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Local and segmental dynamics in modified polystyrene containing chlorine and bromine atoms

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The specific heat capacity of polystyrene and its modifications obtained by substitution of hydrogen atoms in the benzene ring with methyl groups and chlorine and bromine atoms has been measured by differential scanning calorimetry (DSC). The studied temperature range was 300–520 K. The glass transition temperature is found to depend on the character of the substitutions. The frequency shift and change in amplitude of the librational band vibrations have been measured by long-wavelength infrared spectroscopy. A correlation between changes in the activation energy of segmental motion and potential librational barriers is established. The influence of substitutions on the cooperative nature of segmental motion in case of devitrification of the studied polymers is discussed. The excess conformational entropy in polymers below the glass transition temperature is estimated.

Keywords: molecular dynamics, heat capacity, IR spectra, polystyrene and its modifications.

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1. Introduction

The properties of polymeric materials are largely determined by molecular mobility — the torsional-oscillatory and larger-amplitude rotational motions of atomic groups of various sizes, detected and studied by various methods. Of particular importance are the motions of chain segments accompanied by rotational-isomeric transitions, i. e., conformational mobility in block polymers. The conformational mobility occurs below the glass transition (devitrification) temperature in small regions of polymer molecules comparable in size to the size of a statistical segment (Kuhn segment) and containing a few monomeric links of the polymer chain. A cooperative conformational mobility associated with the correlated motion of these segments unfreezes above the glass transition temperature. The manifestation and combination of these forms of molecular motions in the context of the inherently wide variation of features of their molecular and supramolecular structure in different polymers determines the complexity of analyzing and describing the thermophysical characteristics of polymers, in particular, heat capacity.

The potential barriers or activation energies of conformational mobility are determined by the cohesive forces of intermolecular interaction (IMI) and the rotational-isomeric barriers that determine the flexibility of the polymer chain. In turn, cohesive forces are an obstacle to the manifestation of mobility in the finer scale parts of polymer macromolecules — individual monomer links, which is realized in the form of so-called torsional oscillations. 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, questions concerning more localized, small-scale (within the monomeric link) mobility and its relationship to segmental dynamics need further elucidation. The main objective of the present work was to elucidate the effect of the subtle variation of the benzene ring structure on the temperature dependence of the heat capacity of polystyrene.

2. Experiment

The segmental dynamics of the cooperative glass transition process and the mobility of a monomer link with modified side groups were studied in this paper by differential scanning calorimetry (DSC) and long-wavelength IR spectroscopy in the terahertz ($< 100\,\mathrm{cm}^{-1}$) range on a model series of polystyrene (PS)-based polymers. PS (sample № 1) was modified by substituting methyl groups (sample № 2) and / or chlorine atoms (sample № 3) and bromine atoms (sample № 4) for hydrogen atoms in the benzene rings of the side groups of the macromolecular polymer macromolecules [3].

3. Results

3.1. IR Spectra

Figure 1 shows the absorption spectra of the studied samples in the range of ($< 100\,\mathrm{cm}^{-1}$). The spectra show peaks with maximum values in the range $15-20\,\mathrm{cm}^{-1}$ and a descending broad shoulder toward decreasing frequency.

