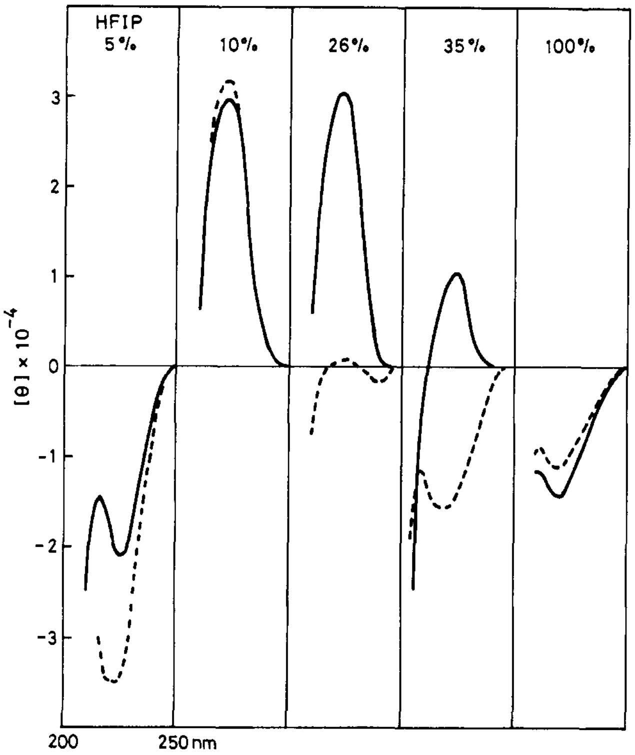

Figure 2. Circular dichroism spectra associated with the amide $n-\pi^*$ transition before (—) and after (- - -) photoirradiation in the mixed solvents of various DCE/HFIP compositions.

series in DCE is left hand helical for the copolymers with less than 40% azo [β-*p*-(phenylazo)phenethyl L-aspartate] residues whereas it is right hand helical for the copolymers with more azo residues. The polymer with 100% azo residues exhibits poor solubility in DCE. Thus I is the polymer with the highest azo residues among the soluble polymers prepared. In an attempt to check the solvent effect on the conformation[11] of *trans*-I, HFIP was added up to 20% to the DCE solution of I. This led to a solvent-induced right-handed helix → left-handed helix transition as shown in Figure 1. Upon further addition of HFIP, I undergoes a left-handed helix → random coil transition. Bradbury et al. reported similar phenomenon, though in their case the conformational transition was induced by addition of trifluoroacetic acid or dichloroacetic acid to chloroform solutions of copolymers of β-ethyl L-aspartate and β-benzyl L-aspartate.[11b] The random form of I yielded the anomalous value of $[\theta] \sim -15\,000$, which is also in agreement with the result of Bradbury et al. This solvent-induced conformational transition may arise from an alteration of the energy balance as a consequence of hydrogen bonding of HFIP to the side-chain ester group.

Photoirradiation was carried out on the solutions of I at various solvent compositions, using a Corning 7-37 filter which passes the light of 320–390 nm with a 500-W Xenon lamp (percent cis: 70–80 in the photostationary state). The results of photoirradiation are shown in Figures 1 and 2. The trend of light-induced conformational change around 5% HFIP is the one from the left-handed helix to the right-handed helix. At 10% HFIP the trend is inverted and the polymer tends to take a fully left-handed helix. The fully left-handed helix at 20% HFIP is insensitive to light. On further increase in the HFIP content, I again becomes sensitive to light, showing a tendency of conformational change from left-handed helix to random coil with the attainment of maximum ellipticity difference $\Delta[\theta] \sim 28\,500$ at 26% HFIP. When the HFIP content reaches 50%, I is in a random-coil conformation and is hardly affected by photoirradiation. Further increase in the HFIP content causes no significant conformational change although there exists a slight decrease in the absolute ellipticity.

These phenomena suggest the important role of environment in realizing remarkable photoresponsive behavior on natural and synthetic photosensitive macromolecular systems. We are currently investigating the decay process from cis to trans configuration in the mixed solvents in connection with the main-chain conformation.

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Variable Temperature High-Resolution Carbon-13 NMR Spectra of Solid Fluoropolymers

It is now well-established that ^{13}C NMR spectra in which resolution approaches that of the liquid state can be obtained for solid hydrocarbon polymers by employing a combination of resolution (dipolar decoupling and magic-angle spinning) and sensitivity (cross-polarization) enhancement techniques.[1-5] In this communication, we re-

