Investigation of the Interactions and Phase Behavior in Poly(dimethylsiloxane) and Poly(methylphenylsiloxane) Blends

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ABSTRACT: The phase behavior of mixtures of linear poly(dimethylsiloxanes) (PDMS) and poly(methylphenylsiloxanes) (PMPS) with narrow molar mass distributions was studied by a static wide-angle light scattering technique. Reversible-phase separations were exhibited as cloud temperatures at and below their respective critical temperatures. An upper critical solution temperature (UCST) behavior was found, and the critical temperature increased with increasing molar mass of the PMPS component. The data were analyzed to determine the polymer/polymer interaction parameter, Λ, for the PDMS/PMPS pairs as a function of temperature and concentration based on the Flory–Huggins theory for the free energy of mixing per unit volume of polymer mixture. The polymer/polymer interaction parameters obtained from the critical points of the blends were compared with those reported previously from equilibrium swelling studies of PDMS model networks swollen with linear methylphenylsiloxane oligomeric diluents.

Introduction

The polyorganosiloxanes $-[RR'SiO]_y-$, where R and R′ are organic substituents, are by far the most important of the polymeric materials having inorganic skeletal backbones. The poly(dimethylsiloxane) (PDMS; R = R′ = CH_3) and poly(methylphenylsiloxane) (PMPS; R = CH_3, R′ = C_6H_5) homopolymers in particular have developed a wide variety of applications over the last 50 years. The commercial products from polyorganosiloxanes include highly mobile fluids, elastomers, and cross-linked resins—all of which show much better thermal stabilities than the corresponding organic polymers.[1] A wide variety of applications also result from the unique surface properties of the polyorganosiloxanes.[2]

The investigation of miscibility in polymer/polymer blends continues to be of considerable fundamental and technological importance.[3-7] A wide variety of methods have been used to determine binary polymer/polymer interaction parameters including cloud points measurements, a variety of scattering techniques, and gas sorption measurements via inverse gas chromatography. In the area of organic polymers, the number of chemically dissimilar polymer pairs that form miscible blends continues to grow. Although there has been some interest in the miscibility of polysiloxanes and organic–polysiloxane block copolymers with organic polymers,[8] studies of blends where both components are inorganic polymers have been neglected. A number of advantageous reasons exist for studying miscibility in polysiloxane/polysiloxane blends including the following: the polymers can be conveniently prepared as sharp fractions having a variety of molar masses; the polysiloxanes typically have glass transition temperatures and melting temperatures that are well below room temperature; the materials are highly thermally stable. These factors give the possibility of studying the miscibility of long-chain molecules over a much wider range or "window" of temperatures than is typically possible for organic/organic polymer blends. Furthermore, all of the experimental techniques mentioned above[3-7] for investigating interaction parameters are applicable to polysiloxane/polysiloxane mixtures.

Siloxane elastomers of well-defined structure can be readily prepared, and the linear siloxanes are mobile fluids up to relatively high degrees of polymerization. Thus, it may also be possible in the case of the polyorganosiloxanes to obtain useful thermodynamic information from network swelling studies. In a previous investigation, the interaction parameter χ_1 for the PDMS/PMPS system was evaluated using PDMS model networks swollen with linear oligomeric methylphenylsiloxane diluents.[9] The results showed a small positive χ_1 value which increased with increasing molar mass between cross-links, M_c, at room temperature, and the findings also suggested that a phase boundary may be found for linear PDMS and PMPS mixtures.

In this work a light scattering technique was applied to measure the phase separation temperatures (cloud points) for mixtures of linear PDMS and PMPS. The polymer/polymer interaction energy density parameter Λ_c at the critical point was determined in each case, and the dependence of Λ on temperature and composition were evaluated.

Experimental Section

Materials. The linear poly(dimethylsiloxane) (PDMS) and linear poly(methylphenylsiloxane) (PMPS) fractions used in the present study were prepared by methods described in detail previously.[10-12] The linear trimethylsilyl-terminated PDMS $(CH_3)_3SiO[(CH_3)_2SiO]_ySi(CH_3)_3$ was obtained from a Dow Corning D.C. 200 series fluid. The linear trimethylsilyl-terminated PMPS samples $(CH_3)_3SiO[(C_6H_5)(CH_3)SiO]_ySi(CH_3)_3$ were prepared by anionic ring-opening polymerization. Vacuum fractional distillation and preparative gel permeation chromatography (GPC) were utilized to prepare fractions of the linear siloxanes having narrow molecular weight distributions. The polymers were characterized by using gas chromatography, HPLC, and analytical GPC and all had heterogeneity indexes (M_w/M_n) of ≤ 1.08 (see Table I). The PMPS samples were shown by 300-MHz ^1H NMR to be stereochemically atactic.[13] Before use, the PDMS and PMPS samples were extensively dried by placing in a vacuum oven at 70 °C for 48 h.

