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Conformation and Structural Relaxation of Partially Disentangled Poly(vinyl chloride) Prepared by Freeze-Extracting Dilute Solutions

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ABSTRACT: The partially disentangled poly(vinyl chloride) (PVC) samples were prepared by freeze-extracting from dilute PVC/THF solutions. The conformation of these samples was investigated by infrared and Raman spectroscopy. The structural relaxation behaviors were studied by differential scanning calorimeter (DSC). The results showed that the PVC samples prepared from dilute solutions with concentrations lower than 0.25% were in the expanded state with fewer entanglements. The conformation and structural relaxation of PVC depended strongly on the entanglements in polymers, and the structural relaxation rate increased with decreasing chain entanglements, which is in good agreement with the modeling predictions.

Introduction

The detailed microstructure of poly(vinyl chloride) (PVC) is very important in determining its physical properties and processing characteristics and the properties of the products. Commerial available PVC is mainly in amorphous state with small amount of crystallites. Infrared spectroscopy has been utilized extensively to study the molecular structure of PVC. Much infrared work has been directed toward the detailed assignment of its spectral bands, especially the crystalline vibrational modes and the conformationally sensitive carbon−chlorine stretching modes.[1−4] Raman spectroscopy can also provide some useful information about the crystalline structure of PVC.[5−8] In the carbon−chlorine stretching region, the band at 638 cm^{-1} was assigned as crystalline bands, and the ratio of the heights of 638 and 695 cm^{-1} has been shown to be strongly sensitive to changes in molecular conformation and/or crystal structures.[7,8]

Structural relaxation is the process by which amorphous materials in the glassy state approach a state of thermodynamic equilibrium. This process is detected through the time evolution of thermodynamic properties such as specific volume or enthalpy, as well as mechanical or dielectric properties. Differential scanning calorimetry (DSC) has revealed enthalpy relaxations occurring near T_g in glassy polymers aged after a wide variety of treatments. Illers and Gray and Gilbert observed sub-T_g endothermic peaks in annealed PVC samples which had been rapidly quenched and found that the magnitude and temperature of peaks increased with increasing annealing time.[9,10] Petrie et al. demonstrated that the magnitude of the DSC endothermic peak at T_g provided a quantitative measure of the enthalpy relaxation which had occurred during prior annealing at temperatures somewhat below T_g.[11,12] Matsuoka has suggested that dilation under tensile stress increases the enthalpy of the glass, reducing the relaxation time and therefore increasing the rate of enthalpy relaxation during annealing.[13]

In studying PVC samples, Hodge et al. have found that enhancement of sub-T_g endothermal peaks resulted from pretreatments that produce a state of increased enthalpy at the start of the annealing process, including thermal quenching, mechanical compression, and dilation by tensile stress or by a swelling vapor.[14,15] Huang et al. studied the influence of entanglements on the structural relaxation behavior of polycarbonate.[16] They found that the single-chain sample might be in a more equilibrium state and showed a lower relaxation enthalpy. In the present work, a series of PVC samples freeze-extracted from PVC/THF solutions at various polymer concentrations were prepared. The concentration dependence of the polymer conformation and crystallinity was studied by a spectroscopic method. The structrual relaxation behavior of disentangled PVC was studied by the DSC measurement and found to be different from that of the much entangled sample.

Experimental Section

The polymer used in this experiment was a commercial, suspension-polymerized PVC, obtained as a free-flowing white powder with an intrinsic viscosity of 1.01 dL/g measured in THF, corresponding to an average molecular weight of 6.2×10^4.

The freeze-extracted samples were prepared by dissolving the desired amount of PVC in THF solvent to obtain PVC/THF solution with concentrations varied from 0.05% to 2%. The solution was then poured into liquid nitrogen to freeze the binary system in a fraction of a second. The THF solvent was extracted by adding a large amount of cold ethanol into the frozen PVC/THF system. The powdered PVC was separated by ultracentrifugation and dried under vacuum at room temperature.

