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Synthesis and Structure-Property Relationships of Low-Dielectric-Constant Fluorinated Polyacrylates*

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11.1. INTRODUCTION

Dielectric constant is directly proportional to the capacitance of a material. Present computer operations are limited by the coupling capacitance between circuit paths and integrated circuits on multilayer boards since the computing speed between integrated circuits is reduced by this capacitance and the power required to operate is increased.^{1†} If the dielectric constant is reduced a thinner dielectric provides equivalent capacitance, and the ground plane can be moved closer to the line, so that additional lines can be accommodated for the same cross-talk. Thus, the effect of a low dielectric constant will be to increase the speed of the signal and improve the density of the packaging, and this will result in improved system performance.²

With recent trends toward microminiaturization and utilization of very thin conductor lines, close spacings, and very thin insulation, greater demands are being placed on the insulating layer. Reductions in such parasitic capacitance can

*This chapter is the fifth in a series of articles by these authors, entitled "Processable Fluoropolymers with Low Dielectric Constants."

†The relationship of capacitance C with dielectric constant K_s can be expressed as $C = AK_s\epsilon_0/d$, where A is area, d is distance, and $\epsilon_0 = 8.85418 \times 10^{-14}$ F/cm.

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Fluoropolymers 1: Synthesis, edited by Hougham *et al.*, Plenum Press, New York, 1999.

be achieved in a number of ways through the proper selection of materials and the design of circuit geometry. In 1988 St. Clair *et al.*³ reported a reduction of dielectric constant to 2.39 by chemically altering the composition of a polyimide backbone to reduce the interactions between linear polyimide chains and by the incorporation of fluorine atoms. In 1991 Cassidy *et al.*⁴ reported a reduction of dielectric constant to 2.32 for the hexafluoroisopropylidene-containing polyarylates and copolyarylates. In 1992 Snow *et al.*⁵ reported that the thermally induced trimerization of a perfluorohexamethylene-linked aromatic cyanate resin to a cyanurate-linked network gave a dielectric constant between 2.3 and 2.4. In 1993 Babb *et al.*⁶ stated that the thermally induced cyclodimerization of a trifluorovinyl aryl ether to a perfluorocyclobutane aromatic ether polymer gave a dielectric constant of 2.40. What is common to all four cases is that they involve incorporating fluorine into polymers as a means of reducing the dielectric constant.

Fluorine is different from the other halogens in the elemental state or when bonded in chemical compounds. Fluorine is the most electronegative element, and when bonded to other atoms, it polarizes the bond, drawing electrons to it. As fluorine replaces hydrogen, the C—F bond shortens and simultaneously the bond strength increases. This shortening and strengthening of the C—F bond with increasing substitution is in striking contrast to the chlorinated or brominated methanes, in which essentially constant bond lengths and bond strengths are observed for all substituted methanes. These are general characteristics of the C—F bond in almost all fluorinated organic compounds.

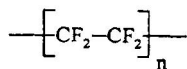
The highly polar nature of the C—F bond has been used to provide some high-performance characteristics in comparison with their hydrogen-containing or other halogen-containing analogues. Fluorine-containing epoxies or acrylics generally exhibit resistance to water penetration, chemical reaction, and environmental degradation; they also show a combination of unusual properties including low surface tension, low friction coefficient, high optical clarity, low refractive index, low vapor transmission rate, and exceptional electromagnetic radiation resistance.

Poly(tetrafluoroethylene) (PTFE), which is also known by DuPont's trade-name Teflon, is a solid at room temperature and has a dielectric constant in the range of 2.00–2.08,* while its monomer, tetrafluoroethylene, is a gas at room temperature. PTFE is exceptionally chemically inert, has excellent electrical properties and outstanding stability, and retains its mechanical properties at high temperatures. The problem with PTFE is that it is not processable. A family of commercial polymeric materials known as Teflon AF is believed to be a

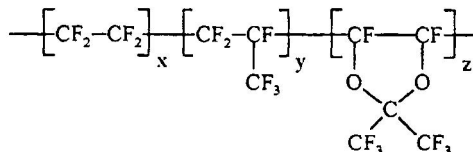
*See Licari and Hughes¹ pp. 378–379, Table A-13: Dielectric Constants for Polymer Coatings (at 25°C).

