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Surface Modification of Poly(chlorotrifluoroethylene) with Methyllithium

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ABSTRACT: The reaction of poly(chlorotrifluoroethylene) film with methyllithium has been investigated with regard to mechanism and product structure. Contact angle, ESCA, UV-vis, ATR IR, SEM, and gravimetric analyses as well as a solution model reaction indicate the incorporation of methyl groups and unsaturation in the outer few tens of angstroms. The mechanism involves a metal-halogen exchange, loss of lithium fluoride, and subsequent addition of methyllithium.

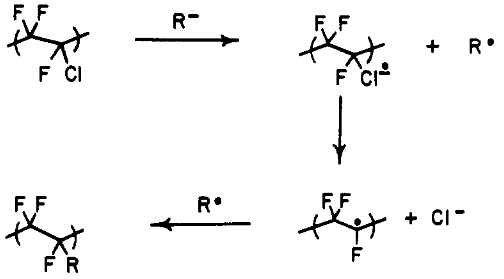
Introduction

The extent to which the science of organic chemistry can be applied to organic functional groups confined to two dimensions has not be tested.[1,2] We have been studying polymer surface chemistry in this regard and have developed refined methods for introducing functionality onto the surfaces of poly(vinylidene fluoride)[3] and poly(tetrafluoroethylene).[4] As substances for monitoring surface reactivity, these materials have certain advantages: because they are organic polymers, the mobility of the surface functional groups (position on the 3D to 2D continuum) is sensitive to temperature and can thus be controlled. Because the polymers are resistant to chemical attack, a wide variety of reactions can be carried out without affecting the bulk. Films of these materials have the integrity necessary to perform gravimetric analysis.[5] The bulk of these materials is UV-vis transparent; thus the observation of surface functional groups by standard transmission spectroscopy is possible. The carbon region of the ESCA spectra is lucid with regard to changes because fluorinated carbon has an especially high (binding energy) chemical shift.[6] The synthesis of these substrates, however, is difficult; derivatizing chemically resistant polymers normally requires severe conditions and limiting the reaction to the surface has proved challenging. We recently reported the surface-selective dehydrofluorination of poly(vinylidene fluoride).[3] This derivatization owes its surface selectivity to an autoinhibitive phase-transport step.

Danielson et al.[7-10] have studied the reactions of alkyl- and aryllithium reagents with PCTFE powder (<44 μm) and propose the mechanism detailed in Scheme I to explain the incorporation of alkyl and aryl groups. They report extensive, sometimes complete reaction and no apparent surface selectivity. These reports have prompted us to reinvestigate these reactions, under less severe conditions, with regard to their products, mechanisms, and potential as surface-selective modifications.

Ultimately, we wish to study the chemistry of small amounts (submonolayer to monolayer coverage) of polar functional groups (carboxylic acids, aldehydes, and alcohols) on polymer film surfaces. This type of film is amenable to several analytical techniques (contact angle, ESCA, gravimetric analysis, and SEM) but does not contain functional groups in concentrations high enough for less sensitive, but information-rich spectroscopies such as NMR and IR. For this reason, we have used PCTFE powder and low molecular weight PCTFE oil in diethyl ether solution in addition to PCTFE film to obtain the results reported here. We emphasize that solution reactions may be different from surface reactions and inferring that something occurs on the surface because it does in solution is dangerous, for reasons we have presented elsewhere.[3] We have used PCTFE oil as a model substrate: we fully expect that certain model reactions will not proceed on surfaces. High surface area powder was used to check for similarities and differences between solution and surface reactions.

Scheme I
Proposed[10] Mechanism for Alkylation and Arylation of PCTFE



Experimental Section

Materials. PCTFE film (Kel-F 81 film, 3M Co.) was uniformly 1.27 × 10^{-2} cm thick and had a density of 2.20 g/cm^3. The film was extracted in refluxing dichloromethane (30 min) and dried in a vacuum oven (24 h, 60 °C, 0.05 mm) to constant mass. This procedure gave films that were consistently free from contaminants. PCTFE oil was obtained from Polysciences and purified by distillation (bp 60-160 °C, 0.05 mm). PCTFE powder was obtained from Afton Plastics (Kel-F 81 resin). Diethyl ether and tetrahydrofuran (Fisher reagent grade) were distilled from sodium benzophenone dianion and stored under nitrogen. Benzyl chloride was obtained from Aldrich and distilled on a vacuum line (0.05 mm) from calcium hydride. Diphenylacetic acid (Aldrich) was purified by sublimation (100 °C, 0.05 mm). Methyllithium (0.47 M in ether), phenyllithium (1.7 M in cyclohexane/ether), and benzene-d_6 (Gold Label) were used as obtained from Aldrich.

