Analysis of rapid chain dynamics in isochronal dielectric measurements of polymers

Yuning Yang, Wei-Chi Lai, and Shaw Ling Hsu[a)]
Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003, USA; Physics Department, University of Massachusetts, Amherst, Massachusetts 01003, USA; and NSF Materials Research Science and Engineering Center, University of Massachusetts, Amherst, Massachusetts 01003, USA

(Received 1 March 2007; accepted 13 June 2007; published online 2 August 2007)

Fast dynamics within the microwave frequency range (approximately gigahertz) in polymer systems as a function of temperature (in the range from 20 to 190 °C) were studied using high frequency dielectric spectroscopy. The frequency of radiation was varied from 0.5 to 18 GHz. The isochronal dielectric loss data were taken to eliminate the complexity arising from the frequency-independent, temperature-dependent background loss in the condensed phase. These studies were conducted for poly(caprolactone) (PCL), poly(ethylene oxide) (PEO), poly(ethylene oxide) with methoxy end group (PEO-CH_3), PLA-*b*-PEO-*b*-PLA triblock copolymers, and several polymers with high glass transition temperatures. These polymers possess glass temperatures ranging from −62 °C (PCL) to 110 °C (PMMA). One broad relaxation process was found only for polymers (PCL, PEO, and PLA-*b*-PEO-*b*-PLA) with low glass transition temperatures. The effect due to end groups was investigated by comparing the results of PEO with hydroxy versus methoxy end groups. The measured relaxation process was determined not to be associated with end groups. The results from temperature-dependent dielectric spectroscopy indicate that the relaxation process follows an Arrhenius T dependence suggesting that it is due to local motions. The activation energy of the relaxation process was measured and investigated based on the coupling model. The results suggest that the observed relaxation process behaves as a Johari-Goldstein β relaxation. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2756036]

INTRODUCTION

The molecular dynamics of relaxation in glass-forming systems, including many small molecules and polymers, have been studied extensively in the past few decades using numerous experimental techniques.[1–5] These include microscopic methods such as inelastic and quasielastic neutron scattering,[1] inelastic x-ray scattering, dynamic light scattering, dielectric spectroscopy, and NMR,[4] as well as macroscopic measurements such as dynamic mechanical thermal analysis.[2] It was found that polymers share some temporal dependence with all glass-forming materials but understandably also possess some special characteristic features. The common features include three types of relaxation processes, the α process, the β process, and the fast picosecond process, which are observed in most glass-forming materials including polymers and small molecules.[3,5,6] In addition to these common features, polymers also have their characteristic relaxation associated with the conformational transitions of polymer chains referred to as an elemental relaxation process (E process).[7] For the β process, further classification has been carried out. The β process, which bears strong correlation to the α process,[8] is classified as the Johari-Goldstein β relaxation.[9] In this study, we focus on the dynamics of polymers in the condensed phase within the microwave frequency range as a function of temperature.

The use of microwave radiation in organic synthesis[10,11] and polymer processing[12,13] has recently increased significantly and exhibits several attractive attributes.[11,13,14] From both fundamental and practical perspectives, it is of great importance to understand the details of how microwave radiation affects polymers from a molecular dynamics perspective. Although there have been extensive studies on the dynamics of polymers over decades of frequency (10^{-4}–10^{12} Hz), relatively little effort has been focused on the dynamics of polymers in the condensed phase within the microwave frequency range (approximately gigahertz). In this investigation, the molecular dynamics of polymers in the condensed phase are studied by high frequency dielectric spectroscopy as a function of temperature. Here we report the isochronal dielectric spectrum as a function of temperature at fixed frequencies for a number of polymers. The isochronal spectrum is used to eliminate the complexity arising from the frequency-independent, temperature-dependent background loss in the condensed phase.[15] The temperature dependence of relaxation time is analyzed based on the coupling model in order to identify the relaxation process.[16,17]

Any instrument providing microwave radiation with varying frequency is typically complex and of relatively high cost. Monitoring temperature is problematic as conventional thermocouples cannot be used in a microwave field.[12] In this

[a)]Author to whom correspondence should be addressed. Tel.: 413-577-1125; Fax: 413-545-0822. Electronic mail: slhsu@polysci.umass.edu

TABLE I. Polymer samples used in dielectric measurements.