FT-Raman spectra of PVC powder were recorded with 1.064 nm excitation, using a Bruker RFS100 FT-Raman spectrometer. FT-IR spectra were recorded using a Bruker IFS66V FT-IR spectrometer. For IR measurements, the freeze-extracted samples were annealed for 1 h at 100 °C to observe the conformational changes. The powdered samples were dispersed

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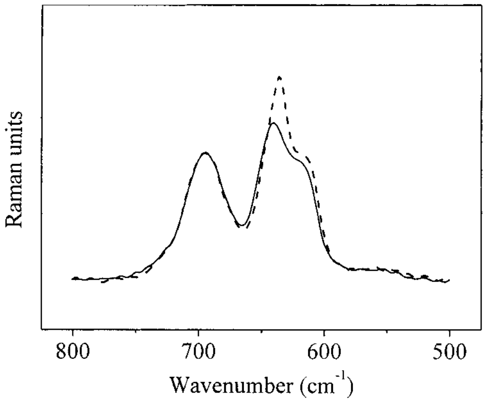

Figure 1. Raman spectra in the carbon−chlorine stretching region of PVC samples freeze-extracted from (solid line) 2% and (dashed line) 0.1% PVC/THF solution.

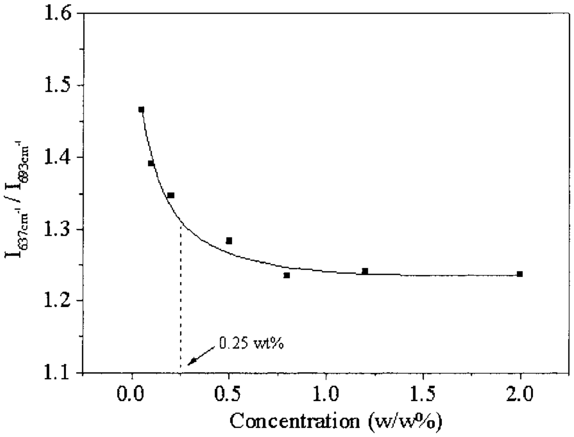

Figure 2. Plot of the Raman intensity ratio of $I_{638cm^{-1}}/I_{695cm^{-1}}$ vs the original solution concentration.

in KBr pellets. The differential scanning calorimeter (DSC) measurement was run on a Perkin-Elmer model DSC-7 system at a 20 °C/min heating rate. All the thermal annealing processes for DSC scans were carried out in the calorimeter.

Results and Discussion

Figure 1 shows the Raman spectra of freeze-extracted PVC in the carbon−chlorine stretching region. Two major peaks are directly observable at 638 and 695 cm^{-1}, the peak at 638 cm^{-1} is assigned as a crystalline band, and the ratio of the intensities of these two peaks ($I_{638cm^{-1}}/I_{695cm^{-1}}$) has been shown in previous work to be strongly sensitive to changes in molecular conformation and/or crystal structures.[7,8] From Figure 1 it can be seen that the band intensity at 638 cm^{-1} for the sample prepared from dilute solution (0.1%) is obviously stronger than that prepared from semidilute solution (2%). The relationship between the ratio of $I_{638cm^{-1}}/I_{695cm^{-1}}$, and the original solution concentration is shown in Figure 2. We can find that the ratio of $I_{638cm^{-1}}/I_{695cm^{-1}}$ increases with decreasing solution concentration at the concentration region lower than 0.5%. When the solution concentration is higher than 0.5%, the ratio of $I_{638cm^{-1}}/I_{695cm^{-1}}$ becomes invariant with solution concentration. The turning point of the relative intensity−concentration curve in Figure 2 is located at about 0.25 wt %. Robinson et al. examined PVC samples taken at various stages of conversion by Raman spectroscopy.[17] For the 2% sample only, a peak attributed to chain folding was detected, suggesting that the crystallite formation would occur under conditions of least entanglement/lowest viscosity. Our Raman spectroscopic study indicated that the freeze-extracted sample from very dilute PVC/THF solution was partially disentangled, and some ordered crystalline structures existed in this sample.

