Thermochimica Acta, 163 (1990) 161–168
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

EFFECTS OF WATER AND ALCOHOLS ON MOLECULAR MOTION OF PERFLUORINATED IONOMER MEMBRANES

Yuka Miura and Hirohisa Yoshida
Department of Industrial Chemistry, Tokyo Metropolitan University, 2-1-1, Fukazawa, Setagaya-ku, Tokyo 158 , JAPAN

SUMMARY

Effects of water and alcohols on the molecular motion of perfluorosulfonate ionomer Nafion having five kinds of inorganic and organic ions were investigated by dynamic viscoelastic and differential scanning calorimetric measurements. Ionomer showed five tan δ peaks; α , β , β', γ' and γ relaxations in dry state. Absorbed water slightly affected tan δ peaks, however, absorbed alcohol influenced the molecular motion of ionomers. Ionomers showed two glass transitions in dry state corresponding to the α and β relaxations. In the ethanol content above 0.08, samples showed one glass transition at 140 K irrespective of counter ion. The dynamic viscoelastic spectrum of the ethanol-dry sample was more simple than that of original sample. The molecular rearrangement occurred in the ethanol absorbed state.

INTRODUCTION

The perfluorinated ionomers, which have tetrafluoroethylene unit as main chain and ionic groups in side chain, have recently become important in the electrochemical industry since they have the high chemical stability and selectivity for ions and molecules. The high selectivity of perfluorinated ionomers is expected to due to the complex highly structure consisted of the hydrophobic fluorocarbon phase, hydrophilic ionic area and a small amount of crystallinity (ref.1). The small angle x-ray scattering works supported the core-shell model constituted by ionic cluster as a core, fluorocarbon phase as a shell and intermediate ionic phase as matrix (refs.2,3). The swelling behaviour with various solvents suggested that Nafion® had at least two swelling sites corresponding to the different solubility parameters (ref.4). The dynamic mechanical properties of Nafion® having various counter ions have been investigated using a torsion pendulum method (ref.5,6). Three mechanical relaxations were observed. The α relaxation was correlated to the molecular motion of ionic cluster and the β and γ relaxations were related to that of hydrophobic fluorocarbon phase (ref.6). The ion selectivity of ionomers was explained by the cluster-network model (ref.7). This model was also employed to explain the mechanism of membrane separation for the alcohol-water systems (refs.8,9). However, it is necessary to discuss the

0040-6031/90/$03.50

molecular selectivity of ionomers not only from the viewpoint of structure but also from the standpoint of molecular motion. In this study, the effects of water and alcohols on the molecular motion of ionomers having inorganic and organic monovalent ions were investigated by dynamic viscoelastic and differential scanning calorimetric measurements.

EXPERIMENTAL

Samples

The perfluorosulfonate ionomer Nafion® supplied from E. I. du Pont de Nemours & Co. Inc. was used through this study. The equivalent weight of Nafion® was 1,100 g/eq. The supplied polymer was converted to the acid form by acid hydrolysis. Five kinds of monovalent ions, such as lithium [Li^+] , potassium [K^+] , ammonium [$NH_4{}^+$] , dimethylammonium [$(CH_3)_2NH_2{}^+$] and tetramethylammonium [$(CH_3)_4N^+$] were used as the counter ions of ionomer. The degree of neutralization was about 90 % for all ions. Ionomer samples were soaked in distilled water, ethanol and methanol for various period in order to control the content of water and alcohol.

Measurements

A Seiko thermal analysis system SSC 5000 connected with a differential scanning calorimeter DSC 200 equipped with cooling apparatus was used. DSC curves were obtained in the temperature ranging from 100 to 500 K, sample weights were 5-10 mg, the scanning rate was 10 K/min. Temperature and enthalpy were calibrated using 1,2-dichloroethane, water and indium as the standard. The extrapolated onset temperature (ref.10) was employed as the glass transition temperature (Tg).

The dynamic viscoelastic properties of samples were measured by a Seiko dynamic mechanical spectrometer DMS 100 connected with a Seiko Rheol. Station SDM 5500. Dynamic viscoelastic spectra were obtained in the temperature ranging from 150 to 500 K, the sample size was 4 mm (width) x 30 mm (length) x 0.2 mm (thickness), the scanning rate was 2 K/min. The shear mode was employed at frequency ranging from 0.1 to 10 Hz. Temperature was calibrated using indium and dynamic shear modulus was calibrated using chloroprene rubber as the standard.

