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Relation between Main and Normal Mode Relaxations for Polyisoprene Studied by Dielectric Spectroscopy

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ABSTRACT: Broadband dielectric spectroscopy (10^{-2}–10^6 Hz) is employed to study the relation between α relaxation and normal mode process for oligomeric polyisoprene samples of different molecular weights. It is shown that α relaxation and normal mode process merge above the Vogel temperature of the α relaxation. This means that the Rouse model is not applicable to the normal mode relaxation near the glass transition. Further, this result is discussed from a microscopic point of view in terms of the different temperature dependences of the two relevant length scales, the correlation length for the α relaxation ξ and the end-to-end vector of the polymer chain. A quantitative evaluation gives more evidence that there exists a characteristic length scale for the α relaxation which is in the order of magnitude of 2–3 nm at the glass transition temperature.

I. Introduction

Relaxations in polymers are controlled by very different length scales ranging from local to very cooperative motions. The segmental motion responsible for the α relaxation is regarded as local and should cover only a few repeating units. On the other hand, the so-called normal mode process (n relaxation), related to the fluctuation of the end-to-end vector, is highly cooperative and involves the whole polymer chain. As has been well established for low molecular weight (unentangled) polymers at high temperatures compared to their glass transition temperature T_g, the normal modes of chains and their viscoelastic[1] and dielectric[2-10] properties, with respect to their dependence on molecular weight, are in good agreement with the modified Rouse model for undiluted polymers.[11] This theory predicts for the time dependence of the mean end-to-end vector

$$\langle r(0)r(t)\rangle/\langle r^2\rangle = (8/\pi^2)\sum(1/p^2)\exp(-t/\tau_p) \tag{1}$$

$$\tau_p = \zeta N^2 b^2/3\pi^2 kTp^2 \qquad p = 1, 3, 5, ... \tag{2}$$

where τ_p is the relaxation time for the pth normal mode, N is the number of chain segments with bond length b, and ζ is the monomeric friction coefficient.

Most dielectric measurements on so-called type A polymers[4] having a dipole component parallel to the chain contour show that the temperature dependence of a characteristic relaxation time τ_n for the normal mode process obeys the Vogel/Fulcher/Tammann/Hesse (VFTH) equation[12-14]

$$\log \tau_n = \log \tau_{\infty,n} + \frac{A_n}{T - T_{0,n}} \tag{3}$$

where $\tau_{\infty,n}$ and A_n are constants and $T_{0,n}$ is the so-called Vogel temperature. This temperature dependence is rationalized by introducing a temperature-dependent monomeric friction coefficient $\zeta(T)$. From a molecular point of view $\zeta(T)$ should be controlled by the segmental motion, and because (as is well-known) the temperature dependence of the relaxation time of the α relaxation τ_α also obeys the VFTH equation,[12-14] both processes should have the same monomeric friction coefficient, with $T_{0,n} = T_{0,\alpha}$.

The relation between normal mode and α relaxations has been previously studied by several authors,[2-8,15-17] providing experimental evidence[16,17] that normal mode and α relaxations merge at a significantly higher temperature than $T_{0,\alpha}$. Also, from a theoretical point of view, the coupling model introduced by Ngai predicts a breakdown of the Rouse model in the vicinity of the glass transition.[18,19] Recent broadband dielectric experiments[20,21] on a series of oligomeric poly(propylene oxide)s (PPO) also deliver a much stronger temperature dependence of τ_α than that of τ_n as the temperature approaches T_g. But because the PPO samples show an anomaly with respect to their glass transition temperature,[20] it is not clear from these experiments whether this behavior is general or not.

Because the Rouse model is fundamental in polymer physics, it seems important to clarify the relation between normal mode and α relaxations on another polymer system. In the present paper dielectric measurements on oligomeric polyisoprene (PI) samples having an in-chain dipole moment[5,9] are carried out. The relaxation of the end-to-end vector therefore shows up in the spectrum of the dielectric permittivity as a discernible relaxation mode. These experiments show the same behavior as observed for the PPO system, a much stronger temperature dependence of τ_α than that of τ_n in the vicinity of T_g. This behavior is discussed by assuming that the characteristic length connected with the α relaxation shows a stronger temperature dependence than the end-to-end vector of the polymer chain. Also, a new approach estimating the length scale of the α relaxation at T_g is presented. The obtained values are of the order of magnitude predicted by the fluctuation approach to the glass transition.[22-24]

