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The effect of field inhomogeneities and molecular diffusion on the NMR transverse relaxation behaviour of polymer melts

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The formation of spin-echoes in the Carr–Purcell–Meiboom–Gill (CPMG) NMR experiment on rubbery polybutadiene (PBD) has been studied as a function of temperature and CPMG inter-pulse spacing. The influence of internal field gradients, and of diffusional motion of the polymer segments during the inter-pulse periods is demonstrated. The CPMG decays are well described by diffusion equations for the case of diffusion of particles through connecting cylinders. Microscopic voids of diameter of ~0.5 nm adjacent to the reptating chain segments are suggested to be responsible for the magnetic field gradients.

(Keywords: polymer melt; NMR T_2 relaxation; molecular diffusion)

INTRODUCTION

The NMR transverse relaxation or T_2 decay of entangled polymers has been of interest for many years, providing information on both the structure and dynamics of polymer chains. Of particular interest has been the multi-exponential nature of the decays. In a series of papers from several groups[1–6] the relative intensities associated with each exponential time constant have been assigned to distinct structural features in the polymer. For example in crosslinked polydimethylsiloxane[2] the rapidly decaying part of the T_2 decay has been assigned to structures such as chemical or physical crosslinks. The slower decay has been similarly assigned to free chains. In this manner the extent of crosslinking or polymerization in polymers can be followed in a quantitative manner[2–5]. In a similar analysis[6] the initial rapid decay in the T_2 relaxation of molten polyethylene has been assigned to regions of residual order in the melt and comprised of the chains which make up the lower temperature crystalline regions. The proportion of the rapidly decaying component follows closely the d.s.c. crystallinity after cooling below the melting point.

In a second set of papers the transverse relaxation decay has been described by the fundamental processes which are suggested to occur during reptation of the chains. A hierarchy of motions is proposed ranging from individual segmental reorientation to reptation of the segments through the tube supported by the surrounding chains to, finally, renewal of the tube, The time constants for these processes range from 10^{-10} to 10^{-2} s for a polymer of moderate molecular weight (2×10^5)[7–9]. Kimmich[7] was able to determine the molecular weight scaling laws for the above correlation times from the frequency dependence of the spin-lattice relaxation times T_1 and spin-spin relaxation time T_2. This approach was extended by Callaghan and co-workers[10,11] to lower frequencies with measurements of rotating frame relaxation times in polyethylene and poly(ethylene oxide)[10,11], and this enabled measurements of the tube renewal time.

Finally, Cohen-Addad and Dupeyre[12,13] and Brereton *et al.*[14,15] have used a scale-invariant model of the dipolar interactions in the polymer chain to describe the spin-spin relaxation processes. In this approach the details of the local motion are neglected, as the rate of reorientation is assumed to be rapid on the NMR time-scale. In contrast, the dipolar interactions of larger numbers of spin-pairs is treated as a whole, leading to a rescaling of the dipolar interactions. Motion in the rescaled chain was then described by a Gaussian process. This analysis, and that of Kimmich[7–9], leads to the prediction of an intrinsically non-exponential decay of magnetization for entangled chains.

Detailed interpretations of the relaxation times of a polymer in terms of models of structure and dynamics as referenced above require accurate and reliable experimental measurements. Transverse relaxation times can be measured with the Carr–Purcell–Meiboom–Gill (CPMG) pulse sequence[16,17], a sequence which was initially designed to minimize the effect of magnetic field inhomogeneities across the sample[16]. Kimmich and co-workers[18,19] were the first to report that the decay of magnetization in molten polymers during the CPMG pulse sequence diverged strongly from the decay of magnetization observed in free precession, despite the external magnetic field being highly homogeneous. They concluded that the sequence was refocusing magnetization

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which was dephasing due to the presence of inhomogeneities in the magnetic field in the sample itself. The field inhomogeneities were suggested to arise from the presence of voids in the bulk sample. Subsequently, Geschke and co-workers[20–22] studied this phenomenon in molten polyethylene with the CPMG and the Hahn echo sequences. Their analysis assumed a Lorentzian distribution of field gradients throughout the sample, and suggested that the size of the voids increased with increasing temperature and decreasing molecular weight. The presence of voids was suggested further to be related to the memory effect in polyethylene melts[21]. These authors also demonstrated that magic angle spinning (MAS) can remove the effect of the internal field gradients in polyethylene at 423 K[20,22].

