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Structural Studies of Polymers with Hydrophilic Spacer Groups. 2. Infrared Spectroscopy of Langmuir–Blodgett Multilayers of Polymers with Fluorocarbon Side Chains at Ambient and Elevated Temperatures

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Revised Manuscript Received January 31, 1989

ABSTRACT: Multilayered Langmuir–Blodgett films of preformed polymers containing fluorocarbon side chains and hydrophilic spacer groups in the main chain have been investigated by IR spectroscopy. Grazing incident reflection and transmission measurements have been utilized to obtain information on the orientation of the side chains at room temperature and at elevated temperatures. Results indicate that the side chain is tilted relative to the surface normal unlike their hydrocarbon analogues, which are perpendicular to the surface. Although this angle of tilt increases at higher temperatures, it is shown that the initial orientation of the side chains returns when the film is cooled to ambient. This is found to be true even for temperatures as high as 150 °C in the homopolymer and 180 °C in the $m = 5$ copolymer, indicating that the main-chain spacer plays a major role in the high-temperature stability of these materials. The contribution of the rigid fluorocarbon side chain in this inherent thermal stability is discussed.

Introduction

Although much of the interest in Langmuir–Blodgett (LB) films has been in amphiphilic molecules containing hydrocarbon chains, there is an increasing realization that chemical modification of the long-chain amphiphiles so as to contain other structures can lead to novel surface properties.[1-4] Of recent interest has been the incorporation of CF$_2$ sequences into the structure of these lipidlike structures[5-8] with the result that liposomes, monolayers, and multilayers have all since been studied. Although the surface properties changed, no significant enhancement of the thermal and mechanical integrity was observed.

In an attempt to further improve the long-term thermal stability of LB films, the polymerization of a series of perfluorocarbon molecules containing reactive groups was investigated and compared[9] to that of their hydrocarbon analogues. An alternative approach[10] was more recently initiated to introduce polymeric properties into LB layers by the formation of a complex of a perfluorinated lipid and a polyelectrolyte counterion. Both methods found that the LB films exhibited increased stability, but their behavior at elevated temperatures was not explicitly addressed.

In general, reports of LB films of preformed polymers with fluorocarbon side chains are rare. An initial attempt[11] was made to create such novel structures by attaching perfluorocarbon chains to a polymer backbone containing random reaction sites. The nature of such a reaction is such that a random copolymer is produced. In another method, free-radical polymerization of reactive monomers containing fluorocarbon side chains was shown[12] to be successful. With this synthetic approach both a homopolymer and a series of copolymers containing varying amounts of hydrophilic comonomer units resulted. It is this set of polymers that are the subject of an IR investigation in this work. Grazing incident reflection and standard transmission measurements have been obtained on the homopolymer ($m = 0$) and two of the copolymers ($m = 1, 5$; see Figure 1) at ambient and elevated temperatures. The extent of orientation of the fluorocarbon side chain was specifically addressed as a function of backbone spacer length and sample temperature.

Experimental Section

Synthesis. The homopolymer and the copolymer $m = 1, 5, 10$ (Figure 1) were synthesized by radical polymerization in solution. A lipid monomer 1*H*,1*H*,2*H*,2*H*-perfluorodecyl methacrylate and a hydrophilic comonomer 2-HEA (2-hydroxyethyl acrylate) were used.

The polymerizations were performed in dry trifluorotoluene in the case of the homopolymer and in dry dioxane in the case of the copolymers. As initiators, 5 mol % of TBPIPC (*tert*-bu-

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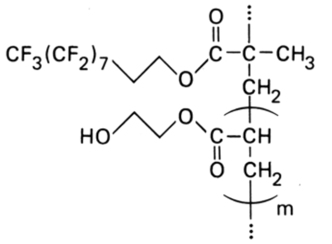


Figure 1. Chemical structures of preformed polymers with perfluorinated side chains; $m = 0$ represents the homopolymer and $m = 1$, 5, and 10 the copolymers used in this study.

