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The Dipolar-Correlation Effect on the Stimulated Echo. Application to Polymer Melts

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The quotient of the amplitudes of the stimulated and the primary echoes generated by a three-pulse sequence is strongly affected by dipolar coupling if motional averaging is incomplete. This effect can be experimentally discriminated from echo attenuation by relaxation and diffusion. A method is established on this basis which permits studies of molecular order and dynamics. The time scale is particularly long and is limited only by spin–lattice relaxation. A theory is presented which links the echo amplitudes with the dipolar-correlation function. The echo attenuation curves have been calculated for correlation functions decaying according to exponential and power laws. The results are compared with experimental data of entangled poly(ethylene oxide) and poly(dimethylsiloxane) melts. It is shown that power-law correlation functions are a suitable basis for the description of the observed phenomena. © 1995 Academic Press, Inc.

INTRODUCTION

The stimulated echo (*1*) following a sequence of three RF pulses with flip angles of preferably 90° is normally considered under motional narrowing conditions. The appearance of a distinct echo of this sort requires an inhomogeneous external magnetic field, but dipolar interaction among the spin-bearing particles is averaged out in the NMR time scale. Under such circumstances, the attenuation of the echo is a matter of transverse and longitudinal relaxation (*1*), translational (particle) diffusion (*2*), and—in the special case of very long polymers—potential spin diffusion (*3*).

The purpose of this study is to show that there are additional phenomena affecting the amplitude of the stimulated echo if the secular part of dipolar interaction is not completely averaged out in the evolution intervals of the stimulated-echo pulse sequence. This is of particular interest with anisotropic media such as polymers and liquid crystals. A promising perspective is that a method can be established on this basis permitting us to record dipolar-correlation functions up to extremely long times merely limited by the spin–lattice relaxation time T_1.

In the following, we consider the pulse sequence

$$(\pi/2)_x \cdots \tau_1 \cdots (\pi/2)_{-x} \cdots \tau_1 \cdots (\text{pr. echo}) \cdots (\tau_2 - \tau_1) \cdots (\pi/2)_y \cdots \tau_1 \cdots (\text{stim. echo}) \quad [1]$$

in the presence of a gradient $\mathbf{G} = \nabla B_0(\mathbf{r})$ of the external magnetic-flux density $\mathbf{B}_0$. The subscripts of the RF pulse symbols represent the rotating-frame direction of the RF amplitude $\mathbf{B}_1$. The only echoes of interest here are the primary echo and the stimulated echo. All other Hahn echoes (*1*) will not be considered.

For simplicity, we begin with the density-operator treatment of a representative pair of two equivalent spins $\frac{1}{2}$, $\mathbf{I}_k$ and $\mathbf{I}_l$. With respect to the formation of echoes in the course of the pulse sequence, this restriction to two-spin systems causes no loss of generality. However, the final conclusions concerning the dipolar-correlation effect refer to large systems consisting of $N \gg 1$ spins so that the central-limit theorem (*4*) for the probability density of the dipolar frequency offsets can be applied (*5*).

The local rotating-frame Hamiltonian is composed of an RF term, $\mathcal{H}_{RF}$, a second term representing the local field-gradient offset, $\mathcal{H}_g$, and the secular part of dipolar coupling, $\mathcal{H}_d^{(0)}$,

$$\mathcal{H} = \mathcal{H}_{RF} + \mathcal{H}_g + \mathcal{H}_d^{(0)}, \quad [2]$$

where

$$\mathcal{H}_g = -\hbar\gamma(\mathbf{G}\cdot\mathbf{r})(I_{kz} + I_{lz}) = -\hbar\Omega_g(\mathbf{r})(I_{kz} + I_{lz}) \quad [3]$$

and

$$\mathcal{H}_d^{(0)} = \hbar\Omega_d(I_{kz}I_{lz} - \tfrac{1}{3}\mathbf{I}_k\cdot\mathbf{I}_l) \approx \hbar\Omega_d I_{kz}I_{lz}. \quad [4]$$

The dipolar coupling constant (in angular-frequency units) is defined by $\Omega_d = 3\mu_0\gamma^2\hbar(1 - 3\cos^2\theta_{kl})/(8\pi r_{kl}^3)$, where r_{kl} and θ_{kl} are the polar coordinates of the internuclear vector.

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