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# Influence of Entanglements on the Glass Transition and Structural Relaxation Behaviors of Macromolecules. 1. Polycarbonate

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ABSTRACT: We obtained the single-chain polycarbonate sample by a new fast evaporation method and found that the polycarbonate sample obtained by this method is completely amorphous, while the polycarbonate sample obtained by other methods all have a certain degree of crystallinity. The glass transition temperature ($T_g$) of the sample decreases with the decreasing of concentration when the concentration of the prepared solution is below the critical value. The critical concentration we obtained from the $T_g$ dependence of concentration is 0.9% g/mL and is in accord with that obtained by viscometry and light scattering methods directly from the solution. The structural relaxation behavior is found also different from that of a normal bulk sample of polycarbonate. The enthalpic peak of the single-chain sample is lower than that of the bulk one, which corresponds to the lower glass transition temperature. The peak of the single-chain sample is lower and broader, and the relaxed enthalpy is much lower compared with that of the bulk sample. These results have been explained in terms of the effect of entanglement on the mobility of the segments in polymer and the compact conformation in the single-chain sample.

## Introduction

When a very dilute polymer solution in the absence of any polymer−polymer interactions is dried by a special method, a specific structure is expected to be obtained; i.e., the individual polymer chain is isolated without chain entanglement and overlapping.

However, obtaining single-chain polymer particles is very difficult because usually removal of solvent from the solution causes an increase in concentration, and ultimately it causes entanglement of polymer chains. Therefore, special techniques are required.

Isolated single- or pauci-chain polymer particles can be obtained using several different methods, all relying on isolation of the molecules from dilute solutions. Once the polymer is dissolved, the rapid addition of a bad solvent can lead to precipitation of isolated single-chain polymer particles.[1−4] Alternatively, the solution can be rapidly frozen and the solvent removed subsequently by sublimation, leaving isolated single-chain particles.[5−7] A variety of spray methods have also been used to generate isolated polymer particles. These rely on the evaporation of the solvent from droplets of dilute solutions containing single polymer molecules.[8−14] Recently, Kumaki developed a new method to obtain single-chain particles of polymers; they were obtained by spreading dilute polymer solution in benzene on a water surface.[15,16]

In the present work, another method was developed by us to obtain single-chain particles. That is, by dropping dilute polymer solution in which the boiling point of the solvent is far below 100 °C into boiling water, the solvent will evaporate in a split second, leaving isolated polymer on the water surface. As the solvent evaporation process is very fast, the obtained solid polymer chain would remain in the isolated state as they were in the solution.

In the single-chain sample the polymer chain is isolated from each other; thus, entanglement between different polymer chains which is ubiquitous in the normal bulk polymer state is absent in the single-chain sample. Many properties of the single-chain sample are reported different from that of the normal bulk polymer. Studies showed that the single-chain samples have higher crystallinity and very rapid crystallization rate compared with the usual crystallization from the melt in isotactic polystyrene[17−19] and polycarbonate.[20] In the freeze-dried a-PS, some absorption bands characteristic of the specific structure of freeze-dried a-PS were found.[21,22] Dai et al. reported that the glass transition temperature of the freeze-dried sample is approximately 10 °C lower than that of the normal bulk sample in a-PS.[23]

All of the results suggest that the properties of the isolated single-chain polymer particles are different from the normal bulk samples as chain entanglements and overlapping in the former are absent.

In this study, the glass transition temperature of polycarbonate obtained by the fast evaporation method from different concentration solutions was determined by DSC, and the concentration dependence of the glass transition temperature was found. The physical aging behavior of the single-chain sample was also found to be different from that of the bulk sample.

## Experimental Section

Bisphenol-A polycarbonate was kindly supplied by Tianjin Chemical Plant of China. The polycarbonate had a mass-average molecular weight $\overline{M}_w$ of 1.7 × 10$^4$ and molecular weight distribution $\overline{M}_w/\overline{M}_n$ of 1.79.

