=== **POLYMERS** ===

Study of Fast Relaxation in a Glassy Polymer by Far-IR Spectroscopy

V. A. Ryzhov

Ioffe Institute, Russian Academy of Sciences, St. Petersburg, 194021 Russia
e-mail: v.ryzhov@mail.ioffe.ru
Received December 12, 2016

Abstract—The temperature dependence of the far-IR spectra of glassy polymethylmethacrylate is studied in the range of $\nu = 10–130$ cm^{-1} at temperatures from 90 to 420 K. The analysis of the spectra revealed absorption corresponding to two rapid relaxation processes: (1) 180°-rotation of the OCO plane of the side groups and (2) reorientation of the links of the main chain. The activation energies of these processes are determined.

1. INTRODUCTION

The development of the molecular mechanisms of segmental dynamics in polymers has been considered in a large number of theoretical and experimental studies that have led to an understanding of the nature of the main relaxation transitions. At the same time, issues concerning a more local, small-scale (within a side group or a chain link) mobility need further clarification, especially since macro- and microdynamics in polymers are closely interrelated. Note that the main method for studying the local dynamics of polymer molecules, that is, molecular dynamics simulation, although very informative, cannot determine all the details of the dynamics.

More recently, Raman spectroscopy began to be involved in the study of processes that are faster than segmental rearrangements in macromolecules; this method showed the possibility of a uniform description of both individual and collective molecular mobility [1]. It was important to establish the fact that in the Raman spectra of polymers in the range 0.03–3 THz (~1–100 cm^{-1}) both the torsional oscillation of individual links (the librational band) and their collective motion (the "bosonic" peak) are manifested, as well as the relaxation component ("β-fast" loss) at quasi-elastic scattering frequencies [2, 3].

The nature of the fast molecular processes observed in low-frequency spectra is now actively discussed in publications, including those based on the data obtained by far-IR (FIR) spectroscopy, which makes it possible to specify their mechanisms [4, 5]. In the model of coupled modes of the vitrification theory, these processes are referred to the manifestation of β-relaxation preceding the structural relaxation [6]. The contribution of elementary processes such as local conformational reorientations in the main chain and side groups is considered [7]. This ambiguity in the attribution of fast processes in polymers is explained by the fact that often it is conducted using phenomenological concepts based on such averaged characteristics of the substance as free volume, viscosity coefficients, diffusion, etc.

Molecular-kinetic theories based on the concepts of the genetic relationship of vibrational and relaxation forms of motion, can specify more confidently the mechanisms of molecular motions responsible for the picosecond dynamics of molecules [8]. An example of such an approach can be found in [9], where it was established that the relaxation component at quasi-elastic scattering frequencies in the Raman spectra of polystyrene and polycarbonate, measured in the range of 3–1000 GHz at temperatures below the glass transition temperature, is caused by temperature-activated transitions through the barrier with a height of ~500 K [10].

The possibility to determine the value of the activation energy of fast rearrangements in polymethylmethacrylate (PMMA) from changes in the spectral parameters of low-frequency absorption with temperature was also used in the present work to elucidate the nature of the relaxation contribution to the FIR spectra of this polymer.

