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N V Surovtsev†§, T Achibat†, E Duval†, A Mermet† and V N Novikov‡

† Laboratoire de Physico-Chimie des Matériaux Luminescents, Université Lyon I-URA No 442
du CNRS, 43, boulevard du 11 Novembre 1918, Bâtiment 205, 69622 Villeurbanne Cedex,
France
‡ Institute of Automation and Electrometry, Russian Academy of Sciences, Novosibirsk, 630090,
Russia

Abstract. Quasielastic light scattering (QLS) in the glassy polymer poly(methylmethacrylate) is investigated in the temperature range 12–470 K. Raman spectra were measured in the frequency interval 3–600 cm^{-1}. The detailed temperature dependence of the Raman intensity at some fixed frequencies, $\omega = 5$, 8, 20 cm^{-1} is obtained. The influence of the quenching on the QLS is investigated. It is shown that there are two characteristic temperature regions with different dependences of the QLS intensity on temperature. The first one is for $T < 50$–80 K, where the reduced Raman intensity increases with a characteristic activation energy of the order of 30 K. The second region is the high-temperature one: $T > 80$–100 K. Here the relaxation time is nearly constant while the reduced Raman intensity increases with an activation energy of the order of 700 K up to the glass transition temperature T_g. The spectral dependence of the relaxation contribution, found by a subtraction of the lowest-temperature (12 K) spectrum from the current one, $I(T, \omega)/(n(\omega) + 1)$, demonstrates a relaxational β peak which weakly depends on temperature. Its characteristic frequency is of the order of its width and is equal to 8–10 cm^{-1}. The peak can be well fitted by a Lorentzian. The data obtained are considered within the frames of the existing models of QLS.

1. Introduction

Quasielastic light scattering (QLS) in glasses occupies a spectral region $\omega < 50$–100 cm^{-1}. In this region there is a light scattering excess, i.e., the intensity $I(\omega, T)$ of the scattered light increases with temperature faster than the Bose factor $n(\omega, T) + 1$ which corresponds to scattering on harmonic vibrations. In spite of a series of experimental and theoretical investigations devoted to this problem (Jäckle 1981, Winterling 1975, Theodorakopoulos and Jäckle 1976, Nemanich 1977, Yasuoka *et al* 1986, Gochijaev and Sokolov 1989, Fleury and Lyons 1976, Heiman *et al* 1979, Gochijaev *et al* 1991, Parshin 1994) the nature of QLS is still not well understood. It is generally believed that QLS arises due to structure relaxation processes and has much in common with ultrasonic attenuation and far-infrared absorption in glasses (Jäckle 1981). There are some models for the QLS in glasses. One of the earliest models (Theodorakopoulos and Jäckle 1976) uses direct coupling of the light to relaxing polarizabilities: it is assumed that two-state defects exhibit different dielectric susceptibility. The hopping of the defect from one metastable configuration to another with a characteristic relaxation time $\tau(T)$ gives rise to QLS. The model predicts a constant depolarization ratio

§ On leave from the Institute of Automation and Electrometry, Russian Academy of Sciences, Novosibirsk, 630090, Russia.

which is determined by the difference of the polarizability tensors in the two alternative states. Although the model reasonably describes the respective experimental data in silica glass below room temperature (Jäckle 1981), it shows discrepancy with the experiment above room temperature and it fails to fit both the temperature and spectral dependence of QLS in As_2S_3 glass (Nemanich 1977, Gochijaev and Sokolov 1989). Probably, by varying the distribution function of the activation energy, the polarizability difference and other quantities one can obtain a good fit of the spectral and temperature dependences of QLS in terms of thermally activated relaxation of two-state defects; however, a principal question about the depolarization ratio remains unexplained.

One of the important properties of the QLS is the constancy of the depolarization ratio ρ over the spectrum: in particular, the depolarization ratio is the same both for the light scattering excess and the first-order vibrational spectrum. As has already been pointed out (Jäckle 1981), the natural explanation is that whatever the mechanism of relaxation, it couples to the light by indirect coupling via the vibrational degrees of freedom. This conclusion is essential for inorganic glasses like silica with $\rho \simeq 0.3$ or chalcogenides with $\rho \simeq 0.5$, i.e. for glasses with specific values of ρ inside the interval 0–0.75. For polymers $\rho = 0.75$ and therefore the above arguments have to be taken with caution because different mechanisms based on the transverse character of vibrations can be responsible for this limiting value of the depolarization ratio (Novikov *et al* 1995).

