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Molecular Dynamics of Polycarbonate Chains at the Interface of Polycarbonate/Polystyrene Heterogeneous Blends

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ABSTRACT: As monitored by DNP-selected dipolar rotational spin-echo ^{13}C NMR, interfacial-PC chains in thin-film PC/PS blends (see previous paper for notation) have less motion than PC chains in the bulk.

Introduction

Having generated and identified a ^{13}C NMR signal arising exclusively from PC chains near the PC/PS interface, we can now perform NMR relaxation experiments to characterize the microscopic dynamics of these chains. A difference pulse sequence is used similar to that shown in Figure 5 (part 1), but which includes a period for carbon dephasing under the influence of dipolar coupling to protons isolated from one another by multiple-pulse H–H decoupling.[1] Thus, the full experiment involves monotoring the dephasing of DNP-enhanced ^{13}C NMR magnetization of interface-PC chains in a thin-film PC/PS blend by dipolar rotational spin-echo (DRSE) ^{13}C NMR spectroscopy.[2] The results of DRSE experiments have been well established for the characterization of the molecular chain dynamics of synthetic polymers[2–8] and proteins.[9,10]

Experiments

DNP-Selected DRSE ^{13}C NMR. A semiwindowless MREV-8 sequence[11] was combined with DNP CPMAS ^{13}C NMR spectroscopy for DRSE experiments with DNP selection (Figure 1). A DNP difference selects the PC chains at the interface of the PC/PS blend. In the first half of this alternate-block experiment the carbon magnetization is prepared with a 1.0-s microwave irradiation at the difference of the electron and proton Larmor frequencies (Figure 1). The resulting DNP-enhanced proton magnetization is transferred to carbons by a standard 1.0-ms matched spin-lock contact at 50 kHz. In the second half of the experiment, the carbon magnetization is prepared just with the standard cross-polarization transfer; the microwave irradiation is delayed until after ^{13}C data acquisition has been completed.

During the first rotor period of each half of the experiment, immediately after the cross-polarization contact, protons are decoupled from carbons by an 87-kHz rf field. The H–H multiple-pulse decoupling is applied for a variable time during the second rotor period following the carbon 180° refocusing pulse. This results in a two-dimensional NMR experiment[12] during one time dimension of which carbon magnetization is allowed to evolve under C–H coupling while H–H interactions are suppressed by semiwindowless MREV-8 decoupling. The accumulated signal from the first half of the experiment is substracted from that of the second half.

The semiwindowless MREV-8 H–H multiple-pulse decoupling was composed of eight 3.0-μs pulses with four windows[13–15] of 2.4 μs each for a total cycle time, t_c, of 33.6 μs. The 87-kHz 3-μs pulses were slightly larger than 90° for better refocusing.[16] Sixteen MREV-8 cycles exactly fit into one rotor period with 1859-Hz magic-angle sample spinning. However, in some experiments, the number of the MREV-8 cycles varied from zero (no MREV-8 pulses during the second rotor period) to only eight. Because the time-domain data are symmetrical,[2] the evolution corresponding to the ninth to fifteenth MREV-8 cycles can be constructed from that for the first to seventh MREV-8 cycles. The percent refocusing is the ratio of the intensities of the carbon signals obtained experimentally with a full sixteen MREV-8 cycles to that obtained with zero MREV-8 cycles. Typically, 70–80% of the protonated aromatic-carbon signal of PC refocused. Full refocusing is not observed because of incomplete H–H decoupling.[3,17] A 16-point Fourier transform was used to produce a 16-point dipolar frequency spectrum[18] with the imaginary buffer set equal to zero. For an isolated ^{1}H–^{13}C spin pair, the pure absorption spectrum is a symmetrical dipolar Pake pattern[19] broken up into spinning sidebands.[20]

Carr-Purcell NMR. Cross-polarization, magic-angle spinning echo amplitudes were measured using a rotor-synchronized, Carr-Purcell refocusing sequence. Following a standard H–C cross-polarization transfer at 50 kHz, carbon magnetization is allowed to evolve for an integral number of rotor periods, nT_r (Figure 2). This is followed by a ^{13}C 180° chemical-shift refocusing pulse. Signal detection starts $2n$ rotor periods after the completion of the cross-polarization transfer.[21] A 50-kHz C–H dipolar decoupling field was used throughout the evolution and detection periods. The Carr-Purcell experiment was performed on a total of four samples all based on PC(^{13}C): two polycarbonates and two thin-film blends. The polycarbonates were PC(^{13}C) and a physical mixture of PC(^{13}C) and BDPA, denoted by PC(^{13}C)/*. The thin-film blends were the PC(^{13}C)/PS(^{12}C/*) and PC(^{13}C)/PS(^{2}D/*) samples whose preparation is described in part 1.

