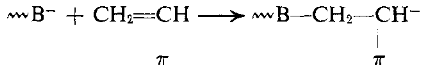
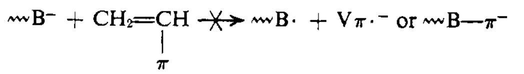
These model system studies with pyrene can be translated to the real polymerization systems and explain the anomalous results obtained in some of the block copolymer syntheses. Addition of 1-vinylpyrene monomer to a solution of living polybutadiene, $\sim B^-$, results in normal block copolymer formation. Apparently, the diene anion reacts more rapidly by addition to the vinyl function (eq 5) than with the pyrene nucleus (eq 6). Once all the diene anions have been converted to $BV\pi^-$, the polymerization of the 1-vinylpyrene segment proceeds in a normal manner.



$$\sim B^- + CH_2{=}\underset{\pi}{CH} \longrightarrow \sim B{-}CH_2{-}\underset{\pi}{CH^-} \qquad (5)$$



$$\sim B^- + CH_2{=}\underset{\pi}{CH} \not\longrightarrow \sim B\cdot + V\pi\cdot^- \text{ or } \sim B{-}\pi^- \qquad (6)$$

In the reverse addition sequence, *i.e.*, addition of butadiene monomer to $\sim V\pi^-$, it appears that the expected crossover reaction occurs and the polybutadiene anion is formed. However, this anion can either continue to polymerize any available butadiene monomer or react with the high local concentration of pyrene rings in the polyvinylpyrene segment of the copolymer. The reaction sequence is illustrated in eq 7–9, where $(\pi)_n$ refers to a pyrene ring on the $PV\pi$ segment of the copolymer chain.

$$\sim V\pi^- + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow \sim V\pi{-}B^- \qquad (7)$$

$$\sim B^- + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow \sim BB^- \qquad (8)$$

$$\sim B^- + (\pi)_n \longrightarrow \sim B\cdot + (\pi)_n\cdot^- \qquad (9a)$$

$$\text{or } \sim B(\pi)_n^- \qquad (9b)$$

Reactions 7 and 8 will result in block copolymers of well-defined structure and composition, whereas reactions 9a and 9b will yield ill-defined copolymer materials. The electron-transfer reaction products shown in reaction 9a lead to chain termination and chain coupling, whereas pseudotermination and branching occur as a result of the addition reaction shown in eq 9b. Our model studies with pyrene indicate, however, that block copolymer formation (eq 8) is the preferred reaction mode in nonpolar solvents at moderate or low temperatures.

Acknowledgments. The authors gratefully acknowledge Mr. W. J. Stauffer for his fine technical assistance during this study, Dr. D. J. Williams for the esr measurements, and Dr. E. Vanzo for several fruitful discussions.

Synthesis of Block Polymers for Desalination Membranes. Preparation of Block Copolymers of 2-Vinylpyridine and Methacrylic Acid or Acrylic Acid

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ABSTRACT: Block copolymers containing cationic and anionic sequences were synthesized by the "living" anionic polymerization of 2-vinylpyridine and various methacrylate and acrylate esters, followed by the hydrolysis of the ester sequence to the free acid. These copolymers were soluble in either strongly acid or strongly basic aqueous media, but insoluble at neutral pH values, indicating that they were polyampholytes. The reduced specific viscosity of these polymers increased with dilution in protic solvents in a manner characteristic of a polyelectrolyte, but the viscosity in aprotic solvents was linearly related to the concentration. Salt rejection and flux rate of a dynamically formed membrane of the block polymers were found to be dependent on pH. Except for the region of 6.5–4.5, the isoelectric range of the block polymer, good salt rejection was observed; the flux rate was maximum near the isoelectric point.

A potentially important method for the desalination of water is membrane reverse osmosis. In studies of salt rejection, cation-exchange and anion-exchange membranes have been shown to have widely different, but sometimes complementary, selectivities for the rejection of different salts.[1–4] Thus a copolymer containing anionic and cationic blocks possibly could exhibit a more uniform rejection of all salts. In addition, the polymer compatibility present in a block copolymer could lead to the formation of a membrane carrying a random distribution of charged domains throughout the microstructure; however, a polymer containing this block structure of an acid sequence followed by a base sequence has not been reported. A copolymer having these uniform block lengths is reported.

Block copolymers of 2-vinylpyridine and various methacrylic acid esters or acrylic acid esters were synthesized by "living" anionic polymerization at low temperature (−78°). Base and acid hydrolysis of the ester sequences produced the block copolymers poly(2-vinylpyridine-*b*-methacrylic acid) and poly(2-vinylpyridine-*b*-acrylic acid). (In this paper, the -*b*- designation is used in reference to block copolymers exclusively.)

Results and Discussion

Preparation of Block Copolymers. For poly(2-vinylpyridine-*b*-methyl methacrylate) as well as poly(2-vinylpyridine-*b*-trimethylsilyl methacrylate), the block ratio con-

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(1) K. A. Kraus, H. O. Phillips, A. E. Marcinkowsky, J. S. Johnson, Jr., and A. J. Shor, *Desalination*, 1, 225 (1966).

