Preparation and Solution Properties of Ionomer Originated from Styrene–Coumarin Copolymer

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SYNOPSIS

A novel ionomer was successfully prepared by lactone ring opening of styrene–coumarin copolymer, containing 9.28 mol % of coumarin, with aqueous NaOH solution. Its solution properties in methanol, including reduced viscosity and surface tension, were investigated as a function of temperature, concentration, and pH value. The reduced viscosities of the ionomer solution decrease smoothly with increasing temperature and concentration. Moreover, the viscosities of the ionomer solution (0.3 g/dL MeOH) are ca. twofold of the copolymer solution (0.3 g/dL THF) between 25 and 45°C. It increases from ca. 0.14 to 0.59 dL/g as pH value decreases from 10.6 to 6, then decreases slightly and reaches a constant value of 0.47 dL/g below pH 4.7. The surface tension of methanol solution decreases with increasing concentration and reaches an asymptotic value of 24.1 dyne/cm as the concentration is above 0.50 g/dL due to the surface-active effects. These properties can be related to the balance between hydrogen bonding and charge–charge interactions that occur along the ionomer backbone. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Coumarin, 2-chromenone, naturally occurs in trace amounts in various plants, particularly in some kind of fruits, as a component in aromatic flavors. In 1902, Ciamician and Silber found that coumarin dimerized on photoirradiation in ethanol or in an aqueous medium.[1] Since then, the photocyclodimerization of coumarin has received a lot of attention among organic chemists and has been studied extensively.[2–8] It gives four types of dimers (anti head-to-head, anti head-to-tail, syn head-to-head, and syn head-to-tail) on photoirradiation, of which the product ratio is influenced predominantly by the multiplicity in the [2 + 2] photochemical reactions. The ring-opening reaction of the anti head-to-head coumarin dimer with various nucleophiles has been studied thoroughly.[9–13] Coumarin is attached to the polymer chain and its photocyclodimerization reactivity was investigated by Chuo et al.[14] We first reported direct

radical copolymerization of styrene with coumarin, through its 3,4-double bond in lactone.[15] The resulted copolymers contain, in the main chain, lactone rings that can be opened by bases such as amine, water, alcohol, etc.

Novel ionomers can be prepared from the styrene–coumarin copolymer by lactone ring opening with basic reagents such as NaOH aqueous water, aqueous pyridine, and aliphatic primary amines. The anionic species are $-COO^-Na^+$ and/or $-\phi-O^-Na^+$ derived from carboxylic acid and/or phenolic hydroxyl groups of the opened lactones. It will exhibit a solution viscosity greater than the original styrene–coumarin copolymer as a result of more extended coils due to the repulsive interactions of anionic charges along the ionomer chain. The ionomer chain will be collapsed upon the addition of acid due to diminished electrostatic repulsions as the ionic charges along the coils disappear gradually. Consequently, the characteristics of the ionomer can be realized from the behaviors of titration, the effects of pH value on viscosity, the effects of pH value on surface tension, and so on. These are interesting phenomena and subjects worth exploring from both

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practical and academic points of view. And this novel ionomer possesses potential applications as a compatibilizer, polymeric dispersant, and surfactant.

In this work, a novel ionomer originated from the styrene–coumarin copolymer were prepared by opening its lactone rings in NaOH aqueous solution. The characteristics and solubility of the ionomer are reported in detail. The solution properties of the ionomer, including reduced viscosity and surface tension, were investigated thoroughly as a function of pH value, temperature, concentration, and time.

EXPERIMENTAL

Chemicals

Coumarin was purchased from Merck and purified by recrystallization in ethanol before polymerization. Styrene was (Merck) purified by distillation under reduced pressure before use. 2,2'-Azobisisobutyronitrile (AIBN) was (Wako Chemical Co.) recrystallized from methanol. Other chemicals were pure reagents and used as received or purified by the conventional method.

Copolymerization and Compositional Analysis

To a 20-mL, two-necked glass reactor were added with 22.87 g of coumarin (0.156 mol), 5.42 g of styrene (0.052 mol), 0.85 g of AIBN, and 65 mL of benzene. The mixture was allowed to react at 60°C for 8 h after degassing with dry nitrogen for 30 min. The copolymers were isolated by filtration after precipitating in a large amount of methanol and then dried *in vacuo* for 48 h. (yield, 44.3%).

