Direct Observation of Dynamic Tube Dilation in Entangled Polymer Blends: A Combination of Neutron Scattering and Dielectric Techniques

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We report a microscopic observation of the time-dependent dynamic tube dilation process on iso-frictional bidisperse melts. By applying neutron spin echo (NSE) and dielectric techniques on blends of long polyisoprene (PI) chains with short PI additives with different topology, we access the dynamics of the tube dilation process on a molecular scale. The time-dependent tube dilation is directly revealed by NSE as an additional time dependence of the dynamic structure factor in the local reptation regime. We identify the characteristic time of tube dilation as the terminal time of the additive.

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Nowadays it is well accepted that the unique rheological properties of high molecular weight polymer melts are controlled by entanglements: topological constraints imposed by the mutually interpenetrating and uncrossable polymer chains. In the tube model for entangled chains, these constraints are represented by a tube that restricts the lateral motion of the polymer chain probe within its diameter d . In the ideal tube model proposed by Edwards and de Gennes [1,2], the relaxation of the probe chain—i.e., its escape at $t > 0$ from the initial tube ($t = 0$)—takes place by the reptation mechanism. However, in reality, other mechanisms compete with reptation, mainly, contour length fluctuations (CLF)—fluctuations of the length of the tube—and constraint release (CR), referring to probe motion driven by the motions of the surrounding matrix chains. A simplified version of the many-body CR mechanism is the dynamic tube dilation (DTD), where CR effects are represented by an increase with time of the tube diameter. The idea of DTD was first introduced by Marrucci [3], who proposed that even in a homopolymer melt the portion of the chain that has escaped from the original tube acts as a solvent for the remaining tube sections. CR in general becomes very important in the case of polydisperse melts and binary blends, especially where long polymer chains are mixed with short additives of the same chemistry (iso-frictional blends) but sometimes of different polymer architecture.

Different mechanisms and models (see, e.g., [4–7]) have been proposed to explain and predict CR effects in iso-frictional polymer blends with different values of the

so-called Struglinski-Graessley parameter [8]: $r_{SG} \equiv N_L N_e^2 / N_S^3$, where N_L and N_S are the number of monomers in the long and short chains, respectively, and N_e is the number of monomers corresponding to the entanglement mass. While for $r_{SG} < 1$ the predictions from different models [4,5] seem to agree (long chain reptation in an undilated bare tube), this is not the case for $r_{SG} \geq 1$. Doi *et al.* [4] proposed a DTD mechanism for the relaxation of the long chains, while Viovy *et al.* [5] assume that the undilated bare tube reptates in a “supertube” defined by long-long chains entanglements. Most of these models predict chain relaxation in the so-called terminal regime of the viscoelastic behavior, where, e.g., within a DTD mechanism, the tube would reach its final dilated value. Accordingly, the experimental studies are usually based on macroscopic rheological or dielectric techniques (see, e.g., [9–13]). A direct experimental microscopic observation of the time dependence of the CR or DTD mechanisms remains elusive [14,15]. It is generally assumed [15] that the time scale of these processes is beyond the accessible times by neutron spin echo (NSE)—the microscopic technique often used to address reptation problems in polymers at molecular level [16].

In this work we combine dielectric spectroscopy (DS) and NSE to address the dynamics of long polyisoprene (PI) chains in iso-frictional blends with “additives” of two different topologies: short PI linear chains and star-branched PI. First, by means of DS in the terminal range we confirm a dilated tube mechanism for long chains relaxation. Second, we demonstrate that the connected

TABLE I. Number-averaged (M_n), weight-averaged (M_w) molecular weights, and polydispersity index ($PDI = M_w/M_n$) of hPI (protonated polyisoprene) and dPI (deuterated polyisoprene) polymers investigated in this work.

