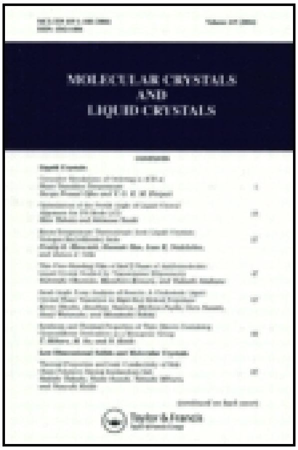

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Molecular Dynamics Study in PU/PBDO Anisotropic Elastomers by Proton NMR Relaxometry

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In this work we present a proton spin-lattice relaxation study of the molecular dynamics in an urethane/urea anisotropic elastomer film and in the two precursor pre-polymers, using conventional and fast field cycling NMR techniques. The precursor pre-polymers used were polypropylene oxide with three isocyanate terminal groups (PU) and polybutadiene diol (PBDO). The proton spin-lattice relaxation time T_1 dispersions were obtained at several different temperatures in the frequency range of 4 kHz to 100 MHz. The results show that while the molecular dynamics in the two precursor pre-polymers is well explained by the Rouse model, the solid elastomer film exhibits a relaxation dispersion where regions I, II and III of molten chain dynamics are clearly seen. The solid anisotropic elastomer film shows a molecular dynamical behaviour similar to other isotropic networks.

Keywords: anisotropic elastomers; molecular dynamics; NMR

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INTRODUCTION

Polypropylene oxide/polybutadiene bi-soft segment urethane/urea elastomer films were shown to exhibit anisotropic mechanical and swelling properties [1,2]. When subjected to a particular treatment they also exhibit an unusual mechanico-optical behaviour [1,3]. Initially studied for the preparation of pervaporation membranes [4], these systems were shown later to develop, upon a specific treatment [2,3], mechanically induced periodic structures that can scatter light efficiently yielding light modulation capabilities to these systems. The band structures that develop in the treated elastomer films at rest, after a series of stretching relaxation cycles, show wave vectors along the stretching direction, wave lengths in the micrometer region, amplitudes in the range of hundredths of microns and are thus capable of producing strong light scattering effects. In order to identify any correlation between the particular properties of these elastomers and possible differences in the molecular dynamics when compared to isotropic networks, we have initiated a proton NMR relaxometry study of untreated films [2] and precursor pre-polymers.

Fast Field-Cycling (FFC) proton NMR relaxometry [5,6] has been used extensively in the study of molecular dynamics in polymer melts, polymer networks [6–9] and in liquid crystalline systems [5,12,13]. This technique has proven to be a convenient tool to detect changes in behaviour at the molecular level, in particular when FFC NMR techniques are combined with conventional measurements in high frequency regime [5,6].

EXPERIMENTAL

The polypropylene oxide based isocyanate terminated triol (PU) and the polybutadiene diol (PBDO) prepolymers were dissolved in toluene (solid content 40 wt%) and mixed with one drop of dibutyltin dilauryate (DBTDL). The prepolymer PU (chemical structure in Fig. 1) was supplied from Portuguese petrochemical industry (CPB). The molecular weight was approximately 3500. The PBDO acquired from Aldrich has a number average molecular weight of 2800 and contains 20–30 wt% vinyl, 10–25 wt% cis-1, 4 and 50–60 wt% trans-1, 4 isomers. The catalyst was supplied by Aldrich and the toluene pro analysis by Merck.

The chemical reaction between PBDO and PU, in the molar ratio of 3:2, under nitrogen atmosphere, was allowed for 30 minutes (Fig. 1). The mixture was then casted and sheared simultaneously by moving a casting knife at a controlled shear rate ($v = 5\,\text{mm/s}$) see Figure 2.