Winterling proposed a model for QLS based on the disorder induced scattering from damped sound waves (Winterling 1975). In this approach the vibrational response function is modified by the introduction of a memory function which is determined by the deviation from the harmonic behaviour. This model is generalized in order to take all vibrational modes up to the boson peak into consideration (Jäckle 1981, Gochijaev *et al* 1991). The model explains naturally the constancy of the depolarization ratio over the low-frequency spectrum. However, the microscopic origin of the memory function and, respectively, the mechanisms of relaxation are still not well understood. Jäckle supposed that structural defects in a glass, each of which can exist in two different atomic configurations, could be responsible for the memory function (Jäckle 1981). Gochijaev *et al* (1991) supposed that the memory function arises due to linear interaction of the boson peak modes with some purely relaxational modes of unspecified nature. In this phenomenological picture, the evolution of the QLS and of the boson peak with temperature was described at $T \geqslant T_g$, in good agreement with experimental data on Raman scattering in glycerol and some other small-molecule organic materials (Gochijaev *et al* 1991). However, the microscopic origin of the relaxational mode is unclear in this model, so that the coupling constant between the boson peak mode and the relaxational one, as well as the relaxational time τ, are fitting parameters.

The present paper is devoted to the investigation of QLS in the glassy polymer poly(methylmethacrylate) (PMMA). We measured both frequency and temperature dependences of the QLS in a broad temperature interval from 12 K to 470 K. Special attention was paid to the influence of the quenching on the QLS. We made an analysis of the data obtained within the frames of the existing models of structural relaxation and QLS in glasses. It is shown that the characteristic relaxation time τ decreases with increasing temperature when T is less than 80–100 K; τ is nearly constant at higher temperatures. It means that the light scattering excess increase at $T \geqslant 100$ K is due to a corresponding increase in the number of relaxation centres but not due to any temperature variation of the relaxation time.

2. Experiment

The PMMA samples were manufactured by the Norsolor Company (France). The number-average molecular weight, $\tilde{M}_n = 58000$ g mol^{-1}, was assessed by gel permeation chromatography. The pellets were processed by extrusion to manufacture 12 mm plates. The quenched samples of PMMA were obtained from the annealed ones by heating them for 30 minutes at $T = 440$ K and after that cooling in water at $T = 273$ K.

The intensity of the polarized Raman scattering from an argon laser beam with a wavelength $\lambda = 514.5$ nm was measured. The spectra were obtained using a five-grating monochromator Z40 provided by Dilor. The width of the slits was chosen such that the elastic component of the scattered light was completely suppressed at 3 cm^{-1}. The suppression was controlled by the comparison of the shape of the low-frequency spectra measured at different magnitudes of slit widths. The sample temperature in the illuminated region was measured using the Stokes/anti-Stokes ratio. The measurements were carried out in the temperature interval of 12–470 K. The low-frequency spectra were normalized using optical lines near 602 and 813 cm^{-1}. The spectral shape of these lines did not depend on temperature. All experimental results which are presented in this paper are obtained by normalization of the integral over the peak near 813 cm^{-1}.

3. Results

In figure 1 the Raman spectrum of PMMA at room temperature is shown. The boson peak is clearly seen at 16 cm^{-1}. The reduced spectra $I_r(\omega, T) = I(\omega, T)/(n(\omega) + 1)$ for temperatures $T = 12$ K, 99 K, 250 K, 300 K, 370 K and 470 K are presented in figure 2. The spectra in figure 2 show that the reduced intensity of the light scattering increases with increasing temperature.
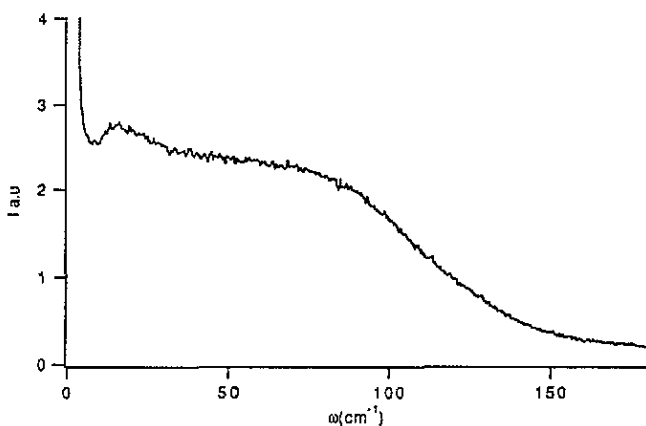

Figure 1. Representative Raman spectrum of PMMA at room temperature.

We investigated in detail the dependence of the reduced intensity on temperature. To this end, the measurements of the light scattering at fixed frequencies were carried out with accumulation times higher than those used in the measurements of regular spectra. The results for three frequencies, $\omega = 5$, 8 and 20 cm^{-1}, are presented in figure 3.