In any NMR experiment where a range of fields is experienced by the sample, full account must be given to the effect of motion. In his original paper on spin-echoes Hahn[24] demonstrates the effect of diffusion of small molecules during the spin-echo experiment in the presence of a constant gradient across the sample. The loss in phase coherence experienced as the spins move through the field gradient was reflected in a decrease in the echo amplitude which was a function of the gradient strength and self-diffusion constant. Expressions for the decay in echo amplitude during the CPMG sequence were derived by Carr and Purcell[16] and Torrey[23]. It was explicitly noted that the rate of decay was a function of the inter-pulse spacing in the CPMG experiment[16]. This fact has not previously been taken into account in measurements of transverse relaxation decays in molten polymers, which, from the above discussion, experience local field inhomogeneities. If the polymer chain segments experience a change in local field due to motion during the experiment it follows that the interpretation of the time constants of the CPMG decay may be in error. Accordingly, we report in this paper the dependence of the echo amplitude on inter-pulse spacing in experiments on polybutadiene as a function of temperature and relate this to the motion of the polymer chain segments across the field gradients existing within the bulk sample.

EXPERIMENTAL

The polybutadiene (PBD) sample was BR1220 obtained from Phillips Petroleum, and contained 99% *cis*-1,4 double bonds. The samples were used as received, and sealed in 7 mm Pyrex tubes after evacuation for 24 h to 10^{-4} mmHg. Identical results were obtained for several samples in the presence of air. For spinning experiments the samples were finely cut and placed in ZrO_2 rotors. The NMR measurements were carried out on a Bruker MSL300 using either a commercial 7 mm MAS probe, or a modified horizontal coil variable temperature ^{1}H probe. π-pulse times of 3 μs and pulse recycle delays of 5 s were used in all experiments.

The CPMG decays were analysed with a fitting program employing the Marquardt–Levenberg algorithm. As discussed below, the decay in the presence of fast sample spinning was fitted to the stretched exponential function. The decays for the non-spinning samples were fitted by multiplying the decay obtained with fast-spinning by an additional function.

RESULTS

Figure 1 shows the CPMG decays for PBD recorded at 302 K with a range of inter-pulse spacings. It can be seen that the inter-pulse spacing dramatically effects the time constants for the decay. This phenomenon has been observed by us for several polymers including polyisobutylene, PBD, polystyrene and polyethylene, and therefore appears to be a general phenomenon in polymer melts, and not just isolated to either glassy or semicrystalline polymers. We have confirmed that the lengthening of the decay is not due to spin-locking by confirming that an experiment with the π-pulses in phase with the initial $\pi/2$-pulse gave identical results to the CPMG experiment.

The decay curves shown in *Figure 1* are clearly not well described by a single exponential time constant. The results of fitting the experimental data in *Figure 1* to the stretched exponential relaxation function [equation (1)] are shown in *Table 1*. Use of the stretched exponential function is not meant to imply that the parameters of best fit in *Table 1* have any physical significance. A fit of

