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MOLECULAR WEIGHT DISTRIBUTION OF THE ACRYLONITRILE-VINYL ACETATE COPOLYMER PREPARED BY REDOX POLYMERIZATION^{*1}

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ABSTRACT

The molecular weight distributions were estimated for the acrylonitrile-vinyl acetate copolymers (93:7 in weight), which were prepared by continuous polymerization in aqueous medium with the persulfate-bisulfite-ion redox system under the conditions of water/monomer ratio varied in the range from 4 to 1.75 in weight.

The molecular weight distributions were evaluated by $\bar{M}_v/\bar{M}_n$ ratios estimated from viscosity and osmotic measurements, and by $\bar{M}_w/\bar{M}_n$ ratios estimated from gel permeation chromatography. The molecular weight distributions of these polymers were so broad that $\bar{M}_w/\bar{M}_n$ ratio varied between 4 and 6. No marked difference was observed in the molecular weight distribution of the polymers prepared under the conditions mentioned above.

1. INTRODUCTION

The continuous polymerization in aqueous medium using the persulfate-bisulfite-ion redox initiation system is important in production of acrylonitrile (AN) polymers. Studies¹⁻⁴⁾ on the polymerization system with low water/monomer ratios have been reported previously, but studies on the effect of water/monomer ratio on the polymer properties and polymerization behaviors do not seem to be sufficient. The authors studied⁵⁾ the properties of polymer slurry and the structures of polymer particles of AN-vinyl acetate (VAc) copolymers (93:7 in weight) which were prepared in the range of water/monomer ratio from 1.5 to 4.0. We have observed that the structure of the polymer particle became more

compact with decreasing water/monomer ratio, resulting in reduced water contents of dewatered cakes at filtration of the polymer slurry and increased bulk densities of the polymer. It is the main object of this report to reveal the influence of these differences in the polymer particles on the molecular weight distribution (M.W.D.).

2. EXPERIMENTAL

2.1 Materials

Commercial grade AN and VAc were used for polymerization. Deionized water was used. Commercially available reagents were used without further purification. First grade potassium persulfate (KPS) and sodium hydrogen carbonate (NaHCO_3) were used as an initiator and buffer, respectively. Special grade sulfur dioxide (SO_2) was used as a bisulfite ion source and ferrous sulfate (FeSO_4) as a promoter. Special grade sodium thiocyanate (NaSCN) and distilled N,N-dimethyl formamide (DMF) were used for the measurements of polymer solution properties.

2.2 Polymerization Procedures

A reaction vessel having a capacity of 83 l of complete mixing type was charged with water

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adjusted to pH 3.0 with sulfuric acid and it was heated under nitrogen. Feed of monomers and aqueous solutions of KPS, SO_2 , NaHCO_3 and FeSO_4 was started at a given temperature. The time from start of feed to beginning of overflow from the reactor was adjusted to a given dwell time with the amount of water charged initially. The running time of the polymerization was about 24 hours except for 8 hours of expt. No. 7. The slurries of polymer were taken as samples for evaluation after about 15 hours from start up of polymerization except for about 6 hours in case of expt. No. 7. After the polymerization was stopped by inhibitor solution, the slurry was filtered and washed. The dry polymer sample was obtained by drying the filtered cake at 85°C for 90 min. To evaluate the dewatering property of the slurry of polymers, the water content of the cake thus obtained being measured by using a leaf tester at the filtration vacuum of 200 mmHg and at the depth of the cake of 1.0 cm.

2.3 Viscometry

Specific viscosity (η_{sp}) was measured at 30°C in DMF or in DMF containing 0.1M NaSCN (0.1M NaSCN/DMF) with a Ubbelohde type viscometer.

Intrinsic viscosity $[\eta]$ was obtained as η_{sp}/C extrapolated to $C=0$ according to eq. (1)

$$\eta_{sp}/C = [\eta] + k' [\eta]^2 C \quad (1)$$

where C is polymer concentration, η_{sp} specific viscosity and k' the Huggins' constant.

2.4 Osmometry

Osmotic pressure (π) of polymer solution was measured in the range of concentration (C) from 0.1 to 0.5 g/dl in DMF at 30°C with Mechrolab High Speed Membrane Osmometer Model 501.

