SHORT COMMUNICATIONS

Changes in Electrical Resistance of Ionic Copolymers Caused by Moisture Sorption and Desorption

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For the past decade, a number of studies have been carried out on the electrical conductivity of various polymers, including conjugated polymers such as polyacetylene¹ and polypyrrole, and ionic conductive polymers such as polyethers dissolving inorganic salts.² Our attention has been directed to the applicability of ionic copolymers to humidity sensors, since the electrical resistance of ionic copolymers depends significantly on environmental temperature³ and relative humidity.⁴ The present investigation is concerned with the diffusion behavior of water molecules in ionic copolymers electrically sensitive to humidity.

The ionic copolymers listed in Table I were synthesized from ionic and nonionic monomers in aqueous media. Potassium persulfate was used as an

initiator for anionic copolymers and 2,2'-azobisisobutyramidine dihydrochloride for cationic copolymers. The following abbreviations were used: Nonionic monomer, methyl methacrylate, MMA; Ionic monomers, sodium methacrylate, NaMA; sodium styrene sulfonate, NaSS; sodium 2-acrylamido-2-methylpropane sulfonate, NaAMPS; methacryloyloxyethyltrimethylammonium chloride, MEDMACl; methacryloyloxyethyltrimethylammonium chloride, METMACl; and methacryloyloxyethyltrimethylammonium chloride, MEDMOcAcI. The counter ions selected were univalent ones such as Na⁺ or Cl⁻.

The electrical resistance of copolymers at 1 kHz was measured by using a pair of comb-shaped electrodes at 30°C at selected relative humidities

Table I. Response time of various ionic copolymers

Copolymer			Response time	
Ionic monomer M ₁	Nonionic monomer M ₂	[M ₁] ^a	min	
		[M ₁]+[M ₂]	Sorption process	Desorption process
NaSS	MMA	0.36	40	> 180
NaAMPS		0.21	20	> 180
NaMA		0.31	10	> 180
MEDMACl		0.35	5	50
METMACl		0.12	2	6
MEDMOcAcI		0.35	2	3.5

^a Molar fractions $[M_1]/([M_1]+[M_2])$ of copolymers were determined by titration for anionic copolymers and by elemental analysis for cationic copolymers.

Figure 1. The electrical resistance vs. the relative humidity curve and the moisture sorption isotherm of poly(MMA-co-MEDMOcAcI).

Figure 2. Response characteristics of poly(MMA-co-MEDMOcAcI). Changes in electrical resistance were recorded as a function of time when the relative humidity was quickly changed from 40 to 60% RH in the sorption process, and *vice versa* in the desorption process.

when the copolymers were in equilibrium with the surroundings. To measure the response to humidity change, the humidity of the surroundings was changed rapidly from 40 to 60% RH during sorption and from 60 to 40% RH during desorption.

The response time was defined as the time in which the electrical resistance reaches the value corresponding to 59% RH during the sorption process and that corresponding to 41% RH during the desorption process. The amount of water sorbed by the copolymer films was measured with a

quartz spring balance mounted inside the vacuum line.

The resistance vs. relative humidity curve and the moisture sorption isotherm of poly(MMA-co-MEDMOcAcI) are shown in Figure 1. From the figure, it can be seen that the electrical resistance of the ionic copolymer decreases exponentially with increasing relative humidity in the range from 20 to 80% RH, while the amount of water sorbed by the copolymer is also a function of the relative humidity and increases with increasing humidity. Similar behavior was observed for other ionic copolymers. Possible charge carriers may be the counter ions formed by dissociation during the moisture sorption.

Figure 2 shows the electrical resistance of the copolymer plotted against time when the relative humidity was changed quickly at time zero. The response time of the various copolymers is summarized in Table I. Two interesting phenomena can be seen. First, the response time is larger in the desorption process than in the sorption process. Second, the response time significantly depends on the ionic monomer species used. Comparison of the chemical structures of the ionic monomers leads to the conclusion that the most important factor governing the response time is the hydrophobicity of ionic groups. The response time was shorter in the following order:

It is well known^{5,6} that the diffusive behavior of water molecules through polymeric membranes depends on the polymer species and that the diffusion coefficient in hydrophobic polymers such as polydimethylsiloxane and polyethylene is much larger than in hydrophilic polymers such as polyamide, polyvinyl alcohol, and cellophane. The order in eq 1 may be explained on the basis of this fact. For hydrophilic polymers, the diffusion coefficient increases with increasing water concentration in the polymers.^{5,6} This implies that the diffusion of water molecules is retarded more in the desorption process than in the sorption process.

In summary the water molecules hydrated to the ionic groups of copolymers play an important role in ionic conductive behavior, and the response time may be used as a quantitative parameter for the

diffusion of water molecules through ionic copolymers. A detailed account of the response properties of ionic copolymers and the ionic conductive behavior due to moisture sorption is now being prepared for publication.

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