

Acrylic Polyester Resins Containing Perfluoropolyethers Structures: Synthesis, Characterization, and Photopolymerization

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ABSTRACT: Poly(ϵ -caprolactone-*b*-perfluoropolyether-*b*- ϵ -caprolactone) (PCL–PFPE–PCL) block copolymers having different PCL block lengths and end-capped with methacrylate groups were prepared and characterized. Spectroscopic analyses confirmed the expected molecular structure of the products. After UV curing, the films revealed the presence of two amorphous phases, corresponding to fluorinated and hydrogenated moieties, respectively. The material containing long PCL blocks showed also a crystalline phase. Surface properties of the UV-cured films were evaluated: The surfaces have a very high hydrophobic character in spite of the presence of many polar OH groups present in the polymeric network and a high hysteresis in wetting. An enrichment of fluorine at the air-side surface was shown by contact-angle measurements, except when long PCL sequences are present. The θ_{adv} angles decreased by increasing the content of PCL, that is, by decreasing the content of fluorine. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 651–659, 2000

Key words: acrylic polyester resins; block copolymers; poly(ϵ -caprolactone); perfluoropolyethers; photopolymerization; surface characterization

INTRODUCTION

The use of fluorinated monomers and oligomers for coatings is very attractive, due to the peculiar characteristics given by the fluorine presence, such as hydrophobicity, chemical stability, and weathering resistance, release properties, and a low coefficient of friction, water impermeability, and a small refractive index. Different fluorinated monomers have been already used for many ap-

plications and their properties discussed in several articles.^{1–3} The hydrophobic character of fluorine-containing polymers is well known, together with other peculiar properties such as high heat and chemical resistance, good toughness and flexibility at very low temperature, low surface energy, and low friction coefficient. Fluorine-containing polymers having some peculiar characteristics, in particular, surface properties, can be obtained by polymerization of fluorinated monomers or surface fluorination of traditional polymeric materials. Both approaches show some drawbacks such as the necessity to use great amounts of fluorinated monomers in order to

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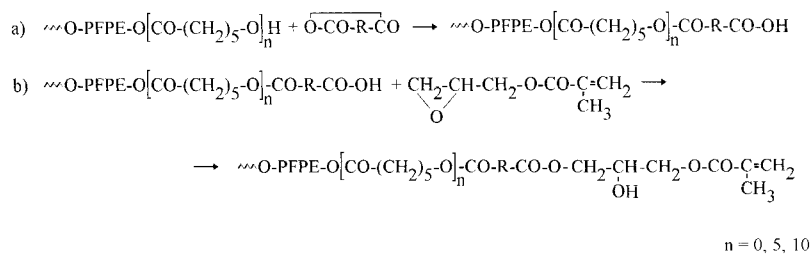


Figure 1 Reaction scheme for the preparation of fluorinated acrylic polyesters.

achieve a significant surface modification and the high cost of surface fluorination of a previously molded item.

In previous works, we studied coatings which contained small amounts of acrylic monomers having perfluoroalkyl branches and we investigated the influence of the monomer structure and its concentration on the film formation and on its final properties.^{4,5} In this context, it seems very interesting to explore the use of perfluoropolyether (PFPE) structures for obtaining, after curing, new coatings for the protection of different substrates. The UV-curing technique has interesting advantages in the preparation of polymeric networks, mainly because it makes it possible to have a high productivity, saves energy, does not require solvents, and avoids environmental pollution.⁶

PFPE-functionalized macromers have already been introduced into epoxy systems,⁷ into polyester polymers,^{8,9} unsaturated polyester resins,¹⁰ and polyurethane systems^{11,12}. The new materials show interesting and peculiar performances, joined with unusual surface properties. Pursuing this research, we decided to use these building blocks for the preparation of UV-curable systems. First, a preliminary report on PFPE bisacrylates, obtained by reaction of the fluorinated macrodiol with acryloyl chloride, was published.¹³ Then, we adjusted a different synthetic route in order to link the PFPE segments to the polymeric network and made the bis-CH₂OH-terminated PFPE macromers able to react with the isocyanate-ethyl methacrylate: PFPE bisurethane-methacrylate derivatives (PFEUMA) were obtained. These oligomers were then successfully subjected to UV curing.¹⁴

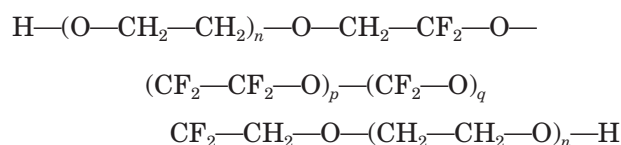
The presence of reactive functional groups in telechelic PFPE¹⁵ makes possible their modification with simple reactions in order to obtain fluorinated additives having improved and controlled miscibility characteristics toward the hydrogenated thermosetting resins, such as vinyl ester resins (VER).

