Gas Chromatographic Study of the Interactions in Styrene–Dimethylsiloxane Block Copolymers and Blends

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ABSTRACT: The biphasic structure of a series of dimethylsiloxane–styrene block copolymers of various composition (22<% PS<84) and molecular weight ($2 \times 10^4 < \bar{M}_n < 11 \times 10^4$), obtained by sequential anionic polymerization, has been studied by differential scanning calorimetry, electron microscopy, and small-angle X-ray scattering. The thermodynamics of the interactions between various probes and the block copolymers or the homologous homopolymer mixtures were investigated by gas chromatography either above (120–180 °C) or below (50–80 °C) the PS glass-transition temperature. The experimental data related to the liquid state were taken into account within the framework of the Flory–Huggins theory. It allows the determination of the polymer–polymer interaction parameter as a quantitative measure of the PDMS–PS incompatibility for the block copolymers; it yields the variations of the interaction parameters with temperature, the nature of the probe, and the copolymer composition and molecular weight. A tentative analysis of the interaction between *n*-decane and the block copolymer in the glassy state yields an estimate of the contribution of the adsorption of the probe at the surface of the PS domains to the total specific retention volumes. Accordingly, it is shown that most of the surface of the PS domains is accessible to the probe.

The study of the thermodynamics of the interactions between a homopolymer and a volatile probe by gas–liquid chromatography[1,2] has been enlarged to the investigation of ternary systems, containing a probe and blends of two nonvolatile components with at least one macromolecular chain. Examples of mixtures that were studied follow: poly(dimethylsiloxane) with *n*-tetracosane (n-C_{24}) and di-*n*-octyl phthalate (DOP);[3] plasticized systems like poly(vinyl chloride) (PVC)–DOP;[4] blends of compatible homopolymers such as PVC–poly(ϵ-caprolactone)[5] or polystyrene–poly(vinyl methyl ether);[6] and finally, block copolymers such as polystyrene–poly(tetrahydrofuran).[7] The methodology implies the preliminary analysis of the interactions between the volatile probe 1 and each of the two nonvolatile components 2 and 3 and, then, the study of their mixture 2–3. In general, the experimental results may be taken into account through the classical Flory–Huggins theory which leads to the derivation of the three different interaction parameters χ_{12}, χ_{13}, and $\chi_{1(2,3)}$. Furthermore, this information allows the determination of the χ_{23} interaction parameter, a direct thermodynamic measurement of the compatibility of the two nonvolatile components.[3-6]

We have focused our interest on biphasic systems (blends or block copolymers of incompatible chains) and, in the present work, we have applied the gas–liquid chromatography technique to the study of the thermodynamics of interactions in the poly(dimethylsiloxane) (PDMS)–polystyrene (PS) systems with a double aim: (a) to compare the diblock PDMS–PS or triblock PDMS–PS–PDMS copolymers and the homologous blends of the two homopolymers in the liquid state, within a temperature range (120–180 °C) higher than the PS glass-transition temperature; and (b) to investigate the segregation phenomena and the domain sizes within a temperature range (50–80 °C) lower than the T_g of PS using a nonsolvent for PS as the volatile probe. Under such conditions, the contribution of the PS domains to the probe retention is restricted to adsorption phenomena at the available surface.[8,9]

Experimental Section

The synthesis of the PDMS–PS block copolymers was carried out by anionic polymerization of hexamethylcyclotrisiloxane (D_3) initiated by living poly(styryllithium) carbanions in homogeneous solution as already described in the literature.[10-12] The experimental conditions may be summarized as follows. PDMS–PS diblock copolymers–styrene polymerization: benzene/*sec*-butyllithium/30 °C. D_3 block copolymerization: tetrahydrofuran (THF)/D_3/55 °C.

PDMS–PS–PDMS triblock copolymer–styrene polymerization: THF/naphthalene–lithium/−70 °C. D_3 block copolymerization: D_3/55 °C.

