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Solid-State Fluorine-19 Nuclear Magnetic Resonance Study of Fluorocarbon Polymers

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ABSTRACT: ^{19}F NMR at 338.7 MHz, with high-speed magic-angle spinning (MAS), has been used to study a number of fluorocarbon polymers. Systems studied were copolymers of vinylidene fluoride and hexafluoropropene, copolymers of vinylidene fluoride and chlorotrifluoroethene, and terpolymers of vinylidene fluoride, tetrafluoroethene, and hexafluoropropene. High-resolution spectra of all samples were obtained by using MAS speeds greater than 18 kHz. Structural assignments of chemical shifts in terms of five-carbon (pentad) sequences were made on the basis of solution-state studies. Sufficient resolution is obtained under high-speed MAS conditions to determine the relative concentration of each carbon pentad present. Monomer composition can also be determined from the ^{19}F MAS NMR data. Agreement with known compositions, when available, is good.

Introduction

Some of the initial applications of NMR spectroscopy to the determination of the structure of polymers was accomplished by using ^{19}F NMR on liquid samples.[1-4] A number of studies followed and led to a better understanding not only of the structure of polymers but also of the reaction rate constants governing the addition of particular monomers to a growing polymer chain.[5-18] A major advantage of ^{19}F NMR in polymer studies is the large chemical shift range for this nucleus. The effect of nearest and next-nearest neighbors on the chemical shift of a particular fluorine is readily measured.[3] Thus, it is possible to determine the number and type of monomer sequences present in a fluorocarbon polymer.[5-18] However, high-resolution ^{19}F NMR studies of polymers have been limited to solution-state spectra and have often employed low molecular weight polymers.

The need for a practical high-resolution technique for solid samples of these kinds of polymers is underscored by the fact that most known solvents must either be used at high temperature[14] or cause spectral overlap.[19] Furthermore, the ability to obtain spectra of undissolved polymers allows one to examine a polymer directly in the state in which its common structural applications depend.

^{19}F NMR measurements on solid samples using multiple-pulse methods[20] have yielded such parameters as the principal values of the chemical shift tensor,[21,22] but the chemical shift fine structure normally present in solution-state studies were not present in those studies. A high-resolution solid-state ^{19}F NMR study of fluoroapatite and fluorohydroxyapatite using magic-angle spinning (MAS) has appeared,[23] but successful ^{19}F MAS NMR studies of solid fluorocarbon polymers have not previously been published. This situation is probably a manifestation of the different characters of the anisotropic interactions present in the apatite and fluorocarbon polymer systems. For the apatite minerals high-resolution solid-state ^{19}F MAS NMR spectra can be obtained[23] by using moderate sample-spinning speeds (e.g., 3–5 kHz) because the dominant cause of line broadening is due to inhomogeneous interactions—chemical shift anisotropy and ^{19}F–^{19}F dipolar interactions between rather remote nuclei.[24] While the apatite spectra are complicated by the presence of spinning sidebands, isotropic chemical shifts can still be obtained.

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Table I
Polymer Designations and Monomer Components

polymer[a]	monomer components
FC 2260	CH_2CF_2 and CF_3CFCF_2[b]
FC 2145	CH_2CF_2 and CF_3CFCF_2[b]
FLS 2690	CH_2CF_2 and CF_2CF_2 and CF_3CFCF_2[c]
FT 2481	CH_2CF_2 and CF_2CF_2 and CF_3CFCF_2[c]
Kel-F 3700	25% CF_2CFCl + 75% CH_2CF_2
Kel-F 800	75% CF_2CFCl + 25% CH_2CF_2

[a] 3M designation. [b] Composition of sample FC 2260 differs from that of sample FC 2145.[27] [c] Composition of sample FLC 2690 differs from that of FT 2481.[27]

The high density of fluorine atoms in fluorocarbon polymers yields strong and homogeneous ^{19}F–^{19}F dipolar interactions, and hence ^{19}F MAS NMR spectra are still severely broadened at the highest sample spinning speeds that until recently have been available. In order to average effectively the strong homonuclear dipole–dipole interactions present in these systems and obtain high-resolution solid-state ^{19}F NMR spectra with MAS techniques, higher spinning speeds are required.[25] We have recently reported on the development of such high-speed MAS technology.[26] Results obtained on Kel-F (3M corporation), a homopolymer of trifluorochloroethylene (–CF_2CFCl–) have shown that high-resolution solid-state ^{19}F MAS NMR spectra can be obtained at spinning speeds greater than about 14 kHz for this type of polymer system.[26] Here we report further and more detailed results on high-speed MAS ^{19}F NMR studies of copolymers of vinylidene fluoride (CH_2CF_2) and hexafluoropropene (CF_3CFCF_2), copolymers of CH_2CF_2 and CF_2CFCl, and terpolymers of CH_2CF_2, CF_3CFCF_2, and tetrafluoroethene (CF_2CF_2).

Experimental Section

Materials. The polymers investigated were supplied by 3M Corp.[27] The 3M designation, which we use throughout the paper, and corresponding monomer components of each polymer are summarized in Table I. All samples were used as received.

^{19}F NMR Measurements. All ^{19}F NMR spectra were recorded at 338.7 MHz on a modified NT-360 spectrometer. The MAS spectra were obtained by using a modified version[26] of the MAS spinning system developed at Delft University.[28] Torlon 4203 (Amoco Chemical Corp.) was used to fabricate the rotors, which have a 4.5-mm outer diameter and a sample volume of 25 μL. Rotational frequencies up to 17 kHz were obtained with air as the drive and bearing gas. Higher rotational frequencies were reached by using a mixture of helium and air as the drive gas and air for the bearing gas. All spectra were recorded without decoupling, using a pulse–acquire–delay pulse sequence. $\pi/2$ pulses of 7-μs duration were used. We have determined that relaxation delays of 10 s are sufficiently long to ensure quantitative peak intensities. Chemical shifts were measured with respect to polytetrafluoroethene (Teflon), which was assigned a chemical shift of 0 ppm.

Results and Discussion

Overview. Typical behavior of the ^{19}F NMR spectra obtained as a function of MAS spinning speed for the fluorocarbon polymers is shown in Figure 1 for sample FT 2481. The dependences of the ^{19}F spectra of the other samples on MAS speed are similar. Some general comments on these results are in order. The static spectrum in Figure 1 shows three very broad features. The large line widths of the peaks are due to a number of effects; these are (a) range of isotropic chemical shifts, (b) chemical shift anisotropies, (c) ^{19}F ^{19}F dipolar interactions, and (d) ^{19}F–^{1}H dipolar interactions. For the samples containing –CF_2–$CF(Cl)$– monomer units, there are also ^{19}F–Cl dipolar interactions.

