

Neutron Scattering Study of the Vibration-Relaxation Crossover in Amorphous Polycarbonates

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(Received 9 February 1994)

We report on neutron scattering observations of the fast picosecond relaxation in two amorphous polycarbonates. Contrary to previous experience, one already observes these fast relaxations far below the glass transition, at temperatures where they cannot be related to the flow process. An explanation in terms of low-barrier structural relaxations is proposed.

PACS numbers: 63.50.+x, 64.70.Pf

Neutron and Raman spectra of undercooled liquids have been investigated intensively within the last decade. One finds a universal transition from harmonic or quasi-harmonic vibrations above 1 or 2 meV to strongly anharmonic behavior at lower frequencies. This behavior is found in covalent, molecular, and ionic substances as well as in polymers. The general appearance is that of a fast picosecond relaxation superimposed on a temperature-independent vibrational density of states. At present, the only theoretical concept explaining the universality of this phenomenon is the mode coupling theory [1], which links these fast relaxations to the slow relaxation of the flow process and has been used to fit numerous neutron [2] and light scattering [3] experiments.

In this Letter we report measurements on two polycarbonates. The polycarbonates are polymers with an unusually high glass temperature T_g . We investigated BPA-PC [polycarbonate of 2,2-bis(4-hydroxyphenyl)-propane with $T_g = 423$ K] and BPZ-PC [polycarbonate of 1,1-bis(4-hydroxyphenyl)-cyclohexane with $T_g = 441$ K]. It was found that the fast relaxation appears already deep in the glassy phase, long before the flow processes become observable on an experimental time scale. As will be seen, the scattering at room temperature is similar to that from polymers with glass temperatures much below room temperature. This implies that the broad quasielastic feature observed has nothing to do with the flow process, but is an intrinsic feature of the glass itself.

The methyl groups of the BPA-PC sample were deuterated [BPA-PC- d_6] in order to suppress the signals from their rotational motion. The BPZ-PC sample, without any methyl group, was fully protonated. The molecular weights determined by viscosimetry were $M_w = 165\,000$ g/mol ($M_w/M_n \approx 5$, BPA-PC) and $M_w = 21\,300$ g/mol ($M_w/M_n \approx 2$, BPZ-PC). Both samples were hot pressed above T_g to obtain thin plates with scattering probabilities of around 10%.

The experiments were done at the cold triple axis spectrometer HER at the beam port C1-1 of the JAERI reactor at Tokai, Japan. The measurements were performed with a fixed wavelength of 4 Å of the incoming neutrons and an energy resolution (FWHM) of 0.25 meV. The main spectra were taken in energy gain of the neutron, at a constant momentum transfer of $Q = 2.75$ Å⁻¹ and at several temperatures between 10 and 300 K. In order to determine the Debye-Waller factors, constant-energy scans at 0, -0.5, -1.5, and -2.5 meV were taken, both at room temperature and at 10 K. A vanadium measurement and several empty can measurements were also done.

The spectra were corrected for background contributions and for the spectrometer sensitivity. After further corrections with the effective Debye-Waller factors and the detailed balance factor, the different scans were scaled to a common temperature of 50 K via multiplication by 50 K/ T (T temperature). For a perfectly harmonic solid, such a procedure should yield identical spectra at each temperature within experimental error.

Figure 1 shows that this is not the case for BPA-PC. One does indeed find the harmonic expectation fulfilled at higher frequencies, above about 2 meV. At the low temperature maximum at 1.3 meV (the so-called boson peak, another universal feature of glasses [4]), there is an increase of the intensity with increasing temperature. This increase is even more pronounced at lower frequencies and looks like a broad relaxational feature emerging on top of the lower part of the vibrational spectrum. That relaxational feature is much too broad to be explained by any of the well-studied secondary relaxations of BPA-PC [5]. Similar results were found for the BPZ-PC sample. In that second case, one finds even a decrease of the normalized intensities above 2 meV with increasing temperature.

