branches are randomly situated along the polymer backbone in LDPE. This might have some effect on the observed branch contents obtained by PHGC.

As was discussed in Table I, if we can achieve enough separation of the resulting isoalkanes above the C_{12} region, the amyl branch contents could be determined by PHGC. In that event, the estimated butyl branch contents migh be lower than those in Table V since the data in Table I predict that 5M in the C_{11} region, utilized as the key peak for butyl branches, also is expected to be formed from the amyl branch structure. In addition to the higher resolution of pyrograms, the use of well-studied model polymers is a very important factor in obtaining reliable results. Further work along these lines is currently in progress.

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Inverse Gas Chromatography Studies of Poly(dimethylsiloxane)-Polycarbonate Copolymers and Blends

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ABSTRACT: The specific retention volumes of a series of volatile probes on stationary phases consisting of homopolymers of poly(dimethylsiloxane) (PDMS) and bisphenol A polycarbonate (PC) as well as block copolymers and blends of these substances were evaluated in terms of the Flory-Huggins approximation. The polymer-solvent, χ_{12}, and normalized polymer-polymer, χ_{23}', noncombinatorial free energies of mixing were determined in each case. χ_{23}' was studied as a function of block length of PC in the copolymer, the chemical structure of the probes, and the copolymer or blend composition. In addition, the morphologies of phase-separated copolymers were analyzed from the specific retention volumes of *n*-decane, a solvent for PDMS and a nonsolvent for PC, at temperatures below the polycarbonate glass transition. The data obtained were compared to morphological information obtained from differential scanning calorimetry, electron microscopy, and small-angle X-ray scattering. Measured χ_{23}' values reflected in all cases the known incompatibility of PDMS and PC in the copolymers and blends. Also, useful information on the copolymers' morphology was obtained by studying the retention behavior of the *n*-decane probe below the PC glass transition. The specific retention volume for the microphase-separated copolymers under these conditions indicated whether the PDMS phase was continuous or not and, in some cases, the actual surface area of the PC domains. Diameters of domains (assuming rod or lamellar geometry) ranging from 180 to 700 Å were calculated from the results.

Introduction

The study of the thermodynamics of interaction between a stationary homopolymer and a volatile probe molecule by gas chromatography[1] (IGC) has been extended to the study of ternary systems containing blends of two nonvolatile components and a volatile probe. Truly miscible mixtures, such as poly(vinyl chloride)-poly(ϵ-caprolactone)[2] and polystyrene-poly(vinyl methyl ether)[3] have been analyzed in terms of the Flory-Huggins theory to determine the well-known interaction parameters χ_{12}, χ_{13}, $\chi_{1(23)}$, and finally χ_{23}, the noncombinatorial parts of the free energy of mixing, where 1 designates the volatile probe. Hence, χ_{23} is directly related to polymer-polymer compatibility.

Recently, inverse gas chromatography (IGC) has been used to study microphase separation phenomena and domain size in block copolymers containing fundamentally incompatible components.[4,5] Basic thermodynamic quantities of such systems were also estimated. Galin and Rupprecht have successfully analyzed domain sizes in poly(dimethylsiloxane)-polystyrene (PDMS-PS) block copolymers by using volatile probes which were chosen specifically to dissolve in only the siloxane phase.[4] In this type of investigation the gaseous probe was passed over the phase-separated stationary polymer which was maintained at a temperature between the T_g's of each phase. Thus, in this particular work the column temperatures were less than 100 °C. Under such conditions the retention of the probe is restricted to adsorption on the glassy phase and bulk absorption in the liquid-like phase. This behavior, along with the assumption that the accessibility of the probe molecule to each phase is not influenced by the presence of the other, allows one to calculate the surface area of the liquid-glassy interface by measuring the partition coefficent for surface adsorption on the glassy

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Table I
Column and Composition Parameters of the Poly(dimethylsiloxane)-Polycarbonate Copolymers, Homopolymers, and Blends

column	block M_n PDMS	block M_n PC	% loading	mass of polymer, g	wt % PDMS	$[\eta]_{CH_2Cl_2}{}^{25°C}$, dL/g
1	10000	3400	4.64	0.433	69.7	0.94
2	5000	3400	5.13	0.510	57.2	1.38
3	random copolymer		6.85	0.324	49.0	0.68
4	10000	11500	8.80	0.869	42.0	0.88
5	10000	11500	4.32	0.405	42.0	0.88
6	5000	6300	9.54	0.767	41.0	1.1
7	10000	16000	4.80	0.231	36.3	1.60
8	10000	19000	4.64	0.423	32.2	0.80
9	PDMS		11.75	0.881		
10	PDMS		7.20	0.591		
11	Merlon		10.0	1.043		0.53[a]
12	Merlon		0.45	0.096		
13	Merlon		11.2	0.993		
14	PDMS/PC blend (B_1)		13.2	0.860	77.2	
15	PDMS/PC blend (B_2)		14.1	0.986	63.9	
16	PDMS/PC blend (B_3)		11.3	0.341	57.1	
17	PDMS/PC blend (B_4)		19.7	2.00	53.9	
18	PDMS/PC blend (B_5)		12.4	0.630	49.0	
19	PDMS/PC blend (B_6)		10.0	0.425	42.2	
20	PDMS/PC blend (B_7)		11.4	0.635	25.5	

