Thermodynamics of the lower critical threshold line in solutions of cyclic and linear poly(dimethylsiloxane)s in tetramethylsilane

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The main features of the critical line in presure–temperature–composition space for mixtures containing either a linear or a cyclic poly(dimethylsiloxane) (PDMS) in tetramethylsilane (TMS) are predicted through the use of the Patterson modification of Prigogine's corresponding-states theory, which incorporates the cell model of a liquid together with a simple van der Waals dependence of the configurational energy on volume. Two main kinds of critical lines are obtained: one is a continuous line for those mixtures with a small chain-length difference between the components, leading to a fairly good prediction of the liquid–vapour critical temperatures of the pure substances; and the other is a broken line for mixtures with a large chain-length difference between the polymer and solvent, indicating the occurrence of a lower critical threshold temperature (*LCTT*) at low polymer concentrations. A full set of temperature and pressure reduction parameters for both linear and cyclic oligomers and PDMS are reported, and are used as the basis for all the calculations with no adjustment whatsoever. It is predicted that the system of minimum chain length to show an *LCTT* is that containing a PDMS of 24 skeletal bonds, compared to the methane–hexane system in the n-alkanes, thus giving an insight into the more flexible and more expanded nature of the PDMS series. Results for the interaction parametert χ_1 confirm that any difference in chemical nature between TMS and the PDMS series may be largely ignored since the structural term $c_1\tau$ alone can account for the *LCTT* behaviour.

(Keywords: poly(dimethylsiloxane); thermodynamics; *LCTT* behaviour)

INTRODUCTION

The occurrence of lower critical end-points or threshold temperatures is rare in mixtures of molecules of similar size and is observed only in a small number of, chiefly, aqueous solutions of amines, ketones, alcohols and highly polar polymers. For a long time it was believed that mixtures that exhibit a lower critical threshold temperature (*LCTT*) were restricted to this kind of solution[1], since such systems exhibit a common pattern of molecular interactions in which by increasing the temperature the number of H bonds is decreased and thus the potential-energy dissimilarity between the 'unlike' molecules prevails for a region of partial miscibility.

It was not until much later[2] that a *LCTT* was shown to be a completely general phenomenon for solutions of polymers in low-molar-mass solvents. This fact had scarcely been noticed previously because it generally lies well above the boiling point of the solvent, and indeed often occurs at temperatures close to the solvent liquid–vapour critical point.

By contrast, it is now well recognized that the solubility of a polymer in a solvent depends on subtle differences between the polymer and the solvent. At low temperatures, chemical dissimilarity may give rise to an upper critical threshold temperature (*UCTT*) while at high temperatures there exists an *LCTT* which is caused essentially by the large difference between the liquid–vapour critical temperatures of the components of the mixture. These facts make polymer mixtures *peculiar* since the *LCTT* can lie well above the *UCTT*, unlike the more common, although still relatively rare, occurrence of closed-loop immiscibility in which the *LCTT* invariably lies below the *UCTT*. In this work the choice of solvent was intended to minimize such dissimilarity, and we have observed no *UCTT* behaviour in any of the systems discussed here.

Patterson and coworkers[3–6] have given a qualitative explanation of the *LCTT* in polymer mixtures in terms of the free-volume difference between polymer and solvent. According to this treatment, the solvent is more expanded than the polymer, and this 'free-volume dissimilarity' arises from the difference in size or chain length between the polymer and solvent molecules.

A mixture of a polymer in a chemically identical homologous solvent of low molecular weight has little 'contact-energy dissimilarity', but nevertheless the free-volume dissimilarity persists and becomes the direct cause of the two-liquid phase separation. In this context mixing resembles the condensation of a gas (solvent) into a dense medium (polymer).

In this paper we discuss mixtures of substances of similar chemical nature, since it has been demonstrated

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that tetramethylsilane (TMS) behaves better as the forerunner of the dimethylsiloxane series than methane does to the n-alkanes[7]. Since for such substances only the free-volume dissimilarity is significant in giving rise to the liquid–liquid phase separation, attention will be focused on the following: (a) the demonstration that, for the more flexible and more expanded dimethylsiloxanes, compared to the n-alkanes, the appearance of the *LCTT* is associated with a much larger chain-length difference between polymer and solvent than in the otherwise analogous unihomologous n-alkane mixtures; (b) the search for the linear and cyclic PDMS first to exhibit an *LCTT* with the monomeric member of the series; (c) an analysis of the extent to which the cyclic PDMS polymers differ from the linear PDMS polymers in the relative positions of their *LCTT*s; (d) an attempt to predict, in this our first theoretical approach to the problem, the critical lines in the pressure–temperature–composition space for PDMS mixtures by applying the principle of corresponding states and a cell theory used before with success by Patterson and Delmas[8] for unihomologous mixtures of n-alkanes; and to (e) confirm, through the evaluation of the interaction parameter χ_1, the negligible influence of the molecular or energy dissimilarity between TMS and the PDMS compared to the contribution made by the free-volume or structural dissimilarity.

