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Temperature evolution of the interaction of relaxation processes with local dynamics at terahertz frequencies in polimers with hydrogen bonds

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At terahertz frequencies, the torsional-vibrational 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, which is especially important for molecular mobility in polymers. We have studied polymers with hydrogen bonds (polyamide-6 and polyvinyl chloride) at temperatures from 90 to 400 K in the range 0.25−4 THz using far-infrared spectroscopy. Three general features were observed in the spectrum of dielectric losses, $\varepsilon''(\nu)$ (a) at temperatures well below the glass transition (T_g), these losses are represented by the low-frequency wing of the absorption peak due to the libration of polymer monomer units. (b) At $0.7T_g < T < T_g$, additional temperature-dependent losses are observed, which can be associated with the manifestation of secondary relaxation processes. (c) At temperatures above T_g, primary α-relaxation processes become the dominant contribution to terahertz losses. The results obtained show that the evolution of terahertz losses with temperature is caused by a change in the structure of hydrogen bonds, which, apparently, is universal for systems with similar intermolecular interactions.

Keywords: polymers, terahertz IR-spectra, temperature dependence, α- and β-relaxations, hydrogen bonding.

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1. Introduction

Glassy materials with intermolecular hydrogen bonds, including polymers, have intriguing physical properties which long since are a subject of active experimental and theoretical research [1,2]. Dielectric, Raman and terahertz IR-spectra demonstrate a striking similarity of molecular dynamics for a wide range of such disordered systems [3]. Dielectric spectroscopy at low frequencies records the occurrence of primary α- and secondary β-relaxation, as well as the existence of faster relaxations on the boundary between radio- and terahertz frequencies [4]. Raman spectroscopy and neutron scattering spectroscopy in the terahertz frequency range show that all glasses and polymers manifest excess oscillations here, the so-called boson peak (BP) [5]. The additional (as compared to the Debye model) vibrational modes, of the type of correlated torsional modes in a chain of several tetrahedrons in amorphous quartz, are associated with the presence of a medium-range order in unordered environments [6]. Interaction of radiation of the far IR-range with a glassy solid body at higher frequencies is described in terms of vibrational state density (VSD), which forms a band of librational vibrations of its dipole groups [7].

While interaction between reorientational motion and various relaxation processes has been studied in detail [8], little is known about the interrelation of this large-scale mobility with local torsional-vibrational (librational) dynamics.

The present paper studies, by means of IR-spectroscopy in the terahertz range, the origin of experimentally observed dielectric losses in polyamide-6 and polyvinylchloride polymers at frequencies from 0.25 to 3 THz in the temperature range of 90 to 400 K, which comprises the glass transition temperature T_g. The literature gives only limited data about dielectric losses at frequencies close to terahertz frequencies, obtained for polymers and glasses by other methods [9].

2. Procedure

Experiments were carried out on films of block atactic polyvinylchloride (PVC) and polyamide-6 (PA-6) with number-average molecular weights $M_n \sim 5 \cdot 10^5$ g/mol and $\sim 3 \cdot 10^5$ g/mol, respectively, $\sim 100\,\mu$m thick, made by pressing at 150°C and curing for 3−5 h at 110°C. Spectra in the far infrared range (FIR-spectra) were recorded by two spectrometers: in the range of 8−50 cm^{-1} — by the LGU spectrometer [10] upgraded by means of an OAP-7 receiver and a new filtration system; in the range of 50−150 cm^{-1} — by the FIS-21 Hitachi spectrometer. Spectra were recorded with a resolution of 1−2 cm^{-1}, signal/noise ratio being approximately 100. The frequency measurement error was 2−3 cm^{-1}. The measurement error for absorption coefficients $k(\nu) = (t)^{-1}\ln(I_0/I)$, where I_0 and I are intensities of incident radiation and radiation that passed through a sample with thickness t respectively, was 5–10%. Spectra in the temperature range of 90 to 400 K were measured using a cuvette-cryostat with crystalline quartz windows. FIR-spectra in the range from room temperature to 400 K were obtained using a temperature-controlled cuvette with sapphire windows. Heat insulation in both cases was achieved by placing the cuvettes in vacuum. Sample temperature was measured using a copper–constantan thermocouple, its stability was not lower than $\pm 2^\circ$C. Up to five parallel measurements were performed in the range of 8 to $50\,\mathrm{cm}^{-1}$ for each temperature.