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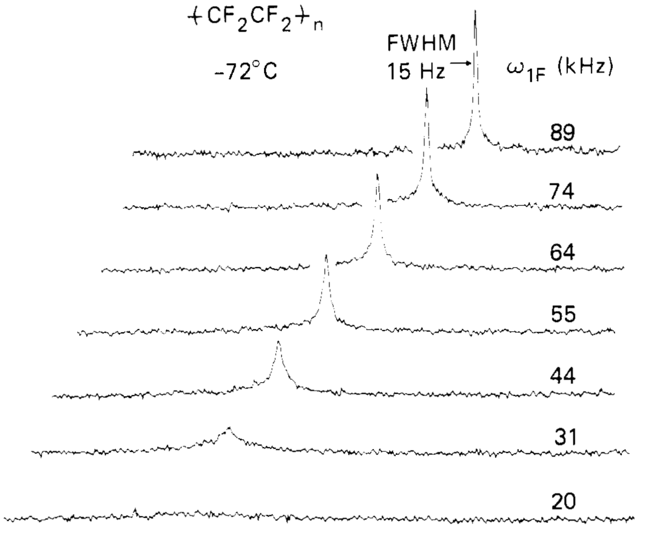

Figure 1. Magic-angle spinning (MAS) ^{13}C spectra of PTFE at -72 °C as a function of the ^{19}F decoupling field, ω_{1F}, kHz. Each spectrum was obtained from a 2K FT of 256 FID accumulations with a cross-polarization (CP) time of 3.0 ms and an experiment repetition time of 2 s. The spectra are displayed on a normalized scale. For further details see ref 10.

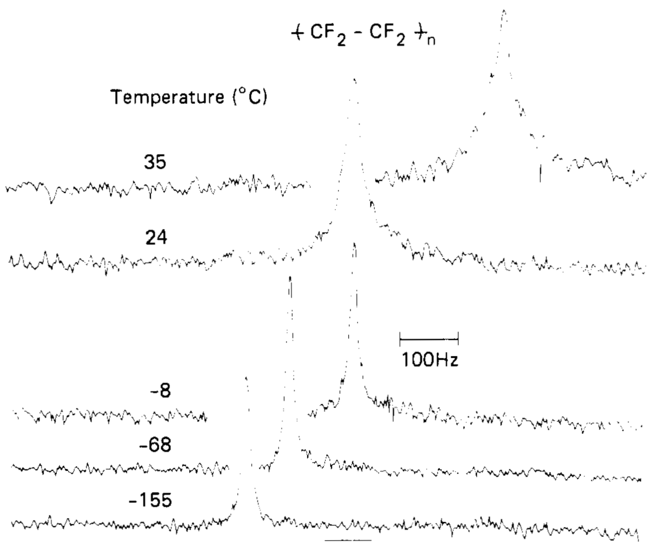

Figure 2. Fluorine-decoupled, MAS ^{13}C spectra of PTFE as a function of temperature. Spectra were obtained from a 2K FT of 300 FID accumulations with a CP time of 5.0 ms and an experiment repetition time of 2.0 s. The ^{19}F decoupling field was 89 kHz in each case.

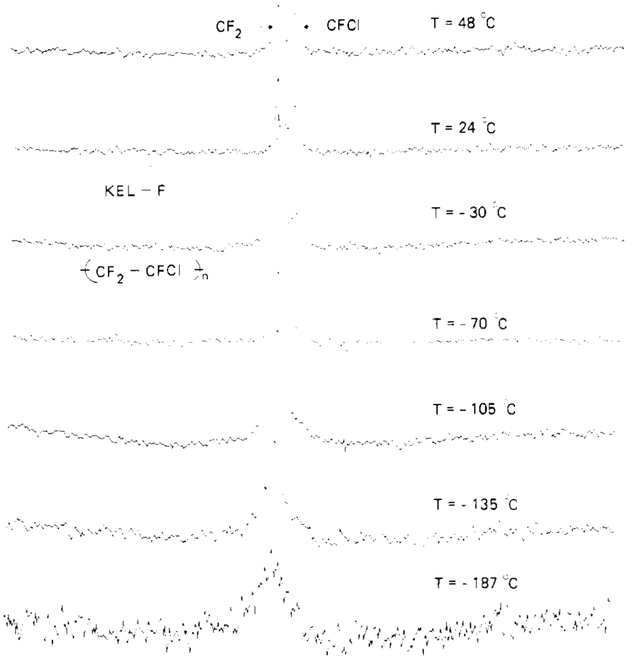

Figure 3. Fluorine-decoupled, MAS ^{13}C spectra of PCTFE as a function of temperature. Spectra were obtained with a CP time of 5.0 ms and an experiment repetition time of 2.5 s. Spectra represent a 2K FT in each case; the number of FID accumulations varied from 1K to 5K.

port the extension of these techniques to obtain ^{13}C spectra of bulk fluoropolymers. Specifically, preliminary results are presented on variable-temperature magic-angle spinning studies of poly(tetrafluoroethylene) (PTFE) and poly(chlorotrifluoroethylene) (PCTFE).