In order to find the purely relaxational part of the Raman spectra we subtracted the
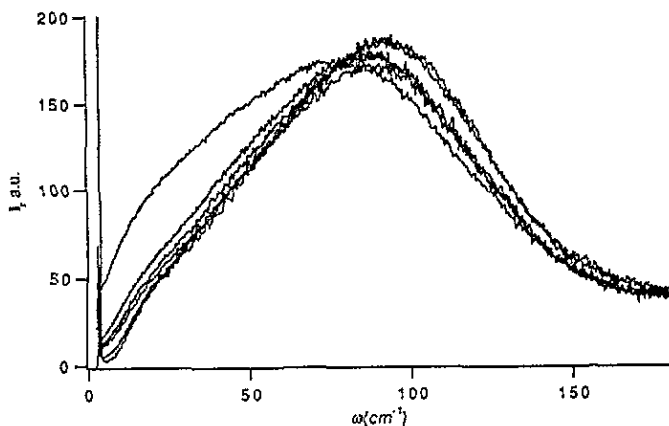
Figure 2. The reduced Raman spectra $I_r(\omega) = I(\omega)/(n(\omega)+1)$ in PMMA for six temperatures: $T = 12$ K, 99 K, 250 K, 300 K, 370 K and 470 K. The sequence of the spectra in the figure corresponds to this series of temperatures from bottom to top at small frequencies.
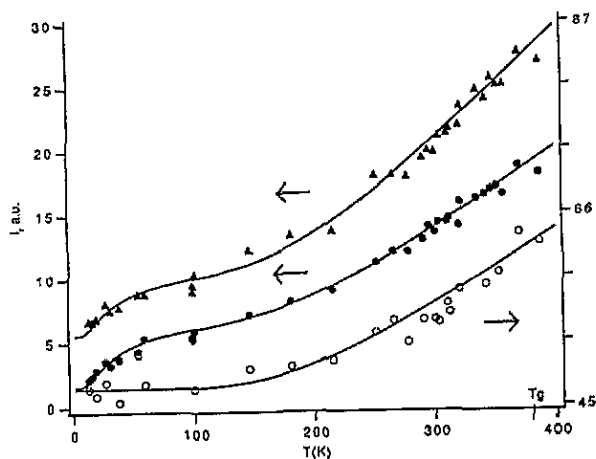

Figure 3. Temperature dependence of the reduced Raman intensity in PMMA for three frequencies: 5 cm^{-1} (solid circles), 8 cm^{-1} (solid triangles) and 20 cm^{-1} (open circles). Solid lines: fit by the formulae (4.1)–(4.3). Left vertical scale is for 5 and 8 cm^{-1} curves, right vertical scale is for the curve at 20 cm^{-1}.

spectrum at 12 K from the ones at higher temperatures. In figure 4 the difference

$$\Delta I_r(\omega, T) = I_r(\omega, T) - I_r(\omega, T = 12 \text{ K}) \tag{3.1}$$

for $T = 99$, 250, 300, 370 and 470 K is presented. Since the temperature dependence of the vibrational part is much weaker than that of the relaxational one, the former almost completely vanishes in the subtraction procedure. In order to decrease the influence of the mismatching of the vibrational spectra at low and high temperatures on the shape of the spectra, we present in figure 5 the spectra $\Delta I_r(\omega, T)/\omega$. This normalization corresponds to the direct Raman spectrum at high T, when $\omega(n(\omega) + 1) \simeq T$.

In figure 6 the normalized spectra of a quenched sample are shown at $T = 315$ K and 15 K. Qualitatively, the spectra of the quenched and of the annealed samples are very similar; the only difference is quantitative: the quenched sample spectra generally show higher QLS intensity than those of the annealed sample. However, beginning from $T = 60$–80 K the
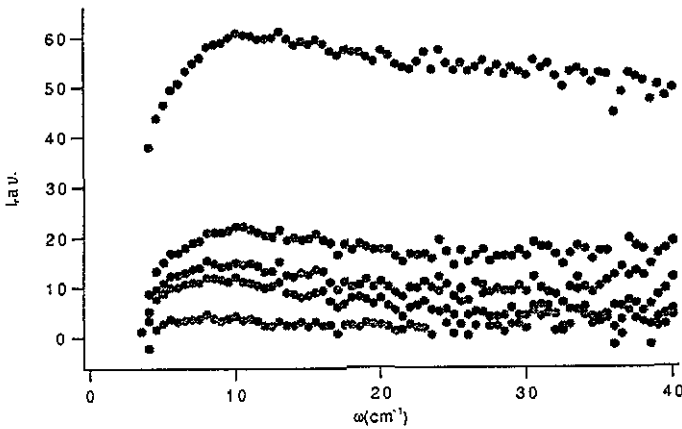
Figure 4. The spectra of the difference $I_r(\omega, T) - I_r(\omega, T = 12 \text{ K})$ between the reduced Raman intensity in PMMA at temperatures $T = 99$ K, 250 K, 300 K, 370 K, 470 K (from bottom to top, respectively) and the one at 12 K.
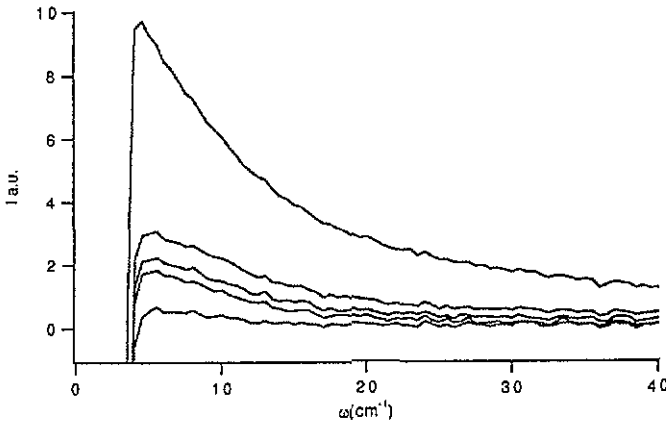