An account of the experimental results obtained for mixtures containing TMS as solvent is given together with the theoretical treatment.

EXPERIMENTAL

In a previous paper[9] we have given a full account of the experimental procedure followed for the determination of the *LCTT* of mixtures containing either linear or cyclic PDMS in the two tetramethyl solvents, TMS and 2,2-dimethylpropane (neopentane).

A large range of polymer samples of carefully separated fractions and differing chain lengths were tested in search of the smallest molecule to show a *LCTT*. It is observed experimentally that the shortest-chain-length linear PDMS to show two-liquid phase separation contains 166 backbone atoms. For the cyclic PDMS, a *LCTT* was attained for chain length greater than 266 atoms. In both cases the *LCTT* was found to be within 0.1% of the liquid–vapour critical point of the pure solvent. For the remaining higher-molar-mass samples, the *LCTT* values were about 10 K below that reference mark.

PREDICTION OF THE CRITICAL LINE

The most important assumption of the corresponding-states theory regarding chain molecules lies in the recognition of the different extents to which the pure liquid components, and the mixtures themselves, are expanded at any finite temperature *T*.

A characteristic difference between a polymeric and a monomeric liquid is the relatively low thermal expansion coefficient of the fomer, so that when a monomer and a polymer are mixed, their free volume (i.e. the volume available for expansion) per molecule changes on mixing, giving rise to an associated change in the enthalpy and the entropy of mixing. In the context of a cell theory, the molecules of the 'expanded' volatile solvent are located in smaller cells when mixed with a 'dense' polymer, while those of the polymer will be in larger ones. These changes, however, will not necessarily neutralize each other and ΔV_{mix} will then have a non-zero, usually negative, value.

The variant of the theory that is of interest for this work is that which supposes that the mixing functions and the properties of the mixture can be predicted from the known measured properties of the pure components. Therefore, the phase behaviour in the polymer–monomer mixtures that have been studied can be predicted semiquantitatively by a treatment based on the difference in thermal expansion of the components.

The method developed by Patterson and Delmas[8] for the prediction of the critical line in the pressure–temperature–composition space for mixtures of molecular chains is based on the simple smoothed-potential cell model of Prigogine and collaborators[10] in combination with a volume-dependent configurational energy based on a simple van der Waals liquid. According to Prigogine's corresponding-states principle in the form developed by Hijmans[11] for pure chain-molecule liquids, the molar configurational thermodynamic quantities are related to dimensionless reduced quantities (~) through reduction parameters (*), which are functions of a reduced temperature and pressure. Accordingly:

$$\begin{aligned} V(n,p,T) &= V^*(n)\tilde{V}(p,T) & V^* &= N_A (r^*)^3 r(n) \\ G(n,p,T) &= U^*(n)\tilde{G}(p,T) & U^* &= N_A \varepsilon^* q(n) \\ S(n,p,T) &= S^*(n)\tilde{S}(p,T) & S^* &= N_A k_B c(n) \\ &\text{and} & p^* &= S^*T^*/V^* \end{aligned} \qquad (1)$$

where the characteristic energy and size parameters ε^* and r^* have the same values for molecules of different chain length as long as they belong to the same homologous series, k_B and N_A are Boltzmann's and Avogadro's constants, respectively.

For the mixture the averages are required, hence:

$$G(p,T) = \langle U^* \rangle \tilde{G}(\langle \tilde{p} \rangle, \langle \tilde{T} \rangle) \qquad (2)$$

where

$$\langle U^* \rangle = x_1 U_1^* + x_2 U_2^* \qquad (3)$$

and

$$\langle \tilde{T} \rangle = x_1 \tilde{T}_1 + x_2 \tilde{T}_2 = T/\langle T^* \rangle \qquad (4)$$

The surface fraction x_1 is not necessarily equal to the volume or segment fraction φ_1 given by:

$$\varphi_1 = x_1 V_1^*/\langle V^* \rangle = x_1 r_1/(x_1 r_1 + x_2 r_2) \qquad (5)$$

but a simple case occurs if q and r, the effective number of segments in energy and volume, respectively, are in approximately the same proportion for the two components: for such a case $q_1/r_1 = q_2/r_2$, then $\varphi_i = x_i$. This assumption is obeyed by the dimethylsiloxanes[12], and is probably a reasonable approximation for all pairs of homologues if it can be safely assumed that the differences in the interactions between end and middle groups are negligible.