The crude copolymer samples were fractionated by precipitation at 25 °C using benzene–methanol as a solvent–nonsolvent system. The fractions were analyzed by elemental analysis and UV spectrometry at 262 nm in chloroform (ϵ = 2.10 L/(g cm)) for the determination of the PS content according to literature.[13] The average molecular weights were measured by osmometry ($\bar{M}_n$) in toluene solution at 35 °C (Mechrolab 52 membrane osmometer) and by light scattering ($\bar{M}_w$) in ethyl acetate solution at room temperature for λ 5460 Å (Fica 50 apparatus) using the values of the specific refractive index increments calculated according to

$$(\mathrm{d}n/\mathrm{d}c)_{\mathrm{cop}} = \omega_{\mathrm{PS}}\,(\mathrm{d}n/\mathrm{d}c)_{\mathrm{PS}} + \omega_{\mathrm{PDMS}}\,(\mathrm{d}n/\mathrm{d}c)_{\mathrm{PDMS}}$$

where ω is the weight fraction of each component and dn/dc = 0.220 and 0.032 mL/g for PS and PDMS, respectively.[12]

The molecular parameters of the fractions selected for the gas chromatographic studies are given in Table I.

It should be pointed out that the block copolymer linearity may be perturbed by some defects like macrocyclic structures arising from the well-known ring–chain equilibrium of living PDMS which may occur to a low extent during the anionic block copolymerization, even in the presence of lithium as counterion.[14]

The measurements by differential scanning calorimetry (DSC) were carried out on a Perkin-Elmer DSC2 apparatus between −140 and 120 °C using the following experimental conditions: sample weight, 6–15 mg; thermal treatment of the sample, heating rates 5–40 °C/min and cooling rates 40 and 160 °C/min. All samples were systematically annealed at 120 °C before measurement and all data were taken on subsequent runs. The glass-transition temperatures were conventionally chosen at the inflexion point of the curves and the melting temperature at the top of the endotherm peak.

The gas chromatographic technique and the preparation of the columns were described in our previous works.[9,15] The copolymers were deposited from their solution in benzene on two different inert supports previously treated with HMDS. These supports are Chromosorb W and glass beads of specific surface area of 0.20 and 0.016 m^2/g, respectively. The retention times were converted into specific retention volumes corrected to 0 °C; V_g^0 and the $\chi_{1(2,3)}$ parameters were calculated using eq 5 of ref 3, assuming that the specific volume of block copolymers and blends is the weight average of the specific volumes of the parent homopolymers. The physical parameters of the solvents and of the two polymers are the same as those previously used.[9,15]

The electron micrographs were obtained with a Hitachi HU 11CS electron microscope. Films were prepared by casting one drop of a 5% benzene solution of the block copolymer on a water

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Table I
Compositions, Molecular Weights, and Transition Temperatures (Heating Rate 10 °C/min) of the Copolymers (B, T) and of the Blends (M)

				T_g, °C[c] (PS)		T_m, °C (PDMS) in copolym		T_g, °C (PDMS) in copolym
sample	% wt PS	$\overline{M}_n$	$\overline{M}_w$	in copolym	in homopolym			
B_1	22.4	72 300	108 000	98 (93)	(88)	−43	−38	−125
B_2	45.8	57 100	64 600	102 (93)	(97)	−44	−39	−126
B_3	70.9	23 000	24 700	92 (87)	(88)	−53		−140
B_4	83.6	46 800	53 000	100 (95)	(98)			
T_3	63.1	118 000	131 700	101 (95)	(99)	−42		−127
		$\overline{M}_n$[a]	$\overline{M}_n$[b]					
M_1	23.2	25 000	17 000		(96)			
M_2	68.0	76 000	30 000		(99)			
M_3	69.3	25 000	4 000		(96)			
L_1	70.7	76 000	30 000					
L_2	68.4	76 000	30 000					

[a] $\overline{M}_n$ of the PS. [b] $\overline{M}_n$ of the PDMS. [c] The number in parentheses is related to the temperature taken at the intersection of the extrapolation of the base line with that of the inflection.

surface. The films were transferred to a carbon-coated copper grid and examined at 50 or 75 kV.

