

Polymer Complex from Copolymers of Acrylonitrile and Ionic Vinyl Benzyl Compounds

MASAO SENUMA, SHIGERU KUWABARA, and KYOJI KAERIYAMA,
*Research Institute for Polymers and Textiles, 1-1-4, Yatabe-Higashi,
Tsukuba, Ibaraki, Japan 305, FUMIO HASE, Seimi Chemical Co., LTD.,
3-2-10 Chigasaki, Chigasaki-shi, Kanagawa, Japan 253, and*
YUKIO SHIMURA, *Kantogakuin University, Chemistry Department, 4834
Mitsuura, Kanazawa-ku, Yokohama, Japan 236*

Synopsis

Copolymerization of sodium vinyl benzyl sulfonate (VBS) or vinyl benzyl trimethyl ammonium chloride (VBQ) with acrylonitrile (AN) gave polyelectrolytes of preferable solution viscosities. The blending of these two copolymers in *N,N*-dimethyl formamide (DMF) produced polymer complexes with ionic linkages, of which the following properties were examined. The maximum in the $\tan \delta$ temperature was increased by complex formation. Freundlich-type dye adsorption and much better dyeability than on polyacrylonitrile was observed. Electric resistivity decreased with the introduction of ionic moiety. Permeability of water increased with the number of ionic sites. Homogeneous films could be cast from DMF and dimethyl sulfoxide (DMSO) solutions.

INTRODUCTION

Cationically and anionically charged polymers are known to be capable of producing polymer complexes of both practical and interesting characteristics by simply blending the two components. For example, the polymer complexes from sodium polystyrene *p*-sulfonate and poly-*p*-vinyl benzyl trimethyl ammonium chloride have been especially widely studied and commercialized under the trade name of Ioplexes[®]. The ionic linkages between the polymer main chains enhance both the strength and the stability of the produced polymer complexes. At the same time, uncomplexed ionic sides on the polymer chains facilitate the absorption of water, dyes, or biologically active materials.¹⁻³

As an extension of the above concept of polymer complexes to conventional polymers, acrylonitrile copolymers with sodium vinyl benzyl sulfonate or with vinyl benzyl trimethyl ammonium chloride were prepared and the complexes of the copolymers have been examined for their viscosity behavior, viscoelastic properties, electric resistance, dyeabilities, and for their properties as separation membranes.

EXPERIMENTAL

Materials

Sodium vinyl benzyl sulfonate (Seimi Chem., Co.) was prepared from *m*, *p*-mixture (60% meta) of chloromethyl styrene by the successive reaction with sodium iodide and sodium sulfite (Fig. 1).

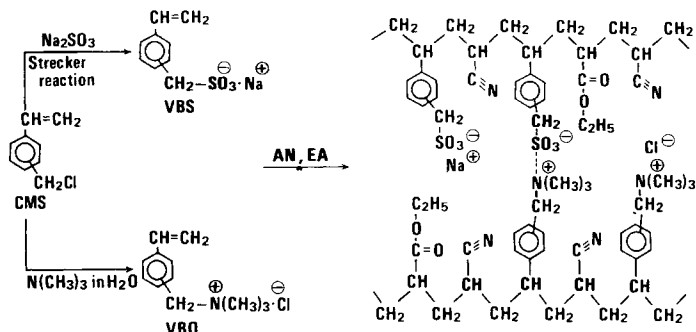


Fig. 1. Reaction scheme.

Vinyl benzyl trimethyl ammonium chloride (Seimi Chem., Co) was prepared in 50% aqueous solution from the same *m, p*-mixture of chloromethyl styrene and trimethyl amine.⁴

Acrylonitrile and ethyl acrylate (EA) were of reagent grade and were used after distillation. All other reagents were of reagent grade and used as supplied.