Differentiation of the total Gibbs function of the mixture with respect to the composition at constant pressure yields the critical conditions:

$$(\partial^2 G/\partial x^2)_{p,T} = (\partial^3 G/\partial x^3)_{p,T} = 0 \qquad (6)$$

With the Flory–Huggins approximation for the combinatorial entropy[13], differentiation of the total Gibbs function of the mixture yields the expression for the chemical potential of the solvent as:

$$\begin{aligned}\Delta\mu_1/RT = {} & \ln(1-\varphi_2)+(1-r^{-1})\varphi_2 \\ & +(U_1^*/RT)\{\tilde{G}(\langle\tilde{p}\rangle,\langle\tilde{T}\rangle)-\tilde{G}(\tilde{p}_1,\tilde{T}_1) \\ & +\varphi_2(\tilde{T}_1-\tilde{T}_2)[\partial\tilde{G}(\langle\tilde{p}\rangle,\langle\tilde{T}\rangle)/\partial\langle\tilde{T}\rangle]_{\langle\tilde{p}\rangle}\} \quad (7)\end{aligned}$$

Differentiation of equation (7) gives the critical conditions as:

$$\begin{aligned}& [1/(1-\varphi_2)+1/r\varphi_2] \\ & \quad +(U_1^*/RT)(\tilde{T}_1-\tilde{T}_2)^2(\partial^2\tilde{G}/\partial\langle\tilde{T}\rangle^2)_{\langle p\rangle}=0 \quad (8)\end{aligned}$$

and

$$\begin{aligned}& [1/(1-\varphi_2)^2-1/r\varphi_2^2] \\ & \quad -(U_1^*/RT)(\tilde{T}_1-\tilde{T}_2)^3(\mathrm{d}^3\tilde{G}/\mathrm{d}\langle\tilde{T}\rangle^3)_{\langle p\rangle}=0 \quad (9)\end{aligned}$$

The calculation of the critical line requires a model for the dependence of G on p and T, and since:

$$(\partial^2\tilde{G}/\partial\langle\tilde{T}\rangle^2)_{\langle p\rangle}=-\tilde{C}_p/\langle\tilde{T}\rangle \quad (10)$$

the critical conditions given by equations (8) and (9) may be written in terms of the reduced configurational heat capacity $\tilde{C}_p$.

The volume dependence of the configurational energy can be found from the smoothed-potential cell model of Prigogine and coworkers. Later, Flory and collaborators[14] developed a similar theory, so that:

$$\tilde{U}=-\tilde{V}^{-1} \quad (11)$$

The cell model yields:

$$\tilde{C}_p^{-1}=(1-\tfrac{2}{3}\tilde{V}^{-1/3})-2(1-\tilde{V}^{-1/3})/(\tilde{p}\tilde{V}^2+1) \quad (12)$$

with the equation of state:

$$\tilde{T}=(\tilde{p}\tilde{V}+\tilde{V}^{-1})(1-\tilde{V}^{-1/3}) \quad (13)$$

so that the critical conditions in terms of $\tilde{C}_p$ are obtained as:

$$\tilde{C}_p^{-1}(\langle\tilde{p}\rangle,\langle\tilde{T}\rangle)=c_1\tau^2(\langle T^*\rangle/T_1^*)[1/(1-\varphi_2)+1/r\varphi_2] \quad (14)$$

and

$$\begin{aligned}\mathrm{d}\tilde{C}_p^{-1}/\mathrm{d}\ln\langle\tilde{T}\rangle = {} & -\tilde{C}_p^{-1}-c_1\tau \\ & \times[(1/r)-\varphi_2/(1-\varphi_2)^2]/ \\ & [(1/r)+\varphi_2/(1-\varphi_2)] \quad (15)\end{aligned}$$

It can be seen from equations (14) and (15) that this approach involves the calculation of the temperature reduction parameters for both the solvent (T_1^*) and the long-chain solute (T_2^*), and also the structural parameter group (τc_1) given by:

$$\tau=(1-T_1^*/T_2^*) \quad (16)$$

which reflects differences in free volume between components, and c_1 is the effective number of segments in the monomer from the point of view of the entropy. This last term is well understood through the definition of $3c$ as the number of external degrees of freedom of a molecule[4].

