

Temperature Evolution of the Interaction of Relaxation Processes with Local Dynamics at Terahertz Frequencies in Polymers with Hydrogen Bonds

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Abstract—At terahertz frequencies, the torsional vibration motion is associated with dielectric relaxation in disordered solids with hydrogen bonds. The interaction between these processes is still poorly understood, especially at temperatures below the glass transition temperature especially important for the molecular mobility in polymers. We studied polymers with hydrogen bonds (polyamide-6 and polyvinyl chloride) at temperatures from 90 to 400 K using far IR spectroscopy in the range of 0.25–4 THz. The following three common features were observed in the spectrum of dielectric losses $\epsilon''(\nu)$: (i) at temperatures well below the glass transition temperature (T_g), these losses are represented by the low-frequency wing of the absorption peak due to libration of monomer units of the polymers; (ii) in the range of $0.7T_g < T < T_g$, additional temperature dependent losses are observed, which may be associated with the manifestation of secondary relaxation processes; (iii) at temperatures above T_g , the primary α relaxation processes predominantly contribute to terahertz losses. The obtained results show that the evolution of terahertz losses with temperature is caused by a change in the structure of hydrogen bonds, which seems to be common for systems with similar intermolecular interactions.

Keywords: polymers, terahertz IR spectra, temperature dependence, α and β relaxation processes, hydrogen bond

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1. INTRODUCTION

Glass materials with intermolecular hydrogen bonds, including polymers, show intriguing physical properties that have long been the subject of rigorous studies, both experimental and theoretical ones [1, 2]. Dielectric, Raman, and terahertz IR spectra show striking similarities in the manifestation of molecular dynamics for a wide range of this kind of disordered systems [3]. At low frequencies, dielectric spectroscopy records the manifestation of primary α and secondary β relaxation processes, as well as the existence of faster relaxations at the boundary between the radio and terahertz frequency ranges [4]. In the terahertz frequency range, Raman and neutron scattering spectroscopy show that all glasses and polymers exhibit excessive vibrations, the so-called “boson peak” (BP) [5]. These additional (compared to Debye’s model) oscillation modes of the type of correlated torsional vibrations in a chain of several tetrahedra in amorphous quartz are associated with the presence of an intermediate order in disordered media [6]. At higher frequencies, the interaction of radiation of the far infrared (FIR) range with a glass solid is described in terms of the density of vibration states (DVS), which

forms a band of libration oscillations of its dipole groups [7].

Though the interaction between reorientation motion and various relaxation processes has been studied quite in detail [8], little is known about the relationship of this large-scale mobility with local torsional vibration (libration) dynamics.

Using IR spectroscopy in the terahertz range, the origin of experimentally observed dielectric losses in polyamide-6 and polyvinyl chloride polymers in the frequency range from 0.25 to 4 THz at temperatures from 90 to 400 K, including the glass transition temperature (T_g) region, is investigated in this study. Only limited data on dielectric losses at frequencies close to the terahertz range are available in the literature, which were obtained for polymers and glasses by other methods [9].

2. EXPERIMENTAL

The experiments were performed on the films obtained from block atactic polyvinyl chloride (PVC) and polyamide-6 (PA-6) polymers with a thickness of

about 100 μm by pressing at 150°C and exposing them to 110°C for 3–5 h with average molecular weights M_n of around 500000 and 300000 g/mol, respectively. The FIR spectra were recorded on the two spectrometers: the LSU spectrometer operating in the range of 8–50 cm^{-1} [10], which was upgraded by means of an OAP-7 detector and a new filtration system; an FIS-21 Hitachi spectrometer operating in the range of 50–150 cm^{-1} . The spectra were recorded with a resolution of 1–2 cm^{-1} with a signal-to-noise ratio of about 100. The error in the measurement of frequency was 2–3 cm^{-1} . The error in the measurement of absorption coefficient $k(\nu) = \tau^{-1} \ln(I_0/I)$ (where I_0 and I are the intensities of the incident beam and the radiation passed through a sample with thickness t , respectively) was 5–10%. To measure spectra in the temperature range from 90 to 400 K, a cryostat cell with crystalline quartz windows was used. The FIR spectra in the range from room temperature to 400 K were recorded using a thermostated cell with sapphire windows. Thermal insulation in both cases was achieved by placing the cells in a vacuum. The temperature of the sample was measured with a copper–constantan thermocouple; its stability was not lower than $\pm 2^\circ\text{C}$. In the range from 8 to 50 cm^{-1} , up to five parallel measurements were performed for each temperature.

