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An investigation of the thermodynamic interactions of oligomeric cyclic methylphenylsiloxanes in siloxane melts and blends

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Abstract

The miscibility of cyclic poly(methylphenylsiloxanes) (PMPS) with molar masses less than 1000 g mol^{-1} have been studied in mixtures with either cyclic or linear poly(dimethylsiloxane) (PDMS). In all cases, an upper critical solution temperature (UCST) was observed and interaction parameters were determined from the phase boundaries. The results were compared with those from our previous studies of linear–linear PDMS–PMPS and cyclic–linear PDMS–PMPS polymer blends. The cyclic–linear PMPS–PDMS and cyclic–cyclic PMPS–PDMS blends in this investigation were found to have higher interaction energy density parameters than the corresponding linear–linear PDMS–PMPS homopolymer blends that we have reported elsewhere. An isomer effect upon the phase separation behavior was also seen for the isolated pure stereoisomers of cyclic PMPS in mixtures with linear PDMS. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Blends; Miscibility; Upper critical solution temperatures

1. Introduction

High molar mass linear siloxane polymers –[R$_1$R$_2$SiO]$_y$– may be prepared by the ring-opening polymerization of small ring siloxanes [R$_1$R$_2$SiO]$_x$, where x is usually three or four. As such reactions often involve ring-chain equilibration, this approach results in a distribution of cyclics being formed in addition to the parent linear siloxane polymer. The presence of these small cyclics may be detrimental to the properties of the desired polymer in its applications. In the case of the dimethylsiloxane system ($R_1 = R_2 = CH_3$), removal of the small cyclics may easily be achieved by distillation under vacuum. The individual small cyclic dimethylsiloxanes have been isolated and characterization has show that only the trimer (D$_3$) and octamer (D$_8$) are solids at room temperature [1,2]. Further, these cyclics are all soluble in the high molar mass linear PDMS polymer at room temperature for the concentrations typically obtained in bulk polymerization, so that phase behavior does not present any problems for the PDMS commercial fluids or elastomers.

In the case of the methylphenylsiloxane system ($R_1 = CH_3$, $R_2 = C_6H_5$) higher concentrations of cyclics are seen under equilibrium conditions when compared to PDMS. Further, removal of the small cyclics by distillation under vacuum is very difficult due to their low vapor pressures. Cyclic methylphenylsiloxanes, of which there are various structural isomers, may be synthesized by the hydrolysis of dichloromethylphenylsilane. When successfully isolated, a number of these pure stereoisomers are found to be solids at room temperature [3,4]. Thus the linear oligomeric or polymeric PMPS formed by ring-chain equilibration may contain a solid crystal precipitant in the final products, which is seen to form slowly in the PMPS melt at room temperature. These crystallized mixtures, which include isomers of the two trimers (P$_3$), four tetramers (P$_4$) and four pentamers (P$_5$) etc., have melting temperature higher than those of the cyclic dimethylsiloxanes (D$_3$, D$_4$, D$_5$ etc.). Further, the solubility and other physical characteristics of these small cyclics also differ from the linear analogs that have the same number of repeat units.

Cyclic siloxanes typically show changes in their physical properties as the ring size increases. A comparison between the cyclic siloxanes and their linear siloxane analogs, i.e. rings and chains having the same molar mass and substitutent groups, have been reported [2,5,6,7]. As the size of the ring increases the difference between certain bulk properties of cyclic siloxanes such as density and glass transition temperature and the analogous linear siloxanes is often reduced. However, it should also be noted that few

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

Compound	M_n (g/mol)	M_w/M_n	n_n[a]	$\rho_{298\ K}$ (g/cm^3)[b]	T_g/T_m (°C)
PDMS (linear)[b]	1110	1.02	25.6	0.943	−130.1/–
PDMS (cyclic)[b]	1420	1.05	38.4	0.972	−121.2/–
PMPS (cyclic)[c]	731	1.04	10.7	1.213	−30/–
$[(CH_3)(C_6H_5)SiO]_4$ [P_4-(I)]	544.9	1	8	1.180[d]	–/99
$[(CH_3)(C_6H_5)SiO]_4$ [P_4-(II)]	544.9	1	8	Na	–/58
PMPS (linear)[b]	1890	1.06	25.4	1.109	−48.2/–

[a] The number of skeletal bonds n for the linears $(CH_3)_3SiO[(CH_3)SiRO]_ySi(CH_3)_3$ were taken to be 2*y* and the number of skeletal bonds for the cyclics $[(CH_3)SiRO]_x$ were taken to be 2*x*.

[b] See Refs. [13,17,26].

[c] Data from Ref. [13].

[d] See Ref. [15].

experimental studies exist to date which address the effect of topology/molecular architecture on the phase behavior of siloxane mixtures.

In our previous studies of poly(dimethylsiloxane)-poly(methylphenylsiloxane) homopolymer blends [8–10], we have discussed the significance of miscibility for the linear–linear blends [8], effect of end-groups in the linear–linear blends [9], and topology/molecular architecture effects of large cyclics in cyclic–linear blends [10]. These considerations, along with the separation problems of the cyclics in commercial linear PMPS as described above, have prompted us to also perform studies of the fundamental thermodynamic interactions of small cyclic methylphenylsiloxanes in siloxane melts.

