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Infrared Study of Helix Reversal in "Nafion"[1] Perfluorinated Membranes and Precursors†

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ABSTRACT: Backbone disorders, known as helix reversals in poly(tetrafluoroethylene) (PTFE), are observed in "Nafion" perfluorinated membranes and precursors. The formation energy is 1 kcal/mol and is independent of the nature and number of vinyl ether side groups. The soliton- or domain-like nature of these defects is discussed.

Introduction

"Nafion" perfluorinated membranes have been studied extensively because of their extraordinary electrochemical properties and commercial application in chloralkali cells.[2,3] The sulfonate ion-exchange polymer is obtained by hydrolysis from a precursor copolymer (XR) of tetrafluoroethylene and the sulfonyl vinyl ether $CF_2{=}CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$.[2,3] The precursor can also react with ethylenediamine (EDA) to form a sulfonamide polymer.[4] The unique transport properties[5,6] observed in these perfluorinated ionomers when submerged in an electrolyte have been correlated to the spontaneous segregation of the aqueous phase into conductive ion-containing domains randomly distributed in the insulating fluorocarbon matrix.[6,7] According to a recent elastic model,[8] the average size of these domains is controlled by the tensile property of the polymer and several other factors such that, qualitatively, a flexible and deformable polymer can support larger clusters than a stiff and rigid one. It is then important to know whether a rigid or flexible rod model would be more appropriate for "Nafion" perfluorinated membranes.

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Table I
Samples Studied in This Investigation[a]

EW	N	XR(SO_2F)	SO_3K	EDA	PTFE
1800	13	+	+	+	
1500	10	+	+	+	
1050	6	+	−	−	
					+

[a] The approximate integer of TFE units between adjacent vinyl ether groups is given in the second column. For simplicity, the perfluorosulfonyl fluoride, perfluorosulfonate, and perfluorosulfonamide polymers are abbreviated by XR(SO_2F), SO_3K, and EDA, respectively.

The rigid rod model is adequate if atomic size would control backbone rigidity. Accordingly, both the vinyl ether side group and the fluorocarbon main chain should be quite stiff because of the steric interference of neighboring fluorine atoms.[6] Nevertheless poly(tetrafluoroethylene) (PTFE) and perfluoroalkanes are known to be sufficiently flexible so that the sense (or pitch or handedness) of a molecular helix can be easily reversed. The resultant disorder is known as a helix reversal.[9-14] It had been observed experimentally by infrared (IR) spectroscopy[9] and also anticipated theoretically from conformational calculations.[13] The formation energy was estimated to be 1.2 and 1.8 kcal/mol, respectively, from IR[9] and calorimetric[10] data on PTFE, 1.1 kcal/mol from dipole moments of isolated dihydroperfluoroalkanes,[11] and 0.9–2.0 kcal/mol from model calculations.[9,12-14]

We present here a temperature-dependent IR study of PTFE, perfluorinated ionomers, and precursors to gain insight into the backbone flexibility of fluoro polymers in general. In particular, we want to delineate the influence of side groups on backbone disorders. Our data are discussed in the next section; we conclude that helix reversals exist in general, regardless of the existence, nature, and density of side groups. The formation energy is about 1 kcal/mol for the samples listed in Table I. This value is consistent with the values quoted above for PTFE and perfluoroalkanes. The soliton-like nature of these disorders is discussed in the last section.

Data Acquisition

The IR absorbances of thin films of PTFE, "Nafion" perfluorinated membranes, and their precursors were recorded on a Digilab FTS-14 infrared spectrophotometer with a nominal resolution of 4 cm^{-1}. The film temperature was controlled by an R&II temperature cell and ranged between approximately −30 and +110 °C. The types of samples that we have investigated are listed in Table I.

Spectral Analysis

The principal signature[9] of a helix reversal in PTFE consists of a doublet occurring between 600 and 700 cm^{-1}. This doublet is extremely temperature sensitive, as shown in Figure 1; over the same temperature range, other spectral regions exhibit negligible changes. The peak at 640 cm^{-1} arises from a wagging mode[15] of the CF_2 group in a normal helical conformation whereas the lower energy split-off band at 625 cm^{-1} originates from the helix reversal.[9] Room-temperature spectra for PTFE and a TFE/perfluorosulfonyl fluoride copolymer (XR) of equivalent weight (EW)[16] 1100 are compared in Figure 2. The most interesting, new, spectral features for the XR 1100 EW polymer are the strong absorption band peaking at 606 cm^{-1} and a distinct shoulder occurring at 665 cm^{-1}. Their thermal response is shown in Figure 3 for an XR polymer of 1500 EW. In contrast to the 640–625-cm^{-1} doublet, which is extremely sensitive to temperature, the new peak and shoulder hardly exhibit any observable temperature dependence. Their origins are explored below with sulfonamide polymers and hydrolyzed XR polymers.