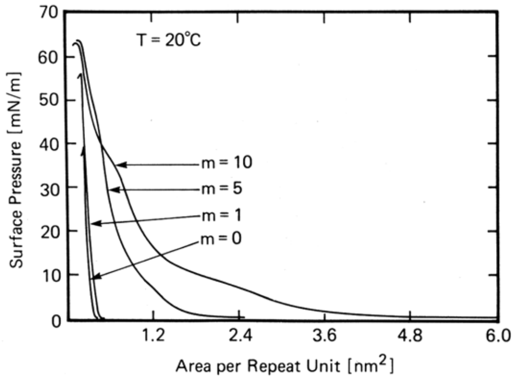


Figure 2. Surface pressure–area diagrams of the polymers with different main-chain spacer length, m (m = 0, 1, 5, 10).

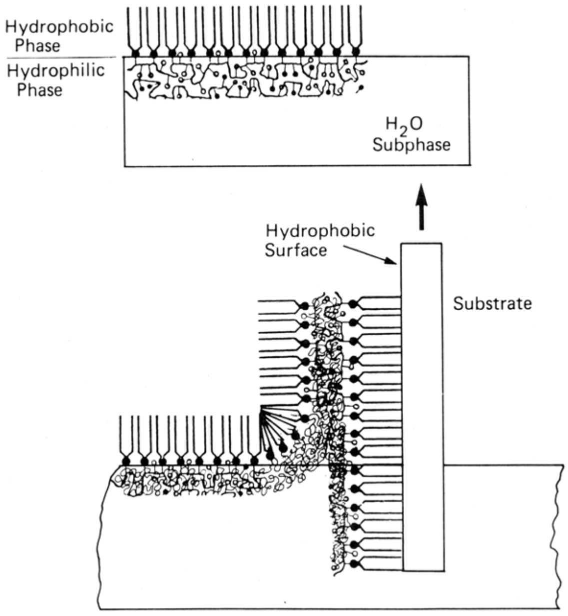
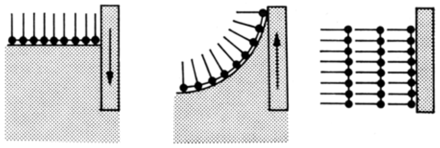
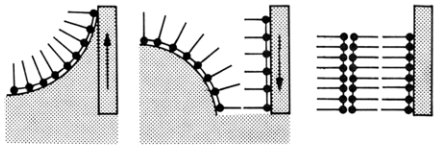


Figure 3. Schematic diagram of polymeric monolayer and the deposition process to build multilayers.



Z-type deposition



Y-type deposition

Figure 4. Different types of deposition of monolayers onto a solid support.

tylperoxyisopropyl carbonate) was used for the homopolymer while only 2.5 mol % of AIBN (azoisobutyronitrile) was used for the copolymers. The mixtures were flushed with argon for 15 min and then degased three times. The polymerizations took place for 18 h at 90 °C in the case of TBPIPC and for 10 h at 60 °C in the case of AIBN.

The polymeric lipids were obtained by precipitation in methylene chloride (homopolymer) and in hexane (copolymers). The polymers were characterized by TLC and IR and ^{1}H NMR spectroscopy. The composition of the statistical copolymers was determined by microanalysis.

Film Preparation. The homopolymer was spread from Freon-113 and the copolymers from chloroform/methanol solutions (9/1 by volume), respectively, both having a concentration of about 0.5 mg/mL.

In Figure 2 the spreading behavior of the polymers m = 0, 1, 5, and 10 with fluorinated side chains is shown at 20 °C.[12] These pressure–area curves indicate that all polymers are able to self-organize into densely packed monolayers. This can be seen in the solid analogue phases of the steep rise of the isotherms. The occupied area at the collapse pressure is almost identical for all polymers (0.25 nm^2 per repeat unit) independent of the different concentration of the hydrophilic comonomer. With increasing main-chain spacer length (comonomer concentration) a dramatic change of the isotherm occurred at $m = 5$, which also showed large fluid analogue phases. However, the isotherms also show that with a high concentration of the hydrophilic comonomer the solid analogue phase is still retained, but there is a stabilization effect on the monomolecular layers. In addition there is an increase of the collapse pressures with increasing spacer length from the homopolymer $m = 0$ to the copolymer $m = 5$.