Composition of the styrene–coumarin copolymer was determined by elemental analysis and calculated from percent C and percent H data by eqs. (1) and (2), in which m and n represent the number of moles of styrene and coumarin in the copolymer, respectively.

$$\% \ C/12.011 = 8m + 9n \qquad (1)$$

$$\% \ H/1.0079 = 8m + 6n. \qquad (2)$$

After m and n were determined for the copolymer by using matrix algebra, compositional data (mol %) were calculated according to eqs. (3) and (4).

$$\text{mol \% of styrene} = m/(m + n) \qquad (3)$$

$$\text{mol \% of coumarin} = n/(m + n). \qquad (4)$$

Preparation of Ionomer

To a 150-mL flask were added 6 g of the styrene–coumarin copolymer containing 9.28 mol % coumarin, 60 mL dioxane, and 40 mL 5N NaOH$_{(aq)}$. The mixture was allowed to react at 60°C for 12 h. Pink precipitates gradually appeared in the progress of the reaction. The precipitates were isolated by filtration, followed by successive washing with 20 mL benzene and 40 mL distilled water. The final products were then collected by filtration and dried *in vacuo* for 48 h (yield, 84.6%).

Measurements

Infrared spectra (IR) were recorded using an IR spectrophotometer, model IR-810 from Japan Spectroscopic Co., at a resolution of 4 cm^{-1}. ^{1}H-NMR spectra were recorded using a Bruker 200 MHz-FT NMR spectrometer. The compositions of the copolymer were determined on a Heraeus CHN-O-RAPID Elemental Analyzer. The molecular weight of copolymers was measured with a gel permeation chromatography (GPC) apparatus equipped with three Shimadzu columns (Shimpack, #801, 8025, 804). A Shimadzu RID-6A detector was calibrated with monodisperse polystyrene standards from Du Pont. The flow rate was 0.5 mL/min tetrahydrofuran (THF) at 25°C. The reduced viscosities were measured by a Fargo-WD Ubbelohde capillary viscometer. The pH values were determined by a Automatic Titrator from TOA Electronics Ltd. The surface tensions were measured with a surface tensiometer (model GBVP-A3 from Kyogo Interfacial Scientific Co.).

RESULTS AND DISCUSSION

Characteristics and Solubility of Ionomer

The preparation route of the ionomer from styrene and coumarin is shown in Scheme 1. The monomer reactivity ratios of styrene (M_1) and coumarin (M_2) are $r_1 = 50$ and $r_2 = 1.04$, respectively.[15] The radical copolymerizability of coumarin is much lower than that of styrene. Therefore, an excess of coumarin (coumarin/styrene = 3/1 mol) is employed in copolymerization to obtain a copolymer containing higher coumarin content. However, this tactic results in low conversion (44.3%) of the copolymerization due to the very low reactivity of the coumarin comonomer. This would be ascribed to the steric hindrance caused by its 1,1'-disubstituted structure.
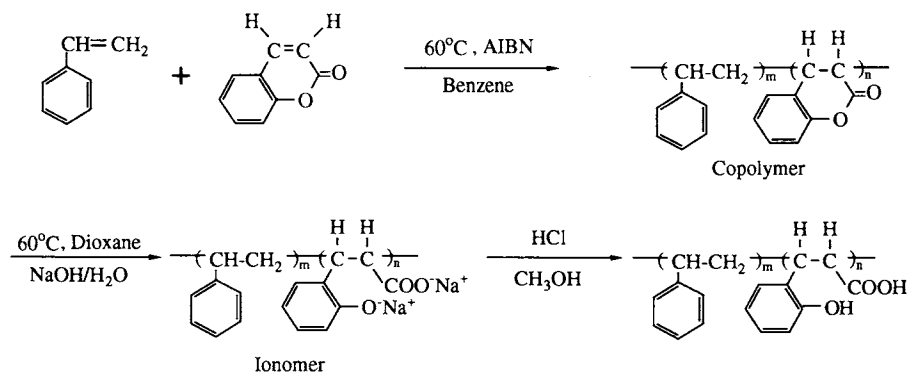
Scheme 1

In this work, the styrene–coumarin copolymer used contains 9.28 mol % of coumarin residues as determined by elemental analysis. The number-average molecular weight of the copolymer is about 8650 as determined by GPC using monodisperse polystyrene as standard. The IR spectrum of the styrene–coumarin copolymer is shown in Figure 1, in which clearly the specific absorptions are at 1760 cm^{-1} (lactone), 1150–1250 cm^{-1} (C—O—C), and 700–800 cm^{-1} (monosubst. or disubst. benzene).

