Macromolecules 1994, *27,* 1571-1577

Monolayers and Langmuir–Blodgett Films of Poly(*N*-acylethylenimines) with Hydrocarbon and Fluorocarbon Side Chains

J. M. Rodríguez-Parada,* M. Kaku, and D. Y. Sogah[†]

DuPont Central Research and Development,[‡] *Experimental Station,*
P.O. Box 80328, Wilmington, Delaware 19880-0328

Received July 16, 1993; Revised Manuscript Received November 30, 1993[●]

ABSTRACT: A series of poly(*N*-acylethylenimines) with hydrocarbon and fluorocarbon side chains varying in length from 6 to 17 carbon atoms were prepared by cationic ring-opening polymerization of 2-oxazolines. The behavior of monolayers of these materials at the air–water interface was studied in a Langmuir trough, and multilayer Langmuir–Blodgett (LB) films were prepared. Both monolayer behavior and LB film formation were strongly dependent on the size and nature of the side chains. Polymers with short hydrocarbon side chains (6–11 carbon atoms) form fluid liquidlike condensed monolayers in which the polymer backbone is at the water surface and the side chains are tilted toward the air. They can be easily transferred onto solid substrates, and uniform LB films can be prepared. Their thickness depends on the length of the polymer side chains. Polymers with longer side chains form only rigid monolayers which tend to crystallize after the initial compression, and LB films of these materials can be prepared only with difficulty. Similar behavior was observed for polymers with fluorocarbon side chains, with the only difference that the same effects are observed at shorter side-chain lengths (usually 3 less carbon atoms).

Introduction

Polymeric Langmuir–Blodgett (LB) films have been receiving increasing attention in recent years due to their superior mechanical and thermal stability over films of low molecular weight amphiphiles. Due to the possibility of making ordered structures, these films are finding more and more applications especially in the fields of electronics and optics.[1,2]

The simplest method to fabricate polymeric LB films is by deposition of monolayers of preformed polymers.[3,4] This method has the advantage that further processing of the films is not necessary, as opposed to polymerization of LB films prepared from amphiphilic monomers.[5–8] Although many classes of polymers have been studied at the air-water interface, only certain types can be used successfully for the fabrication of LB films. One of these types is comblike polymers with well-defined hydrophilic and hydrophobic groups which resemble low molecular weight amphiphiles.[9–20] Monolayer formation and LB film preparation in these polymers are determined by the balance of hydrophilic and hydrophobic interactions. Most comblike polymers studied are amphiphilic materials which have hydrophilic backbones and hydrophobic side chains. Although problems exist in the organization and transferring of monolayers of this type of polymer, some have been solved by the introduction of strong hydrophilic head groups and hydrophobic side chains placed regularly along the polymer chain,[10,18] as well as by the introduction of flexible spacers to decouple the motions of the backbone from the side chains.[11,14]

Besides varying the hydrophilicity of the backbone in comblike polymers, the hydrophobicity of the side chains can also be easily varied. One approach is to change the size of the alkyl side chains. Increasing their length increases the hydrophobicity of the polymer although it may also affect the packing of the side chains. Even though many polymers with different sizes of alkyl side chains have been investigated, there are very few systematic studies[13,16–18] in the literature about the effect of side-chain length on monolayer formation. In addition to influencing the behavior of monolayers, it also determines the incremental thickness in LB films prepared from them.

Another approach to change the hydrophobicity of the side chains in these polymers is to change the nature of the side chains. Substituting hydrocarbon side chains by fluorocarbon accomplishes this. In general, fluorocarbons are more hydrophobic and rigid than their hydrocarbon analogs and usually are not miscible with them. Due to these unique physical properties, low molecular weight amphiphiles containing fluorocarbon moieties have been studied at the air–water interface.[21–25] However, there are only a few reports in the literature about monolayers and LB films of comblike polymers with fluorocarbon side chains.[26–28]

In a previous publication[29] we have shown that poly(*N*-acylethylenimines) with hydrocarbon side chains form stable monolayers at the air–water interface and that uniform LB films can be easily prepared from them. The *N*-acylethylenimine backbone is well suited for monolayer formation since it is very hydrophilic and highly regular. The side chains are attached to the backbone on every third atom, which is a nitrogen, and tend to alternate on both sides of the main chain.[30] Furthermore, these polymers are prepared by cationic ring-opening polymerization of 2-oxazolines[31] which is a living polymerization and allows better control of the polymer architecture.

In this paper we describe the effect of varying hydrocarbon side-chain length on monolayer formation and LB film preparation of this type of polymer. The effect of replacing hydrocarbon side chains by perfluorinated side chains is also presented.

Experimental Section

Techniques. Pressure–area (π–A) isotherms were measured with a computer-controlled Lauda film balance FW-2 (Lauda GmbH, Germany), while preparation of LB films was carried out in a two-trough deposition system (KSV 5000; KSV Instruments, Finland) at 20 ± 0.1 °C. Both troughs were mounted on vibration isolation tables and inside laminar flow hoods. Deionized water,

---

[†] Present address: Department of Chemistry, Cornell University, Ithaca, NY 14853.

[‡] Contribution No. 6457.

[●] Abstract published in *Advance ACS Abstracts,* February 1, 1994.

0024-9297/94/2227-1571$04.50/0

passed through a Barnstead NANOpure II system, with resistivity higher than 17 MΩ cm was used as the subphase. Spreading solutions of the polymers with hydrocarbon side chains were prepared in HPLC-grade chloroform with concentrations between 0.5 and 1.0 mg/mL. Solutions of polymers with fluorocarbon side chains were prepared in chloroform or trichlorotrifluoroethane (Freon 113) containing 1–5% (by volume) hexafluoroisopropyl alcohol. Appropriate amounts (20–200 μL) were spread on the water surface, and the formed monolayers were then compressed at speeds ranging from 0.05 to 0.50 nm²/repeat unit·min. Normally several π–A curves were measured using different compression speeds and different spreading volumes to ensure reproducibility.

