Novel Low Refractive Index Self-Cross-Linking Fluoroterpolymers with Very Low Surface Tension and Good Adhesion to Substrates

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SYNOPSIS

A novel family of fluoroterpolymers was prepared, containing perfluoroalkylethyl methacrylate (PFAEM), methacrylic acid (MAA), and 2-hydroxyethyl methacrylate (2-HEM) residues. The refractive index of the fluoroterpolymers is in the range of $1.3675 \leq n \leq 1.4275$. The surface tension of cured thin films falls in the interval from 15 mN/m to as low as 8 mN/m. Upon heating, these polymers undergo thermally initiated self-cross-linking and develop tenacious bonding to substrates. The associated chemical reactions and products were identified by IR spectroscopy and some thermogravimetric scans. The spectra indicate that the reaction products are ester and anhydride groups. In general, the formation of esters occurs more rapidly and requires lower temperatures ($\geq 110°C$) than does the formation of anhydrides. Prolonged heating, especially at higher temperatures ($\geq 150°C$), favors the formation of anhydrides. When the molar ratio of MAA to 2-HEM is substantially larger than 1.0, the formation of anhydride is favored; when the ratio is 1 : 1, the formation of ester is favored; and when the molar ratio is much smaller than 1.0, the rate of formation of both esters and anhydrides is greatly reduced. In the case of the fluoroterpolymers, the formed esters and anhydrides essentially originate exclusively from the MAA and 2-HEM and seem not to involve any attack on the PFAEM residues. Only after very long heating at the higher temperatures employed, some loss of C—F band intensity was noted. In a copolymer of PFAEM and MAA, a substantial and rapid attack by the acid on the ester group in the PFAEM residues takes place under relatively mild conditions. Such and more drastic conditions appear not to affect at all a homopolymer of PFAEM alone. This suggests that in the fluoroterpolymers the more polar MMA and 2-HEM tend to aggregate close together, so that, when heated, they preferentially react with each other, forming both esters and anhydrides. In the absence of 2-HEM, the MAA may react with itself or with PFAEM, producing only anhydride groups. Both esters and anhydrides may be intermolecular and/or intramolecular, resulting in a cross-linked system in which the cross-link concentration is directly related to the combined amount of ester and anhydride groups. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The patent literature is replete with examples of fluorocopolymers used for optical fiber coatings, optical cladding, and similar applications. Many of these copolymers consist of perfluoroalkylethyl–acrylate or methacrylate and another, cross-linkable comonomer. Most frequently, the cross-linking is a radiation-initiated free-radical addition polymerization, requiring the exclusion of air oxygen or, conversely, very thick polymer layers. Furthermore, during network formation by such a mechanism, a good chance exists for a significant fraction of monomeric and oligomeric species not to be incorporated into the growing network. This may lead to subsequent diffusion of these species, affecting the properties of the coatings and posing environmental hazards. To avoid all these problems, a novel family

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of fluoro*ter*polymers was recently developed in our laboratory.[1] As applied to the substrate, it contains no monomers. By virtue of the ability of the reactive groups in the terpolymer to react with each other upon heating, infinite polymer networks are created by thermally driven cross-linking of a system insensitive to the presence or absence of oxygen in the atmosphere. Among other properties, the fluoroterpolymer family possesses a combination of low refractive index, n, low surface energy, γ_s, and good adhesion to substrates. In this section, the above properties will be discussed in general and how their combination may be obtained by the correct design and creation of a polymeric material. In the following sections, the synthesis and characterization of the fluoroterpolymer family will be described, followed by the experimentally determined properties of the fluoroterpolymers. Then, infrared (IR) and thermal studies will be presented and discussed, elucidating the nature of the condensation reactions leading to highly cross-linked networks grafted to substrates provided these contained reactive sites.

(a) Low Refractive Index, n

The refractive index, n, of a substance is directly related to its molar refraction, R, and inversely dependent on its molar volume, V, by either of the following relationships[2]:

$$n = \left(\frac{1 + 2\frac{R_{LL}}{V}}{1 - \frac{R_{LL}}{V}} \right)^{1/2} \quad (1)$$

or

$$n = 1 + \frac{R_{GD}}{V} \quad (2)$$

where the subscripts LL stand for Lorentz and Lorenz and GD stands for Gladstone and Dale. The values of R_{LL} or R_{GD} are directly dependent on the constitutive groups in the material and the nature of the bonding between them and can be added up by the group contribution method from tables of contributions such as given in Ref. 2. The molar volumes, V, may either be measured directly or calculated from group contributions.[2] A glance at these tables reveals that the smallest group contributions to the molar refraction, R, are due to the presence of fluorine atoms and ether oxygens in the material, whereas the largest contributions are from heavy groups such as iodine atoms and aromatic and cy-

clohexyl rings. The relationships between molar volume and composition are not as straightforward, but one notes that aromaticity, double bonds, and the heavy halogens clearly contribute to increase the material density, ρ, of the material. This increase is inversely proportional to the molar volume:

$$V = \frac{M}{\rho} \quad (3)$$

where M is the molar weight. We further know that, on the average, the density of amorphous polymers is about 90% that of the same polymers in the crystalline phase.

The index of refraction, n, was empirically related to certain thermodynamic properties of organic materials[3]:

$$n = (\delta_d + 5.55)/9.55 \quad (4)$$

where δ_d is the component of the solubility parameter due to dispersion forces:

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_H^2. \quad (5)$$

Here, δ = solubility parameter, δ_p = solubility parameter due to dipole forces, and δ_H = solubility parameter due to hydrogen bonding or other donor-acceptor interactions. The parameter δ^2 is known as the cohesive energy density, e_{coh}, and is defined as

$$\delta^2 = e_{coh} = \frac{\Delta E_{vap}}{V} \quad (6)$$

where ΔE_{vap} is the energy of vaporization of the material. In the case of polymers, where degradation precedes vaporization, eq. (6) is replaced by

$$\delta^2 = e_{coh} = \frac{E_{coh}}{V} \quad (7)$$

where E_{coh} is a molar cohesive energy, usually estimated from comparative swelling or dissolution experiments in liquids with known values of δ^2. It is important to recognize, then, that the index of refraction of certain nonpolar and non-hydrogen-bonding polymers may be estimated from the dispersion contribution to their solubility parameter δ_d.

We therefore conclude that in order to prepare a relatively low refractive index polymer it should be designed to contain the following structural features:

The polymer should contain a as high as possible number of fluorine and ether oxygen atoms; at the same time, it should include no aromatic rings or cyclic structures, no high halogens or atoms with high atomic number, and no double bonds. Furthermore, the polymer should be as nonpolar as possible. The molar volume should be as large as possible, which calls for large and complex aliphatic structures, excluding any aromaticity or condensed ring structures. Finally, the polymeric material should be as random as possible, prohibiting any backbone tacticity or any other form of chain regularity that may lend itself to ordering and the development of crystallinity.

(b) Low Surface Tension, γ_s

A system possesses excess surface energy because the molecules in the surface are subjected to a different environment from those in the bulk.[4] For a liquid, the surface tension and surface energy are identical, but for solids, they are slightly different. In our case, the surface tension was estimated from the equilibrium contact angles, θ_L, of liquids on the polymer surfaces:

$$\gamma_L \cos \theta_L \approx \gamma_s - \gamma_{SL} \qquad (8)$$

where γ_L, γ_S, and γ_{SL} are, respectively, the surface tensions of the liquid, solid, and solid–liquid interface. The theory of surface tension components[5] assumes that γ_S is separable into two linear additive terms:

$$\gamma_s = \gamma_s^d + \gamma_s^p \qquad (9)$$

where γ_S^d is the surface tension due to dispersion forces and γ_S^p is the polar component due to dipole forces and hydrogen-bond effects. By measuring the contact angle θ_L of several liquids with the same polymer, the values of γ_S^d and γ_S^p may be obtained:

$$(1 + \cos \theta_L)\gamma_L$$
$$= 2[(\gamma_L^d \gamma_S^d)^{1/2} + (\gamma_L^p \gamma_S^p)^{1/2}] \qquad (10)$$

In the majority of our measurements, two families of liquids were used: polar and nonpolar. Then, the data were plotted against $1 - \cos \theta_L$, curves were fitted to the points using second-order polynomial curve fitting, and the values of γ_S obtained from the extrapolated point at $1 - \cos \theta_L = 0$.

As will be shown below, the measured surface tensions were far smaller than those calculated from the average composition and molar volumes of the fluoroterpolymers. In general, surface tensions calculated from group additivity,[2] from cohesive energy density,[2]

$$\gamma \approx 0.75 e_{\text{coh}}^{2/3} \qquad (11)$$

and from Parachor[6,7] values, P,

$$\gamma = (P/V)^4 \qquad (12)$$

were twice or more larger than the measured ones. On the other hand, values measured and calculated for polytribromostyrene were reasonably close. This indicates that in the latter polymer the surface and bulk composition are the same and that in the case of the fluoroterpolymers the surface composition differs from the bulk.

For release applications, where very low surface tension is highly desirable, it is advantageous to design a polymeric coating in which the groups with lowest surface tension preferentially migrate to the surface. At the same time, these groups should not migrate to the coating–substrate interface because this will tend to reduce the adhesion between coating and substrate.

(c) Adhesion to Substrates

Good adhesion depends on the work of adhesion, Wa, being large and a thorough and complete wetting of the substrate by the applied coating.[4] The work of adhesion is a thermodynamic property

$$Wa = \gamma_a + \gamma_s - \gamma_{as} \qquad (13)$$

where γ_a is the surface tension of the adherend layer; γ_s, the surface tension of the substrate; and γ_{as}, the interfacial surface tension. In a fashion similar to cohesive energy densities, the surface tensions may contain contributions due to interatomic dispersion forces, dipole–dipole interactions, hydrogen bonds, etc. Collecting the polar contributions together, and writing the interfacial interactions as a geometric mean term, we can represent γ_{as} as

$$\gamma_{as} = \gamma_a + \gamma_s - 2(\gamma_a^d \cdot \gamma_s^d)^{1/2} - 2(\gamma_a^p \cdot \gamma_s^p)^{1/2} \qquad (14)$$

where the superscripts stand for dispersion and polar contributions. The adhesion tension, T, of this system is

$$T = \gamma_s - \gamma_{as} \qquad (15)$$

or

$$T = 2(\gamma_a^d \cdot \gamma_s^d)^{1/2} + 2(\gamma_a^p \cdot \gamma_s^p)^{1/2} - \gamma_a \qquad (16)$$

If we denote the polarity of the substrate $P_s = (\gamma_s^p/\gamma_s)$ and the polarity of the adherend $P_a = (\gamma_a^p/\gamma_a)$, it can be shown that for the maximum value of T, $(\partial T/\partial P_a)_{\gamma_a\gamma_sP_s} = 0$, which leads to the result $p_a = p_s$. Thus, the optimum thermodynamic wettability condition is obtained when the *polarities* of the adherend and substrate are exactly the same.[4]

The above indicates that good adhesion depends not only on enhanced spreading due to a large difference between the higher surface tension of the substrate and the lower surface tension of the adherend, but also on the polarities of both being as close as possible. The practical absence of polarity is, of course, the reason why the low surface tension polytetrafluoroethane does not adhere to higher surface tension, more polar substrates.

The kinetics of wetting also plays a role in adhesion. Therefore, the adherend is dissolved in a low molecular weight low viscosity solvent and/or low-M additives are added to the high-M polymeric adherend to increase the rate of spreading and enhance wetting and tack.

