Properties of Films Obtained by UV-Curing 4,4′-Hexafluoroisopropylidenediphenoldihydroxyethylether Diacrylate and Its Mixtures with the Hydrogenated Homologue

R. BONGIOVANNI,[1] G. MALUCELLI,[1] A. POLLICINO,[2] A. PRIOLA[1]

[1]Dipartimento di Scienza dei Materiali e Ingegneria Chimica, Politecnico di Torino, c. Duca degli Abruzzi 24, 10129 Torino, Italy

[2]Istituto Chimico della Facoltà di Ingegneria, Università di Catania, v.le A.Doria 6, 95125 Catania, Italy

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ABSTRACT: A new ultraviolet (UV)-curable acrylic monomer, 4,4′-hexafluoroisopropylidene-diphenoldihydroxyethylether diacrylate, was synthesized: it was cured as a film and its properties compared with those of its fully hydrogenated homologue. The introduction of two CF_3 groups into the monomer did not change its reactivity in the UV-curing reaction, but increased the glass transition temperature (T_g) of the cured polymeric film, decreased its refractive index (n), and lowered its surface tension. The fluorinated and the hydrogenated monomers were completely miscible and give homogeneous films: the T_g and n values were found linearly dependent on the fluorinated monomer content. The surface properties were deeply influenced by the presence of fluorine; a surface enrichment of the fluorinated monomer was evidenced by X-ray photoelectron spectroscopy analyses on the surfaces of the films obtained from mixtures of the two monomers. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 979–983, 1997

Key words: acrylated bisphenol A; UV-curing; surface properties; optical properties

INTRODUCTION

The introduction of fluorinated groups in polymer chains receives increasing attention as the improvement of their surface behavior, dielectric and optical properties, chemical stability, and solvent resistance allows interesting applications.[1,2]

In this context, 4,4′-hexafluoroisopropylidene diphenol has been proposed as a component of modified epoxy–resins: better chemical, thermal, and mechanical properties were obtained.[1] Therefore it seemed interesting to introduce this structure in an ultraviolet (UV)-curable system and to compare its performance with the corresponding nonfluorinated product.

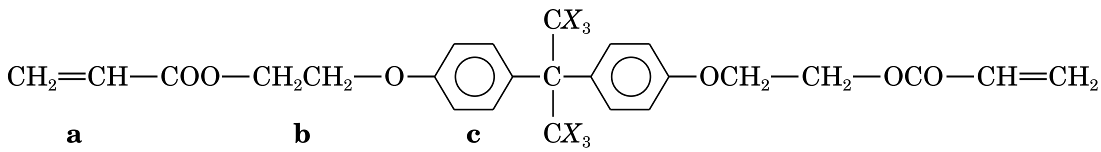
In this work we report an investigation on the properties of the films obtained by UV curing 4,4′-hexafluoroisopropylidenediphenoldihydroxyethylether diacrylate (BHEDAF) compared with the corresponding hydrogenated product (BHEDA). These monomers were used either pure or mixed in different ratios: both the surface and the bulk properties, such as the glass transition temperature (T_g) and the refractive index (n), were investigated.

EXPERIMENTAL

4,4′-isopropylidenediphenoldihydroxyethylether diacrylate (BHEDA) was kindly supplied by UCB

Correspondence to: A. Pollicino

(Drogenbos, Belgium). BHEDAF was synthesized by esterification with acrylic acid of the corresponding diol, kindly supplied by Atochem (Nanterre, France). The experimental procedure is described elsewhere.[3] The structure of the oligomers BHEDA and BHEDAF is reported below:



where X = F for BHEDAF, X = H for BHEDA, and a, b, and c indicate the different hydrogen groups, evidenced by nuclear magnetic resonance analysis.

In Figure 1 the ^{1}H-NMR spectrum of BHEDAF in $CDCl_3$ is reported. The main signals are the following:

- protons of type **a:** three bands in the range 5.8–6.6 ppm.
- protons of type **b:** two bands in the range 4.3–4.5 ppm.
- protons of type **c:** two bands in the range 6.9–7.4 ppm.

Table I collects other data in order to complete the information on the ^{1}H-NMR spectrum and check the purity of the product. Their $\overline{M_n}$, measured by vapor pressure osmometry, and their acrylic functionality are very close to the theoretical values. Moreover, the residual acid number is very low.

