

Fractionation of Acrylonitrile Copolymers.

I. Development of a Method*

G. R. COTTEN and W. C. SCHNEIDER, *Research Laboratories, American Cyanamid Company, Stamford, Connecticut*

1 INTRODUCTION

Although the need for a reliable fractionation method for acrylic polymers has been recognized for some time, a survey of published studies on the molecular weight distribution in acrylonitrile polymers reveals that the determination of the exact form of distribution is beset with a number of difficulties, some of which are unique to the polyacrylonitrile-dimethylformamide system. The aim of the present study was to develop a fractionation method that could be employed not only for the correlation of changes in polymerization conditions with the molecular weight distribution of the resultant polymer, but also for a study of the effect of molecular weight distribution on the physical properties of the final product. It is worthy of note that in the second case fractionation is the only satisfactory technique for studying the effects of changes in molecular weight distribution independently from any effects of long-chain branching. A modification of polymer distribution by a change in reaction conditions usually produces a different degree of branching in the polymer and, hence, a difficulty in separating the two effects.

After some preliminary experiments, it was decided that the partial precipitation technique would most likely meet the objectives of this study and all further work was limited to this method. A literature search was made (Table I), and the various precipitating systems reported there were critically examined. For reasons that will become apparent later, the work was further limited to the precipitant consisting of two parts *n*-hexane plus one part ether.⁵

In all fractionation work, it is generally true that the amount and quality of information gained by any technique is proportional to the expenditure of time and labor. The major difficulty is the fact that neither of the two basic assumptions, made for the purpose of calculating the molecular weight distribution by Schulz's method,⁸ is obeyed. Namely, the fractions usually overlap each other beyond the center points of adjacent fractions, and they do not have a symmetrical molecular weight distribution. In

* Paper presented at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September 1962.

order to minimize the error so introduced, two general procedures have been widely employed: either the polymer is divided into a large number of fractions, or the fractions are purified by a multistage fractionation tech-

TABLE I
Fractionation of Acrylonitrile Polymers by Partial Precipitation from Solutions in Dimethylformamide

Nonsolvent	Reference
<i>n</i> -Heptane-ether (1:1)	Herrent ¹
<i>n</i> -Heptane (at 60°C.)	Bisshops ²
<i>n</i> -Heptane, followed by 2% aqueous CaCl ₂ soln.	Mikhailov and Zelikman ³
Water	Krigbaum and Kotliar ⁴
<i>n</i> -Hexane-ether (2:1)	Peebles ⁵
Ethanol	Anderson ⁶
Lauryl alcohol	Stéfani et al. ⁷

nique. These possibilities have also been explored during the present work.

2 EXPERIMENTAL

The polymer was usually precipitated from 1.5% solution in dimethylformamide by gradual addition of the precipitant (2 parts *n*-hexane + 1 part ether). By this method the polymer was fractionated into approximately 7-8 primary fractions, which were subsequently refractionated to give a total of 40-50 secondary fractions.

The intrinsic viscosity of each secondary fraction was measured in dimethylformamide at 30°C. with the use of a Cannon-Ubbelohde viscometer. The intrinsic viscosity results were converted into the weight-average molecular weight by using the relationship of Cleland and Stockmayer, extended to higher molecular weights by Miller et al..

$$[\eta] = 2.27 \times 10^{-4}(\bar{M}_w)^{0.75} \quad (1)$$

which was derived for pure acrylonitrile polymer having a sharp molecular weight distribution.

Whenever it was desired to precipitate the whole polymer from solution in dimethylformamide, approximately 30-40% of ethanol was added, followed by approximately 15-20% of a saturated solution of ammonium carbonate in water. The fine precipitate so obtained was filtered, washed with hot water (to decompose the ammonium carbonate), followed by washing with ethanol and drying.

All the experimental polymers were prepared in aqueous suspension using a continuous reactor system.