LB films were prepared by the vertical deposition method. Monolayers were transferred onto 25 × 50 mm silicon wafers (Semiconductor Processing Co., Type P; resistivity 15–25 Ω·cm, orientation 100). Usually the first layer was deposited in the upward trip at 2 mm/min while subsequent layers were deposited at speeds ranging from 5 to 20 mm/min. Film thickness was determined by ellipsometry with an automatic Rudolf Research AutoEL III instrument. Refractive indices of 1.46 and 1.30 were used for polymers with hydrocarbon and fluorocarbon side chains, respectively. Normally the average value of 40 points was taken.

Differential scanning calorimetry (DSC) was performed with a DuPont 9900 system at 10 °C/min under a nitrogen atmosphere. Molecular weights of polymers were determined by gel permeation chromatography (GPC) in a Waters HPLC 150C. Polymers with hydrocarbon side chains were run in THF using PS standards for calibration. Polymers with fluorocarbon side chains were run in hexafluoroisopropyl alcohol (HFIP) against PET standards.

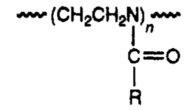
Monomer Synthesis. 2-Alkyl-2-oxazolines were prepared either from alkanenitriles or from the corresponding acid derivatives as described in the literature.[31,32] 2-(*n*-Perfluoroalkylethyl)-2-oxazolines were prepared from 3-perfluoroalkylpropionitriles. The following example illustrates the preparation of one of these monomers.

2-(*n*-Perfluorooctylethyl)-2-oxazoline. A total of 186 g (0.393 mol) of 3-(*n*-perfluorooctyl)propionitrile, 2.6 g (0.008 mol) of cadmium acetate dihydrate, and 200 mL of *n*-butanol were charged into a 1-L round-bottomed flask equipped with a thermometer, reflux condenser, dropping funnel, inert gas inlet and outlet, and magnetic stirbar. The flask was placed into an oil bath at 120 °C, and 28.5 g (0.466 mol) of ethanolamine was added dropwise. A slow flow of argon was maintained to carry off the ammonia formed during the reaction. The reaction mixture was stirred under these conditions for 48 h. At the end of the set reaction time the brown solution was cooled to room temperature and transferred to a 500-mL distillation flask attached to a Vigreux column and a distillation head. The butanol and excess ethanolamine were removed first by distillation under reduced pressure (water aspirator). Then the 2-oxazoline monomer was distilled off at 69 °C and 0.015 mmHg. A total of 165 g of a clear liquid which solidifies upon standing at room temperature was obtained. The monomer was further purified by dissolving it in 800 mL of chloroform and passing the solution through a column with basic alumina. After removal of the solvent in a rotary evaporator, the product was distilled again under high vacuum. Final yield: 157 g (77%). ¹H NMR ($CDCl_3$): δ 2.4–2.6 (m, $R_fCH_2CH_2$–), 3.85 (t, $-CH_2N-$), 4.28 (t, $-CH_2O-$). Elem anal. Calcd for $C_{13}H_8F_{17}NO$: C, 30.19; H, 1.56; N, 2.71; F, 62.45. Found: C, 30.58; H, 1.75; N, 2.98; F, 62.52.

Polymerizations. Polymerization of fluorinated monomers was carried out using *N*-methyl-2-(*n*-perfluorooctylethyl)-2-oxazolinium triflate as initiator while 2-alkyl-2-oxazoline polymerizations were initiated with *N*-methyl-2-methyl-2-oxazolinium triflate. These initiators were synthesized by the reaction of the corresponding oxazoline with methyl trifluoromethanesulfonate and were stable at room temperature if stored under an inert atmosphere. The following example illustrates their preparation.

***N*-Methyl-2-(*n*-Perfluorooctylethyl)-2-oxazolinium Triflate.** Into a dry 1-L round-bottomed flask equipped with a thermometer, dropping funnel, and magnetic stirbar and under an argon atmosphere were placed 50 g (0.305 mol, large excess) of methyl trifluoromethanesulfonate and 300 mL of anhydrous ethyl ether. The solution was cooled to 0 °C in an ice water bath, and 25 g (0.048 mol) of 2-(*n*-perfluorooctylethyl)-2-oxazoline was added slowly dropwise. A white precipitate forms during the addition, and the reaction is mildly exothermic. After the addition the reaction was allowed to stir and warm up to room temperature slowly. The precipitated product was filtered under an argon atmosphere, washed with anhydrous ethyl ether several times in the filter, and dried under vacuum. A total of 32 g (97% yield) of white crystals was obtained. ¹H NMR (CD_3CN): 2.64 (t of t R_fCH_2–), 3.04 (t, $-CH_2CNO-$), 3.30 (s, CH_3N-), 4.15 (t, $-CH_2N-$), 4.90 (t, $-CH_2O-$).

Table 1. Characterization of Poly(*N*-acylethylenimines) with Hydrocarbon Side Chains



$$\sim(CH_2CH_2N)_n\sim \quad N{-}C(=O){-}R$$

polymer R	$\bar{M}_w$[a]	$\bar{M}_n$[a]	T_m[b] (°C)	ΔH_m[b] (J/g)	monolayer thickness[c] (nm)
nC_6H_{13}	44 000	32 800	161	37	10
nC_8H_{17}	48 300	35 000	156	37	13
$nC_{10}H_{21}$	48 400	19 100	151	36	16
$nC_{11}H_{23}$	68 400	34 900	152	33	18
$nC_{12}H_{25}$	74 400	36 700	145	31	20
$nC_{13}H_{27}$	45 600	19 600	146	32	26
$nC_{14}H_{29}$	49 700	25 500	139	30	
$nC_{15}H_{31}$	104 000	48 400	142	27	
$nC_{17}H_{35}$	48 400	31 900	133	25	

[a] By GPC in THF against polystyrene standards. [b] By DSC at 10 °C/min. [c] By ellipsometry on LB films. Monolayers deposited at 30 mN/m.