Polymer	M_n (kg/mol)	M_w (kg/mol)	PDI
hPI-80k	82.7	83.5	1.01
dPI-80k	87.6	90.2	1.03
hPI-12k	11.6	11.7	1.01
dPI-12k	11.9	12.4	1.04
hPI-star	47.0	47.4	1.01
dPI-star	42.9	43.4	1.01

time-dependent tube dilation can be directly accessed by NSE. We identify the characteristic time for CR as the terminal time of the short component.

Nearly monodisperse long-linear PI as well as additives (short-linear and 8-arm star-branched PI) were synthesized by anionic polymerization. The corresponding deuterated polymers were also synthesized to prepare samples for NSE with suitable contrast. The main characteristics of these polymers are indicated in Table I. The entanglement mass of PI is $M_e \approx 5$ kg/mol. Then, long-linear PI has $Z = M/M_e \approx 16$ entanglements per chain and the short-linear PI, $Z \approx 2.4$. For the star-branched PI we also obtained $Z \approx 2.4$ because the molecular mass of one arm is $M_{\text{arm}} \approx 6$ kg/mol ($Z = 2 \times M_{\text{arm}}/M_e$ [17,18]). Blends of long-linear PI chains and the two additives at a volume fraction of the long-linear PI chains $\phi_L = 0.5$ were prepared by dissolving both components in n-hexane. The samples for neutron scattering experiments contained 10% of long protonated PI chains in the otherwise deuterated material. With this labeling, we can selectively access the static and dynamic single chain structure factor of the long PI chains within the corresponding bulk. Considering the molecular weights given in Table I, we can estimate that $r_{\text{SG}} \approx 1.3$ –1.4 for our blends.

Small angle neutron scattering (SANS) measurements performed at the SANS-instrument D11 [19,20] (ILL, Grenoble, France) show that the conformation of long-linear PI chains follows an unperturbed Gaussian random walk, which—within the experimental uncertainties—does not change in the presence of additives [see Supplemental Material (SM) [21] Sec. I for details about the SANS characterization (Fig. S1)]. The average radius of gyration is $R_g = 9.7$ nm.

In polymers like PI, having both local dipole moments parallel and perpendicular to the chain backbone, the terminal relaxation range can be nicely assessed by DS [6,24–26]. The imaginary part of the complex dielectric permittivity $\epsilon''(f)$ [or the derivative of the real part, $d\epsilon'(f)/d\ln f$, with $\ln f$ being the natural logarithm of the frequency f] shows a low frequency peak known as “normal mode”. In the case of entangled polymers this peak reflects the chain disentanglement; i.e., it directly marks

FIG. 1. Dielectric results obtained on mixtures of long PI chains with short linear chains (empty squares) and stars (filled diamonds). Filled circles show the pure long chains bulk results for comparison. The magnitude represented is the natural-log frequency derivative of the real part of the dielectric permittivity (sign changed). Data have been normalized according to the values of the segmental relaxation peak at 230 K (see SM [21]). The vertical arrow marks the frequency corresponding to τ_d^s for star additives deduced from NSE properly translated to 290 K by the temperature dependence given in the SM [21]. Inset: temperature dependence of the ratio between the frequency of the maximum of the long-chain normal mode in each mixture and in the homopolymer (same symbol code; lines show the average values).

the reptation time τ_d [$\tau_d = 1/(\pi f_{\text{max}})$] where f_{max} is the frequency of the maximum of the peak). Figure 1 shows the results obtained for PI-80k (long-linear PI) and the two blends investigated: PI-80k with PI-12k linear and PI-80k with (PI-6k) 8-star. For pure PI-80k only the normal mode peak is observed in the represented frequency range. For the blends, there are two peaks that correspond to the normal modes of both components. In the high-frequency range all curves tend to merge towards the peak corresponding to the α relaxation (out of the window at the temperature shown). This peak is the same for the three samples [see SM [21] Sec. II where the dielectric results on the α process are shown for a temperature of 230 K (Fig. S2)] confirming the iso-frictional character of the samples investigated. We note that the normal mode peak corresponding to the PI-80k is shifted to high frequency in the presence of additives. The inset shows that this shift is constant in the high-temperature range and slightly different for the blends with either short linear PI or with 8-arm star PI. In the tube model, the tube diameter d is related to the reptation time as $d = [3R_E^6/(\pi^2 W \ell^4 \tau_d)]^{1/2}$ where R_E is the end-to-end distance and $W \ell^4$ the Rouse rate [16]. Then, taking into account the iso-frictional state (same $W \ell^4$) and that the conformation of the long linear chains does not change with blending ($R_E = \sqrt{6}R_g$ is constant, as shown

