Synthesis and Surface Properties of Films Based on Solventless Liquid Fluorinated Oligoester

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Received March 31, 2000; Revised Manuscript Received June 23, 2000

ABSTRACT: Two kinds of solventless liquid oligoesters, linear and three-armed, were synthesized by direct esterification of a mixture of diacids and diol or triol. The molecular weights of such oligoesters are in the range 800−1000. Linear oligoesters have a single melting point of between −5 and 0 °C while only one glass transition temperature at about −60 °C was found for three-armed oligoesters. The oligoesters were partially end-capped with a perfluoroalkyl group by reacting with perfluoroalkyl acid chloride. A polymeric film was prepared from the homogeneous mixture of normal and fluorinated oligoesters and a liquid polyisocyanate cross-linker and cured at elevated temperatures. As the fluorine content in the films increases from 0 to about 1.4 wt %, the surface tension of the top surface decreases as much as 20 mN/m, indicating that the top surface is mainly occupied by low surface energy fluorine-containing species. The surface enrichment of fluorine-containing species is confirmed by X-ray photoelectron spectroscopy (XPS) investigations. The fluorine level at about 5 nm depth is about 20−80-fold above its stoichiometric level, whereas the fluorine level at the surface becomes almost saturated at the fluorine content of about 1 wt %. Thus, a fluorine-rich surface with low surface energy can be readily produced based on solventless liquid oligoester systems. The driving force for the surface segregation (self-stratification) of fluorine-containing species comes apparently from the big difference of surface energy between oligoesters and their fluorinated counterparts.

Introduction

Self-stratifying coatings, namely coatings capable of producing multilayer structure in one operation, have been of increasing research interest recently.[1−6] Two direct advantages are offered: economic advantage of combining two or more operations in one and intercoat adhesion being improved. The driving force leading to self-stratification may be the incompatibility between polymer components, including the surface tension difference, cross-linking effect, and so on. A number of research groups have demonstrated various self-stratifying coatings, which were however mainly solvent-borne.[2−6] Other systems such as powder[1,7] and water-borne coatings[8] have been seldom studied. Meanwhile, the use of solvent in coatings has been becoming increasingly stringent in the world, and it is of importance to develop solventless (environmentally friendly) self-stratifying coatings. Here we will describe a solventless liquid coating system that is able to stratify during curing. The ultimate goal is to make an ideal coating that combines the best bulk properties with the optimized surface properties.

Fluorinated polymers have many properties that are desirable in coatings,[9−11] for example, water and oil repellency and cleanability by lowering the surface energy of the film.[12−25] The fluorine can be incorporated into the polymer main chain, e.g., by using fluorinated diols[14−17] or diacids, or on the side chain by introducing acrylate monomers with a long perfluoroalkyl group.[9,18−22] Surface tension reduction could also be realized by chemically grafting fluorinated groups to polymers.[25]

However, the previous studies have focused mainly on solvent-borne systems, i.e., most of the polymers were synthesized in solution and most of the films were prepared by solution spin casting. The use of organic solvents not only increases the expenses of application but also gives off VOCs (volatile organic compounds) or HAPs (hazardous air pollutants). Furthermore, most of the methods employed some difficult techniques[20−24] in order to achieve surface enrichment of fluorine, like using block copolymer with one block containing fluorine segments prepared by anionic polymerization. Specific handling of the polymerization is normally required. Besides, in most of the previous studies, a relatively large amount of fluorinated substances was used. The current work will provide an easy approach to prepare solventless liquid oligoesters[26] that are end-capped with a perfluoroalkyl group. A thin fluorine-rich top layer can be formed through self-stratification in such solventless liquid oligoester systems by cross-linking with a polyisocyanate agent, without dealing with any potential problems associated with organic solvents, and the fraction of fluorinated substances is not necessarily large for surface segregation. The occurrence of fluorine enrichment in the top surface of the films was examined by contact angle measurements and X-ray photoelectron spectroscopy (XPS).

