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Influence of Intermolecular Entanglements on the Glass Transition and Structural Relaxation Behaviors of Macromolecules. 2. Polystyrene and Phenolphthalein Poly(ether sulfone)

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ABSTRACT: The effect of entanglements on the glass transition and structural relaxation behaviors has been studied for polystyrene (PS) and phenolphthalein poly(ether sulfone) (PES-C) samples by fast evaporation of the solution of concentrations varying from above the overlapping concentration to far below it, and compared to the results we have studied previously in PC. It has been found that for all the polymers we have studied, in the concentrated solution region, the T_g of the samples obtained from solution are independent of the change of concentration and are very close to that of normal bulk samples, whereas in the dilute solution region the T_g of the samples decrease with the logarithm of decreasing concentration. The critical concentrations that divide the two distinct regions for the three polymers are 0.9% g/mL for PC, 0.1% g/mL for PS, and 1% g/mL for PES-C. The decrease of T_g of the samples is interpreted by the decrease of intermolecular entanglements as the isolation of polymer chains, and the entanglement of polymer chains restrained the mobility of the segments. The structural relaxation behavior of the polymers is also found to be different from that of normal bulk samples. The enthalpies of single-chain samples are lower than that of the bulk ones, which correspond to the lower glass transition temperature; the peaks are lower and broader, and the relaxed enthalpy is much lower as compared to that of bulk samples. In the three polymers we have studied, the influence of change of entanglements on both the decrease in glass transition temperature and relaxed enthalpy is the most significant for PS and the least for PES-C. It is indicated that the interactions in the flexible polymers are weak; thus, the restraint of the entanglements on the mobility of the segments plays a more important role in the flexible polymers, and the change of entanglement in the flexible polymers has a more significant influence on the physical properties.

Introduction

The properties of single-chain samples with less chain entanglements have been studied in different polymers such as isotactic[1−3] and atactic polystyrene[4−6] and polycarbonate;[7] the properties which varied from the absorption bands in the Fourier transform infrared spectroscopy (FTIR) to the crystallization and glass transition behaviors are found to be different from that of normal bulk samples. All of the results indicate that there are distinguished differences between the single-chain samples and the normal bulk ones and also suggest that a certain structural change occurs during the process of the preparation of samples, and the conformational structure in the solution may be preserved.

In the previous paper[8] we have introduced a new method, that is, the fast evaporation method, to obtain the single-chain sample and have found that the polycarbonate sample obtained by this method is completely amorphous, while the PC sample obtained by other methods from the solution has a certain degree of crystallinity without exception. And the glass transition temperature of the sample decreases with the decreasing of concentration when the concentration of the prepared solution is below the critical value. The structural relaxation behavior found is also different from that of the bulk sample.

Doi and Edwards have proposed a correlation between the entanglement density and the unperturbed chain dimension of polymers[9]

$$M_e = B^{-2}(\langle R^2\rangle_0/M)^{-3}\rho^{-2}N_A^{-2} \qquad (1)$$

where ρ is the polymer density, M_e is the molecular weight between entanglements, B is a constant of order unity, and N_A is the Avogadro constant.

Aharoni[10] divided the entanglements of polymers into flexible, semiflexible, and rodlike groups, and the number of chain atoms between entanglements, N_c, correlated with the values of the characteristic ratio C_∞ or the Kuhn step length A are nicely divisible into the three groups above.

The unperturbed chain dimensions and entanglement molecular weight of some polymers such as polystyrene (PS), bisphenol A polycarbonate (PC), and bisphenol A polysulfone (PSF) are listed in a review by Fetters et al.[11] These data indicate that the unperturbed chain dimensions and entanglement molecular weights of these polymers are different from each other as the rigidities of the polymer chains are different. Thus, it is predicted that the influence of entanglement on these polymers may also be different.