Langmuir–Blodgett multilayers (Figure 3) were prepared on a commercially available film balance (Joyce Loebl) modified to include a Teflon tank. The water in the subphase was purified by deionization and passed through a Barnstead nanopure filtration system. The surface pressure of the monolayers was monitored by a Wilhelmy pressure pickup system. The monolayers of the preformed polymers were transfered at 20 °C either onto zinc selenide disks (1-in. diameter) or onto a 200-nm layer of silver evaporated on glass microscope slides (1 in. × 3 in.). When silver-coated glass slides were used as substrates, the transfer mechanism changed for the perfluorinated polymers from a Y-type deposition (See Figure 4) after the first dip to a Z-type where only a monolayer was transferred upon withdrawal. For the zinc selenide substrates, there was a transferability problem. Where for the homopolymer a reproducible Y-type mechanism was observed, the copolymers $m = 1$ and $m = 5$ did not show constant transfer ratios upon insertion of the substrate. Therefore, the plotted spectra had to be normalized to the CF_2 stretching vibration, and it should be noted that only the relative intensities should be used for comparison with the isotropic and the grazing incidence reflection spectra.

The zinc selenide disks were cleaned with a chloroform/methanol mixture (1/1), then treated by water spray, deionization bath, isopropyl alcohol water exchanger, and dried at 100 °C. The microscope slides were first cleaned in an oxidative acid solution and then passed through the same cleaning procedure as described above. The silver substrates were coated directly after evaporation of the metal film.

The surface pressure used for deposition was increased from 30 mN/m for the homopolymer, to 35 mN/m for the copolymer $m = 1$, and to 50 mN/m for $m = 5$. Surface pressures during the deposition process were chosen accordingly to guarantee transferral of the condensed phase of the polymeric monolayers and to ensure monolayer stability. A dipping speed of 0.25 cm/min was chosen for all the polymers. Drying periods of 20 min between subsequent dips are necessary to prevent retransfer of the previously deposited monolayer to the water surface during the next dip downward. This was most notable for the copolymer m = 5 with the highest hydrophilic comonomer content.

Spectroscopy. All infrared measurements were made with an evacuated IBM IR 98 Michelson interferometer. The spectra were recorded at 4-cm^{-1} resolution by using a room-temperature

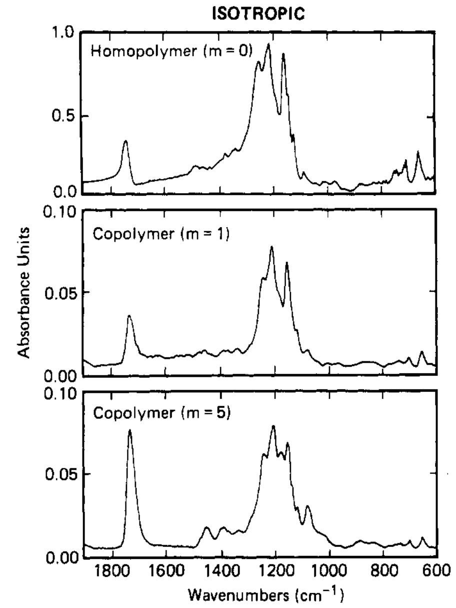


Figure 5. IR transmission spectra of solvent cast films of homopolymer ($m = 0$) and copolymers ($m = 1, 5$) on KBr (resolution = 4 cm^{-1}; 250 scans).

Table I
IR Band Assignments for Homopolymer and Copolymer

Ho ($m = 0$)[a]	Co ($m = 5$)	assignment
1740 m	1740 s	ν(C=O)
	1460 w	δ(CH$_2$)
	1400 w	w(CH$_2$)
	1370 w	ν(CF$_2$)
	1340 w	ν(CF$_2$)
1260 s	1260 s	ν_a(CF$_2$), r(CF$_2$)
1220 s	1220 s	δ(CCC), ν(CC)
	1180 s	ν(C-O-C)
1160 s	1160 s	ν_s(CF$_2$), δ(CF$_2$)
1110 w	1110 sh	
	1080 m	ν(C-O-H)
740	740 w	r(CH$_2$)
710	710 w	r(CF$_2$), w(CF$_2$)
660 m	660 m	w(CF$_2$)

[a] From spectrum of homopolymer (m = (0); ν, stretch; δ, scissors; r, rock; w, wag.

deuterated triglycine sulfate (DTGS) detector. To obtain spectra with high signal-to-noise ratios, 2500 scans had to be collected.

