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Modified Double Lattice Model for Oligoethylene/Oligostyrene Blends

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Summary. Experimental data on oligostyrene/oligoethylene blends (from 5/11-mer to 50/11-mer) reported in the previous paper are interpreted using a modified double lattice model. The approach successfully describes the unusual chain length dependence of the upper critical solution temperature which is observed in this system.

Keywords. Polystyrene; Alkanes; Upper critical solution temperature; Blend; Liquid–liquid equilibrium; Modified double lattice model.

Introduction

Polystyrene and polyethylene are probably the two most common polymers produced by the chemical industry. Unfortunately this polymer pair also forms a classical example of polymer incompatibility. As a result recycling of these materials is more difficult than would otherwise be the case. Although the long-chain polymers are incompatible, it is possible to quantify the extent of the immiscibility by studying the chain length dependence of the solubility of mixtures of oligomers. Then semi-empirical or theoretical methods to extrapolate the data into the long-chain polymer/polymer regime are used. We have already reported studies on the effects of pressure [1], branching [2], end-groups [3], and oligoethylene chain length [4] on solubilities in polystyrene/oligoethylene and oligostyrene/oligoethylene systems. The components of these oligo-blends have different chemical structures. The classical *Flory* theory is limited to the description of blends and solutions of components with similar monomer structure [5], but recently a number of approaches have been developed to describe binary mixtures with components of different monomer structures [6–8]. In this paper we apply the

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modified double lattice model (mDLM) of *Oh* and *Bae* [6] to interpret the chain-length dependence of the UCSTs (upper critical solution temperatures) in some oligostyrene/oligoethylene blends.

Modified Double Lattice Model (mDLM)

A new double-lattice model for the description of binary polymer solutions exhibiting both UCST and LCST (lower critical solution temperature) behavior (Fig. 1) was recently introduced by *Oh* and *Bae* [6]. This model introduced a new kind of interaction parameter and a simplified expression for the *Helmholtz* energy of mixing. According to the classical *Flory-Huggins* theory the *Helmholtz* free energy of mixing for a binary polymer mixture is given by Eq. (1) [5, 6, 9–12].

$$\Delta A/N_r kT = (\phi_1/N_1)\ln\phi_1 + (\phi_2/N_2)\ln\phi_2 + \chi_{OB}\phi_1\phi_2 \tag{1}$$

N_r is the total number of lattice sites, k is *Boltzmann*'s constant, ϕ_1 and N_1 are the volume fraction and the number of segments of the first component (in this case the oligoethylene), ϕ_2 and N_2 are the volume fraction and segment number of the second component (the oligostyrene), and χ is a parameter which describes the excess free energy of mixing. The *Oh* and *Bae* modification introduces a new parameter defined by $\chi = \chi_{OB}$ which is defined by Eq. (2) and now incorporates the chain-length dependence [6].

$$\chi_{OB} = C_\beta\left(\frac{1}{N_2}-\frac{1}{N_1}\right)^2 + \left(2+\frac{1}{N_2}\right)\tilde{\varepsilon} - \left(\frac{1}{N_2}-\frac{1}{N_1}+C_\gamma\tilde{\varepsilon}\right)\tilde{\varepsilon}\phi_2 + C_\gamma\tilde{\varepsilon}^2\phi_2^2 \tag{2}$$

In Eq. (2), $\tilde{\varepsilon}$ is the reduced interaction energy which is described by Eq. (3), where ε_{11}, ε_{22}, and ε_{12} quantify the energetics of nearest-neighbor segment–segment interactions, and the parameters C_β and C_γ depend on N-mer chain length [6, 18] following Eqs. (4) and (5).

$$\tilde{\varepsilon} = \varepsilon/kT = (\varepsilon_{11}+\varepsilon_{22}-2\varepsilon_{12})/kT \tag{3}$$

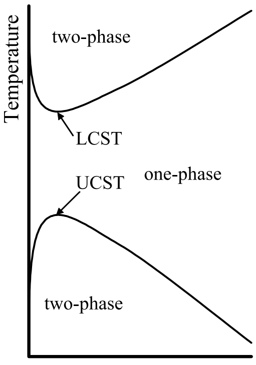

Fig. 1. Schematic representation for a binary polymeric mixture (solution or blend) exhibiting both UCST and LCST behaviour

$$C_\beta = 0.1080 + \frac{0.0647}{0.4907 + (N_1 - 1)} \tag{4}$$

$$C_\gamma = 1.1529 + \frac{1.1035}{0.0738 + (N_1 - 1)} \tag{5}$$

The critical conditions then follow from Eqs. (6) and (7).