Considering the well-known compatibility of poly(ϵ -caprolactone) (PCL) with several different polymers,¹⁶ poly(ϵ -caprolactone-*b*-perfluoropolyether-*b*-(ϵ -caprolactone) (PCL-PFPE-PCL) block copolymers having different PCL block lengths were prepared in order to have samples with controlled compatibility with various polymers. After end-capping with methacrylate groups, these oligomers can be photopolymerized alone or in a mixture with other curable resins. In this article, we report the synthesis and the characterization of PCL-PFPE-PCL block copolymers end-capped with methacrylate groups and their photopolymerization.

EXPERIMENTAL

Materials

The fluorinated macromer was a commercial product named Fomblin Z-DOL® TX (supplied by Ausimont and indicated by TX2) having the following structure:



in which CF₂CF₂O and CF₂O units, randomly distributed along the chain and with a *p/q* ratio of ≈ 0.9 , represent the perfluoropolyether component. The poly(ethylene oxide) chain is the end-capping segment and contains the hydroxyl functional group with an average value *n* of 1.5. The number-average molecular weight of TX2, determined by ¹⁹F-NMR, is 2200. The macromer was employed as received without further purification. In Figure 1, TX2 is also schematically indicated as HO-PFPE-OH.

PCL-PFPE-PCL block copolymers were obtained by bulk polymerization of the ϵ -caprolactone monomer onto the hydroxyl terminal groups

of TX2 in the presence of a suitable catalyst, with formation of ABA-type block copolymers having two hydroxyl terminal groups.¹⁷ The employed samples were characterized by PCL blocks having an average degree of polymerization of 5 [sample indicated by TX2CL(5)] and of 10 [sample indicated by TX2CL(10)], respectively.

Before use, chlorendic anhydride (CA, 1,4,5,6,7,7-hexachloro-5-norbornene-2,3-dicarboxylic anhydride; Aldrich Chemicals, Milwaukee, WI) was purified by crystallization from *n*-hexane, glycidyl methacrylate (GM; Aldrich Chemicals) was distilled at reduced pressure, and toluene (Aldrich Chemicals) was distilled and dried at atmospheric pressure on calcium hydride.

Modification of Fluorinated Oligomers

Preliminary tests showed that a direct reaction between TX2 and GM did not take place. Thus, modification of TX2 with CA is necessary to allow the further reaction with GM.

Modification of TX2, TX2CL(5), and TX2CL(10) with CA

TX2 was reacted with CA (molar ratio 1:2), in bulk, under mechanical stirring, at 120°C for 2 h; the final product was named TX2-CA. Analogously, the TX2CL(5) and TX2CL(10) copolymers were reacted with CA (molar ratio 1:2) in a toluene solution (2:1 vol/vol with respect to the reactants), under mechanical stirring, at the refluxing temperature for 3.5 h; the final products, after elimination of the solvent, were named TX2CL(5)-CA and TX2CL(10)-CA, respectively.

Modification of TX2-CA, TX2CL(5)-CA, and TX2CL(10)-CA with GM

TX2-CA was reacted with GM (molar ratio 1:2) in bulk, under mechanical stirring, at 90°C for 1.5 h; the final product was named TX2-CA-GM. Analogously, the TX2CL(5)-CA and TX2CL(10)-CA copolymers were reacted with GM (molar ratio 1:2) in a toluene solution (2:1 vol/vol with respect to the reactants), under mechanical stirring, at the refluxing temperature for 4 h. The final products, after elimination of the solvent, were named TX2CL(5)-CA-GM and TX2CL(10)-CA-GM, respectively.