2. Experimental

2.1. Materials

2.1.1. Preparation of cyclic PDMS, linear PDMS and cyclic PMPS

The linear PDMS $(CH_3)_3SiO[(CH_3)_2SiO]_ySi(CH_3)_3$ was prepared with trimethylsilyl end-groups as reported earlier [8]. Cyclic PDMS $[(CH_3)_2SiO]_x$ and cyclic PMPS $[(CH_3)(C_6H_4)SiO]_x$ were each prepared by ring-chain equilibration reactions carried out in toluene at 110°C with diglyme as a promoter, followed by fractionation using vacuum fractional distillation and preparative gel permeation chromatography, as described in detail previously [11–14].

The number-average molar masses M_n of the various siloxanes and their polydispersities (M_w/M_n) were characterized using a gel permeation chromatograph (Waters) that was calibrated using standard cyclic and linear siloxane samples (the chromatograms were corrected for axial broadening effects) and also by high performance liquid chromatograhy (HPLC) using gradient elution (THF/methanol). The characterization data for the cyclic PDMS, cyclic PMPS and linear PDMS are summarized in Table 1. The values of the polydispersity index of the samples were close to unity, indicating very narrow molar mass distributions. The PDMS materials were clear, viscous liquids at room temperature and the PMPS materials characteristics are given in Table 1.

2.1.2. Preparation of the stereoisomers of 2,4,6,8-tetramethyl-2,4,6,8-tetraphenylcyclotetrasiloxane

The presence of non-symmetrical substituents on silicon for the small cyclic oligomeric PMPS leads to a mixture of configurational isomers. A few of these individual stereoisomers have been successfully isolated and identified. The four isomeric cyclic methylphenylsiloxane tetramers, which were obtained by the hydrolysis of methylphenyldichlorosilane, were first separated and characterized by Hickton and coworkers [4]. The configurational structure of these four stereoisomeric 2,4,6,8-tetramethyl-2,4,6,8-tetraphenyl cyclotetrasiloxanes are shown in Fig. 1. Because of the similarity in the properties among the four isomers, it is quite difficult and time consuming to separate each isomer from an isomeric mixture.

Two of the isomers, (I) and (II), were isolated here for a study of the effect of stereochemical configuration on the miscibility of siloxane–siloxane mixtures. A liquid mixture of the four isomeric cyclic tetramers was kindly provided by Dr A. Revis of the Dow Corning Corporation. Upon standing at room temperature for several weeks, the mixture slowly precipitated some solid crystalline material. The melting temperature of the resulting crystalline mixture was analyzed by a melting point apparatus (Fisher Scientific Inc.) and by Differential Scanning Calorimetry (Perkin–Elmer DSC-7). The composition of this crystalline mixture was also analyzed by proton NMR spectroscopy (Bruker 250 MHz) at room temperature, using deuterated chloroform as the solvent and TMS as reference. Analysis of the crystal mixture showed that two isomers P_4-(I) and P_4-(II), as designated in Fig. 1, dominated the composition but that it also contained small amounts of isomers P_4-(III) and P_4-(IV). This crystalline mixture was then washed with methanol and carefully fractionated to give each pure isomer, using a repeated melting-crystallization method to