terpolymer of tetrafluoroethylene, perfluoropropylene, and 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole (a derivative of hexafluoroacetone). It is reported to have a dielectric constant in the range of 1.89–1.93 and to be more processable than PTFE.⁷

Teflon



Teflon AF



Very recently we⁸ reported on a class of processable heavily fluorinated acrylic resins that exhibit dielectric constants as low as 2.10, very close to the minimum known values. In this chapter we report on the preparation of a series of processable heavily fluorinated acrylic and methacrylic homo- and copolymers that exhibit dielectric constants as low as 2.06, and the factors that affect the reduction of dielectric constant from structure–property relationships is elucidated.⁹

11.2. EXPERIMENTAL

Only two typical examples in monomer preparation are described here.

11.2.1. Materials

Triethylamine was fractionally distilled from lithium aluminum hydride under nitrogen and acryloyl chloride was distilled under nitrogen. 1,1,2-Trichlorotrifluoroethane (Freon 113) was distilled from phosphorus pentoxide under nitrogen. Azobisisobutyronitrile (AIBN) was used as received. Methyl ethyl ketone peroxide (MEKP) (9% Organic Peroxide VN 2550) was obtained from Witco. Alumina (neutral, Brockman activity 1, 80–200 mesh) was obtained from Fisher Scientific Co. All reagents were obtained from Aldrich unless otherwise specified.

11.2.2. Techniques

Infrared spectra were obtained with a Perkin-Elmer 1800 and a Nicolet Magna-IR 750 FTIR spectrophotometer, and the absorption frequencies are reported in wave numbers (cm^{-1}). NMR spectra were obtained with BZH-300 and CA-F-300 Bruker FTNMR 300 MHz spectrometers. Chloroform-d was used as solvent, and all chemical shifts are reported in parts per million downfield (positive) of the standard. ^1H -NMR and ^{13}C -NMR chemical shifts are reported relative to internal tetramethylsilane, while ^{19}F -NMR chemical shifts are reported relative to internal fluorotrichloromethane, R_f values were obtained from silica gel thin-layer chromatography developed with a mixture of 1.5 mL methylene chloride and three drops of acetone. The number of hydrate water molecules was calculated from the integration of ^1H -NMR spectra.

11.2.2.1. Preparation of Etherdiacrylate **6** from Etherdiol

1,3-Bis-(2-hydroxyhexafluoro-2-propyl)-5-(4-heptafluoroisopropoxy-1,1,2,2,3,3,4,4-octafluoro-1-butyl)benzene, b.p. $95^\circ\text{C}/10\text{ mm}$, was prepared by the multistep route reported by Griffith and O'Rear.¹⁰ Elemental analysis showed it to be anhydrous, but after long storage it had 0.5 H_2O as water of hydration. R_f 0.36; ^1H -NMR δ 8.35 (s, 1H, 2-ArH), 8.09 (s, 2H, 4, 6-ArH), 4.14 (s, 2H, -OH), 2.13 (s, 1H, H_2O); IR (neat) 3620 and 3515 br (OH), 3125, 1618, 1468, 1365, 1350–1100(CF), 1005, 992, 980, 948, 938, 900, 872, 841, 800, 775, 768, 758, 738, 728, 707, 690, 668, 621 cm^{-1} .

The etherdiacrylate **6** was prepared by a modification of the procedure of Griffith and O'Rear.¹¹ To a solution of etherdiol (3 g, 3.78 mmol) in Freon 113 (10 ml) in an ice-water bath under nitrogen, triethylamine (0.791 g, 7.81 mmol) in Freon 113 (5 ml) was added dropwise in 10 min. After 10 min more, acryloyl chloride (0.707 g, 7.81 mmol) in Freon 113 (5 ml) was added dropwise in 20 min; a precipitate formed immediately. After stirring for 2 h at room temperature, filtration through Celite to remove the solid, followed by evaporation at room temperature *in vacuo*, 3.02 g of a viscous liquid was obtained.