Film Preparation

The mixtures of the pure acrylated oligomers with 4% (w/w) of the photoinitiator (2-hydroxy-2-

methyl-1-phenylpropan-1-one, Darocure 1173, from Merck) were coated onto glass plates with a calibrated wire wound applicator to obtain a film thickness of about 100 μm . Coated sheets were then irradiated with a medium-pressure mercury lamp with a light intensity on the film of about 10 mW/cm², working in a small box equipped with a quartz window under a pure N₂ atmosphere (O₂ content <20 ppm).

TX2-CA-GM and TX2CL(5)-CA-GM are liquid at room temperature with quite high viscosity values; by increasing the number of PCL blocks, the copolymers tend to crystallize: therefore, the TX2CL(10)-CA-GM copolymer needs to be warmed above its melting point before the photopolymerization occurs.

Free films were obtained by peeling them from the glass plate and completing the curing process by irradiating the other side of the film. The irradiation time was continued until a constant double-bond conversion was reached (about 20 s). The complete procedure was reported previously.¹⁸

ANALYTICAL TECHNIQUES

Molecular Characterization of Modified Fluorinated Oligomers

FTIR analysis was performed on a Bruker IFS48 instrument. ¹H-NMR analysis was performed on a Varian Gemini System 300-MHz instrument using as a solvent a CDCl₃/1,1,2-trichloro-1,2,2-trifluoroethane mixture (1:1 vol/vol) for the sample TX2-CA and CDCl₃ for all other samples.

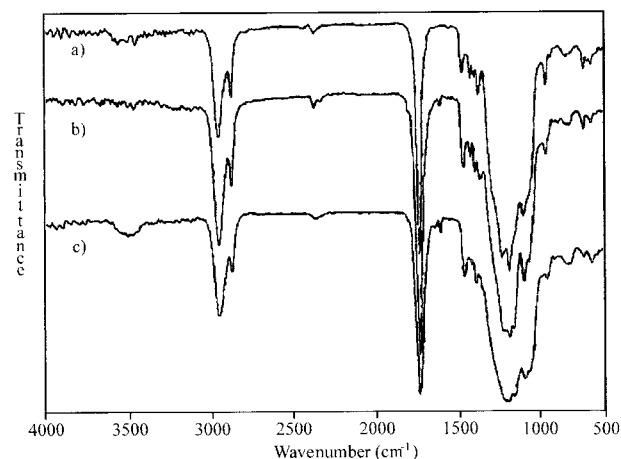


Figure 2 FTIR spectra of (a) TX2CL(10), (b) TX2CL(10)-CA, and (c) TX2CL(10)-CA-GM.

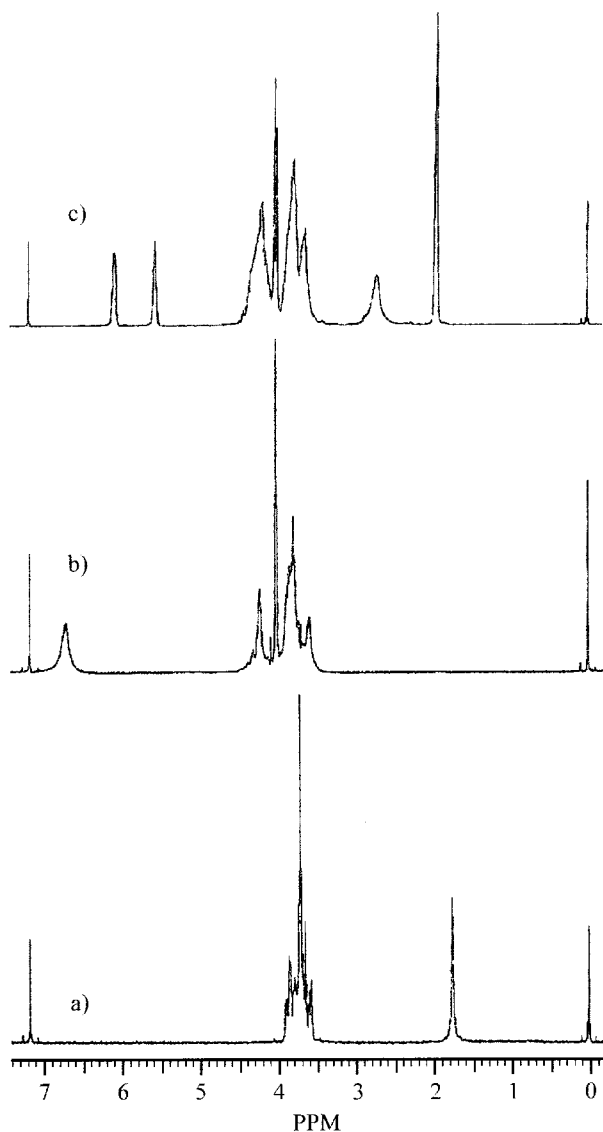


Figure 3 $^1\text{H-NMR}$ spectra of (a) TX2, (b) TX2-CA, and (c) TX2-CA-GM.

