Colloid Polym Sci 275:187–191 (1997)

SHORT COMMUNICATION

M. Appel
G. Fleischer
J. Kärger
I. Chang
F. Fujara
A. Schönhals

# Transient entanglement behaviour in a poly(propylene glycole) melt: A field gradient NMR self-diffusion study

Received: 6 September 1996
Accepted: 13 November 1996

M. Appel[1] · G. Fleischer (✉) · J. Kärger
Universität Leipzig
Fakultät für Physik und Geowissenschaften
Institut für Experimentelle Physik I
Linnestraβe 5
04103 Leipzig, Germany

I. Chang
Universität Mainz
Institut für Physikalische Chemie
Jakob-Welder-Weg 15
55099 Mainz, Germany

F. Fujara
Universität Dortmund
Experimentelle Physik III
Postfach 500 500
44221 Dortmund, Germany

A. Schönhals
Institut für Angewandte Chemie
Rudower Chaussee 5
12484 Berlin, Germany

[1] *Current address*:
Exxon Research and Engineering Company
Annandale, New Jersey 08801, USA

**Abstract** We report measurements of the temperature dependence of the self-diffusion of a poly(propylene glycole) in the melt. Two kinds of magnetic field gradient NMR are used: pulsed field gradient NMR with large field gradients and static field gradient NMR in a specially designed cryomagnet. The emphasis is put on large field gradients. The (true) long-time self-diffusion coefficients are compared with those calculated from normal-mode relaxation times in dielectric spectroscopy using the Rouse model. They agree very well. For temperature below about 270 K, a time-dependent self-diffusion coefficient appears which is an indication of anomalous diffusion. At 253 K we observe complete transient entanglement behaviour of the PPG melt. These results are discussed in comparison with dielectric and other experimental data.

**Key words** Poly(propylene)glycole – transient entanglements – field gradient NMR – self-diffusion – dielectric relaxation

## Introduction

In many polymer systems transient entanglement behavior is observed if network junctions of finite lifetime exist [1]. Specific intramolecular interactions can lead to temporally network junctions, e.g. hydrogen bonds [2] or the dissolution of outer blocks of a triblockcopolymer in microemulsion droplets, whereas the inner block is dissolved in the continuous phase [3]. For molecular weights $M$ greater than the entanglement molecular weight $M_e$ entanglements with a finite lifetime act like temporal network junctions.

The transient entanglement behavior of poly(propylene glycole) (PPG) in the melt was detected by ultrasonic investigations [2]. Further indications were obtained by NMR [4], dielectric spectroscopy [5, 6] and pulsed field gradient NMR [7]. In this work, we report on new field gradient NMR investigations of the self-diffusion of a poly(propylene glycole) melt using very large field gradients produced with a specially designed cryomagnet [8].

At ambient temperatures, we observe common self-diffusion, whereas at low temperatures, anomalous diffusion is observed, i.e., a time-dependent apparent self-diffusion coefficient. This behaviour is typical for restricted diffusion and caused by segmental fluctuations of the chains fixed in the transient network.

The monomeric units of poly(propylene glycole) possesses in addition to an electric dipole moment which is perpendicular to the polymer backbone a component of the dipole moment that is parallel to the chain. These macromolecules are known as type A polymers [9]. For such systems the motion of the whole polymer chain, called normal-mode relaxation, can be studied by dielectric spectroscopy. This process shows up in the dielectric spectra besides the segmental motion as a discernible relaxation peak [10]. Usually, the dielectric normal mode relaxation is described by the Rouse theory [10] where the relaxation time of the $p$th mode is given by [11]

$$\tau_p = \zeta_0 N^2 b^2 / 3\pi^2 kTp^2 , \tag{1}$$

where $\zeta_0$ is the segmental friction coefficient, $b$ the segment length and $N$ the number of segments in the chain. $kT$ has the usual meaning. As discussed by Baur and Stockmayer [9] and later in Ref. [12], in PPG samples which have two opposing sequences of parallel dipole components the major contribution to the dielectric spectrum comes from the second mode with $p = 2$.