Figure 5. The same spectra as in figure 4 in normalization $I(\omega)/(\omega(n(\omega) + 1))$. The sequence of the curves corresponds to $T = 99$ K, 250 K, 300 K, 370 K, 470 K (from bottom to top, respectively).

difference decreases with decreasing temperature and at the lowest T of the experiment, 15 K, the spectra of the quenched and of the annealed samples are practically the same.

4. Discussion

4.1. Temperature dependence

The temperature dependences of the reduced intensities $I_r(\omega)$ at 5 and 8 cm^{-1} are very similar (figure 3). At small temperatures I_r has nearly a constant value and begins to grow smoothly at $T \geqslant 150$–200 K. It means that at $T \leqslant 100$ K the vibrational contribution at these frequencies is predominant. At 5 and 8 cm^{-1} the temperature dependence of the reduced intensity exhibits an additional feature in comparison with that at 20 cm^{-1}: a comparatively sharp drop at $T \leqslant 60$–80 K. This means that at least two different relaxation processes make a contribution to the quasielastic spectrum of PMMA, one of them being
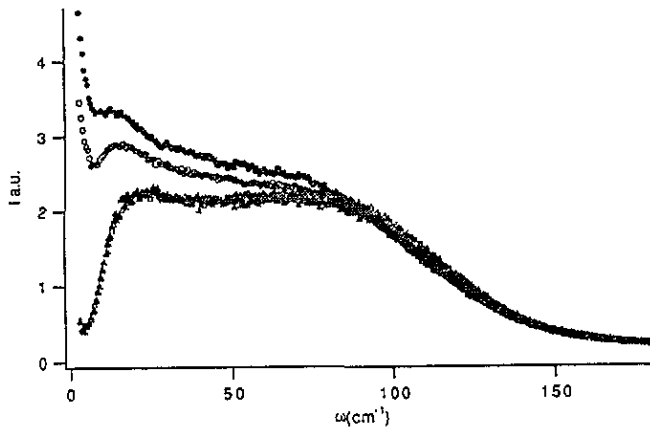
Figure 6. Reduced Raman spectra of quenched sample of PMMA at 315 K (solid circles, upper curve) and 15 K (solid triangles, bottom curve). For comparison, respective Raman spectra of the annealed sample are shown by open circles for 315 K (middle curve) and by open triangles for 15 K (bottom curve). The latter curve is practically indistinguishable from the spectrum of the quenched sample at the same temperature 15 K.
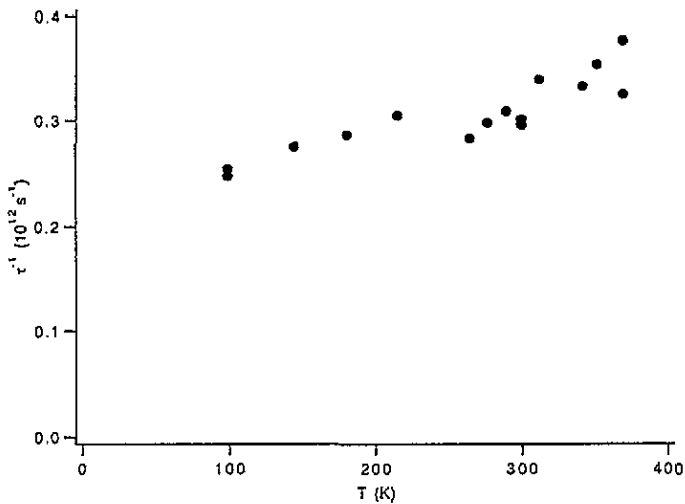

Figure 7. Temperature dependence of the relaxation time τ as defined by fitting of the difference spectra by the Lorentz curve.

important at high temperatures $T > 100$ K and the other one being predominant at low temperatures, $T < 60$–80 K.