The liquid was dissolved in a mixture of methylene chloride (20 ml) and Freon 113 (10 ml); filtration through neutral alumina (1 g) gave a clear filtrate. It was cooled in an ice bath, washed twice with 1.3 N sodium hydroxide (10 ml), washed with water (10 ml), dried over anhydrous sodium sulfate, percolated and washed through a column of neutral alumina (3 g) twice, and evaporated *in vacuo* at room temperature for 3 h to give a colorless viscous liquid **6** (1.38 g, yield 40%). R_f 0.92; IR (neat) 3118, 1772, 1637, 1468, 1410, 1365, 1350–1100 (CF), 1055, 1040, 992, 900, 878, 848, 800, 770, 759, 740, 728, 718, 670 cm^{-1} ; ^1H -NMR δ 7.68 (s, 2H, 4,6-ArH), 7.63 (s, 1H, 2-ArH), 6.61 (d, $J = 17\text{Hz}$, 2H), 6.29 (d, $J = 17, 10\text{Hz}$, 2H), 6.13 (d $J = 10\text{ Hz}$, 2H), 1.57 (s, 2H, H_2O indicated 1.0 H_2O as water of hydration); ^{19}F -NMR $[-\text{c}(\text{CF}_3)_2-]$ -81.10

$[-CF(CF_3)_2]$, -81.35 ($-O-CF_2-$), -112.28 ($Ph-CF_2-$), -123.09 ($-OCF_2-CF_2-$), -124.99 ($Ph - CF_2-CF_2-$), -145.75 $[-CF(CF_3)_2]$; ^{13}C -NMR 82.42 [hept, $J = 30.6$ Hz, $-C(CF_3)_2-$], 121.26 [q, $J = 289.7$ Hz, $-C(CF_3)_2-$], 125.80 (s, 4,6-aromatic C—H), 127.07 (br. s, 1,3-aromatic C), 128.96 (s, 2-aromatic C—H), 130.32 t, $J = 25.0$ Hz, 5-aromatic C), 129.42 (s, $CH_2 = CH-$), 135.29 (s, $CH_2 = CH-$), 160.74 (s, $-COO-$).

11.2.2.2. Preparation of Triacrylate **3** from Triol

1,3,5-Tris (2-hydroxy-hexafluoro-2-propyl)benzene was prepared by a multi-step route according to the procedure of Soulen and Griffith.¹² This compound was hygroscopic as also observed by Griffith and O'Rear.¹⁰ R_f 0.15; IR (KBr pellet) 3660, 3618, 3590 and 3513 (OH), 3125, 1465, 1300–1100(CF), 1026, 1013, 980, 891, 775, 730, 709, 693 cm^{-1} ; 1H -NMR δ 8.25 (s, 1H, ArH), 4.44 (s, 1H, $-OH$), 2.11 (s, 1.5H, H_2O indicated 2.25 H_2O as water of hydration).

The triacrylate **3** was prepared by a procedure similar to that described for the synthesis of etherdiacrylate **6**. Triol (2.176 g, 3.78 mmol), triethylamine (1.517 g, 15.0 mmol) and acryloyl chloride (1.358 g, 15.0 mmol) were used. After filtration and evaporation, 1.82 g of a viscous liquid was obtained. It was dissolved in a mixture of methylene chloride (20 ml) and Freon 113 (20 ml), and a gelatinous solid was removed by filtration through neutral alumina (1 g). The filtrate was purified by percolation and washing through a column of neutral alumina (3 g) twice. Evaporation at room temperature in vacuo for 3 h gave 1.12 g (40% yield) of **3** as a very viscous colorless liquid, which upon standing at $-13^\circ C$ became a semisolid. 1H -NMR δ 7.53 (s, 3H), 6.57 (d, $J = 17$ Hz, 3H), 6.24 (d, d, $J = 17$, 10 Hz, 3H), 6.06 (δ , $J = 10$ Hz, 3H) indicated that no water of hydration was present. This semisolid is, however, hygroscopic. R_f 0.85; IR (KBr pellet) 3515, 3130, 2920, 2850, 1770, 1635, 1630, 1412, 1350–1100 (CF), 1090, 1055, 995, 940, 900, 802, 750, 740, 725, 715, 689, 669 cm^{-1} ; 1H -NMR δ 7.51 (s, 3H), 6.60 (d, $J = 17$ Hz, 3H), 6.28 (d, d, $J = 17$, 10 Hz, 3H), 6.11 (d, $J = 10$ Hz, 3H), 1.56 (s, 3H, H_2O) indicated 1.5 H_2O as water of hydration. ^{19}F -NMR -70.86 ; ^{13}C -NMR 80.53 [hept. $J = 30.5$ Hz, $-C(CF_3)_2-$], 121.30 [q, $J = 289.4$ Hz, $-C(CF_3)_2-$], 125.82 (s, 2,4,6-aromatic C—H), 127.11 (br. s, 1,3,5-aromatic C), 128.80 (s, $CH_2 = CH-$), 135.10 (s, $CH_2 = CH-$), 160.61 (s, $-COO-$).