Experimental Section

Materials. The diacids, including adipic acid (>99%), glutaric acid (>99%), and azelaic acid (about 88%), 1,4-butanediol (>98%), and 1,1,1-trimethyloylpropane (TMP, >99%) were purchased from Merck and used as received. A dialkyl tinoxide with a trademark of FASCAT 4101 was used as catalyst for direct esterification. Perfluoroalkyl agents, like pentadecafluorooctanoic acid (PFOA, 97%) and perfluorooctanoyl chloride (PFOC, 97%), were purchased from Fluorochem and used as received. A polyisocyanate cross-linker, under the trademark Desmodur N3300 and composed of the isocyanurate trimer of hexamethylene diisocyanate, was obtained from

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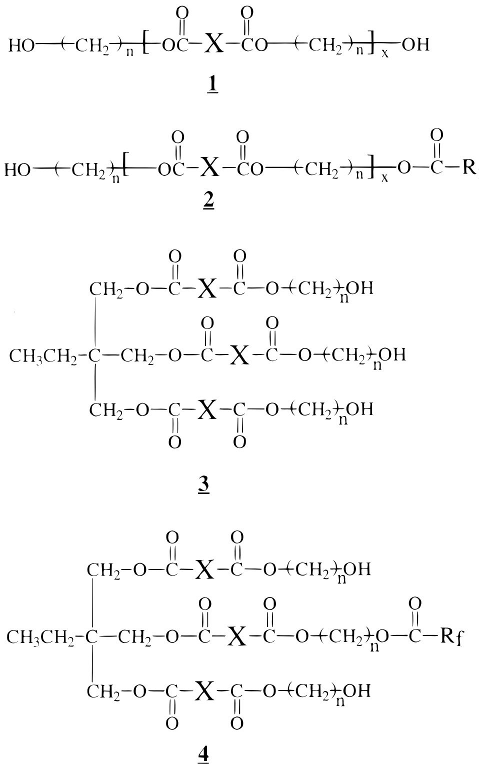


n = 4, 6
X = mixture of $(CH_2)_3$, $(CH_2)_4$, and $(CH_2)_7$
$R_f = (CF_2)_mCF_3$

Figure 1. Chemical structures of synthesized oligoesters.

Table 1. Surface Tension of Liquids at 20 °C (mN/m)

liquid	γ_L	γ_L^d	γ_L^p
water	72.8	22.1	50.7
methylene iodide	50.8	44.1	6.7

Table 2. Molecular Weights of the Solventless Liquid Oligoesters

oligoester[a]	area(H_β, 4.1 ppm)/ area(H_α, 3.7 ppm)	MW by ^1H NMR	hydroxyl no. (mg KOH/1 g)	MW by titration
Oligo-II-1	3.7	874	119	939
Oligo-II-1-F	4.3		110	
Oligo-II-2	3.6	833	133	840
Oligo-III-1	2.5[b]	914	184	915
Oligo-III-1-F	3.1[b]		137	

[a] Oligo-II and -III represent the oligoesters from diol and triol, respectively; an "-F" means the partially fluorinated oligoester. Oligo-II-1-F is the product of Oligo-II-1 and PFOA, while Oligo-III-1-F is the product of Oligo-III-1 and PFOC. [b] The peak area is the sum of a few split peaks around 4.1 and 3.7 ppm, respectively.

Bayer AG. Aluminum panels (0.6 × 76 × 152 mm) were purchased from Q-Panel Co.

Synthesis of Solventless Liquid Oligoesters. Two kinds of such oligoesters, linear or three-armed, were synthesized by direct esterification between a mixture of diacids and a diol or a triol (TMP). A typical synthesis procedure for oligoesters from diol (**1** in Figure 1, with both chain ends being hydroxyl group, and Oligo-II-1 in Table 2) is described as follows. To a 500 mL four-neck flask equipped with a mechanical stirrer, Dean-Stark trap, reflux condenser, thermometer, and nitrogen inlet was added a mixture of diacids (adipic acid, glutaric acid, and azelaic acid, 0.12 mol each), 1,4-butanediol (0.48 mol), and FASCAT 4101 (0.1% of total weight). The flask was gradually heated to 140 °C, raised to 200 °C over 3 h, and then kept at 200 °C until the amount of water collected in the Dean-Stark trap reached 95% of the theoretical amount. The three-armed oligoesters based on TMP could be prepared similarly. For example, for Oligo-III-1 (Table 2), the starting mixture included 0.1 mol of TMP, 0.3 mol of 1,4-butanediol, and three diacids of 0.1 mol each. The ideal structure would be **3** in Figure 1, but the product would actually be a mixture of different oligoesters.