To clarify the nature of the relaxation, we fitted $I_r(T)$ by an activation law. To fit the reduced intensity at 5 cm^{-1} one needs at least two exponentials, one being for low temperatures, another for high temperatures; additionally, we add a temperature independent term to take into account the vibrational contribution. By a least-squared fit we obtained the following expression for $I_r(\omega = 5$ cm$^{-1}, T)$:

$$I_r(\omega = 5 \text{ cm}^{-1}, T) = 1.6 + 6\exp(-32/T) + 84\exp(-750/T). \tag{4.1}$$

The corresponding curve is shown in figure 3. According to equation (4.1) there are two activation energies for the relaxation at 5 cm^{-1}: 32 and 750 K. The latter energy is typical

of the order of magnitude for many glasses and is also observed in ultrasonic attenuation (see, e.g., (Galperin *et al* 1989), where the existence of a singularity in the barrier height distribution in glasses is seen at a temperature of the order of $\sim$500 K). The relaxation process with the lower activation energy, $E = 30$ K, is hardly seen at $\omega = 8$ cm^{-1} and is not observed at all at $\omega = 20$ cm^{-1} (see figure 3). The respective fits of the temperature dependences at 8 and 20 cm^{-1} are the following:

$$I_r(\omega = 8 \text{ cm}^{-1}, T) = 5.6 + 6\exp(-32/T) + 120\exp(-750/T) \tag{4.2}$$

$$I_r(\omega = 20 \text{ cm}^{-1}, T) = 47 + 112\exp(-750/T). \tag{4.3}$$

In equations (4.1)–(4.3) the vibrational contribution increases with frequency. The ratio of the vibrational terms at 8 and 5 cm^{-1} is equal to 3.5. Supposing that for the vibrational contribution $I_r(\omega) \propto \omega^n$, from the condition $(8/5)^n = 3.5$ we found $n = 2.7$. This result is in good agreement with the respective Raman data for very low frequencies in various glasses where the behaviour $I_r \propto \omega^3$ is usually observed (see, e.g., Parshin 1994, Carini *et al* 1993, Duval *et al* 1993). The vibrational contribution at $\omega = 20$ cm^{-1}, however, does not follow an ω^3 dependence since this frequency is close to the maximum of the boson peak.

Some models, which will be discussed below, predict a power law for the Raman intensity temperature dependence, linear or quadratic. In order to check this prediction we fitted the experimental data by a quadratic polynomial. In the interval 100–370 K for $\omega = 5$ cm^{-1} the best fit is

$$I_r(\omega = 5 \text{ cm}^{-1}, T) = 1.05 \times 10^{-4}T^2 + 4. \tag{4.4}$$

For the frequency 8 cm^{-1} there is a wide interval from 12 to 200 K where the temperature dependence is practically linear, $I_r(\omega = 8 \text{ cm}^{-1}, T) = 3.8 \times 10^{-2}T + 5.5$, $T \leqslant 200$ K. At $T \geqslant 200$ K the dependence can also be well represented by a quadratic one: $I_r(T, \omega = 8 \text{ cm}^{-1}) = 1.6 \times 10^{-4}T^2 + 6$. For $\omega = 20$ cm^{-1}, over the whole temperature interval a quadratic polynomial is a good fit:

$$I_r(\omega = 20 \text{ cm}^{-1}, T) = 1.5 \times 10^{-4}T^2 + 40.5. \tag{4.5}$$

4.2. Spectral dependence

Let us now turn to the spectral dependence of QLS. In order to find the relaxational part of the QLS spectrum we will use an approximation in which the intensity of Raman scattering is presented as a sum of the vibrational and the relaxational contributions:

$$I_r(\omega, T) = I_r^{vib}(\omega, T) + I_r^{rel}(\omega, T). \tag{4.6}$$

It is difficult to separate both contributions from the total intensity. There is a weak dependence of the vibrational contribution on temperature due to a softening of the structure as T increases. One can expect that the relative change of the vibrational spectrum will be of the same order as that of the sound velocity. For PMMA at room temperature, $\partial v_l/\partial T = -250$ cm s^{-1} K^{-1}, $\partial v_t/\partial T = -200$ cm s^{-1} K^{-1}, $v_l = 2.69 \times 10^5$ cm s^{-1}, $v_t = 1.34 \times 10^5$ cm s^{-1} (Encyclopedia of Polymer Science and Engineering, 1985). Using these values, we obtain for the relative change of the sound velocity $\partial \ln v_l/\partial T = 0.9 \times 10^{-3}$, $\partial \ln v_t/\partial T = 1.6 \times 10^{-3}$. So, we can expect that the relative changing of the sound velocity over the temperature interval of $\sim$400 K (from 12 K up to T_g) for PMMA does not exceed 0.4–0.6. On the other hand, the intensity of QLS at 5 and 8 cm^{-1} increases by a factor of six in this temperature interval (figure 3).

