End Group Effects on the Phase Behavior of Polymer Blends: Poly(dimethylsiloxane) and Poly(methylphenylsiloxane) Blend

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ABSTRACT: A computational method, using the Flory−Huggins lattice model, the extended random copolymer theory, and a molecular modeling method to account for the end group effect on the χ interaction parameter and on the value of the temperature where the phase separation of a polymer blend occurs, is proposed. The overall χ interaction parameters are calculated based on the individual segmental interaction parameters of the end groups and the monomeric units in the polymer. The individual segmental interaction parameters are calculated from a combination of the Flory−Huggins lattice model and molecular simulation techniques. The χ interaction parameters of poly(dimethylsiloxane) (PDMS) and poly(methylphenylsiloxane) (PMPS) blends are calculated, and the results are compared with those from the experiment.[1,2] The end groups on PDMS and PMPS are α,*ω*-trimethylsilyl and α,*ω*-dimethylsilanol. The simulation results indicate that the end groups and their fractions in polymers at low molecular weights can significantly affect the χ interaction parameters and the phase separation temperatures. For example, in the case of blended polymers having 14 repeat units, the critical solution temperature of α,*ω*-trimethylsilyl-terminated PDMS and α,*ω*-dimethylsilanol-terminated PMPS is found to be 192 °C lower than that of α,*ω*-dimethylsilanol-terminated PDMS and α,*ω*-trimethylsilyl-terminated PMPS.

Introduction

Low molecular weight polymers have a relatively high ratio of end groups that are chemically different from the rest of the chains; hence different physical properties are expected when they are compared with high molecular weight polymers.[3] Poly(organosiloxanes) of well-defined structures with different end groups can be readily prepared. Therefore, such systems can provide the opportunity to study both qualitatively and quantitatively the end group effects for many physical properties. For example, it was found that the adsorbed amounts of different end-functionalized poly(dimethylsiloxanes) (PDMS) of low molecular weight on silica and aluminum surfaces from carbon tetrachloride solution were in the following order:[4]

$$\text{HO}- > \text{H}- > \text{CH}_3- > \text{CH}{=}\text{CH}$$

where HO− is hydroxyl-terminated PDMS, H− is hydrogen-terminated PDMS, CH_3- is methyl-terminated PDMS, and $CH_2{=}CH-$ is vinyl-terminated PDMS. Thus, the results indicated that PDMS with end groups having a high surface affinity such as the HO− group will adsorb to a greater extent.

The characteristics of Langmuir monolayer formation from PDMS oligomers terminated with methyl, hydroxyl, epoxide, carboxyl, or amine functionalities were affected by their end group types.[5] The monolayers of PDMS oligomers with strong anchors, such as amine, were compressed into close-packed structures, whereas PDMS with weak anchors, such as methyl, formed a helical state.

Another study found that amine, hydroxyl, and methyl end groups had different effects on the surface tension of PDMS oligomers.[6] The surface tension increased with molecular weight for the methyl-terminated PDMS, decreased with molecular weight for the amine-terminated PDMS, and was nearly independent of molecular weight for the hydroxyl-terminated PDMS. It was also shown[7] that alkylamine end groups, which had a high surface energy, led to depletion of the terminal groups at the vacuum−polymer interface for α,*ω*-difunctional PDMS oligomers.

The end groups were capable of modifying the interfacial tension between different polymers.[8−10] When polybutadiene had carboxyl groups at the ends of the chains, it formed complexes at the interface with PDMS chains having amine functionalities as end groups, despite the fact that polybutadiene is immiscible with PDMS. Blends of polybutadiene and PDMS terminated with amine end groups showed a reduction of interfacial tension by as much as 30% compared with methyl-terminated end groups. The interfacial tension reduction for the amine-terminated PDMS was attributed to the change in the interactions resulting from the end group substitution.

It was found that for low molecular weight poly(propylene glycol), the upper critical solution temperature values, T_C, of PDMS and poly(propylene glycol) terminated with acetylated groups at both ends were lower by approximately 50 °C as compared with hydroxyl-terminated poly(propylene glycol).[11] It was also reported that a decrease in mutual miscibility was observed as the molecular weight of the less polar component was raised. Therefore, a chain length of optimum miscibility exists for the glycol component in blends of low molecular weight dimethylsiloxane and low molecular weight poly(propylene glycol).

It is difficult to predict the role of the end groups as a tool to modify the properties of various polymer blends before experimental measurements are performed. This paper attempts to estimate the effect of the end groups upon the properties of blended polymers, using for validation purposes a system which consists of poly(methylphenylsiloxane) (PMPS) mixed with poly(dimethylsiloxane) (PDMS).