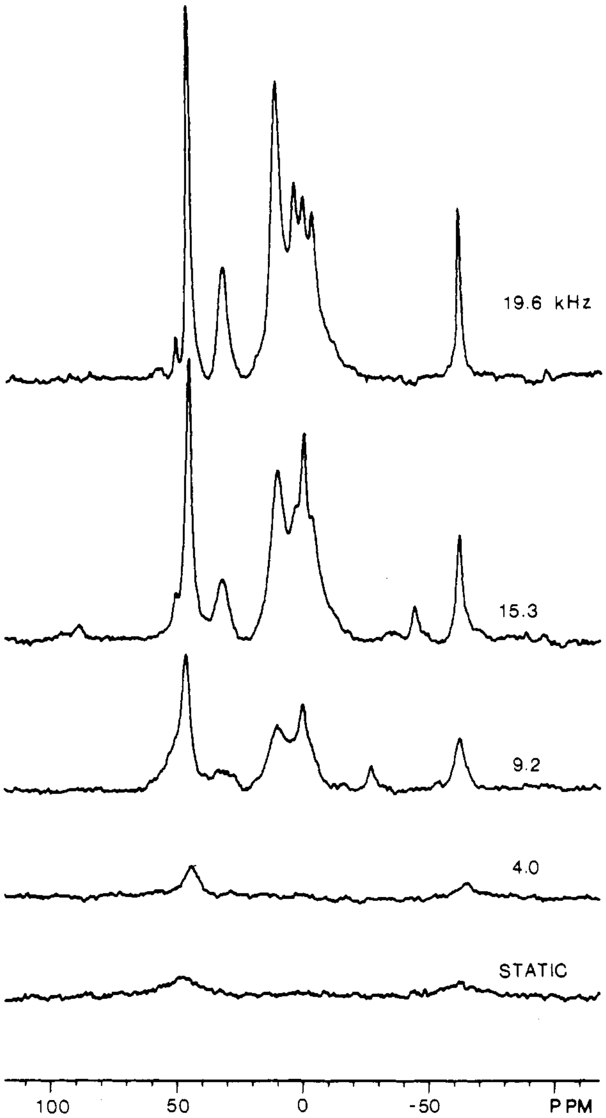

Figure 1. 338.7-MHz ^{19}F MAS spectra of sample FT 2481 as a function of MAS speed.

In the various polymers studied, as represented by the spectra of Figure 1, the static line widths of the –CF_3 (low shielding 40–60 ppm) and >CF– (high shielding –60 to –70 ppm) groups are only about 9 kHz each. Hence, the resonance lines of these two fluorine moieties are significantly narrowed at intermediate MAS spinning speeds, e.g., $\lesssim 9$ kHz.[24] The relative ease of narrowing the resonance lines of these two groups are inherent properties of their structures. The relatively small static ^{19}F line width (i.e., widths for a static sample) of the –CF_3 group probably comes about because the fluorine atoms rapidly rotate about the axis of the C–C bond between the –CF_3 carbon and the attached carbon of the polymer backbone; i.e., there is fast rotational averaging of the ^{19}F–^{19}F dipolar interactions of the –CF_3 group and MAS is effective in reducing further the residual ^{19}F line width that one observes for the static sample.[29] For the >CF– group, ^{19}F–^{19}F dipole–dipole interactions are reduced in magnitude because of the relatively isolated positions of the fluorine of this moiety in the polymer. The dipolar interaction is a function of the inverse cube of the internuclear separation[29] and is rapidly reduced as the separation between nuclei increases. Thus, for >CF– groups, static line widths are relatively small and narrow resonance lines are obtained at intermediate spinning speeds.

The static line width of the –CF_2– (intermediate shielding, 40 to –20 ppm) region of the spectrum is about 20 kHz. The larger line width for this moiety is due to (1)

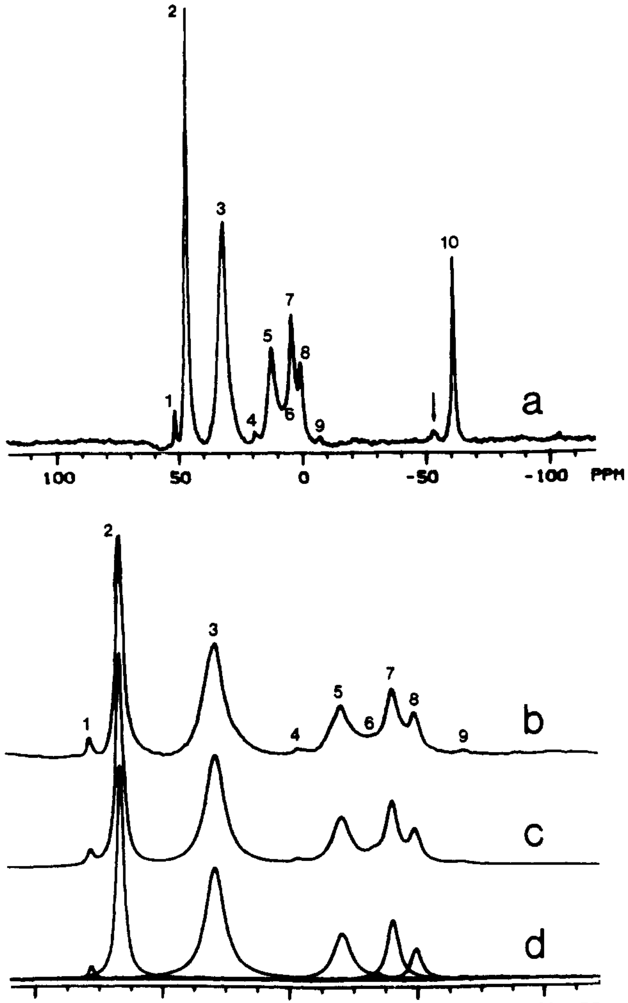

Figure 2. 338.7-MHz ^{19}F MAS spectra of sample FC 2260: (a) 18.2-kHz MAS spectrum (an arrow indicates a spinning sideband); (b) CF_3 and CF_2 regions of (a); (c) computer simulation of (b); (d) deconvolution of peaks corresponding to (c).

