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Universal features of the manifestation of the relationship between local and segmental dynamics of polymers at terahertz frequencies in IR spectra

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Low-frequency IR- spectra of glassy polymers were obtained and analyzed at temperatures from 90 to 400 K. Temperature changes in the IR- spectra in the range from 10 to 140 cm^{-1} show three universal features: low-temperature, corresponding to the torsional-vibrational motion of monomer units, high-temperature, due to the influence of primary relaxation (glass transition) and intermediate, caused by the activation of conformational mobility in chains at a temperature of β -transition. This versatility extends both to polymers with universal chain-to-chain interactions and to those with hydrogen bonds.

Keywords: IR spectra, excess density of vibrational states, bosonic peak, molecular dynamics, α - and β -relaxations.

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Introduction

A large number of theoretical and experimental studies have been devoted to the investigation of the molecular mechanisms of segmental dynamics, which led to an understanding of the nature of the main and secondary relaxation processes in polymers [1,2]. At the same time, issues concerning more local, small-scale (within the limits of a side group or chain link) mobility need further clarification, especially since macro- and microdynamics in polymers are closely interrelated [3,4]. It should be noted, that the main method of studying the local dynamics of polymer molecules — molecular dynamic modeling (MD), although very informative, still does not determine all the details of dynamics. Relatively recently, inelastic neutron scattering spectroscopy [5], Raman spectroscopy, has been involved in the study of processes faster than segmental rearrangements in macromolecules [6] and terahertz spectroscopy in the time domain (the so-called THz-TDS spectroscopy [7]), which showed the possibility of a uniform description of both individual and collective mobility of molecules [8]. It was important to establish the fact that in the spectra of amorphous polymers in the range 0.03–3 THz (~ 1 –100 cm^{-1}) appears as a torsional oscillation of individual links („microscopic peak“ — libration band), and their collective motion (peak „excess VDOS“ — bosonic peak), as well as the relaxation component („ β -fast“ losses) at quasi-elastic scattering frequencies [9]. It was found, in particular, that the temperature evolution of IR absorption spectra at terahertz frequencies is due not so much to a change in the anharmonicity of torsional-oscillatory motion with temperature, as to the restructuring of the intermolec-

ular bonds (IBs) system in the polymer during relaxation transitions. Such sensitivity to intermolecular interactions, energetically close to terahertz photons, gives reason to speak about the universality of the manifestation of the interdependence of vibrational and relaxation processes in polymers at terahertz frequencies [10].

This paper consisted in experimental verification of this assumption on polymers with different IBs types between chains. We investigated the origin and temperature evolution of relaxation losses and IR absorption in polymers polystyrene (PS) and polymethylmethacrylate (PMMA) with van-der-Waals (v-d-w) and dipole-dipole interactions between their chains, as well as in polymers with hydrogen bonds (HB): polyamide (PA-6) and polyvinyl chloride (PVC).

Procedure

The experiments were carried out on plates of block atactic PS and PMMA with average molecular weights $M_n \sim 2 \cdot 10^5$ g/mol and $M_n \sim 3 \cdot 10^5$ g/mol (at polydispersity $M_w/M_n = 1.03$ and 1.08) thick ~ 300 and $100 \mu\text{m}$, respectively, obtained by pressing at 423 K, pressure 150 kgF/cm^2 and exposure in current 3–5 h at temperatures 10–15 K above the glass vitrification temperature. To obtain the spectra of PA-6 and PVC, samples were used in the form of films with a thickness of $100 \mu\text{m}$, which were cast from solutions in phenol and dichloroethane, respectively. The average numerical molecular weights of PA-6 and PVC samples were $M_n \sim 5 \cdot 10^5$ g/mol and $\sim 3 \cdot 10^5$ g/mol with polydispersity 2.08 ± 0.05 and 1.94 ± 0.05 , respectively.

Infrared spectra were recorded on two spectrometers: from 8 to 50 cm^{-1} (0.24–1.5 THz) on a spectrometer developed at LSU and upgraded at FTI using a -7 OAP receiver and a new filtration system, and from 50 to 135 cm^{-1} (1.5–4.5 THz) on the FIS-21 Hitachi spectrometer. Spectra were recorded with a resolution of 1–2 cm^{-1} , signal/noise ratio being approximately 100. The error in measuring the frequency was 2–3 cm^{-1} , the error in measuring the absorption coefficient $k(\nu) = (t)^{-1} \ln(I_0/I)$, where I_0 and I — the intensity of the incident and transmitted radiation through the sample with a thickness t , respectively, was 5–10%.

