rate of 20 °C/min. The time of crystallization (1–2 h) was selected according to dilatometry kinetic results in order that at least complete primary crystallization could be safely assumed. In most cases, secondary crystallization may have occurred to a small extent. The thermograms were obtained at various heating rates (s = 10, 5, 2.5, 1.25, and 0.31 °C/min), and the melting temperatures t_m of the copolymers were taken from the peak position of the endotherm. As already observed on PEO homopolymer,[11] t_m values are a continuously decreasing function of the heating rate, and we selected the values obtained at 0.31 °C/min, wich are quite close to those extrapolated at $s = 0$. The degree of crystallinity τ was deduced from the total area of the melting endotherm, assuming $\Delta H = 47.0$ cal/g for the enthalpy of fusion of PEO crystal.[11] The accuracy of the t_m and τ values is about ±0.3 °C and 4%, respectively.

Small-Angle X-ray Scattering. SAXS experiments were carried out as previously described for PEO homopolymers.[9] For copolymers crystallized at temperature t_c we have checked that the X-ray patterns obtained either at the same temperature or after cooling to 25 °C do not show any significant differences, and the measurements were thus systematically performed at 25 °C. For copolymers in the liquid state ($t > t_m$), temperature was regulated to ±0.1 °C. In general, the X-ray patterns exhibit a set of moderately well-defined lines and their sharpness cannot be improved by annealing. Nevertheless, the Bragg spacings may be measured with sufficient accuracy (3–5%) to allow the derivation of the structural parameters according to classical methods which have been recently reviewed in the case of block copolymers.[12] The following literature data have been used: cross section of the PEO chain, 21.4 Å^2; molar mass per unit length along the c axis, 15.82 Å^{-1}.[13]

3. Gas Chromatography. The preparation of the columns was described in our previous work: The copolymers were coated from benzene solution onto HMDS-treated glass beads and then packed into 0.25-in. stainless steel tubes about 1-m long. The column loading within the range 0.6–1.3%, leading to polymeric film thickness between 4000 and 8000 Å, was systematically checked by Soxhlet extraction. The experimental retention times were converted into specific retention volumes corrected to 0 °C in the usual way.[14] The physical parameters of the solvents are the same as those previously used[15] except for octamethylcyclotetrasiloxane.[16] The specific volumes υ_2 for PDMS[10] and υ_3 for PEO[9] are computed according to literature equations: υ_2^{-1} (g/cm^3) $= 0.9919 - 8.925 \times 10^{-4}t + 2.65 \times 10^{-7}t^2 + 3 \times 10^{-11}t^3$ ($20 < t < 207$ °C); $\upsilon_3 = 0.9217 + 6.9 \times 10^{-4}(t - 70)$ ($70 < t < 120$ °C).

Preliminary experiments carried out on the 2-10-2 copolymer within the temperature range investigated (40–100 °C) have shown that $V_g°$ values are independent of the amount of volatile probe and independent of the gas vector flow rate (8–30 mL/min), whatever the probe nature, solvent, or nonsolvent of either block. Moreover, the surface-to-volume ratio of the polymeric film has no influence on the $V_g°$ values within the narrow range of column loading we used. These results were expected for experiments performed with liquid polymeric phases. The identical behavior we observed for copolymers in their semicrystalline state points out three important features: the interactions of the probe with the amorphous liquid fraction occur without any significant kinetic effects; the crystalline PEO fraction does not contribute to the retention of the probe; and adsorption phenomena at the gas–liquid interface are negligible. It should be noted that the probes we selected (benzene, toluene, n-heptane, cyclohexane, and p-dioxane) are restricted to nonpolar compounds which are unable to provide strong specific interactions (hydrogen bonding, for instance) with PEO or PDMS.

Results and Discussion

A representative DSC thermogram of copolymers cooled from the melt to −180 °C at 30 °C/min shows well-defined thermal transitions which are easily identified as follows: −135 °C, glass transition of the PDMS chains;[17] −67 °C, glass transition of the PEO fraction;[18] 50–57 °C, endothermic peak related to the melting of the crystalline PEO fraction.

These features suggest that the copolymers are semicrystalline materials which are characterized by the coexistence of different segregated chemically homogeneous domains: crystalline PEO lamellae and an amorphous binary phase where PDMS and PEO are sufficiently well separated to exhibit their own characteristic glass transition temperatures.