II. Experimental Section

Four oligomeric poly(*cis*-1,4-)isoprene samples were measured with different molecular weights from 1000 to 8000, purchased from Polymeric Standard Service Mainz, Germany. The sample characteristics are summarized in Table I. For dielectric measurements the sample was kept between two gold-plated stainless steel electrodes (diameter 20 mm) with a spacing of 50 ± 1 μm maintained by fused silica fibers. The temperature of the sample was controlled by a nitrogen gas jet heating system[25] covering a broad temperature range with a resolution of ±0.02 K. To determine the isothermal dielectric behavior, characterized by the complex dielectric permittivity

$$\epsilon^*(f) = \epsilon'(f) - i\epsilon''(f) \tag{4}$$

(f, frequency; ϵ', real part; ϵ'', imaginary part; $i = -1^{1/2}$) in a frequency range from 10^{-2} to 10^6 Hz, a Schlumberger frequency-

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Table I
Molecular Characteristics of the Polyisoprene Samples

sample	M_w	M_n	M_w/M_n
PI-1	1400	1230	1.11
PI-4	3830	3540	1.08
PI-5	4700	4500	1.04
PI-8	8400	8160	1.03

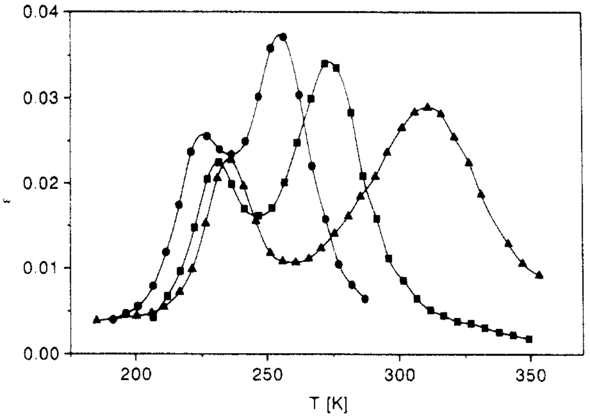

Figure 1. ϵ'' vs temperature at a frequency of 10^4 Hz for different samples. (●) PI-1; (■) PI-4; (▲) PI-8.

response analyzer FRA 1260 with a buffer amplifier of variable gain was used.[25] A part of this work was carried out during a stay in the dielectric group of the Max-Planck-Institut für Polymerforschung at Mainz.

Figure 1 shows ϵ'' vs temperature for the samples PI-1, PI-4, and PI-8 at a frequency of 10^4 Hz. Clearly two relaxation processes, indicated by peaks in $\epsilon''(f)$, can be seen assigned to the α relaxation (low-temperature peak) and to the normal mode process (high-temperature peak).

For a quantitative analysis and to determine $f_{p,i}$ (i = n, α), the frequency of maximum loss, for each process also in the case of strong overlapping of the α and the normal mode relaxation, an evaluation method[26] based on the model function introduced by Havriliak and Negami (HN function)[27] was applied. The HN function reads

$$\epsilon^*(f) - \epsilon_\infty = \frac{\Delta\epsilon}{(1 + (if/f_0)^\beta)^\gamma} \qquad (5)$$

with the HN parameters $\Delta\epsilon$ (intensity), f_0 (characteristic frequency which is nearly equal to the peak frequency f_p) and $\epsilon_\infty = \epsilon'(f)$ for $f \gg f_p$. The fractional shape parameters β and γ ($0 < \beta, \beta^*\gamma \leq 1$) are related[24] to the slopes of ϵ'' for low and high frequencies with respect to f_0: $m = \beta = \partial \log \epsilon''/\partial \log f$ for $f \ll f_0$ and $n = \beta\gamma = -\partial \log \epsilon''/\partial \log f$ for $f \gg f_0$. The Debye limit, which is characteristic for the motion of small isolated molecules, is given by $m = n = 1$.

In the case where both relaxation peaks are covered by the experimental frequency window, two HN functions are simultaneously fitted to the experimental data to determine the HN parameters for each process. In the other cases an additional power law Af^δ is added to determine the influence of neighboring processes.[28] Both normal mode and α relaxations are well described by this procedure (cf. Figure 2) where the accuracy in the determination of the shape parameters β and γ is ±0.05 and in f_0 ±10%.

