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Journal of Magnetic Resonance 236 (2013) 41–46

Contents lists available at ScienceDirect

Journal of Magnetic Resonance

journal homepage: www.elsevier.com/locate/jmr

Study of translational dynamics in molten polymer by variation of gradient pulse-width of PGSE

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ARTICLE INFO

Article history:
Received 15 April 2013
Revised 6 August 2013
Available online 27 August 2013

Keywords:
Magnetic resonance
Molten polymers
Diffusion
Gradient spin echo
Rouse model
Tube/reptation
Velocity correlation function

ABSTRACT

Pulsed gradient spin echo is a method of measuring molecular translation. Changing Δ makes it sensitive to diffusion spectrum. Spin translation effects the buildup of phase structure during the application of gradient pulses as well. The time scale of the self-diffusion measurement shortens if this is taken into account. The method of diffusion spectrometry with variable δ is also less sensitive to artifacts caused by spin relaxation and internal gradient fields. Here the method is demonstrated in the case of diffusion spectrometry of molten polyethylene. The results confirm a model of constraint release in a system of entangled polymer chains as a sort of tube Rouse motion.

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1. Introduction

Pulsed-gradient spin-echo (PGSE) is a powerful NMR method of measuring molecular motion Refs. [1–3]. A PGSE sequence consists of two gradient pulses of duration δ, strength G, and the leading edges are separated by a time interval Δ. The pulses are interspersed by a π RF pulse. PGSE is sensitive to mean squared displacement (MSD) in the limit of short gradient pulses [4]. This approach has its roots in the intrinsic property of the spin echo of having a form known in probability theory as the characteristic functional of a random variable. In the case of spin echo this variable is the velocity fluctuation of spin bearing particle. The link between characteristic functional and the probability density function is through the Fourier transformation (FT). This relation is known in the PGSE measurement with short gradient pulses, where FT of signal dependence with respect to gradient amplitude is the spin displacement probability distribution in the interval between the gradient pulses, Δ [5,4]. For pulses with finite width center-of-mass propagator can be used instead Ref. [6]. The theory of probability offers also an alternative method, in which the spin echo attenuation is directly related to the velocity autocorrelation function [7].

In complex systems (biological or porous systems) MSD depends on Δ. This led to the development of the method of measuring apparent diffusion coefficient (ADC) Ref. [8]. ADC is in a simple relation with the diffusion spectrum (DS). DS is a FT of velocity autocorrelation function. ADC is usually measured by changing Δ in the PGSE experiment. The sensitivity of PGSE is limited to the interval of frequencies extending from zero to the upper limit proportional to $1/\Delta$. Thus, PGSE is not suitable for direct DS measurement. However, it works well when a DS model is known. With suitable magnetic-gradient manipulation e.g. modulated gradient spin echo (MGSE) or oscillating gradient spin echo (OGSE), direct sampling of DS is possible Ref. [9,8].

Measurements with PGSE are effective for long diffusion times or low frequency part of the DS. The problem arises at higher frequencies which implicate the use of short Δ and strong magnetic gradients. This is often hard to implement experimentally. Another problem of the method is additional attenuation caused by background or internal magnetic field gradient. Several methods were proposed to minimize this effect Refs. [10,11]. If time of the spin echo changes with changing Δ, transverse relaxation must also be taken into account.

In cases where details of the non-zero frequency part of the diffusion spectrum are of interest and background gradient cannot be neglected, it is of advantage to sample the diffusion spectrum by varying δ instead of Δ. This is particularly true, when the limit of shortest possible diffusion time Δ has been reached [12,6]. As shown in Ref. [13,14], the frequency range of PGSE method can be extended by measuring the attenuation dependence on the width of gradient pulses δ instead on Δ.

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http://dx.doi.org/10.1016/j.jmr.2013.08.003

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This paper describes the results of the diffusion spectrum measurements of melted polymer with a broad span of characteristic displacements that are a consequence of restricted diffusion. A study of molecular dynamics by PGSE requires gradient pulses shorter than the characteristic times of investigated motion. This condition cannot be always fulfilled, because of the gradient coil induction. For the study of faster molecular motion, we need to analyze the effect of motion on the buildup of spin phase structure during the gradient pulse δ, and not in the time interval between the pulses Δ. This approach permits observations of molecular motion on the time scale below millisecond and displacement in the range of 50–100 nm [14], which is in the range of segmental tube/reptation displacements.