1. Degrees of Crystallinity. The dilatometric curves of the different copolymers show the classical sigmoidal shape characterized by three successive steps: an induction period which is a complex function of the degree of supercooling $t_m - t_c$ and of the copolymer structure; a fairly fast primary crystallization step; and a so-called secondary crystallization process which leads to a slow monotonic increase of the degree of crystallinity. In most cases the secondary crystallization process remains moderate, within the range 5–10%, but it may reach values as high as 7 and 14% (see Table II). More important than for pure PEO or even than for PEO α,ω-octadecyl diether[8] it may be tentatively attributed to the polydispersity of the samples (slow crystallization of the shortest chains). The experimental values of the degree of crystallinity τ are collected in Table II. For a given t_c, $t_c = 40.8$ °C, for instance, the degrees of crystallinity τ measured by DSC are systematically higher than those calculated from dilatometric data (primary crystallization). This increase may be partly explained since DSC measurements take into account the secondary crystallization process which occurs during the crystallization time (1–2 h) we selected. On the other hand, the experimental enthalpy values include, besides the enthalpy of fusion of the crystalline PEO fraction, the enthalpy of partial mixing of the liquid PDMS and PEO chains. Thus, the DSC measurements probably lead to overestimated degrees of crystallinity and only the primary crystallization data derived from dilatometric experiments will be considered in the following discussion.

Within the temperature range 34.9–47.0 °C for PEO 6000 and 34.6–50.8 °C for PEO 10000, crystallinity is independent of the crystallization temperature. This is in sharp contrast with the usual behavior of semicrystalline homopolymers, for which crystallinity is a decreasing function of the supercooling $t_m - t_c$. For instance within the same range of supercooling, PEO H6000 and H10000 homopolymers[9] and even PEO H10000 α,ω-octadecyl diether[8] show a definite increase of crystallinity of 14, 10,

Table II
Crystallinity and Melting Temperature of the Block Copolymers

	degree of crystallinity τ (±0.02)						t_m, °C		
	DSC		dilatometry						
sample	25 °C	40 °C	34.9 °C	40.8 °C	47.0 °C	50.8 °C	DSC[c]	dilatometry[c]	chromatography[d]
1-6-1	0.58	0.63	0.547	0.555[b]	0.553	0.583	52.2	53.8	
2-5-2[a]	0.66	0.68		0.652	0.662		50.6	53.8	
2-6	0.70						51.8		
5-6-5	0.62	0.66		0.616	0.616	0.653	52.5	56.8	52.5
1-10-1	0.59	0.64	0.585	0.560	0.558	0.541	55.7	58.0	56.0
2-10-2[a]	0.65	0.67	0.625	0.610[b]	0.600	0.620	54.0	58.8	55.2
2-10	0.70						57.1		
5-10-5	0.66			0.685		0.682	55.0	58.5	54.7

[a] See Table I. [b] The secondary crystallization process increases τ values from 0.555 to 0.597 and from 0.610 to 0.695. [c] ±0.5 °C. [d] ±2 °C.

and more than 15%, respectively. The only slight increase in crystallinity, about 6%, has been observed in the case of the H6000 block of 1-6-1 and 5-6-5 copolymers for the lowest values of the degrees of supercooling within the t_c temperature range 47.0–50.8 °C.

Whatever the degree of supercooling, the crystallinity of the PEO block in the copolymer is significantly lower than that of the homologous homopolymers. The following τ values measured at 40.8 °C and for identical $t_m - t_c$ values are quite representative: $\tau = 0.55–0.62$ with respect to $\tau = 0.825$ for H6000 chains;[9] $\tau = 0.55–0.68$ with respect to $\tau = 0.800$ for H10000 chains.[9]

Such a decrease of crystallinity has already been observed whenever both ends of the PEO chain are linked with sterically hindered groups incompatible with the PEO crystal: long-chain alkyl radicals,[19] aromatic[20] or aliphatic[21] urethane functions in segmented PEO, and propylene oxide–ethylene oxide PO–EO–PO triblock copolymers.[22]

For a given PEO block in the copolymers the crystallinity τ is an increasing function of the chain length of the PDMS end blocks. When the PDMS molecular weight goes from 1.0×10^3 to 4.5×10^3, the crystallinity increases by as much as 13 and 24% for H6000 and H10000 sequences, respectively. It should be noted that the increase of the PDMS chain length implies a simultaneous structural change from hexagonal to a lamellar structure (see below). This may be a possible explanation for the observed increase of crystallinity since the lamellar structure, as expected, allows an easier organization of the PEO blocks. However, Booth et al.[22] have noticed similar trends in lower molecular weight propylene oxide–ethylene oxide triblock copolymers showing a single type of lamellar structure.