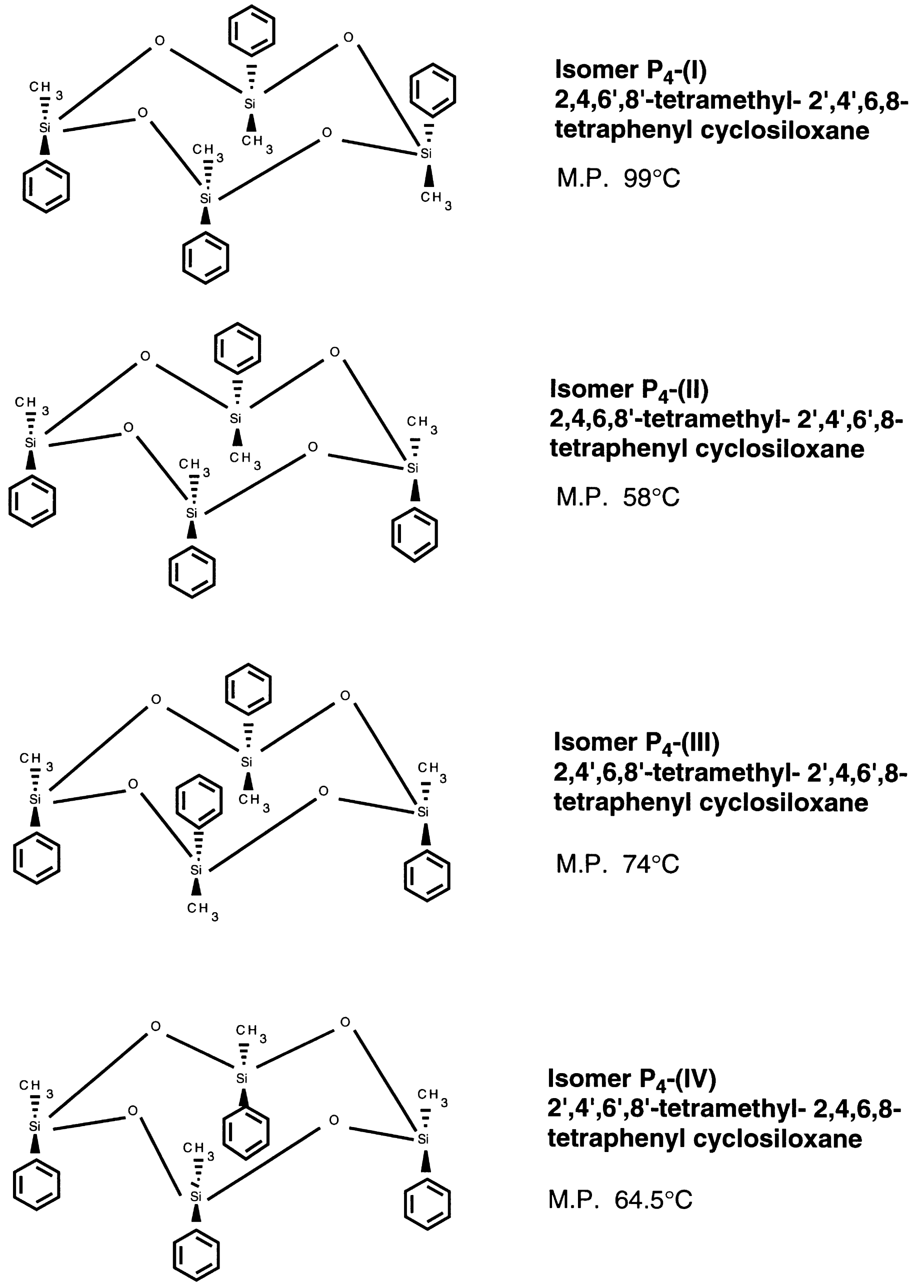

Fig. 1. The four configurational isomers of 2,4,6,8-tetramethyl-2,4,6,8-tetraphenylcyclotetrasiloxane.

remove the unwanted fractions. Two crystal isomers were obtained, showing melting temperature peaks in their DSC thermograms at 99.0 ± 0.2°C and 58.0 ± 0.2°C, respectively, which corresponded to isomer P_4-(I) and isomer P_4-(II). Each isomer was isolated in sufficient quantities in order to carry out the investigations described below. The NMR spectra of the methyl-protons of isomer P_4-(I) and isomer P_4-(II) are presented in Fig. 2a and b, respectively. The correlation of the NMR methyl-proton shift with respect to the stereochemical environment in the 2,4,6,8-tetramethyl-2,4,6,8-tetraphenylcyclotetrasiloxanes, for the isomers P_4-(I) and P_4-(II), may be attributed to the specific methyl proton environments. As expected P_4-(I) is stereoregular in its ring structure as shown by the presence of an alternating meso (m) - racemic (r) sequence and therefore displays only one type of methyl-proton shift. The P_4-(II) isomer has a stereoregularity in its ring structure that is of the diad order m–m–r–r and so it displays three kinds of methyl-proton environment for the proton NMR. These measurements have been confirmed using previously reported values of the chemical shifts [4,15] which are given in Table 2 for comparison. The integration curves of the NMR spectra in Fig. 2 indicate that each isomer was of a high purity.

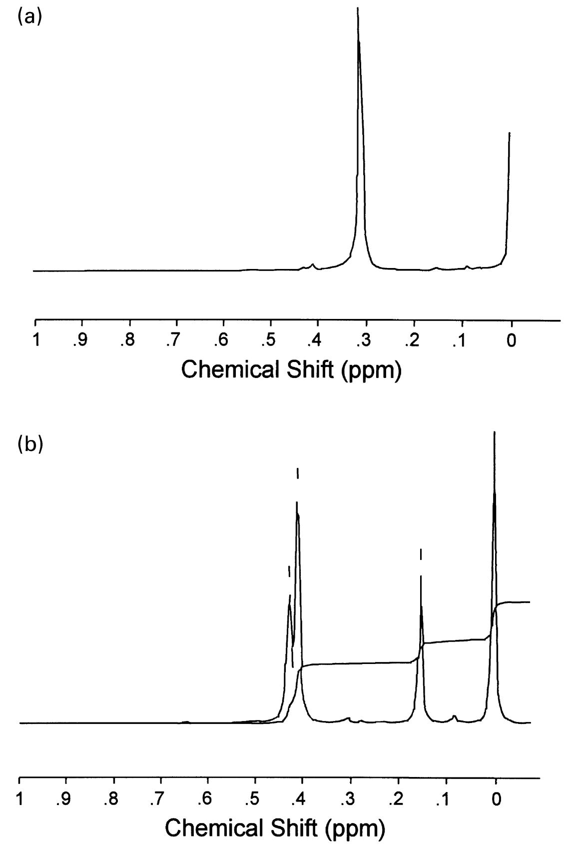

Fig. 2. 250 MHz proton NMR spectra of the pure: (a) P_4-(I); and (b) P_4-(II) stereoisomers.

2.2. Blends and measurements of phase behavior

The cloud points were established using a static light scattering instrument, in which a photometer was used to detect the intensity at a 90° scattering angle. The detailed procedure of the measurement has been described in earlier publications [8,16]. Each sample was well mixed at the miscible temperature, under vacuum (10^{-2} Torr) and contained in a sealed tube. The cloud temperature was 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. Since PDMS and PMPS each possess low glass transition temperatures and high thermal stability, we can work within a wide stable temperature window for these experiments without any reaction or degradation taking place. Our previous studies, on PDMS–PMPS polyorganosiloxane blends [8–10], also showed a phase separation in the melt phase.

Using a binary combination of PDMS and PMPS, four PDMS–PMPS blends were investigated, that involved varying their topology/architecture (linear and cyclic), stereochemistry and molar mass. In order to utilize thermodynamic theory, the composition of the mixtures was converted from weight fraction to volume fraction by using the following values of density as a function of temperature and molar mass [13,14,17].