Number average molecular weight ($\bar{M}_n$) was obtained as π/C extrapolated to $C=0$ according to eq. (2). The second virial coefficient (A_2) was also obtained by eq. (2)

$$\frac{\pi}{C} = RT \left(\frac{1}{\bar{M}_n} + A_2 C \right) \quad (2)$$

where R is gas constant.

2.5 Gel Permeation Chromatography (GPC)

Two kinds of systems were used for GPC measurement. One was a conventional type, Water Associates Model 200 with the column system (G 4000S + G 5000S + G 6000S + G 7000S: each column length, 4 feet; made by Toyo Soda Manu-

facturing Co., Ltd.). GPC measurement was performed in 0.1M NaSCN/DMF at 30°C : polymer solution injected, 0.3 g/dl $\times$ 2 ml; flow rate, 1 ml/min. The other system was a GPC of high speed type constructed by our Research Laboratory with a constant feed pump (Milton Roy Co.), an injector (Waters Associates Inc.) and differential refractometer (Waters Associates Inc.). Another measurement was performed with the column system (GMiX₆ + GMiX₆: each column length, 2 feet; made by Toyo Soda Manufacturing Co., Ltd.) in 0.1M NaSCN/DMF at 30°C : polymer solution injected, 0.2 g/dl $\times$ 0.5 ml; flow rate, 2.2 ml/min.

M.W.D. of sample from No. 1 to No. 4 was measured by the conventional type GPC and that of sample from No. 4 to No. 7 by high speed type GPC.

3. RESULTS AND DISCUSSION

Polymerization conditions under various water/monomer ratios and some properties of the polymers are summarized in Table 1. As previously described⁵⁾, with decreasing water/monomer ratios in polymerization, the polymer particles became more compact, so that bulk densities of polymers increased and water contents of dewatered cakes decreased.

3.1 Intrinsic Viscosity and $\bar{M}_n$

In Fig. 1 and Fig. 2, plots of η_{sp}/C vs. C in 0.1M NaSCN/DMF and π/C vs. C in DMF for No. 1–No. 4 samples are shown. In all cases linear relations were obtained, and values of η_{sp}/C or π/C were easily extrapolated to $C=0$. Intrinsic viscosity, Huggins' constant, $\bar{M}_n$ and the second virial coefficient are shown in Table 2. $\bar{M}_v$ in Table 2 were obtained by equation (4) described later. Heterogeneity index, $\bar{M}_v/\bar{M}_n$ ratio, was used in place of $\bar{M}_w/\bar{M}_n$, since $\bar{M}_w$ was not obtained by direct measurement. $\bar{M}_v/\bar{M}_n$ ratios for No. 1–No. 4 samples were roughly 6 and no marked difference was observed in $\bar{M}_v/\bar{M}_n$ ratio of polymers prepared under the condition of water/monomer ratio varied from 4.0 to 2.5.

3.2 Evaluation of M.W.D. from GPC

Masuzawa et al.^{6–8)} have already studied on M.W.D. of polyacrylonitrile (PAN) by GPC. They have shown⁷⁾ that M.W.D. of PAN prepared by redox system could not be properly evaluated by GPC measurement in DMF, because M.W.D. show

Table 1 Polymerization conditions^a with various water/monomer ratios and some properties of polymers

Expt. No.	Water/monomer (wt.ratio)	SO ₂ /KPS (mol.ratio)	Temperature (°C)	Dwell time (min)	Agitation speed (rpm)	Bulk density of polymer ^b (g/cm ³)	Water content of the cake ^c (% dry basis)
1	4.0	10	50	60	214	0.26	183
2	3.2	10	50	60	260	0.34	
3	2.5	10	50	70	260	0.39	160
4	2.5	10	50	70	240 ^b	0.41	
5	1.75	6.5	55	89	260	0.51	—
6	1.75	10	55	89	260	0.46	103
7	2.0	10	50	82	260	0.44	135

a Molar ratio of SO₂ to NaHCO₃ was fixed to 1.3 in order to keep pH of the polymerization system 3.0. Fe²⁺ was fed 0.4 ppm by weight of monomer.

b Bulk density of dry power.

c Filter cake after dewatering slurry at leaf test.