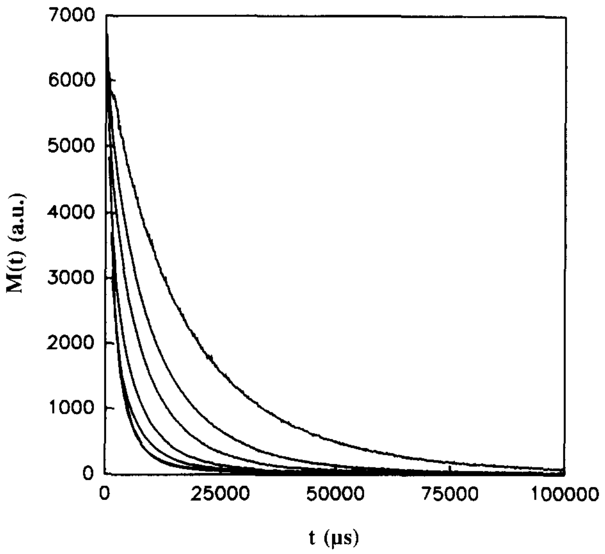

Figure 1 CPMG decays for PBD at 302 K as a function of inter-pulse spacing, τ. The curves with increasing time constants of decay (slower decay) were recorded with inter-pulse spacings, τ, of 1 ms, 800 μs, 600 μs, 400 μs, 200 μs and 100 μs. The longest decay was recorded with MAS

Table 1 Results of fitting CPMG decays to a stretched exponential function. The uncertainties in T_2 and β are ± 4 and ± 0.001, respectively

τ (μs)	302 K	320 K	340 K	360 K	380 K
100 T_2 (μs)	8608	11 650	15 756	19 378	24 714
β	0.805	0.803	0.802	0.799	0.811
200 t_2 (μs)	5458	7350	9862	11 728	15 478
β	0.738	0.728	0.732	0.709	0.728
400 T_2 (μs)	1664	2498	3034	3810	5720
β	0.541	0.551	0.524	0.519	0.543
600 T_2 (μs)	186	174	236	516	1148
β	0.367	0.337	0.332	0.355	0.386
800 T_2 (μs)	16	52	40	66	194
β	0.288	0.310	0.284	0.285	0.311
1000 T_2 (μs)	50	64	84	126	342
β	0.335	0.325	0.319	0.320	0.353
MAS T_2 (μs)	16 540	23 071	30 460	39 092	48 121
β	0.889	0.890	0.877	0.890	0.900

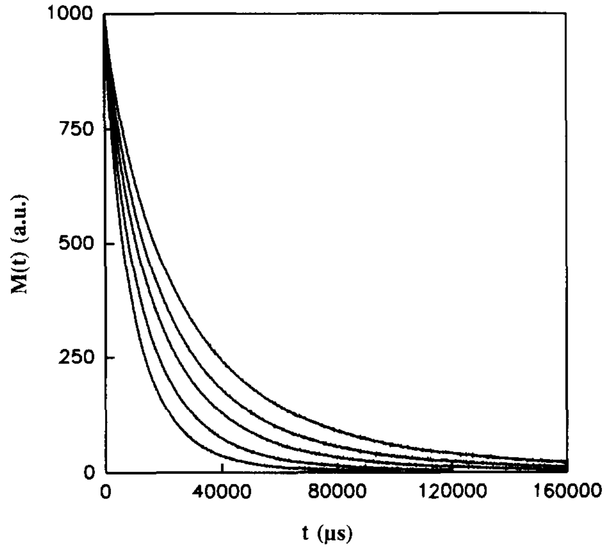

Figure 2 CPMG decays for PBD as a function of temperature recorded with an inter-pulse spacing of 100 μs. The curves with increasing time constants of decay (slower decay) were recorded at 302 K, 320 K, 340 K, 360 K and 380 K

comparable quality could be obtained using a two-exponential decay function. The stretched exponential function was chosen, however, since it requires a smaller number of variables to describe the data.

$$M_{x,y}(t) = M_0 \exp(-t/T_2)^{\beta} \qquad (1)$$

It has been shown by Geschke *et al.*[20,22] that rapid sample spinning is effective at averaging the differences in local field, and the CPMG decay in the presence of spinning therefore reflects the intrinsic relaxation of the molecules. The CPMG decay of PBD recorded in the presence of sample spinning shown in *Figure 1* can be seen to be longer than without sample spinning and is independent of the choice of inter-pulse spacing, τ; the results of fitting this decay to a stretched exponential function are also given in *Table 1*. The values of the intrinsic relaxation times and width parameters were used in subsequent calculations of the effect of internal field inhomogeneities on the CPMG decay.