11.2.2.3. Preparation of Polymer “Cylindrical Donuts” from Monomers

In order to prepare the samples for dielectric-constant measurements, etherdiacrylate **6** was mixed with a trace amount of AIBN at room temperature in a cylindrical donut mold made from General Electric RTV 11 silicon molding compound. The donuts had an outer diameter of 7.0 mm, an inner diameter of 3.0 mm, and a thickness of 3.0 mm; the semisolid triacrylate **3** was mixed with a

trace amount of liquid MEKP with some heating to obtain a clear liquid; equal masses of **6** and **3** were also mixed with MEKP with some heating.

For polymerization the filled donut molds were kept under an inert atmosphere, the temperature was raised to 85°C over 2 h, and then kept at 85–100°C for 20 h. Homopolymers and 50/50 (w/w) copolymers were obtained.

11.2.2.4. Dielectric Constant Measurements

Dielectric constant (DE) values are reported as “permittivity” with the symbol ϵ or K . The polymer cylindrical donuts were used for the measurement of DE on a Hewlett-Packard 8510 automated network analyzer. The analyzer is capable of measuring 401 data points over a frequency band of 500 MHz to 18.5 GHz. Typically S11 and S21 values, which correspond to reflection and transmission, respectively, are measured and then these values are used to calculate the permittivity and permeability.

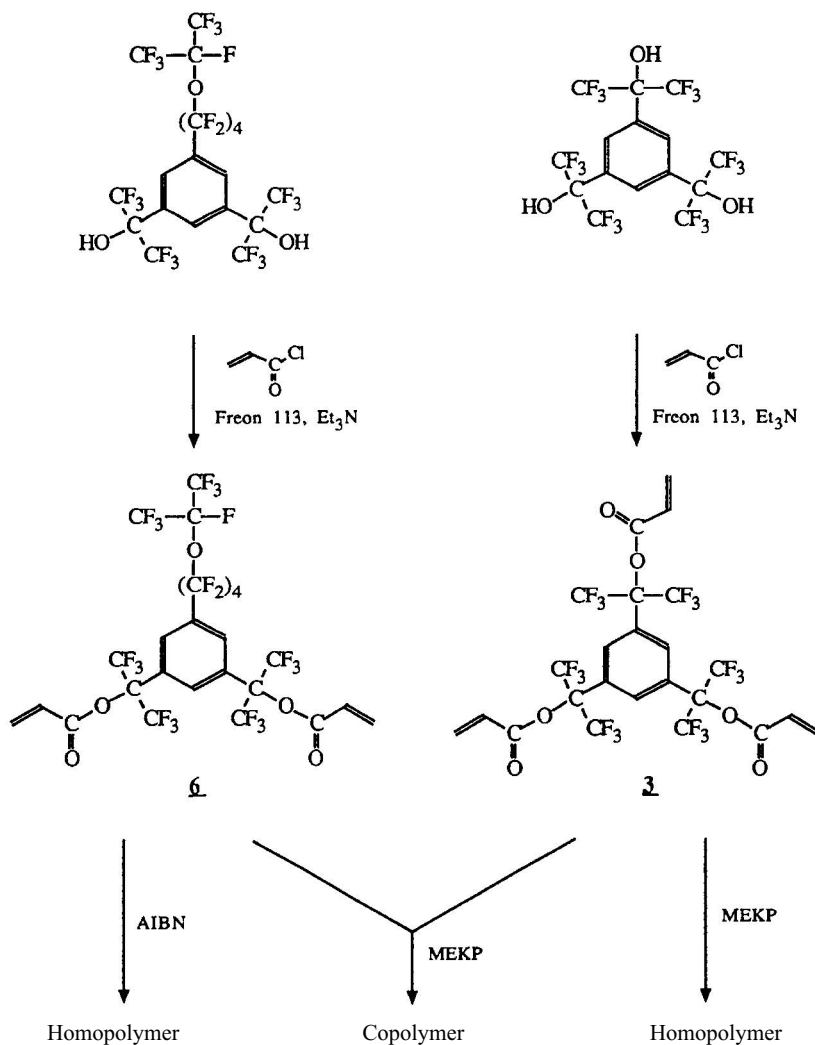
Samples stood at room temperature in air prior to testing; measurements were run at room temperature and approximately 25% relative humidity (RH). A virgin PTFE sheet (MMS-636-2) was obtained from Gilbert Plastics & Supply Co. and cut into the same cylindrical donut size. The result for PTFE reported here is the average of the DE values measured for three samples.