Film Characterization

The film thickness was measured using a Minitest 3000 instrument (Elektrophysik Köln, Germany). The double-bond conversion was determined by Fourier-transform infrared spectroscopy (FTIR) by measuring the change of the area of the absorption band at 1635 cm^{-1} before and after UV irradiation. The FTIR measurements were performed using an ATI Mattson Genesis Series II spectrometer.

The gel content was determined by measuring the weight decrease after 24-h treatment at room temperature with chloroform. DSC analyses were

performed using a Perkin-Elmer 2C or a Mettler DSC 20 instrument in the range -120 to $+150^\circ\text{C}$ with a heating rate of $10^\circ\text{C}/\text{min}$.

Dynamic mechanical analyses (DMTA) were performed on an MK II Polymer Laboratories instrument at a 1-Hz frequency in the tensile configuration. The size of the specimen was about $14 \times 9 \times 0.1\text{ mm}$. The storage modulus, E' , and the loss factor, $\tan \delta$, were measured from -150°C up to the temperature at which the rubbery state was attained. The T_g value was assumed as the maximum of the loss factor curve.

Contact-angle measurements were performed with a Kruss G1 instrument. The measurements were made in air at room temperature by the

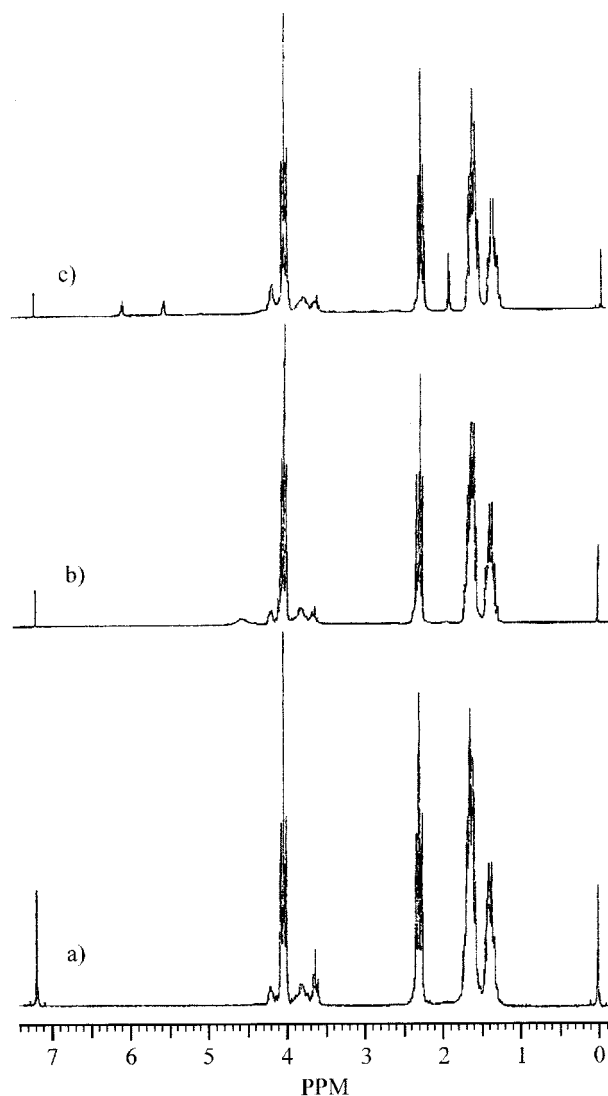


Figure 4 $^1\text{H-NMR}$ spectra of (a) TX2CL(10), (b) TX2CL(10)-CA, and (c) TX2CL(10)-CA-GM.