Finally, it is well known that the interaction parameter χ_1 plays a very important role in the study of phase behaviour of dilute polymer solutions. The Prigogine theory[10] leads to the following expression for the interaction parameter[15,16]:

$$\chi_1=-(\tilde{U}_1/RT)\nu^2+(\tilde{C}_{p1}/2R)\tau^2 \quad (17)$$

where $\tilde{U}_1$ is the solvent configurational energy or $-\tilde{U}_1$ its vaporization energy, $\tilde{C}_{p1}$ is the solvent configurational heat capacity at zero pressure, and ν^2 is a term characterizing molecular differences between the polymer and solvent molecules, while τ^2 is the explicit term dealing with the free-volume differences between the two species.

Both $\tilde{U}_1$ and $\tilde{C}_{p1}$ can be expressed in terms of the van der Waals-type volume dependence of the configurational energy of the liquids (equation (11)). At the critical temperatures, equation (17) becomes:

$$\chi_1=0.5(1+r^{-1/2})^2 \quad (18)$$

where χ_1 is now the critical value of the interaction parameter and an implicit function of the terms $c_1\nu^2$ (energy dissimilarity), $c_1\tau^2$ (volume dissimilarity) and r, which can be taken as the ratio of molar volumes of the polymer and solvent. This equation, however, does not indicate whether this critical value yields an upper or a lower critical temperature, although for the systems of this work only *LCTT* behaviour was observed.

For homologous polymer and solvent mixtures, the term involving energy or molecular dissimilarity $c_1\nu^2=0$ or is very small compared to $c_1\tau^2$. In this case, equation (17) can be written as:

$$\chi_1=(\tilde{C}_{p1}/2R)\tau^2 \quad (19)$$

and the difference between the values calculated for χ_1 by means of equations (18) and (19) would be a direct indication of the degree of solute–solvent molecular dissimilarity.

REDUCTION PARAMETERS

The temperature and pressure reduction parameters for the polymer samples of this work have their origin in a phenomenological corresponding-states study performed before for the linear dimethylsiloxane oligomers dimer to hexamer[17]. More recently, this approach was extended to include TMS, the cyclic oligomers tetramer and pentamer, and three long-chain molecules, one cyclic and two linear PDMS[18]. A least-mean-squares fit yields the following relations for the reduction parameters, for numbers of backbone atoms n exceeding 7:

$$\begin{aligned}T^*/\mathrm{K} &= 6583[1-3.39/(n+5)] \\ V^*/\mathrm{cm^3\,mol^{-1}} &= (n-0.941)/0.029 \quad (20) \\ c/\mathrm{K} = S^*/R &= 0.8033+0.17n\end{aligned}$$

Table 1 contains the number-average number of skeletal bonds n_n, the pressure and temperature reduction parameters p^* and T^*, respectively, and the ratio r of numbers of segments for both the linear (L) and cyclic (R) poly(dimethylsiloxane)s to those of the monomer TMS.

For the solutions, the reduction parameters were taken as the averages, so that the calculations were performed by using:

$$\langle p^*\rangle=\varphi_1 p_1^*+\varphi_2 p_2^* \quad (21)$$

and

$$\langle T^*\rangle=\varphi_1 T_1^*+\varphi_2 T_2^* \quad (22)$$

after the values for the pure components were determined through the phenomenological corresponding-states treatment mentioned above.

Table 1 Symbol, number-average number of skeleton bonds, pressure and temperature reduction parameters, and the ratio of number of segments for TMS and the cyclic and linear poly(dimethylsiloxane)s

Sample	n_n	p^* (MPa)	T^* (K)	$r=r_2/r_1$
TMS	2	373	3921	1
Cyclic				
R1	83	277	6329	42
R2	154	274	6442	77
R3	264	272	6500	132
R4	364	271	6526	193
R5	504	271	6539	252
Linear				
L1	102	275	6376	51
L2	166	273	6453	83
L3	267	272	6501	134
L4	393	271	6527	197
L5	488	271	6538	244
L6	573	271	6544	286
L7	818	271	6556	409

