

Evolution of the Dynamics in 1,4-Polyisoprene from a Nearly Constant Loss to a Johari–Goldstein β -Relaxation to the α -Relaxation

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ABSTRACT: The Johari–Goldstein (JG) secondary relaxation, presumed to be universal, has never been seen in 1,4-polyisoprene (PI) by dielectric spectroscopy, despite very many measurements extending over the past half-century. By using a high-resolution capacitance bridge, we are able to show the existence of a secondary relaxation in PI that has the properties of the JG process. Measurements were also carried out at lower temperatures, which probe the dynamics of chain units “caged” by neighboring segments comprising the local structure. The caged dynamics precede by decades of time the JG relaxation and, from general physical principles, are also expected to be a property of all glass-forming materials. Collectively, the caged dynamics and JG relaxation serve as precursors to structural relaxation (i.e., the glass transition) and thus are of central importance to understanding vitrification. The present data show that the dynamics of caged PI repeat units are manifested as a nearly constant loss (NCL). This NCL has been found in other glass-formers, both molecular and polymeric, and its temperature dependence in PI is similar to that for other materials. The experimental results are consistent with the predictions from the coupling model.

Introduction

Substances having diverse chemical and physical structures vitrify, with the glass transition phenomenon characterized by dynamic and thermodynamic properties common to all glass-formers. An immense amount of experimental data has been accumulated over the years, particularly on the structural α -relaxation; nevertheless, a consensus regarding a theory of the glass transition is lacking.^{1,2} Fundamental understanding requires examination of the dynamics that precede (earlier in time) the cooperative α -relaxation, since these faster processes serve as the precursor to structural relaxation. At early times, before either rotational or translational diffusion has transpired, molecular motions are confined to a “cage”, defined by the intermolecular potential of neighboring molecules. For molecular glass-formers, caging is effected by the neighboring molecules, while for polymers, a segment is caged by segments from other chains as well as repeat units from the same chain. In both cases, the caging is effected by intermolecular (intersegmental) repulsive forces. The short time dynamics within the cage, occurring before the onset of structural relaxation, are of fundamental interest. One familiar short-time process is the secondary relaxation, which is local (noncooperative) and thermally activated. However, at times shorter than the secondary relaxation, but longer than the Boson peak or Poley absorption,³ the motions of the caged molecules are not well understood. Herein, we refer to the processes in this regime as caged dynamics.

The best-known description of the caged dynamics is from mode coupling theory (MCT),⁴ based on nonlinear coupling of density fluctuations in condensed matter. According to MCT, the caged relaxation is the so-called

fast β -process, which transpires at temperatures above a critical temperature, T_c . When the time dependence of this β -process is Fourier transformed to a susceptibility, the imaginary part, $\chi''(\nu)$, has a minimum defined by two power laws, ν^{-b} and ν^a , on the respective low- and high-frequency sides. The exponents a and b are related by the equation $[\Gamma^2(1-a)/\Gamma(1-2a)] = [\Gamma^2(1+b)/\Gamma(1+2b)]$, where Γ is the gamma function. The susceptibility minimum has a frequency dependence that bears no resemblance to the loss associated with a relaxation process, and hence the fast β -process of MCT is not a relaxation in the conventional sense. Note that the MCT β -process is distinct from the above-mentioned secondary relaxations commonly observed in glass-formers; the latter are genuine relaxations, involving local rotation and/or translational diffusion (in MCT parlance, these comprise the slow β -process). According to MCT, the fast β -process is followed by the α -relaxation, described by the Kohlrausch–Williams–Watts (KWW) function

$$\phi(t) = \exp[-(t/\tau_\alpha)^{\beta_{\text{KWW}}}] \quad (1)$$

where τ_α is the α -relaxation time and β_{KWW} is a fraction less than unity.^{5,6} Thus, MCT regards its putative β -process to be the precursor of structural relaxation.

