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Onset of the Fast Process in Amorphous Polypropylene as Detected by Quasielastic Neutron-Scattering and Electron Spin Resonance Techniques

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ABSTRACT: Local chain dynamics of atactic polypropylene, a typical amorphous vinyl polymer, has been studied by both quasielastic neutron scattering and macroradical decay measurements by electron spin resonance to detect the fast process of picosecond order observed for most amorphous materials. It was found that the fast process sets in at the Vogel−Fulcher temperature T_0, similar to observations for other simple polymers, suggesting that the fast process is a precursor of the glass transition. In coincidence with the onset of the fast process, the acceleration of the macroradical decay is also observed in the vicinity of T_0, indicating a close connection of both phenomena. This is the first experimental evidence for the fast process from two independent measurements.

Introduction

The fast process of picosecond order has been observed by quasielastic neutron and Raman scattering in various glass-forming materials including organic and inorganic materials and polymers.[1,2] In some cases, especially for polymers with simple chemical structures of the diene[3−6] and vinylidene[7] type, the onset temperature T_f of the fast process agrees with the Vogel−Fulcher (VF) temperature T_0, which occurs at about 50 K below the calorimetric glass transition temperature T_g for most amorphous polymers.[8] It is extremely hard to detect T_0 directly by usual dynamical measurements in a glassy state, but it is indirectly determined by fitting the VF equation (see eq 1) or the Williams−Landel−Ferry (WLF) equation to temperature dependence of the α-relaxation time obtained by mechanical or dielectric measurement. The VF temperature T_0 is sometimes called the “ideal” glass transition temperature, i.e., an experimentally inaccessible temperature in the limit of infinitely slow cooling. However, the value of T_0 is not affected by the time scale of the experiment, whereas the calorimetric glass transition temperature T_g depends on the time scale. Therefore, T_0 is considered to be a fundamental property of the sample. The correlation between T_f and T_0 strongly suggests that the fast process is a precursor of the α-process or the glass transition.

In contrast to the observations for simple polymers, the fast process of polymers with large side groups or large internal degrees of freedom is observed far below the Vogel−Fulcher temperature T_0.[9−11] In the case of polystyrene, for example, the fast process started appearing at ∼200 K, or ∼120 K below T_0. Such a low onset temperature has been assigned to subtransitions like the β- and/or γ-process due to phenyl group motions or the internal degrees of freedom.[10,11] This indicates that the onset at T_0 is a typical feature for simple main-chain polymers. In order to confirm this, it is very important to verify the correlation between T_f and T_0 for some typical pure amorphous vinyl polymers, which has never been reported as far as we know. In addition it is desired to find some experimental support for the fast process from independent measurements.

In the previous paper,[12] we have investigated the kinetic behavior of free radicals in a series of five amorphous polymers by electron spin resonance (ESR) spectroscopy. It was found that the decay process in the polymers exhibits an acceleration in the sub-T_g region regardless of the detail chemical structure as well as of the type of macroradical, in-chain or end-chain. Moreover, the onset temperature of acceleration T_{tr} from an Arrhenius plot was found to correlate with the VF temperature T_0 for some polymers. It suggests that the acceleration of decay at around T_0 is related to the onset of segmental dynamics already in the glassy state of the polymer matrices investigated.

In this work, we have studied microscopic chain dynamics of a typical amorphous vinyl polymer, atactic polypropylene (a-PP), in parallel by a quasielastic neutron-scattering (QENS) technique and an ESR investigation of macroradical decay. The aims of this study are (i) to confirm the correlation between T_f and T_0 for a simple amorphous vinyl polymer and (ii) to confirm that the macroradical decay in a-PP is accelerated by the fast process by verifying the correlation among T_{tr}, T_f, and T_0.