Table II
^{19}F Chemical Shifts, Probable Structural Assignments, and Peak Areas for Sample FC 2260

peak	chem shift,[a] ppm	% area	structural assignment[b]
1	51.1	1.2	$-CH_2-CF_2-CF(CF_3{}^*)-CF_2-CH_2-$[d,e]
2	46.6	25.3	$-CF_2-CF_2-CF(CF_3{}^*)-CH_2-CF_2-$[d,e]
3	31.8	36.2	$-CF_2-CH_2-CF_2{}^*-CH_2-CF_2-$[d,e]
4	18.8	0.4	$-CF_2-CH_2-CF_2{}^*-CF(CF_3)-CF_2-$[d,e]
5	11.9	13.8	$-CF_2-CH_2-CF_2{}^*-CF_2-CF(CF_3)-$[e]
6	6.8	1.6	$-CF_2-CH_2-CF_2{}^*-CF_2-CH_2-$ + $-CH_2-CF_2-CF_2{}^*-CH_2-CH_2-$[d]
7	3.9	11.6	$-CH_2-CF_2-CF_2{}^*-CF(CF_3)-CH_2-$[d,e]
8[c]	0.4		
9	−7.3	0.5	$-CF_2-CF(CF_3)-CF_2{}^*-CF_2-CF(CF_3)-$[f]
10	−61.8	9.4	$-CF_2-CF_2-CF^*(CF_3)-CH_2-CF_2-$[d,e]

[a] Relative to Teflon. [b] Asterisk indicates relevant moiety. [c] $(CF_2CF_2)_n$ impurity in Torlon 4203. [d] Reference 9. [e] Reference 17. [f] See text.

Table III
^{19}F Chemical Shifts, Probable Structural Assignments, and Peak Areas for Sample FC 2145

peak	chem shift,[a] ppm	% area	structure assignment[b]
1	50.9	1.9	$-CH_2-CF_2-CF(CF_3{}^*)-CF_2-CH_2-$[d,e]
2	46.4	30.8	$-CF_2-CF_2-CF(CF_3{}^*)-CH_2-CF_2-$[d,e]
3	31.4	30.1	$-CF_2-CH_2-CF_2{}^*-CH_2-CF_2-$[d,e]
4	18.5	0.8	$-CF_2-CH_2-CF_2{}^*-CF(CF_3)-CF_2-$[d,e]
5	11.6	9.8	$-CF_2-CH_2-CF_2{}^*-CF_2-CF(CF_3)-$[e]
6	10.4	1.3	$-CF(CF_3)-CH_2-CF_2{}^*-CF_2-CF(CF_3)-$[d]
7	6.5	2.6	$-CF_2-CH_2-CF_2{}^*-CF_2-CH_2-$ + $-CH_2-CF_2-CF_2{}^*-CH_2-CH_2-$[d]
8	3.6	11.4	$-CH_2-CF_2-CF_2{}^*-CF(CF_3)-CH_2-$[d,e]
9[c]	0.0		
10	−5.2	0.9	$-CF_2-CF(CF_3)-CF_2{}^*-CF_2-CF(CF_3)-$[f]
11	−61.7	10.4	$-CF_2-CF_2-CF^*(CF_3)—CH_2-CF_2-$[d,e]

[a] Relative to Teflon. [b] Asterisk indicates relevant moiety. [c] $(CF_2CF_2)_n$ impurity in Torlon 4203. [d] Reference 9. [e] Reference 17. [f] See text.

a substantial range of chemical shifts and (2) larger net dipolar interactions. When MAS speeds the order of the static line width are used ($\gtrsim$15 kHz), all the major features in the spectrum that are readily seen in the 19.6 kHz spectrum are apparent.

Individual Samples. FC 2260. Figure 2a shows the 18.2-kHz ^{19}F MAS NMR spectrum obtained for sample FC 2260, a copolymer of CH_2CF_2 and CF_3CFCF_2. Chemical shifts and probable structural assignments for each peak are given in Table II. Throughout this paper, the particular fluorine site on which we focus for a chemical shift assignment is indicated by an asterisk. The majority of the carbon pentad assignments for each chemical shift were made with reference to the liquid-state work of Ferguson[9] and of Murasheva and co-workers.[17] All the major features apparent in the ^{19}F NMR spectra of the solubilized polymer[9,17] are readily measured with high-speed MAS techniques. Nevertheless, some lines observed in solution-state studies have insufficient intensity and chemical shift separation from neighboring major peaks to be resolved with the MAS spinning speeds used in this study. The only peak that cannot be assigned in the solid-state MAS spectrum by direct comparison with solution-state spectra is peak 9, with a chemical shift of −7.3 ppm. A structure of the type $-CH_2-CF_2-CF_2{}^*-CF_2-CH_2-$ has a reported chemical shift of −2 to −3 ppm.[17] However, this structure is considered highly unlikely, because neither monomer component contains consecutive $-CF_2-$ groups and the formation of such a defect structure is apparently negligible.[9] Experimental error in chemical shifts can also be ruled out, since the precision of our chemical shift measurements is about ±0.5 ppm. Thus, an additional carbon pentad that previously has been undetected[9,17] may have been formed in the synthesis of this copolymer. Possible carbon pentads that might merit consideration are $-CH_2-CF(CF_3)-CF_2{}^*-CF_2-CF(CF_3)-$ and $-CF_2-CF(CF_3)-CF_2{}^*-CF_2-CF(CF_3)-$. These sequences were not considered in earlier studies, because of the assumed inability of CF_3CFCF_2 to self polymerize under the polymerization conditions employed.[9,17] Later in this paper chemical shifts for these two types of pentads are assigned values of −12.5 (Table V) and −5.2 ppm (Table III), respectively, for other polymers on the basis of comparisons with liquid-sample data.[30] The −7.3 ppm value for peak 9 of the FC 2260 spectrum falls between these two assigned chemical shifts; nevertheless, it is perhaps not justifable to make firm decisions on the basis of small differences in deviations from the assigned values. In addition, it is possible that some cross-linking agents may be present in this commercial elastomer, and this could give rise to "anomalous" peaks with low intensities.

Figure 2a also shows that sufficient resolution is obtained with 18.2-kHz MAS that one should expect to be able to carry out a computer deconvolution of the overlapping peaks in the $-CF_3$ and $-CF_2-$ regions of the spectrum. Such a computer deconvolution simulation is shown in Figure 2c. All resonance lines were fit by using

Lorentzian functions. Theoretical evidence exists for the use of Lorentzian a function; i.e., a resonance line that is broadened in the static case by homonuclear dipolar interactions becomes Lorentzian under fast MAS spinning conditions.[31] (Detailed line-shape analysis as a function of MAS speed will be the subject of a future report.) Inspection of Figure 2b–d shows that the computer simulation adequately reproduces the measured spectrum. Relative integrated intensities for each peak of sample FC 2260 are given in Table II. No correction for the intensity of the spinning sideband was made as this sideband is attributable to the $(CF_2CF_2)_n$ impurity in Torlon 4203.

Knowledge of the relative amounts of carbon pentads permits the calculation of relative reactivity ratios when the monomer feed ratios are known.[32] The monomer feed ratios are not known for the samples investigated in this study; thus a calculation of this type is precluded.