[a] $CHCl_3$ solvent.

polymer. A determination of the specific retention volumes of the probe on the copolymer and on the liquid-like polymer separated is also required.

A block copolymer series based on PDMS and polycarbonate (PC) was selected for investigation by IGC. These thermoplastic elastomers have interesting properties, some of which can be rationalized in terms of the great dissimilarity of the two block units (2.6 $cal^{1/2}$ $cm^{-3/2}$ solubility parameter units apart). Vaughn et al.[6] at General Electric first reported synthesis of such copolymers. Since that time there have been a number of investigations of mechanical properties,[7] glass transition behavior,[8] and various aspects of the morphology of these materials.[9-17] In our own laboratories $-(A-B)_n-$block architectures were explored[18] on bulk compositions ranging from 17 to 66% PC by weight. Mechanical behavior varied from elastomeric to ductile-glassy as the percentage of PC increased. Preferential migration of the PDMS component of these materials to the surface of a sample was also recently reported from our laboratories;[19] block length was found to be quite important in influencing enrichment of the siloxane component on the surface of the sample. The surface morphology of siloxane copolymers has also been briefly reviewed[42] and was discussed in an earlier book by one of the authors.[43]

In addition to the alternating block materials discussed above, out IGC studies included columns produced by solution coating blends of PC and PDMS. The homopolymers and a "randomly coupled" block copolymer were also investigated.[19] All of these copolymer materials were previously found to have microphase-separated morphologies. Our principal concern was to delineate how useful IGC might be in determining their thermodynamic quantities of interest, such as the amount of interphase mixing of the two components.

To complement the IGC method of microphase domain area evaluation, small-angle X-ray scattering, differential scanning calorimetry, and transmission electron microscopy were employed.

Experimental Section

Apparatus. The gas chromatograph used was a dual-column Bendix Model 2300 with a thermal conductivity detector; the column oven temperature was controlled within ±0.5 °C and monitored with a platinum resistance thermometer. Inlet pressures were monitored with a mercury manometer to within 1 torr. Flow rates of the helium carrier gas were measured at the column outlet with a soap bubble flowmeter.

Small-angle X-ray scattering (SAXS) measurements and the derivation of the structural parameters from the observed peak spacings were carried out in the usual way.[20,21] DSC measurements were conducted on a Perkin-Elmer DSC-2 instrument between 100 and 500 K. Heating rates of 10 K/min and cooling rates of 40 K/min were employed. The glass transition temperatures were defined as the inflection points of the base-line shift while the melting points were assigned according to the endotherm peak's position.

The transmission electron micrographs were obtained with a JEOL 100C electron microscope. Films were prepared by casting one drop of a 2% chloroform solution of the block copolymer on a water substrate. The films were transferred to a copper grid and examined at 60 kV.

Polymers. The perfectly alternating block copolymers used in this study were synthesized from hydroxyl-terminated polycarbonate oligomers derived from bisphenol A and phosgene and dimethylamino-terminated PDMS using the silyl amine–hydroxyl reaction.[22] Accurate average block lengths for each of the oligomer precursors were obtained by UV spectrophotometry[23] and by end group titration.[19] Estimates of the number of block units in the block copolymers were made by comparing the intrinsic viscosity data in Table I with other PDMS–PC block copolymers of known number-average molecular weight synthesized in our laboratory. The results indicated that $\bar{M}_n$ is between 5×10^4 and 1.0×10^5. Of course, the number of block units in the copolymer depended on the block sizes, and a wide range for this number is expected and easy to calculate. Size exclusion chromatography on typical preparations show a unimodal, symmetric peak.[19]

The weight fraction of the components in the PDMS–PC copolymers was determined by proton NMR (the absorbance of PDMS methyl and PC aromatic hydrogens). The latter technique was accurate to ±1% but yielded values somewhat lower than calculated from the block lengths of the copolymer due to exclusion of cyclic siloxane oligomer in the copolymer synthesis.[19]

The "randomly coupled" block or segmented copolymer used in this study was synthesized using a PDMS oligomer of low molecular weight ($\bar{M}_n \sim 2000$) which reacted in situ with phosgene and bisphenol A monomer. Full details of this synthesis are given elsewhere.[19]

The homopolymers used in this study were a commercial bisphenol A polycarbonate ($\bar{M}_v = 3 \times 10^4$) obtained from Mobay and a 3-hydroxypropyl-terminated PDMS ($\bar{M}_n = 2.3 \times 10^4$) purchased from Silar Laboratories.

