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Sub-Rouse Modes in Polymers Observed by Dielectric Spectroscopy

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ABSTRACT: One of the characteristic features of polymer dynamics is the existence of additional relaxation processes that are related to connectivity of monomers in polymer chain and are absent in small molecular liquids. These processes are usually described as purely entropic Rouse modes and appear on time scales much longer than segmental (structural) relaxation in polymers. They are commonly observed by mechanical relaxation spectroscopy and are detected as normal modes in dielectric spectra of some polymers (where dipole moment accumulates along the chain). Here we present the evidence of additional modes that appear in dielectric relaxation spectra of some polymers between the segmental and Rouse modes. We identified these modes as sub-Rouse modes, the same as those previously found by mechanical spectroscopy. We also demonstrate that these modes are not detected in the dielectric loss spectra of many polymers. Moreover, existence of these modes does not correlate with the existence of dipole moment along the polymer chain. A possible explanation of this behavior is discussed.

1. Introduction

Similar to other glass-forming systems, polymers have local secondary relaxation(s) and primary (local segmental) relaxation, which is responsible for the glass transition. The primary relaxation is the result of cooperative motions of repeat units of different chains in some cooperatively rearranging volume, believed to be a few nanometer size at temperatures near T_g.[1] Because of chain connectivity, there are additional relaxation modes with characteristic times longer than the primary relaxation and involving more repeat units along a single chain. When considering the viscoelasticity of a high molecular weight uncross-linked polymer, the chain modes are responsible for the observed softening dispersion (or the glass−rubber transition region), the rubbery plateau, and the terminal relaxation and flow.[2] For a low molecular weight and unentangled polymer, there is no rubbery plateau but still the chain modes account for the viscoelastic response at times beyond the primary relaxation. The Rouse model generalized to undiluted polymers has proven to offer adequate description of the chain modes in unentangled polymers as well as the high compliance part of the softening dispersion of entangled polymers. In this model, a polymer chain is represented as a sequence of n equivalent randomly oriented subchains. Each subchain contains a sufficient number of repeat units such that configurational rearrangements within the submolecule are fast compared with the time scale under consideration and the end-to-end distribution of each of these subchains is Gaussian. The usual normal-coordinate analysis leads to a series of n normal modes of motion with purely entropic nature, each of which has an exponential correlation function, $\exp(-t/\tau_p)$, where τ_p is the relaxation time governing motions of the pth mode and $p = 1, 2, ..., n$.

Dielectric spectroscopy has been used routinely to observe the primary relaxation of many polymers. In addition to the primary relaxation, normal modes with longer relaxation times have been observed in a few polymers, such as poly(propylene glycol),[3] polyisoprene,[4,5] poly(oxybutylene),[6] poly(hexyl isocyanate),[7] and poly(styrene oxide),[8] that have a component of the dipole moment parallel to the polymer chain backbone. So far, no dielectric relaxation study has reported observation of any additional modes in between the normal modes and the segmental relaxation. Moreover, in amorphous polymers as well as in small molecular glass-formers, the shape of the dielectric loss peak of the structural relaxation was reported to be asymmetric and with the low-frequency side varying linearly with frequency, i.e., $\varepsilon''(\nu) \propto \nu$. In this paper, we report dielectric relaxation measurements in high molecular weight poly(isobutylene) (PIB) and polyisoprene (PIP) that show the presence of the additional modes at frequencies lower than the segmental loss maximum. Following the nomenclature proposed by Santangelo et al.,[9] we ascribe these modes to sub-Rouse relaxation. In the case of PIB, dielectric measurements were made also on the historic NBS-PIB sample in which the sub-Rouse modes were found previously by mechanical measurements.[10−12] From the collection of our dielectric relaxation data and analysis of literature data, it is clear that many other polymers do not exhibit sub-Rouse modes in the dielectric relaxation spectra. Moreover, our analysis suggests that the appearance of the sub-Rouse modes in the dielectric spectra is not connected directly to accumulation of the dipole moment along the chain. A possible explanation is given.

