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Polymer segmental dynamics and entanglement constraint

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The relaxation time (T_e) associated with the transition from liquid-like behaviour to pseudo solid-like behaviour for polybutadiene and polyisoprene, as observed in simple Bloch decay n.m.r. experiments, is shown to be linearly dependent upon the polymer molecular weight. This transition begins at the critical molecular weight, M_c, as classically defined by a variety of rheological experiments. The linear dependence of T_e upon molecular weight, using a simple diffusion model, requires the length scale over which the relaxation is operative to be independent of total polymer molecular weight. The experimental results identify the length scale associated with this relaxation time to be the length scale represented by the critical molecular weight (M_c); this process is observed to be virtually independent of temperature over the range 300–350K for polybutadiene. The n.m.r. experiments utilized are found to be sensitive to chain dynamics on the length scale corresponding to the critical molecular weight, not the total polymer molecular weight. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Nuclear magnetic resonance spectroscopic characterization[1] of the chain dynamics of polymeric melts, gels and concentrated solutions has been of considerable interest recently. In these experimental studies a variety of n.m.r. methods have been utilized to examine the transition from the liquid-like state to the pseudo solid-like state for a variety of polymers. These n.m.r. methods have utilized the residual dipolar interaction that remains when the vast majority of the nuclear spin–spin interactions have been averaged to zero by rapid segmental motion. However, in spite of a substantial number of n.m.r. studies, there are still some uncertainties in the relationship of the relaxation times observed in these experiments and the molecular dynamics that they reflect[2–5].

The manifestation of entanglement coupling effects upon the chain segmental dynamics can be separated into three regimes: (a) polymers of sufficiently low molecular weight such that they show no effects of entanglements and behave as simple liquids; (b) somewhat longer chain polymers where topological constraints produced by entanglements begin to inhibit longer range dynamics and hence exhibit a molecular weight dependence; and (c) a sufficiently high molecular weight regime where a fully developed entanglement network exists and pseudo solid-like behaviour is observed. In regime (a) the viscosity typically follows Debye behaviour[6] and the chain dynamics can be treated using the Rouse model[2]. The viscosity of polymer melts have a linear dependence on molecular weight up to a critical molecular weight, M_c, where the dependence changes from 1.0 to 3.4. M_c is interpreted as the onset of entanglement coupling in a variety of rheological experiments and is also found to be the onset of regime (b) in the n.m.r. experiments. M_c has a unique value for each polymer and is independent of the molecular weight of the polymer[7].

In regime (c) a fully entangled, high molecular weight, polymer melt produces a solid-like response in a simple n.m.r. Bloch decay experiment, but with a residual dipolar coupling of the order of a few hundred Hz—which is much less than is observed in a rigid solid (10–50 kHz). Again, the onset of this plateau behaviour has been noted in rheological observations of the steady state compliance, where above a critical value denoted as M'_c (several times M_c) the compliance is independent of M[7]. The averaged dipolar coupling, as measured by the n.m.r. linewidth or as reflected in the relaxation rate, decreases with decreasing molecular weight, as motional averaging becomes more effective in the transition from regime (c) to regime (b). Incomplete motional averaging of the spin–spin interaction occurs when the chain entanglements dissociate on a longer time than the time scale of the n.m.r. measurement. Cohen-Addad's[8] comprehensive work in this field has clearly demonstrated that one can identify this pseudo solid-like response of the spin system using sample spinning. It is well understood that the dipolar linewidth in a solid can be reduced by spinning the sample at a frequency of the order of or greater than the magnitude of the spin–spin interactions. In particular, if the spinning axis is perpendicular to the magnetic field, a reduction by a factor of 2 is observed in the linewidth[9]. The molecular weight dependence of the sample spinning experiment can be substantially obscured by polydispersity; hence, monodisperse polymers are required to enable one to quantitatively interpret the molecular weight dependence of the residual dipolar interaction. In this note we describe the use of n.m.r. measurements of the proton linewidth (with and without sample spinning) for a series of nearly monodisperse polymers covering a range of molecular weights encompassing the three regions described above. The objectives

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are to more clearly delineate the onset of entanglement coupling via n.m.r., compare this result to independent determinations of M_c and M'_c, and to determine if the molecular weight scaling of the n.m.r. relaxation time in the partially entangled regime can provide insight into the dependence of this process on the entanglement molecular weight and the polymer molecular weight.

