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Crystallization and Relaxation Behavior of Partially Disentangled Poly(vinyl chloride) Prepared from Large Molecule Solvent Dioctyl Phthalate

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ABSTRACT: Poly(vinyl chloride) (PVC) samples for the conformation and structural relaxation studies were prepared by freeze-extracting the solutions in various solvents and with varying concentrations. The partially disentangled PVC samples could be obtained by freeze-extracting very dilute PVC/tetrahydrofuran (THF) and PVC/dimethyl phthalate (DMP) solution (0.05 wt %), while the PVC sample remains in an entangled state after freeze-extracting the concentrated solutions in THF and in DMP. Surprisingly, the extent of interpenetration of PVC chain decreases, even in concentrated solution in dioctyl phthalate (DOP) (5 wt %), which is contrary to accepted theories. DSC and infrared spectroscopic studies showed that a higher ordered conformation could be achieved for the disentangled specimens recovered from concentrated solution in DOP than for the entangled samples prepared from THF and DMP. DSC heating curves showed strong and sharp endothermal peaks for the disentangled polymer after sub-T_g annealing. The structural relaxation behavior of the disentangled PVC freeze-extracted from DOP solutions is more predominant, which is in good agreement with the modeling predictions.

Introduction

It is well-known[1] that atactic poly(vinyl chloride) (PVC) is a low crystalline polymer. Commercial PVC contains less than 10% crystalline segments. But this relatively low level of order has a surprisingly significant effect on both its processing and properties. As early as 1926, Flumiani[2] reported that the dispersion state of PVC in the solution could be influenced by temperature, the various heating period, the aging of the solution, the solvent itself, and even the method of preparation of different concentrations of the solution. Despite numerous studies[2−6] dealing with the gelation and aging process of PVC solutions, the mechanism of formation and the structure of PVC physical gel have still not been fully elucidated. It is generally accepted that the cross-links in these gels are tiny crystallites, although according to Guenet et al.,[7] hydrogen bonding also plays an important role. Effects of polymerization temperature,[8] heat treatment,[9,10] and processing temperature[11] on crystalline of PVC have been investigated. However, until now, little has been done on the conformation and structural relaxation of PVC affected by solvent because of the complexity of the solvents applied.

In our previous work, we prepared partially disentangled PVC samples by the freeze-extraction method from dilute PVC/THF solutions and found that the conformation and relaxation behavior of PVC depended strongly on the entanglements in polymers.[12] We also found that the molar volume of solvents plays an important role in the entanglement state of polymer in solution.[13−15] Therefore, it is necessary for us to explore the effect of solvent on the conformation of PVC. In this work, we selected a normal plasticizer DOP, which has large molar volume, as well as DMP and THF, as the solvents for PVC.

Some attempts[16−18] have been made to study the extent of flexible-chain interpenetration as a function of solution concentration. Work in those laboratories has demonstrated that freeze-drying of polymer solution may lead to a metastable state solid, which could crystallize easily. It was assumed[19,20] that the extent of chain entanglement remains unchanged during the rapid freezing so that, after removal of the frozen solvent by sublimation, the material should retain a memory of the chain interpenetration that has existed in the original solution. In this study PVC samples for the conformation and structural relaxation studies were prepared by freeze-extracting the solutions in various solvents and with varying concentrations.

Experimental Section

The polymer used in this experiment was a commercial low-temperature polymerized PVC with an intrinsic viscosity of 1.63 dL/g measured in THF, corresponding to an average molecular weight of about 11.3×10^4. The solvents, dioctyl phthalate (DOP), dimethyl phthalate (DMP), and tetrahydrofuran (THF), were commercially available and purified by filtration before use.

The freeze-extracted samples were prepared by dissolving the desired amount of PVC in THF at room temperature and in DOP and DMP at 120 °C. The solutions were then poured into liquid nitrogen to freeze the binary system in a fraction of second. Solvent was extracted by adding a large amount of cold ethanol into the frozen system at about −10 °C and was stirred for 24 h with a magnetic stirring bar. The powdered PVC was then separated by ultracentrifugation and dried under vacuum at room temperature. The separated PVC specimens were then repeatedly extracted with ethanol and dried at room temperature until reaching a constant weight. This procedure ensured no solvent residual in the dried powder.