The MCT description of caged dynamics is restricted to temperatures above T_c . However, there exists a plethora of experimental data for both above and well below T_c , which must be reconciled with any theoretical description. At lower temperatures, the duration over which molecules are caged is extended because the primary and secondary relaxations that cause decay of the cage are slower. Since the caged dynamics continues to longer times at lower temperatures, it should be experimentally observable over a wider frequency range at $T < T_c$ than for $T > T_c$. Dielectric data for both small molecules and polymers show^{7–12} that at lower temperatures the caged dynamics can be described by a slowly

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decreasing function of frequency, $\sim\nu^{-\lambda}$ (where λ is a small positive exponent), or as a logarithmic function of ν . Similar behavior is found in glassy, molten, and even crystalline ionic conductors for temperatures at which the ions are caged and thus unable to move to another site in the experimental time range.⁷ The variation of this dispersion with frequency is very weak, and hence, in the field of ionic conductors, it is referred to as the nearly constant loss (NCL). A good example is the glass-forming molten salt, $0.4\text{Ca}(\text{NO}_3)_2-0.6\text{KNO}_3$ (CKN), which is both a glass-former and an ionic conductor.⁷

The observation of the NCL in glass-formers is not limited to dielectric relaxation measurements. Dynamic light scattering experiments on polyisobutylene,¹³ poly-(methyl methacrylate),¹⁴ and glycerol¹⁴ have revealed a nearly constant loss in the imaginary part of both the depolarized and polarized susceptibilities, $\chi''(\nu)$, at high frequencies ($\geq\text{GHz}$) for temperatures ranging from below T_g to near or above T_c . Studies of several organic glass-forming liquids¹⁵ found a power law decay of the optical Kerr effect response given by t^{-1+c} , where $c \approx 0.1$ at temperatures below the T_c of MCT. Since the optical Kerr effect signal is the Fourier transform of the imaginary part of the susceptibility,¹⁵ the latter is a nearly constant loss.

At high temperatures, NCL as a background loss can give rise to a minimum in the susceptibility, having ν^{-b} and ν^a dependences on the low- and high-frequency sides. This occurs at high temperatures (such as above T_c), when τ_α becomes short. Then, the temporal extent of the NCL is reduced by the encroaching high-frequency flank of the α -loss peak, which has a $\nu^{-\beta_{\text{KWW}}}$ dependence on the low-frequency side (viz., the one-sided Fourier transform of eq 1), which can give rise to the ν^{-b} dependence of the susceptibility minimum. On the high-frequency side, there is always a contribution from the low-frequency flank of the Boson peak or Poley absorption. Thus, the structural relaxation at high temperatures (for which τ_α is typically on the order of nanoseconds), in combination with the Boson peak and the NCL, can yield a minimum in the susceptibility, as observed by dielectric, neutron, and light scattering experiments at sufficiently high temperatures.⁴ This explains why τ_α invariably has this magnitude ($\sim 10^{-9}$ s) at T_c , where T_c is obtained by extrapolation of the MCT scaling laws. It is also obvious that the susceptibility minimum predicted by the standard MCT cannot account for the NCL.

At T_c and above, with τ_α in the range of nanoseconds, all nontrivial secondary relaxations have merged with the α -relaxation. Under these conditions, the claim of MCT that the caged dynamics is the precursor of the α -relaxation has validity. However, at lower temperatures, the secondary relaxation and the α -relaxation become well-separated in time. Since the secondary relaxation falls intermediate in time between the faster caged dynamics and the slower α -relaxation, evidently the secondary relaxation must play some role in the development of the α -relaxation. However, it is not uncommon, particularly in studies of polymers, to regard the secondary β -relaxations as having no role in the glass transition. This idea is justified for those β -relaxations involving intramolecular degrees of freedom; i.e., isolated motion of only some atoms in a flexible chain, such as any pendant groups. However, Johari and Goldstein (JG) showed that this is not generally the

case, by their discovery of β -relaxations in glass-formers comprised of completely rigid molecules.¹⁶⁻¹⁸ This intriguing finding implies that some β -relaxations reflect local motions involving essentially the entire molecule,¹⁹ and it is these secondary relaxations which are denoted Johari–Goldstein (JG) relaxations.²⁰⁻³⁸ For polymers without side groups, such as 1,4-polybutadiene, the β -relaxation obviously belongs to this category. In some polymers having pendant groups, for example poly-(methyl methacrylate) (PMMA) and poly(ethyl methacrylate) (PEMA), the secondary relaxations have been shown to entail motion of a side group, together with small-angle rocking of a portion of the chain backbone;^{39,40} thus, essentially all atoms of the repeat unit participate, and thus the motion is a JG process. JG relaxations serve as the precursor of the α -relaxation, in accord with experimental data showing the existence of various relations between the dynamic and thermodynamic properties of JG relaxation and the α -relaxation.^{8,9,23,34,41} One example is the anticorrelation of the fractional exponent β_{KWW} for the structural relaxation (eq 1) with $(\log \tau_\alpha - \log \tau_\beta)$, where τ_β is the JG relaxation time.^{23,41}