EXPERIMENTAL

Samples of 1,4 polybutadiene (PB) with molecular weights in the range of 420–4 × 10^6 were obtained from Scientific Polymer Products Inc. Samples of polyisoprene (PIP) with molecular weights in the range of 1000–3 × 10^5 were obtained from Polysciences Inc. The polydispersities of these polymers were below 1.2, except for the highest molecular weight (> 300 000) polybutadienes which had polydispersities of 1.5. Polybutadienes with polydispersities of less than 1.1 and molecular weights from 4.8 × 10^4 to 3.9 × 10^6 were obtained from Dr L. J. Fetters of Exxon Research and Engineering Company. All samples were degassed and vacuum sealed in 5 mm n.m.r. tubes prior to measurement.

The n.m.r. measurements were made on a modified Bruker SXP 20-100 spectrometer using Techmag software and interfacing. The proton n.m.r. observations were made at 90 MHz using a RF pulse length of 10–20 μs. The n.m.r. probe was modified with a stator capable of rapid (≈300 Hz) sample spinning perpendicular to the magnetic field of a resistive electromagnet (2.1 Tesla).

Measurements were made as a function of temperature in the range 300–350K. The non-spinning linewidth of the samples ranged from 10 to 300 Hz with increasing molecular weight. The proton n.m.r. lineshapes could be simulated within experimental error by a sum of Lorentzian lineshapes for all molecular weights. Typical non-spinning lineshapes are shown for PIP along with the Lorentzian lineshape fits in *Figure 1.* The two peaks reflect the chemical shift between the methine protons, and the sum of the methylene and methyl protons. The fit uses a sum of two Lorentzian lineshapes weighted accordingly. The simulations of the experimental data were used to permit a more accurate determination of the linewidths.