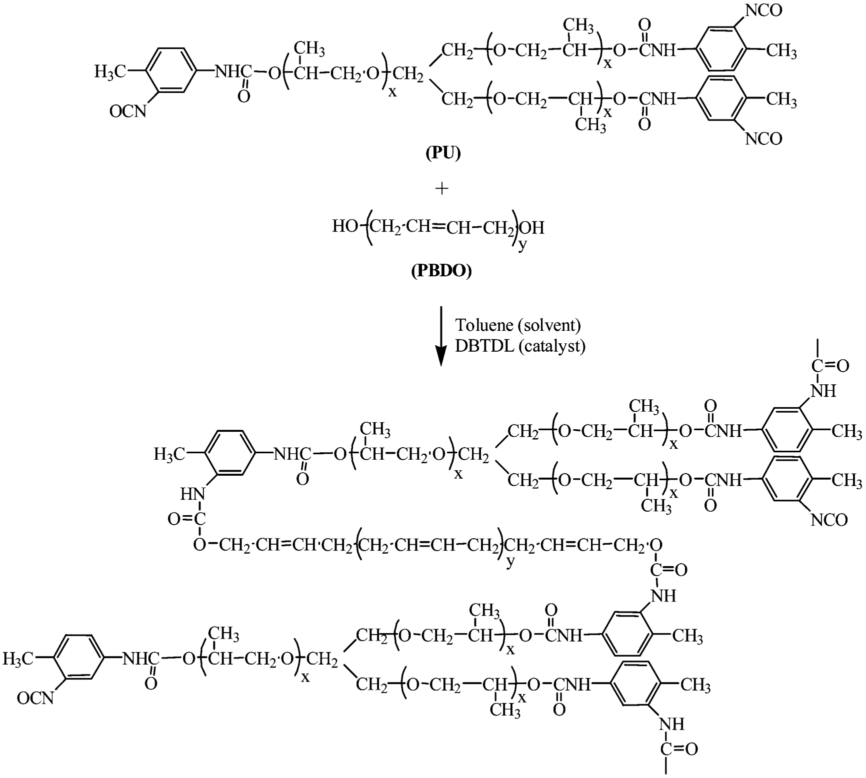

FIGURE 1 First chemical reaction involved in the synthesis of the elastomer and schematic representation of the network (y = 20 and x = 50).

After being cured in an oven at 70–80°C for 3.5 h, the film was carefully removed from the glass substrate, exposed to air and continued curing for at least 72 h in atmospheric moisture. The final thickness of the film was measured using a Mitutoyo digital micrometer.

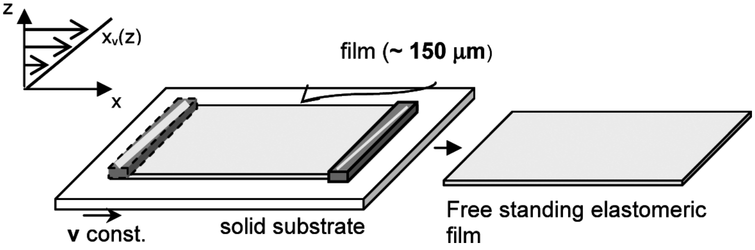

FIGURE 2 Preparation of elastomeric free standing films.

The NMR samples were prepared using standard FFC NMR glass tubes 9 mm thick. The samples were place inside the spectrometers probe heads and then heated to the desired temperatures. Two NMR spectrometers were used to obtain the experimental results here presented. For high frequency T_1 measurements a conventional inversion-recovery rf pulse sequence and a Bruker SXP 4–100 MHz spectrometer were used. For frequencies below 3 MHz a home build FFC NMR spectrometer was used [13]. The T_1 measurements for a given low Larmor frequency ($\nu_L = \gamma B_E/2\pi$), where γ is the proton giromagnetic ratio, are made by sampling the evolution of the magnetization when the external magnetic field is suddenly switched from a fixed high value B_P to the low value B_E where it remains for a given time τ. The magnetic field is then switched back to its high value and a rf pulse in resonance with the high field Larmor frequency ($\nu_L = \gamma B_P/2\pi$), is applied to produce a free induction decay (FID) with initial amplitude proportional to the value of the sample ^1H spins' magnetization after time τ. Therefore, although the spin system evolves in the low magnetic field the detection of the FID is made at the high field thus assuring a good signal-to-noise ratio [5,6].

RESULTS AND DISCUSSION

The network obtained has two kinds of nets that consist of urethane and urea links. The urethane covalent net results from the reaction of the three ended groups of polypropylene oxide-based isocyanate-terminated triol (PU) with polybutadiene diol (PBDO) hydroxyl groups (Fig. 1). The urea net corresponds to the reaction of the excess PU isocyanate groups with moisture.