3 RESULTS AND DISCUSSION

3.1 Mechanism of Precipitation Process

The influence of different nonsolvents on the kinetics of precipitation of methyl methacrylate-acrylonitrile copolymer were followed by measuring the change in turbidity with time, using a photocell to estimate the intensity of scattered light. Ethanol was chosen as a typical highly polar nonsolvent, while a mixture of (*n*-hexane and ether) was used to study the behavior of a nonpolar precipitant. A typical set of results is shown in Figure 1.

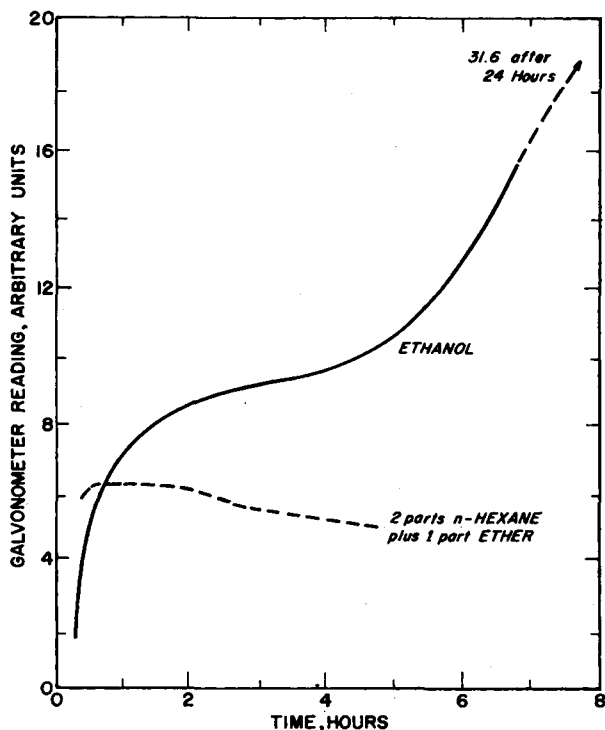


Fig. 1. Turbidimetric curves for two precipitants and 1.5% solution of copolymer A in dimethylformamide.

On addition of ethanol, the precipitation seems to take place in two stages: after an initial rapid precipitation during the first hour, the turbidity of the solution reaches a fairly steady level and does not change appreciably for some 4 hr. At the end of this period, the turbidity increases very rapidly again. The intrinsic viscosity of precipitate collected by centrifugation at different time intervals was measured, and it was concluded that the polymer precipitated in order of decreasing molecular weight. No such effect was observed on addition of the hexane-ether precipitant.

A possible explanation of this behavior is that on addition of ethanol the solvation layer is destroyed, however, individual particles remain stabilized by electrical charges. Miller and Millikan¹⁰ have shown, using electrophoresis measurements, that the negative charge on the particles of polyacrylonitrile can be due to the presence of a few acrylic acid groups in the polymer chain. Some rough calculations indicated that the observed mobility of such particles could be accounted for if approximately one monomer unit per ten thousand were hydrolyzed.

The addition of the hexane-ether mixture not only removes the solvation layer but also lowers appreciably the dielectric constant of the medium. This reduces the dissociation of the carboxylic acid groups and hence reduces the residual charge on the particles. Some change in the opposite direction arises from the decreased dielectric constant of the bulk medium, but in general, this provides insufficient compensation. Climie and White¹¹ report that time-dependent molecular aggregation occurs when benzene is added to a solution of polyacrylonitrile in dimethylformamide. However, we were not able to precipitate the polymer on a macroscopic scale by addition of benzene, diethyl ether, chloroform, or carbon tetrachloride, although all of these solvents have a low dielectric constant. On the other hand, the polymer could be easily precipitated by addition of *n*-hexane, *n*-heptane, or petroleum ether. It appears, therefore, that the bulk precipitation process depends not only on the dielectric constant of the bulk liquid, but also on the polarity of individual bonds in the molecule of the precipitant.

The above experiments show the disadvantage of using any high dielectric constant nonsolvent as a precipitant for copolymers of acrylonitrile and methyl methacrylate dissolved in dimethylformamide. Such precipitants are inherently not capable of giving sharp polymer fractions, since the precipitation process becomes controlled by changes in electrical charge on polymer particles and/or reduction in electrostatic forces, which in turn are not significantly influenced by the precipitating agent unless its dielectric constant is appreciably lower than that of dimethylformamide.