2. Experimental Section

Two samples of PIB were used in this study. One is from the original 1949 batch distributed by Marvin from the U.S. National Bureau of Standards, NBS (now NIST). This sample is referred to as NBS-PIB ($M_w = 1.56 \times 10^6$). The NBS-PIB sample we used came from D. J. Plazek at the University of Pittsburgh. It was stored in a freezer since received in 1949. The absence of unsaturation in PIB makes the polymer quite resistant to degradation. Creep measurements of its terminal zone behavior carried out in 1995[10] verified that the material has not changed over the past 50 years. This test indicated the NBS-PIB sample we measured undergoes no change when stored until the present

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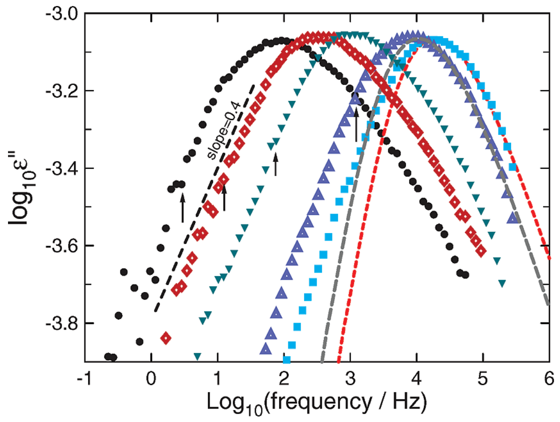

Figure 1. Loss spectra of NBS-PIB for different temperatures. Arrows indicate position of the sub-Rouse modes estimated from mechanical spectroscopy data.

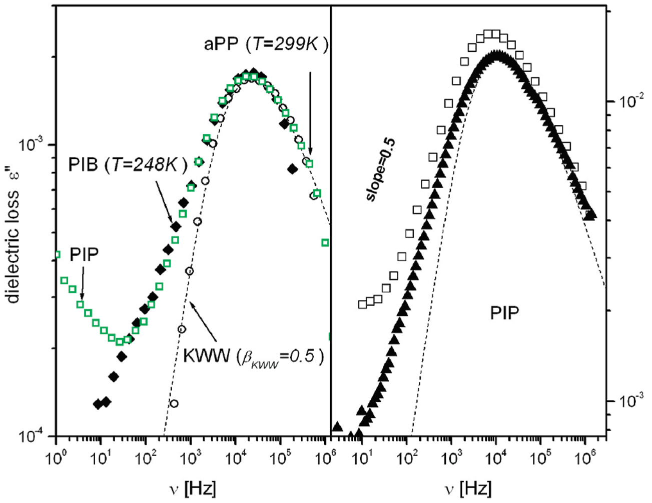

Figure 2. Left panel: loss spectra of PIP (open squares), PIB (filled diamonds), and aPP (open circles) measured for the same segmental relaxation time. Dashed line represents the KWW fit with $\beta_{\mathrm{KWW}} = 0.5$. Right panel: dielectric loss spectra of PIP with two molecular weights, 138k (empty squares) and 1 million (filled triangles), measured for the same segmental relaxation time.

times. The exact polydispersity of the NBS-PIB is not known, except that it is quite monodisperse as we were told. In any case, our interest in the present work on PIB is limited to the sub-Rouse relaxation at frequencies not far below the local segmental relaxation, and polydispersity at so high molecular weight should have no effect on the results. Another PIB sample (synthesized at the University of Akron) has the molecular weight $M_{\mathrm{n}} = 12\,200$ and very low polydispersity $M_{\mathrm{w}}/M_{\mathrm{n}} = 1.02$. Two PIP samples are from commercial source (Polymer Source) and have molecular weights of $M_{\mathrm{n}} = 10^6$ (polydispersity index = 1.05) and 138 000 (polydispersity index = 1.01). Polystyrene samples (Scientific Polymer) have $M_{\mathrm{n}} = 540$ (polydispersity index = 1.07) and $M_{\mathrm{n}} = 205\,000$ (polydispersity index = 1.08), respectively. For atactic polypropylene dielectric results were obtained for the same sample as used by Ediger for NMR measurements.[13] Polycaprolactone (PCL) sample from Sigma-Aldrich has $M_{\mathrm{n}} = 200\,000$. All samples were used as received without further purification.

Dielectric measurements were performed using a Novocontrol Alpha impedance analyzer in the frequency range from 1 mHz to 3 MHz at different temperatures. Liquid samples (low-M_{n} polymers) were placed into a parallel-plate capacitor with 20 mm diameter, and glass fibers with 40 μm diameter were used as spacers between the electrodes. The PCL sample was melted at ca. 333 K inside the capacitor. All other high-M_{n} polymers were in the form of amorphous wax and were placed inside the capacitor and slightly pressurized (with pressure of ca. 1 MPa). The sample capacitor was mounted in the fixture and placed in the cryostat. The temperature control was achieved through Novocontrol Quatro Cryosystem, and data analysis was performed using the Novocontrol WinFit program.