Fig. 1 η_{sp}/C versus C of polymer samples in 0.1M-NaSCN/DMF at 30°C: ○, expt. No. 1, ⊙, No. 2, ⊗, No. 3, ●, No. 4 in Table 1.

unusual curves owing to the strong acid groups of the polymers originated from initiators. This is considered to be due to the unusual expansion of polymer chains caused by electrostatic interactions of the strong acid groups. They also have shown that correct M.W.D. could be obtained by GPC measurement in such a solvent system as 0.1M NaSCN/DMF. Hence, in this study, GPC measurement was performed in 0.1M NaSCN/DMF. Calibration curve is necessary to calculate M.W.D. and several kinds of average molecular weight. The universal calibration curve prepared from poly-

Fig. 2 π/C versus C of polymer samples in DMF at 30°C: ○, expt. No. 1, ⊙, No. 2, ⊗, No. 3, ●, No. 4 in Table 1.

styrene is not applicable to PAN as previously stated⁶). Hence it is necessary to make new calibration curve with monodisperse polymers prepared from the polymer concerned in this study. To obtain such polymers the AN/VAc copolymers (AN/VAc 93/7 in weight) prepared under the condition corresponding to expt. No. 1 in Table 1, were fractionated by the precipitation fractionation. Details of fractionation method are described elsewhere⁹). Intrinsic viscosity, $\bar{M}_n$ and

Table 2 Molecular weight and related data of polymer samples

Sample ^a No.	$[\eta]^b$ (dl/g)	k'	$\bar{M}_n$ $\times 10^{-4}$	Pn^c	$A_2 \times 10^4$ (mol.ml/g)	$\bar{M}_v^d$ $\times 10^{-4}$	$\bar{M}_v/\bar{M}_n$
1	1.49	0.324	2.09	378	2.51	11.9	5.69
2	1.54	0.327	2.07	374	4.59	12.5	6.04
3	1.52	0.320	2.05	371	5.71	12.3	6.00
4	1.54	0.326	2.10	380	5.05	12.5	5.95

a Sample No. 1 – No. 4 corresponds to Expt. No. 1 – No. 4 in Table 1.

b Obtained by extrapolation to $C = 0$ in Fig. 1

c Number average degree of polymerization

d $[\eta] = 7.486 \times 10^{-4} \bar{M}_v^{0.650}$ (0.1M – NaSCN/DMF, 30°C)

Table 3 Intrinsic viscosity and molecular weight of fractions of the AN/VAc copolymer sample^a

Fr. No.	$[\eta]$ (dl/g) ^b	$[\eta]$ (dl/g) ^c	$\bar{M}_n \times 10^{-4}$	$\bar{M}_v^d \times 10^{-4}$	$(\bar{M}_n \times \bar{M}_v)^{1/2}$ $\times 10^{-4}$	$\bar{M}_v/\bar{M}_n$
1	2.74	2.51	9.85	26.3	16.1	2.67
2	2.30	2.16	12.0	22.3	16.4	1.86
3	2.07	1.98	10.1	18.0	13.5	1.78
4	1.73	1.71	6.42	14.0	9.48	2.18
5	1.38	1.35	4.13	10.0	6.43	2.42
6	0.850	0.847	2.80	5.10	3.05	1.82

a Prepared under the conditions corresponding to Expt. No. 1 in Table 1.

b Measured in DMF at 30°C

c Measured in 0.1M NaSCN/DMF at 30°C

d $[\eta] = 4.57 \times 10^{-4} \bar{M}_v^{0.70}$ (DMF, 30°C, Senuma's equation)

related data of fractionated polymers are shown in Table 3.

$\bar{M}_v$ was calculated from $[\eta]$ on 2nd column by the eq. (3) obtained by A. Senuma et al.¹⁰⁾

$$[\eta] = 4.57 \times 10^{-4} \bar{M}_v^{0.70} \text{ (DMF, 30°C)} \quad (3)$$

$[\eta]$ measured in 0.1M NaSCN/DMF was correlated to $\bar{M}_v$ above evaluated, to obtain equation (4).

$$[\eta] = 7.486 \times 10^{-4} \bar{M}_v^{0.650} \text{ (0.1M NaSCN/DMF, 30°C)} \quad (4)$$

The exponent of $\bar{M}_v$ of eq. (4) is smaller than that of eq. (3), so that 0.1M NaSCN/DMF is a poorer solvent than DMF for PAN.