In order to be able to compare terahertz IR spectra with dielectric loss spectra $\epsilon''(\nu)$, absorption coefficient $k(\nu)$, and refractive index $n(\nu)$ should be converted into the real and imaginary parts of the dielectric function according to the method proposed in [11], as follows:

$$\hat{\epsilon}(\nu) = \epsilon'(\nu) + i\epsilon''(\nu) = \hat{n}(\nu)^2,$$

$$\hat{n}(\nu) = n(\nu) + i\kappa(\nu),$$

$$\kappa(\nu) = (k(\nu)/\nu)(c/4\pi),$$

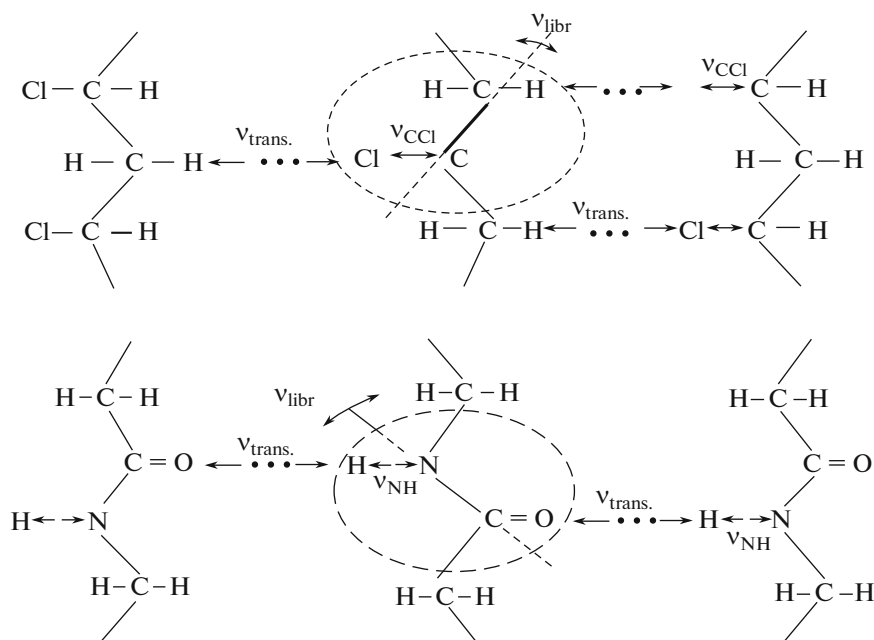
$$\epsilon'(\nu) = n(\nu)^2 - \kappa(\nu)^2,$$

$$\epsilon''(\nu) = 2n(\nu)\kappa(\nu) = (k(\nu)/\nu)(n(\nu)c/2\pi),$$

where $\hat{\epsilon}(\nu)$ is the complex dielectric function; $\hat{n}(\nu)$ is the complex refractive index and $n(\nu)$ is its real part, the dispersion of which is calculated from the Kramers–Kronig ratio using data on the temperature dependence of absorption coefficient $k(\nu)$; $\kappa(\nu)$ is the extinction coefficient; c is the speed of light in vacuum; ϵ' is the dielectric constant; ϵ'' is dielectric losses. Given $n(\nu) \approx \text{const}$ in the studied frequency range [12, 13], $\epsilon''(\nu) \approx \text{const } k(\nu)/\nu$.

3. RESULTS AND DISCUSSION

The dielectric loss spectra of PVC and PA-6 in the terahertz IR range at temperatures from 90 to 400 K are given on a logarithmic scale in the $\epsilon''(\nu) = k(\nu)/\nu$ coordinates in Figs. 1 and 2, respectively. One can see that the dielectric losses barely depend on the temperature at low temperatures and represent a low-frequency wing of the doublet absorption band in the FIR spectrum of PVC with maxima at 64 and 90 cm^{-1} , which is ascribed to the translational motion at weak hydrogen bonds (HBs) of the $\text{CH}\dots\text{Cl}$ type in the CH_2CCl groups of conformationally different chains (see scheme below) [14]. The dielectric losses at low temperatures in the spectrum of PA-6 appear in the shape of a low-frequency wing of the absorption band at 105 cm^{-1} , which is ascribed to the translational motion on hydrogen bonds of the CONH group [15] (see scheme below).