Polymers are macromolecular systems characterized by a complex internal microstructure with large span of length scales. A lot of scientific interest has been devoted to an extremely complex problem of molecular dynamics in molten polymers, where high density, entanglements, chain-bonds and cross-links prevent the formulation of an explicit theory even on larger intra-molecular length scales. The discussion is usually based on highly simplified models such as the Rouse model [15] and the tube/reptation model [16,17], where "reptation" describes a snake-like creeping of a polymer chain during the Brownian motion along a fictive tube formed by adjacent polymer chains (see Fig. 2). These models neglect the details of the chain structure and are consequently only applicable to the length scales, on which a polymer molecule behaves as a highly flexible chain with universal properties. Mathematical simplicity involving very small number of free parameters attributes to the popularity of these models. Although investigation of polymer dynamics has a long-standing record using various experimental techniques shedding the light on various time and length scales of polymer motion, these models remain debatable. In the reptation model, which qualitatively well describes the dynamic properties of dense polymers, a chain performs a curvilinear diffusion along a tube representing the topological constraints exerted by the surrounding chains. The model predicts anomalous segment motion, involving transitions between four different regimes characterized by the dependence of the segmental MSD on time.

By using NMR methods, the self-diffusion coefficient of molten polymers and polymer solutions has been measured either indirectly through the analysis of spin relaxation data [18–21] or directly by the attenuation of the gradient spin echo that displays the phase decoherence of spin-bearing particles moving randomly in the applied magnetic field gradient [19].

PGSE studies of polymer dynamics quite convincingly confirm the validity of the Rouse model in the case of dilute and semidilute polymers [22–25] but not so clearly the tube/reptation model for the dense polymers [19,26–28]. The PGSE is able to measure diffusion in the interval of Δ from 10 ms to 3 s [29], where the shortest interval is limited by the strongest applicable gradients. This method is able to detect the segment displacement in the range of 200–450 nm assuming the self-diffusion coefficient D of high molecular weight polymer melts on the orders 10^{-15}–10^{-12} m^2 s^{-1}. Polymer chain reptation displacements are smaller than 100 nm and are not detectable with a conventional PGSE experiment. A test of tube/reptation model by measuring diffusion of nanoscopic strands of linear, mono-disperse poly (ethylene oxide) embedded in the artificial cross-linked methacrylate matrices is described in Ref.[30].

2. Theory

By treating the spin dephasing as a characteristic functional of the stochastic process with the molecular velocity as the random variable, the spin echo attenuation is given by [7,31,9]

$$\ln S/S_0 = \frac{1}{\pi}\int_0^\infty |q(\omega)|^2 D(\omega)d\omega, \tag{1}$$

in which S_0 is the magnitude of the spin echo in the absence of magnetic field gradient, $q(t) = \gamma\int_0^t G_{eff}(t')dt'$ is dephasing, $q(\omega) = \int q(t)e^{i\omega t}dt$ its spectrum and diffusion spectrum $D(\omega)$ is the velocity autocorrelation spectrum of molecular motion [32]

$$D(\omega) = \int_0^\infty \langle \Delta v_z(t)\Delta v_z(0)\rangle e^{i\omega t}dt. \tag{2}$$

Here, $\Delta v_z(t) = v_z(t) - \langle v_z(t)\rangle$ is the velocity fluctuation in the direction of the effective magnetic field gradient G_{eff} [33,34] applied along the z-axis.

A PGSE sequence (Fig. 6) consists of two gradient pulses of strength G separated by a time interval Δ and its dephasing power spectrum is given by

$$|\mathbf{q}(\omega)|^2 = 16\gamma^2 G^2 \frac{\sin^2(\omega\delta/2)\sin^2(\omega\Delta/2)}{\omega^4}. \tag{3}$$

The power spectrum, shown in Fig. 1, samples the DS around zero frequency.

Inevitable in heterogeneous samples is the presence of steady magnetic gradient caused by susceptibility effects G_i. The contribution of this internal gradient field is described in appendix. Its power spectrum is included in Fig. 1. Plots for different δ indicate impact of internal gradient at low frequencies. Variable δ PGSE is suitable for measuring DS at higher frequencies because the width of the PGSE power spectrum changes more than the width of the corresponding internal gradient power spectrum.