A well-adhering coating should, therefore, contain chemical groups that will contribute to enhance the polarity of the coating and bring it to the range of the substrate. A system containing both dipole–dipole and hydrogen-bond contributions is preferred over a system containing only one such contribution because of its broader compatibility. During application, the system must be sufficiently fluid in order to encourage rapid spreading, uniform coating, and good wetting.

EXPERIMENTAL

(a) Materials

Guided by the desirable large number fraction of fluorine atoms and constrained by commercial availability, we initially elected to use perfluoroalkylethyl methacrylate (PFAEM) and perfluoroalkylethyl acrylate monomers as the major components in the polymers to be prepared. The PFAEM is sold by DuPont as a mixture of monomers having up to 20 fluorinated carbon atoms,[8] under the trade name Zonyl-TM®. The perfluoroalkylethyl acrylate is also a mixture of monomers with up to 16 fluorinated carbon atoms[9] sold by Hoechst-Celanese under the trade name NUVA-FH®. Polymers prepared from NUVA-FH acrylates were of lower molecular weights than those from the polymethacrylates and of lower solubility, a stronger tendency to precipitate out of the polymerization mixture, and a stronger tendency to haze up. Therefore, we shall describe below only polymers prepared from Zonyl-TM. Those prepared from NUVA-FH will be discussed only in the context of their X-ray diffraction patterns.

The nonfluorinated monomers were obtained at the highest purity from chemical supply houses. They were purified from polymerization inhibitors by passing through the appropriate columns prior to use. Polymerization initiators were kept refrigerated and used as received. All polymerization solvents were obtained from supply houses in spectroscopic grade and used without further purification. Solvents for workup were of reagent grade.

(b) Polymer Synthesis

A typical laboratory-scale polymerization procedure follows: A three-neck round-bottom flask containing a large magnetic stirring "egg" is immersed in a thermostated oil bath on a stirring hot plate. A stream of dry nitrogen is introduced through one of the necks to keep the reaction mixture under nitrogen atmosphere throughout the reaction. Another neck is stoppered. Through this neck, the polymerization initiator is added by momentarily opening the stopper. The third neck is equipped with a pressure-equalizing dropping funnel. On top of this dropping funnel, a long vigeraux condenser is placed equipped on the top with a very narrow exit. Extra solvent is placed in the dropping funnel, which is dropped into the reaction vessel in order to compensate for loss of solvent that may arise from the combination of nitrogen flow and elevated reaction temperature. With the above arrangement, each drop of solvent (which can also be a solution of a very reactive monomer in the same solvent) is swept by the nitrogen flow in the opposite direction.

The desired proportion of the monomers is weighed into the three-neck round-bottom flask. A typical and convenient preparation, coded 6A, follows: Here 101.97 g PFAEM monomer mixture (DuPont's Zonyl-TM), 12.70 g methacrylic acid (MAA), 12.94 g 2-hydroxyethyl methacrylate (2-HEM) were weighed into the flask. Their percentage weights were 79.91% PFAEM, 9.95% MAA, and 10.14% 2-HEM. To this mixture, 250 mL tetrahydrofuran (THF) were added. The solution volume should be about half the volume of the flask. The mixture was stirred under nitrogen flow with very slow heating to ca. 40°C for about 1 h. Then, added to the clear solution was 0.38 g (0.3% by weight based on total monomer weight) of 2,2'-azobis(2-methylpropanenitrile) (AIBN) (DuPont's VAZO® 64), a convenient free-radical polymerization ini-

tiator.[10] The reaction mixture was slowly brought up to around 63°C and the reaction was allowed to proceed for several hours. Then, the mixture was poured into a crystallization dish and most of the THF evaporated. The residual material was washed and comminuted in methanol, the unreacted monomeric species washed away, and the powdery white polymer dried under high vacuum at temperatures not exceeding 50°C. The intrinsic viscosity of the polymer was determined in a glass viscometer at 25°C in 1 : 1 v/v mixture of THF and 1,3-bis(trifluoromethyl)benzene. A value of $[\eta] = 0.23$ dL/g was obtained. Fluorine and proton NMR analyses indicated that the monomer composition in the terpolymer is rather close to the feed composition.

The above procedure may be repeated in the good solvent glacial acetic acid (AA) and in the marginal solvents methyl ethyl ketone (MEK) or methyl isobutyl ketone (MIBK). In all cases, the highest polymerization temperature is a few degrees below the boiling point of the solvent. The lowest polymerization temperature is determined by the dissolution temperature of the PFAEM mixture in the solvent (usually around 40–45°C). Within that range, the free-radical initiator AIBN was found to be very convenient. The volume of solvent can be reduced down to about 1.2 times the total monomer weight. Smaller amounts of solvent in the polymerization mixture resulted in a poorly controlled reaction and the development of cross-linked gels. Another, very convenient, method for the workup calls for the addition of a substantial amount of the solvent, e.g., THF or AA, to the reaction vessel after the reaction is completed. The mixture is then allowed to cool to room temperature before the stirring is stopped. The polymeric product precipitates down and the straw-colored clear supernatant solvent containing unreacted monomers, impurities, etc., is decanted off. A fresh batch of solvent is added and then the polymer is comminuted by passing it with water through the blender. The white powdered fluoroterpolymer is then washed with methanol several times and finally dried under dynamic vacuum.

The methacrylate fluoroterpolymers remain in hot THF or AA only when the combined weight fraction of the nonfluorinated monomers is 8% or higher. When terpolymers very rich in PFAEM are prepared in THF or AA, they start precipitating out with the progress of reaction. In such cases, a better solvent was found to be 1,1,2-trichlorotrifluoroethane at reflux temperature.

For the purpose of identifying and assigning IR spectral bands, as well as determining the refractive index and critical surface energy of polymers very rich in PFAEM, a fluorohomopolymer (coded 6B) and a fluorocopolymer were also prepared and analyzed. The fluorohomopolymer consists of a polymerized mixture of the PFAEM monomers. The fluorocopolymer (coded 14B) contains the PFAEM mixture and the MAA, and no hydroxy-containing monomers.

(c) Characterization and Infrared (IR) Studies

The only solvents for the fluoroterpolymers were found to be mixtures of THF and 1,3-bis(trifluoromethyl)benzene (hexafluoroxylene, HFX). A 1 : 1 v/v THF/HFX mixture was most commonly used, but for the fluoropolymers rich in the PFAEM monomer, solvent systems richer in HFX were necessary. To check on the cross-linking efficiency, a series of coating samples from each polymer was used, starting with the air-dried one and proceeding with samples heated (cured) at increasing temperatures and prolonged durations. All heatings were conducted in ambient atmosphere. In all cases, the air-dried coatings dissolved completely. The coatings exposed to increasingly harsh curing conditions showed ever-decreasing levels of dissolution, swelling, breaking apart, and peeling off the substrates. Well-cured coatings showed none of the above, indicating a very high cross-link density.

IR spectra of the virgin and heat-cured fluoropolymers were obtained using a Perkin-Elmer 983 ratio-recording double-beam dispersive IR spectrophotometer. The polymeric samples were cast on KBr windows from solution and air-dried. The thickness of the polymeric films was verified by using a pretreatment scan. Then, the films on the KBr windows were exposed to the desired temperature under flowing air, first to drive off all the solvent and then to cross-link the fluoropolymers. The IR data were good enough to indicate trends but too scattered to derive kinetic constants from. Thermal scans were obtained using a DuPont 9900 DSC instrument with the samples under nitrogen flow and a DuPont 9900 TGA instrument with the samples under argon. In both instruments, the heating rate was 10°C/min.

Solution properties were measured in a 1 : 1 v/v mixture of THF and HFX. Dilute solution viscosity was measured in this mixture at 25°C using internal dilution Cannon-Ubbelohde glass viscometers with solvent efflux time longer than 100 s. Light scattering was performed in a Chromatix KMX-6 low-angle laser light-scattering photometer at room temper-

ature. The refractive index increments were measured in a KMX-16 differential refractometer. The GPC was performed in a Waters 501 GPC system with a set of 500, 10^3, and 10^5 Ultrastyragel® columns. The flow rate was 1 mL/min and the detector was a Waters 401 differential refractometer.

The composition and purity of the polymeric products were evaluated from NMR scans of ^{19}F, ^{13}C, and ^1H nuclei of the fluoropolymers in deuteriated solvents such as DMSO and $CHCl_3$ and undeuterated 1 : 1 THF/HFX. The scans were obtained in a Varian XL-400 NMR spectrometer.

The surface tension, γ_s, of the fluoropolymers was measured from their contact angles with the 16 liquids listed in Table I. To evaluate the effects of hydrogen bonding on surface tension, two subsets of the liquids were used: one hydrogen-bonding and the other, nonbonding. They are so identified in the table.

The index of refraction, n, of the fluoropolymers was measured with a Metricon instrument on thin layers deposited on substrates with known refractive index and cured for various times at 150 ± 30°C. Wide-angle X-ray diffraction (WAXD) patterns were obtained from powdered fluoropolymers tightly packed in aluminum sample holders. The patterns were obtained in a Philip APD3600 automatic diffractometer operating in parafocus mode with monochromatized $CuK\alpha$ radiation. After back-

ground subtraction, peak width at half-height was measured on the only "sharp" reflection the WAXD patterns contained.
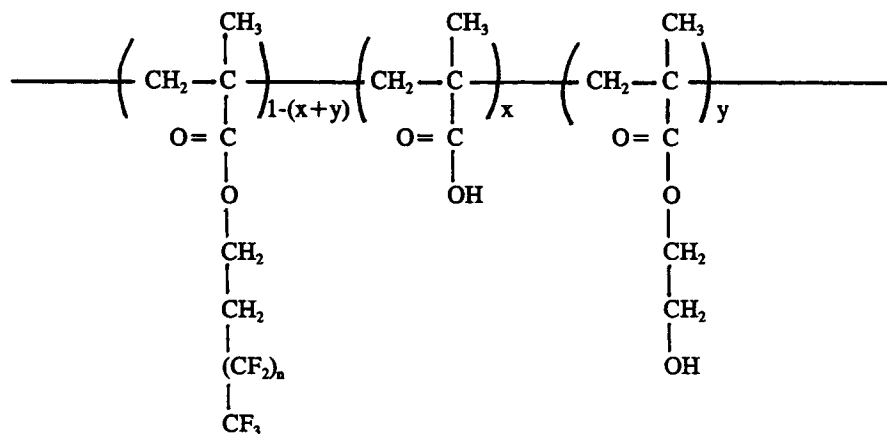
Qualitative estimates of the adhesion of the fluoropolymers to various substrates were gathered from various qualitative tests common in the coating (paint) industry. Among these tests, we enumerate parallel scratch tests (ca. 2 mm between scratches), cross-hatch scratch (1.5–2 mm between scratches) combined with masking tape and Scotch tape (3M No. 610) lift tests,[11] repeated rubbing with a standard eraser, pencil hardness tests (indentations by pencils of increasing hardness), and, in the case of flexible substrates, a 180° folding or crease test. In all instances, the coatings were observed under an optical microscope at 100× magnification. The tests were conducted on coatings up to 3 μm in thickness with increasing levels of cross-linking. In addition to adhesion estimates, these tests give us a qualitative appreciation of the robustness of the coating materials.

