JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 3, March 2007, p. 633 - 636

NMR observation of the residual dipolar interaction in some polymeric samples

M. TODICA
"Babes-Bolyai" University, Faculty of Physics, 400089 Cluj-Napoca, Romania

The relaxation of the transverse magnetization of the protons attached to the polymeric chains and the pseudo-solid echoes were observed for the molten polybutadiene by NMR method. The function that characterizes the fluctuations of the polymeric segments can be estimated from the analysis of the experimental data collected in a large temperature domain

(Received November 15, 2006; accepted December 21, 2006)

Keywords: NMR spin-spin relaxation, Residual dipolar interaction, Pseudo-solid echoes

1. Introduction

The dipolar interaction between the nuclear spins is the main mechanisn that governs the relaxation of the transverse magnetization of the protons attached to the polymeric chains [1,2]. The residual dipolar interaction between the nuclear spins is determined by the entanglements between the polymeric chains. The effect of this interaction on the relaxation of the transverse magnetization can be observed by a special NMR pulse sequence called the *pseudo-solid echo* [2,3]. The specific behavior of the relaxation function of the transverse magnetization is determined by two mechanisms: the anisotropy of the local segmental motions between the entanglements and the fluctuation of the entanglements [2,4,5]. These mechanisms are strongly influenced by the temperature that leads to important modification of the properties of the pseudo-solid echoes. In this work we observed the modification of the slopes of the pseudo-solid echoes for the molten polybutadiene in a large temperature domain. Preliminary analysis of the experimental data leads to the possibility to evaluate the function that characterizes the fluctuation of the polymeric segments.

2. Experimental

We studied the molten polybutadiene PB, with the microstructure 36% "trans 1,4", 10% vinyl and the molecular mass 190 000 g/mole, in the temperature range 274-334 K. The samples were enclosed in NMR tubes (diameter 8 mm) and sealed under a primary vacuum. The NMR measurements were performed with CXP Bruker spectrometer at the resonance frequency 45 MHz. The relaxation of the transverse magnetization was observed by the Carr-Purcell sequence [6] and the residual dipolar interaction was investigated by the pseudo-solid echoes pulse sequence [3]. The temperature of the samples was controlled within 1 K.

3. Results and discussion

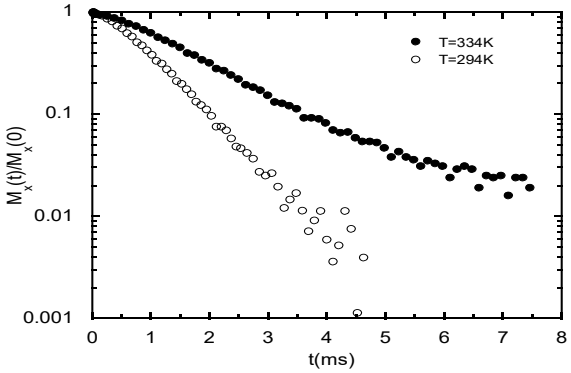

Fig. 1. The relaxation curves of the molten polymer observed at the temperatures: T=334 K and T=294 K.

The dynamics of the polymeric chains is determined by the elementary local rapid rotations of the polymeric segments [4,7]. These motions are almost isotropic for a completely free chain and the dipolar interaction between the nuclear spins attached to the polymeric chain is averaged to zero. In this case the relaxation of the transverse magnetization is characterized by a long decay function [2].

In the majority of the polymeric samples, the dynamics of the polymeric segments is restricted by the entanglements. The polymeric segments are not completely free to move and the dipolar interaction between the nuclear spins is not averaged to zero, (the residual dipolar interaction). The relaxation curves are complex and cannot be approximated by a single exponential, (Fig. 1).