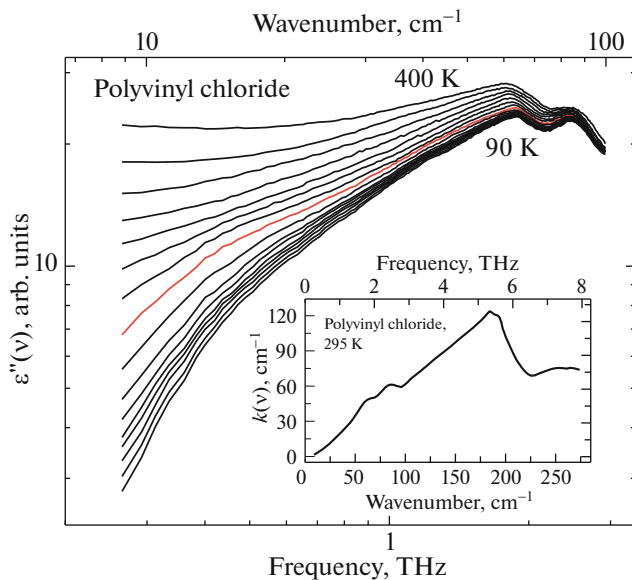


Fig. 1. Dielectric losses $\varepsilon''(\nu)$ of PVC at terahertz frequencies of 0.25–3 THz in the temperature range of 90–400 K with an interval of 25 K. The inset to the figure shows the FIR spectrum in the $k(\nu)$ coordinates for PVC at 295 K in the range of 8–275 cm^{-1} , which includes the studied range of terahertz frequencies.

With an increase in the temperature, these high-frequency peaks in the dielectric loss spectra of PVC and PA-6 increase in the intensity and shift to the low frequency region by 3–4 cm^{-1} due to the weakening of HBs and an increase in the anharmonicity of oscillations. However, the intensity of the low-frequency band wing increases to a substantially greater extent than that of the high-frequency band, especially at frequencies below the BP, which looks like an inflection on spectral curves at 0.43 and 0.54 THz in the coordinates shown in Figs. 1 and 2, respectively.

This observed increase in the dielectric losses with temperature can be associated with the manifestation of primary dielectric relaxation, the peak of which is outside the frequency range available for measurement at low temperatures and quickly shifts to terahertz frequencies at temperatures above T_g .

Obviously, the manifestation of relaxation contribution at terahertz frequencies is also determined by a change in the intermolecular interactions (in this case, HBs), since it is known that bound OH groups in systems with HBs become free at temperatures above T_g [16], thereby increasing molecular mobility.

The fact that spectral changes with temperature are more substantial at terahertz frequencies than at frequencies of manifestation of the torsional vibration motion allows us to use this range to obtain information about the relationship and mutual influence of local and large-scale (segmental) dynamics. Information on how the system moves from the vibrational

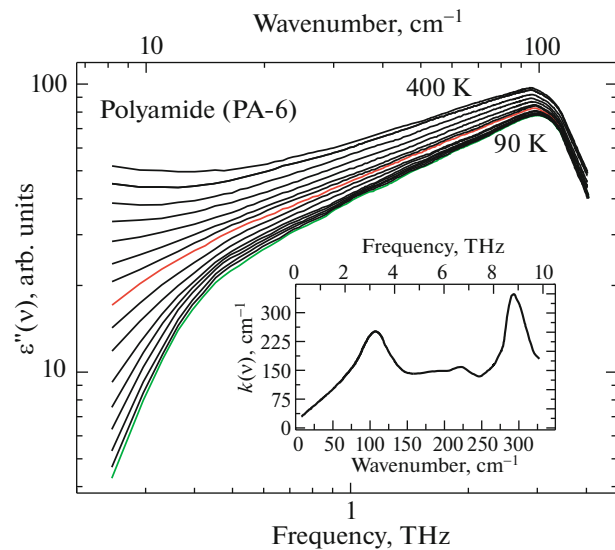


Fig. 2. Dielectric losses $\varepsilon''(\nu)$ of PA-6 at terahertz frequencies of 0.25–4 THz in the temperature range of 90–400 K with an interval of 25 K. The inset to the figure shows the FIR spectrum in the $k(\nu)$ coordinates for PA-6 at 295 K in the range of 8–325 cm^{-1} , which includes the studied range of terahertz frequencies.

mobility to relaxation mobility—which ultimately leads to structural changes—is also important.