RESULTS AND DISCUSSION

The general structure of the fluoropolymers prepared in this study is described in Scheme 1:

Table I   Liquids Used for Contact-Angle Measurements of Fluoropolymers

No.	Liquid	Surface Tension (mN/m = dyne/cm)	H-bonding
1	Water	72.6	Yes
2	Glycerin	63.4	Yes
3	Formamide	58.2	Yes
4	1,2,6-Trihydroxylhexane	51.8	Yes
5	Diiodomethane	50.8	No
6	Ethylene glycol	47.7	Yes
7	1-Bromonaphthalene	44.6	No
8	1-Methylnaphthalene	40.6	No
9	Diethyl phthalate	36.6	No
10	Dioctyl phthalate	30.0	No
11	Hexadecane	27.6	No
12	1-Butanol	24.6	Yes
13	Decane	23.9	No
14	Ethanol	22.8	Yes
15	2-Propanol	21.7	Yes
16	Hexane	18.4	No

$$
\mathrm{-\!\!-\!\!-}\!\!\left(\!CH_2\!-\!\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle O=\!C}{|}}{C}}\!\right)_{\!\!1-(x+y)}\!\!\!\left(\!CH_2\!-\!\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle O=\!C}{|}}{C}}\!\right)_{\!\!x}\!\!\left(\!CH_2\!-\!\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle O=\!C}{|}}{C}}\!\right)_{\!\!y}\!\!\mathrm{-\!\!-\!\!-}
$$

Left branch: $O=C$, O, CH_2, CH_2, $(CF_2)_n$, CF_3

Middle branch: $O=C$, OH

Right branch: $O=C$, O, CH_2, CH_2, OH

Scheme 1

More than 50 different fluoropolymers were prepared with compositions ranging from $x + y = 0$ up to $x + y = 48$ wt %, but most were in the interval of $15 \le x + y < 35$ wt % where the balance of properties was closest to our expectations. NMR spectroscopy showed that in most instances the ratio of the PFAEM to the nonfluorinated monomers in the purified polymers were rather close to their ratios in the feed mixture. A comparison between the feed composition and NMR-determined composition of two typical terpolymers is shown in Table II.

In all but one of the NMR analyses of the fluoroterpolymers, there was a slight overestimate of PFAEM at the expense of the nonfluorinated monomers. The reason for this is not understood at present.

The copolymerization of fluoromonomers with strongly hydrogen-bonding (H-bonding) monomers demands a solvent system with the following combination of properties: (a) At the polymerization temperature, all the monomers must be highly soluble in it, (b) the polymeric product must remain in solution throughout the polymerization, (c) the solvent must not interfere with the polymerization to an extent that may prevent the formation of high-M polymers, and (d) the solvent must possess the appropriate miscibility with other solvents, volatility, and boiling point, etc., to facilitate a reasonable workup for the polymers under conditions that will not cause them to cross-link or degrade.

After an extended search, we have found for methacrylate monomers only two good solvents endowed with all the above properties and two marginal ones: The good solvents are tetrahydrofuran (THF) and glacial acetic acid (AA), and the marginal solvents are methyl ethyl ketone (MEK) and methyl isobutyl ketone (MIBK). For acrylate monomers, only THF was deemed to be useful. To maintain monomer and polymer solubility, the polymerizations had to be conducted at elevated temperatures in all cases. These were always higher than 45°C and lower than ca. 90°C and limited by the boiling temperature of the polymerization solvent. It was found that, as a rule, higher monomer concentrations produced polymers with higher solution viscosities (higher-M) than polymerizations with lower monomer concentrations (say, volume/weight solvent to monomers of ≥ 2). Interestingly, the intrinsic viscosities of polymers prepared in AA were not significantly higher than those of the analogs prepared in THF.

Table II   Relationship between Feed and Polymer Composition

Polymer Code	Feed Composition in Mol %			NMR Composition in Mol %		
	PFAEM	MAA	2-HEM	PFAEM	MAA	2-HEM
6A	43.25	34.15	22.60	45	30	25
40A	43.50	28.25	28.25	51	24	25

The viscosities of the fluoroterpolymers were generally low, with the intrinsic viscosity $[\eta]$ in the range of 0.15–0.35 dL/g. At first, these low values appear to be inconsistent with the mechanical properties of films of the fluoroterpolymers, which imply modest or high molecular weight and not a very low one. The inconsistency is resolved when we recall that the average molecular weight of each PFAEM monomer is 543, corresponding to $n = 7.2$ in Scheme 1 and resulting in rather short and stubby chains with very high molecular weight. For example, chains of the fluoromethacrylate homopolymer (6B) are less than 20% the length of chains of polystyrene or poly(methyl methacrylate) (PMMA) of the same molecular weight! The relative shortness and large "thickness" of the fluoroterpolymer chains result in low intrinsic viscosities for high-M polymers.

The refractive index of the mixed THF/HFX solvent is very close to that of the fluoroterpolymers. In fact, it is identical with that of the terpolymer 6D. Because of the closeness of the refractive indices of solvent and solute, light-scattering and GPC studies were found to be extremely hard, if not impossible. Osmotic pressure determinations of M_n are also impossible because of the solvent being a mixture. Because of the above problems, only two fluoroterpolymers were successfully analyzed. Because of the problems with light scattering, a GPC instrument equipped with highly sensitive detector was used. The molecular weights were determined by direct analogy with monodisperse PMMA hydrodynamic volume and by a universal curve based on considerations of intrinsic viscosity and elution time. In the case of the terpolymer 6A, light scattering indicates a M_w of 910,000, but we believe that some aggregation might be possible. All the molecular weights are listed in Table III.

From Table III it is obvious that if we accept even the smallest M_w values they correspond to polymers with decent chain lengths and degrees of polymerization of the order of several hundreds. Because of the intrinsic viscosity values and mechanical performance similarity to most other fluoroterpolymers in this study, we conclude that their molecular weights are also in the same range, namely, M_w of a few hundred thousands.

Qualitative tests indicated that the fluoroterpolymers undergo self-cross-linking and bonding to appropriate substrates when heated in the temperature range of ca. 130–200°C from 30 min up to 4 h. When deposited on glass and silicon substrates, for example, it was found that curing the fluoroterpolymers at 150°C for only 30 min resulted in the coating falling apart when placed in boiling DMF. Coatings cured for 1 h lifted off the substrate in small patches. Coatings cured for 2 h partially lifted off the substrate in large patches, and coatings cured for 4 h neither lifted off the substrate nor swelled nor broke apart.

DSC scans on several fluoroterpolymers showed a broad and smooth exotherm, starting at ca. 125°C and terminating at about 225°C, indicating a chemical reaction taking place over this temperature interval. TGA scans indicate that the major weight loss of the fluoroterpolymers (see Figs. 1 and 2) start at temperatures not lower than ca. 280°C.

Several TGA scans, in Figures 1–4, indicate that typical fluoroterpolymers such as 6A in Figure 1 and 40A in Figure 2 lose only about 3% of their weight in the 125–215°C temperature interval. The fluorohomopolymer 6B in Figure 3 also loses about 3% of its weight and the fluorocopolymer 14B in Figure 4 lost about 15% of its weight upon heating to 225°C. The copolymer contains only the PFAEM and MAA residues. IR spectroscopy results, to be discussed below, showed that, upon heating, the copolymer 14B loses a substantial fraction of its IR bands' intensity associated with C—F bonds. The combination of TGA and IR instructs us that, upon heating the copolymer, the free acid groups form anhydrides by reacting with one another or by attacking the ester moieties in the fluorinated residues, forming an anhydride group and splitting off a fluorinated alcohol that evaporates off during the curing process.
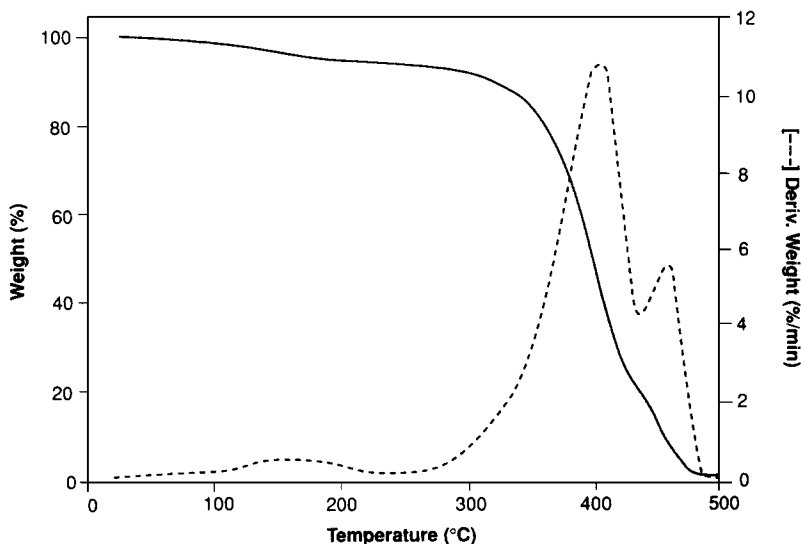
Table III Characterization of Fluoroterpolymers[a]

Code	Wt % PFAEM	$[\eta]$ (dL/g)	M_w (L.S.[b])	$M_{w,\text{PMMA}}^{\text{GPC}}$	$M_{w,\text{universal}}^{\text{GPC}}$	$(M_w/M_n)_{\text{PMMA}}^{\text{GPC}}$
6A	80	0.23	910,000	300,000	640,000	1.9
6D	90	0.20	—	—	—	—
6E	65	0.18	—	200,000	440,000	1.7

[a] 6D is isorefractive with the solvent.
[b] L.S. = light scattering.

Figure 1 Percent weight loss and rate of weight loss of the fluoroterpolymer 6A, as measured by TGA.

In the case of the fluoroterpolymers, this mode of attack does not happen, and the free acids react preferentially either with themselves or with the 2-HEM residues, forming anhydrides and ester groups. The weight loss of the terpolymers upon curing appears to involve, hence, mostly water losses during the condensation reactions. The similarity with the fluorohomopolymers is not understood at present, but may imply that most of the weight loss of the homopolymer up to ca. 225°C is involved with de-

hydration processes that do not split off perfluoroalkylethyl alcohols.