Table I $^1\text{H-NMR}$ Assignments

1	$\overbrace{\text{CH}_2\text{-(CH}_2)_3\text{-CH}_2\text{-O-CO}}^{\text{a b c}}$	a: 2.65 ppm, 2H; b: 1.80–1.85 ppm, 6H; c: 4.25, 2H
2	$\text{—CH}_2\text{-(CH}_2)_3\text{-CH}_2\text{-O-CO—}$ a b c	a: 2.30 ppm, 2H; b: 1.40–1.65 ppm, 6H; c: 4.05, 2H
3	$\text{—PFPE—CF}_2\text{—}\underbrace{\text{CH}_2\text{—O(CH}_2\text{—CH}_2\text{—O)}_{1.5}\text{H}}_a$ b	a: 3.50–4.00 ppm, 8H; b: 2.20 ppm, 1H
4	$\text{—PFPE—CF}_2\text{—}\underbrace{\text{CH}_2\text{—O(CH}_2\text{—CH}_2\text{—O)}_{0.5}\text{—CH}_2\text{—CH}_2\text{—O—}}_a\text{(CO—CH}_2\text{—(CH}_2)_3\text{—CH}_2\text{—O)}_n\text{—CO—CH}_2\text{—(CH}_2)_3\text{—CH}_2\text{—OH}$ b c d e c d f	a: 3.70–3.95 ppm, 6H; b: 4.25 ppm, 2H; c: 2.30, 2H; d: 1.40–1.65, 6H; e: 4.05, 2H; f: 3.65, 2H
5	$\overbrace{\text{O—OC—CH—R—CH—CO}}^{\text{a}} \text{ (CA)}$	4.17 ppm, 2H
6	$\text{CH}_2\text{=}\overset{\text{a}}{\underset{\text{CH}_3 \text{ b}}{\text{C}}}\text{—CO—O—}\overset{\text{c}}{\text{CH}_2}\text{—}\overset{\text{c}}{\underset{\text{O}}{\text{C}}}\text{—}\overset{\text{c}}{\text{CH}_2}$	a: 5.62 ppm, 1H, 6.19 ppm, 1H; b: 1.99 ppm, 3H; c: 2.68 ppm, 1H, 2.88 ppm, 1H, 3.28 ppm, 1H, 4.03 ppm, 1H, 4.50 ppm, 1H

sessile drop technique; advancing and receding angles were obtained by increasing or decreasing the drop volume until the three-phase boundary moved over the surface. The microsyringe needle was kept immersed inside the drop during the measurements. On every sample, at least nine measurements were performed, placing the liquid drops in different parts of the sample surface; their difference in the average value was no more than 2° .

RESULTS AND DISCUSSION

FTIR Analysis

The information obtained from the FTIR analysis gave an indication of the type of functional groups involved in the modification reactions. FTIR spectra of TX2CL(10), unmodified and modified with CA and GM, are reported in Figure 2. Thus, from a qualitative point of view, it can be noted that, with respect to unmodified copolymer TX2CL(10) [Fig. 2(a)], the spectrum of TX2CL(10)–CA [Fig. 2(b)] exhibits a marked decrease of the broad band at $3300\text{--}3600\text{ cm}^{-1}$ according to the reaction of hydroxyl with the anhydride groups. On the contrary, the spectrum of TX2CL(10)–CA–GM [Fig. 2(c)] shows the appearance of a broad peak in the region related to the stretching vibrations of hydroxyl groups, as expected from the reaction between the carboxyl terminal

groups of TX2CL(10)–CA and the epoxy group of GM. Similar considerations can be made for the other products.

$^1\text{H-NMR}$ Analysis

In Table I is reported the attribution of $^1\text{H-NMR}$ peaks for starting materials and final products.

Modification of TX2, TX2CL(5), and TX2CL(10) with CA

The spectrum of TX2–CA [Fig. 3(b)] indicates that the signal related to the methylene groups of PFPE adjacent to the hydroxyl groups [(3.9 ppm in Fig. 3(a)] is shifted at 4.2–4.3 ppm after esterification and has almost the same intensity of the signal of the CH groups of CA [4.05 ppm, slightly shifted in respect to the cyclic structure reported in Table I (5)], because of the ring-opening esterification: this is an indication that the expected reaction between the hydroxyl terminal groups of PFPE with anhydride groups occurred. Reaction can be assumed complete because the ratio between signals of the esterified methylene groups and of the remaining methylene groups of PFPE is 1:3, as expected.