The existence of the JG relaxation is considered to be universal among glass-formers.¹⁶⁻¹⁸ Likewise, caged dynamics, manifested as the NCL, may be regarded as a general property of glass-formers. In this work, we consider a glass-former, 1,4-polyisoprene, for which neither the JG relaxation nor the NCL has been reported in previous relaxation studies.⁴²⁻⁵⁸ From broadband relaxation measurements under optimal conditions, we show that these two features of the dynamics do indeed exist in PI. Moreover, the respective temperature dependences of the JG relaxation time and the dielectric strength, $\Delta\epsilon_\beta$, as well as the NCL, are all in accord with the properties of these processes seen in other glass-formers. The results are compared with the predictions from the coupling model.^{7-9,19}

Experimental Section

The linear 1,4-polyisoprene (high cis), obtained from A.F. Halasa of the Goodyear Tire & Rubber Co., was prepared by anionic polymerization using *n*-butyllithium initiator. The nominal molecular weight was 500 000 Da, and the calorimetric $T_g \approx 203$ K. Isothermal dielectric spectra were measured over the frequency range 10 Hz–100 kHz using a CGA-83 capacitance measuring assembly. (This instrument is a prototype of the commercially available Andeen-Hagerling capacitance bridge.) The measurements employed a cell similar to that described elsewhere,⁵⁹ but with a solid 2 mm piece of brass used as the “high” electrode. This cell was mounted on a coldfinger of a Precision Cryogenics dewar, and the temperature was controlled using a LakeShore Cryotronics DRC 82C temperature controller. Other measurements were made using an IMass Inc. time domain dielectric spectrometer, having a frequency range of 10^{-4} – 10^4 Hz, in combination with a Delta Design 9023 liquid nitrogen cooled oven. A parallel plate geometry (25 mm diameter with sample thickness between 0.05 and 0.15 mm) was employed, with a guard ring on the detector side. Samples were allowed to equilibrate at least 1 h after attaining the desired temperature, with replicate measurements used to ensure thermal equilibration.

Results and Discussion

Johari–Goldstein Relaxation. The complex dielectric susceptibility of the prominent α -relaxation is routinely measured using conventional dielectric instruments. Shown in Figure 1 are the data obtained using

