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Low surface energy polymeric films from partially fluorinated photocurable solventless liquid oligoesters

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Summary

We have recently shown that low surface energy polymeric films can be readily obtained from partially fluorinated hydroxyl-end-capped solventless liquid oligoesters by thermal curing [1]. Photocurable liquid oligoesters can be prepared by further substituting the remaining hydroxyl end groups with acrylic double bonds. A conventional photoinitiator containing 2-hydroxy-2-methylpropiophenone was used to cure the liquid oligoesters. As the fluorine content increases from 0 to about 1.57 wt %, the surface energy decreases by about 14 mN/m. The fluorine level in the outer few nanometers is significantly greater than that in the bulk, as revealed by XPS studies. The driving force for the surface segregation of fluorinated species comes from the large difference in surface energy between the oligoesters and their fluorinated counterparts.

Introduction

The purpose of our recent research is to manipulate self-stratifying polymeric systems, towards the goal of combining the best bulk properties with the optimum surface properties. One of the potential applications for such systems is a self-stratifying coating, where two direct advantages are offered: economic advantage of combining two or more application procedures in one, and an improved intercoat adhesion without sacrificing either bulk or surface properties. The driving force leading to self-stratification may be the incompatibility between polymer components, e.g., a large difference in the surface energy.

A few research groups have demonstrated various self-stratifying coatings, which include primarily solvent-borne systems [2-4] and, very occasionally, powder [5] and water-borne systems [6]. Many fundamental aspects regarding the stratification kinetics and mechanisms have not been fully addressed so far. On the other hand, the use of solvent in coatings has been becoming increasingly stringent in the world, and it is necessary to develop solventless (environmentally friendly) self-stratifying coatings. We therefore have been focusing on the following systems: solventless liquid polymer systems, water-borne systems, and powder systems.

In a previous paper [1], we have shown that self-stratified polymeric films with low surface energy (about 20-25 mN/m) can be readily obtained by using a thermally curable system composed of a partially fluorinated hydroxyl end-capped solventless liquid 3-armed oligoester and a liquid polyisocyanate crosslinker. The oligoester possesses a Tg of around -60 °C and an *M*n of 800 - 1000. Polymeric films were prepared from a mixture of normal and partially fluorinated oligoesters and a liquid polyisocyanate crosslinker, and cured at elevated temperatures. As the fluorine content in the films increases from 0 to about 1.4 wt %, the surface energy of the coating surface at the air/coating interface decreases by as much as 20 mN/m, indicating that this surface is mainly occupied by low surface energy fluorine-containing species. The fluorine level at the surface is dozens of times higher than that in the bulk. Meanwhile, the fluorine level at the surface becomes almost saturated at a fluorine content of about 1 wt %. Such a thin layer with low surface energy may introduce many interesting properties to a coating, such as increased hydrophobicity and oleophobicity, improved weatherability, low coefficient of friction, and so on [7].

In comparison with thermal curing, photocuring is a faster and less energy-consuming process and has been recently employed to obtain low surface energy films by Bongiovanni et al [8-13]. In most cases, they used a special fluorinated oligomer, perfluoropolyether, which is difficult to synthesize and mainly located in the middle of polymer main chains. Significant surface energy decrease was also reported in various UV curable systems containing fluorinated acrylic monomers [14-15].

The current work is a continuation of the previous research. After the fluorination of some hydroxyl groups, the remaining hydroxyl end groups in the 3-armed oligoester are further substituted by acrylic double bonds. The partially perfluoroalkyl-end-capped double-bond-containing oligoester can be readily photocured under UV irradiation. A thin fluorine-rich top layer can be also formed through self-stratification in such a solventless liquid oligoester system. A number of techniques will be employed to characterize the surface segregation of these novel fluorinated species.