Methods. Contact angles were measured with a Rame-Hart telescopic goniometer. Gravimetric analysis consisted of measuring the mass change that occurred with reaction using a Cahn 29 electrobalance. UV-vis spectra were obtained with a Perkin-Elmer Lambda 3A. Transmission spectra of films were obtained with a film-holding attachment. Infrared spectra of films were obtained with a micro ATR IR attachment and a 0.5-mm-thick germanium (45°) crystal; spectra of gaseous products were obtained with a sealed 10-cm gas cell. Proton NMR were obtained with a Perkin-Elmer R32. ESCA spectra were obtained with a Kratos XSAM 800 (Mg Kα source). Scanning electron micrographs were obtained with a JEOL 100 STEM. Gas chromatographic analyses were performed with a Hewlett-Packard 5790A gas chromatograph at 25 °C (15% AN 600 10 ft × $^1/_8$ in. column) for the analyses of chlorobenzene. Fluoride analyses were performed with a Corning fluoride-sensitive electrode and a Fisher Accumet pH meter. Chloride analyses were performed by Volhard titration.[11]

Standardization of Methyllithium and Phenyllithium. Diphenylacetic acid (0.1 g) was placed in a nitrogen-purged Schlenk tube containing a magnetic stirbar, and 10 mL of tet-

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Table I
Contact Angle, UV-Vis, and Gravimetric Changes in PCTFE Film upon Reaction with Methyllithium

reactn time, min	contact angle $\theta_{adv}/\theta_{rec}$ (water)	A_{270}	mass loss, μg
0	(104 ± 1)/(80 ± 1)	0	
2	(90 ± 1)/(54 ± 1)	0.02	3 ± 1
10	(84 ± 1.5)/(50 ± 1)	0.06	9 ± 1
20	(80 ± 1)/(49 ± 2)	0.10	19 ± 1

rahydrofuran was added. The lithium reagent was diluted with THF (1:5) in a calibrated Schlenk tube and this was added dropwise via cannula to the stirred diphenylacetic acid solution. The end point was taken as the first appearance of yellow.

Reaction of PCTFE Film with Methyllithium. A 2.0 × 1.5 cm sample of PCTFE film was placed in a nitrogen-purged Schlenk tube and covered with 10 mL of diethyl ether. The tube was placed in a bath at −78 °C for 15 min and 0.5 mL of methyllithium was added. The reaction was allowed to proceed at −78 °C for the desired time, and then methanol (5 mL) was added. The film was successively washed with 100 mL of 1 N HCl, 3 × 100 mL of distilled water, and 3 × 100 mL of methanol. The films were then dried at 0.05 mm for 24 h before contact angles were measured. The films were further dried to constant mass (24 h, 60 °C, 0.05 mm) before other measurements were made.

Reaction of PCTFE Oil with Methyllithium. PCTFE oil (1.0 g) was dissolved in 10 mL of diethyl ether in a Schlenk tube and placed in a bath at −78 °C for 15 min before the addition of methyllithium. Methyllithium solution was prepared in a graduated tube under nitrogen by diluting the desired amount to 15 mL with diethyl ether. This solution was also cooled in a bath at −78 °C for 15 min prior to its dropwise addition (over 15 min) to the stirred polymer solution. After the addition was complete, the reaction was stirred at −78 °C for an additional 15 min, allowed to warm to room temperature, at which temperature it was maintained for 15 min, and quenched with 5 mL of methanol. Pentane (GC internal standard) (0.5 mL) was added and the mixture was analyzed by GC. The reaction mixture was then extracted with 3 × 30 mL of 0.1 M nitric acid. The organic layer was concentrated to an oil by rotary evaporation and was further dried for 24 h at 50 °C and 0.05 mm. The aqueous layers were combined and analyzed for chloride and fluoride. The gaseous products from this reaction could be isolated with a series of traps at temperatures of 0, −78, and −200 °C. The analytical results are summarized in Table II.

Reaction of PCTFE Oil with Methyllithium and Benzyl Chloride. This reaction was carried out as above except that prior to warming, the solution was purged with nitrogen for 10 min, 1.5 mL of benzyl chloride was added via syringe, and then the reaction was stirred an additional 15 min.