$$\begin{aligned}
&\frac{\partial(\Delta\mu_1/kT)}{\partial\phi_2}\\
&\quad = \frac{-1}{1-\phi_2} + \left(1 - \frac{N_1}{N_2}\right)\\
&\quad + 2\left[r_1 C_\beta\left(\frac{1}{N_2} - \frac{1}{N_1}\right)^2 + \left\{\left(\frac{N_1}{N_2} - 1\right) + N_1 C_\gamma \tilde{\varepsilon}\right\}\tilde{\varepsilon} + N_1\left(2 + \frac{1}{N_2}\right)\tilde{\varepsilon}\right]\phi_2\\
&\quad - 6\left[\left\{\left(\frac{N_1}{N_2} - 1\right) + N_1 C_\gamma \tilde{\varepsilon}\right\}\tilde{\varepsilon} + N_1 C_\gamma \tilde{\varepsilon}^2\right]\phi_2^2 + 12 N_1 C_\gamma \tilde{\varepsilon}^2 \phi_2^3 = 0
\end{aligned} \tag{6}$$

$$\begin{aligned}
&\frac{\partial^2(\Delta\mu_1/kT)}{\partial\phi_2^2}\\
&\quad = \frac{-1}{\left(1-\phi_2\right)^2}\\
&\quad + 2\left[r_1 C_\beta\left(\frac{1}{N_2} - \frac{1}{N_1}\right)^2 + \left(\left(\frac{N_1}{N_2} - 1\right) + N_1 C_\gamma \tilde{\varepsilon}\right)\tilde{\varepsilon} + N_1\left(2 + \frac{1}{N_2}\right)\tilde{\varepsilon}\right]\\
&\quad -12\left[\left\{\left(\frac{N_1}{N_2} - 1\right) + N_1 C_\gamma \tilde{\varepsilon}\right\}\tilde{\varepsilon} + N_1 C_\gamma \tilde{\varepsilon}^2\right]\phi_2 + 36 N_1 C_\gamma \tilde{\varepsilon}^2 \phi_2^2 = 0
\end{aligned} \tag{7}$$

Results

Critical volume fraction and ε/k are obtained from Eqs. (6) and (7) using the experimental UCSTs from Ref. [4].

$$N_2 = \frac{V^u_{m2(vdW)} \cdot M_{w2}}{V_{m,CH_2(vdW)} \cdot M^u_{w2}} \tag{8}$$

N_2 is given by Eq. (8) where $V_{m,CH_2(vdW)}$ (=10.23(cm^3/mol)) is the molar *van der Waals* (*vdW*) volume of a CH_2 group, which occupies one lattice site [13] and $V_{m2(vdW)}$ and M_{w2} are the molar *vdW* volume and molecular weight of *PS*, respectively. Superscript u represents a repeating unit of PS. Based on the meaning of Eq. (8), the value of N_2 used in this calculation is not the physical chain length itself, but is rather the molar volume ratio of the oligostyrene and the CH_2 group. Therefore, $N_2 = 77.373$ from Eq. (8). If N_2 is fixed by Eq. (8), the critical composition and interaction energy of each system is automatically determined from critical conditions in Eqs. (6) and (7). These results are shown in

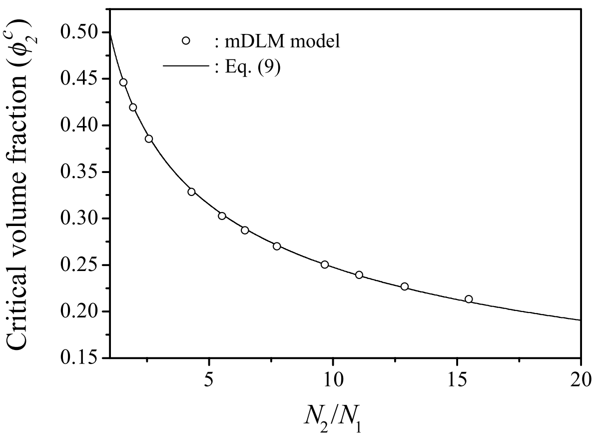

Fig. 2. Critical volume fraction of a 11-unit oligostyrene plus oligoethylenes blend *vs.* the ratio of chain lengths of the two oligomers (one of them with fixed and the other one with variable chain-length)