2. EXPERIMENTAL

The experiments were carried out using films of bulky atactic polymethylmethacrylate with a number-average molecular weight of ≈ 500 000 g/mol and a thickness of ~100 μm, obtained by pressing at 150°C and holding for 3–5 h at 110°C. FIR-spectra were recorded using two spectrometers: a spectrometer of developed in the Leningrad State University, modern-
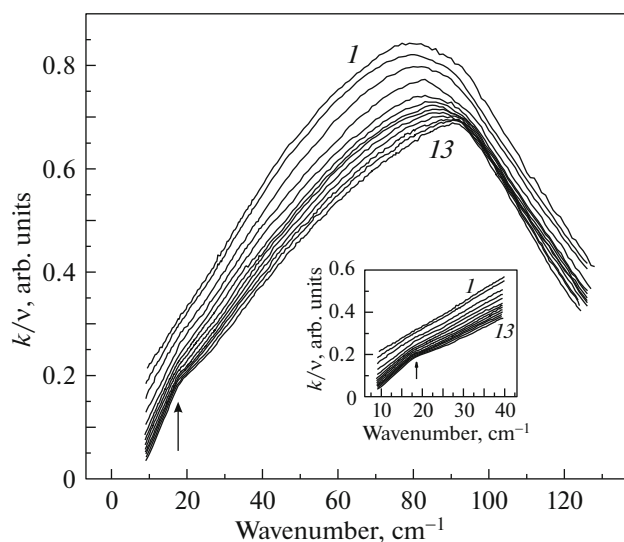
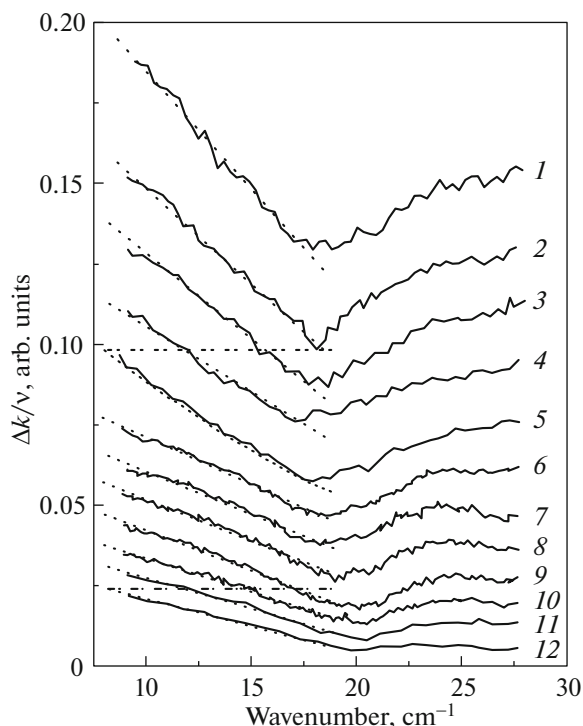**Fig. 1.** Reduced FIR spectra of PMMA in the range of 10–130 cm^{-1} at different temperatures (T, K): (*1*) 420, (*2*) 403, (*3*) 368, (*4*) 333, (*5*) 293, (*6*) 273, (*7*) 253, (*8*) 233, (*9*) 193, (*10*) 173, (*11*) 153, (*12*) 123, and (*13*) 90. Inset: initial sections of the curves in an enlarged scale; arrows mark the position of the boson peak in the spectra.


Fig. 2. Spectra obtained by subtraction of a PMMA spectrum at 90 K from PMMA FIR spectra at temperatures from 420 to 123 K; notations are the same as in Fig. 1.

ized with an OAP-7 receiver and a new filtration system, in the range of 10–50 cm^{-1} [11] and a FIS-21 Hitachi spectrometer in the range of 50–150 cm^{-1}. The spectra were recorded at a resolution of 1–2 cm^{-1} with a signal-to-noise ratio of approximately 100. The error in measuring the frequency was 2–3 cm^{-1}, the error in measuring the absorption coefficient $k = (t)^{-1} \times \ln (I_0/I)$ (where I_0 and I were the intensity of the incident radiation and the radiation transmitted through the sample of thickness t, respectively) was 5–10%. To measure the spectra in the temperature range from 90 to 273 K, a cuvette-cryostat with windows made of crystalline quartz was used. FIR spectra in the range from room temperature to ~413 K were obtained using a thermostated cuvette with sapphire windows. Thermal insulation in both cases was achieved by placing the cuvettes in a vacuum. The temperature of the sample was measured with a copper–constantan thermocouple; its stability was within ±2°C. Up to five parallel measurements were carried out for each temperature in the range from 10 to 50 cm^{-1}.

3. RESULTS AND DISCUSSION

The FIR spectra of PMMA are shown in Fig. 1 as a function of k/ν on ν. The plotting of FIR spectra in these coordinates makes it possible to compare them with the Raman spectra given in the coordinates of $I(\nu)/(N + 1)$, where $I(\nu)$ is the measured scattering intensity, and $N + 1$ is the Bose factor.

As the reduced Raman spectra of PMMA, recorded at 5–150 cm^{-1} for different temperatures

[12], the reduced FIR spectra of PMMA have an intense band at ~90 cm^{-1} with a singularity at frequencies close to the position of the boson peak (BP) in the Raman spectra.