Experimental

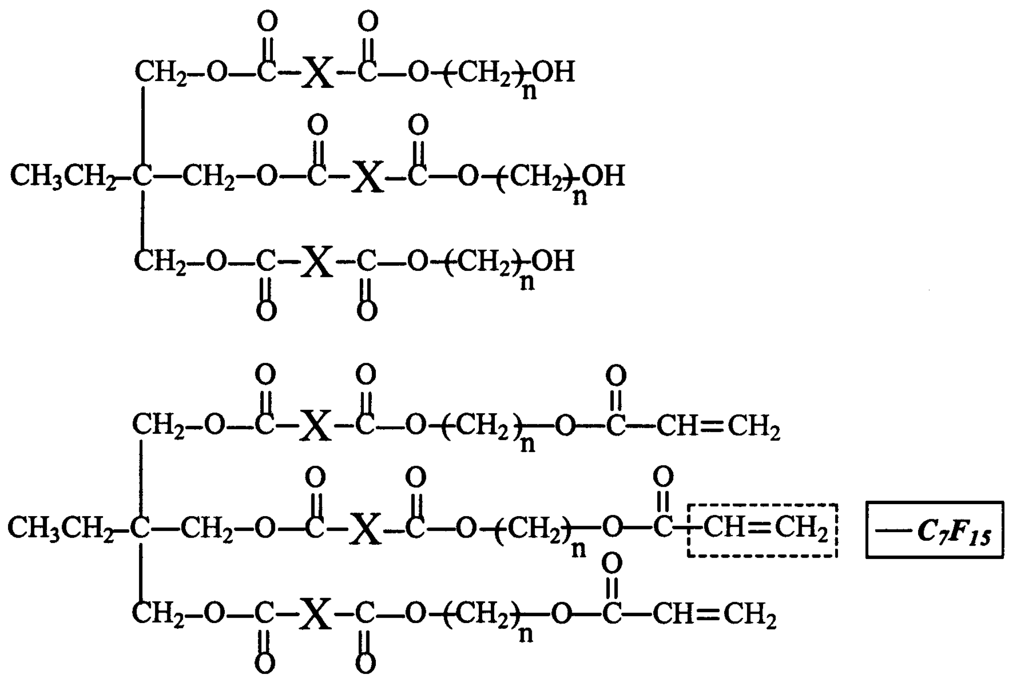
Materials

Acryloyl chloride (96%) and perfluorooctanoyl chloride (PFOC, 97%) were purchased from Aldrich Co. and Fluorochem Ltd., respectively, and used as received. Triethylamine and toluene were purchased from Merck and dried with anhydrous $MgSO_4$ before use. The photoinitiator DAROCUR 1700, comprising 75 % of 2-hydroxy-2-methylpropiophenone and 25 % of bisacyl phosphin oxide, was obtained from Ciba Specialty Chemicals and used without further purification.

Synthesis of Partially Fluorinated Photocurable 3-Armed Liquid Oligoesters

The synthesis of hydroxyl end-capped 3-armed solventless liquid oligoester (**1** in Figure 1) has been described in detail elsewhere [1], based on 1,4-butanediol, trimethyloylpropane, glutaric acid, adipic acid, and azelaic acid. The synthesis of partially fluorinated photocurable 3-armed liquid oligoester (**2** in Figure 2) is as follows. The first step is the partial fluorination. For instance, 10.0 g of liquid oligoester **1** (about 0.035 mol OH) and 0.21 g of dried triethylamine (10 % molar excess over PFOC) were firstly dissolved in 50 mL of dried toluene. 0.83 g of PFOC ($1.9X10^{-3}$ mol, 1/18 of the total OH amount) was then added dropwise under ice bath. The temperature was raised to ambient temperature and the reaction remained overnight. Following the partial fluorination, the remaining OH groups were further replaced by acrylic double bonds, through dropwise addition (under ice bath) of 3.62 g (0.04 mol) of acryloyl chloride diluted by 10 mL of toluene. The formed HCl was absorbed by additional 4.01 g of dried triethylamine. After another overnight reaction, the produced salt, $(CH_3CH_2)_3HN^+Cl^-$, was removed by filtration and the solution was distilled under reduced pressure to remove toluene, the left triethylamine, and unreacted acryloyl chloride. After drying under vacuum at 30 °C for 24 hours, the partially fluorinated photocurable liquid oligoester was obtained.

A non-fluorinated photocurable oligoester was also synthesized in a similar way without using PFOC. The fluorine content in the films can thus be adjusted by varying the ratio of partially fluorinated oligoester and non-fluorinated species.



1

2

X = equimolar mixture of $(CH_2)_3$, $(CH_2)_4$, and $(CH_2)_7$; n = 4

Figure 1. Structures of hydroxyl end-capped 3-armed liquid oligoester (1) and partially fluorinated photocurable 3-armed liquid oligoester (2) with a ratio between C_7F_{15} and $CH{=}CH_2$ being approximately 1/17.