RESULTS AND DISCUSSION

The ratio of non-spinning to spinning proton linewidth (at

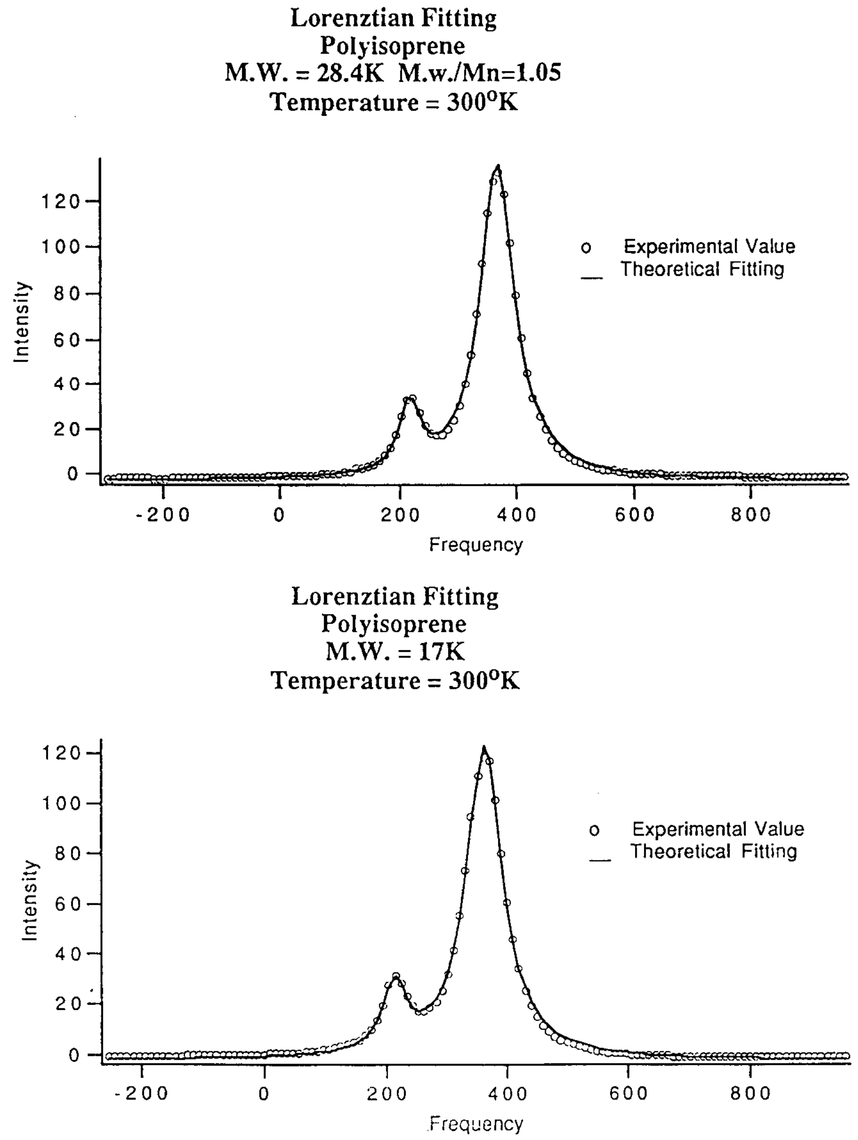

Figure 1 Experimental proton n.m.r. lineshapes (circles) for polyisoprene fitted by a sum of Lorenztian lineshapes (lines)

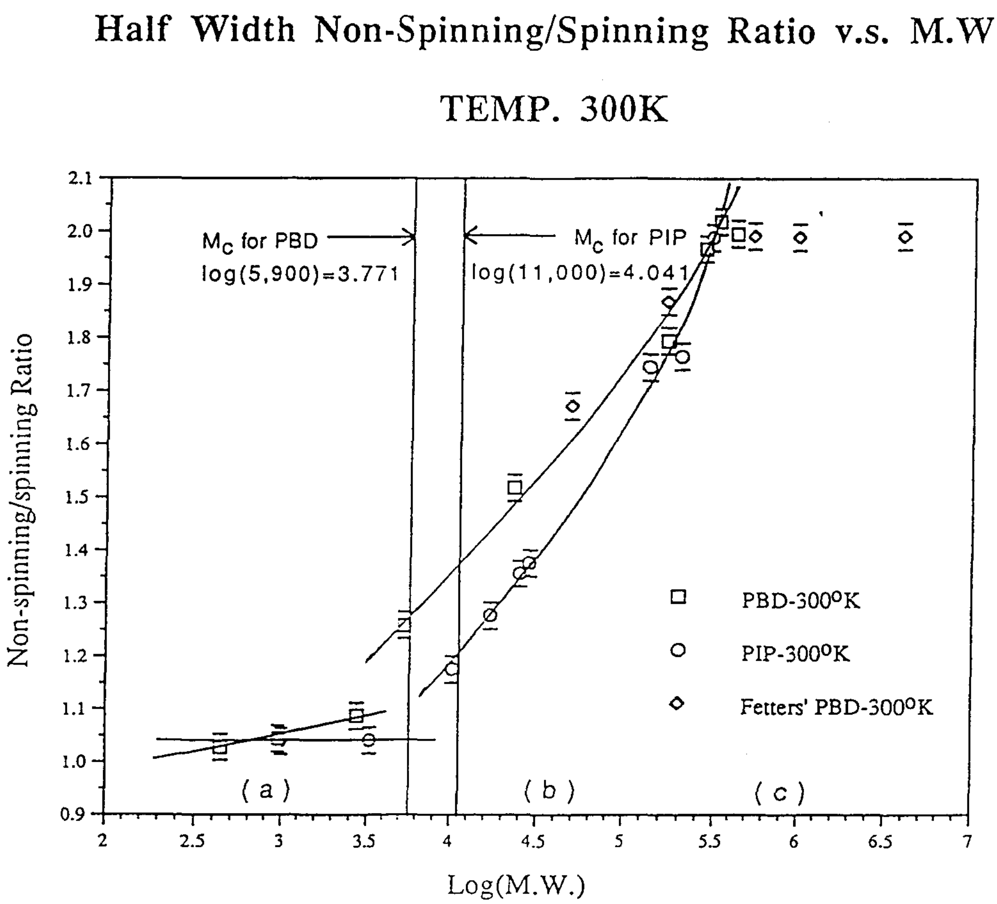

Figure 2 Ratio of the non-spinning to spinning proton n.m.r. linewidth versus molecular weight (*M*) for polybutadiene and polyisoprene at 300K. The liquid like regime (a), the regime of partial entanglement coupling (b), and the pseudo solid-like fully entangled regime (c) are identified