The CPMG decay curves for PBD were also recorded as a function of temperature (*Figure 2*). The results of the fit to the stretched exponential function, given in *Table 1*, show that as the temperature is increased the decays become slower.

DISCUSSION

The observation of differences between the FID of a molten polymer, and the response to a CPMG sequence was first reported by Kimmich and co-workers[18,19] in a study of molten polyethylene. Kimmich *et al.*[18,19] suggested that the differences between the FID and the CPMG decay are due to the presence of local field inhomogeneities within the sample. They ruled out the influence of residual dipolar broadening since this would not be refocused by the π pulses in the CPMG train. The field inhomogeneities were suggested by them to arise from the presence of voids in the polymer matrix[18,19]. A calculation by Kimmich of the effective difference in field expected for spherical voids in a melt gave differences in local B_0 field of the order of magnitude expected from the NMR lineshape (1–1.5×10^{-5} T). The calculations of Singer and Geschke[21] are of a similar magnitude. Our results support the conclusions of these authors that the response of the system to the CPMG decay is due to internal field inhomogeneities, but differs in the analysis of the effects of motion.

The data in *Table 1* shows that for a given value of the inter-pulse spacing, τ, the form of the exponential decay, as represented by the stretched exponential width parameter, β, is very close to being independent of temperature. This fact seems to explain the success of comparative studies using the CPMG sequence, since, as is demonstrated by the results here, the proportions of the two components in a two-component fit will be approximately constant when a single value of τ is used for all samples, however, the values of the rate constants will depend strongly on the choice of τ.

The dependence of the response of the CPMG experiment on inter-pulse spacing has not been previously noted for molten polymers, and is important for understanding the dynamic nature of the experiment. Early experiments by Hahn[24] and Carr and Purcell[16] predicted a τ dependence in a spin-echo experiment on a simple liquid undergoing self-diffusion in the presence of an external field gradient. Carr and Purcell[16] initially suggested that their experiment would eliminate the effect of field gradients when the inter-pulse spacing became very small. We indeed observe that as τ is decreased the CPMG decay approaches the intrinsic T_2 decay. It is evident from *Figure 1* that the polymer segments experience a change in magnetic field, due to diffusional motion, during the CPMG experiment, and that the time-scale of the change is comparable to the CPMG inter-pulse spacing.

The general case of decay of magnetization in an NMR experiment, in the presence of a gradient, can be written as the product of two terms[22]:

$$M(t) = f(t)\psi(t) \qquad (2)$$

where $f(t)$ is the decay function due to the intrinsic T_2 processes and can be represented, as above, by the stretched exponential function [equation (1)]. The function $f(t)$, which can be measured by averaging the local internal fields in the sample with rapid sample spinning, is given in the bottom line of *Table 1*. $\psi(t)$ is the decay function which describes the dephasing of the magnetization due to motion of the polymer segments through an inhomogeneous magnetic field (either external or internal to the sample). Carr and Purcell[16] have shown that for a simple liquid undergoing Brownian motion in the presence of a constant gradient the perturbing function $\psi(t)$ has the form:

$$\psi_{\mathrm{CPMG}}(t) = \exp(-\gamma^2 G^2 D t^3 / 12 n^2) \qquad (3)$$

Here γ is the gyromagnetic ratio, G is the field gradient (in T m^{-1}), D is the diffusion constant (m^2 s^{-1}) and n is the number of π pulses before data acquisition. Since in the CPMG experiment $n = t/(2\tau)$, equation (3) is best written as:

$$\psi_{\mathrm{CPMG}}(t) = \exp(-\gamma^2 G^2 D \tau^2 t / 3) \qquad (4)$$

The decay function $f(t)$ for PBD at each temperature was convoluted with equation (4) with a range of possible