Films were prepared by UV curing the pure acrylates and their mixtures under nitrogen at-

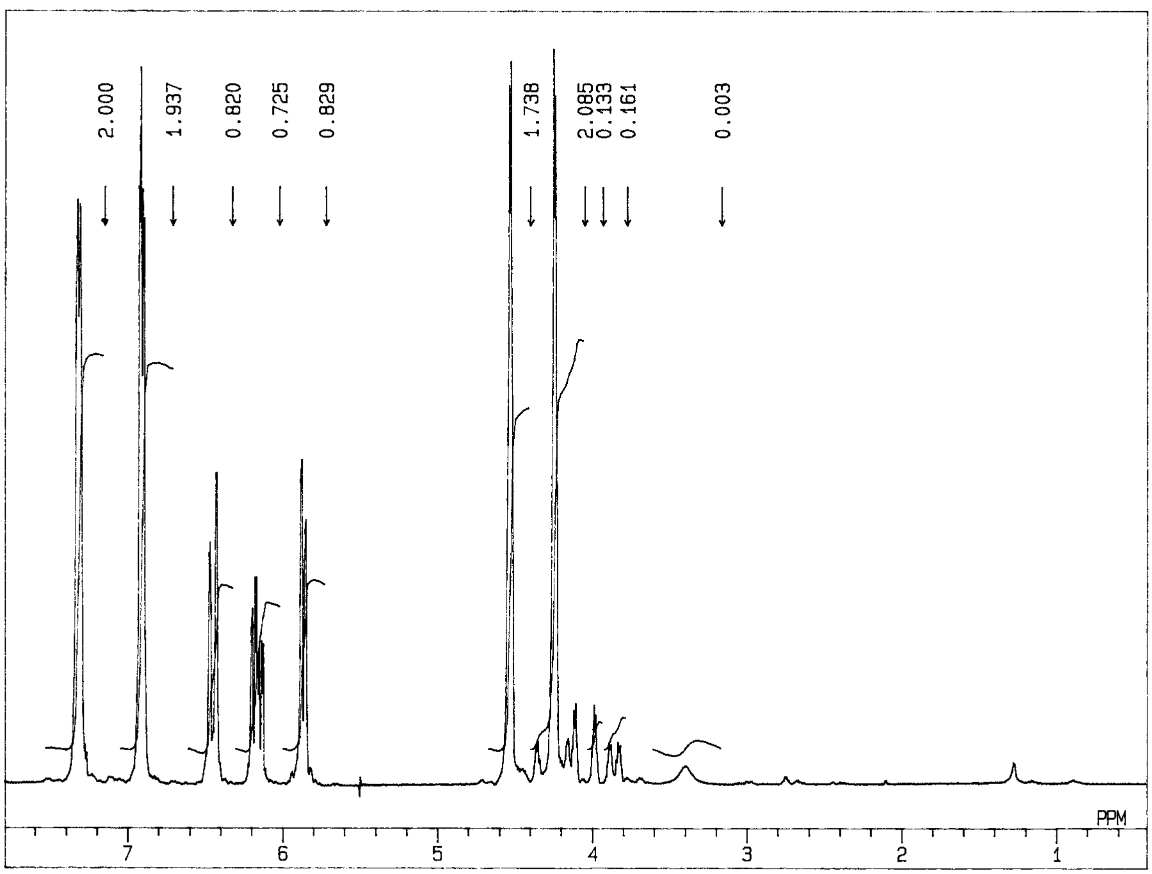


Figure 1 ^{1}H-NMR spectrum of BHEDAF in $CDCl_3$.

Table I Properties of BHEDA and BHEDAF

Property	BHEDA	BHEDAF
$\bar{M}_n$ (theoretical value)	428	536
$\bar{M}_n$ (experimental value)	424	533
Acid number[a]	6.3	2.1
Acrylic functionality	1.9	2.0

[a] Weight of KOH in mg for 1 g of sample.