The wide angle X-ray diffraction of ionomers was measured by a MAC science MXP¹⁸ X-ray diffractometer with Cu-Kα operated at 40 KV and 200 mA. The degree of crystallinity of ionomer was determined by the diffraction peak separation method.

RESULTS AND DISCUSSION

Fig.1 shows dynamic viscoelastic spectra of ammonium and alkylammonium salts of Nafion® in dry state at 1 Hz. Loss tangent (tanδ) curve of $NH_4{}^+$ salt sample showed five peaks, which were named α, β, β', γ' and γ relaxations from higher temperature as same as the viscoelastic behaviour of alkali metal salt type of perfluorocarboxylate ionomers (ref.11). Among five relaxations, the α peak shows the highest intensity and the β and β' relaxations appear as a shoulder of lower intensity. As can be seen in Fig.1, the α peak intensity also depended on the counter ions. For the $(CH_3)_2NH_2^+$ salt sample which shows the lowest α relaxation peak temperature, the β relaxation peak overlaps with the α peak. All samples showed the same γ peak temperature, however, the peak intensity seemed to depend on the counter ion. The $(CH_3)_4N^+$ salt sample showed the highest γ intensity without the γ' relaxation.

The tan δ peak temperatures of samples having various ions in dry state at 1 Hz were listed in Table 1. The apparent activation energy of relaxations which were calculated from the frequency dependence of tan δ peak temperature and the degree of crystallinity (Xc) were also shown in Table 1.

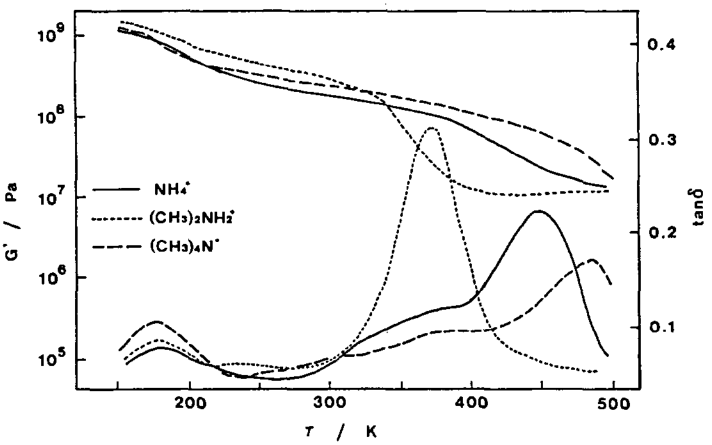

Fig.1 Dynamic viscoelastic spectra of ammonium and alkylammonium salts Nafion in dry state at 1 Hz.

TABLE 1

Tan δ peak temperatures of Nafion® with different counter ions in dry state at 1Hz.

counter ion	α (KJ/mol)*1	β	β'	γ'	γ (KJ/mol)	Xc
NH_4^+	449 K (208)	374 K	326 K	216 K	179 K (74)	7.3%
$(CH_3)_2NH_2^+$	374 (255)	-	-	234	179 (72)	5.1
$(CH_3)_4N^+$	484 (308)	380	310	-	177 (79)	6.5
Li^+	448 (237)	335	301	215	170 (74)	7.1
K^+	481 (219)	363	-	234	175 (50)	5.7
H^+	393	-	267	204	175	6.8

*1 Figures in parentheses show the apparent activation energy.

According to Kyu and Eisenberg (ref.6) , the α peak temperature was influenced by the degree of neutralization as well as by the degree of crystallinity. As both values of degree of neutralization and crystallinity of samples used in this study were almost the same, the α peak temperature depended on the type of counter ions.

Fig.2 shows dynamic viscoelastic spectra of NH_4^+ salt sample with different conditions such as dry (a), water absorbed (b; ca. 2wt%), methanol absorbed (c; ca. 16wt%) and ethanol absorbed state (d; ca. 26wt%) at 1 Hz. The dry sample shows the γ relaxation peak and the γ' relaxation as a shoulder of lower intensity, however, the water absorbed sample shows the γ' relaxation peak which is the same intensity as the γ peak. On the other hand, the alcohol absorbed samples show the γ' relaxation peak at around 200 K accompanied with the γ relaxation as a shoulder. The γ' peak intensity of the alcohol absorbed samples was the same as that of the β relaxation of dry sample. The γ' peak temperature sifted to lower temperature with the increase of alcohol content. The effect of water content on the γ' peak temperature was uncertain, because it was difficult to change water content without ice formation in this temperature range. Since storage shear modulus (G') of the water and alcohol absorbed samples increased at room temperature, the tan δ peak observed at around 300 K was due to the evaporation of absorbed materials.