In this paper we examined the influence of the change of entanglements on the glass transition and structural relaxation behaviors of polystyrene and phenolphthalein poly(ether sulfone) (PES-C) and compared that to the polycarbonate we have studied. PES-C is a novel thermoplastic which is a linear aromatic polymer with the chemical structure as shown in Figure 1: as there is a prodigious phenolphthalein pendent group in the backbone, the chain of PES-C is very rigid and has a glass transition temperature as high as 260 °C (deter-

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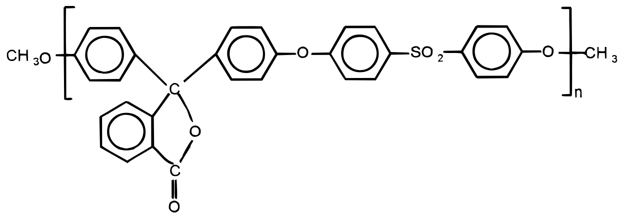

Figure 1. Chemical structure of phenolphthalein poly(ether sulfone) (methyl oxide terminated).

mined by DSC); according to the theory about the correlation between the rigidity of the polymers and the unperturbed chain dimension, the unperturbed dimension of PES-C is much larger than that of PSF.

Experimental Section

The atactic polystyrene sample with molecular weight $\overline{M}_w = 3.45 \times 10^5$ and dispersity $\overline{M}_w/\overline{M}_n = 1.24$ was obtained from Gaoqiao Chemical Plant of Shanghai (China). The PES-C sample was obtained from Xuzhou Engineering Plastics Co. (China) and purified by fractional precipitation before use; the molecular weight of the purified sample was $\overline{M}_w = 2.03 \times 10^4$ and distribution $\overline{M}_w/\overline{M}_n = 1.37$.

Reagent grade chloroform was used after distilled twice from a quartz still. The glass apparatus was etched by a potassium bichromate−sulfuric acid mixture and subsequently thoroughly rinsed with doubly distilled water.

Single-chain particles of polystyrene and PES-C were obtained as described in the Experimental Section of the previous paper.[8]

The differential scanning calorimetry was run on a Perkin-Elmer DSC-7 system. Indium metal was employed for temperature calibration, and the data were evaluated with respect to sapphire as a heat capacity standard. The heating rate was 10 °C min^{-1} where a nitrogen gas purge was used. The fluffy single-chain polymer samples were pressed under room temperature at 53 kbar into pellets before DSC scanning in order to abstain from the error that might be caused by the different thermal transfer effect.

Sample weights were between 6 and 11 mg, and the unaged glasses were formed by cooling at 20 °C min^{-1} to $T_g - 70$ °C after holding for 10 min at $T_g + 50$ °C to erase the previous thermal history for both the single-chain sample and bulk sample. Aged glasses were subjected to the same thermal treatment, but first cooled to the chosen T_a, held for the required t_a, then finally cooled to $T_g - 70$ °C prior to the data acquisition heating scan. The structural thermal history stability of the samples was monitored by recycling through the chosen thermal history several times without aging.

Results and Discussion

Glass Transition Temperature Dependence of Concentration. The PS and PES-C samples obtained by the fast evaporation method from different concentrations of solution are scanned by DSC, the glass transition temperatures are determined from the DSC scans, and the concentration varies from 5% to 10^{-5} g/mL, that is, from above the critical concentration to far below it.

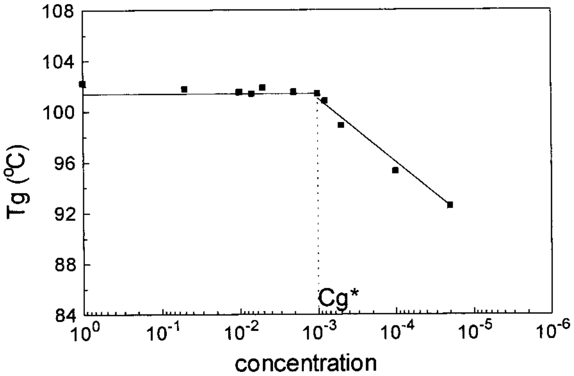

Figure 2. Glass transition temperature of polystyrene samples obtained by the fast evaporation method from different concentrations.

