High and low molecular weight crossovers in the longest relaxation time dependence of linear cis-1,4 polyisoprene by dielectric relaxations

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Abstract The dielectric relaxation of cis-1,4 Polyisoprene [PI] is sensitive not only to the local and segmental dynamics but also to the larger scale chain (end-to-end) fluctuations. We have performed a careful dielectric investigation on linear PI with various molecular weights in the range of 1 to 320 kg/mol. The broadband dielectric spectra of all samples were measured isothermally at the same temperature to avoid

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utilizing shift factors. For the low and medium molecular weight range, the comparisons were performed at 250 K to access both the segmental relaxation and normal mode peaks inside the available frequency window (1 mHz–10 MHz). In this way, we were able to observe simultaneously the effect of molecular mass on the segmental dynamics—related with the glass transition process—and on the end-to-end relaxation time of PI and thus decouple the direct effect of molecular weight on the normal mode from that due to the effect on the monomeric friction coefficient. The latter effect is significant for low molecular weight ($M_w < 33$ kg/mol), i.e., in the range where the crossover from Rouse dynamics to entanglement limited flow occurs. Despite the conductivity contribution at low frequency, careful experiments allowed us to access to the normal mode signal for molecular weights as high as $M_w = 320$ kg/mol, i.e., into the range of high molecular weights where the pure reptation behavior could be valid, at least for the description of the slowest chain modes. The comparison between the dielectric relaxations of PI samples with medium and high molecular weight was performed at 320 K. We found two crossovers in the molecular weight dependence of the longest relaxation time, the first around a molecular weight of 6.5 ± 0.5 kg/mol corresponding to the end of the Rouse regime and the second around 75 ± 10 kg/mol. Above this latter value, we find a power law compatible with exponent 3 as predicted by the De Gennes theory.

Introduction

The chain dynamics of linear polymers is one of the basic and classical problems of polymer physics; thereby, it has been the subject of intensive investigation, both experimentally and theoretically, over many years. Rouse theory (Rouse 1953) and the reptational tube model introduced first by de Gennes (1971) and developed by Doi and Edwards (1986) are the two fundamental theoretical approaches to describe the molecular relaxations of unentangled and entangled polymers, respectively. Concerning the dynamics of entangled polymer many corrections (as Contour Length Fluctuation or Constraints Release) to the pure reptation have been attempted to obtain a totally predictive theory (Viovy et al. 2002; McLeish 2002). It is also a well-known fact that the different regimes describing the polymer dynamics are function of their molecular weight and molecular weight distribution. Abdel-Goad et al. (2004), using rheology measurements coupled with an empirical winter relaxation BSW model, obtained three different exponents (1, 3.4, and 3) in the molecular weight dependence of the zero shear viscosity. In a recent work (Riedel et al. 2009), the validity of the Rouse model for unentangled polymer melts have been tested in full detail by using broadband dielectric spectroscopy (BDS). Previous BDS studies on the molecular weight dependence of the normal mode relaxation time showed a crossover from the unentangled dynamics to the entanglement regime (Boese and Kremer 1990; Yasuo et al. 1988; Adachi and Kotaka 1993; Watanabe 2001; Watanabe et al. 2002). However, none of them has been able to access the crossover to the exponent 3 expected by the pure reptation theory which, as aforementioned, has been detected for the viscosity.

In this paper, we have carefully investigated the dynamics of 1,4-*cis*-poly(isoprene), which was obtained by anionic polymerization with a narrow distribution of molecular weights over a broad molecular weight range: M_w in the range 1–320 kg/mol. PI is a A-type polymer, i.e., BDS experiments are sensitive to the large chain motion involving end-to-end vector fluctuations (normal mode). As BDS is particularly sensitive to the slow chain modes, it gives a quite direct access to the longest relaxation time since it can be obtained from the dielectric loss peak frequency. In that way, we will detail how careful BDS experiments allow detecting the two different crossovers from the Rouse up to the pure reptation regime. Entanglement effects in BDS spectra will be also analyzed. Finally, the possible influence of the narrow molecular weight distribution of the samples on the dielectric loss shape will be discussed.

