

CLOUD POINT CURVES OF POLY(ETHYLENE GLYCOL)/POLY(PROPYLENE GLYCOL) MIXTURES AND THEIR THERMODYNAMIC EXPLANATION*

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ABSTRACT

In the study of poly(ethylene glycol) (PEG) and poly(propylene glycol) (PPG) mixtures not only a bimodal shape but also a reverse trend of the dependence on molecular weight of the cloud point curves were observed.

This trend indicates that the miscibility of the studied mixtures decreases as the molecular weight of one component decreases. The excess volumes of the mixtures show that the interaction parameter between two components decreases at first and increases after passing a minimum as the concentration of one component increases. This supports the explanation of Koningsveld on the bimodal shape of cloud point curves. Based on a binary interaction model a formula was derived revealing that the interaction between PPG and the end group of PEG and the hydrogen bonding interaction between ether and hydroxy end group inner or inter PEG molecules are not favorable for mixing. The latter interaction is an "attractive" force in PEG molecules. The two interactions are responsible for the observed abnormal dependence.

The miscibility of oligomers has become an attractive topic for research, the reason is 1) the molecular weight of such oligomers is large enough to bear the basic characteristics of long chain molecules. Thus the study of oligomer miscibility can give some hints to high polymers. 2) Usually such substances are liquids, after mixing a thermodynamic equilibrium is easily established. The methods of studying phase equilibrium in small molecules can be applied to oligomers without difficulty. For instance, the phase diagram and heat of mixing of oligomer mixtures can be measured accurately. Therefore, the miscibility study of oligomers will conduct to a more clear picture of the origin of miscibility, instead of studying polymer blends.

One of the authors had joined in publishing a paper on the miscibility of poly(ethylene glycol)/poly(propylene glycol) methylethers^[1]. For simplicity, the hydroxy end groups of oligomers were transformed to methoxy groups, to avoid the hydrogen bonding interaction. In this paper we will report some results of the same oligomer pairs, but, with the hydroxy end groups. In the latter case two types of hydrogen bonding are introduced in the mixtures. These are hydroxy-hydroxy and hydroxy-ether of the molecular chain bonding. We expect to obtain more informations from such a complicated system.

EXPERIMENTAL

1. Materials

PEG are the chromatographic reagents with molecular weight 200, 400, 600, 1000 and 1500,

respectively. All the samples were dried in a vacuum oven at 50°C for at least 2 weeks.

PPG are also the chromatographic reagents with molecular weight 1025 and 2050, respectively. The samples were dried in a vacuum oven at 50°C for at least 2 weeks.

2. Measurement of cloud point curve (CPC)

In a glass tube of diameter 5 mm PEG and PPG in proper ratio were filled. The mixture was homogeneous and transparent after stirring by using a small stick of stainless steel at high temperature, and then was cooled down at a rate of 1°C/min. The cloud point temperature was recorded at which the mixture became turbid. A CPC was drawn through all the cloud points of the mixtures with different compositions.

3. Measurement of density

The homogeneous and transparent mixture was filled in a density bottle and then thermostated at $\pm 0.03^\circ\text{C}$. The density of liquid was measured from high to low temperatures at an interval of 10°C , until the turbidity was seen in the mixture.

From the densities of pure components and mixture d_1 , d_2 and d_m , and the weight fractions of the components in the mixture w_1 and w_2 , the excess volume ΔV_m can be obtained.

$$\Delta V_m / V = 1/(w_1/d_1 + w_2/d_2)d_m - 1 \quad (1)$$

where V is the total volume of mixture at $\Delta V_m = 0$. A negative ΔV_m indicates that a volume contraction takes place after mixing.

RESULTS AND DISCUSSION

1. Time dependence of the measured binodal

A binodal is a boundary where a stable single phase exists in a mixture, beyond this boundary the mixture is meso-stable or unstable. A boundary between the latter two regions is a spinodal. The binodal should have no dependence on the observation time in the thermodynamic meaning. This is true in small molecules. Because of a very slow process of diffusion of segments the phase separation in polymer blends takes a long time. What we observed is usually only at a certain stage of the phase separation in polymer blends, depending on the method of observation. For oligomer mixtures there is a good fluidity, a thermodynamic equilibrium should be easy to reach in a short time. Although a CPC is usually thought to be in between the binodal and the spinodal^[2], it can be said that the CPC of oligomer mixtures is near to the binodal. In Figs.1 and 2 are shown the CPCs of PEG / PPG mixtures. Above the CPC is one phase region, under the curve the mixture will undergo a phase separation.