	Mn (g/mol)	Source	T_g (°C)
PCL	1 000	Solvay Co.	−62
PEO	8 000	Aldrich Co.	−60
PEO	2 000	Aldrich Co.	−60
PEO-CH_3	2 000	Aldrich Co.	−60
PVAc	170 000	Acros Organics	30
PLA	2 000	Polymer Source	54
PLA	100 000	Cargill/Dow	54
Nylon 6	100 000	Aldrich Co.	63
PS	250 000	Acros Organics	100
PMMA	120 000	Aldrich Co.	114
PLA-*b*-PEO-*b*-PLA	13 000[a]	Synthesized	[b]

[a]Degree of polymerization of each block: 35/200/34.
[b]T_g was not observed using differential scanning calorimetry.

study, in a relatively simple configuration, we used a network analyzer (HP8510C) and temperature control unit to achieve dielectric measurements at elevated temperatures and in the entire microwave frequency domain for polymers in the condensed state. Dielectric studies were conducted for poly (caprolactone) (PCL), poly(ethylene oxide) (PEO), poly (vinyl acetate) (PVAc), poly(lactic acid), polystyrene (PS), nylon 6, and poly(methyl methacrylate) (PMMA). These polymers all possess polar backbones and/or side groups and a wide glass transition temperature variance (−62–114 °C). PLA-*b*-PEO-*b*-PLA triblock copolymer was also studied in order to characterize molecular weight effects of each block and possible block coupling. The isochronal spectra were obtained within the range from room temperature up to 190 °C. Relaxation processes were found to be present in PCL, PEO, and PLA-*b*-PEO-*b*-PLA. Molecular dynamics and the coupling mechanism are discussed and interpreted based on the dielectric dispersion behavior of these polymers as a function of temperature and frequency.

EXPERIMENTAL SECTION

The PEO, PEO-CH_3, nylon 6, and PMMA used in this study were purchased from Aldrich Chemical. The PCL sample was obtained from Solvay. PLA (100 K) was provided by Cargill/Dow. PLA (2000) was obtained from Polymer Source. The PVAc and PS were obtained from Acros Organics. The PLA-*b*-PEO-*b*-PLA copolymer was synthesized by co-workers (research group of Professor Gregory Tew). The glass transition temperatures T_g and molecular weights for each sample are tabulated in Table I. Samples studied have glass transition temperatures ranging from −62 to 114 °C. They can be categorized into two groups, a low T_g (PCL and PEO) and a high T_g group (PVAc, PLA, nylon 6, PS, and PMMA). All samples were used as received.

Each sample was first placed in a 5 ml beaker in a vacuum oven above its melting temperature for 1–2 h to ensure complete melting. The samples were then cooled in a vacuum oven to room temperature. Sample thickness in the beaker was approximately 1 cm. Dielectric data were collected using an open-ended coaxial probe (HP85070B) and a computer controlled network analyzer (HP8510C) over a frequency range of 0.5–18 GHz. Before each experiment, the sample was heated above the melting temperature (T_m) and the probe immersed into the molten sample to ensure good contact. The thermocouple was fixed between the sample and surface of the probe. The entire assembly was placed on a hot plate to be heated. The data were then obtained from room temperature to about T_m+60 °C with a heating rate of 2–3 °C/min. In order to eliminate the complexity arising from the frequency-independent, temperature-dependent background loss, the dielectric data were taken as a function of temperature at fixed frequencies (isochronal spectrum).

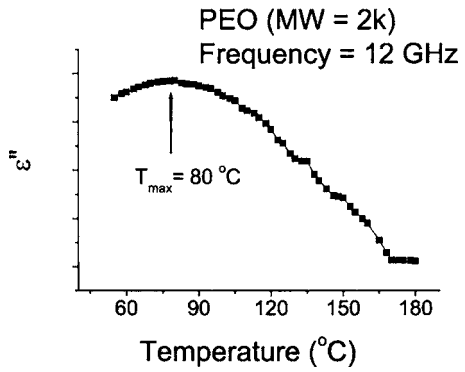

FIG. 1. Dielectric loss factor ε'' as a function of temperature at 12 GHz for amorphous poly(ethylene oxide) (MW=2000).

