Polypyrrole-Based Conducting Polymer Alloy Films: Physical Properties and Film Morphology

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ABSTRACT: The electrochemical polymerization of pyrrole on an electrode covered with an insulating polymer film produces novel conducting polymer alloy films of polypyrrole (PPy) and the insulating polymer. The relationship between physical properties and the film structure of the alloy film was studied by using poly(vinyl chloride) and vinylidene fluoride–trifluoroethylene copolymer as insulating polymers. The incorporation of PPy into the film greatly increases the electrical conductivity of the alloy film and improves the mechanical property in the high-temperature region. However, the effect of the PPy amount on the physical properties varies by the insulating polymers. This effect can be explained in terms of the film morphology, which was studied by scanning electron microscope observation of the alloy films before and after solvent extraction.

Introduction

Various aromatic compounds can be polymerized by electrochemical oxidation in a solution containing a supporting electrolyte. The reaction involves the subtraction of hydrogen from the monomer, forming fully conjugated aromatic polymers.[1] The simultaneous electrochemical doping of electrolyte anions renders these polymers highly electrically conducting. The highest conductivity of electrochemically produced conducting polymers, about 500 S/cm for poly(3-methylthiophene),[2] is almost comparable to that of doped polyacetylene. Among these electrochemically produced polymers, polypyrrole (PPy) shows the most attractive properties, such as high conductivity of more than 300 S/cm,[3] good stability in ambient conditions, and film-forming property on an electrode surface. However, several drawbacks limit the application of PPy for practical use as a conducting polymer. These films are very hard, deeply black in color, and cannot be produced with a controlled conductivity. Moreover, relatively long polymerization time is necessary to make a film with a practical thickness, typically greater than 10 μm.

Recently several groups[4,5] have reported that the electrochemical polymerization of pyrrole occurs on an electrode substrate whose surface is coated with an ordinary insulating polymer film. In this case, monomer molecules and the electrolyte anions can diffuse into the polymer films when the electrolyte solution is adjusted according to the kind of polymer used. The polymerization starts around the interface between the electrode surface and the polymer film. The resultant PPy grows inside the polymer film, forming a novel electrically conducting polymer alloy film. We have confirmed that a number of insulating polymer films can be easily changed into electrical conductors by alloying with PPy. This process has great potential not only in improving the film quality of electrochemically produced conducting polymers but also in realizing PPy-based functional devices due to the wide freedom of design in the electrical and optical properties of conducting films.[6]

In this paper, the physical properties and the morphology of PPy-based conducting polymer alloy films were investigated by using two kinds of insulating polymers with quite different properties. One is poly(vinyl chloride) (PVC) (Wako Pure Chemicals, M_w = 70 000), which is chosen as an amorphous and relatively high glass-transition temperature (T_g) polymer. Vinylidenefluoride–trifluoroethylene copolymer (PVDF–TrFE) (Daikin), which is known to show ferroelectric property,[7] is a highly crystalline and low T_g polymer.

Experimental Section

Table I summarizes the properties and experimental conditions of the two insulating polymers used. Films (20 μm thick) were formed on indium–tin oxide (ITO) coated glass substrate by casting at 35 °C. The ITO substrate with a polymer film was immersed in an acetonitrile-based polymerization solution containing 1 mol/L of pyrrole and 0.3 mol/L of tetraethylammonium p-toluenesulfonate (Tokyo Kasei) as a supporting electrolyte. Pyrrole (Tokyo Kasei) was polymerized by applying a constant voltage of 2–5 V between the ITO electrode and Pt-plated Ti meshes as a counterelectrode. The amount of PPy was controlled by measuring charge density using a digital Coulomb meter (PAR-379). After the polymerization, the film was washed with ethanol and stripped from the substrate.

