Macromolecules 1984, *17*, 1585-1591 **1585**

ification known[7,8] to be introduced in PE by mechanical processing. Furthermore, group theoretical analysis of the primitive unit cell indicated that a single rotatory lattice mode should be spectroscopically active and appear only in the Raman spectrum.

Normal coordinate calculations[9,26-30] and INS measurements[31-33] support the presence of a low-frequency *c*-axis lattice mode that is both IR and Raman inactive. It was concluded that the only known type of defect model that could account for the presence of LAM in these CEPE crystals while also being responsible for a breakdown in the optical selection rules was a 180° twist boundary or a 360° gently twisted disclination as suggested by Reneker and Mazur.[24]

Registry No. PE, 9002-88-4.

References and Notes

(1) B. Wunderlich and T. Arakawa, *J. Polym. Sci., Part A*, **2**, 3697 (1964).
(2) D. C. Bassett, *Polymer*, **17**, 460 (1976).
(3) U. Leute and W. Dollhopf, *Colloid Polym. Sci.*, **258**, 353 (1980).
(4) D. C. Bassett, S. Block, and G. J. Piermarini, *J. Appl. Phys.*, **45**, 4146 (1974).
(5) J. F. Rabolt and C. H. Wang, *Macromolecules*, **16**, 1698 (1983).
(6) W. F. X. Frank, H. Schmidt, B. Heise, G. W. Chantry, E. A. Nicol, H. A. Willis, and M. E. A. Cudby, *Polymer*, **22**, 17 (1981).
(7) K. Tanaka, T. Seto, and T. Hara, *J. Phys. Soc. Jpn.*, **17**, 873 (1962).
(8) T. Seto, T. Hara, and K. Tanaka, *Jpn. J. Appl. Phys.*, **7**, 31 (1968).
(9) M. Tasumi and T. Shimanouchi, *J. Chem. Phys.*, **43**, 1245 (1965).
(10) A. O. Frenzel and J. P. Butler, *J. Opt. Soc. Am.*, **54**, 1059 (1964).
(11) S. Krimm and M. Bank, *J. Chem. Phys.*, **42**, 4059 (1965).
(12) G. D. Dean and D. H. Martin, *Chem. Phys. Lett.*, **1**, 415 (1967).
(13) J. W. Fleming, G. W. Chantry, P. A. Turner, E. A. Nicol, H. A. Willis, and M. E. A. Cudby, *Chem. Phys. Lett.*, **17**, 84 (1972).
(14) B. Fanconi, *J. Appl. Phys.*, **46**, 4124 (1975).
(15) M. G. Broadhurst, *J. Res. Natl. Bur. Stand., Sect. A*, **66A**, 241 (1962).
(16) Y. Kikuchi and S. Krimm, *J. Macromol. Sci., Phys.*, **B4**, 461 (1970).
(17) P. C. Painter, J. Havens, W. W. Hart, and J. L. Koenig, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 1237 (1977).
(18) K. Matsushige and T. Takemura, *J. Cryst. Growth*, **48**, 343 (1980).
(19) L. B. Shih and R. G. Priest, *Bull. Am. Phys. Soc.*, **28**, 476 (1983).
(20) G. Strobl and W. Hagedorn, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 1181 (1978).
(21) P. J. Hendra, H. P. Jobic, E. P. Marsden, and D. Bloor, *Spectrochim. Acta*, **33A**, 445 (1977).
(22) J. R. Scherer, R. G. Snyder, and S. J. Krause, *J. Phys. Chem.*, **83**, 626 (1979).
(23) D. H. Reneker and B. Fanconi, *J. Appl. Phys.*, **46**, 4144 (1975).
(24) D. Reneker and J. Mazur, *Polymer*, **24**, 1387 (1983).
(25) M. Tasumi, T. Shimanouchi, and T. Miyazawa, *J. Mol. Spectrosc.*, **9**, 261 (1962).
(26) T. Kitagawa and T. Miyazawa, *Rep. Prog. Polym. Phys. Jpn.*, **8**, 53 (1965).
(27) M. Tasumi and S. Krimm, *J. Chem. Phys.*, **46**, 755 (1967).
(28) R. T. Harley, W. Hayes, and J. F. Twisleton, *J. Phys. C., Solid State Phys.*, **6**, L167 (1973).
(29) J. Barnes and B. Fanconi, *J. Phys. Chem. Ref. Data*, **7**, 1309 (1978).
(30) M. Kobayashi, *J. Chem. Phys.*, **70**, 4797 (1979).
(31) G. J. Safford, A. W. Naumann, and F. T. Simon, *J. Chem. Phys.*, **45**, 3787 (1966).
(32) W. R. Myers and P. D. Randolph, *J. Chem. Phys.*, **49**, 1043 (1968).
(33) L. Berghmans, G. J. Safford, and P. S. Leung, *J. Polym. Sci., Polym. Phys. Ed.*, **9**, 1219 (1971).

Dynamic Mechanical Properties of Perfluorocarboxylate Ionomers

Y. Nakano and William J. MacKnight*

Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003. *Received July 12, 1983*

ABSTRACT: Two perfluorocarboxylate ionomers of different ion-exchange capacities (IEC) of 1.25 and 1.80 mequiv/g were studied to determine their dynamic mechanical behavior, water uptake, and rates of neutralization. These polymers consist of a fluorocarbon backbone containing short side chains on the end of which the carboxylate functionality resides. They are quite similar in many ways to the more familiar perfluorosulfonate ionomers that have been studied extensively. Methyl esters, free acids, and sodium, potassium, cesium, silver, barium, magnesium, and tetrabutylammonium salts were examined. In the case of the 1.25 mequiv/g IEC resin, a two-phase morphology consisting of a fluorocarbon matrix and a dispersed "ionic" phase could well explain the observed relaxation behavior for all the salts with the exception of the tetrabutylammonium salt. It, as well as the free acid in the dry state and the ester precursor, appeared to be single-phase materials. The derivatives of the 1.80 mequiv/g IEC resin showed no unambiguous evidence for phase separation. This was attributed to their high polar group content (ca. 36 mol %). The effect of polar diluents such as water and ethylene glycol could be accounted for in the above framework. In general, these perfluorocarboxylate polymers absorb much less water and show much slower neutralization rates than similar perfluorosulfonate polymers.