Light Scattering Measurements. The cloud points were established using a static light scattering instrument, in which a photometer (EG&G HUV-1100BG) was used to detect the scattered light intensity at a 90° scattering angle.[14] The appropriate amounts of the two polymer samples were carefully weighed into a glass tube. The tube was evacuated under vacuum (10^{-2} Torr) and then sealed. The sample to be investigated was first placed in a heated silicone oil bath, which was stirred by means of a magnetically activated stirrer, in order to initially estimate the temperature at which the polymer mixture became single phase. The sample was then mounted in the furnace of the light scattering system, whose temperature was determined

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Table I
Characterization of the Poly(dimethylsiloxane) and Poly(methylphenylsiloxane) Samples

sample	M_n, g/mol	M_w, g/mol	M_w/M_n
PDMS (linear)	1110	1135	1.02
PMPS (linear)	1890	2003	1.06
PMPS (linear)	2240	2420	1.08

Table II
Composition of the Polymer Blends and Their Cloud Point Temperatures

blend sample no.	vol fractn, ϕ_{PDMS}	cloud temp T_c, K	blend sample no.	vol fractn, ϕ_{PDMS}	cloud temp T_c, K
B-1-01	0.32	420	B-2-02	0.30	470
B-1-02	0.50	448	B-2-03	0.42	492
B-1-03	0.60	455	B-2-04	0.54	513
B-1-04	0.65	456	B-2-05	0.57	519
B-1-05	0.72	451	B-2-06	0.59	520
B-1-06	0.74	450	B-2-07	0.67	515
B-1-07	0.83	438	B-2-08	0.84	494
B-1-08	0.92	413	B-2-09	0.93	468
B-2-01	0.13	406			

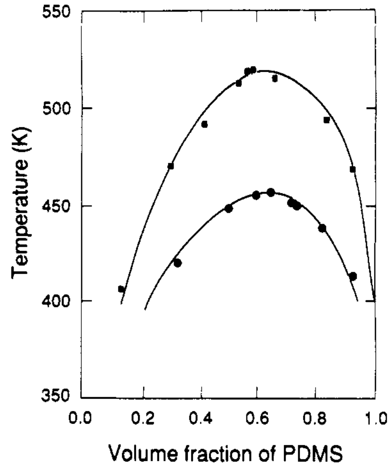

Figure 1. Cloud point temperatures of the linear homopolymer mixtures of PDMS and PMPS. The squares were obtained for blend 1, which contained PMPS of M_n = 1890 g/mol, and the circles were obtained for blend 2, which contained PMPS of M_n = 2240 g/mol, the PDMS being of M_n = 1100 g/mol for both blends. The binodal curves were calculated using eq 3.

by an electrical temperature controller. The cloud temperature was then measured by cycling within a 10 K range of the phase separation temperature at heating and cooling rates of 2.0, 1.0, and 0.5 K/min. The equilibrium cloud point was established in each case by extrapolating the recorded data of scattered intensity and temperature to a zero cycling rate.

Results and Discussion

PDMS/PMPS Phase Diagrams. The cloud points obtained for mixtures containing the linear PDMS fraction and linear PMPS fractions of different molecular weight are shown in Table II. The composition of the mixture was converted from weight fraction to volume fraction by use of the following values of density ρ (in g/cm^3) as a function of temperature and molecular weight. For the linear poly(dimethylsiloxane) fraction[12,15]

$$\rho = 1.2666 - 1.0986 \times 10^{-3}T \tag{1}$$

and for linear poly(methylphenylsiloxanes)[16]

$$1/\rho = 0.7303 + 4.4893 \times 10^{-4}T + (0.1814T + 16.3684)/M \tag{2}$$

where T is in kelvin and M is the molar mass in grams per mole.