The existence of the residual dipolar interaction is easily evidenced by forming the pseudo-solid spin echoes [3,7]. The following pulse sequence was used:

$$\left(\frac{\pi}{2}\right)_y - \frac{\tau}{2} - (\pi)_y - \frac{\tau}{2} - \left(\frac{\pi}{2}\right)_{-x} - \left[\frac{t_1}{2} - (\pi)_y - \frac{t_1}{2} - (echo)\right]_n \quad (1)$$

The first pulse $\left(\frac{\pi}{2}\right)_y$ flips the magnetization in the transverse plane. The next two pulses, the $(\pi)_y$ applied at the instant $\tau/2$ and the $\left(\frac{\pi}{2}\right)_{-x}$ applied at the instant τ after the beginning of the relaxation of the transverse magnetization, are responsible for the formation of the pseudo-solid echo. From theoretical point of view, the effect of these pulses is equivalent to the effect of the rotation matrix applied to the Hamiltonian of the spin system. As result the time derivative of the relaxation function $M_x(\tau)$ at the instant $t=\tau$ before the $\left(\frac{\pi}{2}\right)_{-x}$ pulse is equal to its opposite value at the instant $t=\tau_+$ immediately after the $\left(\frac{\pi}{2}\right)_{-x}$ pulse. This corresponds to the formation of one echo [2,3,7]. The next part of the sequence corresponds to the standard Carr-Purcell multiple spin echo sequence with t_1 the distance between the echoes. The effect of this pulse sequence on the spin system is very well presented in the references [2,3,7].

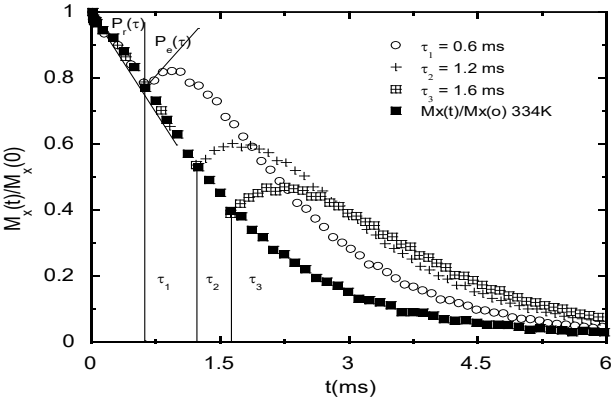

Fig. 2. The pseudo-solid echoes generated at different instants τ, τ_1=0. 6ms, τ_2=1.2 ms, and τ_3=1.6 ms, for the molten polymer at T=334 K.

The delay τ is chosen in function of the desired time domain of the relaxation process subject of the observation. We were interested for the fast decay of the relaxation function and we set the value of this parameter in the domain 0.3 to 1.6 ms. The parameter t_1 is chosen for better definition of the relaxation curves of the transverse magnetization, and its value was 80-100μs for ours experiments.

For a given value of the delay τ the pseudo-solid echo observed at different temperatures correspond to different time domains of the relaxation of the transverse magnetization and theirs amplitudes are different. At T=334 K and τ=0.6 ms the pseudo-solid echo corresponds to the beginning of the relaxation process, and its amplitude is important. At T=274 K and the same instant τ the pseudo-solid echo is observed towards the end of the relaxation process and its amplitude is smaller compared to the amplitude of the pseudo-solid echo recorded in the same conditions at high temperatures.

The most important characteristic observed in our study was the temperature dependence of the slopes of the relaxation function and of the pseudo-solid echoes. At high temperatures the slopes of these curves are almost symmetric, (Fig. 2). When the temperature decreases the modification of the slope of the pseudo-solid echoes is more important, (Fig. 3). To explain this behavior we must take into account the following suppositions. The entanglements are strongly influenced by the temperature, but theirs dynamics is very slow compared to the dynamics of the local polymeric segments. The relaxation of the transverse magnetization is governed by two dynamic mechanisms, the rapid motions of the polymeric segments and the fluctuations of the entanglements [2,7,8]. The relaxation function $M_x(t)$ can be expressed by the product of two functions:

$$M_x(t) = M_x^e(t) * \Phi_e(t) \tag{2}$$

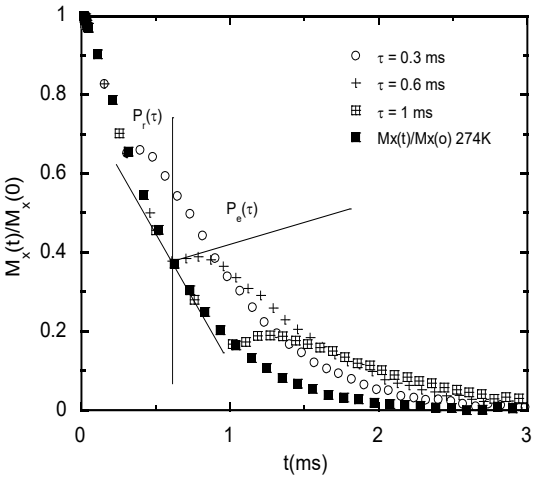

Fig. 3. The pseudo-solid echoes generated at different instants, τ=0.3ms, τ=0.6ms, and τ=1ms, at T=274 K. The slopes of the pseudo – solid echoes and of the relaxation functions are not symmetric.