Introduction

Perfluorinated sulfonate and carboxylate ionomers have been the subject of numerous investigations in recent years, largely because of their technological interest as membranes in the water-swollen form.[1] The sulfonated ionomers have received more attention than the carboxylated ionomers, but the latter show very interesting properties somewhat distinct from the former. A recent study[2] of a commercial perfluorocarboxylate ionomer membrane indicates that the polymer contains only about 50% of its polar groups in the form of carboxylates, with the rest being sulfonates. Naturally, this tends to complicate the interpretation and obscure the differences between the two forms. In the present paper we present the results of a dynamic mechanical relaxation study of two perfluorinated derivatives, including esters, acids, and salts. The results clarify and supplement the assignments of relaxation peaks to particular mechanisms made previously. They also include the effect of polar diluents such as water and ethylene glycol on the relaxation behavior.

Especially striking is the similarity of the relaxation behavior of the perfluorinated carboxylate derivatives to

0024-9297/84/2217-1585$01.50/0

Table I
Drying Conditions for the Perfluorinated Carboxylate Derivatives

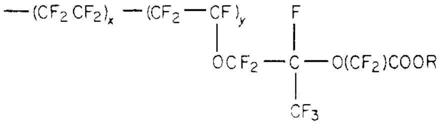
derivatives	conditions
Na salt	160 °C, 24 h in vacuo
free acid	110 °C, 4 h in vacuo
Ag and NBu_4 salts	110 °C, 4 h in vacuo
K, Cs, Mg, Ba, and Zn salts	160 °C, 6 h in vacuo

hydrocarbon carboxylate ionomers studied previously.[3]

Experimental Section

Materials. The perfluorinated carboxylate polymers studied were kindly provided by Asahi Glass Co.[4] in the form of 0.25-mm-thick films. Two derivatives were examined of ion-exchange capacities 1.25 mequiv/g (19 mol %) and 1.80 mequiv/g (36 mol %), respectively. At these levels of polar groups, the polymers are completely amorphous under all conditions.[1]

The structure of these polymers is[1]



They were originally provided in the methyl ester form (R = CH_3).

Due to the fact that previous studies had indicated appreciable quantities of sulfur in commercial samples similar to those studied here,[2] the sulfur content was determined by energy-dispersive X-ray analysis (EDAX). No sulfur was detected, confirming that the polar substituents were present wholly as carboxylates.

In the ester form, the polymers were processible and could be compression molded at 250 °C and 15000 lb/in.[2] All of the other derivatives except for the tetrabutylammonium salts were either infusible or underwent chemical decomposition at the temperature of flow. In the ester case, films were compression molded to a 0.5-mm thickness for dynamic mechanical measurements. Measurements on the other derivatives were made at a thickness of 0.25 mm.

Preparation of Derivatives. Sodium Salts. The esters were first treated with 25% aqueous NaOH at 90 °C for 24 h, washed with water, and boiled in water for 1 h. The degree of conversion to the sodium salt was assessed by gravimetry and infrared spectroscopy. The carboxyl absorption band initially present at 1780 cm^{-1} shifted to 1680 cm^{-1} (asymmetric carboxylate stretch) upon neutralization. Neutralization was complete in all cases.

Films were dried at 160 °C for 24 h in vacuo prior to measurements.

Free Acids. The sodium salts were converted to the carboxylic acid forms by treating the films with 2 N aqueous HCl at 90 °C for 24 h, followed by washing with water and boiling in water for 1 h. The degree of conversion to the acid form was again assessed by gravimetry and was complete in all cases. Infrared analysis showed that the asymmetric carboxylate stretching vibration at 1680 cm^{-1} shifted to 1775 cm^{-1} (carboxyl stretch).

Films were dried at 110 °C for 4 h in vacuo prior to measurements.

Various Salts. The free acids were neutralized by treating with aqueous solutions of the appropriate salts; 0.1 N KOH, CsOH, $AgNO_3$, $MgCl_2$, $BaCl_2$, and $ZnCl_2$ were employed. Tetrabutylammonium hydroxide (1 N) was used to prepare the quaternary ammonium salt.

All conversions were assessed by gravimetry. The films were washed with water and then boiled in water for 1 h with the exception of the tetrabutylammonium salts, which are water soluble under these conditions.

Partial Neutralization. A series of partially neutralized sodium salts was prepared by treating the free acids with 0.1 N aqueous NaOH at 25 °C for various times. The degrees of neutralization were assessed by gravimetry.

Films were washed with water and boiled in water for 1 h. Subsequently they were dried at 110 °C for 4 h in vacuo.

Measurements. Dynamic mechanical measurements were carried out with a dynamic mechanical thermal analyzer (DMTA) manufactured by Polymer Laboratories. This is a forced frequency device capable of operating between 0.01 and 90 Hz over a temperature range from −150 to +250 °C. The film samples are mounted in such a way that they undergo dual cantilever bending as a mode of deformation. All measurements were made at 1 Hz except for the ester and acid forms, where measurements were also carried out at 10 Hz. In all cases a heating rate of 5 °C/min was used.