III. Results and Discussion

A. Shape Parameters. In agreement with the literature[9,10] for the shape parameters of the segmental model $m_\alpha \approx 0.6$ and $n_\alpha \approx 0.34$ independent of the temperature and of the molecular weight are found. In contrast to this result, the shape parameters for the normal mode process show a different behavior. The low-frequency parameter m_n is approximately unity for all samples studied, whereas the high-frequency parameter n_n depends on molecular weight as shown in Figure 3. The molecular weight dependence of n_n can be well described by

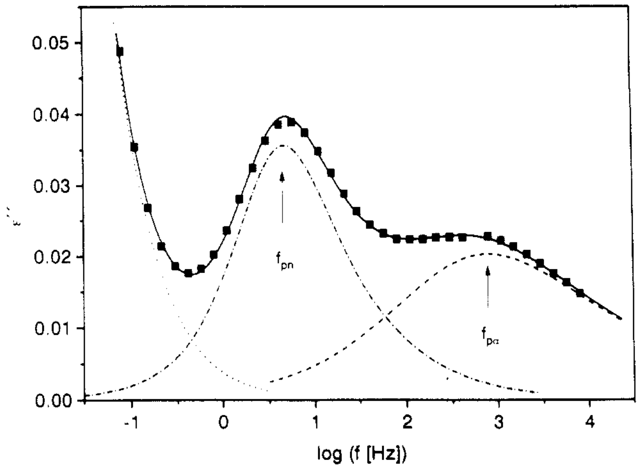

Figure 2. Decomposition of the measured ϵ''-frequency dependence into the α relaxation (dashed line), into the normal mode relaxation (dashed-dotted line), and into the conductivity contribution (dotted line) for PI-1 at 216 K. The solid line is the fit-function.

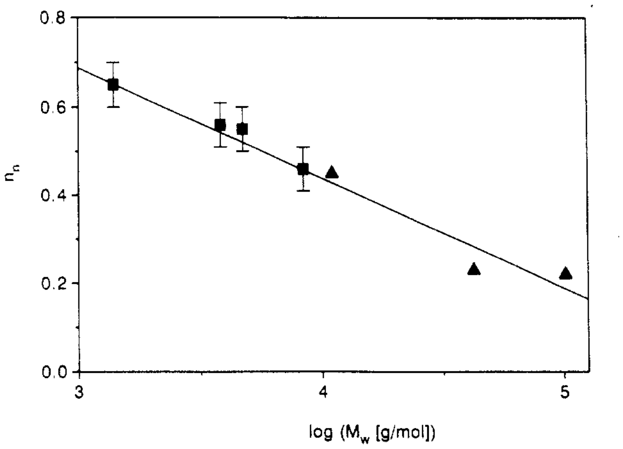

Figure 3. Molecular weight dependence of the shape parameter n_n. (■) This work; (▲) ref 7.

$$n_n(M_w) = 1.435 - 0.249 \log (M_w) \qquad (6)$$

Although the samples are relatively monodisperse (see Table I), the absolute value of n_n does not agree with the parameters given in ref 9 but coincide very well with the data given by Adachi and Kotaka[7] (cf. Figure 3) and can be described also by eq 6.

From eq 1 $m_n = 1$ and $n_n = 0.7$ independent of molecular weight are obtained. So in general one has to state that molecular weight dependence of n_n is in contrast to the Rouse model, as also discussed in ref 9. Recently, Pakula and Geiler[29] have carried out computer simulations for cooperative relaxation in dense macromolecular systems. The conformational relaxation in a system of linear chains is characterized by the end-to-end vector correlation function which shows a strong nonexponential behavior depending on molecular weight. The model takes into consideration a large variety of cooperative rearrangements as well as a large variety of local structural situations. The close packing restricts the motion of any element in the system until some other elements move with these elements cooperatively. The observed experimental behavior is in accordance with this model. In particular, the extrapolation of n_n to the molecular weight of the repeating unit using eq 6, leading to $n_n = 0.944$ which is near the Debye limit, delivers strong support for this simulation. These