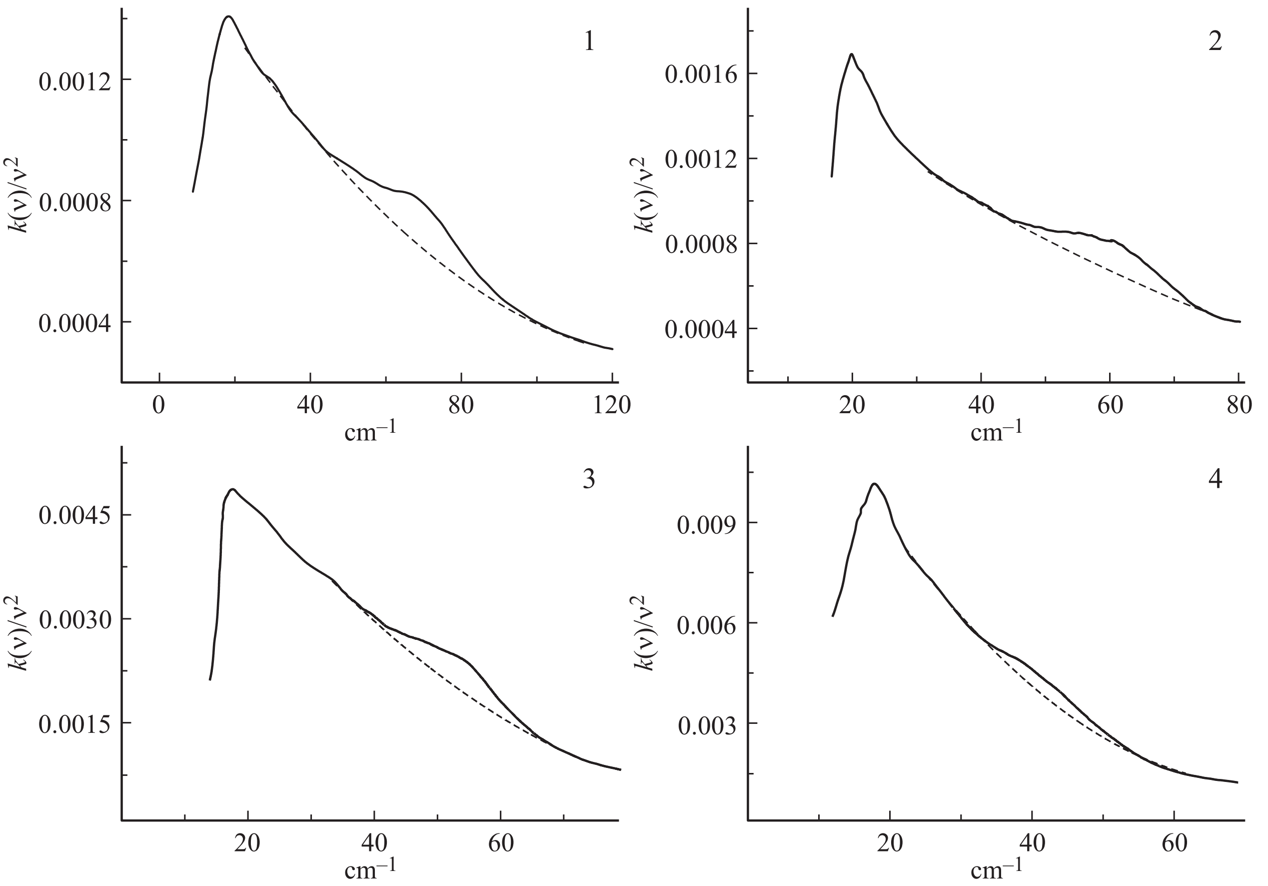

Figure 1. IR spectra of PS (*1*) and modifications of polystyrene: *2* — poly (2,5-dimethyl-styrene), *3* — poly (4-chloro-2,5-dimethyl-styrene), *4* — poly (4-bromo-2,5-dimethyl-styrene).

Anomalies in the range of 50–80 cm^{-1} are observed on the descending arm, associated with the manifestation of torsional vibrations of the aromatic ring in individual monomeric units (the so-called „microscopic peak“ — librational band, in which absorption occurs by the so-called „Poley mechanism“ [4], and is the main component of the IR spectra of polymers in the range below 150 cm^{-1}). This band was identified by the difference between the experimental dependence $k(\nu)/\nu^2 = F\,(\mathrm{cm}^{-1})$, shown in Figure 1, and „base“ line $F_0\,(\mathrm{cm}^{-1})$ shown as a dashed line in the same figure. „The baseline“ was plotted using the principle of best fit with the dependence $k(\nu)/\nu^2 = F\,(\mathrm{cm}^{-1})$ outside the anomaly on the descending arm. It was found that the best match was observed when the „base“ line was analytically represented by a polynomial $F_0\,(\mathrm{cm}^{-1}) = \mathrm{A} + \mathrm{B}\nu + \mathrm{C}\nu^2$, where A, B, and C are constants whose variation achieved the best match with the experimental dependence outside the anomaly. The „librational“ bands thus selected are shown in Figure 2.