As already mentioned, PGSE samples the whole lower part of the DS spectrum and is not suitable for direct sampling. However, if a model DS is known, the integral in Eq. (1) can be evaluated and parameters of the model can be fitted to the experimental results.

The models of molecular dynamics commonly describe the molecular MSD time dependence. $D(\omega)$ in Eq. (1) is derived as a Fourier transformation of MSD: $D(\omega) = -\frac{\omega^2}{2}FT[\langle\Delta z^2(t)\rangle]$. In the Rouse model of entangled polymer melt dynamics [15] the segment MSD is given as a sum of modes, which can be approximated in the case of a long chain [35] as

$$\begin{aligned}\langle\Delta z^2(t,N)\rangle_R) &= 2D_c t + \frac{4}{3}\sum_{p=1}^{N}\left\langle X_p^2\right\rangle\left(1 - e^{-p^2 t/\tau_R}\right)\\ &\approx \frac{4\sqrt{\pi}}{3}\left\langle X_1^2\right\rangle\sqrt{\frac{t}{\tau_R}}.\end{aligned} \tag{4}$$

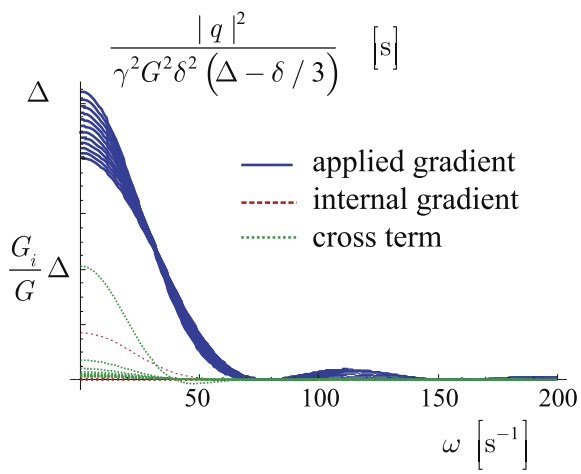

Fig. 1. Normalized spin dephasing power spectra for PGSE sequence (solid, blue line) for different values of δ, as used in experiment, with corresponding background (dashed, red) and cross (dotted, green) terms.

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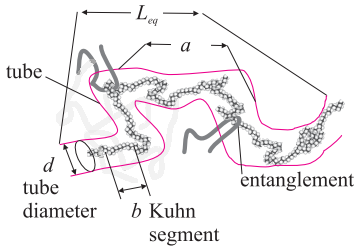

Fig. 2. Entangled polymer chains constitute a tube confining a single chain.

Here, N is the number of Kuhn segments of length $b, D_c = \frac{k_B T}{N\xi}$ is the center-of-weight diffusion coefficient, ξ is the effective friction drag on the monomer, $\langle X_p^2 \rangle = \frac{Nb^2}{2\pi^2 p^2}$ is the amplitude of the p-mode and $\tau_R = \frac{2\langle X_1^2 \rangle}{3D_c}$ is known as the Rouse relaxation time.

In a dense polymer, intermolecular entanglements localize a macromolecule inside a curved tube. In a short intervals, the part of the chain between the adjacent entanglements moves as anticipated in the Rouse model with MSD $\langle \Delta z^2(t, N_e) \rangle_R$ in which N_e corresponds to the number of Kuhn segments between the two entanglements. In the intermediate time regime, as segment displacements reach the tube "walls", topological confinement forces the chain to move in a reptile manner (reptation) along the tube [16,17]. The Rouse MSD in the curvilinear coordinates $\langle \Delta z^2 \rangle_{rept} \propto d\sqrt{\langle \Delta z^2(t, N) \rangle_R}$ describes the chain motion along the tube, where d is the effective tube diameter. The correlations with the initial conformation are lost at longer times, when the polymer chain creeps out of the tube. This process is disengagement self-diffusion with MSD $\langle \Delta z^2 \rangle_d = 2D_d t$ [16]. The replacement of the Rouse MSD, Eq. (4), in these expressions gives an overall MSD time dependence proportional to $t^{1/2}$ at short times. In the intermediate tube/reptation regime the mode is changed from $t^{1/4}$ to $t^{1/2}$. Following the chain disengagement from the tube at $\tau_d = \frac{N^2 a^2}{\pi^2 N_e^2 D_c}$, MSD is proportional to t [19]. a is the tube length between the entanglements. These different diffusion modes are shown in Fig. 3.