11.3. RESULTS AND DISCUSSION

11.3.1. Monomers and Polymers

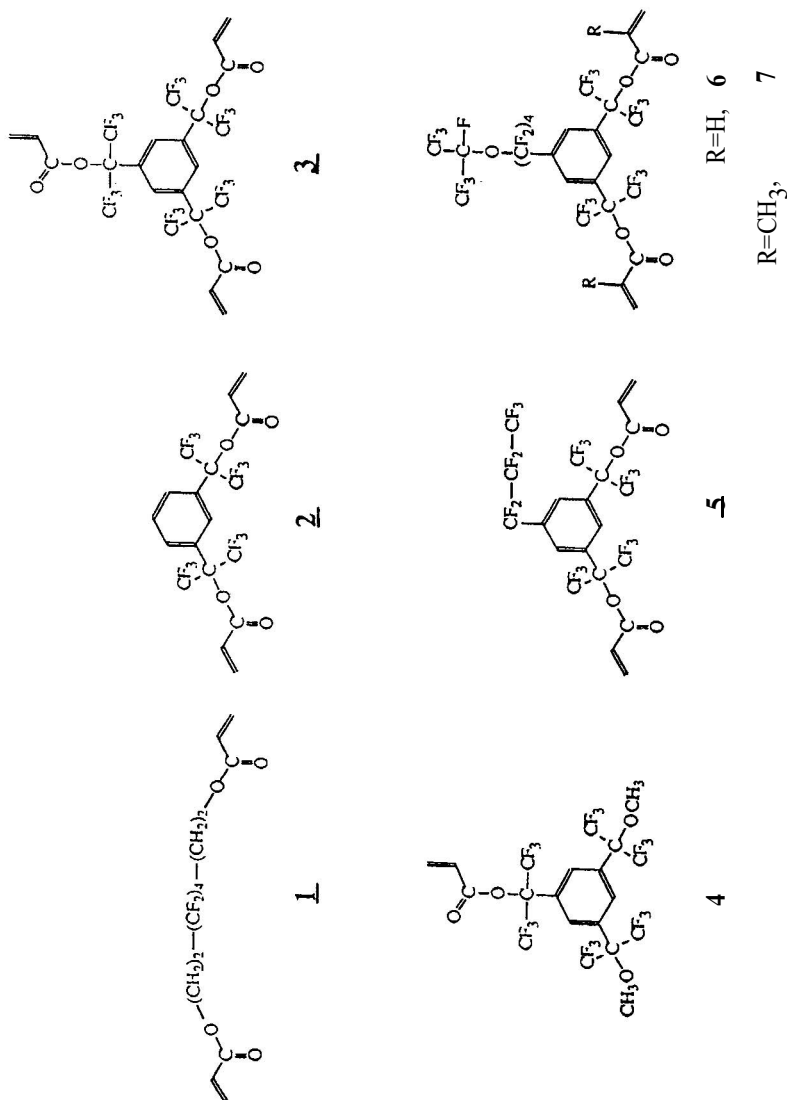
The preparation of fluorinated alcohols was carried out in multistep routes according to the reported procedures.^{10,12} The synthesis of acrylic and methacrylic esters as shown in Table 11.1 was carried out in a fluorocarbon solvent such as Freon 113 by the reaction of the respective fluorinated alcohol with acryloyl chloride or methacryloyl chloride and an amine acid acceptor such as triethylamine with examples shown in Scheme 1. Other attempts to esterify the fluoroalcohols directly with acrylic acid or acrylic anhydride were not successful.¹¹ Product purification by distillation was not feasible because of the temperature required, but purification by percolation of fluorocarbon solutions through neutral alumina resulted in products of good purity identified by TLC, FTIR, and ¹H-, ¹³C-, and ¹⁹F- FTNMRs.