half maximum) as a function of molecular weight is shown in *Figure 2* for both PB and PIP at 300K. These data illustrate the expected trends:[1] regime (c), where the linewidth is reduced upon spinning by a factor of two—corresponding to pseudo solid-like behaviour at high molecular weight; regime (a), where there is no dependence of the linewidth on spinning at low molecular weight; regime (b), where there is a strong dependence of the linewidth on molecular weight and hence the onset of entanglement coupling is evidenced. It is demonstrated that the onset of entanglement coupling as detected through the n.m.r. linewidths occurs at the literature values for M_c for the two polymers (PB $M_c = 5900$[7]; PIP $M_c = 11\,000$[10]). The M_c values depend on the polymer microstructure. The PB used was 58% cis (as determined by n.m.r.) which may be compared to that in ref. 7 which is quoted as approximately 50% cis. The PIP used here was 76% cis (from n.m.r.) compared to those in ref. 10 which ranged from 72% to 84% cis.

The proton linewidth for the non-spinning sample of PB as a function of molecular weight is shown in *Figure 3* for a series of temperatures. The data show a small temperature dependence from 300 to 350K. The slope of the linewidth versus molecular weight, for regime (b), in *Figure 3* reflects the scaling of the n.m.r. relaxation with polymer molecular weight in the entanglement regime.

In the fully entangled (high molecular weight) regime, the motional averaging of the n.m.r. linewidth, δ, will only be observed when the correlation time, T_e, of the motion is of the order of or smaller than the inverse of the linewidth, $1/\delta$. If the motional correlation time is much greater than $1/\delta$ then this is identified as the pseudo solid regime. This corresponds in terms of the steady state compliance behaviour to being above the critical value M'_c. For PB, the pseudo solid-like regime exists above a molecular weight of 135 000, where δ is approximately 250 Hz and is essentially independent of molecular weight. If $T_e < 1/\delta$ this corresponds to regime (a), the low molecular weight regime, where there are no significant entanglement coupling effects and we observe $\delta = 10$ Hz. In the intermediate regime, the n.m.r. linewidth is sensitive to motions with a time scale of the order of 10^{-2}s; furthermore, in this regime the nuclear spin system is in the rapid exchange limit and $\delta \propto T_e$.

T_e represents the characteristic time for relaxation of the constraint(s) which prevents isotropic segmental motion. It is clear from *Figure 3* that δ and hence T_e scale linearly with M in this region; this linear scaling is apparent in other n.m.r. data[1,4], but has not always been recognized. If the disentanglement process is assumed to be diffusive in nature, then $T_e \propto L^2/D$ (where D and L are the diffusion constant and the length scale over which the constraint is effective). If D were proportional to M^{-1} then $T_e \propto M$ and L scales as M^0; note, that if D were to be proportional to M^{-2}, then the non-physical result that the length scale for disentanglement would be inversely proportional to the molecular weight would result. The parallel between M_c and M'_c (determined by rheology), and the beginning and end of the transition region (as observed by n.m.r.) is straightforward. I.e. the onset of entanglement behaviour at M_c is essentially identical for the rheological and n.m.r. measurements; the relationship between M'_c as determined by steady state compliance and the onset of the plateau region