Samples swollen with water or ethylene glycol were also examined. Films were immersed in the diluents at room temperature, and the weight of diluent uptake was measured. Boiling water was used for the free acid forms.

The drying conditions for the various derivatives are summarized in Table I.

After drying, films were mounted quickly (<5 min) in the DMTA and measurements were carried out under dry nitrogen.

Results

Table II summarizes the tan δ peak temperatures of all the mechanical dispersion regions observed in the dried forms of these derivatives. Five dispersions are observed in the sodium salts. These are labeled α, β, β', γ', and γ in decreasing order of temperature. All of the other derivatives exhibit fewer than five relaxation regions.

Figures 1 and 2 summarize the relaxation behavior of the methyl esters at 1 and 10 Hz. Only two relaxations are evident, the β and the γ. The free acid forms show similar behavior. Three relaxation regions appear, the β, γ', and γ, and the β relaxation moves to higher temperatures than in the ester derivatives.

Figures 3 and 4 show the relaxations observable in the alkali metal salts. All of these salts exhibit α and γ relaxations but some of the intermediate temperature dispersions are not evident in all the derivatives.

Table II
Temperatures (°C) of Mechanical Relaxations in the Perfluorinated Carboxylate Derivatives

	1.25 mequiv/g IEC						1.80 mequiv/g IEC					
	deg of neut, %	γ	γ'	β'	β	α	deg of neut, %	γ	γ'	β'	β	α
Me ester												
1 Hz		−55			30			−53			14	
10 Hz		−50			35			−47			21	
acid												
1 Hz		−74	−40		68			−76	−43		62	
10 Hz		−63	−20		76			−60	−20		70	
Na salt	101	−65	−30	55	205	245	106	−63	−25	40	210	248
K	96	−58		50	165	207	95	−60		50	170	210
Cs	96	−57		50	(160)	195	97	−55		50		195
Ag	66	−70	−15	50		198	94	−68	−20	45		215
$N(C_4H_9)_4$	102	−76			63	85	105	−76			55	
Mg	103	−63		50	205	228	84	−63		60	200	229
Ba	67	−62	−20	70		225	77	−65	−18	90		273
Zn	95	−63	−20	75		210	76	−66	−20	75		205

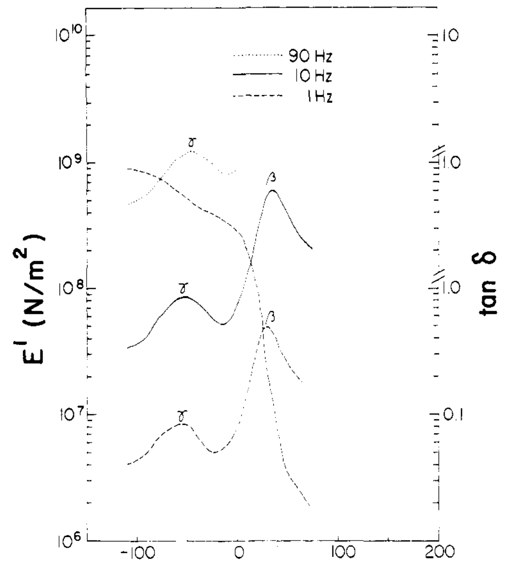


Figure 1. Temperature dependencies of E' and tan δ at 1, 10, and 90 Hz for the methyl ester derivative of the 1.25 mequiv/g IEC perfluorinated carboxylate polymer.

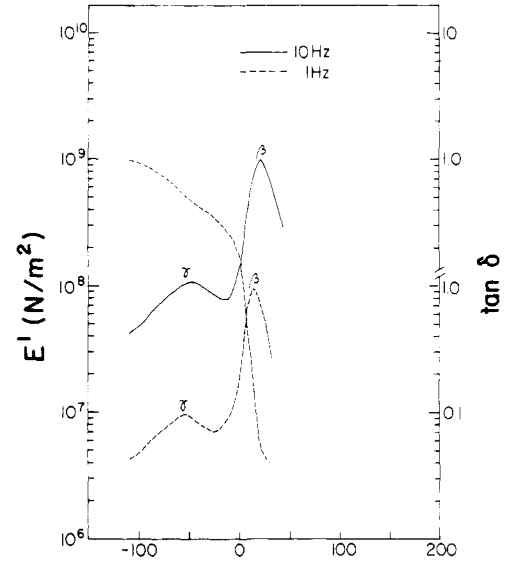


Figure 2. Temperature dependencies of E' and tan δ at 1 and 10 Hz for the methyl ester derivative of the 1.80 mequiv/g IEC perfluorinated carboxylate polymer.

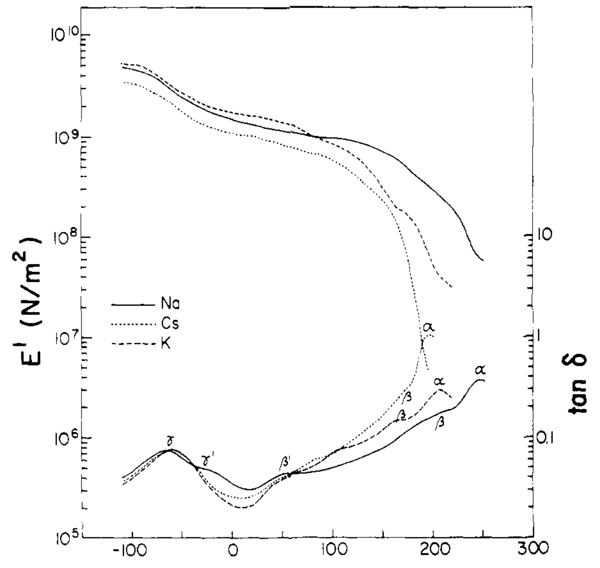


Figure 3. Temperature dependencies of E' and tan δ at 1 Hz for the Na, K, and Cs salts of the 1.25 mequiv/g IEC perfluorinated carboxylate polymer.