Material and methods

Polymers

1,4-*cis*-Poly(isoprene) samples were provided by Polymer Source. They were synthesized by living anionic polymerization of isoprene in a-polar media. After polymerization, the poly(isoprene) backbone is constituted mainly by *cis* units (80%). The molecular weight (M_n) and polydispersity index (determined from size-exclusion chromatography experiments) of the samples investigated are listed in Table 1. To avoid oxidation, PI samples were stored at −25°C. In addition, before the experiments, samples were dried in a vacuum oven at 70°C for 24 h to remove any trace of solvent and humidity.

Dielectric spectroscopy

A broadband dielectric spectrometer, Novocontrol Alpha analyzer, was used to measure the complex dielectric permittivity, $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$, $\omega = 2\pi f$, in the frequency (f) range 10^{-2}–10^6 Hz. The samples were placed between parallel gold-plated electrodes of 20 mm diameter. The value of the gap between the electrodes was fixed to 0.1 mm (by a narrow PTFE cross shape piece). The measurements accuracy in the whole frequency range was better than $2 \cdot 10^{-4}$ for the dielectric loss permittivity. Isothermal measurements were performed every 10° over the temperature range 220–350 K using a temperature controller based on N_2-gas jet stream (Novocontrol). The temperature stability so obtained resulted in all the cases better than ±0.1 K.

Table 1 Microstructure of the samples investigated in this work

Sample code	M_n [kg/mol]	M_w [kg/mol]	I_p	T_g [K]]
PI-1	1.1	1.2	1.11	194
PI-3	2.7	2.9	1.06	203
PI-11	10.1	10.5	1.04	209
PI-35	33.5	34.5	1.04	210
PI-82	76.5	82	1.07	210
PI-145	138	145	1.07	210
PI-320	281	320	1.14	210

M_n average molecular weight, M_w weight-averaged molecular weight, I_p polydispersivity index, T_g glass transition temperature determined from the middle point of the DSC trace at a heating rate of 10 K/min after cooling down at the same rate

Results

Figure 1 presents the raw data of the dielectric loss permittivity of some of the PI samples investigated. The broad frequency window of BDS (eight decades in a single spectrometer) permits to measure the two relaxations—segmental and normal mode—at the same isothermal measurement for most of the samples. It is apparent that the segmental dynamics (α-relaxation) of PI has relaxation times that are essentially independent on the chain molec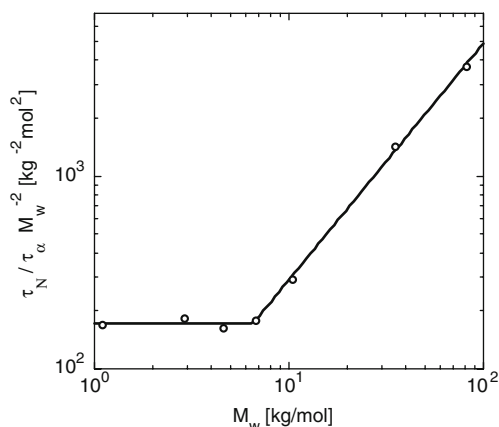ular weight as far it is above 10 kg/mol, whereas the normal mode relaxation shifts rapidly to lower frequencies on increasing molecular weight. This fast variation of the normal mode relaxation peak prevents detecting it at this temperature for molecular masses higher than about 50 kg/mol. Thus, we will first focus the analysis on the samples with lower molecular mass. First, it should be noticed that for very low molecular masses the observed changes in the longest relaxation time could be attributed to two different sources. On one hand, the intrinsic slowing down of the end-to-end fluctuations as the chain length increases, and on the other hand, the changes in the local friction coefficient arising because the significant changes in the end chain groups accompanying the changes in molecular weight. As a signature of these changes the glass transition temperature of the small molecular weight samples is significantly lower than that obtained for molecular weights higher than 10 kg/mol, which remains essentially constant ($T_g = 210$ K). As can be seen in Fig. 1, this last behavior is also found for the dielectric α-relaxation. Thus, in order to disentangle this effect on the normal mo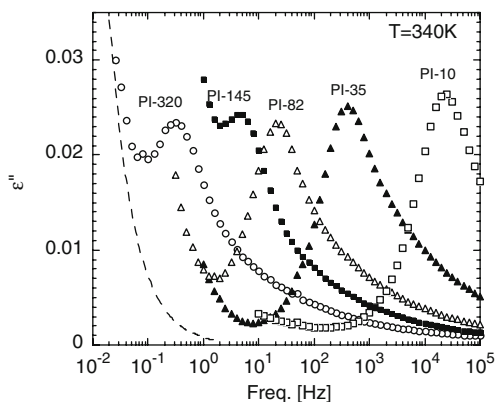de relaxation time from that directly related with the chain length, the ratio of the normal mode time scale to that of the α-relaxation was evaluated. The obtained result is shown in Fig. 2. For completeness, data from other two PI samples previously measured in our laboratory are also included, namely for PI samples with values of $M_w = 6.7$ kg / mol and $M_w = 4.6$ kg/mol. To increase the plot sensitivity to changes between the different regimes, a factor of M_w^{-2} has been applied to the ratio between the characteristic times (reciprocal of the peak angular frequency) of the two relaxation processes, i.e., τ_N / τ_α. From this plot, it becomes evident that the M_w^2 dependence expected for unentangled polymers on the basis of the Rouse theory is fulfilled for samples with molecular weight below 6.5 ± 0.5 kg/mol. This value is actually only slightly higher than that of the molecular mass between entanglements ($M_e = 5$ kg/mol) obtained from neutron scattering experiments. However, this value is clearly out of the uncertainty of the crossover molecular weight between the two regimes detected from the present experiments. The exponent describing the higher molecular mass range considered in this plot was 3.2 ± 0.1 which is distinctly lower, but close, to the 3.4 usually found in rheological experiments (Ferry 1980). It is noteworthy that imposing this exponent to fit our data will result in a higher value of the crossover molecular weight, thus increasing the discrepancy with the reported/admitted value of M_e mentioned above. It is noteworthy that, as it is well known, the ratio τ_N / τ_α will change with temperature (Ding and Sokolov 2006). Nevertheless, the previous results will not change significantly using data at other