2. Melting Points. The melting zone of all the copolymers is spread over a wider temperature range than that of pure PEO: DSC thermograms show a single asymmetric endothermic peak with a width at half-height of about 2.5 °C vs. 1.3 °C for the homologous PEO. This characteristic broadening may arise from the copolymer polydispersity. On the other hand, dilatometry and DSC experiments carried out at the same heating rate of 0.3 °C/min on samples of identical thermal history crystallized at $t_c = 25$ °C are expected to lead to directly comparable t_m values (see Experimental Section), as already observed for α,ω-dialkoxypoly(ethylene oxide).[8] Nevertheless, for PDMS–PEO–PDMS copolymers, differences in the observed values may be as high as 4 °C for some samples (Table II) and they are outside the limit of experimental error. We have no satisfactory explanation for a such discrepancy. The t_m values derived from the DSC thermograms seem to be more clearly defined and more reliable, and, moreover, they are quite close to those determined independently from gas chromatography experiments, as described in section 4 (see Table II). Thus, the DSC values of the melting temperature were systematically preferred for comparison with literature data, most often obtained from the same technique.

The melting temperatures of the copolymers are systematically lower than those of the homologous PEO homopolymers crystallized under identical supercooling conditions (the number of chain folds ν and hence t_m are well-defined for the homopolymer): $t_m = 52.1 \pm 0.4$ °C for copolymers 1-6-1, 2-6-2, and 5-6-5 vs. $t_m = 60.7$ for H6000 ($\nu = 1$); $t_m = 55.3 \pm 1.3$ °C for copolymers 1-10-1, 2-10-2, and 5-10-5 vs. $t_m = 61.8$ °C for H10000 ($\nu = 3$). This characteristic melting point depression is quite similar to that already observed in urethane-segmented PEO[20] and in triblock PO–EO–PO copolymers.[22] PEO H10000 α,ω-octadecyl diether, however, shows a melting behavior close to that of the PEO precursor[8] ($t_m = 61.0$ °C vs. $t_m = 61.8$ °C).

The melting point depression we observed for our copolymers may be correlated with possible higher chain folding numbers (see below) and with the modification of the interfacial free energy at the crystal surface because of the presence of PDMS blocks in the amorphous phase.

Within the crystallization temperature range 25–40 °C, t_m is nearly independent of t_c, but a possible increase of t_m for very low degrees of supercooling cannot be completely ruled out.

Finally, for a given PEO central block, the variations of t_m with the chain length of the PDMS end blocks do not show any well-defined trend.

3. Organized Structures of the Block Copolymers. Two main features can be drawn from the X-ray scattering experiments carried out on copolymers crystallized at 25 °C:

SAXS patterns show two diffraction lines which are consistent with long-range structural order typical of a two-phase structure: PDMS and PEO chains are segregated into different domains according a regular periodic distribution throughout the space. An ordered structure was not unexpected for such block copolymers in spite of the low molecular weight of their blocks because of the high incompatibility of the PEO and the PDMS (see below, gas chromatography section). That the X-ray patterns are independent of crystallization temperature t_c and any annealing points out, as previously discussed, that the copolymer is quenched in a metastable and poorly crystallized structure without any possibility of structural reorganization.

WAXS patterns similar to that of pure PEO[13] confirm that the PEO chains are partly crystallized within their microdomains.

Table III
Structural Parameters of the Block Copolymers Measured at 25 °C

sample	structure	structural parameters[a]
1-10-1	hexagonal	$D = 184$, $R = 42$, $S_{\mathrm{PDMS}} = 81$
2-10-2	hexagonal	$D = 214$, $R = 53$, $S_{\mathrm{PDMS}} = 133$
1-6-1	hexagonal	$D = 190$, $R = 53$, $S_{\mathrm{PDMS}} = 64$
5-10-5	lamellar	$d_{\mathrm{PDMS}} = 214$, $d_{\mathrm{PEO,c}} = 114$, $d_{\mathrm{PEO,a}} = 57$
5-6-5	lamellar	$d_{\mathrm{PDMS}} = 250$, $d_{\mathrm{PEO,c}} = 74$, $d_{\mathrm{PEO,a}} = 54$

[a] d, D, and R in Å; S in Å^2.

Moreover, SAXS patterns obtained at temperatures higher than the melting point of the PEO block show the presence of a single diffuse diffraction line, but this feature is not sufficient to prove unambiguously the persistence of a long-range order.

All of the structural parameters given in Table III (dimensions of the domains, and specific surface S available for a molecule at the interface) have been calculated according to simple geometrical considerations,[12] assuming, in a first approach, additivity of the specific volumes of the different components and sharp phase separation between the different domains.