Spectra in the temperature range from 90 to 273 K were measured using a cuvette-cryostat with crystalline quartz windows. The temperature control in it was carried out by changing the flow rate of cold nitrogen in the heat exchanger assembled on the cuvette body. Infrared spectra in the temperature range from room temperature to ~ 400 K were obtained using a thermostatic cuvette with sapphire windows and an electric stove heater, switched on to maintain the desired temperature by an electronic potentiometer with a regulating device. Heat insulation in both cases was achieved by placing the cuvettes in vacuum. The temperature on the sample was measured with a copper-constantan thermocouple, its stability was not lower than ± 2 K. Up to 90 K samples were cooled in about 30 min and left to balance for 20 min before the start of measurements. For all subsequent measurements, the samples were heated at an interval of 25–30 K and left to balance for 15 min at each heating stage.

Up to 5 or more parallel measurements were carried out for each temperature in the range from 8 to 50 cm^{-1} .

Results and their discussion

Figures 1 and 2 show the IR absorption spectra of PS, PMMA, PVC and PA-6 at terahertz frequencies. They are presented in double logarithmic coordinates $k(\nu)/\nu$ so that they can be compared with the dielectric spectroscopy data presented in the coordinates of dielectric losses — $\varepsilon''(\nu)$. Since $\varepsilon''(\nu) = cn(\nu)k(\nu)/2\pi\nu$, where c — the speed of light, $n(\nu)$ — refractive index, at $n(\nu) \approx \text{const}$ in the studied frequency range $\varepsilon''(\nu) \propto k(\nu)/\nu$.

It is seen that the dielectric losses (absorption in terms of optical spectroscopy) of the studied polymers at frequencies of the terahertz IR range (0.24–4.5 THz) in the range of 90–210 K is practically independent of temperature. At low temperatures, they are represented by a high-frequency absorption band with a break (shoulder) on the low-frequency wing. This is the so-called microscopic peak (MP), which in the long-wavelength IR spectra of polymers is attributed to absorption by the Poley mechanism caused by rotational vibrations (libration) of the monomeric units of macromolecules [4]. The attribution of the fracture on the low-frequency wing of the MP follows from the spectra on the insets to Fig. 1 and 2, represented