Reaction of PCTFE Oil with Phenyllithium. The reaction was carried out as above for methyllithium except tetrahydrofuran was used as the solvent in place of diethyl ether and 0.5 mL of decane was added as the GC internal standard. The analytical results are summarized in Table III.

Reaction of PCTFE Powder with Phenyllithium. PCTFE powder (0.1 g) was placed in a nitrogen-purged Schlenk tube and covered with 10 mL of tetrahydrofuran. The tube was placed in a bath at −78 °C for 15 min and 0.5 mL of phenyllithium was added. The reaction was allowed to proceed at −78 °C for 10 min and 0.5 mL of methanol was added; 0.5 mL of decane was added and the mixture was analyzed by GC. The resulting suspension was extracted with 3 × 30 mL of 0.1 M nitric acid. The aqueous layers were combined and analyzed for chloride and fluoride. The polymer was isolated by filtration.

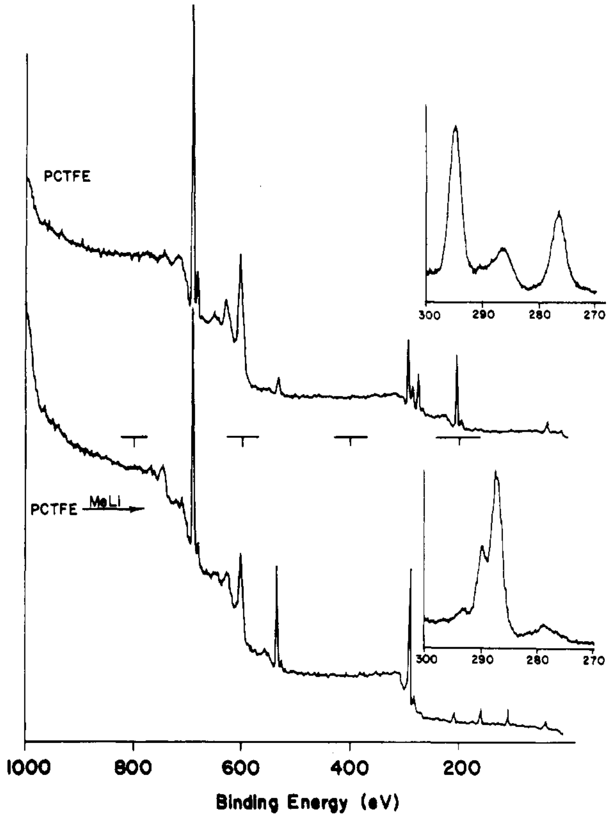


Figure 1. ESCA spectra of PCTFE film and PCTFE film after reaction with methyllithium for 5 min.

Table II
Quantitative Analyses of Products of PCTFE Oil-Methyllithium Reactions

equiv of MeLi/ equiv of PCTFE	F equiv	Cl equiv	MeCl equiv
0.50	0.38 ± 0.04	0.12 ± 0.01	0.53 ± 0.15
0.68	0.55 ± 0.06	0.13 ± 0.01	0.44 ± 0.12
1.2	1.14 ± 0.10	0.19 ± 0.02	0.93 ± 0.09

Results and Discussion

When PCTFE film is allowed to react with excess methyllithium in diethyl ether followed by hydrolytic work up, contact angle data, ESCA, UV-vis, and gravimetric analyses indicate that a reaction has taken place: Table I and Figure 1 summarize these results. The contact angles fall as the reaction proceeds. This decrease is likely a result of polar groups introduced in the workup (see below) and the reaction of the lithiated polymer with oxygen or carbon dioxide: the increase in oxygen (532 eV) is apparent in the ESCA spectra. The ESCA spectra also indicate the complete loss of CF_2 (295 eV) and Cl (277 eV). The UV-vis spectra indicate a gradual increase in absorbance at 270 nm, which can be attributed to conjugated double bonds. Gravimetric analysis indicates a steady decrease in mass. Scanning electron microscopy shows that there is no change in microtopography at a resolution of 60 Å and ATR IR spectra exhibit no changes. The sampling depth at these ATR IR conditions (Ge, 45°) is 0.5 μm at 1500 cm^{-1}. These results by themselves indicate only that a somewhat surface-sensitive reaction has taken place and suggested very little concerning the structure of the product. Except for the appearance of unsaturation, the results are consistent with the reported mechanism (Scheme I).[10]