The self-diffusion coefficient $D$ of the chain corresponds to the zeroth Rouse mode. It is given by

$$D = kT/\zeta_0 N . \tag{2}$$

For the product of $\tau_p D$ we obtain

$$\tau_p D = \langle R^2 \rangle / 3\pi^2 p^2 , \tag{3}$$

where $\langle R^2 \rangle = Nb^2$ is the mean squared end-to-end distance of the chain. Therefore, one can calculate $D$ from dielectric data and known $\langle R^2 \rangle$.

The goals of this work are (i) to verify Eq. (3), i.e., to compare the dielectric measurements of PPG from Ref. [13] with self-diffusion measurements and (ii) to look for transient entanglement behaviour of the PPG by the detection of spatially limited fluctuations of the polymer chain segments. For the latter task field gradient NMR with a large space resolution, i.e., with very high field gradients, is necessary. To our knowledge, only one paper has until present been published on this topic in which the segmental fluctuations in swollen polybutadiene networks are detected [14].

## Experimental

For the pulsed field gradient NMR we refer to the papers of Kärger et al. [15, 16]. The experiments were carried out as described e.g. in Ref. [17]. From the echo attenuation $\Psi$ in a stimulated echo experiment with applied pulsed field gradients the self-diffusion coefficient $D$ is calculated according to the Tanner–Stejskal equation

$$\Psi = \exp(-q^2 Dt) , \tag{4}$$

where $q = \gamma\delta g$ is the absolute value of a generalized scattering vector [18]. $\gamma$ is the gyromagnetic ratio of the proton, the nucleus under consideration, $\delta$ the width and $g$ the magnitude of the field gradient pulses. The diffusion time $t$ is the distance of the two field gradient pulses ($t \gg \delta$). For free diffusion the mean square distance of a species travelled in the diffusion time $t$ between the two field gradient pulses is

$$\langle z^2 \rangle = 2Dt . \tag{5}$$

If the diffusion becomes restricted, the dependence of $\langle z^2 \rangle$ on the diffusion time is weaker than with the first power of $t$, and for completely restricted diffusion $\langle z^2 \rangle$ is independent of $t$. In this case a diffusion coefficient derived from the experimental echo attenuation curve with Eq. (4) is an apparent one: $D_{\text{app}}$. It depends on the diffusion time as $D_{\text{app}} \sim t^{-1}$. The echo attenuation then characterizes the barrier distances and not the molecular mobility of the diffusing species ("dynamic imaging" [19]). The pulsed field gradient NMR experiments were carried out at two home-built spectrometers at resonance frequencies of 60 and 400 MHz. The maximum applied field gradients were 23 and 25 T/m, respectively.

The echo attenuation in the static field gradient NMR experiment additionally contains an echo attenuation due to transverse nuclear magnetic relaxation since the distance $\tau_{\pi/2}$ between the two first $\pi/2$-rf pulses is varied in the experiment, a time window in which $T_2$-relaxation takes place. Therefore, in this case the right-hand side of Eq.(4) must be multiplied by $\exp(-2\tau_{\pi/2}/T_2)$, and $\delta$ is to be replaced by $\tau_{\pi/2}$. In one experiment $T_2$ and $D$ must be evaluated by a fitting procedure (if $T_2$ is not known from a separate measurement). With decreasing temperature $T_2$-relaxation becomes faster and diffusion slower so that at some instant the echo attenuation becomes dominated by $T_2$-relaxation and an accurate determination of $D$ is no longer possible. This is the limiting factor for determining low self-diffusion coefficients with this method. Nevertheless, due to the large field gradients (200 T/m can be reached [8] as compared with about 50 T/m for pulsed field gradient NMR [20]) with static field gradient NMR the lower limit of self-diffusion coefficients can be extended at least by one order of magnitude.

The measurement and data evaluation of the dielectric spectroscopy is described in Refs. [13, 27]. The PPG with a nominal molecular weight of 4000 was purchased from Waters Associates (MA, U.S.A.) and used without further treatment. This PPG consists of two chain parts with opposing sequences of dipole moments.