Experimental Section

Sample. Amorphous a-PP with molecular weight $M_w = 1.02 \times 10^6$ and polydispersity $M_w/M_n = 2.4$ was studied. The glass transition temperature T_g, determined by differential scanning calorimetry (DSC) (Perkin-Elmer, DSC-7) with a heating rate of 20 °C/min, is 259 K.

Neutron-Scattering Measurements. Quasielastic neutron scattering measurements were carried out with inverted geometry time-of-flight (TOF) spectrometers LAM-40[13] and LAM-80ET[14] installed at the pulsed spallation cold neutron source in the National Laboratory for High Energy Physics (KEK), Tsukuba, Japan. The energy resolutions of LAM-40 and LAM-80ET are ∼0.2 and ∼0.02 meV, and the energy windows are below 10 and 0.5 meV, respectively. The length of the scattering vector Q at the elastic position ranges from 0.2 to 2.6 Å^{-1} for LAM-40 and from 0.2 to 1.64 Å^{-1} for LAM-80ET. The measurements were carried out at 18−330 K. The observed TOF spectrum was converted to the dynamical

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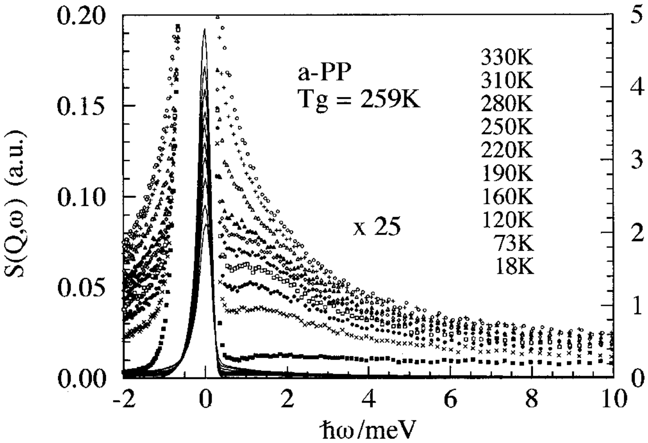

Figure 1. Dynamic scattering laws, $S(Q,\omega)$, of a-PP measured with LAM-40 as a function of temperature. Solid lines show the whole profile of the spectra indicated by symbols, which are expanded by a factor of 25.

scattering law $S(Q,\omega)$ after correcting for empty can scattering, counterefficiency, self-shielding, and the incident neutron spectrum.

Macroradical Decay Measurements. Macroradicals were generated by γ-irradiation with a ^{60}Co source with a dose rate of 0.8 kGy/h in vacuum at 77 K. The total radiation dose was 4.8 kGy.

Spectral and kinetic studies of macroradicals were carried out with an X-band ESR spectrometer (Varian E-4) equipped with a temperature controller (E-257). The initial macroradical concentrations and their time evolutions were calculated using the strong-pitch standard by means of a computer (IBM-PC). The macroradical decay was investigated as a function of temperature; the temperature was increased stepwise at intervals of 10 K from 173 to 263 K, and at each step the sample was kept for 36 min. The time changes of macroradical concentrations were evaluated by the second-order kinetic equation.

Results and Discussion

Fast Process by Quasielastic Neutron Scattering. Dynamic scattering laws, $S(Q,\omega)$, of a-PP observed with LAM-40 are shown in Figure 1 as a function of temperature covering the glass transition temperature T_g (=259 K). These spectra were obtained by summing up seven spectra at scattering angles of 16°, 32°, 48°, 64°, 80°, 96° and 112° because the shapes of the spectra are almost independent of the scattering angle. The sharp peak at around $\hbar\omega = 0$ meV is due to the elastic scattering, which represents an immobile component within the energy resolution $\delta\epsilon$ (=0.2 meV) or a component slower than $h/\delta\epsilon$, where h is the Planck's constant, and the intensity decreases with increasing temperature. On the other hand, the counterparts of the elastic scattering, inelastic and quasielastic scattering parts, increase with temperature. A very broad inelastic scattering peak, the so-called *low-energy excitation* peak or Boson peak, is observed at 1.2−1.5 meV at low temperatures below the glass transition temperature T_g. As the temperature increases to a temperature slightly below the glass transition temperature T_g, the shape of the spectrum changes from inelastic-like to quasielastic-like, suggesting that the fast process initiated below T_g.