In order to compare terahertz IR-spectra with spectra of dielectric losses $\varepsilon''(\nu)$, absorption coefficient $k(\nu)$ and refraction index $n(\nu)$ are converted using the method suggested in [11], into the real and imaginary parts of the dielectric function:

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

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

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

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

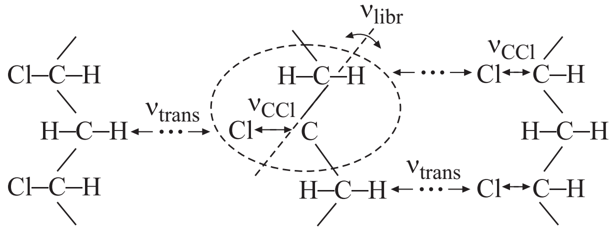
$$\varepsilon''(\nu) = 2n(\nu)\kappa(\nu) = \big(k(\nu)/\nu\big)\big(n(\nu)c/2\pi\big),$$

where $\hat{\varepsilon}(\nu)$ — complex dielectric function, $\hat{n}(\nu)$ — complex refraction index, $n(\nu)$ — its real part dispersion of which is calculated according to the Kramers–Kronig relation using the data about temperature dependence of absorption coefficient $k(\nu)$, $\kappa(\nu)$ — extinction coefficient, c — speed of light in vacuum, ε' — permittivity, ε'' — dielectric losses. Since $n(\nu)$ can be considered a constant quantity in the studied frequency range [12,13], $\varepsilon''(\nu) \approx \mathrm{const} \cdot k(\nu)/\nu$.

3. Results and discussion

Fig. 1, 2 show on a logarithmic scale the spectra of dielectric losses $\varepsilon''(\nu)$ for PVC and PA-6 in the terahertz IR range at temperatures of 90 to 400 K.

It is seen that dielectric losses at low temperatures are virtually independent from temperature and are a low-frequency wing of a doublet absorption band with the maxima at 64 and $90\,\mathrm{cm}^{-1}$ in the FIR-spectrum of PVC, which is related to translational motion on weak hydrogen bonds (HB), of type CH…CCl, groups of CH_2CCl in conformationally differing chains [14] (see the fragment of the structural formula).



Dielectric losses at low temperatures in the spectrum of PA-6 are a low-frequency wing of the absorption band at $105\,\mathrm{cm}^{-1}$, which is related to translational motion on

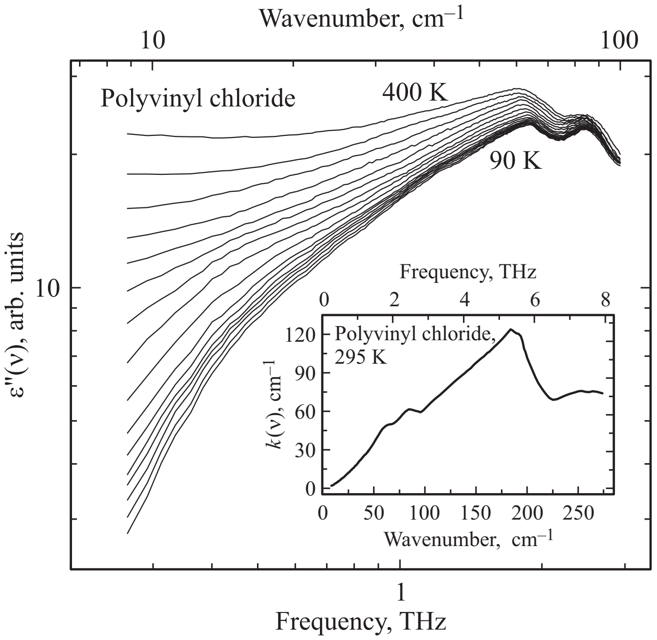


Figure 1. Dielectric losses $\varepsilon''(\nu)$ for PVC in the frequency range of 0.25–3 THz at temperatures varying within 90–400 K with an interval of 25 K. The insert shows the FIR-spectrum $k(\nu)$ of PVC at 295 K in the region of $8{-}275\,\mathrm{cm}^{-1}$, comprising the studied range of terahertz frequencies.