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TABLE I

THE RELATION BETWEEN THE MOLAR RATIOS OF MONOMERS CHARGED AND OF THE MOLAR RATIO OF BLOCK SEQUENCES IN THE POLYMER[a]

Acrylate charged	Molar ratio of monomers charged acrylate/2-vinylpyridine	Molar ratios of block sequences in polymer	[η]
Methyl methacrylate	1.09	1.05	0.38[b]
Methyl acrylate	16.40	0.81	0.29[b]
Isopropyl acrylate	1.92	0.95	0.36[b]
tert-Butyl acrylate	1.25	0.87	0.36[b]
Trimethylsilyl methacrylate	0.78	0.74	0.23[c]
Trimethylsilyl methacrylate	0.86	0.98	0.48[c]
Trimethylsilyl methacrylate	2.16	2.25	0.37[c]

[a] Polymerization solvent tetrahydrofuran; polymerization temperature −78°. [b] In benzene. [c] In dimethyl sulfoxide.

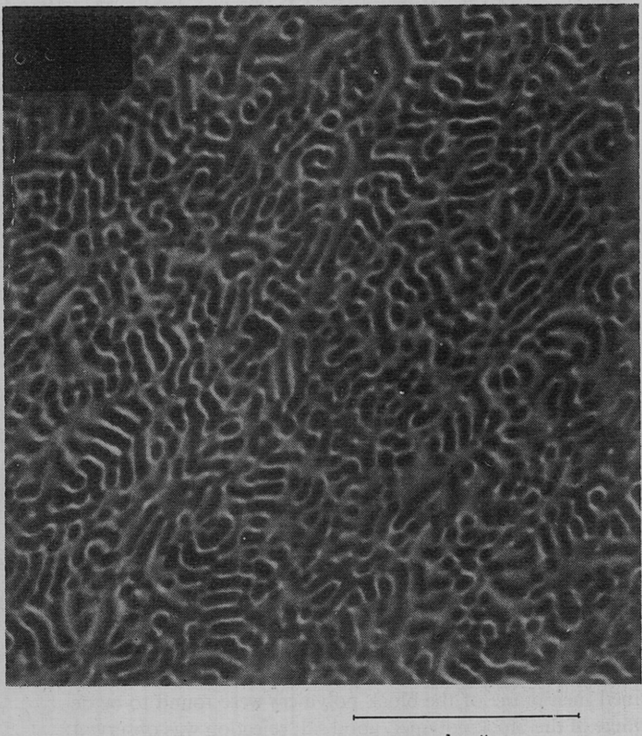

Figure 1. Electron micrograph of poly(2-vinylpyridine-*b*-methyl methacrylate).

tained in the polymers was found to be approximately equal to the molar ratio of monomers charged (Table I); therefore, block polymers of 2-vinylpyridine and trimethylsilyl methacrylate containing sequences of various lengths could be prepared simply by varying the ratio of monomers charged in the polymerization.

In order to prepare a block polymer containing a given amount of poly(alkyl acrylate), alkyl acrylate in excess of the theoretical amount had to be added to the living poly(2-vinylpyridine) anion system (Table I). The ratio of alkyl acrylate charged to that incorporated in the polymer varied with the alcohol portion of ester. Generally, the greater the steric hindrance presented by the alcohol portion, the lower the ratio necessary to obtain a 1:1 block polymer. Self-termination competes with the anionic propagation of the alkyl acrylate, thereby reducing the amount of this block in the polymer.[5]

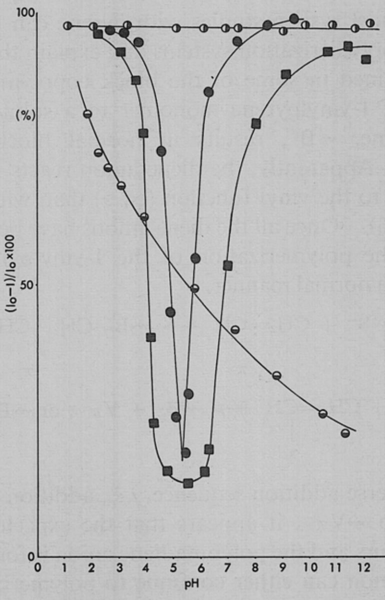

Figure 2. Turbidimetry of hydrolyzed copolymers and polymer blend: (●) block copolymer, (◑) poly(MAA), (■) random copolymer, (⊖) polymer blend.