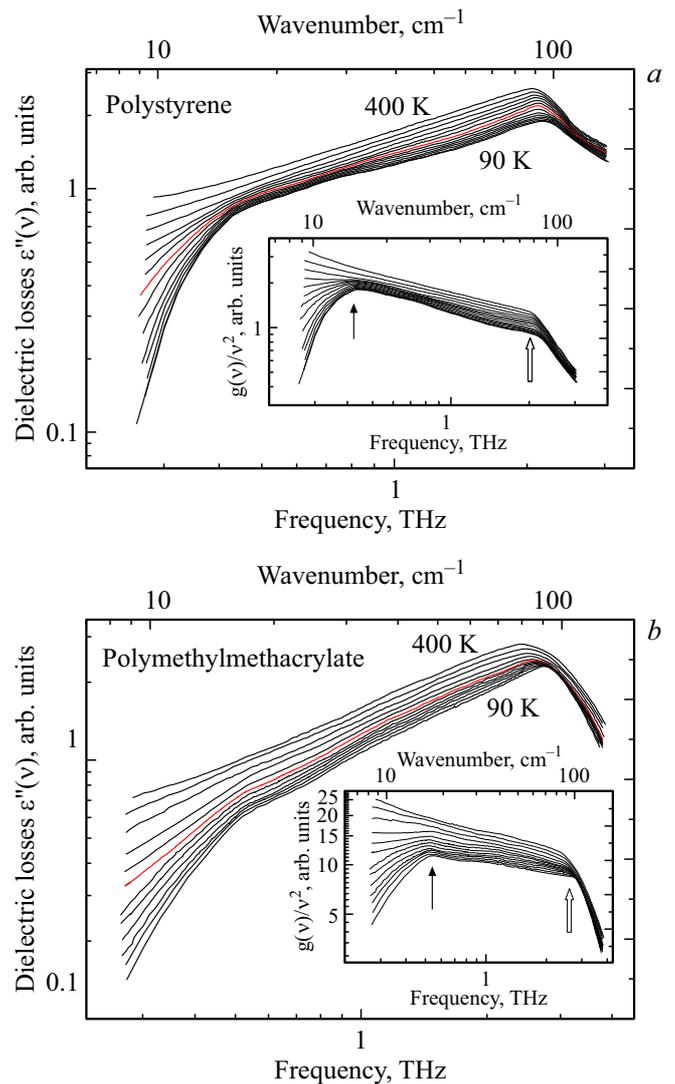


Figure 1. Dielectric loss spectra $\varepsilon''(\nu)$ PS (a) and PMMA (b) at terahertz frequencies 0.24–4.5 THz in the temperature range 90–400 K with an interval of 30 K. The color highlights the spectrum of $\varepsilon''(\nu)$ at a temperature of T_g . The insets to the figures show the spectra of the excess (in comparison with the Debye) density of vibrational states (excess VDOS) in the coordinates $g(\nu)/\nu^2$. The arrows \uparrow and $\hat{\uparrow}$ show the position of the maxima „excess VDOS“ and absorption by the Poley mechanism (microscopic peak), respectively.

in the coordinates $g(\nu)/\nu^2$, where $g(\nu) = k(\nu)$ — the density of vibrational states. The fracture frequency, the maximum of the excess (in comparison with the Debye) density of vibrational states (excess VDOS) is located on them. In low-frequency Raman-spectra of polymers represented in coordinates $I(\nu) = I_{ex}(\nu)/\nu[n(\nu) + 1]$, where $I_{ex}(\nu)$ — is the intensity of the scattered light, and $n(\nu) = [\exp(h\nu/kT) + 1]^{-1}$ — bose-factor, the peak at this frequency is called the Bosonic peak (BP) [11]. The appearance of additional quasi-local vibrational modes is associated with the existence of medium-order and

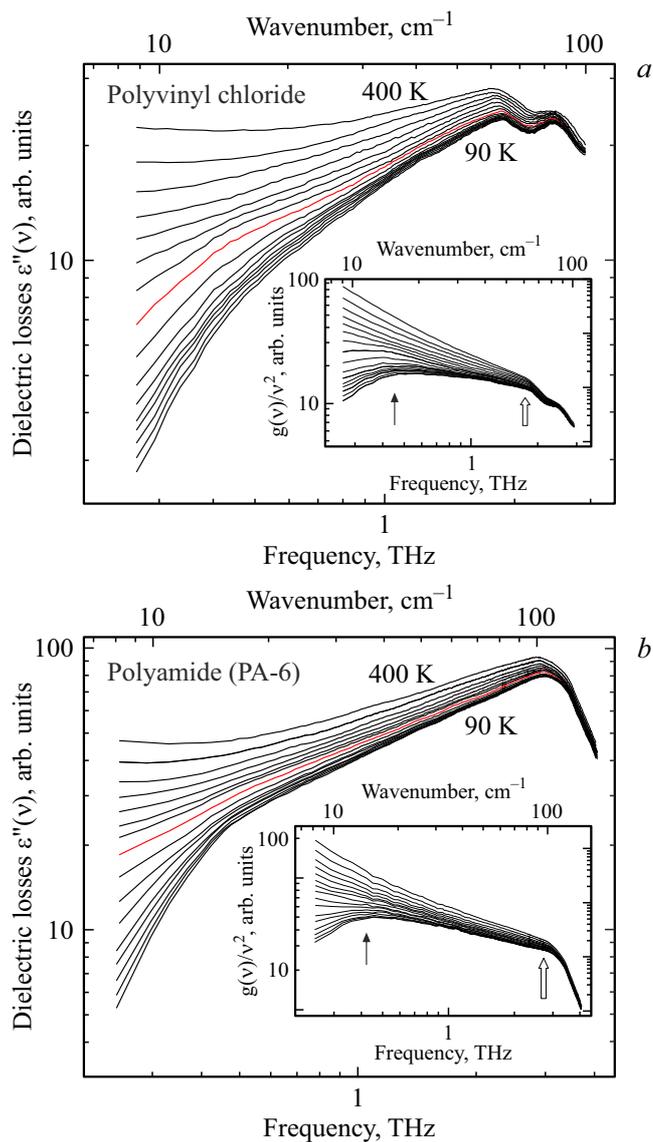


Figure 2. Dielectric loss spectra $\epsilon''(\nu)$ PVC (a) and PA-6 (b) at terahertz frequencies 0.24–4.5 THz in the temperature range 90–400 K with an interval of 25 K. The color highlights the spectrum of $\epsilon''(\nu)$ at a temperature of T_g . The insets to the figures show the spectra of the excess (in comparison with the Debye) density of vibrational states (excess VDOS) in the coordinates $g(\nu)/\nu^2$. The arrows \uparrow and \downarrow show the position of the maxima „excess VDOS“ and absorption by the Poley mechanism (microscopic peak), respectively.