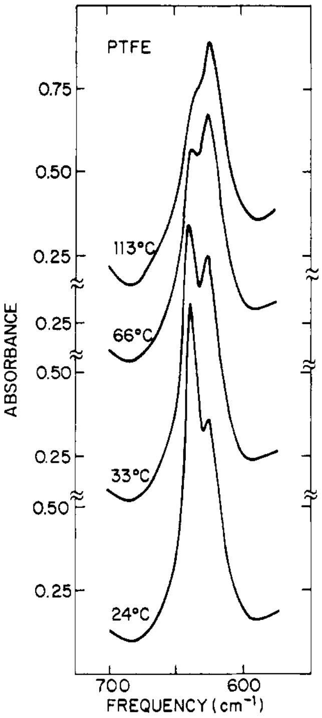

Figure 1. IR absorbance and its temperature dependence for PTFE in the spectral range of interest. The temperature-sensitive doublet arises from helix reversal (cf. ref 9).

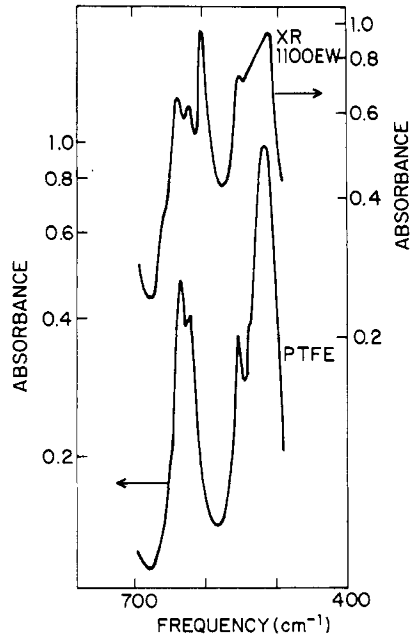

Figure 2. Comparison of IR spectra for PTFE and an 1100 EW TFE/perfluorosulfonyl fluoride copolymer (XR). Note, in particular, the very intense absorption peak at 606 cm^{-1} and a distinct shoulder at 665 cm^{-1} present in the XR spectrum.

The 606-cm^{-1} peak has markedly diminished in the sulfonamide polymers and shifted in frequency in hydro-

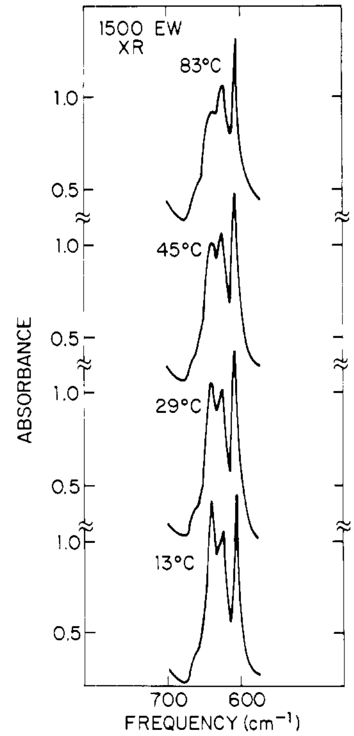

Figure 3. Temperature dependence of IR absorbance for a 1500 EW XR polymer. In contrast to the doublet, the peak at 606 cm^{-1} and the shoulder at 665 cm^{-1} are temperature insensitive.

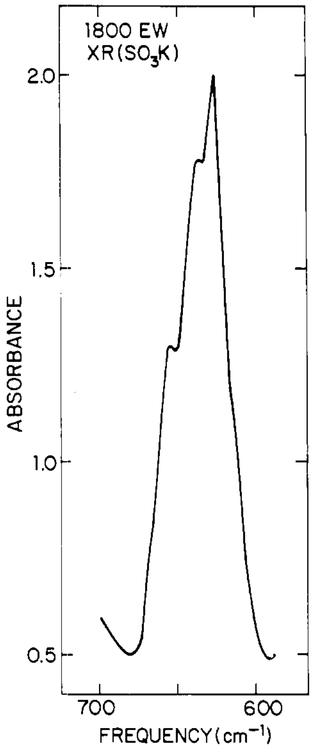

Figure 4. Typical absorption spectrum for perfluorosulfonate polymers. The 606-cm^{-1} absorption band was weakened and shifted to higher frequency. This particular sample is in the potassium salt form, XR(SO_3K).