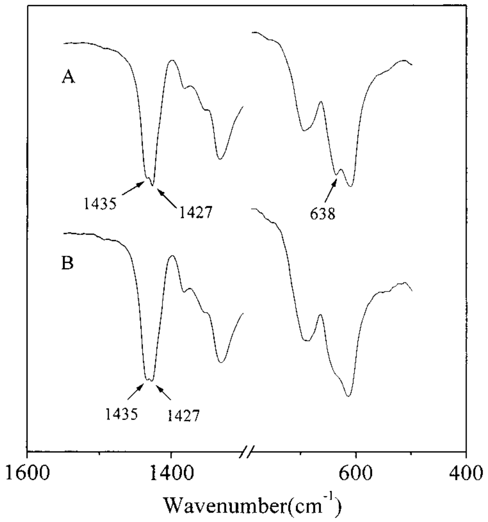

Figure 3. FT-IR spectra of annealed PVC samples freeze-extracted from (A) 0.1% and (B) 2% PVC/THF solution.

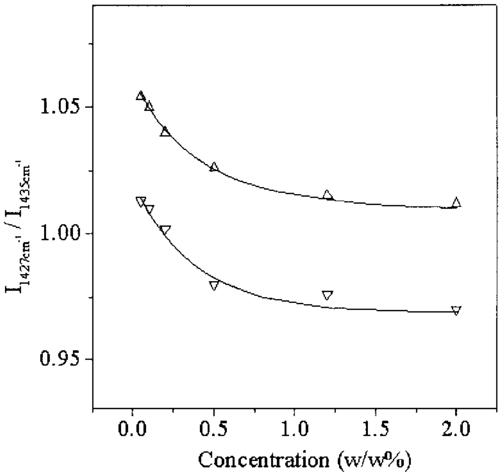

Figure 4. Plots of the IR intensity ratio of $I_{1427cm^{-1}}/I_{1435cm^{-1}}$ vs the original solution concentration: lower, before annealing; upper, after annealing at 100 °C for 1 h.

Infrared spectroscopy can provide some useful information for reflecting the crystallinity level in PVC. Many infrared bands were considered to be related to the crystalline structures of PVC. Here, the methylene deformation at 1427 cm^{-1} and carbon−chlorine stretching vibration at 638 cm^{-1} were used as crystalline bands as referred in most studies and the ratio of intensities of the 1427 and 1435 cm^{-1} bands ($I_{1427cm^{-1}}/I_{1435cm^{-1}}$) as a relative measure of crystallinity.[1] Figure 3 shows the FT-IR spectra of annealed PVC samples freeze-extracted from 0.1% and 2.0% solutions, respectively. The $I_{1427cm^{-1}}/I_{1435cm^{-1}}$ ratio was obtained by computer separation of the doublet into two Lorentzians under the assumption that the integral absorbance coefficients are the same for both bands. The $I_{1427cm^{-1}}/I_{1435cm^{-1}}$ ratio decreased sharply with increasing solution concentration both before and after annealing as illustrated in Figure 4. When the solution concentration is higher than 0.5%, the ratio of $I_{1427cm^{-1}}/I_{1435cm^{-1}}$ did not vary significantly with solution concentration. It can be found that the

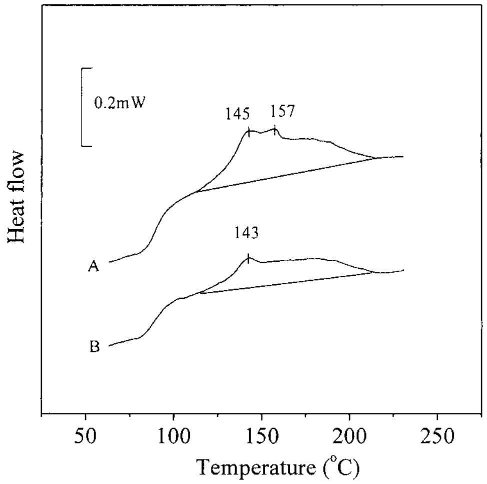

Figure 5. DSC curves of PVC freeze-extracted from 0.1% (A) and 2% (B) PVC/THF solution, recorded after annealing at 100 °C for 3 h.