Copolymerization

The general procedure was to charge acrylonitrile 0.875 mol, EA 0.075 mol, sodium vinyl benzyl sulfonate 0.05 mol, DMF 61.7 g, and water 3.2 g into a four-necked flask. To this mixture was added a DMF solution of 2,2'-azobisisobutyronitrile (AIBN) 0.1 g. The solution was agitated with nitrogen and polymerized for 20 h at 55°C. The DMF solution was concentrated under reduced pressure and precipitated with methanol. The product was further purified in refluxing acetone.⁵⁻⁸

Formation of Polymer Complexes

The copolymer with 5 mol% anionic moiety (sodium vinyl benzyl sulfonate) 0.8 g was dissolved in DMF 20 ml. To this was gradually added an equimolar solution of the copolymer containing a cationic moiety (vinyl benzyl trimethyl ammonium chloride). The resulting opaque solution was concentrated under reduced pressure and poured into methanol as discussed above. The precipitated polymer complex was purified in refluxing acetone and dried in vacuo; isolated yield was 68%.

Analysis of Copolymer Composition

Copolymer composition was analyzed by infrared spectroscopy (IR). Homopolymers of sodium vinyl benzyl sulfonate and vinyl benzyl trimethyl ammonium chloride were mixed with polyacrylonitrile in different ratios and the mixtures were compared with the copolymers by comparing the IR absorption intensity of C_6H_5- 1500 cm^{-1} or 890 cm^{-1} against the $-CN$ 2250 cm^{-1} .

Preparation of Films

DMF solution (5 wt%) of ionic copolymer was cast onto a 13×8 cm² glass plate in a desiccator and evacuated at 10 mmHg for 1 h at room temperature. The cast film on the glass plate was peeled off, fixed with a plastic frame and washed overnight with running water. A soft and slightly opaque film with a thickness of 25 μ m was obtained after drying.

Films of the polymer complex were also obtained using DMSO as the casting solvent. Depending on the composition of the polymer complexes, aqueous DMSO with NaI was also used. For example, copolymers with 10% cationic and anionic moieties were dissolved separately in mixed solvent of DMSO (3.5 wt% solution). Blending of the two solutions gave precipitates which redissolved upon heating at 55°C for 15 min. The clear solution did not precipitate any more and could be cast into films as described above.

Measurement of Viscoelasticity

Cast films were drawn to triple their length at 120°C and heat set at 130°C for 10 min. They were cut in the size of 5×30 mm² (Ca. 25 μ m thick), fixed in a Toyoseiki Vibron DDV-1, and measured for $\tan \delta$ at the speed of 0.5–2.0°C/min.

Measurement of Electric Resistance

The film samples were cut in circular sheets of 20 mm diameter, fixed in a Toyoseiki Thermal Stimulated Current Meter, and measured for bulk electric resistance in the temperature range from room temperature to 150°C, at the rate of 1°C/min. Similarly, surface electric resistance was measured at 25°C, 60% relative humidity (RH).

Dye Absorption

Copolymers with anionic and cationic moieties (each containing 0.5–20 mol% ionic sites), polymer complexes therefrom, and also polyacrylonitrile were dyed in the powdery state with acidic dye (C. I. Acid Violet 3, abbr. as V. V.) and basic dyes (C. I. Basic Blue 9, abbr. as M. B.; C. I. Basic Green 4, abbr. as M. G.). After equilibrium dyeing at 60°C, dyes remaining in the solutions were measured with a Shimadzu spectrophotometer UV-240.

Permeation Measurement

Polymer complex films were cut in sheets of 40 mm diameter and fixed to a permeation cell consisting of two 125 ml compartments which were separated vertically by the sample film of 3.8 cm² effective area.⁹ Pure water and aqueous solutions of NaCl, KCl, and CaCl₂ in concentrations described in the figures were put in each compartment and the water was allowed to permeate through the film without applying pressure. The flux was measured by the rise of the meniscus in the tube attached to the compartment for solution. The change of salt concentration was followed conductometrically.