From Table 3, $\bar{M}_v/\bar{M}_n$ ratios of fractionated polymers are roughly 2, so that these fractions are

not monodisperse. Hence, it is not obvious what kind of average molecular weight corresponds to the peak of elution curve of GPC for the fractionated polymers. If M.W.D. of the samples conforms to Wesslau's distribution¹¹⁾, it is shown that $(\bar{M}_w \times \bar{M}_n)^{1/2}$ is the average molecular weight (MPGPC) corresponding to the peak of elution curve of GPC. In this study, $(\bar{M}_v \times \bar{M}_n)^{1/2}$ was used as MPGPC, $\bar{M}_w$ being replaced with $\bar{M}_v$.

Fig. 3 shows the correlation between MPGPC $\times [\eta]$ (0.1M NaSCN/DMF) and the elution count of the peak of GPC. The same correlation curve for polystyrene are also shown in Fig. 3, though the former did not conform to the latter universal calibration curve. Eq. (5) was obtained as calibration curve for this polymer from the correlation

Fig. 3 Hydrodynamic volume versus elution volume for polystyrene and AN/VA copolymer in 0.1M NaSCN/DMF at 30°C: ○, polystyrene ($M=M_w$); ●, AN/VA copolymer ($M=(M_n \times M_v)^{1/2}$).

curve of Fig. 3.

$$Q = [\eta] \cdot M = 7.486 \times 10^{-4} \cdot M^{1.650} \\ = 18.69 - 1.140V + 4.463 \times 10^{-2} \cdot V^2 \\ - 7.558 \times 10^{-4} V^3 \quad (5)$$

$\bar{M}_n$, $\bar{M}_w$, $\bar{M}_z$ and M.W.D. can be calculated by eq. (5) from GPC curves. Fig. 4 shows GPC curves for No. 1–No. 4 samples. $[\eta]$, $\bar{M}_n$, and $\bar{M}_w$ were calculated by equation (5) from GPC curves shown in Fig. 4.

Calculated values of $\bar{M}_n$ were larger than the observed ones. It is considered that it might be caused by the presence of impurities in low molecular weight region⁷⁾. Although the calculated $\bar{M}_w/\bar{M}_n$ ratios were smaller than the observed values, no marked difference exists in M.W.D. of No. 1–No. 4 samples. Fig. 5 shows integral molecular weight distribution curves for No. 1 and No. 4 samples. No marked difference in M.W.D. was observed in the curve.

Curves of No. 4–No. 7 samples obtained by the high speed GPC are shown in Fig. 7. The results of high speed GPC measurements were analysed by calibration curve derived from fractionated

Fig. 4 GPC curves of the polymer prepared under the conditions of expt. No. 1, No. 2, No. 3 and No. 4 in Table 1.

Fig. 5 Integral molecular weight distribution curve: —, No. 1; ---, No. 4 in Table 1.

polymers in Fig. 6. The calculated values are listed in Table 5. This GPC system was inferior to the conventional type GPC in resolving power because the slope of the curve in Fig. 6 was larger than that of Fig. 3. Hence $\bar{M}_n$ calculated for No. 4 sample in Table 5 was larger than that of Table 4.

Although $[\eta]$, $\bar{M}_n$, $\bar{M}_w$ and $\bar{M}_z$ calculated for No. 5–No. 7 samples were larger than those listed in Table 4, $\bar{M}_w/\bar{M}_n$ ratios were approximately 5 and comparable to those in Table 4. Based on these results, it is concluded that no marked change occurs in M.W.D. of polymers produced

Fig. 6 Hydrodynamic volume versus elution volume for polystyrene and AN/VA copolymer in 0.1M-NaSCN/DMF at 30°C: ○, polystyrene ($M = M_w$); ●, AN/VA copolymer ($M = (M_n \times M_w)^{1/2}$).

Fig. 7 GPC curves of the polymer prepared under the conditions of expt. No. 5, No. 6, No. 7 and No. 4 in Table 1: -----, No. 4.