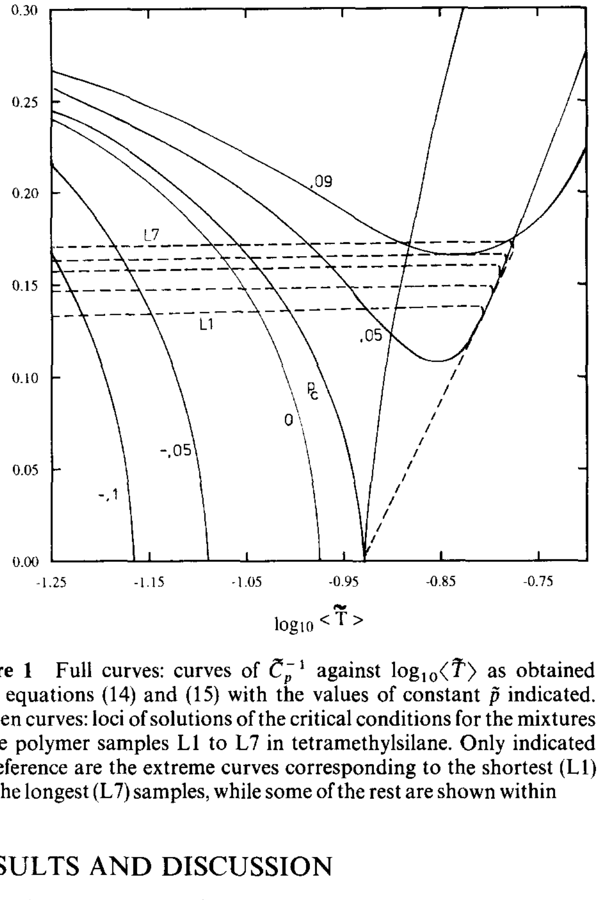

Figure 1 Full curves: curves of $\tilde{C}_p^{-1}$ against $\log_{10}\langle\tilde{T}\rangle$ as obtained from equations (14) and (15) with the values of constant $\tilde{p}$ indicated. Broken curves: loci of solutions of the critical conditions for the mixtures of the polymer samples L1 to L7 in tetramethylsilane. Only indicated for reference are the extreme curves corresponding to the shortest (L1) and the longest (L7) samples, while some of the rest are shown within

RESULTS AND DISCUSSION

In order to test both the procedure followed for the calculation of the critical lines and the reliability of our computer programs, a full set of calculations was carried out using the data given by Patterson and Delmas[8] for the n-alkanes. The results obtained for the mixtures of methane + hexane, methane + octane and methane + decane were identical to those reported by them and so it was considered that the programs had passed the test.

The gas–liquid critical line was then calculated for the mixtures with TMS as the first component and the heavier cyclic and linear PDMS as the long-chain second component. For the calculations the reduction parameters were taken from *Table 1*, whereas the entropy-related term c_1 for TMS was found to be equal to 1.133[18].

Figure 1 shows a selection of the curves of $\tilde{C}_{p1}$ as calculated from equation (14) for the van der Waals model. The plots of $\tilde{C}_{p1}$ against $\log_{10}\langle\tilde{T}\rangle$ have some chosen typical values of $\langle\tilde{p}\rangle$ indicated. If a calculation was made for each value of φ_2, then *Figure 1* shows the values of $\langle\tilde{p}\rangle$ and $\log_{10}\langle\tilde{T}\rangle$ to give the correct value of $\tilde{C}_{p1}$ and the slopes of $\tilde{C}_{p1}$ against $\log_{10}\langle\tilde{T}\rangle$ to satisfy the critical conditions.

Since the number of systems discussed here is very substantial, in *Figure 1*, and those following thereafter, we show only the critical lines for a few representative mixtures identified by the symbol given to the long-chain component, chiefly a few of the linear PDMS, since for mixtures containing cyclic PDMS the results became graphically very similar. The locus of the critical conditions for these systems is shown as φ_2 moves from the smallest values to 1 as a loop around which the point moves clockwise; it ends at $\tilde{C}_{p1}$ equal to zero and $\tilde{T}=0.1187$, corresponding to the critical point of the pure components. At low φ_2 values, the locus has moved from negative values of $\langle\tilde{p}\rangle$, showing that an *LCTT* occurs in these systems as the critical line crosses the vapour pressure of the solution. At even lower values of φ_2 the locus has moved to even more negative values of $\langle\tilde{p}\rangle$ and, in all these cases, composition regions exist where there is no solution of equations (14) and (15). This is due to the greatly increased value of r for the systems containing a long-chain polymer in a short monomeric solvent, and shows up as an artefact of the model used. This was also observed by Patterson and Delmas for methane + long-chain alkane mixtures. For this last reason alone, the loop appears open to the left of the plot in *Figure 1*.