by SANS), the ratios of the time scales shown in the inset of Fig. 1 translate into ratios of the tube diameter for the long linear PI chains: $d(\phi_L = 0.5)/d_o \approx 1.39$ (for the blend with short linear additive) and $d(\phi_L = 0.5)/d_o \approx 1.34$ (for the blend with star additive). d_o means the tube diameter corresponding to pure long linear PI (PI-80k); i.e., $\phi_L = 1$. These results indicate effective tube dilation for long-linear PI terminal chain dynamics in the blends, supporting the DTD approach of Doi *et al.* for $r_{SG} > 1$ [4]. We note that for $\phi_L = 0.5$, the values found for $d(\phi_L = 0.5)/d_o$ correspond to a dynamic dilation exponent, α , [$d = d_o \phi^{-\alpha/2}$] of $\alpha \approx 1$ and $\alpha \approx 0.8$ for the blend with short-linear PI and star-branched PI respectively. In the framework of this DTD representation of the CR processes due to the additives, we should expect an effective time-dependent tube diameter $d(t)$ in the time regime shorter than the terminal relaxation that should affect the chain dynamic structure factor $S(Q, t)/S(Q, 0)$ that can be measured by NSE at a suitable temperature. With these ideas in mind, we have carried out NSE measurements on pure PI-80k and on the blends investigated by means of IN15-NSE [27] (ILL, Grenoble, France) at $T = 423$ K. The results obtained at the three Q values investigated are shown in Fig. 2. The chain dynamic structure factor of the long chains (PI-80k) is not appreciably affected at short times by the additives—the expected result from the isofrictional character of the samples. Only above ≈ 100 ns, a progressively more pronounced decay of $S(Q, t)/S(Q, 0)$ is found for the blends with respect to the pure PI-80k reference sample. For describing the chain dynamics in this reference system (PI-80k) and according with the approach followed for DS, we have considered a simple ideal reptation mechanism. This means that the tube diameter obtained (d_o) should, in principle, be considered as an effective reference tube diameter that likely includes CLF and CR effects in the pure (PI-80k) system.

In the framework of the reptation model the chain dynamic structure factor can be expressed as [28]

$$\frac{S(Q, t)}{S(Q, 0)} = \left[1 - \exp\left(-\frac{Q^2 d^2}{36}\right) \right] S^{\text{loc}}(Q, t) + \exp\left(-\frac{Q^2 d^2}{36}\right) S^{\text{esc}}(Q, t) \quad (1)$$

where $S^{\text{loc}}(Q, t)$ and $S^{\text{esc}}(Q, t)$ reflect local reptation and escape process from the tube (creep motion), respectively. In general, in order to fit the NSE data it is assumed that $S^{\text{esc}}(Q, t) \approx 1$ in the time window covered by NSE. In our case, since we know from DS the reptation time controlling $S^{\text{esc}}(Q, t)$, we have checked the validity of such approach [21] (SM, Sec. IV) and fixed $S^{\text{esc}}(Q, t) \equiv 1$ in the following. On the other hand, in the original formulation, $S^{\text{loc}}(Q, t)$ is only valid for $t > \tau_e$, where τ_e is the entanglement time, which is not well defined experimentally. Here, we have replaced $S^{\text{loc}}(Q, t)$ by a phenomenological