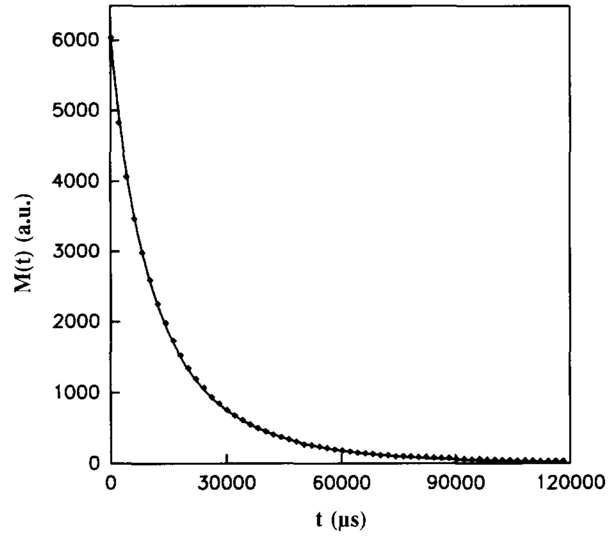

Figure 3 Example of the fit of the experimental data to equations (2) and (5) which model the diffusion of chain segments through a path described by connecting cylinders. The experimental data (◆) were recorded at 302 K with an inter-pulse spacing of 100 μs. For clarity only every tenth experimental point is plotted here.

values for G and D. A satisfactory fit to the experimental data could not be obtained.

The observation that the CPMG decay is a function of the inter-pulse spacing, τ, indicates that during the CPMG sequence the local fields at the nuclei are time dependent. The failure of equation (4) to describe the CPMG decays indicates that the change in field is not due to Brownian-type diffusion in a uniform field gradient. Two additional possible explanations can be offered, namely that field gradients are time dependent as suggested by Kimmich *et al.*[18,19] and Geschke *et al.*[20–22], or that the polymer chain segments themselves undergo non-Brownian molecular displacement during the NMR experiment. In this work we examine the model of displacement of the chain segments across a field gradient which is more or less static on the time-scale of the NMR experiment. We favour this model over the model of time dependent gradients since displacement of a chain segment via the reptation process is energetically more favoured than movement of a large number of chain segments necessary for fluctuation of the voids responsible for the field gradient. We have noted that at temperatures immediately above the glass transition temperature the CPMG decay shows no dependence on the inter-pulse spacing, τ, presumably because the reptation of the polymer chain at these temperatures is slow. At these temperatures T_2 determined from the inverse of the NMR linewidth is identical to that determined by the CPMG method, and reflects the range of local magnetic fields present in the sample. As the temperature is increased the linewidth is little affected, indicating that the fields themselves are not averaged by increasing motion. However, T_2 determined by the CPMG sequence increases (*Figure 2*), and the dependence of T_2 on the inter-pulse spacing becomes more pronounced. At these temperatures diffusional motion of the polymer chain segments or reptation allows displacement of the polymer chain across the internal field gradients. The most simple model of a field gradient is a linear gradient across the chain segment of interest.

The motion of individual chain segments in polymer melts has been described by de Gennes[25] and Doi and Edwards[26] by the reptation model, in which motion of the polymer occurs within a curvilinear 'tube' defined by the surrounding polymer matrix. Such curvilinear diffusion deviates strongly from the Brownian model. In particular the root-mean-square displacement of a segment of the polymer chain depends on $t^{1/4}$ in the reptation model, but is linear with time for Brownian motion of a small molecule. Recently, Fleischer and Fujara[27] have obtained evidence for this scaling law in poly(ethylene oxide) melts using a pulsed field-gradient experiment.