RESULTS AND DISCUSSION

Copolymerization

Acrylonitrile and ethyl acrylate along with ionic monomers were copolymerized radically either in aqueous media, DMF or DMSO, or aqueous organic media. Some of the important results are summarized in Table I.

Dissociation of the monomer ions complicated the copolymerizations and copolymer composition was uneven in the suspension copolymerization in aqueous media. Homogeneous copolymerization in aqueous DMF gave better results but the viscosities of the obtained copolymers still varied significantly as a function of the amounts of water, initiator and polymerization temperature (Fig. 2). The solubilities of sodium vinyl benzyl sulfonate and vinyl benzyl trimethyl ammonium chloride in DMF were quite low, and consequently copolymerization of ionic monomers in DMF containing small amounts of water gave inhomogeneous copolymer emulsion and accordingly low conversion. Copolymerization in DMF containing large amounts of water gave gelled copolymers which were difficult to purify. The preferable water content in DMF was less than 20%.^{10,11}

Viscosities of Copolymers and Polymer Complexes

Most of the copolymers showed comparatively high viscosity values. Viscosity-concentration curves measured in DMF were similar to polyelectrolytes, and yielded characteristically higher η_{sp}/C values at low concentration. Addition of the inorganic salt NaI depressed the dissociation of polymer ions and gave normal straight lines.¹²⁻¹⁴

When cationic and anionic copolymers were blended in equimolar amounts, the resulted mixtures showed lower viscosities than the original copolymers regardless of the contents of ionic moieties in the copolymers (Fig. 3). Formation of ionic linkages between both copolymers as the result of the elimination of counter ions Na^+ and Cl^- is responsible for the lowering of viscosities.¹⁵ Addition of a strong electrolyte such as NaI also lowered the viscosity, thus giving a dotted straight line. The viscosity-concentration relationship of the polymer complex is shown in Figure 4. In

TABLE I
Copolymerization Results

Expt. no.	Monomers ($\times 10^2$ mol %)				Temp. (°C)	Time (hr)	Conversion (%)	Viscosity $[\eta]^a$
	AN	EA	VBS	VBQ				
1	92	7.5	0.5	0	60	16	68	1.5
2	92	7.5	0	0.5	55	16	72	1.6
3	87.5	7.5	5	0	55	20	67	1.2
4	87.5	7.5	0	5	55	20	65	1.2
5	82.5	7.5	10	0	55	18	49	0.81
6	82.5	7.5	0	10	55	18	43	0.89

^a The values were measured in DMF at 25°C, but No 3, 4, 5, and 6 were measured under the condition which was further added 0.02 mol/l NaI.

Monomer concentration in total, 20%; water content in DMF, 5%; AIBN, 0.6 g.

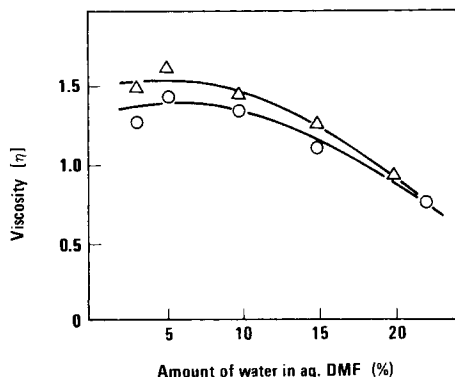


Fig. 2. $[\eta]$ and polymer concentration: (Δ): Cationic copolymer with 0.5 mol% VBQ; (\circ): Anionic copolymer with 0.5 mol% VBS. Polymerization condition: 20 wt % monomer, 0.6 g AIBN, 60°C, 16 h.

contrast to the polyelectrolyte curves for the original copolymers, a normal curve was obtained for the blended copolymers which we suggest is proof of the formation of polymer complex.

Reactivities of Ionic Monomers and Acrylonitrile in the Copolymerization

Contents of the ionic moiety in the copolymers were examined from IR absorption intensities. Somewhat larger incorporation of ionic moieties was found, but the discrepancy was small and good monomer reactivity ratios can be determined (Fig. 5).