crystallinity of samples prepared from dilute solutions (lower than 0.2%) is obviously higher than that prepared from more concentrated solutions. After annealing, a distinct shoulder band at 638 cm^{-1} appeared for the samples prepared from 0.1% solution as can be seen in Figure 4, while no observable changes occurred for samples prepared from other solutions with concentration higher than 0.5%. This indicated that, for the partially disentangled PVC sample prepared from very dilute solutions, some more perfect crystalline structures could be formed rapidly after annealing just above its glass transition temperature. Xue et al. have found that the coils of the freeze-dried i-PS or freeze-extracted PET from dilute solution were in the expanded state with fewer entanglements which could crystallize upon annealing at a much higher rate than the i-PS or PET prepared from more concentrated solutions.[18,19]

To study further the crystallizability of partially disentangled PVC sample prepared from very dilute solution, we also measured the DSC thermograms of PVC samples after annealing. The melting traces in DSC curves for PVC powder reported in the literature were usually broad and featureless,[20] and two or three peaks often appeared in the annealed samples.[21] Figure 5 shows the DSC curves recorded after annealing at 100 °C for 3 h for PVC samples freeze-extracted from 0.1% (Figure 5A) and 2% (Figure 5B) PVC/THF solution. The melting region covers from about 120 to 210 °C. Compared with Figure 5B, a new peak at 157 °C appears in Figure 5A, which can be attributed to the melting of material crystallized at the annealing temperature,[21] and the total melting enthalpy in Figure 5A is much higher than that in Figure 5B. This result indicated that for the partially disentangled PVC sample crystalline structures could be formed rapidly after annealing above its glass transition temperature, which was in agreement with the vibrational spectroscopy results.

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.[22] 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 in a striking manner because of the interpenetration of the molecular coils.[23] Recently, Qian et al. have put forward a concept of a concentration boundary C_s of solutions well below C^* ($C^*/C_s > 40$) on the basis of the studies of excimer fluorescence experiments.[24] Some recent measurements have focused on the consequences of rapidly taking polymers with flexible chains from dilute solution regime to a concentrated state. Measurements of nonradiative energy transfer between a mixture of donor- and acceptor-labeled polystyrene freeze-dried from the dilute solution suggested that the neat polymer obtained be comprised of nonoverlapping collapsed coils.[25,26] The concentration of the solution for polystyrene used in these reports was 0.83 g/dL. This is 4 times more dilute than the critical concentration, C^*, at which overlap of the polystyrene chains would commence.[27] The study of the crystallizability of freeze-extracted poly(ethylene terephthalate) (PET) from solutions with different concentrations found that there was a concentration boundary near 0.2% for the crystallizability of PET: near the boundary concentration the macromolecular chains contain a considerable amount of segments with few chain entanglements.[19] In this study, we find that there is a concentration boundary at about 0.25% for PVC, near which the chain coils contain a considerable amount of segments with few chain entanglements.

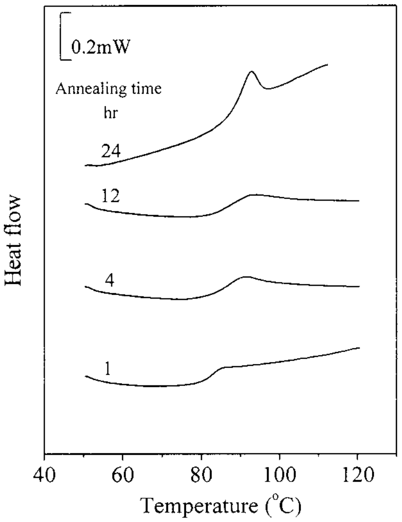

Figure 6. DSC curves for PVC sample freeze-extracted from 2% PVC/THF solution after annealing at 80 °C for the indicated times.

Annealing of amorphous polymers below the glass transition temperature produces changes in many physical properties. A particularly convenient property for the study of annealing is enthalpy, because of the availability of accurate and sensitive DSC instruments. Figure 6 shows the DSC curves for PVC sample freeze-extracted from 2% PVC/THF solution after annealing at 80 °C for the indicated times. Typical sub-T_g endothermic peaks are observed in these annealed samples. It shows common relaxation behavior of amorphous polymers as studied by Hodge et al.[14] The magnitude and temperature of peaks increase with increasing annealing time.