The small-angle X-ray scattering (SAXS) measurements and the derivation of the structural parameters from the observed peak spacings on the X-ray patterns obtained at 25 °C on the polymeric films (thickness ~ 0.1 cm) were carried out as usual.[16]

Results and Discussion

1. Thermal Transitions of the Block Copolymers by DSC. We observed, in general, the transitions of both blocks (Table I). PDMS: glass transition between −140 and −120 °C; melting points at −44 and −40 °C; the endothermic peak corresponding to the second melting point is no longer visible at higher heating rates (40 °C/min for instance). Furthermore, for those samples quenched at 160 °C/min, an exothermic peak appears at −108 °C. All of these features are in good agreement with literature data on pure PDMS.[17] PS: glass transition in the range 85–102 °C. The variations of the glass-transition temperature may be readily taken into account considering the corresponding variations of the molecular weight of the PS block.[18] On the other hand, the difference between the T_g of the PS block in the copolymer and that of the homologous PS homopolymer of the same molecular weight never exceed 4 °C. This feature is in sharp contrast with the characteristic behavior of PS–polyisoprene diblock copolymers studied by Roovers et al.,[19] where the lowering of the T_g of the PS block is by far higher. The presence of individual thermal transition points of each block at almost the same temperature of the corresponding homopolymers may be considered as an argument for a complete segregation of the blocks and a biphasic structure for the copolymers, over the whole range of molecular weight and composition we have investigated. According to Saam et al.,[20] such behavior may be readily explained by the high interfacial contact energy in the PS–PDMS block copolymers owing to the very strong incompatibility of the two blocks.

2. Block Copolymer Structure by Electron Microscopy and Small-Angle X-ray Scattering. The electron photomicrographs of the samples B_1 (22.4% PS) and B_2 (45.8% PS) in the form of very thin films cast from benzene solution clearly show typical segregated structures of PS and PDMS domains where chains of the same chemical nature have aggregated to form spaghetti-like microphases. Similar features were already observed by SAAM et al.[10] on a diblock PS–PDMS (40% PS) film cast from toluene solution. SAXS patterns are not very well defined showing a poor structural organization, but they may be improved in a significant manner after the films are annealed at 150 °C for 24 h. The patterns are consistent with a rodlike structure characterized by the dispersion of PS rods in a PDMS matrix. This is also true for the B_2 sample for which a lamellar structure was expected from its composition ($V_{\text{PS}}/V_{\text{PDMS}} = 0.77$) and from literature data.[21]

For B_4 (83.6% PS) and T_3 (63.1% PS) block copolymers phase inversion occurs, and the structure may be described as a dispersion of PDMS rods in a PS matrix.

For the B_3 copolymer, electron microscopy definitely shows a lamellar structure in spite of its high styrene content (70.9% PS). This feature may be tentatively correlated with its rather low molecular weight ($\bar{M}_n = 23\,000$) and has already been observed by Saam et al.[20] on a very similar copolymer (70.9% wt PS, $\bar{M}_n = 28\,600$).

We have collected in Table II the values of the domain sizes directly measured by electron microscopy or deduced from SAXS measurements. Moreover, we have calculated the distance $\bar{L}$ of the most remote chain atom in the unperturbed PS or PDMS block from one of its chain ends, assuming that the block conformation in the copolymer film always obeys Gaussian statistics similar to the homopolymer in its Θ state: $\bar{L}_{\text{Å}} = 1.2(6^{1/2})(\bar{S}_\theta^2)^{1/2}$[22] with $(\bar{S}_\theta^2)_{\text{Å}}^{1/2} = 0.300\bar{M}_w^{0.50}$ for PS and $(\bar{S}_\theta^2)_{\text{Å}}^{1/2} = 0.266\bar{M}_w^{0.50}$ for PDMS.[23] It may be seen that the PS rod diameter ($2R$) is roughly twice the calculated $\bar{L}_{\text{PS}}$ value and that the PDMS phase thickness ($d - 2R$) is close to the $\bar{L}_{\text{PDMS}}$ value.[24] In our opinion, such an agreement, already observed by Saam et al.[10] on similar copolymers, is not to be taken as definite proof of a given conformation of the blocks in the copolymer.

3. Study of the PS–PDMS Block Copolymers and Blends by Gas Chromatography. We have investigated the thermodynamics of the interactions of our block copolymers with various probes within the temperature range 50–180 °C choosing three types of solvents: benzene and toluene (goods solvents for both blocks), n-heptane (n-C_7) and n-decane (n-C_{10}) (selective solvents of the PDMS block), and dioxane (selective solvent of the PS block). The variations of ln V_g^0 vs. $1/T$(K) are generally linear for the copolymers in the glassy and liquid states. The glass-transition temperature of PS is visualized as a simple change in the slope of the straight lines for the copolymers rich in PDMS. For the copolymers rich in PS (>60% by weight) and using a nonsolvent of PS as probe, the experimental curve presents the classical S shape around the T_g temperature (Figure 1).

