Studies of cyclic and linear poly(dimethylsiloxane)s: 31. Effect of molecular architecture/topology on blends of poly(methylphenylsiloxane) and poly(dimethylsiloxane)

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The phase behaviour of binary mixtures of cyclic poly(dimethylsiloxane) (PDMS) and linear poly(methylphenylsiloxane) (PMPS) was investigated using a static wide-angle light-scattering technique. Evidence for the effect of component molecular architecture/topology (cyclic or linear) on the phase separation of blends was sought through cloud point measurements and by examining the composition dependence of the resulting phase diagram. The cyclic–linear blend exhibited an upper critical solution temperature (*UCST*) and showed a dependence on the molecular architecture/topology in that the critical temperature T_c for the cyclic–linear blend was lower than expected when compared with PDMS–PMPS blends in which both components had a linear polymeric structure. The interaction energy density parameter Λ_{12} for the polymers was evaluated via the Flory–Huggins treatment for the thermodynamics of mixing of two polymers. The blending of cyclic PDMS led to a lower Λ_{12} when compared with the corresponding linear–linear binary blend, again because of the chain architecture/topology effect. For this *UCST* system, it thus appears that PDMS cyclics are more soluble/compatible than their linear analogues of the same degree of polymerization. These findings are consistent with the current, but very limited, experimental data in the literature for large ring systems.

(Keywords: poly(dimethylsiloxane); poly(methylphenylsiloxane); polymer blends)

INTRODUCTION

In previous publications of this series we have described the preparation and properties of cyclic poly(dimethylsiloxane) (PDMS) sharp fractions containing up to several hundred skeletal bonds[1]. Such studies have included a comparison of their bulk, solution and surface properties with those of their commercial linear analogues and also with the predictions of the various theories for cyclic polymers[2-4].

Much attention has been focused on polymer blends since the mid-1980s in both academic and industrial research laboratories. Phase separation behaviour, compatibility, morphology, mechanical properties, etc. have been extensively studied for a wide variety of blend systems[5-7]. Most of the investigations to date have been centred on polymer blend systems where both components are linear polymers. There is now a range of synthetic polymers with various molecular architectures/topological structures and their properties have attracted much attention recently[2,4,8-11]. Well characterized examples such as cyclic and star polymers are of fundamental interest in the field of polymer blends but their properties in this area have received little attention to date.

In order to compare the various theories against the experimental results, reliable values of polymer–polymer interaction parameters are clearly needed. This investigation follows previous studies on miscibility and the determination of the polymer–polymer interaction parameters for linear–linear PDMS–poly(methylphenylsiloxane) (PMPS) polyorganosiloxane blends[12,13] in which the effects of both chain length and end-groups were studied. The current work is concerned with characterizing the miscibility by a wide-angle light-scattering technique of a binary siloxane homopolymer blend in which one component of the mixture is cyclic.

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Table 1 Characterization of the poly(dimethylsiloxane) and poly(methylphenylsiloxane) samples

Compound	M_n (g mol^{-1})	M_w/M_n	n_n[a]	T_g[b] (°C)	ρ_{298K}[c] (g cm^{-3})
PDMS (cyclic)[c]	1420	1.05	38.4	−121.2	0.972
PMPS (linear)[c]	1890	1.06	25.4	−48.2	1.109

[a] The number-average number of skeletal bonds n_n for the linear PMPS $(CH_3)_3SiO[(CH_3)(C_6H_5)SiO]_ySi(CH_3)_3$ is taken to be $2y$ and the number of skeletal bonds for the cyclic PDMS $[(CH_3)_2SiO]_x$ is taken to be $2x$

[b] See refs 16 and 17

[c] See refs 18 and 19

EXPERIMENTAL

Preparation of materials

The linear PMPS $(CH_3)_3SiO[(CH_3)(C_6H_5)SiO]_ySi(CH_3)_3$ was prepared with trimethylsilyl end-groups as reported earlier[14]. The cyclic PDMS $[(CH_3)_2SiO]_x$ was prepared by a ring–chain equilibrium reaction in toluene at 110°C and fractionated by vacuum fractional distillation and preparative gel permeation chromatography as described in detail elsewhere[14,15].