For comparison the isotropic spectra of the polymers were taken by casting the bulk material from solutions onto KBr disks (1-in. diameter). The grazing incidence reflection spectra (electric field vector is perpendicular to the surface, $E_\perp$) were taken from seven layers on silver substrates. A standard Harrick Scientific reflection accessory with adjustable grazing angle between 80° and 88° was used in conjunction with a heating device to study the temperature-induced molecular reorganization of these organic films. Only those groups that have a component of their change in dipole moment oriented perpendicular to the film would be observed. The transmission spectra (electric field vector is parallel to the surface, $E_\parallel$) were obtained from six layers on each side of a zinc selenide disk.

Results and Discussion

Isotropic Films of Homopolymer (m = 0) and Copolymers (m = 1, 5). Shown in Figure 5 are the IR transmission spectra of isotropic films of the homopolymer ($m = 0$) and copolymers ($m = 1, 5$) obtained in the 1900–600-cm^{-1} region. The CH$_2$ stretching region (2800–3100 cm^{-1}) is not included since only two very weak broad bands were observed in this region attributable to CH$_2$ groups which are in very low concentration in the homopolymer (see Figure 1).

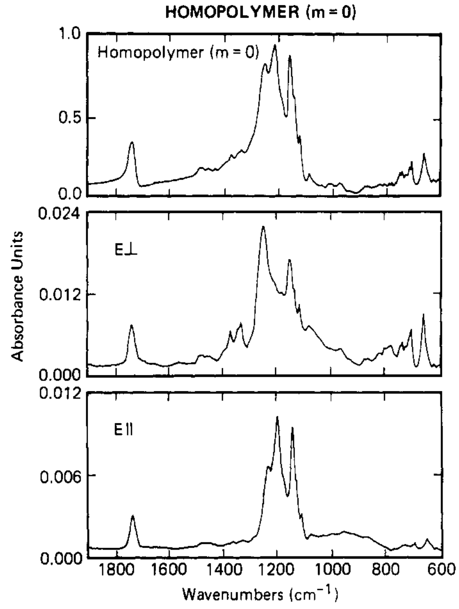


Figure 6. Comparison of grazing incidence reflection ($E_\perp$) and standard transmission ($E_\parallel$) measurements of homopolymer (m = 0). Spectrum of isotropic sample included for ease in comparison (resolution = 4 cm^{-1}; 2500 scans).

The 1900–600-cm^{-1} region can be subdivided into three regions which contain IR bands of observable intensity. The higher frequency region contains only one band at 1740 cm^{-1} resulting from a C=O stretching vibration (ν(C=O)) in the side chain and in the hydrophilic spacer groups. Hence as observed in the $m = 5$ copolymer, the intensity of this band has increased significantly due to the addition of five spacer groups per repeat unit.

The second region of interest is that between 1500 and 1000 cm^{-1}, which is dominated by bands associated with motions of the CF$_2$ groups at 1260 (ν_a(CF$_2$) + r(CF$_2$)) and 1160 cm^{-1} (ν_s(CF$_2$) + δ(CF$_2$)).[13] In addition the band at 1220 cm^{-1} is attributed to stretching and bending of the carbon skeleton of the fluorocarbon helix. As seen in the $m = 5$ copolymer spectrum several additional bands attributable to the main-chain spacer appear with the most intense at 1180 cm^{-1} characteristic of ν(C–O–C) of the ester group contained in the spacer.[14] There are also weaker bands found in the 1400-cm^{-1} region which are due to scissors and wagging motions of the CH$_2$ groups added in the copolymer main-chain spacer. Likewise the band at 1080 cm^{-1}, shown to increase in intensity in the copolymer, is assigned to the ν(C–O–H) of the spacer unit. Several other bands are also present, but their intensity is very weak and their exact origin unknown.