DRSE Refocusing. Following a ^{13}C inspection pulse the carbon magnetization was allowed to evolve under chemical shift *only* and under combined chemical-shift and C–H dipolar interactions. The magnetization was sampled 16 times each rotor period (see Figure 1, part 4). The details of these experiments and results on homogeneously doped PC will be discussed in part 4. In this paper, only the multiple-sampling results on PC and inhomogeneously doped PC obtained under combined chemical-shift and C–H dipolar interactions will be presented. These results demonstrate the effect of aggregated BDPA on the degree of carbon magnetization refocused under the application of H–H multiple-pulse decoupling.

Results

DNP-Selected DRSE ^{13}C NMR. The time evolution of the ^{13}C magnetization of the ^{13}C-labeled, protonated, aromatic carbons of PC at the interface of the thin-film PC/PS blend, PC(^{13}C)/PS(^{12}C/*), is shown in Figure 3. The DRSE data for the protonated, aromatic carbons of bulk PC and the protonated, aromatic carbons of bulk PS are also shown in the same figure. The intensity of the ^{13}C magnetization is plotted as a function of the number of semiwindowless MREV-8 cycles used in the H–H multiple-pulse decoupling. The plots are normalized so that the first points of all three curves match. The decay of the interface-PC magnetization is intermediate to those for bulk PC and bulk PS.

Line Widths by Carr-Purcell NMR. Spin-echo ^{13}C NMR spectra of four PC samples are shown in Figure 4. The stacked plots are of chemical shift versus the number

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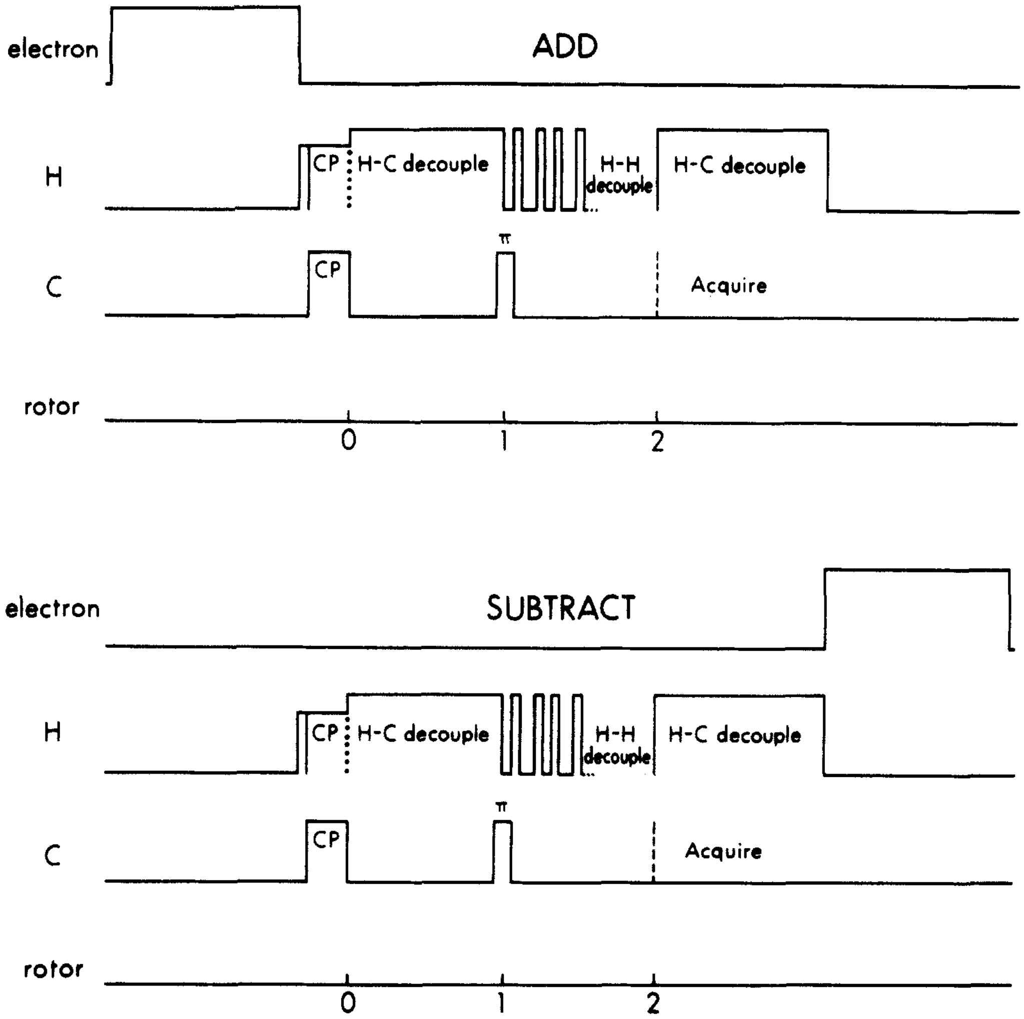