Preparation of Poly(2-vinylpyridine-*b*-methyl methacrylate) and Poly(2-vinylpyridine-*b*-alkyl acrylate). Block polymers containing acid and base sequences were prepared by the hydrolysis of the ester sequence of block polymers of 2-vinylpyridine and methyl methacrylate, trimethylsilyl methacrylate, and alkyl acrylate. The hydrolysis of the ester of poly(2-vinylpyridine-*b*-methyl methacrylate) and poly(2-vinylpyridine-*b*-alkyl acrylate) was carried out in acid media at room temperature. From the nmr spectrum (3.6 ppm, OCH_3) and combustion analysis data, the poly(methyl methacrylate) sequence was found to be less than 90% hydrolyzed (Table II). In the acid hydrolysis of poly(methyl methacrylate), the configuration of polymer chain has been shown to be an important factor in determining the extent of hydrolysis.[6-9] The poly(methyl methacrylate) sequence in the block polymer was found to be amorphous by ir. Hydrocarbon solvents, *e.g.*, toluene, have to be used for the preparation of polymer containing the isotactic poly(methyl methacrylate) sequences at the low temperatures which are necessary to retain the living poly(2-vinylpyridine) anion.[10,11] Since poly(2-vinylpyridine) is insoluble in hydrocarbon solvents at low temperature, an isotactic methyl methacrylate sequence could not be obtained under the polymerization conditions necessary to prepare a block copolymer. The solubility and the solution properties of these partially hydrolyzed polymers (>75%) were nearly the same as those of poly(2-vinylpyridine-*b*-methyl methacrylate), however.

The block polymers of 2-vinylpyridine and alkyl acrylate were completely hydrolyzed by treatment with acid, as shown

[5] W. E. Goode, F. H. Owens and W. L. Myers, *J. Polym. Sci.*, **47**, 75 (1960).

[6] W. E. Goode, F. H. Owens, R. P. Fellman, W. H. Snyder and J. E. Moore, *ibid.*, **46**, 317 (1960).

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[8] J. Semen and J. B. Lando, *Macromolecules*, **2**, 570 (1969).

[9] E. Klesper, W. Gronski and V. Barth, *Makromol. Chem.*, **139**, 1 (1970).

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[11] M. Fontanille and P. Sigwalt, *Bull. Soc. Chim. Fr.*, 4087 (1967).

TABLE II
HYDROLYSIS OF BLOCK POLYMERS

Block polymer	Hydrolysis method	Time, hr	Temp, °C	Degree of hydrolysis, %
Poly(2-vinylpyridine-*b*-methyl methacrylate)	Concd H_2SO_4	72	30	90
Poly(2-vinylpyridine-*b*-methyl acrylate)	NaOH (15% aq soln):hexamethylphosphoramide 1:10	12	60	58
Poly(styrene-*co*-2-vinylpyridine-*b*-methyl methacrylate)[a]	NaOH (15% aq soln):hexamethylphosphoramide 1:10	12	60	48
Poly(2-vinylpyridine-*b*-isopropyl acrylate)	Concd H_2SO_4	72	30	100
Poly(α-methylstyrene-*b*-2-vinylpyridine-*b*-isopropyl acrylate)[a]	Concd H_2SO_4	24	30	100
Poly(2-vinylpyridine-*b*-*tert*-butyl acrylate)	Concd H_2SO_4	72	30	100
Poly(2-vinylpyridine-*b*-*tert*-butyl acrylate)	NaOH (15% aq soln):hexamethylphosphoramide 1:10	12	60	32
Poly(2-vinylpyridine-*b*-trimethylsilyl methacrylate)	NaOH (5% aq soln)	12	30	100

[a] A dianionic initiator was used which produced a block structure of the type C–B–A–B–C.

by the absence of the ester methyl group by nmr and by combustion analyses. The facile hydrolysis of these alkyl acrylate sequences compared to the methyl methacrylate sequence may be explained by the intramolecular hydrolysis mechanisms proposed for poly(alkyl acrylate) or poly(methyl methacrylate).[12,13]

The hydrolysis of trimethylsilyl methacrylate sequence of poly(2-vinylpyridine-*b*-trimethylsilyl methacrylate) was carried out in basic media at room temperature. Complete hydrolysis occurred, as was confirmed by the absence of a Si–CH_3 absorption in the ir (840 and 1260 cm^{-1}) and nmr spectra (0.2 ppm) and by combustion analysis. The complete hydrolysis was possible even under much milder conditions than reported for the hydrolysis of poly(trimethylsilyl methacrylate).[14]

Poly(2-vinylpyridine-*b*-methyl methacrylate) was shown by electron microscopy to be made up of laminar domains (Figure 1). These domains disappeared after hydrolysis, possibly because the interaction of the oppositely charged blocks causes a complete mixing of the two different blocks.

Poly(2-vinylpyridine-*b*-methacrylic acid) and Poly(2-vinylpyridine-*b*-acrylic acid). Poly(2-vinylpyridine-*b*-methacrylic acid) and poly(2-vinylpyridine-*b*-acrylic acid) were insoluble in common organic solvents up to 100°, but could be dissolved in hot aprotic solvents such as dimethyl sulfoxide and hexamethylphosphoramide above 100°. The block polymer remained dissolved in the aprotic solvent even after the solutions were allowed to cool to room temperature. These polymers were also soluble in formic acid and sulfuric acid; they were almost completely soluble in strongly acid media (pH <3) or in alkaline aqueous media (pH >8), but precipitated at intermediate pH values. The behavior of these polymers in aqueous solution was remarkably different from that of a polymer blend of poly(2-vinylpyridine) and poly(methacrylic acid) (Figure 2). The range of pH values through which the polymer solution remained turbid is greater for a random copolymer than for a block polymer.