The shape of the segmental relaxation of polymers is invariably wider than for a Debye process. The asymmetrically broadened frequency dispersion of the dielectric spectrum, originating from the interactions between repeat units, is fitted by the one sided Fourier transforms of the Kohlrausch−Williams−Watts (KWW) function:[14,15]

$$\phi(t) = \exp\left[-(t/\tau)^{\beta_{\mathrm{KWW}}}\right], \quad 0 < \beta_{\mathrm{KWW}} \leq 1 \qquad (1)$$

3. Results

Isothermal dielectric loss data of NBS-PIB at several temperatures above T_{g} are presented in Figure 1. The loss peak of the primary (segmental) relaxation is obviously broadened on the low-frequency side. Normally, the low-frequency side of the dielectric loss spectrum of structural relaxation is well approximated by the linear dependence on frequency: $\varepsilon''(\nu) \propto \nu$. Surprisingly, the PIB spectra exhibit the low-frequency slope with sublinear frequency dependence, $\varepsilon''(\nu) \propto \nu^{\alpha}$, with the exponent $\alpha \sim 0.4$ (Figure 1). This exponent seems to be independent of temperature, at least in the temperature range from 213 to 258 K.

Similar stretching of the low-frequency side of the segmental spectrum is observed in PIB sample with $M_{\mathrm{n}} = 12\,200$ (Figure 2). Both PIP samples also show strongly stretched low-frequency flank of the local segmental loss spectrum with the exponent $\alpha \sim 0.5$. PIP belongs to the family of polymers for which the normal-mode process is also detected in the dielectric spectra. The rise of the loss with decreasing frequency starting at about 20 Hz in Figure 2a is due to the onset of contribution from the chain (Rouse) normal modes. The low-frequency flank of the local segmental relaxation can be seen even better in the spectra of higher M_{n} sample because the rise of the loss caused by the chain modes is shifted to lower frequency (Figure 2b). Again, the low-frequency flank of the local segmental relaxation is broadened as it is in PIB spectra.

On the other hand, the a-PP spectrum exhibits the usual behavior, i.e., asymmetric loss peak, skew toward high-frequencies, and the low-frequency flank has with the slope $\alpha \sim 1$ (Figure 2a). The same slope $\alpha \sim 1$ is observed in the dielectric loss spectra of PS at low and high molecular weight as well as in the spectra of polycaprolactone (PCL) (Figure 3). We emphasize that PCL also belongs to the same class of polymers as PIP, where the dipole moment accumulates along the chain, and normal (chain) modes appear in the dielectric relaxation spectra. Yet, no stretching is visible on the low-frequency side of the loss peak (see inset in Figure 3).

4. Discussion

Loss spectrum of the primary (structural) relaxation in small molecular systems usually has asymmetric shape with high-frequency tail having sublinear frequency dependence and linear frequency dependence on the low-frequency side. In the case of polymers, additional relaxation (chain modes) appears at frequencies significantly below the primary (local segmental) relaxation. These modes exist due to chain connectivity in polymer molecules. It is expected, however, that the local segmental relaxation in polymers should be similar to the structural relaxation in small molecules. Our analysis (Figures 2 and 3) shows that some polymers indeed have dielectric spectrum of segmental relaxation similar to small molecules with no stretching on the

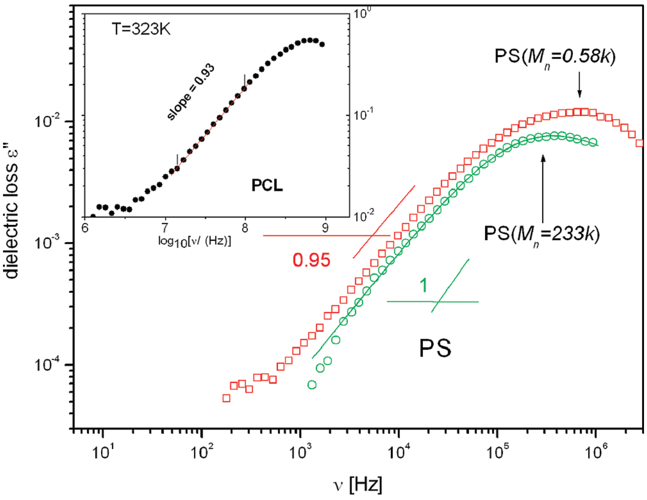

Figure 3. Dielectric loss spectra of PS with two molecular weights, 233K (T = 433 K) and 580 (T = 313 K), measured for the same segmental relaxation time. Inset shows spectrum measured in PCL at T = 323 K.