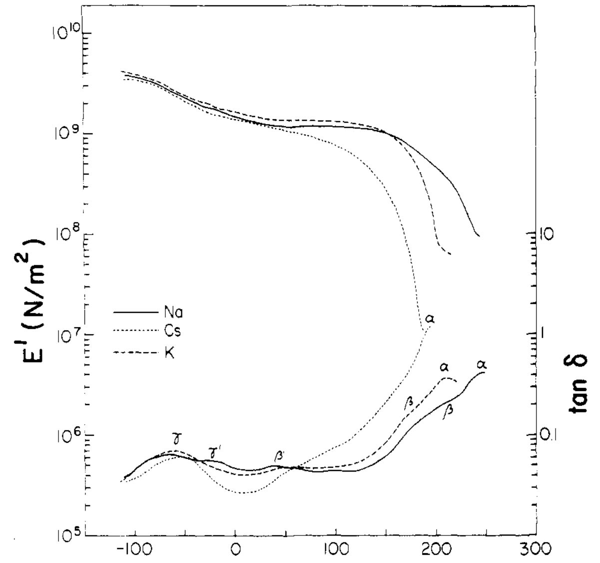


Figure 4. Temperature dependencies of E' and tan δ at 1 Hz for the Na, K, and Cs salts of the 1.80 mequiv/g IEC perfluorinated carboxylate polymer.

Figures 5 and 6 present the temperature dependencies of E' and tan δ for the silver and tetrabutylammonium salts. The behavior of the silver salt is quite similar to that of the alkali metal salts, but the tetrabutylamonium salt is quite different, being now more like the ester or acid derivatives than any of the salts.

Figures 7 and 8 show the changes in the relaxation behavior in a series of partially neutralized sodium salts. In the case of the lower IEC derivatives (1.25 mequiv/g), it can easily be seen that the α dispersion, appearing upon neutralization, rapidly moves to higher temperatures with increasing neutralization while the β relaxation remains largely unchanged in temperature, although decreasing in magnitude. In the case of the 1.80 mequiv/g IEC derivative, Figure 8, no such clear-cut separation occurs, and a single or perhaps merged relaxation peak shifts to higher temperatures with increasing neutralization.

The effects of polar diluents on the various relaxation regions are summarized in Table III. In analogy with the behavior of other ionomers, one would expect water to plasticize the ionic interactions, leaving relaxational behavior associated with the nonpolar matrix unaffected. Although water causes the γ and γ' relaxations to merge in the sodium salts, it has little or no effect on the α and β relaxations. This is because, at the high temperature of the latter relaxations, the rate of water loss from the sample is faster than the rate of measurement. As a result, a less volatile solvent, ethylene glycol, was examined. Ethylene glycol exhibits a large plasticizing effect on the temperature of the α relaxation and has some effect on the β relaxation also. The effect of water is very clearly observable in the partially (14%) neutralized sodium salt of the 1.25 mequiv/g IEC derivative. Here, the α and β relaxations are at low enough temperatures so that water is retained during the measurement, and its effect is to shift the α dispersion much more to lower temperatures (ΔT = 48 °C) than the β dispersion (ΔT = 29 °C). The effect of water on the carboxylic acid derivatives is sig-

Table III
Effects of Solvents on the Mechanical Relaxation Temperatures (°C) of the Perfluorocarboxylate Derivatives

	1.25 mequiv/g IEC					1.80 mequiv/g IEC				
	solvent content	γ	γ'	β	α	solvent content	γ	γ'	β	α
acid										
dry		–74	–40	68			–76	–43	62	
water swollen	7.9% 3.5 H_2O/COOH	–75	–55	35	78	18.4% 5.7 H_2O/COOH	–75	–55	58	
Na salt										
dry		–65	–30	210	245		–63	–25	210	245
water swollen	17.3% 7.7 H_2O/COOH	–43		208	245	36.3% 11.2 H_2O/COOH	–48		210	240
ethylene glycol swollen	22.4%	–38		77	145	19%	–40		80	125
Na salt (14% neut)										
dry		–70	–30	68	134					
water swollen	9.3% 4.1 H_2O/COOH	–70	–53	40	87					

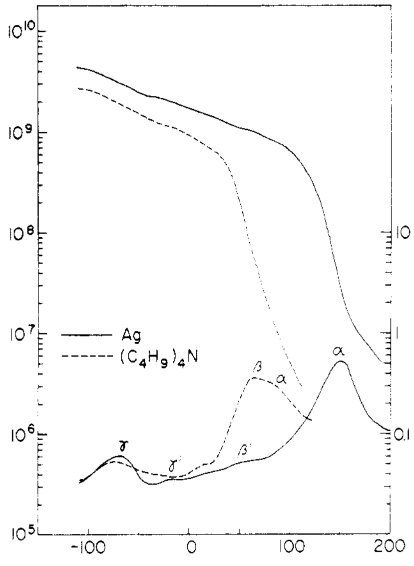


Figure 5. Temperature dependencies of E' and tan δ at 1 Hz for the tetrabutylammonium and silver salts of the 1.25 mequiv/g IEC perfluorinated carboxylate polymer.