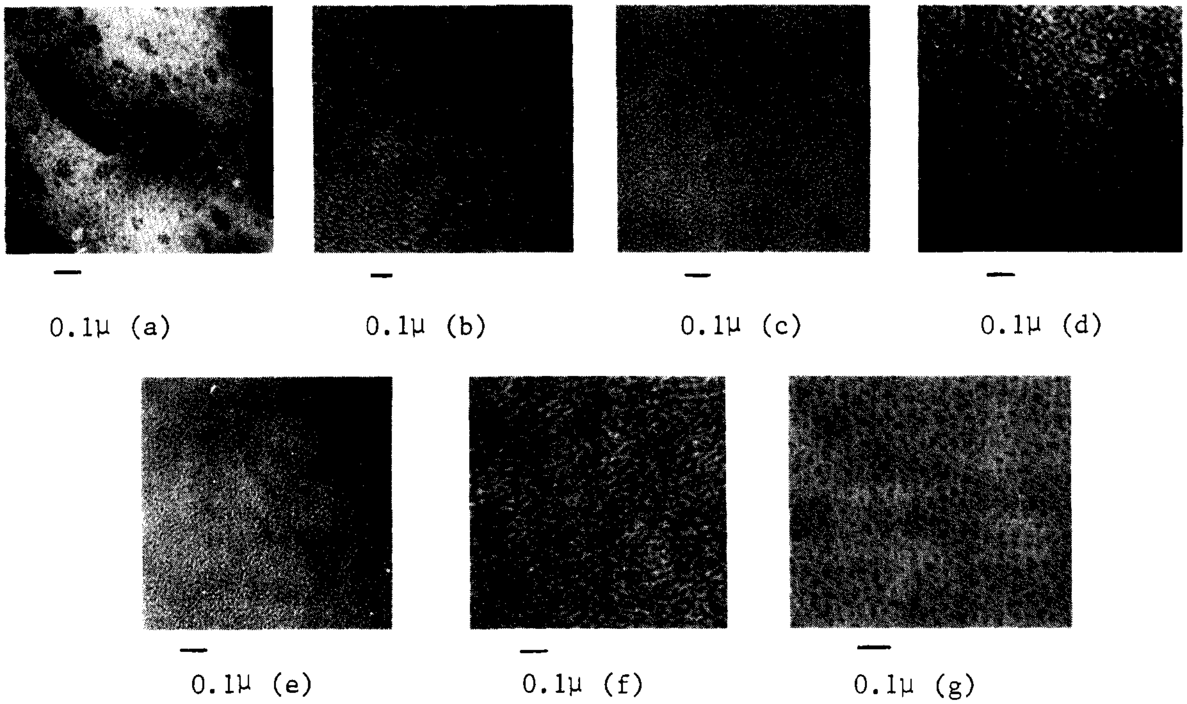

Figure 1. Electron micrographs of PDMS-PC copolymers. Block molecular weights: (a) randomly coupled copolymer; (b) 10000-3400; (c) 5000-3400; (d) 10000-11500; (e) 5000-6300; (f) 10000-16000; (g) 10000-19000.

The blends were made from the above commerical homopolymers and were produced by successive coating of the two materials on the support from a solution of methylene choride. Both possible sequences of coating were examined and found to have no influence on the results. The weight fraction of each component of the blend was assumed to be determined by the initial stoichiometry.

Stationary Phases. Column parameters for each of the stationary phases are listed in Table I. The inert support used for the columns, with the exception of column 12, was a Johns-Manville 60-80 mesh Chromosorb W, AW, and treated with dimethylchlorosilane. A 60-80 mesh glass bead support (surface area of 0.014 m^2/g) was used in column 12 specifically to provide information for calculating the partition coefficient for adsorption of the probe on PC.

To coat a support, the particular polymer system was dissolved in methylene chloride and precipitated on the support by stirring and slow evaporation of the solvent. Percent column loadings were obtained from Soxhlet extractions of the coated supports with chloroform or, as in the case of the glass beads, directly from the known amounts of polymer and support. Specific retention volumes, $V_g°$, of each probe were obtained by using the common expression involving the product of the flow rate, retention time, and gas compressibility factor.[1] All retention volumes were extrapolated to zero flow rate and zero probe concentration in order to obtain a true equilibrium measurement of the activity of the probe at infinite dilution. The experimental range of retention volumes measured for a particular probe-polymer interaction was ±1% of $V_g°$ for those polymers in which only one column was examined and ±3.5% for those in which additional columns were considered.