The molar masses of the siloxanes and their polydispersities (M_w/M_n) were characterized using gel permeation chromatography (Waters) calibrated with standard siloxane samples, with corrections being applied for axial broadening effects. The characterization data for the cyclic PDMS and linear PMPS are summarized in *Table 1*. The values of the polydispersity index for the samples were close to unity, indicating very narrow molar mass distributions. The materials were clear, viscous liquids at room temperature.

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. The appropriate amounts of the two polymers were carefully weighed into a glass tube. The tube was evacuated under vacuum (10^{-2} torr; 1 torr $\approx$ 133.3 Pa) 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 estimate the temperature at which the polymer mixture became a single phase. The sample was then mounted in the furnace of the light-scattering system, whose temperature was determined 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^{-1}. The equilibrium cloud point was established in each case by extrapolating the recorded data of scattered intensity and temperature to a zero cycling rate. Since PDMS and PMPS have low glass transition temperatures[16,17], we had a wide and stable temperature window for these experiments without any reaction or degradation taking place, as in our earlier studies on polyorganosiloxane blends[12,13] which showed a phase separation in the melt phase.

RESULTS AND DISCUSSION

In order to utilize thermodynamic theory, the compositions of the mixtures were converted from weight fractions to volume fractions using the following equations for density as a function of temperature and molar mass[18–20]. For cyclic poly(dimethylsiloxane)

$$\rho_{(C)} = 1.237 - (8.87 \times 10^{-4})T \qquad (1)$$

and for linear poly(methylphenylsiloxane)

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

where T is in kelvin and M is the molar mass.

Cloud temperatures and phase diagram

The observed reversible cloud temperatures as determined by the light-scattering technique are shown in *Table 2*. Considering deviations of the data from experimental error, all measurements were repeatedly analysed and had deviations in temperature $T \leqslant \pm 2.0$°C and composition $\phi \leqslant \pm 1.0\%$. The obvious phase boundary, as approximated by the observed cloud points for the blend mixtures of PDMS and PMPS, exhibited a maximum in the form of an upper critical solution temperature (*UCST*). The near-symmetrical phase diagram of the PDMS–PMPS blend had a maximum critical temperature at 60 vol% PDMS. Similar *UCST* phase behaviour was also seen in our earlier studies on linear–linear PDMS–PMPS blends[12,13].

Comparison with theory

The phase diagram and critical temperature obtained from experimental measurements of phase separation temperatures (cloud points) for the PDMS–PMPS mixtures were used to interpret the polymer chain architecture effect. Theoretical approximations based on corresponding state theory[21,22] and Flory's equation of state[23] thermodynamics offer a good understanding of compatible polymer blends. In this work, the cyclics were treated by the established binary blend theory; however, deviations from the results for linear polymeric chains are to be expected. Therefore, by simply comparing the results with the corresponding results for a linear–linear blend system, the discrepancy in the interaction energy density parameter Λ_{12}, calculated using the Flory–Huggins theory of linear polymeric systems for the cyclic–linear blend system at critical conditions, was used to index the architecture/topology effect.

In an analysis based on the Flory–Huggins theory[24–26], where there are no specific interactions, the free energy of mixing decreases with increasing temperature. Therefore, the existence of *UCST* phase behaviour is predicted. The Flory–Huggins equation for the free energy of mixing

Table 2 Compositions of the polymer blends and their cloud temperatures

Blend	Volume fraction ϕ_{PDMS}	Cloud temperature T_c(K)
B-1-01	0.245	401
B-1-02	0.402	429
B-1-03	0.483	438
B-1-04	0.592	442
B-1-05	0.668	440
B-1-06	0.750	428
B-1-07	0.886	408

per unit volume of a polymer mixture can be written as[27]

$$\Delta G_{\mathrm{m}} = RT\left(\frac{\phi_1 \ln \phi_1}{V_1} + \frac{\phi_2 \ln \phi_2}{V_2}\right) + \Lambda_{12}\phi_1\phi_2 \qquad (3)$$

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 equation (3) is the combinatorial part of the free energy of mixing as given by the Flory–Huggins treatment[26]. The Λ in the last term is the interaction energy density parameter, which is generally a function of temperature, pressure and composition of the mixture. To compare Λ in equation (3) with the interaction parameter χ of the Flory–Huggins equation, it is noted that Λ and χ are related to each other by

$$\chi = \Lambda V_{\mathrm{r}}/RT \qquad (4)$$

where V_{r} is a volume of reference.