For the disentangled PVC sample, the relaxation behavior is quite different from the previous study. Figure 7 shows the DSC curves recorded after annealing

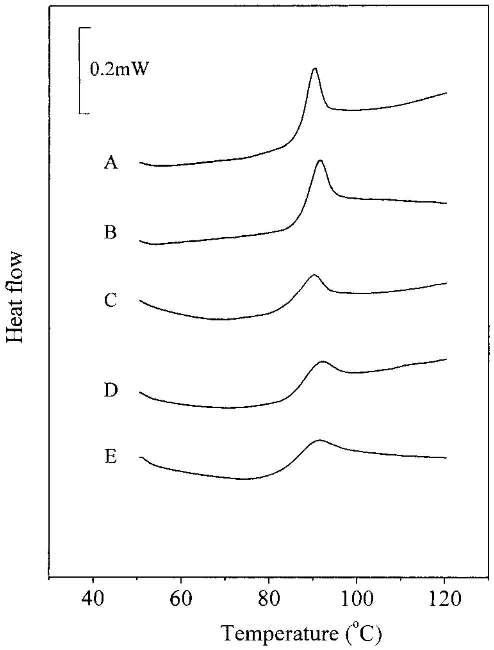

Figure 7. DSC curves recorded after annealing at 80 °C for 2 h, for PVC samples freeze-extracted from PVC/THF solution with different concentrations: A, 0.1%; B, 0.2%; C, 0.5%; D, 1.2%; E, 2.0%.

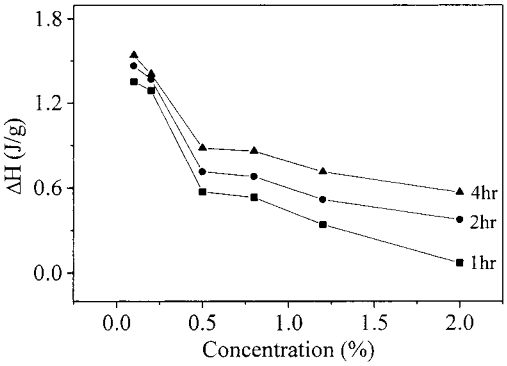

Figure 8. Plots of endothermic enthalpy ΔH vs the original solution concentration for the indicated annealing time.

at 80 °C for 2 h, for PVC samples freeze-extracted from PVC/THF solution with different concentrations. It can be seen that the magnitude of the endothermic peak is strongly dependent upon the pretreatment, i.e., upon the original solution concentration before freeze-extracting. The plots of endothermic enthalpy ΔH vs the original solution concentration for the indicated annealing time are illustrated in Figure 8. For the same annealing time, the endothermic enthalpy increases rapidly with decreasing solution concentration. With increasing annealing time, the difference of the ΔH value originating from the solution concentration decreases. Figure 9 shows the relationship between ΔH and log t_e (t_e = annealing time) for two samples freeze-extracted from 0.1% and 2% PVC/THF solutions, respectively. As studied previously,[14] ΔH is a linear function of log t_e when t_e is sufficiently short that the annealing glass is still far from equilibrium. At long t_e, ΔH becomes constant as the annealed glass approaches equilibrium. From Figure 9 it can be found that the sample prepared from very dilute solution (0.1%) possesses obviously higher enthalpy relaxation rate than that prepared from more concentrated solution (2%), and its relaxation enthalpy ΔH increases very slowly after annealing for several hours, indicating the approach to the equilibrium enthalpy of this PVC sample.

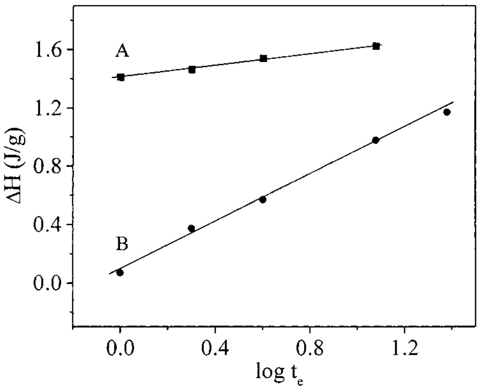

Figure 9. Plots of endothermic enthalpy ΔH vs log t_e for PVC samples freeze-extracted from (A) 0.1% and (B) 2% PVC/THF solutions.