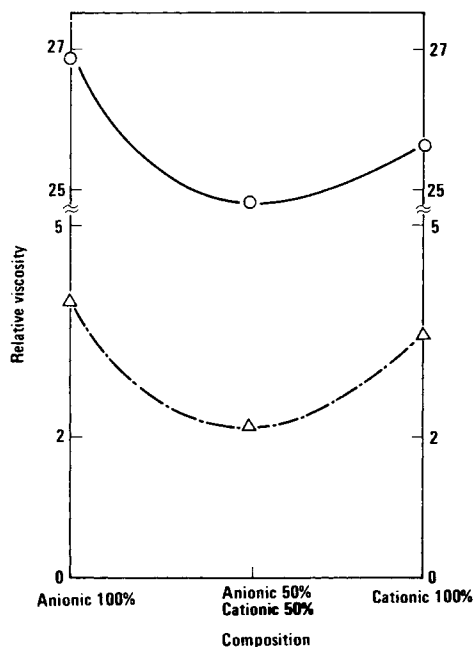


Fig. 3. Relative viscosities for copolymers and polymer complexes: (\circ): in 5 wt% DMF solution; (Δ): in 0.8 wt% DMF solution measured at 25°C, 5 mol% ionic moiety.

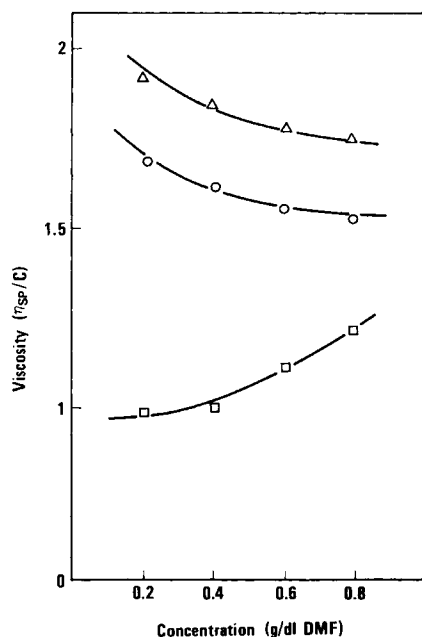


Fig. 4. Solution viscosity of the polymer complexes; (Δ): Cationic copolymer with 0.5 mol% VBQ; (\circ): Anionic copolymer with 0.5 mol% VBS; (\square): Polymer complex from equimolar ionic copolymers measured at 25°C.

Viscoelastic Properties

Viscoelastic properties of the copolymers and the polymer complexes are shown in Figure 6. The maximum $\tan \delta$ values for the polymer complexes appeared at higher temperatures than for anionic and cationic copolymer

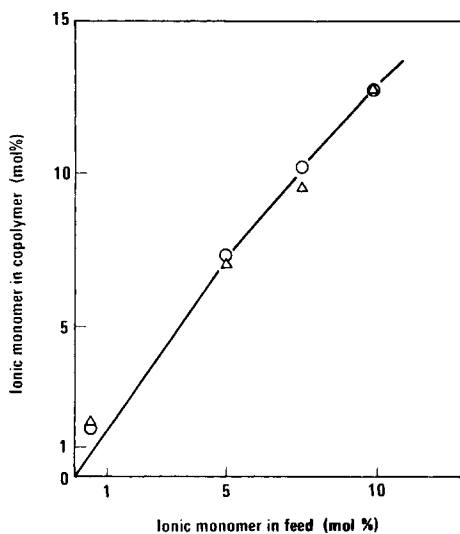


Fig. 5. Polymer composition as a function of monomer composition: (Δ): Cationic copolymer with VBQ; (\circ): Anionic copolymer with VBS.