The conductivity of the films was evaluated from the surface resistance measurements of both film sides by means of a 4-terminal method. The mechanical properties of films were investigated from the measurements of dynamic modulus of elasticity (E, dyn/cm^2) by using a longitudinal viscoelastometer (Toyo Baldwin, Rheovibron DDV-III-EA). The film morphology was studied by scanning electron microscope (SEM, JEOL JSM-840) observations of alloy films. To obtain information about the growth of PPy chains inside the polymer film, a soluble base polymer component was extracted from the alloy film with tetrahydrofuran. This extraction left PPy components, which were still filmlike in most cases and which were subjected to SEM observations.

Results and Discussion

Electrical Properties. As PPy starts to grow from the film side attached to the ITO electrode surface, only the electrode side of the film becomes conductive in the early stage of polymerization. The surface side contacted with the polymerization solution is insulating at first and shows conductivity after PPy chains reach the surface side.[8] This means that the conductivity of both film sides is considerably different and cannot be defined accurately. Thus, the film conductivity should be evaluated by the surface resistance values of the two film sides.

Figures 1 and 2 show the surface resistances of PVC/PPy and PVDF–TrFE/PPy alloy films, respectively, produced at 2 V as a function of charge density. In all cases the electrode side of the films was conducting. A small amount of charge density drastically decreases the surface resistance, and with the increase of charge density the resistance values are gradually reduced. On the other hand, the surface side that was insulating with a small charge density becomes conducting at a charge density greater than 1.0 C/cm^2 for PVC and 0.5 C/cm^2 for PVDF–TrFE. At these critical charge densities, the resistance values show a relatively large variation among samples. At the higher charge densities the resistance

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Table I
Polymer Films Used as Base Films[a]

polymer	composition, wt %	T_g, °C	cast solvent
poly(vinyl chloride) (PVC)	homopolymer	81	ethyl methyl ketone/tetrahydrofuran, 1:1
vinylidene fluoride–trifluoroethylene copolymer (PVDF–TrFE)	VDF/TrFE, 52.3:47	−35	ethyl methyl ketone/acetone, 1:1

[a] Film thickness: 20 μm.

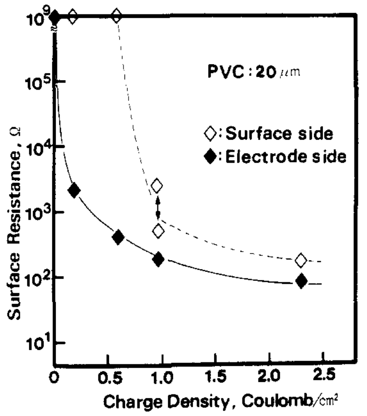


Figure 1. Surface resistances of PVC/PPy alloy films prepared at 2 V with various charge densities.

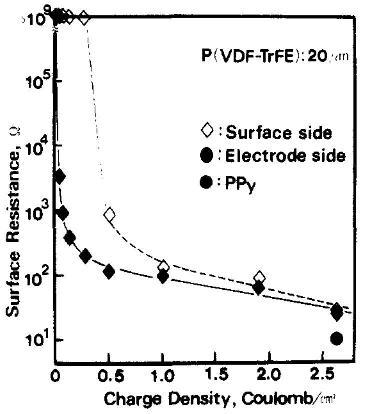


Figure 2. Surface resistances of PVDF–TrFE/PPy alloy films prepared at 2 V with various charge densities.

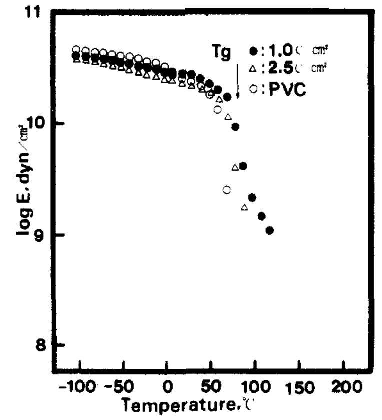


Figure 3. Temperature dependence of dynamic modulus of elasticity of PVC and PVC/PPy films.