UV Curing

The photocurable liquid oligoesters with different fluorine contents were mixed with 2 wt % of photoinitiator, DAROCUR 1700. The mixture was applied on clean aluminum substrates with a square applicator and then photocured by a mercury UV lamp under N_2 atmosphere. The UV light energy applied depended on the speed of the conveyer belt and was around 300 mJ/cm^2 in total for each sample.

Characterization Techniques

^{1}H NMR spectra were recorded on a Varian 400 spectrometer at 25 °C operating at 400.162 MHz, with $CDCl_3$ as the solvent. Infrared spectra were collected on a Mattson Polaris TM FTIR spectrometer at a resolution of 4 cm^{-1}. Glass transition temperatures (Tg) of oligoesters and films were determined on a Perkin Elmer Pyris 1 DSC instrument at a heating rate of 10 °C/min. Static contact angles were measured with deionized water and diiodomethane (>99%, Merck) on a contact angle microscope (G10, Krüss, Hamburg). The contact angles were averaged with 3-4 drops, and the difference was normally within 2°. X-ray photoelectron spectroscopy (XPS) spectra were collected at an electron takeoff angle of 0° (between surface normal and the analyzer axis) on a VG Ionex system equipped with a VG Clam II analyzer and Mg Kα X-ray source operating at 250 W. All C_{1s} peaks corresponding to hydrogen carbon were calibrated at a binding energy of 285.0 eV to correct for charging.

Results and Discussion

Characterization of partially fluorinated photocurable liquid oligoesters

The synthesis of partially fluorinated oligoester has been discussed in detail elsewhere [1,16]. After the first partial fluorination step, the remaining hydroxyl groups were further substituted by acrylic double bonds. The proton NMR spectra are shown in Figure 2. Before modification, a group of peaks in the range of 3.4 - 3.7 ppm (H_α in Figure 2) correspond to the methylene hydrogen next to a hydroxyl group. After the introduction of acrylic double bonds, not only these peaks disappeared since they changed into the methylene hydrogen next to an ester group, but also distinct peaks in the range of 5.6 - 6.4 ppm emerged in accordance with three hydrogens in the acrylic double bond ($H_=$). In addition, a small peak at 4.4 ppm (H_β’ in Figure 2) indicates the existence of the methylene hydrogen next to a perfluoroalkyl ester group. The peak area ratio between H_β’ and $H_=$ gives a C_7F_{15}/double bond ratio of about 1/20, which is in accordance with the starting experimental design (1/17).

The modification was also monitored by FTIR. As can be seen in Figure 3(b), after the partial fluorination a new peak originating from the perfluoroalkyl group appeared at 734 cm^{-1}, and a shoulder at 1780 cm^{-1} corresponds to the carbonyl next to C_7F_{15}. Meanwhile the intensity of the broad peak at around 3500 cm^{-1} decreased a bit (peaks are normalized according to CH stretch at 2942 cm^{-1}), suggesting a partial substitution of hydroxyl groups. Following the second modification step, OH absorption disappeared completely; besides, a number of new adsorptions emerged at 1637, 1407, 988, and 810 cm^{-1} [Figure 3(c)], which can be attributed to the double bonds.

A transparent film could be readily obtained by photocuring a mixture of partially fluorinated photocurable oligoester, normal photocurable oligoester, and a small amount of photoinitiator at ambient temperature for about 1 min. An infrared spectrum was collected for a photocured film (Figure 4). All adsorptions corresponding to double bonds either disappeared or decreased drastically, indicating that the majority of acrylic double bonds have been reacted. The glass transition temperature increased from -60 °C for the liquid oligoester to -22 °C for the photocured film.