cohesive inhomogeneity in disordered media on the scales of 1–4 nm [12]. In polymers, the linear size of the coherence region of these additional torsional-vibrational excitations is comparable to the size of a chain section of several monomeric links [4,13]. At low temperatures, the intensities of MP and „excess VDOS“ only slightly increase, and their maxima shift to lower frequencies due to an increase in the amplitude and anharmonicity of oscillations from - due to weakening of interchain interactions.

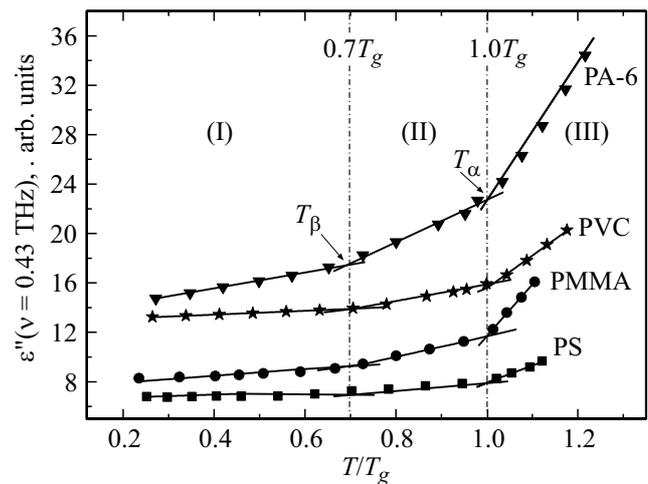


Figure 3. Graphs of the dependence of dielectric losses on temperature $\epsilon''(\nu)(T/T_g)$ in the studied polymers at a frequency $\nu = 0.43 \text{ THz}$. The solid lines show the linear approximation of dependence $\epsilon''(T/T_g)$ in modes (I), (II) and (III). T_β and T_α are the points of intersection of linear approximation (I) with (II) and (II) with (III), respectively.

The main changes in the spectra take place at temperatures above the glass vitrification temperature T_g , especially at the lowest frequencies. So, in the range from 90 K to T_g , losses at the frequency $\nu = 0.24 \text{ THz}$ increase by only 20–30%, and at 400 K they are almost an order of magnitude higher than at 90 K. It is natural to assume that at elevated temperatures these temperature-dependent losses are associated with the manifestation of primary dielectric relaxation, the maximum of which is outside the frequency range available for measurements at low temperatures and rapidly shifts at temperatures above T_g to terahertz frequencies. However, this explanation requires clarification, since, as can be seen from Fig. 3, the graphs of the dependence of the intensity of losses of $\epsilon''(\nu)(T/T_g)$ from temperature are not monotonic, but show at least two modes of growth of dielectric losses with temperature.

It is known that relaxation dynamics in flexible-chain polymers is realized and controlled by acts of intermolecularly co-operated (α - process near T_g) segmental motion, as well as local kinetically independent conformational mobility of individual sections of the chain in areas of less dense packing (the Johari–Goldstein process [14] near T_β). In the theoretical approach describing the relaxation behavior of polymers: the theory of coupled modes (mode-coupling theory (MCT) [15]), except for low-frequency α - and β - processes high-frequency β -relaxation (fast β -relaxation) is also predicted. It is believed that the rapid β -relaxation occurs due to the „rattling“ (rattling) movement of molecules in an environment formed from neighboring molecules.