Fig. 1 Raw BDS data showing the normal mode and the α-relaxation of the lower molecular weight PI samples at 250 K


Fig. 2 Longest and segmental relaxation time ratio as a function of the molecular weight at 250 K. The *vertical axis* is scaled by M^2 to emphasize the transition from the Rouse to the intermediate regime. The *solid line* corresponds to the description of the data with a sharp crossover between two power law regimes with different exponents (see text)

temperatures because the changes in the value τ_N / τ_α will be very similar for all the samples having different molecular weights, and consequently, the resulting molecular weight dependence would be unaltered.

After analyzing the molecular weight dependence of the end-to-end fluctuations in the low and moderate molecular weight range, now we will focus the attention in the highest accessible molecular weights. In the high molecular weight range, the comparison among the different samples has to be performed at a significantly higher temperature due to the dramatic slowing down of the chain dynamics. The more suitable temperatures are those where the normal mode loss peak of the sample with the highest molecular weight occurs in the slow frequency range of the experimental window. An additional factor that has to be taken into account is the fact that by increasing temperature, the conductivity contribution to the dielectric losses becomes more prominent. The conductivity contribution appears as a ω^{-1} increasing of the dielectric losses. This is an important issue even for high-quality samples when the experiments require accessing to the low frequencies at temperatures far above T_g. This situation is illustrated in Fig. 3 for the raw data of the PI sample having the highest investigated molecular weight. It is apparent that at 340 K, the normal mode peak can be well resolved from conductivity for this sample, but it would be hard to resolve the normal mode relaxation at this temperature for a sample with a significantly higher molecular weight. Furthermore, increasing temperature would not improve the situation since the overlapping of the conductivity contribution with the normal mode relaxation will also increase. This is a serious limitation of the dielectric methods for investigating the slowest chain dynamics in highly entangled systems. Nevertheless, as shown in Fig. 3, resolving the
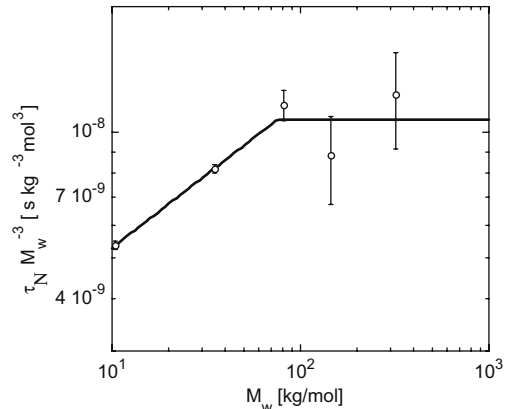
Fig. 4 Longest relaxation time from the higher molecular weight PI samples. The graph is scaled to M^3 to emphasize the crossover from the intermediate to the reptation regime. The *solid line* corresponds to the description of the data with a sharp crossover between to power law regimes with different exponents (see text)