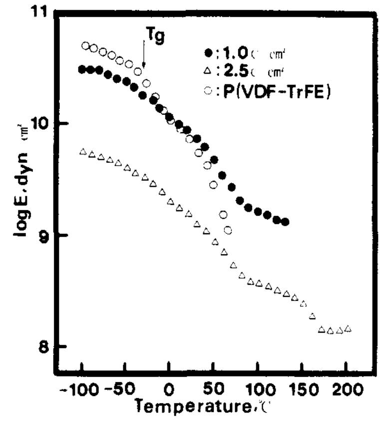
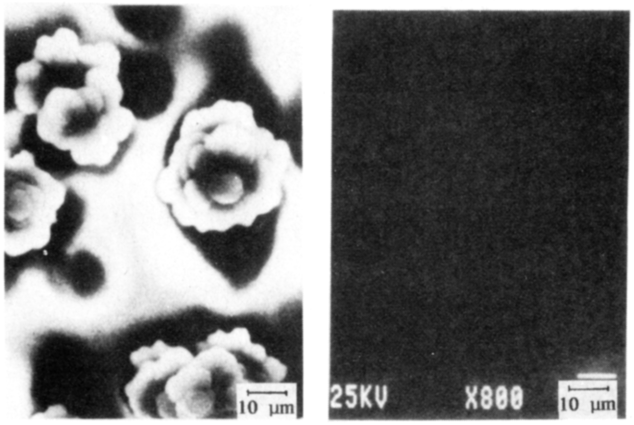


Figure 4. Temperature dependence of dynamic modulus of elasticity of PVDF–TrFE and PVDF–TrFE/PPy alloy films.

values become almost constant, indicating PPy chains grow on the surface side all over the film. Polymerization at a voltage higher than 2 V decreases the critical charge density. As a high applied voltage also increases the electrolytic current, PPy chains rapidly reach the film surface. For example, only 2–3 min at 5 V is necessary to produce 25-μm-thick PVC/PPy alloy films with a conductivity of 0.2–1 S/cm.

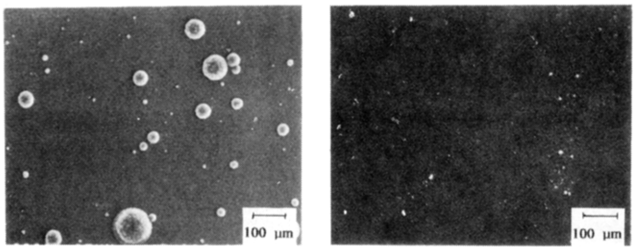
In PVDF–TrFE/PPy, the resistance value of the surface side becomes almost identical with that of the electrode side, whereas PVC/PPy alloy films show a substantial difference between the two values. This result is closely related with the film morphology, which is discussed in a later section. In PVDF–TrFE/PPy alloy film, the maximum conductivity obtained so far is 15 S/cm (a surface resistance of 20 Ω) at a charge density of 2.5 C/cm^2. The weight measurements of the alloy films before and after the solvent extraction revealed that this film contains about 28 wt % PPy by the polymerization of 2.5 C/cm^2 at 2 V. The same polymerization conditions on a neat ITO electrode produces 7–8-μm-thick pure PPy films with a surface resistance of 10 Ω, which is almost half that of 28-μm-thick PVDF–TrFE/PPy alloy films. In ordinary conducting polymer composites where fine carbon-black particles are simply mixed in the polymer matrix, carbon contents must be more than 80 wt % to get such a high conductivity. When the carbon content is 30 wt %, the conductivity of the composite film is about 10^{-3}–10^{-4} S/cm, which is lower by 5–6 orders of magnitude than that of the filler itself. These indicate how effectively PPy can render the film conductive. This effectiveness could be achieved by the formation of continuous conducting paths in the polymer film. On these points, these conducting films are clearly different from ordinary conducting composites and should be regarded as a new class of polymer alloys.