Lamellar Structure. Lamellar structures have been observed for the copolymers in the medium composition range (40 < PEO wt % < 65), in good agreement with the general behavior of block copolymers.[12] The structure of an idealized sheet of total thickness D is composed of the superposition of three successive layers of different thickness d corresponding to the crystalline PEO lamellae ($d_{\mathrm{PEO,c}}$), the amorphous PEO layer ($d_{\mathrm{PEO,a}}$), and the liquid PDMS layer (d_{PDMS}). The number of chain folds ν in the crystalline lamella deduced from its thickness is in very good agreement with that deduced from the specific surface S available for a molecule at the interface; this can be taken as a proof of the good self-consistency of the model and of the calculated structural parameters. For copolymer 5-10-5, the value $\nu \sim 3$ for the PEO H10000 block is identical with that of the PEO precursor crystallized with the same degree of supercooling. On the other hand, the PEO H6000 block in copolymer 5-6-5 shows a higher folding index, $\nu \sim 2$, than that of the corresponding PEO homopolymer, $\nu = 1$.

Cylindrical Hexagonal Structures. These structures have been observed for the PEO-rich copolymers (PEO wt % > 70). They may be described by the regular distribution of the PDMS liquid chains within infinitely long cylinders of radius R located at the nodulus of a bidimensional hexagonal lattice defined by the distance D between the axis of two neighboring cylinders; the PEO matrix is partly crystallized. Such a structure is analogous to those previously observed by Kawai et al.[23] on polyisoprene–poly(ethylene oxide) copolymers. Our experimental data do not allow a quantitative description of the organization of the crystalline PEO lamellae and of the amorphous phase within the PEO matrix.

4. Gas Chromatography Studies. For all probes the variations of $V_g°$ with $1/T$ show the classical shape already observed for semicrystalline polymers characterized by a $V_g°$ minimum value at a temperature quite close to the melting point of the PEO block as determined by DSC (see Table II). One exception should be noted: the variations of $\ln V_g° = f(1/T)$ for the copolymer of lowest PEO content, sample 5-6-5, using n-heptane as a probe, are quite linear within the temperature range 30–80 °C. The lack of any minimum at the melting point can be reasonably interpreted by taking into account the very weak increase of the contribution of the PEO fraction to the total retention volume when going from the semicrystalline state (~3%) to the liquid state (~10%), for n-heptane, a nonsolvent of the PEO chains. Benzene, a strongly interacting solvent for both blocks, leads to the expected $V_g°$ minimum value for the same sample. On the other hand, for a given probe and a given temperature the retention volumes are quite independent of the whole thermal history of the column: this specific feature is in good agreement with the behavior of the copolymer studied by all previous techniques and characterized by a nearly constant degree of crystallinity. It should be noted that the well-known chain unfolding which occurs for pure PEO homopolymer when increasing crystallization or annealing temperatures can be clearly observed by inverse gas chromatography.[26]

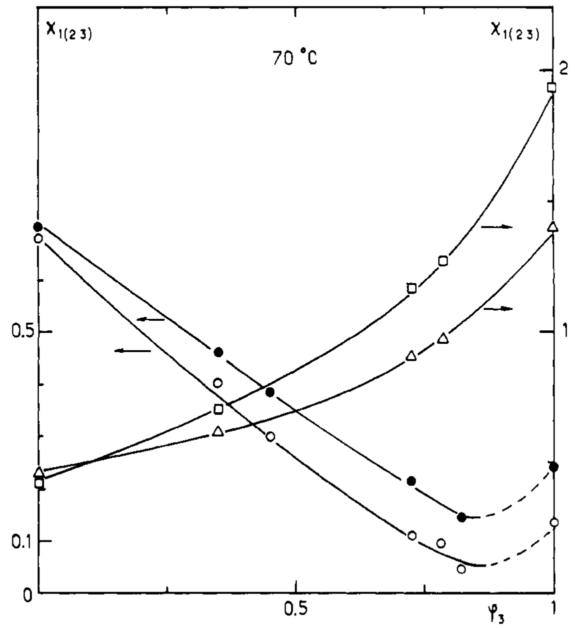


Figure 1. Variation of the $\chi_{1(23)}$ interaction parameter at 70 °C vs. the volume fraction ϕ_3 of PEO in the copolymers: (○) C_6H_6; (△) C_6H_{12}; (●) $C_6H_5CH_3$; (□) n-C_7H_{16}.