So, the dependence of the vibrational contribution on T is much weaker than that of the relaxational one. This gives us the possibility of determining $I_r^{rel}(\omega, T)$ at a temperature T in a rough approximation as the difference between the total spectrum at this temperature and the one at very low temperature where the relaxational contribution is negligible. The lowest temperature used in the present experiment is 12 K. So, let us suppose that $I_r^{vib}(\omega, T) \simeq I_r^{vib}(\omega, T = 12\,K)$. The relaxation contribution to the reduced Raman intensity found in this approximation is shown in figure 4. It is an increasing function of the frequency in the interval $3 < \omega < 8\text{--}10$ cm^{-1} and demonstrates a pronounced peak with a maximum at $\omega = 8\text{--}10$ cm^{-1}. This peak corresponds to the one of the fast β relaxation observed in some supercooled liquids (Götze and Sjögren 1992). The position and the width of the peak practically do not depend on temperature at $T > 100$ K in contrast to the slow β relaxation process which is usually observed in glassy materials at lower frequencies. The similar observation was made in inelastic neutron scattering spectra of polybutadiene, where it was found that the width of the low-frequency excess scattering does not depend on temperature (Frick and Richter 1995).

4.3. Models of QLS

4.3.1. Single relaxation time For the interpretation of the experimental data let us consider a simple relaxation model of quasielastic light scattering. The relaxational part of the reduced intensity of QLS, $I_r^{rel}(\omega, T)$, which is the generalized susceptibility $\chi''(\omega, T)$, can be written in the form (Jäckle 1981):

$$I_r^{rel}(\omega, T) = \frac{I(\omega, T)}{(n(\omega) + 1)} \propto \sum_i \frac{b_i(\omega, T)\omega\tau_i}{1 + (\omega\tau_i)^2} \qquad (4.7)$$

where $\tau_i(T)$ are relaxation times distributed according to some law; parameters $b_i(\omega, T)$ depend on the particular mechanism of relaxation and characterize the strength of the relaxation process. In the simple Debye approximation with only one relaxation time $\tau(T)$ and one constant b we will have

$$I_r^{rel}(\omega, T) \propto \frac{b\omega\tau}{1 + (\omega\tau)^2}. \qquad (4.8)$$

Applying the Debye formula to the experimental data for I_r^{rel} we found that qualitatively it well describes the peak near $\omega = 8\text{--}10$ cm^{-1}. The most interesting result is that the effective relaxation time τ practically does not depend on temperature at $T > 100$ K (see figure 7) while the intensity of QLS strongly increases as T increases at all temperatures (figure 3).

Let us now apply some models existing in the literature to describe the experimental data. We begin with the soft-potential model (SPM) (see, e.g., reviews Parshin 1994, Galperin *et al* 1989, Klinger 1988).

4.3.2. Soft potential model According to Jäckle (1981), as a consequence of the fluctuation–dissipation theorem, the reduced Raman intensity in amorphous solids can be expressed via the ultrasonic absorption coefficient:

$$I_r(\omega, T) = al^{-1}/\omega \qquad (4.9)$$

where a is a constant. In the soft-potential model, the absorption coefficient is a sum of three terms,

$$l^{-1} = l_{res}^{-1} + l_{rel,DWP}^{-1} + l_{rel,HO}^{-1}. \qquad (4.10)$$

The first term in the r.h.s. of equation (4.10) corresponds to some resonance absorption by harmonic oscillators; this term does not contribute to the relaxation spectrum (3.1). The second term appears due to thermally activated processes in double-well potentials (DWP). In the SPM, the distribution function $F(\Delta, V)$ of the energy difference between two minima, Δ, and of the barrier height V is taken as independent of Δ. For frequencies ω such that $\omega\tau_0 \ll 1$ ($\tau_0 \simeq 10^{-13}$ s) an expression is obtained (see, e.g., Parshin 1994, Gurevich *et al* 1994)

$$l^{-1}/\omega \propto (T/W)^{3/4} \ln^{-1/4} \frac{1}{\omega\tau_0}. \qquad (4.11)$$

Here the parameter W is of the order of a few kelvin. This expression does not properly describe the temperature dependence of the reduced Raman intensity in any of the measured temperature intervals. One can see more or less similar behaviour at $\omega = 5$ cm^{-1} and $T < 80$ K, but the temperature dependence (4.11) is too weak in comparison with the experimental one.

The third term in the r.h.s. of equation (4.10) corresponds to relaxation scattering on (quasi)harmonic oscillators. There are various regimes of scattering, depending on the temperature and on frequency. The frequency and temperature interval of the present experiment corresponds to the cases of intermediate and high frequencies in terms of the papers by Parshin (1994) and Gurevich *et al* (1994). Intermediate frequencies have an upper limit: $\omega \ll W(2T/E_c)^2$, where E_c is of the order of the boson peak frequency, i.e. in our case 20 cm^{-1} and for polymers typically $W \approx 1$–3 cm^{-1} (Parshin 1994). Harmonic oscillators with $\omega\tau \simeq 1$ give the main contribution. For these frequencies SPM gives (Parshin 1994, Gurevich *et al* 1994)