The phase boundaries, as approximated by the cloud points, are shown in Figure 1 for the mixtures of PDMS and PMPS. In contrast to a previous study[17] in which phase diagrams of the lower critical solution temperature (LCST) were shown for cyclic and linear PDMS in tetramethylsilane and neopentane solution, the PDMS/PMPS system here, which has a comparable degree of polymerization for each component, showed an upper critical solution temperature (UCST). It can also be seen that the symmetrical phase diagrams of PDMS/PMPS blends have a maximum in the range 50–60% volume fraction of PDMS for each pair. The critical temperature T_c increased with an increase in degree of polymerization of one of the components as expected. Such UCST phase behavior has also been reported for mixtures of poly(methylphenylsiloxane) and polystyrene.[18,19] A recent study has also described the phase behavior of PDMS/poly(diethylsiloxane) mixtures.[20,21]

Comparison of Experimental Results with Theory. The miscibility and the phase behavior of polymer mixtures are governed by the Gibbs free energy of mixing. Using an analysis based on the Flory–Huggins theory[22] for polymer/solution systems where there are no specific interactions, the free energy of mixing decreases with increasing temperature. Therefore, the existence of a UCST phase behavior is predicted.[22] The appropriate free energy of mixing expression for representing polymer/polymer interactions of polymer mixtures based on the classical Flory–Huggins theory has been described by Roe,[23] where the free energy of mixing per unit volume of polymer mixture may be written as

$$\Delta G_m = RT\left[\frac{\phi_1 \ln \phi_1}{V_1} + \frac{\phi_2 \ln \phi_2}{V_2}\right] + \Lambda\phi_1\phi_2 \tag{3}$$

where ΔG_m is the free energy of mixing per unit volume of the mixture, V_1 and V_2 are the molar volumes, and ϕ_1 and ϕ_2 are the volume fractions of the components. The first term in eq 3 is the combinatorial part of the free energy of mixing as given by the Flory–Huggins treatment.[22] The second term contains Λ, the interaction energy density parameter in units of calories per cubic centimeter, which includes all the other contributions to the free energy of mixing that are not accounted for by the combinatorial entropy of mixing represented in the first term. The interaction energy density parameter is generally a function of temperature, pressure, and composition of the mixture. To compare the interaction energy density parameter, Λ, in eq 3 with the interaction parameter χ of the conventional Flory–Huggins equation for polymer mixtures which exhibit UCST behavior, it is noted that Λ and χ are related to each other at a temperature T by $\chi = \Lambda V_r/RT$, where V_r is the volume of reference.[14,24] For a polymer/solvent system, V_r is defined as the molar volume of the solvent molecule, whereas for a polymer/polymer mixture, V_r is assumed to be equal to the volume of a segment or a lattice site.

The experimental data shown in Figure 1 were analyzed on the basis of the Flory–Huggins theory for the phase behavior of binary mixtures. The calculated binodal curves are shown with experimental data points. Because the interaction energy density Λ is regarded as an adjustable parameter having a temperature and composition dependence, in order to analyze the binodal curve, Λ may be represented by[14]

$$\Lambda = \lambda_0 + \lambda_1\phi + \lambda_2 T \tag{4}$$

and the best fit values of λ_0, λ_1, and λ_2 for the cloud points

Table III
Critical Conditions of Each PDMS/PMPS Blend from Cloud Point Measurements and the Interaction Parameters[a] Λ_c and χ_c

blend no.	PDMS M_n	PMPS M_n	T_c, K	ϕ_c	Λ_c,[b] cal/cm^3	Λ_c,[c] cal/cm^3	χ_c,[d] cal/cm^3
1	1110	1890	456	0.64	0.972	1.051	0.122
2	1110	2240	518	0.59	1.048	1.027	0.112

[a] Calculated at the critical point. The critical temperature and critical composition were estimated from the cloud point curves in Figure 1. [b] Calculation based on the curve fitting eq 1 and eq 6.[c] Calculation based on eq 7. [d] Calculation based on the average lattice volume of PDMS and PMPS and Λ_c at the temperature T_c.

Table IV
Interaction Parameters for Bimodal PDMS Networks at Equilibrium Swelling Measurement with Linear MPS Oligomers[9]

network no.[a]	PDMS M_c	MPS M_d[b]	temp, K	χ_1[c]	χ_1[d]
NA-01	9050	298.6	298	0.184	0.114
NA-02	7010	298.6	298	0.165	0.102
NA-03	2230	298.6	298	0.128	0.079
NB-01	2400	298.6	298	0.044	0.027
NB-02	2400	434.8	298	0.250	0.155
NB-03	2400	571.0	298	0.219	0.136

[a] NA samples are bimodal network of PDMS with M_n 21 300 and 880 g/mol, NB samples are bimodal network of PDMS with M_n 21 300 and 440 g/mol. [b] M_d, molar mass of linear methylphenylsiloxane oligomer used as the diluent. [c] Calculated by using eq 8. [d] χ_1 after correcting by the temperature factor of 298/480.

determined by means of a nonlinear least-squares algorithm. The values thus evaluated for the two sets of mixtures containing PDMS and PMPS in Figure 1 are given by

$$\text{blend 1} \qquad \Lambda = 3.58 + 0.77\phi - 0.0068T \tag{5}$$

$$\text{blend 2} \qquad \Lambda = 4.65 + 0.83\phi - 0.0079T \tag{6}$$

where ϕ is the volume fraction of poly(dimethylsiloxane) and the temperature is in kelvin. The Λ_c values for each blend at the critical temperature and composition were thus determined using the above equations and are listed in Table III.