Mobile Phases. High-purity solvents were used as received from the manufacturers. No GC-detectable impurities were noted.

Results and Discussion

Thermal Analysis. Table II contains the observed thermal transitions for the PDMS and PC homopolymers and copolymers as obtained from DSC experiments. All of the copolymers studied had lower glass transition temperatures and/or melting temperatures only slightly less than those of the pure PDMS homopolymer. The first, second, and fourth block copolymers listed, incorporating short PC sequences, had upper glass transitions, T_{g_2}, less than those of the corresponding homopolymers, suggesting that the microphase separation in these materials was not complete. The "randomly coupled" block copolymer had an upper glass transition temperature which seemed particularly high for material incorporating short PC sequences. Since it was prepared by a unique chemical route compared to the other block copolymers, further experiments were conducted to define its anomalous behavior. Electron microscopy indicated that large-scale separation into regions rich in siloxane and carbonate was taking place. Apparently the kinetics of the random coupling reaction yielded chains which were extraordinarily rich in either the siloxane or carbonate component. The electron micrograph is shown in Figure 1a, where relatively large phase-segregated regions may be noted.

Table II
DSC Transition of
Polydimethylsiloxane-Polycarbonate
Copolymers and Homopolymers

$\overline{M}_n \times 10^{-3}$ PDMS/PC	T_{g_1}, °C	T_c, °C	T_m, °C	T_{g_2}, °C
10/3.4	−125	−100	−63	87
5/3.4		−107	−50	105
random	−126			102
10/11.5	−132	−105	−70	144
5/6.3	−127	−99	−56	127
10/16	−145	−108	−60	142
10/19	−131			143
PDMS	−125	−98	−54 (−45)	
Merlon				146
PC oligomer[a]				125
PC oligomer[b]				136

[a] $\overline{M}_n = 3400$. [b] $\overline{M}_n = 6000$.

Polymer-Solvent Interaction. The polymer-solvent interaction parameters and the specific retention volumes from which they were calculated are tabulated in Table III. In all four solute (probe) and two homopolymer cases the data were collected above the PC glass transition in order to ensure equilibrium diffusion of the probes into the polymers. In order to verify that equilibrium operating

Table III
Specific Retention Volumes (cm³/g) and Polymer-Solvent Interaction Parameters of the Homopolymers

solvent	parameter	160 °C PDMS	160 °C PC	180 °C PDMS	180 °C PC	195 °C PDMS	195 °C PC
toluene	V_g°	13.6	11.0				
	χ_{12}	0.60	0.52				
decane	V_g°	40.1	8.59	24.5	5.63	19.5	4.20
	χ_{12}	0.47	1.70	0.46	1.60	0.35	1.57
ODCB	V_g°	48.3	69.2	32.2	39.3	25.8	30.8
	χ_{12}	1.02	0.37	0.92	0.43	0.81	0.33
CB	V_g°	21.5	20.9	14.2	14.5	11.3	10.4
	χ_{12}	0.69	0.43	0.68	0.37	0.62	0.41

conditions were in effect for each column, Arrhenius plots of ln (V_g°) vs. reciprocal temperature were made and found to be linear.

The equation used to calculate χ_{12} was the usual expression derived from the Flory–Huggins lattice approximation:[24]

$$\chi_{12} = \ln \frac{273.2Rv_2}{V_g^\circ P_1^\circ V_1} - 1 - \frac{P_1^\circ(B_{11} - V_1)}{RT}$$

Here V_1 and v_2 are the molar volume of the probe and the specific volume of the polymer, B_{11} is the second virial coefficient of the gaseous probe, and P_1° is its vapor pressure at temperature T. A term involving the ratio of molar volumes was dropped from the equation since it was numerically insignificant. The polymer and probe properties used in the calculations were determined from data taken from Van Krevelen,[25] Galin[26] (PC and PDMS specific volumes), Olabisi[27] and Dreisback[28] (vapor pressure and specific volume of the probe), and Reid[29] (virial coefficients).

The χ_{12} values calculated show that two of the potential solutes examined, *o*-dichlorobenzene (ODCB) and decane, are selective for PC and PDMS, respectively. The other two are mutual solutes for both the polymers. This result was expected from the available solubility parameter data.[30] ODCB and decane have solubility parameters of 10.0 and 6.6 (cal/cm³)$^{1/2}$, respectively, close to the values of 10.0 (cal/cm³)$^{1/2}$ for PC and 7.5 (cal/cm³)$^{1/2}$ for PDMS. The mutual solutes' solubility parameters, 8.9 (cal/cm³)$^{1/2}$ for toluene and 9.5 (cal/cm³)$^{1/2}$ for chlorobenzene, fall between those of PC and PDMS, thus indicating their lack of strong affinity for either material.