The last region of interest is that between 600 and 800 cm^{-1}. In this region are found two medium bands at 660 and 710 cm^{-1} which result from a combination of rocking and wagging vibrations of the CF$_2$ groups.[13] A third band at 740 cm^{-1} is somewhat broad and weak, similar to that at 1470 cm^{-1}, indicating that it is most probably associated with the CH$_2$ rocking vibration. It is this band that splits into multiple components in the IR of crystalline n-alkanes and is indicative, in that case, of the number of molecules per unit cell.[15]

Polarized IR Studies of Homopolymer and m = 5 Copolymer. Figures 6 and 7 show the IR spectra of LB multilayers of the homopolymer and the copolymer (m = 5) obtained by using both grazing incidence reflection ($E_\perp$) and standard transmission ($E_\parallel$) measurements. For ease in comparison, the spectra of the isotropic films are included. As is obvious from the dichroic spectra obtained from the LB films of the homopolymer, a significant

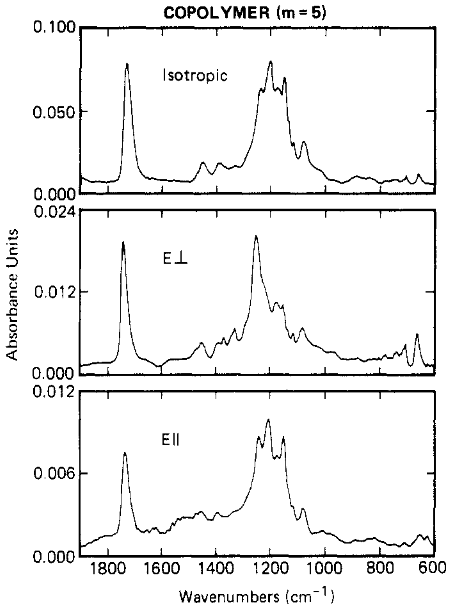


Figure 7. Comparison of grazing incidence reflection ($E_\perp$) and standard transmission ($E_\parallel$) measurements of copolymer (m = 5). Spectrum of isotropic sample included for ease in comparison (resolution = 4 cm^{-1}; 2500 scans).

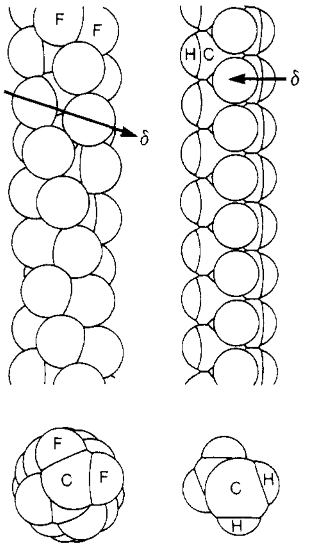


Figure 8. Molecular structure[8] of a fluorocarbon $(CF_2)_n$ and a hydrocarbon chain $(CH_2)_n$. At the bottom the cross section of both C–C chains is shown.

amount of molecular orientation exists. The most dramatic changes are observed in the 1000–1400-cm^{-1} region. The $\nu_a(CF_2)$ vibration at 1260 cm^{-1} dominates the $E_\perp$ spectrum, while its intensity is considerably reduced relative to the 1220-cm^{-1} band in the $E_\parallel$ spectrum. The former is perpendicularly polarized relative to the fluorocarbon helical axis, while the latter exhibits parallel polarization.[16,17] However, as shown in Figure 8, the 1260-cm^{-1} band has a component of the change in dipole moment (dP/dQ) that is parallel to helical axis because dP/dQ of $\nu_a(CF_2)$ lies in the CF_2 plane, which in the case of a helix is tilted (see Figure 8) compared to its CH_2 analogue in planar n-alkanes. This is also true for the 1160-cm^{-1} band because it has a contribution from $\delta(CF_2)$ that also has a change in dipole moment which lies in the CF_2 plane and hence is also tilted relative to the helical axis. Perhaps the most useful band is that at 1220 cm^{-1} whose change in dipole moment lies parallel to the fluorocarbon axis. In Figure 5 it is clear that this band is strong in $E_\parallel$ and weaker in $E_\perp$ relative to $\nu(C{=}O)$, which is isotropically oriented in the homopolymer. This strongly suggests that the fluorocarbon side-chain axis is tilted relative to the surface normal as schematically illustrated in Figure 9. The change in intensity of the 1260- and 1160-cm^{-1} bands in $E_\perp$ and $E_\parallel$ is consistent with this orientation of the side chain.