FIG. 2. Chain dynamic structure factor measured by NSE for PI chains at 423 K and the three Q values investigated (squares: $0.05 \text{ \AA}^{-1}$; circles: $0.09 \text{ \AA}^{-1}$; diamonds: $0.13 \text{ \AA}^{-1}$). Empty symbols correspond to the pure PI system and filled symbols to PI chains (matrix) in the presence of short linear (a) and 8-arm stars (b) additives. Solid lines are the description of the dynamic structure factor of pure PI based on pure reptation mechanism. Dashed lines correspond to the phenomenological model described in the text for the PI chains in the presence of the additives, for which the tube diameter increases according to the dotted lines.

stretched exponential function. Thus, the full expression employed to describe the dynamic structure factor in the NSE window was

$$\frac{S(Q, t)}{S(Q, 0)} = \left[1 - \exp\left(-\frac{Q^2 d^2}{36}\right) \right] \exp\left[-\left(\frac{t}{\tau}\right)^\beta\right] + \exp\left(-\frac{Q^2 d^2}{36}\right). \quad (2)$$

This function nicely describes the experimental data (see Fig. 2) and its choice, instead of the full theoretical expression for $S^{\text{loc}}(Q, t)$, does not affect the value deduced of d , within uncertainties. A value of $\beta \approx 0.59$ was found to give a reasonable description of the experimental data of pure long-linear PI (PI-80k), and the characteristic times τ were 175 ns ($Q = 0.05 \text{ \AA}^{-1}$), 68 ns ($Q = 0.09 \text{ \AA}^{-1}$), and

29 ns ($Q = 0.13 \text{ \AA}^{-1}$). The value obtained of the effective tube ($d_o = 64 \text{ \AA}$) is similar to that previously reported [29,30].

Once the NSE reference data corresponding to pure long-linear PI are analyzed, we can investigate the effect of the dynamics of the additives (CR effects) on the chain dynamics of these long PI chains in the blends. To do so, we have considered a simple phenomenological model inspired by the DTD ideas [3]. We base our modeling on the following facts: (i) at the entanglement time of PI ($\tau_e \approx 90 \text{ ns}$ at 423 K [29]), the measured dynamic structure factors from the long labeled PI chains in both, the pure homopolymer melt and in the blends, almost coincide; i.e., at τ_e the long PI chains feel the same “tube” (d_o) in both systems; (ii) a comparison of the dielectric normal mode peak of the blend and that of the pure matrix at the temperature of the NSE measurements reveals the dilated tube diameter (d_∞) at the terminal time of the long chain and suggests that the dilation occurs in the relaxation range of the fast component of the blend [see SM [21] Sec. V where the dielectric normal mode peaks of the matrix in the blend and that of the pure matrix are compared (Fig. S5)]; and (iii) as in the case of the reported MD simulations [15], the measured dynamic structure factor for the long PI chains in the blends cannot be described by imposing a time-independent fully dilated tube (d_∞ with the value deduced from the DS results [see SM [21] Sec. VI where the dynamic structure factors with constant fully dilated tube diameters and/or varying β parameter are shown (Figs. S6, S7, S8)]. As alluded to in the introduction, DTD assumes a tube diameter that increases with time. Our observations suggest just this phenomenon: an “effective” time-dependent tube for the long PI chains in the blends growing from d_o to d_∞ in the time range of the relaxation of the fast component of the blend. Accordingly, we have defined