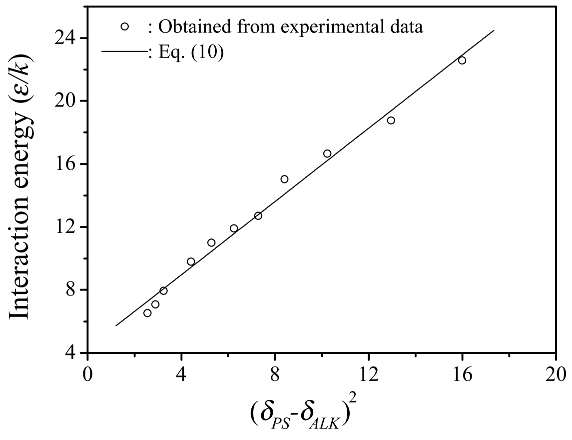

Fig. 3. The *Hildebrand* solubility parameter dependence of the interaction energy in a 11-unit oligostyrene plus oligoethylenes; solid line represents Eq. (10), symbols represents results calculated from experimental data of Ref. [4] using Eqs. (6) and (7)

Figs. 2 and 3. The chain length dependence of the calculated critical compositions in the *Flory-Huggins* model can be expressed by $\phi_c \propto (N_2/N_1)^{-0.5}$, while in this mDLM model ϕ_c is given by Eq. (9).

$$\phi_c = \frac{1}{1 + (N_2/N_1)^{0.483}} \tag{9}$$

Thus, the present model is less sensitive to the ratio of chain lengths of the two components (Fig. 2), but this exponent is slightly closer to the one (0.4) given by experiments and recent theories ([14] and references therein). We assume that ε/k is related to *Hildebrand* solubility parameters. Using the experimental cloud point data and Eqs. (6) and (7), ε/k can be expressed by Eq. (10), where δ_{PS} and

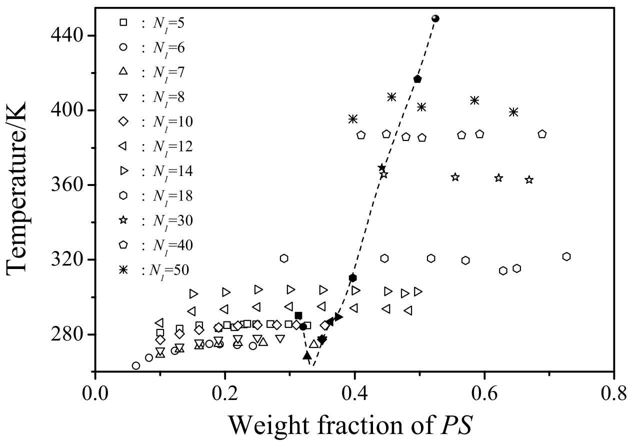

Fig. 4. Cloud point and critical points of some oligoethylene/oligostyrene systems; the chain-length of the oligoethylenes (*n*-alkanes) can be seen in the insert (N_1), the oligostyrene has fixed (approx. 11 units) chain length; empty symbols: experimental cloud points from Ref. [4], full symbols: calculated critical points; the dashed line connecting the critical points (B-spline) has no physical basis but facilitates reading this figure

δ_{ALK} are the *Hildebrand* solubility parameters of polystyrene and alkane compounds, respectively.

$$\varepsilon/k = 4.308 + 1.163(\delta_{PS} - \delta_{ALK})^2 \qquad (10)$$

As shown in Fig. 3, the values of ε/k increase linearly with $(\delta_{PS} - \delta_{ALK})^2$, that is, the system gets more immiscible. Critical points calculated by the present model are compared to the cloud point curves from Ref. [4] (Fig. 4). It can be seen that these points are not far from the extrema (maximum or local minimum) of the cloud point curves, *i.e.* the assumption to take the temperatures corresponding to these extrema as UCSTs [4] is justified. In a strictly binary system, the critical point is at the maximum; the shift of the critical point is caused by the polydispersity in a pseudo-binary system. No polydispersity effects are included in the model. Hence, the model gives the critical points as maxima in the cloud point curve.

In Fig. 5, the generalized UCST's from Eqs. (6) and (7) are compared with those from Eqs. (9) and (10).

