Articles

Cohesional Entanglement of Amorphous Polymer in Glass State as Probed by Equilibrium Swelling in a "Non-Solvent"[†]

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The equilibrium swelling of the system Polystyrene (PS) ($M = 1.7 \times 10^5$, monodisperse)/diethyl ether at 30 ℃ and 35 ℃ has been studied in detail in quiescent state for a time span over 150 d. Arguments are given to show that the swelling process in a "non-solvent" is a network swelling rather than a phase separation process. It is different from the cloud point curve (CPC) experiment studied in literature, where the experiment starts from a one-phase solution, so that the cohesional entanglement present in the solid polymer is disrupted by dissolution. The cohesional entanglement structure of the solid polymer, on the contrary, is retained in the concentrated phase on swelling, at least in the initial stage. The course of swelling as presented by the curve $V_s(t)$ was found to proceed in three stages, where V_s is the volume of the concentrated phase. In the first and third stages of $V_s(t)$, the curve goes up smoothly, while in the second stage the curve $V_s(t)$ shows large up and down jumps, indicating probably a readjustment in the network structure. Some results on a monodisperse PS sample of $M = 5.8 \times 10^5$ and a polydisperse sample of $M = 2.0 \times 10^5$ are also given. The values of V_s observed at swelling equilibrium are not in accord with the expected cloud point temperature. The cloud point curve represents a phase separation process occurring in local regions (space limited to µm) and in time scale of the order of minute, while the process $V_s(t)$ occurred in the whole space of the concentrated phase, in time scale of days. For quantitative characterization of the network present in the concentrated phase, a precise value of the polymer-solvent interaction parameter χ is needed.

Keywords　　polymer/solvent system, PS/Et$_2$O, PS/Me$_2$CO, UCST and LCST, equilibrium swelling, cohesional entanglement, cloud point curve

Introduction

Chain entanglement in rubbery and fluid state of an amorphous polymer is a characteristic feature of the condensed state of long chain macromolecules. The entanglement concept was established through studies of melt viscosity behavior, in respect to the molar mass dependence of melt viscosity and network-like visco-elasticity. Recently it was argued to be of the nature of van der Waals crosslinking through local nematic interaction, rather than topological in nature, between two or three neighboring chains of a few repeating units long along each chain, so that it has been termed "cohesional entanglement".[1,2] So far polymer scientists refrained to speak of entanglement in the glass state. However, when an amorphous polymer sample is quenched from its fluid or rubbery state, in which chain entanglement does exist, to a glass state it is no doubt that chain entanglement will be frozen and retained in the glass state. That is, cohesional entanglement network exists in the glass state of an amorphous polymer. In this work an attempt was made to explore the entanglement network in amorphous atactic polystyrene (PS) by a traditional method of solvent swelling as applied to a chemically crosslinked network. But here we have to use a "non-solvent" so that PS does not eventually dissolve in the solvent.

For the term "non-solvent" we refer to the system like PS/acetone or PS/diethyl ether,[3] when the molar mass M of PS is smaller than 10^4, homogeneous single phase solution can be obtained showing both upper critical