The computer simulation permits the ^{19}F spectra of the fluorocarbon polymers to be corrected for the tetrafluoroethylene (TFE) impurity signal that is found at 0 ppm in the spectrum of the Torlon 4203 used to fabricate the sample spinners. This correction is applied to the total intensity of the $-CF_2-$ region of each spectrum and allows the relative amounts of the monomer components of the fluorocarbon polymer to be calculated.

Because hexafluoropropene is the only source of $-CF_3$ and $>CF-$ groups in this copolymer, the fractional number (N_{HFP}) of CF_3CFCF_2 (HFP) monomers in the polymer, FC 2260, can be accounted for either in terms of $>CF-$ or $-CF_3$ resonances. Hence

$$N_{HFP} = n_{10} \tag{1a}$$

$$N_{HFP} = \tfrac{1}{3}(n_1 + n_2) \tag{1b}$$

where n_i is the relative intensity of carbon pentad number i as defined by a peak number in Figure 2a. A difference in the value of N_{HFP} obtained by using eq 1a and 1b is a measure of the experimental error associated with the integrated intensities of Table II. Since peak 5 in principle has contributions from $-CF_2-$ groups of both monomers, the number of CH_2CF_2 (VF) monomers present, N_{VF}, is most readily given for this polymer by

$$N_{VF} = \tfrac{1}{2}(n_3 + n_4 + n_5 + n_6 + n_7 + n_9) - N_{HFP} \tag{2}$$

Substitution of the integrated intensities of Table II into eq 1a and 2 gives as the result that sample FC 2260 is composed of 71% CH_2CF_2 while use of eq 1b and 2 yields a composition of 72% CH_2CF_2 in this polymer. Comparison with the known composition of this polymer is not possible.[27] However, for Kel-F 3700 and Kel-F 800, for which the monomer compositions are known,[27] the present ^{19}F MAS NMR analyses yield results which agree within experimental error (see below).

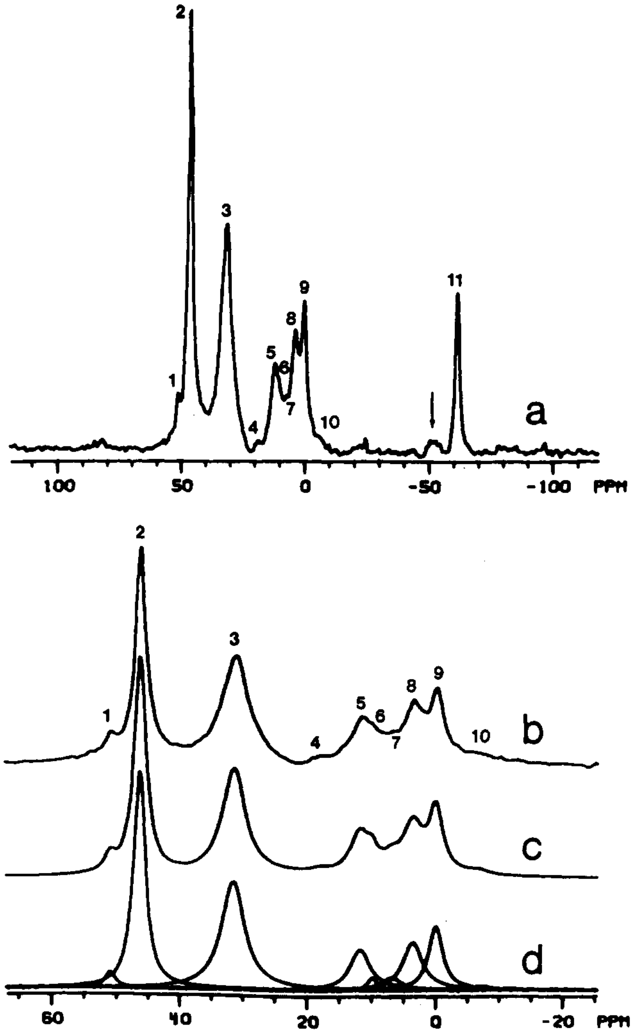

Figure 3. 338.7-MHz ^{19}F MAS spectra of sample FC 2145: (a) 18.0-kHz MAS spectrum (an arrow indicates a spinning sideband); (b) CF_3 and CF_2 regions of (a); (c) computer simulation of (b); (d) deconvolution of peaks corresponding to (c).

FC 2145. Figure 3a shows the 18.0-kHz ^{19}F MAS NMR spectrum of sample FC 2145, another copolymer of CH_2CF_2 and CF_3CFCF_2. Chemical shifts and probable structural assignments for each peak are given in Table III. Note the presence of an additional carbon pentad, $-CF(CF_3)-CH_2-CF_{2*}-CF_2-CF(CF_3)-$ (peak 6, Table III), not observed in sample FC 2260. The appearance of this pentad may be due to the overall increased concentration of CF_3CFCF_2 monomers in this polymer relative to sample FC 2260 (see below). Probable structural assignments were made in complete analogy with those of sample FC 2260, again using the results of solution-state studies.[9,17] A computer simulation of the $-CF_3$ and $-CF_2-$ regions of the spectrum is shown in Figure 3c,d. Relative integrated intensities are given in Table III. No correction for the intensity of the spinning sideband was made as this sideband is attributable to the $(CF_2CF_2)_n$ impurity in Torlon 4203. Calculations similar to that for sample FC 2260 yield the conclusion that sample FC 2145 is composed of 63% or 62% CH_2CF_2 when $N_{HFP} = n_{11}$ or $N_{HFP} = \frac{1}{3}(n_1 + n_2)$, respectively. The 1% deviation in the amount of CH_2CF_2 calculated in this manner is a measure of the experimental error associated with the integrated intensities listed in Table III.

FLS 2690. The 18.3-kHz ^{19}F MAS NMR spectrum of sample FLS 2690, a terpolymer of CH_2CF_2, CF_2CF_2, and CF_3CFCF_2, is shown in Figure 4a. Chemical shifts and probable structural assignments for each resonance are given in Table IV. Probable structural assignments were made in analogy to those of sample FC 2260. One additional carbon pentad, with a chemical shift of −3.5 ppm, is present in this terpolymer that is not present in the copolymers of CH_2CF_2 and CF_3CFCF_2 (Figures 2 and 3). The structural assignment of this additional resonance is $-CH_2-CF_2-CF_2{}^*-CF_2-CH_2-$,[17] and is due to the presence of the monomer CF_2CF_2 in this polymer. A computer simulation of the $-CF_3$ and $-CF_2-$ regions of the spectrum is shown in Figure 4c,d. Relative integrated intensities are given in Table IV. No correction for the intensity of the spinning sideband was made as this sideband is attributable to the $(CF_2CF_2)_n$ impurity in Torlon 4203. The monomer composition of this terpolymer can be calculated because the ^{19}F NMR spectrum is sufficiently resolved to permit structural assignments to be made on the basis of