In the case of PCL–PFPE–PCL block copolymers, conversion can be evaluated by comparing signals ranging from 3.6 to 4.3 ppm of TX2CL(10) and TX2CL(10)–CA [Fig. 3(a,b), respectively]: This latter shows a decrease of signal resonating in the

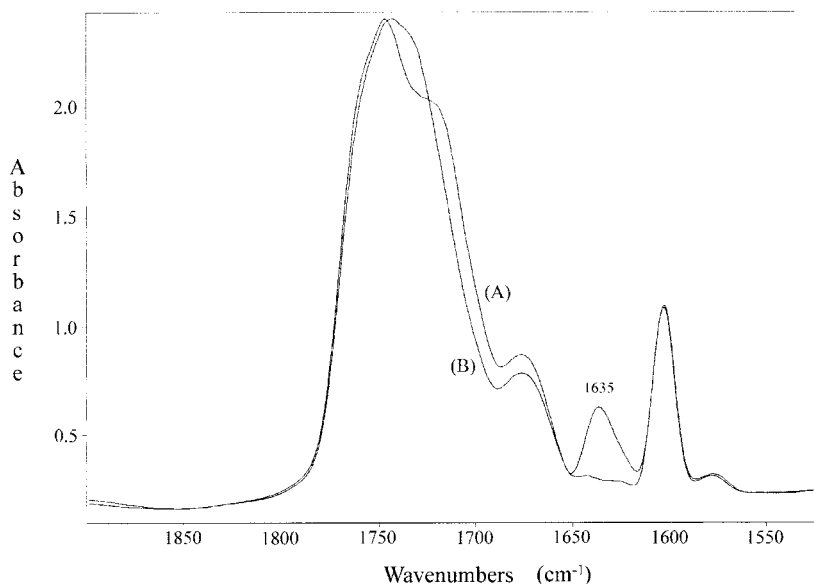


Figure 5 FTIR spectra of a TX2-CA-GM (curve A) before and (curve B) after UV irradiation.

region where the methylene groups adjacent to the hydroxyl terminal groups of PCL blocks (3.6–3.7 ppm) are located together with increase of the complex signal ranging from 3.95 to 4.15 ppm related to CH groups of CA residue, to esterified methylene groups after reaction with CA, and to the predominant methylene groups adjacent to ester groups of PCL blocks. Signal variations of TX2CL(10)-CA with respect to the unmodified copolymer indicate that the esterification reaction of the hydroxyl groups of TX2CL(10) takes place quantitatively. Similar considerations can be made for TX2CL(5),

in which the lower PCL content makes the quantitative determination of conversion easier.

Modification of TX2-CA, TX2CL(5)-CA, and TX2CL(10)-CA with GM

Spectra of TX2-CA-GM [Fig. 3(c)] and of TX2CL(10)-CA-GM [Fig. 4(c)] appear quite complex because of the superimposition of different signals in the region ranging from 3.2 to 4.5 ppm; however, it is possible to note the disappearance of signals corresponding to unreacted epoxy

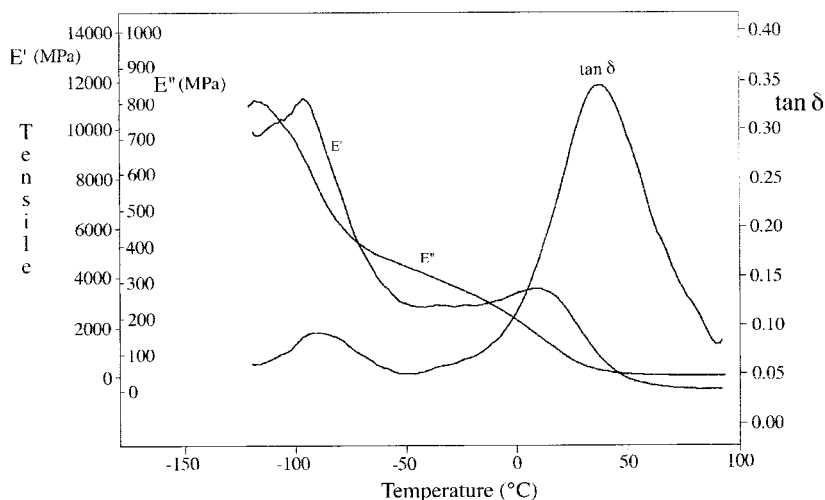


Figure 6 DMTA spectrum of a UV-cured TX2-CA-GM film (thickness about 100 m).