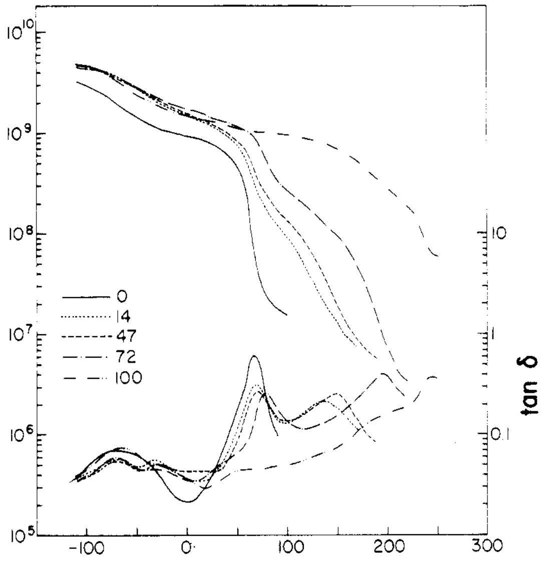


Figure 7. Temperature dependencies of E' and tan δ at 1 Hz for a series of partially neutralized sodium salts of the 1.25 mequiv/g IEC perfluorinated carboxylate polymer.

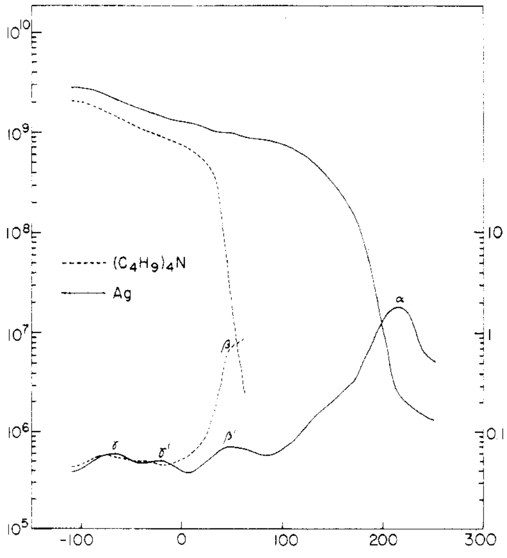


Figure 6. Temperature dependencies of E' and tan δ at 1 Hz for the tetrabutylammonium and silver salts of the 1.80 mequiv/g IEC perfluorinated carboxylate polymer.

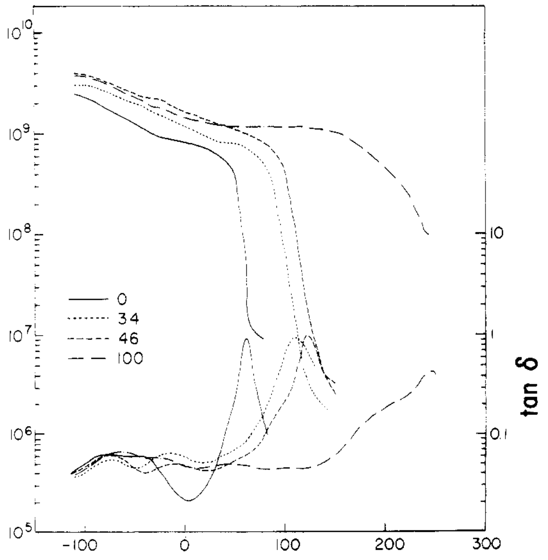


Figure 8. Temperature dependencies of E' and tan δ at 1 Hz for a series of partially neutralized sodium salts of the 1.80 mequiv/g IEC perfluorinated carboxylate polymer.

nificant and quite different for the two different IEC's. In the 1.25 mequiv/g IEC sample, water splits the single β relaxation observed in the dry state into two partially merged peaks. It also affects the shape of the γ-relaxation region. For the 1.80 mequiv/g IEC sample, the β peak is broadened and decreased in temperature, but no splitting

Table IV
Salt and Free Acid Water Uptake for the Perfluorocarboxylate Derivatives

	1.25 mequiv/g IEC			1.80 mequiv/g IEC		
		water uptake, wt %			water uptake, wt %	
	deg of neut, %	4 days in sol at 25 °C	boiled for 1 h	deg of neut, %	4 days in sol at 25 °C	boiled for 1 h
H			7.6			23
Na salt		36	41		91	101
K	97	8.6	19	97	20	68
Cs	92	8.5	13	94	22	50
Ag	72	5	5	61	17	61
$N(C_4H_9)_4$	102	12		105	18	
Mg	103	12	15	83	27	38
Ba	41	6.5	7.3	74	20	18
Zn	95	11	11	84	27	35

Table V
Rates of Neutralization to Na Salts of Perfluorocarboxylate Derivatives

1.25 mequiv/g IEC		1.80 mequiv/g IEC	
time, min	deg of neut, %	time, min	deg of neut, %
40	14	2	13
90	47	7	34
140	61	17	52
200	72	32	71

is observed. The behavior in the γ-relaxation region is similar to that for the lower IEC sample.

The water uptake data for the various salts and the carboxylic acid derivatives are summarized in Table IV. For the 1.25 mequiv/g IEC derivatives the amounts of water absorbed on boiling for 1 h are in the order $Na^+ > K^+ \geq Mg^{2+} > Cs^+ > Zn^{2+} > Ba^{2+} > H > Ag^+$. In the 1.80 mequiv/g IEC derivatives, the order is $Na^+ > K^+ > Ag^+ > Cs^+ > Mg^{2+} > Zn^{2+} > H > Ba^{2+}$. In general, these derivatives absorb much less water than the corresponding sulfonic acid derivatives.[1] The relative order of absorption among the various cations is very similar in the two cases. It was impossible to obtain data for the tetrabutylammonium salts because these derivatives are fully soluble in boiling water.