The function $M_x^e(t)$ is associated to the anisotropy induced by the entanglements, and $\Phi_e(t)$ is associated to the dynamics of the polymeric segments. The pseudo-solid echoes are generated at different instants τ. The slope $P_r(\tau)$ of the relaxation function at these instants represents the derivative of the total relaxation function $M_x(t)$.

$$P_r(\tau) = \frac{dM_x^e(t=\tau)}{dt}\Phi_e(t=\tau) + M_x^e(t=\tau)\frac{d\Phi_e(t=\tau)}{dt} \tag{3}$$

When the pseudo-solid echoes impulsion sequence is applied, the evolution of the transverse magnetization after the delay τ is described by the equation:

$$\tilde{M}_x(t) = \tilde{M}_x^e(t) * \Phi_e(t) \tag{4}$$

The slope $P_e(\tau_+)$ of the echo function at the instant $t = \tau_+$ immediately after the pseudo-solid echo pulse sequence is given by the equation [2, 3]:

$$P_e(\tau_+) = \frac{d\tilde{M}_x^e(t=\tau_+)}{dt}\Phi_e(t=\tau_+) + \tilde{M}_x^e(t=\tau_+)\frac{d\Phi_e(t=\tau_+)}{dt} \tag{5}$$

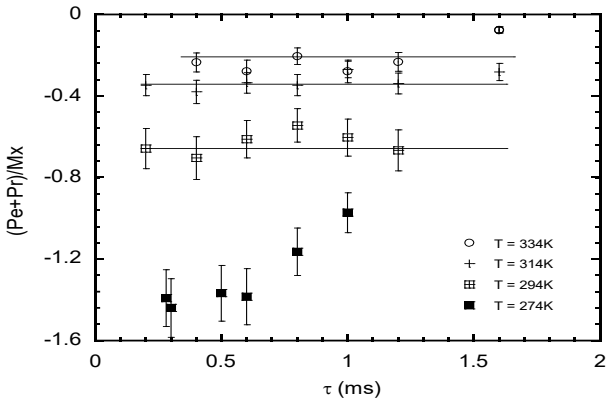

Fig. 5. The values of the expression $[P_r(\tau)+P_e(\tau)]/M_x(\tau)$ calculated at different instants τ and different temperatures.

The function $\Phi_e(t)$ is invariant to the pseudo-solid echo impulsion sequence, [2, 3]. Then:

$$\frac{d\Phi_e(t=\tau_+)}{dt} = \frac{d\Phi_e(t=\tau)}{dt} \tag{6}$$

The slope of the function $\tilde{M}_x^e(t=\tau_+)$ is the inverse of the slope of the function $M_x^e(\tau)$,[2,3].

$$\frac{d\tilde{M}_x^e(t=\tau_+)}{dt} = -\frac{dM_x^e(t=\tau)}{dt} \tag{7}$$

The amplitude of the relaxation function at the instant τ, immediately before and after the pulse $\left(\frac{\pi}{2}\right)_{-x}$ is the same [3].

$$M_x^e(t=\tau) = \tilde{M}_x^e(t=\tau_+) \tag{8}$$

From equations (2), (3), (5), (7) and (8) we obtain:

$$\frac{P_r(\tau)+P_e(\tau_+)}{M_x(\tau)} = \frac{1}{2\Phi_e(\tau)}\frac{d\Phi_e(\tau)}{dt} \tag{9}$$

The equation (9) represents the logarithmic derivative of the function $\Phi_e(\tau)$ at each instant τ. We can reconstruct this function if many pseudo-solid echoes are generated at different instants τ. For each value of τ we estimated the slopes $P_r(\tau)$, $P_e(\tau_+)$ and the amplitude of the relaxation function $M_x(\tau)$. These estimations were done in the experimental error limits 10% to 20%.