All polymerizations were carried out in bulk under an argon atmosphere with monomer to initiator ratios varying from 100/1 to 500/1. The reactions were usually started at 80 °C and kept at this temperature until the polymerization mixture became so viscous that it could not longer be stirred. Then the temperature was gradually raised to 130 °C to finish off the polymerization. A typical example follows.

Poly[2-(*n*-perfluorooctylethyl)-2-oxazoline]. Into a 50-mL single-neck, round-bottomed flask equipped with a magnetic stirbar were placed 5 g (0.0097 mol) of 2-(*n*-perfluorooctylethyl)-2-oxazoline and 0.0132 g (0.000 02 mol) of *N*-methyl-2-(*n*-perfluorooctylethyl)-2-oxazolinium triflate initiator. The flask was filled with argon and stirred in an oil bath at 80 °C. After 1.5 h the polymerization mixture was a white solid. The temperature was raised to 130 °C, and the reaction was continued for an additional 3.5 h. After cooling to room temperature the polymer was dissolved in hexafluoroisopropyl alcohol, precipitated into methanol, filtered off, washed, and dried under vacuum at 80 °C overnight. A total of 4.33 g of a fine white powder was obtained.

Results and Discussion

Poly(*N*-acylethylenimines) with Hydrocarbon Side Chains. Table 1 lists the polymers with hydrocarbon side chains prepared along with their molecular weights and DSC characterization. The polymers were of moderate molecular weights, and their melting temperatures decrease as the length of the side chain increases. Most of them have been reported in the literature.[32] The molecular weights reported, although they were determined by GPC and are relative to other polymer standards, are generally lower than expected from the monomer to initiator ratios. Also the molecular weight distributions are rather broad (1.3–2.3). This is due to the fact that polymerization of 2-alkyl-2-oxazolines under the conditions used (e.g., in bulk) is usually accompanied by extensive chain transfer.[33] However, we have shown previously that the behavior of this type of polymer at the air–water interface is independent of molecular weight at degrees of polymerization higher than about 10.[29]

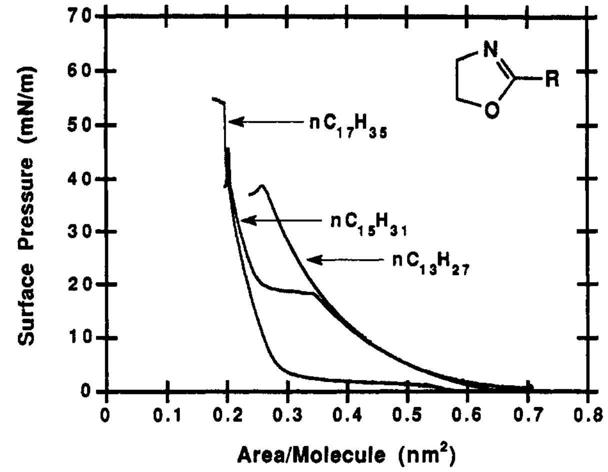


Figure 1. π–A isotherms of 2-alkyl-2-oxazoline monomers.

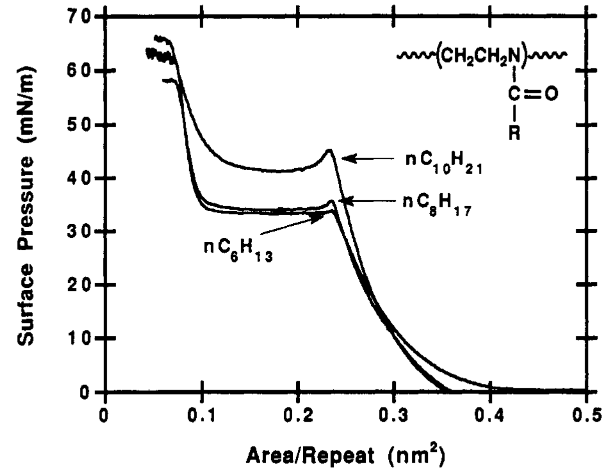


Figure 2. π–A isotherms of poly(N-acylethylenimines) with hydrocarbon side chains of 6, 8, and 10 carbon atoms.

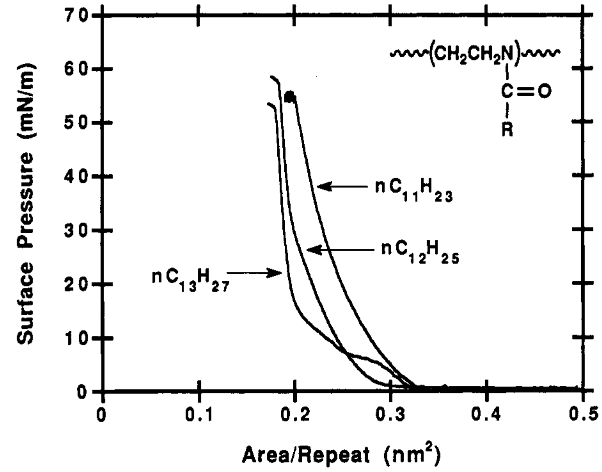


Figure 3. π–A isotherms of poly(N-acylethylenimines) with hydrocarbon side chains of 11, 12, and 13 carbon atoms.

Some of the 2-alkyl-2-oxazoline monomers themselves form monolayers at the air–water interface. Figure 1 shows the surface pressure–area (π–A) isotherms for some of these materials. Monomers with less than 12 carbon atoms in the side chain do not form monolayers as they are too soluble in water. This behavior is typical for hydrocarbon amphiphiles.[34] 2-Tridecyl-2-oxazoline forms an expanded monolayer which collapses at about 40 mN/m with an area per molecule at collapse of 0.25 nm^2. This indicates that even at collapse the side chains are not closely packed, since a value of 0.18–0.20 nm^2/molecule is usually found for close-packed monolayers of hydrocarbon amphiphiles.[34] The monomer with C14 side chains forms a slightly more stable monolayer which exhibits a similar π–A isotherm.