The graphs in Fig. 3 show how the dielectric losses in the terahertz range change with temperature at a frequency taken arbitrarily close to the frequency of the maximum

excess density of vibrational states (VDOS or BP) at 0.47 THz (16.0 cm^{-1}) in the studied polymers. The graphs are plotted in the coordinates $\varepsilon''(T/T_g)$. The scaled temperature T/T_g on the abscissa axis was used to compare the general characteristics of the glassy state of these two polymers. It can be seen from the graphs that in all cases there are not two, but three modes of temperature dependence of dielectric losses: one, designated (I), — these are practically temperature independent losses at temperatures far from the glass vitrification temperature and the other, designated (III), — this is a sharp increase in losses when $T > T_g$. The graph clearly shows, especially for PVC and PA-6, another intermediate process (II) — the beginning of the growth of losses when approaching the glass vitrification temperature. Moreover, both in the case of PVC and in the case of PA-6, the crossover from mode (I) to mode (II) occurs at $T_1 = 0.7T_g$, and from mode (II) to mode (III) — at $T_2 = 1.0T_g$, as in the charts for PS and PMMA.

For PVC, the glass vitrification temperature (at α -transition) $T_g = 350 \text{ K}$, and for PA-6 $T_g = 330\text{--}350 \text{ K}$; i.e. for PVC $T_1 = 245 \text{ K}$ and $T_1 = 230\text{--}245 \text{ K}$ for PA-6. The temperatures of the β -transition representing the local conformational mobility in these polymers [16] have similar values. Losses due to reorientational mobility of a macromolecule, in addition to the purely vibrational contribution, start manifesting themselves in the dielectric loss spectrum and increasing from temperature T_β .

Unlike PVC and PA-6, temperature changes in dielectric losses in PS and PMMA at T_β (for PS $T_\beta = 315 \text{ K}$, for PMMA $T_\beta = 285 \text{ K}$ [16]) are not so noticeable. Obviously, the transition from limited torsional oscillations in chains to local conformational mobility is carried out here only due to a gradual increase in the amplitudes of torsional-vibrational motion and the accumulation of angular vibrational displacements in macromolecules with a weakening with temperature of universal (van-der-Waals) interactions between them.

A strong increase in dielectric losses (Fig. 3), starting from T_g , in the studied polymers can be associated, as already noted, with the contribution of the main relaxation process in polymers: α -glass vitrification, the peak of which at a temperature above T_g shifts to high frequencies and its high-frequency wing can fall into the terahertz region. However, α -relaxation is too slow a process to manifest itself at THz-frequencies at T_g , therefore it is more correct to assume that the sharp increase in losses is due to the influence of primary relaxation on the local terahertz dynamics of polymer chains controlled by a change in the IBs system at vitrification.

The influence of α -relaxation on local dynamics also explains the growth of losses in PVC and PA-6, starting from T_β ; in the case of van-der-Waals interactions between the circuits in PS and PMMA this effect is less noticeable. Interestingly, PS and PMMA refer to polymers in the dielectric loss spectra of which α - and β -processes are not

separated from each other and are represented by one wide band [17].

The graph in Fig. 3 also shows that some minor temperature changes in the spectra exist at temperatures below T_β (in the mode (I)). Theoretically, they can be associated with the contribution of other secondary relaxations, such as fast (fast- β) relaxation, which is attributed to translational vibrations (rattling) of a molecule in a cell formed by its immediate environment [15]. And also with a low-frequency offset and broadening with a temperature of -due to the anharmonicity of the highest frequency band in the presented spectra — absorption by the Poley mechanism.

So, the same scenario of the temperature evolution of dielectric losses at terahertz frequencies shows that intermolecular and interchain bonds play the same role in both primary and secondary relaxation. Such a scenario, seems to be supported by a universal change in the structure of intermolecular bonds in polymers and with the van-der-Waals and with the hydrogen-binding nature of the interaction. And the fact that the type of temperature dependence of dielectric losses undergoes fractures at temperatures of T_β and T_g relaxation transitions indicates the relationship of local dynamics with relaxation at terahertz frequencies.

With a more detailed consideration of the universality of the temperature behavior of IR absorption at terahertz frequencies discussed above, it should be clarified that the temperature gradients of loss growth — coefficients B of the linear approximation of the dependence $\varepsilon''(T/T_g) = A + BT/T_g$ (table) — the spectra of the studied polymers differ markedly. Despite the fact that in the first -, they grow equally in the row of PS, PMMA, PVC and PA-6, and in the second-, the gradient B_g is always greater than the gradient B_β , from Fig. 3 and the table it can be seen that for polymers with van-der-Waals bonds, the transition from (II) mode to (III) mode occurs more sharply than for polymers with hydrogen bonds.