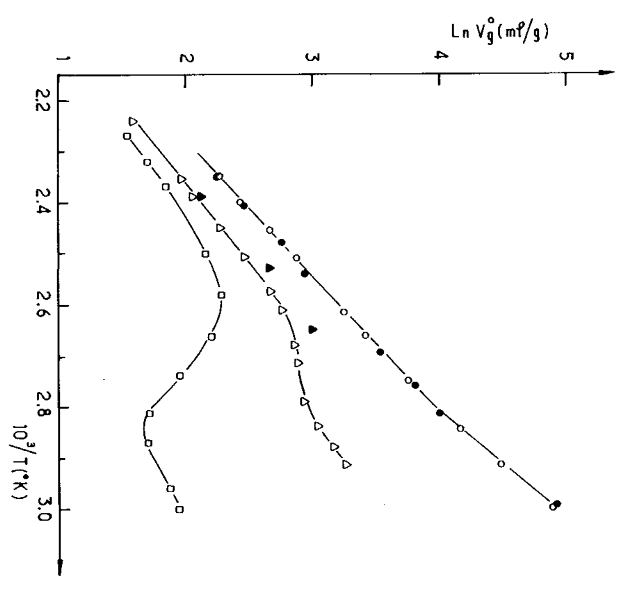

Figure 1. The effect of copolymer composition and column loading on the retention diagram of *n*-heptane (copolymer/Chromosorb W): B_2, ○ ~20% and ● ~5%; T_3, △ ~20% and ▲ ~5%; and B_4, □ ~20%.

Thermodynamics of the Interactions in the Liquid State within the Temperature Range 120–180 °C. In the liquid state, the interactions between the various probes and the stationary phase are restricted to dissolution phenomena. The variations of flow rate of the gas vector and of the column loading may affect the experimental V_g^0 values. We have checked that these influences are negligible in all cases, except for PS-rich copolymers and their poor solvents like aliphatic hydrocarbons. We have thus performed the required corrections (≤5%), extrapolating the experimental data to zero flow rate and to infinite column loading. In the whole range of composition and when using a good solvent of both sequences, the V_g^0 values for block copolymers are systematically higher than the corresponding values for the homopolymers we have previously measured.[9,15] For a preferential solvent of either PS or PDMS, the V_g^0 values of the block copolymers are within the range defined by the homopolymers.

The calculation of the interaction parameter $\chi_{1(2,3)}$ was performed within the framework of the Flory–Huggins theory using the modified equation of Patterson et al.[3] The knowledge of the χ_{12} and χ_{13} interaction parameters from previous studies allows the derivation of the polymer 2–polymer 3 χ_{23} interaction parameter by means of the relation

$$\chi_{1(2,3)} = \phi_2\chi_{12} + \phi_3\chi_{13} - \frac{V_1}{V_2}\chi_{23}\phi_2\phi_3 \qquad (1)$$

where ϕ are the volume fractions of the polymers in the mixture and V are the molar volumes. The values of the interaction parameter χ_{23}' normalized to the size of the probe molecule $\chi_{23}' = \chi_{23}V_1/V_2$ are collected in Table III together with the values of χ_{23}/V_2. The latter seem more reliable for a comparison of the experimental data obtained with probes of different molar volumes.

Equation 1 is strictly valid only for homogeneous mixtures of compatible homopolymers. Its use for biphasic structures of incompatible blends or block copolymers where the components 2 and 3 belong to the same molecule is questionable and it may be considered as a rough but convenient approximation. Because of the lack of any

Table II
Structural Parameters of the Copolymers as Derived from EM and SAXS Measurements at 25 °C

		$\bar{L}$, Å			structural parameters, Å	
sample	% wt PS	PS	PDMS	structure of the block copolymer	EM	SAXS
B_1	22.4	110	188	rods of PS	$d = 450$, $2R = 240$	$d = 470$, $2R = 250$
B_2	45.8	138	138	rods of PS	$d = 450$, $2R = 270$	$d = 450$, $2R = 310$
B_3	70.9	106	65	lamellae	$d_{PS} = 350$, $d_{PDMS} = 160$	
B_4	83.6	168	70	rods of PDMS		
T_3	63.1	230	116	rods of PDMS	$d = 350$, $2R = 130$	