The isotherm for the C15 monomer shows formation of an expanded monolayer as the monomer is compressed to about 22 mN/m. At this point a transition region starts and eventually a condensed monolayer is formed. It then collapses at 47 mN/m with an area per molecule of 0.19 nm^2, indicating well-packed hydrocarbon chains. The C17 compound forms only condensed monolayers which collapse at about 55 mN/m and 0.19 nm^2/molecule. As expected, increasing the length of the hydrocarbon chain in these monomers increases the tendency to form more stable condensed monolayers with higher collapse pressures.

Attempts to prepare LB films of these monomers on hydrophilic silicon substrates were not successful. A single monolayer is deposited on the upward trip upon withdrawing the substrate through the monolayer. However, on the downward trip the monolayer is removed from the substrate.

Contrary to the monomers, all poly(N-acetylethylenimines) prepared form stable monolayers at the air–water interface. Even polymers with six carbon atoms in the side chain formed monolayers. The behavior of these monolayers depends strongly on the length of the side chains, and in general three different types of isotherms were observed. Figure 2 shows typical π–A isotherms for the polymers with 6, 8, and 10 carbon atoms in the side chains. All curves exhibit a "knee" and a "plateau" region. The average area occupied by each polymer repeat unit at the knee is 0.23–0.24 nm^2 for the three materials. This is larger than the cross-sectional area of an alkyl chain, indicating that the alkyl chains are not densely packed at or below the knee pressures and the monolayer is in a liquidlike state.

Compression–expansion of these monolayers shows that for pressures below the knee the isotherms are perfectly reversible and there is no hysteresis. However, on compression to areas smaller than at the knee, excessive hysteresis is observed. When the film is compressed beyond the knee, it collapses. When compression is limited to areas within the plateau region, the monolayer respreads on decompression. This is often referred to as reversible collapse of the monolayer.[35] However, when the monolayer is compressed beyond the plateau region, irreversible collapse occurs.

The behavior of this type of monolayer was found to be independent of the polymer molecular weight and has been explained before.[29] It was suggested that at low surface pressures the polymer molecules lie flat on the water surface with the side chains tilted toward the air. As the pressure increases, the side chains tilt further away from the water. At the knee the side chains are roughly perpendicular to the interface. At areas below the knee the polymer backbones must be partially lifted from the water surface, producing irregular and partially collapsed film structures. The extent of the collapse will determine whether or not the monolayers will reform upon decompression.

Figure 3 shows the π–A curves obtained for polymers with 11, 12, and 13 carbon atoms in the side chains. Unlike those of polymers with shorter side chains, the isotherms do not show a plateau region. The curve for the C11 polymer is very similar to those of the previous polymers up to the knee point. It is perfectly reversible and indicates formation of a liquidlike monolayer. It collapses at about 54 mN/m (higher than the knee pressure for monolayers of polymers with shorter side chains) and 0.20 nm^2/repeat,

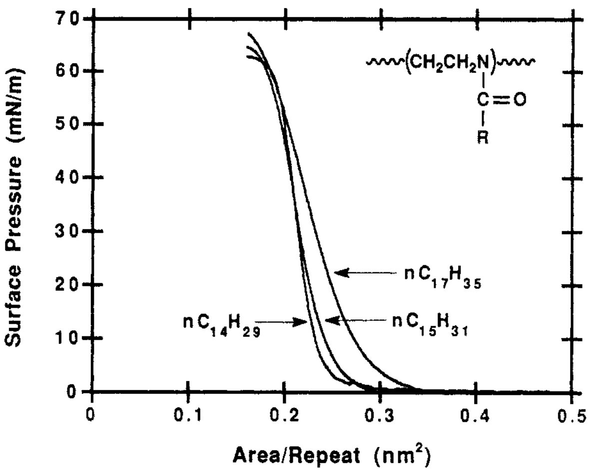


Figure 4. π–A isotherms of poly(N-acylethylenimines) with hydrocarbon side chains of 14, 15, and 17 carbon atoms.

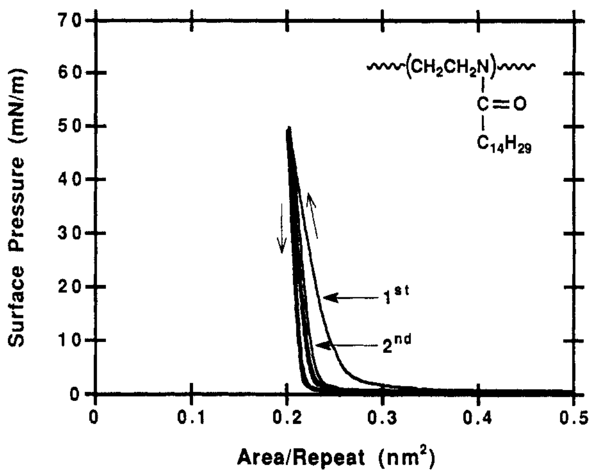


Figure 5. Compression–expansion isotherms of poly(N-pentadecanoylethylenimine).

indicating also a tighter packing of the hydrocarbon side chains at this point.

The polymer with C12 side chains shows an isotherm corresponding to a more condensed monolayer. Two different regions can be seen. They resemble the liquid-condensed (up to about 30 mN/m) and solid (up to collapse at 58 mN/m) states of monolayers of low molecular weight amphiphiles,[34] although the transition point is not as sharp as the one seen for these compounds. However, this is expected for high polymers because they usually form more viscous monolayers.

Monolayers of the C13 polymer show, in addition to the condensed phases observed for C12, an expanded phase below 5 mN/m. As the monolayer is compressed above this pressure, there is a transition to a condensed phase, and finally above approximately 15 mN/m a solidlike monolayer which collapses at about 52 mN/m is obtained. Isotherms for both C13 and C12 polymers are reversible and show little or no hysteresis. Both show at high surface pressures average areas of 0.18–0.19 nm^2/repeat unit, indicating tightly packed alkyl side chains in these solid phases.