The T_1 frequency dispersions obtained at different temperatures for the pre-polymers and the solid elastomer film are shown in Figures 3a and 4 respectively, along with the fits to be discussed next. Since it is reasonable to assume the absence of "entanglements" in the two pre-polymers, based on their molecular weight, we tried a model fit to the experimental results considering the Khazanovich NMR relaxation formula for the Rouse Model [6–9] given by

$$T_1 = -\frac{\beta}{\tau_S \ln(\omega\tau_S)} \quad (\omega\tau_S << 1). \tag{1}$$

The time τ_s is the Rouse relaxation time of a Kuhn segment corresponding to the shortest mode and follows an Arrhenius temperature dependence with activation energy E_a and a pre-factor $\tau_{S\infty}$.

$$\tau_S = \tau_{S\infty} e^{\frac{E_a}{k_B T}}, \tag{2}$$

Figures 3(a–c) show the model curves obtained by simultaneous fitting both the frequency and temperature spin lattice relaxation time T_1 dependences for each pre-polymer. As it can be observed the model fits

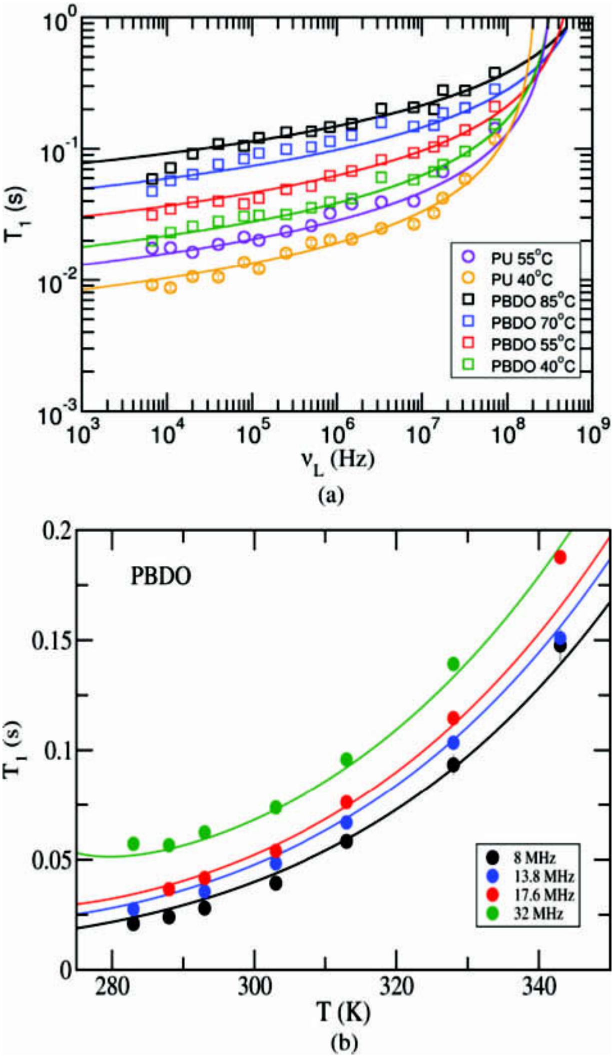

FIGURE 3 a) Frequency dependence of the proton spin-lattice relaxation time T_1 for PU and PBDO at several temperatures and Rouse model simultaneous fits to the frequency and temperature dependences of T_1 for PU and PBDO; b) and c) temperature dependence of T_1 at different frequencies for PBDO and PU respectively and corresponding fits.

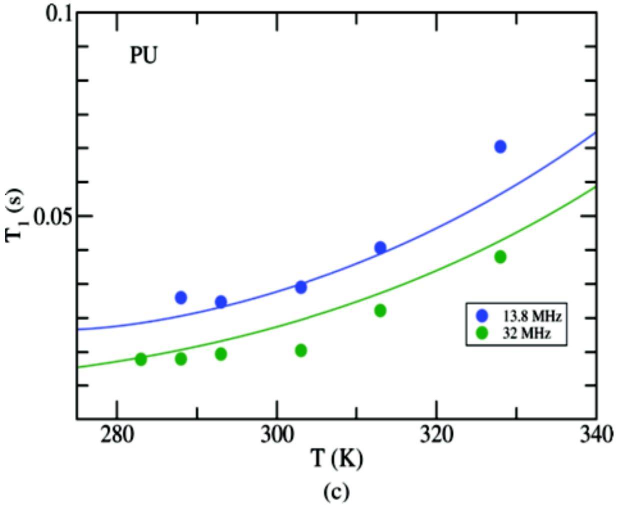

FIGURE 3 Continued.