The lactone ring-opened copolymer is a pink solid. Its IR spectrum is quite different from that of the original copolymer as shown in Figure 2. The characteristic absorptions are at 1590 cm^{-1} (—COO$^-$Na$^+$), 1400 cm^{-1} (—COO$^-$), and 1220 cm^{-1}(—ϕ—O). Clearly the specific absorptions of lactone group of the original copolymer obviously disappear. However, it cannot be confirmed directly from its ^{1}H-NMR spectra, because the chemical shifts of the coumarin and styrene residues overlap
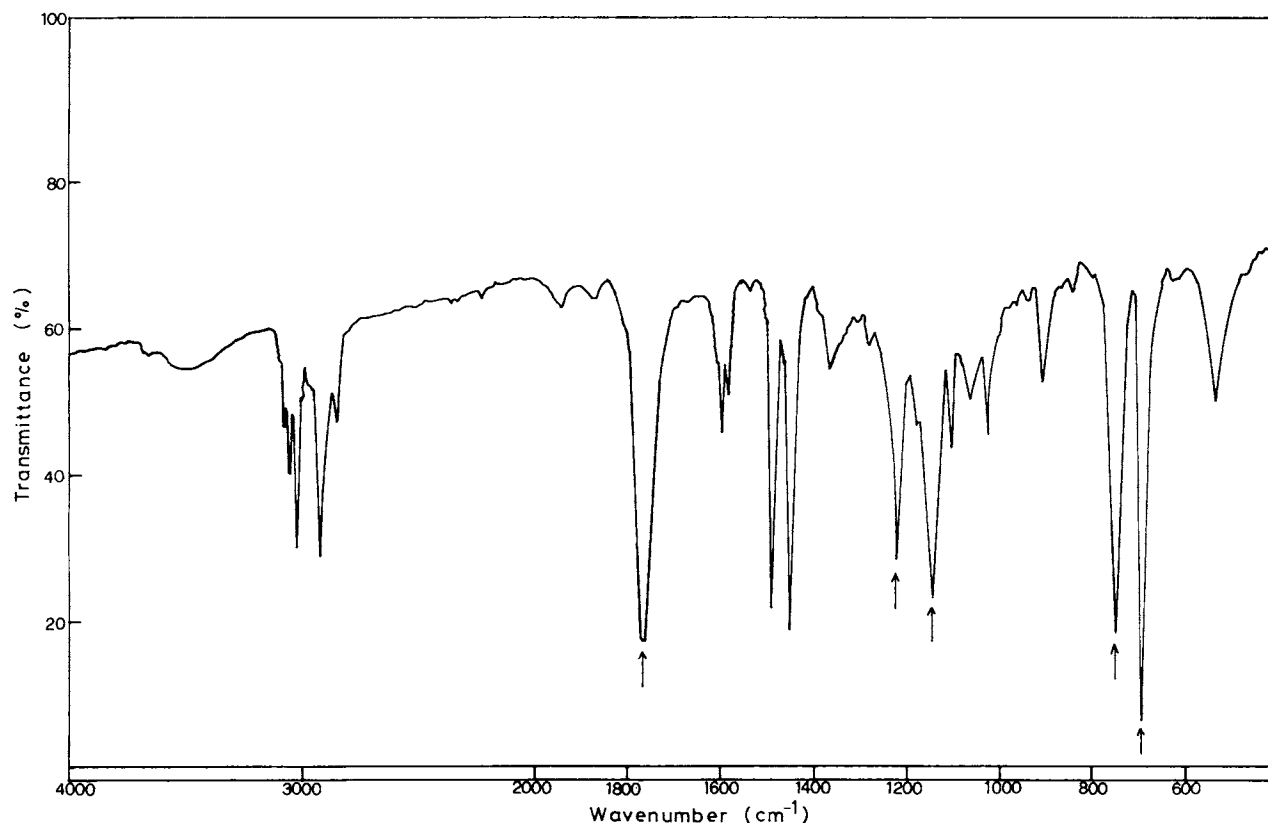