The dotted line in Fig. 5 is the result obtained from *Weimer-Prausnitz* theory [4, 15, 16]. The solid line shows the result of the present calculation. It can be seen that the agreement between experimental and theoretical results is satisfying and the existence of the minimum in UCST *vs.* N_1 (although more pronounced than the experimental one) is confirmed.

The theta temperature for *PS*1241/polyethylene "quasi-solutions" (where *PS*1241 acts as a solvent for high chain-length polyethylenes) can be determined using the recent results. Using the first three points (the only linear part) of Fig. 6, 1360 ± 50 K as theta temperature can be obtained. This is much higher than the one obtained from the experimental data (650 ± 10 K), suggesting that for a good description of long-chain mixtures more experimental data from the higher chain region are necessary. Further details on this topic can be found in Ref. [4].

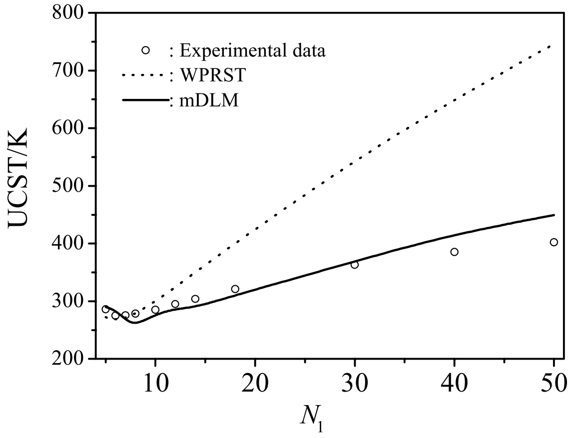

Fig. 5. The chain-length dependence of the Upper Critical Solution Temperature (UCST) in an 11-unit oligostyrene plus oligoethylenes blend; symbols represent experimental data, dashed line represents the *Weimer-Prausnitz* theory [4], solid line represents the recent model

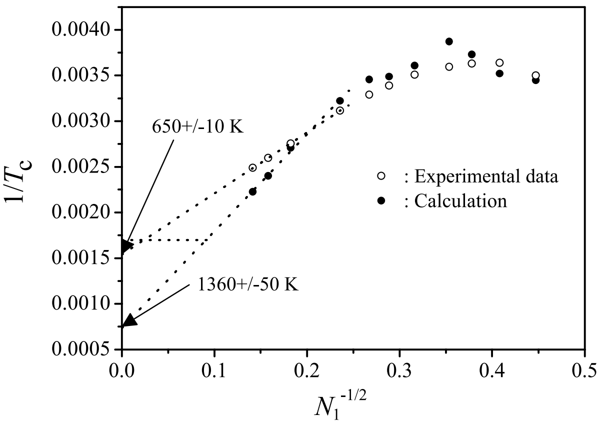

Fig. 6. *Shultz-Flory* plot ($N_1^{-1/2}$ *vs.* $1/T_c$) for the studied oligostyrene/oligoethylene mixtures; predicted theta temperatures are marked by arrows, degradation temperature of long-chain linear polyethylene [17] marked by vertical dotted line

Conclusion

Experimental UCST data of oligostyrene/oligoethylene blends (polystyrene, $M_w = 1241$, approx. 11-unit with *n*-alkanes from pentane ($N_1 = 5$) to pentacosane ($N_1 = 50$) published in our previous paper [4] are well described using the modified double lattice model of *Oh* and *Bae* [1].

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List of Symbols

UCST upper critical solution temperature; LCST lower critical solution temperature; N segment number in general; N_1 number of carbon atoms in the alkanes (segment number); N_2 polystyrene segment number; M_w weight-average molecular weight; Θ theta temperature; ΔA *Helmholtz* energy of mixing; N_r total number of lattice sites; ϕ_1 volume fraction of the oligoethylene; ϕ_2 volume fraction of the oligostyrene; χ_{OB} *Oh–Bae* interaction parameter; $\tilde{\varepsilon}$ reduced interaction energy; ε_{11}, ε_{22}, ε_{12} corresponding nearest-neighbor segment–segment interactions; C_β, C_γ chain-length dependent universal functions; $V^u_{m2(vdW)}$ molar *van der Waals* volume of the polystyrene repeating unit; $V_{m,CH_2(vdW)}$ molar *van der Waals* volume of a CH_2 group; M_{w2} molecular weight of the polystyrene; T_c liquid–liquid critical temperature; δ_{PS} *Hildebrand* solubility parameters of polystyrene; δ_{ALK} *Hildebrand* solubility parameters of alkane compounds.

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