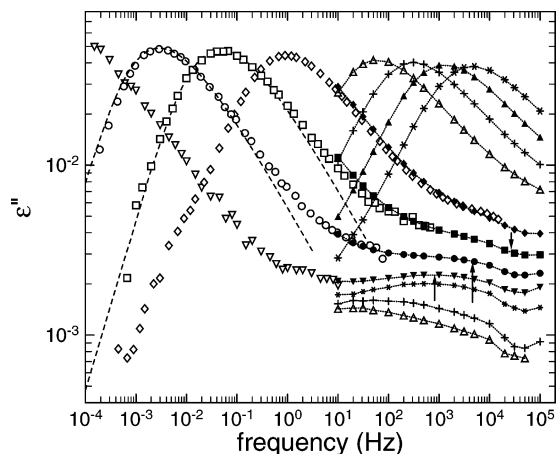


Figure 1. Dielectric loss spectra of PI. The data at 216.0 (\diamond), 211.15 (\square), 208.15 (\circ), and 204.15 K (∇) were obtained using the IMass time domain dielectric analyzer. All the other data, which start at 10 Hz and continue up to 100 kHz, were taken with the CGA-83 capacitance bridge. There is good agreement of the CGA-83 data at 216.7 (\blacklozenge), 212.7 (\blacksquare), 208.7 (\bullet), and 204.7 K (\blacktriangledown) with the IMass data at 216.0 (\diamond), 211.15 (\square), 208.15 (\circ), and 204.15 K (∇), respectively, after the latter have been shifted horizontally by an amount determined from the VFTH (eq 2) temperature dependence of the α -relaxation frequency (see Figure 2) to account for the slight differences in temperature. The other eight spectra were obtained only using the CGA-83. The spectra that show α -loss maxima correspond (from right to left) to $T = 236.7$ (*), 232.7 (\blacktriangle), 228.7 (+), and 224.7 K (\triangle). The lower three CGA-83 curves, which show β -loss peaks, were taken (starting from the bottom) at 169.7 (\triangle), 181.7 (+), and 200.7 K (*). The vertical arrows mark the locations of the calculated primitive relaxation frequencies, ν_0 , at (from right to left) 212.7 (\blacksquare), 208.7 (\bullet), and 204.7 K (\blacktriangledown). The locations of these ν_0 should be compared with the secondary relaxation peaks at these temperatures.

the IMass time domain dielectric analyzer at 216.0 (\diamond), 211.15 (\square), 208.15 (\circ), and 204.15 K (∇). At each of these temperatures, the data were obtained for frequencies up to 10^4 Hz. However, the losses at the higher frequencies are low and exhibit large scatter, particularly at lower temperatures. Consequently, no useful information is obtained for frequencies much beyond ν_{α} , the frequency at the maximum of the α -loss peak. For this reason, the data in Figure 1 have been truncated. To probe the response at higher frequencies, we employ the high-precision CGA-83 capacitance bridge. Note that these data, over the frequency range 10 Hz–100 kHz, exhibit no appreciable scatter at any temperature (Figure 1). The α -relaxation measurements from the two instruments agree to within the experimental error.

The dielectric α -relaxation times defined as the reciprocal of the angular frequency at the loss maximum ($1/(2\pi\nu_{\alpha})$), which is somewhat larger than the τ_{α} defined by eq 1) are shown in an Arrhenius plot in Figure 2, along with the fit to the Vogel–Fulcher–Tammann–Hesse (VFTH) equation⁶⁰

$$\log \tau_{\alpha} = -14.35 + \frac{721.3}{T - 163.24} \quad (2)$$

The dielectric T_g , defined by $\tau_{\alpha}(T_g) = 100$ s, is 207.4 K. There is a small (ca. 0.5 deg) temperature difference between the two experiments; however, the CGA-83 data at 216.7 (\blacklozenge), 212.7 (\bullet), 208.7 (\blacksquare), and 204.7 K (\blacktriangledown) match well the IMass data at 216.0 (\diamond), 211.15 (\square), 208.15 (\circ), and 204.15 K (∇). These small differences are corrected by shifting the IMass loss data for each

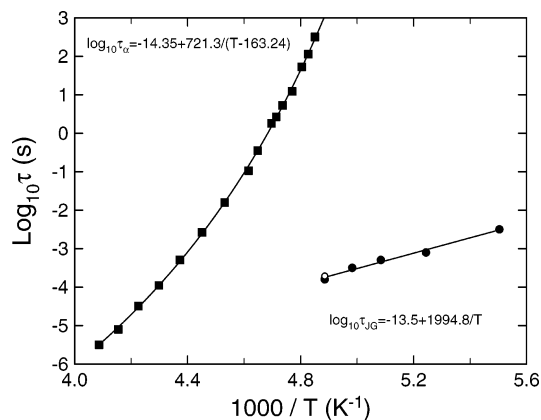


Figure 2. Temperature dependence of the α -relaxation (\blacksquare) and JG β -relaxation (\bullet) times in PI, along with the respective VFTH and Arrhenius fits. The single open circle is the calculated primitive relaxation time at 204.7 K.

temperature horizontally along the frequency axis, with the amount of the shift determined from the VFTH equation. For example, the 216.0 K IMass data are shifted 0.179 decade toward higher frequency in order to match the CGA-83 measurements at 216.7 K.