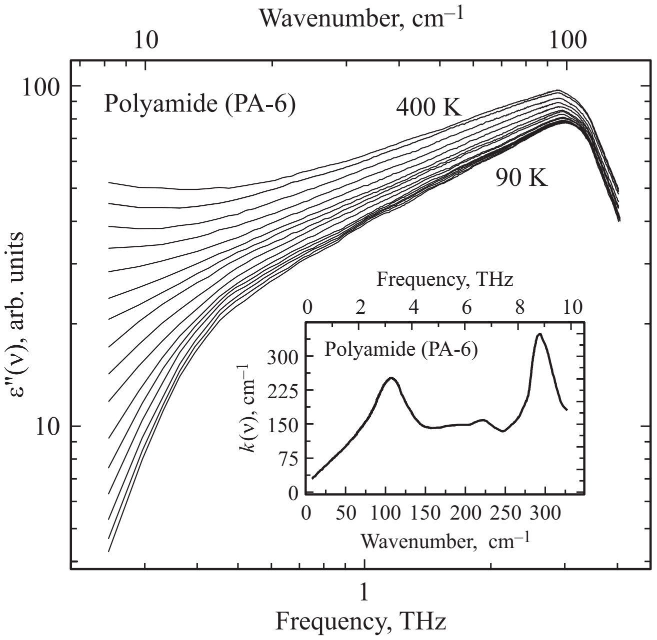
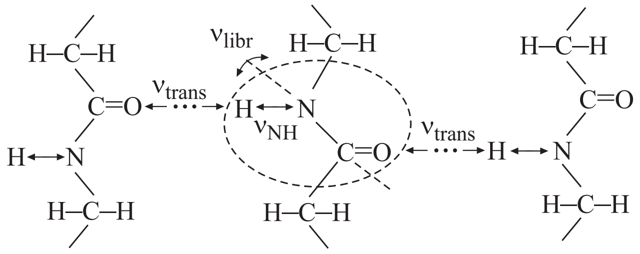


Figure 2. Dielectric losses $\varepsilon''(\nu)$ for PA-6 in the frequency range of 0.25–4 THz at temperatures varying within 90–400 K with an interval of 25 K. The insert shows the FIR-spectrum $k(\nu)$ of PA-6 at 295 K in the region of $8{-}325\,\mathrm{cm}^{-1}$, comprising the studied range of terahertz frequencies.

weak hydrogen bonds of the CONH group [15] (see the fragment of the structural formula).



With temperature rise, these high-frequency peaks in the dielectric loss spectra of PVC and-6 are intensified and shift by $3-4\,\mathrm{cm}^{-1}$ towards low frequencies due to HB weakening and increase of anharmonicity of vibrations. However, in this case intensity of the low-frequency wing of the band increases considerably more than that of the high-frequency one, particularly at frequencies below the BP, which in the coordinates used in Fig. 1, 2 looks like a bend on the spectral curves at 0.43 and 0.54 THz, respectively.

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

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

The fact that spectral changes with temperature at terahertz frequencies are more significant that at the frequencies of torsional-vibrational motion manifestation, allows for using this range to obtain information about the interrelation and mutual influence of the local and large-scale (segmental) dynamics. It is also important to know how the system changes over from vibrational to relaxational mobility, which eventually gives rise to structural changes.