Mechanical Property. PVC/PPy alloy films are relatively hard because no plasticizer is included in the film. On the other hand, PVDF–TrFE/PPy alloy films are relatively flexible. This difference originates from the film nature of the base polymers, particularly the T_g of polymer. Figures 3 and 4 show the results of dynamic moduli (E) of PVC/PPy and PVDF–TrFE alloy films, respectively, and show a close relation with the T_g of the base polymers. In a temperature region lower than T_g for both cases, a slight decrease in E was observed as compared with pure base films. However, E in a higher temperature region was improved by alloying with PPy. Particularly, PVDF–TrFE/PPy alloy films withstand temperatures up to 140 °C without deformation, which is well above the softening point of PVDF–TrFE.



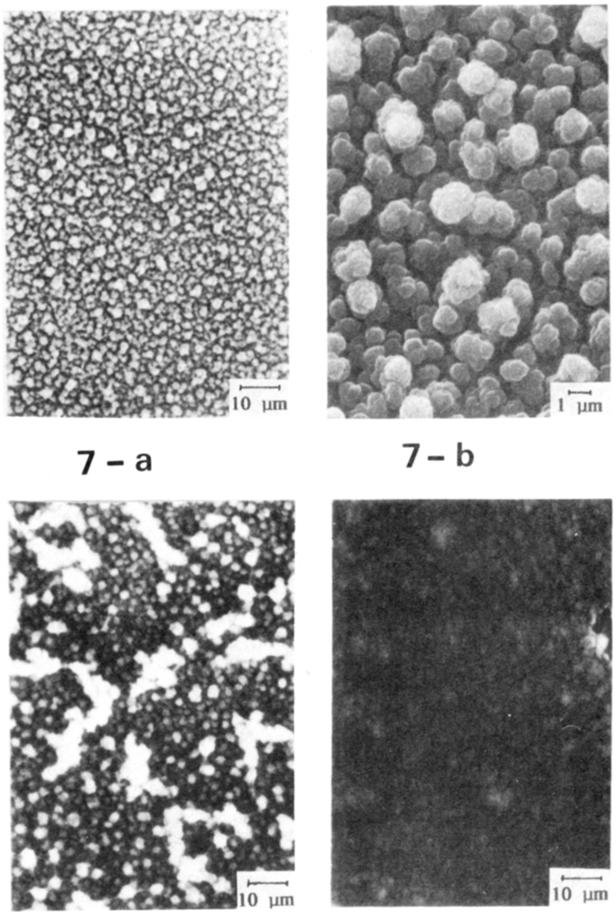
5 – a 5 – b

Figure 5. SEM pictures of PVC/PPy alloy films prepared at 5 V and 0.5 C/cm^2: (a) surface side; (b) electrode side.



6 – a 6 – b

Figure 6. SEM pictures of PVDF–TrFE/PPy alloy films prepared at 2 V and 0.5 C/cm^2: (a) surface side; (b) electrode side.



7 – a 7 – b

7 – c 7 – d

Figure 7. SEM pictures of extracted PVC/PPy alloy films: (a) surface side prepared at 2 V and 0.5 C/cm^2; (b) higher magnification picture of sample in 7(a); (c) surface side prepared at 5 V and 0.5 C/cm^2; (d) electrode side of sample in (a).

Two polymers exhibit a distinctive difference in E for films prepared at a charge density of 2.5 C/cm^2. PVC/PPy alloy films show no significant change by the charge density, that is, PPy content, while E of PVDF–TrFE/PPy alloy films decreased by 1 order of magnitude by alloying about 30 wt % PPy. This result may also be explained by an examination of the film morphology in the next section. The polymerization voltage does not affect E when the charge density is relatively small.

Film Morphology. In the SEM observation of alloy films without a thin metal coating, nonconducting surfaces give a brightly white picture due to the charging-up of incident electrons. This phenomenon is very effective in judging whether the material is conductive or not. SEM photographs could not be taken for the surface side of the film prepared at a very low charge density due to a charging-up effect, indicating no PPy chain reached the surface side. The electrode side of the alloy films did not show the charging-up in any cases.