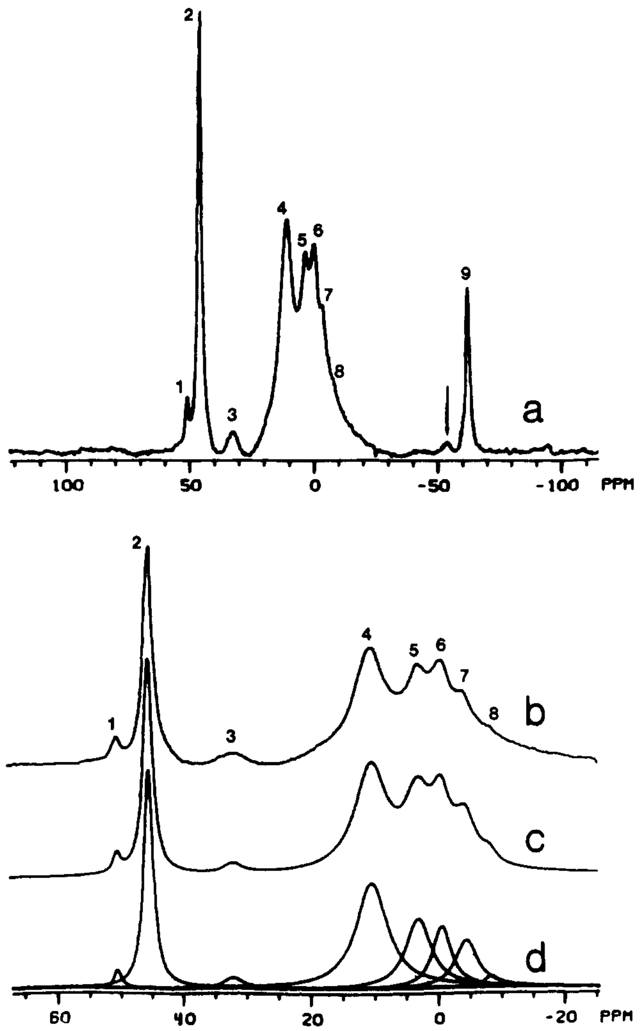

Figure 4. 338.7-MHz ^{19}F MAS spectra of sample FLS 2690: (a) 18.3-kHz MAS spectrum (an arrow indicates a spinning sideband); (b) CF_3 and CF_2 regions of (a); (c) computer simulation of (b); (d) deconvolution of peaks corresponding to (c).

Table IV
^{19}F Chemical Shifts, Probable Structural Assignments, and Peak Areas for Sample FLS 2690

peak	chem shift,[a] ppm	% area	structural assignment[b]
1	50.3	1.4	$-CH_2-CF_2-CF(CF_3*)-CF_2-CH_2-$[d,e]
2	45.3	21.8	$-CF_2-CF_2-CF(CF_3*)-CH_2-CF_2-$[d,e]
3	32.4	1.9	$-CF_2-CH_2-CF_2*-CH_2-CF_2-$[d]
4	10.4	35.6	$-CF(CF_3)-CH_2-CF_2*-CF_2-CF(CF_3)-$[d]
5	3.0	18.8	$-CH_2CF_2-CF_2*-CF(CF_3)-CH_2-$[d,e]
6[c]	-0.5		
7	-3.5	11.2	$-CH_2-CF_2-CF_2*-CF_2-CH_2-$[e]
8	-8.1	1.7	$-CF_2-CF(CF_3)-CF_2*-CF_2-CF(CF_3)-$[f]
9	-62.6	7.4	$-CF_2-CF_2-CF*(CF_3)-CH_2-CF_2-$[d,e]

[a] Relative to Teflon. [b] Asterisk indicates relevant moiety. [c] $(CF_2CF_2)_n$ impurity in Torlon 4203. [d] Reference 9. [e] Reference 17. [f] See text.

five-carbon sequences. Because hexafluoropropene is the only source of $-CF_3$ and $>CF-$ groups in this polymer, the number of CF_3CFCF_2 monomers, N_{HFP}, can be calculated as follows

$$N_{HFP} = n_9 \tag{3a}$$

or

$$N_{HFP} = \frac{1}{3}(n_1 + n_2) \tag{3b}$$

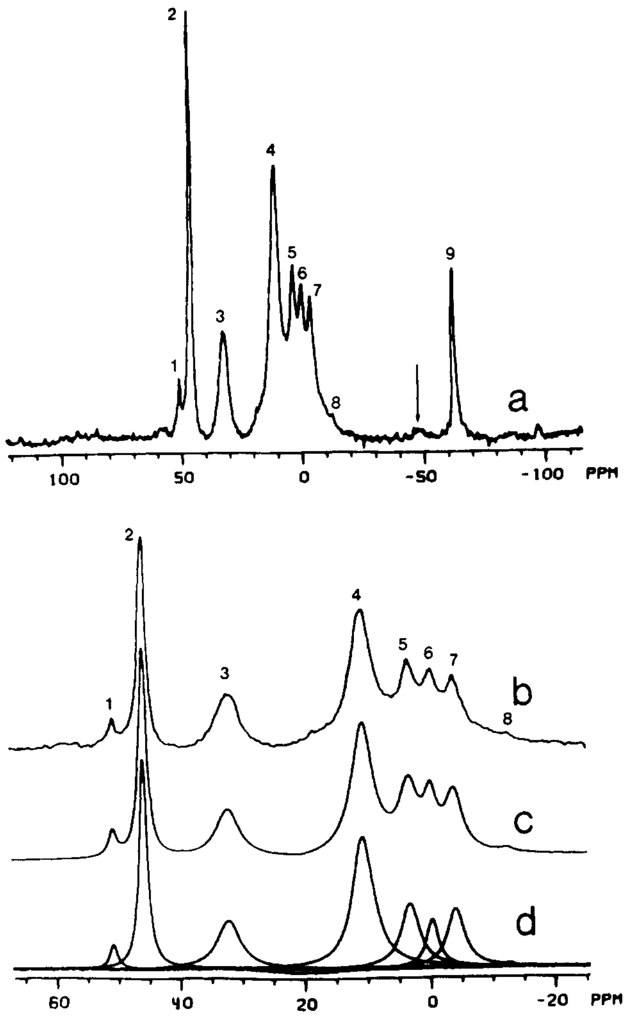

Figure 5. 338.7-MHz ^{19}F MAS spectra of sample FT 2481: (a) 19.6-kHz MAS spectrum (an arrow indicates a spinning sideband); (b) CF_3 and CF_2 regions of (a); (c) computer simulation; (d) deconvolution of peaks corresponding to (c).