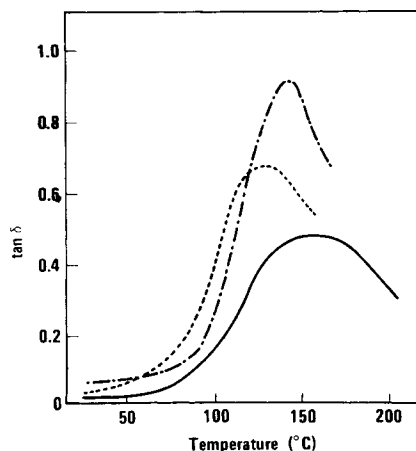


Fig. 6. Tan δ and temperature: (---): Cationic copolymer with VBQ; (···): Anionic copolymer with VBS; (—): Polymer complex; film thickness 25 μm , 5 mol% ionic moiety.

components. Restricted movement of acrylonitrile segments which is suggestive of the formation of ionic crosslinkings in the polymer complexes, contributes to the increase of these thermal properties.

Electric Resistivity

Bulk and surface electric resistivities of polymer complexes are shown in Figure 7. Both resistivities decreased in accordance with the amount of the ionic moieties in the complexes. The introduction of the ionic sites to polyacrylonitrile is thus effective for the reduction of static electricity.

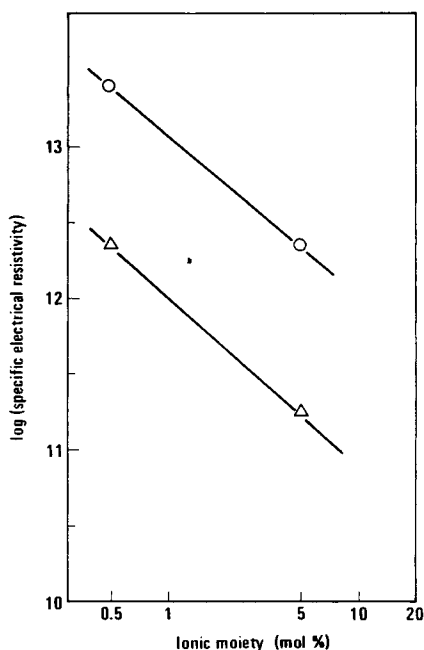


Fig. 7. Electrical resistivity of polymer complex: (○): bulk resistivity ($\Omega\text{ cm}$); (Δ): surface resistivity (Ω); film thickness 30 μm .

Dye Absorption

Figure 8 shows the equilibrium absorption of dyes for anionic and cationic copolymers having 10 mol% ionic moieties and the polymer complexes along with those for acrylonitrile. Both for acidic and basic dyes, the copolymers with ionic moieties gave Langmuir-type isotherms for monolayer absorption while the polymer complex and polyacrylonitrile gave Freundlich-type multilayer absorption. Two types of isotherms suggest the existence of ionic interactions between dyes and copolymers and nonionic ones between dyes and polymer complexes or polyacrylonitrile.¹⁶

Figure 9 shows the apparent saturated absorption vs. the amounts of the ionic moiety in the copolymers. Both copolymers showed much higher saturated absorption (i.e., better dyeability) than polyacrylonitrile. However, the values saturated at 10 mol% ionic moiety. The polymer complexes from the equimolar mixture of anionic and cationic copolymers gave lower saturated absorption than the original copolymers. Their value still increases over 20 mol% ionic moiety. Microstructures of polymer complexes are considered relaxed and nonionic dyeing sites increased with the introduction of ionic moieties.

Permeability

Permeabilities of water and inorganic salts through polymer complex membranes are shown in Figures 10-12. The abscissas of the figures are the difference of the amounts of anionic and cationic moieties in the polymer complexes (i.e., the content of free ionic moiety in molar scale).