Synthesis of Partially Fluorinated Solventless Liquid Oligoesters. The partially fluorinated oligoesters were prepared by reacting the previously synthesized oligoesters (in excess) with perfluoroalkyl acid (e.g., PFOA) or the corresponding acid chloride (e.g., PFOC). A three-armed fluorinated oligoester, **4** (Oligo-III-1-F in Table 2), was prepared by reacting 5.69 g of PFOC (0.013 mol) with 20 g of **3** (Oligo-III-1, about 0.08 mol of hydroxyl group) at 90−120 °C**,** with the latter being in large excess. PFOC was added dropwise into **3** in a period of about 3 h. Fast purging of nitrogen through the reactants would help the removal of the formed HCl. The theoretical fluorine content after partial fluorination is 14.7 wt %, and the actual content is 14 wt % as estimated from end group titration.

Film Preparation. A small amount of fluorinated oligoester was mixed with unfluorinated oligoester at 40 °C under magnetic stirring. An appropriate amount of Desmodur N3300 was then added by maintaining the OH/NCO molar ratio at 1. After a homogeneous mixture was formed, a coating was drawn down on an aluminum panel with a square applicator. The coating was then immediately cured at 80 °C for 30 min. The thickness for dry films was found to be 20−40 μm, as measured using a Twin-Check thickness gauge by List-Magnetic GmbH.

Measurement of Molecular Weight of Oligoesters. The average molecular weights of the synthesized oligoesters could be determined by proton NMR and inferred from the hydroxyl number of the oligoesters. Proton NMR spectra were recorded on a Varian 300 spectrometer using $CDCl_3$ as the solvent. The degree of condensation, d_C, can be estimated on the basis of the area ratio for certain peaks, as shown later.

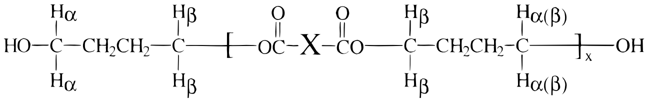
The hydroxyl number, i.e., the number of milligrams of potassium hydroxide equivalent to the hydroxyl groups in 1 g of material, was determined according to a test method, TM-2432 by DSM Resins. In brief, the hydroxyl groups in the oligoester are first acetylated with a known amount of acetic anhydride, the excess anhydride is decomposed with water, and the formed acetic acid is titrated with a methanolic potassium hydroxide solution. The average molecular weight of oligoesters could be deduced from the hydroxyl numbers since chain ends in the oligoesters are hydroxyl groups.

Contact Angle Measurements and Surface Tension Determination. Contact angles were measured with deionized water and methylene iodide (>99%, Merck) on a contact angle microscope (G2, Krüss, Hamburg). Dynamic advancing and receding angles were recorded while the probe fluid was added to and withdrawn from the drop, respectively, by a syringe pump from Harvard Apparatus. The photos of the drop were taken by a MXR CCD Camera from HCS Vision Technologies. The contact angles were measured on both sides of 3−4 drops, the difference was normally within 2°, and the results were averaged. The calculation of surface tension of the oligoester films was based on Wu's harmonic mean approach.[29] The surface tensions of liquids (γ_L) used in this study, as well as their polar (γ_L^p) and dispersion (γ_L^d) components, are listed in Table 1.

XPS Experiments. The XPS spectra were collected on a VG Scientific ESCALAB 200 photoelectron spectrometer with Al Kα irradiation (15 kV, 34 mA) at an electron takeoff angle of 30° (between the film surface and the axis of the analyzer lens). Data handling and analysis were performed on a VGS 5250 Data System. All C_{1s} peaks corresponding to hydrogen carbon were calibrated at a binding energy of 284.6 eV to correct the charging energy shift.

Results and Discussion

Synthesis of Solventless Liquid Oligoesters. Toward the goal to eventually eliminate the organic



$HO{-}C(H_\alpha)_2{-}CH_2CH_2{-}C(H_\beta)_2{-}[OC(=O){-}X{-}C(=O)O{-}C(H_\beta)_2{-}CH_2CH_2{-}C(H_{\alpha(\beta)})_2]_x{-}OH$

Figure 2. Different protons (H_α and H_β) in oligoesters.

solvents in coating systems, one of our strategies is to prepare solventless liquid oligoesters by direct esterification between diol or triol and diacid. The molecular weight of such oligoester will be targeted at around 1000. The use of a mixture of diacids is to reduce the regularity of the ester backbone and, consequently, the crystallinity of the resultant oligoester, which may ensure that the oligoester is in liquid state at ambient temperature. All the chain ends are hydroxyl groups (as shown in Figure 1), which will enable the further cross-linking of oligoester with polyisocyanate. The degree of condensation is controlled stoichiometrically. For example, when targeted degree of condensation for a linear oligoester (e.g., **1**) is 3, the OH/COOH molar ratio in starting raw materials would be 4/3, as previously depicted in Experimental Section. It is essential to remove the byproduct of the condensation (water) in time. At the late stage of reaction, the flow rate of nitrogen is increased to help the water removal and carry the condensation to completion.