The index of refraction of the solid fluoropolymers was found to be extremely insensitive to cure conditions below 200°C. At 150°C, cure times as short as 10 min and as long as 12 h produced the same n values. In Figure 5 are shown the results measured on many of the fluoroterpolymers and the fluorohomopolymer. The values of n show inverse linear dependence on the weight fraction of the flu-
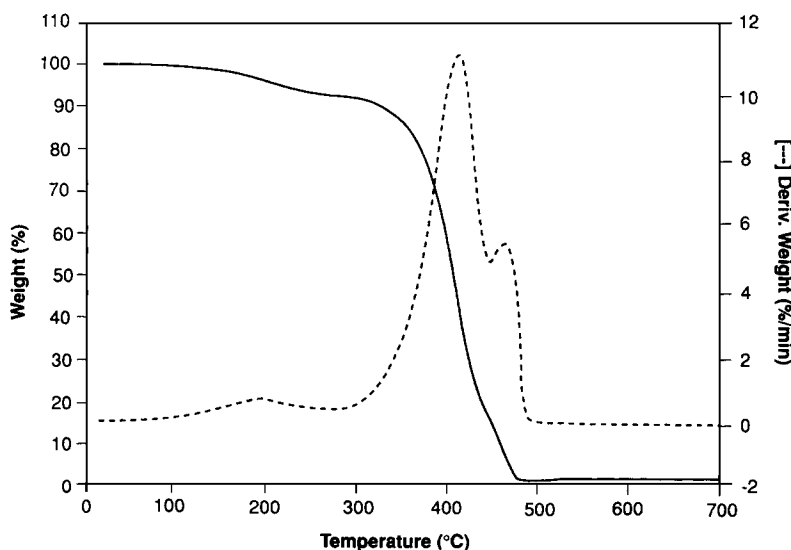
Figure 2 TGA scan of the fluoroterpolymer 40A containing equimolar amounts of MAA and 2-HEM.
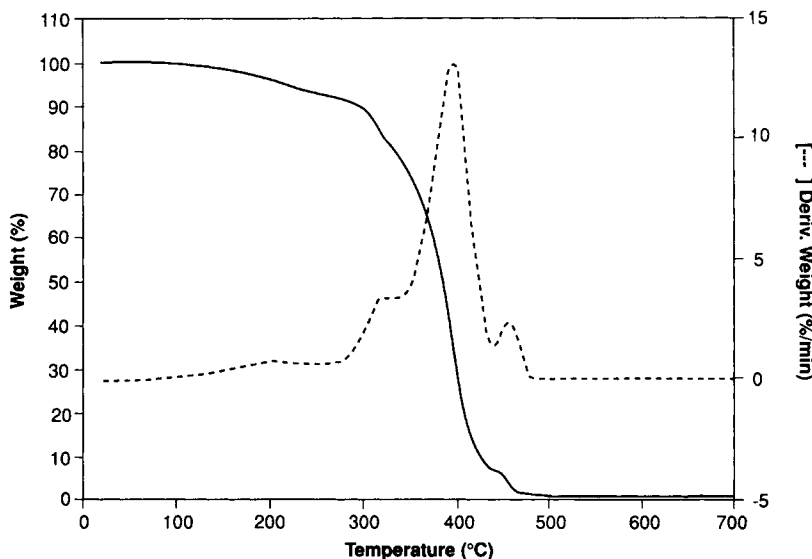
Figure 3 TGA scan of poly(PFAEM) the fluorohomopolymer 6B.

orinated monomer, with the PFAEM homopolymer possessing the lowest refractive index $n \simeq 1.3675$. It is of interest to note that the replacement of 2-HEM (solid circles) with propylene glycol monomethacrylate (solid squares) appears to reduce the values of n, probably due to the presence of ether oxygens and the relatively large free volume associated with amorphous aliphatic polyethers.

Several trial calculations of n according to eq. (2) yielded results within ±3% of the experimental ones.

In these calculations, both volume and molar refraction linear additivity were assumed.

The results of critical surface tension measurements of the fluoroterpolymers and their homopolymer analogs are all collected in Figure 6. In the figure, a line is drawn from $\gamma_s \simeq 27$ to $\gamma_s \simeq 41$ mN/m, giving the values of γ_s as calculated from group additivity according to eq. (11) above. Values of γ_s calculated from Parachor values according to eq. (12) gave closely similar results. Each of the data
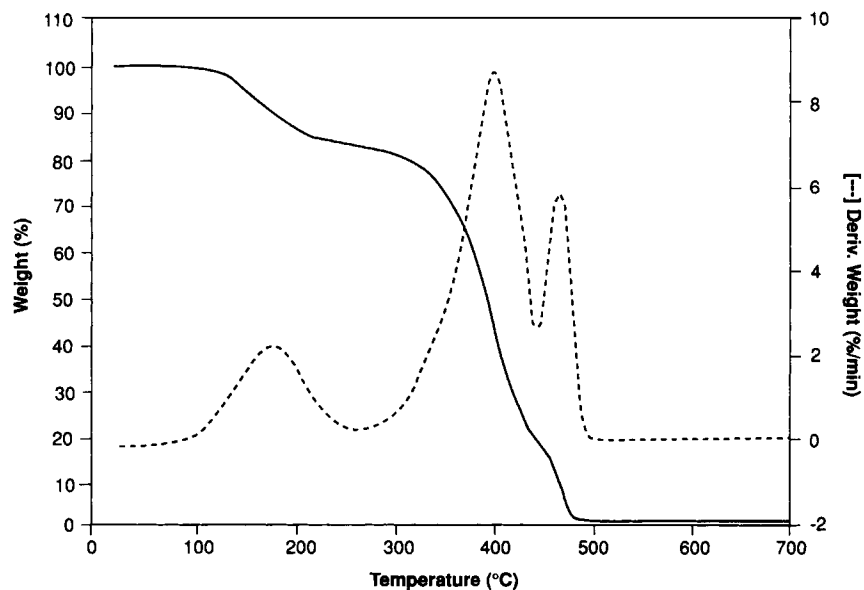
Figure 4 TGA scan of the fluorocopolymer 14B, containing PFAEM and MAA residues.
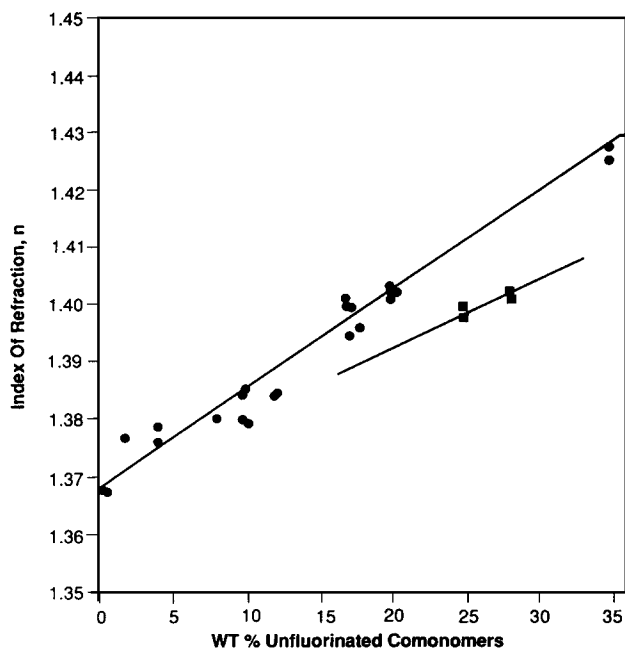
Figure 5 Index of refraction of fluoroterpolymers spun as thin films on glass or silicon substrates and cured at 150 ± 30°C from 10 min up to 4 h: (●) fluoroterpolymers of PFAEM, MAA, and 2-HEM; (■) fluoroterpolymers of PFAEM, MMA, and propylene glycol monomethacrylate. Index of refraction plotted against wt % unfluorinated monomers.

points in Figure 6 was obtained by using all the appropriate solvents in Table I. The most striking thing about the results is that, immaterial of whether measured by H-bonding or nonbonding solvent, they are about half or less the values calculated for the same compositions. In our case, no result was higher than 18 mN/m even when the terpolymer contained less than 50 mol % fluorinated residues. This is a clear indication that in our systems the fluorinated side chains in the homo- and terpolymers are preferentially secreted onto the polymer–air interface. In other words, the immediate surface composition is not identical with the average composition of the polymer and is richer in fluorinated residues than is the rest of the polymer.

It was stated by Wu[12] that the surface tension of a surface consisting of —CF₃ alone is 15 mN/m (= dyn/cm) and that of surface constituted of only —CF₂— is 23 mN/m. Mixtures of the above result in surface tensions in between the above values. On the other hand, in a DuPont brochure entitled *Zonyl® Fluorochemical Intermediates,*[8] the corresponding values are 3–5 and 18.5 mN/m. In light of our low γ_s values, we are inclined to accept the

latter. We conclude that, most likely, the perfluorinated side chains in our homo- and terpolymers are not well-ordered perpendicularly to the surface such that only —CF₃ groups may be detected, but randomly lie on the surface such that both —CF₃ and —CF₂ groups contribute to its tension. Ramharack and Nguyen[13] reached similar conclusions while evaluating several fluorinated homopolymers. They also confirmed the value of 18.5 mN/m for the surface tension of polytetrafluoroethane.

The good spreading on and adhesion of most of the fluoroterpolymers to substrates such as glass, polyamide films, and polyester films indicate that the composition of the fluoroterpolymers at the interface with the substrate contains a significant amount of polar groups such as carboxyls and hydroxyls. This composition may be similar to, or richer than, the composition of the bulk fluoroterpolymers, but is undoubtedly richer in polar groups than the polymer–air interface. From the bulk composition, one may calculate the solubility parameter of the fluoroterpolymers, δ, by group contributions[2]
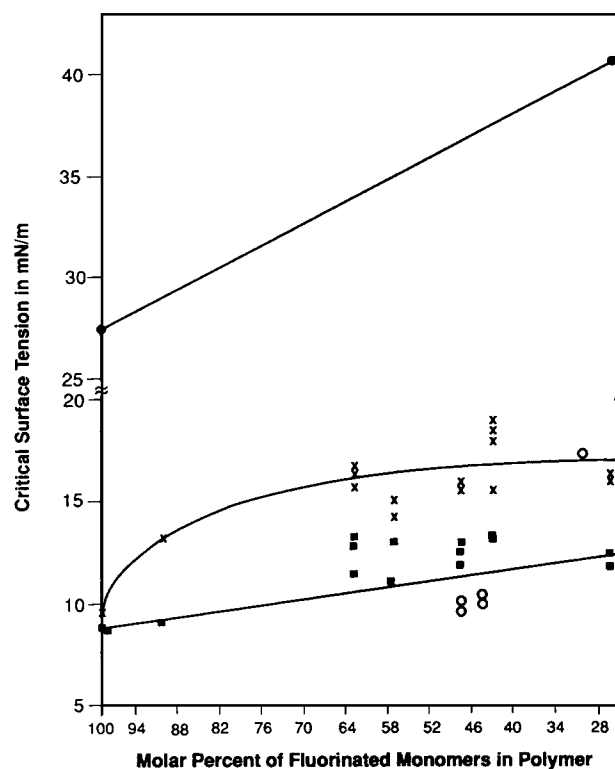
Figure 6 Critical surface tension of fluoroterpolymers. Top: Calculated from group additivity. Bottom: Experimental results from contact angle measurements. (X) H-bonding solvents; (■) nonpolar solvents; (●) too close to differentiate; (○) fluoroterpolymers containing propylene glycol monomethacrylate.
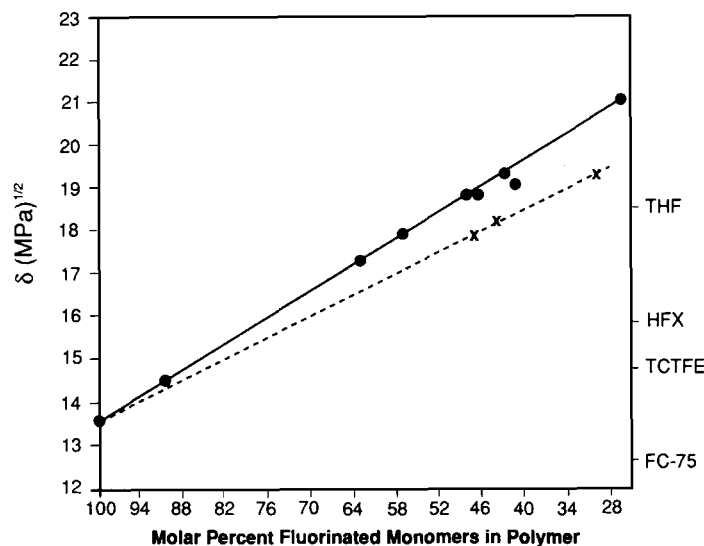
Figure 7   Solubility parameter of fluoropolymers calculated from group contributions, actual molecular weights and molar volumes, and molar contributions, plotted against mol % of fluorinated monomers in polymer. Values of solubility parameters of solvents used in this work are indicated on the right-hand-side ordinate.

assuming linear additivity of the molar volumes and molar additivity of molecular weights. The results are shown in Figure 7, and the calculated values appear to be most reasonable. Solubility parameters of some solvents used in this work are indicated on the right-hand-side ordinate of the figure. FC-75 is perfluoro(n-butyl-2-tetrahydrofuran) with $\delta = 12.7$ (MPa)$^{1/2}$.[14] It is interesting to note that δ of THF falls in the midrange of our fluoroterpolymers but that THF fails as a solvent for these very same polymers.