## Results and discussion

We first present the results of the temperature dependence of the (true) long-range self-diffusion of the PPG in the melt. In Fig. 1 the values measured with field gradient NMR and those calculated from dielectric data with Eq. (3) and $p = 2$ are presented. The input value for $\langle R^2 \rangle$ has been calculated to $(4, 8\,\mathrm{nm})^2$ from data of Refs. [22, 23]. The self-diffusion coefficients for $T \geq 293$ K were measured in Leipzig with PFG-NMR, those for $T \leq 293$ K were measured in Maniz with static field gradient NMR. The agreement of both NMR data is very satisfactory and confirms the reliability of our field gradient spectrometers. The self-diffusion coefficients measured by us are also in good agreement with earlier results from literature [24, 25]. The self-diffusion coefficients calculated from dielectric data with Eq. (3) are consistent with those measured by field gradient NMR. A similar result was obtained for polyisoprene [26]. Obviously, the Rouse model with its simple assumptions describes the dynamics of our polymer rather well. With increasing temperature, a difference between the two curves appears. We attribute this difference to an increasing mean squared end-to-end distance of the PPG (see Eq. (3)) with decreasing temperature, i.e., the chain becomes stiffer on cooling. Also, a different influence of interchain interactions (hydrogen bonds) on the $p = 0$ (diffusion) and higher modes with decreasing temperature may be a reason for this difference. The used value for $\langle R^2 \rangle$ yields continuously increasing deviations with decreasing temperature. The same effect is observed for polyisoprene when comparing PFG-NMR measurements of $D$ with those calculated from dielectric data [26], where, however, the two curves deviate at the high-temperature side.

In Fig. 2 the measured dependence of the apparent self-diffusion coefficient on the diffusion time is shown for five temperatures. As the temperature is lowered to below 268 K, a time dependence of the measured self-diffusion coefficient appears. For times larger than a certain value, which must be interpreted as an entanglement lifetime, we observe free long-time diffusion. For shorter times, the apparent self-diffusion coefficient increases with decreasing diffusion time. This is an indication of anomalous, restricted diffusion. At 253 K, the experimentally accessible time window, we observe almost totally restricted diffusion: $D_{\mathrm{app}} \sim t^{-0.9}$. Consequently, the chain segments move in a spatially limited region. The mean distance of the spatially restricted chain motion is $\langle z^2 \rangle^{1/2} = (2 D_{\mathrm{app}} t)^{1/2}$. We obtain from our experiment 120 nm, nearly independent of the diffusion time. This behaviour is characteristic for chains fixed between network junctions [14] and demonstrates a transient entanglement behaviour of the PPG in the melt. The free long-time diffusion crosses over into the restricted diffusion at that time at which the bend in the curves appears. This cross-over time can be interpreted as the lifetime of the entanglements (for 253 K we have extrapolated the curve in Fig. 2 to the long-time-$D$ extrapolated from the curve in Fig. 1 to 253 K, therefore, this time is not really measured, but the extrapolation fits very well into the curve of Fig. 3, see below).

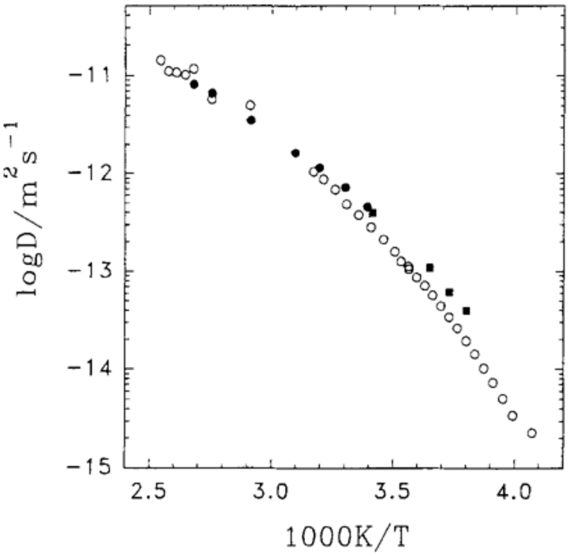

**Fig. 1** Arrhenius plot of the self-diffusion coefficients measured with pulsed (●) and static (■) field gradient NMR and calculated from dielectric relaxation times of the second normal mode with Eq. (3) and $\langle R^2 \rangle$ data from Refs. [22, 23] (○)