It is evident from these spectra that a secondary relaxation is present on the high-frequency side of the α -peak. This secondary relaxation appears as a shoulder at 212.7 K and becomes a broad peak at 208.7 K and lower temperatures. Note that given the weakness of the secondary relaxation in PI, its observation would be very difficult using a conventional dielectric instrument. This explains why it was undetected in all previous dielectric studies of PI, including our own.^{42–58}

Although the data at 216.7, 212.7, and 208.7 K indicate a secondary relaxation is present, a characteristic β frequency cannot be deduced from the broad shoulder in $\epsilon''(\nu)$. At lower temperatures, below T_g , the shoulder evolves into a distinct peak with a peak frequency ν_{β} . The peak relaxation times, $\tau_{\beta} = 1/(2\pi\nu_{\beta})$, are plotted in Figure 2, along with the fit to the Arrhenius equation

$$\log \tau_{\beta} = -13.5 + \frac{1995}{T} \quad (3)$$

The activation enthalpy $E_{\beta} = 38.2$ kJ/mol. The only pendant moiety in PI is the methyl group, whose rotation is very fast at temperatures above T_g , with an activation enthalpy much smaller than the 38.2 kJ/mol we find herein.⁶¹ A mechanical secondary relaxation was reported for PI,⁶² with a relaxation time 3 orders of magnitude faster than the τ_{β} in Figure 2 and having a much weaker temperature dependence. This process is thus more local and not the JG relaxation, since the slower motion involves all atoms of the repeat unit. The E_{β} determined herein for PI is nearly the same as the value of 35.7 kJ/mol reported for the secondary relaxation of 1,4-polybutadiene,²⁴ which is known to be a JG β -relaxation. All indications are that the secondary relaxation of PI involves motion of the entire repeat unit and thus can be classified as a Johari–Goldstein β -relaxation.

The JG process is related to the α -relaxation, as can be demonstrated by a relationship from the coupling model (CM).^{8,9,63–65} Similar to the JG relaxation, the primitive (independent) relaxation of the CM entails motion of the entire molecule and is not cooperative. Thus, the primitive relaxation time, τ_0 , of the model is

expected to be close to the most probable relaxation time of the JG relaxation for any given temperature. The CM's conception of the evolution of the dynamics^{8,9} differs from the conventional view that the JG relaxation is comprised of a broad symmetric distribution of relaxation times, additional to the α -relaxation. At a given temperature and pressure P

$$\tau_{\beta}(T,P) \approx \tau_0(T,P) \quad (4)$$

where τ_0 is calculated from the α -relaxation time by the CM relation^{8,9,63,64}

$$\tau_0 = (t_c)^{1-\beta_{\text{KWW}}}(\tau_{\alpha})^{\beta_{\text{KWW}}} \quad (5)$$

where β_{KWW} (eq 1) describes the time dependence of the α -relaxation and t_c ($\sim 2 \times 10^{-12}$ s) is the characteristic time for the onset of intermolecular cooperativity.⁶⁵ Previous works on various glass-formers have shown that for genuine JG β -relaxations $\tau_{\beta} \approx \tau_0$.^{7-9,19,66} This relation between τ_{β} and τ_0 is striking, in that the former is an experimentally determined quantity, while the latter is calculated via eq 5 using only parameters of the α -relaxation, e.g., τ_{α} and β_{KWW} .

Equation 4 can be tested against the data for PI. First, we fit the asymmetric α -loss peaks at 212.7 and 208.7 K (Figure 1), and two other temperatures, 207.15 and 209.65 K (not shown), to the one-sided Fourier transform of eq 1. This yields $\beta_{\text{KWW}} = 0.47$ independent of temperature (as shown for 212.7 and 208.7 K as dashed lines in Figure 1). Interestingly, the α -loss peak at higher temperatures broadens on the low-frequency side to become nearly symmetric. This behavior is anomalous (in the absence of a conductivity contribution) and is not seen in the dielectric spectra of other polymeric or nonpolymeric glass formers. The broadening is reproducible, both herein using either instrument (Figure 1) and as seen in previous measurements on other 1,4-polyisoprene samples.⁶⁷ The cause of this behavior is unclear, but it may be related to the presence of a dipole moment parallel to the PI chain backbone. It is known that sub-Rouse modes^{68,69} can intrude on the local segmental mode (i.e., the α -relaxation), affecting the apparent shape of the latter. However, this would not explain why the effect is noted herein at higher temperatures only.