Importantly, one may calculate n from the calculated values of δ according to eq. (4), assuming that in this case $\delta = \delta_d$. Using the relationships (7) and (11), one may calculate γ_s from δ, but the resulting value is the one calculated from group additivity as shown in Figure 6 and not in agreement with experiment.

Typical WAXD patterns of our fluoropolymers are shown in Figure 8 for polymers containing PFAEM and in Figure 9 for polymers containing perfluoroalkylethyl acrylates. In Figure 8 are shown the patterns of the homopolymer 6B and the fluoroterpolymer 6A made from 80% PFAEM, 10% MAA, and 10% 2-HEM. In Figure 9, the patterns of the homopolymer 62B and a terpolymer 62J9 containing 83 wt % perfluoroalkylethyl acrylate are shown. In the four diffraction patterns, there is only one relatively sharp reflection at $2\theta \approx 17°$ and a broad halo at $2\theta \approx 40°$. The broad halo corresponds

to d-spacings of $d \simeq 2.24$ Å. From C—F distances of 1.32 Å and a tetrahedral angle of 108°, one calculates a F—F distance of 2.245 Å. We take it, therefore, that the broad halo with $d \simeq 2.24$ Å rep-
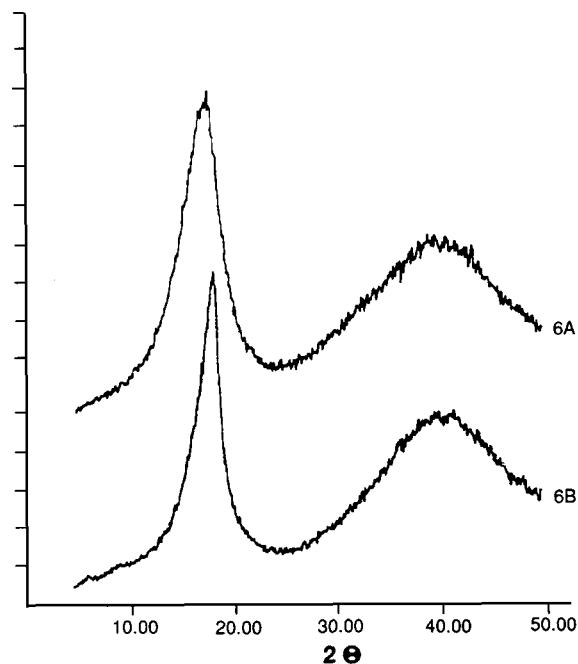
Figure 8   WAXD patterns of fluoropolymers containing PFAEM. Bottom: 6B, PFAEM homopolymer. Top: 6A, Fluoroterpolymer containing 80 wt % PFAEM.
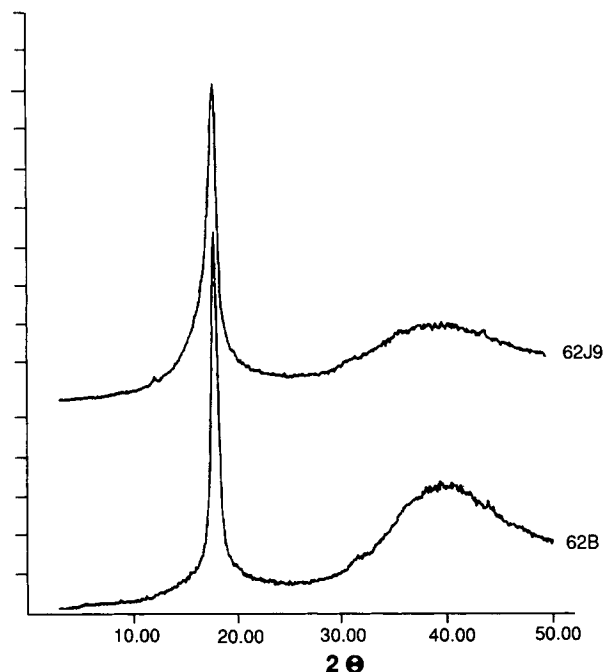
Figure 9 WAXD pattern of fluoropolymers containing perfluoroalkylethyl acrylate. Bottom: 62B, homopolymer of perfluoroalkylethyl acrylate. Top: 62J9, fluoropolymer containing 83 wt % perfluoroalkylethyl acrylate.

resents an average F—F distance in the —CF$_2$ and —CF$_3$ groups along the perfluoroalkyl side chains. Because we see no indication of a reflection in the range of $d = 2.54$ Å, which may arise from a planar zigzag arrangement of the perfluoroalkyl side chains, we believe that these groups are, most likely, somewhat twisted out of planarity and/or possess a significant level of freedom of rotation.

The behavior of the "sharp" reflection at $2\theta \approx 17°$ is interesting. Both its d-spacings and the line width at half-height ($h_{1/2}$ in units of 2θ) increase as more and more unfluorinated comonomers are built into the chain. For fluoroterpolymers containing PFAEM, the d-spacings increase from 4.99 to 5.30 Å and $h_{1/2}$ from 2.5 to 5.0 upon going from 100% to 50% by weight PFAEM. In the case of fluoropolymers containing the perfluoroalkylethyl acrylate monomer mixture, the d-spacings values were practically identical with polymers containing PFAEM, but the line widths were much narrower, increasing from $h_{1/2} = 0.65$ to $h_{1/2} = 1.2$ upon going from 100% fluoromonomer to ~ 80% fluoromonomer. Both phenomena indicate an increasing level of disorder in the systems as the weight fraction of fluoromonomer decreases. The fluoropolymers containing perfluoroalkylethyl acrylate are, however, somewhat more ordered than those containing

PFAEM. The increased disorder is commensurate with the NMR observations indicating that the comonomers in the fluoroterpolymers are present in the chain more or less at random, since no evidence of any backbone tacticity or regularity was ever observed in all our NMR spectra. In agreement with Budovskaya et al.,[15,16] we conclude from the WAXD results that the perfluorinated side chains show a strong tendency toward parallel alignment and cocrystallization. DSC and cross-polarized light microscopy failed to show liquid crystalline behavior in our fluoroterpolymers. The combination of ordered side chains and lack of liquid crystallinity is, however, well documented.[17]

The important facts that the WAXD patterns of our fluoropolymers contained only one "sharp" reflection, that the sharpness of this reflection did not increase with annealing, that the d-spacings did not change, that no additional reflections appeared, and that the polymeric films remained clear upon annealing even when cross-linking did not yet take place all indicate that our PFAEM fluorohomopolymer and, especially, the fluoroterpolymers containing PFAEM are amorphous and remain so upon annealing. Surface tension and refractive index measurements of the fluoroterpolymers gave essentially the same values before and after curing for 4 h at 150°C. All these indicate, and the DSC and TGA scans corroborate, that neither the top surface nor the bulk of the fluoroterpolymers undergo any significant compositional change. On the other hand, as the curing process progresses, the fluoroterpolymer coatings greatly increase their adhesion to substrates and gradually become more internally crosslinked. Uncured, they were relatively weak and adhered to the substrates poorly. However, once cured at temperatures in the interval 130–180°C for, say, 2 h or more, the coatings showed a remarkable improvement in their strength, durability, and adhesion to substrates. As a group, the cured fluoroterpolymers containing 90 to 65 wt % PFAEM withstood very well the qualitative tests aimed at estimating durability and adhesion. Parallel scratch tests, cross-hatch scratch combined with masking tape and with Scotch tape lift-tests, and repeated rubbing with a standard eraser, were administered to fluoroterpolymer coatings cured on substrates such as glass or silicon. Examination under the microscope, at magnifications up to 100×, clearly showed that all these treatments failed to lift the coatings off the substrates. Furthermore, no cracks in the coatings or chipping due to the testing were observed under the same magnification. Pencil hardness tests revealed grooves in the coatings when

Table IV   Compositions of Fluoropolymers Studied by IR Spectroscopy

No.	Polymer Code	Wt % Composition			Mol % Composition		
		PFAEM	MAA	2-HEM	PFAEM	MAA	2-HEM
1	6B	100	0	0	100	0	0
2	14B	82.2	17.8	0	42.22	57.78	0
3	6D	90.1	5.0	4.9	63.39	22.21	14.40
4	40	90	4	6	64.14	18.00	17.86
5	6A	79.9	10.0	10.1	43.14	34.09	22.77
6	40A	80.16	7.91	11.93	43.76	27.26	28.98
7	40B	80.66	5.80	13.54	46.40	21.07	32.53
8	6E	65.0	18.2	16.8	26.29	42.95	30.76

scratched by pencils number 3 and harder. From the nature of the grooves, we qualitatively define the coatings as horny, i.e., neither elastomeric nor brittle and glassy. When abraded with an eraser, the cured coatings gradually became marred and then wore out but did not peel off the substrate even after the eraser penetrated through their whole thickness.

Over 50 different fluoroterpolymer compositions were prepared. From these, several typical ones were selected for thermal scans and IR studies. These are listed in Table IV, together with the fluorohomopolymer 6B and fluorocopolymer 14B used for IR band assignments.

