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Communications to the Editor

Rotational-Echo Double-Resonance NMR To Observe the Interfaces of Heterogeneous Polymer Blends

Gang Tong, Yong Pan,[†] Mobae Afeworki,[‡] Mark D. Poliks,[§] and Jacob Schaefer*

Department of Chemistry, Washington University, St. Louis, Missouri 63130

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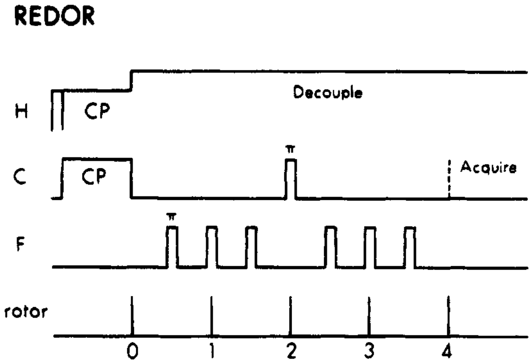

Figure 1. Pulse sequence for rotational-echo double-resonance ^{13}C–^{19}F NMR. After a cross-polarization transfer from protons to carbons to enhance sensitivity, the protons are removed from the experiment by high-power resonant decoupling. Simple *XY* phase alternation of the fluorine π pulses was used to suppress the effects of radio-frequency offsets.

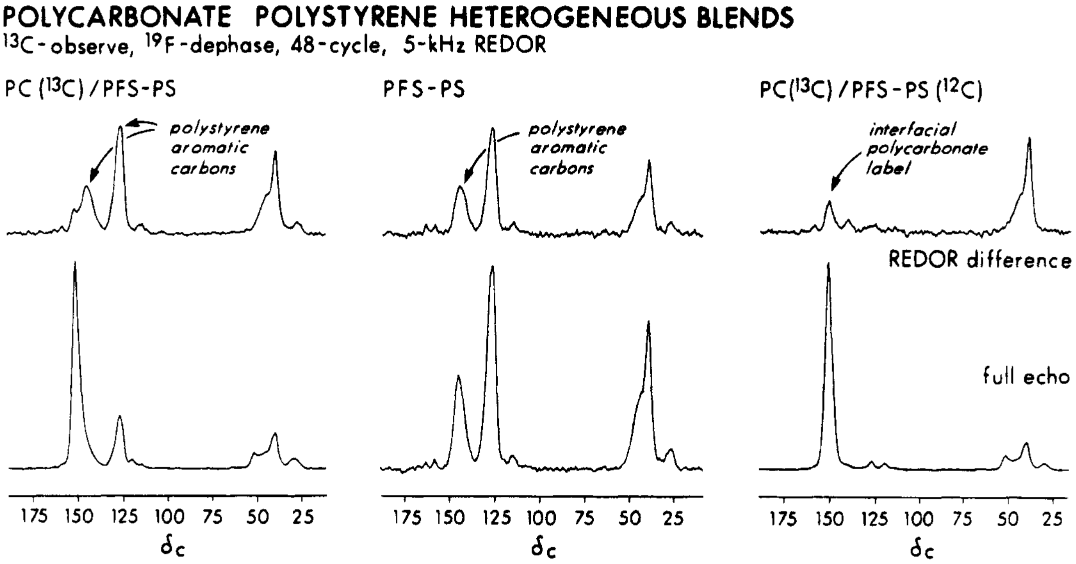

Figure 2. (Left) Carbon-observe, fluorine-dephase REDOR difference (top, ×3) and full-echo (bottom) NMR spectra of a heterogeneous blend of [carbonyl-^{13}C]polycarbonate and poly(*p*-fluorostyrene-*co*-styrene) after 48 rotor cycles of 5-kHz magic-angle spinning. The concentration of polycarbonate in the blend is 10 mol %. The concentration of fluorostyrene in the copolymer is 20 mol %. The blend was formed by coprecipitation from chloroform into methanol. (Middle) REDOR spectra of the copolymer used to make the blend whose spectra are shown at the left, after 48 rotor cycles. The arrow marks the polystyrene aromatic-carbon peak that interferes with quantitation of the polycarbonate interface signal. (Right) Carbon-observe, fluorine-dephase REDOR difference (top, ×5) and full-echo (bottom) NMR spectra of a heterogeneous blend of [carbonyl-^{13}C]polycarbonate and poly(*p*-fluorostyrene-*co*-[^{12}C$_6$]styrene) after 48 rotor cycles of 5-kHz magic-angle spinning. The concentration of polycarbonate in the blend is 10 mol %. The concentration of fluorostyrene in the copolymer is 10 mol %. The blend was formed by coprecipitation from chloroform into methanol.

We are developing a new analytical technique to observe the interfaces of immiscible polymer blends by rotational-echo double-resonance[1] (REDOR) NMR. The experiment involves a stable-isotope label for each component of the blend,[2,3] such as, for example, ^{13}C in polycarbonate and ^{19}F in a copolymer of *p*-fluorostyrene and styrene. Carbon-observe, fluorine-dephase REDOR is performed in two parts, once with dephasing π pulses on the ^{19}F channel (Figure 1) and once without dephasing pulses.[1] The resulting carbon difference signal arises only from those carbons that are near ^{19}F (Figure 2, left), which includes carbons throughout the polystyrene phase (Figure 2, middle) as well as carbons at the interface in the polycarbonate phase. The more rotor cycles that are used for dephasing, the greater the ^{13}C–^{19}F distance that is measured,[4] up to a maximum of about 10 Å. Unwanted polystyrene copolymer REDOR difference signals can be eliminated by using ^{13}C-depleted material (Figure 2, right). The fortuitous distribution of aromatic-carbon chemical shifts for poly(*p*-fluorostyrene) results in no interferences with detection of the polycarbonate label in blends of the two homopolymers (spectra not shown). Interferences from natural-abundance background signals in the copolymer blend system can also be eliminated by a second subtraction using the REDOR difference signal from an *un*labeled polycarbonate blended with the same styrene copolymer. This double difference is due only to labeled polycarbonate at the interface (Figure 3, top) and can