Table 4 Molecular weight and related data calculated from GPC results

Sample ^a No.	$[\eta]^b$ (dl/g)	$\bar{M}_n^b \times 10^{-4}$	$\bar{M}_w^b \times 10^{-4}$	$\bar{M}_z^b \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_z/\bar{M}_w$
1	1.43	2.64	13.6	32.2	5.16	2.36
2	1.38	1.65	13.0	30.1	7.86	2.33
3	1.42	2.80	13.0	28.8	4.65	2.21
4	1.51	3.34	14.6	33.2	4.36	2.28

a Sample No. 1 – No. 4 corresponds to Expt. No. 1 – No. 4 in Table 1.

b Calculated by following eqs. (6) – (9), from Figs. 3 and 4.

$$[\eta] = K^{\frac{1}{a+1}} \sum W_i Q_i^{\frac{a}{a+1}} \quad (6)$$

$$\bar{M}_n = \frac{K^{-\frac{1}{a+1}}}{\sum W_i Q_i^{-\frac{1}{a+1}}} \quad (7)$$

$$\bar{M}_w = K^{-\frac{1}{a+1}} \sum W_i Q_i^{\frac{1}{a+1}} \quad (8)$$

$$\bar{M}_z = K^{-\frac{1}{a+1}} \frac{\sum W_i Q_i^{\frac{2}{a+1}}}{\sum W_i Q_i^{\frac{1}{a+1}}} \quad (9)$$

where K and a are defined in eq. (10).

$$[\eta] = KM^a \quad (10)$$

here, eq. (10) corresponds to eq. (4); $K = 7.486 \times 10^{-4}$,

$a = 0.650$.

W_i is a weight fraction of polymer of molecular weight M_i .

Table 5 Molecular weight and related data of polymers prepared under the condition of Table 1 calculated from GPC results

Sample ^a No.	Nsp ^b	$[\eta]$ ^c	$\bar{M}_n \times 10^{-4}$ ^c	$\bar{M}_w \times 10^{-4}$ ^c	$\bar{M}_w/\bar{M}_n$
5	0.204	2.10	5.64	28.4	5.04
6	0.203	1.97	5.42	25.2	4.64
7	0.189	2.08	5.45	27.9	5.11
4	0.205	1.49	3.73	16.5	4.43

a Sample No. 4 - No. 7 corresponds to Expt. No. 4 - No. 7 in Table 1.

b Nsp denotes reduced viscosity (0.5% polymer in 25°C DMF) x 0.1

c Calculated by the same method as mentioned in Table 4.

under the conditions of water/monomer ratio varied from 4.0 to 1.75 in this polymerization system. $\bar{M}_w/\bar{M}_n$ and $\bar{M}_v/\bar{M}_n$ ratios are apparently larger than the reported values^{12),13)}. Mixing^{14),15)}, heterogeneity¹⁶⁻¹⁹⁾ in polymerization systems, and the polymer composition (PAN and AN-VAc copolymer) are considered to cause the difference in $\bar{M}_w/\bar{M}_n$ ratios to some extent.

Although the marked change in polymer particles occurred in this system with the range of water/monomer ratio from 4.0 to 1.75 as described above partly and in the previous paper⁵⁾, no marked change was observed in M.W.D. of the polymers prepared with this particular range of water/monomer ratio. The result described above is industrially valuable. First, we can choose any level of water to monomer ratio in the range from 1.75 to 4.0 without significant change in polymer qualities connected with those of shaped articles therefrom. In this polymerization system M.W.D. affects strong acid end groups of polymer which directly correlates dyeability of shaped articles¹³⁾. M.W.D. affects the mechanical properties of shaped articles such as fibers, too.^{20),21)} Hence in this range, we can choose the best condition, taking into consideration the factors including dewatering property, bulk density of polymer, conversion rate, KPS/monomer ratio, and agitation power from cost and stability of the process. Secondly, we can produce polymer of normal quality shortly after the start of polymerization without uneconomical production of off grade polymer in large quantity at the start of polymerization.

The results described above show suggestions concerning the mechanism of the polymerization

in this system, too. Effect of water to monomer ratio on M.W.D. had not been known before this study. With decreasing water to monomer ratio, the polymer content in the polymerization system increases and consequently the surface area of polymer particles attacked by radicals in the aqueous phase per unit volume of the aqueous phase increases.²²⁾ Hence, it is supposed²²⁾ that polymerization in the polymer phase would increase to produce comparatively high molecular weight polymer, which would enlarge M.W.D. to some degree. However, the results obtained in this paper show that this effect was not distinctive. No marked difference in M.W.D. from GPC suggests that the mechanism of the polymerization in this system does not change largely in the range of water to monomer ratio from 4 to 1.75. It approximately corresponds to the results of a kinetic study concerning this polymerization system.²³⁾

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REFERENCES

- 1) W. M. Thomas and W. C. Mallison, *Petroleum Refiner*, **40**, No. 5. 211 (1961).
- 2) W. C. Mallison, (American Cyanamid), U.S. Pat. 2,777,832 (1957) and 2,847,405 (1958).
- 3) Charles Clifford Ketter, (E. I. du Pont), U.S. Pat. 2,974,123 (1961).
- 4) Myron Q. Webb and Williamson, (E. I. du Pont), U.S. Pat. 2,992,209 (1961).
- 5) S. Ito and K. Yoshida, *Kobunshi Ronbunshu*, **40**, 307 (1983).