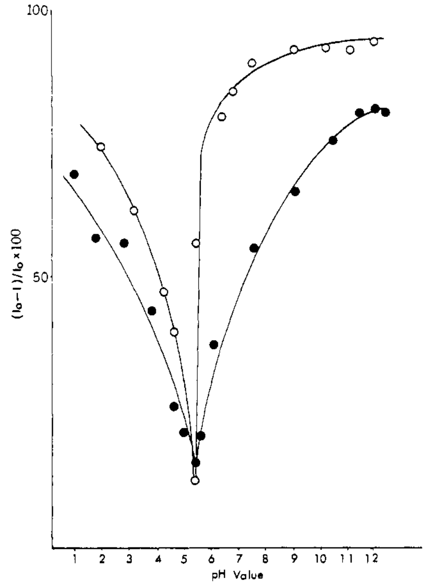

Figure 3. The effect of ionic strength on the turbidity of block polymer (2VP:AA = 1:0.87): (○) before the addition of NaCl, (●) after the addition of NaCl.

The behavior of the block polymer in a solution of varying pH value was similar to that observed for polyampholytes in that the degree of hydrogen bonding is affected by the pH.[15] An increase in ionic strength of a solution of a block polymer leads to an expansion of the polymer chain and greater intermolecular interaction (Figure 3).

The potentiometric titration of poly(2-vinylpyridine-*b*-methacrylic acid) was carried out, and the resulting curve is shown in Figure 4. Two inflections were observed, one at pH 8.10 ascribed to the end point of the methacrylic acid sequence and one at pH 5.25 corresponding to the block polymer's isoelectric point. With block polymers containing various molar ratios of 2-vinylpyridine and methacrylic acid sequences, the isoelectric point, the pH at which maximum

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(13) M. M. Van Keylen, "The Stereochemistry of Macromolecules," Vol. 3, A. D. Keteley, Ed., Marcel Dekker, New York, N. Y., 1968, pp 333–355, and references cited therein.

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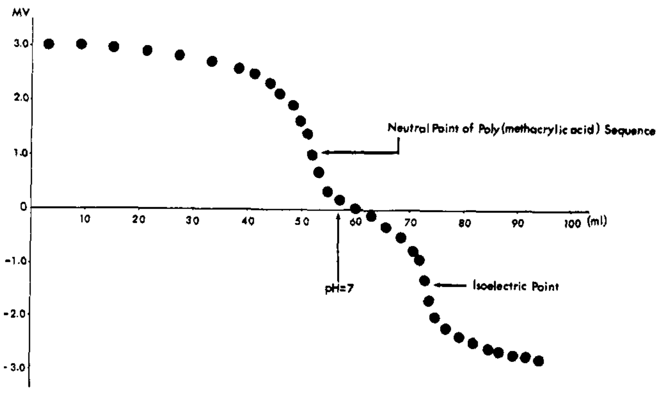

Figure 4. Potentiometric titration of block copolymer sample (2VP:MAA = 1:0.74).

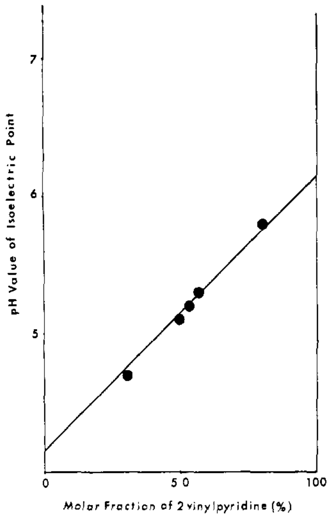

Figure 5. Isoelectric point of block copolymers *vs.* pH.

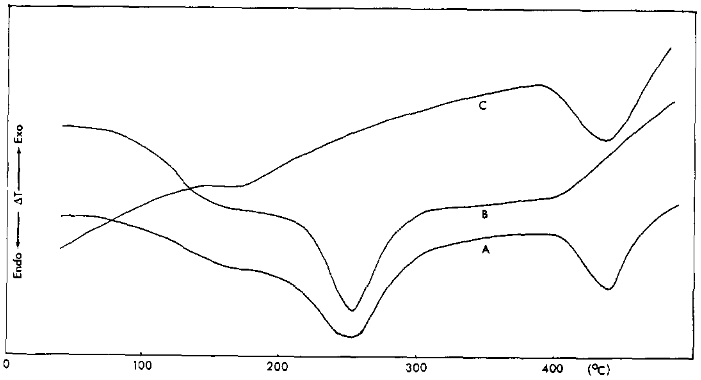

Figure 6. Differential thermal analysis: (A) block copolymer (2VP:MAA = 1:0.74), (B) poly(methacrylic acid), (C) poly(2-vinylpyridine).