lyzed XR polymers. A typical IR absorbance curve from the potassium perfluorosulfonate ionomer is shown in Figure 4. The 606-cm^{-1} peak found in the unhydrolyzed samples has obviously been shifted to a higher frequency and now interferes with the 640–625-cm^{-1} doublet. The peak absorbance also appears to be weakened. Figure 5 compares the room-temperature spectra of two sulfonamide polymers to two unhydrolyzed XR polymers of corresponding EW's. All samples have the same nominal thickness. The 606-cm^{-1} peak was reduced to an insignificant shoulder in EDA-modified samples. These observations together require that the 606-cm^{-1} peak be assigned to the SO_2F group of the XR polymer. The residual shoulder appearing in the sulfonamide samples arises from unreacted SO_2F groups. This peak can thus be used to monitor whether SO_2F has completely reacted with other chemicals. In contrast, the 665-cm^{-1} shoulder is observed in all "Nafion" samples but not in PTFE. It becomes more pronounced as the EW decreases (Figure 6). It is, therefore, assigned to the CF or CF_3 group of the vinyl

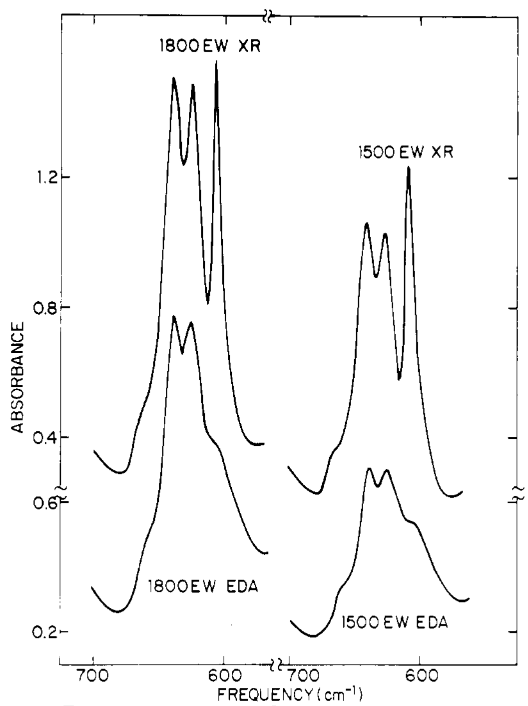

Figure 5. Room-temperature absorption spectra for perfluorosulfonyl fluoride (XR) polymers and perfluorosulfonamide (EDA) polymers at two equivalent weights.

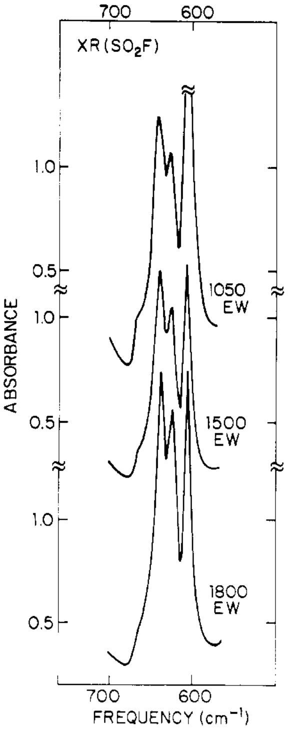

Figure 6. Spectral variation of the 665-cm^{-1} shoulder as a function of the equivalent weight for the XR polymer at 14.5 °C.

Table II
Breakdown of Eq 3 at Sufficiently Low Temperature[a]

sample	T, °C	I_{640}/I_{625} obsd	I_{640}/I_{625} interpolated
PTFE	24	1.57	1.04
1800 EW EDA	−10	1.76	1.30
1500 EW EDA	−28	2.21	1.45
1050 EW XR(SO_2F)	−20	1.96	1.40

[a] Column 4 gives the interpolated value for the ratio I_{640}/I_{625} using eq 3 and the least-squares-fitted values of C and E_d. The same abbreviations as defined in Table I are used here to identify various ionomers and precursors.

ether. Although Figures 4 and 5 indicate that the peak intensities of the doublet are affected by the nature and number of the vinyl ether groups, their ratio (i.e., the relative peak absorbance of the doublet) remains only a function of the absolute temperature. We can thus extract the characteristic formation energy of helix reversals.