It is seen from Fig. 1 that as the temperature increases, the absorption band at ~90 cm^{-1} becomes somewhat broader, its intensity increases, and the maximum shifts by 3–5 cm^{-1} to low frequencies. The latter is obviously due to an increase in the amplitude and anharmonicity of the oscillations because of the weakening of intermolecular interactions. Of special interest is the increase in the intensity of its longwave wing at frequencies below the boson peak, which indicates an increase in the relaxation component of the spectrum [12]. The dynamics of the intensity of the longwave wing of the band is illustrated in Fig. 2, which shows the difference spectra obtained by subtracting the PMMA spectrum at 90 K from them, which, as follows from [12], is basically a purely vibrational contribution.

It is seen from the dependence of the intensity of the difference spectrum on temperature (Fig. 3) that the increase in absorption in the region of 8–20 cm^{-1} is not monotonic. Two stages are clearly seen: "low-temperature" (from 90 to ~260 K) and sharper "high-temperature" (from ~260 to 420 K). Since the temperature at that the conformational mobility in PMMA begins is close to 260 K [13], this suggests that
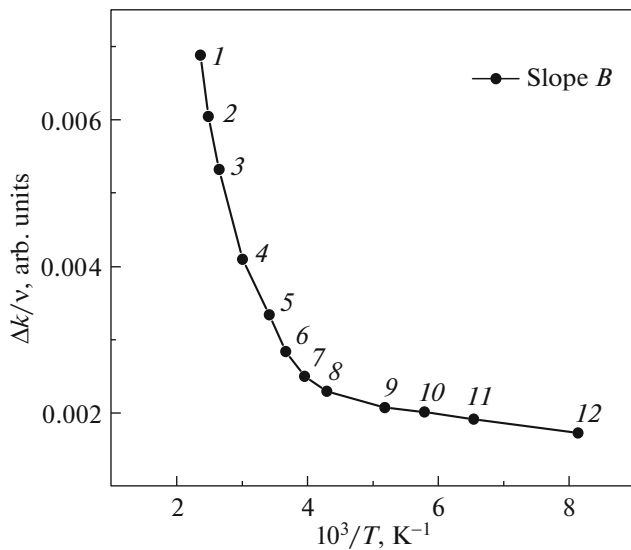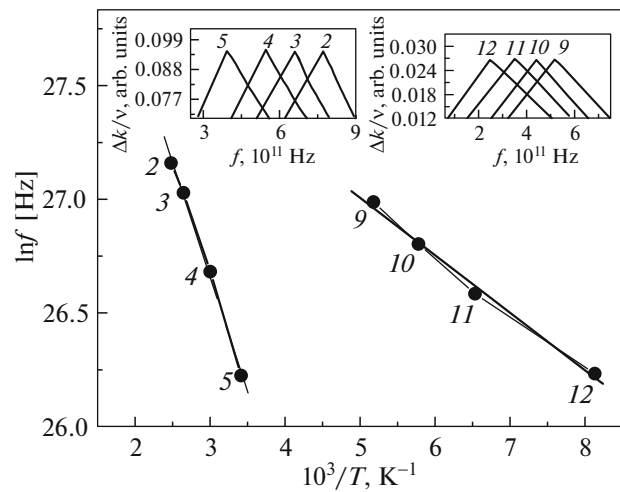
Fig. 3. Temperature dependence of the intensity of FIR spectra PMMA in the region of 8–20 cm^{-1}; notations are the same as in Fig. 1.

Fig. 4. Dependences of the frequency position of the (2–5) high-temperature and (9–12) low-temperature relaxation loss on temperature. Insets: schematic displacement of the peak of these losses with temperature; notations are the same as in Fig. 1.

a sharp increase in the intensity of the difference spectrum is due precisely to this process.

To confirm this assumption, we estimate the height of the potential barrier of the high-temperature relaxation process, using the available experimental data on its temperature shift. For example, as it is performed in dynamic mechanical analysis, differential scanning calorimetry, or dielectric measurements, when the activation energy of the relaxation process is determined from the linear dependence of the frequency shift of the relaxation peak f with temperature $\ln f(1/T)$ and equation $E = -Rd(\ln f)/d(1/T)$, where R is the universal gas constant, and $f = c\nu$ (c is the speed of light in vacuum).