The link between the experimental gas–liquid chromatographic (GLC) data and the thermodynamics of solvent–solute interaction has been extensively developed.[14] The interaction parameter $\chi_{1(23)}$ between an infinitely dilute volatile solute 1 and a polymeric stationary phase constituted by a mixture of homopolymers 2 and 3 is correlated to the specific retention volume $V_g°$ through the relation[24]

$$\chi_{1(23)} = \ln\{273.2R(w_2v_2 + w_3v_3)/P_1V_g°V_1\} - (1 - V_1/V_2)\phi_2 - (1 - V_1/V_3)\phi_3 - (P_1/RT)(B_{11} - V_1) \quad (1)$$

where ϕ and w are the volume fraction and the weight fraction of the components, respectively, v is their specific volume, V is their molar volume, P_1 is the saturation vapor pressure of the volatile probe, and B_{11} is the gas-phase second virial coefficient correcting for nonideality, with all of these parameters taken at T K. The temperature dependence of the χ parameter yields the enthalpic contribution χ_H.

Block Copolymers in the Liquid State. The $\chi_{1(23)}$ parameters are calculated by using the χ_{12} and χ_{13} values previously measured on the corresponding systems.[25,26] The variations of $\chi_{1(23)}$ vs. the composition of the polymeric stationary phase, expressed as the PEO volume fraction ϕ_3, are plotted in Figure 1 for various copolymers and

Table IV
PDMS-PEO Interaction Parameters χ_{23}' and $\chi_{23}/V_2 \times 10^2$ [a] (mol/mL) Measured with Various Probes at Infinite Dilution

	benzene		toluene		cyclohexane		*n*-heptane		*p*-dioxane	
sample	70 °C	100 °C	70 °C	100 °C	70 °C	100 °C	70 °C	100 °C	70 °C	100 °C
1-10-1	1.28 (1.35)	1.26 (1.28)	1.33 (1.19)	1.24 (1.06)			2.16 (1.38)			
2-10-2	0.91 (0.96)	0.95 (0.96)	1.06 (0.95)		1.27 (1.10)	1.27 (1.06)	2.01 (1.28)	2.07 (1.27)		
1-6-1	0.86 (0.91)	0.93 (0.94)	0.96 (0.86)	0.92 (0.79)	1.16 (1.01)	1.05 (0.88)	1.80 (1.15)	1.88 (1.15)		
5-10-5	0.53 (0.56)	0.47 (0.48)	0.60 (0.54)							
5-6-5	0.42 (0.43)	0.37 (0.37)	0.42 (0.38)	0.35 (0.30)	0.75 (0.65)	0.65 (0.55)	1.09 (0.70)	0.85 (0.52)	0.70 (0.78)	0.52 (0.57)

[a] χ_{23}/V_2 in parentheses.

Table V
Enthalpic Contribution χ_H to $\chi_{1(23)}$ Parameter of Some Solvents at Infinite Dilution in Various Copolymers at 70 and 100 °C

	benzene		toluene		*n*-heptane		cyclohexane
sample	70 °C	100 °C	70 °C	100 °C	70 °C	100 °C	70 °C
1-10-1	−0.50	−0.34	−0.27	−0.20			
1-6-1	−0.41	−0.27	−0.25	−0.15	1.51	1.24	1.10
5-10-5	−0.39	−0.14	−0.27	−0.01			
5-6-5	−0.19	0.27	−0.13	0.25	0.35	0.25	0.51

volatile probes at 70 °C. They clearly show strong negative deviations to the additivity, which would be expected if complete segregation of the PEO and PDMS chains in pure microdomains has occurred. This feature suggests that at least a fraction of the polymeric material is constituted by a homogeneous mixture of PEO and PDMS chains: their interaction, characterized by a positive χ_{23} parameter, leads to the observed decrease of the $\chi_{1(23)}$ values with respect to the volume-average ones. Using Scott's equation[27] for homogeneous binary blends, one can easily calculate the $\chi_{1(23)}$ parameter by assuming that the liquid copolymer is made up of three independent and juxtaposed phases: pure PDMS (volume fraction $a\phi_2$), pure PEO (volume fraction $b\phi_3$), and a homogeneous PDMS–PEO phase

$$\chi_{1(23)} = \chi_{12}\phi_2 + \chi_{13}\phi_3 - \chi_{23}'(1 - a)(1 - b)\phi_2\phi_3 \quad (2)$$

Here $\chi_{23}' = \chi_{23}V_1/V_2$.