$$l^{-1}/\omega \propto T\omega^{-1/2}. \qquad (4.12)$$

The linear temperature dependence is clearly seen in a broad interval from 80 to 250 K on the curve $I_r(\omega, T)$ with $\omega = 8$ cm^{-1} (see figure 3) but it is hardly found for the case of $\omega = 5$ cm^{-1}. In any case, the temperature dependence of the reduced intensity becomes a quadratic one at $T > 200$–250 K for all frequency points. Such a transition from a linear to a quadratic law with increasing temperature is in contradiction with the predictions of the SPM. Indeed, according to Parshin (1994) and Gurevich *et al* (1994) at some fixed frequency ω (e.g., 5 cm^{-1}) a quadratic dependence on temperature is expected for the temperature interval $T \ll E_c(\omega/W)^{1/2}/2$, while a linear dependence has to be observed in the region $T \gg E_c(\omega/W)^{1/2}/2$, i.e., according to the SPM, at some fixed frequency with increasing temperature a quadratic temperature dependence has to appear before a linear one, which is in contradiction with our experimental data. Let us note that the power dependence of the QLS intensity on temperature of the type $I_r \propto T^\alpha$ with $\alpha = 0.5$–1.3 was found to be a good fit of the experimental data for samarium phosphate glasses (Brodin *et al* 1994). A conclusion was made about the qualitative agreement of the temperature and frequency dependences of both the QLS with the SPM predictions. However, it seems that there is a qualitative disagreement with the SPM predictions in the succession of the linear and quadratic temperature dependences at a fixed frequency.

The frequency dependence in the interval 10–20 cm^{-1} is qualitatively in agreement with the decreasing function (4.12); however, the experimental data show stronger power dependence than in 4.12. Regarding higher frequencies, it seems that at $\omega > 20$ cm^{-1} there is a relaxation process which masks the simple Cole–Cole or Lorentzian dependence of the peak with a maximum of $I_r(\omega)$ at 8–10 cm^{-1}, so it is impossible to make any definite

predictions on the frequency dependence of the Cole–Cole-like process at $\omega > 20$ cm^{-1}. At high frequencies, $\omega \gg W(2T/E_c)^2$, SPM predicts $\omega\tau \gg 1$ and

$$l^{-1}/\omega \propto T^2/\omega. \tag{4.13}$$

This prediction is in very good agreement with our data for the temperature dependence of $I_r(\omega, T)$ at $\omega = 20$ cm^{-1} (see figure 3 and equation (4.5)). However, as mentioned above, there is no such agreement for the cases of $\omega = 5$ and 8 cm^{-1}. If we suppose that the frequency dependence of the $I_r^{rel}(\omega, T)$ is a superposition of the Lorentz type expression at low frequencies with a maximum near 8–10 cm^{-1} and of a broad feature of unknown nature at high frequencies with a maximum at $\omega = 50$–70 cm^{-1} then the frequency dependence predicted by the SPM is also in reasonable agreement with the results obtained.

As mentioned above, one of the most interesting observations regarding QLS in PMMA is the very weak temperature dependence of the effective relaxation time τ defined as the inverse width of the relaxation peak at 8–10 cm^{-1}. It is unclear how this fact can be explained by the SPM. In particular, the assumption made by Parshin (1994) that the relaxation time τ is determined by a single-phonon process, i.e. by the resonant absorption or emission of phonons, which is temperature independent, can be valid only at not too high temperatures. Our data show that the width of the peak weakly changes in the whole interval from 100 to 470 K; this behaviour can hardly be explained by the single- phonon process.

So, one may conclude that the soft-potential model, in any case in the version presented by Parshin (1994) and Gurevich *et al* (1994), cannot well describe the whole set of the experimental data on QLS in PMMA.

4.3.3. Gilroy–Phillips model

Let us now consider the model of Gilroy and Phillips (1981). It probably can be applied to the low-temperature QLS, $T < 100$ K. To describe the relaxation scattering on double-well potentials, they used a constant value f_0 of the distribution function of Δ, $f(\Delta)$, and an exponential distribution function for barrier heights V,

$$g(V) = \frac{1}{V_0} \exp(-V/V_0). \tag{4.14}$$

They obtained for the susceptibility an approximate expression

$$\chi'' \propto (T/V_0)(\omega\tau_0)^{T/V_0} \tag{4.15}$$

where V_0 is an energy related to T_g. We used this formula to fit the low-temperature part of $I_r(\omega = 5$ cm$^{-1}, T)$. The fit is very good and the expression

$$I_r(\omega = 5 \text{ cm}^{-1}, T) = 1.4 + 0.078T(0.993)^T + 91\exp(-680/T) \tag{4.16}$$

describes the experimental curve in the whole temperature interval quite well. The factor 0.993 in brackets is equal to $(\omega\tau_0)^{(1/V_0)}$. Taking $\omega = 5$ cm^{-1} and $\tau_0 = 10^{-13}$ s, we found $V_0 = 600$ K. This value of V_0 is in agreement with the one obtained by fitting the high-temperature dependence (4.1). At temperatures higher than about 100 K the model cannot fit the experimental data, because, as mentioned above, a different mechanism of relaxation is predominant at these temperatures.