For the cyclic and linear polydimethylsiloxanes

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

$$\rho_{(L)} = 1.2666 - 1.0986 \times 10^{-3} T \tag{2}$$

and for the cyclic polymethylphenylsiloxanes

$$\rho_{(C)} = 1.442 - 7.688 \times 10^{-4} T \tag{3}$$

where T is the temperature in Kelvin.

According to their structure–property relationships, stereoisomers of PMPS cyclotetramer have different melting temperatures due to the difference of their crystal structures. The density of each isomer may also vary. Unfortunately, only isomer P_4-(I) has had its density determined ($\rho_{298\ \mathrm{K}} = 1.180$) at the present time. Although the density is used to calculate molar volume, it is also an important factor in determining the composition and other parameters of the mixture at different temperatures. The value, relative to the molar volume of cyclic PMPS, at the critical temperature in the phase diagram representative of this current investigation, was assumed in each case to follow the prediction described by the relationship expressed in Eq. (3).

2.3. Differential scanning calorimetry

The melting transition temperature of a blend of linear PDMS (1.110 g mol^{-1}) with the cyclic P_4-(I) was measured using a DSC (Perkin–Elmer DSC-7) under nitrogen flow. With reference to the phase diagram which was obtained from cloud point measurements, the sample was first heated to the single phase region, at 40°C above critical temperature of blend, for 3 min. Next the sample was quenched to 50°C and annealed for 15 min. The melting temperature

Table 2
NMR chemical shift (δ) ppm of the 2,4,6,8-tetramethyl-2,4,6,8-tetraphenylcyclotetrasiloxanes

Isomer	Chemical Shift (δ) ppm	Literature[a] (δ) ppm	CH_3 Hydrogen type
Isomer P_4-(I)	0.303	0.281/0.32	2,4,6′,8′
Isomer P_4-(II)	0.426	0.402/0.43	4
	0.408	0.392/0.42	2,6
	0.152	0.148/0.20	8′

[a] See Refs. [4,15].

Table 3
The composition of the polymer blends and their cloud point temperatures (blend samples 1–4)

Sample of blend	Volume fraction ϕ_{PDMS}	Cloud temperature T_c (K)
B-1-01	0.201	388
B-1-02	0.315	404
B-1-03	0.444	421
B-1-04	0.513	424
B-1-05	0.590	420
B-1-06	0.664	410
B-1-07	0.773	400
B-1-08	0.878	375
B-2-01	0.238	395
B-2-02	0.391	419
B-2-03	0.499	432
B-2-04	0.542	428
B-2-05	0.629	423
B-2-06	0.686	412
B-2-07	0.707	411
B-2-08	0.803	395
B-3-01	0.061	313
B-3-02	0.120	338
B-3-03	0.174	357
B-3-04	0.279	364
B-3-05	0.450	368
B-3-06	0.515	371
B-3-07	0.572	367
B-3-08	0.716	361
B-3-09	0.901	323
B-4-01	0.192	343
B-4-02	0.293	354
B-4-03	0.396	359
B-4-04	0.514	358
B-4-05	0.658	352
B-4-06	0.715	348
B-4-07	0.862	312
B-4-08	0.899	298

of sample was then determined by the presence of an exothermic peak and by using the initial temperature. A heating rate of 10 K/min was used.

2.4. Comparison with theory

The phase diagram and critical temperature, obtained in each case from experimental measurements of phase separation temperatures (cloud points) of the PDMS–PMPS blends for different compositions, may be used to interpret chain topology/configuration effects. Theoretical approximations based on corresponding state theory [18–20] and Flory's equation-of state [21,22] offer a fairly good understanding of the thermodynamics of compatible polymer blends, at least in qualitative terms. One has to be careful in using theory developed for linear polymer molecules in the case of cyclic molecules, however. In this study, we assume that the oligomeric cyclics can be treated by the established binary blend theory derived for linear polymeric chains. This means that the interaction energy density parameter Λ_{12}, derived by Flory–Huggins theory can be obtained for each blend and then used as a parameter to compare the discrepancy of miscibility between cyclic blends and linear blends. Based on this assumption, the values were calculated for cyclic blend system under critical conditions to index the effect of molecular architecture.

An analysis based on the Flory–Huggins theory [21], where there are no specific interactions, shows that the free energy of mixing decreases with increasing temperature. Therefore, the existence of an UCST phase behavior is predicted. The Flory–Huggins theory can be written as [16]:

$$\Delta G_m = RT\left[\frac{\phi_1 \ln \phi_1}{V_1} + \frac{\phi_2 \ln \phi_2}{V_2}\right] + \Lambda_{12}\phi_1\phi_2 \tag{4}$$

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. (5) is the combinatorial part of the free energy of mixing as given by the Flory–Huggins treatment [21]. The interaction energy density parameter, Λ, is generally a function of T, p and composition of the mixture. Λ in Eq. (5) and the interaction parameter χ of the Flory–Huggins equation can be related by the following equation

$$\chi = \Lambda V_r / RT \tag{5}$$

where V_r is a volume of reference.

One consequence of the expression of the interaction energy density Λ of Eq. (5) being independent of composition at the critical temperature T_c for phase separation is that

$$\Lambda_c = RT_c(\sqrt{V_1} + \sqrt{V_2})/2V_1V_2 \tag{6}$$

where V_1 and V_2 are the molar volumes of the polymers involved. Therefore, if the polymer molar mass is known, the change in critical temperature on cloud point curve of the blend, due to the variety in cyclic structure, will be proportional to the change in Λ_c.