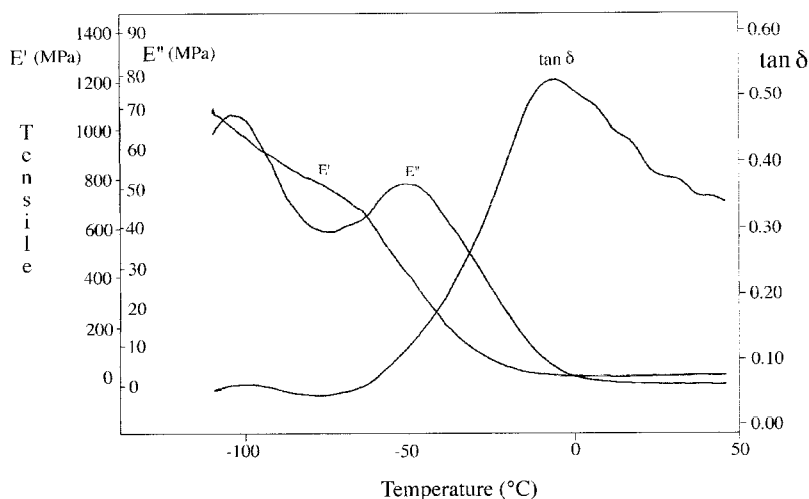


Figure 7 DMTA spectrum of a UV-cured TX2CL(5)-CA-GM film (thickness about 100 μ m).

groups (2.7, 2.9, and 3.25 ppm), indicating a complete conversion. Furthermore, in the case of TX2CL(10)-CA-GM, the ratio between normalized signals of the PCL blocks and of the $\text{CH}_2=\text{C}(\text{CH}_3)$ -methacrylic groups (2.0, 5.6, and 6.2 ppm) is equal to 10, which represents the value expected from stoichiometry. Once again, the same conclusions are valid for TX2CL(5)-CA-GM. In conclusion, information obtained from FTIR and $^1\text{H-NMR}$ analyses indicates that modification reactions with CA and GM take place quantitatively and with the formation of the expected products according to the scheme proposed in Figure 1.

Properties of the Films Obtained After UV Curing

Bulk Properties

The oligomers, with 4% w/w of the photoinitiator added, were UV-irradiated under a N_2 atmosphere using a glass sheet as the substrate. TX2-CA-GM and TX2CL(5)-CA-GM gave completely amorphous and transparent films having rubbery properties. TX2CL(10)-CA-GM was cured at 60°C; it gave an opaque film which showed, by DSC analysis, a crystallinity peak having T_m

= 43°C; the same peak was observed in the thermogram of the starting uncured oligomer.

A typical FTIR spectrum of the film obtained after UV curing of TX2-CA-GM is reported in Figure 5 (curve B) and compared to the oligomer before curing (curve A). The band at 1635 cm^{-1} , due to the methacrylic double bonds, disappears completely after irradiation. Therefore, the double-bond conversion is practically 100%. As far as the other two oligomers are concerned, the double-bond conversion observed showed the following values:

$$\begin{aligned} &\text{TX2CL(5)-CA-GM } 69\% \\ &\text{TX2CL(10)-CA-GM } 56\%. \end{aligned}$$

The incomplete conversion of double bonds can be attributed mainly to dilution effects, which increase by increasing the length of the PCL segments. In any case, these values of conversion are above those of the critical conversion of tetrafunctional monomers calculated from the Flory theory.¹⁹

The determination of the gel content on the films gave the following results:

Table II T_g Values of Cured Films by DMTA

	TX2-CA-GM	TX2-CL(5)-CA-GM	TX2-CL(10)-CA-GM
T_{g1} (°C)	-90	-99	-103
T_{g2} (°C)	+36	-6	-13

Table III Contact Angles of Water on Films Cured on Glass

Sample	θ_{adv} (°)		θ_{rec} (°)		Hysteresis	
	Side		Side		Side	
	Air	Glass	Air	Glass	Air	Glass
TX2-CA-GM	128	98	35	54	93	44
TX2CL(5)-CA-GM	118	93	31	43	87	50
TX2CL(10)-CA-GM	88	85	45	42	43	43

TX2-CA-GM 95%
 TX2CL(5)-CA-GM 88%
 TX2CL(10)-CA-GM 82%.