Figure 5 shows SEM pictures of the two film sides of PVC/PPy alloy films prepared at 5 V and 0.5 C/cm^2. As shown in Figure 1, this film has a conductive surface. The electrode side is very smooth with a very fine structure (Figure 5b), which corresponds to a surface roughness of the ITO electrode. On the surface side of the film many cauliflower-like projections are observed (Figure 5a). The same structure was also observed in the alloy films prepared at a charge density of more than 1.0 C/cm^2 at 2 V and are assigned pure PPy chains growing on the surface because no charging-up is observed. Figure 6 shows PVDF–TrFE/PPy alloy films prepared at 2 V and 0.5 C/cm^2. The projections appearing on the surface have a round shape (Figure 6a). The electrode side of the film is also very smooth (Figure 6b). This difference in the shape of projections could be varied with the solvent used for the polymerization. However, the details of PPy growth inside the film were not revealed from the simple SEM observation of as-grown film.

In order to get this information, we observe the PPy component of the alloy films with SEM after sovlent extraction of the base polymer component. For all extracted samples, no charging-up phenomenon was observed. This suggests that the PPy component can be isolated by solvent extraction with tetrahydrofuran.

Figure 7 shows the SEM pictures of two sides of extracted PVC/PPy alloy films. In Figure 7a, the extracted film prepared at 2 V and 0.5 C/cm^2 has a surface consisting of a number of fine PPy particles with 1–2-μm diameters. As no PPy chain reached the surface side of the alloy film before the solvent extraction, these fine columns seem to be chain ends of growing PPy in the films. A higher magnification picture (Figure 7b) suggests these particles are isolated with each other like columns. On the surface of extracted film prepared at 5 V and 0.5 C/cm^2, large irregular parts are observed on the uniform columnar structure (Figure 7c). However, the cauliflower-like projections observed in Figure 5a disappeared on the extracted film. PPy chains between the extracted film and the projections may not be so strong that the projections drop during the solvent extraction. The irregular structure in Figure 7c could be a part of these connecting PPy chains. The electrode side of the film seems to be very smooth, but shows a vague structure, which is almost the same as the columnar structure (Figure 7d).

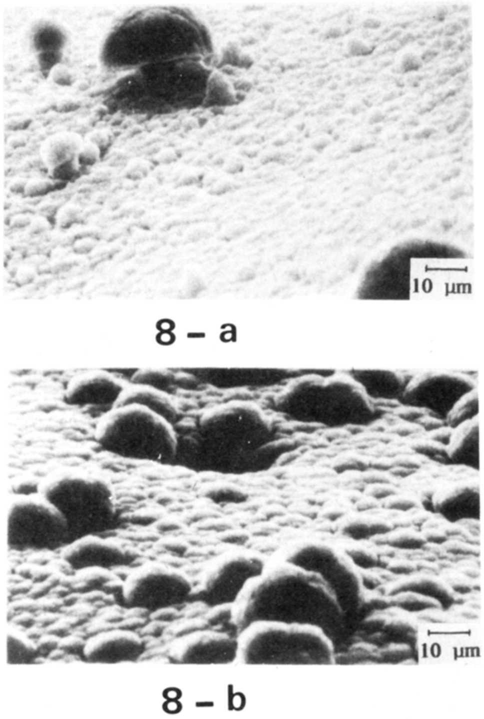


Figure 8. SEM pictures of extracted PVDF–TrFE/PPy alloy films from side view: (a) surface side prepared at 2 V and 0.5 C/cm^2; (b) surface side prepared at 5 V and 2.5 C/cm^2.

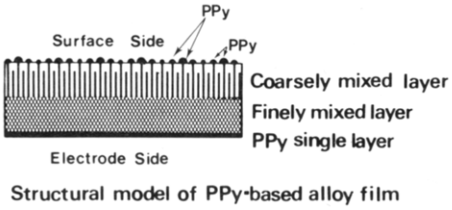


Figure 9. Schematic representation of the structure of PPy-based alloy films.