The diagrams in Figs. 3a and 3b illustrate the temperature evolution of dielectric losses in the studied terahertz range at the frequency close to the frequency of the BP at 0.43 THz (14.3 cm^{-1}) for PVC and 0.54 THz (18 cm^{-1}) for PA-6. The diagrams are given in the $\varepsilon''(T/T_g)$ coordinates. The reduced T/T_g temperature in the abscissa was used to compare the common glass state characteristics of the two polymers.

As can be seen from the diagrams, there are basically three modes of temperature dependence of dielectric losses in both cases: (I) practically temperature-independent losses at temperatures far from the glass transition temperature, (II) a slight increase in the dielectric losses when approaching the glass transition temperature, and (III) a sharp increase in the losses at $T > T_g$. At the same time, the crossover transitions from mode (I) to mode (II) and from mode (II) to mode (III) in both PVC and PA-6 occur at temperatures $T_1 = 0.7T_g$ and $T_2 = 1.0T_g$, respectively.

The glass transition temperature (at the α type of transition) is $T_g = 350$ K for PVC and 330–350 K for PA-6; this means that $T_1 = 245$ K for PVC and $T_1 = 230$ –245 K for PA-6. Such temperatures are close to the temperature of the β type of transition, which corresponds to the local conformational mobility in these polymers [17]. It is temperature T_β that correspond to the temperature, from which the losses caused by the reorientation mobility of the macromolecule begin to

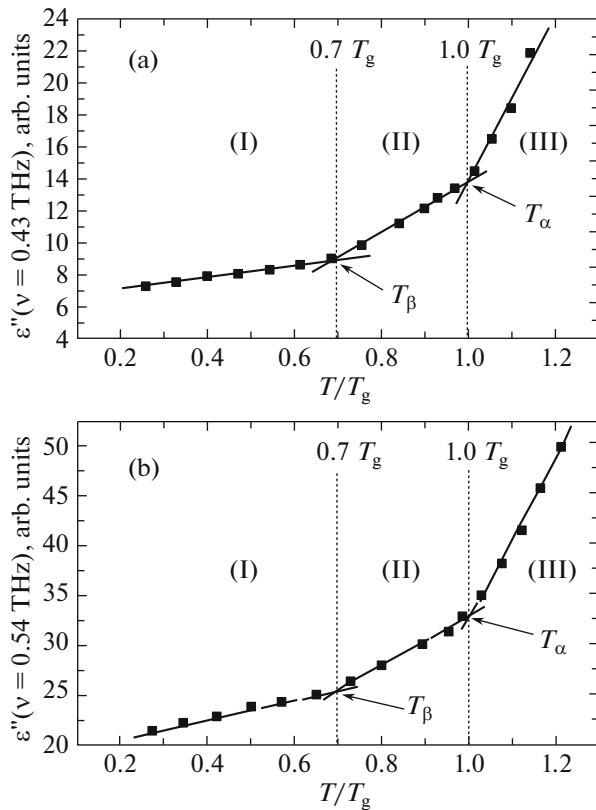


Fig. 3. Dielectric losses $\varepsilon''(T/T_g)$ at frequencies of (a) $\nu = 0.43$ THz for polyvinyl chloride PVC and (b) $\nu = 0.54$ THz for polyamide PA-6. The solid lines show a linear approximation of the $\varepsilon''(T/T_g)$ dependence in modes (I), (II), and (III). Points T_β and T_α are the points of intersection of linear approximations (I) with (II) and (II) with (III), respectively.

appear and grow in the spectrum of dielectric losses in addition to a purely vibrational contribution.

A sharp surge in the dielectric losses at T_g is caused by the contribution of the main relaxation process in polymers, i.e., the α glass transition, the peak of which at a temperature above T_g shifts to high frequencies and its high-frequency wing extends to the terahertz region. It is quite obvious that the manifestation of this contribution at terahertz frequencies is also associated with a change in the intermolecular interactions (in

this case, the HBs), since the bound OH groups in systems with HBs become free at temperatures above T_g , as already been noted above.

The increase in the relaxation contribution at $T_\beta < T_g$ is apparently caused only by weakening of HBs rather than their breaking, but this weakening is sufficient to manifest the reorientation mobility in the macromolecules of PVC and PA-6 due to an increase in the amplitudes of torsional vibration movements with temperature and the accumulation of angular vibrational displacements in the chain [18].