The derivation of the true value of the χ_{23}' interaction parameter from the experimental $\chi_{1(23)}$ data requires knowledge of the volume fractions a and b, which determine the importance and the composition of the mixed interface between the pure PEO and PDMS domains. Because of the lack of any information on these interfaces, we are restricted to calculate a lower limit value for χ_{23}', assuming, as a rough approximation, a homogeneous monophasic structure for the liquid copolymer ($a = b = 0$); these values are collected in Table IV. It may be pointed out that the values should be corrected by a factor as high as 2.0 if, for instance, 30% of the PEO and PDMS were segregated in different domains. In spite of the necessary simplification we made, the positive values of the χ_{23}' parameter thus estimated seem quite reasonable, taking into account the well-known incompatibility of PDMS and PEO, as pointed out, for instance, by the strong difference of their solubility parameters deduced from GLC experiments: δ(PEO) = 9.5, δ(PDMS) = 6.4 at 100 °C.

The analysis of the influence of the probe nature and of the block copolymer structure requires more critical discussion. The reduced value χ_{23}/V_2 should be independent of the probe nature: nevertheless, a significant difference can be noticed between the higher values obtained with a selective solvent of a given block and the lower ones obtained with a good solvent for both blocks. Moreover, this difference is sensitive to copolymer composition. For instance, the χ_{23}/V_2 values measured with either benzene or *n*-heptane are fairly similar for copolymer 1-10-1 (ϕ_3 = 0.812): 1.35 × 10^{-2} and 1.38 × 10^{-2}, respectively. On the contrary, χ_{23}/V_2 strongly increases from 0.43 × 10^{-2} to 0.70 × 10^{-2} for the copolymer 5-6-5 (ϕ_3 = 0.343) when going from benzene to *n*-heptane. These discrepancies may arise from two different origins, which we shall discuss separately: (a) The results obtained with a probe involving specific interactions with any one of the blocks are expected to reflect the specificity and the magnitude of these interactions:[24,27] this is obviously the case of *n*-heptane, a selective solvent of PDMS (χ(n-C_7H_{16}–PDMS) = 0.425 vs. χ(n-C_7H_{16}–PEO) = 1.935 at 70 °C). A common solvent such as benzene is, in fact, a preferential solvent for the PEO blocks, as reflected by its significantly lower χ value (χ(C_6H_6–PEO) = 0.135 vs. χ(C_6H_6–PDMS) = 0.680 at 70 °C). Specific interactions between PEO and benzene, probably involving weak charge transfer complexes between the aromatic ring and the ether bonds,[28] are well-defined by the negative χ_H value of the PEO–C_6H_6 system.[26,29] Moreover, it should be noted that χ_H values are always negative for all the block copolymers even when PDMS is the major component and in spite of the positive χ_H value for the PDMS–C_6H_6 system (Table V).

(b) The correcting factor $(1 - a)(1 - b)$ can obviously take different values, depending on the copolymer composition, and the comparison of the calculated lower limit value of the χ_{23}' interaction parameter may thus be more or less misleading.

As an independent approach to incompatibility phenomena in the PDMS–PEO materials, we have briefly investigated two model systems: PDMS–*p*-dioxane and PEO–octamethylcyclotetrasiloxane. The χ parameters measured at 100 °C are of 1.25 and 2.6, respectively. The PDMS–PEO χ_{23}' values increase from about 0.4 ± 0.1 for the PDMS-rich copolymers to 1.1 ± 0.2 for the PEO-rich copolymers and this trend is in fair agreement with the behavior of the model systems. A better agreement on a

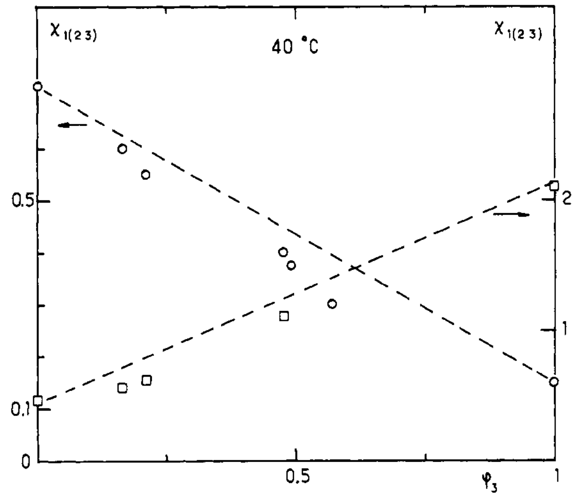


Figure 2. Variation of the $\chi_{1(23)}$ interaction parameter at 40 °C vs. the volume fraction ϕ_3 of PEO in the copolymers: (○) C_6H_6; (□) n-C_7H_{16}.

more quantitative basis cannot reasonably be expected, taking into account the necessary rough assumptions involved in the χ_{23}' calculation.