$$d(t) = d_\infty + (d_o - d_\infty)\varphi(t), \quad (3)$$

where $d_o = 64 \text{ \AA}$ is the effective tube diameter previously obtained for the pure long-linear PI chains and $d_\infty \equiv d(\phi_L = 0.5)$. Its value is obtained from the value of d_o and the ratio $d(\phi_L = 0.5)/d_o$ determined by DS in the terminal regime. $\varphi(t)$ is a normalized function that would reflect the terminal relaxation dynamics of the additive in the blend. In a first approximation, $\varphi(t) \approx \exp(-t/\tau_d^S)$, where τ_d^S is the terminal time of the short additive in the blend. In the following we will use Eq. (3) with this $\varphi(t)$. In the case of linear chain additives, τ_d^S can be directly determined from the dielectric spectra (see Fig. 1) as the time of the normal mode of the short-linear PI in the blend. The value obtained for τ_d^S at 423 K is 1086 ns [see SM [21] Sec. III where the relaxation map from dielectric experiments is shown (Fig. S3)]. The corresponding evolution of $d(t)$ [Eq. (3)] in the NSE window is presented in Fig. 2(a). This figure also shows the dynamic structure

factor for the long-linear PI chains (PI-80k) in the presence of the linear additive calculated in this framework for the three Q values investigated. To do that we have generated Eq. (2) [21] (SM, Sec. IV) with the calculated $d(t)$. According to the isofrictional character of the samples [21] and the insensitivity of the short-time behavior of the NSE results to the presence of additives, β and τ parameters were fixed to the values obtained for pure long-linear PI. The agreement with the experimental data is excellent taking into account that there are no free parameters in this calculation. We also emphasize that, in contrast to the general belief, the time-dependent CR effects (tube dilation) are evident in the NSE dynamic range, as shown in this figure and in the SM [21] [Sec. IV where the time evolution of the apparent tube diameter and model functions are shown in an illustrative example (Fig. S4)].

In the case of the star topology for the additive, the situation is not so clear because the normal mode time is associated with the arm retraction process only. Therefore in this case we have followed the same procedure described above but keeping τ_d^S as a free parameter. We have found the best agreement with the NSE results at the three Q values investigated with $\tau_d^S \approx 1300 \text{ ns}$ [see Fig. 2(b)]. This time amounts to about threefold the value of the arm retraction time deduced from the dielectric normal mode (see Fig. 1). Figure 3 shows that this time is also rather

FIG. 3. Master curve combining data on the imaginary part of the viscosity measured at different temperatures on 50% mixtures of long PI chains with short linear chains (blue empty squares) and stars (red filled diamonds) (see SM [21] Sec. VII where details about the rheological experiments are presented). Circles, crosses and empty diamonds show the pure long chains, pure short chains, and pure stars bulk results, respectively, for comparison. The reference temperature is 293 K. The vertical arrow marks the frequency corresponding to τ_d^S for the blend with star additives deduced from NSE and properly translated to 293 K with the temperature dependence given in the SM [21].

similar to the “terminal time” deduced from the imaginary part of the viscosity $\eta''(\omega)$ corresponding to the star additive in the blend.

In summary, by combining neutron scattering (NSE) and dielectric spectroscopy we have addressed the CR effects produced by short additives with different topology on the dynamics of long-PI chains. By NSE we directly observe the process of time-dependent constraints removal at molecular scale. The characteristic time that governs tube dilation is identified as the terminal time of the additive. We have proposed a simple model inspired by DTD ideas, which nicely describes the NSE data with the model parameters fixed from dielectric results and from the NSE data of bulk long-PI chains. The comparison of some results from our model with available simulation results [15,31] give additional support to our approach [see SM [21] Sec. VIII where the results of the model are compared with MD-simulations results (Fig. S9)]. We note that even considering a single exponential for the CR process (i.e., no distribution of times), the effect of $d(t)$ on $S(Q, t)/S(Q, 0)$ starts to be visible at times rather short in comparison with τ_{add} and of the same order of the entanglement time of long PI chains. A similar situation was observed in the $S(Q, t)/S(Q, 0)$ obtained from MD simulations of long with short linear blends [15]. In that case it was interpreted as a clear signature of a broad distribution of the lifetimes of the topological constraints. Here we demonstrate that this behavior naturally emerges from a simple DTD mechanism without considering any type of distribution.

The supporting data for this Letter are openly available from Institut Laue-Langevin [20,27].

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