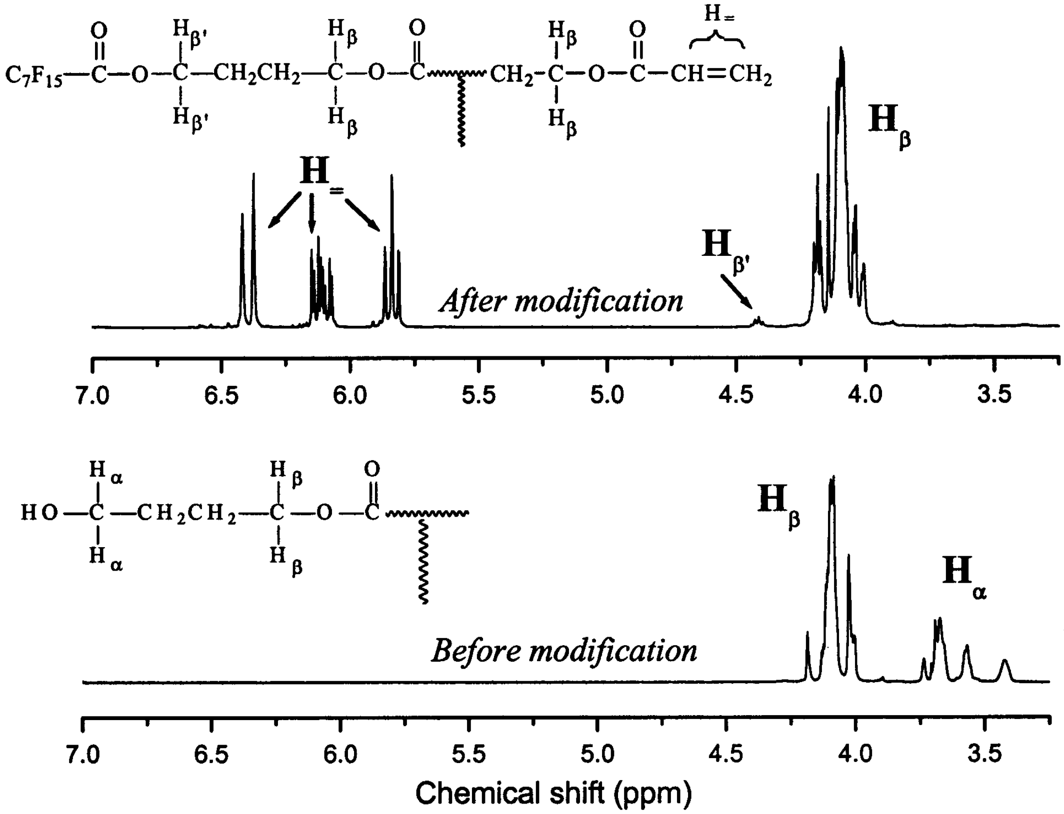


Figure 2. Proton NMR spectra (3.25 – 7.0 ppm) for a 3-armed liquid oligoester before and after modification.

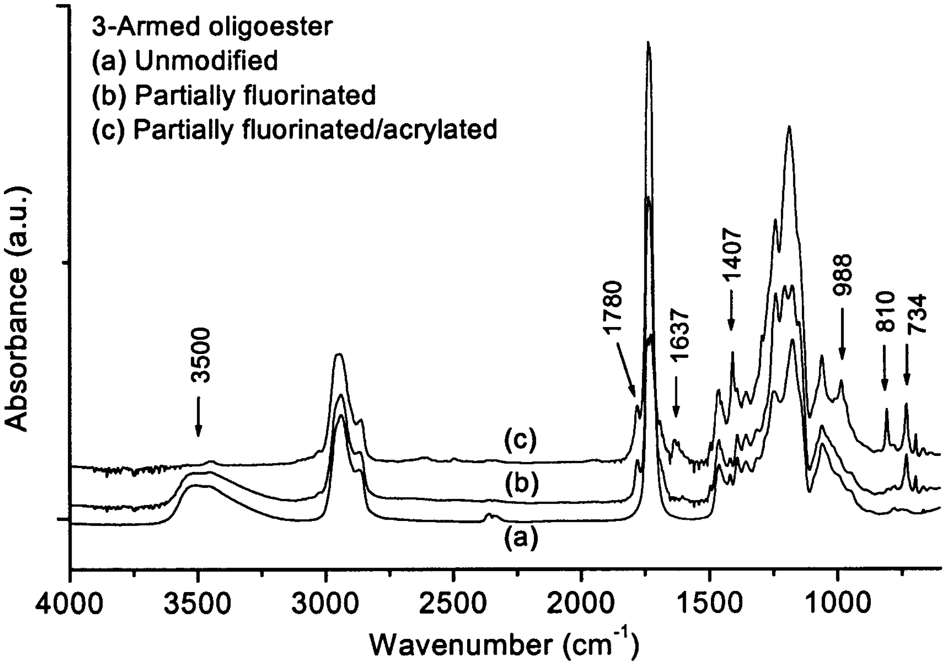


Figure 3. Infrared spectra for a liquid oligoester before and after modification steps.