Permeabilities of water and inorganic salts increased with the content of free ionic moiety for aqueous NaCl, KCl, and CaCl₂ solutions. Both permeabilities decreased as the content of free ionic moiety approached to zero (i.e., to the polymer complex made from the equimolar mixture of anionic and cationic copolymers). This is the same tendency which Markley found

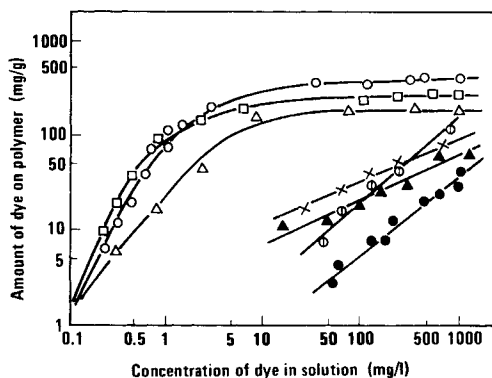


Fig. 8. Equilibrium absorption isotherms of dyes: (○): C. I. Acid Violet 3 on cationic copolymer with 10 mol% VBQ; (□): C. I. Basic Blue 9 on anionic copolymer with 10 mol% VBS; (△): C. I. Basic Green 4 on anionic copolymer with 10 mol% VBS; (X): C. I. Basic Blue 9 on polymer complex with 10 mol% ionic moieties; (⊙): C. I. Acid Violet 3 on polymer complex with 10 mol% ionic moieties; (▲): C. I. Basic Blue 9 on polyacrylonitrile; (●): C. I. Acid Violet 3 on polyacrylonitrile at 60°C, pH 5 (acid dye) and pH 7 (basic dye).

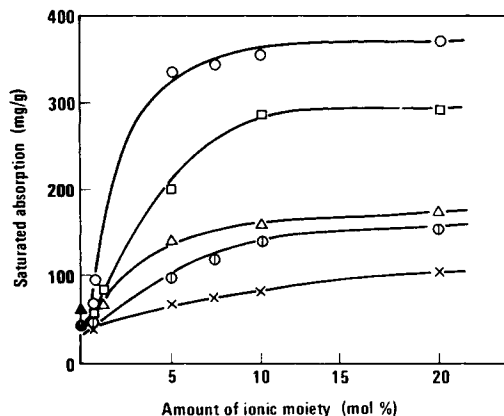


Fig. 9. Saturated absorption and the amount of ionic moiety: (○): C. I. Acid Violet 3 on cationic copolymer with VBQ; (□): C. I. Basic Blue 9 on anionic copolymer with VBS; (△): C. I. Basic Green 4 on anionic copolymer with VBS; (⊙): C. I. Acid Violet 3 on polymer complex with equimolar ionic moieties; (×): C. I. Basic Blue 9 on polymer complex with equimolar ionic moieties; (▲): C. I. Basic Blue 9 on polyacrylonitrile; (●): C. I. Acid Violet 3 on polyacrylonitrile at 60 °C.

on polyvinyl benzyl trimethyl ammonium polystyrene sulfonate.¹⁷ Increased hydrophilicity and accordingly the water contents of the polymer complexes with the increase of ion exchange capacity are considered to increase their water and salt permeability.²

Permeabilities of water in aqueous inorganic salt solutions were in the order of $\text{CaCl}_2 > \text{KCl} > \text{NaCl}$ and those of the salts in the order of $\text{NaCl} > \text{KCl} > \text{CaCl}_2$, which reflected the molecular sizes of the dissolved ions. Polymer complexes rich in anionic moiety showed higher permeability of