Temperature dependence of the elastic scattering intensity $I_{el}(Q)$ observed at $Q = 1.64$ Å^{-1} is shown in Figure 2 as a function of energy resolutions $\delta\epsilon$. The logarithm of $I_{el}(Q)$ decreases linearly with increasing temperature until ~190 K for $\delta\epsilon = 0.02$ meV, i.e., log[$I_{el}(Q)$] $\sim -T$, indicating that the motion observed below this temperature is vibrational, while above ~190 K $I_{el}(Q)$ begins to deviate from the linear relationship and decreases more steeply. Such a deviation may suggest the onset of the fast process at around 190 K, which is about 70 K below T_g. For the energy resolution of $\delta\epsilon$ = 0.2 meV, the extra decrease of $I_{el}(Q)$ at ~190 K is less pronounced but still observed, while for $\delta\epsilon \geq 2$ meV it is no longer observed at 190 K, indicating that the fast process mainly appears in an energy range less than 2 meV.

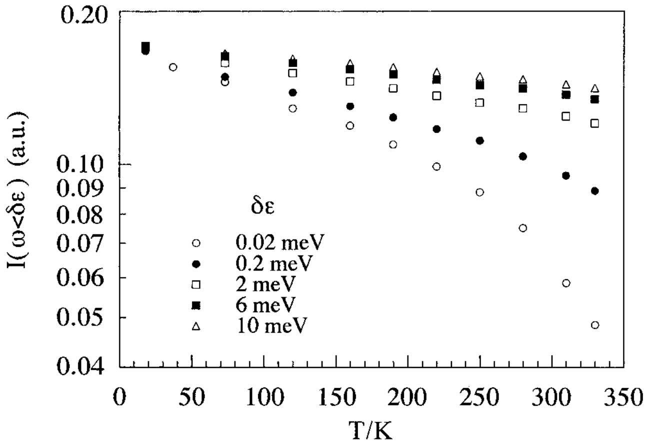

Figure 2. Temperature dependence of elastic scattering intensity $I_{el}(Q)$ at $Q = 1.64$ Å^{-1} for various energy resolutions $\delta\epsilon$. $\delta\epsilon = 0.02$ meV (○), 0.2 meV (●), 2 meV (□), 6 meV (■), and 10 meV (△).

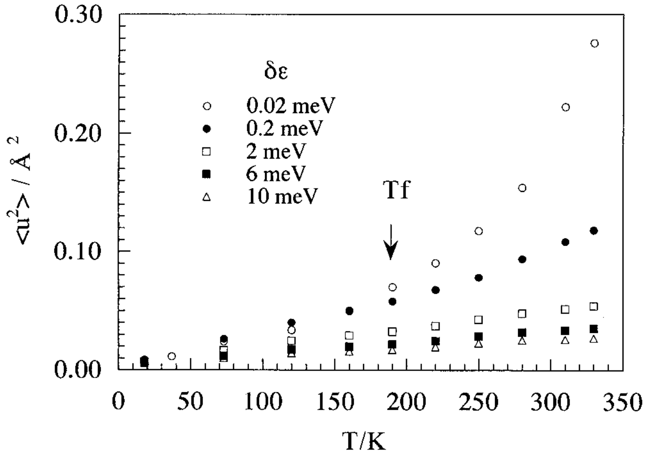

Figure 3. Temperature dependence of mean square displacement $<u^2>$ for various energy resolutions $\delta\epsilon$. $\delta\epsilon = 0.02$ meV (○), 0.2 meV (●), 2 meV (□), 6 meV (■), and 10 meV (△).