Fig.3 shows dynamic viscoelastic spectra of same samples shown in Fig.2 at temperatures above 300 K. From the separate thermogravimetric measurement, about 15 % of absorbed alcohol existed at 320 K and most of

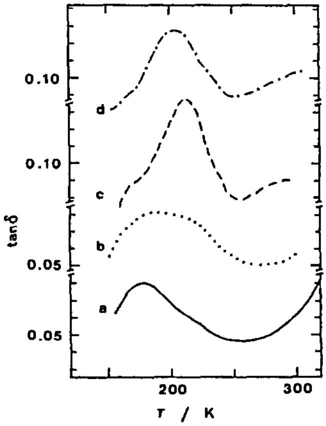

Fig.2 Dynamic viscoelastic spectra of ammonium salt Nafion at 1 Hz in dry (a) , water absorbed (b), methanol absorbed (c), and ethanol absorbed (d) state.

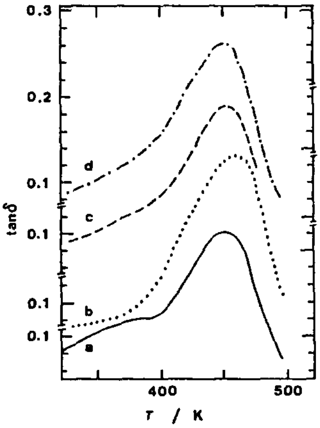

Fig.3 Dynamic viscoelastic spectra of ammonium salt Nafion at 1 Hz in dry (a) , water absorbed (b), methanol absorbed (c), and ethanol absorbed (d) state.

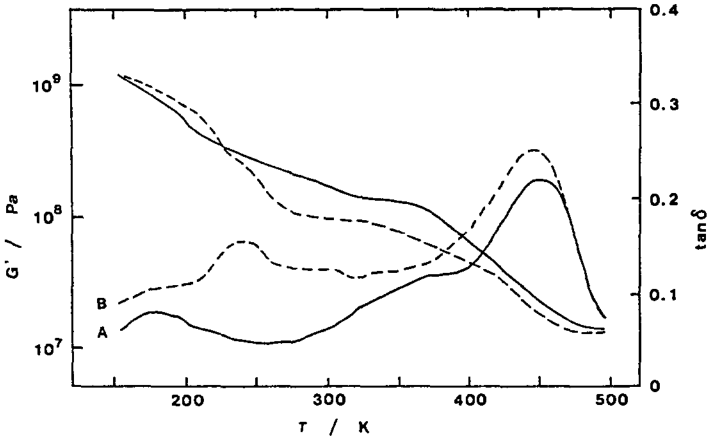

Fig.4 Dynamic viscoelastic spectra of ammonium salt Nafion having different histories at 1 Hz . A : dry sample from water absorbed state , B : dry sample from ethanol absorbed state.

alcohol evaporated at 420 K. Therefore, the absorbed alcohols hardly contributed to the α relaxation peak but to the β relaxation peak. As water molecules remained even at 400 K (ref.12), both α and β peaks would be influenced by absorbed water. The β relaxation peak of the water absorbed sample shifted to lower temperature and became smaller, however, the α peak shifted to higher temperature and the peak intensity increased. The β relaxation of alcohol absorbed samples broadened and merged with the α peak. These facts suggest that the β relaxation may be associated with molecular motion including the ionic group.

Fig.4 shows dynamic viscoelastic spectra of NH_4^+ salt sample in dry state having different histories. Samples were dried from the water absorbed state (A) and the ethanol absorbed state (B). Sample A shows the same spectrum of dry sample shown in Fig.1. For sample B, however, the γ peak shifted to higher temperature and the peak intensity increased. The β peak of sample B disappeared and the α peak temperature shifted to lower temperature and the peak intensity increased. The value of G' of sample B was lower than that of sample A at temperatures above 230 K. The molecular motion of ionomer was influenced by the previous swelling history. The molecular rearrangement including ionic group probably take place in the ethanol absorbed state.