3. Results and discussion

The observed reversible cloud temperatures for each blend, as determined by the light scattering technique are given in Table 3. The level of experimental error was determined by repeating the measurements and were found to show deviations in temperature ($T \leq \pm 2.0$°C) and in composition ($\phi \leq \pm 1.0\%$). The obvious phase boundaries, as approximated by the observed cloud points for the blend mixtures of PDMS and PMPS, exhibited maxima with the form of an upper critical solution temperature (UCST) and were all found to be below 160°C. Similar UCST phase behavior has been observed in our previous studies of linear–linear PDMS–PMPS blends [8–10].

Table 4
Critical conditions for the PDMS–PMPS blends determined from the cloud point measurements and the resulting interaction parameters Λ_c and χ_c

Blend	PDMS M_n	PMPS M_n	T_c (K)[a]	ϕ_c[a]	Λ_c (cal/cm^3)	χ_c[b]
B-1	1420/C	731/C	424	0.52	1.638	0.210
B-2	1110/L	731/C	432	0.49	1.825	0.251
B-3	1110/L	544.9/C-(P_4-I)	371	0.47	2.038	0.300
B-4	1110/L	544.9/C-(P_4-II)	360	0.47	1.987	0.300
B-5[c]	1420/C	1890/L	442	0.60	0.950	0.095
B-6[c]	1110/L	1890/L	456	0.64	1.051	0.122

[a] The critical temperature and critical composition were estimated from cloud point curves shown in Figs. 3–5.

[b] Data calculated based on the average lattice volume of PDMS and PMPS and Λ_c at the temperature T_c.

[c] See Refs. [8,9,10].

3.1. Cyclic–linear PMPS–PDMS and cyclic–cyclic PMPS–PDMS blends

All four blends displayed cloud temperature curves in the form of a UCST phase diagram at temperatures well below their depolymerization/decomposition temperature. The small cyclic PMPS ($M_n = 731$ g/mol) was mixed with cyclic PDMS and linear PDMS in blend B-1 and blend B-2, respectively. The interaction energy densities at the critical temperature Λ_c, were determined for each blend using the relationship given in Eq. (6) and the values are listed in Table 4. The critical temperatures T_c, of the phase diagrams of blends B-1 and B-2 (see Figs. 3 and 4) were estimated from the maximum temperature on the curve and found to be at 424 and 432 K, respectively. The interaction parameter in the cyclic–cyclic blend B-1 was found to be lower than the cyclic–linear blend B-2 despite the higher molar mass of the cyclic PDMS in blend B-1 relative to the linear PDMS in blend B-2.

The cyclic oligomers clearly have no end-groups as compared with the corresponding linear polymers, but also the cyclic organosiloxanes exhibit significant differences in properties, such as specific volume, viscosity, thermal expansion coefficient and latent heat of vaporization ΔH_{vap}, as the size of the ring decreases [5]. In the blend systems described here, since there are no special inter- or intra-molecular interactions among the siloxane chains, a variation of the specific volume per repeat unit in the small rings may cause the oligomeric cyclic PMPS to exhibit an appreciable molecular architecture/topology effect upon the polymer demixing in blends B-1 and B-2. The results may be compared with the blend B-6 reported previously [8–10], that used a linear chains of PMPS, ($M_n = 1890$ g/mol) mixed with same linear PDMS sample as in blend B-2. All the data are listed in Table 4 for purposes of comparison and one observes that higher interaction parameters Λ_c and χ_c, were obtained for blends B-1 and B-2.

The shorter PMPS cyclics, which were designated as P_4-(I) and P_4-(II) for two of the four stereoisomers of 2, 4, 6, 8 tetramethyl 2, 4, 6, 8 tetraphenylcyclotetrasiloxane were prepared at 99% purity, as described above. Two blend systems, B-3 and B-4, were prepared by using a linear trimethylsilyl terminated PDMS ($M_n = 1110$ g/mol) along with either the P_4-(I) or P_4-(II) isomers, respectively. The cloud points determined for the mixtures of these two blend systems are given in Table 3 and plotted in Fig. 5.

Based on Eqs. (4) and (6), the Λ_c value of linear–linear PDMS–PMPS blends is a constant and can be applied for calculation the critical temperature of other PDMS–PMPS

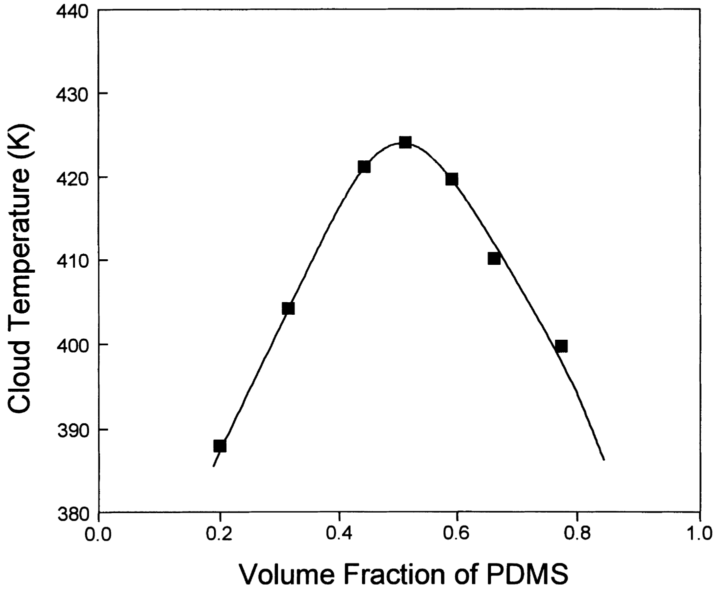

Fig. 3. Cloud point temperatures of the homopolymer mixtures of cyclic PDMS and cyclic PMPS. The cyclic PDMS has a molar mass $M_n = 1420$ g mol^{-1}, the cyclic PMPS has a molar mass $M_n = 731$ g mol^{-1} and the experimental cloud points are designated by squares.