The effects of the end groups on PDMS and PMPS blends on the phase behaviors were studied experimentally in detail.[1,2] In these studies, both PDMS and PMPS had low molecular weights with a repeat unit length from 11 to 15. PDMS was terminated with an

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α, ω-trimethylsilyl or α, ω-dimethylsilanol end group, and PMPS was terminated with an α,ω-trimethylsilyl group. An upper critical solution temperature (UCST) type phase diagram was observed. The results indicated that the interaction parameters of PMPS with a trimethylsilyl end group and PDMS with a trimethylsilyl or dimethylsilanol end group had comparable values, 0.111 and 0.123, respectively, at the critical solution temperature.[1,2] The dimethylsilanol end group on PDMS did not significantly change the phase separation temperature of the PDMS and PMPS blend compared with the trimethylsilyl-terminated PDMS.

All the experimental studies essentially indicated that the end group of a polymer chain can be treated as a chemically and energetically distinctive component from the monomeric units. In particular, experimental measurements have provided evidence that the end groups do influence the χ interaction parameter and the miscibility behavior of a polymer blend. However, measurement of the χ interaction parameter between the end group and monomeric unit by experiment cannot be performed practically. Thus, theoretical calculation is the only means to quantify the end group effect. In this report, we attempt to explain this effect on the phase separation by calculating the χ interaction parameters of PDMS and PMPS blends with and without end group effects, using molecular simulation methods. We also compare the results of the phase separation temperatures with the experimental data.[1,2]

Methodology

The miscibility behavior of a mixture can be described as a phase diagram showing the phase change as a function of temperature and composition. A phase diagram can be calculated from the thermodynamic analysis of the free energy of mixing. The Flory−Huggins lattice model is the simplest and most widely used to calculate the free energy of mixing,[12] and thus the phase diagram. The free energy of mixing per mole of lattice site, ΔG, in the Flory−Huggins lattice model is described as

$$\Delta G/RT = (\phi_1/N_1)\ln\phi_1 + (\phi_2/N_2)\ln\phi_2 + \chi\phi_1\phi_2 \quad (1)$$

The first two terms on the right side of the equation are the contributions from the combinatorial entropy of mixing long-chain polymer. The last term is the contribution from the enthalpy of mixing. In eq 1, ϕ_1 and ϕ_2 are the volume fractions of components 1 and 2, respectively, N_1 and N_2 are the chain lengths (the so-called repeat units) of components 1 and 2, respectively, and χ is the so-called interaction parameter, which is a complex function of temperature, composition, and pressure of the mixture.

One conclusion from the thermodynamic analysis of the Flory−Huggins lattice model is that most blends of high molecular weight polymers will not be miscible. This is a direct consequence of a negligibly small combinatorial entropy of mixing long-chain polymers plus an unfavorable positive enthalpy of mixing, especially when there is no favorable specific interaction between the two polymers such as hydrogen-bonding interactions.

The calculation of the interaction parameter χ_{blend} between two random copolymers, (A_xB_{1-x}) and (C_yD_{1-y}), as shown in the equation below, is known.[13]

$$\chi_{\text{blend}} = xy\chi_{AC} + (1-x)y\chi_{BC} + x(1-y)\chi_{AD} + (1-x)(1-y)\chi_{BD} - x(1-x)\chi_{AB} - y(1-y)\chi_{CD} \quad (2)$$

Here, x and y are the coefficients which can be represented by the mole fraction of A in the AB copolymer and C in the CD copolymer, respectively.[13] χ_{AC}, χ_{BC}, χ_{AD}, χ_{BD}, χ_{AB}, and χ_{CD} are the individual segmental interaction parameters between a given pair of monomers.

In the above mean-field random copolymer model, the χ interaction parameter from a pair in the same copolymer such as the A monomeric unit and the B monomeric unit is subtracted from the overall χ_{blend} interaction parameter by the appropriate amount of these two monomeric units in the copolymer. On the other hand, the χ interaction parameter from a pair in two different copolymers such as the A monomeric unit and the C monomeric unit is added to the overall χ_{blend} interaction parameter by the appropriate amount. This formulation has been successfully applied to explain miscibility behaviors of random copolymer blends.[14−16]