solution temperature (UCST) and lower critical solution temperature (LCST). The phase diagram, as usually determined for such cases by the so called cloud point curve (CPC), shows a single phase solution region between the curve of UCST and that of LCST. As the UCST increases rapidly with M while the LCST decreases rapidly with M, for PS of higher M the CPCs of UCST and LCST cross each other so that the UCST and LCST coalesce. Then the lower and upper two-phase regions merge to give an "hourglass shape" of the phase boundary curve. From Flory-Huggins theory of polymer solutions the binodal curve of the two-phase region below UCST is very much asymmetric, in the sense that the dilute phase, in equilibrium with the concentrated phase, has very low polymer concentration. For example, for a polymer/solvent system of interaction parameter $\chi = 0.65$ and the degree of polymerization of the polymer $DP = 10^2$ and 10^3, the dilute phase concentrations in volume fraction of the polymer (ϕ_p') are 1.02×10^{-2} and 1.22×10^{-3} respectively; and for $\chi = 0.70$ the corresponding dilute phase concentrations are 0.6×10^{-10} and 0.5×10^{-20} respectively.[4] Thus, for PS sample of $M = 2 \times 10^5$ ($DP = 2 \times 10^4$) in the dilute phase $\phi_p' \approx 0$, while in the concentrated phase $\phi_p'' \approx 0.3$. The phase diagram of such a case is degenerated from an hourglass shape to everywhere a two-phase region for $\phi_p \geqslant 0.3$, and the concentrated phase ϕ_p'' is in equilibrium practically with the pure solvent, as shown schematically in Fig. 1. It is interesting to note that for such a polymer/solvent system it is a highly swollen polymer phase in equilibrium with practically the pure solvent, while a usual dilute solution of the polymer can not be obtained. It is in this sense the solvent being here denoted as a "non-solvent", yet the solvent swells the polymer well. Such a system is to be considered in this paper as the case of swelling equilibrium of a polymer network, which is the cohesional entanglement network existing in an amorphous polymer in its glass state.

Experimental

Thee atactic PS samples were used in this work:

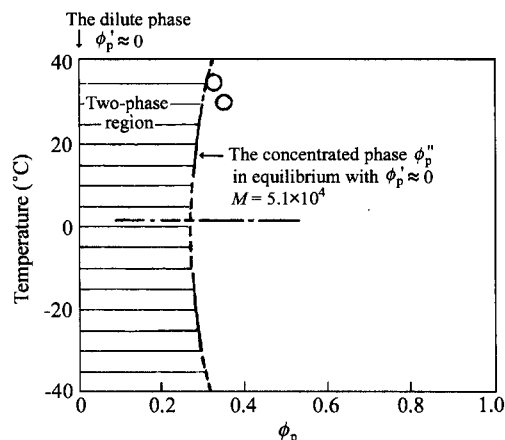| Sample	Polymerization	Source	$M_w \times 10^{-5}$	M_w/M_n
A1	Anionic	Nanjing University	1.68	1.02
A2	Anionic	Nanjing University	5.82	—
B	Free radical	Commercial pellets	1.99	2.42

Fig. 1   Phase diagram by cloud point curve experiment for the system PS/diethyl ether ($M = 5.1 \times 10^4$) from data of Siow et al.[3] The open circles in the figure indicate the experimental results of ϕ_p'' by equilibrium swelling at two temperatures obtained in this work, $M = 1.7 \times 10^5$.

All molar masses given above were determined by size exclusion chromatography. Both the samples A1 and A2 were in short fibrous form and they were processed into small granules for easy introduction into phase equilibrium tube in the following way. The sample was dissolved in tetrahydrofuran (THF) to give a transparent viscous fluid, which was then dropped into water through a pippet to form solid semi-spherical granules to be filtered. THF retained in the granules was removed by extraction with MeOH. After vacuum drying the semi-spherical granules of 2—3 mm diameter were kept in a descicator. The sample B in the form of short cylindrical (3 mm diameter) pellets, ca. 30—50 mg/pellet, was extracted with MeOH to remove impurities and then vacuum dried. The sample was then heated at 120 °C for 30 min to erase the thermal history, quenched in ice-water for 10 min and dried under vacuum. The density determined in a isopropyl alcohol-diethylene glycol density gradient tube at 30 °C was 1.045 g/mL.

Phase equilibrium experiment was carried out using a graduated measuring pipette of 0.5 cm diameter and 25 cm long, the tip end of which was sealed. The volume of the tube from the sealed bottom to one of the graduated marks of the tube was calibrated by filling with a weighed amount of distilled water. The meniscus of water or the meniscus of the concentrated phase in the equilibrium experiment was measured by a cathetometer reading to 0.02 mm, the volume in excess of the calibrated mark was in-