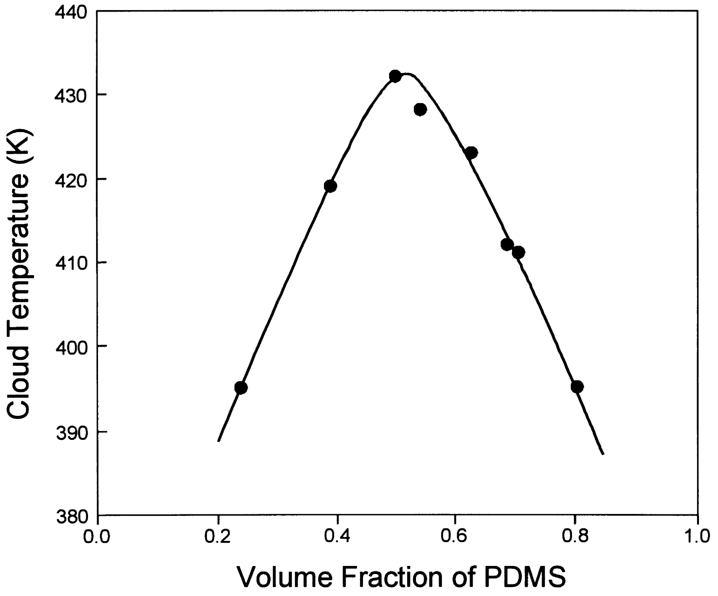

Fig. 4. Cloud point temperatures of the homopolymer mixtures of linear PDMS and cyclic PMPS. The linear PDMS has a molar mass $M_n = 1110$ g mol^{-1}, the cyclic PMPS has a molar mass $M_n = 731$ g mol^{-1} and the experimental cloud points are designated by circles.

blends with similar molar mass [8,16]. The short PMPS tetramers in blends B-3 and B-4 show critical point temperatures that are much lower than the predicted temperatures for the critical point based on the Λ_c value of linear–linear PDMS–PMPS blend (B-6). A comparison of the phase diagrams measured for linear PDMS ($M_n = 1110$ g/mol) with a series of either linear or cyclic PMPS chains in blends B-2 to B-6, indicates a good agreement of a critical composition ϕ_C, that is shifted to lower PDMS content with a decrease in molar mass of the PMPS (see Table 4). The

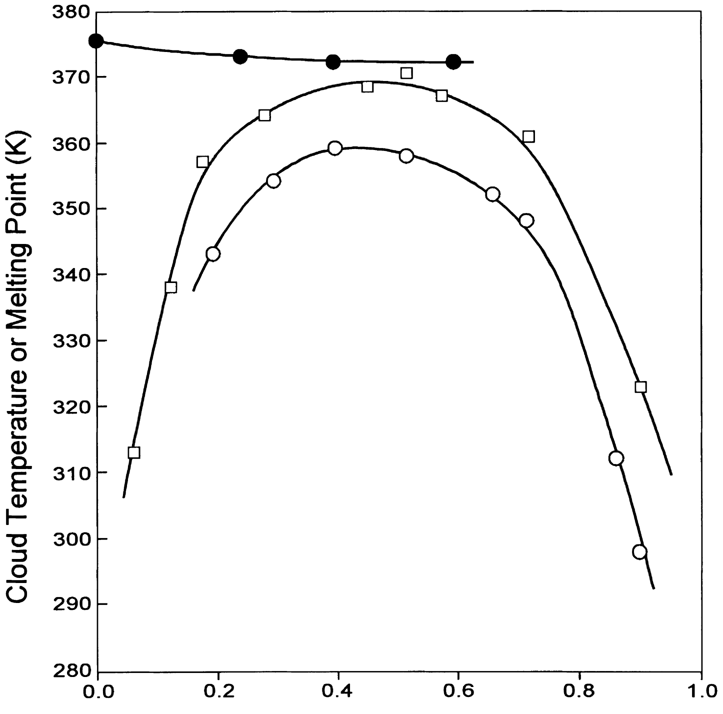

Fig. 5. Cloud point temperatures of the homopolymer mixtures of linear PDMS and the cyclic PMPS stereoisomers. The linear PDMS has a molar mass $M_n = 1110$ g mol^{-1}, the cyclic PMPS are the cyclic siloxane tetramers P_4-(I) and P_4-(II) each having a molar mass $M_n = 544.9$ g mol^{-1} and the experimental cloud points are designated by open squares and open circles, respectively. Also shown are the melting point depressions designated by filled circles for the cyclic siloxane tetramer P_4-(I) mixed with linear PDMS ($M_n = 1110$ g mol^{-1}) as determined by separately by DSC.