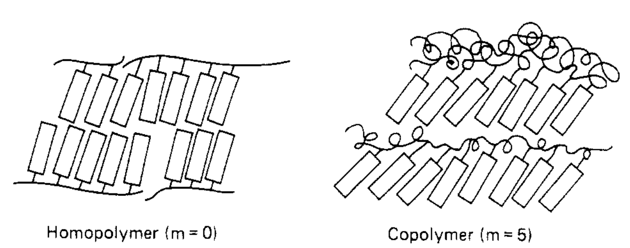


Figure 9. Schematic representation of orientation of fluorocarbon side chains in a bilayer structure (Y type) of homopolymer (m = 0) and a monolayer structure (Z type) of copolymer (m = 5).

Interestingly enough a similar argument can be made for the 660- and 710-cm^{-1} bands. They have contributions from CF_2 wagging and CF_2 twisting, i.e., the change in dipole moment associated with each of these vibrations has a component both parallel and perpendicular to the helical axis although the former is classified as a parallel band.[16,17] As such the intensity of these bands relative to $\nu(C{=}O)$ is strongly supportive of side-chain tilt.

An interesting observation can be made upon comparing the spectra of the homopolymer (Figure 6) to the m = 5 copolymer in Figure 7. Upon the addition of the main-chain spacers, the change in intensity of the 1220-cm^{-1} band relative to $\nu(C{=}O)$ in $E_\perp$ and $E_\parallel$ relative to their counterparts in the homopolymer indicates that the fluorocarbon has increased its tilt relative to the surface normal. The change in intensity of the 1260- and 1160-cm^{-1} bands is also consistent with this increased tilt. This is most probably due to the increased amount of chain flexibility allowed through the incorporation of main-chain spacer groups (see Figure 9).

Hence the picture that arises is one in which the fluorocarbon side chains are forced to tilt increasingly toward the surface normal with increasing comonomer concentration (spacer length) as illustrated in Figure 9. The tilt is somewhat constrained due to the short molecular backbone segments between adjacent side chains and hence is very similar to the semifluorinated fatty acid salts[7] where divalent cadmium ions restricted any change in orientation of the fluorocarbon segments. On the other hand, the introduction of main-chain spacer groups removes these constraints and a larger tilt of the fluorocarbon helix occurs.

Grazing Incidence Reflection Measurements at Elevated Temperatures. To assess the orientational stability of LB films of both the homopolymer and the m = 5 copolymer, IR reflection measurements were made at elevated temperatures. During these studies the temperature of the film was raised, and the IR spectra recorded. The film was then returned to room temperature, and its spectrum obtained again. By this method the recovery of the original state of order and orientation could be monitored.

As discussed previously, the bands in the 100–1400-cm^{-1} region in the $E_\perp$ spectrum of the homopolymer are attributed to vibrations of the CF_2 groups and C–C vibrations of the helical fluorocarbon chain.[13] As shown in Figure 10, this is the region that is most affected by temperatures above 100 °C. The intensity of the 1260-cm^{-1} band increases dramatically, indicating an increase of tilt of the fluorocarbon chain. This is most likely due to the introduction of gauche bonds between the rigid fluoro-

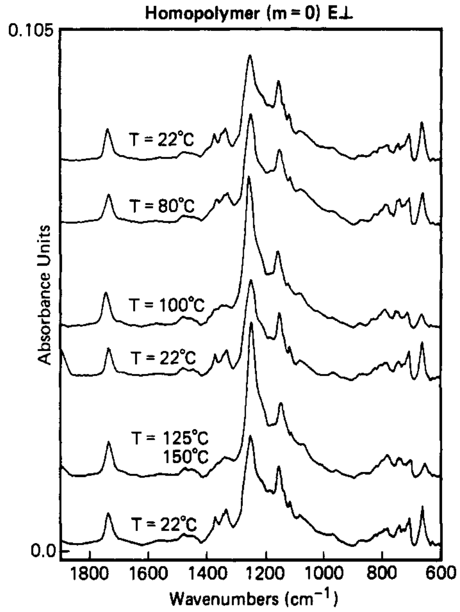


Figure 10. Comparison of IR spectra of C=O and CF_2 (1900–600 cm^{-1}) stretching region of homopolymer (m = 0) as a function of temperature (resolution = 4 cm^{-1}; 2500 scans).

carbon helix and the polymer backbone (see Figure 1). Rotational isomerism about C–O bands is known to occur quite readily at elevated temperatures. In addition rotation about the C–C bond of the short hydrocarbon segment would also lead to an increased side chain tilt. It was this latter mechanism that led to the increased tilt of the fluorocarbon segment in a semifluorinated fatty acid previously studied[7] at high temperatures.