It was possible to gain further insight into the structure of this material as well as the mechanism of the reaction by performing similar experiments on a low molecular weight oil in diethyl ether solution. When PCTFE oil is treated with 0.5–1.2 equiv (based on monomer) of methyllithium in diethyl ether at −78 °C a series of reactions occurs. Analysis of the gaseous products by GC and IR indicates that methyl chloride and no methyl fluoride is produced. Analysis of the salts produced show that it is composed of lithium fluoride and lithium chloride in a molar ratio of 6.0:1. Quantitative data for these reactions

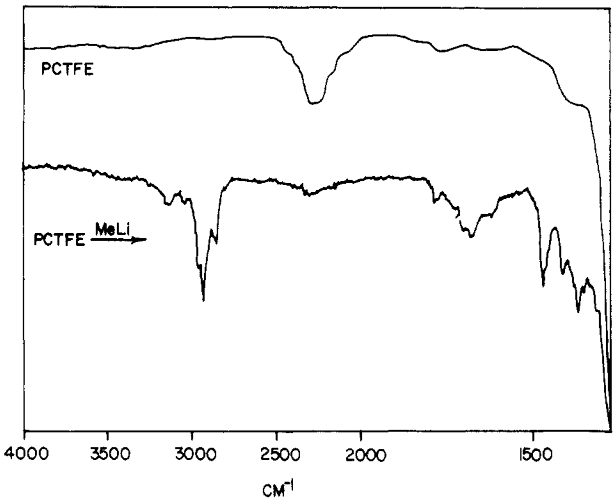


Figure 2. Infrared spectra of PCTFE oil before and after reaction with 0.5 equiv of methyllithium.

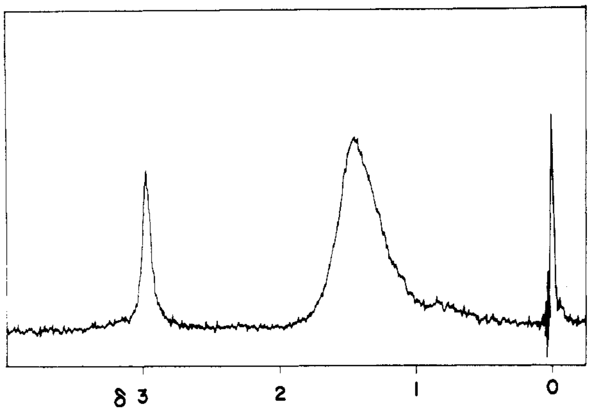


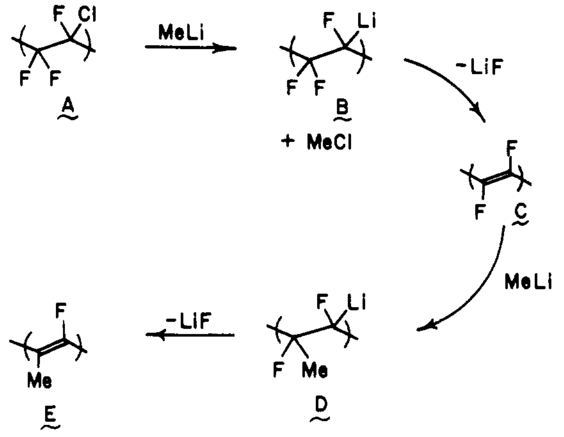
Figure 3. ^{1}H NMR spectrum (90 MHz) of PCTFE oil after reaction with 0.5 equiv of methyllithium and methanol workup.

Table III
Quantitative Analyses of Products of PCTFE Oil–Phenyllithium Reactions

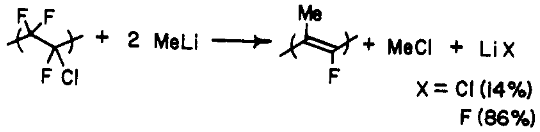
equiv of PhLi/ equiv of PCTFE	F equiv	Cl equiv	PhCl equiv
0.43	0.32 ± 0.03	0.09 ± 0.01	0.35 ± 0.03
0.85	0.69 ± 0.06	0.13 ± 0.02	0.58 ± 0.06
1.3	1.12 ± 0.10	0.19 ± 0.02	0.82 ± 0.08