In Fig.3 is shown the temperature dependence of the excess volume of the studied mixtures. It is seen that a volume contraction occurs when mixing. This is believed as a result of hydrogen bonding interaction in the mixture. The excess volume has a sudden increase when the temperature of mixture decreases to a certain value, which indicates that the phase separation has already taken place in the mixture. In Fig.1 we denoted such temperatures by a dashed curve for PEG600/PPG1025 mixtures, which is 15°C higher than the corresponded CPC. A single point of PEG200/PPG1025 mixture at weight fraction 0.5 was measured in the same manner, which is also 15°C higher than the CPC point. Considering that the measurement of density is a slow process, taking a long time of observation, the dashed curve at higher temperature is reasonable and should

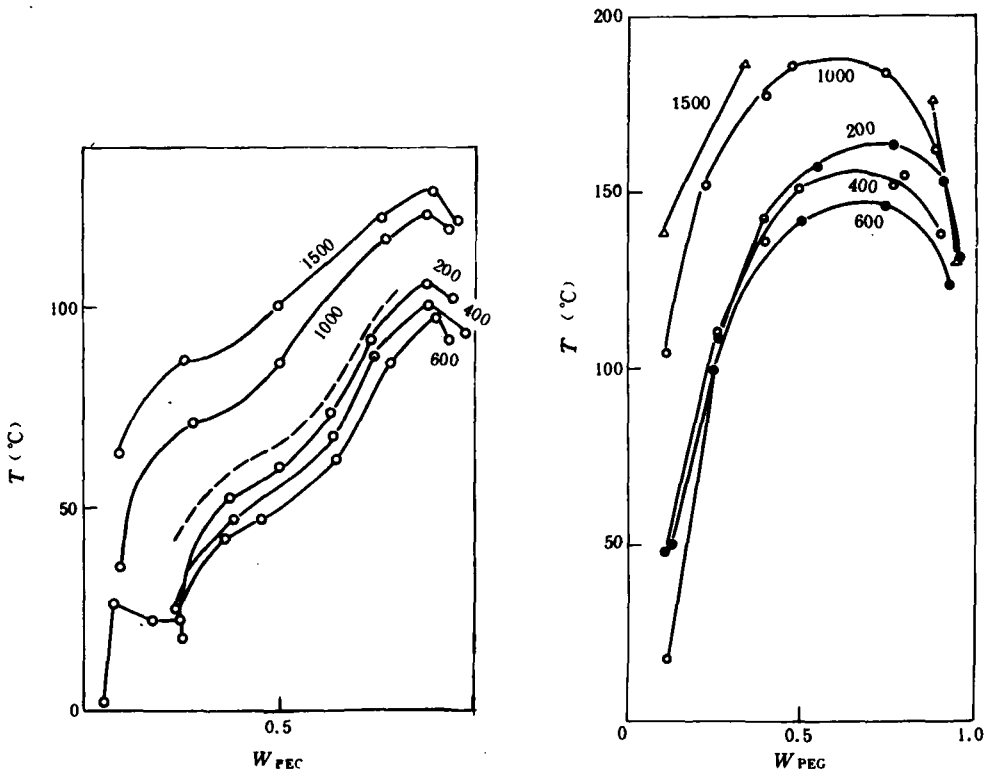


Fig.1 The cloud point curves of PEG/PPG1025 mixtures. Fig.2 The cloud point curves of PEG/PPG2050 mixtures. The molecular weights of PEG are denoted on the curves The molecular weights of PEG are denoted on the curves

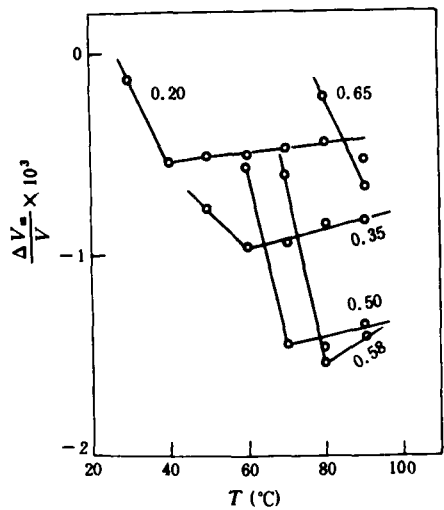


Fig.3 The excess volumes of PEG600/PPG1025 mixtures. The weight fractions of PEG are denoted on the curves

be much near to the real binodal. Therefore, through the observations at two time scales we can see that even in oligomers the measured phase boundaries may still have time dependence.

2. CPC of bimodal shape

We can see that all the CPCs in Figs.1 and 2 have a bimodal shape, the phenomenon first discovered by Allen in 1960^[3]. According to the explanation of Koningsveld^[4], a special composition dependent χ exists in such systems, which is expressed as

$$\chi = \chi_0 + \chi_1\phi_2 + \chi_2\phi_2^2 + \dots \quad 2)$$

where χ is the Flory-Huggins interaction parameter, $\chi_1 < 0$, $\chi_2 > 0$, and ϕ_2 is the volume fraction. With ϕ_2 increasing, χ decreases to a minimum and increases afterwards. This shape of χ dependence is a result of either the change of flexibility of molecular chain during mixing or the effects of non-uniform segment density in mixture, or of both reasons.