Figure 1 IR spectrum of styrene–coumarin copolymer (9.28 mol % of coumarin residues).
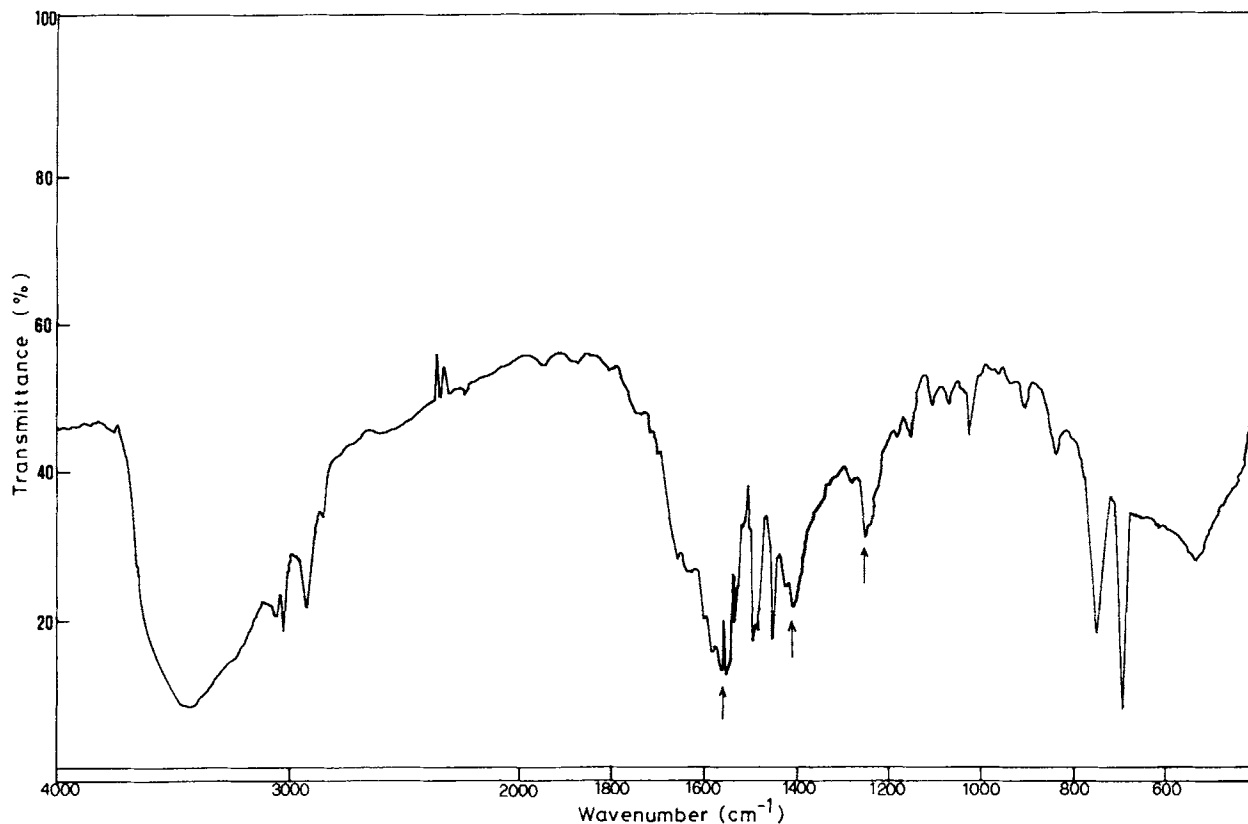
Figure 2 IR spectrum of ionomer derived from the styrene–coumarin copolymer.

each other to form two broad peaks at δ 0.15–3.71 ppm and δ 5.72–8.43 ppm.

The ionomer can be completely dissolved in protic polar solvents such as methanol and ethanol, although the original copolymer is not soluble in these solvents. In fact, methanol is a precipitating solvent of the copolymer. However, it is not soluble in water, benzene, dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), chloroform, toluene, THF, and N,N-dimethylacetamide (DMAc). This fact can be explained by the polarity increase caused by the lactone ring opening and ionization of the carboxylic acid and phenolic hydroxy groups. But the polarity increase is limited by the mole percent of coumarin residues (9.28%) in the main chain and results in insolubility in water.

Effect of Temperature on Viscosity

The effects of temperature on viscosities of the ionomer in methanol (curve A) and the styrene–coumarin copolymer in THF (curve B) are shown in Figure 3. The reduced viscosities of the copolymer and the ionomer decrease slightly with increasing

temperature, suggesting that hydrodynamic volume decreases with temperature for both. This also indicates that the conformational and solvent-associational changes occur as a function of temperature.
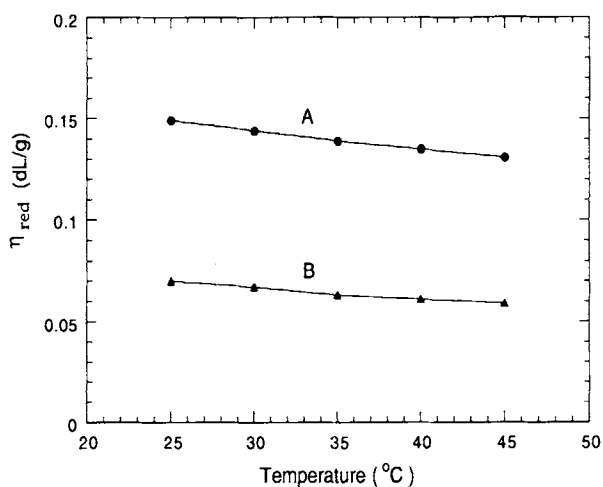