The rates of neutralization for partially neutralized sodium salts are summarized in Table V. These rates are much slower than those reported for perfluorosulfonate derivatives, where 24–36 h was sufficient to obtain fully neutralized species.[5]

Discussion

We shall discuss each relaxation region in turn, starting with the α relaxation.

α Relaxation. The α relaxation occurs only in the salt forms (Table II) and is plasticized by ethylene glycol (Table III). As previously discussed, it is likely that water also plasticizes the α relaxation, but water cannot be retained in the samples during the measurements at the high temperatures of the α relaxation. In analogy with previous results[1,2] we assign the α relaxation to motions accompanying the glass transition of the ionic phase. In early studies of polyphosphate glass transitions, Eisenberg showed that the glass transition temperature (T_g) was proportional to the charge of the cation divided by the distance between the centers of charge for the anion and cation at closest approach[6] ($T_g \propto Z/r$). The polyphosphates are, of course, single-phase materials. However, if the relaxation mechanism in the ionic phase of the perfluorocarboxylate polymers is similar to that in the polyphosphates, a similar correlation should exist for the α-relaxation temperature. Figure 9 shows that this is indeed the case for the alkali metal salts and barium. Silver also falls quite close to the curve but zinc and magnesium show very large deviations, possibly due to the somewhat covalent character of these salts. In any case, the existence of the Z/r correlation for the α relaxation strongly supports the existence of a separate ionic phase in the perfluorocarboxylate salts.

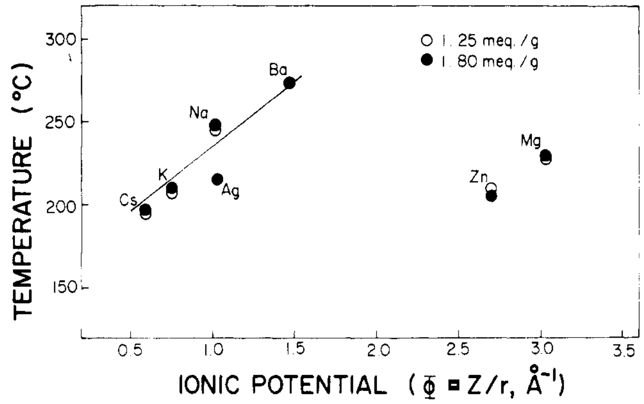


Figure 9. T_g vs. Z/r for the various salts of the perfluorinated carboxylate polymers.

The behavior of the partially neutralized sodium salts further reinforces the assignment of the α relaxation to the ionic phase motions. In the 1.25 mequiv/g IEC derivatives, there is a clear separation between the β and α relaxations, with the former remaining nearly constant in temperature and the latter increasing rapidly with increasing neutralization. This is reminiscent of the behavior observed in a series of partially neutralized sodium salts of a 4.1 mol % poly(ethylene-*co*-methacrylic acid).[3] In the present case, however, the 1.25 mequiv/g IEC derivative contains about 19 mol % carboxylic acid substituent. Nevertheless, there is little doubt about the existence of an "ionic phase" formed by the clustering of the salt groups and a less polar matrix phase in these derivatives. In the 1.80 mequiv/g IEC derivatives, the results are less clear. Here there appears to be only a single relaxation increasing rapidly in temperature with increasing neutralization. The 1.80 mequiv/g IEC derivatives contain about 36 mol % polar substituents and it may be that in this case the "ionic phase" is dominant, with the less polar fluorocarbon component perhaps existing as a dispersed phase if present at all.

When the carboxylic acid derivative of the 1.25 mequiv/g IEC polymer is swollen with water, the single large β relaxation present in the dry material splits into two. The most natural interpretation of this phenomenon would be that water causes the segregation of the acid groups into a separate polar phase. The higher temperature (α) peak in the swollen derivative would then be identified with the glass transition of this polar phase, while the lower temperature (β) peak would be identified with the glass transition of the nonpolar matrix. In other carboxylic acid ionomers,[7] it is generally thought that the free acid groups form hydrogen-bonded dimers but do not associate to form a distinct, dispersed polar phase. However, in most of the ionomers, the concentration of carboxylic acid groups is much less (<10%) than in the perfluorocarboxylate derivatives, and they are usually directly attached to the backbone rather than to the end of a fairly long side chain. Also, the fluorocarbon moiety is presumably much less "hospitable" to carboxylic acid groups than is the hydrocarbon moiety. It has been suggested[7] that water is capable of affecting structural reorganization of ionomers, but the behavior of the 1.25 mequiv/g IEC acid derivative is the first clear indication of the ability of water to actually induce phase separation. The picture is different in the higher 1.80 mequiv/g IEC derivative. Here the β relaxation present in the dry form is plasticized by water to some extent and broadened, but it remains in the form of a single relaxation. This reinforces the idea put forward to explain the behavior of the partially neutralized derivatives of the 1.80 mequiv/g IEC polymer, that, in this case, the concentration of polar groups is so great that the material is essentially single phase under all conditions or that any nonpolar phase is present to only a minor degree.

The behavior of the tetrabutylammonium salts is interesting. Figures 5 and 6 indicate that the highest temperature relaxation observed in these salts is in the vicinity of the β relaxation observed in the free acids. In the 1.25 mequiv/g IEC resin, it appears that there exists a partially merged α and β relaxation at 85 and 63 °C, respectively, but in the 1.80 mequiv/g IEC resin only one relaxation exists at 55 °C. Considering that the α relaxations of all the other salts occur at temperatures in excess of 200 °C, it is clear that ionic interactions are very much weaker in the tetrabutylammonium salts, if they exist at all, than in the others. The solubility of the tetrabutylammonium salts in boiling water also indicates the absence of strong interchain associations in these derivatives.