Fluorine is introduced to reduce the surface tension of oligoester. The partially fluorinated oligoesters were synthesized via the dropwise addition of perfluoroalkyl acid chloride to the normal oligoesters. The reaction temperature is slightly below the boiling point of the acid chloride agent. It is noteworthy to point out that a fast purging of dry nitrogen is required to remove the produced HCl. The largely excessive amount of normal oligoester and the very slow addition of acid chloride allowed us to prepare the structure with at most one perfluoroalkyl end group per oligoester molecule. In the case of the fluorinated oligoester based on diol, each linear oligoester molecule will then have at least one hydroxyl group left after partial fluorination. For three-armed oligoester based on triol, at least two hydroxyl groups would remain. In both cases, the remaining hydroxyl groups will react with isocyanate group during the film formation to ensure the perfluoroalkyl groups are connected to the cross-linked network.

At the very beginning, we also tried to introduce the fluorine into oligoesters by using perfluoroalkyl diacid or diol. In that case the perfluoroalkyl groups are located inside the oligoester chain. It was found that for these systems the surface tension decrease is much less pronounced than that for perfluoroalkyl end-capped oligoesters. This may be due to two factors: perfluoroalkyl end group is more efficient in reducing the surface energy than that located in the middle of the chain, and the CF_3 group could contribute even more in the decrease of surface energy than CF_2.[27]

Characterization of Solventless Liquid Oligoesters. The ^1H NMR spectra for a linear oligoester **1**, and its fluorinated counterpart, **2**, are shown in Figure 3. The peak at 4.1 ppm corresponds to the proton (H_β in Figure 2) in the methylene connected with the ester group ($-CH_2-O-CO-$), while the peak at 3.7 ppm is attributed to the proton (H_α in Figure 2) in the methylene next to the hydroxyl group ($-CH_2-OH$). The degree of condensation, d_C (x), can be calculated from the peak area ratio of H_α and H_β.[26]

$$d_C = \text{area}(H_\beta)/\text{area}(H_\alpha) \qquad (1)$$

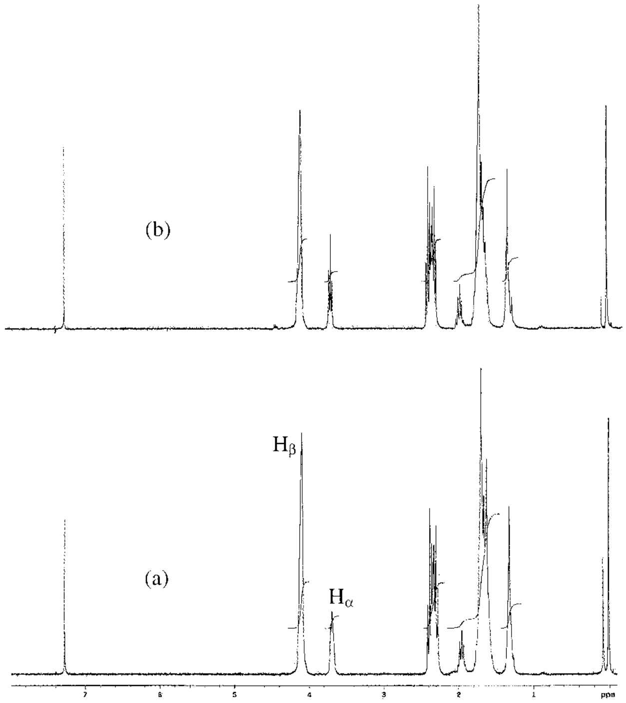


Figure 3. Proton NMR spectra of solventless liquid oligoesters before and after fluorination: (a) Oligo-II-1 and (b) Oligo-II-1-F.

Thus, the average molecular weight (M_n) of the oligoester can be calculated by the following equation

$$M_n = d_C[MW_{(diacid)} + MW_{(diol)} - 2MW_{(water)}] + MW_{(diol)} \qquad (2)$$

where $MW_{(diacid)}$, $MW_{(diol)}$, and $MW_{(water)}$ are the molecular weights of diacids, diol, and water, respectively. The molecular weight of three-armed oligoesters can be estimated similarly, but the d_C would be half of the ratio of area(H_β)/area(H_α) (see **3** in Figure 1). In Table 2 are listed the average molecular weights for various solventless liquid oligoesters; the MWs are in the range 800−1000. The melting points of linear oligoesters are in the range −5 to 0 °C (a single melting transition), as determined by differential scanning calorimetry (DSC) on a Perkin-Elmer 7 instrument. On the other hand, only one glass transition temperature (T_g) at −60 °C was detected for three-armed oligoesters. Low melting temperature or low T_g is indicative of the liquid state of these oligoesters at ambient temperature.