Figure 1. Pulse sequence for dipolar rotational spin-echo ^{13}C NMR of carbons selected by DNP difference. Proton–proton decoupling is done using a semiwindowless MREV-8 sequence. The position of the 180° pulse is synchronized with the end of the first rotor period after the cross-polarization transfer. Data acquisition begins at the end of the second rotor period. The accumulated signal from the first half of the experiment is substracted from that of the second half.

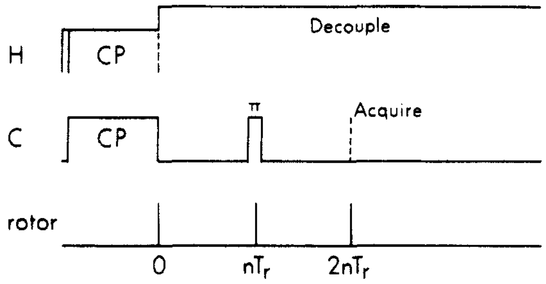

Figure 2. Pulse sequence for cross-polarization, magic-angle spinning spin-echo ^{13}C NMR spectroscopy.

of rotor periods, *n*, preceding the refocusing *π* pulse (see Figure 2). The observed homogeneous line widths, obtained from the echo decays are 34, 50, 38, and 52 Hz for PC(^{13}C), PC(^{13}C)/*, PC(^{13}C)/PS(^{12}C/*), and PC(^{13}C)/PS(^{2}D/*), respectively.

DRSE Refocusing. Figure 5 shows the time-domain evolutions of ^{13}C magnetization under combined chemical-shift and C–H dipolar interactions, with H–H interactions suppressed by MREV-8 pulses for PC(^{13}C) and PC(^{13}C)/*. These data were obtained by a synchronous-detection experiment. Details of the experiment will be presented in part 4. The first points (with $t = 0$ defined by the top of the first echo) of both curves were adjusted to have the same magnitude. Both samples have rotational echoes arising from the refocusing of chemical-shift and dipolar interactions. The echo train of PC(^{13}C/*) decays faster

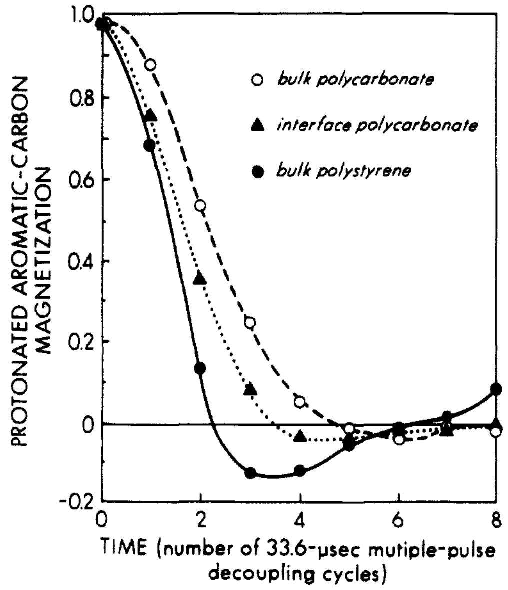

Figure 3. The time evolution of the DRSE ^{13}C NMR signal of the protonated, aromatic-carbon magnetization of homopolymer bulk PS, homopolymer bulk PC, and interfacial PC of a thin-film PC/PS blend. The interface-PC signal is obtained from the *difference* spectra of chains selected by DNP CPMAS ^{13}C NMR using the pulse sequence of Figure 1. Data points are connected for clarity. The relatively fast dephasing of the interfacial-PC signal indicates that PC chains at the interface are more restricted than those in bulk.