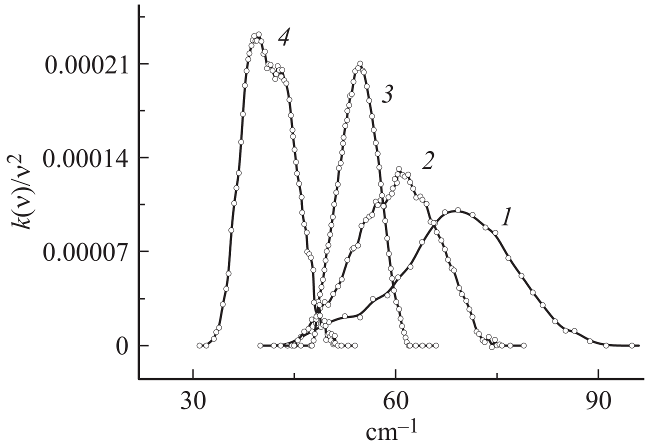

Figure 2. The identified „anomalies“ on the spectra shown in Figure 1. Notations — see Figure 1.

It can be seen from Figure 2 that the introduction of substituents into the benzene ring causes the bands to shift in only one direction — toward longer wavelengths (lower frequencies). A change of the amplitude is observed along with the shift of the bands, also in one direction of the increases compared to the PS.

3.2. DSC

The cooperative conformational mobility associated with the correlated motion of macromolecule segments was studied calorimetrically by analyzing the temperature dependence of the heat capacity $C_\mathrm{p}(T)$. Figure 3 shows these