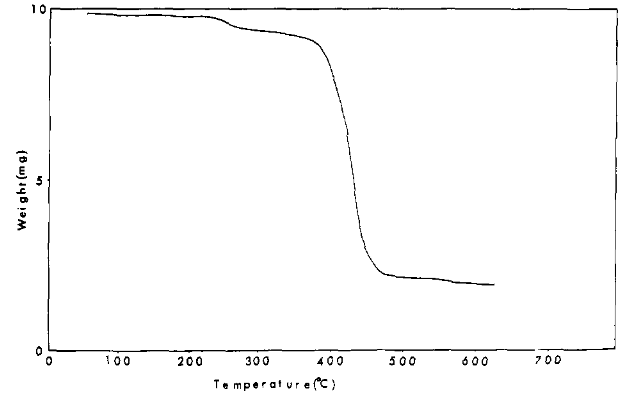

Figure 7. Thermogravimetric analysis of block copolymer (2VP: MAA = 1:0.74).

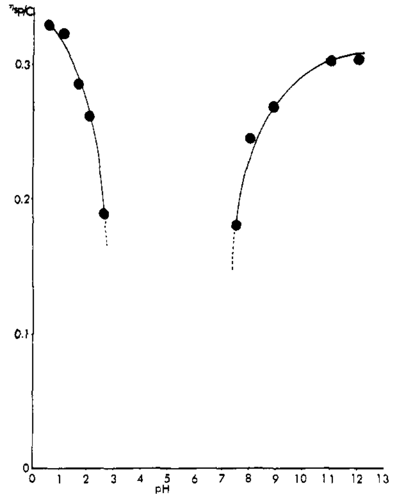

Figure 8. Viscosities of block copolymer *vs.* pH; sample (2VP: MAA = 1:0.74), 0.189%.

turbidity occurs, was found to increase as the content of the 2-vinylpyridine increased. Thus, maximum turbidity results at the pH at which the number of cationic and anionic groups are equal and complete neutralization results. Consequently, poly(2-vinylpyridine-*b*-methacrylic acid) can be synthesized with a desired isoelectric point (Figure 5).

Poly(2-vinylpyridine-*b*-methacrylic acid) showed two endothermic transitions at 220 and 395° by differential thermal analysis (Figure 6). A comparison of the differential thermal analysis of the block copolymer with those of each homopolymer along with the thermogravimetric analysis of the copolymer showed that the 3% weight loss at 220° corresponded to the dehydration of the methacrylic acid block sequence with concurrent polyanhydride formation (Figure 7). The anhydride formation was verified by the appearance of new peaks at 1803 and 1775 cm^{-1} in the ir spectrum after the block polymer was heated at 240° for 1 hr. A second large break appearing at 395° on the thermogravimetric analysis curve results from degradation of the block copolymer.

The viscosity of the block polymer in water and in water–*N*-methylpyrrolidone solutions (1:3) also increases as the pH is varied from the isoelectric point (Figures 8 and 9). Electrostatic repulsions of the net charge carried by the polymer molecule presumedly cause it to unfold, which increases the viscosity. The reduced specific viscosity of the block polymers increased with dilution in formic acid in a manner characteristic of a strong polyelectrolyte (Figure 10). This has been ascribed to the expansion of the polymer chain through repulsion of the protonated 2-vinylpyridine sequences. This increase of the reduced specific viscosity in formic acid, however, was found to occur to a lesser extent upon dilution in water–*N*-methylpyrrolidone (1:3) at pH 12.8. It is possible that the lack of this viscosity increase on dilution is caused by the low solubility of the 2-vinylpyridine block in these solvents which do not allow this block to unfold. Vis-

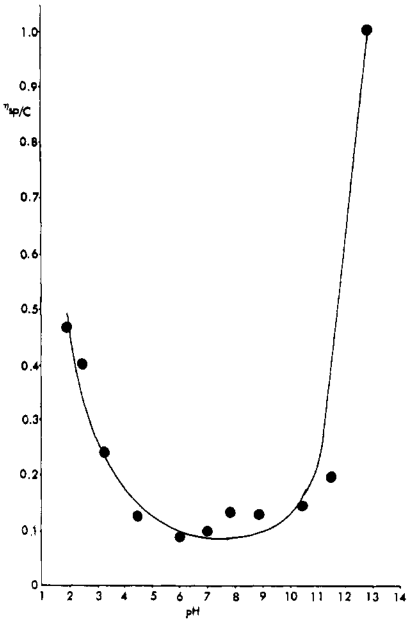

Figure 9. Viscosities of block copolymer *vs.* pH; sample (2VP:MAA = 1:0.87), 0.10% solution in NMP(75)-H_2O(25).

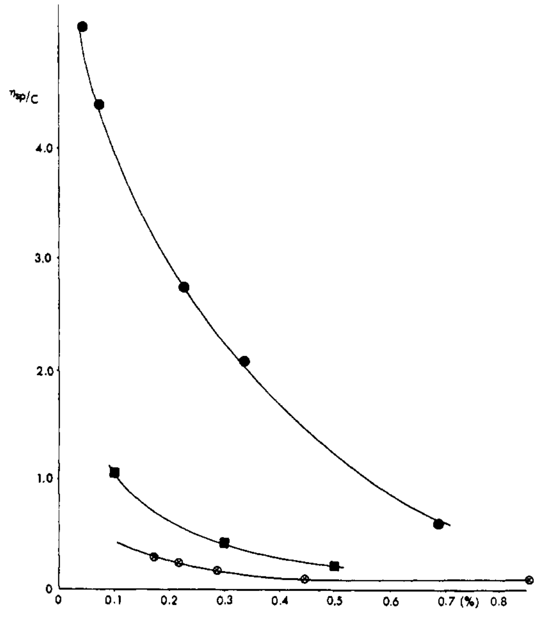

Figure 10. Viscosities of block copolymer in formic acid (●, 2VP:MAA = 1:0.74); alkaline aqueous solution, pH 12.35 (⊗, 2VP:MAA = 1:0.74); and NMP(75)-H_2O(25), pH 12.80 (■, 2VP:MAA = 1:1.14).