The calculation of the influence of non-Brownian motion on the CPMG train is not trivial. The central problem involves obtaining an expression for the distribution of the displacements of the spins, $P(r,t)$. In the original analysis of the effect of gradients on the spin-echo experiment, Hahn[24] used the central limits theorem to show that this must have a Gaussian form. Such an approach is not applicable here, where non-random processes are involved except in the long time limit. Callaghan and Soderman[28], in a pulsed field-gradient NMR study of Aerosol OT/water mixtures, were confronted with a similar problem. The diffusion of water molecules through a series of connected lamellae is the two-dimensional version of the phenomenon of curvilinear diffusion of the polymer chain segments. Similarly, Callaghan and co-workers[29] studied the diffusion of water in wheat kernels, and found a one-dimensional model was appropriate. By considering the limiting conditions of their problem they were able to suggest a function of the following form which models well their echo attenuation plots[28,29]:

$$\psi_{\mathrm{CPMG}}(t)=\int_0^1 \exp[(-kD/N)x^2]\,\mathrm{d}x \qquad (5)$$

where, in the case of a constant steady gradient, $k=\gamma^2G^2\tau^2t$, as distinct from Callaghan and Soderman's paper[28]. Here N is the effective number of linear chain lengths along which a particular chain segment moves. In the limit of large N the diffusion becomes Gaussian, and for $N=1$ the diffusion is akin to diffusion in a capillary. The effect of the term N is to scale the linear diffusion coefficient.

The CPMG curves for PBD were analysed using equation (5) as the perturbing function, $\Psi(t)$, in equation (2). The decay in the absence of gradients, $f(t)$, obtained from the MAS experiment was subsequently convoluted by the function $\psi_{\mathrm{CPMP}}(t)$ of equation (5), with the value of G^2D/N adjusted to achieve the best fit to the experimental data. A typical fit to the data is shown in *Figure 3*, while the values of the parameters G^2D/N obtained as a function of inter-pulse spacing, τ ($T=302$ K) or temperature ($\tau=100\,\mu$s), are shown in *Figures 4* and *5*, respectively.

It is relevant to note that Callaghan has already considered in some detail the application of the above analysis to curvilinear diffusion in polymer melts[30], but states that gradients large enough for observation of echo attenuation in the pulsed field-gradient experiment are not readily obtainable. It is our conjecture that the gradients present in the polymer melt samples are of sufficient magnitude to allow the observation of the reptation process, but that the gradients extend only over

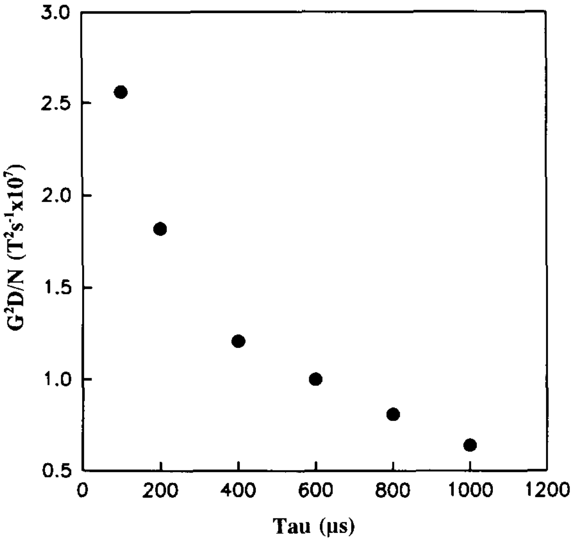

Figure 4 Dependence of the parameter G^2D/N on inter-pulse spacing, τ, at 302 K

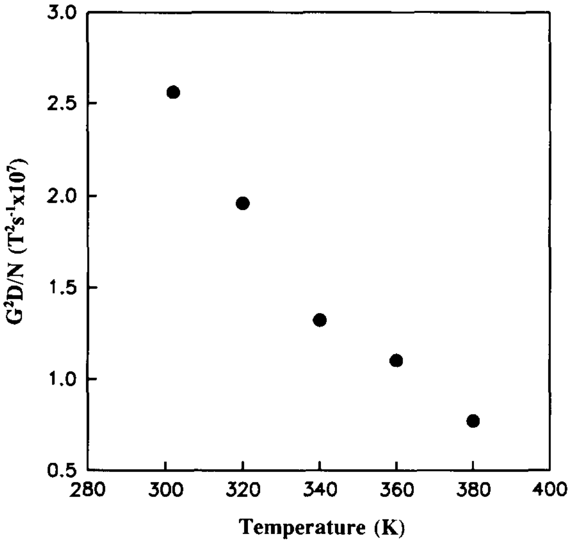

Figure 5 Dependence of the parameter G^2D/N on temperature with an inter-pulse spacing of 100 μs