Earlier data of transient entanglement lifetimes in PPG melts with a molecular weight of 2660 are published in form of a relaxation map by Alig et al. [4]. In Fig. 3 the part with the experimental points from NMR relaxation and ultrasonic data is completed with our data. We have rescaled our data to the molecular weight of 2660 asuming the relation $f \sim M^{-3}$. This dependence was found for PPG by Schlosser and Schönhals [27] at $T = 222$ K, and this can be regarded as a further proof of transient entanglement behaviour of PPG in the melt. For really entangled chains with $M \ll M_e$, $\tau \sim 1/f \sim M^{3.7}$ is observed dielectrically [10] yielding a slightly larger exponent.

As already mentioned, from the data of Fig. 2 at 253 K the mean squared amplitude $\langle z^2 \rangle$ of the chain fluctuations between the transient network junctions can be calculated. We obtain $\langle z^2 \rangle^{0.5} \approx 120$ nm. We have to discuss two questions: at first, which physical process underlies this length scale of 120 nm, and secondly, what happens at 253 K where completely restricted diffusion sets in.

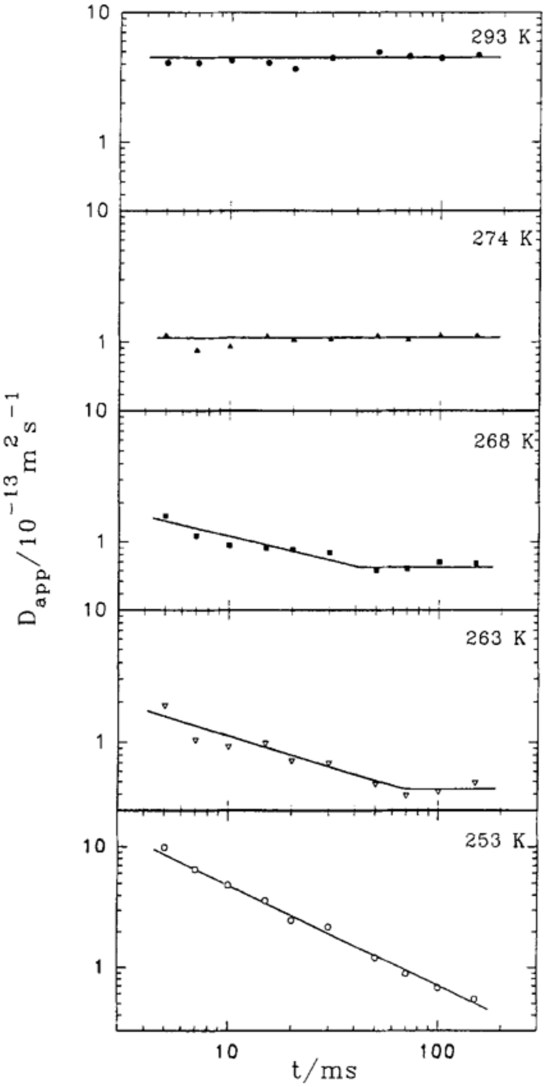

**Fig. 2** Experimental self-diffusion coefficients as function of the diffusion time *t* for different temperatures. Note the occurrence of a time-dependent apparent self-diffusion coefficient at small diffusion times for low temperatures