Reagent grade chloroform was used after being 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 polycarbonate were obtained as described below. A drop of dilute polycarbonate solution was dripped into the boiling water by using a Teflon syringe. The boiling water was kept in a beaker and placed in a constant temperature regulator. The melt point of the chloroform is 67 °C, which is far below the temperature of boiling water. When

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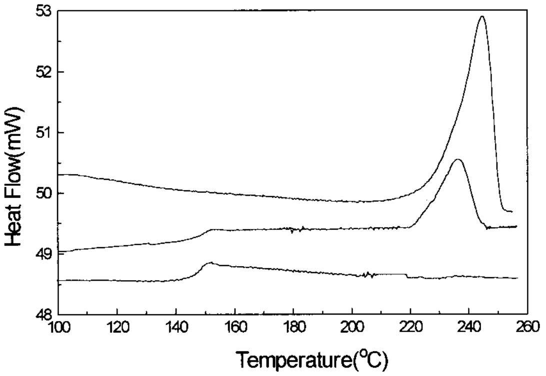

**Figure 1.** DSC scan curves for polycarbonate samples obtained from 5% chloroform solution by different methods (from top to bottom: heat deposition, normal heating evaporation, and fast evaporation).

the solution is dripped into the boiling water, the solvent will evaporate in a split second, leaving the fluffy sample on the water surface. The sample was collected and then kept under vacuum for 1 week at room temperature in order to evaporate the solvent residual and water. This is an important procedure since the remaining solvent inside the polymer powder might act as a plasticizer and thus lower the observed glass transition temperature.

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 polycarbonate sample was pressed at 53 kbar into pellets before DSC scanning in order to abstain from the error that might be caused by the difference of the 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 $T_g + 40$ °C to erase 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 $t_a$, and then finally cooled to 50 °C prior to the data acquisition heating scan. The structural thermal stability of the samples was monitored by recycling through the chosen thermal history several times without aging in order to sure that structural equilibrium was achieved.

## Results and Discussion

**Fast Evaporation Method.** To comprehend the efficiency of the fast evaporation method, the DSC scans of polycarbonate sample obtained from 5% chloroform solution by different methods are listed in Figure 1. These methods are as follows: heat deposition by adding methanol;[24] normal heat evaporation by heating the solution directly; and fast evaporation described in the Experimental Section. From Figure 1 we can find that the polycarbonate sample obtained by heat deposition has the most prominent melt peak. The crystallinity is so high that the glass transition of the amorphous part cannot be distinguished. The sample obtained by the normal heating evaporation method has a certain degree of crystallity but is less than that of the heat deposition sample. The melt enthalpy of the heat deposition sample is 39.6 J/g, and is 7.91 J/g for the normal heat evaporation sample. According to linear relationship between the crystallinity degree and melt enthalpy obtained by Adam et al.,[24] the crystallinity in the two samples are about 25% and 5%, respectively.

In Figure 1 it should be noticed that the sample obtained by the fast evaporation method does not show any melt peak at all, indicating the sample is completely amorphous. This result suggests that fast evaporation method can make the solvent evaporate very rapidly, so the polycarbonate macromolecular chains do not have enough time to crystallize before they separate out from the solution.

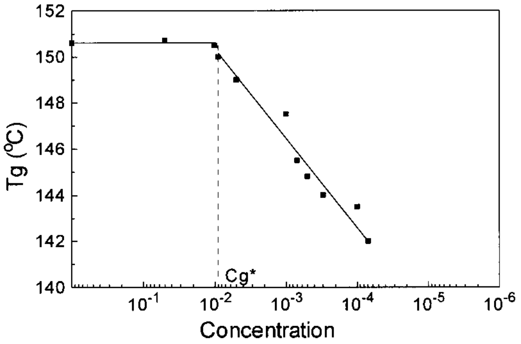

**Figure 2.** Glass transition temperature of polycarbonate samples obtained by the fast evaporation method from different concentrations.

**Glass Transition Temperature Dependence of Concentration.** The polycarbonate 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 scan, and the concentration varies from 5% to $2 \times 10^{-5}$ g/mL, that is, from above the critical concentration to far below it.

Figure 2 shows the dependence of glass transition temperature on the logarithmic concentration of the solution. It can be found that the glass transition temperatures of the samples change with the concentration and can be divided into two regions: In the concentrated solution region, the glass transition temperature of the samples are independent of the change of concentration and very close to that of the normal bulk sample. In the dilute solution region, however, the glass transition temperatures of the obtained samples decrease with the decreasing concentration; there is a linear correlation between the glass transition temperature of the samples and the logarithmic concentration in this region. A critical concentration point between the two regions can be determined; the value is 0.9%. To distinguish that value determined directly in solution, the critical concentration is named as $C_g$*.