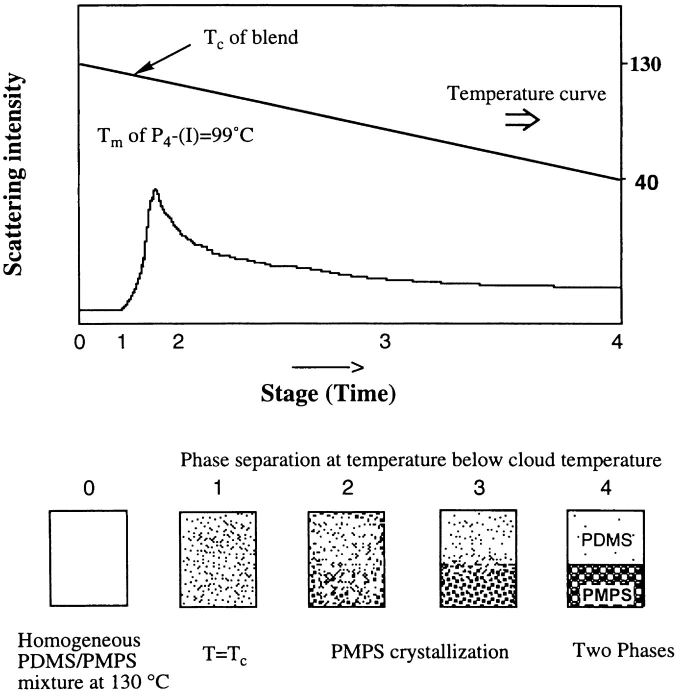

Fig. 6. Schematic of the phase separation and crystallization behavior of the cyclic PMPS stereoisomer in the PDMS–PMPS stereoisomer blends.

interaction parameters Λ_c and χ_c, are expected to be independent of the chain length. Calculations on the basis of the derivative of the Flory–Huggins theory given in Eq. (6) for blends B-3 and B-4 show their Λ_c values to be much higher than those of the linear–linear blend (B-6) and even higher than that of the cyclic PMPS/linear PDMS of blend B-2. It is shown that a decrease in miscibility of the PMPS component results upon incorporating small cyclics. The discrepancy between the interaction parameter from this approximate relationship and the experimental data might result from the specific volume effect on the short cyclic system. Interesting investigations on oligomer effects for other linear polymers have been reported [23–25] and the results were explained by an increase in the free volume of the short linear polymer chain, due to end-group effects. There are no such end-groups in cyclic structures, nevertheless, cyclic polymers may show an effect because due to the topological structure which causes the molecular volume to greatly change. The ring strain for small PDMS cyclics may also cause the molar density to drop [5,26,27]. For these reasons, the molar volume and free volume for short PMPS cyclic in blends may change and thus these changes may facilitate demixing for blends containing small siloxane rings.

The available data is too limited to date to justify any generalization of the cyclic effect, but the results cited above describe the topology or molecular structure effect for cyclic and linear macromolecules from the viewpoint of the thermodynamics of polymer blends. It is well known that it is difficult to treat small siloxane rings as small macromolecules. As the cyclic chain topology may not agree well with the assumptions made by the mean-field model for the Flory–Huggins free energy of mixing, it may not be appropriate to substitute parameters used for the linear structures in blends when a cyclic component is involved. Instead the behavior of small cyclic siloxanes in blends may require individual consideration, which accounts for the molar mass dependence of ring containing systems.

3.2. Stereoisomers of 2,4,6,8-tetramethyl-2,4,6,8-tetraphenylcyclotetrasiloxane in PDMS–PMPS blends

The various stereoisomers have a distinct structural configuration and hence unique physical properties for each form, as illustrated by their different melting points (see Fig. 1). The UCST phase diagrams of the blends B-3 (P_4-(I)) and B-4 (P_4-(II)) display two distinct cloud temperature curves with blend B-3 having a critical temperature 11 K higher than blend B-4. As their molar masses and overall chemical compositions are identical, this behavior must be caused by their configurational difference. In the calculation of interaction parameters at the critical condition based on Eq. (6), we assumed that the two isomers have the same density and that their densities change as a function of temperature in accordance with Eq. (3) for the cyclic PMPS oligomers. The values of Λ_c and χ_c for blends B-3 and B-4 were thus obtained and are listed in Table 4. The minor difference (0.051 in Λ_c and 0.0003 in χ_c) thus results from a difference in the critical temperature ($\Delta T = 11$ K). Generally speaking, the density of the stereoisomers is associated with the melting temperatures and the molecular packing in the crystal form. The specific volume, which follows from the density, effects the miscibility of cyclic stereosiomers in blends and may be assumed to account for the difference between the two-phase diagrams. Since P_4-(I) has a more symmetrical structure, it should have a higher density than P_4-(II). The above assumption that the two isomers have the same density in the calculation may thus be incorrect. It is consequently believed that the value of the interaction energy density parameter Λ_c and Flory–Huggins interaction parameter χ_c,, of blend B-4 should be larger than those calculated here. Stereoregularity plays a very important role in governing the structure and properties of polymers. The tacticity of a polymer clearly has an effect on the miscibility of polymer–polymer blends. In the case of high molar mass polymer blends, PMMA/PVC and PVME/Polystyrene [28,29], are examples of systems where this effect has been studied. Small cyclic siloxane tetramers with different configurations in structure may thus show a correlation with the stereoregularity effect on the blend of large macromolecule. The stereoisomers used in the current study show evidence of the configuration effect on the miscibility of PDMS–PMPS blends. As stereochemical control is possible during the polymerization of the *cis*-trimer for PMPS, this effect may be worth exploring using the PDMS–PMPS model system.