Within the narrow range of temperature investigated (70–100 °C), the χ_{23}' values are nearly constant (variation < 10%) for the PEO-rich copolymers (PEO wt % > 75) but they show a significant decrease with increasing temperature for copolymers of low PEO content (PEO wt % < 50). These results suggest an increase of miscibility of PDMS and PEO with temperature, especially for PDMS-rich copolymers. In connection with this behavior, it may be recalled that dioxane is more soluble in PDMS than octamethylcyclotetrasiloxane in PEO.

Block Copolymers in Their Semicrystalline State. The experimental results were interpreted by taking into account the following two assumptions: the crystalline fraction of the PEO block does not contribute at all to the measured retention volume and adsorption at the amorphous crystalline interfaces is negligible. For a given temperature, the degree of crystallinity of the polymeric film deposited on the glass beads does not differ significantly from its value measured by DSC on bulk samples.

The $\chi_{1(23)}$ values related to the amorphous phase are thus readily derived from the experimental $V_g°$ values and the corrected PEO and PDMS volume fractions. Their variations at 40 °C with the volume fraction of the amorphous PEO in the various copolymers are illustrated Figure 2. The $\chi_{1(23)}$ values are systematically slightly lower than the calculated values, assuming simple additivity of the contribution of the two blocks which is observed when macroscopic phase separation occurs between very large domains.[30] Rough χ_{23}' values were tentatively estimated by using the same equation as previously used for the liquid state. Most of them lie within the range 0.3–0.5 but they may reach a higher value of about 1.2 for the two copolymers of lowest PEO content studied with n-heptane as a probe, a selective solvent for PDMS. As in the previous case of the liquid state, these values are merely lower limits of the χ_{23}' interaction parameters, estimated assuming no segregation of PDMS and PEO in the amorphous phase. Moreover, it has to be pointed out that the calculated χ_{23}' values are extremely sensitive to the copolymer fraction which effectively contributes to the measured retention volume. We have already shown that in block copolymers, a fraction of a given block may escape to the probe when dispersed and masked within the glassy matrix of the other block.[30] Such a situation can obviously occur in a similar way for semicrystalline copolymers, as in our case: χ_{23}' is increased by a factor of about 2 if only 10% of the copolymer is not accessible to the probe. Thus, the segregation of PEO and PDMS chains and the poor accessibility of the amorphous material to the volatile probe each contribute to the same effect: the calculated apparent χ_{23}' parameter may be significantly decreased with respect to its true value. Finally χ_{23}' values calculated at 40 °C are quite close those calculated at 70 °C in the liquid state, and this may be considered as an argument of good self-consistency of our results.

Conclusion

Our studies on PDMS–PEO–PDMS triblock copolymers have led to the following main conclusions: (a) With respect to the PEO homopolymer precursor, the block copolymers are characterized by a strong decrease in crystallinity τ and in melting temperature by the independence of τ upon the crystallization conditions and by the lack of any significant annealing. These specific features are quite typical of the crystallization of the middle PEO block linked at both its end groups to bulky and incompatible chains. (b) In their semicrystalline state the copolymers show the characteristic periodic organization of block copolymers in lamellae or a hexagonal cylindrical structure according to composition. Long-range order remains probably in the liquid state at high temperature as a result of segregation of the PDMS and PEO incompatible chains, but partial miscibility cannot be completely ruled out at the domain interfaces. (c) Estimation of the lower limits of the χ_{23}' interaction parameter leads to reasonable positive value in the range 0.4–1.1. They show only a weak dependence on temperature but they are, on the other hand, an increasing function of the PEO content of the copolymers. These results are in good agreement with the high incompatibility of PDMS and PEO chains even in the low molecular weight range.

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Thermodynamic Miscibility of Various Solutes with Styrene–Butyl Methacrylate Polymers and Copolymers

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ABSTRACT: Inverse gas chromatography has been used to determine the thermodynamic miscibility of molten poly(styrene–*n*-butyl methacrylate) (58 wt % styrene), poly(styrene–isobutyl methacrylate) (80 wt % styrene), and the corresponding homopolymers with various polar and apolar solutes. Infinite-dilution weight fraction activity coefficients, Flory–Huggins χ parameters, and excess partial molar heats of mixing are used as measures of the polymer–probe interaction. The thermodynamic interaction parameters obtained for these systems are self-consistent; i.e., the miscibility of the copolymer is in qualitative agreement with the interpolated behavior of the parent homopolymers. However, this agreement is generally not quantitative. This probably reflects the effects of nearest-neighbor segment interactions on the solution thermodynamics of the copolymer. In addition, a comparison of homopolymer properties reveals only minor differences between molten poly(*n*-, iso-, and *sec*-butyl methacrylates).