The IR spectra of the fluorohomopolymer 6B and the fluorocopolymer 14B are shown in Figures 10 and 11, respectively. The most intensive bands in both spectra appear in the close neighborhood of 1200 cm^{-1} and are clearly assigned to C—F symmetric and asymmetric stretching vibrations.[18,19] An intense and sharp band appears in both figures at 1730–1735 cm^{-1}, which is assigned to the C=O stretching vibrations of the ester groups[18,19] present in both 6B and 14B. A sharp band at 1700 cm^{-1} appears in Figure 11 and not in Figure 10. This band is, hence, clearly assignable to the free carboxylic acid carbonyl stretching mode[18,19] in 14B, which does not exist in the homopolymer 6B. Several less intense bands could be identified as belonging to C—H stretching in the backbone —CH$_3$ group (the doublet at ca. 2990 and 2920 cm^{-1})[18,19] and —CH$_2$— groups (band at ~2965 cm^{-1}),[18,19] and C—H bending at ca. 1480 and ca. 1450 cm^{-1}.[18,19] We have found that the intensity and position of the 2990 cm^{-1} band were totally unaffected by the thermal treatments accorded our polymers. The band at 1480 cm^{-1} seems not to change intensity upon heating, but tended to slowly shift position with the 1450 cm^{-1} band until, after prolonged ex-
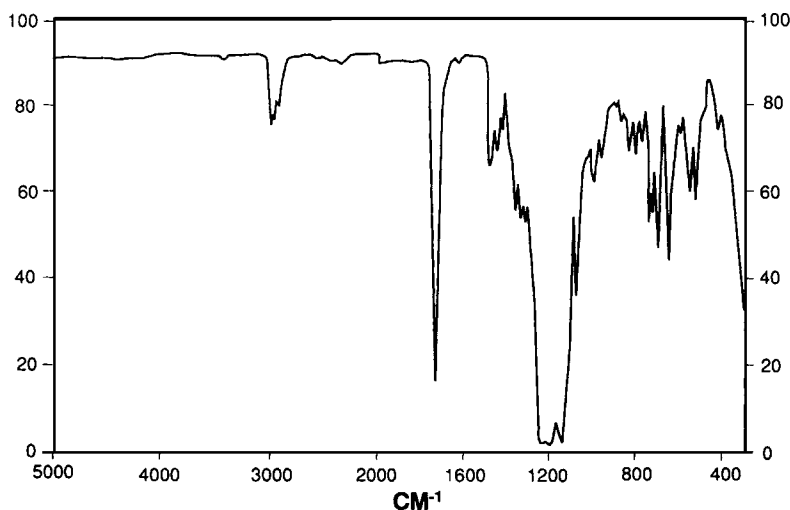
**Figure 10**   IR spectrum of the air-dried fluorohomopolymer 6B.
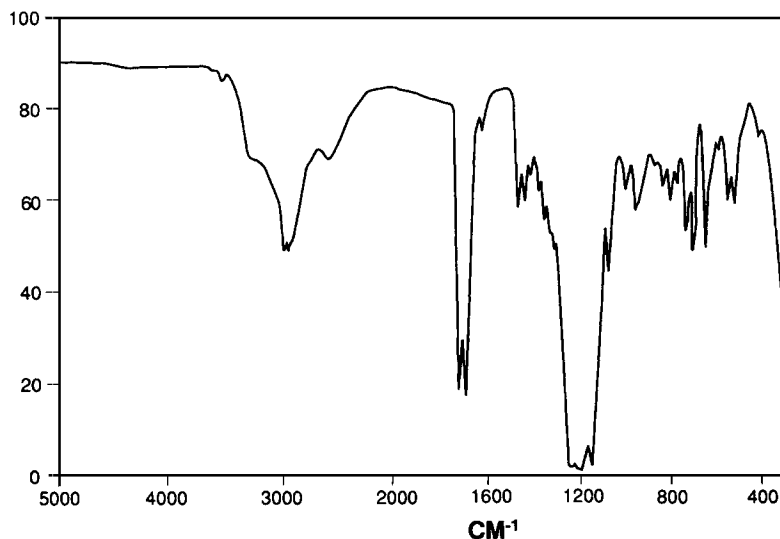
Figure 11 IR spectrum of the air-dried fluorocopolymer 14B.

posure to intense heat, they merged into a single band at 1460 cm^{-1}. In light of the above, we elected the band at 2990 cm^{-1} as an internal reference and used the intensity of variable bands relative to the 2990 cm^{-1} band as a measure of changing concentrations of the respective species. Relative intensities against the 1480 cm^{-1} band were also used occasionally, and it is important to emphasize here that, as long as the 1480 cm^{-1} band did not shift position significantly, the obtained results were within our experimental scatter similar to those obtained from band ratios (relative intensities) against the 2990 cm^{-1} band.

The fluorohomopolymer 6B remains unaffected upon heating and did not cross-link. Spectra ob-

tained after 4 h exposure to 120 and to 180°C were identical with the spectrum in Figure 10. The fluorocopolymer 14B, as all the fluoroterpolymers, undergoes cross-linking and exhibits substantial changes in its IR spectrum upon heating. In Figure 12, the IR spectrum of the fluorocopolymer 14B is shown after 4 h exposure to 120°C. In this case, three new bands appear, at 1800, 1760, and 1020 cm^{-1}. The doublet at 1800 and 1760 cm^{-1} is assigned[18,19] to C$=$O stretching vibrations in an anhydride group. The band at 1020 cm^{-1} is close to the range of anhydride C$-$O vibrations in the literature.[18,19] Because the 1020 cm^{-1} band always appears in our spectra together with the doublet at 1800 and 1760 cm^{-1}, we associate this band with the
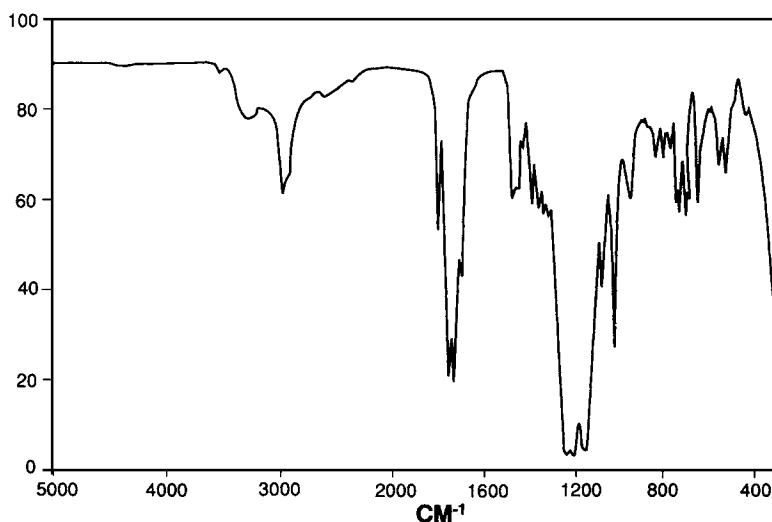
Figure 12 IR spectrum of the copolymer 14B after 4 h at 120°C.

presence of anhydride groups in our fluoropolymers. In fact, we have found that the 1020 cm^{-1} band is so intense and sensitive to the presence of anhydrides that we elected to use its relative intensity as a gauge for quantitative estimates of the amount of anhydrides present in the polymers. A comparison of Figures 11 and 12 shows that while the three anhydride bands intensify the carboxylic acid C═O band at 1700 cm^{-1} decreases in intensity. At the same time, the broad band centered at 3280 cm^{-1} also decreases in intensity. This band is associated with hydrogen-bonded ─OH groups belonging to carboxylic acids.[18,19] From IR spectra of fluoroterpolymers to be shown below, we determine that hydroxylic ─OH groups are associated with a broad band centered at about 3420 cm^{-1}. From the comparison of Figures 11 and 12, we conclude that the appearance of anhydride groups is associated with the disappearance of free carboxylic acid groups. Upon heating, the polymer 14B becomes less and less soluble and swellable in good solvents. This means that it undergoes cross-linking at ever-increasing levels. This, of course, indicates that at least some of the anhydride groups are intermolecular and serve as cross-linking joints in the evolving network. Importantly, all the IR spectra obtained from our systems fail to distinguish between intermolecular and intramolecular anhydride groups. After heating 4 h at 180°C, the picture is different. Here, the anhydride bands at 1800, 1760, and 1020 cm^{-1} are more intense. The acid band at 1700 cm^{-1} is now invisible and the ester band at 1735 cm^{-1} lost so much of its original intensity that now it is only a shoulder on the side of the 1760 cm^{-1} anhydride band. The reduced intensity of the C─F bands around 1200 cm^{-1} indicates that fluorine-containing moieties are being lost together with the loss of ester residues. The IR spectra tell us, hence, that when exposed to prolonged intense heat the copolymer 14B undergoes a reaction in which esters bearing C─F residues are replaced by anhydride groups. At the temperature of the reaction, the fluorinated alcohol byproducts are being, most likely, driven off by evaporation:
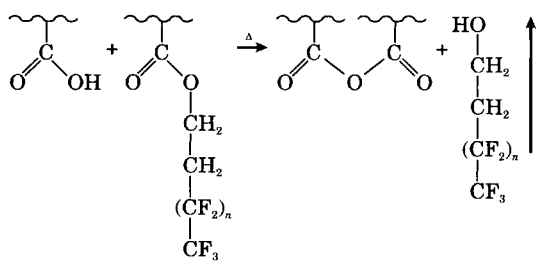
Reaction 1

In the case of fluoroterpolymers, where a sufficient amount of 2-HEM is present, the depletion of PFAEM in favor of anhydride residues required much longer exposure to high temperatures than in the case of the fluorocopolymer 14B. The fluoroterpolymer 6A is a good example. After 2 h at 180°C, no major differences from the air-dried polymer are observed, although a reduction in the 1700 cm^{-1} band intensity and the appearance of the anhydride bands are noticeable. After 4 h at 180°C, the anhydride bands are intense but the ester band at 1730 cm^{-1} is of comparable, if not higher, intensity. Both the hydroxy and carboxy H-bonded envelopes at 3280 and 3420 cm^{-1} are gone. A comparison of spectra of polymers 6A and 14B, obtained after 4 h curing at 180°C, clearly shows that in the copolymer 14B the ester band is greatly reduced in intensity, indicating that in this polymer the ester destruction proceeded much faster than in the fluoroterpolymer 6A. IR spectrum of 6A obtained after 21 h at 170°C indicates that in the presence of 2-HEM in the fluoroterpolymers the ester group destruction is arrested and proceeds very slowly and is discernible only after prolonged exposure at temperatures of 180°C and higher.

We shall now discuss the effects of cure temperature and duration on the thermally initiated reactions occurring during the cross-linking of the fluoroterpolymers. The behavior of the typical fluoroterpolymer 6A will be described in detail as an example of the other members of the fluoroterpolymer series. For conciseness and clarity, the relative intensities of the IR bands of relevance will be plotted against time or temperature. This will make the presentation of dozens of IR spectra unnecessary. For consistency between different samples, all the relative intensities were normalized against the 1730 cm^{-1}/2990 cm^{-1} ratio of the fluorohomopolymer 6B. By so doing, possible effects of time and temperature on the band intensity of unreacted ester groups are accounted for. It is important to emphasize here that concomitantly with the changes in IR spectra most of the fluoroterpolymers prepared in this work undergo self-cross-linking and bonding to appropriate substrates when heated in the temperature range of ca. 120–200°C from 30 min up to 4 h. When deposited on glass and silicon substrates, for example, it was found that curing the fluoroterpolymers at 150°C for only 30 min resulted in the coating falling apart when placed in boiling DMF. Coatings cured for 1 h lifted off the substrate in small patches. Coatings cured for 2 h partially lifted off the substrate in large patches and coatings cured for 4 h neither lifted off the substrate nor swelled or broke
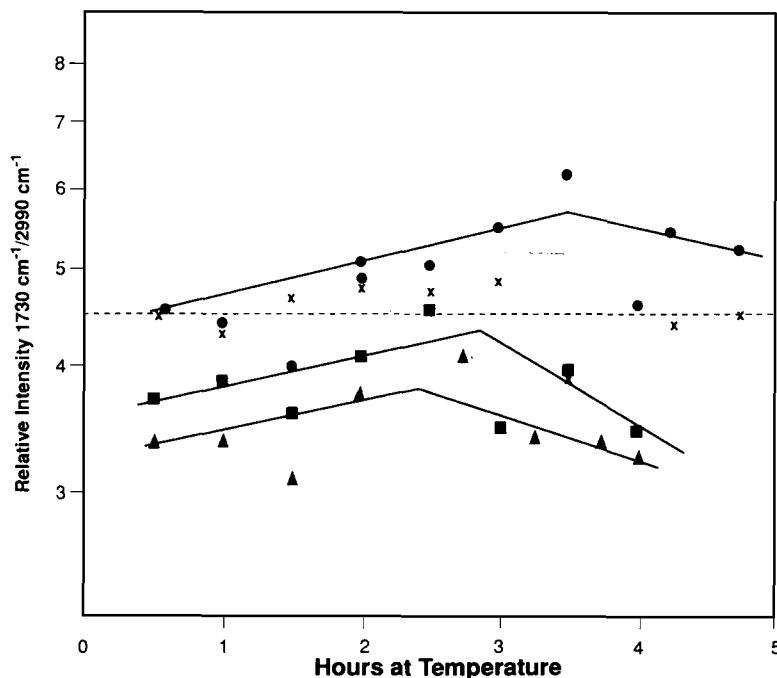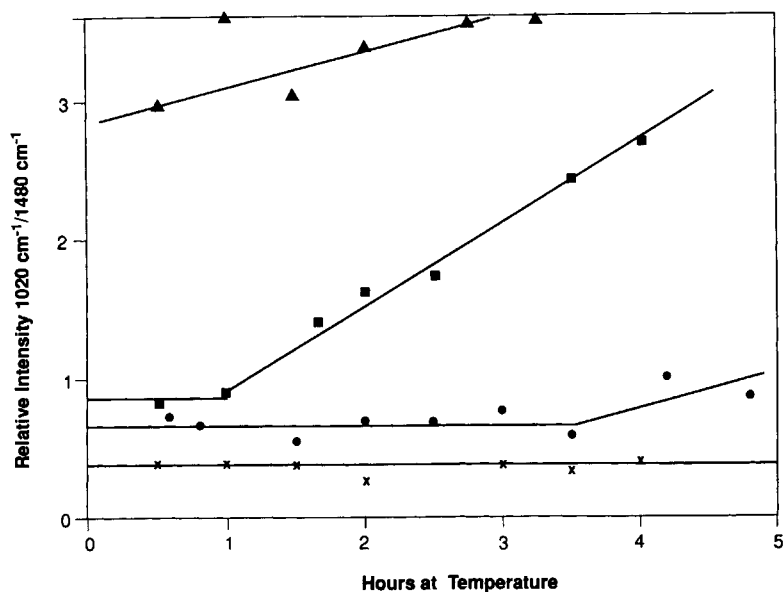
Figure 13 Effect of cure temperature and duration on ester carboxyl groups in the fluoroterpolymer 6A: (x) room temp; (●) 120°C; (■) 150°C; (▲) 180°C. Dashed line = room temperature average. Solid lines indicate trends and are merely guides for the eye.