low-frequency side. The dielectric loss peaks in polymers, such as poly(vinyl acetate), poly(methylphenylsiloxane), poly(methyl-*p*-tolylsiloxane), a-PP, PS, poly(vinyl methyl ether), and BPA-polycarbonate, all have asymmetric shapes that are skew toward high frequencies and have linear frequency variation of $\varepsilon''(\nu)$ on the low-frequency side.[16−22]

However, some polymers show stretched low-frequency slope. So, there must be an additional relaxation between the local segmental and the Rouse modes in these polymers, which is appropriately called sub-Rouse modes. The existence of sub-Rouse modes with length- and time-scale intermediate between local segmental motion, and Rouse modes were proposed and observed in PIB some time ago using mechanical spectroscopy and photon correlation spectroscopy.[10,11] Until now, there has been no report on the observation of the sub-Rouse modes in dielectric spectra. The dielectric relaxation data presented above for PIB and PIP show beyond any doubt the existence of a relaxation process slower than the primary relaxation but faster than the Rouse modes.

The natural question is why PIB and PIP are exceptional in showing the sub-Rouse modes in dielectric relaxation measurements, while aPP, PS, PMPS, poly(methyl-*p*-tolylsiloxane) (PMpTS),[16−20] and many other polymers do not? On the other hand, we know at least for some of these polymers that photon correlation spectroscopy can detect the sub-Rouse modes. For PMPS, there are several such examples including studies on samples with M_w = 4400,[23,24] M_w = 5000,[25] and M_w = 10 500.[15] For PMpTS, photon correlation experiments have found a slower relaxation process than the primary relaxation for samples with M_w = 4500, 15 000, and 42 000 g/mol.[16] Another example from the photon correlation spectroscopy is poly(cyclohexyl methacrylate) plasticized by up to 15% of dioctyl phthalate.[26] Photon correlation spectroscopy had observed the sub-Rouse mode in PIB as well.[10] Creep compliance measurements by Plazek and co-workers on the low-molecular-weight amorphous polymers including polystyrene invariably see the sub-Rouse modes appearing at compliances higher than the maximum value contributed by the primary relaxation.[11] Thus, sub-Rouse mode can be observed more generally for different polymers by photon correlation spectroscopy and mechanical spectroscopy, while dielectric relaxation so far detect this mode in PIB and PIP only.

Here we offer the following rationalization of these experimental facts based on two conditions involving the ordering of dipole moment in polymer chain and the degree of tacticity. Since the sub-Rouse mode involves concerted motion of several repeat units along the chain, its observation by dielectric relaxation depends on existence of resultant dipole moment different from zero value. Because both the Rouse and the sub-Rouse modes are observed for the PIP, it is tempting to assume that both have the same molecular origin related to the component of the dipole moments parallel to the polymer backbone. However, in the case of PIB, chain modes are not detected dielectrically and only the sub-Rouse mode is observed in the dielectric loss spectra. Moreover, in the case of polycaprolactone the Rouse mode is dielectrically observed whereas the sub-Rouse mode is absent (Figure 3). These facts indicate that dipolar origins of these two modes are different. Consequently, the resultant dipole moment responsible for the sub-Rouse modes seems to originate from correlation of the normal dipole moments of monomers within the Gaussian submolecule, which is also responsible for the observation of the primary relaxation. As a result, the sub-Rouse modes observed by dielectric spectroscopy are uncorrelated with the appearance of normal modes. Moreover, because the segmental and the sub-Rouse modes have the same dipolar origin and the length scale of sub-Rouse mode is not much larger than the local segmental one, both processes are closer in time and share some similar characteristics.

However, the question remains why in most of the polymers the sub-Rouse modes are invisible in the dielectric loss spectra whereas all of them have the normal dipole moment in the polymer units? As was mentioned above, the sub-Rouse modes are visible in the dielectric spectra only if the resultant dipole moment from motion of several repeat units within the submolecule is nonzero. For polymers with high randomness in tacticity like aPP, PS, and PMPS, the slope of the low-frequency side of the segmental relaxation peak is equal to 1 because there is no correlation between randomly arranged normal dipole moments within the atactic submolecule. On the other hand, in the case of PIB and PIP, that have no disorder in tacticity; this correlation exists, and the low-frequency tail of the segmental relaxation has slope ~0.5, indicating appearance of the sub-Rouse mode in the dielectric spectra.