FT-IR spectra of the collected PVC were recorded using a Bruker IFS66V vacuum-type FT-IR spectrometer. All of the spectra were taken with 4 cm^{-1} resolution. Differential scanning calorimeter (DSC) measurement was run on a Perkin-Elmer DSC-Pyris 1 system. Temperature calibration was performed using indium as a standard.

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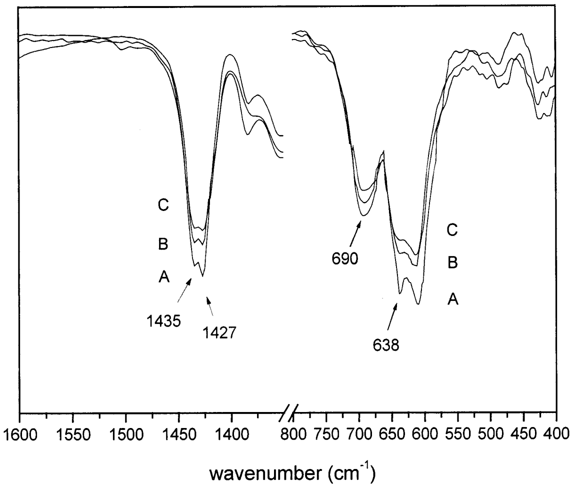

Figure 1. FT-IR spectra of PVC samples freeze-extracted from 5 wt % PVC/DOP (A), PVC/DMP (B), and PVC/THF (C) solutions.

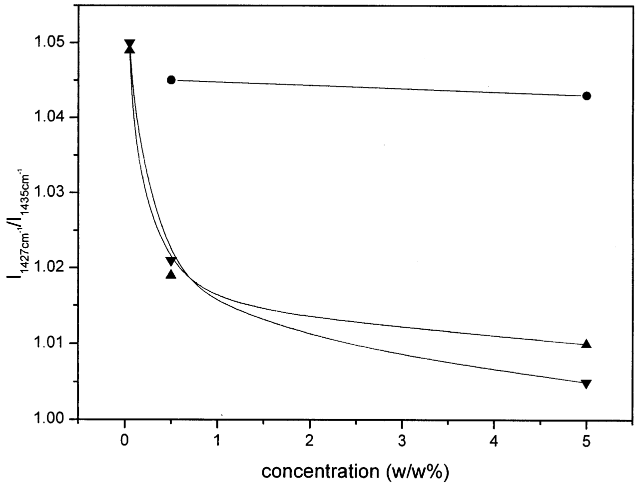

Figure 2. Plots of the IR Intensity ratio of $I_{1427\ \mathrm{cm}^{-1}}/I_{1435\ \mathrm{cm}^{-1}}$ vs the original solution concentration for samples from PVC/THF (▼), PVC/DMP (▲), and PVC/DOP (●) solutions.

Results and Discussion

IR spectra were measured to examine the effect of solvent on the disentanglement of PVC in solutions. Figure 1 shows the FT-IR spectra of PVC freeze-extracted from concentrated solution (5 wt %) in THF, DMP, and DOP. Infrared spectroscopy can provide some useful information for reflecting the morphology in PVC. Many infrared bands were considered to be related to the crystalline structures of PVC. Krimm et al.[21,22] assigned the band at 638 cm^{-1}, the carbon−chlorine stretching vibration of PVC, to long planar syndiotactic sequences. The intensity ratios of 638 and 690 cm^{-1} can be used[23] to measure the content of planar syndiotactic units. Tabb and Koenig[24] assigned the methylene deformation at 1427 cm^{-1} as a crystalline band and the ratio of intensities of the 1427 and 1435 cm^{-1} bands ($I_{1427\ \mathrm{cm}^{-1}}/I_{1435\ \mathrm{cm}^{-1}}$) as a relative measure of crystallinity. In our previous paper, we reported that the PVC sample prepared from very dilute solution in THF was in the expanded state with fewer entanglements which would result a higher crystallinity than samples prepared from more concentrated solution.[12] In the IR spectra shown in Figure 1, the change in relative intensity of the 1427 and 1435 cm^{-1} bands and the increased intensity of a crystalline bands at 638 cm^{-1} in curve A indicate that an ordering takes place in PVC due to effect of partly disentanglement of polymer chain in concentrated solution in DOP. PVC freeze-extracted from 5 wt % in DOP has relatively high content of crystalline units, as shown in Figure 1A, while Figure 1B,C illustrates the amorphous morphology of the polymer samples recovered from PVC/THF and PVC/DMP.