The number of CF_2CF_2 (TFE) monomers, N_{TFE}, is given by

$$N_{TFE} = \frac{1}{2}(n_7 + fn_8) \tag{4}$$

where f is the fraction of CF_2CF_2 monomers incorporated into carbon pentads of the type $-CF_2-CF(CF_3)-CF_2*-CF_2-CF(CF_3)-$. The number of CH_2CF_2 monomers is given by

$$N_{VF} = \frac{1}{2}(n_3 + n_4) \tag{5}$$

The integrated intensities of Table IV may be used to estimate the monomer composition of this polymer. The value of N_{HFP} is taken as the average of N_{HFP} computed from eq 3a and 3b. The value of N_{TFE} is taken as the average of the values computed using eq 4 with $f = 0$ and $f = 1$. The resulting conclusion is that sample FLS 2690 has a composition of 58% CH_2CF_2, 23% CF_3CFCF_2, and 19% CF_2CF_2.

FT 2481. Figure 5a shows the 19.6-kHz ^{19}F MAS NMR spectrum of sample FT 2481, another terpolymer of CH_2CF_2, CF_2CF_2, and CF_3CFCF_2. Chemical shifts and probable structural assignments for each line are given in Table V. Probable structural assignments were made in analogy with those of sample FLS 2690. In addition, the resonance with a chemical shift of -12.5 ppm is tentatively assigned to the structure, $-CH_2-CF(CF_3)-CF_2*-CF_2-CF(CF_3)-$. This assignment is made in analogy with that of peak 10 of sample FC 2145 (Figure 3a) and the previously

Table V
^{19}F Chemical Shifts, Probable Structural Assignments, and Peak Areas for Sample FT 2481

peak	chem shift,[a] ppm	% area	structural assignment[b]
1	50.5	2.3	$-CH_2-CF_2-CF(CF_3*)-CF_2-CH_2-$[d,e]
2	45.6	19.0	$-CF_2-CF_2-CF(CF_3*)-CH_2-CF_2-$[d,e]
3	31.7	13.0	$-CF_2-CH_2-CF_2*-CH_2-CF_2-$[d]
4	10.4	32.1	$-CF(CF_3)-CH_2-CF_2*-CF_2-CF(CF_3)-$[d]
5	3.2	14.0	$-CH_2-CF_2-CF_2*-CF(CF_3)-CH_2-$[d,e]
6[c]	-0.4		
7	-4.1	11.9	$-CH_2-CF_2-CF_2*-CF_2-CH_2-$[e]
8	-12.5	0.5	$-CH_2-CF(CF_3)-CF_2*-CF_2-CF(CF_3)-$[f]
9	-62.2	7.2	$-CF_2-CF_2-CF*(CF_3)-CH_2-CF_2-$[d,e]

[a] Relative to Teflon. [b] Asterisk indicates relevant moiety. [c] $(CF_2CF_2)_n$ impurity in Torlon 4203. [d] Reference 9. [e] Reference 17. [f] See text.

Table VI
^{19}F Chemical Shifts, Probable Structural Assignments, and Peak Areas for Sample Kel-F 3700

peak	chem shift,[a] ppm	% area	structural assignment[b]
1	33.5	14.9	$-CF_2-CH_2-CF_2*-CH_2-CF_2-$
2	32.3	18.3	$-CFCl-CH_2-CF_2*-CH_2-CF_2-$
3	14.4	30.1	$-CF_2-CH_2-CF_2*-CF_2-CFCl-$
4	6.4	1.4	$-CH_2-CF_2-CF_2*-CH_2-CH_2-$ + $-CH_2-CF_2-CF_2*-CFCl-CF_2-$
5	3.0	22.5	$-CH_2-CF_2-CF_2*-CFCl-CH_2-$
6	0.9	10.6	$-CF_2-CF_2-CF*Cl-CH_2-CF_2-$
7[c]	0.3		
8	-6.6	2.2	$-CH_2-CF*Cl-CF_2-$

[a] Relative to Teflon. [b] Reference 18. Asterisk indicates relevant moiety. [c] $(CF_2CF_2)_n$ impurity in Torlon 4203.

demonstrated increased shielding effect of 2.5 ppm of a next-nearest-neighbor $-CH_2-$ group (relative to a $-CF_2-$ group) on the resonance position of a $-CF_2-$ group.[17] This is the right order of magnitude of the chemical shift difference we observe for peak 8 of this polymer (FT 2481) relative to the chemical shift of carbon pentad, $-CF_2-CF(CF_3)-CF_2*-CF_2-CF(CF_3)-$, assigned to peak 10 of sample FC 2145. A computer simulation of the $-CF_3$ and $-CF_2-$ regions of the spectrum is shown in Figure 5c,d. Relative intensities are given in Table V. No correction for the intensity of the spinning sideband was made as this sideband is attributable to the $(CF_2CF_2)_n$ impurity in Torlon 4203. The number of CF_2CF_2 monomers, N_{TFE}, for this polymer is given by

$$N_{TFE} = \tfrac{1}{2}n_7 \tag{6}$$

and a calculation similar to that of sample FLS 2690 shows that sample FT 2481 has a composition of 63% CH_2CF_2, 20% CF_3CFCF_2 and 17% CF_2CF_2.