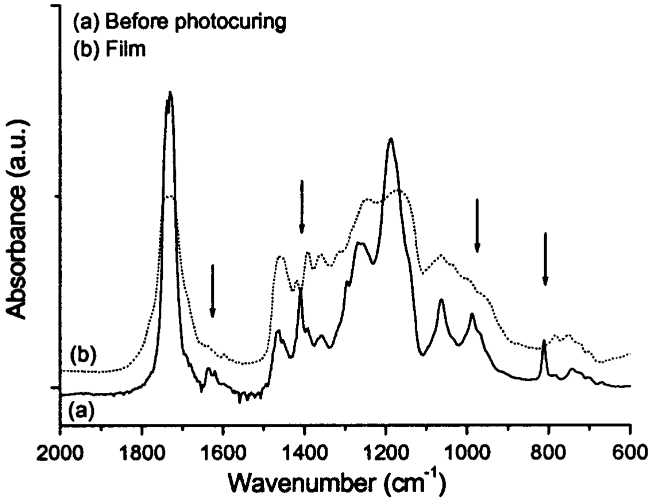


Figure 4. Infrared spectra for (a) a non-fluorinated photocurable liquid oligoester and (b) its photocured film. Arrows indicate the absorptions from double bonds.

Surface properties of photocured films

Figure 5 shows contact angle data of two liquids, i.e. water and diiodomethane, on the films with different fluorine contents as well as the surface energy of these films. As the fluorine content in the film increases from 0 to 1.57 wt % (the fluorine content is calculated on the basis of starting materials), the static contact angles for both water and diiodomethane have an increase of about 20°. It is clearly shown in Figure 5 (left) that the contact angle levels off at a fluorine content of about 0.8 wt %. After that, further increase of the fluorine content does not make a big difference on the contact angle. The surface energy of the films can be calculated by Wu's harmonic mean method [17] (H_2O: $\gamma = 72.8$, $\gamma^d = 22.1$, $\gamma^p = 50.7$; CH_2I_2: $\gamma = 50.8$, $\gamma^d = 44.\ 1$, $\gamma^p = 6.7$, all in mN/m) on the basis of contact angles. The surface energy decreases from 46.0 to 32.5 mN/m as the fluorine content increases to 1.57 wt %. It appears that the content of fluorine-containing species at the surface becomes saturated at the fluorine content of 0.8 - 1.0 wt %. This clearly shows a segregation of fluorinated species at the surface.

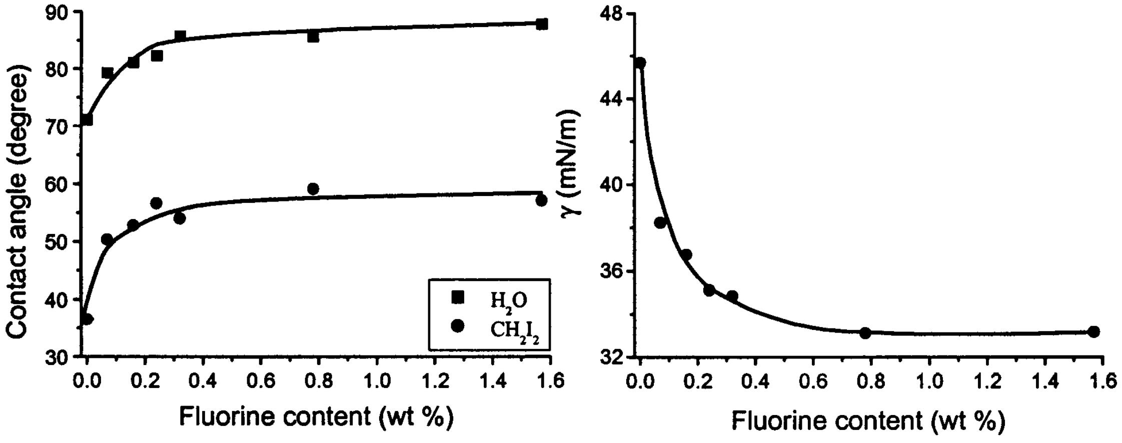


Figure 5. Contact angle of two liquids (left) and surface energy of the films (right) as a function of fluorine content in the films.