apart. In general, the changes in the IR spectra upon heating the fluoroterpolymers involve a reduction in intensity of bands associated with the presence of free carboxylic acid and hydroxyl groups and an intensification in the intensity of bands associated with ester and anhydride groups. The effects of polymer composition variations will be discussed in a subsequent section.

In Figure 13, the relative intensity of the ester band at 1730 cm^{-1} is shown as a function of both heating temperature and time. The dashed horizontal line at 1730 cm^{-1}/2990 cm^{-1} equals 4.5 for samples dried at ambient temperature. The solid lines are for samples cured at 120, 150, and 180°C. The data scatter relegates the lines to be guides to the eye only, but in conjunction with Figures 14–16 below, the breaks in the lines and the conclusions appear to be valid and self-consistent. From Figure 13 we learn that within 30 min at 150 and 180°C a measurable reduction in the ester concentration is already noticeable. No such reduction takes place at 120°C. From the respective starting points, a gradual increase in the ester concentration takes place, at about the same rate for the three temperatures. The length of time the ester concentration increases is dependent on the cure temperature. The onset of decrease in ester concentration starts after

3.5 h at 120°C, 3 h at 150°C, and 2.5 h at 180°C. Concomitantly with the onset of ester depletion, substantial enhancements in the anhydride IR bands are noticeable. In Figure 14, the relative intensity of the 1020 cm^{-1} anhydride band is plotted as a function of temperature and time. Here, the room temperature data should be taken as base line. The 120°C intensities show a break at 3.5 h cure time. The 150°C intensities start increasing after only 1 h at temperature. The 180°C data greatly increased in intensity within the first 30 min of heating, before the sample was first tested. From that point on, an increase in anhydride concentration more moderate than the one at 150°C took place. The combination of Figures 13 and 14 indicates that at 120°C the major product of the thermally initiated reaction is the ester group and that only after ca. 3.5 hours at this temperature anhydride groups start forming at the expense of the ester groups. A low and constant concentration of anhydrides is present, however, throughout the time interval of 0.5–3.5 h, where the ester concentration substantially increases. At 150°C, the onset is much earlier and rate of anhydride formation more intense, but it appears to take a toll on the ester concentration after only about 3 h at temperature. Similar conclusions may be drawn for the 180°C results, but here the effects on ester
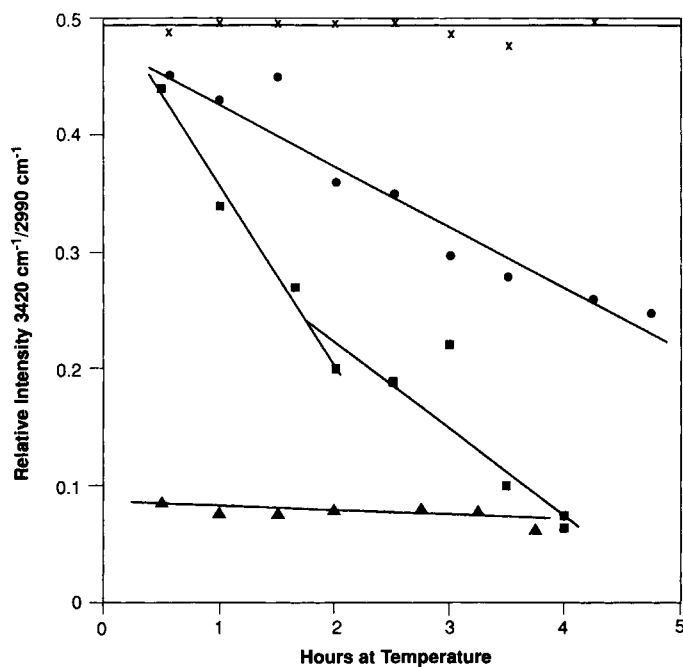
Figure 14 Effect of cure temperature and duration on anhydride concentration in the fluoroterpolymer 6A: (x) room temp; (●) 120°C; (■) 150°C; (▲) 180°C.

depletion become noticeable after only 2.5 h at temperature.

Figures 15 and 16 present the relative intensities of the hydroxyl —OH group at 3420 cm^{-1} and the carboxyl —OH group at 3280 cm^{-1}, respectively. These figures indicate that a drastic reduction in both kinds of —OH groups takes place within the first 30 min of heating at 180°C. From that point on, additional reductions in the —OH concentration are either negligible or nonexistent. When taken together, Figures 15 and 16 indicate that at 120 and 150°C the fluoroterpolymer 6A loses both hydroxylic


Figure 15 Effect of cure temperature and duration on hydroxyl-OH concentration in the fluoroterpolymer 6A: (x) room temp; (●) 120°C; (■) 150°C; (▲) 180°C.
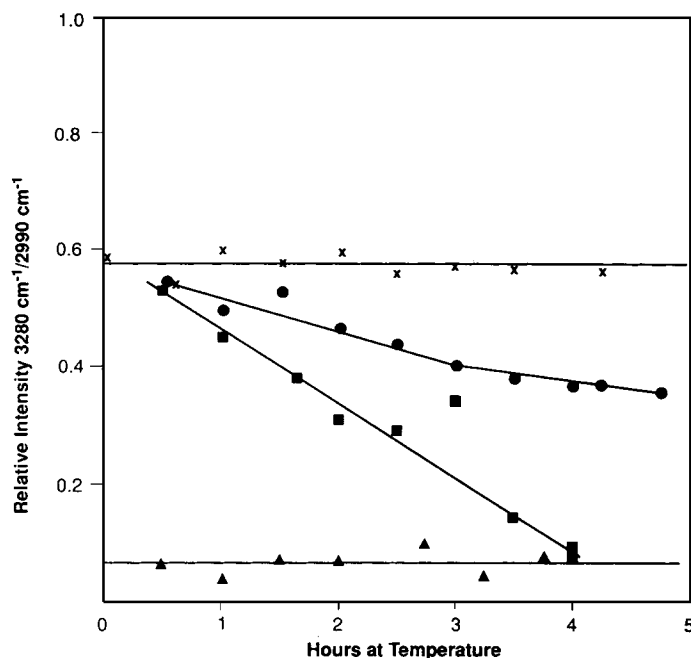
Figure 16 Effect of cure temperature and duration on carboxyl-OH concentration in the fluoroterpolymer 6A: (x) room temp; (●) 120°C; (■) 150°C; (▲) 180°C.

and carboxylic —OH groups. Over the total exposure time, the decrease in concentration of both species is about the same, but along the way, there are intervals where the hydroxylic —OH is depleted faster (initial 2 h at 150°C) and where the carboxylic —OH depletes at a reduced rate (final 2 h at 120°C).

Based on Figures 13–16, we conclude that the first observable reaction taking place upon heating the fluoroterpolymers is the formation of ester groups from the MAA and 2-HEM residues:
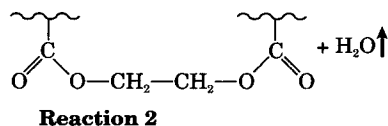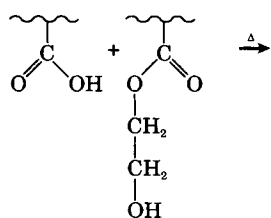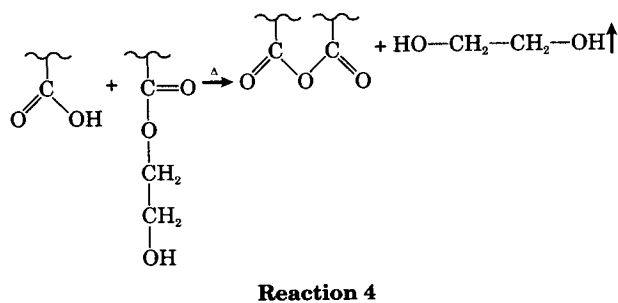

Reaction 2

A slower reaction, requiring more drastic conditions such as exposure to higher temperature (e.g., 180°C) or longer duration (e.g., over 3.5 h at 120°C) is the

formation of anhydride groups. In this case, two reactions may occur, probably simultaneously:
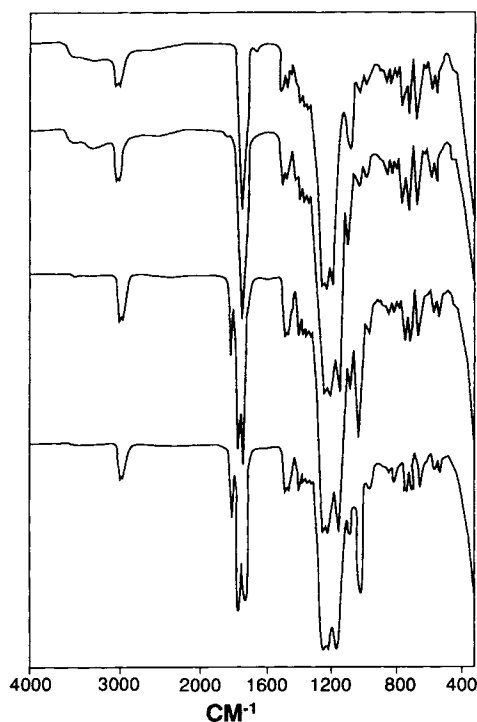