The best support for the proposed idea came from comparison of the data of atactic and head-to-head polypropylene. The chemical structure of polypropylene is related to PIB by replacing a methyl group by hydrogen atom, thus rendering the structure asymmetry and producing a dipole moment normal to the polypropylene backbone. Head-to-head polypropylene, with its repeat unit twice that of aPP, is rendered symmetric with increased ordering of the normal dipole moment. Consequently, the resultant dipole moment responsible for the sub-Rouse modes becomes nonzero, and one should observe them in the dielectric loss spectra of head-to-head PP (hhPP). Indeed, analysis of literature data[27] reveals significant broadening of the low-frequency tail of $\varepsilon''(\nu)$ in hhPP (Figure 4). It would be important to compare other polymers with different randomness in tacticity to further verify this hypothesis.

Finally, we want to emphasize that the classical picture of polymer dynamics based on segmental and chain modes with no modes in between is obviously too simple and inconsistent with experiments.[12] The motion of structural units involved in segmental dynamics (e.g., a few monomers) must be strongly affected by chain connectivity on time scale comparable to or slightly longer than segmental relaxation time. The classical Rouse modes, however, appear on a time scale significantly longer than segmental dynamics and are based on purely entropic forces. There should be modes in between that are slower than segmental modes due to chain connectivity but still faster than the entropically driven Rouse modes. This qualitative argument together with that given in ref 12 justifies the existence of sub-Rouse modes that have been observed earlier in mechanical and

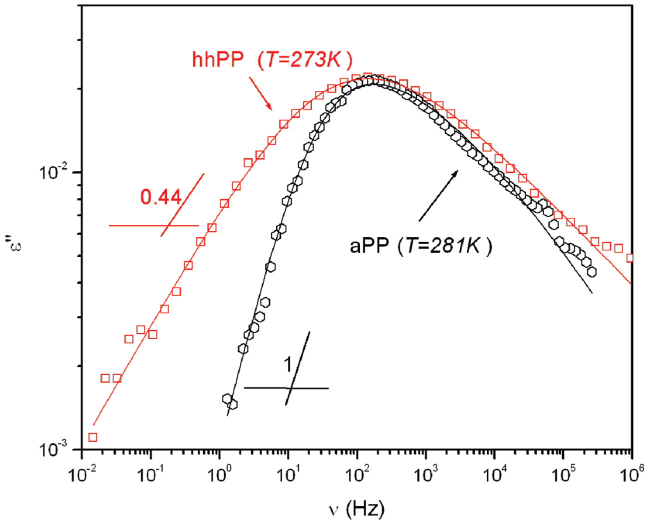

Figure 4. Dielectric loss spectra of aPP (hexagons, T = 281 K) and hhPP (squares, T = 273 K)[27] for the same segmental relaxation time.

photon correlation spectroscopy measurements in polymers. One can interpret in a similar way the results of the recent computer simulations that identified for very short subchains (high p index) relaxation modes with behavior deviating from the expected Rouse behavior.[28] The present study has identified sub-Rouse modes also in dielectric spectra of some polymers (Figures 1−3), but not in all polymers because their appearance depends on the regularity in polymer tacticity.

5. Conclusion

Our dielectric spectroscopy studies reveal unusual shape of segmental relaxation and excess contribution on the low-frequency side of the loss peak in some polymers, such as PIB, PI, and hhPP for the first time. We ascribe this to contribution of the sub-Rouse mode to the dielectric loss spectra of these polymers. The location of the sub-Rouse mode relative to the segmental relaxation, determined from the fractional power law frequency dependence on the low-frequency side of the primary loss peak, is in accord with the previous studies by mechanical and by photon correlation spectroscopy. The absence of this low-frequency excess loss in the dielectric spectra of many other polymers is rationalized using randomness in monomer (dipole) orientations along the chain particularly in atactic polymers. As demonstrated by going from atactic PP to head-to-head PP, where there is decreased randomness in the monomer orientation and consequently increased correlation between the normal dipole moments, it is possible to observe the sub-Rouse modes in head-to-head PP. On the other hand, this unusual condition is not fulfilled in most other polymers, and the prevailing dielectric loss coming from the primary relaxation obscures the presence of the sub-Rouse mode in the dielectric loss spectrum. Unlike in dielectric spectroscopy, the sub-Rouse mode contributes without restriction to the correlation function observed in photon correlation spectroscopy and to compliance in mechanical spectroscopy, and hence they have been found more generally by these techniques in more polymers.

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