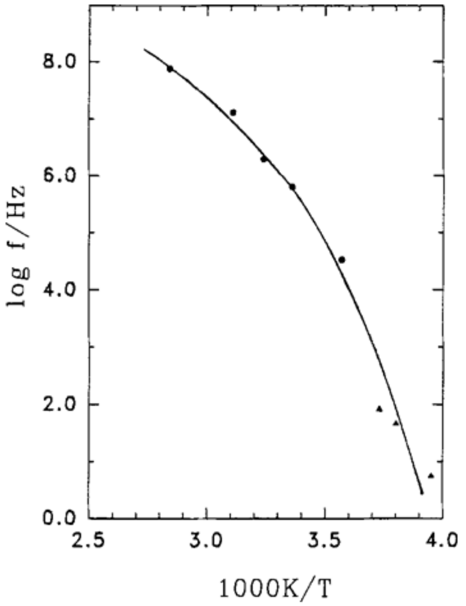

**Fig. 3** Relaxation map of the transient entanglements in the PPG melt. ●: data from Ref. [4] for PPG 2660. ▲: this work for PPG 4000. The data for PPG 4000 are rescaled to the molecular weight 2660 with the relation $f \sim M^{-3}$

The value of 120 nm is too large to be interpreted as resulting from fluctuations of network chains between adjacent transient entanglements. This is also true if one takes into account that the large network chains of the distribution of network chain lengths are strongly weighted in our experiment (the NMR signal contains the mass contribution of the individual chain lengths, and the initial slope of the echo attenuation from which $\langle z^2 \rangle^{0.5}$ is derived weights the largest displacements of the spins [28]). There exists a theoretical work of Donth [29] which assumes the existence of very mobile tubes and diffusing entanglements in entangled polymer melts which allow large amplitudes of chain fluctuations, but nevertheless this model is insufficient to explain our experimental results [30]. The results of our experiments presented in this paper must be interpreted as cooperative fluctuations of the whole gel-like network with amplitudes much larger than the distance between transient network junctions. Since we observe this behaviour at a temperature of 253 K which is about 50 K above the calorimetric glass transition of PPG [13], we must compare our length of 120 nm with the different length scales which are discussed in connection with the glass transition [31]. The only length which seems to play a role in our experiments is the length $\xi_D$ of clusters or "surviving large structures" [31]. But one has to have in mind that field gradient NMR measures the single particle correlation function of polymer segments; therefore a direct comparison is difficult at present.

Investigating the characteristic features of glass transition, Schönhals and Kremer have intensively studied the temperature dependence of the dielectric behaviour of different glass-forming liquids [13]. For PPG they observed at 250 K a characteristic temperature $T_A$ at which the $\beta$-relaxation branches from the $\alpha$-relaxation, i.e., at $T_A$ the cooperative motion of the $\alpha$-process sets in. This is also manifested in the temperature dependence of the relaxation strength $\Delta\varepsilon_A$ of the $\alpha$-process. We believe that the onset of completely transient entangled behaviour of the PPG melt is strongly correlated with the onset of the cooperative motion with decreasing temperature which favours the formation of the transient network junctions between the PPG chain ends.

## Conclusions

Using field gradient NMR with large static and pulsed field gradients the self-diffusion of PPG 4000 in the melt was measured over a broad temperature range. The self-diffusion coefficients measured by field gradient NMR agree very well with the self-diffusion coefficients calculated from the dielectric relaxation time of the second normal mode and the mean-squared end-to-end distance $\langle R^2 \rangle$ of the PPG chain with the Rouse theory. Deviations exist at lower temperatures where possibly $\langle R^2 \rangle$ increases with decreasing temperature. When lowering the temperature the self-diffusion starts at about 270 K to become restricted, and at 253 K we observe almost completely restricted diffusion of the polymer segments in a transient entanglement network. The amplitude of the fluctuations of the chains is derived to about 120 nm, a surprisingly large value. This value cannot be explained with fluctuations of the network chains between adjacent transient entanglements. We believe that we observe cooperative fluctuations of the gel-like network. This is considered to be connected with the onset of cooperative motions of the $\alpha$-process detected at a temperature $T_A \approx 250$ K in dielectric spectroscopy [13].

**Acknowledgments** The authors are obliged to Prof. E. Donth, Universität Halle, for fruitful discussions. G.F., M.A. and J.K. thank the Deutsche Forschungsgemeinschaft for financial support (SFB 294).

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