As stated previously, for a low molecular weight polymer that has a relatively high proportion of chemically different compositions at the two ends, the end groups of the polymer have a strong effect on the phase separation behavior of a mixture. Qualitative analysis using the above random copolymer theory to explain the end group effect on the χ interaction parameter has been described.[9] In order to calculate this effect quantitatively, a polymer mixture with two different end groups can be described as $[A_{(1-n)/2}\,B_nC_{(1-n)/2}]$ and $[X_{(1-m)/2}Y_m\text{-}Z_{(1-m)/2}]$. Here A and C are the two end groups of the ABC polymer, and X and Z are the two end groups of the XYZ polymer. The mole fractions of n and m range between 0.0 and 1.0 and can be calculated from the repeat unit lengths as follows.

$$n = (N_1 - 2)/N_1 \quad (3)$$

$$m = (N_2 - 2)/N_2 \quad (4)$$

We further assume that each end group and repeat unit of the polymer occupies one lattice site in the Flory−Huggins lattice model. We can extend the original method for calculation of the χ interaction parameter between two random copolymers[13] to include the end group effect in two homoplymers with two different end groups. Based on the individual segmental interaction parameters, the overall interaction parameter of the polymer mixture χ_{blend} with the end group effects can be calculated as

$$\begin{aligned}\chi_{\text{blend}} = {} & (1-n)(1-m)\chi_{AX}/4 + (1-n)m\chi_{AY}/2 + (1-n)(1-m)\chi_{AZ}/4 + n(1-m)\chi_{BX}/2 + nm\chi_{BY} + \\ & n(1-m)\chi_{BZ}/2 + (1-n)(1-m)\chi_{CX}/4 + (1-n)m\chi_{CY}/2 + (1-n)(1-m)\chi_{CZ}/4 - \\ & (1-n)n\chi_{AB}/2 - (1-n)(1-n)\chi_{AC}/4 - n(1-n)\chi_{BC}/2 - (1-m)m\chi_{XY}/2 - \\ & (1-m)(1-m)\chi_{XZ}/4 - m(1-m)\chi_{YZ}/2 \quad (5)\end{aligned}$$

The above calculation indicates that the interaction parameter may be decreased if the intramolecular mutual repulsions between the end groups and the main repeat units in the same polymer are sufficiently large to overcome the overall intermolecular interactions of the segments in the two different polymers. For example, a strong repulsive interaction between the A and the C end groups encourages mutual miscibility of the two polymers. It also indicates that the end group effect decreases as the molecular weight of polymers increases and becomes negligible if n and m are close to 1.0, that is, the case for high molecular weight polymers. Equation 5 can also be reduced to the form of eq 2 for a random copolymer blend with an appropriate composition. The above method is only applicable to describe the end group effects to the phase behaviors of monodisperse end-functional polymers.

There has been a recent surge of interest in using molecular modeling and atomistic simulation technologies to study the physical properties of polymeric materials.[17−19] Indeed, a number of molecular modeling techniques have been developed to estimate the miscibility behavior of a polymer blend.[20] For example, a combination of the Flory−Huggins lattice model and molecular simulation techniques was developed to calculate the temperature dependence of the χ interaction parameter of a binary mixture.[21] The method consists of a Monte Carlo sampling with the excluded volume constraint to calculate the heat of mixing associated with the pairwise interaction and the coordination number. This combination of the Flory−Huggins theory and the molecular simulation technique provides an opportunity to study the thermodynamic behavior of a binary mixture.

In our simulation, the following form of the temperature dependence of the energy of mixing, $\Delta w(T)$, in units of kcal/mol is used

$$\Delta w(T) = a + b/T + c/T^2 \tag{6}$$

where a, b, and c are the coefficients specifying $\Delta w(T)$, the energy of mixing for a specific mixture. The above analytical functional form of $\Delta w(T)$, the energy of mixing as a function of temperature, is selected because it generates the least standard deviation in fitting the simulated mixing of energy. The χ interaction parameter and $\Delta w(T)$, the energy of mixing, are related by

$$\chi = \Delta w(T)/(RT) \tag{7}$$

The above algorithm has been implemented in CERIUS2 molecular simulation software.[22] Because we have used the assumption that each end group and repeat unit of the polymer occupies one lattice site in the Flory−Huggins lattice model, in order to minimize the effect caused by the size difference of different segments in using the molecular modeling calculation, we have done the following. The energy of mixing, Δw, is calculated as

$$\Delta w = (z_{12}w_{12} + z_{21}w_{21} - z_{11}w_{11} - z_{22}w_{22})/2 \tag{8}$$

where z_{ij} and w_{ij} ($i,j = 1,2$) are the coordination number as defined in the original Flory−Huggins lattice model and the interaction energy of a particular ij segment pair, respectively. Thus, the averaged values of the calculated interaction energies of w_{AB} and w_{BA} are used to minimize the difference due to the effect caused by the A segment surrounded by the B segment or the B segment surrounded by the A segment. No significant difference was observed between w_{AB} and w_{BA} for the segments included in this study. The details of the procedures as how to account for this effect and the simulation techniques can be found in ref 22. An algorithm to approximate the possible coordination number of nearest neighbors in contact with the central segment was also proposed.[21] The coordination number was explicitly calculated for each of the possible segment pairs using molecular simulations that employ the nearest neighbor packing technique. The effects of polymer connectivity and end groups were also considered. The two ends of a monomeric unit and one end of an end group are connected to other segments, making these positions inaccessible to other segments in the packing. Thus, dummy atoms are introduced at these end positions in the molecular simulation. Any segment in contact with the dummy atoms was rejected in the simulation.