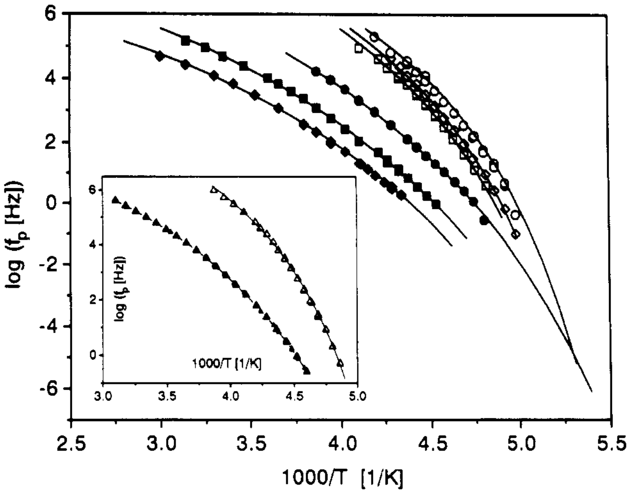

Figure 4. Temperature dependence of the characteristic relaxation frequencies. Open and solid symbols correspond to the α relaxation and to the normal mode process, respectively. (○) PI-1; (△) PI-4; (□) PI-5; (◇) PI-8.

Table II
VFTH Parameters for the α and Normal Mode Relaxations

	α relaxation			normal mode relaxation			
sample	$\log f_\infty$/Hz	A/K	T_0/K	$\log f_\infty$/Hz	A/K	T_0/K	$\log f_s$/Hz
PI-1	10.73	403.3	163.8	10.33	708	142.3	-4.3
PI-4	10.73	416.5	168.1	9.49	664	151.5	-7.1
PI-5	10.73	440.8	164.8	9.26	693	146.3	-6.6
PI-8	10.73	419.2	165.2	8.21	629	151.2	-10.3

results are also in accord with a recent Focker–Planck approach to the chain dynamics of polymers[30] by Ngai and co-workers.

B. Relaxation Frequencies. In Figure 4 $\log f_p$ for the α relaxation as well as for the normal mode process is given. As is known, the temperature dependence of both characteristic relaxation frequencies can be well described by the VFTH equation (eq 3), and the VFTH parameters are collected in Table II. For the α relaxation $\log f_{\infty,\alpha}$ is the vibrational frequency and should not be dependent on molecular weight. For this reason the VFTH parameters for the α relaxation were first determined without any restriction; afterwards, $\log f_{\infty,\alpha}$ was averaged over the four samples to 10.73 ± 0.20, and finally, in a second run, A and T_0 were determined with this fixed value of $\log f_{\infty,\alpha}$. This procedure leads to more stable values of $T_{0,\alpha}$. For the normal mode process the VFTH equation was fitted to the data without any restrictions. An analysis of $f_{\infty,n}$ vs M_w shows that the quadratic dependence on molecular weight expected for polymers below the critical molecular weight is approximately fulfilled. Therefore, the estimated parameters of Table II seem to be sufficiently accurate to permit the extrapolation of f_{pi} to low temperatures shown in Figure 4. This extrapolation demonstrates clearly that α relaxation and normal mode process merge at a temperature T_s, which is higher than the Vogel temperature $T_{0,\alpha}$ of the α relaxation.

In Figure 5 the difference $T_{0,\alpha} - T_{0,n}$ is plotted vs molecular weight. For all samples this quantity is greater than zero and the data can be described well by a straight line with a slope of $-9.332 \times 10^{-4} \pm 2 \times 10^{-4}$ K mol/g. This means that $T_{0,\alpha} - T_{0,n}$ decreases significantly with the molecular weight and that the merging of α relaxation and normal mode process occurs at lower temperatures for higher molecular weights. This is also indicated by the decrease of the merging frequency f_s of the normal mode process and the α relaxation with molecular weight which is given in Table II. To show the consistency of the data, some values taken from the literature are also included. Although these data have a greater scatter, they display the same behavior. The results presented here for the polyisoprene samples are essentially the same as those obtained for the poly(propylene oxide) system[20,21] and provide more experimental evidence that the Rouse model in connection with the conception of the monomeric friction coefficient breaks down in the vicinity of the glass transition. Because this behavior is now found for at least two different materials, it should be regarded as a general feature of polymer dynamics. The first attempt to explain this was made on the basis of the coupling scheme by Ngai.[18,19,21]

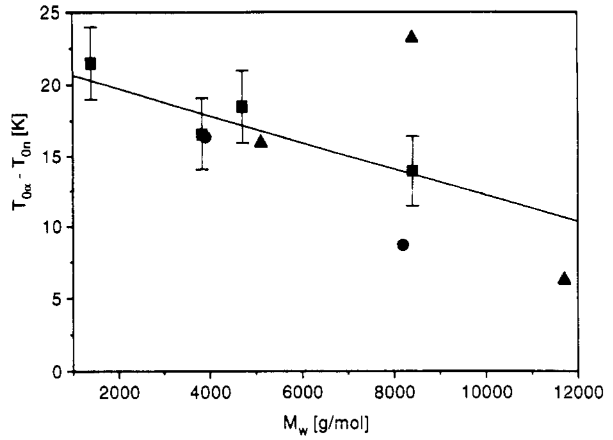

Figure 5. Difference of the Vogel temperatures for α relaxation and the normal mode process vs molecular weight. (■) This work; (▲) ref 8; (●) ref 9.