Isotherms for monolayers from polymers with longer side chains are shown in Figure 4. All these materials form very rigid, condensed monolayers which collapse above 60 mN/m. The area per repeat unit at collapse indicates that the alkyl side chains are closely packed at this point. Even though, at lower pressures, the isotherms look like those of more expanded monolayers, this is only so during the initial compression. Figure 5 shows compression–expansion curves for one of these polymers. After the first cycle to 50 mN/m, the compressibility of the monolayer changes and the following cycles show only a very steep rise in pressure characteristic of solidlike packing. This behavior has been attributed before to rearrangements in the monolayer.[35] Probably when the monolayer is initially spread at the air–water interface, the polymer molecules are uniformly distributed on the surface with their backbones at the interface and the side chains tilted toward the air. As the pressure increases during the first compression, the side chains tilt further away from the water and start packing tightly like in the previous cases. However, since the side chains are now longer, they can crystallize and after releasing the pressure they do not respread to the same state. Instead they could remain on the water surface as islands of crystallites.

From these results, the effect of the side-chain length upon monolayer formation in this class of polymers can be clearly seen. When the side chains are short (6–10 carbon atoms), the polymers form liquidlike compressible monolayers in which all segments of the backbone are lying in the water surface and the side chains are tilted toward the air but not closely packed. As the length of the side chain increases and there are stronger hydrophobic interactions between them, more condensed phases start to appear and solidlike monolayers are formed at high surface pressures (C12 and C13). Polymers with even longer side chains (C14 and above) form only rigid solid monolayers which tend to crystallize after the initial compression.

Fabrication of LB films of all these polymers was attempted by depositing their monolayers onto silicon wafers using the vertical deposition method. Monolayers of polymers which show a plateau in their π–A isotherms (C6, C8, and C10) can be easily deposited onto the solid substrate at pressures below the knee point. Y-type multilayers are normally obtained, but Z-type films of equal quality can also be prepared using a two-trough deposition system: in the downward trip the substrate is passed through pure water and in the upward trip through the monolayer. Deposition ratios are usually 1.0 ± 0.1 in either case. Ellipsometry shows that these films are uniform across the entire substrate area. Even films consisting of 100 or more monolayers show thickness variation of less than 1 nm.

Monolayers of the C11 polymer can also be easily deposited at any pressures below collapse to give very uniform films. Figure 6 shows the plot of thickness of LB films from this polymer, measured by ellipsometry, versus the number of monolayers in the films. As can be seen in the figure there is a very good linear correlation of film thickness with the number of layers.

As the length of the side chain increases, LB film preparation becomes more difficult. Monolayers of C12 can still be deposited easily, but monolayers of C13 are already too rigid at high pressures and the transfer mode seems to change. With even longer side chains (C14, C15, and C17) a single monolayer could be easily transferred onto silicon, but afterward transfer deteriorates rapidly and uniform LB films with a large number of layers could not be obtained under the experimental conditions investigated.

The thickness of monolayers in the LB films of all these materials was measured by ellipsometry, as is also shown in Table 1. As expected, it increases as the side-chain length increases. However, the increment does not correspond to that expected for a fully extended hydrocarbon chain perpendicular to the film. It is actually larger. This

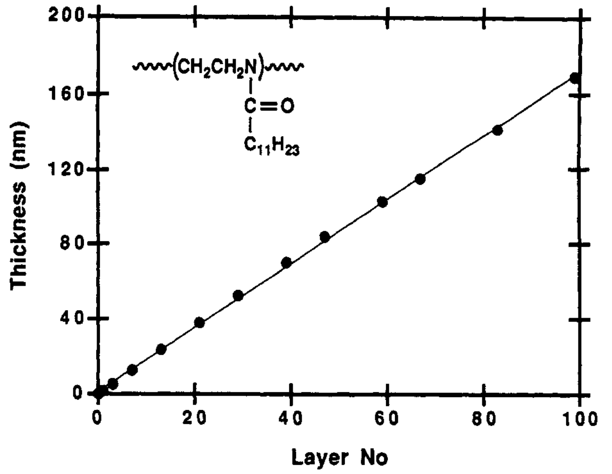
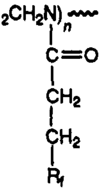


Figure 6. Thickness versus number of monolayers for LB films of poly(*N*-dodecanoylethylenimine). Monolayers deposited onto silicon wafers at 5 mm/min and a surface pressure of 30 mN/m.

Table 2. Characterization of Poly(*N*-acylethylenimines) with Fluorocarbon Side Chains


$$\sim(CH_2CH_2N)_n\sim \; | \; C{=}O \; | \; CH_2 \; | \; CH_2 \; | \; R_f$$

polymer R_f	$\bar{M}_w$[a]	$\bar{M}_n$[a]	T_m[b] (°C)	ΔH_m[b] (J/g)
C_4F_9	41 300	27 800	179	34
C_6F_{13}	54 600	42 100	193	27
C_8F_{17}	42 000	21 500	214	27
$C_{10}F_{21}$			226	27
$C_{12}F_{25}$			236	38

[a] By GPC in HFIP against PET standards. [b] By DSC at 10 °C/min.

suggests that the side chains in these LB films are tilted from the normal to the substrate and that the tilt angle probably decreases as the side-chain length increases. This also agrees with the fact that the π–A isotherms for these materials indicated the formation of more tightly packed phases, hence less tilted side chains, as the side-chain length increases.

It is apparent from all the data that side chains of 10–12 carbon atoms present the best compromise in terms of monolayer stability and LB film formation for this type of materials. Polymers with shorter side chains form monolayers which collapse at lower pressures while monolayers of those with longer side chains are too rigid for the preparation of uniform LB films.