3.2 Fractionation of Copolymer A

An experimental copolymer of methyl methacrylate and acrylonitrile was fractionated using dimethylformamide as a solvent and a mixture (2 parts *n*-hexane + 1 part ether) as a precipitant. In the primary fractionation, the polymer was divided into eight fractions and each of these was subsequently refractionated to give a total of forty-seven secondary fractions. The overall percentage of polymer recovery was 85.3%, calculated on the basis of the weight of the original sample.

The molecular weight distributions within each of the eight primary fractions are shown in Figure 2, where the differential molecular weight distributions were calculated on a weight basis, i.e., the area under each curve is proportional to the weight of that fraction (Table II). The apparent difference between the molecular weight distribution for the whole

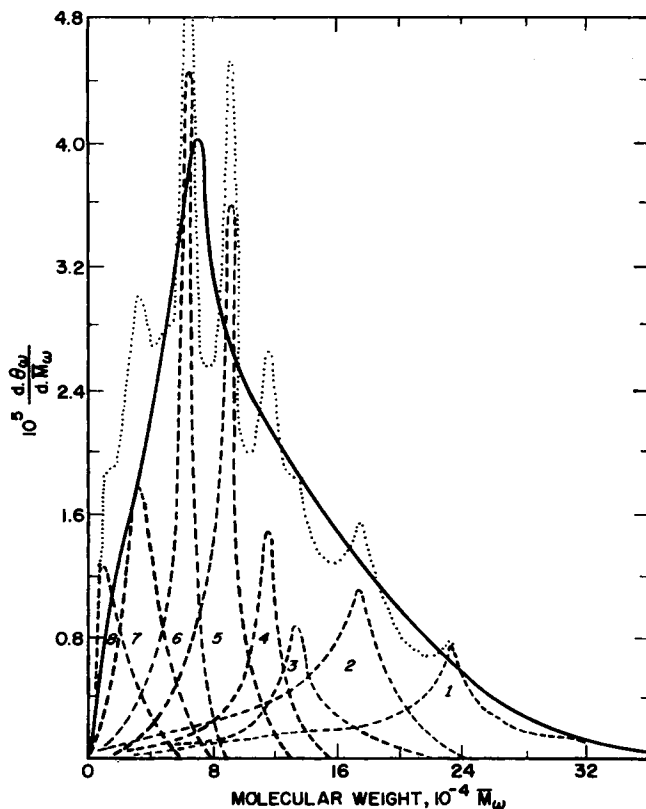


Fig. 2. Differential molecular weight distribution of individual primary fractions and the whole copolymer A: (---) molecular weight distribution of individual primary fractions; (—) molecular weight distribution of the whole polymer as calculated from individual results; (...) molecular weight distribution of the whole polymer as calculated by addition of areas under the curves representing individual fractions.

polymer calculated by addition of individual results for secondary fractions (solid line), and that obtained graphically by addition of areas under the curves for each primary fraction (dotted line) is due to the experimental difficulty of calculating the exact height of the peak in any differential molecular weight distribution curve.

In agreement with the accepted theory⁸ of polymer fractionation, the fractions became progressively sharper as the fractionation was continued; the highest molecular weight fraction had the widest distribution. The molecular weight distributions of the primary fractions appeared, however, to have the shape predicted by Beall's theory,¹² i.e., all distributions were skewed to the left and overlapped each other. The molecular weight distribution was found to depend somewhat on the experimental conditions under which the mixing of precipitant and solution takes place. In particular, it was possible to increase the efficiency of fractionation by addition of a diluent (dimethylformamide) to the precipitant prior to mixing with solu-

TABLE II
Fractionation of Copolymer A

Fraction no.	Weight W , g.	Area under the curve, A , arbitrary units	$10^3 \times W/A$
1	0.837	777	1.08
2	0.890	850	1.05
3	0.514	460	1.12
4	0.514	458	1.12
5	0.817	790	1.03
6	0.713	700	1.02
7	0.548	550	1.00
8	0.305	300	1.02

tion, and by an increase in the rate of stirring. It appears therefore that the unusually large amount of low molecular weight polymer found in the first few fractions, under certain experimental conditions, may be caused by an occlusion process, and that it is not due to the semicrystalline nature of polyacrylonitrile.¹³

