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Dipole-Echo Formation in Three-Pulse-Sequence NMR Experiments on Polymer Systems

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Data from three-pulse NMR experiments, namely, the Goldman–Shen pulse sequence and the stimulated-echo sequence, on partially crystallized poly(ethylene glycol) and tetrafunctional dimethylsiloxane networks are presented. A dipole echo has been observed after a third radiofrequency pulse. Quantum mechanical calculations of the response of the spin system to the three-pulse sequences have been performed, considering only the $z-z$ component of the dipole–dipole spin coupling. The resulting expression suggests dipole-echo formation and is in agreement with experimental data.

INTRODUCTION

The method of pulsed nuclear magnetic resonance offers a considerable variety of radiofrequency pulse sequences for studying morphology and molecular mobility in polymer systems. Among the different techniques, the Goldman–Shen (GS) sequence of three RF pulses (*1*) and the ''stimulated-echo'' (SE) pulse sequence (*2*) are used extensively. The former is employed in experiments aimed at studying spin diffusion between the distinct morphological regions of a polymer sample. The results obtained on polymers lead to an estimation of the sizes and shapes of the supermolecular structures in such systems: crystalline and amorphous phases (*3, 4*) or rigid and mobile domains (*5, 6*). In many cases, this information is beyond the reach of other methods of structural analysis (*7*).

Currently, the SE pulse sequence with a pulsed magnetic-field gradient applied after the first and third RF pulses (*8*) has proven useful in studies of molecular motions in polymer melts and solutions (*9*). The theoretical framework for analysis of data obtained in the three-pulse experiments until now has been based on the Bloch equations derived in terms of the short-correlation-time approximation (*3–6, 8, 9*). This approach, however, is acceptable only for liquid-like samples where the spin–spin interactions are averaged due to rapid isotropic molecular motions over a time much less than the characteristic time intervals of the pulse sequence. It occurs, sometimes, that these conditions do not hold in polymer systems (*10, 11*). In this case, a response of the spin system to the aforementioned pulse sequences reflects the preceding development of the system under the spin–spin interaction in the time interval between the first two RF pulses (*12*).

In this paper, we draw attention to the effects that make their appearance if these three-pulse sequences are applied to polymer systems with dipole–dipole (d–d) couplings nonaveraged during the course of the experiment. We present here evidence for the echo formation resulting from the GS and SE pulse experiments on polymers. Theoretical predictions of this phenomenon are given which follow from the quantum mechanical calculations of the response of the spin system to the three-pulse sequences.

EXPERIMENTAL

The NMR measurements have been carried out with a homebuilt spectrometer operating at a proton frequency of 19 MHz. A magnetic-field gradient with the maximum value of $\sim$0.1 T/m was generated with a quadrupole coil. The application of the pulsed magnetic-field gradient with a duration of 10 μs was sufficient for a total dephasing of magnetization in the transverse plane. The time of establishment of equilibrium in the magnet (the homogeneity of the field H_0) after such a pulse was less than 10 μs. Typically, 20 signals were accumulated at a repetition time exceeding $6T_1$, where T_1 is the spin–lattice time of the sample studied.

The samples under study were partially crystallized poly(ethylene glycol) with molecular mass $\sim$1500 (PEG1500) and tetrafunctional dimethylsiloxane networks with a number of monomers between cross links of about 29 (NET29).

EXPERIMENTAL OBSERVATION OF DIPOLE-ECHO FORMATION IN THREE-PULSE SEQUENCES

The Goldman–Shen Experiments [90°_x—τ_1—90°_{-x}—τ_2—90°_x—*Free Induction Decay* (τ_3)]

In the course of the experiments on partially crystallized polymers, Cheung (*4*) noted that considerable distortion of

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