One consequence of the expression for the interaction energy density parameter Λ of equation (3) being independent of composition at the critical temperature T_{c} for phase separation is that

$$\Lambda_{\mathrm{c}} = RT_{\mathrm{c}}(\sqrt{V_1} + \sqrt{V_2})/2V_1V_2 \qquad (5)$$

where V_1 and V_2 are the molar volumes of the polymers involved. Thus, when the polymer molar mass is kept approximately constant, the cloud point curve shift caused by the cyclic structure will be proportional to the change in Λ_{c}.

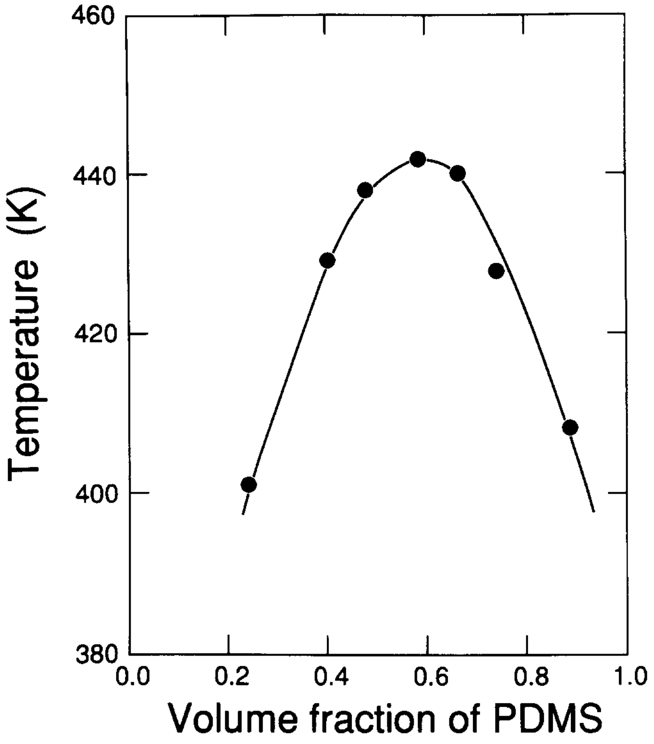

Figure 1 Cloud point temperatures of the homopolymer mixtures of cyclic PDMS and linear PMPS. The cyclic PDMS had a molar mass of 1420 g mol^{-1} and the linear PMPS had a molar mass of 1890 g mol^{-1}. The experimental cloud points are designated by filled circles

Interactions and phase behaviour of blends containing cyclic polymers

The cloud points determined for mixtures containing cyclic PDMS and linear PMPS are shown in *Figure 1*. In accordance with the cloud point measurements for these binary mixtures, the critical temperature and composition were obtained from the maximum in the *UCST* phase diagram. The interaction energy density parameters Λ_{c} and χ_{c} for the cyclic–linear blend were then calculated on the basis of equation (5) and the values are presented in *Table 3*.

Comparing blend 1 and blend 2 in *Table 3*, the molar mass of the cyclic PDMS is higher than that of the linear PDMS; however, the values of both the critical temperature and the interaction energy density are lower for blend 1. This result may be contrasted with the predicted effect of polymer molar mass for linear–linear polymer blends, where the *UCST* phase diagrams have a higher critical temperature T_{c} upon increasing the molar mass of either component. When the polymer molar mass is kept approximately constant, a shift in the cloud point curve because of the cyclic structure may be reflected by a change in Λ_{c}. Based upon the results for the corresponding linear–linear blends 2 and 3, which are listed in *Table 3* for comparison, the parameter Λ_{c} for the cyclic–linear blend should have a comparable value. A deviation from the results for the linear–linear blend system is clearly seen in the case of the cyclic–linear blend. For this *UCST* system, it appears that PDMS cyclics are more soluble/compatible than their linear analogues of the same degree of polymerization.