3.3. Crystal–liquid phase separation

One special characteristic of blends B-3 and B-4 is the possibility of crystallization of the P_4 isomer taking place after cooling the homogeneous blend below the binodal temperature. Depending on the depth to which the temperature is quenched, both the dynamic liquid–liquid phase separation and the isomer crystallization may occur simultaneously. After phase separation was allowed to proceed at room temperature for two months, all of the samples of blend B-3 and the samples B-4-01 and B-4-02 of blend B-4 showed accumulated PMPS isomeric crystals and a clear liquid phase of PDMS. Fig. 6 suggests a possible model for the turbidity behavior in the light scattering measurements. In such cases, the cloudiness was observed to rapidly increase when the temperature was lowered to the cloud point (stage 1). Upon phase separation, the separated phase of the blends may then display a crystallization behavior in the PMPS rich phase. The growing PMPS crystals were gradually deposited in the dense phase in the sample tube leading to a change of the cloudy scattering intensity (stage 2). In the meantime, the cloudiness was gradually reduced due to the density effect on the phase segregation. The detailed phase diagram thus includes a crystal–liquid boundary which may exist in the two-phase region. Such an experimental determination is difficult and beyond the capability of our current light scattering techniques.

The cloud temperatures of blend B-3, which include the critical temperature in the phase diagram, were found to have lower values than the melting temperature of the cyclic component, P_4-(I) ($T_m = 99°C$). This phenomenon implies that the liquid–liquid phase equilibrium can be generally superimposed onto the liquid–crystal equilibrium. In other words, the phenomenon of melting temperature depression, resulting from the crystalline–liquid equilibrium in the range of the miscible phase, could occur in accordance with the phase rule.

In order to further demonstrate this effect, the melting point depression of the cyclic PMPS P_4-(I) by linear PDMS (blend B-3) was determined using DSC. Four mixtures of B-3 were measured and the data are plotted in Fig. 6. Although the melting temperature of each was a little higher than the equilibrium melting point, due to the effect of heating rate in this non-equilibrium measurement, the melting points of the samples clearly show a depression relative to the melting point of the pure P_4-(I) stereoisomer ($\Delta T = 3°C$ for the blends having the highest PDMS content).

4. Concluding remarks

The results obtained in this investigation clearly demonstrate the usefulness of the interaction energy density in the Flory–Huggins treatment for evaluating the difference in thermodynamic behavior between cyclic structures and linear structures in polymer–polymer mixtures. In future it is desirable that cyclic blends should have their own theoretical considerations for their thermodynamics of mixing [20,30,31], which should incorporate the effect of topology/architecture, composition and molar mass. Further studies of polysiloxane containing blends are in progress and should lead to a more complete understanding of the phase behavior of siloxane–siloxane mixtures.

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References

[1] Noll W. Chemistry and technology of silicones, London: Academic Press, 1968.
[2] Semlyen JA. In: Clarson SJ, Semlyen JA, editors. Siloxane polymers, Englewood Cliffs, NJ: Prentice Hall, 1993.
[3] Young CW, Servais PC, Currie CC, Hunter MJ. J Am Chem Soc 1948;70:3758.
[4] Hickton HJ, Holt A, Homer J, Jarvie AW. J Chem Soc (C) 1966;00:149.

[5] Edwards CJC, Stepto RFT. In: Semlyen JA, editor. Cyclic polymers, Amsterdam: Elsevier, 1986 chap. 4.
[6] Semlyen JA et al. Studies of cyclic and linear polydimethylsiloxanes, Part 1–32. Polymer, 1977–1998.
[7] Wright PV, Beever MS. In: Semlyen JA, editor. Cyclic polymers, London: Elsevier, 1986 chap. 3.
[8] Kuo CM, Clarson SJ. Macromolecules 1992;25:2192.
[9] Kuo CM, Clarson SJ. J Eur Polym 1993;29:661.
[10] Kuo CM, Clarson SJ, Semlyen JA. Polymer 1994;35:4623.
[11] Semlyen JA, Wright PV. Polymer 1969;10:543.
[12] Wright PV, Semlyen JA. Polymer 1970;11:462.
[13] Clarson SJ. D Phil thesis. University of York, 1985.
[14] Clarson SJ, Semlyen JA. Polymer 1986;27:1633.
[15] Pierron ED, Hobbs CF, Parker DL, Bauer DJ. J. Heterocyclic Chem 1966;3:533.
[16] Roe RJ, Zin WC. Macromolecules 1980;13:1221.
[17] Jozsef N, Tamas G, Katalin BP. J Organometal Chem 1966;6:603.
[18] Patterson D. Macromolecules 1969;2:672.
[19] Patterson D. J Polym Sci, Part C 1968;26:81.
[20] Patterson D, Robard A. Macromolecules 1979;12:690.
[21] Flory PJ. Discuss Faraday Soc 1970;49:7.
[22] Flory PJ. Principles of polymer chemistry, Ithaca, New York: Cornell University Press, 1953.
[23] Allen G, Gee G, Nicholson JP. Polymer 1961;2:8.
[24] Wolf BA, Blaum G. Makromol Chem 1979;180:2591.
[25] Wolf BA, Blaum G. Makromol Chem 1981;182:1801.
[26] Beevers MS, Mumby SJ, Clarson SJ, Semlyen JA. Polymer 1983;24:1565.
[27] Mitlin VS, Sanchez IC. J Chem Phys 1993;99:533.
[28] Lemieux E, Prud'homme RE, Forte R, Jerome R, Teyssie P. Macromolecules 1988;21:2148.
[29] Beaucage G, Stein RS, Hashimoto T, Hasegawa H. Macromolecules 1991;24:3443.
[30] Barbarin-Castillo JM, McLure IA, Clarson SJ, Semlyen JA. Polym Commun 1987;28:212.
[31] Barbarin-Castillo JM, McLure IA. Polymer 1994;35:3075.