β Relaxation. The results leave little doubt that the β relaxation is associated with micro-Brownian segmental motions accompanying the glass transition of the fluorocarbon phase. It is clear that the polar groups participate in the β relaxation to some extent since its temperature is sensitive to the presence of water. At the high mole percentage of polar groups present in both derivatives, it is not surprising that a significant portion of them should remain in the fluorocarbon phase upon neutralization. The β relaxation in the carboxylic acid derivatives increases significantly in temperature compared to the ester precursors, a result that was also observed in studies of other carboxylate ionomers.[7] In the fully neutralized salts, the β relaxation is present only as a shoulder in the case of the 1.25 mequiv/g IEC derivatives and is difficult to detect at all in the 1.80 mequiv/g IEC derivatives. The temperture of the β relaxation is enormously increased in the salts compared to the free acids or esters and it is clear from this that extensive phase mixing between the fluorocarbon matrix and the polar groups must occur and that the dispersed "ionic phase" must exert a considerable reinforcing effect on the matrix.

In the partially neutralized sodium salts of the 1.25 mequiv/g IEC derivatives, neutralization affects the temperature of the α relaxation to a much greater extent than the β relaxation, consistent with the above interpretation. The significant increase in the β-relaxation temperature does not occur until neutralization degrees of over 70% are achieved.

In the case of the water-swollen acid derivative of the 1.25 mequiv/g IEC polymer, the β relaxation shifts to temperatures comparable to that of the corresponding ester derivatives, while a new α relaxation appears at higher temperatures. Presumably the removal of the hydrogen-bonding carboxylic acid groups from the matrix leads to this decrease in temperature of the β relaxation.

As previously discussed, it seems likely that the 1.80 mequiv/g IEC resin consists primarily of a single polar phase in all of its derivatives. The lack of a clearly defined β relaxation in most of these derivatives supports this interpretation.

β' Relaxation. Despite the extensive results quoted here we are still unable to assign the β' relaxation to a definite relaxation mechanism with certainty. It appears in all the salts of all the derivatives except the tetrabutylammonium salt and is relatively insensitive in temperature to cation type. Whether the long-chain side groups may participate in the β' relaxation is not clear, but the fact that it is somewhat sensitive to water indicates that this may be the case.

γ' Relaxation. The γ' relaxation is absent in the ester precursors, but it is present in the free acids and all of the salts with the exception of the tetrabutylammonium salt. There is little variation in temperature in the γ' relaxation either among derivatives of the same IEC resin or between derivatives of the two different IEC resins investigated. The temperature of the γ' relaxation is decreased significantly upon the addition of water (Table III). Its magnitude is also greater in the 1.80 mequiv/g IEC derivatives than in the 1.25 mequiv/g IEC derivatives. These facts lead us to assign the γ' relaxation to local motions of the portions of the polar side groups that are not phase separated from the fluorocarbon matrix.

γ Relaxation. The γ relaxation occurs at very similar temperatures for a particular derivative regardless of the IEC. Its temperature across the whole series of derivatives is also rather constant except for the ester derivatives whose γ relaxations lie at considerably higher temperatures than the others (Table II). The γ relaxation is also insensitive to the presence of water or ethylene glycol. It therefore appears that the γ relaxation originates from local motions of CF_2 groups in the main chain.

Finally, we may compare the results of Kyu and Eisenberg[8] in a study of the mechanical behavior of perfluorosulfonate ionomers to those obtained here. In general, the perfluorosulfonate derivatives show three major relaxation regions, α, β, and γ, roughly corresponding to those present in the perfluorocarboxylate derivatives. In the case of the salts, the behavior is very similar in the two cases, and the assignments of molecular mechanisms by Kyu and Eisenberg to the relaxations in the perfluorosulfonate salts are identical with our assignments for the perfluorocarboxylate salts. It appears, however, that all of the derivatives studied by Kyu and Eisenberg were muliphase materials, whereas this conclusion is doubtful for the 1.80 mequiv/g IEC perfluorocarboxylate derivatives. In the case of the perfluorosulfonate free acid derivatives, Kyu and Eisenberg observe all three relaxations, while only two are present in the perfluorocarboxylic acids. It is thus concluded that the perfluorosulfonic acids are phase separated while the perfluorocarboxylic acids are not. Similar conclusions apply to the perfluorosulfonate esters vs. the perfluorocarboxylate esters. Kyu and Eisenberg make no distinction between the γ and γ' relaxations but observe that their γ relaxations are sensitive to water. It may be that the two relaxations are merged in the perfluorosulfonate derivatives but not in the perfluorocarboxylate derivatives.

Conclusions

The mechanical relaxation behavior of the 1.25 mequiv/g IEC derivatives is readily interpretable on the basis of the "standard ionomer model". That is, the salt groups aggregate to form a separate microphase that has observable mechanical properties of its own. The fluorocarbon matrix contains considerable quantities of non-phase-separated polar groups and these modify its properties so that it no longer behaves exactly like poly(tetrafluoroethylene). The ester and acid derivatives appear to be one-phase materials in the dry state but it is likely that the acid groups cluster to form a separate polar phase in the presence of water.

The 1.80 mequiv/g IEC derivatives contain such a large quantity of polar groups (36 mol %) that they appear to be primarily one-phase materials regardless of whether they are in the ester, acid, or salt form. Any less polar fluorocarbon phase must be present as a minor component and it must contain very significant quantities of polar groups so that its properties are not very different from those of the polar or "ionic" phase.

The morphology of these derivatives needs to be investigated in detail and small-angle X-ray scattering studies are currently under way.