Figure 2 illustrated the $I_{1427\ \mathrm{cm}^{-1}}/I_{1435\ \mathrm{cm}^{-1}}$ ratio obtained by computer separation of the doublet spectral band into two Lorentzians under the assumption that the integral absorbance coefficients are the same for both bands. The $I_{1427\ \mathrm{cm}^{-1}}/I_{1435\ \mathrm{cm}^{-1}}$ ratio decreased with an increasing solution concentration for samples prepared from solutions in THF and DMP, while the $I_{1427\ \mathrm{cm}^{-1}}/I_{1435\ \mathrm{cm}^{-1}}$ ratio of the sample from the concentrated PVC/DOP solution is nearly as high as that from very dilute solutions in THF and DMP and remains almost unchanged as the DOP concentration is changed. All these results demonstrate that the extent of chain interpenetration in a concentrated solution in DOP is similar to that in the very dilute solutions in THF and in DMP. Partially disentangled PVC can be easily obtained by freeze-extracting a concentrated solution in DOP, a solvent with large molar volume. It has been reported[19,20] that the extent of chain interpenetration remains unchanged during the rapid freezing so that, after removal of the frozen solvent by sublimation, the material should retain a memory of the chain interpenetration that has existed in the original solution. Our results clearly indicate that PVC chains should be partially disentangled in 5 wt % DOP solution, just as in the very dilute solution (0.05 wt %) in THF and in DMP. Therefore, it is easy for PVC chains in DOP solution to aggregate to form partially an ordered structure.

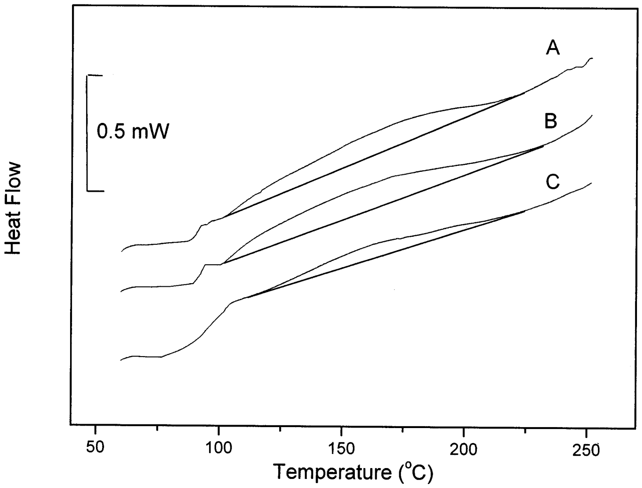

Figure 3. DSC curves of PVC freeze-extracted from 5 wt % PVC/DOP (A), 0.05 wt % PVC/DMP (B), and 5 wt % PVC/DMP solution (C). Note: the heating rate for DSC measurement is 20 °C/min.

To study further the crystallizability of partially disentangled PVC sample prepared from solution in various solvents, we also measured the DSC thermograms of PVC sample. The melting traces in DSC curves for PVC powder reported in the literature were usually broad and featureless.[25] Figure 3 shows the DSC curves recorded for PVC samples freeze-extracted from 5 wt % PVC/DOP (Figure 3A), 0.05 wt % PVC/DMP (Figure 3B), and 5 wt % PVC/DMP solution (Figure 3C). Clearly, the crystallinity of the partially disentangled PVC (Figure 3A,B) is higher than that of the entangled sample (Figure 3C). Figure 4 shows the DSC curves