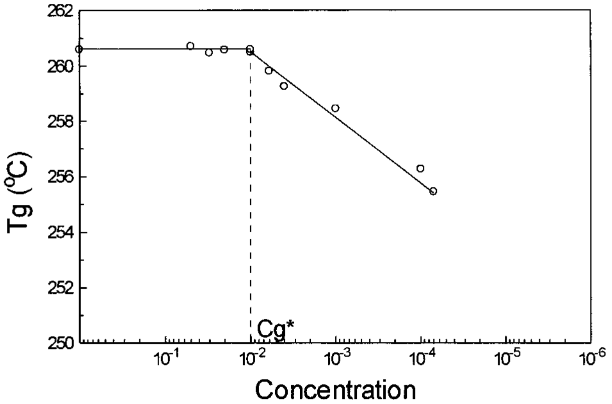

Figure 3. Glass transition temperature of PES-C samples obtained by the fast evaporation method from different concentrations.

Figures 2 and 3 show the dependence of glass transition temperature of the samples obtained by the fast evaporation method on the concentration of the polymers solution for PS and PES-C, respectively. As similar to the case of polycarbonate, the glass transition temperatures of the samples change with the concentration and can be divided into two regions: In the dilute solution region the glass transition temperature of the samples decreases linearly with the decreasing of logarithmic concentration, whereas in the concentrated solution region the glass transition temperatures of the samples remain nearly constant and very close to that of the normal bulk samples. The critical concentration values of C_g* that divided the two regions of the two polymers are 1.0% and 0.1% g/mL, respectively. It should be noted that despite the critical values C_g* are obtained from the change of T_g of solid polymer sample; they reflect that the polymer chains in the solution change from overlap to isolated.

Dilution of high molecular weight, M, polymers with $M \gg Mc$ does not significantly affect the entanglement interaction between polymer chains, as was experimentally observed[12] that the onset of entangled behavior at a concentration c is well approximated by

$$(cM)_c \cong Mc \tag{2}$$

where $(cM)_c$ is the product of concentration and molecular weight at the point of onset of entangled behavior. When the concentration is above the critical value, the T_g of the samples obtained by the fast evaporation method are independent of the concentration and close to the T_g of the normal bulk sample, which suggests that in this concentration range the entanglements between the polymer chains did not change very much compared to the bulk state.

As we have proposed in the previous study,[8] below the critical concentration, the decrease of T_g of the samples obtained from dilute solution by the fast evaporation method is the reason that the isolated state of the polymer chains in the solution retained in the obtained samples; thus, the number of intermolecular entanglements decreases greatly. The decrease of entanglement promotes the mobility of the segments, and the glass transition temperature consequently decreases.

It should be noted that, for the different polymers as well as with different molecular weights, the critical concentration values are different, too. The C_g* value for PC is 0.9% g/mL, 0.1% g/mL for PS, and 1% g/mL for PES-C. For polymer solution, scaling laws are well established and are found to be universal, that is, valid for any polymer molecular weight and polymer species.[13,14] These concentration scaling laws are expressed as functions of the overlap ratio C/C^*, independent of local properties. C^*, the overlap concentration, corresponds to the polymer close packing condition: $C^* \propto N/R^3$. The dilute size R and degree of polymerization N are linked by $R \propto N^v$, with $v = 0.588$ and 0.5 for good solvent and for Θ solvent conditions, respectively. Thus, the correlation between C^* and N is $C^* \propto N^{(1-3v)}$ for good solvent and for Θ solvent are $C^* \propto 1/N^{0.764}$ and $C^* \propto 1/N^{0.5}$, respectively. For both of the cases, the critical concentration value is inversely proportional to the degree of polymerization. That is in agreement with the above results.

Despite the T_g dependence on the change of concentration in the solution for the different polymers we have studied having the same tendency, the influence of the change in concentration of the solution on the extent of the decrease of T_g of the obtained samples is not the same for different species. As can be found in Figures 2 and 3 as well as the previous paper,[8] for the samples obtained from 0.01% g/mL solution by the fast evaporation method, the decrease of T_g in PS is 9.7 °C and in the PC is 9.2 °C, while the decrease of T_g in PES-C is only 5.6 °C. Considering the critical concentration of PS is lower than that of PC and PES-C, the influence of concentration of the preparing solution on the decrease of T_g in PS is more significant. As the T_g of PS is much lower than that of PC and PES-C, the influence of interchain entanglements on the glass transition behavior is also the most significant in PS and the least significant in PES-C. That is, the more flexible the chain of the polymer is, the more significant is the influence of entanglement on the change of T_g.