In general, the perfluorocarboxylate derivatives studied here absorb much less water and show much slower rates of neutralization than comparable perfluorosulfonate derivatives examined previously.

The tetrabutylammonium derivatives, although true salts, exhibits flow at experimentally accessible temperatures and are thus processible. They also dissolve in polar solvents such as dimethylformamide and water.

Acknowledgment. We are grateful to Drs. Ukihashi and Miyake of the Asahi Glass Co. for providing perfluorocarboxylate starting materials. We are also grateful to the Mitsubishi Petrochemical Co. for providing support for one of us (Y.N.). Acknowledgment is made to the Materials Research Laboratory of the University of Massachusetts for use of Central Facilities.

Registry No. $(CF_2{=}CFOCF_2CF(CF_3)OCF_2CO_2H)\cdot(CF_2{=}CF_2)$ (copolymer), 70776-76-0; $(CF_2{=}CFOCF_2CF(CF_3)OCF_2CO_2Me)\cdot(CF_2{=}CF_2)$ (copolymer), 68821-26-1; $(CF_2{=}CFOCF_2CF(CF_3)OCF_2CO_2H)\cdot(CF_2{=}CF_2)$ (copolymer) Na salt, 90481-62-2; $(CF_2{=}CFOCF_2CF(CF_3)OCF_2CO_2H)\cdot(CF_2{=}CF_2)$ (copolymer) K salt, 90481-63-3; $(CF_2{=}CFOCF_2CF(CF_3)OCF_2CO_2H)\cdot(CF_2{=}CF_2)$ (copolymer) Cs salt, 90481-64-4; $(CF_2{=}CFOCF_2CF(CF_3)OCF_2CO_2H)\cdot(CF_2{=}CF_2)$ (copolymer) Ag salt, 90507-09-8; $(CF_2{=}CFOCF_2CF(CF_3)OCF_2CO_2H)\cdot(CF_2{=}CF_2)$ (copolymer) Ba salt, 90481-65-5; $(CF_2{=}CFOCF_2CF(CF_3)OCF_2CO_2H)\cdot(CF_2{=}CF_2)$ (copolymer) Mg salt, 90481-66-6; $(CF_2{=}CFOCF_2CF(CF_3)OCF_2CO_2^-)\cdot(CF_2{=}CF_2)$ (copolymer) Bu_4N^+ salt, 90507-12-3.

References and Notes

(1) (a) M. Escorbes and M. Pineri, in "Perfluorinated Ionomer Membranes", A. Eisenberg and H. L. Yeager, Eds., American Chemical Society, Washington, DC, 1982, Chapter 2. (b) H. J. Yeager, *ibid.*, Chapter 4. (c) H. Ukihashi and M. Yamble, *ibid.*, Chapter 17.

(2) N. G. Boyle, J. M. D. Coey, A. Meaghen, V. J. McBrierty, Y. Nakano, and W. J. MacKnight, in press.

(3) W. J. MacKnight, L. W. McKenna, and B. E. Read, *J. Appl. Phys.*, 38, 4228 (1967).

(4) Flemion is a registered trademark of the Asahi Glass Co.

(5) H. L. Yeager and A. Steck, *Anal. Chem.*, 51, 862 (1979); 52, 1215 (1980).

(6) A. Eisenberg, H. Farb, and L. G. Cool, *J. Polym. Sci., Part A-2*, 4, 855 (1966).

(7) W. J. MacKnight and T. R. Earnest, Jr., *J. Polym. Sci., Part D*, 16, 41-122 (1981).

(8) T. Kyu and A. Eisenberg, Chapter 6 of ref 1.

Concerning the Origin of Broad Bands Observed in the FT-IR Spectra of Ionomers. Cluster Formation or Water Adsorption?

Barbara A. Brozoski,[†] **Paul C. Painter, and Michael M. Coleman***

Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802. *Received July 19, 1983*

ABSTRACT: Water immersion studies of ionomers derived from an ethylene–methacrylic acid copolymer have necessitated a reinterpretation of some of our previously published FT-IR results. The formation of clusters from multiplet structures was inferred from the broadening of the asymmetric carboxylate stretching vibration during annealing studies. However, it is demonstrated that broadening of this band can also be caused by the slow adsorption of water. Experiments performed under vacuum over fresh phosphorus pentoxide substantiate this hypothesis.

Introduction

Perhaps the most widely accepted model of ionomer superstructure is the multiplet–cluster concept advanced by Eisenberg.[1,2] This framework has dominated the interpretation of many vibrational spectroscopic studies to the extent that specific infrared bands and Raman lines have been separately assigned to multiplets or clusters. We were no exception to this general rule and our initial FT-IR studies of the sodium and calcium salts of ethylene–methacrylic acid copolymers were interpreted in terms of Eisenberg's model.[3,4] Specific sharp bands in the spectra of quenched films or films held at elevated temperatures (in the range 70–130 °C) were assigned to multiplets. Broad bands observed upon annealing these films for extended periods of time at room temperature were assigned to clusters. However, as a result of subsequent work on the salts of other group 1 and group 2 elements, we were forced to reevaluate these somewhat simplistic initial assignments.[5] Essentially, we used symmetry arguments to analyze the pattern of sharp bands in the spectra of freshly prepared films. On this basis, we postulated the existence of specific coordinated structures. Because infrared spectroscopy is principally sensitive to short-range order, the bands associated with such local structures should be characteristic of multiplets *and* any such assembly of multiplets in clusters. This revised interpretation left

---

[†] Current address: Experimental Station, E. I. du Pont de Nemours and Co., Wilmington, DE 19898.

0024-9297/84/2217-1591$01.50/0