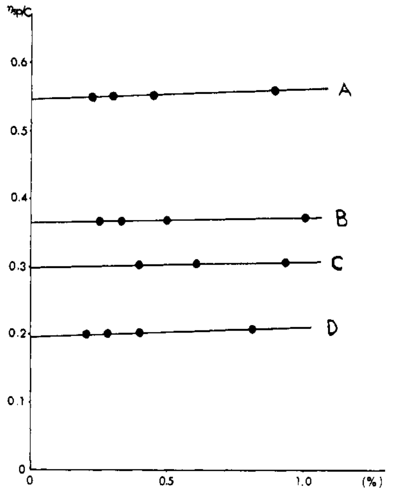

Figure 11. Viscosities of block copolymers in DMSO and NMP: (A) 2VP:MAA = 1:0.86 (DMSO), (B) 2VP:MAA = 1:0.90 (DMSO), (C) 2VP:MAA = 1:0.87 (NMP), (D) 2VP:MAA = 1:0.74 (DMSO).

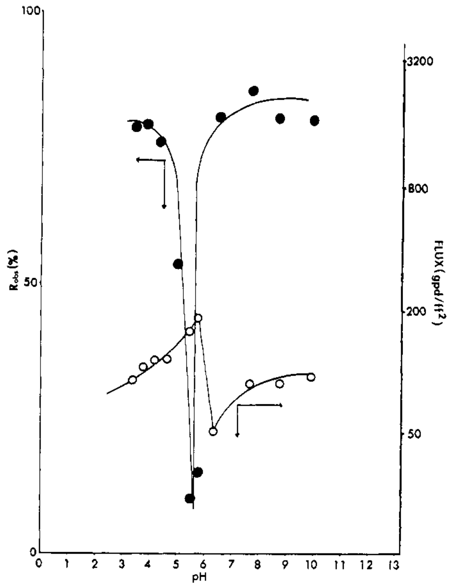

Figure 12. Relationship of salt rejection and flux *vs.* pH; sample (2VP:MAA = 1:0.90), a dynamic single-layer membrane, 0.05 *M* NaCl at 950 psig.

cosities were taken in the aprotic solvents dimethyl sulfoxide and *N*-methylpyrrolidone, and were found to be linearly related to the concentration (Figure 11).

Desalination data were obtained employing a dynamically[16] formed membrane of poly(2-vinylpyridine-*b*-methacrylic acid) (Figure 12). Except for the region of pH 6.5–4.5, the isoelectric range of the block polymer, good salt rejection was observed (60–80%). The flux rate was also found to be dependent on pH, with maximum flux occurring near the isoelectric point, pH 5.5–6.0. This behavior can be accounted for by considering that at the isoelectric point the largest interaction between the 2-vinylpyridine and methacrylic acid blocks occurs, resulting in contraction in the microstructure of the polymer, providing a high porosity of the membrane. The desalination properties of the poly(2-vinylpyridine-*b*-acrylic acid) were quite similar to those of poly(2-vinylpyridine-*b*-methacrylic acid).

Experimental Section

Ir spectra were obtained on a Perkin-Elmer 21 infrared spectrophotometer. Nmr spectra were recorded on a Varian A-60 instrument. The pH values were measured on a Fisher Accumat Model 20 pH meter. A Du Pont 900 differential thermal analyzer was used for differential thermal analysis (differential thermal analysis cell) and thermal gravimetric analysis.

Styrene, α-methylstyrene, and 2-vinylpyridine were distilled under reduced pressure. Further purification was carried out on these monomers by distillation from sodium chips *in vacuo* (10^{-5}

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[16] A. E. Marcinkowsky, K. A. Kraus, H. O. Phillips, J. S. Johnson, Jr., and A. J. Shor, *J. Amer. Chem. Soc.*, **88**, 5744 (1966).

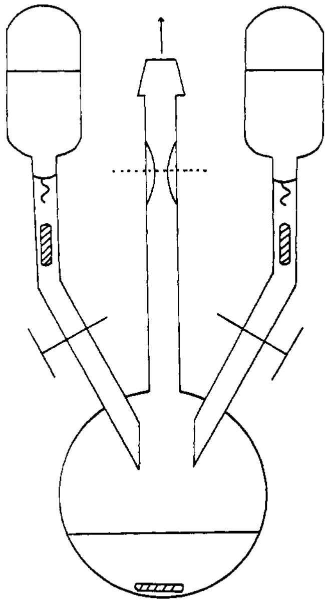

Figure 13. Polymerization apparatus.