are compiled in Table II. UV–vis spectra of the polymeric product indicate the formation of conjugated double bonds (see below). The infrared spectrum of the polymeric product (Figure 2) exhibits absorbances consistent with the presence of methyl groups (2980, 2885, 1450, and 1380 cm^{-1}), carbonyls with α-fluorine (1790 cm^{-1}), and conjugated carbon–carbon double bonds (1750–1600 cm^{-1}). The presence of weak bands above 3000 cm^{-1} may indicate vinyl protons, but these were not observed by NMR and must be present in only small amounts. The proton NMR spectrum (Figure 3) exhibits two resonances: the one centered at 1.45 ppm is due to the methyl groups and the one at 2.98 ppm is due to the methoxy groups introduced in the work up (see below). Obtaining accurate quantitative data for methyl chloride production was difficult due to its volatility. Analogous experiments using phenyllithium were performed as chlorobenzene analysis is straightforward. These data are compiled in Table III.

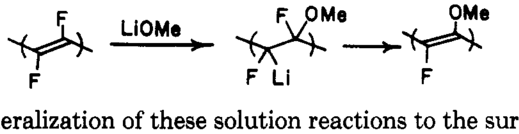
Scheme II
Proposed Series of Reactions by Which Methyllithium Reacts with PCTFE Oil



The reported mechanism[10] (Scheme I) is not consistent with these data. It does not explain the introduction of unsaturation or the production of methyl chloride, chlorobenzene, and fluoride and the data in Tables II and III indicate that the reactions that lead to these products are the principal pathways. That the surface and solution reactions do not proceed by different mechanisms was verified by treating PCTFE powder with phenyllithium and observing chlorobenzene (0.3 mmol) and fluoride (could not quantitate). We propose that the modification takes place by the series of reactions depicted in Scheme II; the modified product consists primarily of a combination of the structures indicated as C and E. The first step is a metal–halogen-exchange reaction forming B and methyl chloride. B is not stable[12] and eliminates fluoride to form C and lithium fluoride. Lithium chloride is also produced in lesser amounts: this can be attributed to the 2% head-to-head[13] linkages and to the formation of rings. The lithium fluoride:lithium chloride ratio (6.0:1) suggests ring formation is an important side reaction. B (or D) could react with oxygen or carbon dioxide to generate the observed carbonyl groups, but this reaction is not general for electrophiles: Benzyl chloride does not react and we infer that neither does methyl chloride and that methyl groups are not introduced via this reaction sequence. A second molecule of methyllithium adds to C, which subsequently decomposes to form E and more salt. Equation 1 summarizes the reaction stoichiometry. The methanolic

 (1)

workup is responsible for the incorporation of methoxy groups (Figure 3). Addition of alkoxides to fluorinated olefins is facile[14] and could occur as depicted in eq 2. E (Scheme II) could undergo the same chemistry.

 (2)

Generalization of these solution reactions to the surface modification is (as discussed above) dangerous. The data presented in Table I and Figure 1 are consistent with the solution reactions, and the reactions of PCTFE powder suggest similarities. A difference exists with regard to the UV–vis spectra (Figure 4). The film shows relatively more absorbance at higher wavelengths (dienes and trienes). This could be due to different reactions or to different extents of reaction: that the film surface reaction involves a large excess of lithium reagent suggests the latter.

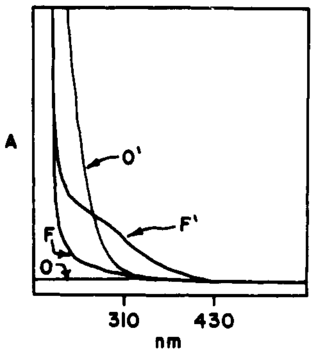
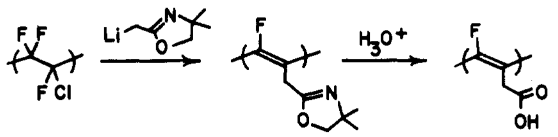


Figure 4. UV–vis spectra of PCTFE oil (O), PCTFE oil after reaction (0.5 equiv) with methyllithium (O′), PCTFE film (F), and PCTFE film after reaction (5 min) with methyllithium (F′).