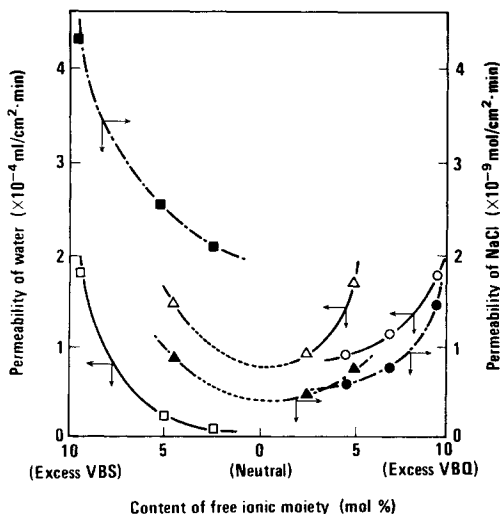


Fig. 10. Permeabilities of water and NaCl: (□): Water, 10 mol% anionic moiety in the complex; (■): NaCl, 10 mol% anionic moiety in the complex; (△): Water, 5 mol% anionic moiety in the complex; (▲): NaCl, 5 mol% anionic moiety in the complex; (○): Water, 0.5 mol% anionic moiety in the complex; (●): NaCl, 0.5 mol% anionic moiety in the complex at 20°C.

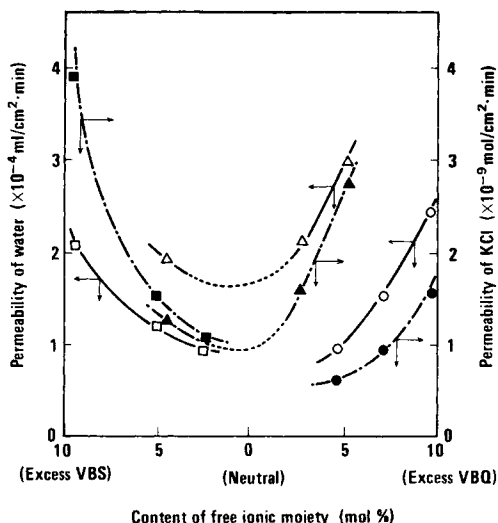


Fig. 11. Permeabilities of water and KCl: (□): Water, 10 mol% anionic moiety in the complex; (■): KCl, 10 mol% anionic moiety in the complex; (△): Water, 5 mol% anionic moiety in the complex; (▲): KCl, 5 mol% anionic moiety in the complex; (○): Water, 0.5 mol% anionic moiety in the complex; (●): KCl, 0.5 mol% anionic moiety in the complex at 20°C.

salts than the complexes rich in the cationic moiety although water permeability was almost the same. This fact can be explained by the attraction of alkali and alkaline earth metal ions by the anionic sites of the polymer complexes.

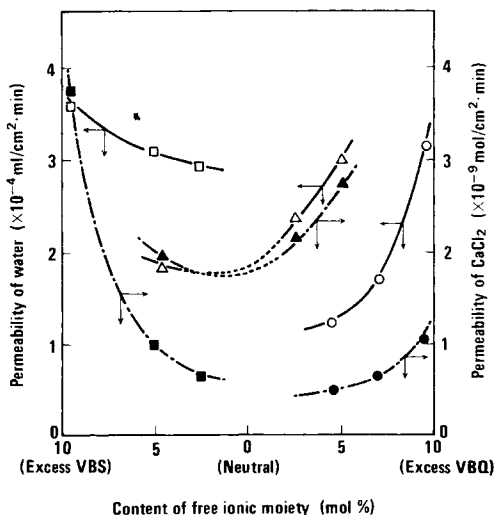


Fig. 12. Permeabilities of water and CaCl_2 : (□): Water, 10 mol% anionic moiety in the complex; (■): CaCl_2 , 10 mol% anionic moiety in the complex; (△): Water, 5 mol% anionic moiety in the complex; (▲): CaCl_2 , 5 mol% anionic moiety in the complex; (○): Water, 0.5 mol% anionic moiety in the complex; (●): CaCl_2 , 0.5 mol% anionic moiety in the complex at 20°C.

CONCLUSION

Radical copolymerization of sodium vinyl benzyl sulfonate and vinyl benzyl trimethyl ammonium chloride with acrylonitrile gave polyelectrolyte of preferable solution viscosities. The blending of these two copolymers in DMF produced polymer complexes with ionic linkages.