The original Flory−Huggins lattice model[12] in eq 1 uses the mole fraction for the mixed components. An alternate route consists of expressing eqs 1 and 2 in terms of volume fraction following the work of Roe and Zin[24] and models to characterize random copolymers.[15,23] In this case, the χ interaction parameter is replaced by the Λ interaction energy density parameter.[15,24] The χ interaction parameter and the Λ interaction energy density parameter are related to each other by

$$\chi = \Lambda V_r/(RT) \tag{9}$$

where V_r is a volume of reference. A detailed discussion as how the coordination number and segment size affects the simulation results can also be found in ref 21 and in the CERIUS2 software manual.[22]

The experiments[1,2] allow for determination of the interaction energy density, and the computational techniques[21] allow for calculation of the interaction energy Δw_{12} between two segments participating in the mixture. For practical purposes, if we address the equivalence between experimental and computed energies, a critical factor is the equality of the energy obtained when one segment (A) is surrounded by the other (B) with the energy obtained when B is surrounded by A. In our example, this was the case.

In all our simulations, a total of 30 000 samples was calculated for every segment pair in order to obtain statistically meaningful data of the pairwise interaction energies. The fitting temperature range between the calculated pairwise interaction energies and the above theoretical model was from 200 to 600 K.

As with any molecular modeling technique, the results depend on the accuracy of the force field employed. The original universal force field parameters[25] were modified to describe siloxane-containing molecules in the condensed state.[26] For the same reason, of using parameters that characterize molecular structures in the condensed state, we used the van der Waals parameters for the carbon and hydrogen atoms in the phenyl rings and hydrocarbons as given by Lii and Allinger.[27]

Results and Discussion

No End Group Effect. In Figure 1, the χ interaction parameter versus temperature from molecular simulation is plotted for the PDMS and PMPS mixture. In Table 1, the number of repeat units, the corresponding critical interaction parameters (χ_C), and the upper critical solution temperature (T_C) from the simulations are given. In this table, the same repeat unit number for both polymers was used to calculate the parameters at critical point. Following the analysis of the Flory−Huggins lattice model, the critical interaction parameter χ_C is equal to $2/N$ when the number of repeat units (N)

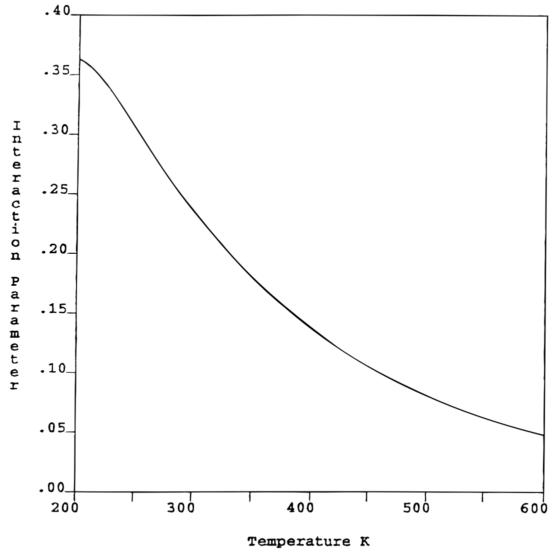

Figure 1. Interaction parameter vs temperature of PDMS and PMPS blend, no end group effects are considered.