The plots in Fig. 3, *a, b* illustrate the temperature evolution of dielectric losses in the studied terahertz range at a frequency close to the BP frequency: at 0.43 THz ($14.3\,\mathrm{cm}^{-1}$) for PVC and 0.54 THz ($18\,\mathrm{cm}^{-1}$) for PA-6. The figures show the dependences $\varepsilon''(T/T_g)$. 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.

The plots show that in both cases there are mainly three modes of temperature dependence of dielectric losses: (I) virtually temperature-independent losses at temperatures far from the glass transition temperature, (II) slight increase of losses upon approach to the glass transition and (III) sharp increase of losses at $T > T_g$. Thereat, both for PVC and for PA-6, a transition from mode (I) to mode (II) and from mode (II) to mode (III) occurs at $T_1 = 0.7T_g$ and $T_2 = 1.0T_g$.

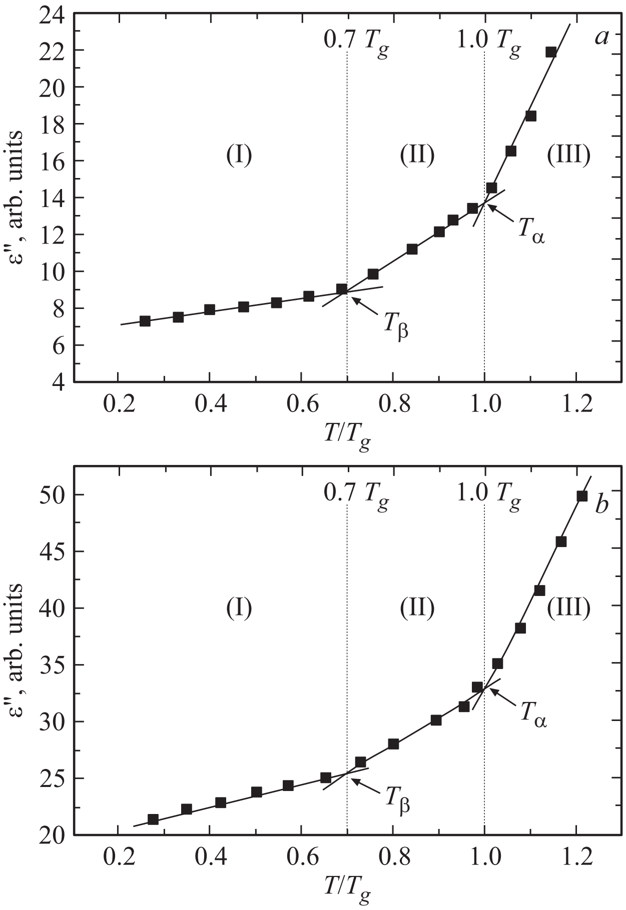


Figure 3. Dielectric losses $\varepsilon''(T/T_g)$ at the frequencies of 0.43 THz for polyvinylchloride (*a*) and $\nu = 0.54$ THz for polyamide PA-6 (*b*). The solid lines show the linear approximation of dependence $\varepsilon''(T/T_g)$ in modes (I), (II) and (III). T_β and T_α are the points of intersection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

Glass transition temperature (at a α-transition) $T_g = 350\,\mathrm{K}$ for PVC and $330-350\,\mathrm{K}$ for PA-6; thus, $T_1 = 245\,\mathrm{K}$ for PVC and $T_1 = 230-245\,\mathrm{K}$ for PA-6. These temperatures are close to the temperature of the β-transition, associated with local conformational mobility in these polymers [17]. 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.

A surge of losses at T_g is a contribution by the main relaxation process in polymers: α-glass transition the peak of which at temperatures above T_g shifts towards higher temperatures and its high-frequency wing enters the terahertz region. It is quite evident that the manifestation of this contribution at terahertz frequencies is also associated with a change of intermolecular interactions (HBs in this case), since it has been already mentioned that the bound OH-groups in systems with HBs become free at temperatures above T_g.