Figures 3a and 3b also show that some minor temperature changes in the spectra also exist at temperatures below $0.7T_g$. They can be caused by other secondary relaxations, such as the rapid β relaxation in polybutadiene [19], which is associated with translational vibrations (rattling) of a molecule in the cell formed by its immediate environment. In addition, a slight red shift and broadening of the lowest frequency vibration bands with temperature due to the anharmonicity—at 64 cm^{-1} in the spectrum of PVC and at 105 cm^{-1} in the spectrum of PA-6 (Figs. 1 and 2)—also contributes to mode (I).

In general, a single scenario of the temperature behavior of the terahertz spectra of polyvinyl chloride and polyamide-6 shows that the intermolecular and hydrogen-bonded origin of interactions in these polymers plays the equal role in both the primary and secondary relaxation processes. The universality of such a scenario should be further tested on other polymers in which van der Waals interactions are predominant.

As a clarification of its versatility, it should be noted that the temperature gradients of dielectric losses in the spectra of PVC and PA-6, i.e., coefficients B of the linear approximation of dependence $\varepsilon''(T/T_g) = A + BT/T_g$ (see Table 1), are nevertheless different: the dielectric losses in the spectrum of PA-6 increase with temperature faster than in the spectrum of PVC. The found effect seems to be associated with the fact that PVC macromolecules have increased rigidity compared to PA-6 molecules, which is determined not only by the bond polarity, but also by the correlation of the motion of neighboring dipoles. The energy of HBs is 8.4 kcal/mol in PA-6 [20] and 3.7 kcal/mol in PVC [21], and the Kuhn segment characterizing the equilibrium stiffness of polymer

Table 1. The temperatures of glass transition and β transition, and the linear analysis of dielectric losses $\varepsilon''(T/T_g) = A + BT/T_g$, as shown in Figs. 3a and 3b*

Polymer	T_g , K	T_β , K	T_β/T_g	B_I	B_{II}	B_{III}	ν_{BP} , cm^{-1}	Hydrogen bond
PVC	350	230–250	0.66–0.72	4	10	52	14 (13)	CH...ClC
PA-6	330–350	220	0.68–0.63	6	24	82	18 (20)	NH...OC

* T_g and T_β are the published temperatures of glass transition and β transition, respectively [17]; B_I , B_{II} and B_{III} are the linear coefficients obtained from the analysis of dielectric losses in modes (I), (II), and (III), respectively; ν_{BP} is the spectral position of the boson peak; the figures in parentheses are taken from [22] for PVC and [23] for PA-6.

chains includes 12 monomeric links in PVC and only 2–3 links in PA-6 [17]. It can be assumed that the increased flexibility of PA-6 macromolecules allows the HB network to respond more dynamically to temperature changes in this polymer compared to PVC.

This result is indicative of the high sensitivity of the terahertz spectra to temperature-dependent changes in the molecular dynamics of macromolecules.

4. CONCLUSIONS

In general, the performed analysis of dielectric losses at terahertz frequencies for two polymers differing in the type of HBs has shown a number of common features in their terahertz IR spectra at temperatures above and below T_g . At the lowest temperatures, the dielectric losses are represented only by the low-frequency wing of the absorption peak due to the torsional vibration movement of monomeric polymer units (at 64 cm^{-1} in the spectrum of PVC and at 105 cm^{-1} in the spectrum of PA-6). Up to temperatures close to the temperature of the β transition in PVC and PA-6, which equals $0.7T_g$, the dielectric losses barely depend on temperature and, thus, the increase in the dielectric losses in the temperature range starting from $T = 0.7T_g$ can be associated with the manifestation of secondary relaxation at terahertz frequencies. The next sharper jump in the dielectric 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 PVC and PA-6. Since the relaxation mobility in polymers is mainly controlled by potential barriers of intermolecular interactions (hydrogen bonds in these particular cases), the manifestation of the local molecular motion at T_g is indicative of the weakening of HBs. A sharp increase in the relaxation contribution to the spectra of dielectric losses with an increase in the temperature to T_g , i.e., the manifestation of segmental mobility, is apparently caused not only by the weakening and breaking of HBs, but also by a change in the network system of hydrogen bonds in the polymers under study. This conclusion is confirmed by the fact that intermolecular interactions play an important role in the primary and secondary relaxation processes and points to the necessity of taking into account the relaxation contribution to the terahertz range of the IR spectrum. Further studies of other objects with and without HBs in the terahertz range are necessary to confirm the universality of the relationship between relaxation processes and low-frequency torsional vibration modes.

CONFLICT OF INTEREST

The author declares that he has no conflicts of interest.

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