These data can be attributed either to the presence of small amounts of unfunctionalized products which increase by increasing the MW of the oligomers and/or to the incomplete double-bond conversion.

In Figures 6 and 7, the dynamic mechanical thermal analysis (DMTA) spectra related to UV-cured TX2-CA-GM and TX2CL(5)-CA-GM films are reported, recorded from -120 to 80°C . The spectra clearly show the biphasic nature of the films, indicating the presence of two T_g values: The former, T_{g1} , is close to the T_g of pure PFPE, and the latter, T_{g2} , is positioned at a higher temperature and can be attributed to a phase containing the hydrogenated moieties of the cured material. The obtained T_g values are reported in Table II.

The T_g values of the fluorine-rich phase are practically unaffected by the length of the hydrogenated segments, in agreement with previous results,¹⁴ while the T_g of the phase containing hydrogenated moieties is strongly decreased by the PCL segments ($T_{g,PCL} = -56^\circ\text{C}$).²⁰ Therefore, we can conclude that, after curing, the films are two-phase systems with an almost pure PFPE

phase and a second homogeneous phase containing PCL and the other hydrogenated moieties.

Surface Properties

The contact-angle values of water were performed on the cured films peeled off from two different substrates: glass and polypropylene (PP). The side in contact with air was labeled the air side, and the other side, the substrate (glass or PP) side. The values of advancing and receding angles and of hysteresis obtained for films peeled off the two above-reported substrates are collected in Tables III and IV.

The θ_{adv} angles decrease by increasing the content of caprolactone, that is, by decreasing the content of fluorine. For TX2-CA-GM and TX2CL(5)-CA-GM films, wettability is lower on the air side, indicating an enrichment of the fluorinated chains at the less polar film-air interface. Similar results were found for oligomers having urethane-acrylate PFPE structures.¹⁴ In the case of TX2CL(10)-CA-GM films, the asymmetry between the two sides practically disappears: therefore, in the presence of great amounts of PCL blocks, the surface enrichment of fluorinated chains on the air side is not evident. The hysteresis values are generally high, indicating a surface heterogeneity of the cured films.

Table IV Contact Angles of Water on Films Cured on PP

Sample	θ_{adv} (°)		θ_{rec} (°)		Hysteresis	
	Side		Side		Side	
	Air	PP	Air	PP	Air	PP
TX2-CA-GM	127	101	36	45	91	56
TX2CL(5)-CA-GM	116	88	32	42	84	46

With the aim to evaluate the effect of the polarity of the substrate on the surface properties, some films were cured on an apolar substrate such as polypropylene and then were subjected to surface analysis. The contact-angle values reported in Table IV indicate that the effect of the apolar substrate is not evident.

CONCLUSIONS

New telechelic macromers containing PCL-PFPE-PCL blocks end-capped with methacrylate groups were synthesized and characterized. Spectroscopic analyses (NMR and FTIR) confirmed the molecular structure of the products.

The films obtained after UV curing, examined by DSC and DMTA, revealed the presence of two amorphous phases, one containing almost pure fluorinated segments, and the other, hydrogenated moieties. The films obtained from the TX2CL(10)-CA-GM resin showed also a crystalline phase, due to the presence of sufficiently long PCL blocks. With the only exception of TX2CL(10)-CA-GM films, the products gave rise to transparent films: therefore, the dimensions of the domains, which have different refractive indices, have to be considered smaller than the wavelength of light.

The surface properties of the photopolymerized films were evaluated: the surfaces have a very high hydrophobic character in spite of the presence of many polar OH groups present in the polymeric network and a high hysteresis in wetting. An enrichment of fluorine at the surface in contact with air with respect to glass or the polypropylene side was found by contact-angle measurements, except for samples with long PCL segments [TX2CL(10)-CA-GM]. The θ_{adv} angles decreased by increasing the content of caprolactone, that is, by decreasing the content of fluorine. The results obtained suggest that the acrylic polyester resins containing PCL-PFPE-PCL blocks give rise, after UV curing, to a multiphase polymeric structure with interesting properties for high-performance applications.

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