The FT of the segment MSD, gives also the overall diffusion spectrum $D(\omega)$ in different modes. With increasing frequencies, $D(\omega)$ goes from a constant D_d at $\omega = 0$ into $\omega^{1/2}$ and $\omega^{3/4}$-dependence in the tube/reptation regime. After passing into the Rouse regime at the frequency $\omega_R = 2\pi/\tau_R$, it exhibits $\omega^{1/2}$-dependence again, which levels into a constant at high frequencies [36]. The DS is shown in Fig. 4.

Replacement of the many-chain problem by a single chain moving in a tube of permanent obstacles, enables a solution, but it is oversimplified due to neglect of the obstacle motion. In real polymers, the motion of adjacent chains leads to the so called "constraint release" [37,38] that causes a reorganization, in which the tube itself may behave as a Rouse chain with the relaxation time proportional to the lifetime of the obstacles τ_{ob}. According to this view [16,39], the tube is considered as a chain, coarse-grained to segments of length a, with the number of segments $\frac{N}{N_e}$, and the curvilinear length of $L_{eq} = \frac{N}{N_e} a = N\frac{b^2}{a}$. This model gives the coarse grained segmental MSD in the form of Eq. (4), $\langle \Delta z^2 \rangle_{Rtube} = \langle \Delta z^2(t, N/N_e) \rangle_R$, in which we replace: $D_c \to D_d = \frac{N_e}{N} D_c, \langle X_1^2 \rangle \to \langle X_1^2 \rangle_{Rtube} = \frac{3L_{eq}a}{2\pi^2}$ and $\tau_R \to \tau_{ob}\frac{N^2}{N_e^2}$. The model of chain reptation in the tube and the tube Rouse motion give identical segmental MSD-s starting as $t^{1/2}$ and evolving to t time dependencies around the terminal time τ_d. In order to determine, which of both modes prevails in the time range $\tau_R < t < \tau_d$, we compare the ratio of their MSD-s

$$\frac{\langle \Delta z^2 \rangle_{Rtube}}{\langle \Delta z^2 \rangle_{rept}} \approx \frac{\sqrt{2}a^2}{\pi^2 d\sqrt{D_c \tau_{ob}}}. \tag{5}$$

According to the original idea [37], the longest relaxation time of the tube Rouse motion in mono-dispersed polymer melt equals to the terminal time of the chains reptation in the tube, $\tau_{ob}\frac{N^2}{N_e^2} = \tau_d$, which amounts to almost equal contributions of both processes to the MSD $t^{1/2}$-dependence. However, recent measurements of the velocity autocorrelation spectra in molten polymers by the method of modulated gradient spin echo [40], show a prevailing role of the tube Rouse motion at low frequencies, which corresponds to long diffusion times of the PGSE method. These data indicate much faster tube reorganization than was previously expected. For polydispersed sample L_{eq} would assume a broad spectrum of values. In the following we use this result to express the low frequency DS of polymer segments from the FT of the tube Rouse MSD as

$$D(\omega) \approx D_d + \sqrt{\frac{\omega}{8\pi^3 \tau_{ob}}} L_{eq}^2 + \cdots \tag{6}$$

The substitution of Eq. (6) together with the spectrum of PGSE sequence from Eq. (A.1) into Eq. (1) gives the spin echo attenuation

$$\ln(S/S_0) = \gamma^2 G^2 \left[D_d \delta^2 \left(\Delta - \frac{\delta}{3} \right) + \frac{\sqrt{8}}{15\pi^2\sqrt{\tau_{ob}}} L_{eq}^2 \left((\Delta - \delta)^{5/2} + (\delta + \Delta)^{5/2} - 2\Delta^{5/2} - 2\delta^{5/2} \right) \right]. \tag{7}$$

The attenuation depends not only on Δ, but also on δ. This is a clear display of the effect of segmental motion on the buildup of spin phase structure during the gradient pulse application. ADC defined here as

$$D_{eff} = \frac{\ln(S/S_0)}{\gamma^2 G^2 \delta^2 (\Delta - \frac{\delta}{3})} \tag{8}$$