Focusing on the fits to the KWW function at 212.7 and 208.7 K, which yield $\beta_{\text{KWW}} = 0.47$, τ_0 is calculated using eq 5 from the τ_{α} at 212.7, 208.7, and 204.7 K. The frequency $\nu_0 = 1/(2\pi\tau_0)$ for each temperature is indicated in Figure 1 by a vertical arrow. For $T = 212.7$ and 208.7 K, the calculated ν_0 is located on the broad shoulder of the JG β -relaxation. For $T = 204.7$ K, ν_0 is near the secondary relaxation peak maximum. This agreement between τ_0 and τ_{β} at 204.7 K is shown in Figure 2 by the location of the single datum (open circle), representing the logarithm of the calculated τ_0 for this temperature. The equivalence of τ_{β} and τ_0 is consistent with the prediction of the coupling model and supports the designation of the observed secondary relaxation in PI as a JG relaxation. Thus, it serves as the precursor to the α -relaxation.

Caged Relaxation: The Nearly Constant Loss. For glass-formers such as PI that have a resolved JG relaxation, the combined dispersions of the α - and β -processes for the equilibrium liquid occupy many decades of frequency. Hence, measurements at frequencies much higher than available herein would be neces-

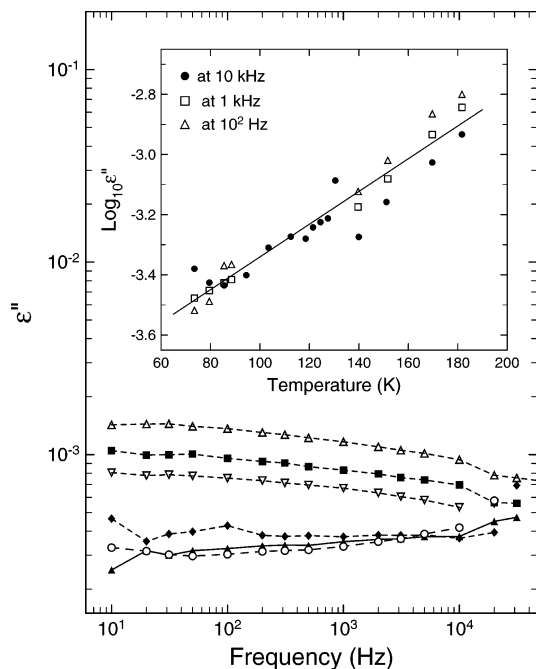


Figure 3. The nearly constant loss measured by the CGA-83 in PI at representative temperatures below T_g . From top to bottom: 169.7 (Δ), 151.7 (\blacksquare), 139.7 (∇), 85.5 (\blacklozenge), 79.5 (\triangle), and 73.5 K (\circ). The inset shows the nearly constant loss as a function of temperature at 0.10, 1, and 10 kHz. The line is a least-squares fit to all data points, which has a slope equal to -184 K^{-1} .

sary to study the shorter-time caged dynamics in PI. Accordingly, to probe the caged dynamics, measurements were made at lower temperatures, below T_g , for which the α - and β -relaxations have moved beyond the lowest available frequencies. The dielectric loss at these lower temperatures is small, necessitating again the use of the CGA-83. The main part of Figure 3 shows the data collected at 169.7 K and several representative lower temperatures. The dispersions are so flat that they are appropriately referred to as the nearly constant loss. The data collected at the three lower temperatures, 85.5, 79.5, and 73.5 K, show some scatter. These ϵ'' data show a slight increase with frequency, rather than the decrease, as seen at higher temperatures. Evidently, there is another process contributing at high frequencies at these lower temperatures. Nevertheless, the variation of ϵ'' is so weak that the loss reflects mainly the NCL. Overall, the weak frequency dependence of ϵ'' of the data in Figure 3 is similar to the NCL found in molecular glass-formers.^{7,8,10,12,29,70-72}

From the data taken at different temperatures, we determined ϵ'' of the NCL at three frequencies: 0.1, 1, and 10 kHz. These values are plotted as $\log \epsilon''$ vs temperature in the inset to Figure 3. The solid line represents the least-squares fit of all the data points, suggesting that the NCL has a temperature dependence given by

$$\epsilon''(T) = 0.456 \exp\left(\frac{T}{79.8}\right) \quad (6)$$

in the temperature range of Figure 3. This weak variation with temperature of the NCL in glassy PI recalls similar behavior found in small molecule glass-formers at temperatures below T_g . The NCL for the latter has a temperature dependence of

$$\epsilon''(T) \propto \exp(T/T_f) \quad (7)$$

with $T_f \approx 33$ K.^{29,70} The same temperature dependence (eq 7) has been found for the NCL in glassy ionic conductors⁷³ and explained^{7,73} in the framework of the coupling model. A similar explanation when applied to caged molecular dynamics readily accounts for the temperature dependence of the NCL in PI and small molecule glass-formers, as given by eqs 6 and 7.