SEM pictures in Figure 8 are extracted PVDF–TrFE/PPy alloy films. PPy chains after extraction are more tightly packed than in PVC/PPy, and on these tight networks some mushroom-like projections are observed (Figure 8a). The caps of the mushroom structure correspond to the round projections observed in Figure 6a. These are supported by the solid stems, which were concealed inside the base film before the extraction. The increase in charge density makes the tight network structure thicker, and then at last the mushroom structures are buried with the network structure at 2.5 C/cm^2 (Figure 8b). This kind of structure may cause a large deterioration in mechanical property as shown in Figure 4. The electrode side is also very smooth in PVDF–TrFE/PPy.

Structural Model and Polymerization Mechanism. From the results on film morphology, the film structure can be schematically described as in Figure 9. The alloy films are a layered structure composed of three parts.[9] The fact that the solvent extraction does not change the structure of the electrode side of the film indicates that a thin and pure PPy layer forms on the electrode side of the film. The second layer is a thick and fine mixture of the base film and PPy chains. This finely mixed layer appears as a columnar structure in PVC/PPy and as a network structure in PVDF–TrFE/PPy. The third layer is mainly an insulating base polymer, where PPy chains grow coarsely up to the film surface and deposit on the film surface forming the projections. This structure indicates that in most cases the electrical conduction on the surface side is attained not within the surface but through a film thickness direction via the continuous first and/or second layer. If the resistance in the thickness direction is not negligible as compared with the surface resistance of the electrode side, the surface side could have a significantly higher resistance than the electrode side. This is the case of PVC/PPy, where the fine PPy chains are coarsely mixed in the third layer. To confirm this, the resistance in the film thickness direction was measured for both films prepared at 2 V and 1.0 C/cm^2. The measurement was carried out by a 4-terminal method using Au electrodes evaporated on both film sides at the same position. In PVC/PPy the resistance values, which varied considerably from sample to sample, were always larger than 0.5 Ω. This result suggests that the conductivity in the film thickness direction is at least 150 times lower than the value obtained from the surface resistance of the electrode side. This high anisotropic conductivity between parallel and perpendicular to the surface could cause the discrepancy in the resistance value between the two film sides in PVC/PPy alloy films. On the other hand, the observed resistance in the film thickness direction in PVDF–TrFE/PPy film was less than 0.05 Ω. This could be due to the tight network structure in the second layer and the solid stem of the mushroom structure in the third layer; almost equivalent surface resistances for the two film sides in PVDF–TrFE/PPy were realized.

From these experimental observations, the polymerization mechanism is speculated as follows. The increase of charge density has two effects on the structure, namely, thickening the finely mixed layer and growing the projections. The contribution of these two effects may depend on the balance of polymerization rate and monomer supply by diffusion. In the polymerization solution there could be a certain distribution of monomer and electrolyte anion concentrations in the film thickness direction. PPy chains, which start to grow from the interface between the electrode and the insulating film, form a network structure in the film. When the polymerization rate is low enough, as in the case of low-voltage polymerization, monomer molecules may be sufficiently supplied to the PPy chain ends, resulting in the formation of a thick second layer. On the other hand, when the material supply by diffusion is less than the polymerization rate, monomer molecules may rapidly disappear around the PPy chain ends, and then PPy chains grow toward the film surface to seek more monomer molecules to be polymerized. This process causes nonuniform propagation among PPy chains, and when some chains reach a certain level in the film earlier than others, the polymerization mainly occurs around these chains. The projections on the film surface could be due to the local and rapid growth of PPy chains.

It is still not clear why a pure PPy layer forms between the electrode and the insulating film in the early stage of the polymerization. However, this layer is very effective in reducing the surface resistance of the electrode side of the film with a very small PPy content, particularly in PVC/PPy alloy films. When this layer was physically removed by oxygen plasma etching, PVC/PPy alloy films lost their conductivity within both film surfaces. This clearly indicates that PPy columns in PVC/PPy films are isolated from each other. On the other hand, the oxygen plasma etching of the electrode side of PVDF–TrFE/PPy alloy films did not change the conductivity significantly because the thick network structure contributes to the conductivity within film surfaces.