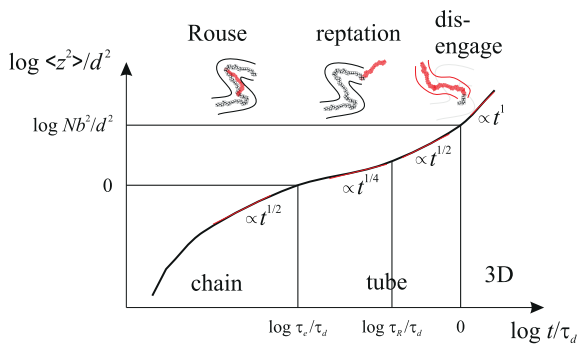

Fig. 3. MSD of entangled polymer segments in different regimes. MSD is proportional to $t^{1/2}$ for the displacements on the order of the tube diameter and times shorter than τ_e. For times up to Rouse time τ_R the MSD is proportional to $t^{1/4}$ which is followed by a crossover to $t^{1/2}$ mode of reptation. On a long scale, for times longer than disengagement time τ_d and displacements longer than chain length, MSD is proportional to t.

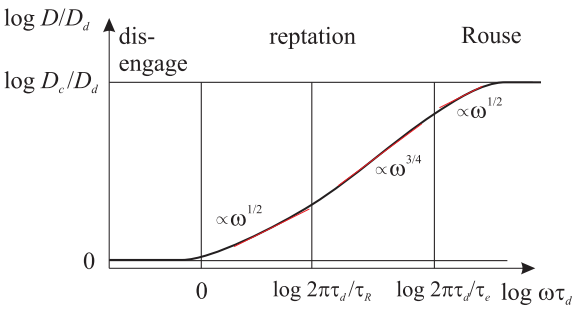

Fig. 4. Diffusion spectra of entangled polymer. At low frequencies the spectra has a constant value D_d corresponding to center of weight diffusion in a long time limit. The diffusion spectrum then increases proportionally to $\omega^{1/2}$ in reptation regime with a crossover to $\omega^{3/4}$ dependence at frequencies of $1/\tau_R$.

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can be approximated for $\delta \ll \Delta$ with the power series in terms of $\sqrt{\frac{\delta}{\Delta}}$

$$D_{eff}(\Delta,\delta) \approx D_d + \frac{1}{\pi^2\sqrt{2\Delta\tau_{ob}}}L_{eq}^2\left(1-\frac{8}{15}\sqrt{\frac{\delta}{\Delta}}+\cdots\right). \quad (9)$$

D_{eff} does not depend on G, as long as the effect of internal gradient can be neglected. Measuring the dependence of ADC on the time interval between gradient pulses Δ looks as the most effective way to extract information about the tube Rouse diffusion, $L_{eq}^2/\sqrt{\tau_{ob}}$. However, internal magnetic field gradients caused by differences in the susceptibility strongly affect measurements of Δ-dependence in molten polymers [19]. Measurement of the PGSE attenuation dependence on δ at fixed Δ reduces these effects to a great extent, as demonstrated in Fig. 5. Figure shows ADC calculated from Eq. (B.1) for the cases with and without internal gradient. The artifact is dominant at short δ, while at longer δ ADC converges into a single curve following linear $\sqrt{\delta/\Delta}$-dependency corresponding to the model without internal gradient described in Eq. (7). As shown in Ref.[14], the variation of gradient pulse width δ instead of Δ also shortens the time range of displacement measurements to below 1 ms, which is enough to give better insight into the polymer dynamics.

3. Method

Measurements were done on a home-made pulsed NMR spectrometer at 60 MHz proton NMR frequency and equipped with magnetic field gradient coil system described in [41]. The sequence is shown in Fig. 6. Lengths of RF pulses used were about microseconds. π RF pulse was applied symmetrically between the gradient pulses. Gradient pulse followed the RF pulse with a delay short enough to be neglected in the signal analysis. The same is true for the echo following the second gradient pulse; however the echo followed the second gradient pulse with a delay large enough that no artifacts were introduced because of the finite gradient fall time.

PGSE attenuation dependence on the duration of gradient pulses was measured by changing the pulse width δ from 1 to 15 ms with an interval between the gradient pulses Δ = 80 ms. Other intervals were tested as well. Measurements were done with gradient fields: 4.38 T/m, 3.04 T/m and 1.34 T/m. Signal attenuation at zero applied gradient is dominated by internal gradient and S_0 can be determined by the extrapolation to δ = 0 as shown in Fig. 7.