Dyeabilities for both acidic and basic dyes were examined and Langmuir-type and Freundlich-type absorption were observed for copolymers and polymer complexes, respectively. The introduction of hydrophilic sites into polyacrylonitrile by copolymerization or by polymer complex formation increased the dyeability.

Homogeneous membranes of the polymer complex were cast from DMF or DMSO solutions and viscoelasticity, electric resistivity, and permeability have been examined. Complex formation by ionic linkages shifted the maximum $\tan \delta$ temperature to higher temperature, increasing the thermal mechanical stability. Electric resistivity decreased with introduction of the ionic moiety. Permeability of water increased with the amount of ionic site in the copolymer.

Acknowledgments are to Dr. A. Okada and Dr. K. Sasaki for their valuable discussion.

References

1. E. Tsuchida, in *Kinosei Kobunshi* (Functional Polymers), Kobunshi Zikkengaku (Experimental Polymer Science Vol. 7), Kobunshi-gakkai Ed., Kyoritsu Pub., Tokyo, 1974, p. 489.
2. H. J. Bixler, A. S. Michaels, *Encyclopedia of Polymer Science and Technology*, Vol. 10, Interscience, New York, 1969, p. 765.
3. E. Tsuchida, Y. Osada, and K. Sanda, *J. Polym. Sci.*, A-1, **10**, 3397 (1972).
4. S. Kori, T. Amakasu, Y. Anodo, Y. Tsuruta, E. Nishihara, and M. Fukui (Seimi Chem.), Jpn. Kokai Tokkyo Koho JP 50, 104290 (1975); *Chem. Abstr.* **83**, P19440r (1975).
5. M. Suzuki, M. Senuma, Y. Shimura, F. Hase, and S. Kori (Agency Inc. Sci. Tech.; Seimi Chem.), Japan Patent JP 53,37445 (1978); *Chem. Abstr.* **89**, P91078h (1978).
6. M. Suzuki, M. Senuma, Y. Shimura, F. Hase, and S. Kori (Agency Ind. Sci. Tech.; Seimi Chem.), Japan Patent JP 53,42805 (1978); *Chem. Abstr.* **89**, P91079j (1978).
7. D. Coleman (Amer. Cyan.), Japan Patent JP 46,27814 (1971); *Chem. Abstr.* **75**, P50329h (1971).
8. A. Nakajima, K. Taketani, and Y. Shimosaka (Jpn Exlan), Japan Patent JP 40,24396 (1965); *Chem. Abstr.* **64**, 5231c (1965).
9. K. Sasaki, T. Suehiro, S. Fujino, and N. Nakabayashi, Sen-i-kobunshi Zairyo Kenkyo-jo Kenkyu-happyokai Sanko Shiryo (Collected Papers at the Annual Symposium of Research Institute for polymers and Textiles) 1977, p. 141. *Chem. Abstr.* **89**, 220858p (1978).
10. H. Tanaka, S. Fujii, and M. Shimamura (Toray), Jpn Kokai Tokkyo Koho JP 49,87788 (1974); *Chem. Abstr.* **82**, 112614 (1974).
11. R. H. Yocum and E. B. Nyquist, *Functional Monomers*, Vol. 1, Wiley-Interscience, New York, 1973, p. 251.
12. L. Yuan, *J. Polym. Sci.* A-2, **10**, 171 (1972).
13. H. Fujita, *J. Polym. Sci.*, **15**, 277 (1955).
14. K. Miyamichi, M. Suzuki, T. Harada, and M. Katayama, *Kobunshikagaku* (Polym. Chem. Jpn.), **21**, 79 (1964).
15. A. S. Michaels, *Ind. Eng. Chem.*, **57**, (10), 32 (1965).
16. T. Vickerstaff, *The Physical Chemistry of Dyeing*, Oliver and Boyd, London, 1954, pp. 93, 274.
17. L. L. Markley, H. J. Bixler, and R. A. Cross, *J. Biomed. Mater. Res.*, **2**, 145 (1968).

Received May 31, 1985

Accepted August 15, 1985