A comparison was made between observed weight-average \bar{M}_w , molecular weight (by light scattering), with that obtained using intrinsic viscosity relationship (1) on the whole polymer, and on individual fractions. In the latter case, eq. (2) was utilized to compute the molecular weight of the whole polymer.

$$\bar{M}_w = \sum w_i M_i \quad (2)$$

where $w_i = C_i/C =$ weight-fraction of i fractions having the molecular weight M_i .

It is worth noting (Table III) that the weight-average molecular weight obtained from the light-scattering data is very close to that calculated from intrinsic viscosity measurements on fractions. The result obtained by measuring intrinsic viscosity of the whole polymer is quite low, and this was expected since the relationship (1) was originally established for polymers having a narrow molecular weight distribution.

Similarly, a comparison was made between the observed number-average molecular weight (by osmotic pressure) \bar{M}_n , and the calculated one (assuming that each secondary fraction is homogeneous) using the equation:

$$\bar{M}_n = 1/\sum(w_i/M_i) \quad (3)$$

TABLE III
Molecular Weight of Copolymer A

Method	$10^{-3} \bar{M}_w$
Observed from light scattering (whole polymer)	115.0
Calculated from intrinsic viscosities of fractions	106.2
Calculated from intrinsic viscosity of the whole polymer	88.0

where w_i and M_i have their usual meaning. Such a calculation may indicate the success of the fractionation process, and in particular, it shows the seriousness of the loss of low molecular weight material. Table IV summarizes such results, and it may be concluded that some low molecular weight material was lost in both fractionation experiments. The difference between the observed and calculated values could be accounted for if approximately 10% of the original polymer were lost and the average molecular weight of that material was 5000. Such an estimate may be quite realistic since only 85.3% of original polymer was recovered at the end of the fractionation.

TABLE IV
Molecular Weight of Copolymer A

Method	$10^{-3} \bar{M}_n$
Observed osmotic pressure (whole polymer)	24.8
Calculated from hexane-ether fractionation data (secondary fractions)	42.5
Calculated from ethanol-ultracentrifuge fractionation data (primary fractions)	49.7

The eight primary fractions were also examined by infrared spectral analysis, and they appeared to have a uniform chemical composition within the accuracy of the technique.

3.3 Large-Scale Fractionation of Copolymer A

The above fractionation method was subsequently employed for the preparation of large fractions from copolymer A. A sample of polymer, 100 g., was dissolved in dimethylformamide to give originally a 2.0% concentrated solution. The primary fractions were separated by careful addition of hexane-ether precipitant and allowing the polymer-rich phase to settle overnight. It was found, however, that when approximately 50% of the total polymer was removed, i.e., the polymer concentration in the solution became 1.0%, the polymer started to precipitate in the form of very fine swollen particles which would not settle under the normal gravitational field. In order to avoid the necessity of using a centrifuge, the whole remaining polymer was precipitated at that point, using a procedure described earlier, and redissolved to give again a 2.0% concentrated solution. In Table V the weights and average molecular weights of each primary fraction are given. The total polymer recovery was 75.4%, and it is thought that the missing polymer was uniformly distributed amongst the fractions.

The molecular weight distribution of each primary fraction was determined by refractionating it again. For each refractionation only 0.8 g. sample was used, and the results were subsequently normalized. As a matter of interest the molecular weight distribution of the whole polymer was computed graphically from individual results and compared with the

TABLE V
Large Scale Fractionation of Copolymer A

Fraction no.	Weight, g.	% of total polymer recovered	$10^{-3} \bar{M}_w$
1	7.09	9.4	213.6
2	8.95	11.9	169.8
3	8.68	11.5	140.6
4	11.92	15.8	104.7
5	8.30	11.0	88.2
6	11.61	15.4	72.5
7	10.57	14.0	46.2
8	8.27	11.0	20.2
Whole polymer	75.39	100.0	102.6

earlier results (Fig. 3). The molecular weight distribution curve as obtained by large scale fractionation technique was adjusted to fit the other curve at the high molecular weight end. The agreement between the two curves is good considering the crudeness of the calculations employed.