Table 1. Critical Interaction Parameters and Critical Solution Temperatures of PDMS and PMPS Blend from the Simulation (No End Group Effects Are Considered)

	repeat unit					
	10, 10	12, 12	14, 14	16, 16	18, 18	20, 20
χ_C	0.200	0.167	0.143	0.125	0.111	0.100
T_C, K	332	366	394	418	440	460

Table 2. Coefficients *a*, *b*, and *c* and the Fitted Standard Deviations of the Energy of Mixing $\Delta w(T)$ for PDMS and PMPS Polymers

interaction pair	*a*	*b*	*c*	std dev
dms, mps	−0.1064	122.3	−14390	0.00254
dms, hms	0.1349	94.76	45170	0.000503
dms, tms	−0.1178	119.5	−19410	0.00291
dms, hsi	−0.1245	17.40	−7609	0.000103
dms, sil	0.1355	312.6	−63860	0.00778
mps, tms	−0.2590	193.8	−35370	0.00530
mps, hms	0.1560	−43.02	59090	0.00222
mps, hsi	−0.1584	102.8	−21640	0.00160
mps, sil	−0.1913	765.1	−124500	0.00451
hsi, sil	−0.02518	399.8	−64640	0.00439
hsi, tms	−0.08359	107.2	−12960	0.00201
hsi, hms	0.1423	158.4	30150	0.000424
sil, tms	−0.2695	881.1	−139800	0.00150
sil, hms	−0.07627	1308	−73440	0.00180
hms, tms	0.04239	78.09	13920	0.000268

Table 3. χ Interaction Parameters among the End Groups and the Repeat Units of PDMS and PMPS Polymers

interaction pair	300 K	400 K	500 K
dms, mps	0.237	0.138	0.081
dms, hms	1.598	0.823	0.508
dms, tms	0.109	0.0750	0.0438
dms, hsi	−0.253	−0.162	−0.121
dms, sil	0.785	0.652	0.509
mps, tms	−0.0101	0.00557	−0.0130
mps, hms	1.123	0.526	0.308
mps, hsi	−0.0942	−0.0461	−0.0396
mps, sil	1.636	1.187	0.846
hsi, sil	0.989	0.718	0.519
hsi, tms	0.217	0.130	0.0794
hsi, hms	1.686	0.914	0.583
sil, tms	1.869	1.333	0.940
sil, hms	5.816	3.440	2.260
hms, tms	0.767	0.408	0.256

for both polymers are the same.[28] The critical solution temperature T_C was calculated from the critical interaction parameter χ_C according to eqs 6 and 7. In Table 2, we list the *a*, *b*, and *c* coefficients and the fitted standard deviations for the energy of mixing $\Delta w(T)$ as given by eq 6 for the PDMS and PMPS mixture.

The simulation results indicate that at room temperature, medium to high molecular weight PDMS and PMPS blends will be phase separated because the χ interaction parameter has a value of approximately 0.24. Low molecular weight PDMS and PMPS will be partially miscible at room temperature. An upper critical solution temperature (UCST) type phase diagram in the temperature range 200−600 K is observed. The same UCST type of phase diagram was experimentally observed for the same temperature range at similar molecular weights for PDMS and PMPS.[2]

The χ interaction parameters were found to be in the range between 0.111 and 0.123 at the critical solution temperature.[2] This is in agreement with the simulated data at similar temperature and concentration conditions if no end group effects are considered. In our simulation model, the χ interaction parameter was assumed to be temperature dependent but concentration independent. However, experimental results found that the χ interaction parameter does depend on the concentration.[1] A concentration-dependent χ interaction parameter would shift the phase separation concentration according to the theoretical calculation.[29] The interested reader is referred to use eqs 41 and 42 in ref 29 to study the effect of the critical solution concentration.

End Group Effects. In this study, both end groups on PDMS and PMPS polymers are α,ω-terminated trimethylsilyl or dimethylsilanol. The structures of the four polymers used in our simulations are $(CH_3)_3SiO[(CH_3)_2SiO]_nSi(CH_3)_3$, $(CH_3)_2(OH)SiO[(CH_3)_2SiO]_nSi(CH_3)_2(OH)$, $(CH_3)_3SiO[(CH_3)(C_6H_5)SiO]_nSi(CH_3)_3$, and $(CH_3)_2(OH)SiO[(CH_3)(C_6H_5)SiO]_nSi(CH_3)_2(OH)$. The effects of the end groups of PDMS and PMPS upon the miscibility behavior were calculated. The abbreviations for the end groups and the repeat units of the PDMS and PMPS used in Tables 2 and 3 are as follows: dms, $-(CH_3)_2SiO-$; mps, $-(CH_3)(C_6H_5)SiO-$; tms, $(CH_3)_3SiO-$ hms, $(CH_3)_3Si-$ sil, $(CH_3)_2(OH)SiO-$; hsi, $(CH_3)_2(OH)Si-$.

In Table 2, we list the *a*, *b*, and *c* coefficients and the fitted standard deviations for the energy of mixing $\Delta w(T)$ as given by eq 6 for the end groups and the repeat units of the PDMS and PMPS polymers. An excellent fit was obtained between the calculated and theoretical free energy values, with the largest standard deviation less than 0.00778 kcal/mol.