Poly(*N*-acylethylenimines) with Fluorocarbon Side Chains. 2-Oxazolines with perfluoroalkyl groups directly attached to the heterocycle ring have been reported.[32,36] However, due to the strong electron-withdrawing effect of the perfluoroalkyl groups, the monomers are not very stable and much less nucleophilic than 2-alkyl-2-oxazolines. Therefore, they do not polymerize as well and give lower molecular weights. In this work we used 2-(*n*-perfluoroalkylethyl)-2-oxazolines which have a two methylene spacer between the oxazoline ring and the fluorocarbon chain to avoid these problems. A brief account of the preparation of these monomers was published by us recently.[37]

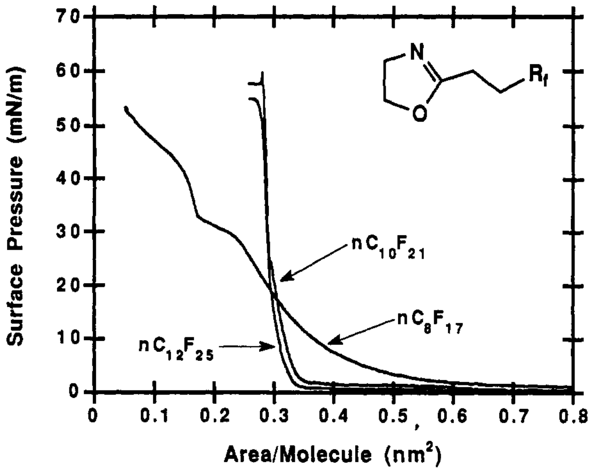


Figure 7. π–A isotherms of 2-(perfluoroalkylethyl)-2-oxazolines.

Table 2 lists the polymers prepared along with their molecular weights and DSC data. They all are white crystalline solids of moderate molecular weights. Their melting temperatures are much higher than those of the corresponding poly(*N*-acylethylenimines) with hydrocarbon side chains of the same length, and unlike them, the melting points increase as the side-chain length increases. This behavior reflects the effect of the fluorocarbon chains which are more rigid than hydrocarbons and melt at higher temperatures. The polymers are insoluble in most common organic solvents. The ones with shorter side chains (4, 6, and 8 perfluorinated carbons) are soluble only in hexafluoroisopropyl alcohol (HFIP) and mixtures of chloroform, methylene chloride, or trichlorotrifluoromethane (F113) with HFIP or trifluoroacetic acid (TFA). Polymers with longer side chains are soluble only in TFA.

π–A isotherms for the perfluorinated 2-oxazoline monomers which form monolayers are shown in Figure 7. Monomers with side chains containing C_4F_9 and C_6F_{13} do not form monolayers at the air–water interface. This is in agreement with literature data for perfluorinated alkanoic acids[21] which form stable condensed monolayers only when the fluorocarbon segment contains seven or more carbon atoms. The isotherm for the monomer with a C_8F_{17} side chain shows initially the formation of an expanded monolayer. It does not show a clear collapse point. As the monolayer is compressed and the pressure rises there is a gradual transition which must correspond to collapse of the monolayer since the areas per molecule at these pressures are smaller than expected for fluorocarbon amphiphiles (0.28–0.33 nm^2/molecule[38–40]). In addition, the monolayer is not stable. It shows large hysteresis in compression–expansion experiments and the curves shift to smaller areas in each cycle, suggesting partial collapse.

Monomers with $C_{10}F_{21}$ and $C_{12}F_{25}$ side chains both form stable monolayers. The isotherm for the $C_{10}F_{21}$ monomer shows formation of a condensed phase at low surface pressures and a transition to a solidlike packing at 25 mM/m. At higher pressures the monolayer is basically incompressible and collapses at about 58 mN/m. In this region the area per molecule is 0.28 nm^2 which agrees very well with that measured for other fluorocarbon amphiphiles that form condensed monolayers.[39] The monomer with the longest side chain ($C_{12}F_{25}$) also forms condensed monolayers which have collapse pressures and areas per molecule similar to the previous one.

As with the 2-alkyl-2-oxazoline monomers, increasing the length of the side chain increases the stability of the monolayers. However, shorter chains lengths are needed for the fluorocarbon monomers than for the hydrocarbon ones to form a stable condensed monolayer due to the higher hydrophobicity of fluorocarbons.

Monolayers of polymers with fluorocarbon side chains were obtained by spreading solutions of the polymers (in

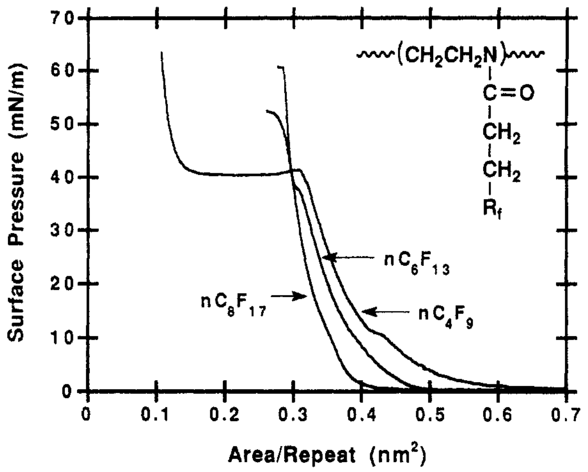


Figure 8. π–A isotherms of polymers with fluorocarbon side chains.

chloroform or F113 containing 1–5 vol % of HFIP) on the water surface. Only the polymers with short side chains formed monolayers which gave reproducible isotherms. Polymers containing $C_{10}F_{21}$ and $C_{12}F_{25}$ side chains were not soluble enough in this mixture to obtain reproducible data. No solvent was found that could be used to spread monolayers of these polymers on the water surface.