A closed loop (not shown) was obtained for all the mixtures containing TMS + oligomers of either linear or cyclic chain. Such a loop never crosses to negative values of $\langle\tilde{p}\rangle$ so that for those systems *LCTT* is not attainable, in agreement with experiment.

Figure 2 was obtained by projecting the critical lines on the $\langle\tilde{p}\rangle$–$\langle\tilde{T}\rangle$ plane for a few chosen systems as mentioned above. Owing to the large chain-length difference between the two components, the loop drops to negative values of $\langle\tilde{p}\rangle$ at low values of φ_2, below the vapour pressure of the solution. The three-phase line and the *LCTT* which thus appear are predicted for all the systems dicussed here.

After introducing the pressure and temperature reduction parameters in *Figure 2*, a full insight into the predicting 'muscle' of this treatment is achieved and *Figure 3* is then obtained. *Figure 3* shows that, at temperatures slightly higher than the critical temperature of pure TMS, the critical line of all the systems undergoes a sharp drop, bringing these lines below the vapour pressure of the solution, and a three-phase line appears, thus predicting the appearance of an *LCTT*. *Figure 4* shows the actual predicted critical temperatures as a function of polymer volume fraction.

The calculated values for the predicted critical solution threshold temperatures are given in *Table 2*. In all cases, the predicted *LCTT* lies below the liquid–vapour critical temperature of pure TMS, 448.60 K, and according to experimental evidence *LCTT* is higher for the shorter-chain polymer samples used. For comparison, *Table 2* also reports the experimental values of *LCTT* from our previous paper[9], together with the value of φ_2 for which these *LCTT* predictions were obtained. However, this

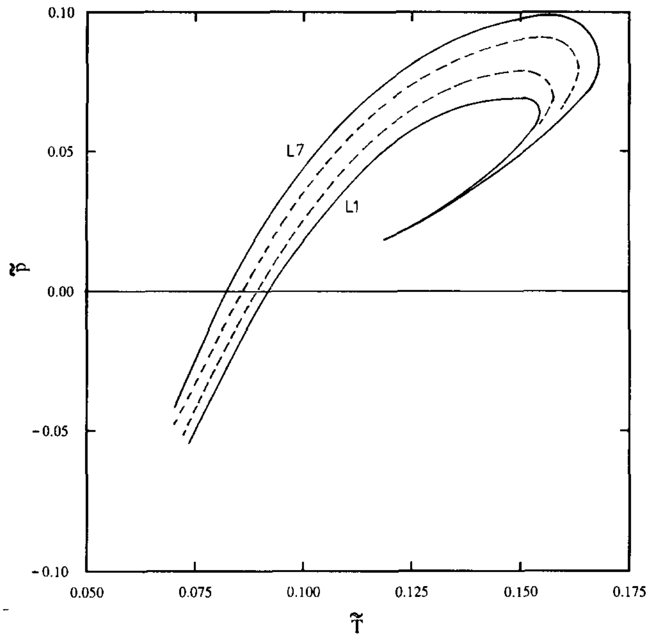

Figure 2 The reduced $\tilde{p}$–$\tilde{T}$ projection of the predicted critical lines for the mixtures of the polymer samples L1 to L7 in tetramethylsilane. Only indicated for reference are the extreme curves corresponding to the shortest (L1) and the longest (L7) samples, while some of the remaining are shown in the broken curves between

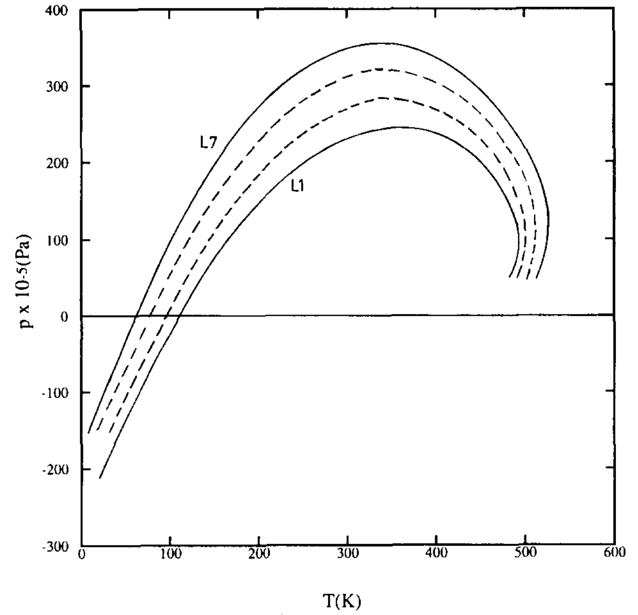

Figure 3 The calculated p–T projections of the critical lines for the mixtures of the polymer samples L1 to L7 in tetramethylsilane. Only indicated for reference are the extreme curves corresponding to the shortest (L1) and the longest (L7) samples, while some of the remaining are shown in the broken curves between