Table II Bulk Properties of Pure BHEDA and BHEDAF Films

Property	BHEDA	BHEDAF
Double-bond conversion	83	82
T_g (°C)	34.1	57.0
n (λ = 580 nm)	1.9827	1.9314

mosphere, coated onto a glass substrate. The film side in contact with the substrate is labelled as the glass side; the opposite one as the air side. As photoinitiator, 2,2-dimethoxy-2-phenylacetophenone was used (4% wt/wt). The curing was performed with a mercury lamp having intensity of 6 mW/cm^2: three shots of 10 s assured a constant conversion of the acrylic double bonds. This value was measured by Fourier transform infrared (FTIR) analysis, using the reference band at 1635 cm^{-1}. The gel content was near 100% for all the samples after extraction with $CHCl_3$ for 24 h.

The surface properties of the films were evaluated through contact angle measurements according to an analytical procedures reported in another work.[4] The liquids used were bidistilled water and methylene iodide. In order to obtain the film surface tension, the data were processed according to the harmonic mean approximation.[5]

The T_g of the films was determined by differential scanning calorimetry analysis (Mettler TA 3000). The refractive index was evaluated at different wavelengths by measuring the reflectance of the film using a UV-near IR instrument (Perkin Elmer, Milan, Italy). The data were processed according to the following expression[6]:

$$R = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2}$$

where n is the refractive index and k the extinction coefficient, as determined by transmission measurements. X-ray photoelectron spectroscopy (XPS) measurements were performed by means of a VC Instrument MT500, equipped with a Clam II analyser, Twin Anod Mg/Al; more information is reported elsewhere.[7]

RESULTS AND DISCUSSION

Homopolymers of BHEDA and BHEDAF

Table II collects a few results on the bulk properties of the homopolymeric UV-cured films. The acrylic double-bonds conversion is rather high and practically the same for both monomers, indicating that the network crosslinking density is similar. On the contrary, BHEDAF films show a higher T_g compared with the hydrogenated (BHEDA) films: in fact, the presence of the trifluoromethyl groups linked to the polymer chain reduces the chain flexibility, in agreement with some recent results of other authors.[8]

The refractive index is lower for BHEDAF than for BHEDA, according to the typical optical behavior of the fluorinated polymers.[1,2,9]

Table III reports the surface properties of the films obtained from the pure monomers. The films containing fluorine show a clear increase of the contact angle with water; as a consequence, the surface tension decreases, mainly due to the lowering of the polar component γ_p.

Copolymers of BHEDA and BHEDAF

BHEDA and BHEDAF are miscible in all ratios. The mixtures can be UV cured in the same conditions as the pure monomers, giving rise to homogeneous and transparent films. Similar values of the double-bond conversion are obtained.

The thermal and the surface properties of the

Table III Surface Properties of Pure BHEDA and BHEDAF Films

Property	BHEDA	BHEDAF
Contact angle (°)		
Air side	$\vartheta = 75°$	$\vartheta = 91°$
Glass side	$\vartheta = 70°$	$\vartheta = 92°$
Surface tension (mN/m)		
Air side	$\gamma = 44.8$	$\gamma = 35.4$
	$\gamma_d = 32.8$	$\gamma_d = 34.2$
	$\gamma_p = 12.0$	$\gamma_p = 1.2$
Glass side	$\gamma = 45.9$	$\gamma = 36.4$
	$\gamma_d = 31.0$	$\gamma_d = 31.4$
	$\gamma_p = 14.9$	$\gamma_p = 5.0$

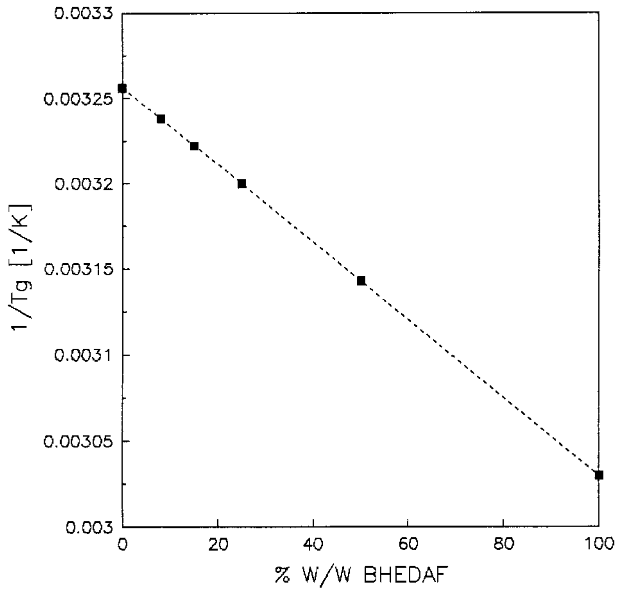


Figure 2 $1/T_g$ as a function of BHEDAF concentration.

films were examined. In Figure 2 the reciprocal of the T_g of these systems is plotted against the film composition. The results can be fitted by the Fox equation, showing that the copolymerization between the two monomers is of the random type.