In the region below 800 cm^{-1} there is additional evidence that the side-chain tilt increases at elevated temperatures. The 600-cm^{-1} band, attributed to a CF_2 wagging vibration,[13] exhibits parallel (to helical axis) polarization, and as shown in Figure 10 it decreases in intensity as the temperature increases.

The interesting result shown in Figure 10 is that the spectrum of the homopolymer returns to its initial form after heating. In fact even after a temperature of 150 °C, the LB films retain their "memory", returning to their initial state of order and orientation. This is readily observed by comparing the bottom spectum of Figure 10 with that at the top. A careful comparison indicates that these spectra are reproducible within the noise limit. Thus this is the first time that such a high-temperature stability for an LB film has been demonstrated by using IR spectroscopy. In the case of the homopolymer, heating to temperatures above 150 °C does not allow a return to the original spectrum obtained at room temperature.

As discussed previously, studies of LB films of the m = 5 copolymer indicate that the fluorocarbon side chain has a larger angle of tilt (see Figure 9) than in the homopolymer. As its temperature is raised (see Figure 11), the 1260-cm^{-1} band increases in intensity while the 660-cm^{-1} band decreases as observed previously in the homopolymer. Thus, as before, the side-chain tilt of the copolymer also increases. In this case, as shown in Figure 11, the reversibility of the spectrum is observed up to 180 °C. This enhanced stability over the homopolymer most likely results from the increased flexibility of the polymer backbone due to the addition of five spacer groups per repeat unit. There is some evidence that the 1180-cm^{-1} ν(CO) vibration of the spacer groups does change as a function of temperature. As shown in Figure 11, at room temperature the 1180-cm^{-1} band is more intense than the fluorocarbon vibration at 1160 cm^{-1}. After cycling to elevated temperatures (80 °C) and returning to ambient temperature, a decrease in intensity of the 1180-cm^{-1} band relative to that at 1160 cm^{-1} is observed. After cyclic heating to 180 °C there is a significant dropoff in intensity of the 1180-cm^{-1} band, indicating that there is some rearrangement of the copolymer backbone spacer groups during heating resulting in a different orientation of C–O bands relative to $E_\perp$. This could be due to some relaxation process similar to the glass transition in which the amorphous backbone reorients into an equilibrium conformation which is more energetically favorable.

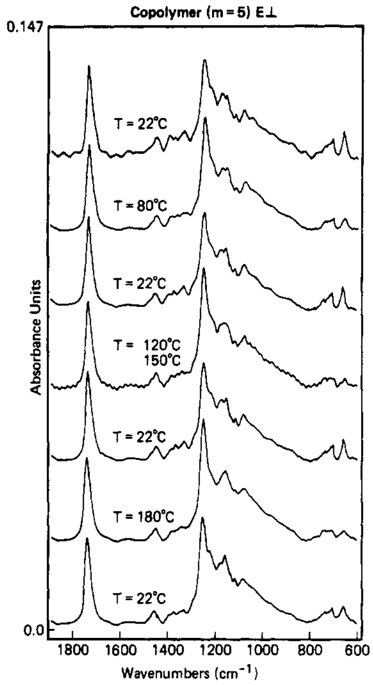


Figure 11. Comparison of IR spectra of C=O and CF_2 (1900–600 cm^{-1}) stretching region of copolymer (m = 5) as a function of temperature (resolution 4 cm^{-1}; 2500 scans).

Conclusion

LB films of preformed saturated polymers containing fluorocarbon side chains and hydrophilic spacer groups in the main chain exhibit the best thermal stability observed thus far by IR spectroscopy. This is attributed to the inherent stability of the fluorocarbon helix and the absence of molecular constraints imposed on the polymer backbone because of the presence of flexible spacer groups. In the case of the homopolymer, the fluorocarbon side chain was found to be tilted relative to the surface normal. This side chain tilt was observed to increase by the addition of backbone spacer groups or the elevation of the temperature. In the latter case the side chain was observed to return to its initial state even after exposure to temperatures as high as 180 °C (m = 5 copolymer).