Figure 8 shows the π–A isotherms for monolayers of these polymers. The polymer containing C_4F_9 in the side chains shows a π–A curve similar to those of poly(2-alkyl-2-oxazolines) with 6, 8, and 10 carbon atoms in the side chains. It has a knee and plateau region at about 40 mN/m. At low pressures a rather expanded liquidlike monolayer exists. As it is compressed there is a transition close to 11 mN/m to a more condensed monolayer. At the knee point the observed area per repeat unit is 0.31 nm^2. This is still larger than that found for a solidlike monolayer of fluorocarbon amphiphiles (0.28 nm^2)[38] but indicates that they are well packed at this point. Compression–expansion experiments show totally reversible isotherms with no hysteresis for pressures below the knee. On compression to areas smaller than that at the knee, the same behavior as in the case of polymers with C6, C8, and C10 hydrocarbon side chains is observed. That is, reversible collapse occurs on compression of the monolayer to areas in the plateau, while irreversible collapse takes place if compression is beyond the plateau region.

The polymer with C_6F_{13} in the side chains exhibits a more condensed monolayer at low pressures than the polymer with C_4F_9 in the side chains. A rather sharp transition is observed at 38 mN/m and 0.30 nm^2/repeat, and at higher pressures the isotherm is very steep, suggesting a solid phase. It finally has a collapse point at 60 mN/m. The area at collapse is 0.28 nm^2/repeat unit, indicating a tight packing of the fluorocarbon side chains in this phase. Compression–expansion experiments show that the isotherm is perfectly reversible with no hysteresis. This behavior is somewhat analogous to that of hydrocarbon polymers with C12 and C13 side chains. It seems to be the transition point between fluid and solid monolayers as the length of the side chains increases.

The π–A isotherm for the polymers with C_8F_{17} in the side chains shows that this polymer forms condensed monolayers at all pressures. They collapse at about 52 mN/m with areas per repeat of 0.27–0.28 nm^2, indicating close packing of the fluorocarbon chains. Compression–expansion experments show some hysteresis after a large rearrangement in the first cycle, just like the poly(*N*-acylethylenimines) with long hydrocarbon side chains (C14, C15, and C17).

Monolayers of all these polymers can be transferred onto silicon substrates to prepare LB films. In the case of the polymer with C_4F_9 side chains, deposition can be made at pressures below the knee point in the isotherm. Y-Type deposition is normally obtained. Z-Type films can also be prepared in a two-trough system as described before. Monolayers deposited at 35 mN/m in the normal Y-mode give very uniform LB films with a thickness of 1 nm per monolayer as measured by ellipsometry. This is the same value as obtained for monolayers of poly(*N*-heptanoylethylenimine), the corresponding polymer with hydrocarbon side chains of the same length.

Monolayers of the poly(2-oxazoline) with C_6F_{13} in the side chains also give very uniform LB films. Monolayers deposited at 35 mN/m (below the transition point to a solid monolayer) give films with a thickness of 1.1 nm per monolayer, while films prepared at 45 mN/m have a thickness of 1.25 nm per monolayer. This suggests that some of the orientation of side chains developed in the monolayer by compressing to smaller areas might be preserved during the deposition and in the films. The polymer with the longest side chains (C_8F_{17}) forms only rigid monolayers which can also be transferred to solid substrates but with much difficulty. The LB films obtained are not very uniform in thickness.

The same trends observed for the polymers with hydrocarbon side chains in terms of monolayer formation and LB film fabrication are also seen for these materials with semifluorinated side chains. Polymers with short side chains form liquidlike compressible monolayers which can be easily deposited onto solid substrates to prepare uniform LB films. As the length of the side chains increases and the hydrophobic interactions between them also increase, more condensed and stable monolayers are obtained which can still be transferred onto solid substrates. After reaching a maximum in stability (optimum side-chain length), increasing the length of the side chains leads only to the formation of very rigid condensed monolayers which cannot be transferred onto solid substrates without destroying their organization and give films that are not as uniform in thickness.

The whole process of monolayer and LB film formation in these comblike polymers depends on the balance of hydrophobic and hydrophilic interactions. If the side chains are too short, the interactions of the hydrophilic groups with water are too strong and the polymer dissolves in water. If, on the other hand, the side chains are too long the hydrophobic interactions among them are stronger and the hydrophilic inteactions with water decrease so that the organization of the polymer at the air–water interface is controlled by the side chains.

Conclusions

Poly(*N*-acylethylenimines) with short hydrocarbon side chains (6–11 carbon atoms) form very fluid liquidlike condensed monolayers in which the polymer backbone is at the water surface and the side chains are tilted toward the air. They can be easily transferred onto solid substrates, and both Y and Z-type LB films consisting of hundreds of layers can be prepared. The films are very uniform across the substrate area, and their thickness depends on the length of the polymer side chains.

Poly(*N*-tridecanoylethylenimine) represents a shift in the behavior of monolayers of these polymers. Its isotherm shows a transition point to a phase with solidlike packing. Uniform LB films of this polymer can still be obtained at low surface pressures. Polymers with hydrocarbon side chains longer than 13 carbon atoms form only rigid monolayers which tend to crystallize after the initial compression. LB films of these materials can be prepared only with difficulty, and they are not as uniform.

Polymers containing perfluoroalkylethyl side chains with 4–12 fluorinated carbon atoms were also prepared and characterized. They are highly crystalline materials with limited solubility. Their melting points are higher than those of the corresponding polymers with hydrocarbon side chains, and they increase with the length of the side chains. Polymers with C_4F_9 and C_6F_{13} in the side chains form condensed monolayers which can be easily deposited onto solid substrates to make uniform LB films. The polymer with C_8F_{17} in the side chains forms only rigid monolayers that transfer with difficulty. Materials with even longer perfluorinated side chains are soluble only in solvents which cannot be used to spread them on the water surface. The overall behavior of these materials at the air–water interface is very similar to that of the polymers with hydrocarbon side chains, the major difference being that the same effects are observed at shorter side-chain lengths. This is expected from the hydrophobicity and rigidity of the fluorocarbon chains.

Acknowledgment. The skillful technical assistance of J. R. Crompton, Jr., and R. A. Morrison is gratefully acknowledged. We are indebted to B. E. Baker, A. Casalnuovo, and E. R. Wonchoba for supplying several of the perfluorinated starting materials.

