

Sequential Copolymers Composed of Basic and Acidic Sequences I. Poly(*N,N*-dimethylaminopropylacrylamide-*b*-acrylic acid)

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ABSTRACT: The block copolymer composed of basic and acidic sequences, poly(*N,N*-dimethylaminopropylacrylamide-*b*-acrylic acid), was prepared by a mechanochemical method. Poly(*N,N*-dimethylaminopropylacrylamide) (PDAPA) was cleaved by ultrasonic irradiation in an aqueous solution of sodium acrylate. The block copolymer was separated as a precipitate from the reaction solution by controlling pH, and then fractionated by stepwise precipitations. The ratio, number of acidic monomer units/number of basic monomer units, was in the range of 0.3—145. The block copolymer showed microphase separation when it was cast from basic (NaOH aq.) or acidic (HCl aq.) solutions.

KEY WORDS Block Copolymer / Basic Sequence / Acidic Sequence / Ultrasonic Irradiation / Microphase Separation /

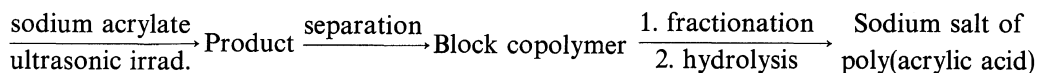
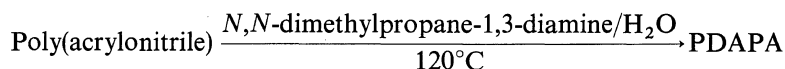
Sequential polymers are very interesting materials, because they show microphase separation, and consequently, they have particular properties. But, for a sequential polymer composed of basic and acidic sequences, they are miscible each other, and thus we can not expect the phase separation.

If this type of sequential polymer shows microphase separation under certain conditions, for example, in the salt form, the field of the use would be expanded widely to charged mosaic membranes, ion exchange resins which are regenerative by heating, etc.¹⁻⁵

The main intentions of this study are to

synthesize a block copolymer composed of basic and acidic sequences and to examine if this copolymer shows the microphase separation.

We have chosen 3-dimethylaminopropylacrylamide (DAPA) and acrylic acid as the basic and acidic monomer units, respectively. To prepare the basic sequence, the method established by Dragan *et al.* was used.^{6,7} A mechanochemical method (ultrasonic irradiation) was applied to synthesize the block copolymer.⁸⁻¹¹ The route to prepare and the method to characterize the block copolymer are shown schematically as follows.



—————→ Degree of polymerization (Viscometry).

EXPERIMENTAL

Poly(acrylonitrile) (PAN) was prepared by the usual emulsion polymerization at room temperature for 60 h (initiator: $K_2S_2O_8$ - $NaHSO_3$, surfactant: sodium laurylsulfate). The average molecular weight obtained by viscometry ($[\eta] = 2.43 \times 10^{-4} M_p^{0.75}$, in *N,N*-dimethylformamide at $25^\circ C$)¹²⁾ was 1.07×10^6 .

PDAPA was prepared by the previously reported method.^{6,7} PAN, *N,N*-dimethylpropane-1,3-diamine and H_2O (amine(mol)/CN(mol) = 5/1, H_2O (mol)/CN(mol) = 1/1) were allowed to react at $120^\circ C$ for 17.6 h. The excess amine and water were removed in vacuum. The residue was dissolved in a benzene/dioxane (about 1/2 in volume ratio) mixture, and the solution was poured into benzene. The precipitate was separated by decantation and dried. The infrared spectra of PAN and PDAPA are shown in Figure 1.

Sodium acrylate (NaAA) was prepared by neutralizing acrylic acid (AA) with equimolar NaOH in a small amount of water, and by precipitating in methanol. The filter cake was washed with acetone and dried.

The preparation method of the block copolymer was as follows. PDAPA and NaAA were dissolved in water, and then the solution was exposed to ultrasonic irradiation, using a Cho-Ompa Kogyo Type UE-300Z20S in a nitrogen atmosphere at 11 – $13^\circ C$ for 2 h. The apparatus for the block copolymer synthesis is shown in Figure 2. The details of the reaction conditions are shown in Table I along with the results.

The method of separation of the block copolymer from the reaction solution is shown in Figure 3. The pH of the reaction solution was adjusted to 1 to precipitate poly(acrylic acid) (PAA) by adding conc. HCl, and then to 2–5 to precipitate the block copolymer by adding NaOH solution. At pH 2–5, PDAPA was still soluble in water. The precipitate was washed by dilute HCl solution (pH 2–5) and

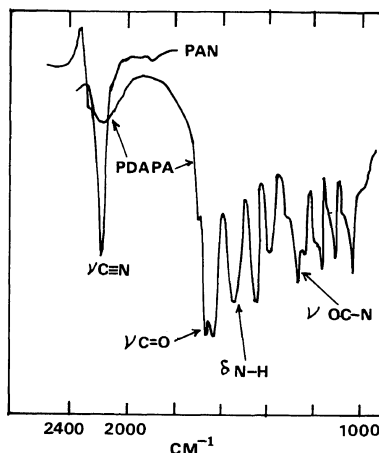


Figure 1. Infrared spectra of raw PAN and PDAPA.