If we consider the structure of a cyclic macromolecule, it is obvious that there are no end-groups. It has been shown that the chemical difference between trimethylsilyl end-groups, i.e. $\mathrm{OSi(CH_3)_3}$, and dimethylsiloxane segments, i.e. $[\mathrm{OSi(CH_3)_2}]$, in linear poly(dimethylsiloxane) has a negligible effect on the mixing of linear PDMS and linear PMPS[12]. In addition, no effect has been found in PDMS–PMPS blends using PDMS with silanol end-groups, i.e. $\mathrm{OSi(CH_3)_2OH}$[13]. It has also been shown that linear PDMS samples of molar mass exceeding 700 g mol^{-1} have a near-constant value of the solubility parameter[28]. The cyclic PDMS and linear PMPS used in the current investigation had molar masses higher than

Table 3 Critical conditions for PDMS–PMPS blends from cloud point measurements and their interaction parameters Λ_{c} and χ_{c}

Blends	PDMS M_{n} (g mol^{-1})	PMPS M_{n} (g mol^{-1})	T_{c}^{a} (K)	ϕ^{a}	Λ_{c} (cal cm^{-3})	χ_{c}^{b}
1	1420 (cyclic)	1890 (linear)	442	0.60	0.950	0.095
2^{c}	1110 (linear)	1890 (linear)	458	0.64	1.051	0.122
3^{c}	1110 (linear)	2240 (linear)	518	0.59	1.027	0.112

[a] The critical temperature and critical composition were obtained from the cloud point curve shown in *Figure 1*

[b] Data calculated based on the average lattice volumes of PDMS and PMPS and the value of Λ_{c} at the temperature T_{c}

[c] Data from refs 12 and 13

this value. We therefore do not anticipate a chemical effect from the end-groups in the present study, despite the relatively low molar masses of the samples. Cyclic polymers do, however, have lower mean-square radii of gyration[29,30] than their linear analogues. Although large cyclics have some physical properties close to those of the corresponding linear polymers, properties which depend on the mean-square radius of gyration are typically different. For example, large, non-entangled rings show a higher value of the diffusion coefficient[31] and lower intrinsic viscosity[32,33]. The ratio of the radii of gyration for flexible linear polymers (l) to cyclic polymers (c) is $\langle s_l^2 \rangle / \langle s_c^2 \rangle \approx 2$, and hence cyclics occupy approximately one third of the volume of their linear analogues having the same molar mass[29,30]. In considering the solution or blend properties, the cyclics have significantly more intramolecular segment–segment contacts than the corresponding linear chains, which should be directly reflected in the free energy of mixing. Thus, this may result in the lower values of the critical temperature and Λ_c that were determined for the cyclic–linear blend.

Recently, phase separation kinetics studies on blends of high molar mass cyclic polystyrene[34] and star-shaped polystyrene[35] with linear poly(vinyl methyl ether) (PVME) have been performed. In both these studies a lower critical solution temperature (*LCST*) was seen; however, the cyclic polystyrene (PS) was observed to phase separate 7–8°C above the PS–PVME linear–linear blend where the components had the same molar mass. This result is consistent with our earlier study[36] in which phase diagrams of the lower critical solution temperature were shown for cyclic and linear PDMS in tetramethylsilane and neopentane solutions. In all cases the cyclic polymers were found to show a higher *LCST* by up to 2.5°C when compared with the linear polymers of the same molar mass.

The available data are still too few to justify generalization of the cyclic effect, but the results cited above demonstrate the architecture/topology effect for cyclic molecules from the viewpoint of the thermodynamics of polymer blends. Furthermore, because the cyclic chain architecture/topology does not fully agree with the assumptions of the Flory–Huggins mean-field model for the free energy of mixing, it is clearly not appropriate to use parameters for the linear structures when a cyclic structure is involved. However, for the purpose of investigating the miscibility relationships of a given cyclic polymer substituted for a linear chain in a blend, this postulate was assumed to be valid here for cyclic molecules. The results thus demonstrate the usefulness of the interaction energy density parameter in the Flory–Huggins treatment in evaluating the difference in thermodynamic behaviour between cyclic structures and linear structures in polymer–polymer mixtures. In future, however, cyclic blends should have their own theoretical considerations, which are required to incorporate the effects of topology, composition and molar mass.

CONCLUSIONS

The phase diagram of PDMS–PMPS blends was determined upon changing the component topological structure from linear PDMS to cyclic PDMS. Comparing the critical temperatures and interaction parameters of the cyclic–linear blend and the corresponding PDMS–PMPS linear–linear blend, a higher miscibility for the blend containing rings was seen for this *UCST* system. Further studies of the properties of cyclic polysiloxanes are in progress.

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