Temperatures of glass transition and β-transition, as well as coefficients B of linear approximation of dielectric losses $\varepsilon''(T/T_g) = A + BT/T_g$ on different areas of dependence $\varepsilon''(T/T_g)$, see Fig. 3, *a, b**

Polymer	T_g, K	T_β, K	T_β/T_g	B_{I}	B_{II}	B_{III}	ν_{BP}, cm^{-1}	HB type
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

* Note. T_g and T_β — temperatures of glass transition and β-transition, respectively, taken from the literature [17]; B_{I}, B_{II} and B_{III} — linear coefficients taken from the analysis of dielectric losses in modes (I), (II) and (III), respectively; ν_{BP} — spectral position of BP; the numbers in brackets are from [22] for PVC and [23] for PA-6.

An increase of the relaxation contribution at $T_\beta < T_g$ is, probably, due not to a break of HBs but only their weakening which, however, is sufficient for reorientational mobility to occur in PVC and PA-6r macromolecules due to an increase of torsional-vibrational motion amplitudes with temperature and accumulation of angular vibrational displacements in the chain [18].

Fig. 3, *a, b* also shows that some slight temperature changes are also present in the spectra at temperatures below $0.7T_g$. They can be caused by other secondary relaxations, for instance, fast (fast-β) relaxation in polybutadiene [19], which is associated with translational vibrations („rattling") of a molecule in a cell formed by its immediate environment. Moreover, a slight red shift and widening with temperature due to anharmonicity of the lowest-frequency vibrational bands (at 64 cm^{-1} in the PVC spectrum and at 105 cm^{-1} in the PA-6 spectrum, see Fig. 1, 2), also contributes to mode (I).

On the whole, a unified scenario of temperature behavior of the terahertz spectra of polyvinylchloride and polyamide-6 shows that the intermolecular, hydrogen-binding nature of interactions in these polymers play an identical role both in primary and secondary relaxation. Universality of this scenario should be further checked on other polymers where van der Waals interactions are prevailing.

We would like to clarify the above-mentioned universality of the temperature behavior of the spectra by stating that the temperature gradients of losses for the PA-6 and PVC spectra — coefficients B of linear approximation of dependence $\varepsilon''(T/T_g) = A + BT/T_g$ (see the table) are yet different: dielectric losses in the PA-6 spectrum increase with temperature faster than those in the PVC spectrum. The revealed effect is, apparently, due to the fact that PVC macromolecules have an increased stiffness as compared to PA-6, which is determined not only by bond polarity, but also by motion correlation of the neighboring dipoles. HB energy is equal to 8.4 kcal/mol in PA-6 [20] and 3.7 kcal/mol in PVC [21], while the Kuhn segment, characterizing the equilibrium stiffness of polymer chains, for PVC includes twelve monomeric units, while for PA-6 — only two−three units [17]. It can be supposed that, due to an increased flexibility of PA-6 macromolecules, the HB grid in this polymer can respond to a temperature change faster than in the case of PVC.

Sensitivity of the above-mentioned analysis method to details of temperature-dependent behavior of spectra indicates the prospect of use of the terahertz range for studying the molecular dynamics of macromolecules.

4. Conclusion

On the whole, the performed analysis of dielectric losses at terahertz frequencies for two polymers, which differ by HB type, at temperatures above and below T_g, has revealed several universal peculiarities in their terahertz IR-spectra. These losses at the lowest temperatures are represented only by a low-frequency wing of the absorption peak, conditioned by torsional-vibrational motion of polymers' monomeric units (at 64 cm^{-1} in the PVC spectrum and at 105 cm^{-1} in the PA-6 spectrum). They virtually do not depend on temperature in case of temperatures close to the temperature of the β-transition in PVC and PA-6, equal to $0.7T_g$, and thus the increase of dielectric losses starting from $T = 0.7T_g$ can be due to secondary relaxation occurring 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. Relaxation contributions at temperatures above T_g become prevailing in the terahertz spectra of PVC and PA-6. Since relaxation mobility in polymers is mainly controlled by potential barriers of intermolecular interactions — hydrogen bonds in this case — the manifestation of local molecular motion at T_β indicates their weakening. A sharp increase of relaxation contribution to spectra at a temperature rise to T_g — a manifestation of segmental mobility — is, apparently, due to not only the HB weakening and break, but also by a change in the hydrogen bond system in the studied polymers. This conclusion confirms the fact that intermolecular interactions play an important role in primary and secondary relaxations, and emphasizes the need for consideration of the relaxation contribution to the terahertz range of the IR-spectrum. Further terahertz studies on all objects with and without HBs are necessary to confirm the universality of the interrelation of relaxation processes with low-frequency torsional-vibrational modes.