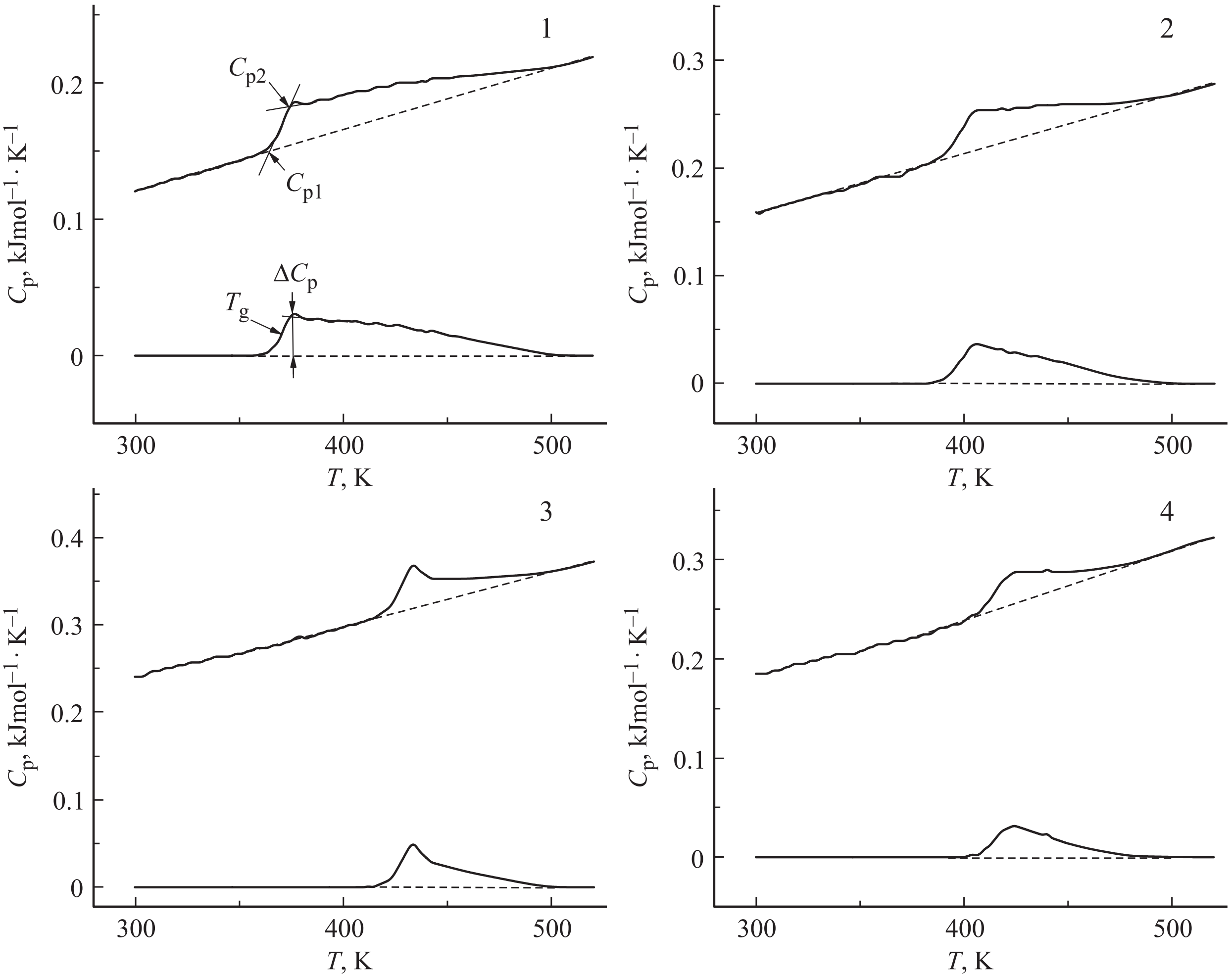

Figure 3. Temperature dependences of the heat capacity $C_p(T)$ and devitrification steps $\Delta C_p(T)$ of samples 1–4 (respectively, Figures 1–4).

dependencies obtained by the DSC method at a scan rate of $V = 10$ K/min for PS samples and modifications.

Results are presented in units of kJ/mol $\cdot$ K, where „mol" corresponds to the molecular weight (MW) of the polymer monomer link. It can be seen that the dependencies are homogeneous in character. C_p relatively gently, monotonously and almost linearly increases with the increase of temperature from 300 to $\sim$ 350–400 K. The cooperative segmental motion is not evident in this temperature range because in this temperature region segmental dynamics is associated with motion obeying the Arrhenius relation, i. e., motion of segments independent of each other [1,5]. A relatively sharp surge of heat capacity occurs in each sample at a different temperature T_g , which corresponds to the transition of the polymer to the devitrified state. In each figure, the heat capacity surges ΔC_p are shown at the bottom of the figure, which look like the steps that characterize the dependences $C_p(T)$ of the polymer transition to the highly elastic devitrified state. The designations C_{p1}, C_{p2} introduced in Figure 1.1, correspond to points on the dependence $C_p(T)$, from which the heat capacity values before $C_p(T < T_g)$ and after $C_p(T > T_g)$ surge ΔC_p were determined. The numerical values of the MW parameters listed above, C_{p1}, C_{p2}, T_g (the temperature corresponding to the middle of the surge), and ΔC_p are given in Table 1.

4. Discussion

The calculation of potential librational barriers based on the experimental data obtained was carried out using the Brot–Darmon model when considering the monomeric link of the polymer chain as a whole as a librator [6,7]. The results of the calculation of the librational barriers of side groups in the macromolecules of PS and its modifications Q_{libr} are given in Table 2, where they are compared with the cohesion energies of the side groups of the same polymers taken from Ref. [8].

Polymers have no relationship between the activation energy of segmental motion Q_β and the cohesion energy E_{coh} assigned to a mole of monomeric links. At the same time, if we conventionally consider a linear polymer to

Table 1. The relationship between the thermodynamic parameters of the step heat capacity and disordered configurational entropy in PS and its modifications. Parameter designations are given in Section 4 and in Figure 3.1; polymer numbers are given in Section 2.

Sample	MW	T_g	C_{p1}	C_{p2}	ΔC_p	δT	ω_s	ω_0	N	n_s	ΔS_0
		K	kJ/mol · K	kJ/mol · K	kJ/mol · K	K	nm^3	nm^3			kJ/mol · K
1	104	372	0.15	0.18	0.032	8.5	3.40	0.085	39	3.6	0.00031
2	132	398	0.21	0.25	0.047	9.5	2.26	0.115	20	2.5	0.00128
3	166	427	0.31	0.36	0.054	11.0	1.44	0.135	11	1.4	0.00258
4	211	415	0.24	0.28	0.041	14.5	1.05	0.138	9	1.1	0.00312

consist of quasi-molecules — statistical segments as kinetic units, then according to [5], a dependence of the following form is true:

$$Q_\beta \approx (0.3 \pm 0.05)E_{\mathrm{coh}}\mathrm{S} + \mathrm{B}, \qquad (1)$$

where Q_β is expressed in kcal/mol$_c$ per 1 mol of kinetic units (segments). A statistical segment consists of 8 monomeric links in polystyrene, i.e. $\mathrm{S} = 8$. The relatively small summand $\mathrm{B} \approx 3$ kcal/mol$_c$, corresponds to the internal rotation barrier for turns around bonds C–C in the flexible chain of vinyl polymers, so called gauche-trans (G–T) transition in act of β-relaxation.