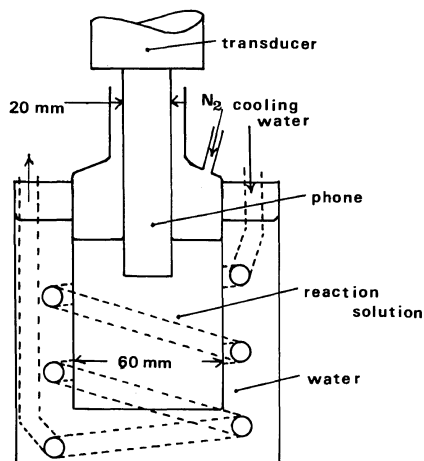


Figure 2. Apparatus to synthesize the block copolymer by ultrasonic irradiation.

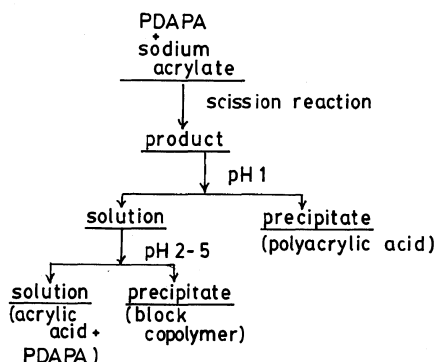


Figure 3. Procedures to prepare the block copolymer and to separate it from the reaction solution.

dried. The reliability of this separation method was confirmed by using PAA, PDAPA, the precipitate at pH 2—5, and the mixture of these polymers for comparison.

The block copolymer thus obtained was dissolved in dilute NaOH solution (pH 11), and then fractionated with methanol as the nonsolvent into five portions (B f-1—f-5). The number of monomer units (DAPA and AA) in each block polymer was determined as follows. The copolymer was hydrolyzed into sodium salt of polyacrylic acid (PNaAA) by refluxing in 1*N* NaOH solution for over 70 h. The product was then precipitated in methanol and dried. It was confirmed by infrared absorption spectroscopy using a Hitachi Infrared Spectrophotometer 285 that *N,N*-dimethylaminopropylamide groups changed completely to carboxylate groups. The degree of polymerization of PNaAA was determined by viscometry³⁾ using an equation, $[\eta] = 4.22 \times 10^{-4} M_p^{0.64}$. The composition (number of AA unit/number of DAPA unit) was calculated from elementary analysis data.

Electron Microscopy

The preparative method of a specimen for electron microscopy was as follows. The block copolymer (one of the sequences was in the salt form) was dissolved in water (about 1 wt%). This solution was dropped on a mesh plate vaporized carbon film, and dried slowly at room temperature. The specimen thus prepared was exposed to methyl iodide vapor in a glass vessel shown in Figure 4 for three days.

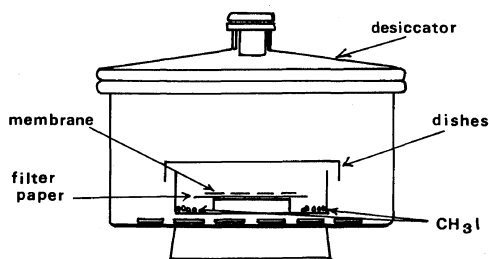


Figure 4. Apparatus to quaternize block copolymer specimens for electron microscopic observation.

Under these conditions, free *N,N*-dimethylaminopropyl groups in the specimen cast from a basic solution were considered to be quaternized quantitatively. When the basic sequences were in the salt form as expected for the specimen cast from HCl solution, this reaction will not occur, and a basic domain was considered to be marked by Cl⁻ ion. The electron microscopic observations were performed using a Hitachi HS-7 type apparatus.

RESULTS AND DISCUSSION

The conditions for the block copolymer synthesis and the results are shown in Table I. First of all, the solutions after ultrasonic irradiation did not show any precipitation or clouding at pH 1, indicating that they did not contain the PAA homopolymer. The block copolymer separation was carried out at pH 4.7, 3.8 and 2.5 for the samples no. B-1, B-2, and B-3, respectively. At these pH values, maximum clouding was observed for each sample in a very dilute solution.