As at high frequencies, the relaxation peak shifts in parallel to itself with temperature, preserving the amplitude and half-width [14], such a dependence can be plotted not only by the position of the maximum. In our case, the peak of the relaxation loss does not fall into the wavelength range under consideration; therefore, the displacement of its frequency was determined from the shift of the low-frequency wing of the difference spectrum with the temperature variation. In Fig. 2, the change in the position of the low-frequency wing at $k/\nu = 0.09$ for high-temperature and at $k/\nu = 0.02$ for low-temperature relaxation processes is shown by horizontal dashed lines.

The dependences $\ln f(1/T)$ obtained in this way are presented in Fig. 4; insets illustrate the displacement of the "peaks" of the selected relaxation processes. The activation energies of the low-temperature and high-temperature processes were determined from the slope of these dependences (B) and equation $E =$ $-8.3B$ (J/mol), which were ~2 and 8 kJ/mol, respectively.

The activation energy of the former is close to the activation energy of fast relaxation in polyvinyl acetate (1.9 kJ/mol), attributed to 180°-rotations of the OCO group [15]. The barrier of the latter fast process corresponds to the difference between the energies of the rotational isomers in PMMA, and the fact that it begins to appear at the temperature of appearance of conformational mobility in PMMA makes it a high-frequency analog of β-relaxation in this polymer.

4. CONCLUSIONS

Thus, the study of the FIR absorption spectra of polymethylmethacrylate in the range of $\nu = 10$–130 cm^{-1} at temperatures from 90 to 420 K showed that they not only contain information about the local vibrational mobility of the monomer units of this glassy polymer but also evidence that the relaxation dynamics is realized in PMMA starting from the β-transition temperature of $T \approx 260$ K. According to the linear dependence of the frequency position of the relaxation loss on temperature, the activation energies of two fast relaxation processes in this glassy polymer are found: 180°-rotations of the OCO plane of the side groups and conformational reorientation of the monomer units.

REFERENCES

1. W. Coffey, M. Evans, and P. Grigolini, *Molecular Diffusion and Spectra* (Wiley Interscience, New York, 1984; Nauka, Moscow, 1987).

2. V. K. Malinovskii, V. N. Novikov, and A. P. Sokolov, Fiz. Khim. Stekla **22**, 204 (1996).

3. G. P. Johari, J. Non-Cryst. Solids **307−310**, 114 (2002).

4. V. A. Bershtein and V. A. Ryzhov, Adv. Polym. Sci. **114**, 43 (1994).

5. V. A. Ryzhov, Phys. Solid State **44**, 2336 (2002).

6. W. Götze and L. Sjogren, Rep. Prog. Phys. **55**, 241 (1992).

7. T. Kanaya and K. Kaji, Adv. Polym. Sci. **154**, 87 (2001).

8. Yu. Ya. Gotlib, A. A. Darinskii, and Yu. E. Svetlov, *Physical Kinetics of Macromolecules* (Khimiya, Leningrad, 1986) [in Russian].

9. N. V. Surovtsev, J. A. Wiedersich, V. N. Novikov, E. Rossler, and A. P. Sokolov, Phys. Rev. B **58**, 14888 (1998).

10. K. S. Gilroy and W. A. Phillips, Philos. Mag. **43**, 735 (1981).

11. V. A. Ryzhov and M. V. Tonkov, in *Molecular Spectroscopy*, Ed. by M. O. Bulanin, Collection of Articles (Leningr. Gos. Univ., Leningrad, 1973), p. 103 [in Russian].

12. N. V. Surovtsev, T. Achibat, E. Duval, A. Mermet, and V. N. Novikov, J. Phys.: Condens. Matter **7**, 8077 (1997).

13. V. A. Bershtein and V. M. Egorov, *Differential Scanning Calorimetry of Polymers: Physics, Chemistry, Analysis, Technology,* Ellis Horwood Series in Polymer Science and Technology (Khimiya, Leningrad, 1990; Ellis Horwood, New York, 1994).

14. H. Z. Cummins, G. Li, Y. H. Hwang, G. Q. Shen, W. M. Du, J. Hernandez, and N. J. Tao, Z. Phys. B **103**, 501 (1997).

15. C. Zhang, V. Arrighi, S. Gagliardi, I. J. McEwen, J. Tanchawanich, M. T. F. Telling, and J.-M. Zanotti, Chem. Phys. **328**, 53 (2006).

Translated by O. Zhukova