Polymer–Polymer Compatibility. Determinations of the polymer–polymer interaction parameter above the PC glass transition were initiated by measuring the specific retention volumes of the probes with each copolymer or blend in the 160–195 °C range. These data were combined with the homopolymer results in Table III in order to make the final thermodynamic calculation. Equations of Patterson et al.[31,32] for polymer–solvent interactions in ternary systems and for the noncombinatorial term of the Scott–Hildebrand ternary solution equation were combined with the previously cited expression for χ_{12}. This resulted in the following equation for χ_{23}', the normalized polymer–polymer interaction parameter:

$$\chi_{23}' = \chi_{23}\frac{V_1}{V_2} = \frac{1}{\phi_2\phi_3}\ln\left[\frac{\nu_2^{\phi_2}\nu_3^{\phi_3}}{\omega_2\nu_2 + \omega_3\nu_3}\,\frac{V_g{}^\circ{}_{1(23)}}{(V_g{}^\circ{}_{12})^{\phi_2}(V_g{}^\circ{}_{13})^{\phi_3}}\right]$$

Here, V_1 and V_2 are the molar volumes of the solvent and polymer, ω_2, ω_3, ϕ_2, and ϕ_3 are the weight and volume fractions of each polymer component, and ν_2 and ν_3 are their specific volumes. In this expression the ratio of the geometric to the weight-average specific volume is close to unity. This means that the assignment of polymer–polymer compatibility by IGC is essentially determined by the ratio of the retention volume of the probe in the copolymer to the volume fraction weighted geometric mean of its retention volume in the two homopolymers. Thus, positive χ_{23}' values, indicating incompatible components, are obtained when this latter ratio is greater than one.

Table IV contains the specific retention volume data for the PDMS–PC copolymers and blends. Three important conclusions can be drawn from this information. First, in

Table IV
V_g° and χ'_{23} Values for PDMS-PC Copolymers and Blends

$\overline{M}_n \times 10^{-3}$ PDMS/PC	blend	parameter	160 °C toluene	160 °C CB	160 °C ODCB	160 °C decane	180 °C CB	180 °C ODCB	180 °C decane	195 °C CB	195 °C ODCB	195 °C decane
10/3.4		V_g°	16.0	26.2	71.9	37.5	17.4	43.0	24.2			
		χ'_{23}	1.20	1.14	1.71	1.73	1.10	1.34	1.92			
5/3.4		V_g°	15.3	26.0	69.2	30.9	17.2	42.3	19.4	13.2	32.8	14.0
		χ'_{23}	0.88	0.91	1.04	1.32	0.84	0.92	1.32	0.85	0.81	0.99
random		V_g°		25.2		26.9	16.2		16.7			
		χ'_{23}		0.74		1.17	0.54		1.10			
10/11.5		V_g°	13.8	24.4	71.4	24.4	16.4	43.3	15.5	12.2	30.4	11.1
		χ'_{23}	0.53	0.60	0.87	1.24	0.58	0.82	1.20	0.52	0.34	0.90
5/6.3		V_g°	14.3	25.3	74.0		17.0	44.7				
		χ'_{23}	0.70	0.74	1.00		0.72	0.94				
10/19		V_g°	13.6	25.3	73.0	20.4	16.5	45.5	13.0			
		χ'_{23}	0.59	0.80	0.85	1.17	0.62	0.98	1.16			
	B_1	V_g°	13.9	22.2								
		χ'_{23}	0.35	0.31								
	B_2	V_g°	13.3	22.6								
		χ'_{23}	0.24	0.32								
	B_3	V_g°		23.2			15.7					
		χ'_{23}		0.43			0.45					
	B_4	V_g°	14.1									
		χ'_{23}	0.54									
	B_5	V_g°	13.3	24.0	63.2		16.1					
		χ'_{23}	0.34	0.55	0.50		0.52					
	B_6	V_g°	14.4	25.0								
		χ'_{23}	0.69	0.70								
	B_7	V_g°	14.0	27.0	79.0		18.0					
		χ'_{23}	0.89	1.19	1.15		1.08					