As the interactions in the flexible chain polymers are weaker, the effect of entanglements on the mobility of the segments is more important than that in the rigid polymer chains. In the rigid chain polymers, the factors that may restrain the mobility of the segments are the electrostatic interaction, the spatial obstacle of bulky groups, and the rotational obstacle in the backbone besides the entanglement. Thus, the influence of entanglement on the mobility of the segments is relatively less significant.

Effect of Entanglement on the Structural Relaxation Behavior. Figure 4 shows the DSC curves of the single-chain sample and normal bulk polystyrene sample annealed at the same aging temperature and for the same time. It is found that, corresponding to the lower glass transition temperature, the enthalpic peak of the single-chain polystyrene sample is also lower than the normal bulk sample. And the shape of the peak of the single-chain sample is also different from that of bulk sample. The peak height of the single-chain sample is lower, but the peak width is wider than that of the normal bulk sample. The same case has been reported in the polycarbonate.[8] Both Sasak et al.[6] and Qian et al.[15] found that there is an exothernal peak near the glass transition region in the polystyrene single-chain sample but cannot be found in the PS and PES-C samples we studied. The enthalpy relaxation data obtained from Figure 4 are listed in Table 1.

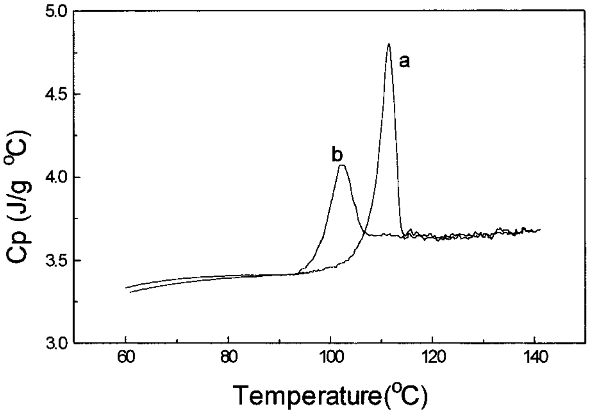

Figure 4. DSC curves of PS samples physical aging at the same temperature (T_a = 90 °C) and for the same time (24 h): (a) normal bulk sample; (b) sample obtained from 0.01% solution by the fast evaporation method.

Table 1. Enthalpy Relaxation Data Obtained from Figure 4

sample	T_g (°C)	T_p (°C)	W_p (°C)	H_p (J/g °C)	ΔH (J/g)
a	105.7	111.5	7.5	1.017	3.65
b	97	102.2	9.1	0.364	1.47

[a] The normal bulk PS sample. [b] The PS sample obtained from 0.01% solution by the fast evaporation method.

It should be noted that the relaxed enthalpy of the single-chain sample is much lower than that of the bulk polystyrene sample, as listed in Table 1.

Hodge et al.[16−18] have predicted the influence of entanglement in polymers on the structural relaxation. They noticed that the extrapolation of the experimental values of $\Delta H(T,t)$ to long times leads to limit values considerably lower than the theoretically predicted ones, and they compared the modeling curves and the experimental curves and find that the models usually predict narrower and higher peaks than the experimental ones after annealing close to T_g. They ascribed the distinctive feature in polymers to the effect of entanglement in the polymer.

In this study, the structural relaxation behavior of the single-chain sample which contain less entanglements is found truly different from the bulk sample, which is in accordance with the prediction aforementioned. But contrary to the above prediction, the result shows that the sample with less entanglements has a broader and lower peak than the normal bulk sample, and the relaxed enthalpy is much lower than the bulk one, which may be the reason that in the single-chain state the isolated polymer chains adopt a highly compact conformation and in a more equilibration state. That is similar to the structural relaxation behavior of the single-chain polycarbonate sample.