Figure 3 Effect of temperature on reduced viscosity of the ionomer in (A) methanol and (B) the copolymer in THF. Concentration: 0.3 g/dL.
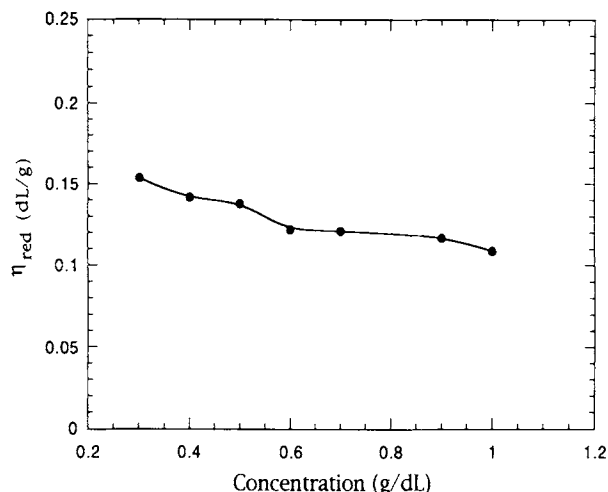
Figure 4   Effect of concentration on reduced viscosity of the ionomer in methanol at 25°C.

The reduced viscosities of the ionomer solution are about twofold of the copolymer solution between 25 and 45°C. This phenomenon is due to greater extension of ionomer chains caused by the repulsive interactions between ionic charges. Further, the viscosity variation of the ionomer solution is slightly greater than that of the copolymer solution. This would be ascribed to gradual disruption of the ionic interactions as temperature increases.[16–18]

Effect of Concentration on Viscosity

Usually, the viscosity of polymer solution increases with increasing concentration. A quadratic dependence of the specific viscosity on polymer concentration is described well by the following expression[19]:

$$\eta_{sp}/C = [\eta] + K'[\eta]^2 C$$

where $[\eta]$ is the intrinsic viscosity, C is the concentration of polymer solution in g/dL, and K' is sometimes called the Huggins constant.

The effects of concentration on the reduced viscosity of the ionomer solution are demonstrated in Figure 4. The reduced viscosities decrease with increasing concentration, which is opposite to that of ordinary polymers. There are two possible reasons for this phenomenon. First, the repulsive forces of ionic charges along the chain extend the coil, so the reduced viscosity of the ionomer is larger even at low concentration. As the concentration increased, the intermolecular charge interactions would allow the ionomer chain to associate and therefore result

in decreased viscosities.[20] Second, the styrene residues in the ionomer chain are the hydrophobic segments to methanol and may associate by the hydrophobic interactions. In other words, the decrease of viscosity would result readily from coils association as concentration increases.[21]

Effect of Concentration on Surface Tension

Because the ionomer contains both hydrophobic polystyrene segments and hydrophilic anionic charges in the main chain, it should behave like a polymeric surfactant in lowering surface tension of the solution. The effects of concentration on the surface tension of the methanol solution are shown in Figure 5. The surface tension first decreases smoothly with concentration, then it reaches an asymptotic value of 24.1 dyne/cm at concentrations greater than 0.5 g/dL. The inflection point corresponds to the critical concentration at which intermolecular cooperative associations through hydrophobic or hydrophilic interactions begin to occur among the ionomers. The critical concentration of this ionomer solution is about 0.30 g/dL. These behaviors may be due to the formation of hydrophobic microdomains because the ionomer possesses both hydrophobic and hydrophilic groups along the polymer chain.[20,22]

Behaviors of Titration

The methanol solution (0.3 g/dL) of as-prepared ionomer is basic and its pH value is about 10.6. Acidification of the solution with protonic acid de-
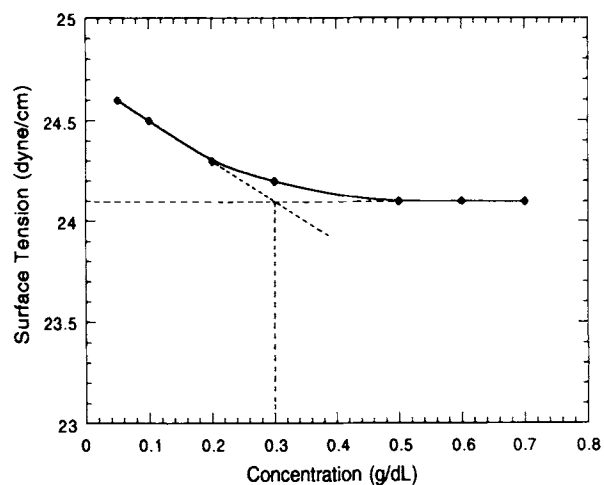