4. Experiments and discussion

The sample of linear polyethylene Standard Reference Material 1482 with narrow molecular weight distribution (M_n = 11,400 g mol^{-1}, M_w = 13,600 g mol^{-1}) was prepared by NIST, Washington DC, USA. Measurements were done on melted polyethylene sample at 426 K. Fig. 7 shows the results of D_{eff} from Eq. (8) for different gradients at Δ = 80 ms. The effective self-diffusion coefficient follows mainly the $\sqrt{\delta/\Delta}$-dependence according to Eq. (9), but deviates from it at short $\delta \approx 1$ ms, as expected from Eq. (B.2) due to effect of susceptibility fields shown in Fig. 5. The effective diffusion coefficient obtained by measurements at shorter Δ = 20 and 40 ms agree mostly with the reported results but were not used in the analysis, because they are not accurate due to the problems with signal acquisition. Namely, the shift of the echo center is more sensitive to the variation of δ at shorter Δ. By neglecting the data at 1 ms, the fit of the experimental data at Δ = 80 ms in terms of Eq. (8) gives the diffusion parameters. The negative slope, which is an evidence of the tube Rouse motion, gives the tube displacement per obstacle lifetime $L_{eq}^2/\sqrt{\tau_{ob}} \sim (1.8 \pm 0.2) \times 10^{-11}$ m^{2}s$^{-1/2}$. The extrapolation to $\delta/\Delta \to 0$ and subtraction of the tube diffusion part according to Eq. (9) give $D_d \approx (3.9 \pm 3) \times 10^{-13}$ m^2 s^{-1}, which is close to the center-of-mass diffusion coefficient for entangled polymers of this length [29,42,43]. The experimental errors are taken from the parameter variations of the least squared fit to Eq. (8) with the assumption of error normal distributions.

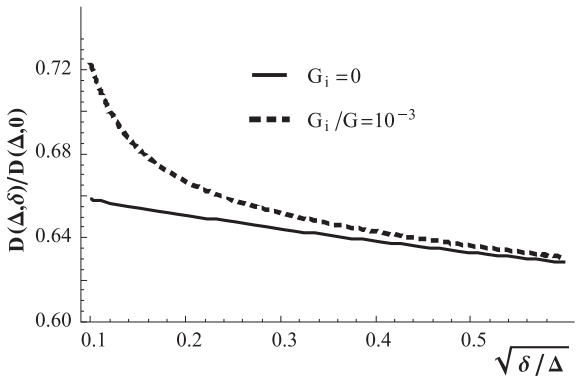

Fig. 5. At short δ susceptibility magnetic field gradient (dotted lines) cause a deviation of the effective diffusion coefficient from the $\sqrt{\delta/\Delta}$-dependence that corresponds with Eq. (7) (solid line).

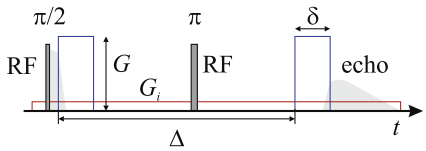

Fig. 6. The PGSE sequence used in the study: two gradient pulses of strength G and duration δ were applied with the leading edges separated by Δ. G_i is the constant internal gradient.

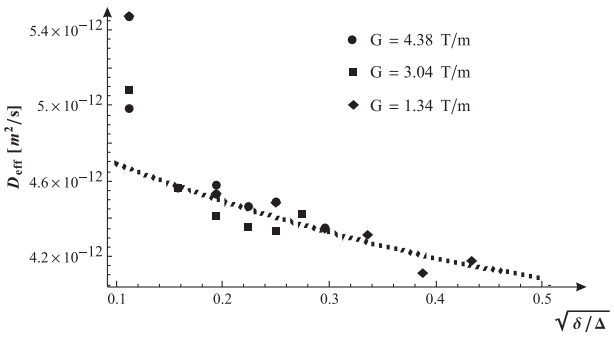

Fig. 7. δ/Δ-Dependence of the effective diffusion coefficient of polyethylene in melt measured with PGSE measurement at Δ = 80 ms and different gradient strengths. Dotted line is the least square fit of Eq. (8) to the experimental data, in which the first points at δ = 1 ms were discarded.