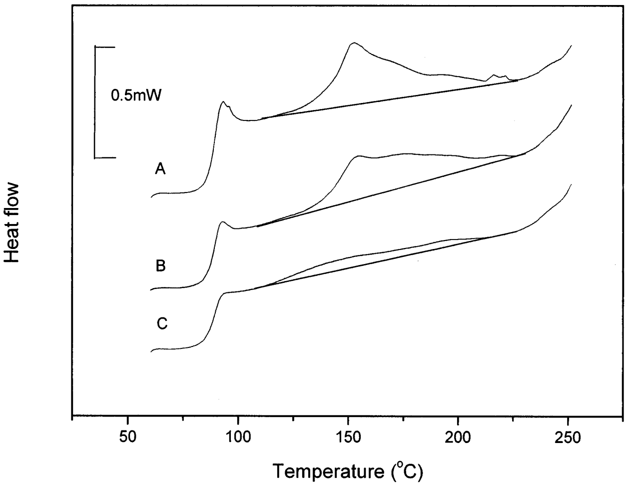

Figure 4. DSC curves of PVC freeze-extracted from 5 wt % PVC/DOP (A), 0.05 wt % PVC/DMP (B), and 5 wt % PVC/DMP solution (C) recorded after annealing at 120 °C for 1 h. Note: the heating rate for DSC measurement is 20 °C/min.

recorded for the above PVC samples after annealing at 120 °C for 1 h. It is proved that after annealing above its glass transition temperature the total melting enthalpy of the disentangled PVC samples are higher than that before annealing. On the other hand, the melting enthalpy in Figure 4A,B is also much higher than that in Figure 4C. These results indicate that for the partially disentangled PVC sample more of the ordered crystalline structures could be formed before and after annealing.

The Flory–Krigbaum theory of the thermodynamic properties of dilute solutions of flexible-chain polymers predicts that the interpenetration of the molecular coils is strongly resisted in good solvent media.[26] As the solution concentration is increased, a point is eventually reached where the total space can no longer accommodate the swollen molecular coils without some chain entanglement. Beyond this “critical concentration”, conventionally denoted by C^*, the dependence of thermodynamic and hydrodynamic properties of the system on polymer chain length and concentration changes because of the interpenetration of the molecular coils.[27] Xue[28] and Bo[18] have found that the coils of the freeze-dried i-PS from very dilute solution (less than 0.04 wt %) were in the expanded state with fewer entanglements which could crystallize upon annealing at a much higher rate. In this study, we demonstrated again that there is a critical concentration at about 0.5 wt % for PVC, above which the chain coils contain a considerable amount of chain entanglements. This value is consistent with the calculated C^* from the scale law[27]

$$C^* \cong \Phi^* \rho_p/\rho_s \cong N^{-4/5} \rho_p/\rho_s \qquad (1)$$

where N is the degree of polymerization and ρ_p and ρ_s are the density of polymer and solvent, respectively. For the PVC sample of degree of polymerization of 1800, the calculated C^* is about 0.5%. To our great surprise, freeze-extracting concentrated PVC solution in DOP (5 wt %) shows characteristics of disentangled chains as shown in Figures 1–3, contrary to accepted theories. The melting enthalpy of the annealed PVC powder prepared from concentrated solution in DOP (Figure 4A) is about the same as that from very dilute solution in DMP (Figure 4B). This suggests again that freeze-extracting concentrated solution in DOP produced a PVC powder with the same level of chain disentanglement as that derived from a dilute solution in DMP.

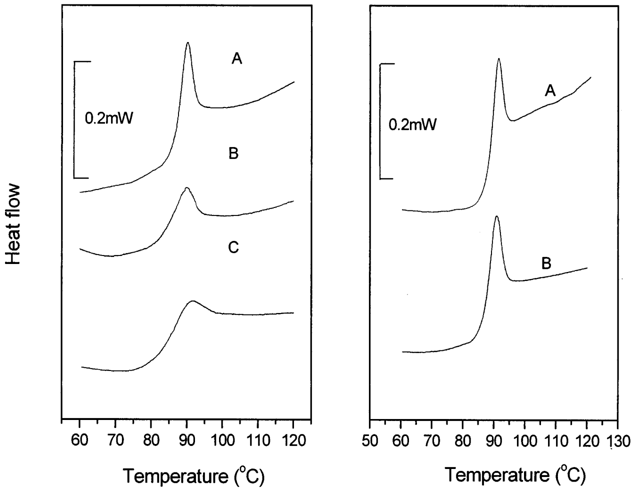

Figure 5. DSC curves for PVC sample freeze-extracted from (left) 0.05 wt % PVC/THF (A), 0.5 wt % PVC/THF (B), and 2 wt % PVC/THF (C) solution and (right) 2 wt % PVC/DOP (A) and 5 wt % PVC/DOP (B) solution after annealing at 80 °C for 2 h. Note: the heating rate for DSC measurement is 10 °C/min.