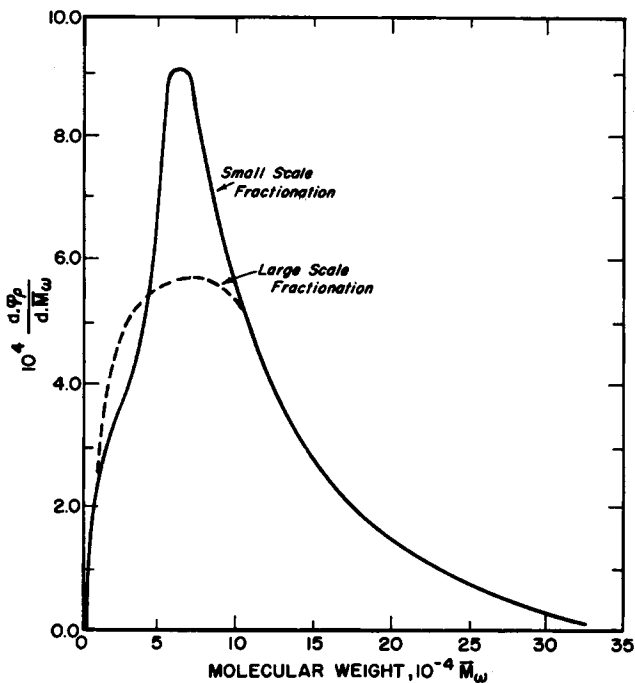


Fig. 3. Differential molecular weight distribution as obtained by two fractionation experiments using copolymer A.

3.4 Fractionation of Terpolymer B

An experimental terpolymer of methylvinylpyridine-vinyl acetate-acrylonitrile was carefully fractionated, by using a two-stage technique

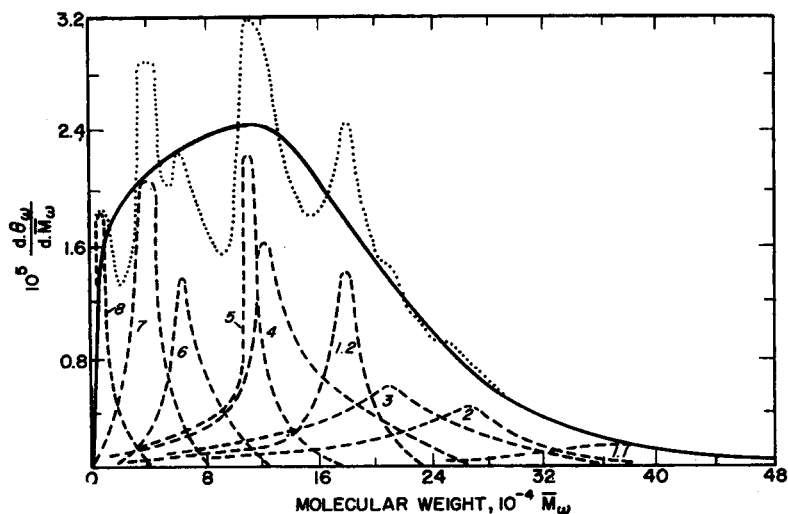


Fig. 4. Differential molecular weight distribution of individual primary fractions and of the whole terpolymer B: (---) molecular weight distribution of individual primary fractions. (—) molecular weight distribution of the whole polymer as calculated from individual results. (...) molecular weight distribution of the whole polymer as calculated by addition of areas under the curves representing individual fractions.