5. Conclusion

PGSE method enables the measurement of segmental translation of polymeric chain by variation of gradient pulse width. This approach effectively reduces artifacts caused by internal gradients and spin relaxation, which commonly effect the PGSE measurement of molten polymer, but requires knowledge of interplay between the molecular motion and the buildup of spin phase structure during the magnetic field gradient action. By using the spectra of the effective gradient and the segmental velocity autocorrelations rendered from the model of tube Rouse motion [39], we obtain the dependence of the PGSE signal attenuation on the variation of gradient pulse width. Result fits well to the data obtained by the measurements of molten polyethylene and provide

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an evidence of the tube Rouse motion model proposed in Ref. [39]. The model that was already confirmed by the method of modulated gradient spin echo [40] reveals the segmental motion in the range of milliseconds. Both data M_w and M_n indicate a sharp distribution of fragment sizes so the effects of polydispersity, which may cause apparently non-classical diffusion behavior, can be neglected in our case.

Acknowledgments

We are grateful to the Slovenian Ministry of Higher Education, Science and Technology for the financial support.

Appendix A. Spectrum of spin dephasing

The spectrum of spin dephasing, $q(t) = \gamma \int_0^t G_{eff}(t')dt'$, of the PGSE with two gradient pulses is

$$q(\omega) = \int_0^\tau q(t)e^{i\omega t}dt = -\gamma G\frac{(1-e^{i\delta\omega})(1-e^{i\Delta\omega})}{\omega^2}. \tag{A.1}$$

The spectrum of steady internal gradient is accordingly $q_i(\omega) = -\gamma G_i\frac{(1-e^{i\Delta\omega})^2}{\omega^2}$. From here the combined squared dephasing spectrum of two pulse gradient G and the constant internal gradient G_i follows as

$$\begin{aligned}|q(\omega)+q_i(\omega)|^2 = &\frac{\gamma^2}{\omega^4}\left[16G^2\sin^2\left(\frac{\delta\omega}{2}\right)\sin^2\left(\frac{\Delta\omega}{2}\right)\right.\\ &+32GG_i\sin\left(\frac{\delta\omega}{2}\right)\sin^3\left(\frac{\Delta\omega}{2}\right)\cos\left(\frac{1}{2}\omega(\delta-\Delta)\right)\\ &\left.+16G_i^2\sin^4\left(\frac{\Delta\omega}{2}\right)\right].\end{aligned} \tag{A.2}$$

only the PGSE part was used in the analysis of ADC.

Appendix B. Polymer motion and the gradient spin echo attenuation

The substitution of Eq. (6) and Eq. (A.2) into Eq. (1) gives the gradient spin echo attenuation

$$\begin{aligned}\ln(S/S_0) = &D_d\gamma^2\left(\delta^2G^2\left(\Delta-\frac{\delta}{3}\right)+\delta GG_i\left(-\frac{2\delta^2}{3}+\delta\Delta+\Delta^2\right)+\frac{2}{3}G_i^2\Delta^3\right)\\ &+\frac{1}{\pi^2\sqrt{2\Delta\tau_{ob}}}L_{eq}^2\gamma^2\\ &\left[G^2\left(-2\delta^{5/2}+(\Delta-\delta)^{5/2}+(\delta+\Delta)^{5/2}-2\Delta^{5/2}\right)\right.\\ &+GG_i\left(-3\delta^{5/2}+3(\Delta-\delta)^{5/2}+(\delta+\Delta)^{5/2}-(2\Delta-\delta)^{5/2}\right.\\ &\left.\left.-4\Delta^{5/2}+\sqrt{32}\Delta^{5/2}\right)+8G_i^2\left(1-\frac{1}{\sqrt{2}}\right)\Delta^{5/2}\right]\end{aligned} \tag{B.1}$$

For $G_i \ll G$, the apparent diffusion coefficient for small δ is expressed as

$$\begin{aligned}\frac{\ln(S/S_0)}{\gamma^2\delta^2G^2\left(\Delta-\frac{\delta}{3}\right)} \approx &D_d\left(1+\frac{\delta G_i}{\Delta G}+\cdots\right)\\ &+\frac{1}{\pi^2\sqrt{2\Delta\tau_{ob}}}L_{eq}^2\left(1-\frac{8\sqrt{\delta}}{15\sqrt{\Delta}}+\frac{4\left(\sqrt{2}-1\right)G_i\Delta}{3\delta G}+\cdots\right).\end{aligned} \tag{B.2}$$

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