theoretical approach predicts the occurrence of *LCTT* for all the polymer samples tested, against the experimental findings that samples L1, R1 and R2 do not show the two-liquid phase separation, and that it was not until very close to the critical temperature of TMS that L2 and R3 achieved their *LCTT*.

We have no data concerning the critical pressures and temperatures of the polymer samples used in this work. According to the results of these calculations it is possible to obtain a prediction of the critical properties of the polymer samples, shown also in *Table 2* under the heading of T_c with values in the range of 479 to 506 K, but no assessment will be attempted on these results for the reasons given above, except to state that, although this approach was shown to be quite accurate by predicting T_c of the n-alkanes[8], it was less reliable for the prediction of the critical pressures of the pure components if no adjustment is made to the reduction parameters used for the calculations. This is just the case in this work, in which the predicted critical pressures for TMS and the pure oligomers are higher than the experimentally determined values by a factor of 4.

Calculations were also performed in order to obtain the value of the interaction parameter χ_1 and its critical value leading to liquid–liquid phase separation for each system, and assessing its critical value at the point where the vapour pressure of the mixture changes sign from negative to positive values. *Table 2* reports the values of χ_1 as calculated from both equations (18) and (19).

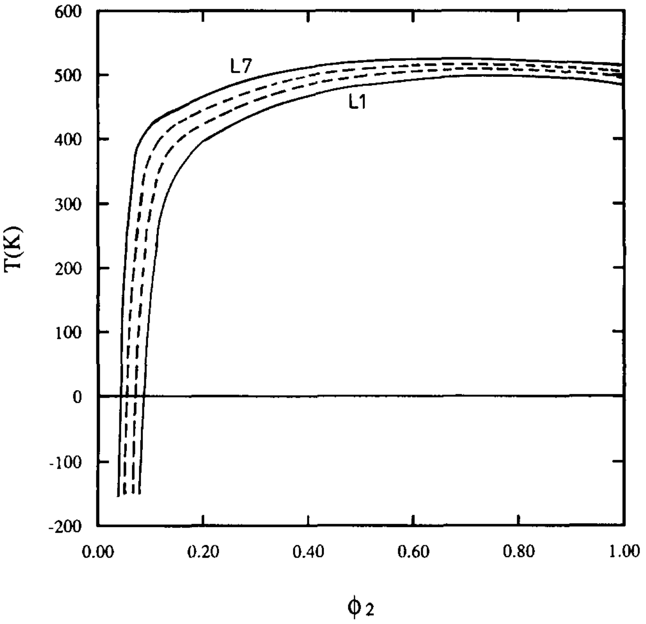

Figure 4 Predicted critical temperatures *versus* volume fraction for the mixtures of the polymer samples L1 to L7 in tetramethylsilane. Only indicated for reference are the extreme curves corresponding to the shortest (L1) and the longest (L7) samples, while some of the remaining are shown in the broken curves between

Table 2 Experimental and predicted *LCTT*, volume fraction φ_2, predicted critical temperature of the pure components, and critical value of the interaction parameter χ_1 for the cyclic and linear PDMS

	LCTT(K)			T_c(K)	χ_1	
Sample	expt	theory	φ_2	theory	eqn (18)	eqn (19)
Cyclic						
R1	–	387	0.0960	479	0.666	0.639
R2	–	369	0.0817	487	0.620	0.593
R3	448	355	0.0676	494	0.591	0.567
R4	445	347	0.0582	497	0.575	0.554
R5	443	341	0.0521	504	0.565	0.547
Linear						
L1	–	381	0.0921	479	0.650	0.621
L2	449	367	0.0798	488	0.616	0.589
L3	446	355	0.0672	494	0.590	0.567
L4	443	346	0.0577	497	0.574	0.553
L5	441	341	0.0528	504	0.566	0.547
L6	440	340	0.0494	505	0.561	0.543
L7	439	335	0.0423	506	0.551	0.536