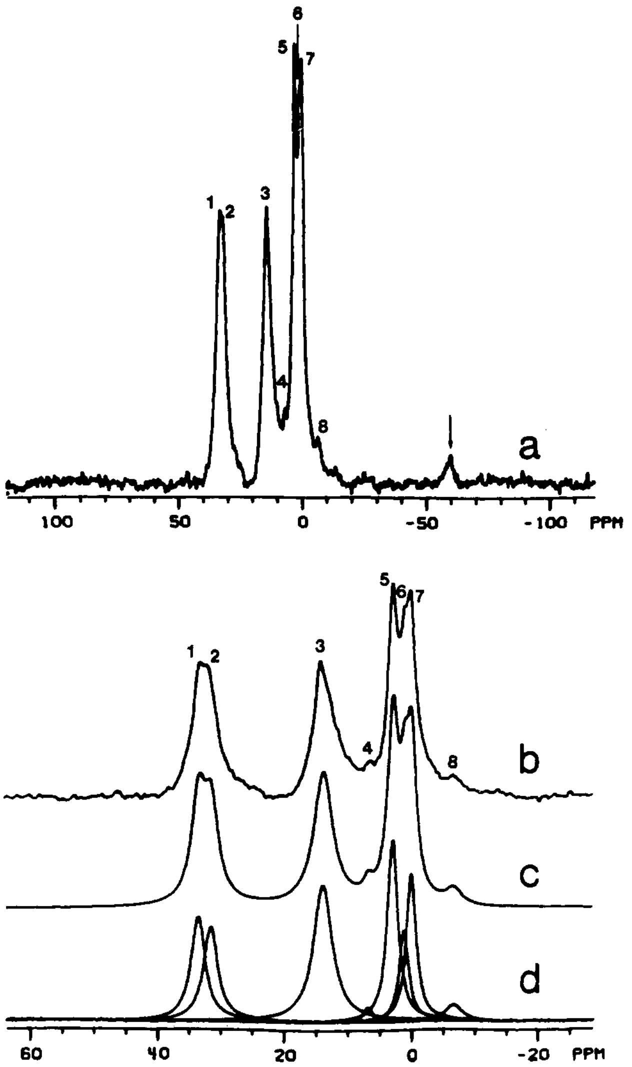

Figure 6. 338.7-MHz ^{19}F MAS spectra of sample Kel-F 3700: (a) 20.1-kHz MAS spectrum (an arrow indicates a spinning sideband); (b) CF_3 and CF_2 regions of (a); (c) computer simulation of (b); (d) deconvolution of peaks corresponding to (c).

Kel-F 3700. The 20.1-kHz ^{19}F MAS NMR spectrum of Kel-F 3700, a copolymer of 75% CH_2CF_2 and 25% CF_2CFCl,[27] is shown in Figure 6a. Chemical shifts and probable structural assignments for each peak are given in Table VI. The source for the structural assignments is the solution-state study of this copolymer of Murasheva and co-workers.[18] A computer simulation of the spectrum is shown in Figure 6c,d. Relative integrated intensities are given in Table VI. No correction for the intensity of the spinning sideband was made as this sideband is attributable to the $(CF_2CF_2)_n$ impurity in Torlon 4203. Knowledge of the intensities allows a check to be made on the peak assignments. The relative intensities of the resonance lines due to $-CF_2-$ groups bonded to $-CFCl-$ groups must be twice that for all resonance lines attributable to $-CFCl-$ groups. Thus, for this particular sample, we can calculate an upper and lower bound for the relative amounts of these two groups. Since $n_6 + n_8$ represents the total $-CFCl-$ content, and peaks 4 and 5 have at least some intensity contributed from $-CF_2-$ groups bonded to $-CFCl-$ groups, it follows that

$$2(n_6 + n_8) = an_4 + n_5 \tag{7}$$

where a is the unknown fraction of peak 4 corresponding to the carbon pentad $-CH_2-CF_2-CF_2*-CFCl-CF_2-$. Substitution of the areas listed in Table VI into eq 7 yields

$$\frac{n_4 + n_5}{2(n_6 + n_8)} = 0.93 \qquad (a = 1) \tag{8}$$

$$\frac{n_5}{2(n_6 + n_8)} = 0.88 \qquad (a = 0) \tag{9}$$

Neither eq 8 or eq 9 yields a value of one for the ratio of N_{-CF_2-} to $2N_{-CFCl-}$; i.e., the sum $an_4 + n_5$ is smaller than its theoretical value even for the most favorable case, $a = 1$. This is a measure of the experimental error associated with the integrated intensities for this polymer and indicates the need for even higher resolution than can be obtained with our present MAS spinning capabilities and static field strength. However, the result for $a = 1$ is closer to the theoretical value, which implies that most of the

Table VII
^{19}F Chemical Shifts, Probable Structural Assignments, and Peak Areas for Sample Kel-F 800

peak	chem shift,[a] ppm	% area[b]	structural assignment[c]
1	41.1	0.3	$-CH_2-CF_2{}^*-CH_2-$
2	14.1	63.2	$-CF_2-CH_2-CF_2{}^*-CF_2-CFCl-$ + $-CF_2-CFCl-CF_2{}^*-CFCl-CH_2-$
3	8.0	2.7	$-CF_2-CH_2-CF_2{}^*-CF_2-CH_2-$
4	3.3	6.2	$-CH_2-CF_2-CF_2{}^*-CFCl-CH_2-$
5[d]	0.0		
6	-4.6	4.0	$-CF_2-CF^*Cl-CH_2-$
7	-7.3	23.7	$-CF_2-CF^*Cl-CH_2-$

[a] Relative to Teflon. [b] Includes contributions from spinning sidebands. [c] Reference 18. Asterisk indicates relevant moiety. [d] $(CF_2CF_2)_n$ impurity in Torlon 4203.

contribution to the intensity of peak 4 comes from the carbon pentad, $-CH_2-CF_2-CF_2{}^*-CFCl-CF_2-$.

An additional check on the validity of the structural assignments can be made by calculation of the relative amounts of the monomer components from the ^{19}F NMR data and comparing with their known concentrations. The total number of CF_2CFCl (TFCE) monomers for this polymer, N_{TFCE}, is

$$N_{TFCE} = n_6 + n_8 \tag{10}$$

while the total number of CH_2CF_2 (VF) monomers, N_{VF}, is

$$N_{VF} = \tfrac{1}{2}(n_1 + n_2 + n_3 + n_4 + n_5) - N_{TFCE} \tag{11}$$

Substitution of the integrated intensities into eq 10 and 11 yields the conclusion that Kel-F 3700 is composed of CH_2CF_2 to the extent of 71%. This is in good agreement with its known value of 75%.[27]

Kel-F 800. Figure 7a shows the 19.9-kHz ^{19}F MAS NMR spectrum of sample Kel-F 800, a copolymer of 25% CH_2CF_2 and 75% CF_2CFCl.[27] Chemical shifts and probable structural assignments for each peak are given in Table VII. The peak areas contain corrections for the intensity due to the presence of spinning sidebands. Peak assignments are based on the solution-state work of Murasheva and co-workers.[18] A computer simulation of the spectrum is shown in Figure 7c,d. Relative integrated peak intensities for each peak are listed in Table VII. Peak 2 is assigned to ^{19}F resonances of two structures, $-CF_2-CH_2-CF_2{}^*-CF_2-CFCl-$ and $-CF_2-CFCl-CF_2{}^*-CFCl-CH_2-$. This is plausible for two reasons. One, this peak has a relatively large line width compared to that of peak 3 of Kel-F 3700. Additionally, if the intensity of peak 2 of Kel-F 800 were due solely to the marked (asterisk) ^{19}F of structure, $-CF_2-CH_2-CF_2{}^*-CF_2-CFCl-$, then the only $-CF_2-$ resonance for which the CF_2CFCl monomer was the source of $-CF_2-$ groups would be peak 4, which makes a very small contribution to the total intensity of the spectrum. This seems unlikely, because CF_2CFCl is present in the largest concentration and thus would be the most likely source of $-CF_2-$ intensity for the ^{19}F spectrum in this copolymer.