Mean square displacement $<u^2>$ has been evaluated from the slope of log[$I_{el}(Q)$] versus Q^2 because $I_{el}(Q)$ is proportional to exp($-<u^2>Q^2$). $<u^2>$ is shown in Figure 3 as a function of temperature. It is proportional to temperature T in the range below ~190 K, corresponding to the fact that log[$I_{el}(Q)$] is proportional to T in the same temperature range (see Figure 2). This again suggests that the motion below ~190 K is vibrational. In the temperature range above ~190 K, $<u^2>$ begins to deviate from the linear relationship and increase more rapidly with temperature for both $\delta\epsilon$ = 0.02 and 0.2 meV, corresponding to the excess decrease of the elastic intensity $I_{el}(Q)$ above ~190 K as seen in Figure 2. These facts must suggest the onset of the fast process above this temperature, which is quite close to the VF temperature T_0. It is noted that two values were reported for T_0 of a-PP: 192 K[15] and 205 K.[16]

We now discuss the counterparts of the elastic scattering, inelastic and quasielastic scattering. In order to confirm the onset of the fast process from the

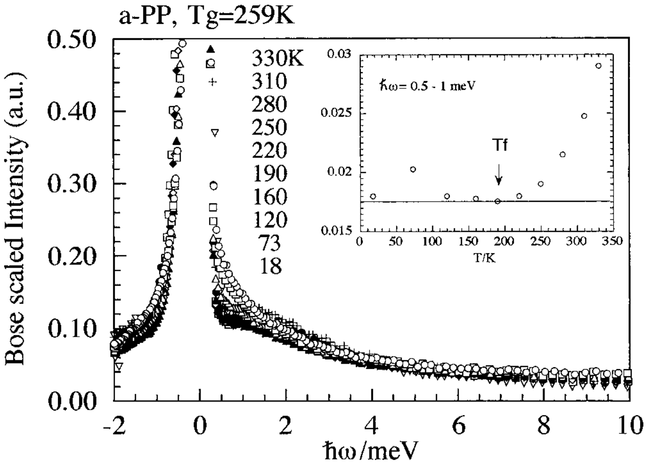

Figure 4. Inelastic scattering intensity in a temperature range of 18−330 K scaled by the Bose factor after correction for the Debye−Waller factor using the mean square displacement obtained for $\delta\epsilon = 0.2$ meV. The reference temperature is T_g (=259 K). Insert shows temperature dependence of inelastic intensity integrated in the energy range of 0.5−1 meV.

quasielastic part, the observed spectra were scaled by the Bose population factor after correction for the Debye−Waller (DW) factor evaluated for $\delta\epsilon = 0.2$ meV. The DW- and Bose-scaled spectra are shown in Figure 4. In the energy region above 3 meV, the Bose scaling works very well both below and above the VF temperature T_0, while in the energy region below ~2 meV, excess quasielastic scattering is clearly observed above ~200 K, suggesting that the onset of the fast process is of picosecond order. The characteristic time evaluated from the spectrum width is about 4 ps, which is almost independent of temperature T and length of the scattering vector Q, suggesting that the fast process is a local motion. This result is similar to those observed for other amorphous polymers. It should be noted that the DW and Bose scaling do not perfectly work for the energy region below ~2 meV even below T_0; the DW and Bose-scaled inelastic scattering intensity at around 75 K is rather large compared with those above 120 K. In order to demonstrate it, the integrated intensity between 0.5 and 1 meV is plotted versus T in the inset of Figure 4. This result may indicate that the DW factor or the mean square displacement $<u^2>$ is energy- or frequency-dependent. This effect has not been taken into account in the present scaling where we used the DW factor evaluated from the elastic scattering intensity, which is an average over all the modes with frequencies outside the energy resolution $\delta\epsilon$ (=0.2 meV). Because of this effect, it is slightly ambiguous to estimate the onset temperature of the fast process from the DW- and Bose-scaled quasielastic scattering spectra, but the fast process seems to appear at around $T_f = 190$ K (see the insert in Figure 4), corresponding to the estimation from $I_{el}(Q)$ and $<u^2>$.