In Figure 3 the refractive index n measured at different wavelengths is plotted as a function of the fluorinated monomer concentration: an almost-linear decrease of n by increasing the BHEDAF content is observed.

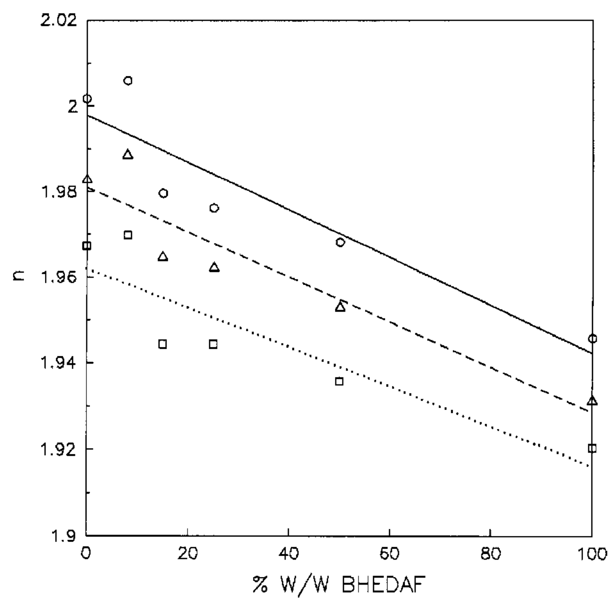


Figure 3 Refractive index as a function of BHEDAF concentration at λ = 530 nm (–○–), λ = 580 nm (–▷–), and λ = 700 nm (–□–).

Table IV Surface Properties of Films from BHEDA–BHEDAF Mixtures

% BHEDAF (w/w)	Surface Tension, γ (mN/m) Air Side[a]	Glass Side[a]
8	43 (12)	44 (12)
15	41 (12)	42 (12)
25	38 (7)	41 (12)
50	39 (7)	41 (12)

[a] γ_p shown in parentheses.

Table IV collects the surface tension values as a function of the fluorinated monomer content. The main results are the following:

1. γ decreases mainly on the air side and its value depends on the fluorinated monomer concentration.
2. The two sides of the films have different γ; the glass side is clearly more polar than the air side.

The asymmetry of the copolymer film surfaces is a very interesting aspect of these systems. It is even more evident examining the surface tension components: γ_p is larger for the glass side and remains constant (12 mN/m), while on the air side it decreases nearly one-half. Similar results were obtained by using fluorinated monoacrylate monomers in the UV-cured systems.[7,10]

Table V collects the XPS analyses performed on the cured films having a BHEDAF content equal to 25%. The F/C ratios clearly show a surface enrichment of BHEDAF on the air side. Analyses at different take-off angles show the existence of a concentration profile of the fluorinated monomer: its concentration decreases going from the air side towards the bulk. These data can ex-

Table V XPS Results for Films Containing 25% BHEDAF

Take-off Angle	F/C Atomic Ratio Glass Side[a]	Air Side[a]
30°	0.069	0.146
90°	0.051	0.114

[a] Theoretical F/C value: 0.060.

plain the increase of contact angle observed with water and the asymmetry of the surface tension on the two sides of the films obtained.

CONCLUSIONS

The results indicate that BHEDA and BHEDAF have similar behaviors in the UV-curing reaction. The substitution of H atoms with F atoms does not change the reactivity of the monomers in the UV-curing reaction. It does bring new properties to the films: a higher T_g value, a higher hydrophobicity, and a higher refractive index.

The evaluation of the properties of the films obtained by UV curing different mixtures of the two monomers shows that:

1. The modification of the bulk properties ($1/T_g$ and n) are linearly dependent on the monomers' concentrations. This behavior is typical of random copolymerization systems.
2. As far as the surface properties are concerned, the films show a high hydrophobicity on the air side and a difference in surface tension between the air side and that in contact with the glass substrate. XPS results allow the interpretation of these data, indicating a surface enrichment of BHEDAF at the air side of the cured films.

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