It can be also seen from Figure 3 and Table 2 that, after partial fluorination, the peak area ratio of H_β over H_α increases a little bit, suggesting that a few hydroxyl groups have been substituted by perfluoroalkyl carbonyl group.

To stoichiometrically match the OH/NCO molar ratio in the film preparation, the content of hydroxyl groups in the synthesized oligoesters must be known prior to the formulation of the coating films. The hydroxyl number can be readily determined by titration, as described in the Experimental Section. The hydroxyl numbers for several oligoesters before and after fluorination are given in Table 2. The molecular weight of oligoesters can also be deduced from the hydroxyl number, considering all chains are ended with a hydroxyl group. The MW values are also listed in Table

Table 3. Contact Angle Data for Films Based on Linear Oligoesters and Polyisocyanate Cross-Linker Cured at 80 °C

film[a]	water contact angle (deg) θ_{adv}	water contact angle (deg) θ_{rec}	CH_2I_2 contact angle (deg) θ_{adv}	CH_2I_2 contact angle (deg) θ_{rec}	surface tension (mN/m)[b] γ_S^d	surface tension (mN/m)[b] γ_S^p	surface tension (mN/m)[b] γ_S
non-F film	78	66	56	46	23.5	13.5	37.0
F-containing film	92	77	78	65	15.2	10.3	25.5

[a] Non-F film was stoichiometrically based on a mixture of Oligo-II-1 and Desmodur N3300, while for F-containing film, 4 wt % of F was incorporated into the Oligo-II-1-F. (Fluorine content in the film is 2.83 wt % after the composition correction for the amount of polyisocyanate cross-linker added.) [b] Surface tension was calculated from advancing contact angles.

2, which are in good agreement with those determined by proton NMR.

Contact Angle and Surface Tension of Oligoester Films. The surface tension of a polymer can be evaluated by various methods. Among them the contact angle method gives the information for the top surface, such as wettability.[27] On the basis of harmonic mean method[28,29] or geometric mean method,[29] one can calculate the surface tension of a film by measuring the contact angles of two different liquids, very commonly water and methylene iodide. Here, we will choose Wu's harmonic mean method. Combining the harmonic mean equation with the Young's equation gives[28,29]

$$(1 + \cos\theta_L)\gamma_L = 4\left(\frac{\gamma_L^d\gamma_S^d}{\gamma_L^d + \gamma_S^d} + \frac{\gamma_L^p\gamma_S^p}{\gamma_L^p + \gamma_S^p}\right) \tag{3}$$

where θ_L is the contact angle of the liquid on a surface, $\gamma = \gamma^d + \gamma^p$, and γ^d and γ^p are the dispersion and polar components of surface tension, respectively. If the γ^d and γ^p of two probe liquids are known, the dispersion and polar components of solid surface tension (γ_S^d and γ_S^p) can be obtained by solving the two simultaneous equations. Thus, the dispersion and polar characters of the surface will also be monitored.

Shown in Table 3 are contact angle data for the films based on linear oligoesters **1** and **2** and polyisocyanate cross-linker. The films were cured at 80 °C for 30 min. Compared to the film containing no fluorine, when about 2.8 wt % of fluorine was introduced to the film, both advancing and receding angles saw a considerable increase for both probe liquids, water and methylene iodide. The contact angle measurement was repeated either a few weeks later or after the film was rinsed with acetone. The change of the contact angle was found within ±2°, implying the film surface was quite stable, and the decrease of surface tension was not caused by the existence of small fluorine-containing molecules which otherwise would have been removed by acetone. The increase of contact angle by the addition of fluorinated species corresponds to the decrease of the surface tension of the film, i.e., from 37.0 to 25.5 mN/m.

We also estimated the surface tension by the so-called group contribution theory.[30] For oligoester **1**, with $x = 3$, the calculated γ is 42 ± 3 mN/m, while for fluorinated oligoester **2**, γ is 28 ± 3 mN/m. Although this is a rough estimation, the closeness between the predicted value and the measured surface tension value for the normal and partially fluorinated oligoesters suggests, to some extent, that the uppermost layer of the film is mainly occupied by the species with a perfluoroalkyl group, $(CF_2)_6CF_3$, which is the source of the lower surface energy. The big difference in surface tension between normal and fluorinated oligoesters is the driving force leading to the enrichment of F-containing species at the surface. This is also one of the most important strategies to prepare self-stratifying coatings.