all of the PDMS-PC copolymer systems the probe molecules had retention volumes which exceeded the volume fraction geometric mean of retention volumes as measured in the homopolymers found in Table III; the data reflected the known incompatibility of PDMS and PC in every case. Second, a comparison of the retention volumes of the probes on block copolymers 4, 5, and 6, as listed in Table I, indicated that there was little influence of the block size on retention as long as the percent PDMS did not vary widely. This conclusion is certainly valid in block lengths varying from about 5000 up to about 10 000 in molecular weight. Even in the randomly coupled material, which was overall approximately 8 wt % richer in PC and which was found to be macroscopically phase separated, no dramatic variation in retention volumes was seen. Third, the retention volumes found for the "blends" indicated there was a low degree of mixing in these systems; the values of $V_g°$ are seen to be generally smaller than those obtained for the corresponding copolymers. However, it is important to note that the blends occasionally exhibited retention volumes almost identical with those of the copolymer (B_6 and the randomly coupled copolymers form an example, as one might expect from the factors cited above). The retention volume apparently cannot be used to distinguish a copolymer from a blend prepared as in our work.

Results similar to the above have been reported by Klein and Widdecke.[33] They observed that changes in the overall composition of polystyrene-polybutadiene systems could be determined from the retention volume data, but not structural details. Block copolymers, random copolymers, and blends were found to have retention volumes equal to the weight average of the values for the appropriate homopolymers.

The calculated χ_{23}' values are also given in Table IV. It is important to note the models used to calculate these values are rigorously applicable only to homogeneous systems. The microscale associated with such total solubility is not totally unambiguous for polymers, however, particularly where "mixing" of components may be possible. In microphase-separated block copolymers and in low-compatability blended systems, these thermodynamic values of the interaction parameter can best be thought of as an approximation whose worth is currently being evaluated in several laboratories.

Examining Table IV again, we see that rather similar, positive χ_{23}' values were obtained for the randomly coupled block copolymer and for the microphase-separated block copolymers for any given probe series. In previous IGC studies positive χ_{23}' values were obtained for microphase-separated PDMS-PS block copolymers and for ethylene-vinyl acetate[34] copolymers, indicating the incompatability of copolymer constituents. In our work, one can see by examining Table IV that rather similar positive χ_{23}' values were also obtained for all of the copolymers having a common probe. More specifically, the χ_{23}' values for the three copolymers of nearly the same percent by weight PDMS are not altered, within experimental error, by block dimensions. To emphasize this point, the 5000-6300 and 10 000-11 500 PDMS-PC block copolymers along with the randomly coupled copolymer all have χ_{23}' parameters within ±0.15 of each other (see Error Analysis). It is important to note, however, that the influence of degree of phase separation is difficult to decipher; PDMS-PC copolymers which are homogeneous, i.e., which exhibit only one glass transition, have yet to be synthesized. An unambiguous conclusion concerning the influence of degree of phase separation on the χ_{23}' parameter cannot be made without such a copolymer.

The values of χ_{23}' obtained for the copolymers indicate there is a dependence on three factors: the nature of the probe used, the composition of the polymer or blend, and the temperature at which the parameter was measured.

The effect of structure of the probe on χ_{23}' has been interpreted[35] as arising from its preferential interaction with one of the two types of polymer segments. Such selective probes do not "sense" the three varieties of intermolecular contacts possible in the copolymers and blends, e.g., PDMS-PDMS, PDMS-PC, and PC-PC, in proportion to concentration. Instead, the selective probes, ODCB and decane in our case, detect a relatively low concentration of the chains for which they are nonsolvents. This increases the observed specific retention volume (and the χ_{23}') values relative to those which would be obtained by a truly random mixing of the probe and polymer. The mutual solvents, on the other hand, exhibit a more random "sampling" of the molecular environment of the stationary phase due to the equal affinities thay have for both. A better measure of the polymer-polymer interaction is likely in this case.

Regarding the seven "blends", χ_{23}' values measured in our laboratory are, in general, smaller in magnitude than those obtained for the copolymers. This seems to contradict one's expectations about compatibility being improved as blocks are linked together.[36] But, data scatter is large and any correlation is weak at best. Previous work[4,31,37] on blends by IGC has indicated that not only the magnitude but also the sign of χ_{23}' can be unreliable for predicting solubility of one polymer in another when they are relatively insoluble overall. It may be that artifacts of the column coating procedure enter the results; more likely it is the breakdown of the theoretical framework, where a true ternary component system does not exist.

The effect of temperature on χ_{23}' is as expected. As temperature increases the values of χ_{23}' overall decreases for the copolymers. This result arises from two factors. First, as the temperature is raised, the probes *o*-dichlorobenzene and decane become less selective and they show less preferential interaction with either chemical type. Second, the polymers themselves become more compatible, as we confirmed by observations with a hot-stage polarizing microscope. All of the perfectly alternating block copolymers of Table I showed better phase mixing with increasing temperature by a decrease in their birefringence from 160 to 200 °C. It should be kept in mind, however, that rheological studies on highly incompatible block copolymers often show a two-phase character existing in the melt.