RESULTS AND DISCUSSIONS

Dielectric data are typically obtained and presented either in the form of isothermal spectrum (the frequency is varied and temperature fixed) or in the form of isochronal spectrum (the temperature is varied and frequency fixed). It has been shown that for amorphous materials in the condensed phase, the isochronal spectrum can eliminate the complexity arising from the frequency-independent, temperature-dependent background loss.[15] In our study, the dielectric loss of polymers in the condensed phase and the associated dielectric data are presented in the form of an isochronal spectrum. In the polymers studied, PVAc, PLA, nylon 6, PS, and PMMA have relatively high T_g's (30–114 °C). The data for these polymers indicate that the dielectric loss factor ε'' increases monotonically with increasing temperature. Therefore, no relaxation process is induced by the microwave signal. Poly(ethylene oxide) and poly(caprolactone) have low glass transition temperatures, T_g −60 and −62 °C, respectively. Figure 1 shows the loss factor ε'' as a function of temperature at 12 GHz for PEO (MW =2000). In this case, the loss factor ε'' reaches a peak value at the coupling temperature $T_{\max}$=80 °C. This indicates that some relaxation process is induced by the microwave signal. The relaxation time τ of the process at 80 °C should match the frequency of the microwave, that is, $\tau(T=80\ ^\circ\mathrm{C})=1/f$ =1/(12 GHz). According to the time-temperature superposition principle, the coupling temperature $T_{\max}$ is expected to shift to higher temperature at higher frequency. This is indeed observed for these two polymers. For PCL, the peak of the dielectric loss factor shifts to higher temperature with increasing frequency, as shown in Fig. 2. The quantitative

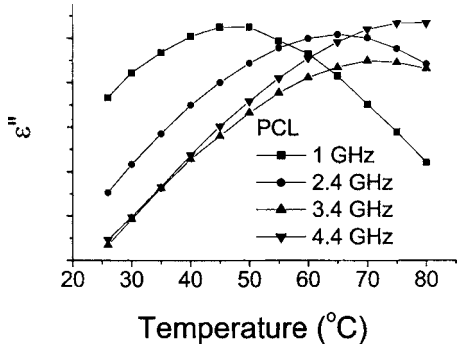

FIG. 2. Dielectric loss factor ε'' as a function of temperature at various frequency for poly(caprolactone) (MW=1000).

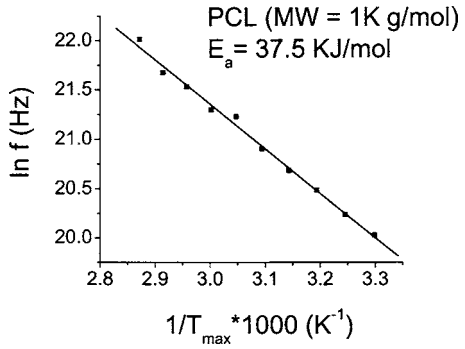

FIG. 3. $\ln(f)$ vs $1/T$ plot for poly(caprolactone) (MW=1000).

trend of this shift provides the temperature dependence of relaxation time. The mechanism of the relaxation process is discussed below.

Many experimental techniques have shown that there are generally three types of relaxation in glass-forming materials: the α process, the β process, and the fast picosecond process.[3,5] As mentioned above, polymers can possess another process associated with the conformational transition and referred to as the E process.[7] The relaxation time of each type of relaxation has different temperature dependence. For the β and E relaxations, the temperature dependence of the relaxation time is described by the Arrhenius equation