Table 4. Contact Angle Data for Films Based on Three-Armed Oligoesters and Polyisocyanate Cross-Linker Cured at 80 °C

film[a]	wt % of added F	water contact angle (deg) θ_{adv}	water contact angle (deg) θ_{rec}	CH_2I_2 contact angle (deg) θ_{adv}	CH_2I_2 contact angle (deg) θ_{rec}	surface tension (mN/m)[b] γ_S^d	surface tension (mN/m)[b] γ_S^p	surface tension (mN/m)[b] γ_S
F-0	0	63	54	38	29	29.7	18.9	48.6
F-1	0.18	86	63	51	35	27.6	8.4	36.0
F-2	0.36	91	69	59	41	24.6	7.1	31.7
F-3	0.72	93	70	60	40	24.6	6.3	30.9
F-4	1.43	96	72	64	41	23.3	5.5	28.8

[a] Films were based on a mixture of Oligo-III-1 and Oligo-III-1-F, and the stoichiometric amount of Desmodur N3300. Fluorine content in the film was calculated from the recipe for oligoester synthesis and the amount of polyisocyanate cross-linker added. [b] Surface tension was calculated from advancing contact angles.

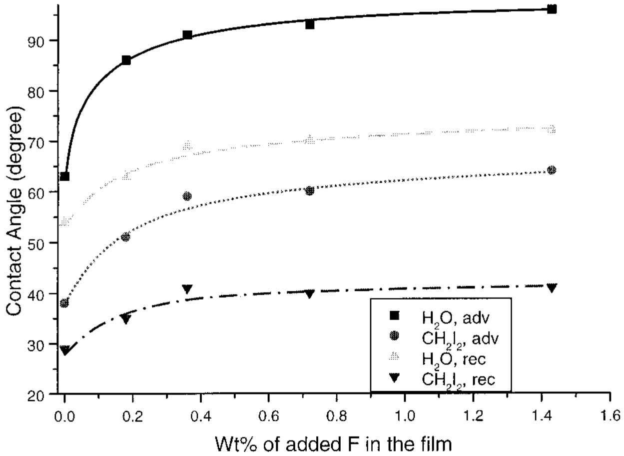


Figure 4. Contact angle change as a function of fluorine content in films cured at 80 °C and based on three-armed oligoesters and polyisocyanate cross-linker.

On the other hand, the packing of perfluoroalkyl group at the surface is far away from the close packing. For self-assembled perfluoroalkyl acid monolayer (close-packed CF_3), the water advancing contact angle is 112°–120°,[31] and even for poly(tetrafluoroethylene) (PTFE) film (CF_2 packing), the angle is measured to be 109°.[32] The highest value in our experiments is about 98°. Therefore, on the basis of the current contact angle data, it is hard to envisage any picture on polymer orientation and architecture at the air–polymer interface. The observed contact angle hysteresis, on the other hand, may imply that the domains of hydrocarbon-rich species (with higher surface tension) are also present at the surface. The film surface roughness in the 10 μm × 10 μm range is within 5 nm, as observed on a Dimension 3100 AFM from Digital Instruments, Santa Barbara, CA, under tapping mode, and it is therefore not the source for contact angle hysteresis. One other possible cause for the hysteresis is the surface rearrangement upon the exposure to the testing liquids, or so-called "kinetic hysteresis".[27,33]

In Table 4 and Figure 4 are shown the contact angle data for the film cured at 80 °C for 30 min based on three-armed oligoesters and polyisocyanate cross-linker. As the content of fluorine in the film increases from 0 to 1.43 wt %, the advancing contact angle for water increases more than 30°, while that of methylene iodide has an increase of about 25°. It is clearly shown in Figure 4 that the contact angles level off at the fluorine content of about 0.5−1 wt %. After that, further increase of fluorine content does not make a big difference on the contact angle. The decrease of the surface tension of the films demonstrates a similar trend, as listed in Table 4. It appears that the content of fluorine-containing species at the surface becomes saturated at the fluorine content of 0.5−1.0 wt %. At the fluorine content of 1.43 wt %, the surface tension of the film was measured to be 29 mN/m, much lower than the film where no fluorine was involved (48 mN/m). This, once again, clearly shows a segregation of fluorine-containing species at the surface.