Table 2 summarizes the calculation of the height of barrier Q_β for local segmental motion by the relation (1) as well as the values Q_β/S, showing the fraction of the activation barrier of segmental motion attributable to one monomeric link, i.e., the value Q_β per mole of monomeric links. The latter can be compared to the magnitude of the side-group libration barrier, since Q_{libr} is one of the summands forming the segmental motion barrier. Internal rotation barriers, intermolecular interactions between the C–H groups of the polymer main chain are involved in the formation of the segmental motion barrier in addition to the librational barrier. However, comparison of the values of Q_β/S and Q_{libr} shows that the latter account for the major share in the formation of the segmental motion barrier.

The calorimetric data, as inferred from Figure 3, show that substitutions in the benzene ring cause a shift in the devitrification temperature toward higher values compared with the initial PS. This can be explained by the fact that the activation barriers of the elementary acts of segmental motion occurring during devitrification, due to intermolecular or cohesive interactions, increase in the samples of modified PC (see Table 2).

Table 2. The relationship between potential libration barriers and parameters of local segmental mobility in PS and its modifications. The polymer numbers are given in Section 2

Sample	Q_{libr}	E_{coh}	Q_β	Q_β/S
	kcal/mol	kcal/mol	kcal/mol$_c$	kcal/mol
1	2.18	8.64	23.7	2.9
2	2.44	10.60	28.4	3.5
3	3.18	13.10	34.4	4.3
4	2.64	14.40	37.5	4.7

The heat capacity surges ΔC_p represent a manifestation of the so-called conformational heat capacity associated with the unfreezing of cooperative segmental motion. Several segments of neighboring polymer chains are involved in each act of such motion. According to modern terminology, the number of such segments n_s is associated with the concept of „degree" of cooperativity.

The extent or „degree" of cooperative motion n_s near the glass transition temperature T_g can be estimated from the volume of the substance ω involved in the act of such motion. ω was calculated using the following relationship:

$$\omega = kT_g^2 \Delta C_p^{-1}/\rho(\delta T)^2,$$

where

$$\Delta C_p^{-1} = \Delta C_p/(C_{p2} \cdot C_{p1});$$

$C_p(T < T_g)$ and $C_p(T > T_g)$ — heat capacities before and after the surge ΔC_p at T_g, ρ is the density, and $\delta T = \Delta T_g/2$ is the half-width of the glass transition interval [9]. Then, since $\omega = n_s \cdot \omega_s$, it is possible to determine the desired value n_s.

The calculation results given in Table 1 show that the introduction of substituents into the benzene ring causes not only an increase in the glass transition temperature T_g, but also decreases the volume of the substance ω involved in the act of such motion. The degree of cooperativity decreases from $n_s = 3.6$ estimated for the PS to $n_s = 1.1$ calculated for the PS modification with Br. It should be noted that the value of $n_s = 3.6$ is close to the ratio of the activation volumes of cooperative and independent (Arrhenius) segmental motion, i.e., the ratio ω/ω_s, which is $\approx 4 \pm 1$ and obtained from the internal friction spectra of samples subjected to static shear stresses during the tests [5]. The decrease of the index of the degree of cooperativity n_s for the modifications down to a value close to unity for the PS modification with Br, i.e., to the index characterizing the Arrhenius segmental motion, indicates a stepwise degeneration of the cooperative segmental motion in the series of the studied modifications.

A similar effect is observed in case of polymer plasticization, when the introduction of a plasticizer significantly increases the excess configurational entropy (ΔS_0) in the

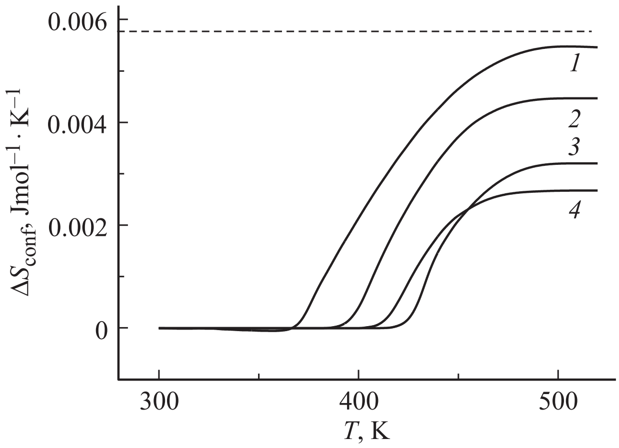

Figure 4. Determination of the conformational entropy $\Delta S_{\mathrm{conf}}(T)$ from the DSC data shown in Figure 3. See Figure 1 for notations.