C. Characteristic Length Scale for the Glass Transition. The understanding of the α relaxation is one of the central problems of condensed matter physics. Adam and Gibbs[31] treated the α relaxation as a cooperative process by introducing a cooperatively rearranging region (CCR) defined as the smallest volume element that can relax to a new configuration independently of neighboring regions. For this reason the CCR can be regarded as the correlation volume (correlation length ξ^3) for the α relaxation. These ideas were used and further developed in the fluctuation approach[22,23,32] to the glass transition. Within the framework of this model the correlation length ξ can be estimated from DSC measurements.[23]

To discuss the relationship between α relaxation and normal mode process from a more microscopic point of view, we use this concept where the strong decrease of $f_{p,\alpha}$ with decreasing temperature is explained by a strong temperature dependence of the correlation length $\xi(T)$ which diverges[31,22,23] as T approaches $T_{0,\alpha}$. The fluctuation approach to the glass transition[22,23,32] gives $\xi \sim 1/(T - T_{0,\alpha})^{2/3}$ with $\xi(T_g) \approx 2$–3 nm for polymers. On the other hand, the normal process is related to the fluctuation of the end-to-end vector,[4,5,9,29] which increases with molecular weight but scarcely changes with temperature.[33] Because the temperature dependences of the two length scales are different, the merging of these processes should take place when, by lowering the temperature, the correlation length for the α relaxation is increased to the order of magnitude of the end-to-end distance

$$\xi(T_s) \approx \langle R^2 \rangle^{1/2} \qquad (7)$$

Since $\langle R^2 \rangle$ increases with M_w, the merging of both processes should shift to a lower temperature for a higher molecular weight as can be seen in Figure 5 (or Table II). For a quantitative determination of $\langle R^2 \rangle$ the relationship found by Hadjichristidis and co-workers[34] for dilute polyisoprene solutions

$$\langle R^2\rangle^{1/2}/nm = 0.08M_w^{1/2} \qquad (8)$$

is used. To apply this formula to the studied undiluted oligomeric melts, it has to be assumed, first, that the chain dimensions for dilute solutions and melts are similar, as was predicted by Flory and found for polystyrene melts using neutron scattering[35] and, second, that the characteristic ratio is independent of molecular weight. From calculations for poly(ethylene terephthalate) using the isomeric rotational state model, it turns out[33] that the second assumption is fulfilled for a degree of polymerization greater than approximately 10.

For the polyisoprene sample with the lowest molecular weight, PI-1, having a degree of polymerization of 15, eq 8 gives for $\langle R^2\rangle^{1/2}$ 2.9 nm. This value corresponds very well to the length scale for α relaxation obtained from the fluctuation approach to the glass transition.[20-22,31] This quantitative agreement gives more evidence that there exists a characteristic length scale for the α relaxation which is in the order of magnitude of 2–3 nm at the glass transition temperature T_g.

IV. Conclusions

The shape of the normal mode process shows a clear dependence on molecular weight where the extrapolation to the molecular weight of the repeating unit gives nearly the Debye limit. These experimental results support the model of cooperative rearrangement developed by Pakula and Geiler[29] for the normal mode process.

As with the poly(propyleneoxide) system,[20,21] it was found that also for polyisoprene the characteristic relaxation frequency $f_{p,\alpha}$ for the α relaxation shows a much stronger temperature dependence than that of $f_{p,n}$, the characteristic frequency of the normal mode process, as the temperature approaches the glass transition temperature. This means that the application of the Rouse model to the normal modes breaks down in the vicinity of the glass transition.