The increase in losses (absorption) with temperature is explained by the fact that with an increase in the amount of thermal energy and molecular mobility in the system, the intensity of changes in dipole moments increases, to which these losses are proportional. Intuitively, it is clear that these changes are stronger at the defrosting temperature of segmental mobility (T_g) than in the interval of local mobility, starting from T_β in the (II) mode. And then it is natural to assume that in the case of weak van-der-Waals intermolecular interactions, the change in molecular mobility with temperature will be more significant than in the case of polymers with stronger hydrogen bonds.

Another refinement of the universality of the temperature behavior of terahertz spectra concerns polymers with VS. The temperature loss gradients of the PA-6 and PVC spectra are still different: the dielectric losses in the PA-6 spectrum grow with temperature faster than in the PVC spectrum. The discovered effect is explained by the fact that PVC macromolecules have increased rigidity compared to PA-6: the Kuhn segment for PVC includes 12 links, and for

Glass vitrification temperatures and β -transitions together with linear dielectric loss analysis $\varepsilon''(T/T_g) = A + BT/T_g$ (as shown in Fig. 3)

Polymer	T_g, K	T_β, K	T_β/T_g	B_I	B_{II}	B_{III}	ν_{BP}, cm^{-1}	μ_{ef}, D	Type MMB
PS	373	300	0.80	1.7	1.9	14	15(15.5)	0.42	v-d-w
PMMA	380	290	0.76	4.7	5.3	42	18(18.5)	1.33	v-d-w
PVC	350	250	0.72	4.0	10	52	14(13.0)	1.73	HB
PA-6	330	220	0.68	6.0	24	82	18(20.0)	3.20	HB

Note. * T_g and T_β — glass vitrification temperatures and β -transitions, respectively, taken from the literature [16]; B_I , B_{II} and B_{III} — linear coefficients obtained from the analysis of dielectric losses in (I), (II) and (III) modes, respectively; ν_{BP} — spectral position BP. The numbers in parentheses are taken from the papers [18–20]; μ_{ef} — dipole moment [21].

PA-6 — only 2–3 links [16]. As a result, the increased flexibility of the macromolecules PA-6 allows the BC grid in this polymer to react more dynamically to temperature changes than in the case of PVC. The Kuhn segments of PS and PMMA are almost the same [16,22], and the fact that the increase in temperature losses in PMMA is more significant than in PS can only be due to the fact that $\mu_{ef} PMMA > \mu_{ef} PS$ (table).

The data presented in Fig. 3 and in the table indicate the increased sensitivity of the analysis method described above to the details of the temperature-dependent behavior of the spectra, as well as the prospects of using the terahertz range to study the molecular dynamics of macromolecules.

Conclusion

In general, the analysis of dielectric losses at terahertz frequencies for polymers with a different type of molecular bond between the chains (van-der-Waals in the case of PS and PMMA and VS in the case of PVC and PA-6) at temperatures above and below T_g showed a number of universal features in terahertz IR spectra. At the lowest temperatures, these losses are represented only by the low-frequency wing of the absorption peak caused by the torsional-vibrational motion of monomeric polymer links (at 80 cm^{-1} and 95 cm^{-1} in the PS and PMMA spectra and at 64 cm^{-1} and 105 cm^{-1} in the spectra of PVC and PA-6, respectively). Up to temperatures close to the β -transition temperature equal to $0.7T_g$, they practically do not depend on temperature and, thus, the increase in dielectric losses (more noticeable in the case of PVC and PA-6), starting from $T_1 = 0.7T_g$, may be associated with the manifestation of secondary relaxation at terahertz frequencies. The next, sharper surge of losses occurs at $T = T_g$, when the high-frequency wing of the α -process shifts to the terahertz range. At temperatures above T_g , relaxation contributions become predominant in the terahertz spectra of all studied polymers. Since relaxation mobility in polymers is mainly controlled by potential barriers of intermolecular interactions, the manifestation of

local molecular motion at T_β indicates their weakening. A sharp increase in the relaxation contribution to the spectra with an increase in temperature to T_g — the manifestation of segmental mobility — is caused, apparently, not only by the weakening and rupture of the VS, but also by a change in the system of these bonds in the studied polymers. This conclusion confirms the fact that intermolecular interactions play an important role in primary and secondary relaxations, and also emphasizes the need to take into account the relaxation contribution to the terahertz range of IR spectra.