The overall compositional dependence of χ_{23}' on percent PC indicated the interaction of PC with PDMS is poor for copolymers very rich in PDMS. The 10 000-3400 block copolymer exhibits χ_{23}' values significantly larger than those of the remaining copolymers. Other trends are difficult to establish from the IGC data.

Domain Size Measurements. The PDMS-PC/*n*-decane system was examined well below the glass transition of PC (50-75 °C). The partition coefficient for PC adsorption was calculated for column 12 with the expression[37]

$$\ln V_g° = \ln K + \ln A_2 - (\Delta H_a/RT) - \ln W$$

Here, A_2 is the specific surface area of the glass beads (0.302 m^2), K is the partition coefficient, W is the weight of polymer on the column, and $-\Delta H_a$ is the heat of adsorption. The values of ln K and $-\Delta H_a$ were found to be -11.3 and 9.1 kcal/mol, respectively, at 60 °C.

By assuming the probe was integrally accessible to both PDMS and PC, the surface area of the PC domains (A)

Table V
PC Domain Diameters of the PDMS-PC Copolymers As Determined by Inverse Gas Chromatography, Small-Angle X-ray Scattering (SAXS), and Electron Microscopy (EM)

column	$\overline{M}_n \times 10^{-3}$ PDMS/PC	vol % PC	$V_g°$	domain area, m^2/g	calcd PC domain diameter, Å	exptl domain diameter, Å	
						SAXS	EM
1	10/3.4	26.2	1465	95.1	300	100	120
2	5/3.4	37.9	1165	47.6	700		110
3	random	45.9	840	3.6			
4	10/11.5	53.0	1300	93.0	180	160	175
5	10/11.5	53.0	1260	87.0	190	160	175
6	5/6.3	53.7	1240	83.9	200		135
7	10/16	58.9	1200	83.2	200		195
8	10/19	63.2	250				
	PDMS		1630				
	Merlon		36.2				

could be determined from the specific retention volume of the copolymer ($V_g°$)

$$V_g° = \omega V_{g,b}° + (1 - \omega) V_{g,a}°$$

$$\ln A = \ln V_{g,a}° - \ln K + \Delta H_a / RT$$

where $V_{g,b}°$ is the specific retention volume for bulk absorption n the PDMS homopolymer, $V_{g,a}°$ is the specific retention volume for PC absorption, and ω is the weight fraction of PDMS.

The specific retention volumes of the copolymers and the calculated surface areas at 60 °C are presented in Table V. Two important observations can be made concerning these data. We note that $V_g°$ and the calculated surface area of the PC domains in the randomly coupled copolymer are considerably lower than in any of the block copolymers of similar composition. This result is easily accounted for by reference to the electron micrograph of this particular copolymer (Figure 1a). The phases present are of an order of magnitude larger than those of the block copolymers. Consequently, the contribution of adsorption at the interphase to the retention volume is drastically reduced.

Also, in comparing results from columns seven and eight, a discontinuity in the observed retention volume appears with increasing PC content in the block copolymers. Apparently, the probe loses access to much of the PDMS phase; PDMS is suggested to have become discontinuous in this composition range, allowing the PC domains to block the small molecule penetration. This conclusion is supported by the electron micrographs shown in Figure 1. In Figure 1b–f the siloxane phase is apparently continuous while Figure 1g indicates clearly that the 10 000–19 000 PDMS–PC block copolymer has the siloxane phase dispersed in a PC continous phase.

Structural information obtained by the electron micrographs and also by SAXS was then compared to the calculated PC surface areas. The electron micrographs indicate the block copolymers have structures similar to those reported by Saam[38] and Matsuo[39] for microphase-separated block copolymers of PDMS–PS and polystyrene–polybutadiene (PS–PB), respectively. Our PDMS-rich block copolymers (volume percent >60) exhibited a spaghetti-like discontinuous phase similar to their PDMS–PS copolymers. This structure can be pictured as being a variation of the cylindrical structure reported for PS-PB. The PC apparently forms a number of coiled rows on a given plane which, when considered in three dimensions, would be cylinder-like.