In Table II, the results of the fractionation of the block copolymer are shown. At pH 4.7, B-1 f-5 was obtained whose composition (AA/DAPA) is 0.3 (mol/mol). In B-2 and B-3, the ratios of f-5s were 4.8 and 2.7, respectively. B-2 and B-3 were separated from more acidic solutions than B-1. It seems that if the block copolymer separation is carried out from more basic solutions, the block copolymer rich in the basic sequence can be obtained. The difference in the composition of f-5s in B-2 and B-3 must be caused by the different volume fraction of methanol where f-5s were fractionated.

In Table III, the degrees of polymerization of PNaAA obtained by the hydrolysis of the block copolymer are shown. The value is very small compared to that of raw PAN (2.0×10^4). If the degree of polymerization did not decrease in the PDAPA synthesis, PDAPA was considered to be cleaved very frequently under the ultrasonic irradiation judging from the degree of polymerization of PNaAA in

Table I. The conditions of block copolymer preparation and the results

	Sample No.	B-1	B-2	B-3
Conditions of preparation	PDAPA (g)	12.8	10.0	11.1
	NaAA (g)	12.8	23.1	33.3
	NaAA (mol)	1.7	3.8	5.0
	DAPA (mol)	4.7	3.8	2.5
	pH ^a	4.7	3.8	2.5
Results	Yield (g)	7.2	11.9	19.4
	NaAA (mol) ^b	3.0	12.1	12.1
	DAPA (mol)			

^a pH at which the block copolymer was separated from reaction solution.

^b Polymer composition.

Table II. Fractionation of block copolymer

Sample No.	Fraction	wt%	NaAA (mol) ^a DAPA (mol)
B-1	f-1	10	145
	f-2	2	9.3
	f-3	6	6.0
	f-4	54	4.7
	f-5	28	0.3
B-2	f-1	25	48.8
	f-2	50	14.0
	f-3	Trace	13.0
	f-4	6	7.0
	f-5	18	4.8
B-3	f-1	2	70.0
	f-2	9	79.5
	f-3	13	15.8
	f-4	73	10.8
	f-5	2	2.7

Fractionation system: NaOH (pH 11) (solvent)-methanol (nonsolvent) at room temperature.

^a Block copolymer composition from elementary analysis.

Table III. This suggested that almost all of the ends of a DAPA sequences are conjugated with AA sequences.

The titration curve of the block copolymer is shown in Figure 4. The neutralization points of DAPA and AA sequences are not distinguished in both the cases where the titrations

Table III. The results of hydrolysis and number of monomer units (degree of polymerization of PNaAA)

Sample No.	B-1 f-4	B-2 f-2	B-3 f-4
$\frac{AA \text{ (mol)}^a}{DAPA \text{ (mol)}}$	4.7	14	10.8
Reaction time (h)	70	70	117
Degree of hydrolysis	98.2	97.5	98.6
$[\eta] \text{ (dl g}^{-1}\text{)}^b$	0.32	0.33	0.60
DP ^c	370	370	940

^a Polymer composition, determined by elemental analysis.

^b $[\eta]$ of the polymer after hydrolysis (in 2N NaOH aq., at 25°C).

^c Degree of polymerization of PNaAA calculated from viscometric relation.

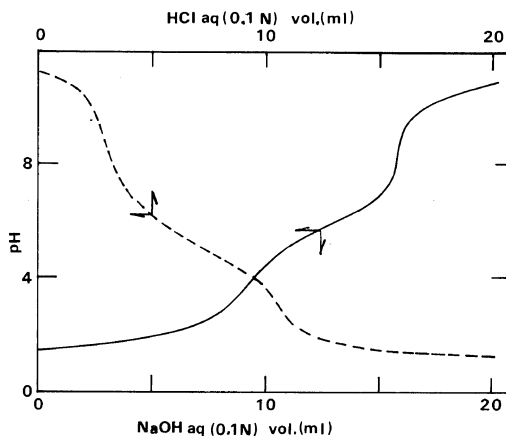


Figure 5. Potentiometric titration of the block copolymer (B-3 f-4; 80 mg/100 ml; clouding was observed at pH 2–8).

were started from basic and acidic solutions. The inflection points at pH 7.5–11 and pH 1.5–2 correspond to the neutralization of excess NaOH and HCl. It was not possible to determine the composition of the block copolymer by this titration method.

The electron microscopic observation is shown in Figure 5 for two samples. As clearly shown, the phase separation is observed for both the specimens prepared from the basic and acidic solutions. The dark part is the quaternized (or in salt form) DAPA sequence.