The χ interaction parameters among the end groups and the repeat units of the PDMS and PMPS polymers were calculated from the *a*, *b*, and *c* coefficients in Table 2 according to eqs 6 and 7. The data at 300, 400, and 500 K are listed in Table 3. The differences of the χ interaction parameters between various segment pairs confirm that the end groups and the repeat units interact differently. Thus, the theoretical calculations can be used to quantify the end group effect on the phase behavior of a polymer blend.

This approach is based on the estimation of the χ interaction parameter as a result of electrostatic and van der Waals interaction energies. Our data indicate that the electrostatic interaction is the main contribution to the immiscibility behavior, a positive χ interaction parameter. Contribution from the van der Waals term is much smaller, but in most pairs it is negative, which would increase miscibility. Therefore, the final χ interaction parameter is determined by the balance

Table 4. Simulated Interaction Parameters and Critical Solution Temperatures of α,*ω*-Trimethylsilyl-Terminated PDMS and α,*ω*-Trimethylsilyl-Terminated PMPS Blend

	repeat unit					
	10, 10	12, 12	14, 14	16, 16	18, 18	20, 20
T_C, K	248	298	340	368	397	420
χ = 300 K	0.152	0.165	0.174	0.181	0.187	0.192
χ = 350 K	0.116	0.125	0.133	0.138	0.143	0.146
χ = 400 K	0.088	0.095	0.101	0.105	0.108	0.112
χ = 450 K	0.068	0.073	0.078	0.081	0.083	0.086
χ = 500 K	0.052	0.056	0.060	0.062	0.064	0.066

Table 5. Simulated Interaction Parameters and Critical Solution Temperatures of α,*ω*-Dimethylsilanol-Terminated PDMS and α,*ω*-Dimethylsilanol-Terminated PMPS Blend

	repeat unit					
	10, 10	12, 12	14, 14	16, 16	18, 18	20, 20
T_C, K	248	299	340	369	397	422
χ = 300 K	0.152	0.165	0.174	0.181	0.187	0.192
χ = 350 K	0.116	0.125	0.132	0.138	0.143	0.146
χ = 400 K	0.088	0.095	0.101	0.105	0.109	0.112
χ = 450 K	0.068	0.073	0.077	0.081	0.083	0.086
χ = 500 K	0.052	0.056	0.059	0.062	0.064	0.065

Table 6. Simulated Interaction Parameters and Critical Solution Temperatures of α,*ω*-Dimethylsilanol-Terminated PDMS and α,*ω*-Trimethylsilyl-Terminated PMPS Blend

	repeat unit					
	10, 10	12, 12	14, 14	16, 16	18, 18	20, 20
T_C, K	417	436	458	474	491	508
χ = 300 K	0.358	0.328	0.314	0.299	0.288	0.284
χ = 350 K	0.276	0.254	0.242	0.230	0.222	0.218
χ = 400 K	0.216	0.198	0.188	0.179	0.172	0.169
χ = 450 K	0.171	0.156	0.148	0.140	0.135	0.132
χ = 500 K	0.137	0.124	0.117	0.111	0.106	0.104

Table 7. Simulated Interaction Parameters and Critical Solution Temperatures of α,*ω*-Trimethylsilyl-Terminated PDMS and α,*ω*-Dimethylsilanol-Terminated PMPS Blend

	repeat unit					
	10, 10	12, 12	14, 14	16, 16	18, 18	20, 20
T_C, K	195	228	266	300	330	358
χ = 300 K	0.102	0.108	0.116	0.125	0.132	0.139
χ = 350 K	0.073	0.079	0.085	0.092	0.098	0.104
χ = 400 K	0.053	0.058	0.063	0.068	0.073	0.077
χ = 450 K	0.039	0.042	0.046	0.050	0.054	0.058
χ = 500 K	0.029	0.031	0.034	0.037	0.040	0.043

between the electrostatic and the van der Waals interaction energies. This may be an explanation for the different behaviors of the χ interaction parameter listed in Table 3 for different pairs.

The summary of the χ interaction parameters of PDMS and PMPS with different end groups and the critical solution temperatures at a defined repeat unit number is presented in Tables 4–7. These data were calculated from the *a*, *b*, and *c* coefficients in Table 2. In these tables, the same number of repeat units for both polymers was used to calculate the critical solution temperatures and the value of the χ interaction parameters.