$$\tau(T) = \tau_\beta \exp\left(\frac{E_a}{kT}\right), \tag{1}$$

where E_a is the activation energy of motion and τ_β the prefactor. Activation energy E_a is a constant during motion as there is no global structural change. In plotting $\ln(f)$ versus $1/T$ [Williams-Landel-Ferry (WLF) plot], the slope will be a constant if the motion can be described by the Arrhenius equation. For the α process, the temperature dependence of the relaxation time is described by the WLF equation[18]

$$\log \frac{\tau}{\tau_s} = \frac{-8.86(T-T_s)}{101.6+T-T_s}, \tag{2}$$

where T_s/τ_s are the reference temperature/relaxation time. In this case, the $\ln(f)$ is not proportional to $1/T$ because the motion involves global structural change. The fast picosecond process has no significant temperature dependence, i.e., the relaxation time is on the order of a picosecond and does not change with temperature.[3] The temperature dependence of relaxation times measured for PCL and PEO-CH_3 are shown in Figs. 3 and 4, respectively. As can be seen from both plots, the data can be fitted to a straight line suggesting an Arrhenius process. The activation energy E_a and the prefactor τ_β are calculated for both polymers based on the slope and the y intercept of the straight line. The activation energies are E_a=37.5 kJ/mol for PCL and E_a=29.1 kJ/mol for PEO-CH_3. And the prefactors are $\tau_\beta = 7.7\times10^{-7}$ ns for PCL and $\tau_\beta = 2.8\times10^{-5}$ ns for PEO-CH_3. The prefactor is extremely small because τ_β corresponds to the relaxation time at infinitely high temperature. Since the E process is associated with the conformational transition, the activation of the E process is approximately equal to the energy barrier of a single C–C bond rotation, which is approximately 2–3 kJ/mol.[7] Values for PCL and PEO are significantly higher than bond rotation indicating that the relaxation process in the two polymers is not due to conformational transitions. On the other hand, the Johori-Goldstein (JG) β process is assumed to involve the motion of the whole monomeric repeat unit.[3,5,19] Based on the coupling model,[16] there is a quantitative relationship between the activation energy of the β process E_β and the glass transition temperature T_g for the JG β process[20–22],

$$E_\beta = 24RT_g, \tag{3}$$

where R is the gas constant. An empirical relationship was first suggested in the late 1990s,[22] then theoretically derived based on the coupling model.[20] Therefore, the ratio E_β/RT_g is expected to be approximately 24 for the JG β relaxation. For a PCL sample, the measured activation energy is 37.5 kJ/mol. With a T_g=211 K, the E_β/RT_g should be 22. For a PEO-CH_3 sample, a similar calculation leads to E_β/RT_g=18. These values agree reasonably well with the expected value of 24. The results therefore suggest that the relaxations observed in PEO and PCL behave as a JG β relaxation. In order to estimate the size of the dynamic unit involved in the relaxation process, we followed an approach combining the Rouse theory and the Verdier-Stockmayer model first proposed by Adachi in 1989.[23] Based on the Rouse theory,[24] the relaxation time τ_n for the normal mode process is given by

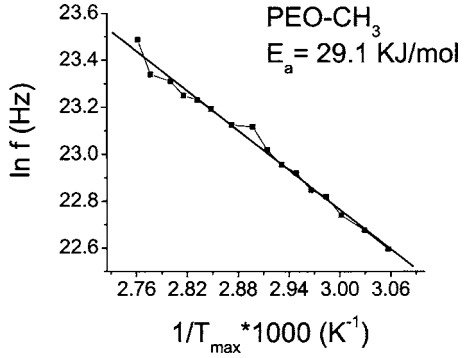

FIG. 4. $\ln(f)$ vs $1/T$ plot for poly(ethylene oxide) with CH_3 end group (MW=2000).

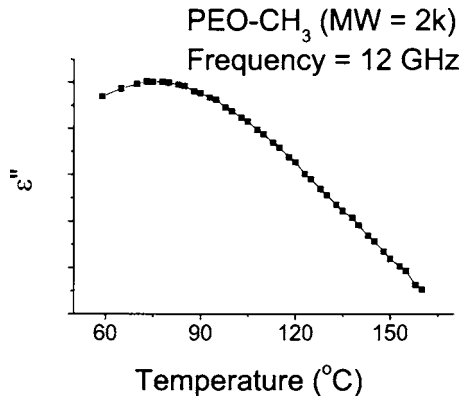

FIG. 5. Dielectric loss factor ε'' as a function of temperature at 12 GHz for poly(ethylene oxide) with CH_3 end group.