The results of Fig. 1 look qualitatively similar to many neutron and light scattering results in many other

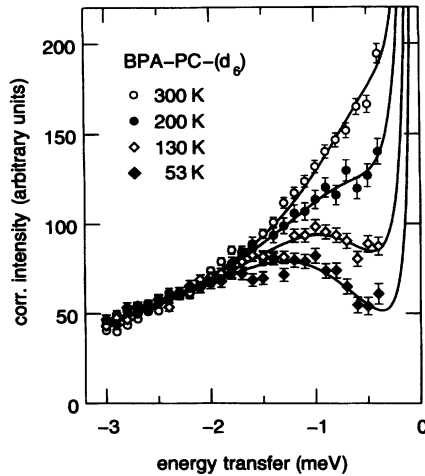


FIG. 1. Bose and Debye-Waller factor scaled neutron spectra of BPA-PC at four different temperatures below the glass transition temperature $T_g = 423$ K. The continuous lines are fits in terms of sound waves, additional vibrations, and classical relaxations, as described in the text.

substances, not only in polymers, but also in other glass formers. So far, however, this kind of spectrum has been taken to be typical for the undercooled liquid state, while our data show it far below the glass transition. In fact, our room temperature spectra look roughly like those of polyethylene [6], polybutadiene [7], polyisobutylene [8], polyvinylchloride [9], and polystyrene [10], though some of the polymers (the polycarbonates and polystyrene) are frozen glasses and the others are highly mobile liquids.

From Fig. 1, it is difficult to decide whether one has a mere onset of fast relaxations or a simultaneous vibrational softening. There are several other cases [8,11], however, where one observes a pronounced softening of the boson peak as the fast relaxations set in. In BPA-PC, Brillouin scattering measurements [12] show a strong temperature dependence of the sound velocities even below the glass temperature. Again, that softening cannot be attributed to the secondary relaxations, because the Brillouin frequencies are too high. So before dealing with the fast relaxation, one has to account for a temperature-dependent vibrational density of states with the proper Debye low frequency limit

$$g_D(\omega) = \frac{M\omega^2}{6\pi^2\rho} \left(\frac{1}{v_l^3} + \frac{2}{v_t^3} \right) \equiv \frac{3\omega^2}{\omega_D^3}, \quad (1)$$

where v_l and v_t are the longitudinal and transverse sound velocities, respectively, M is the atomic mass, ρ is the mass density, and ω_D is the (temperature-dependent) Debye frequency.

Unfortunately, the available theoretical models fail to describe the observed vibrational softening. The mode coupling theory [1] does not account for the boson peak at all. Though one can explain the boson peak [13] within

the phenomenological soft potential model [14,15], our fit of the 53 K data in terms of that model gave a poor fit at higher temperatures. Therefore, we decided to describe the vibrations by the following empirical form, taking the boson peak frequency ω_b as a free parameter

$$S_{\text{vib}}(Q, \omega) = \frac{3k_B T Q^2}{2M\omega_0^2} \left(\frac{A + \omega^2}{B + \omega^4} \right)^{1/2}, \quad (2)$$

with

$$A = \frac{\omega_0^4 \omega_b^4}{\omega_D^6 - 2\omega_0^4 \omega_b^2}, \quad B = \frac{\omega_D^6 \omega_b^4}{\omega_D^6 - 2\omega_0^4 \omega_b^2}.$$

The frequency ω_0 is another free parameter describing the height of the approximate $1/\omega$ decay of the scattering for frequencies above the boson peak. ω_D is not a free parameter, but is given by the Brillouin sound velocities according to Eq. (1). Fortunately, both the longitudinal as well as the transverse sound velocities have been measured in BPA-PC at and above room temperature [12], so the Debye limit could be calculated at room temperature and extrapolated to lower temperatures. For BPZ-PC, we used the BPA-PC values.