The surface modification reaction appears to be less surface selective than the two-phase dehydrofluorination of poly(vinylidene fluoride):[3] it does not, however, exhibit autocatalysis and pitting. If the stoichiometry in eq 2 is assumed, the mass losses at 2-, 10-, and 20-min reaction times correlate with average reaction depths of 45, 136, and 285 Å, respectively. The contact angle data further suggest that the reaction is not surface selective: changes within the sampling depth (several angstroms) of this technique are occurring after an average of many tens of angstroms of material have reacted.

Work in progress concerns extending this chemistry to introduce surface polar functional groups (alcohols, aldehydes, and carboxylic acids). The strategy involves protecting-group chemistry. Carboxylic acids have been introduced by using the chemistry in eq 3.



(3)

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Registry No. PCTFE, 9002-83-9; phenyllithium, 591-51-5; methyllithium, 917-54-4.

References and Notes

(1) For a discussion of the theory of chemistry in reduced dimensions, see: Astumian, R. D.; Schelly, Z. A. *J. Am. Chem. Soc.* **1984**, *106*, 304.
(2) For a discussion of chemistry in noninteger dimensions between two and three, see: Pfeifer, P.; Avnir, D. *J. Chem. Phys.* **1983**, *79*, 3558.
(3) Dias, A. J.; McCarthy, T. J. *Macromolecules* **1984**, *17*, 2529.
(4) Costello, C. A.; McCarthy, T. J. *Macromolecules* **1984**, *17*, 2940.
(5) Bonafini, J. A.; Dias, A. J.; Guzdar, Z. A.; McCarthy, T. J. *J. Polym. Sci., Polym. Lett. Ed.* **1985**, *23*, 33.
(6) Clark, D. T. In "Polymer Surfaces"; Clark, D. T., Feast, W. J., Eds.; Wiley-Interscience: New York, 1984; p 309.
(7) Huth, J. A.; Danielson, N. D. *Anal. Chem.* **1982**, *54*, 930.
(8) Siergiej, R. W.; Danielson, N. D. *J. Chromatogr. Sci.* **1983**, *21*, 362.
(9) Siergiej, R. W.; Danielson, N. D. *Anal. Chem.* **1983**, *55*, 17.
(10) Danielson, N. D.; Taylor, R. T.; Huth, J. A.; Siergiej, R. W.; Galloway, J. G.; Paperman, J. B. *Ind. Eng. Chem. Prod. Res. Dev.* **1983**, *22, 303.*
(11) Vogel, A. I. In "A Textbook of Quantitative Inorganic Analysis"; Longmans Green and Co.: London, 1961; p 267.
(12) Kobrich, G. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 41.
(13) Cais, R. E.; Kometani, J. M. *Proc. Org. Coat. Appl. Sci. Div. Am. Chem. Soc.* **1983**, *48*, 216.
(14) Chambers, R. D.; Mobbs, R. H. *Adv. Fluorine Chem.* **1965**, *4*, 54.

Fluorescence Study of Factors Affecting the Complexation of Poly(acrylic acid) with Poly(oxyethylene)

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ABSTRACT: Complex formation between poly(acrylic acid) (PAA) and poly(oxyethylene) (POE) was studied by following changes in the emission of dansyl-labeled PAA (Dan-PAA). Addition of POE with a molecular weight of 24 000 (POE-24) to Dan-PAA produced an up to eightfold increase of fluorescence with a blue shift of the maximum. Addition of much higher molecular weight POE led to a relatively small increase of fluorescence, and the emission maximum was *red-shifted*, suggesting increased exposure of the dansyl label to water. This was interpreted as indicating that Dan-PAA stretched out and was in contact with POE only at widely separated regions. The model was supported by the observation that addition of POE-24 to the Dan-PAA complex with high molecular weight POE leads to emission changes similar to those seen when POE-24 is added to Dan-PAA alone. Also, displacement of Dan-PAA from POE complexes by unlabeled PAA leads first to a sharp drop but later to an increase of fluorescence, indicating that Dan-PAA is first liberated in a stretched state before contracting to its equilibrium extension. An acrylic acid copolymer with 9 mol % acrylamide forms POE complexes similar to those of PAA although polyacrylamide does not complex with POE. This suggests than an uninterrupted sequence of interacting groups is not important in the formation of PAA–POE complexes.

Introduction

It has been known for a long time that poly(acrylic acid) (PAA) forms an association complex with poly(oxyethylene) (POE).[3] This phenomenon has been studied in great detail by Kabanov and his associates, who concluded early, on the basis of solution viscosity data and pH shifts accompanying the complex formation, that the process is highly cooperative and that the complex contains stoi-