At the critical temperature of the mixture the second and third partial derivatives of the Gibbs free energy with respect to ϕ_{2c} in eq 3 are simultaneously zero, and hence, one consequence of the interaction energy density parameter, Λ, of eq 3 being independent of composition at the critical temperature T_c for phase separation is that

$$\Lambda_c = RT_c(\sqrt{V_1} + \sqrt{V_2})^2/2V_1V_2 \tag{7}$$

where V_1 and V_2 are the molar volumes of the polymers involved. In Table III, the critical temperature, composition, and interaction energy density parameters Λ_c and χ_c for the mixtures are presented. When the effect of polymer molar mass is considered, it is noted that the critical temperatures T_c for UCST phase diagrams have a higher value upon increasing the molar mass of a component, whereas Λ_c and χ_c have values comparable (see Table III) to the Λ values obtained from the binodal curves as described above.

The interaction parameter χ may also be evaluated experimentally by several methods based on equilibrium thermodynamic properties.[25] A convenient experimental technique for the determination of the χ parameter is the measurement of equilibrium swelling of polymer networks. Polyorganosiloxanes have been studied by vapor sorption and swelling equilibria in order to determine the χ parameters with organic solvents.[26-28] Flory has studied the thermodynamics of swollen networks,[29] and the effect of cross-link density on the polymer/solvent interaction parameter at equilibrium swelling was also analyzed.[30,31] It is noted that χ is a function of polymer concentration and does depend on the cross-link density due to both different degrees of swelling and the fact that the junction points are chemically slightly different from the network chains. The χ value for swollen networks at low cross-linking density approach a limiting value, which is typically the same as that measured by other techniques for polymer/solvent systems. In a recent study[9] the interaction parameters, χ, for PDMS model networks with various molar mass between junctions swollen with linear methylphenylsiloxane oligomers were reported. The χ values were calculated from the Flory–Rehner theory[32] corrected by deformation factor as[9]

$$M_c = \frac{F_\varphi \rho V_1[(2\upsilon_{2m}/\phi) - \upsilon_{2m}{}^{1/3}]}{\ln (1 - \upsilon_{2m}) + \upsilon_{2m} + \chi_1 \upsilon_{2m}{}^2} \tag{8}$$

where M_c is molar mass between cross-links, $F_\varphi = 0.7$ is a factor characterizing the extent to which the deformation in swelling approaches the affine limit for the tetrafunctional PDMS networks ($\phi = 4$), V_1 is the molar volume of the diluent, υ_{2m} is the volume fraction of polymer network, and ρ is the density of the polymer. The values are listed in Table IV for purpose of comparison with the results obtained in the present study. The χ parameters from the network swelling data ($\chi = 0.155 - 0.027$) have values comparable to the data reported for blends in this work ($\chi = 0.122 - 0.111$). The semiquantitative result was obtained of a trend of decreasing χ with decreasing M_c or with increasing molar mass of the oligomeric diluents.[9,26,33] A comparison of the χ values between the two systems is complicated because the components do not have the same structure and chain length and were investigated at different temperatures (see the correction factor in the final column of Table IV). In the swollen model network studies, the oligomeric diluents have a higher proportion of trimethylsilyl end groups and are therefore somewhat different chemically from the corresponding higher molar mass linear polymers. More generally, the network topology is not consistent with the assumptions of the mean-field model of the Flory–Huggins theory for polymer solutions. Thus it may not be appropriate to evaluate and compare quantitatively the interaction parameters with those from the linear structures when the network structure effect is considered. Polymers, however, may have a variety of topological structures such as linear, ring, star, branched, and ladder chains and also three-dimensional network structures, where the chain flexibility, free volumes of mixing, etc., are directly reflected in the free energy of mixing. Thus, a change in critical temperature and interaction parameter obtained on the basis of different topological structure is of fundamental interest in polymer science. For certain lengths of polymer chain between junction points (low cross-linking density) in the network's structure, however, an interaction parameter comparable to that obtained for polymer/polymer blends may be obtained[34] and the χ parameter governed by the chemical structure of repeat units involved.

The results obtained in this work demonstrate the usefulness of the interaction energy density parameter in Flory–Huggins treatment to evaluate the phase behavior of the PDMS/PMPS binary blend system and the possibility of a correlation with the results from swollen polymer networks. Further studies of blends of cyclic and linear polysiloxanes are in progress.

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