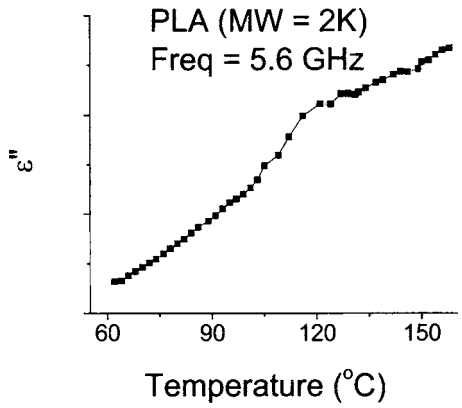

FIG. 6. Dielectric loss factor ε'' as a function of temperature at 5.6 GHz for poly(lactic acid) (MW=2000).

$$\tau_n = \eta N^2 a^3/(3\pi^2 k_B T), \tag{4}$$

where η is viscosity, N the total number of dynamic units in a polymer chain, and a the size of the dynamic unit involved in the relaxation process. The Verdier-Stockmayer model provides a relationship between relaxation time τ_n for the normal mode process and relaxation time τ_s for the local modes,[25] which is given by

$$\tau_n = K(N-1)^2 \tau_s, \tag{5}$$

where K is a constant ranging from 0.8 to 1.1, and N the total number of dynamic units in the chain. Combining Eqs. (4) and (5) gives us

$$\tau_s = \eta a^3/(3\pi^2 k_B T), \tag{6}$$

where we have taken K to be 1 and N equal to $N-1$ by approximation. Based on Eq. (6), the order of magnitude of the size can be approximately calculated. For PEO of molecular weight 2000 g/mol at temperature 60 °C, it is

$$\tau_s = a^3 \times 10^{18}\ (\mathrm{s}). \tag{7}$$

Based on our experimental data, relaxation time τ is measured to be 1 ns at 60 °C; thus the size of the dynamic unit a is approximately 1 nm. This size is comparable to the size calculated in the same approach by Adachi *et al.*[23] and Hyde and Ediger[26] for polyisoprene based on dielectric spectroscopy and time-resolved optical spectroscopy. Adachi *et al.* concluded that slightly more than one monomer unit is involved in polyisoprene dielectric relaxation. Hyde and Ediger reached a similar conclusion on size of the local mode, which is 8–12 Å based on optical spectroscopy. This size agrees with the assumption that the JG β relaxation involves motion of the whole monomeric repeat unit.

Since JG β relaxation involves only the motion of the monomeric repeat unit, it is expected that the end group should have no effect on the relaxation behavior in our system. For confirmation, measurements were carried out for PEO with –OH and $–CH_3$ end groups. The dielectric loss factor ε'' as a function of temperature at 12 GHz for PEO-OH and PEO-CH_3 is shown in Figs. 3 and 5, respectively. These clearly indicate that there is virtually no difference between –OH end groups and $–CH_3$ end groups. The –OH end group and $–CH_3$ end group have totally different polarities, the –OH end group being polar and the $–CH_3$ end group being nonpolar. If the end group motion is responsible for coupling to the microwave, these two polymers should display quite different dielectric behavior as only polar groups couple to the microwave signal. The lack of response of the end group is consistent with the conclusion that the observed relaxation process can be assigned to the JG β process.