Fig.5 shows DSC curves of NH_4^+ salt sample with various ethanol content. The dry sample (A) shows two glass transitions at 324 K and 415 K. These glass transitions corresponded to the α and β relaxations. The lower Tg was influenced by annealing at temperatures from 300 K to 380 K. The dry sample

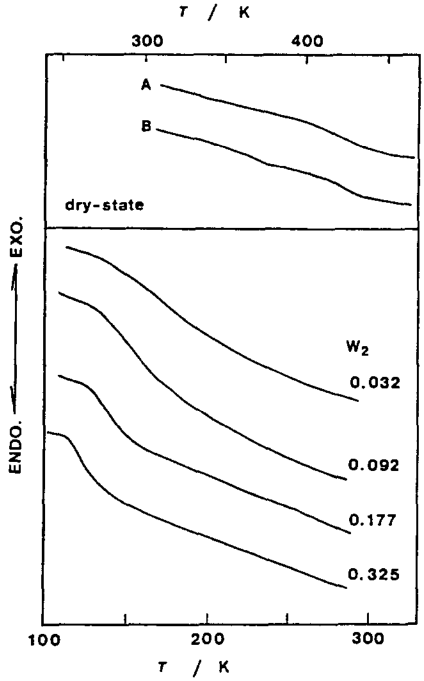

Fig.5 DSC curves of ammonium salt Nafion in dry and in ethanol absorbed state. Dry samples A and B are quenched and annealed samples.

annealed at 353 K for 1 hr (B) shows the endothermic peak due to the enthalpy relaxation at 380 K. In the ethanol content above 0.08, sample showed one Tg. With increasing ethanol content, Tg shifted to lower temperature and the heat capacity difference between glassy state and super-cooled liquid state at Tg (Δ Cp) increased. Since the evaporation of water overlapped glass transition, Tg of the water absorbed sample was uncertain, however, the lowering Tg was not observed. For samples having water content above 4 wt%, only melting of ice was observed (ref.13). Water molecules in the ionic cluster hardly acted as a plasticizer of ionomer, however, alcohol molecules penetrated into fluorocarbon matrix and affected Tg of ionomer.

Fig.6 shows the relationship between Tg and ethanol content for Li^+ and NH_4^+ salt samples. Tg decreased remarkably with increasing ethanol content. The Tg values of two components system were calculated by the additivity law as presented in the following equation.

$$\ln Tg = (w_1 \Delta Cp_1 \ln Tg_1 + w_2 \Delta Cp_2 \ln Tg_2)/(w_1 \Delta Cp_1 + w_2 \Delta Cp_2) \qquad (1)$$

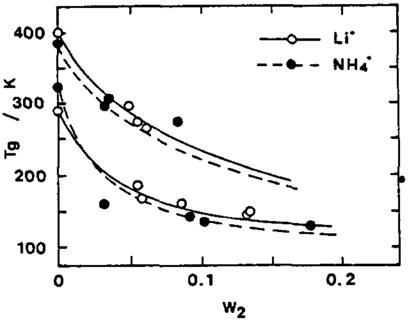

Fig.6 Tg changes with ethanol content for lithium and ammonium salts Nafion.

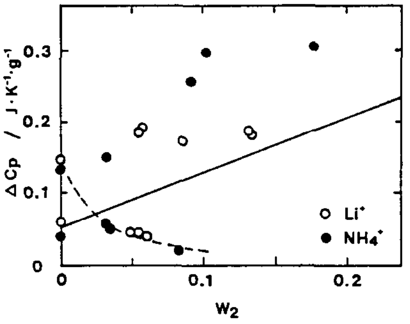

Fig.7 ΔCp changes with ethanol content for lithium and ammonium salts Nafion.

where, w_i and ΔCp_i were weight fraction and ΔCp of i-th component, respectively. The subscripts 1 and 2 denoted ionomer and ethanol, respectively. The values of Tg_2 and ΔCp_2 used for calculation were 95 K and 0.83 J/K g (ref.14). The solid and broken lines shows the calculated values using eq. (1) for Li^+ and NH_4^+ salt samples, respectively. Usually, eq. (1) described the relationship between Tg and composition in the homogeneous mixture systems such as the polymer blend systems (ref.15) and the water-polysaccharide systems (ref16). In the ethanol content range above 0.08, Tg approached to a constant value in spite of type of counter ion. As the experimental values agreed with the calculated Tg, ethanol molecules distributed homogeneously in ionomer at ethanol content above 0.08.