Conclusion

The polymerization of pyrrole on an electrode covered with an insulating polymer film produces novel conducting polymer alloy films in which highly conducting PPy is mixed to form continuous conducting paths. The physical properties and the morphology were investigated by using PVC and PVDF–TrFE as insulating polymer films. The conductivity is greatly increased with the PPy amounts incorporated in the film. The alloying process does not change the mechanical property of the insulating film and improves the thermal stability of the film in a high-temperature region. The structure of alloy films has been revealed by SEM observation of extracted film, and the physical properties are closely related with the film morphology.

Registry No. PPy, 30604-81-0; PVC, 9002-86-2; (TrFE)-(PVDF) (copolymer), 28960-88-5.

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Vinylpyridinium Ionomers. 1. Influence of the Structure of the Ion on the State of Aggregation in Random Styrene-Based Systems[1]

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ABSTRACT: The thermal and dynamic mechanical properties of random styrene ionomers containing various vinylpyridinium groups have been examined. The properties of the materials were found to be independent of the structure of the ion. The glass transition temperatures of these ionomers were found to increase regularly with increasing ion content, at a rate of about 3.5 °C/(mol % ions). In contrast with styrene ionomers with pendant anionic groups studied before, the vinylpyridinium ionomers showed only one peak in their loss tangent curves, associated with the T_g of the matrix. The absence of a second, higher temperature peak suggests the absence of clusters in these ionomers, at least at temperatures above their T_g. The storage modulus curves are in agreement with this conclusion.

Introduction

Over the past few decades, ionomers have been the subject of a large number of investigations.[2,5] Early studies brought to light the unique properties of these materials and suggested a range of applications. This encouraged further research in an attempt to understand the phenomena responsible for these properties and thus enable researchers to produce materials capable of answering very specific needs.

Fundamental investigations have focused on relatively few types of backbones and even fewer kinds of ionic groups; these few systems have been studied extensively, using numerous techniques to probe different aspects of their behavior. Polyethylene, poly(tetrafluoroethylene), and polystyrene, as well as some elastomers, have probably been the most widely investigated backbones. A relatively new family of ionomers based on the polypentenamer backbone has also been investigated.[4] Other systems have been examined, although not as extensively. Variation of other parameters, such as the nature of the ion and the counterion, the ion content, and the position of the ion relative to the chain, has provided a better understanding of the factors influencing the properties of ionomers. Most of the studies have been conducted on salts of carboxylic acids, the most common being methacrylic and acrylic acids as well as carboxystyrene. Sulfonic acids have been introduced on certain backbones. Investigations of ionomers carrying a positive charge have been limited mostly to a few vinylpyridinium systems.

Ion Aggregation in Ionomers. It is well-known that ionic compounds have a tendency to aggregate in media of low dielectric constant.[6] A similar, but somewhat more complex behavior may be expected in ionomeric systems in the bulk, since the majority of the backbones studied are of relatively low polarity.

The first attempt made to describe this phenomenon theoretically is probably that of Eisenberg.[7] Several other treatments have been published more recently.[8–11] Briefly, Eisenberg suggests that aggregation is governed by two opposing tendencies, association between ion pairs ($\Delta G < 0$) and stretching of the polymeric chain segments when such an association between ion pairs occurs ($\Delta G > 0$). The formation of two different types of aggregates is postulated: multiplets and clusters. The association of ion pairs into multiplets is shown to be limited solely by spatial restrictions, as the electrostatic energy gained is much greater than the work done to deform the chains. Multiplets are thus considered to be an association of a relatively small number of ion pairs (<8) and to be completely coated with nonionic chain material. Clusters are suggested to result from the aggregation of multiplets; since the latter are completely coated with nonionic material, clusters are expected to include chain segments. In contrast with the multiplets, the difference between the electrostatic and the elastic forces involved in the forma-

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