Figure 5   Variation of surface tension with concentration for the ionomer in methanol at 25°C.

creases the concentration of ionic charges in the main chain. This abrupt polarity change should change the solubility of the ionomer significantly. Titration curves of the ionomer solution with $0.1N$ $HCl_{(aq)}$ at 25°C are shown in Figure 6. The aspect of the ionomer solution changes from pink into colorless at pH 6–7. This is the equivalent point of the phenolic hydroxyl groups in the ionomer chain. Further, there is an equivalent point at pH 4–5 as measured by automatic titrator. It is conjectured that this is an equivalent point of the carboxylic acid. Besides, the white solids begin to precipitate out as the pH value below 2, then the pH values remain almost constant regardless of the addition of $HCl_{(aq)}$. The IR spectrum of the white precipitates is shown in Figure 7. The characteristic absorptions are at 3200–3600 cm^{-1} (hydroxy groups of carboxylic acid and phenol), 1706 cm^{-1} (carbonyl groups of carboxylic acid), and 1223 cm^{-1} ($-\phi-O$). By comparing Figure 7 with Figure 1, it is found that the absorption of lactone rings at 1760 cm^{-1} is absent in the acid-precipitated products. Therefore, it is inferred that the pendant carboxylic acid and phenolic hydroxyl groups are not closed to form original lactone rings under the acidic condition.

Effect of pH Value on Reduced Viscosity

Because the ionomer contains carboxylic acid moieties, its reduced viscosity should be influenced significantly by the pH value of the solution. Figure 8 illustrates the dependence of the reduced viscosity on pH value of the ionomer solution. The reduced viscosity first increases with decreasing pH value from ca. 0.14 dL/g (at pH 10.6) to a maximum value of 0.59 dL/g (at pH 6.0), then decreases a little to 0.47 dL/g at pH 4.7. The reduced viscosity remains constant at 0.47 dL/g below pH 4.7.

In general, the electrostatic repulsions and the degree of ionization of carboxylic or phenolic hydroxyl groups decreases with decreasing pH value and lead to less extended chain structure in solution. Nevertheless, the acidified ionomer solution exhibits greater viscosities ($\eta_{red} = 0.47$ dL/g) than the original ionomer ($\eta_{red} = 0.14$ dL/g). This would be due to formation of hydrogen bonding between solvent (MeOH) and the carboxylic acid or phenolic hydroxyl groups of polymer backbone.[23,24] When pH value is in the range of 6–10.6, the viscosity is predominantly influenced by the hydrogen-bonding interactions and electrostatic repulsions. Therefore, the increased viscosity with decreasing pH value is due to enhanced hydrogen-bonding interactions at
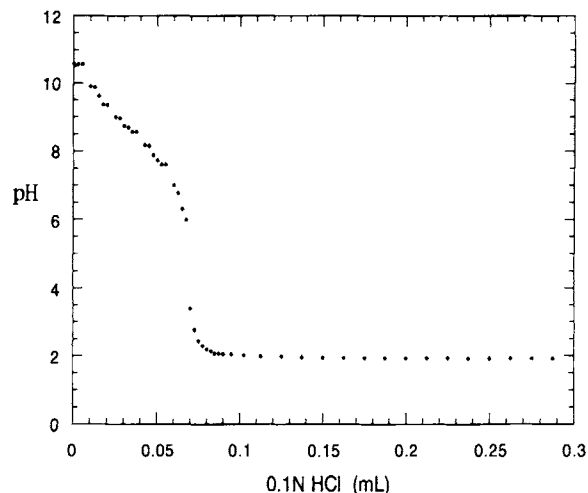

Figure 6 Titration curve of the ionomer (0.3 g/dL methanol) with $0.1N$ $HCl_{(aq)}$ at 25°C.

this stage. The slight decrease in viscosity below pH 6 is explained by the assumption that only hydrogen-bonding interactions contributed to viscosity buildup at this stage. The reduced viscosity remains constant as the pH value is below 4.7; it should be ascribed to the fact that the ionic species ($-COO^-Na^+$ and $-\phi-O^-Na^+$) in ionomer completely transform into carboxylic acid and phenolic hydroxyl groups.

Effect of pH Value on Surface Tension

The surface tension of polymer solution is contributed by dispersion surface tension (r^d) and polar surface tension (r^p)[25]

$$r = r^d + r^p.$$

The dispersion surface tension is affected by the length of the side chain, the packing of side chains, the nature of the main chain, etc. Moreover, the polar surface tension include mainly hydrogen-bonding interactions.