Furthermore, the dielectric data for the block copolymer were measured to assess the effect of block copolymerization on JG β relaxation. It has been shown that PLA homopolymer does not couple to the microwave while PEO homopolymer does. When blocks of PLA are linked to the PEO blocks on both ends, the behavior of the PEO block responding to microwave radiation should prove very informative and of interest. PLA-*b*-PEO-*b*-PLA triblock copolymer has been extensively studied for other purposes in our laboratory. The degree of polymerization of each block is 34/200/34, i.e., the PLA block molecular weight is 2400 and the PEO is 8900. The dielectric data of PLA-*b*-PEO-*b*-PLA copolymer, PLA homopolymer with MW=2000 g/mol, and PEO homopolymer with MW=8000 g/mol are all shown in Figs. 6–8. The dielectric loss factor versus T for PLA (2000) at 5.6 GHz is shown in Fig. 6. This set of data for low molecular weight PLA is similar to that obtained for higher molecular weight PLA (MW=100 000 g/mol) and no relaxation is observed. The dielectric loss factor versus T for PLA-*b*-PEO-

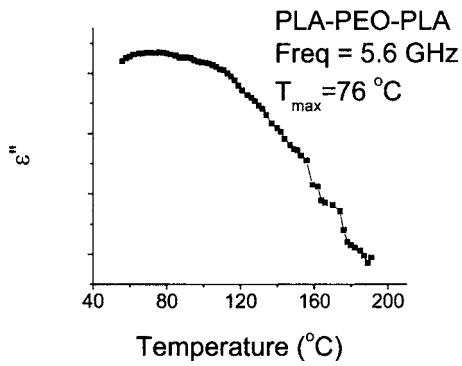

FIG. 7. Dielectric loss factor ε'' as a function of temperature at 5.6 GHz for poly(lactic acid)-*b*- poly(ethylene oxide)-*b*- poly(lactic acid) triblock copolymer.

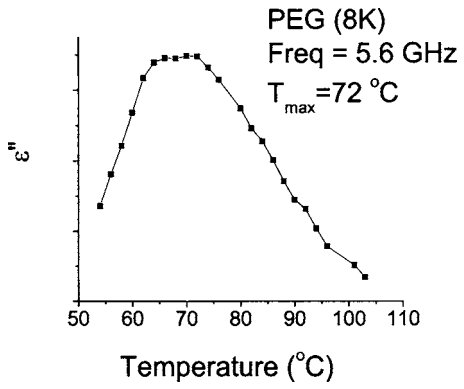

FIG. 8. Dielectric loss factor ε'' as a function of temperature at 5.6 GHz for poly(ethylene oxide) (MW=8000).

b-PLA copolymer and PEO (8000) at 5.6 GHz are shown in Figs. 7 and 8, respectively. A relaxation peak was observed for both. The PEO block in the copolymer still responds to the microwave radiation in a manner similar to the PEO homopolymer. The presence of the PLA block does affect the behavior of PEO block. In the copolymer, the transition is broader than that of the PEO homopolymer suggesting that the distribution of relaxation time τ is broader due to the presence of PLA block. Another effect is that the coupling temperature $T_{\max}$ of copolymer (76 °C) is slightly higher than that of the PEO homopolymer (72 °C). This is due to the fact that the two PLA blocks on both sides of PEO may reduce mobility and thereby increase the "rigidity" of the PEO block. However, the overall effect of PLA blocks is not significant. Therefore, block copolymerization does not have an important effect on the JG β relaxation upon exposure to microwave radiation.

CONCLUSIONS

Isochronal dielectric spectra of 11 polymers in the condensed phase within the microwave frequency range have been obtained as a function of temperature. These polymers possess a broad glass transition temperature range (−62–110 °C). The three polymers (PCL, PEO, and PEO-CH_3) with low glass transition temperature (−62 and −60 °C) show significant relaxation upon microwave radiation. The copolymer PLA-*b*-PEO-*b*-PLA also shows a relaxation due to the presence of the PEO block. The results from temperature-dependent dielectric spectroscopy indicate that the relaxation process follows Arrhenius T dependence. The activation energy E_a was calculated and the relationship between E_a and T_g was analyzed by the coupling model. The results suggest that the relaxation processes observed in our systems behave as the JG β process. Moreover, the calculation based on the Rouse theory and the Verdier-Stockmayer model indicates that the motion is at a very localized scale, which agrees with the assumption that the JG β process involves motion of the whole monomeric repeat unit. The effect of end groups was investigated and the conclusion reached that the end group is not associated with the relaxation process. Studies on the copolymer PLA-*b*-PEO-*b*-PLA indicate that block copolymerization does not significantly affect the JG β process.