- 6) T. Masuzawa, K. Kamada and T. Yoshihara, *Reports on Progress in Polymer Physics in Japan*, Vol. XVI, 127 (1973).
- 7) T. Masuzawa, K. Kamada and T. Yoshihara, *Reports on Progress in Polymer Physics in Japan*, Vol. XVII, 75 (1974).
- 8) T. Masuzawa, K. Kamada and T. Yoshihara, *Reports on Progress in Polymer Physics in Japan*, Vol. XVIII, 19 (1975).
- 9) Paper contributed to *J. Appl. Polym. Sci.*, by S. Ito, C. Okada and K. Kamada entitled "Distributions of End Groups and Comonomer of the Acrylonitrile-Vinyl Acetate Copolymer from Redox Polymerization" (in press).
- 10) A. Senuma, H. Sato and N. Yamada, *15th Symposium of High Polymer (Japan)*, Nov. 19, 1966, Abstracts of Papers.
- 11) H. Wesslau, *Markromol. Chem.*, **20**, 111 (1956).
- 12) L. H. Peebles, Jr., P. B. Thompson, Jr., J. R. Kirby, and M. E. Gibson, *J. Appl. Polym. Sci.*, **16**, 3341 (1972).
- 13) L. H. Peebles, Jr., *J. Appl. Polym. Sci.*, **17**, 113 (1973).
- 14) K. G. Denbigh, *Trans. Faraday Soc.*, **43**, 648 (1947).
- 15) M. Harada, W. Eguchi, S. Nagata, *Chem. Eng. (Japan)*, **26**, 583 (1962).
- 16) W. M. Thomas, *Fortschr. Hochpoly. Forsch.*, **2**, 401 (1961).
- 17) H. Shirouchi, S. Yuguchi and M. Watanabe, *Kogyo Kagaku Zasshi*, **67**, 1063 (1964).
- 18) C. H. Bamford and A. D. Jenkins, *Proc. Roy. Soc., Ser. A* 216 (1953) S. 515.
- 19) G. R. Cotten, W. C. Schneider, *J. Appl. Polym. Sci.*, **7**, 1243 (1963).
- 20) Y. Fujisaki, *Kobunshi Kagaku*, **18**, 667 (1961).
- 21) M. Takahashi, *Kogyo Kagaku Zasshi*, **65**, 114 (1962).
- 22) S. Ito, a paper in preparation.
- 23) S. Ito, *Kobunshi Ronbunshu*, **42**, 865 (1985).

レドックス重合により得られたアクリロニトリル- 酢酸ビニル共重合体の分子量分布*

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アクリロニトリル/酢酸ビニル共重合体(93/7重量比)を SO_2 /過硫酸カリウム系レドックス開始剤を用い水系連続重合により製造するに当り、重合条件として水/モノマー比を4.0(重量比)より1.75の範囲で小さくしていくと、得られたポリマー粒子はち密になり、かさ密度は大きく、生成スラリーのポリマー保水性は小さくなることを既に認めたが、このような見かけ上のポリマー形態の差がポリマーの分子量分布に影響するかどうかを知るため水/モノマー比を4.0より1.75まで変えて得られたポリマーの分子量分布を評価した。分子量分布は粘度及

び浸透圧測定より求めた $\bar{M}_w/\bar{M}_n$ 比並びに既検討の塩を添加したDMF溶媒を用いるGPCより求めた $\bar{M}_w/\bar{M}_n$ 比により評価した。ポリマーの分子量分布は広く $\bar{M}_w/\bar{M}_n$ 比は4~6の間で変動しているが、水/モノマー比の影響による顕著な差は認め難いものであった。

*この報文を「低水/モノマー比におけるアクリロニトリル水系連続重合の研究(第7報)」とする。

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