Conflict of interest

The author declares that he has no conflict of interest.

References

[1] E. Kremer, A. Loidl. The Scaling of Relaxation Processes. Springer International Publishing AG, Leipzig (2018). 325 p.

[2] G. Biroli, J.P. Garahan. J. Chem. Phys. **138**, 12A301 (2013).

[3] E.P.J. Parrot, A. Zeitler. Appl. Spectrosc. **69**, *1*, 1 (2015).

[4] W. Götze. Complex Dynamics of Glass-Forming Liquids. Oxford University Press, N.Y. (2009). 362 p.

[5] V.N. Novikov, A.P. Sokolov, B. Stube, N.V. Surovtsev, E. Duval, A. Mermet. J. Chem. Phys. **107**, 1057 (1997).

[6] S.D. Bembenek, B.B. Laird. J. Chem. Phys. **114**, 2340 (2001).

[7] V.A. Bershtein, V.A. Ryzhov. Adv. Pol. Sci. **114**, 43 (1994).

[8] K.L. Ngai. Relaxation and Diffusion in Complex Systems. Oxford University Press, N.Y. (2011). 425 p.

[9] S. Kastner, M. Köhler, V. Goncharov, P. Lunkenheimer, A. Loidl. J. Non-Cryst. Solids **357**, 510 (2011).

[10] V.A. Ryzhov, M.V. Tonkov. In: Molekulyarnaya spektroskopiya / Ed. by G.S. Denisov. LGU, L. (1973). P. 108 (in Russian).

[11] L. Duvillaret, F. Garet, J.-L. Coutaz. IEEE J. Sel. Top. Quantum Electron. **2**, 739 (1996).

[12] Y-S. Jin, G-J. Kim, S-G. Jeon. J. Korean Phys. Soc. **40**, 513 (2006).

[13] S. Wietzke, C. Janden, M. Reuter, B.M. Ficsher, M. Koch, J. Mol. Struct. **1006**, 41 (2011).

[14] A.V.R. Warrier, S. Krimm. Macromolecules **3**, 709 (1970).

[15] W.F.X. Frank, H. Fiedler. Infrared Phys. **19**, 481 (1979).

[16] A. Barkatt, C.A. Angell. J. Chem. Phys. **70**, 901 (1979).

[17] V.A. Bershtein, V.M. Yegorov. Differentsialnaya skaniruyushchaya kalorimetriya v fizikokhmii polimerov. Khimiya, L. (1990). 248 p. (in Russian)

[18] Ya.ya. Gotlib, A.A. Darinsky, Yu.E. Svetlov. Fizicheskaya kinetika makromolekul. Khimiya, L. (1986). 272 p. (in Russian)

[19] R. Zorn, A. Alegria, A. Arbe, J. Colmenero, D. Richter, B. Frick. J. Non-Cryst. Solids **235–237**, 169 (1998).

[20] N. Nagai, T. Imai, R. Fukasawa, K. Kato, K. Yamauchi. Appl. Phys. lett. **85**, 4010 (2004).

[21] G. Wypych. PVC Degradation and Stabilization. ChemTec Publishing, Toronto (2008). 466 p.

[22] E. Duval, T. Achibat, A. Boukenter, B. Varrel, R. Calemczuk, B. Salce. J. Non-Cryst. Solids **190**, 258 (1995).

[23] P. Papanek, J.E. Fischer, N.S. Murthy. Macromolecules **35**, *10*, 4175 (2002).