ACKNOWLEDGMENTS

The authors express thanks to Fang Lu and Professor Sigfrid Yngvesson for permitting the use of the microwave instrument in the Electrical Engineering Department. This work was supported by the National Science Foundation, Grant No. CTS 0304217, and the National Science Foundation Materials Research Science and Engineering Center.

[1] D. Richter, A. J. Dianoux, W. Petry, and J. Teixeira, *Dynamics of Disordered Materials* (Springer, Berlin, 1989).
[2] A. J. Dianoux, W. Petry, and D. Richter, *Dynamics of Disordered Materials II* (North-Holland, Amsterdam, 1993).
[3] T. Kanaya and K. Kaji, Adv. Polym. Sci. **154**, 87 (2001).
[4] R. Zorn, J. Phys.: Condens. Matter **15**, R1025 (2003).
[5] K. L. Ngai, J. Non-Cryst. Solids **275**, 7 (2000).
[6] K. L. Ngai and M. Paluch, J. Phys. Chem. B **107**, 6865 (2003).
[7] T. Kanaya, T. Kawaguchi, and K. Kaji, Macromolecules **32**, 1672 (1999).
[8] K. L. Ngai, Macromolecules **32**, 7140 (1999).
[9] K. L. Ngai and M. Paluch, J. Chem. Phys. **120**, 857 (2004).
[10] R. N. Gedye, F. E. Smith, and K. C. Westaway, Can. J. Chem. **66**, 17 (1988); R. A. Abramovitch, Org. Prep. Proced. Int. **23**, 685 (1991); A. G. Whittaker and D. M. P. Mingos, J. Microwave Power Electromagn. Energy **29**, 195 (1994).
[11] D. M. P. Mingos and D. R. Baghurst, Chem. Soc. Rev. **20**, 1 (1991).
[12] P. Albert, M. Holderle, R. Mulhaupt, and R. Janda, Acta Polym. **47**, 74 (1996).
[13] J. Palacios and C. Valverde, New Polym. Mat. **5**, 93 (1996).
[14] D. A. C. Stuerga and P. Gaillard, J. Microwave Power Electromagn. Energy **31**, 87 (1996); A. Loupy, A. Petit, J. Hamelin, F. Texier-Boullet, P. Jacquault, and D. Mathe, Synthesis **9**, 1213 (1998).
[15] S. H. Chung, K. Pathmanathan, and G. P. Johari, J. Polym. Sci., Part B: Polym. Phys. **24**, 2655 (1986).
[16] K. L. Ngai and K. Y. Tsang, Phys. Rev. E **60**, 4511 (1999).
[17] K. L. Ngai, J. Phys.: Condens. Matter **15**, S1107 (2003).
[18] M. L. Williams, R. F. Landel, and J. D. Ferry, J. Am. Chem. Soc. **77**, 3701 (1955).
[19] K. L. Ngai, P. Lunkenheimer, C. Leon, U. Schneider, R. Brand, and A. Loidl, J. Chem. Phys. **115**, 1405 (2001).
[20] K. L. Ngai and S. Capaccioli, Phys. Rev. E **69**, 031501 (2004).
[21] A. Kudlik, C. Tschirwitz, T. Blochowicz, S. Benkhof, and E. Rossler, J. Non-Cryst. Solids **235**, 406 (1998).
[22] A. Kudlik, C. Tschirwitz, S. Benkhof, T. Blochowicz, and E. Rossler, Europhys. Lett. **40**, 649 (1997).
[23] K. Adachi, Y. Imanishi, and T. Kotaka, J. Chem. Soc., Faraday Trans. 1 **85**, 1083 (1989).
[24] P. E. Rouse, J. Chem. Phys. **21**, 1272 (1953).
[25] P. H. Verdier and W. H. Stockmayer, J. Chem. Phys. **36**, 227 (1962).
[26] P. D. Hyde and M. D. Ediger, J. Chem. Phys. **92**, 1036 (1990).