Introduction

Since the pioneering work of Smidsrod and Guillet,[1] numerous investigators have used inverse gas chromatography (IGC) to determine physicochemical parameters characterizing the interaction of small amounts of volatile solutes with polymers.[2-4] It has been established that reliable infinite-dilution weight fraction activity coefficients, Flory–Huggins χ parameters, and excess partial molar heats of mixing can be readily determined with this technique. In the present work, the sensitivity of these thermodynamic interaction parameters to structural modifications of several poly(butyl methacrylates) is investigated. In addition, the melt behavior of two styrene–butyl methacrylate copolymers has been investigated, and the results have been compared with those for the corresponding homopolymers. This investigation is part of a continuing study of the thermodynamic properties of styrene–methacrylate homopolymers, copolymers, and blends.

Experimental Section

Materials. All solutes were chromatoquality or reagent grade and were obtained from standard laboratory supply sources. Polystyrene (PS: $\bar{M}_w$ = 110 000, $\bar{M}_w/\bar{M}_n$ < 1.06) was obtained from Polysciences. Poly(*n*-butyl methacrylate) (PnBMA: $\bar{M}_w$ = 320 000, $\bar{M}_n$ = 73 500), poly(isobutyl methacrylate) (PiBMA: $\bar{M}_w$ = 300 000, $\bar{M}_n$ = 140 000), and poly(*sec*-butyl methacrylate) (PsBMA: density = 1.052 g cm^{-3}) were obtained from Aldrich. Poly(styrene–*n*-butyl methacrylate) ($\bar{M}_w$ = 70 000–75 000, $\bar{M}_w/\bar{M}_n$ $\simeq$ 2.0–2.3, MI = 15.5) containing 58 wt % styrene and poly(styrene–isobutyl methacrylate) ($\bar{M}_w$ $\simeq$ 70 000) containing 80 wt % styrene are random copolymers which were obtained from internal sources (Xerox Corp.). Chromosorb G (AW-DMCS treated, 70/80 mesh) was obtained from Johns-Manville.

Columns. The polymers were coated from a benzene solution onto Chromosorb G. After drying in a vacuum oven for ca. 72 h at 60 °C, the coated support was resieved and the packed into 0.25-in o.d. copper columns. Silanized glass wool was used to block the ends of the column. The exact percent loading of polymer on the support (weight of polymer/weight of polymer plus support) was determined by calcination, using a suitable blank correction. A complete description of the columns is given in Table I.

Table I
Stationary Phase and Column Parameters

polymer	loading, % (w/w)	wt of polymer, g	length of column, cm
PS	7.45	1.1778	152.4
PnBMA	8.19	1.2656	152.4
PiBMA	8.20	0.9860	121.9
		0.3463	50.8
PsBMA	8.00	1.0194	121.9
P(S-nBMA)	8.03	1.2763	152.4
P(S-iBMA)	10.62	1.2987	119.4

Instrumentation. IGC measurements were carried out on a Hewlett-Packard 5830A gas chromatograph equipped with a dual flame ionization detector. The oven temperature was measured with a precision of ±0.01 °C with a Hewlett-Packard platinum resistance thermometer. Carrier gas (prepurified nitrogen) flow rates were measured from the end of the column with a water-jacketted soap bubble flowmeter. The net retention time of the probe (±0.01 min) was determined from the peak maxima retention times for the probe and methane (a marker to correct for dead volume in the column). Column inlet and outlet pressures were read from a mercury manometer (±0.05 mmHg).

The solutes and marker were injected manually with a 10-μL Hamilton syringe (<0.01 μL). The solutes were characterized by symmetrical elution peaks and generally exhibit little sample size dependence at low injection volumes, low carrier gas flow rates (5–20 cm^3/min), and moderate column loadings ($\simeq$8%). Galin and Rupprecht[5] have shown that under these conditions the opposite influences of surface adsorption and gas flow rate are nearly equivalent, so that the experimental V_g° value is quite close to the bulk V_g° value. Columns were conditioned at temperatures ca. 100 °C above T_g for 2–3 h prior to use.

Data Reduction. Specific retention volumes, V_g° (cm^3/g), were computed from the relation[6]

$$V_g^\circ = t_N F J / w_L \tag{1}$$

where t_N is the net retention time for the probe, w_L is the weight of polymer in the column, J is the James–Martin correction factor

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