The results from the simulation indicate that the miscibility temperatures of PDMS and PMPS with different end groups depend on the type of the end groups and their concentrations in the PDMS and PMPS polymers. For example, the χ interaction parameter at 300 K and critical solution temperatures of an α,*ω*-trimethylsilyl-terminated PDMS and α,*ω*-trimethylsilyl-terminated PMPS blend with 14 repeat units are 0.174 and 340 K, whereas those for a PDMS and PMPS blend without the end group effects are 0.237 and 394 K.

Comparison of the PDMS and PMPS blends with and without including the end group effect shows that only the blend of α,*ω*-dimethylsilanol-terminated PDMS and α,*ω*-trimethylsilyl-terminated PMPS increases the critical solution temperature (Table 6). The other three blends decrease the critical solution temperature (Tables 4, 5, and 7). The overall interaction parameters are decreased as shown in Tables 4, 5, and 7. This decrease of the χ interaction parameter is due to the fact that the repulsive intramolecular interactions between the end groups and the main repeat units on the same polymer are sufficiently large to overcome the overall intermolecular interactions between the segments on the two different polymers, as shown in Tables 4, 5, and 7. However, in Table 6, the intramolecular mutual repulsions between the end groups and the main repeat units on the same polymer are smaller than the overall intermolecular interactions of the segments in the two different polymers, the overall χ interaction parameter increases, and a higher phase separation temperature is observed.

Our results also indicate that the end groups and their fractions in the polymers can significantly affect the miscibility temperatures at low molecular weights. For example, the critical solution temperature of the α,*ω*-trimethylsilyl-terminated PDMS and α,*ω*-dimethylsilanol-terminated PMPS blend is 192 °C lower than that of the α,*ω*-dimethylsilanol-terminated PDMS and α,*ω*-trimethylsilyl-terminated PMPS blend when 14 repeat units are considered. PDMS and PMPS containing 10–20 repeat units would be considered as low molecular weight polymers. As expected, the end group effects decrease when the molecular weights of the polymers increase. This trend is shown in Table 8, which lists the simulated χ interaction parameters of α,*ω*-dimethylsilanol-terminated PDMS and α,*ω*-dimethylsilanol-terminated PMPS blend. In the last column of Table 8, the χ interaction parameters for PDMS and PMPS with no end groups are also listed. The χ interaction parameters for PDMS and PMPS both with α,*ω*-dimethylsilanol groups is 0.192 for 20 repeat units, 0.220 for 60 repeat units, and 0.229 for 100 repeat units at 300 K. Therefore, with the increase of the number of repeat units, the χ interaction parameter approaches the value of 0.237, where no end group effects were

Table 8. Simulated Interaction Parameters of α,*ω*-Dimethylsilanol-Terminated PDMS and α,*ω*-Dimethylsilanol-Terminated PMPS Blend with the Repeat Unit Change

	repeat unit							
	10, 10	15, 15	20, 20	40, 40	60, 60	80, 80	100, 100	no end groups
χ = 300 K	0.152	0.182	0.192	0.212	0.220	0.224	0.229	0.237
χ = 350 K	0.116	0.139	0.146	0.162	0.168	0.171	0.174	0.181
χ = 400 K	0.088	0.106	0.112	0.123	0.128	0.130	0.133	0.138
χ = 450 K	0.068	0.082	0.086	0.094	0.098	0.100	0.102	0.106
χ = 500 K	0.052	0.063	0.070	0.073	0.075	0.077	0.078	0.081

considered. The χ interaction parameters for PDMS and PMPS blends where the polymer chains have other endgroups behave similarly when the degree of polymerization increases.

Further analysis of the results also indicates that the changes of critical solution temperatures and χ interaction parameters with the same type of end groups on the two polymers (Tables 4 and 5) are much smaller than those with two different types of end groups (Tables 6 and 7). This is expected because the changes of the enthalpy are smaller for the same type of end groups on the two polymers than those with different end groups. The interactions between the same type of end groups on the two polymers are athermal.

Compared with the experimental data for similar molecular weight α,ω-trimethylsilyl-terminated PDMS and α,ω-trimethylsilyl-terminated PMPS blend,[1] the simulated critical solution temperature is approximately 100 °C lower. However, the simulated critical solution temperature is in agreement with the experimental data for the α,ω-dimethylsilanol-terminated PDMS and α,ω-trimethylsilyl-terminated PMPS blend.[2]

Conclusions

The method described in this paper to calculate the end group effect on the χ interaction parameter and phase separation temperature of a polymer blend is an extension of the mean field theory calculation of the χ interaction parameter of a random copolymer blend.[13] The overall χ interaction parameter was calculated based on the individual segmental interaction parameters of the end groups and the monomeric units in the polymer. The individual segmental interaction parameters were calculated from a combination of the Flory–Huggins lattice model and molecular simulation techniques.