The onset temperature T_f thus estimated is about 190 K, which is obviously below T_g and close to the VF temperature T_0, confirming the correlation between T_f and T_0. The VF temperature is usually determined by fitting the VF equation (eq 1) to the temperature dependence of the α-relaxation time τ estimated from mechanical or dielectric relaxation measurement:

$$\log \tau = \log \tau_\infty + \frac{B}{T - T_0} \tag{1}$$

Here, B is constant and τ_∞ is the α-relaxation time at infinite temperature. The VF temperature T_0 is considered to be a temperature at which the α-process would be completely frozen under the infinite slow cooling rate. It means that T_0 has a nature of the α-process which governs the glass transition directly. From the present observation that the onset temperature of the fast process coincides with the VF temperature, $T_f = T_0$, we directly conclude that the fast process is a precursor of the glass transition, at least for a-PP without any large side groups or internal degrees of freedom.

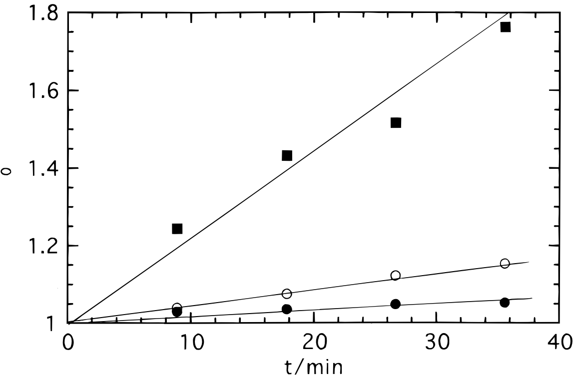

Figure 5. Test of second-order kinetics for macroradical decay in a-PP at 183 K (●), 223 K (○), and 263 K (■).

Finally, it should be noted that effects of methyl group motion were not detected in the present measurements. It is probably because methyl group motion is out of the energy window in the present measurements, though there is a possibility that the slightly lower onset temperature than T_0 is due to this effect. Furthermore, the characteristic time of the fast process is independent of temperature as mentioned above, meaning that the activation energy is almost zero. This indicates that the fast process is not related to the methyl group rotation with an activation energy of 12.1 kJ/mol.[17]

Macroradical Decay Rate by ESR. In the next step we studied the macroradical decay rate of a-PP by an ESR technique in order to see if the onset of the fast process at T_0 can be detected with a technique different from quasielastic neutron scattering. Figure 5 shows the results to test the second-order kinetic model for the decay reaction of alkyl tertiary macroradicals[18] at several temperatures: 183, 223, and 263 K. Linearity of these dependences confirms the validity of a bimolecular character for the decay process:

$$\frac{1}{C} - \frac{1}{C_0} = k_{\text{eff}}\, t \tag{2}$$

where C and C_0 are the total macroradical concentrations at time t and $t = 0$, respectively, and k_{eff} is the effective second-order decay rate constant. An Arrhenius plot of the decay rate constants is given in Figure 6. Three regions of different kinetic behavior are seen. An analysis of these regions in terms of the Arrhenius equation:

$$k_{\text{eff}}(T) = k_{\text{o,eff}} \exp\left[-\frac{E_{\text{eff}}}{RT}\right] \tag{3}$$

leads to the effective activation parameters summarized in Table 1.