Polymer solution theory indicates that there is an overlap concentration, $C$*, where physical contact among macromolecular coils starts as proposed by de Gennes.[25] Below $C$*, it is generally assumed that macromolecules exist as isolated single-chain coils in solution. However, Qian et al. suggested a dynamic contact concentration ($C_S$), at which coils have already contacted due to molecular motion, and they argued that only below $C_s$ are coils well-separated in solution. $C_s$ is usually 1−2 orders of magnitude lower than $C$*.[26]

It is interesting that the critical concentration we obtained here is well in the range of the values determined by viscometry and light scattering methods directly from the solution,[27] which implies that the sample obtained by the fast evaporation method remains the state in the prepared solution.

Kumaki[15] and Festag et al.[14] obtained the single-chain sample by different methods, and they concluded the same result; that is, the number of single-chain particles increases with the decreasing of concentration. Thus, it is reasonable to assume that below the critical

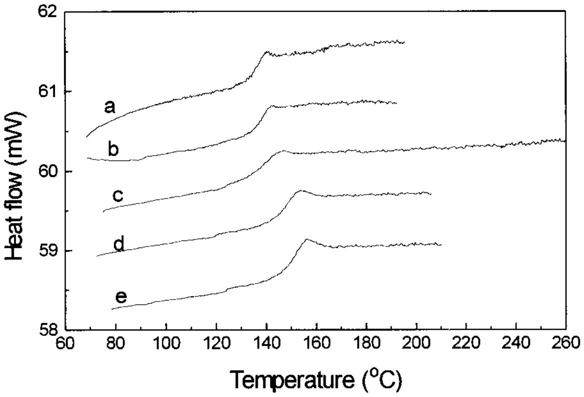

**Figure 3.** DSC curves of PC samples obtained from different approaches: (a) sample obtained from 0.01% solution by fast evaporation method in the first scan (up to 200 °C), (b) the sample in the second scan, (c) the sample in the third scan (up to 260 °C), (d) the sample in the fourth scan, and (e) the normal bulk sample.

concentration, as the concentration decreases, the number of the single-chain particles also increases, and the glass transition temperature of the obtained sample consequently decreases.

Entanglements develop from the interpenetration of random-coil chains and are important in determining rheological, dynamic, and fracture properties. The studies on entanglement are usually made in the solution in which the polymer interaction with the solvent and the properties of the polymer are influenced by the solvent; thus, the effect of entanglements on the properties of the polymer itself is difficult to determine.

Other properties such as crystallization behavior and IR absorbance spectra of the polymer also have been reported to change with the prepared concentration by the freeze-dried method.[17−22] Dai et al. also reported the decrease of glass transition temperature of polystyrene sample obtained by the freeze-dried method.[23]

In the samples obtained by the fast evaporation method, as the concentration of the prepared solution decreased, the number of single-chain particles increased; thus, intermolecular entanglements which are ubiquitous in the bulk polymer will decrease greatly. The existence of entanglements is usually considered to prohibit the mobility of the segments in the polymer. Thus, the decrease of entanglement promotes the mobility of the segments, and the glass transition temperature consequently decreases.

Another reason the glass transition temperature can decrease may be the degradation of the molecular chain during the prepared processing. The following results except the possibility of degradation in the single-chain sample. Figure 3 shows the DSC curves of polycarbonate sample made by the fast evaporation method under three scannings. The first scan of the virgin single-chain polycarbonate sample has a very low glass transition temperature compared to that of the normal bulk sample. The $T_g$ of the treated sample in the second scan is the same as in the first scan even after heating the sample up to 200 °C, which is 50 °C higher than the $T_g$ of the polycarbonate sample. In the first three scans, $T_g$ is about the same and 10 °C lower than the normal PC, which implies that the congregate state of the sample does not change in the scan temperature range. However, the DSC curve D scanned after heating the sample to 260 °C became similar to curve E, which is recorded from the normal bulk PC sample. Under the temperature of 260 °C the polycarbonate sample is in a state of melt; thus, the movement of the whole macromolecular chain can be achieved. The intermolecular chain entanglement comes into being over again through interchain penetration; as a result, the glass transition temperature of the sample is close to that of the normal bulk sample. Below the temperature of 200 °C, the movement of the whole chain is restrained, and the isolated single-chain state remained; thus entanglement cannot formed, and the glass transition temperature of the single-chain sample remains unchanged in the temperature region.