Table III
PDMS–PS Interaction Parameters χ_{23}' and $[\chi_{23}/V_2] \times 10^2$ mol/mL Measured with Various Probes

	120 °C		150 °C						180 °C	
sample	toluene	*n*-C_7	benzene	toluene	*n*-C_7	*n*-C_{10}	dioxane	chloroform	toluene	*n*-C_{10}
B_1	0.67 (0.56)	1.19 (0.70)	0.54 (0.50)	0.58 (0.47)	0.86 (0.48)	1.01 (0.45)	0.91 (1.03)		0.50 (0.38)	0.80 (0.34)
B_2	0.80 (0.67)	1.60 (0.95)	0.51 (0.48)	0.62 (0.50)	0.87 (0.49)	0.92 (0.41)	0.59 (0.67)		0.50 (0.38)	0.70 (0.30)
B_3	0.36 (0.30)	1.30 (0.77)	0.20 (0.19)	0.26 (0.21)	0.71 (0.40)	0.90 (0.40)	0.40 (0.45)		0.25 (0.19)	0.47 (0.20)
B_4	0.80 (0.67)		0.42 (0.39)	0.45 (0.36)	0.95 (0.53)	1.03 (0.46)			0.35 (0.27)	0.50 (0.21)
T_3	0.44 (0.37)	0.79 (0.47)	0.26 (0.24)	0.32 (0.26)	0.63 (0.35)	0.82 (0.36)	0.41 (0.46)	0.27 (0.31)	0.19 (0.14)	0.38 (0.16)
M_1				0.52 (0.42)		0.74 (0.33)				
M_2				−0.54 (−0.43)		−0.12 (−0.05)				
M_3				0.18 (0.14)		0.68 (0.30)				

theoretical argument, its justification may be found a posteriori in the calculated χ_{23}' values. For the copolymers, the χ_{23}' values are always positive and their order of magnitude appears quite reasonable, as expected from the well-known incompatibility of PS and PDMS chains. For the polymer blends, however, the χ_{23}' values are generally lower than those of the homologous block copolymers and, in the particular case of the M_2 mixture (homopolymers of the highest molecular weight), they are negative. These meaningless values may be correlated with those already obtained by Patterson et al. for PDMS-tetracosane systems.[3] As a rough guide, it may be estimated that eq 1 still remains meaningful for incompatible block copolymers where segregation leads to highly dispersed microdomains of relatively small size (300-500 Å for our samples) but that it is not valid for incompatible polymeric mixture where segregation leads to macrophase separation in very large domains (0.5-1 μm).

The variations of χ_{23}'/V_1 are a complex function of the copolymer composition, of the temperature, and of the probe affinity for the copolymer.

Influence of the Probe Nature. Whatever the composition of the copolymer is and at all temperatures studied the χ_{23}'/V_1 values do not show any significant difference, provided that comparison is restricted to different probes of the same affinity for the copolymer: good solvents for both chains (benzene and toluene) or preferential solvents of the PDMS (n-C_7 and n-C_{10}). The first case is thought to lead to the more reliable average value of polymer-polymer interaction parameter: $\chi_{23}' \sim 0.50 \pm 0.05$ at 150 °C. As more or less expected,[3] this value is quite close to the χ_{12} value 0.46 for the PDMS-benzene or toluene systems at the same temperature. When comparison is made between probes of different affinities for the copolymer, two factors are to be taken into account: temperature and composition. The observed differences between χ_{23}'/V_1 values for aromatic and aliphatic hydrocarbons are a decreasing function of temperature and a decreasing function of the PS content in the copolymers. For instance, the increase of the χ_{23}'/V_1 value upon going from toluene to n-heptane is noticeable for all copolymers at 120 °C, it is still significant but lower at 150 °C for PS-rich copolymer (more than 50% in weight), and it finally becomes negligible at 180 °C. The behavior of dioxane, preferential solvent of PS block, is quite symmetric; at 150 °C, the χ_{23}'/V_1 values are an increasing function of the PDMS content of the block copolymer. This complex dependence of the χ_{23}'/V_1 parameter on the nature of the probe may be interpreted as the result of the preferential interaction phenomena of the probe with a given chain (for instance n-alkanes-PDMS) and of possible low rates of diffusion of the probes (especially for poor solvents such as aliphatic hydrocarbons) into the PS domains for the lowest temperature which may be close to their glass transition.