Obviously, Eq. (2) is just one of many possible choices. We made sure, however, that it describes the shape of the boson peak in a number of different substances. Later on, an argument will be given in support of the $1/\omega$ high-frequency limit of Eq. (2). In any case, with the correct Debye frequency, it supplies the proper baseline for the quasielastic scattering at low frequencies.

The quasielastic part of the scattering was described in terms of two different assumptions. The first of these was the mode coupling approach [1] with $S_{\text{rel}}(Q, \omega) = [1 - f_Q(T)]\omega^{a-1}$, which was supposed to describe the high-frequency part of the relaxations (β relaxation) with the temperature-dependent parameter $f_Q(T)$ and the temperature-independent parameter a . With $a \approx 0.3$, the fit required a high-frequency cutoff of the relaxational scattering around 1 meV in order to keep the high-frequency intensity low enough.

The second treatment of the relaxational scattering was based on Wigner's result [16] of a semicircle for the eigenvalue distribution of a symmetric random matrix. In this approach, the randomness of the elements of the dynamical matrix of the glass is supposed to lead to an approximately constant eigenvalue density $P(\lambda) = 1/\omega_0^2$ around the eigenvalue $\lambda = 0$. The eigenvalue density is normalized to three states per atom as usual. The approach is closely related to the soft potential model [14,15].

The eigenmodes are described in terms of normal coordinates A_λ . The kinetic energy of the mode is $A_\lambda^2/2$, so the contribution of the mode to the atomic mean square displacement must be of the order of $\langle A_\lambda^2 \rangle / M$, where M is the average atomic mass. In order to be able to deal with modes with a negative eigenvalue λ , they must be localized, which implies a positive stabilizing fourth order

term in their potential. Neglecting a possible asymmetry of the potential, one has

$$V(A_\lambda) = \frac{\lambda}{2} A_\lambda^2 + \frac{\nu_4}{4} A_\lambda^4, \quad (3)$$

where ν_4 , the coefficient of the fourth order term, is inversely proportional to the number of atoms participating in the mode and is related to the crossover energy W between tunneling states and vibrations of the soft potential model by

$$W = (\hbar^4 \nu_4 / 16)^{1/3}. \quad (4)$$

If λ is positive and large enough to neglect the influence of the fourth order term, one has a vibrational mode with a frequency ω , where $\lambda = \omega^2$. These modes give rise to a vibrational density of states $g_+(\omega) = 2\omega/\omega_0^2$ at higher frequencies.

The modes with a negative λ move in double-well potentials with minima at $\pm A_{\min}$ with $A_{\min}^2 = |\lambda|/\nu_4$. The barrier height is $E_a = \lambda^2/4\nu_4$, and the second derivative of the potential at A_{\min} is $2|\lambda|$. Thus a potential with a high enough barrier gives two contributions to the spectrum: (i) a more or less harmonic vibration within one of the two wells and (ii) a relaxational contribution from jumps over the barrier.

If one sums the vibrational contributions from positive and negative λ , one finds a high-frequency limit for the vibrational density of states of $3\omega/\omega_0^2$, consistent with the vibrational scattering Eq. (2). Two-thirds of this are due to positive eigenvalues and one-third comes from the vibrations within a double-well potential.

In order to calculate the relaxational scattering from the double-well potentials, one assumes that the anharmonic interaction between different modes acts like a stochastic force on a given mode [17], giving rise to a Langevin equation with a friction term γ . γ is the third parameter of the model, assumed to be the same for all these localized modes. The vibrational spectrum of Eq. (2) has to be convoluted with a Lorentzian of the half-width $\gamma/2$.