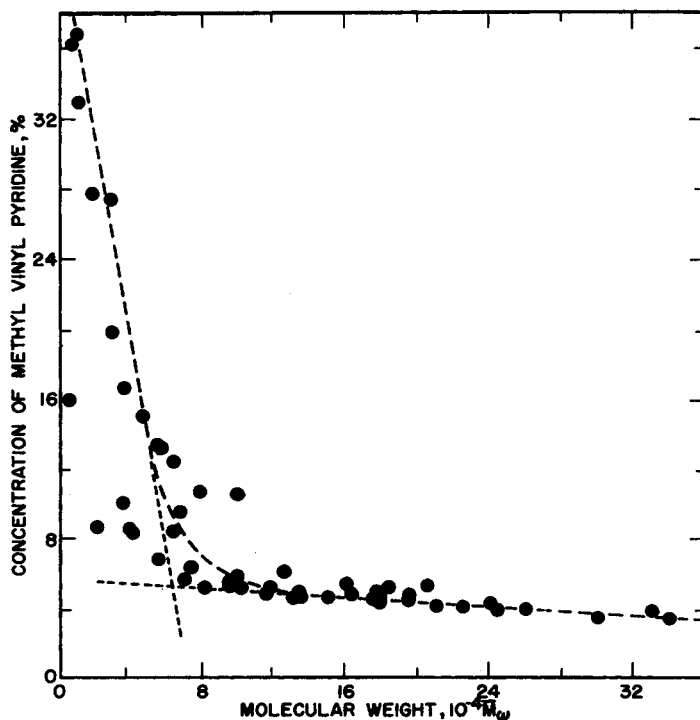


Fig. 5. Chemical distribution within the terpolymer B.

described earlier. A total of 58 secondary fractions was obtained, and the overall percentage of polymer recovery was 89.0% based on the weight of original sample.

The differential molecular weight distribution (Fig. 4) was calculated by addition of all the individual fractions (solid line) and by addition of areas under the curves for the primary fractions (dotted line). The results obtained by the first method were subsequently smoothed, and this may account for the appreciable difference between the two graphs in molecular weight region approximately of 60,000–100,000. In spite of these differences, both graphs indicate that the polymer has a double peak distribution.

The concentration of methylvinylpyridine was determined in all of the secondary fractions using an ultraviolet spectrophotometric method which was calibrated by a chemical method previously described.¹⁴ The results so obtained are shown in Figure 5, where the concentration of methylvinylpyridine in each fraction is plotted against the molecular weight of that fraction. It can be seen that the points fall on two straight lines, meeting in the region of molecular weight of 60,000–100,000, and it is interesting that this corresponds to the break in the molecular weight distribution curve in Figure 4.

The concentration of vinyl acetate in several selected secondary fractions was measured using infrared analysis. The results are summarized in Table VI, and it is seen that the concentration of vinyl acetate is somewhat lower in the lower molecular weight polymer, although the relative proportion of vinyl acetate to acrylonitrile remains nearly constant and the same as in the whole polymer.

TABLE VI
Chemical Composition of Terpolymer B

$10^{-3} \bar{M}_w$	MVP, %	VA, %	AN, %	Ratio AN, %/VA, %
330	3.8	6.1	90.1	14.8
94	5.3	5.6	89.1	15.9
72	6.4	5.9	87.7	14.9
54	13.3	5.7	81.1	14.2
29	19.8	5.5	74.7	13.6
10	36.8	4.2	59.0	14.0
Whole polymer	6.8	5.8	87.4	15.1

The present results support an earlier suggestion¹⁵ that acrylonitrile in aqueous suspension polymerizes by two simultaneous mechanisms: (a) homogeneous polymerization of single radicals in solution, and (b) heterogeneous growth of radicals present in stable suspended polymer particles. Further, the data presented here are in full agreement with findings of Wishman, et al.,¹⁶ who studied similar polymers prepared, however, by batch polymerization.

The weight-average molecular weight of the whole polymer was calculated from fractionation data [eq. (2)], assuming all fractions to be homogeneous, and compared with the values obtained from intrinsic viscosity result on the whole polymer, and light-scattering measurements (Table VII).