terpolated from the cathetometer readings between two adjacent 1 mL marks on the pipette. The sample specimen in granular form was introduced into the bottom of the tube and then the tube was drawn on a gas flame to make a neck of about 1.5 mm inside diameter at 2 cm from the top. The swelling solvent (ca. 4 mL) was introduced into the tube by a syringe. The tube was immersed in liquid nitrogen or ice water up to about 1 cm over the solvent level in the tube, and then the tube was sealed using a gas flame. The tube containing the sample and swelling solvent was put in a water thermostat for equilibrium measurement at constant temperature, the fluctuation of which was within ±0.02 ℃. When the PS granules became swollen and coalesced to form a seemingly homogeneous phase and a clear meniscus appeared between the concentrated and the dilute phases, the counting of swelling time was started. This took about 4 d for the samples A1 and A2 in diethyl ether at 30 ℃, and 16 d for the sample B, apparently because of much smaller specific surface area of the melt processed pellet sample B, as compared to the samples re-precipitated from solution. Long term observations were carried out to follow the changes of the volume of the concentrated phase under quiescent condition up to 200 d. The volume in mL of the concentrated phase per gram PS sample is denoted as V_s. From V_s the volume fraction of the polymer in the concentrated phase ϕ_p'' is calculated, $\phi_p'' = (V_s \rho_p)^{-1}$ where ρ_p is density of the polymer.

Results and discussion

Swelling equilibrium of PS in diethylether and acetone

The observed changes of the volume of the concentrated phase of the systems PS/diethyl ether and PS/acetone for the samples used leveled after ca. 100 d and 50 d, respectively. These volumes are regarded as equilibrium values as given in Table 1, expressed in mL/(g PS).

Table 1   Volume of equilibrium swelling, V_s, in mL/(g PS)

Sample	Solvent	Temp. (℃)	V_s	ϕ_p''	χ_{calcd}
	diethyl ether	30	2.74	0.35	0.66
A1	diethyl ether	35	3.00	0.32	0.64
	acetone	30	2.16	0.44	0.72
	acetone	35	2.14	0.45	0.72
A2	diethyl ether	35	2.92	0.33	0.65
B	diethyl ether	30	2.61	0.37	0.67

When this equilibrium is considered as a phase separation of a polymer/solvent system having a UCST and $\phi_p' \approx 0$, we can apply Flory-Huggins theory of polymer solutions to give[4]

$$\ln \phi_1' + (1 - 1/m)\phi_p' + \chi\phi_p'^2 = \ln \phi_1'' + (1 - 1/m)\phi_p'' + \chi\phi_p''^2 \quad (1)$$

$$\ln \phi_p' - (m - 1)\phi_1' + m\chi\phi_1'^2 = \ln \phi_p'' - (m - 1)\phi_1'' + m\chi\varphi_1''^2 \quad (2)$$

where the subscript 1 means the solvent while the subscript p means the polymer, and m is the degree of polymerization of the polymer. When $\phi_p' \leqq 0$, $\phi_1' \leqq 1$, and $m \gg 1$, Eq. (1) becomes

$$\ln(1 - \phi_p'') + \phi_p'' + \chi\phi_p''^2 = 0 \quad (3)$$

which gives the value of ϕ_p'' at equilibrium. It is well known that the theory is qualitatively good for accounting the UCST of the polymer/solvent system, but quantitatively the theoretical binodal curve falls at too high ϕ_p' and too low ϕ_p'' values at equilibrium.[4] For the observed ϕ_p'' values listed in Table 1, we get from Eq. (1) values of the χ parameter between 0.64—0.67 for PS/diethylether and 0.72 for PS/acetone. It is of course true that acetone is a poorer solvent for PS than diethylether. The values of the χ parameter calculated from Flory-Huggins theory are overestimated, the actual values must be somewhat lower. From Eq. (2) we can calculate the value of ϕ_1'. For example, for the system PS (A1)/diethyl ether at 30 ℃, $\phi_p'' = 0.35$, $\chi = 0.66$, $m = 1590$, substituting these values in Eq. (2)

$$\ln \phi_p' - (m - 1)\phi_1' + m\chi\varphi_1'^2 = \ln \phi_p'' - (m - 1) \cdot (1 - \phi_p'') + m\chi (1 - \phi_p'')_2$$

we get $\phi_p' = 8 \times 10^{-23}$. This means that the simplification $\phi_p' \leqq 0$ used in evaluating χ from Eq. (1) is self-consistent. An attempt of experimental measurement of ϕ_p' by fluorescence failed as the concentration is much below the detection limit.