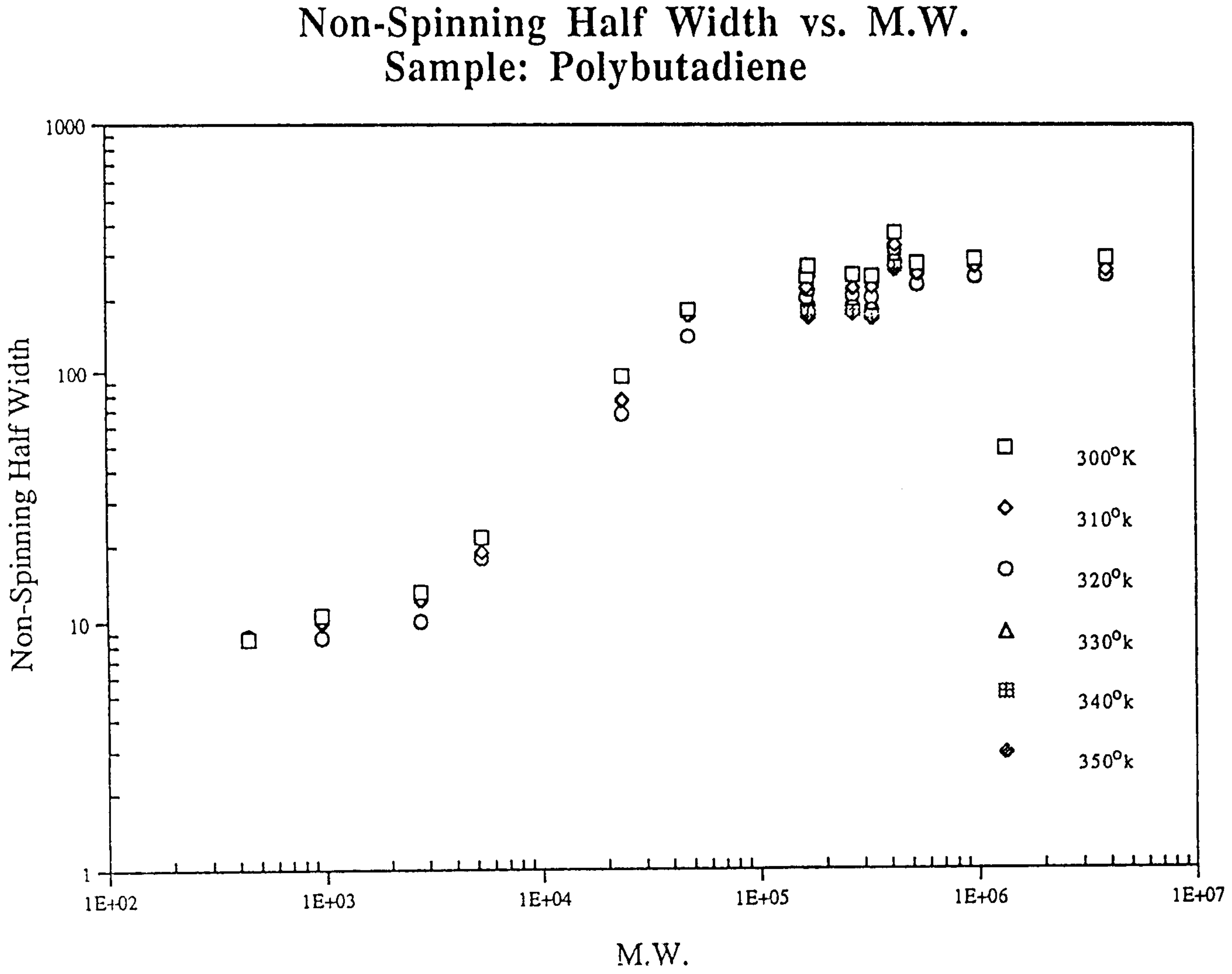

Figure 3 Non-spinning linewidth for polybutadiene versus molecular weight (*M*) at various temperatures

in the n.m.r. linewidth have similar origins. The deviation from plateau behaviour in the steady state compliance (J_e^0) is a measure of how solid-like the system is and this is the same conceptual description used in n.m.r. Graessley[11] suggests that M'_c is related to the spacing between entanglements and predicts a ratio of 1.8 for M'_c/M_c. Experimentally the ratio is typically found to vary from 2 to 6, the value for PIP being 6.0[7] and the n.m.r. value from our data is approximately 20. The difference between the rheological and n.m.r. measurements of solid-like behaviour is due to the two methods having different sensitivity to very slow motions.

CONCLUSIONS

The relaxation time (T_e) associated with the transition from liquid-like behaviour to pseudo solid-like behaviour for PB and PIP, as observed in simple Bloch decay n.m.r. experiments, has been shown to be linearly dependent upon the molecular weight of the polymer. T_e, which is the relaxation time for the constraint preventing chain segments from executing an isotropic motion, exhibits this linear dependence upon molecular weight as the molecular entanglement coupling regime is entered at M_c (the critical molecular weight as determined from a variety of rheological experiments). Furthermore, this linear dependence implies that the length scale over which the relaxation is operative is independent of molecular weight for any diffusive model where $D \propto M^{-1}$. The experimental results identify the length scale associated with this relaxation time (T_e) to be the length scale represented by the critical molecular weight (M_c); the length scale associated with this relaxation is observed to be virtually independent of temperature over the range 300–350K for polybutadiene. The Bloch decay n.m.r. experiments utilized in this work are sensitive to chain dynamics only on the length scale corresponding to the critical molecular weight, not the total polymer molecular weight.

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