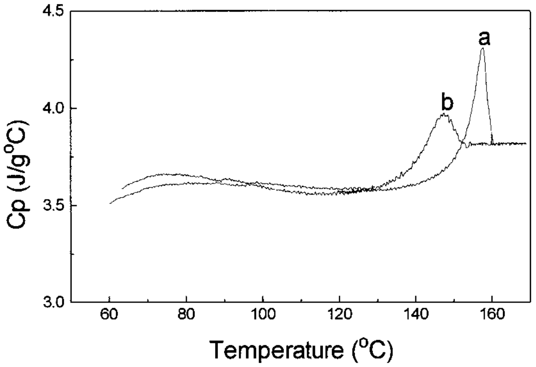

**Figure 4.** DSC curves of PC samples physical aging at the same annealing temperature ($T_a$ = 120 °C) and for the same time (120 h): (a) normal bulk sample; (b) sample obtained from 0.01% solution by the fast evaporation method.

**Table 1. Enthalpy Relaxation Data Obtained from Figure 4**

| sample[a] | $T_g$ (°C) | $T_p$ (°C) | $W_p$ (°C) | $H_p$ (J/(g °C)) | $\Delta H$ (J/g) |
|---|---|---|---|---|---|
| a | 155 | 157.5 | 6.7 | 0.458 | 1.97 |
| b | 147 | 149.6 | 10.2 | 0.227 | 0.88 |

[a] Sample a is the normal bulk PC sample, and sample b is the single-chain PC sample obtained from 0.01% solution by the fast evaporation method.

**Effect of Single-Chain State on the Structural Relaxation Behavior.** Sasak et al. reported that the IR spectra of the single-chain atactic polystyrene sample obtained by the freeze-dried method is different from that of bulk sample, which implies that the microstructure of the single-chain sample underwent change compared to the normal bulk sample. Since the structural relaxation behavior involves the rearrangement of the microstructure in the polymer,[28] the structural relaxation behavior of the single-chain sample may be different from the bulk sample.

Figure 4 shows the DSC curves of the single-chain sample and normal bulk polycarbonate sample annealed at the same aging temperature for the same time. From Figure 4 we can find that, corresponding to the lower glass transition temperature compared to the normal bulk sample, the enthalpic peak of the single-chain polycarbonate sample is also lower than that of the bulk sample. The shape of the peak of the single-chain sample is different from that of bulk sample, too. The peak height of the single-chain sample is lower but the peak width is wider than that of the normal bulk sample. The enthalpy relaxation data obtained from Figure 4 are listed in Table 1.

We can recognize that an exothermic peak precedes the glass transition in the single-chain sample in Figure 4. This peak corresponds to the enthalpy difference between the single-chain structure and a nonequilibrium glassy state (or at least the melt state in equilibrium), indicating that the enthalpy in the single-chain state is lower than that in the normal bulk state.

It is worth pointing out that the relaxed enthalpy of the single-chain sample is much lower than that of the bulk polycarbonate sample, as listed in Table 1.

The influence of entanglement in polymers on the structural relaxation has been predicted by Hodge[29] and Gomez Ribelles[30] as well as by Cowie.[31] 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 found 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, we find that the structural relaxation behavior of the single-chain sample which contains less entanglements is truly different from the bulk sample, which is in accordance with the prediction mentioned previously.

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. de Gennes has pointed out that in single-chain systems the requirement of adequate space filling necessarily implies that the polymer chains adopt a highly compact conformation.[25] Thus, the obtained single-chain sample might be in a more equilibration state, and the relaxed enthalpy is much lower. The difference also exists in the polystyrene and poly(ether sulfone)[32] we have studied.

## Conclusion

In this work we obtained the single-chain sample of polycarbonate by a new fast evaporation method and found that the polycarbonate sample obtained by this method is completely amorphous, while the polycarbonate sample obtained from solution by other methods has a certain degree of crystallinity without exception. The glass transition temperature of the sample decreases with the decreasing of concentration when below the critical concentration, and the critical concentration value we obtained from the $T_g$ dependence of concentration is 0.9% g/mL, which is in accordance with that one obtained by viscometry and light scattering methods directly from the solution. All of the results suggest that the fast evaporation method can efficiently remove the solvent and the remaining polymer chain in the state when it is in solution. The decrease of glass transition temperature is considered as the single-chain sample which contains less entanglements, thus promoting the mobility of the segments in the polymer. The structural relaxation behavior is also found to be different from that of a normal bulk sample in polycarbonate. The enthalpic peak of the single-chain sample is lower than that of the bulk one, which corresponds to the lower glass transition temperature. The peak is lower and broader, and the relaxed enthalpy is much lower when compared with that of the bulk sample. That can be explained as the single-chain sample adopts a highly compact conformation; thus, the sample is in a more equilibrium state.

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