a short distance in the sample, or are periodic in nature as suggested by Singer and Geschke[21]. The ^{1}H NMR linewidths for these samples were 500 Hz at 302 K, which corresponds to an inhomogeneity of the magnetic field of 1.1×10^{-5} T. The calculations of Kimmich *et al.*[18,19] predict a linewidth of 3–4 kHz for a void model in the absence of motional narrowing. The observed lower linewidth here arises either from an error in the estimated values of magnetic susceptibility used by Kimmich *et al.* or by partial averaging of the gradient by restricted anisotropic motion of chain segments.

The values of G^2D/N obtained from our fits to the experimental data are of the order of $10^{-7}\,\mathrm{T}^2\,\mathrm{s}^{-1}$. We can estimate a value of the self-diffusion coefficient, D, to be of the order of $10^{-15}\,\mathrm{m}^2\,\mathrm{s}^{-1}$, from pulsed field-gradient NMR experiments[27]. If diffusion is restricted to a single cylindrical segment ($N=1$) we arrive at a value of the field gradient $G = 10^4\,\mathrm{T\,m}^{-1}$. Singer and Geschke also suggested the presence of gradients of the same order of magnitude in molten polyethylene[21]. Using the above model of spherical voids, a gradient of this magnitude would be present in the proximity of voids of radius of 0.5 nm. Voids of this dimension have been measured in polymers both above and below the glass transition temperature measured by a range of different techniques including small-angle X-ray scattering[31], fluorescent probes[32] and positron annihilation spectroscopy[33]. Such an excellent agreement between the predicted void sizes and recent other experimental results is gratifying, and supports the use of the model of diffusion of chain segments across field inhomogeneities produced by microscopic voids.

For PBD across the temperature range 300–380 K G^2D/N decreases from 2.6×10^{-7} to $8 \times 10^{-8}\,\mathrm{T}^2\,\mathrm{s}^{-1}$ with increasing temperature (*Figure 5*). At first inspection this result appears surprising, since the curvilinear diffusion constant is expected to increase by an order of magnitude across this temperature range[34]. We believe, however, that as the individual chain segments undergo reptation through the tight tube, the effective diffusion coefficient (D/N) will be decreased by traversal of an increasing number of linear chain segments, i.e. the term N increases. In addition the increase in the rate of diffusion may be partially offset by a decrease in the local field gradient, G, which may be partially averaged by motion. A small decrease in linewidth at the highest temperatures supports this view. In addition, the term G^2D/N decreases with increasing inter-pulse spacing, τ, as seen in *Figure 4*. We again attribute this to an increase in N with increasing τ, since the effective diffusion time is directly proportional to the inter-pulse spacing. This result is directly comparable to the decrease in D at longer times in polystyrene–isoprene block copolymers measured by pulsed field-gradient NMR by Fleischer *et al.*[34] which was similarly ascribed to restriction of the diffusional pathway.

CONCLUSIONS

The observed dependence of the CPMG T_2 decay on the inter-pulse spacing demonstrates that account must be taken of diffusional motion during T_2 measurements of polymer melts. Specifically the choice of the inter-pulse spacings strongly affects the time constants of the T_2 decay. Good agreement between the experimental data and results of calculations using a model of diffusion of chain segments through a path described by connecting cylinders suggests that the CPMG experiment is sensitive to primary reptation processes. The model provides estimates of the size of the field gradient responsible for the above effect, and consequently estimates of the size of the voids producing the gradients. The estimated void sizes are in good agreement with previous measurements by a range of different techniques.

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