Recently, Sokolov and co-workers⁷⁴ carried out dynamic light scattering measurements on PI in the gigahertz to terahertz range, at temperatures from about 153 K to about 240 K. The spectral range is much higher than that of the dielectric instruments used herein, and accordingly the measured temperature range was higher. Sokolov et al.⁷⁴ observed the NCL in the susceptibility spectra of the glassy state ($T < T_g$), having a frequency dependence of $\chi''(\nu) \propto \nu^{-0.15}$ and a weak temperature dependence. These results are consistent with the behavior at lower temperature reported herein, supporting our identification of the dielectric loss in Figure 3 as originating from the caged dynamics manifested as the NCL. At temperatures above T_g , the NCL is much more sensitive to temperature, suggesting that it "senses" the glass transition. Such interesting behavior can be interpreted using the coupling model.⁷⁵

Conclusions

Among amorphous polymers, PI has been widely studied, both dielectrically and mechanically, by many workers.^{42–58} The spectra show only the local segmental mode (i.e., the α -peak in the dielectric spectrum) and the normal modes. No evidence of the presence of a secondary relaxation has been reported (note the trivial methyl group rotation is dielectrically inactive). On the other hand, the works of Johari and Goldstein^{16–18} and others^{20–38} indicate that a secondary relaxation of the Johari–Goldstein kind is universal, existing in all glass-formers. This apparent conundrum is resolved from our dielectric loss measurements with greater sensitivity and resolution than heretofore, leading to the discovery that a weak JG relaxation is indeed present in PI. Our conclusion that this β -relaxation is a genuine JG process is consistent with the fact that its activation enthalpy in the glassy state is quite close to the value for the JG relaxation in 1,4-polybutadiene (a polymer without side groups, whereby the secondary relaxation necessarily involves the entire repeat unit). Additional support for the identification of the β -peak in PI as a JG process is the correspondence between the most probable relaxation time, τ_β , and the primitive relaxation time of the coupling model, τ_0 . Conformance to eq 4 has been shown previously for Johari–Goldstein relaxations in other glass-formers.^{8,9,19,66}

At times prior to τ_β , the PI segments remain caged, and the dielectric spectra reflect the dynamics constrained within the cage, which has the form of a NCL. Recent experiments using dielectric relaxation,^{7–12,72} scattering,^{13,14} and the optical Kerr effect¹⁵ have all shown that the NCL is quite general, having been observed in inorganic, polymeric, and small molecule glass-formers. We find herein that the intensity of the NCL in PI at temperatures below T_g has a weak temperature dependence, in accord with eq 7 and the behavior of other glass-formers and glassy ionic conductors. Our identification of the NCL in PI is corroborated by recent dynamic light scattering measurements in the

gigahertz to terahertz range on the same polymer.⁷⁴ At these higher frequencies, the light scattering data reveal that the NCL exists not only in the temperature range of the present experiments but also at temperatures up to ca. 20% above T_g .

Notes Added in Proof. After the present paper was in the publication stage, an extension of the standard MCT appeared [Götze, W.; Sperl, M., cond-mat/0401536; <http://lanl.arXiv.org>], with a nearly logarithmic decay of the correlation function obtained for temperatures near the MCT critical temperature T_c . Although this extension addresses the NCL phenomena near T_c , MCT still does not account for the NCL at temperatures well below T_c , as observed herein for PI.

We recently became aware of a review article by Rault [Rault, *J. Non-Cryst. Solids* **2000**, 271, 177] reporting a secondary β -process in PI. Although ref 62 herein was cited by Rault as the source for this information, the original work was actually by Pechhold and Blasenbrey [Pechhold, W.; Blasenbrey, S. *Kautsch. Gummi Kunstst.* **1972**, 25, 195], who found a " γ -relaxation" in mechanical measurements on semicrystalline PI.

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