A calculation similar to that for Kel-F 3700 shows that Kel-F 800 has a composition of 23% CH_2CF_2. This is in good agreement with its known composition of 25%.[27]

It is also possible to determine the relative contributions made by the carbon pentads, $-CF_2-CH_2-CF_2{}^*-CF_2-CFCl-$ and $-CF_2-CFCl-CF_2{}^*-CFCl-CH_2-$, to the intensity of peak 2 for this polymer

$$\frac{N_{VF}}{N_{VF} + N_{TFCE}} = \frac{n_1 + An_2 + n_3}{n_1 + n_2 + n_3 + n_4} \tag{12}$$

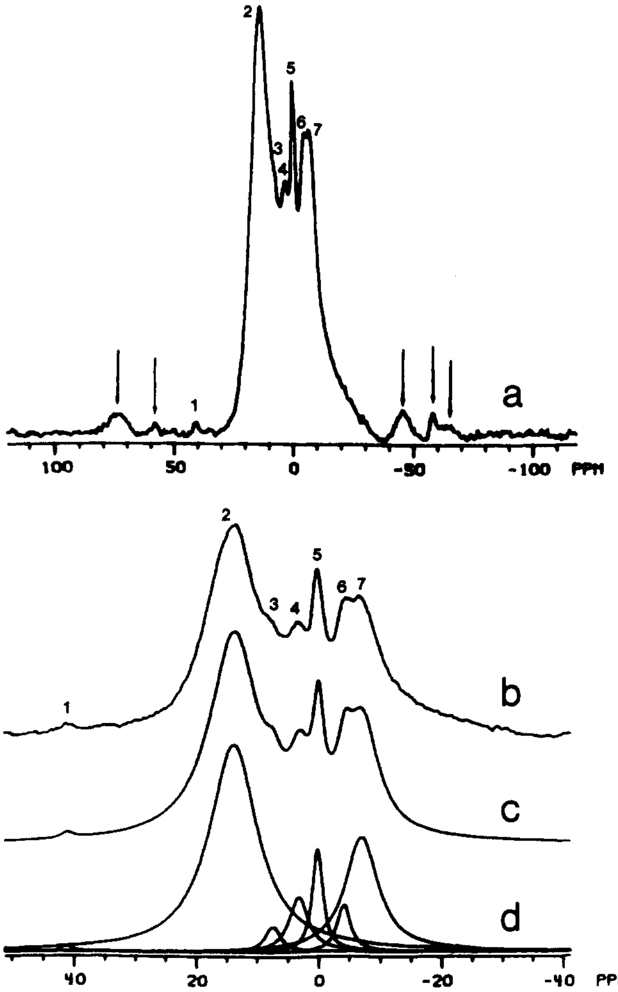

Figure 7. 338.7-MHz ^{19}F MAS spectra of sample Kel-F 800: (a) 19.9-kHz MAS spectrum (arrows indicate spinning sidebands); (b) CF_3 and CF_2 regions of (a); (c) computer simulation of (b); (d) deconvolution of peaks corresponding to (c).

where A is the fraction of integrated NMR intensity contributed to peak 2 by carbon pentad, $-CF_2-CH_2-CF_2{}^*-CF_2-CFCl-$. Substitution of the relative intensities given in Table VII into eq 12 yields the result that 23% of the intensity of peak 2 is due to this carbon pentad, supporting the hypothesis that a large contribution to the intensity of this peak is from $-CF_2-$ moieties bonded to $-CFCl-$ groups.

Conclusions

High-speed magic-angle spinning permits the direct observation of high-resolution ^{19}F NMR spectra of solid fluorocarbon polymers. The detail provided in these spectra allows the direct assignment of individual resonances associated with specific carbon pentad structures and provides a powerful approach for the structural characterization of such systems. In addition, the nature of the dominant anisotropic interactions present in these systems indicates that improved results should be obtained by using higher MAS spinning frequencies and larger magnetic fields.

Although the present study does not attempt to discriminate between crystalline and amorphous components in the materials studies, the level of resolution provided by high-speed MAS should make it possible to address this issue via strategies that discriminate through differences in relaxation behavior. Such studies have been initiated.

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Registry No. (HFP)(VF) (copolymer), 9011-17-0; (TFCE)(VF) (copolymer), 9010-75-7; (HFP)(TFE)(VF) (copolymer), 25190-89-0.

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Pulsed Dynamic NMR of Fibers from Thermotropic Liquid-Crystal Polymers

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ABSTRACT: Semiflexible liquid-crystal polyesters were melt spun into highly oriented fibers with tensile moduli up to $E = 22$ GPa and studied by pulsed dynamic NMR techniques. Analysis of the various ^{2}H NMR experiments provided detailed information about molecular order and dynamics of these systems. As-spun and annealed fibers are characterized by a high degree of orientational and conformational order of the polymer chains. In addition, practically all director axes are aligned in draw direction. High modulus and strength result from these highly oriented chain configurations. Molecular motion in annealed fibers is heterogeneous, as two components are detected. One component exhibits similar fast dynamics as observed in the anisotropic melt (liquid-crystalline phase), while the other shows a drastic motional decrease (crystalline phase). Decomposition of various NMR relaxation curves into two components yields a crystallinity of (55 ± 5)%, subject to the annealing conditions. However, the degree of order is independent of the thermal history, in agreement with only subtle changes of the mechanical properties upon annealing.

Introduction

Thermotropic liquid-crystal main-chain polymers (LCPs) have attracted considerable attention within the last years. This is due to their ease in melt processing and expected good mechanical properties which suggest potential application as high-modulus fibers and moldings.[1-3] From the chemical point of view three basic types of polymers can be distinguished: (i) rigid homopolymers, (ii) random copolymers, and (iii) semiflexible homopolymers.

Completely rigid homopolymers often exhibit lyotropic mesophases in the presence of a suitable solvent. The lack of thermotropic mesomorphism for these systems is attributed to the undesirable high melting temperatures being higher than the corresponding decomposition temperatures.[4] Thus, the reduction of the melting temperature is the main objective in getting thermotropic LCPs with stable mesophases. This can be achieved either by random rigid copolymers[5] or by semiflexible homopolymers having alternating rigid and flexible residues within the repeating unit.[6] In recent years both types of LCPs have been investigated in detail. In particular, pulsed dynamic NMR of deuteron (^{2}H) labeled polymers has successfully been employed for a comprehensive molecular characterization of these systems.[7]

Although melt spinning data and fiber studies for a number of thermotropic copolymers have been reported,[8-10] only limited information about fibers of semiflexible homopolymers is available.[11,12] In this paper we present pulsed ^{2}H NMR studies of melt spun fibers from nematic polyesters, containing a flexible spacer. Variation of pulse sequence and pulse separation provides the large number

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