normal mode peak was possible for all the samples investigated, although the contribution from conductivity will increase the uncertainty in the peak position for the samples with very high molecular weight. Figure 4 shows the molecular weight dependence of the slowest relaxation time for the high molecular weight regime obtained from the data presented in Fig. 3. Trying to increase the sensitivity of the plot to possible changes in behavior, the data have been multiplied by M_w^{-3}, which would produce a molecular weight independent result for a pure reptation regime. Despite the uncertainties involved, our results evidence that for the highest molecular weight samples, the molecular mass dependence approaches the pure reptation regime expectation. The line in Fig. 4 corresponds to a crossover from and exponent 3.35 to a pure reptation-like regime. The small difference between this exponent and that obtained above from Fig. 2 is more likely due to the fact that the sample with the lower molecular weight considered in Fig. 4 has a significantly lower glass transition temperature, an effect not considered in Fig. 4. The crossover molecular weight obtained from Fig. 4 is 75 ± 10 kg/mol, i.e., it corresponds to about 15 times M_e. This value is slightly lower than that determined from viscosity data (Abdel-Goad et al. 2004).

Discussion

The results previously described showed three different regimes for the molecular weight dependence of the chain longest relaxation time in PI, one below 7 kg/mol following the Rouse model prediction as expected for a non-entangled polymer melts, other above 75 kg/mol

Fig. 3 Normal mode of the high molecular weight PI samples. *Dashed line* represents the calculated conductivity contribution to the dielectric losses for the PI-320 sample

where the reptation theory provides a good description and an intermediate one, where the polymer is entangled but other mechanisms (like contour length fluctuations or constraints release) in addition to reptation would control the whole chain dynamics. In a recent publication, we have shown that the Rouse model provides a very satisfactory description of the whole normal mode relaxation of unentangled PI once the narrow sample polydispersity is properly taken into account. On the other hand, in the rheological experiments above referred (Abdel-Goad et al. 2004), it was shown that the viscosity of high molecular weight PI samples conforms well the reptation theory predictions. Thus, we decided to test up to what extent the pure reptation theory is able to describe the normal mode relaxation spectrum of the highly entangled PI samples. This test can evidence the ability of the reptation theory to capture the main features of the slowest chain dynamics, despite the well-documented failure of the reptation theory in accounting for the whole chain dynamics, even in the high molecular weight range. This is clearly evidenced by the reported mismatching of the normalized dielectric and rheological spectra (Watanabe 2001). To this end, we compared our experimental data on the high molecular mass samples with the corresponding reptation theory predictions for the end-to-end vector relaxation, which reads as:

$$\left\langle \vec{R}(t) \cdot \vec{R}(0) \right\rangle \propto \sum_{p:odd} \frac{1}{p^2} \exp\left(-\frac{p^2 t}{\tau_d}\right) \tag{1}$$

where p refers to a given normal mode and τ_d is the disengagement (reptation) time, which would correspond in good approximation to τ_N. The corresponding expression for the normal mode dielectric relaxation would be:

$$\varepsilon''(\omega) \propto \sum_{p:odd} \frac{1}{p^2} \frac{\omega \tau_d / p^2}{1 + \left(\omega \tau_d / p^2\right)^2} \tag{2}$$

Figure 5 shows the direct comparison between the experimental data for some of the samples investigated (symbols) having all of them the lowest available polydispersity index (~1.05) and the pure reptation theory prediction (solid line). Both vertical and horizontal scaling factors have been applied to obtain a good matching of the peaks. It should be noted that the possible conductivity contributions to the normal mode relaxation were subtracted. The inset shows separately the data of the highest molecular weight sample because it has a markedly broader molecular weight distribution (polydispersity index 1.14).
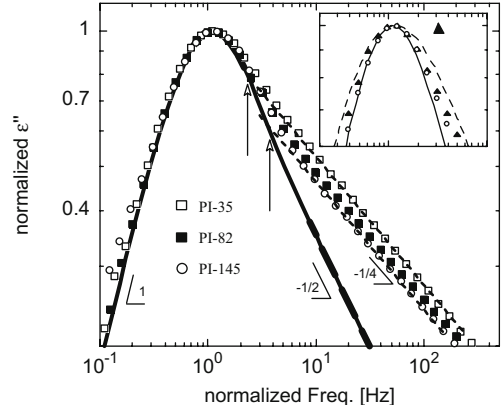
Fig. 5 Comparison of the BDS data of high molecular weight (*symbols*) with pure reptation theory (*solid line*). *Dashed straight line* showing the 1/4 power law behavior of the samples with PI 35 and PI 145 are also shown. The *vertical arrows* indicate the crossover frequency between both regimes. The *inset* presents for comparison the highest molecular weight data (PI 320) with a high polydispersity (1.14) with that of smaller polydispersity (1.04). The *dashed line* represents what would be the reptation theory expectation when a very crude approximation is used to account the effect of the molecular weight (see text)