4.3.4. Multiple-order Raman scattering

The contribution of the multiple-order Raman scattering to the QLS was discussed in the review by Jäckle (1981). The influence of such scattering on the acoustical Raman spectra of amorphous solids was investigated recently

in a series of papers by Zwick *et al* (see, e.g., Zwick and Carles 1993, Chehaidar *et al* 1994a, 1994b). We believe that multiple-order Raman scattering can hardly explain our experimental data on QLS. It is known that the depolarization ratio is the same for the one-phonon spectrum in the spectral region of the boson peak and for the low-frequency QLS (Jäckle 1981), being 0.3 for SiO_2, 0.4–0.5 for chalcogenide glasses and 0.6–0.75 for polymers. It is difficult to understand this property within the frame of multiple-order scattering. Additionally, in the inelastic neutron scattering experiments it was found that the intensity of the low-frequency excess scattering in polybutadiene (which corresponds to QLS) depends on the momentum transfer q in the same manner as the intensity of the boson peak, suggesting a common origin (Frick and Richter 1995). Although one can not definitely exclude the multiple-order Raman scattering as the source of QLS, it seems that its contribution is in any case small in comparison with the relaxational one at small frequencies.

4.4. Influence of quenching

Let us turn now to the QLS in quenched samples of PMMA. As one can see in figure 6 the intensity of QLS is higher in the quenched PMMA sample than in the annealed sample at the same temperature. However, at low temperatures the QLS intensity in the quenched sample tends to the same value as in the annealed one. The high-temperature behaviour of the reduced intensity can be well fitted by approximately the same activation parameters as in the case of annealed samples. One can introduce a parameter which is defined as the ratio $\mu(T)$ of the QLS intensity of the quenched to that of the annealed samples at 5 cm^{-1}:

$$\mu(T) = I_{quen}^{rel}(\omega = 5 \text{ cm}^{-1}, T)/I_{ann}^{rel}(\omega = 5 \text{ cm}^{-1}, T). \tag{4.17}$$

We found that this ratio is practically independent of temperature and is equal to 1.8–2.2 in the temperature interval 100–370 K. So, the temperature dependence of the QLS intensity in the quenched sample can be connected to that of the annealed sample by the expression $I_{quen}^{rel}(T) = \text{constant} \times I_{ann}^{rel}(T)$. It means that the activation energies for the QLS of the quenched sample are nearly the same as those for the annealed one while the other factors are higher for the quenched sample by a factor of two. One of the possible explanations is that the number of the relaxation centres increases due to annealing while the nature of the centres and their activation energy are the same.

As pointed out above, at low temperatures the ratio $I_{quen}(T)/I_{ann}(T)$ tends to unity, figure 6. Such a behaviour can be explained very easily, if one assumes that at very low temperature the relaxational contribution to the light scattering becomes less than the intensity of the Raman scattering on harmonic vibrations. In this case the scattering intensities on both annealed and quenched samples are determined by the density of vibrational states. The latter is the same in both samples with the accuracy of the order of a few per cent, in accordance with the changes of the sound velocity and density.

5. Conclusion

In this work the quasielastic light scattering in quenched and annealed samples of PMMA was investigated. The measurements were carried out in the temperature interval from 12 to 470 K, but the main attention was paid to the temperature interval below the glass transition. Detailed temperature dependences of the intensity of QLS at some fixed frequencies, 5, 8 and 20 cm^{-1}, were found. The existence of two different relaxation mechanisms is revealed: one of them is predominant at temperatures $T < 60$–80 K, another one is responsible for

the relaxation at $T > 100$–150 K. It is shown that the former mechanism of relaxation may correspond to some temperature induced activation relaxation in double-well potentials. The nature of the latter one, the high-temperature mechanism of relaxation remains unclear. It has a relaxation time ($\tau^{-1} = 0.3$–0.4×10^{12} s^{-1}) which very weakly depends on temperature while the QLS intensity strongly increases with temperature. The quenching of the samples leads to an increase of QLS; the activation energies of the relaxation process in the quenched samples are nearly the same as in the non-quenched ones, whereas the increasing of the pre-exponential factor is much more pronounced.

The frequency and temperature dependences of the QLS were analysed in the frame of the soft-potential model (Parshin 1994, Galperin *et al* 1989, Gurevich *et al* 1994). It is shown that the SPM can well describe some isolated parts of the temperature and frequency dependences of the QLS in PMMA. However, there are some inconsistencies which make it impossible to describe the whole picture of QLS in PMMA by the soft-potential model, in any case, in the formulation in which it is presented in Parshin (1994), Gurevich *et al* (1994). A new model which can describe the quasielastic scattering in glasses is needed.

Acknowledgments

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