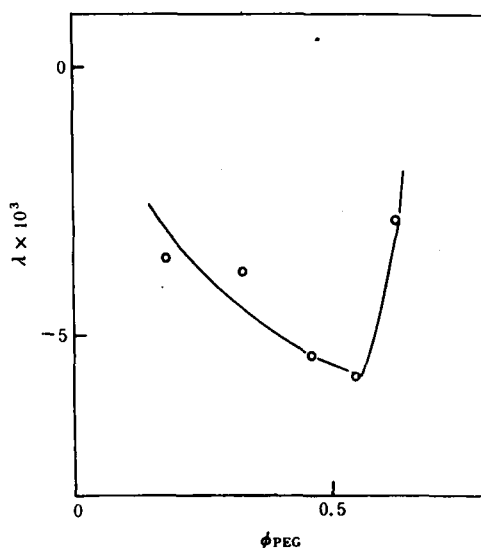


Fig.4 The interaction parameter λ in the PEG600/PPG1025 mixtures, calculated from the excess volume at 90°C

In Fig.4 we plotted an interaction parameter λ , which was calculated from Eq.3:

$$\Delta V_m / V = \lambda \phi_1 \phi_2 \quad 3)$$

λ is analogous to parameter χ ^[5]. It is seen that λ is indeed composition dependent as Eq.2. Based on $\Delta V_m / V$, we can obtain parameter χ from the Flory equation of state theory. χ has a similar shape as λ . Therefore, our measurement supports Koningsveld's theory. In our system there are strong hydrogen bonding interactions. It may change the flexibility of chain molecules after mixing. Also it is possible that the orientation effect in the mixture may lead to an inhomogeneous distribution of the segments of two components.

3. Reverse trend of molecular weight dependence of CPC

A reverse trend of molecular weight dependence of CPC is seen in Figs.1 and 2. The normal trend of dependence is that the CPC moves to a lower temperature range with molecular weight decreasing, the mixture becomes more miscible. This is due to the contribution of entropy of mixing. In our mixtures the molecular weight of PPG is fixed, we can observe such a normal dependence if the molecular weight of PEG is larger than 600. But when the molecular weight of

PEG is smaller than 600, an abnormal dependence on molecular weight occurred.

In order to find an explanation, we turn to the so-called binary interaction model, which was suggested by Paul in 1984^[6]. This model was originally designed for the analysis of polymer blends in which at least one component was a copolymer. Later on it was used for the miscibility of stereoregular polymers, if the polymer was taken as a copolymer of *d* and *l* configuration units^[7-9].

In this paper we try to use this model for polymers which having strong interacting end groups, if we take the polymer as a special triblock copolymer. For instance, PEG(A) can be looked as a polymer block of dimethyl ether (1) with two residuals of methanol (2) as the end blocks. Also PPG(B) can be taken as a polymer block of methyl ethyl ether (3) with one residual of methanol (2) and one residual of ethanol (4) as the end blocks. Fig.5 is a schematic presentation of the above arguments, based on the binary interaction model.

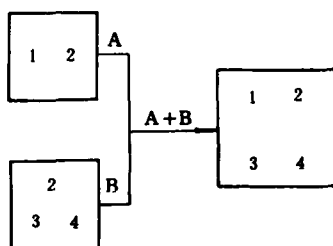


Fig.5 A schematic presentation of PEG/PPG mixture, based on the binary interaction model.

1—4 are residuals of dimethyl ether, methanol, methyl ethyl ether and ethanol, respectively

The heat of mixing of the mixture can be written as

$$\Delta H_m = V(B_{12}\phi_1\phi_2 + B_{13}\phi_1\phi_3 + B_{14}\phi_1\phi_4 + B_{23}\phi_2\phi_3 + B_{24}\phi_2\phi_4 + B_{34}\phi_3\phi_4) - V_A B_{12}\phi'_1\phi'_2 - V_B(B_{23}\phi''_2\phi''_3 + B_{24}\phi''_2\phi''_4 + B_{34}\phi''_3\phi''_4) \quad (4)$$

with

$$V = V_A + V_B \quad (5)$$

$$\phi_A + \phi_B = 1 \quad (6)$$

$$\phi_1 + \phi_2 + \phi_3 + \phi_4 = 1 \quad (7)$$

$$\phi'_1 + \phi'_2 = 1 \quad (8)$$

$$\phi''_2 + \phi''_3 + \phi''_4 = 1 \quad (9)$$

The first bracket of Eq.4 is the interaction term of 1,2,3 and 4 units in the mixture, the second is that of 1 and 2 units in PEG, and the third term is that of 2,3 and 4 units in PPG. Eq.14 can be finally obtained if the volume fractions without primes were substituted by the ones with primes. The volume fraction without primes is the quantity in the mixture, the other two with single and double primes are the volume fractions in PEG and PPG, respectively.