Influence of the Copolymer Structure. In order to avoid any complication arising from preferential interaction of the probe with a given chain, the variations of the χ_{23}' parameter with polymer structure have been studied with a good solvent for both polymers as the volatile probe. Furthermore, they may reflect complex influences of the molecular weights of the individual blocks and of the composition which are not independent parameters for block copolymers. For diblock copolymers of molecular weights higher than 3×10^4 and of styrene content increasing from 22 to 84%, the χ_{23}' values calculated for benzene are in the range 0.45-0.54. Taking into account an average accuracy of about 10% of the experimental values, it may be seen that χ_{23}' parameters are slightly dependent on copolymer composition with a significant decrease for the PS-rich copolymers. The diblock copolymer of the lowest molecular weight ($\bar{M}_n$ = 24 700, % PS = 70.9) and the triblock copolymer of high molecular weight ($\bar{M}_n$ = 115 000, % PS = 63.1) definitely show lower χ_{23}' values of approximately 0.24 and 0.32, respectively.

In a general way, the positive χ_{23}' values reflect the incompatibility of the PS and PDMS chains; this incompatibility is reduced as expected for low molecular weight chains and may depend, on the other hand, on copolymer structure, as clearly shown by the significant decrease of the χ_{23}' parameter when going from the diblock to the triblock copolymer.

Influence of Temperature. In the whole range of composition, whatever the probe is, the χ_{23}' values are a decreasing function of temperature, showing an increase of compatibility of PS and PDMS with increasing temperature. Nevertheless, χ_{23}' remain positive even at the highest temperature of 180 °C, suggesting that the block copolymers should behave always as biphasic systems with segregated domains of PS and PDMS. This feature is easily checked by examination of the block copolymers films by the polarizing microscope; a well-defined birefringence may be noticed up to 300 °C.

Comparison between Block Copolymers and Homopolymer Mixtures. As a rough approximation, the experimental $V_g{}^0{}_{23}$ values of the homopolymer mixtures are linearly correlated with the $V_g{}^0$ values of their two components by means of the simplified relation

$$V_g{}^0{}_{23} = \omega_2 V_g{}^0{}_2 + \omega_3 V_g{}^0{}_3 \qquad (2)$$

where ω_2 and ω_3 are the weight fractions of polymers 2 and 3 in the mixture. This relation only means that the polymer mixtures behave quite separate and juxtaposed macrophases. As already pointed out, eq 1 is not valid for such a biphasic structure even in a first approximation since it leads to inconsistent χ_{23}' values with respect to the well-ascertained incompatibility of PS and PDMS.

Study of the PDMS-PS/*n*-Decane Systems below the Glass Transition of the PS Polymer within the Temperature Range 50-80 °C. For PDMS-rich copolymers (>60% PDMS), the shape of the elution peak remains symmetrical, but it is by far wider and shows only a slightly longer elution time than for the homopolymer mixtures. This feature implies a greater equivalent height of the theoretical plate H for the copolymer. The influence of the gas vector flow rate and of the amount of injected probe is weak (<5%), but nevertheless we have systematically extrapolated the data to zero flow rate and probe amount. The variations of ln $V_g{}^0$ vs. $1/T$ are linear and the ΔH experimental values derived from the slopes are within the range defined by the enthalpies of the homopolymer-solute interactions: vaporization of the n-decane from its infinitely dilute solution in the bulk of PDMS ($-\Delta H_b$ = 11.1 kcal/mol) and from its infinitely dilute adsorption layer at the PS surface ($-\Delta H_s$ = 9.3 kcal/mol) (latent heat of vaporization of n-decane at 60 °C $\Delta H_v \simeq$ 11.6 kcal/mol).