The deviations revealed during the discussion of the universality of the temperature behavior of terahertz spectra indicate an increased sensitivity of the analysis method described above to the details of the temperature-dependent behavior of the spectra and the prospects of using the terahertz range to study the molecular dynamics of macromolecules.

Conflict of interest

The authors declare that they have no conflicts of interest.

References

- [1] K.L. Ngai. *Relaxation and Diffusion in Complex Systems* (Oxford Press: NY, 2011).
- [2] Yu.Ya. Gotlib, A.A. Darinskii, Yu.E. Svetlov, *Fizicheskaya kinetika makromolekul* (Khimiya, L., 1986). (in Russian).
- [3] W. Coffey, M. Ivens, P. Grigolini. *Molekulyarnaya diffuziya i spektry* (Nauka, M., 1987). (in Russian).
- [4] V.A. Bershtein, V.A. Ryzhov. *Adv. Pol. Sci.*, **114**, 43 (1994). DOI: 10.1007/BFb0008694.
- [5] U. Buchenau, A. Wishniewski, M. Ohl, E. Fabiani. *J. Phys.: Condens. Matter.*, **19** (20), 205106 (2007). DOI: 10.1088/0953-8984/19/20/205106
- [6] L.V. Kulik, L.L. Rapatsky, A.V. Pivtsov, N.V. Surovtsev, S.V. Adichtchev, I.A. Grigor'ev, S.A. Dzuba. *J. Chem. Phys.*, **131**, 064505 (2009). DOI: 10.1063/1.3206909
- [7] M.T. Ruggiero. *J. Infrared, Millimeter, and Terahertz Waves*, **41**, 491 (2020). DOI: 10.1007/s10762-019-00648-3
- [8] S.N. Taraskin, S.I. Simdyankin, S.R. Elliott, J.R. Neilson, T.Lo. *Phys. Rev. Lett.*, **97**, 055504 (2006). DOI: 10.1103/PhysRevLett.97.055504
- [9] P. Lunkenheimer, A. Loidl. *Phys. Rev. Lett.*, **91**, 20 (2003). DOI: 10.1103/PhysRevLett.91.207601
- [10] P.J. Parrott, J.A. Zeitler. *Appl. Spectrosc.*, **69**, 1 (2015). DOI: 10.1366/14-07707
- [11] L. Hong, B. Begen, A. Kisliuk, C. Alba-Simionesco, V.N. Novikov, A.P. Sokolov. *Phys. Rev. B.*, **78**, 134201 (2008). DOI: 10.1103/PhysRevB.78.134201
- [12] V.K. Malinovskiy. *FTT*, **41** (5), 805 (1999). (in Russian).
- [13] V.A. Ryzhov. *Opt. i spektr.*, **127** (12), 895 (2019). (in Russian). DOI: 10.21883/OS.2019.12.48682.340-18
- [14] G.P. Johari, M.J. Goldstein. *Chem. Phys.*, **53** (6), 2372 (1979).
- [15] E. Kremer, A. Loidl. *The Scaling of Relaxation Processes* (Springer International Publishing AG: Leipzig, 2018).
- [16] V.A. Berstein, V.M. Egorov. *Differential scanning calorimetry in polymer physicochemistry* (Khimiya, L., 1990).
- [17] S. Bose, S. Schmid, T. Larsen, S. Keller, A. Boisen, K. Almdal. *J. Polym. Sci. B*, **53**, 1035 (2015). DOI: 10.1002/polb.23745

- [18] E. Duval, T. Achibat, A. Boukenter, B. Varrel, R. Calemczuk, B. Salce. *J. Non-Cryst. Solids*, **190**, 258 (1995).
DOI: 10.1016/0022-3093(95)00274-X
- [19] V.N. Novikov, A.P. Sokolov, B. Stube, N.V. Surovtsev, E. Duval, A. Mermet. *J. Chem. Phys.*, **107**, 1057 (1997).
DOI: 10.1063/1.474453
- [20] P. Papanek, J.E. Fischer, N.S. Murthy. *Macromolecules*, **35** (10), 4175 (2002). DOI: 10.1021/ma011218o
- [21] *Polymer Handbook*. Ed. by J. Brandrup, E.H. Immergut (Wiley-Interscience, NY, 1989).
- [22] R. Everaers, H.A. Karimi-Varzaneh, N. Hojdis, F. Fleck, C. Svaneborg. *Macromolecules*, **53** (6), 1901 (2020).
DOI: 10.48550/arXiv.1808.03509