The effect of the curing temperature on film surface properties was also investigated. When the coating was cured at 120 °C for 30 min, the contact angle changes for both liquids have a similar tendency with those of the films cured at 80 °C. The only major difference lies in that the contact angle change following the increase of fluorine content is less pronounced for the 120 °C-cured films than for their 80 °C-cured counterparts. This may be due to the faster reaction rate at 120 °C between hydroxyl groups in oligoester and isocyanate group in Desmodur N3300, which leads to the faster formation of the cross-linked network. As a direct consequence, the viscosity of the system would become high enough in a short period (compared to the case where a curing temperature of 80 °C was used) to prevent the migration of fluorine-containing low surface energy species. More work is under way on this issue. It is thus important to choose an appropriate curing temperature for the preparation of self-stratified films where a cross-linker is involved. It would be ideal if, by doing this, we could make the most of the very low level fluorine-containing species (lower than 2 wt % of fluorine) while achieving the best surface enrichment of low surface energy species at the surface in a period as short as possible.

XPS Analysis of Oligoester Films. In the XPS experiment, the sample of interest is irradiated with Al Kα X-ray as the kinetic energy of the emitted photoelectron is recorded. The analysis depth, *d*, is controlled by the mean free path[34] of the ejected photoelectron through the following simplified equation[35]

$$d = 3\lambda \sin \theta \tag{4}$$

where λ is the inelastic mean free path of electron and θ is the takeoff angle (between the film surface and the axis of analyzer lens). A nondestructive depth profile analysis of the outer about 10 nm of the film surface can be obtained by changing the takeoff angle. For typical polymer systems, a 90° takeoff angle corresponds to an integrated depth sensitivity of about 10 nm. In our experiments, the takeoff angle is 30°, and the detection depth is then around 5 nm.

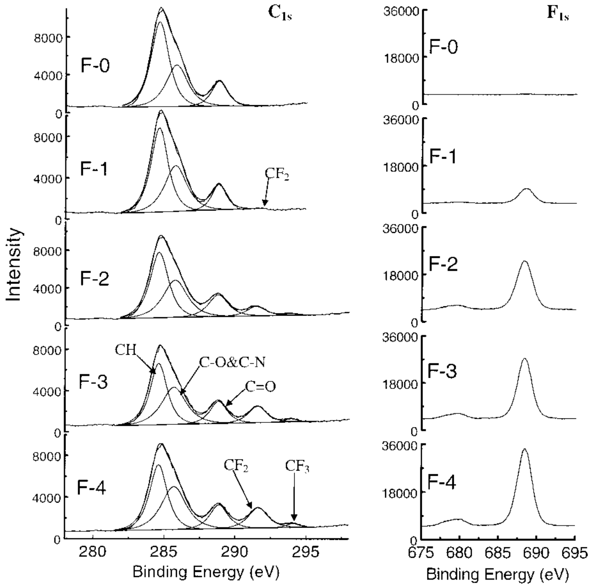


Figure 5. High-resolution XPS spectra of the films cured at 80 °C from a mixture of Oligo-III-1 and Oligo-III-1-F and the stoichiometric amount of Desmodur N3300. The takeoff angle is 30°.

Table 5. XPS Data for Films Based on Oligoesters and Polyisocyanate Cross-Linker

sample		F/C int ratio	surf. F/C atomic ratio	stoich F/C ratio	F surf. enrichment factor[b]
Oligo-III	F-0	0.022[a]	0.0044	0	
	F-1	0.53	0.11	0.0021	52
	F-2	1.77	0.36	0.0043	84
	F-3	2.27	0.46	0.0085	54
	F-4	2.52	0.51	0.017	30
Oligo-II-1	non-F	0.138[a]	0.028	0	
	F-containing	3.33	0.68	0.035	20

[a] Instrumental memory effect. [b] [Measured atomic F/C ratio]/[stoichiometric F/C ratio].

The C_{1s} and F_{1s} regions of the XPS spectra for the film surfaces with or without fluorine are shown in Figure 5. For codes of the films see Table 4. These films were cured at 80 °C, based on a mixture of Oligo-III-1 and Oligo-III-1-F and the stoichiometric amount of Desmodur N3300. The films from the linear oligoesters gave similar XPS spectra. In the C_{1s} region of these spectra, discrete peaks can be assigned to different functional groups. The peak assignments are (in electronvolts, after charging correction) as follows: C−H, 284.6; C−O/C−N, 285.8; C═O, 288.8; CF_2, 291.5; and CF_3, 293.9.