In principle, the narrowing of ^{13}C resonance lines in bulk fluoropolymers by "solid-state" methods[6] is no more difficult than that in hydrocarbons. However, there is a significant experimental difference between the two cases with respect to removal of the heteronuclear (C–H or C–F) dipolar broadening. The fluorine nucleus exhibits a range of isotropic chemical shifts ca. 20-fold greater than that of the proton.[7] In solids, typical fluorine chemical shift anisotropies display a corresponding relationship to their proton counterparts.[8a] The consequence of such large dispersions in the fluorine resonance is that larger decoupling fields are required for removal of C–F dipolar broadening of carbon resonance lines than for C–H broadening in analogous cases.[8b] To illustrate, magic-angle spinning ^{13}C spectra of PTFE (60% crystalline) obtained at -72 °C as a function of the ^{19}F decoupling field strength (ω_{1F}) are presented in Figure 1.[9,10] For semicrystalline polyethylene, PE, spectra with fwhm of $\lesssim$5 Hz can be obtained from the crystalline region with 35–40 kHz of proton decoupling.[4] At this same ^{19}F decoupling field, PTFE yields a 50–70 Hz resonance line with large wings at its base. The difference in resolution achieved in the two polymers is attributed mainly to less efficient dipolar decoupling in PTFE caused by "off-resonance" effects[11] arising from the large ^{19}F chemical shift anisotropy.[12-14] At the magnetic field of 1.4 T, the nonaxially symmetric ^{19}F powder pattern encompasses a frequency range of ~8 kHz as opposed to an ~330 Hz frequency range for the ^{1}H powder pattern in PE.[15] As is evident in Figure 1, the ^{13}C resonance line in PTFE does narrow significantly at larger values of ω_{1F} with the minimum ^{13}C line width (15 Hz fwhm) being observed at the maximum available decoupling field (89 kHz). The smooth decrease in the PTFE line width up to the maximum decoupling field[16] suggests that residual fluorine dipolar broadening accounts, in part, for the 15 Hz line width observed at this field strength. (Other sources of residual broadening include magnetic field inhomogeneities, spinner instabilities, and distribution of isotropic shifts in amorphous regions.)[3,4]

^{13}C magic-angle spinning spectra of PTFE as a function of temperature[17] are shown in Figure 2. The line width (15 Hz) of the CF_2 resonance remains essentially constant until the temperature regime (15–25 °C) is reached, above which a broadening of 2–3-fold ensues. This broadening appears to reflect the 19 °C first-order transition which has been observed in PTFE by numerous techniques including ^{19}F broad-line NMR[18] and more recently by ^{19}F NMR with the use of a multipulse narrowing scheme.[13,14] The transition is associated with the onset of rotation of molecules in crystalline regions about the long axis of the helical chain.[18] The resulting anisotropic motion is sufficient to give rise to motional broadening[1] of the carbon resonance. The same temperature-induced broadening phenomenon is also observed for a 95% crystalline sample of PTFE, thus establishing that the effect occurs in crystalline regions.

Magic-angle spinning ^{13}C spectra of PCTFE obtained as a function of temperature are shown in Figure 3. At 48 °C, the two carbon resonances of the repeat unit are clearly resolved with the line at higher field being assigned to the CFCl carbon. Line widths in the spectrum are ca. 60–70 Hz fwhm.[19] As the temperature is lowered, the CFCl resonance begins to broaden and the appearance of a two-line spectrum is lost. The source of broadening is not C–F dipolar coupling as the ^{19}F rigid lattice line width is reached at ca. 20 °C[20] and the fwhm of the CF_2 carbon resonance does not change measurably above or for a 100 °C range below this temperature. Thus, the differential broadening of the CFCl resonance is attributed to a residual dipolar interaction of this carbon with the quadrupolar chlorine nucleus. In organic systems, chlorine nuclei often experience large quadrupole coupling constants.[21] Depending on the ratio of the Zeeman and quadrupole interaction energies, the chlorine spins may be oriented along the Zeeman field or fixed at some definite orientation in the principal axis system of the molecular electric field gradient tensor.[22] If the Cl moments are coupled more strongly to the electric field gradient than to the Zeeman field, the C–Cl dipolar interaction will not be removed by magic-angle spinning.[23] In the Zeeman field of 1.4 T, this interaction appears to broaden the C–Cl resonance in PCTFE at temperatures below ambient. The separation of the resonances at higher temperature appears to be coupled to molecular motion in the polymer. Glass transition temperatures[20] for PCTFE are ca. 40 °C. Thus, at 48 °C, motion in the polymer backbone is presumably sufficient to cause the Cl spin–lattice relaxation rate to be rapid enough to induce near-complete "self-decoupling" of the C–Cl dipolar interaction.[24] Well below T_g, the small amplitude of oscillatory motions may be insufficient to cause rapid quadrupolar relaxation and thus C–Cl dipolar broadening ensues. Effects on the CF_2 resonance are strongly attenuated by the r^{-3} dependence of the dipolar interaction; however, at temperatures below −135 °C the broadening of the CF_2 carbon is apparent.

These results on PTFE and PCTFE demonstrate that well-resolved ^{13}C spectra can be obtained on solid fluoropolymers by magic-angle spinning and ^{13}C-$\{^{19}F\}$ dipolar decoupling. From the spectral data obtained as a function of temperature, it is also clear that useful information on motion and structure in these materials can be ascertained from variable temperature spinning studies. A full report on fluoropolymer systems, including work on fibers, will be forthcoming.[25]

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