From Fig. 5, it becomes apparent that in the high frequency side of the loss, peak deviations from the reptation predictions on the end-to-end vector fluctuations persist even for the highest molecular weight investigated. Whereas the high frequency behavior expected from the reptation theory is a power law with exponent $-1/2$, the experimental data present and exponent $-1/4$ (see Fig. 5), which would be a signature of the relevance of chain contour length fluctuations at least in this high frequency side of the normal mode relaxation. Nevertheless, it is also clear that the range of these deviations reduce when increasing molecular weight. The vertical arrows in Fig. 5 show that a factor of 5 increasing in molecular weight makes the crossover frequency to increase in a factor of about 2. By inspection of the rheological data reported by Abdel-Goad et al. (2004), it is also apparent that in the very high molecular weight range where the viscosity scales as predicted by reptation theory, the terminal relaxation is far from being properly described by this theory.

Eventually, the normal mode description by the pure reptation theory could be obtained only at extremely higher molecular weights, for which, as aforementioned, the dielectric experiments will not be suitable for investigating the extremely slow chain dynamics. Concerning this, it has been shown (McLeish 2002) that for polyethylene, the frequency dependence of the loss shear modulus verifies the reptation prediction only for a molecular weight as high as of 800 kg/mol, which for this polymer corresponds to about 400 times M_e,

i.e., it would correspond to about 3,000 kg/mol for PI. Taking the above-calculated shift of the crossover frequency into account, for this limiting molecular weight, the crossover frequency would occur at around 20 Hz, and the failure of the repetition theory description would be hardly detectable by using the same scale as in Fig. 5.

Figure 5 also shows that both the maximum and the low frequency side of the loss peak are well accounted by the reptation theory without any evident deviation, except for the sample having a broader distribution of molecular weight, which shows a distinctly broader normal mode peak (see inset of Fig. 5). This comparison evidences that the molecular weight distribution have a noticeable effect on the normal mode spectrum shape. The effect of the molecular weight distribution on the normal mode was properly accounted for in an unentangled PI sample (Riedel et al. 2009) by assuming that the contributions from chains in the sample with distinct molecular weight simply superimpose. When we tried the same approach with the higher molecular weight samples (dashed line in the inset of Fig. 5), it becomes evident that the situation for well-entangled polymers is different. Even by using the smallest polydispersity (1.04), the calculated response overestimates by far the broadening of the peak for the sample with highest polydispersity (1.14). Thus, for highly entangled polymers, the effect of the molecular weight distribution on the normal mode is less evident than that observed in the unentangled polymer case. In fact, the complete disentanglement of a chain involves also the motions of the chains around, which would have a different molecular weight, being, therefore, the resulting time scale some kind of average of those corresponding to the ideally monodisperse melts. As a result, the longest relaxation time in highly entangled melts should not depend greatly on the molecular weight distribution, provided it is not very broad.

Conclusion

BDS experiments on PI have allowed us to detect two crossovers in the molecular weight dependence of the end-to-end relaxation time. The first corresponds to the crossover from the range where the Rouse theory is applicable to the entangled limited range, being the crossover molecular weight 6.5 ± 0.5 kg/mol, i.e., slightly above the molecular weight between entangle-

ments. The crossover from the intermediate range to the behavior predicted by the pure reptation theory is found at around 75 ± 10 kg/mol, which corresponds to 15 times the molecular weight between entanglements. Despite of the fact that the reptation theory is able to describe the molecular weight dependence of the slowest relaxation time for these high molecular weight samples, the shape of the normal mode spectrum is still markedly different from that expected by this theory. Eventually, only at a much higher molecular weight (hundred times the molecular weight between entanglements) the reptation theory could completely describe the normal mode relaxation associate to the chain dynamics. Unfortunately, dielectric experiments in this range are not feasible.

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