solid state of the polymer, i. e., at temperatures below the glass transition temperature. In this case, the degree of cooperativity decreases and approaches a value corresponding to an independent (noncooperative) Arrhenius mechanism of segmental motion.

It is possible to estimate the excess configurational entropy in our case by the difference between the maximum configurational entropy $\Delta S_{\max}$ and the configurational entropy $\Delta S_{\mathrm{conf}}(T)$. The latter is a function of temperature and is calculated from the area of the glass transition step when heated above the glass transition temperature by the relationship $\Delta S_{\mathrm{conf}}(T) = \int \Delta C_{\mathrm{p}} d(\ln T)$. The maximum configuration entropy $\Delta S_{\max}$, which is reached at temperatures above the melting point for crystalline polymers or the transition temperature of an amorphous polymer into „true" liquid state, is equal to the so-called mixing entropy, the value of which is $S_{\max} = R \ln 2$ per mole of polymer chain segments.

The calorimetric data obtained in the present work allow the function $\Delta S_{\mathrm{conf}}(T)$ to be calculated from the curves shown in Figure 3 at the bottom of each figure. Figure 4 shows such calculations. In the same figure, the dashed line indicates the limiting value of the configurational entropy, i. e., $\Delta S_{\max}$. Thus the sought value ΔS_0 will be determined by the relation $S_0 = R \ln 2 - \int C_{\mathrm{p}} d(\ln T)$.

The numerical values ΔS_0 calculated from this relation and presented in Table 1 show that the stepwise degeneration of cooperative segmental motion in a number of studied modifications of polystyrene is due to the growth of excess configurational entropy (ΔS_0) in the solid state of the polymer, i. e., at temperatures below the glass transition temperature. It can be assumed that the detected effect is related to the fact that modification of the ring by substitutions leads not only to changes in the electronic structure of the benzene ring, affecting the change in the interaction of the segment with its surroundings, but also to the action of some steric factor. The latter may be attributable to an increase in the volume of the link (which is roughly proportional to the increase in the mass of the link), which itself leads to a hindrance of mobility due to steric hindrances, even without taking into account the change in atomic interactions.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] K.L. Ngai. Relaxation Diffusion in Complex Systems. Oxford University Press: New York (2011), p. 835.

[2] Yu.Ya. Gotlib, A.A. Darinsky, Yu.E. Svetlov. Fizicheskaya kinetika makromolekul. Izd. „Himiya", Leningrad, 1986, p. 272. (in Russian).

[3] A.F. Dokukina, M.M. Koton. Vysokomol. soyed., **1**, 1129 (1959).

[4] P. Lunkenheimer, A. Loidl. Phys. Rev. Lett. **91**, 20 (2003).

[5] V.A. Bershtein, V.M. Egorov. Differential Scanning Calorimetry of Polymers: Physics, Chemistry, Analysis, Technology. Ellis Horwood. N. Y. (1994), p. 253.

[6] W.T. Coffey, G.P. Johary, Ya.P. Kalmykov, S.V. Titov. J. Phys. Condens. Matter. **15**, 152961 (2003). DOI: 10.1088/0953-8984/15/19/301; C. Brot, I. Darmon. Molec. Phys. **21**, 785 (1971). DOI: 10.1080/00268977100101941

[7] V.A. Ryzhov. Optika spektrosk., **129**, 292 (2021). DOI: http://dx.doi.org/10.21883/OS.2021.03.50655.264-20

[8] D.W. Van Crevelen. Properties of Polymers: Their Correlation with Chemical Structure: Their Numerical Estimation and Prediction from Additive Group Combinations. 3rd ed. Amsterdam and London: Elsevier, 1990, p. 414; D.W. Van Crevelen. Properties and chemical structure of polymers. M: Khimiya, 1976, c. 414.

[9] E. Donth. J.Non-Crys.Solids, **53**, 325 (1982).

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