The three block copolymers of intermediate PDMS content also exhibit a cylinder-like structure; however, the volume fraction of PC in the materials has been increased to the extent that PC appears to be continuous. This conclusion is supported by the tensile stress–strain response of similar perfectly alternating block copolymer studied previously in this laboratory.[18] A Kerner analysis[40] of the modulus data of solution-cast samples of a 15 000–16 000 PDMS–PC block copolymer and of a 10 000–16 000 PDMS–PC copolymer revealed that the PC phase was continuous. A lamellae-like structure is probably an adequate description of the morphology. Recently published electron micrographs of PDMS–PC block copolymers varying from 22 to 69 wt % PC were similar to ours and were described as having a "sponge-like" structure.[41]

The diameters or thicknesses of the PC phases were calculated, using the above structural information, from the surface areas and are tabulated in Table V. This table also lists the corresponding numbers obtained from SAXS and the electron micrographs. The agreement between the two sets of data is good for two of the block copolymers with a lamellar structure, but less satisfactory for the remaining copolymers having a continuous PDMS phase. This is not surprising in view of the DSC results, where some mixing of the siloxane and carbonate phase was indicated for the PDMS-rich copolymers and the 5000–6300 PDMS–PC block copolymer. This mixing would act to isolate the IGC probe from some of the PDMS and eliminate the well-defined interface for PC adsorption. Consequently, there would be a lowering of the retention volume of the probe and in calculated domain radii, which were larger than those obtained by the other techniques. On the other hand, the DSC data obtained for the remaining copolymers with a lamellar structure indicated a sharply phase-separated system; the IGC-determined domain sizes showed little effect of isolation of the probe from PDMS. The agreement between the calculated lamellae thickness and those observed by SAXS and electron micrographs was good in this case.

Error Analysis. The errors in the measured interaction parameters and the PC domain radii were estimated from the range of specific retention volumes obtained for duplicate columns of the same polymer and also for duplicate measurements on the same column. Absolute errors of ±0.03 and ±0.30 were obtained for the polymer–solvent and normalized polymer–polymer interaction parameters, respectively, and ±7.0% for the PC domain radii. The relative error was from 33 to 100% of the values for the thermodynamic parameters and ±3.5% for the radii. In the case of the χ values, the smallest errors were observed when different probes and temperatures on the *same* columns were compared (±0.10 for χ_{23}' and ±0.01 for χ_{12}), while the largest errors occurred when comparisons of values for different copolymers and homopolymers (±0.15–0.20 for χ_{23}' and ±0.03 for χ_{12}) were made. Our observations definitely confirm those of others regarding the importance of column preparation in IGC.[37]

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π-Helical Conformation of Poly(β-phenethyl L-aspartate)

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ABSTRACT: The left-handed π-helical conformation is found in a solid-state modification of poly(β-phenethyl L-aspartate). The helix contains approximately 4.25 residues per turn with a unit height along the helix axis of 1.17 Å. Atomic coordinates are presented for the model constructed with the standard dimensions of bond lengths and bond angles and torsion angles of ϕ(N–C$^\alpha$) = 50.7°, ψ(C$^\alpha$–C′) = 73.6°, and ω(N–C′) = 177°. The hydrogen bond formed between the C=O group of the *n*th residue and the NH group of the $(n + 5)$th residue is inferred to be weak from the infrared spectra. Poly(β-phenethyl L-aspartate) exists also as as right-handed α-helix and a β-pleated-sheet structure. Structures and transitions between modifications are discussed.

Pauling and Corey[1,2] proposed two helical conformations (the α and γ helices) for polypeptide chains by considering some structural restrictions. By the notation of Bragg, Kendrew, and Perutz,[3] these helices are denoted as 3.6_{13} and 5.1_{17}, respectively.[4] Several other helices were also proposed, for instance, 2.2_7,[5] 3_{10} (the δ helix),[6] 4.4_{16} (the π helix),[7,8] and so on. Donohue estimated the strain energy for these models and suggested the possibility of the δ and π helices.[6] The 3_{10} helix was once suspected for poly(α-aminoisobutyric acid),[9] but its existence has not yet been firmly established.[10]

The π helix has a 16-atom ring of hydrogen bonds formed between the C=O group of the *n*th residue and the NH group of the $(n + 5)$th residue. The 4.4_{16}-helix model proposed by Low et al.[7,8] has an axial translation per residue, *h*, of 1.15 Å, and a small distortion (about 4°) in the bond angle τ(N,C$^\alpha$,C′). A conformation similar to the π helix is presented for alternating poly(γ-benzyl D,L-glutamate), in which the D and L residues assume different orientations with two kinds of hydrogen bonds (14 and 16 atoms in the rings).[11] The π helix as proposed by Low et al. has not been found so far.

The conformational versatility of poly(aspartate esters) has been extensively investigated. Poly(β-benzyl L-aspartate) (PBLA) exists as a left-handed α helix (α_L) in chloroform solution, the helix sense being opposite to the normal sense of L polypeptides.[12,13] The PBLA film obtained from chloroform solution exhibits an X-ray dif-