From a microscopic point of view this experimental result is discussed by assuming different temperature dependences of the two relevant length scales, the correlation length ξ for the α relaxation and the end-to-end vector of the polymer chain. A quantitative analysis gives more experimental evidence that the length scale for the α relaxation is in the order of magnitude of 2–3 nm predicted by the fluctuation approach to the glass transition.[22-24,32]

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References and Notes

(1) Ferry, J. D. *Viscoelastic Properties of Polymers*; Wiley: New York, 1980.
(2) Stockmayer, W. H.; Baur, M. E. *J. Am. Chem. Soc.* **1964**, *86*, 3485.
(3) Baur, M. E.; Stockmayer, W. H. *J. Chem. Phys.* **1965**, *43*, 4319.
(4) Stockmayer, W. H. *Pure Appl. Chem. Phys.* **1967**, *15*, 247.
(5) Adachi, K.; Kotaka, T. *Macromolecules* **1984**, *17*, 120.
(6) Adachi, K.; Kotaka, T. *Macromolecules* **1985**, *18*, 466.
(7) Adachi, K.; Kotaka, T. *J. Mol. Liq.* **1987**, *36*, 75.
(8) Adachi, K.; Kotaka, T. *Macromolecules* **1988**, *21*, 157.
(9) Boese, D.; Kremer, F. *Macromolecules* **1990**, *23*, 829.
(10) Stühn, B.; Stickel, F. *Macromolecules* **1992**, *25*, 5306.
(11) Rouse, P. E. *J. Chem. Phys.* **1953**, *21*, 1272.
(12) Vogel, H. *Phys. Z.* **1921**, *22*, 645.
(13) Fulcher, G. S. *J. Am. Ceram. Soc.* **1925**, *8*, 339.
(14) Tammann, G.; Hesse, W. *Z. Anorg. Allg. Chem.* **1926**, *156*, 245.
(15) Beevers, M. S.; Elliot, D. A.; Williams, G. *Polymer* **1979**, *20*, 785.
(16) Plazek, D. J.; O'Rourke, M. O. *J. Polym. Sci. A2* **1971**, *9*, 209.
(17) Plazek, D. J. *Polym. J.* **1980**, *12*, 43.
(18) Ngai, K. L.; Plazek, P. J. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 619.
(19) Ngai, K. L.; Plazek, P. J.; Deo, S. S. *Macromolecules* **1987**, *20*, 3047.
(20) Schlosser, E.; Schönhals, A. *Colloid Polym. Sci.* (in press).
(21) Ngai, K. L.; Schönhals, A.; Schlosser, E. *Macromolecules* **1992**, *25*, 4915.
(22) Donth, E. *Glasübergang*; Akademie Verlag: Berlin, 1981.
(23) Schick, C.; Donth, E. *Phys. Scr.* **1991**, *43*, 423.
(24) Fischer, E. W.; Donth, E.; Steffen, W. *Phys. Rev. Lett.* **1992**, *43*, 139.
(25) Kremer, F.; Boese, D.; Meier, G.; Fischer, E. W. *Prog. Colloid Polym. Sci.* **1989**, *80*, 129.
(26) Schlosser, E.; Schönhals, A. *Colloid Polym. Sci.* **1989**, *267*, 963.
(27) Havriliak, S.; Negami, S. *J. Polym. Sci., Polym. Symp.* **1966**, *14*, 89.
(28) Expanding the HN function for low and high frequencies compared to f_0, it becomes obvious that the limiting behavior is given by power laws. For this reason for the α relaxation a power law at low frequencies is added to consider the influence of the high-frequency tail of the normal mode relaxation ($-1 < \delta < 0$). On the other hand, for the normal mode a high-frequency power law is used to weight the low-frequency behavior of the α relaxation ($0 < \delta < 1$).
(29) Pakula, T.; Geiler, S. *Macromolecules* **1987**, *21*, 2909.
(30) Ngai, K. L.; Peng, S. L.; Skolnick, J. *Macromolecules* **1992**, *25*, 2184.
(31) Adam, G.; Gibbs, J. H. *J. Chem. Phys.* **1965**, *43*, 139.
(32) Schneider, K.; Schönhals, A.; Donth, E. *Acta Polym.* **1981**, *32*, 471.
(33) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Wiley: New York, 1969.
(34) Hadjichristidis, N.; Zhongde, X.; Fetters, L. J.; Roovers, J. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 743.
(35) Cotton, J. P.; Decker, D.; Benoit, H.; Farnoux, B.; Jannink, G.; Ober, R.; Picot, C.; des Cloizeaux, J. *Macromolecules* **1974**, *7*, 863.