References and Notes

(1) Roberts, G. G. *Langmuir–Blodgett Films*; Plenum Press: New York, 1990.
(2) Ulman, A. *An Introduction to Ultrathin Organic Films from Langmuir–Blodgett to Self-Assembly*; Academic Press: San Diego, 1991.
(3) Tredgold, R. H. *Thin Solid Films* **1987**, *152*, 223.
(4) Hodge, P.; Davis, F.; Tredgold, R. H. *Philos. Trans. R. Soc. London, A* **1990**, *330*, 153.
(5) Cemel, A.; Fort, T., Jr.; Lando, J. B. *J. Polym. Sci., Polym. Chem. Ed.* **1972**, *10*, 2061.
(6) Tieke, B.; Lieser, G.; Wegner, G. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 1631.
(7) Rabe, J. P.; Rabolt, J. F.; Brown, C. A.; Swalen, J. D. *Thin Solid Films* **1985**, *133*, 153.
(8) Pasquier, C.; Tieke, B.; Zahir, S.; Bosshard, C.; Günter, P. *Chem. Mater.* **1991**, *3*, 211.
(9) Tredgold, R. H.; Winter, C. S. *Thin Solid Films* **1983**, *99*, 81.
(10) Winter, C. S.; Tredgold, R. H.; Vickers, A. J.; Khoshdel, E.; Hodge, P. *Thin Solid Films* **1985**, *134*, 49.
(11) Elbert, R.; Laschewsky, A.; Ringsdorf, H. *J. Am. Chem. Soc.* **1985**, *107*, 4134.
(12) Mumby, S. J.; Swalen, J. D.; Rabolt, J. F. *Macromolecules* **1986**, *19*, 1054.
(13) Oguchi, K.; Yoden, T.; Sanui, K.; Ogata, N. *Polym. J.* **1986**, *18*, 887.
(14) Laschewsky, A.; Ringsdorf, H.; Schmidt, G.; Schneider, J. *J. Am. Chem. Soc.* **1987**, *109*, 788.
(15) Duda, G.; Schouten, A. J.; Arndt, T.; Lieser, G.; Schmidt, G. F.; Bubeck, C.; Wegner, G. *Thin Solid Films* **1988**, *159*, 221.
(16) Watanabe, M.; Kosaka, Y.; Oguchi, K.; Sanui, K.; Ogata, N. *Macromolecules* **1988**, *21*, 2997.
(17) Miyashita, T.; Mizuta, Y.; Matsuda, M. *Br. Polym. J.* **1990**, *22*, 327.
(18) Davis, F.; Hodge, P.; Towns, C. R.; Ali-Adib, Z. *Macromolecules* **1991**, *24*, 5695.
(19) Schouten, A. J.; Wegner, G. *Makromol. Chem.* **1991**, *192*, 2203.
(20) Penner, T. L.; Schildkraut, J. S.; Ringsdorf, H.; Schuster, A. *Macromolecules* **1991**, *24*, 1041.
(21) Bennett, M.; Zisman, W. A. *J. Phys. Chem.* **1963**, *67*, 1534.
(22) Kunitake, T.; Okahata, Y.; Yasunami, S. *J. Am. Chem. Soc.* **1982**, *104*, 5547.
(23) Elbert, R.; Folda, T.; Ringsdorf, H. *J. Am. Chem. Soc.* **1984**, *106*, 7687.
(24) Laschewsky, A.; Ringsdorf, H.; Schmidt, G. *Thin Solid Films* **1985**, *134*, 153.
(25) Naselli, C.; Swalen, J. D.; Rabolt, J. F. *J. Chem. Phys.* **1989**, *90*, 3855.
(26) Sekiya, A.; Ishida, H.; Tamura, M.; Watanabe, M. *Chem. Lett.* **1987**, 1593.
(27) Schneider, J.; Erdelen, C.; Ringsdorf, H.; Rabolt, J. F. *Macromolecules* **1989**, *22*, 3475.
(28) Tamura, M.; Sekiya, A.; Song, B.-K. *Chem. Lett.* **1990**, 1027.
(29) Kaku, M.; Hsiung, H.; Sogah, D. Y.; Levy, M.; Rodriguez-Parada, J. M. *Langmuir* **1992**, *8*, 1239.
(30) Litt, M.; Rahl, F.; Roldan, L. G. *J. Polym. Sci., Polym. Phys. Ed.* **1969**, *7*, 463.
(31) Kobayashi, S.; Saegusa, T. In *Ring-Opening Polymerization*; Ivin, K. J., Saegusa, T., Eds.; Elsevier Applied Science: New York, 1984; Vol. 2, Chapter 11.
(32) Bassiri, T. G.; Levy, A.; Litt, M. *J. Polym. Sci., Polym. Lett. Ed.* **1967**, *5*, 871.
(33) Litt, M.; Levy, A.; Herz, J. *J. Macromol. Sci., Chem.* **1975**, A9, 703.
(34) Gaines, G. L., Jr. *Insoluble Monolayers at Liquid–Gas Interfaces*; Interscience: New York, 1966; Chapter 4.
(35) Gaines, G. L., Jr. *Langmuir* **1991**, *7*, 834.
(36) Miyamoto, M.; Aoi, K.; Saegusa, T. *Macromolecules* **1988**, *21*, 1980.
(37) Sogah, D. Y.; Kaku, M.; Shinohara, K.-I.; Rodriguez-Parada, J. M.; Levy, M. *Makromol. Chem., Macromol. Symp.* **1992**, *64*, 49.
(38) Nakahama, H.; Miyata, S.; Wang, T. T.; Tasaka, S. *Thin Solid Films* **1986**, *141*, 165.
(39) Wolf, S. G.; Deutsch, M.; Landau, E. M.; Lahav, M.; Leiserowitz, L.; Kjaer, K.; Als-Nielsen, J. *Science* **1988**, *242*, 1286.
(40) Gaines, G. L., Jr. *Langmuir* **1991**, *7*, 3054.