If the equilibrium is considered as solvent swelling of the entanglement network in the PS glass sample, in the framework of Flory-Huggins theory, we can get the molar mass of the chain strands between the crosslinking points of the network, M_c, from the following equation[5]

$$-[\ln(1 - \phi_p'') + \phi_p'' + \chi\phi_p''^2] = (\rho_p V_1/M_c) \cdot (\phi_p''^{1/3} - \phi_p''/2) \quad (4)$$

where ρ_p is density of the polymer and V_1 is molar volume of the solvent used. However, in order to calculate the value of M_c, a precise value of χ is needed. For example, for the data of the system PS (A1)/diethyl ether at 30 ℃, $\rho_p = 1.045$ g/mL, $V_1 = 110$ mL, if we take $\chi = 0.65$, 0.60 and 0.55, we get M_c values 6.1×10^4, 7.0×10^2 and 4.5×10^2 respectively. In the absence of a precise value of χ, only a qualitative comparison of the network M_c can be made by comparing the value of ϕ_p'', a higher value of ϕ_p'' means a larger value of M_c. The views of phase separation against network swelling will be discussed later.

Three stages of long term swelling equilibration

The course of long term swelling (swelling time t over 100 d) as shown for example by the curve $V_s(t)$ in Fig. 2 for the sample PS (A1) in diethyl ether indicates that the behavior of swelling consists of three consecutive stages. In Fig. 2, at $t = 123$ d the swelling, at 30 ℃, reached close to equilibrium, then the temperature of the thermostat was increased to 35 ℃. At $t = 183$ d, the temperature was brought back to 30 ℃ and at $t = 230$ d the temperature was decreased to 25 ℃.
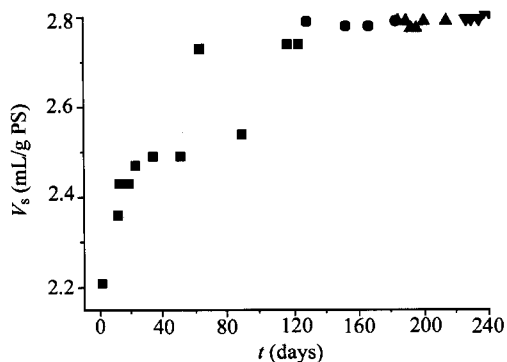

Fig. 2 The course of swelling of the sample PS (A1) in diethyl ether. ■—at 30 ℃ up to 123 d; ●—the swelling temperature increased to 35 ℃ at $t = 123$ d; ▲—the temperature of swelling brought back to 30 ℃ at $t = 183$ d; ▼—the temperature of swelling decreased to 25 ℃ at $t = 230$ d.

During the first stage of swelling the curve $V_s(t)$ increases steadily in separate steps up to $t = 50$ d. This is more clearly seen in Fig. 3a for swelling of the sample PS (A1) in diethyl ether at 35 ℃, and in Fig. 3b for