Owing to their liquid or semisolid nature, monomers are easy to process into polymers. For radical polymerization the use of solid AIBN for liquid monomers at room temperature and liquid MEKP for semisolid monomers or a mixture of liquid and semisolid monomers with some heating is convenient. During the course of curing at 85–100°C for 22 h the problem of surface inhibition of free radicals by oxygen from the air can be avoided by inert-gas blanketing.



Scheme 1

In 1H -NMR spectra, the acrylates showed a characteristic ABX pattern in the region of δ 6.8–6.0 with a pair of doublet couplings for each vinyl proton, while the methacrylates showed a characteristic AB pattern in the region of δ 6.5–5.8 with an equivalent singlet peak for each vinyl proton. The monomers purified by percolation over alumina contained no detectable hydrate water or polymerized impurities.

Table 11.1. Summary of Data for Dielectric Constant Measurements^a

R=H,

R=CH₃,

Polymer		Dielectric constant			
Monomer used	Fluorine content (%) ^d	0.0 GHz	3.0 GHz	9.0 GHz	15.0 GHz
1	41.50	2.31	2.41	2.36	2.36
2	43.99	2.26	2.25	2.28	2.27
3	46.32	2.23	2.23	2.23	2.22
(3 + 6) ^b	51.58	2.22	2.23	2.24	2.22
(4 + 5) ^b	52.27	2.21	2.22	2.22	2.19
5	52.60	2.18	2.21	2.16	2.15
6	56.85	2.11	2.10	2.12	2.13
7	55.14	2.07	2.06	2.08	2.10
PTFEc	75.98	1.96	1.98	1.99	—

^a See Experimental Section for details.

^b 50/50 (w/w).

^c Polytetrafluoroethylene (MMS-636-2) from Gilbert Plastics & Supply Co.

^d Calculated.

As expected, the homopolymers and the 50/50 (w/w) copolymers are semitransparent, hard solids, and some shrinkage in volume is observed during curing. In an uncured state they are frangible, but when totally cured they acquire a more resilient character. The degree of polymerization can be easily monitored with an FTIR spectrophotometer as shown in Figure 11.1, e.g., by examining the intensity of the absorption frequencies at 1635 and 1410 cm^{-1} that