As dissolution phenomena of n-decane, a good solvent for PDMS, are quite negligible for PS below its glass-transition temperature,[9] the retention volume measured for both block copolymers and homologous mixtures arises from the contributions of dissolution of the probe in the bulk of PDMS domains and of its adsorption at the surface of PS ones, as expressed by the following relation:

$$V_g{}^0{}_{\text{exp}} = \omega V_g{}^0 s(\text{PS}) + (1 - \omega) V_g{}^0 b(\text{PDMS}) \qquad (3)$$

Table IV
Estimation of the Surface Area of the PS Domains from Gas Chromatographic Measurements in the Glassy State with *n*-Decane as Probe

column	surface area of support,[a] m^2	wt % polymer/support	$V_g^0(C_{10}$, 60 °C), cm^3/g	A of PS domains, m^2	$2R$, A
B_1 (1)	0.275	20.48	1660	8.20 ± 0.3	290
(2)	0.271	5.01	1630	1.80 ± 0.1	320
B_2 (1)	0.087	16.74	1320	2.39	530
(2)	0.191	6.18	1350	2.07 ± 0.06	495
(3)	0.219		1370	2.49 ± 0.07	470
B_3 (1)	0.188	20.13	1035	8.15 ± 0.15	310
B_4	0.295	19.21	60		
T_3 (1)	0.113	20.43	410		
(2)	0.245	4.71	380		
M_1	0.276	5.00	1325	0.27 ± 0.08	
M_2	0.188	22.53	550	0.26 ± 0.06	
L_1	0.221	19.17	500	0.22 ± 0.1	
L_2	0.352	19.87	532	0.21 ± 0.2	

[a] Chromosorb W (specific surface area 0.2 m^2/g) in all cases but for run B_2 (3) (glass beads (0.016 m^2/g)).

where ω is the weight fraction of the PS in the PDMS–PS system. Using the V_g^0b(PDMS) values previously determined for the homopolymer (1660 cm^3/g at 60 °C), the V_g^0s(PS) contribution term may be derived from the V_g^0 experimental measurement. Assuming that the adsorption enthalpy ΔH_s and the surface partition coefficient K of the *n*-decane in our PDMS–PS systems possess the same values as for the model *n*-decane–PS system,[9] the surface area A of the PS domains accessible to the probe may be estimated through the relation[8]

$$\ln A = \ln V_g^0 s + \ln W - \ln K + \frac{\Delta H_s}{RT} \tag{4}$$

W is the weight of PS.

It should be pointed out that this basic additivity relationship implies that PS and PDMS are integrally accessible to the probe molecule. Obviously this would not be the case of a specific film structure characterized by the dispersion of isolated PDMS domains in an impermeable PS matrix (PS > 60%, $\bar{M}_n > 40\,000$).

The calculated A values at 60 °C are collected in Table IV. For the homopolymer mixtures they have to be discussed taking into account the method of polymer film deposition onto the surface of the inert support.

When PS and PDMS homopolymers are deposited successively (run L_1), the PS surface area is identical to that determined in the absence of the PDMS layer and is quite close to the surface area of the support; this may be considered as a posteriori justification of our previous assumption that the adsorption enthalpy ΔH_s and the partition coefficient K of the *n*-decane at the PDMS–PS interface are not essentially different from these at the PS–carrier gas interface. Nevertheless, this assumption remains a convenient approximation, which may find further justification in the reasonable results obtained for copolymers (see as described below).

When PS is deposited on the support previously recovered with a PDMS layer (run L_2), the surface area of the PS is only about 60% of that of the Chromosorb. This significant decrease merely reflects the incompatibility of PS and PDMS, which does not allow a regular spreading of PS chains on the PDMS surface, but rather promotes the aggregation of PS in more concentrated domains of smaller surface. The contribution of the bulk sorption of the *n*-decane into the PDMS through defects of the PS layer to the experimental V_g^0 value remains predominant.

When PS and PDMS are simultaneously deposited on the support from their solution in a common good solvent such as benzene, the measured surface area of PS macrodomains is slightly higher than the surface area of the support (runs M_1 and M_2). This suggests a dispersion of PS domains of high surface in a permeable PDMS matrix that we have been able to check directly by optical microscopy.

The block copolymer films were systematically deposited on the inert support from their solution in benzene, a good solvent for both blocks; their structures determined by small-angle X-ray scattering and electron microscopy have already been discussed. Two different cases may be considered, depending on whether the matrix is permeable (PDMS) or impermeable (PS).