swelling at lower temperature, 25 ℃. The step by step increase of $V_s(t)$ is genuine, as it was reproducible in different runs and it appeared so in all experiments done in this work. From the view point of network swelling this seems to be the manifestation of the act of the opening of weak cohesional entanglement point by the solvent at the instant of the step increase. These weak (rather easily opened) cohesional entanglement points are very probably formed at lower temperatures during quenching of the solid sample after erasing the thermal history. The time scale of the observation was of the order of days. The growth of $V_s(t)$ curve took dozens of days, and the growth curves for the samples PS (A1) and PS (B) are comparable in this stage as shown in Fig. 4, the former being a mono-disperse sample while the latter a poly-disperse one.
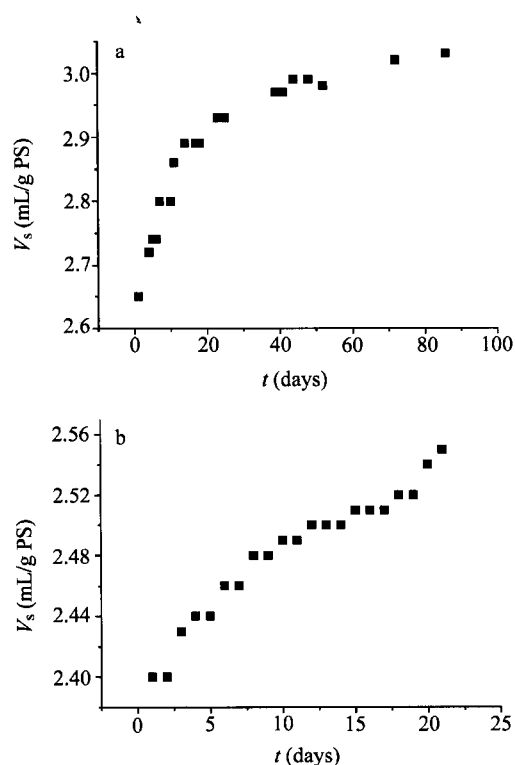

Fig. 3 The first stage of swelling of the sample PS (A1) in diethyl ether at 35 ℃ (a) and at 25 ℃ (b).

During the second stage of swelling the curve $V_s(t)$ shows large up and down jumps till $t \geqslant 100$ d. These large jumps in V_s were also reproducible and common to all cases studied, so it is believed to be genuine, but rather difficult to really understand. Jumping up of the curve indicates the disruption of cohesional entanglement points and jumping down indicates the creation of new co-

hesional entanglement points in the concentrated phase. This would mean some re-adjustment of the network structure occurring during this stage of swelling. The other possible origin of the phenomenon is explained as follows. When V_s is small, the swollen polymer is in a rubbery state. The swollen granules of the polymer would not interpenetrate each other, and the inter-granular boundaries remain until the swollen polymer reaches a fluid state in the time scale of the experimental observation.[6] Thus, the second stage of swelling is a transition from rubbery state to fluid state, whence the swollen rubbery granules begin to merge and the solvent present in the interstitial volume, which consists of the solvent only, between contacts of swollen granules will be squeezed out of the concentrated phase, causing a large drop of V_s. This transition to a fluid state also renders the entanglement network to become a relaxing network,[6] leading to the possibility of readjustment of the network structure. It is reasonable to expect that when M_c is large enough (i . e . V_s large enough), the thermal motion of these chain strands at this temperature could lead to the possibility of encountering the neighboring chain strands to form new cohesional entanglment points between them. If this would be the case, the subsequent swelling equilibrium would not reflect the original cohesional entanglement network structure of the starting sample in its glass state. Further studies are needed for elucidating the nature of this second stage of swelling.
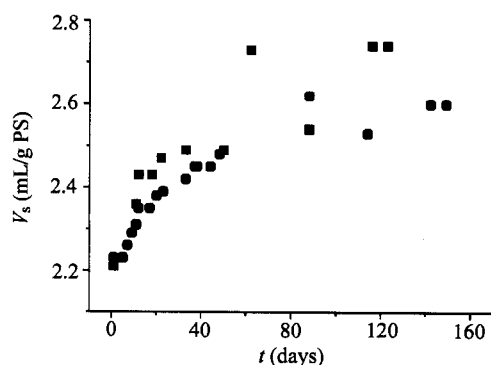

Fig. 4   Comparison of the equilibrium swelling at 30 ℃ of the monodisperse sample PS (A1) of $M = 1.7 \times 10^5$ (■) and the polydisperse sample PS (B) of $M = 2.0 \times 10^5$ (●).