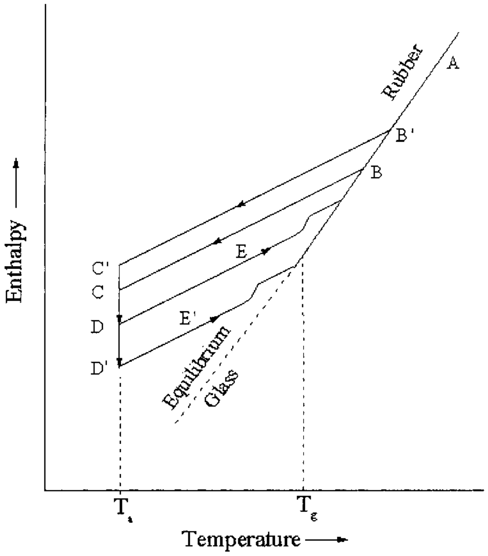

Figure 10. Schematic enthalpy vs temperature diagram.

The observed effects may be illustrated on the schematic enthalpy–temperature diagram shown in Figure 10. For a sample cooled into the glassy state, say along with ABC, and annealed at T_a somewhat below T_g, the enthalpy relaxes along CD; a subsequent DSC scan, tracing path DEBA, shows an endothermic peak superposed on the T_g step, i.e., the well-known "T_g overshoot". For the PVC sample prepared from very dilute solution, it would be frozen in a higher level of enthalpy (AB′C′). The enthalpy relaxes along C′D′ during annealing at T_a; a subsequent DSC scan, tracing path D′E′B′A, shows an enhanced DSC peak. This indicated that a greater degree of relaxation occurred during annealing (C′D′). Hodge et al. explained the increased enthalpy in vapor preswelling to be volume dilation.[14] Our experimental results suggest that other preannealing treatments also produce a high-enthalpy state and a consequent enhancement of relaxation during annealing. As discussed above, the coils of the freeze-extracted PVC from dilute solution were in the expanded state with fewer entanglements. 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.[23] The expanded macromolecular coils freeze-extracted from dilute solution will contract rapidly into collapsed coils upon annealing, resulting in an enhancement of enthalpy relaxation and consequent intensified DSC peaks.

The fast enthalpy relaxation rate and strong and sharper endothermic peak for the disentangled PVC sample indicated that the entanglement in polymers would affect strongly on the structural relaxation behavior. Matsuoka and Hodge's studies have demostrated that the enhancement of sub-T_g endothermic peaks and fast enthalpy relaxation rate resulted from the increased enthalpy at the start of the annealing process produced by pretreatments.[13,14] Thermal analysis and infrared results showed that partially disentangled sample could form partial crystalline structures rapidly after annealing at 100 °C. This indicated that the sample freeze-extracted from very dilute solution was situated at a high energy level so that crystallization might occur more easily during annealing period. In studying the structural relaxation behaviors of glassy polymers, Hodge, Gomez Ribelles, and Cowie noticed that the extrapolation of the experimental values of ΔH to long times led 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 predicted narrower and higher peaks than the experimental ones after annealing close to T_g.[28-30] They ascribed the distinctive feature in polymers to the effect of entanglement in the polymer. Our results showed that the PVC samples prepared from THF solution with concentration lower than 0.25% are in the less chain entanglement state. This suggested that the conformation and structural relaxation of PVC depended strongly on the entanglements in polymer, and the structural relaxation rate increased with decreasing entanglements, which is in good agreement with their modeling predictions.

Conclusion

Raman and infrared spectroscopic studies showed that the PVC samples prepared from dilute solutions with concentrations lower than 0.25% were in the expanded state with fewer entanglements which could partially crystallize upon annealing at a much higher rate than that prepared from more concentrated solutions. The melting behavior of annealed samples also showed crystallization ability in samples prepared from dilute solution. DSC results showed that the amorphous part in the thus-prepared disentangled samples were in a high-enthalpy state and could relax in a rapid rate during annealing. The structural relaxation behaviors of PVC depended strongly on the entanglements in polymers, and the relaxation rate increased with decreasing chain entanglements, which is in good agreement with the modeling predictions.

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