We utilized this method to evaluate the function $\Phi_e(\tau)$ at different temperatures. At high temperatures, in the domain of variation of the parameter τ, we obtained in the limit of the experimental errors, a constant value for the expression $[P_r(\tau)+P_e(\tau)]/M_x(\tau) = k$, (Fig. 4). In this case $\Phi_e(\tau)$ can be approximated by an exponential function:

$$\Phi_e(\tau) = A\exp(2k\tau) \tag{10}$$

The values of the constant k are the followings: k= -0.65 at T=294 K, k= -0.35 at T=314 K and k= -0.23 at T=334 K. This exponential dependence is characteristic for the functions describing the relaxation of the transverse magnetization, and suggests the similitude between the inverse of the parameter k and an apparent spin-spin relaxation time $T_{2e} = \frac{1}{2|k|}$. We can rewrite the expression of the function $\Phi_e(\tau)$ using this new parameter in similar form as the relaxation function of the transverse magnetization:

$$\Phi_e(\tau) = A\exp\left(\frac{-\tau}{T_{2e}}\right) \tag{11}$$

This relaxation time can be associated to the fluctuations of the polymeric segments.

At low temperatures, at θ=274 K, the expression $[P_r(\tau)+P_e(\tau)]/M_x(\tau)$ do not represents a constant, (Fig. 4). The function $\Phi_e(\tau)$ can't be approximated by an exponential function. The expression of the function $\Phi_e(\tau)$ at this temperature cannot be obtained by this algorithm. The change of the shape of the function $\Phi_e(\tau)$ above and below the temperature θ modify the shape of the total relaxation function $M_x(t)$ and the slopes of the pseudo-solid echoes. This change indicates a modification of the mechanism of the fluctuations of the polymeric segments between the entanglements that results in a modification of the dipolar interaction between the nuclear spins [8,9,10].

3. Conclusions

The relaxation of the transverse magnetization of the nuclear spins attached to the polymeric chains is governed by the dipolar interaction. This interaction is strongly influenced by the dynamics of the polymeric segments and by the fluctuations of the entanglements. The entanglements between different polymeric chains induce

important anisotropy of the dipolar interaction. The dominance of this anisotropy is responsible for the residual dipolar interaction and is correlated to the pseudo-solid behavior of the relaxation curves of the transverse magnetization. The analyze of the slopes of the pseudo-solid echoes in function of the temperature leads to the possibility to estimate the expression of the function $\Phi_e(t)$. In the domain of high temperatures this function is exponential. Important modifications of the slopes of the pseudo-solid echoes were observed at low temperatures and were associated to the modification of the function $\Phi_e(t)$. Below the temperature θ=274 K the function $\Phi_e(t)$ is not exponential. The change of the shape of this function can be associate to the modification of the dynamics of the polymeric segments between the entanglements.

References

[1] A. Abragam, The Principles of Nuclear Magnetism, (Clarendon Press, Oxford, 1961).
[2] J. P. Cohen-Addad, NMR and Fractal Properties of Polymeric Liquids and Gels, (Pergamon Press, London, 1992).
[3] J. P. Cohen-Addad, Carlo Schmit, Polymer, **29**, 883 (1988).
[4] P. G. de Gennes, Scaling Concepts in Polymeric Physics, (Cornell University Press, New-York, 1979).
[5] J. D. Ferry, Viscoelastic Properties of Polymers, 3rd. edn. (John Wiley, New York, (1980).
[6] H. Y. Carr, E. M. Purcell, Phys. Rev. **94**, 630 (1954).
[7] J. P. Cohen-Addad, Physical Properties of Polymeric Gels, (John Wiley, Chichester, 1996).
[8] M. Todica, Int. J. Mod. Phys. B, **19**, 1771 (2005).
[9] J. P. Cohen-Addad, A. Labouriau, J. Chem. Phys. **94**, 3242 (1991).
[10] J. P. Cohen-Addad, E. Soyez, A. Viallat, Macromolecules **25**, 1259 (1992).

*Corresponding author: tami@phys.ubbcluj.ro