In the calculation of the relaxational spectrum, one assumes a jump rate of $\gamma(E_a/k_B T) \exp(-E_a/k_B T)$ in the double wells, corresponding to the weak damping case of Kramer's classical treatment [18]. Integrating over all double wells with barriers higher than $k_B T$, one gets

$$S_{\text{rel}}(Q, \omega) = \frac{4k_B T Q^2}{M \omega_0^2} \int_1^\infty dv \frac{2v \gamma \exp(-v)/\pi}{4v^2 \gamma^2 \exp(-2v) + \omega^2}. \quad (5)$$

Note that all our assumptions tend to overestimate the relaxational contribution: the weak damping assumption, the assumption of a constant density of eigenvalues (numerical work in liquids shows a decrease of the mode density towards higher negative eigenvalues [19]), and the neglect of any asymmetry of the potentials. Even so, the fit results attribute most of the anomalous intensity increase to a softening of the vibrations.

The curves in Fig. 1 were obtained by summing the contributions from the vibrations, Eq. (2), and from the relaxations, Eq. (5). The three parameters, the frequency ω_0 , the boson peak frequency ω_b , and the vibrational relaxation rate γ , were adapted at each temperature.

The frequency ω_0 was found to be essentially temperature-independent, with a slight tendency to increase at higher temperatures. Assuming the full monomer mass [236 a.u. for BPA-PC-(d₆) and 294 a.u. for BPZ-PC], frequencies ω_0 of about 6 to 7 meV were obtained. That means that one has $4\frac{1}{2}$ vibrational degrees of freedom per monomer below that frequency. Since there are 6 soft torsional degrees of freedom per monomer along the main chain, expected to appear below 10 meV in the vibrational dynamics of the polymer [20], those values for ω_0 seem reasonable.

With respect to the vibrational relaxation rate γ , one expects a linear increase with temperature for a quasiharmonic spectrum with anharmonic third order interactions. The results in Fig. 2 correspond roughly to that expectation. In addition, the value at room temperature (about 0.1 meV) is of a reasonable order of magnitude for both polymers, of the same order as values measured in crystals near to their melting temperature [21].

One finds a pronounced softening of the boson peak frequency ω_b (see Fig. 2). According to the fit, ω_b decreases by a factor of 2 between 53 K and room temperature, while the sound velocity decreases only by 20%. At present, there is no obvious explanation for such a strong softening.

Finally, we note that polycarbonate is one of the most fragile polymers [22] in Angell's classification [23]. As pointed out by Sokolov *et al.* [24], the relaxational contribution of the spectrum of a glass former tends to become stronger with increasing fragility. The results reported here may be typical for a very fragile substance.

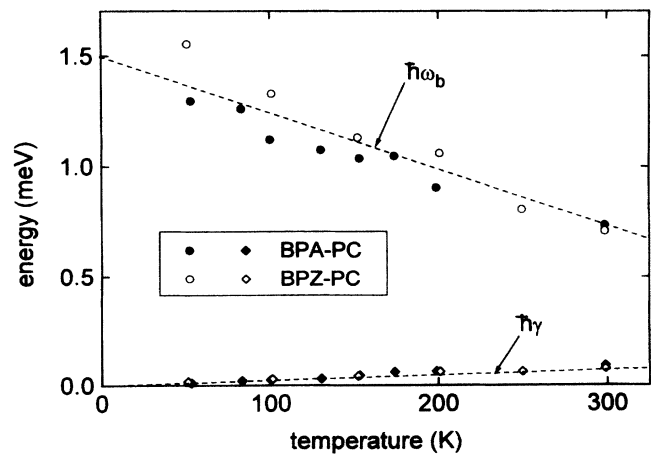


FIG. 2. Temperature dependence of the fit parameters for BPA-PC and BPZ-PC. The dashed lines are guides for the eye.

This work was supported as a Japan-Germany Collaboration Project by the Yamada Foundation, and U. B. and K. K. thank this foundation for financial support during this. C. S. gratefully acknowledges financial support by the BMFT Project No. ZBY 260 558 on polycondensates. We are grateful to Dr. Y. Oohara and Dr. H. Yoshizawa for their competent help with the experiments.

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