Fig.7 shows ΔCp changes with ethanol content for Li^+ and NH_4^+ salt samples. For the ethanol content range between 0 and 0.08, the value of ΔCp of higher Tg decreased and became hard to observe. The value of ΔCp of lower Tg increased extremely and approached to the constant value at ethanol content above 0.08. The solid line shows the linear additivity of ΔCp between ionomer and glassy ethanol. This fact suggested that ethanol molecules distributed homogeneously in ionomer at ethanol content above 0.08.

Two glass transitions observed in the dry sample supported the heterogeneous structure of perfluorinated ionomer. As pointed out by other researchers, ionic groups existed heterogeneously in the ion cluster and the fluorocarbon matrix. The α relaxation was associated with the glass transition of the ion-rich phase including the ion cluster. The β and β' relaxations related to the fluorocarbon matrix having different portion of ionic group. The molecular motion of ionomer was slightly influenced by absorbed water which existed in the ion cluster. Absorbed alcohol molecules diffused into not only the ionic cluster but also the fluorocarbon matrix and decreased Tg of ionomer. The γ' relaxation observed for the alcohol absorbed sample was associated with the glass transition of the alcohol swollen ionomer. In the ethanol swollen state, the molecular rearrangement occurred and the ionic group distributed homogeneously. Therefore, the ethanol-dry sample showed more simple dynamic viscoelastic spectrum than that of original sample. These facts suggested that the heterogeneous structure of perfluorinated ionomer might be the metastable state.

REFERENCES

1. A.Eisenberg and H.L.Yeager (Ed.) in Perfluorinated Ionomer Membranes, (ACS Symposium Ser. 180), Am.Chem.Soc., Washington D.C., (1982) pp1-8
2. M.Fujimura, T.Hashimoto and H.Kawai, Small-angle x-ray scattering study of perfluorinated ionomer membranes 2, Macromolecules, 15 (1982) 136-144
3. D.Lee, R.A.Register, C.Yang and S.L.Cooper, Methylenebis(p-phenyl isocyanate)-based polyurethane ionomers 1, Macromolecules, 21 (1988) 998-1004
4. R.S.Yeo, Dual cohesive energy densities of perfluorosulphonic acid membrane, Polymer, 21 (1980) 432-435
5. S.C.Yeo and A.Eisenberg, Physical properties and supermolecular structure of perfluorinated ion-containing polymers, J.Appl.Polym.Sci., 21 (1977) 875-898
6. T.Kyu and A.Eisenberg, Mechanical relaxations in perfluorosulfonate ionomer membranes: Perfluorinated Ionomer Membranes, in: A.Eisenberg and H.L.Yeager (Ed.), (ACS Symposium Ser. 180) Am.Chem.Soc., Washington D.C., (1982) pp93
7. T.D.Gierke, G.E.Munn and F.C.Wilson, The morphology in Nafion perfluorinated membrane products, J.Polym.Sci.,Phys.Edn., 19 (1981) 1687-1704
8. I.Cabasso and Z.Liu, The permselectivity of ion-exchange membranes for non-electrolyte liquid mixtures I., J.Membrane Sci., 24 (1985) 101-119
9. I.Cabasso, Z.Liu and T.Makenzie, The permselectivity of ion-exchange membranes for non-electrolyte liquid mixtures II., J.Membrane Sci., 28 (1986) 109-122
10. S.Nakamura, M.Todoki, K.Nakamura and H.Kanetsuna, Thermal analysis of polymer samples by a round robin method I., Thermochim.Acta, 136 (1988) 163-178
11. Y.Nakano and W.J.MacKnight, Dynamic mechanical properties of perfluorocarboxylate ionomers, Macromolecules, 17 (1984) 1585-1591
12. N.J.Bunce, S.J.Sondheimer and C.A.Fyfe, Proton NMR method for the quantitative determination of the water content of the polymeric fluorosulfonic acid Nafion-H, Macromolecules, 19 (1986) 333-339
13. Y.Miura and H.Yoshida, Behaviour of water in the perfluorinated carbon polymer with alkyl ammonium ions, Polymer Preprints Japan, 37 (1988) 1062
14. H.Suga and S.Seki, Thermodynamic investigation on glassy states of pure simple compounds, J.Non-Crystalline Solids, 16 (1974) 171-194
15. P.R.Couchman, Compositional variation of glass transition temperature 2, Macromolecules, 11 (1978) 1156-1161
16. H.Yoshida, T.Hatakeyama and H.Hatakeyama, Glass transition of hyaluronic acid hydrogel, Kobunshi Ronbunshu,46 (1989) 597-602