As the fluorine content in the film based on three-armed oligoesters and polyisocyanate cross-linker increases from 0 to 1.43 wt %, the peaks corresponding to CF_2 and CF_3 become more and more obvious, indicating the increasing surface enrichment of fluorine at the surface. As listed in Table 5, the fluorine over carbon (F/C) intensity ratio increases upon the increase of the stoichiometric fluorine content. On the basis of the F/C intensity ratio, we were able to estimate the F/C atomic ratio. In the analysis of XPS data, a uniform distribution of atoms is assumed, and the element ratios are then determined by using XPS sensitivity factors[24,34]

$$\frac{n_a}{n_b} = \frac{I_a}{I_b}\frac{I_b^\infty}{I_a^\infty}\frac{n_a^\infty}{n_b^\infty} \tag{5}$$

where *n* is the atomic density, *I* is the XPS signal density, and n^∞ and I^∞ are the atomic density and signal for the pure material. Wheeler reported that for PTFE standard film the F/C intensity ratio is 9.8,[36] which equals an F/C atomic ratio of 2/1. The calculated F/C atomic ratio for our systems is also given in Table 5 and plotted as a function of the fluorine content in the film in Figure 6. The stoichiometric F/C atomic ratio is well

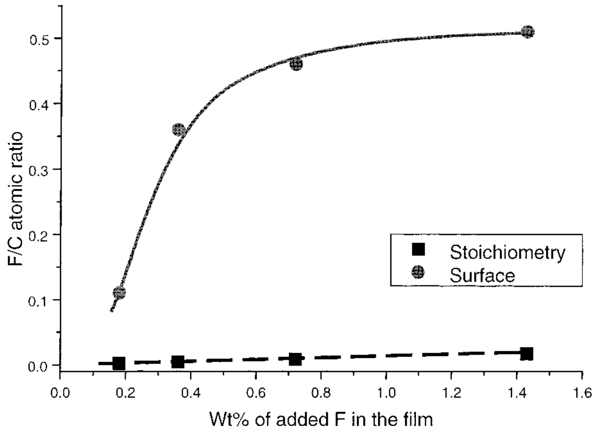


Figure 6. Surface F/C atomic ratio as a function of fluorine content in the films cured at 80 °C from a mixture of Oligo-III-1 and Oligo-III-1-F and the stoichiometric amount of Desmodur N3300.

below 0.02, but at the surface much more fluorine-containing species segregate. For example, when the stoichiometric F/C ratio is only 0.0043, the surface F/C atomic ratio is 0.36, about 80-fold higher than the former. In this series of samples, the surface excess of fluorine (at a depth of about 5 nm) ranges from 30- to 80-fold above the corresponding stoichiometric levels. This surface enrichment is quite close to the results in the literature,[18] where the surface excess of fluorine was observed in the acrylic polymers containing about 1.5 wt % of (perfluoroalkyl)ethyl methacrylate using a so-called "single shot addition" copolymerization. For the film based on linear oligoester, the surface enrichment of fluorine is also unambiguous (see Table 5). Figure 6 also clearly indicates that the surface F/C ratio becomes almost unchanged at the fluorine content of about 1 wt %. This is in good agreement with the contact angle measurements as depicted in Figure 4. It appears to be true that with the addition of fluorinated species containing only 1 wt % of fluorine, we are able to produce a fluorine-rich surface with much lower surface energy. Such films have shown good repellency against water and common organic solvents. It is anticipated that with angular dependence XPS or dynamic secondary ion mass spectroscopy (SIMS) we shall be able to show that the fluorine concentration decreases when the depth increases into the film.

Conclusion

It has been demonstrated in this paper that the surface with very low energy could be produced through the self-stratification in solventless liquid oligoester systems cured with a liquid polyisocyanate cross-linker, where organic solvent was eliminated. So-called "environmentally friendly" coating systems can therefore be developed. It has been shown from the contact angle and XPS investigations that only as low as 1.5 wt % of fluorine level is sufficient in producing a surface with a surface energy of about 29 mN/m. The fluorine level at the surface is dozens of times higher than that in the bulk. The top layer is mainly composed of fluorine-containing species. Such a thin low surface energy layer may introduce many interesting properties to a coating, such as chemical resistance, low friction, and so on. The investigations on the properties are under way.

Acknowledgment. This study was supported by CW-PPM in The Netherlands. The authors are grateful to Wouter van Gennip for XPS measurements and to Robert van de Grampel for his beneficial discussions.

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MA0005771