For the copolymer of the highest PDMS content (sample B_1, 77.6% PDMS), the experimental surface area deduced from gas chromatography experiments leads to a calculated diameter of about 290 Å for the PS cylinders, in rather good agreement with the values directly deduced from SAXS and electron microscopy measurements, 240 and 250 Å, respectively. This suggests that all the surface of the rodlike PS domains is readily accessible to the *n*-decane probe through the permeable PDMS matrix in which they are dispersed. When the PS content reaches 45.8% (sample B_2) with a slight increase of the size of the corresponding domains (cf. Table II), the gas-chromatography measurements lead to a too low surface area and to a too high diameter (470 Å). It seems that 30% of the surface area of the PS domains is no longer accessible to the probe. Our calculations imply that all the bulk of the PDMS matrix contributes to the total retention of the probe, but, as shown by electron microscopy, a low fraction of PDMS may be found in microdomains surrounded by PS and thus may be isolated from the *n*-decane probe. In this case, the calculated contribution of the PDMS is overestimated and that of PS underestimated. Moreover, the experimental broadening of the elution peaks suggests that the measurements may be perturbed by kinetic effects arising from a slow diffusion of the probe into the biphasic "tortuous" material. For the block copolymers, the measurement of the surface area of the cylindrical PS domains dispersed in the permeable PDMS matrix by gas chromatography has to be considered with caution and checked by independent methods.

For PS-rich copolymers (PS > 60%, $M_n > 40\,000$), the permeable PDMS domains are dispersed and isolated in the impermeable PS matrix, and their contribution to the probe retention is thus drastically reduced; this leads to a strong decrease of the experimental retention volumes.

For the block copolymer of the highest PS content (B_4, 83.6% PS), assuming that the PS surface is close to that of pure PS deposited on the support in the same conditions, the contribution of PDMS domains to the probe retention may be roughly determined as an underestimated value; 15%, at least, of the PDMS remain accessible to the *n*-decane at the surface and through defects of the copolymer film. For the triblock T_3 copolymer (63.1% PS), 55% of the PDMS contributes to the probe retention, according to the same calculations.

In the particular case of the B_3 sample (70.9% PS), the specific retention volume remains relatively high in spite of the high content of PS; this specific feature may be correlated with the lamellar structure of the copolymer. Assuming that all the PDMS layers are readily accessible to the probe, the thickness of PS lamellae may be estimated to be approximately $d_{PS} = 310$ Å. This value is in fairly good agreement with that directly measured by electron microscopy.

Conclusion

The main conclusions derived from our study of the PDMS–PS systems may be summarized as follows:

DSC, electron microscopy, and SAXS measurements on the block copolymers have allowed the determination of the shape and size of the different domains in these biphasic materials.

The gas–liquid chromatographic measurements performed on block copolymers in the liquid state (120–180 °C) readily allow the derivation of the χ_{23}' polymer–polymer interaction parameter, which may be considered as a quantitative measure of block incompatibility; the more significant χ_{23}' values are obtained with a good solvent of both blocks as probe, provided that the temperature is well above the PS glass-transition point. In such conditions (150 °C, benzene or toluene as probe), the average χ_{23}' value of about 0.5 for the PS–PDMS is much higher than that of the PS-polyisoprene system at 25 °C, $\chi_{23} \sim 0.14$.[25] This difference may explain why a sharp phase separation may occur in PDMS–PS block copolymers even in the low molecular weight range. Finally, the incompatibility of the two blocks is a decreasing function of temperature and an increasing function of molecular weight as expected. For polyblends in the liquid state, the specific retention volume of a given probe is merely the weight average of specific retention volume for the parent homopolymers, as a result of macrophase separation.

The gas–solid chromatographic measurements performed on blends and block copolymers in the glassy state ($50 < t < 80$°C) with a selective solvent of PDMS (*n*-decane) as probe have been tentatively analyzed and used to calculate the contribution of the probe adsorption at the surface of the PS domains to the total specific retention volume. The overall polymer–probe interaction process strongly depends on the morphological and structural characteristics of the polymeric film: macro (blends) vs. microphase (block copolymers) segregation and chemical nature of the matrix and of the dispersed phase (composition and molecular weight). In spite of these complex influences, the gas–solid chromatographic measurements lead to quite meaningful values of the surface area of PS domains for the copolymers characterized by a dispersion of the PS rods in a PDMS matrix, or by a lamellar structure.

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