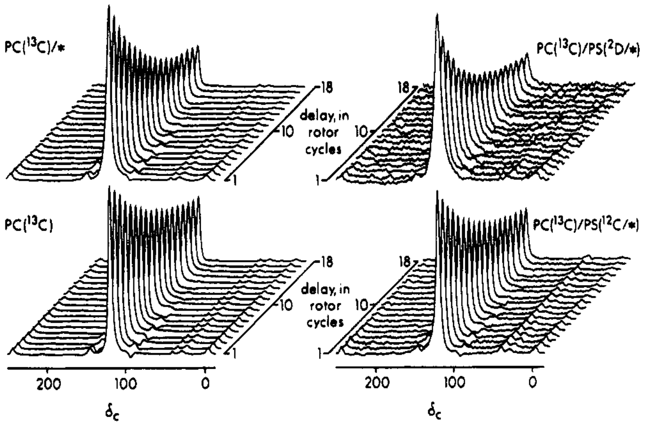

Figure 4. Cross-polarization, magic-angle spinning, rotational-echo ^{13}C NMR spectra of PC(^{13}C) (lower left), PC(^{13}C)/* (upper left), PC(^{13}C)/PS(^{12}C/*) (lower right), and PC(^{13}C)/PS(^{2}D/*) (upper right). These two-dimensional stacked spectra were obtained by plotting the chemical shift as a function of the number of rotor periods, *n*, using the pulse sequence of Figure 2. The peaks near δ_C 0 and 250 are spinning sidebands.

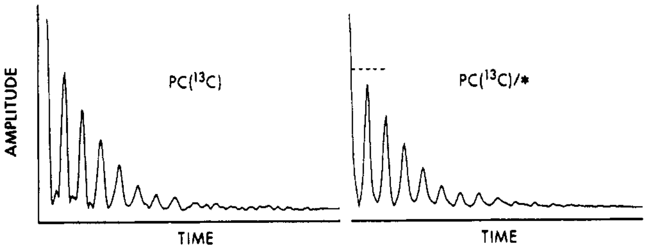

Figure 5. Rotational echoes of PC(^{13}C) and PC(^{13}C)/* under a combination of chemical-shift and dipolar interactions. The refocusing of the rotational echoes is affected by the presence of inhomogeneously mixed BDPA. The horizontal dashed lines represent the echo amplitude of PC(^{13}C) at the end of the second rotor period. The top of the first echo defines the left-hand side of each plot.

than that of PC(^{13}C). After $2T_\rho$ ($n = 1$) the refocusing for PC(^{13}C) is 74% and that for PC(^{13}C)/* is 62%.

Discussion

DNP-Selected DRSE ^{13}C NMR. After the application of only one cycle of semiwindowless MREV-8 pulses, the ^{13}C magnetization of bulk PS decreases by about 30%, whereas that of bulk PC decreases by only about 10% (Figure 3). Moreover, the ^{13}C magnetization of the bulk PS is substantially negative after only three semiwindowless MREV-8 cycles, while that of bulk PC is barely negative after five MREV-8 cycles. Restricted molecular motion results in fast DRSE dephasing of ^{13}C magnetization.[18] Because the aromatic-carbon magnetization in bulk PS dephases faster than that in bulk PC, PS aromatic carbons have less motion than PC aromatic carbons. The faster dephasing for bulk PS is attributed primarily to the absence of averaging of C–H dipolar interactions by π flips about the ring C_2 axis.[18]

The dephasing of the ^{13}C magnetization of the DNP-selected interfacial-PC signal is intermediate to that of bulk PC and bulk PS (Figure 3). Thus, interfacial-PC aromatic carbons have less motion than bulk PC aromatic carbons, but more motion than bulk PS aromatic carbons. This reduction of interface-PC motion relative to bulk-PC motion can be explained in terms of the interference with cooperative, interchain motions. Presumably, the dense, or at least atypical, packing of PC chains near the impenetrable PS barrier[22] inhibits the lattice dilation necessary to enable a ring π flip.[23]

DRSE and Carr-Purcell Refocusing. The presence of free radicals in PC broadens ^{13}C-resonance lines and reduces the efficiency of MREV-8 decoupling. The free radicals do not have to be molecularly dispersed in the PC chains to produce these effects. Inhomogeneous mixing of BDPA with PC reduces the refocusing in both DRSE and Carr-Purcell echo experiments (Figures 4 and 5). Because the DNP-selected DRSE ^{13}C NMR experiments on blends were performed on narrow lines arising from protonated, aromatic carbons not affected by molecularly dispersed BDPA and not close to aggregated BDPA, the appropriate control for the DRSE dephasing is bulk PC chains in PC homopolymer (Figure 3), not bulk PC chains in PC(^{13}C)/PS(^{12}C/*). In the latter sample, some PC chains are near BDPA aggregates and so are subject to local susceptibility variations.

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