The lowest temperature region is characterized by low values of the decay rate constants dominated by the low effective activation energy and the very low preexponential factor. With increasing temperature the

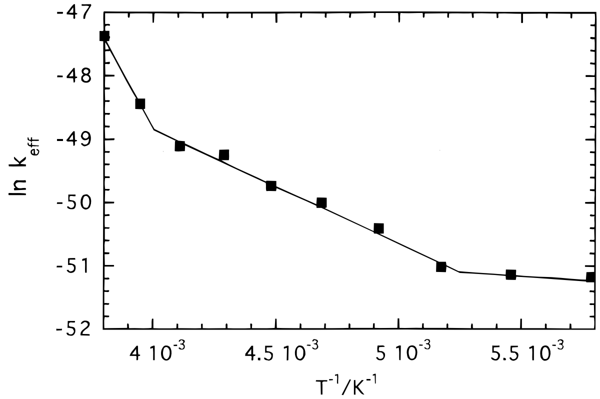

Figure 6. Arrhenius plot of the macroradical decay rate constant k_{eff}.

Table 1. Arrhenius Analysis of the Macroradical Decay in a-PP

region	ΔT(K)	$k_{o,eff}$ (g/spin·s)	E_{eff} (kJ/mol)
I	173−193	$(2.3 \pm 0.2) \times 10^{-22}$	2 ± 0.2
II	203−243	$(4.1 \pm 0.4) \times 10^{-19}$	14 ± 0.5
III	253−263	$(5.6 \pm 0.2) \times 10^{-10}$	57 ± 1

decay process accelerates, and the first transition temperature $T_{tr,1}$ can be obtained by solving a system by two linear equations with respect to T. The result is $T_{tr,1} = 190$ K. This value is in a quite acceptable agreement with the onset temperature for the fast process T_f from the above-mentioned neutron-scattering measurements. This coincidence indicates a close connection of both phenomena which can be outlined as follows. In the first temperature region the decay of persisting macroradicals, localized in great vicinity, occurs due to small scale mobility, perhaps by bond reorientation from a deformed state to the presence of an unpaired radical site. As the temperature is increased through $T_{tr,1}$ more distant free radical centers have a chance to approach due to the relatively larger scale mobility. The activation energy for the decay in the second kinetic region reaches a value slightly exceeding one rotational potential barrier for conformational transition. This suggests a possible role of such mobility under favorable local free volume and energy conditions. Because the fast process is independent of Q, i.e., very localized, and with a very low activation energy, such a rapid motion may ensure the migration of small free volume entities and consequently their accumulation in the vicinity of transforming bond in the polymer matrix. Thus, this fast mobility type enables the higher activation energy motion in the glassy state which controls the approaching more distant reactants into the contact decay situation. Note that in the quasielastic neutron-scattering measurements, we do not see the relatively large scale mobility below T_g. It is probably because such a mobility is not so frequently detected by neutron scattering. As the temperature is further increased we observe the second acceleration at about 250 K. This $T_{tr,2}$ is in a good agreement with the value of the glass transition temperature from DSC measurements: $T_g = 259$ K. This very good correspondence indicates that the decay of distant reactants is influenced by segmental mobility in the elastic state of a-PP. This segmental motion is of the conformational origin as evidenced by 2D ^{13}C NMR spectroscopy on the same polymer sample.[19] This is supported by recent microstructural analysis of the glass transition phenomenon which suggests an existence of sufficient free volume holes for the above-mentioned conformation segmental motion.[20]

Conclusions

In this paper, we have studied local chain dynamics of a-PP, a typical amorphous vinyl polymer, by quasielastic neutron scattering and by macroradical decay measurements by ESR. It was found that the onset temperature of the fast process of picosecond order coincides with the Vogel−Fulcher temperature T_0, similarly to observations for other simple polymers, confirming that the fast process is a precursor of the glass transition without any assumptions. In the macroradical decay study we observed the acceleration of the decay constant at a transition temperature $T_{tr,1}$ which agrees well with the onset temperature T_f of the fast process and the Vogel−Fulcher temperature T_0. This provides strong evidence that the macroradical decay in a-PP is accelerated by the fast process.

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