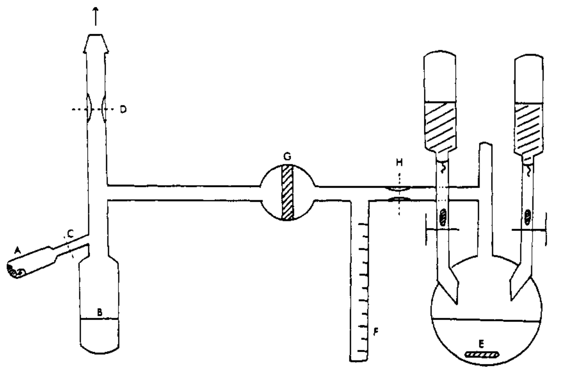

Figure 14. Polymerization apparatus.

mm) into a sodium-coated ampoule. The monomers were then distilled into a graduated ampoule for storage until needed.

Methyl methacrylate and alkyl acrylate were dried over anhydrous sodium sulfate, distilled from calcium hydride under reduced pressure, and dried over sodium and stored in the same manner as α-methylstyrene.

Trimethylsilyl methacrylate was synthesized by the base-catalyzed reaction of methacrylic acid and trimethylsilyl chloride to give a 57% yield of ester, bp 52° (20 mm).[11] Further purification was carried out in the same manner as for methyl methacrylate. *Anal.* Calcd for $C_7H_{14}O_2Si$: C, 53.06; H, 8.84. Found: C, 53.20; H, 8.83.

Block Polymerization. (1) Butyllithium-Initiated Block Polymerization. A polymerization apparatus was prepared by connecting ampoules containing tetrahydrofuran solutions of 2-vinylpyridine and methyl methacrylate or trimethylsilyl methacrylate to a vessel, as shown in Figure 13. The vessel was evacuated on a high-vacuum system and flushed with nitrogen and a solution of butyllithium in heptane was introduced into the vessel under nitrogen by means of a hypodermic syringe. The solvent was removed by evacuation and the vessel was sealed and placed in a Dry Ice–methanol bath. After 30 min, the tetrahydrofuran solution of 2-vinylpyridine was introduced into the polymerization vessel by means of a break-seal. The color of the reaction system changed to red. After an additional hour, the tetrahydrofuran solution of methyl methacrylate or trimethylsilyl methacrylate was added to the polymerization system. The red color of living polymer anion disappeared immediately. The polymerization reaction was allowed to continue for another hour and the reaction was terminated by the addition of a small amount of methanol. The yield of polymeric product obtained was above 95% in the block polymerization of 2-vinylpyridine and methyl methacrylate as well as that for 2-vinylpyridine and trimethylsilyl methacrylate.

TABLE III
ISOLATION OF BLOCK POLYMER OF 2-VINYLPYRIDINE AND METHYL METHACRYLATE

Fraction	Weight, g
Methanol soluble	0.8
Acetonitrile soluble	1.0
Insoluble	3.1
Total polymer	4.9

TABLE IV
ISOLATION OF BLOCK POLYMER OF 2-VINYLPYRIDINE AND TRIMETHYLSILYL METHACRYLATE

Fraction	Weight, g
Methanol soluble	0.2
Methanol insoluble[a]	4.6
Total polymer	4.8

[a] Homopoly(TSM) could not be removed from the block polymer. However, this homopolymer was removed as poly(methacrylic acid) after hydrolysis and was found to be almost negligible.

(2) Sodium-Initiated Block Polymerization. The apparatus shown in Figure 14 was used to prepare the block polymer of the structure C–B–A–B–C. Sodium was distilled from ampoule A to ampoule B under high vacuum. After sealing the system at C, ampoule B was coated with sodium, and known aliquots of α-methylstyrene and tetrahydrofuran were distilled into B. The apparatus was then sealed at D and placed in a constant-temperature bath at 30°. The color of the reaction system was orange-red. The tetrahydrofuran solution of living poly(α-methylstyrene) was poured into the graduated tube F through the sintered glass filter G. From F, a given volume of the tetrahydrofuran solution of living poly(α-methylstyrene) was transferred to the polymerization vessel E. The polymerization apparatus was sealed at H and placed in a Dry Ice–methanol bath. The remainder of the procedure followed for this block polymerization was the same as in the *n*-butyllithium-initiated block polymerization.

Fractionation and Characterization of Block Polymers. The solvent and the unreacted monomer in the polymerization mixture were evaporated. In the case of the block polymer of 2-vinylpyridine and methyl methacrylate, homopoly(2-vinylpyridine) and inorganic compounds produced from the catalyst were extracted with methanol, and homopoly(methyl methacrylate) was extracted with acetonitrile. The average amounts of each fraction in block polymerizations of 2-vinylpyridine and methyl methacrylate are given in Table III. The insoluble fraction was poly(2-vinylpyridine-*b*-methyl methacrylate), obtained in a yield of 63%; ir 1730 (C=O) and 1595 cm^{-1} (C=N); nmr ($CDCl_3$) δ 0.9 (s, 3), 1.6–2.0 (broad s, 5), 3.6 (s, 3), 6.6 (s, 1), 6.8 (s, 1), 7.1 (s, 1), and 8.2 (s, 1).