Reaction 3

and
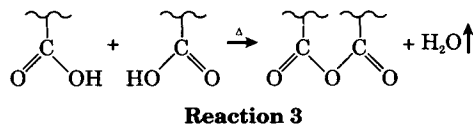
Reaction 4

Under the conditions of these reactions, no measurable reduction in the intensity of C—F bands was ever noted. This means that in the fluoroterpolymers the formation of anhydrides by the attack of acid on an ester group is limited to the attack of MAA on the ester group of 2-HEM and not on the ester group of the PFAEM.
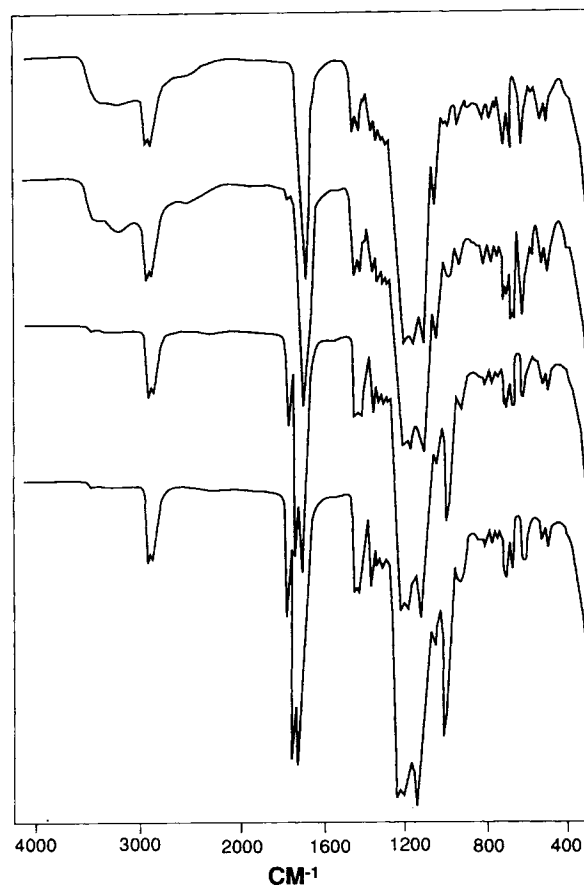
The IR results are consistent with the TGA scans in Figures 1–4: Very small weight losses are asso-

ciated with the cross-linking reactions in the fluoroterpolymers 6A and 40A, a minute weight loss occurs in the homopolymer 6B, and a large weight loss of about 15% in copolymer 14B. This large weight loss of 14B should be combined with the substantial drop in C — F band intensity observed upon curing at 180°C to indicate that, in the case of 14B, the formation of anhydride groups is accompanied by the loss of C — F-bearing groups, i.e., the perfluoroalkylethyl alcohol (as in Reaction 1). The very small weight loss in the fluoroterpolymers 6A and 40A, taken together with the fact that no reduction in the C — F band intensity is noticed for both polymers, indicates that in these fluoroterpolymers the formation of anhydrides is associated with a loss of water or ethylene glycol (Reactions 3 and 4) and not perfluoroalkylethyl alcohol. IR scans indicate that the results and conclusions for 6A and 40A are representative of most of the fluoroterpolymers investigated in this work.

Two experiments were performed to gauge the effects of composition on the thermally induced condensation reactions in the fluoroterpolymers. In the first experiment, three fluoroterpolymers were compared, in which the total amount of nonfluori-

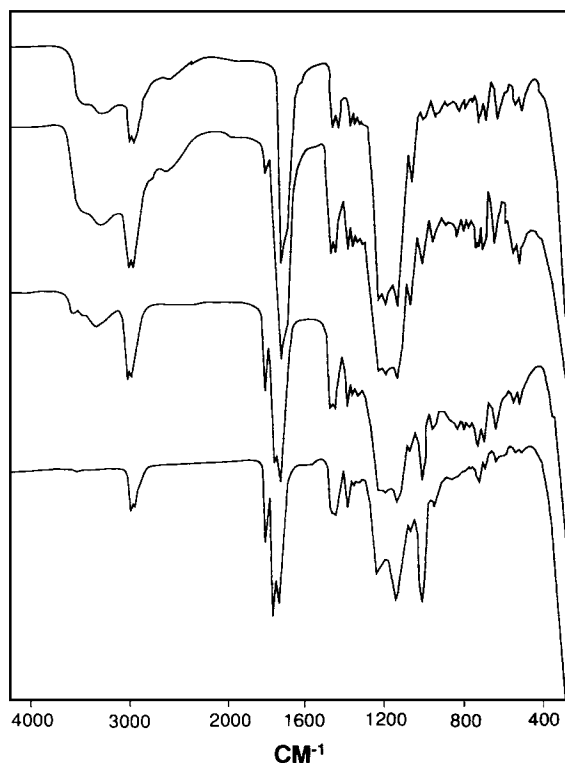**Figure 18** Thermal history of the fluoroterpolymer 6A. Same conditions as in Figure 17.

Figure 17 Thermal history of the fluoroterpolymer 6D. From top to bottom, the spectra were taken from samples dried in air, heated 4 h at 120°C, heated 4 h at 150°C, and heated 4 h at 180°C.

nated monomers was increased upon going from 6D through 6A to 6E. In each of these polymers, the weight percent of the MAA and 2-HEM were kept about equal. In the second experiment, three polymers were compared in which the total weight percent of nonfluorinated monomers was kept constant at about 20%. In these polymers, the molar ratios of MAA to 2-HEM was changed such that in 6A the molar ratio was 3 : 2 MAA/2-HEM; in 40A, 1 : 1; and in 40B, 2 : 3. Thus, the two experiments allow us to follow the effects of total nonfluorinated monomers in the system and of the molar ratios of both these monomers.

The effects of changes in the total amount of nonfluorinated monomers on the rate of formation of ester and anhydride groups can be gathered from a close scrutiny of Figures 17–19. In this series, we must recall that the composition is molarly richer in the MAA than in the 2-HEM, a condition preferring the formation of anhydrides. The IR spectra in Figure 17 reflect the thermal history of the fluoroterpolymer 6D, containing 90.1 : 5.0 : 4.9 wt %

Figure 19 Thermal history of the fluoroterpolymer 6E. Same conditions as in Figures 17 and 18.

PFAEM/MAA/2-HEM. From top to bottom, the four spectra in Figure 17 were taken from samples dried in air, cured 4 h at 120°C, cured 4 h at 150°C, and cured 4 h at 180°C. In Figure 18, the spectra obtained from 6A, containing 79.9 : 10.0 : 10.1 wt % PFAEM/MAA/2-HEM, are shown. In Figure 19, the spectra of 6E, containing 65.0 : 18.2 : 16.8 wt % PFAEM/MAA/2-HEM, are shown. The sequence of spectra in both these figures are identical with the sequence described above for 6D in Figure 17. As expected, comparison of the air-dried spectra in Figure 17 shows the relatively low-intensity IR bands at 3420 and 3280 cm^{-1}, belonging to hydroxylic and carboxylic —OH groups, and their increasing intensity upon going to Figures 18 and 19, respectively. The intensity of the ester band at 1730 cm^{-1} remains about the same, but the acid band, visible as a shoulder on the 1730 cm^{-1} band, increases in intensity upon going from 6D through 6A to 6E. Upon heating for 4 h at 120°C, the bands at 3420 and 3280 cm^{-1} changed slightly. The relative intensity of the 1730 cm^{-1} band increased somewhat. A very small amount of anhydride is already observable (bands at 1800 and 1020 cm^{-1}) coupled with a small reduction in the acid band at 1700 cm^{-1}. It should be noted that the intensity of the band at

3420 cm^{-1} relative to that at 3280 cm^{-1}, especially for 6A and 6E, slightly decreased upon heating. The above indicates that upon heating to 120°C both esters and anhydrides were created. After 4 h at 150°C, practically all the —OH groups in 6D have vanished. A small amount of —OH remained in 6A and a much larger amount in 6E. The amounts of ester remained about the same as they were at 120°C. The concentration of anhydride groups greatly increased upon going from 120 to 150°C, with the largest increment in 6D and the smallest in 6E. After 4 h at 180°C, the —OH bands vanished in all three polymers. The relative intensity of the ester band remains about the same. Because the —OH and free acid bands in 6D were depleted already at 150°C, no change occurred in this polymer upon going to 180°C. In the cases of 6A and 6E, where some —OH bands were clearly visible after 4 h at 150°C, they essentially disappeared after 4 h at 180°C. At the same time, the intensity of the anhydride bands increased in amounts commensurate with the decrease in —OH band intensities.

Next, the effects of changes in the molar ratios of MAA to 2-HEM were evaluated (while keeping their total wt % in the fluoroterpolymers constant). From the IR spectra, the relative intensities of the ester group, 1730 cm^{-1}/2990 cm^{-1}, and the anhydride group, 1020 cm^{-1}/2990 cm^{-1}, were calculated. The results for 2 h exposure to various temperatures are shown in Figure 20. The results for 4 h exposure, not shown here, reflected the onset of the appearance at ca. 150°C of larger concentrations of anhydride groups and a small reduction in the amount of ester groups in the polymers richer in MAA. At 180°C, the amounts of anhydride for all three polymers were larger than after 2 h. The concentration of esters was lower in 6A and 40A, while it still continued to increase in 40B. From this we conclude that exposure of fluoroterpolymers, whose compositions fall in the range covered in Table IV, to heat of up to 180°C for up to 2 h, preferentially produces more esters than anhydrides. An increase in cure time to 4 h starts depleting the ester concentration in favor of a more rapidly growing anhydride concentration. When the total amount of nonfluorinated monomers is increased, it takes longer to consume all the —OH moieties, but the combined amounts of ester and anhydride are larger than in polymers very rich in PFAEM. The ratios of ester to anhydride depend on composition and cure conditions. In systems very rich in MAA, a larger amount of anhydride eventually is formed. In systems rather poor in MAA, a larger amount of ester is formed, but the rate of reaction is slower than in other polymers. It appears
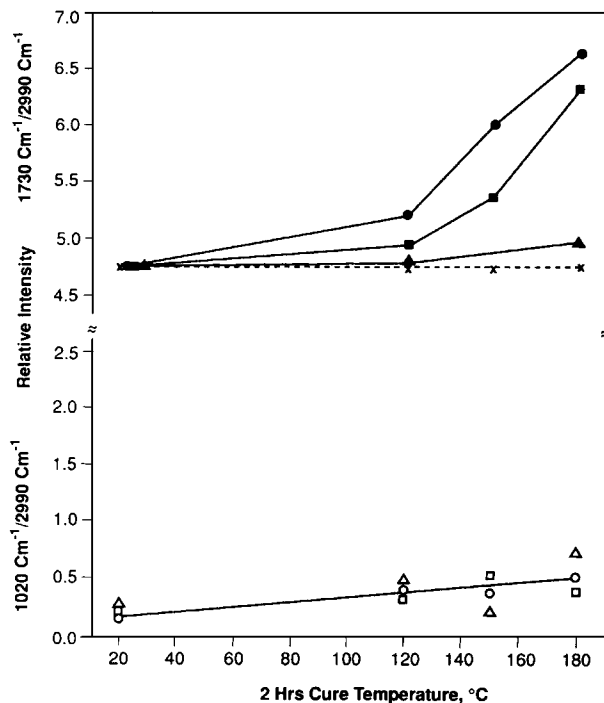
Figure 20 Effect of 2 h heating at various temperatures on the concentrations of esters and anhydrides in three fluoroterpolymers. Solid symbols = esters; empty symbols = anhydrides. ($\bullet$, $\bigcirc$) 6A; ($\blacksquare$, $\square$) 40A; ($\blacktriangle$, $\triangle$) 40B.

that the best compositions, conducive to the creation of most esters, are those with about equimolar amounts of MAA and 2-HEM. A slight favoring of the free acid seems not to affect the results significantly. The best cure conditions seem to be the exposure of the fluoroterpolymers for about 2 h to temperatures up to 180°C or for up to 4 h at temperatures not higher than 140°C. At temperatures of 110°C and lower, no reaction and no cross-linking takes place even after 8 h at temperature.

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