Structural relaxation is the process by which amorphous materials in the glassy state approach a state of thermodynamic equilibrium.[29–33] This process is detected through the time evolution of thermodynamic properties such as specific volume or enthalpy as well as mechanical or dielectric properties. A differential scanning calorimeter (DSC) can be used to record enthalpy relaxations occurring near T_g in glassy polymers aged after a wide variety of treatments. Gray and Gilbert[9,34] observed sub-T_g endothermic peaks in annealed PVC samples, which had been rapidly quenched. However, our work indicated that for the disentangled PVC sample the relaxation behavior is quite different from the previous study.

The left figure in Figure 5 shows DSC curves recorded after annealing at 80 °C for 2 h, for PVC sample freeze-extracted from PVC/THF solution with different concentration. Typical sub-T_g endothermic peaks are observed in this figure. It is clear that the magnitude of the endothermic peak is strongly dependent on the pretreatment, i.e., on the original solution before freeze-extracting. The plots of endothermic enthalpy ΔH vs the original solution concentration for samples from PVC/THF and PVC/DMP solutions are illustrated in Figure 6. Obviously, under the same annealing conditions, the endothermic enthalpy increases rapidly with decreasing concentration, while for a sample freeze-extracted from concentrated PVC/DOP solution (5%) (see right panel in Figure 5 and upper curve in Figure 6) the relaxation enthalpy ΔH is almost as high as for the sample prepared from very dilute THF solution (0.05%). Clearly, a greater degree of relaxation occurred for the disentangled sample during annealing. De Gennes[27] 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. The expanded macromolecular coils were in a metastable state after freeze-extracting, which would contract rapidly into collapsed coils upon annealing, resulting in an enhancement of the enthalpy relaxation and consequent intensified DSC peaks. The strong

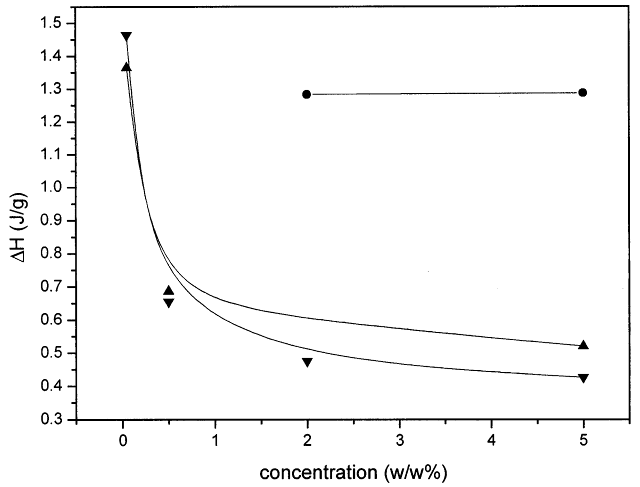

Figure 6. Plots of endothermic enthalpy Δ*H* vs the original solution concentration for samples from PVC/THF (▼), PVC/DMP (▲), and PVC/DOP (●) solutions.

endothermic peak for the disentangled PVC sample indicated that the entanglement in polymers would affect strongly the structural relaxation behavior, and the relaxation rate increased with decreasing chain entanglements, which is in good agreement with the modeling predictions.

Conclusion

Infrared spectroscopy and DSC studies showed that the PVC samples prepared from concentrated solution in DOP (5 wt %) were in the expanded state with fewer entanglements which would crystallize to a higher crystallinity than the samples prepared from DMP and THF solutions. DSC results showed that the amorphous part in thus-prepared disentangled samples were in a high-enthalpy state and could relax at a rapid rate during annealing. The extent of interpenetration decreases even in concentrated solution in DOP, contrary to accepted theories. Additionally, we reported recently that isotactic polystyrene, PET, and isotactic PMMA could be also easily crystallized in some large solvent such as PEG oligomer or epoxy resin.

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