For the block polymer of 2-vinylpyridine and trimethylsilyl methacrylate, poly(2-vinylpyridine) and inorganic compounds produced from the catalyst were extracted with methanol (Table IV). Homopoly(trimethylsilyl methacrylate) could not be removed before hydrolysis because the solubility of homopoly(trimethylsilyl methacrylate) was similar to that of poly(2-vinylpyridine-*b*-trimethylsilyl methacrylate): ir 1730 (C=O), 1595 (C=N), and 1266 and 840 cm^{-1} (Si—CH_3); nmr (dimethyl-d_6 sulfoxide) δ 0.2 (s, 9), 0.9 (s, 3), 1.6–2.0 (broad s, 5), 6.6 (s, 1), 6.8 (s, 1), 7.1 (s, 1), and 0.2 (s, 1).

For the block polymer of 2-vinylpyridine and alkyl acrylate, the polymer mixture obtained from the block polymerization was initially precipitated by pouring the polymer solution into Skelly B. The precipitated polymer was dried under reduced pressure, and extraction with toluene separated poly(2-vinylpyridine-*b*-alkyl acrylate) and homopoly(alkyl acrylate) from the toluene-insoluble homopoly(2-vinylpyridine). The toluene-soluble polymers were precipitated by pouring the solution into Skelly B; the precipitated polymer was dried and extracted with methanol to separate the block polymer from the methanol-insoluble homopoly(alkyl acrylate). The block polymer was isolated from methanol by evaporation. The amounts of each fraction for the block polymer of 2-vinylpyridine and *tert*-butyl acrylate are shown in Table V. The block ratios for the various block polymers were determined by combustion analysis (Table I).

The solution viscosities of the polymers were determined in benzene solution or DMSO solution at 30°.

Block Polymer Hydrolysis. The hydrolysis of poly(methyl methacrylate) sequences and poly(alkyl acrylate) sequences in the block polymers were carried out in acidic media. About 0.3 g of polymer was added to 50 ml of sulfuric acid, and nitrogen gas was bubbled vigorously through the sulfuric acid to provide mixing. The polymer gradually dissolved and the reaction mixture became brown. The flask was then cooled in an ice bath and the polymer was precipitated by the addition of cold diethyl ether. The precipitated polymer was filtered, washed with ether, and dried under reduced pressure.

The hydrolysis of the poly(trimethylsilyl methacrylate) sequence in the block polymer was carried out in alkaline media. About 1 g of polymer was suspended in 20 ml of 5% aqueous sodium hydroxide and the solution was stirred for 12 hr at room temperature. The block polymer containing the polyacid sequence was precipitated by adjusting the pH of the solution to 5 with hydrochloric acid. The homopoly(methacrylic acid) impurity contained in the block polymer was completely removed owing to its solubility in the aqueous solution at pH 5. The block polymer was filtered, washed with water and ether, and dried under reduced pressure.

The base hydrolysis of the poly(alkyl acrylate) sequence in the block polymer was carried out under more vigorous conditions (Table II). However, the hydrolysis was not complete. A quantitative determination of the extent of the hydrolysis was based on comparisons of the nmr spectra and combustion analysis before and after the hydrolysis treatment (Table II).

TABLE V
ISOLATION OF BLOCK POLYMER OF 2-VINYLPYRIDINE AND *tert*-BUTYL ACRYLATE

Fraction	Weight, g
Toluene insoluble	0.4
Toluene soluble and methanol insoluble	0.2
Toluene and methanol soluble	3.6
Total polymer	4.2

Turbidimetric Titration. Polymer solutions for turbidimetry were prepared by dissolving about 0.4 g of polymer in 200 ml of about 0.05 *N* aqueous alkaline solution. The pH values of these polymer solutions were varied by the addition of a 0.1 *N* HCl solution. Known volumes of the polymer solution were removed at various pH values and the turbidity of each sample was measured on a Bausch and Lomb Spectronic 20 instrument at a wavelength of 525 nm. A nonturbid polymer solution did not absorb at this wavelength.

Electron Microscopy. The block polymers of 2-vinylpyridine and methyl methacrylate were prepared for electron microscopy by cutting the plastic-embedded polymer with a diamond knife at 700 Å with a Porter Blum Mt-2 ultramicrotome. The sample was stained with osmium tetraoxide vapor for 30 hr, viewed, and photographed.

Transmission techniques were utilized for the hydrolyzed block polymer, poly(2-vinylpyridine-*b*-methacrylic acid). The specimens were cast as films on stainless-steel grids from formic acid solutions. The films were washed by dipping them into a 37% methanol solution of 0.1 *N* sodium hydroxide.

Desalination Measurements. Salt rejection of a dynamically prepared membrane[16] of a hydrolyzed block polymer was measured on a 0.45-μ Millipore support at Oak Ridge National Laboratory.

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