are quite good and support the initial hypothesis for the Rouse chain dynamics considered. E_a, $\tau_{s\infty}$ and β were the three fitting parameters considered and their values for PU and PBDO are listed in Table 1. These values are quite compatible with others obtained in similar

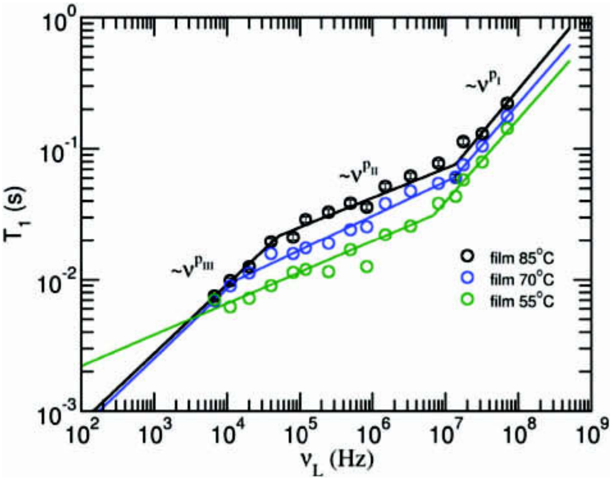

FIGURE 4 Frequency dependence of proton spin-lattice relaxation time T_1 for the solid elastomer film at three different temperatures and power laws fits to the frequency dependence of T_1.

TABLE 1 Fitting Parameter Values for PU and PBDO as Explained in the Text

	$\tau_{S\infty}/S$	$E_a/(kJ\ mol^{-1})$	β/s^2
PBDO	1.369×10^{-15}	32	9.394×10^{-11}
PU	1.970×10^{-14}	27	7.378×10^{-11}

systems [8]. Rouse dynamics is predicted for unconfined polymer chains in a viscous medium and has been observed in different polymer melts with molecular weights below the critical value (Mc) [6,9,14].

The T_1 dispersion in the solid elastomer film is clearly distinct from the one detected in the pre-polymers as the chain dynamics is now conditioned by constraints imposed by the cross-links between the chains. The T_1 dispersion is seen to follow power laws in three distinct regions, respectively I, II and III as is shown in Figure 4. In regions I and II the proton T_1 frequency dispersions are dominated by intra-chain dipolar interactions while in the region III, which appears at lower frequencies, segment diffusion becomes relevant and corresponds to a dominance of the inter-segment dipolar interactions contribution to the relaxation rate. Regions I and II correspond to the high and the low mode number limit respectively of the renormalized rouse dynamics model where the chain entanglement effects are considered in the generalized Langevin equation through a memory term [6,10,11].

In the lowest temperatures, the frequency window studied only allows for the detection of two regions, I and II, well fitted by power laws. The power law exponents and the transition frequencies determined from the fits are given in Table 2. The power law exponents quoted in literature take the values 0.5 in region I, 0.25 in region II and 0.5 in region III for network polymers in the appropriate frequency windows. In the region I, the exponent of the power law fitted

TABLE 2 Fitting Parameter Values for the Power Law Exponents and Transition Frequencies Obtained at Different Temperatures in the Solid Elastomer Film

T/K	P_I	P_{II}	P_{III}	$f_{t\ I\text{-}II}/Hz$	$f_{t\ II\text{-}III}/Hz$
328	0.63	0.24	–	6.847×10^6	–
343	0.64	0.26	0.53	1.309×10^7	1.318×10^4
358	0.66	0.22	0.52	1.380×10^7	5.197×10^4

to our data is slightly above the values found in the literature while in regions II and III the obtained parameters are in agreement with the values reported for other systems [6–9].

CONCLUSION

It was found that for the pre-polymers PU and PBDO the T_1 dispersion data can be well described by the Khazanovich NMR relaxation formula for the Rouse Model [6]. A simultaneous fit of the frequency and temperature T_1 dependences produced high quality fits for both PU and PBDO data which validates the description of the relaxation.

The T_1 dispersions in the elastomer film show a distinct behaviour characterized by the presence of characteristic power laws in three frequency windows, respectively regions I, II and III. The results obtained for this anisotropic elastomer film are similar to those found for isotropic polymer networks [6,8] and do not seem to evidence a clear feature that could be linked with the particular mechanical behaviour exhibited by these elastomers. Further work will be done in order to investigate this point.

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