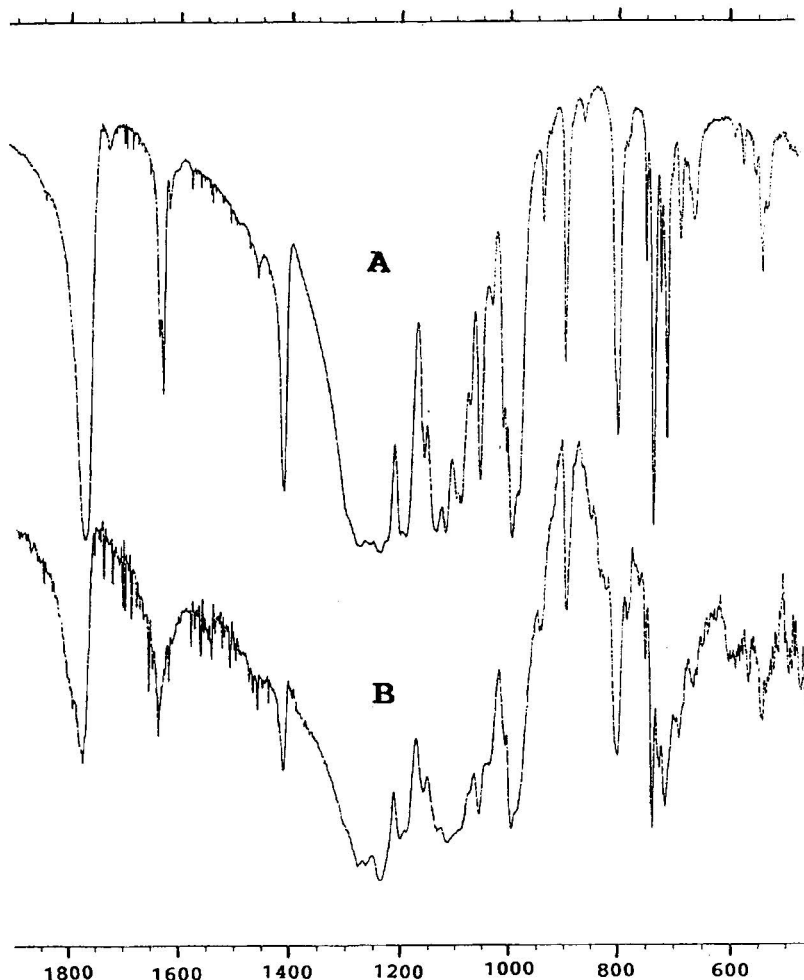


Figure 11.1. FTIR (KBr pellet) spectra of (A) triacrylate 3 and (B) its curing with AIBN at 100°C for 18 h.

are assigned to the acrylate functional groups. In all cases, the filled donut molds were degassed and kept under inert gas for curing at up to 100°C for 20 h.

Since each acrylate group is difunctional, the diacrylates are tetrafunctional while the triacrylates are hexafunctional. For polymerization of the polyfunctional monomers at sufficiently high degrees of conversion, the branching must result in the formation of cross-links to give a three-dimensional network.

The fluoroacrylic polymers are high-modulus, low-elongation plastics, which are brittle in the sense that all thermosetting polymers are brittle. However, they are tough, rugged materials not easily damaged by impact or mechanical abuse.

11.3.2. Dielectric Constant and Structure–Property Relationships

In order to validate the accuracy of our measurements, three samples of virgin PTFE in the same cylindrical donut size were measured and found to have average DE values around 1.96–1.99, which are close to the reported values 2.0–2.08.* Summarized results of the DE measurements on the polymer donuts are shown in Table 11.1. All the new polymer exhibit low DEs, around 1.06–2.41, over a wide frequency region of 500 MHz to 18.5 GHz; the variation of DE values over the measured frequency region is within 0.03, which indicates a wide-range frequency independence.

Basically, the effect of a higher fluorine content on the polymer backbone or side chain will be the reduction of polymer chain–chain electronic interactions, which further results in a reduction of DE. This effect was observed by St. Clair *et al.*,³ but only on the polymer backbone.

In a comparison of **5** and **6** (see Table 11.1), the existence of a perfluoroalkyl ether linkage seems to play an important role in further reducing the DE values. Teflon AF and **6** both have low dielectric constants and contain ether linkages. Since the dielectric constant of Teflon AF is lower than that of Teflon, which has a higher fluorine content, it appears that the ether linkage has an effect in lowering the DE. The Teflon AF has been reported by Resnick⁷ as the lowest dielectric constant (1.89–1.93) of any polymer thus far.