The χ interaction parameters and phase separation temperatures of poly(dimethylsiloxane) and poly(methylphenylsiloxane) blends with and without end group effects were calculated, and the results are in agreement with the experimental data.

Experimentally, it was observed that at high molecular weight, the end group does not have a significant effect upon the polymer miscibility. However, the simulation results indicated that the end groups and their fractions in the polymers significantly affect the miscibility temperatures at low molecular weights. For example, the critical solution temperature of the α,ω-trimethylsilyl-terminated PDMS with the α,ω-dimethylsilanol-terminated PMPS blend was 192 °C lower than that of the α,ω-dimethylsilanol-terminated PDMS and the α,ω-trimethylsilyl-terminated PMPS blend when 14 repeat units were considered. This method should be applicable for studies of the interaction parameter and phase separation temperature due to the end group effect for other low molecular weight polymer blends.

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References and Notes

(1) Kuo, C. M.; Clarson, S. J. *Macromolecules* **1992**, *25*, 2192.
(2) Kuo, C. M.; Clarson, S. J. *Eur. Polym. J.* **1993**, *29* (5), 661.
(3) Fox, T. G.; Flory, P. J. *J. Polym. Sci.* **1954**, *14*, 315.
(4) Patel, A.; Cosgrove, T.; Semlyen, J. A.; Webster, J. R. P.; Scheutjens, J. M. H. M. *Colloids Surf. A* **1994**, *87*, 15.
(5) Lenk, T. J.; Lee, D. H. T.; Koberstein, J. T. *Langmuir* **1994**, *10*, 1857.
(6) Jalbert, C. T.; Koberstein, J. T.; Yilgor, I.; Gallagher, P.; Krukonis, V. *Macromolecules* **1993**, *26*, 3069.
(7) Jalbert, C. T.; Koberstien, J. T.; Balaji, R.; Bhatia, Q.; Salvati, L., Jr.; Yilgor, I. *Macromolecules* **1994**, *27*, 2409.
(8) Anastasiadis, S.; Gancarz, I.; Koberstein, J. T. *Macromolecules* **1988**, *21*, 2980.
(9) Fleischer, C. A.; Koberstein, J. T.; Krukonis, V.; Wetmore, P. A. *Macromolecules* **1993**, *26*, 4172.
(10) Fleischer, C. A.; Morales, A. R.; Koberstein, J. T. *Macromolecules* **1994**, *27*, 379.
(11) Wolf, B. A.; Schuch, W. *Makromol. Chem.* **1981**, *182*, 1801.
(12) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(13) Zhikuan, C.; Karasz, F. E. *Macromolecules* **1992**, *25*, 4716.
(14) Kambour, R. P.; Bendler, J. T.; Bopp, R. C. *Macromolecules* **1983**, 16, 753.
(15) Paul, D. R.; Barlow, J. W. *Polymer* **1984**, *25*, 487.
(16) Cowie, J. M. G.; McEwen, I. J.; Nadvornik, L. *Macromolecules* **1990**, *23*, 5106.
(17) *Computer Simulation of Polymers*; Roe, R. J., Ed.; Prentice-Hall: Englewood Cliffs, NJ, 1991.
(18) Gelin, B. R. *Molecular Modeling of Polymer Structures and Properties*; Hanser Publishers: New York, 1994.
(19) *Atomistic Modeling of Physical Properties of Polymers*; Monnerie, L., Suter, U., Eds.; Springer: New York, 1994.
(20) Case, F. H.; Honeycutt, J. D. *Trends Polym. Sci.* **1994**, *2*, 259.
(21) Fan, C. F.; Olafson, B. D.; Blanco, M.; Hsu, S. L. *Macromolecules* **1992**, *25*, 3667.
(22) CERIUS2 User's Reference Manual, version 1.6; Molecular Simulations, Inc.: Burlington, MA.
(23) ten Brinke, G.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1983**, *16*, 1827.
(24) Roe, R. J.; Zin, W. C. *Macromolecules* **1980**, *13*, 1221.
(25) Rappe, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard, W. A., III; Skiff, W. M. *J. Am. Chem. Soc.* **1992**, *114*, 10024.
(26) Grigoras, S.; Qian, C.; Crowder, C.; Harkness, B.; Mita, I. *Macromolecules* **1995**, *28*, 7370.
(27) Lii, J. H.; Allinger, N. L. *J. Am. Chem. Soc.* **1992**, *111*, 8576.
(28) de Gennes, P. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(29) Qian, C.; Mumby, S. J.; Eichinger, B. E. *Macromolecules* **1991**, *24*, 1655.

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