Because the same ionomers were investigated, the polar surface tension is the main factor in determining the surface tension of the ionomer solution. The effect of pH value on the surface tension of ionomer solution is illustrated in Figure 9. The surface tensions gradually increase with decreasing pH value, suggesting that hydrogen-bonding interactions increase gradually with decreasing pH value due to the fact that the ionic species progressively transform to carboxylic acid or phenolic hydroxyl groups. Nevertheless, the variation of the surface
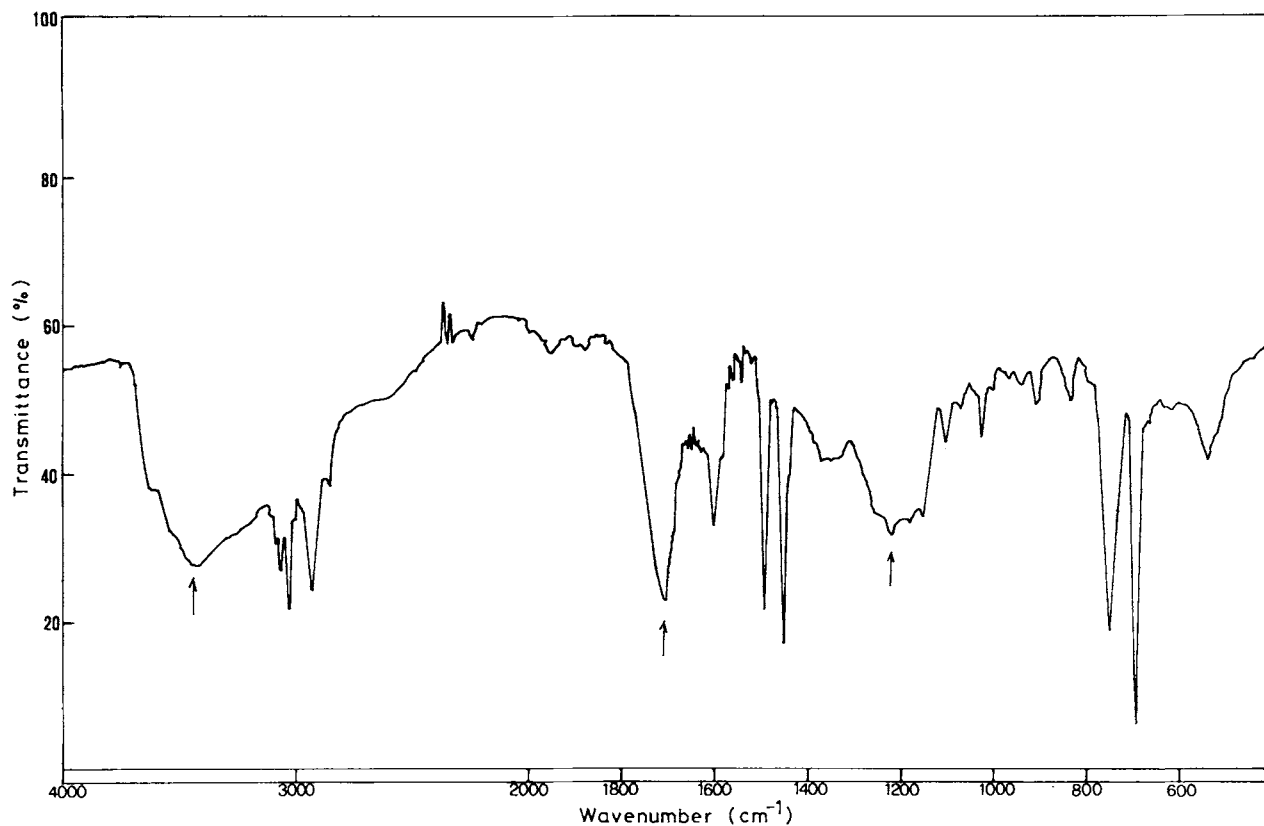
Figure 7 IR spectrum of the precipitates obtained from acidification of the ionomer methanol solution.

tension between pH 2 and 11.75 is smaller than 1 dyne/cm.