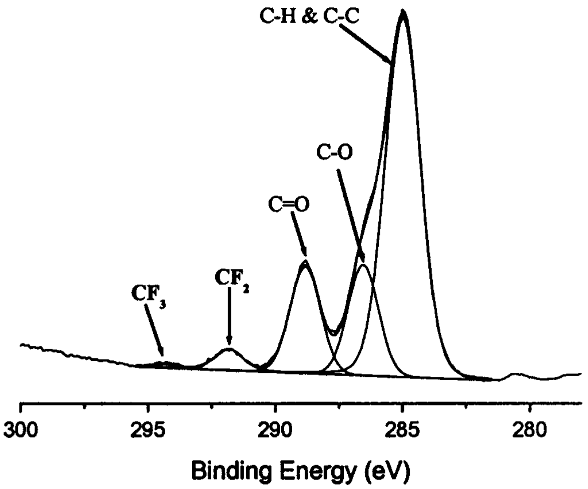


Figure 6. C_{1s} **XPS spectrum for the photocured film with 0.78 wt % of fluorine.**

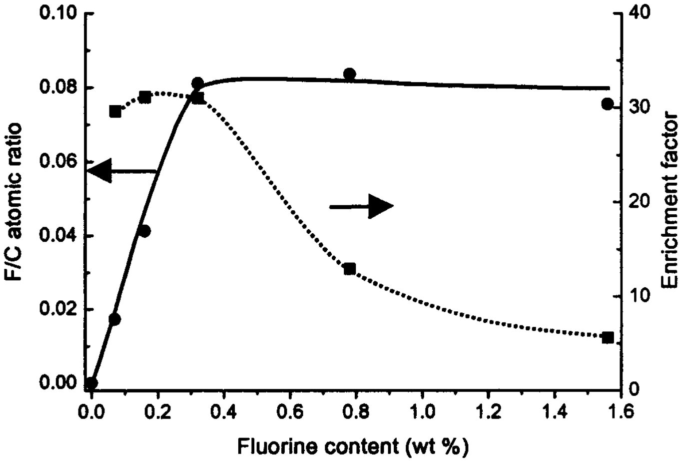


Figure 7. Surface F/C atomic ratio and surface enrichment factor of fluorine as a function of fluorine content in the photocured films.

The chemical composition at the surface of photocured films was examined by XPS. A take-off angle of 0° corresponds to a probe depth of about 10 nm [18]. The C_{1s} region of the XPS spectrum for the sample containing 0.78 wt % of fluorine is shown in Figure 6. Five distinctive peaks can be assigned to C-C & C-H, C-O, C=O, CF_2, and CF_3, respectively. On the basis of curve-fitting data, the F/C atomic ratio at about 10 nm depth can be calculated from the relative intensity of the CF_x peaks with respect to the total C_{1s} peak [18,19], as given in Figure 7. As the fluorine content increases, the surface F/C atomic ratio increases steadily until reaching a plateau level. This is consistent with contact angle results. Also shown in Figure 7 is the surface enrichment factor of fluorine, which is defined as the ratio between surface F/C and stoichiometric F/C level. In this series of samples, the surface excess of fluorine in the first 10 nm of the films ranges from 5- to 35-fold above the corresponding stoichiometric level.

In the photocured films, however, the surface enrichment of fluorinated species is less pronounced in comparison with the previously reported thermally cured oligoester films [1], where a surface enrichment factor of as high as 80 at about 5 nm depth (about 60 at *10* nm depth) was observed. The lower extent of fluorine enrichment is also evidenced by the less pronounced decrease of surface energy with the addition of similar level of fluorine in the photocured films than in the thermally cured films. There are presumably a few reasons. First of all, the chemical structure is not same in two systems: there is a large quantity of urethane moiety in the thermally cured films, which appears to have a higher surface energy than other components. Secondly, in the case of photocuring the crosslinking reaction is finished within 1 min., which allows much less time for low surface energy species to migrate towards the surface in comparison with the thermally cured system. Thirdly, photocuring is performed at ambient temperature; this may also limit the diffusion of fluorine-containing species. All of these may contribute to the lower extent of fluorine enrichment at the surface in the photocuring systems. Further investigation, for instance, by varying fluorinated tail length, is under way towards the better understanding of the segregation kinetics.

Conclusion

It has been demonstrated in this paper that low surface energy polymeric films can be readily obtained by photocuring the partially fluorinated photocurable solventless liquid oligoesters. The introduction of about 1.57 wt % of fluorine can effectively decrease the surface energy by about 14 mN/m. The fluorine level at the surface is dozens of times greater than that in the bulk, thus the top layer is mainly composed of fluorinated species.

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