On entering the third stage of swelling the curve $V_s(t)$ reverts to smooth going and approaches an equilib-

rium state, the value of V_s remaining unchanged for long time. It is interesting to note that in Fig. 2 at $t = 124$ d the thermostat temperature was increased to 35 ℃, the curve $V_s(t)$ shows a small jump to $V_s = 2.82$ and then stabilized at $V_s = 2.79$ for 60 d. During the temperature increase the concentrated phase appeared cloudy, but after staying at 35 ℃ for more than 10 h it became transparent. Then at $t = 184$ d the thermostat temperature was brought back to 30 ℃, but the value V_s stayed unchanged for 26 d. Even when the thermostat temperature was decreased to 25 ℃ at $t = 230$ d, the value of V_s still remained unchanged until the experiment finished at $t = 239$ d. This last branch of the curve $V_s(t) = 2.79$ remaining constant from $t = 124$ to 239 d reflects the network structure of the concentrated phase at 35 ℃. A cooling from 35 to 25 ℃ did not lead to the formation of any new cohesional entanglement points in the time scale of the experiment. This temperature irreversibility of V_s after equilibrium contradicts the view of phase separation, which should be reversible, but understandable from the view of network swelling. The formation of new cohesional entanglement points, for example in the case of sub-T_g annealing at low temperatures may take months to years. Similar behavior like Fig. 2 was observed for the samples PS (A2) and PS (B) in diethyl ether.

The swelling of PS (A1) in diethyl ether at 25 ℃ shown in Fig. 3b after 21 d was interrupted by transferring the tube containing the swelling system to an oil bath at 120 ℃ so that the concentrated phase was immersed below the oil level of the bath. The volume of the concentrated phase V_s was observed to decrease drastically from 2.55 to 1.59 mL/g PS in 12 h. During this period the dilute phase, which was situated above the level of oil in the bath, did not show any tendency to boil. The concentrated phase, which had been annealed at 120 ℃ for 12 h, appeared transparent when the tube was removed from the oil bath, although it might be cloudy during the temperature increase from 25 to 120 ℃. This high temperature annealing of the concentrated phase apparently led to a significant creation of new cohesional entanglement points in the concentrated phase. When this tube was removed from the oil bath at 120 ℃ and put back to the thermostat at 30 ℃ counted as $t' = 0$, a swelling curve $V_s(t')$ was observed which ended up to an equilibrium V_s value of 2.70 mL/g PS after 120 h as (being not changed up to 157 d) shown in Fig. 5, which comparable to the value 2.73 mL/g PS of Fig. 2. This confirms that

new cohesional entanglement points were formed on 120 ℃ annealing of the concentrated phase resulting from 21 d swelling at 30 ℃. These newly formed entanglement points could be gradually opened up by the solvent at 30 ℃.
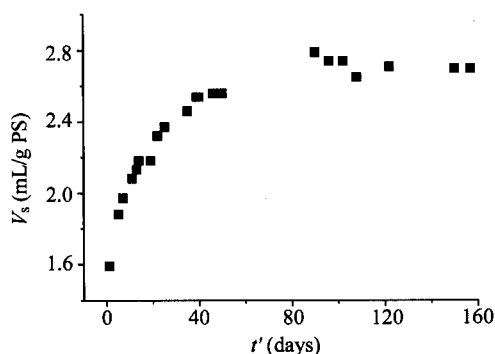

Fig. 5 The course of re-started swelling $V_s(t')$ of the sample PS (A1) in diethyl ether at 30 ℃ after being swelled for 21 d at 30 ℃ ($V_s = 2.55$ mL/g PS) and then at 120 ℃ for 12 h (V_s dropped to 1.59 mL/g PS).

The swelling behavior of the PS samples in acetone was similar to that in diethyl ether described above, but the equilibrium values of V_s were much smaller and reached at much shorter time. As an example, for the system PS (A1) in acetone at 35 ℃ the equilibrium V_s value of 2.14 mL/g PS was reached in less than 30 d, as compared to the corresponding equilibrium V_s value of 3.00 mL/g PS after 72 d in diethyl ether.