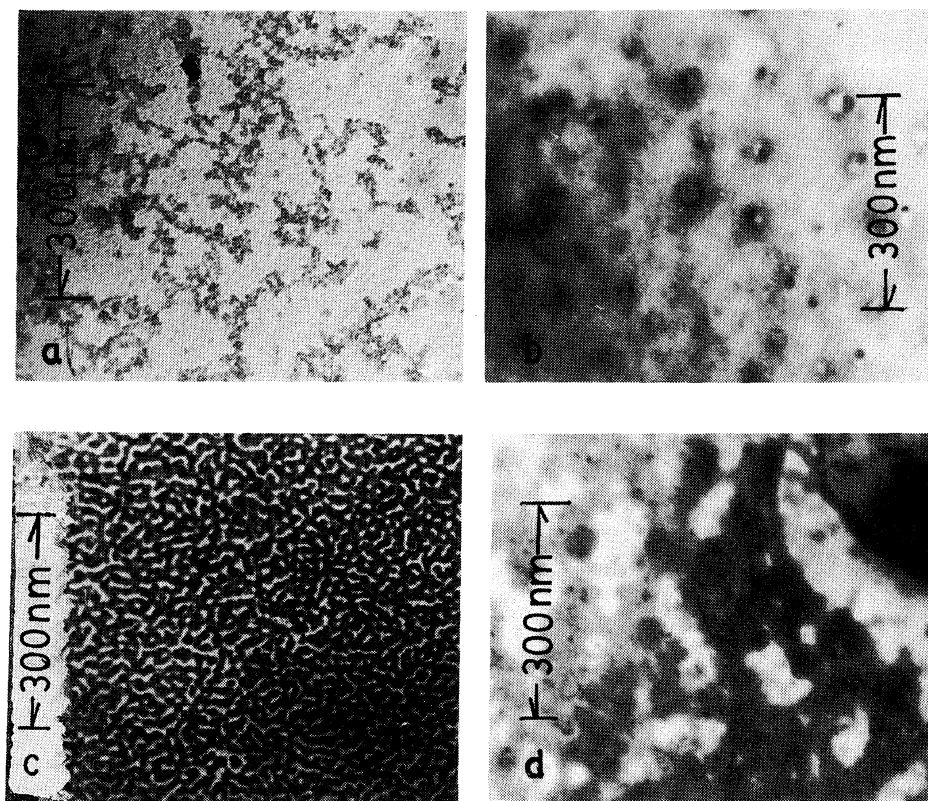


Figure 6. Electron microscopic observation

B-1 f-5. AA (mol)/DAPA (mol)=0.3:

- a) Casting solv.; HCl aq. pH 1.35.
- b) Casting solv.; NaOH aq. pH 10.76.

B-2 f-5. AA (mol)/DAPA (mol)=4.8:

- c) Casting solv.; HCl aq. pH 1.20.
- d) Casting solv.; NaOH aq. pH 10.39.

In comparison of a) and b), or c) and d), the domain size (diameter and thickness) is smaller and the phase separation is neater when casting was carried out from acidic solutions.

As the conclusion, the block copolymer composed of the weak base and weak acid sequences (DAPA and AA) showed micro-phase separation in both the cases of casting from basic or acidic solutions.

The application of this type of the sequential copolymer to a thermoregenerative ion exchange resin will be reported in the next article.

REFERENCES

1. J. N. Weinstein and S. R. Caplan, *Science (Washington, D.C.)*, **161**, 70 (1968).
2. M. Kurihara, M. Kamachi, and J. K. Stille, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 587 (1973).
3. A. Chapiro, A. M. Jendrychowska-Bonamour, and S. Mizrahi, *Eur. Polym. J.*, **12**, 773 (1976).
4. Y. Matsushita, H. Choshi, T. Fujimoto, and M. Nagasawa, *Macromolecules*, **13**, 1053 (1980).
5. H. Funabashi, Y. Miyamoto, Y. Isono, T. Fujimoto, Y. Matsushita, and M. Nagasawa, *Macromolecules*, **16**, 1 (1983).
6. S. Dragan, V. Barboiu, I. Pertrariu, and M. Dima, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 2869 (1981).
7. S. Dragan, I. Pertrariu, and M. Dima, *J. Polym. Sci.*,

- Polym. Chem. Ed.*, **19**, 2881 (1981).
8. M. Pike and W. F. Watson, *J. Polym. Sci.*, **9**, 229 (1952).
 9. D. J. Angier and W. F. Watson, *J. Polym. Sci.*, **18**, 129 (1955).
 10. D. J. Angier and W. F. Watson, *J. Polym. Sci.*, **20**, 235 (1956).
 11. R. J. Ceresa, "Block and Graft Copolymers," Butterworth, London, 1962, p 65.
 12. R. L. Cleland and W. H. Stockmayer, *J. Polym. Sci.*, **17**, 473 (1955).
 13. A. Takahashi, N. Hayashi, and I. Kagawa, *Kogyo Kagaku Zasshi (J. Chem. Soc. Jpn., Ind. Chem. Sec.)*, **60**, 1059 (1957).