Acknowledgment. J. Rabolt acknowledges partial support of this work by Office of Naval Research Chemistry Division.

Registry No. (2-HEA)(1*H*,1*H*,2*H*,2*H*-perfluorodecyl methacrylate) (copolymer), 120059-75-8; 1*H*,1*H*,2*H*,2*H*-perfluorodecyl methacrylate (homopolymer), 26338-99-8.

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Antiplasticization and Crystallinity in Poly(vinyl chloride)

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Received July 14, 1988; Revised Manuscript Received December 1, 1988

ABSTRACT: The rise in tensile modulus observed in formulations of poly(vinyl chloride) (PVC) at low concentrations of tricresyl phosphate (TCP) can be influenced and even eliminated according to the way the sample is prepared or treated prior to measurement. All pretreatments that were found to eliminate crystallinity in the sample (quenching, chlorination of the polymer) also produced samples that failed to show the rise in modulus associated with antiplasticization. Formulations where the plasticizer was introduced at room temperature rather than by heating also showed a lack of an antiplasticization effect. Wide-angle X-ray diffraction measurements cannot be analyzed in a straightforward manner, since orientation effects are detected. In spite of this, the experimental data as a whole point to a strong correlation between the rise in modulus and the presence of a crystalline phase at low levels of TCP in PVC formulations.

Introduction

Among the questions that still remain to be answered regarding PVC's unique response to plasticizers, one aspect that has received intermittent attention is the unexpected phenomenon of antiplasticization. The apparently anomalous increase in modulus and tensile strength, together with a decrease in elongation, at low concentrations of plasticizers has been known for many years. This unforeseen change in mechanical properties was first assigned to possible experimental difficulties in preparing homogeneous samples for testing.[1] There was no inmediate explanation as to why small quantities of plasticizer (a liquid at room temperature) should lead to higher values of modulus and tensile strength. A straightforward application of any law of mixtures would predict a steady decrease in those properties with increasing plasticizer content, which is exactly what occurs once a threshold or critical plasticizer concentration has been passed.

Since later studies have shown that this effect is observed consistently though with different intensity according to the plasticizer, two lines of reasoning have been proposed. Horsley in 1957 carried out one of the few studies to date that have tried to correlate changes in crystallinity with the antiplasticization effect.[2] Though the X-ray evidence presented is limited by the state of knowledge on PVC crystallinity at the time, he presents semiquantitative data based on WAXD flat-plate transmission photographs. The three haloes he refers to are taken to be, in order of increasing diameter, the 200 reflection, the 110 reflection, and the unresolved group of the 210, 201, and 111 reflections. All three haloes are superimposed on the two broad amorphous background reflections. He reports a sharpening and increase in intensity of the two outermost haloes with respect to the innermost one, this effect being more prominent in the plasticizer concentration range where the maximum in modulus is observed. He also found that quenching of the samples prior to mechanical testing eliminates the rise in modulus associated with antiplasticization. Later work reported by Lebedev et al.[3] studied basically the same phenomenon, this time using WAXD diffractometer traces, with corrections for the scatter of the plasticizer. They report that the intensity of the reflection at $2\theta = 17°$ (that is, the 110 reflection) goes through a maximum in the concentration range of plasticizer where also a maximum in strength and modulus is measured.

The other line of explanation that has been proposed involves polymer–plasticizer associations that are believed to have a stiffening effect on the chain at low concentrations of plasticizer, therefore acting as cross-links in the structure. Ghersa was the first to propose this, together with a possible crystallization effect concurring, depending on the type of plasticizer.[4] Pezzin et al.[5] propose that this sort of association could explain the disappearance of the PVC β peak, as evidenced from dynamic mechanical studies on slightly plasticized PVC. The loss in mobility would explain, according to this model, the observed rise in tensile modulus. Kinjo and Nakagawa[6] carried out further studies using a wide range of plasticizers and arrived at a similar explanation.

In light of present knowledge regarding the crystallizing capability of PVC in the presence of solvents (including plasticizers)[7] a new look will be taken at the possible relation between changes in physical structure and its effect

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