The structural relaxation behavior of the single-chain sample and normal bulk PES-C sample annealed at the same temperature and time are shown in Figure 5. It is similar to the cases of polycarbonate and polystyrene, the temperature of the enthalpic peak of the single-chain PES-C sample is also lower than that of the bulk sample, and the peak height of the single-chain sample is lower but the peak width is wider than that of the

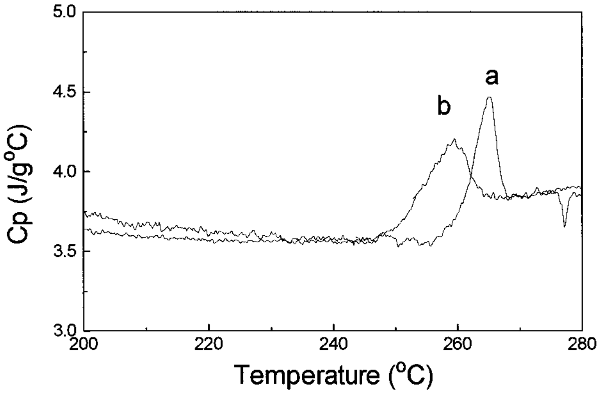

Figure 5. DSC curves of PES-C samples physical aging at the same temperature (T_a = 230 °C) and for the same time (85 h): (a) normal bulk sample; (b) sample obtained from 0.01% solution by the fast evaporation method.

Table 2. Enthalpy Relaxation Data Obtained from Figure 5

sample	T_g (°C)	T_p (°C)	W_p (°C)	H_p (J/g °C)	ΔH (J/g)
a	258.7	265.1	7.6	0.624	2.67
b	252.7	259.4	11.1	0.302	1.72

[a] The normal bulk PES-C sample. [b] The PES-C sample obtained from 0.01% solution by the fast evaporation method.

normal bulk sample. From the enthalpic relaxation data listed in Table 2 we can find that the relaxed enthalpy of the single-chain sample is also much lower than that of the bulk PES-C sample.

Like the entanglements on the decrease of glass transition temperature for the different polymers we have discussed above, the changes of structural relaxation behavior for the three polymers are also different. As for the samples obtained from 0.01% g/mL solution by the fast evaporation method, the relaxed enthalpy of the single-chain polystyrene sample is only 40% of the normal bulk sample and that of the polycarbonate is 45%, while for the PES-C it is 65%. (The detailed data can be found in Tables 1 and 2 as well as in ref 8.) It can be found that the effect of entanglements on the change of structural relaxation behavior is more significant for the flexible polymer than that of the rigid polymer. This is similar to the influence of entanglements on the glass transition behavior of the polymers.

Conclusion

The effects of entanglements on the glass transition and structural relaxation behaviors have been studied for PS and PES-C by fast evaporation of the solution of concentrations varying from above the critical overlapping concentration to far below it, and compared to the results we have studied previously in PC. It have been found that for all the polymers we have studied the glass transition temperature of the obtained samples changes with the concentration and can be divided into two regions: In the concentrated solution region, the T_g of the samples are independent of the change of concentration and very close to that of normal bulk samples, while in the dilute solution region the T_g of the obtained samples decrease linearly with the decreasing of logarithmic concentration. The critical concentrations that divide the two distinct regions for the polymers with different molecular weights are 0.1% g/mL for PS and 1% g/mL for PES-C. These results suggest that the polymer chains in the samples obtained by the fast evaporation method retained the state in solution. The decrease of T_g of the samples is explained by the decrease of intermolecular entanglements as the isolation of polymer chains and the entanglement of polymer chains restrained the mobility of the segments. It was also found that the influence of entanglement on the decrease of glass transition temperature in the flexible polystyrene is more significant than the rigid phenolphthalein poly(ether sulfone).

The structural relaxation behaviors of the polymers are also found to be different from that of normal bulk samples. The enthalpies of single-chain samples are lower than that of the bulk ones, which correspond to the lower glass transition temperature; the peaks are lower and broader, and the relaxed enthalpies are much lower as compared to that of bulk samples. In the three polymers we have studied, the difference in structural relaxation between the single-chain sample and the normal bulk one is the most significant for PS and the least for PES-C, which is similar to the glass transition behavior. It is indicated that the interaction in the flexible polymers are weak; thus, the restraint of the entanglements on the mobility of the segments plays a more important role in the flexible polymers, and the change of entanglement in the flexible polymers has a more significant influence on the physical properties.

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