Cloud point curve (CPC)

Polymer/solvent systems exhibiting both a UCST and a LCST were usually studied by the method of so called cloud point curve. The experiment starts with a polymer/solvent system in a sealed cell at a concentration and temperature so that a single-phase solution could be obtained. Then the system is subjected to a temperature scan at a given rate (0.1—0.2 ℃/min) of either temperature decrease or temperature increase. At certain temperature during the scan a first appearance of cloudiness of the solution detected by visual observation or by a photo-electronic device is taken as the cloud point. For a system having both UCST and LCST, the cloud point appears on decreasing temperature scan as well as on the increasing temperature scan. A small glass sealed magnetic

stirrer may be introduced into the cell for stirring to guarantee a more homogeneous solution, as a polymer solution at $\phi_p > 0.3$ is usually rather viscous. The cloud points obtained from starting solution concentrations (ϕ_p) usually in the region up to 0.3 give us the cloud point curve (CPC). In case the molar mass of the polymer sample is higher than 1×10^4, a starting homogeneous one-phase solution may not exist. Then the system is subject to an applied external hydraulic pressure which enhances the goodness (*i.e.* miscibility with the polymer) of the solvent[7] to obtain a single-phase solution to start with. The cloud points are to be determined at several applied pressures so that the data can be extrapolated to zero applied pressure. The problem here is how to look at the physical nature of a CPC. So far some people take CPC as the binodal of phase separation, and some people take CPC as the spinodal of phase separation. As the measurement is a temperature scanning experiment, the CPC observed is expected to be scanning rate dependent. In view of the fact that for polymer solutions at concentrations higher than the entanglement concentration the relaxation time would be much greater than the time scale of the temperature scanning experiment, CPC obtained should not be regarded as a thermodynamic equilibrium entity. One should consider the CPC as a phase transition in a limited space scale and time scale of experimental observation. The space limitation comes from slow heat conduction of the polymer solution, so that the first appearance of the cloudiness must come from the layer of the solution in direct contact with the cell wall. From the cloudiness to visible light, the phase-separated domains must be in the order of 0.5 µm size. This also implies a very rapid process of phase separation. The time limitation comes from the transient nature of the temperature, which causes the phase transition. The time scale is of the order of less than a minute. In contrast, in an equilibrium swelling experiment of the system PS/diethyl ether what observed represents processes occurred in the whole space of the system and on a time scale of the order of days.

The cloudiness of the solution usually appears very fast when the temperature of the solution is brought across the transition temperature. It is also difficult to believe that CPC represents a binodal curve, but rather it may be more possibly a spinodal curve. This fast spinodal phase separation leads to phase-separated droplets of microscopic size to give the cloudiness. Anyway the CPC on the temperature-concentration diagram is not a true phase dia-

gram in thermodynamic equilibrium. In the case of the system PS ($M_n = 1.8 \times 10^5$)/cyclohexane where a miscibility gap exists between UCST and LCST, the experimental CPC and binodal of true phase separation equilibrium curve of the UCST branch did show some significant difference.[8]

In CPC experiment the starting solution is a one-phase solution, so the entanglement history of the solid polymer in glass state has been erased by its dissolution in the solvent. On the contrary the swelling experiment carried out in this work starts from a solid polymer in glass state in contact with a solvent, which can not dissolve the polymer. So at least in the first stage of swelling the entanglement network structure present in the glass state is retained in the concentrated phase but swollen by the solvent in contact. Even at the swelling equilibrium the values of ϕ_p'' calculated from V_s values at equilibrium should not be the same as the concentration at this temperature on CPC. The CPC's for the PS samples used in this work were not determined. However, it is still possible to show that the values of ϕ_p'' and its temperature dependence from CPC and from V_s of equilibrium swelling are different. According to the reported results[3] the mid-point temperature of UCST and LCST is almost independent on the molar mass of the sample, so this mid-point temperature for PS (A1) in diethyl ether should be around 1.4 °C, shown as the dotted line in Fig. 1. Below this dotted line the cloud point temperature should decrease with increasing ϕ_p'', while above this dotted line the cloud point temperature should increase with increasing ϕ_p''. Now the swelling equilibrium experiments of this work show that when the swelling temperature decreased the observed ϕ_p'' value increased. This contradicts the CPC behavior, as these temperatures are well above 1.4 °C. These two equilibrium ϕ_p'' values for swelling at 35 and 32 °C are also indicated in Fig. 1. This confirms that swelling equilibrium curve and CPC on the temperature-concentration diagram are different as discussed above.