Formation Energy

The peak absorbances I_{640} and I_{625} of the doublet are related to the population density n_j of the normal (j = 640) and defect (j = 625) states, respectively, by

$$I_j = a_j n_j d \qquad (1)$$

where a_j is the absorptivity for the jth state and d is the length of the sample. Assuming Boltzmann statistics, i.e.,

$$n_j = k_j e^{-\epsilon_j/RT} \qquad (2)$$

the defect energy E_d ($=\epsilon_{625} - \epsilon_{640}$) with respect to the normal state can be obtained from the relative absorbance:

$$I_{640}/I_{625} = Ce^{E_d/RT} \qquad (3)$$

where

$$C = (a_{640}/a_{625})(k_{640}/k_{625}) \qquad (4)$$

In the above equations, R is the universal gas constant, T is the absolute temperature, ϵ_j is the energy of the jth state, and k_j is a prefactor that includes possible degeneracy of states. After background correction,[17] the ratio I_{640}/I_{625} was plotted semilogarithmically against T^{-1} for all samples (except the four points listed in Table II) in Figure 7. From the ensuing least-squares fit, the formation energy E_d was determined to be 0.9 ± 0.1 kcal/mol, and the prefactor was 0.2.[18] Within our experimental accuracy, E_d is consistent with the published values quoted earlier for PTFE and perfluoroalkanes. The present data further indicate that backbone disorders in fluorocarbons are strictly a local phenomenon and independent of the presence and nature of any side groups.

Equation 3 is known to break down when T becomes near or drops below the 30 °C crystalline–disorder transition in PTFE.[9,19] In "Nafion" perfluorinated membranes, the same crystalline–disorder transition has been observed to be weakened (in strength) and depressed (in temperature) progressively with decreasing EW.[20] Thus eq 3 is obeyed even below 30 °C in perfluorinated ionomers and precursors. However, deviations can still be detected at sufficiently low temperatures as listed in Table II.

Discussion

Brown's IR data[9] on PTFE suggest that helix reversals exist at all temperatures, but their formation energy is higher and population less numerous at low T.[19] Helix reversals thus contribute prominently to the conformational entropy and thermodynamics.[21] Our low-T data (~−30 °C), albeit limited, seem to suggest a similar picture for perfluorinated ionomers and precursors.

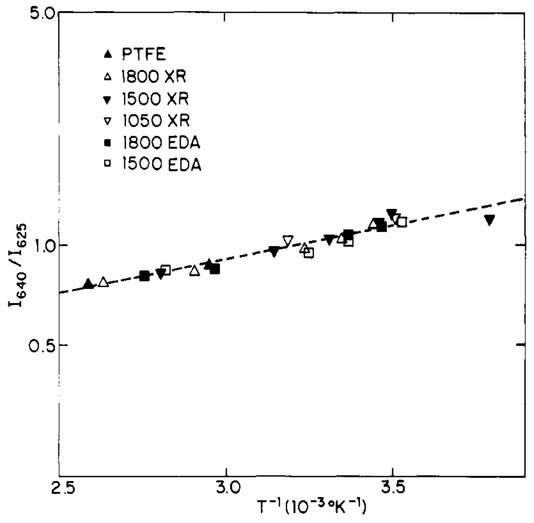

Figure 7. Relative absorbance for the doublet as a function of temperature. Four low-temperature data (Table II) were excluded from this composite plot.

To reconcile conflicting X-ray diffraction[22] and NMR[23] data from crystalline PTFE, Clark[24] proposed that the helix reversal points segregated into planes normal to the chain axes, separating the right-handed helix domains from the left-handed helix domains. Conceptually, these planes are similar to the magnetic domain walls, which are known to exhibit a solitary behavior.[25] For a single fluorocarbon chain, the right- and left-handed helical backbone conformations are isomorphic with the two degenerate all-trans states found in polyacetylene.[26] A helix reversal is thus like a domain wall in an Ising spin chain[25] or like a soliton,[27] similar to the one suggested for polyacetylene.[26] The difference may lie in the spatial extent. Usually, these excitations are sufficiently extended so that a continuum sine–Gordon or ϕ^4 model[28] is adequate; but here the soliton-like structure may be sufficiently narrow to require a discrete description. In addition, unlike polyacetylene, which is a semiconductor, PTFE and related perfluoro ionomers are wide-bandgap insulators[29] such that electronic excitations are not expected to couple into helix reversals to form charged solitons.