$$\phi_1 = \phi'_1\phi_A \quad (10)$$

$$\phi_2 = \phi'_2\phi_A + \phi''_2\phi_B \quad (11)$$

$$\phi_3 = \phi''_3\phi_B \quad (12)$$

$$\phi_4 = \phi''_4\phi_B \quad (13)$$

We now have

$$\Delta H_m = V B_m \phi_A \phi_B \quad (14)$$

with

$$B_m = B_1\phi'_1 + B_2\phi'_2 - B_{12}\phi'_1\phi'_2 - B_0 \quad (15)$$

$$B_1 = B_{12}\phi''_2 + B_{13}\phi''_3 + B_{14}\phi''_4 \quad (16)$$

$$B_2 = B_{22}\phi''_2 + B_{23}\phi''_3 + B_{24}\phi''_4, B_{22}=0 \quad (17)$$

$$B_0 = B_{23}\phi''_2\phi''_3 + B_{24}\phi''_2\phi''_4 + B_{34}\phi''_3\phi''_4 \quad (18)$$

B_1 and B_2 characterize the interactions between residuals 1 and 2 with polymer B . B_0 is the interaction in polymer B . B_{ij} is the interaction parameter between i and j segments. B_m is the effective interaction parameter between A and B polymers.

The heat of mixing measurements showed that B_{13} is positive and all the other B_{ij} are negative^[1,10]. Thus, from Eqs.17 and 18 we know that B_2 and B_0 are negative. We can not determine the sign of B_1 from Eq.16, because although B_{12} and B_{14} are negative, B_{13} is positive and we do not know exactly the magnitude of these B_{ij} parameters. However, we still assume a negative B_1 in accordance with the solubility fact that PPG dissolves in dimethyl ether. According to the same reason we assume further that $B_2 > B_0 > B_1$. A primary test showed that the ethylene glycol/PPG1025 mixture was not miscible even at much higher temperatures, as compared with the PEG200/PPG1025 mixture.

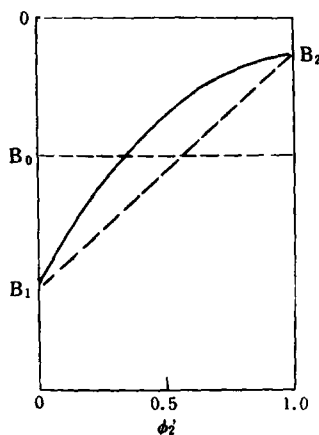


Fig.6 The interaction parameter B_m as a function of the volume fraction of hydroxyl end groups in PEG

Now B_m can be drawn as in Fig.6. We assume that one dimethyl ether or one methanol molecule takes a same volume. Therefore, $\phi'_2 = 1$ in ethylene glycol, $\phi'_2 = 2/3$ in the dimer of ethylene glycol, and $\phi'_2 = 0$ in the high molecular weight PEG, etc. In Fig.6 in the part of curve $B_1\phi'_1 + B_2\phi'_2 - B_{12}\phi'_1\phi'_2$ where the curve is above B_0 , the heat of mixing ΔH_m of the mixture is positive, which is not favorable for mixing. We can see that with decreasing molecular weight of PEG, ϕ'_2 increases, the value of $B_1\phi'_1 + B_2\phi'_2 - B_{12}\phi'_1\phi'_2$ increases, an originally negative ΔH_m becomes positive finally. If only ΔH_m is considered, the miscibility of the mixture would decrease with the molecular weight of PEG decreases. Since what we studied are oligomers, the contribution of ΔS_m is not negligible. This term will make the miscibility increase with decreasing the molecular weight of PEG. The two contrary factors decide that the miscibility of our system increases at first and decreases afterwards as the molecular weight of PEG decreases.

In conclusion, the binary interaction model shows that two factors lead to the observed reverse dependence of the CPC on the molecular weight. One is $B_2 > B_0$, which decides that the B_m curve goes from negative to positive. This general trend of the B_m curve makes the miscibility decreasing with smaller molecular weight of PEG. Another is $B_{12} < 0$, which means that there is an "attractive" force between the structure units 1 and 2 in PEG. The B_m curve becomes convex, moving to the higher molecular weight range of PEG. So we can see the abnormal phenomenon from PEG600 downwards. Many reports have shown that the "repulsive" force between the structure units in a copolymer may enhance the miscibility of the polymer blends^[6]. Here we present an example that the "attractive" force between the structure units in PEG is partially responsible for the decrease of miscibility of the corresponded mixtures.

Keywords:

Cloud point curve; Poly(ethylene glycol); Poly(propylene glycol); Binary interaction model; Thermodynamics.

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