Aging Effect

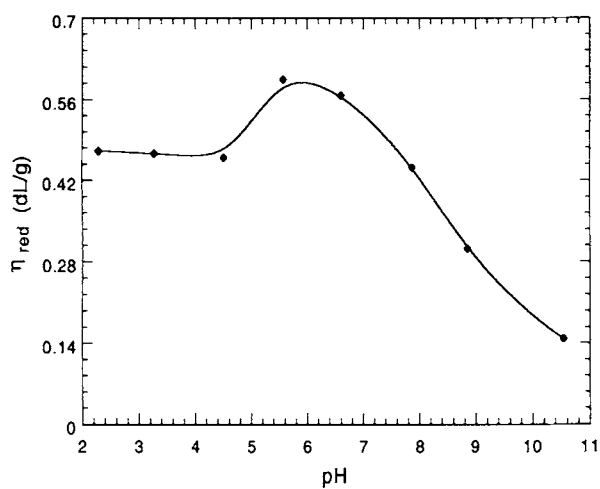To assess the stability of the ionomer solution, pre-

Figure 8 Viscosity variations at different pH value. Concentration: 0.3 g/dL ionomer solution in methanol at 25°C.
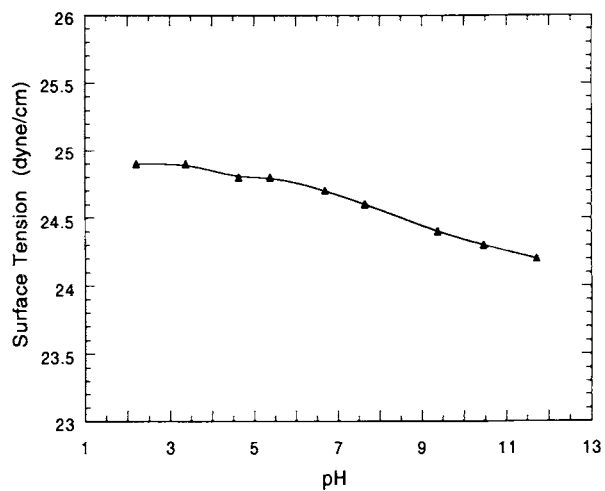

Figure 9 Surface tension variations at different pH value. Concentration: 0.3 g/dL ionomer solution in methanol at 25°C.
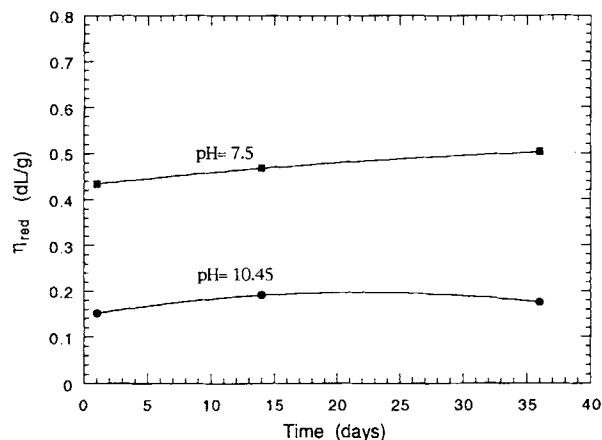

Figure 10 Viscosity variation of the ionomer solution (0.3 g/dL methanol) with time.

liminary aging studies were conducted for 36 days. Water-soluble copolymers with hydrophobic substituents often exhibit time-dependent reorganization in the solution.[26,27] These changes are thought to result from variations in solvation and hydrogen bonding. Finally, polymer conformation will transform to the most thermodynamically stable one and the viscosity of the polymer solution will be a constant with time.[17,18]

Reduced viscosity versus time plots for the ionomer solutions at pH 7.5 and 10.45 are shown in Figure 10. At pH 10.5 the reduced viscosity shows an initial increase during dissolution followed by a gradual decrease with time. However, at pH 7.5 the viscosity increases slightly with time. The different trends in viscosity variations with time may be attributed to conformational changes resulting from changes in interchain and intrachain hydrogen bonding in methanol solution.[28]

CONCLUSIONS

A novel ionomer, containing $-COO^-Na^+$ and $-\phi-O^-Na^+$ groups, has been successfully prepared from styrene-coumarin copolymer by lactone ring opening with aqueous NaOH solution. The reduced viscosities of the ionomer solution (0.3 g/dL MeOH) are about twofold of the copolymer solution (0.3 g/dL THF) between 25 and 45°C. The reduced viscosity decreases with increasing concentrations, suggesting that interchain association of the ionomer is favored by increasing concentrations. It increases with decreasing pH value (from pH 10.6 to 6) and reaches a maximum value of 0.59 dL/g at pH 6,

then decreases slightly to a constant 0.47 dL/g below pH 4.7. These behaviors are explained by the electrostatic repulsion and hydrogen-bonding interactions. Surface tensions of the ionomer solution decrease with concentration as a result of the surface-active effects, and the critical concentration of the ionomer is about 0.3 g/dL. It increases with decreasing pH value due to increased hydrogen-bonding interactions. The ionomer solution shows little aging within 1 month.

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