Another interesting observation is as follows. When the swelling system PS (A1)/diethyl ether in equilibrium at 30 °C was removed from the thermostat and left at room temperature (20—18 °C) for quite some time (months), the concentrated phase being transparent. When it was put in a water bath and heated up at a rate of roughly 1 °C/min, a cloud point was observed. During the heating up process, cloudiness started to develop at 25 °C, starting from the top of the phase boundary extending toward

the whole concentrated phase at 30 °C. Then the concentrated phase remained cloudy in the course of further heating up to 82 °C whence the run was stopped. When the system was taken out from the water bath, standing at room temperature (18.5 °C), it came back to the original state of transparency in 10—15 min. The cloud point temperature was found to be about the same for the sample subjected to swelling at temperatures of 35, 30 and 25 °C to get equilibrium. The CPC for PS/diethyl ether of $M = 1.7 \times 10^5$ used in this work is expected to lie in the region of higher concentrations than that of $M = 5.1 \times 10^4$ shown in the temperature concentration diagram of Fig. 1. These results seem to indicate that the concentrated phase of the swelling equilibrium in local sense and in limited time scale (temperature scan) behaves like the solution in CPC measurement to show the cloud point of local phase separation. This local phase separation is reversible so that the system reverts to a transparent concentrated phase on being brought back to 18.5 °C. Experiments described in previous paragraphs show that cloudiness of the concentrated phase, developed on heating up to 35 °C a swollen PS/diethyl ether system which had been in equilibrium at 30 °C and vanished on long standing (hours) at 35 °C. This means that the local phase-separated concentrated phase at 35 °C reverts to the transparent state of swelling equilibrium on long standing at this temperature.

Conclusions

(1) The equilibrium swelling experiment differs from the cloud point curve experiment in the state of PS chains in the concentrated phase. In the former case the cohesional entanglement network present in the solid sample is retained in the concentrated phase, at least in the initial stage of swelling. In the latter case the cohesional entanglement network present in the solid sample is disrupted on dissolution.

(2) The swelling process as represented by $V_s(t)$ curve proceeds in three stages. In the first stage the increase of V_s occurs steadily in step by step processes. In the second stage the curve $V_s(t)$ shows large up and down jumps, indicating a transition of the concentrated phase from a rubbery state to a fluid state of relaxing network, leading to readjustment of the entanglement network structure by disrupting existing entanglement points and creating new entanglement points. In the third stage the curve goes smoothly and finally reaches equilibrium.

(3) The process $V_s(t)$ is a network swelling process, not a phase separation process. The process proceeds in the whole space of the concentrated phase, in a time scale of the order of days.

(4) The cloud point curve on the other hand represents a phase separation process occurring in local regions (space limited to the order of μm), and in time scale of the order of minute, being not a true phase diagram in thermodynamic equilibrium.

(5) At a given temperature the ϕ_p'' value at swelling equilibrium at given temperature T_1 differs from the value at this temperature on CPC. Furthermore this swelling equilibrium value of ϕ_p'' (at T_1) stays unchanged when the system is brought to a lower swelling temperature T_2. This irreversibility on lowering the temperature signifies that the swelling process is a network swelling rather than a phase separation, which should be reversible with temperature changes.

(6) The concentrated phase after swelling equilibrium does show a space and time limited phase separation process, i. e. the appearance of cloudiness, on being heated up crossing over the corresponding CPC. However, on long standing at this temperature or bringing back to temperatures below the corresponding CPC the cloudy concentrated phase reverts to a transparent state of equilibrium swelling.

(7) For a quantitative characterization of the cohesional entanglement network present in the concentrated phase, a precise value of the polymer-solvent interaction parameter χ determined by an independent method is needed.

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