Table 3 Pressure and temperature reduction parameters, and the liquid–vapour critical temperatures for the linear and cyclic dimethylsiloxane oligomers

			T_c (K)	
Substance	p^* (MPa)	T^* (K)	theory	reported
TMS	373	3921	463	448.6[a]
Linear				
Dimer	358	4420	522	516.6[b]
Trimer	343	4718	557	562.9[b]
Tetramer	335	4970	587	599.4[b]
Pentamer	324	5158	609	629.0[b]
Hexamer	318	5291	625	653.2[b]
Cyclic				
Tetramer	363	4860	574	586.5[c]
Pentamer	347	5180	611	593.0[d]

[a] From ref. 19
[b] From ref. 20
[c] From ref. 21
[d] From ref. 22

Finally, calculations were carried out for the mixtures TMS + linear (dimer to hexamer) and cyclic (tetramer and pentamer) dimethylsiloxane oligomers, so that a prediction of the critical temperatures of the pure oligomers could be obtained and a comparison with values reported in the literature would be possible. *Table 3* lists together the predicted and literature-reported values of T_c, where the disagreement amounts to no more than 3%.

If is worth noting that the iterations in the execution of the computer programs were performed with increments of only 0.0001 in the values of φ_2, since the changes in both $\tilde{C}_{p1}$ and $\mathrm{d}\tilde{C}_{p1}/\mathrm{d}\log_{10}\langle\tilde{T}\rangle$ are very sharp in the low concentration range.

CONCLUSIONS

The treatment described in this work has given the essential features of the critical lines for binary mixtures of TMS + linear or cyclic PDMS over a very wide range of chain lengths without recourse to any adjustment in the pressure or temperature reduction parameters.

For the systems containing a short-chain-length dimethylsiloxane, there is a calculated continuous critical line (not shown) together with an excellent prediction of the liquid–vapour critical temperature for the less volatile component, as shown for both the linear and cyclic oligomers of *Table 3*. When the chain-length difference between components is increased, the critical line is broken at very low concentrations of the longer molecules, thus predicting the occurrence of an *LCTT*.

In general, the relative differences in the known reduction parameters for the polymers used make it hard to predict qualitatively the relative differences between linear and cyclic chains observed in the experiments. However, on the basis of T^* alone we should expect theory to reproduce the results in accordance with the criteria:

$$T^*(\text{cyclic}) < T^*(\text{linear}) \quad \text{and} \quad LCTT(\text{cyclic}) > LCTT(\text{linear})$$

as observed in the experimental part of this work for those solutions containing polymers of similar chain length. However, in detail the predicted values of *LCTT* are insensitive to whether the polymer is cyclic or linear in nature.

The theory as it stands, together with the reduction parameters used for the predictions, cannot give a finer prediction of the relative *LCTT*s mentioned above, chiefly because the predictions are within an overall range of 46 K, compared to only 10 K for the experiments. Also, the reduction parameters are very similar in value for both kinds of species if their chain lengths are similar, yielding predictions of about the same order.

However, the pattern shown by the predicted *LCTT* and φ_2 values is according to experience. In general, the *LCTT* decreases as the polymer chain length increases, but theory gives this variation in steps of about four times the experimentally observed values and also the predicted *LCTT* values lie, chiefly, nearly 100 K below the experimental range. This was observed and discussed also by Patterson and Delmas who pointed out that this was to be expected for polymer mixtures in general.

Computations were also made in order to determine the system with the shortest chain-length difference to show an *LCTT*. For this procedure the reduction parameters p^* and T^* were calculated by the general expressions given in equation (20) in terms of n, and also r was determined. According to these calculations, theory predicts that *LCTT* should be shown by a PDMS of $n_n = 24$ skeletal bonds, short of the experimental evidence for $n_n = 166$ or $n_n = 264$ for the linear and cyclic PDMS, respectively, but large when compared to the series of the n-alkanes for which the 'monomer' methane + hexane is predicted as the system with the smallest chain-length difference to show an *LCTT*.

Two differing approaches were compared in the calculation of the critical value of the interaction parameter χ_1, one based on Flory's theory and the other based on a free-volume dependence only, directly related to a phenomenological corresponding-states treatment. Both sets of calculations, shown in *Table 2*, indicate that molecular dissimilarities between TMS and the cyclic or linear PDMS contribute only marginally to the value of χ_1, whereas the free-volume dissimilarity accounts for up to 97% of its value, thus confirming once again the unihomologous nature between TMS and the poly(dimethylsiloxane)s.

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