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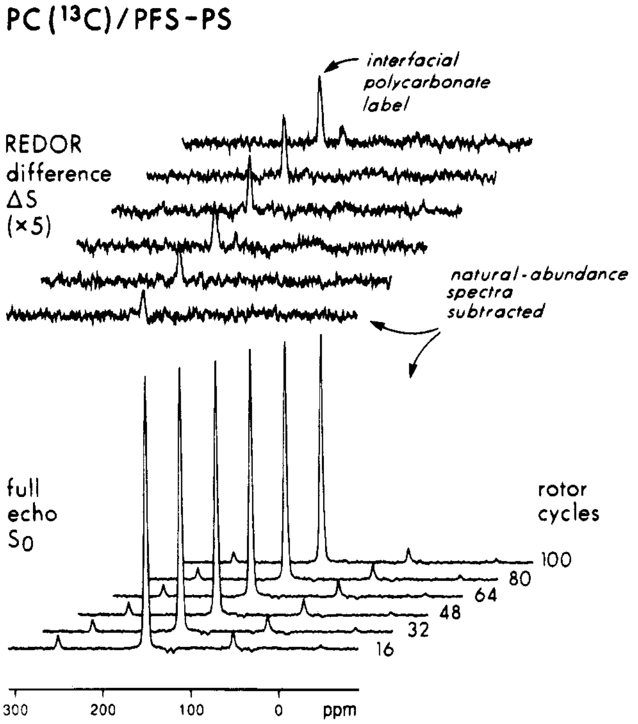

Figure 3. Carbon-observe, fluorine-dephase REDOR NMR spectra of a heterogeneous blend of [carbonyl-^{13}C]polycarbonate and poly(*p*-fluorostyrene-*co*-styrene) as a function of the number of rotor cycles of 5-kHz magic-angle spinning. This is the same blend whose spectra appear in Figure 1 (left). The natural-abundance background has been subtracted from both top and bottom sets of spectra. The REDOR difference (top) arises exclusively from polycarbonate carbons at the interface.

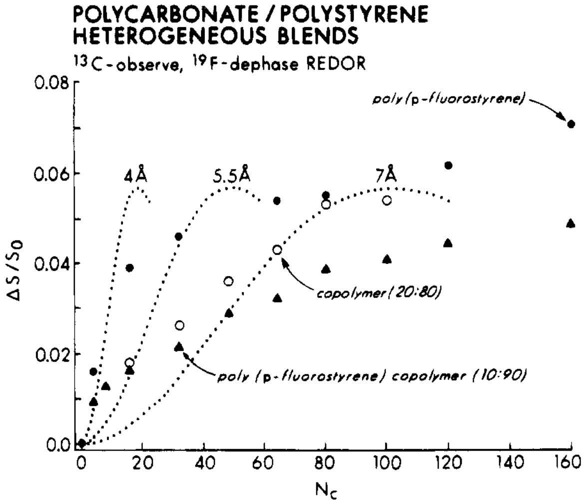

Figure 4. REDOR dephasing for three heterogeneous blends of [carbonyl-^{13}C]polycarbonate and poly(*p*-fluorostyrene) homo- and copolymers, as a function of N_C, the number of rotor cycles of 5-kHz magic-angle spinning. The dotted lines show REDOR dephasing calculated for isolated ^{13}C$-^{19}$F pairs.

be used to examine directly the structure[3] and dynamics[5] of chains at the interface.

A simple, isolated-pair analysis[6] of the carbon-observe, fluorine-dephase REDOR difference due solely to polycarbonate at the interface (dotted lines, Figure 4) shows qualitatively that the shortest distance between the carbonyl carbon of polycarbonate and the *p*-fluoro ^{19}F of the styrene copolymer is between 4 and 7 Å. A few ^{13}C$-^{19}$F couplings are missing for the copolymers relative to poly(*p*-fluorostyrene) because of the lower concentration of fluorine labels, and this results in less dephasing. A quantitative analysis of $\Delta S/S_0$ requires a model to specify the placement of one or more dephasing ^{19}F centers near each ^{13}C label. (This kind of analysis is in progress.) There are no significant concentrations of polycarbonate chains kinetically trapped in the polystyrene phase during coprecipitation of the blends of Figure 4 because the observed REDOR differences do not decrease with prolonged annealing at 180° (data not shown), a temperature well above the polycarbonate glass transition temperature. If we make the assumption that the polycarbonate chains stacked at the interface form successive layers, each 10 Å in depth, then the 5% $\Delta S/S_0$ (Figure 4, $N_C = 100$) observed for all three blends means that 1 polycarbonate chain in 20 is at the interface. Thus, the polycarbonate phase in these coprecipitated blends is 200 Å thick (infinite slab) or 400 Å in diameter (polycarbonate spheres embedded in a continuous polystyrene matrix). These estimates are influenced by the microroughness of the interface, a feature of the blends that is currently under investigation.

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References and Notes

[†] Present address: Corporate Research Division, The Procter & Gamble Company, Cincinnati, OH 45239.

[‡] Present address: Department of Chemistry, Asmara University, Asmara, Eritrea.

[§] Present address: Systems Technology Division, IBM, Endicott, NY 13760.

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