It has been reported¹³ that in the preparation of polyimides the more flexible *meta*-linked diamine systematically gave lower DE values than the corresponding *pura*-linked system and that this may be related to free volume in the polymer since the *meta*-substituted systems should have a higher degree of entropy. Therefore, the symmetrical *meta*-substitution in our aromatic structure may result in a reduction of DE.

In a comparison of **6** and **7**, a reduction of DE was observed when acrylate was replaced by methacrylate and this may be related to the free volume in the

*See Licari and Hughes¹ pp. 378–379, Table A-13: Dielectric Constants for Polymer Coatings (at 25°C).

polymer since the bulkier methacrylate should have more steric hindrance than the acrylate.

The wide-range frequency independence of these low DEs and the processability of these monomers suggest many potential applications. In particular, it is known that the addition of a fluorine-containing group to the polymer backbone will reduce the polymer chain-chain electronic interactions, which will result in a reduction of DE as reported by St. Clair *et al.*¹³ However, the DE for the polymer from **6** (fluorine content 57%) is at most 0.13 below that for the polymer from **3** (fluorine content 46%), which may indicate that a minimum value has nearly been reached.

11.3.3. Processability and Applications

The liquid or low-melting solid monomers can be cured to the solid state by incorporating a curing catalyst and heating the mixtures below the decomposition temperature. Moreover, the cured solids are transparent and hard polymers formed of three-dimensional networks with moderate thermostability.

In the course of curing, the viscosity vanes from thin to syrupy liquids. This is convenient for impregnating reinforcing materials, such as fiberglass scrim, used in making wiring or circuit boards for electronics applications.

A compound containing two or three unsaturated groups would be expected to polymerize to a cross-linked, solid, and nonlinear thermosetting polymer. Fluorinated compounds that have only one unsaturated group can be used in a mixture with our monomers to polymerize to a solid polymer of a thermoset nature and this is a convenient way to enhance the ease of processing.

11.3.4. Lower Dielectric Constants?

Dielectric constants of these materials can be further lowered by known means such as by incorporating air bubbles into the materials or by inhibiting crystallization. A difference of a couple of hundredths in the DE value may be important when one is at the low extremes. Recently Singh *et al.* calculated the DEs of polyimide films from the measured free volume fraction and found that the calculated values, are close to the experimental result.^{14,15*}

In 1991 Groh and Zimmerman¹⁶ estimated the theoretical lower limit of the refractive index of amorphous organic polymers by using the Lorentz-Lorentz equation and reported the lower limit to be very close to 1.29, while in 1979 Dislich¹⁷ proposed a limit of about 1.33 from a screening of published polymer data.

*The calculation was based on the relation: $1/\epsilon = (1-f)/\epsilon_R + f/\epsilon_{Air}$, where ϵ_R is the value of ϵ for zero free volume fraction, which can be obtained from the plot of ϵ vs. f .

The amorphous Resnick Teflon AF terpolymer has the lowest refractive index in the range of 1.29–1.31 and also the lowest DE in the range of 1.89–1.93. Furthermore, Groh and Zimmermann¹⁶ reported that functional groups with a high fluorine content, such as CF₃ and CF₂, have the lowest refractive index contribution. The value for the ether group is also remarkably low, while the values for the carbonyl and carboxyl groups are high. In view of the good agreement between the refractive index and the DE on amorphous organic polymers, the opportunity to obtain the former in the range of 1.89–2.06 by modifying our synthesis is high.

11.4. CONCLUSIONS

In this work we have demonstrated that a new class of heavily fluorinated acrylic and methacrylic resins can be efficiently synthesized and then cured to solid form with radical initiator at elevated temperatures. These cured resins were found to have low dielectric constants, which are close to the minimum known values for Teflon and Teflon AF. In contrast to tetrafluoroethylene, our monomers are processable owing to the fact that they are liquids or low-melting solids, and moreover are soluble in common organic solvents. Lower dielectric constants are obtained as fluorine contents on the polymer backbone or side chain increase, when acrylate is replaced by methacrylate, when ether linkages are present in the fluorocarbon, and when aromatic structure is symmetrically *meta*-substituted.

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*These references are part of a series of articles, entitled "Processable Fluoropolymers with Low Dielectric Constants."