The idea of a solitary wave in polymer is not new. In addition to transport and spin resonant effects in polyacetylene,[26] the α relaxation of polyethylene has recently been attributed to solitons by Mansfield[30] and by Skinner and Wolynes.[31] The helix reversal discussed here appears to be another interesting example of this class of large-amplitude excitations.[32] At low temperature, the IR and NMR spectra, X-ray diffraction pattern, and thermodynamic and statistical properties of fluoro polymers could well be consistently accounted for by a double sine–Gordon model,[33] chosen to mimic the two trans states of the four-state rotational isomeric model.[10,11]

In conclusion, fluoro polymers are quite flexible torsionally. The energy required to disrupt a TFE molecular helix is only 1 kcal/mol and is independent of the nature and number of side groups.

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Registry No. Poly(tetrafluoroethylene), 9002-84-0; Nafion EW 1050, 85304-43-4; Nafion EW 1500, 63496-25-3; Nafion EW 1800, 85304-44-5.

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(17) A linear base line is employed to correct for the background. The measured absorbance is the peak-to-base line value.
(18) $C < 1$ is most likely due to different absorptivities, arising from different symmetries, of the normal and reversed helical states. For example, the cis and gauche states of 2,3-difluoropropene have very different microwave and far-IR absorptivities (cf.: English, A. D.; Scharpen, L. H.; Ewool, K. M.; Strauss, H. L.; Harris, D. O. *J. Mol. Spectrosc.* **1976**, *60*, 210).
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Investigation on Ion Binding in Synthetic Polyelectrolyte Solutions Using Rare Earth Metal Fluorescence Probes[1]

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ABSTRACT: The rare earth metal fluorescence probe technique was applied for the elucidation of the binding of metal ions to polyelectrolytes. We have observed that the presence of synthetic polyelectrolytes such as poly(sodium acrylate) (PAA) and poly(sodium ethenesulfonate) (PVS) enhances considerably the fluorescence intensity of the Tb^{3+} ion in aqueous solution. This result was accounted for by the fact that the Tb^{3+} ion was bound to asymmetrically arranged polyanions. The formation of a unique asymmetric environment surrounding the Tb^{3+} ion led to the increased transition probability for the fluorescence, and the resulting fluorescence of the Tb^{3+} ion was greatly enhanced. With poly(sodium methacrylate) and poly(sodium styrenesulfonate), the fluorescence intensity of the Tb^{3+} ion did not increase appreciably. When the methyl and phenyl groups were attached to the polymer chain, the polymer became less flexible and the multidentate complex formation between the Tb^{3+} ion and carboxylate or sulfonate became more difficult. When the Tb^{3+} ion solutions were titrated with Li-, Na-, K-, and Rb-PAA salts, the fluorescence intensity of the Tb^{3+} ion increased sharply over a small range of the PAA salt concentration and reached a constant value at higher concentration. We calculated the binding constants, K (M^{-1}), of these PAA alkali salts with the Tb^{3+} ion and found them to be 300, 390, 500, and 610, respectively, in the presence of Li, Na, K, and Rb. This order was attributed to the competition reaction between Tb^{3+} and alkali metal ions for the binding to polyacrylate. Addition of a large excess of NaCl to the solution of the PAA-Na salt and Tb^{3+} increased the fluorescence intensity of the Tb^{3+} ion. This result indicated that the electrostatic repulsion of the polymer chain was reduced by addition of NaCl and then the polymer became more compact. Such contraction would facilitate the multidentate complex formation of the Tb^{3+} ion with the carboxylate group. When EDTA was added to the solution of the PAA-Tb^{3+} complex, the fluorescence of the Tb^{3+} ion was drastically decreased and this result suggested that EDTA binds Tb^{3+} much more strongly than PAA.

Introduction

The extremely low activity coefficients of counterions in polyelectrolyte solutions are attributed to two types of association of counterions to polyions. One type of binding is referred to as "diffuse" or "ion atmosphere binding", where the counterions are localized in the area of the polyelectrolyte domain due to the large electrostatic forces and have some mobility. Another type of binding is "site binding", where the counterions are attracted to specific sites of the polyions through the formation of the complex.[2]

Positive evidence for site binding has been accumulated from studies of dialysis equilibrium,[3] dilatometric measurements,[4] UV spectroscopy,[5,6,19] and potentiometric titrations of synthetic polyelectrolytes. Site binding of counterions to biological polymers has been studied by NMR,[7] fluorescence,[8] and dichroism measurements.[8]

There has been a great stimulation of interest in the absorption and fluorescence of rare earth metal ions in

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