TABLE VII
Molecular Weight of Terpolymer B

Method	$10^{-3} \bar{M}_w$
Observed from light scattering	200.0
Calculated from intrinsic viscosities of fractions	141.6
Calculated from intrinsic viscosity of the whole polymer	128.0

The results reported here are in a much poorer agreement than those obtained on copolymer A. In this connection it should be pointed out that Bushuk and Benoit¹⁷ have shown already that too high a molecular weight can result from light-scattering data for copolymers owing to fluctuation in chain composition. The magnitude of this effect increases rapidly as the absolute value of the refractive index increment dn/dc approaches zero, and as the polydispersity of chemical composition increases. The results obtained on terpolymer B may be in appreciable error, as compared with those on copolymer A, since the fractionation data already indicated that the terpolymer has a very inhomogeneous chemical composition: also the value of dn/dc in dimethylformamide was equal to $0.077 \text{ (g./ml.)}^{-1}$.

4 CONCLUSIONS

The fractionation method developed during the present study is a compromise between a multistage and single-stage fractionation. It is experimentally simpler to perform than a multistage fractionation technique, and the results obtained are in agreement with theoretical predictions. Further, the method can easily be modified for preparation of large fractions as may be required for further study into basic polymer properties.

The molecular weight distributions of primary fractions were shown to overlap each other and be skewed to the left. However, molecular weight results were not sufficiently accurate to warrant numerical computations based on Beall's theory.

The authors wish to thank Mr. D. T. Szokolay for assisting in experimental work, and Miss M. Van Weenen for light-scattering measurements.

References

1. Herrent, P., *J. Polymer Sci.*, **8**, 346 (1952).
2. Bisshops, J., *J. Polymer Sci.*, **17**, 81 (1955).
3. Mikhaïlov, N. V., and S. G. Zelikman, *Kolloid. Zh.*, **18**, 717 (1956).

4. Krigbaum, W. R., and A. M. Kotliar, *J. Polymer Sci.*, **32**, 323 (1958).
5. Peebles, L. H., *J. Am. Chem. Soc.*, **80**, 5603 (1958).
6. Anderson, R. E., private communication.
7. Stéfani, R., M. Chevraton, J. Terrier, and C. Eyrand, *Compt. Rend.*, **248**, 2006 (1959).
8. Schulz, G. V., (a) *Z. physik. Chem.*, **A179**, 321 (1937); (b) *ibid.*, **B47**, 155 (1940).
9. Miller, M. L., P. A. Button; R. F. Stamm, L. Rapoport, and E. H. Gleason, paper presented at the Meeting-in-Miniature, New York Section American Chemical Society, March 1956.
10. Miller, M. L., and R. C. Millikan, paper presented at the 127th American Chemical Society meeting, Cincinnati, March 1955.
11. Climie, I. E., and E. F. T. White, *J. Polymer Sci.*, **47**, 149 (1960).
12. Beall, G., *J. Polymer Sci.*, **4**, 483 (1949).
13. Booth, C., and L. R. Beason, *J. Polymer Sci.*, **42**, 93 (1960).
14. Streuli, C. A., *Anal. Chem.*, **27**, 1827 (1955).
15. Dainton, F. S., P. H. Seaman, D. G. L. James, and R. S. Eaton, *J. Polymer Sci.*, **34**, 209 (1959).
16. Wishman, M., F. E. Detoro, M. C. Booty, C. Felton, and R. E. Anderson, *J. Appl. Polymer Sci.*, **7**, 833 (1963).
17. Bushuk, W., and H. L. Benoit, *Can. J. Chem.*, **36**, 1616 (1958).

Synopsis

The mechanism of precipitation of acrylonitrile polymers was investigated using different nonsolvents. The effect of the dielectric constant and the polarity of individual bonds in the molecule of precipitant is discussed briefly. A methyl methacrylate-acrylonitrile copolymer was successfully fractionated from dimethylformamide solution, using a two-stage fractionation technique, and a mixture of (2 parts *n*-hexane + 1 part ether) as a precipitant. The molecular weight distributions of primary fractions were skewed to the left and overlapped each other. A large, 100-g. sample of the same copolymer was separated into eight primary fractions, which on refractionation gave a result substantially the same as that obtained by the small scale experiment. An experimental terpolymer of methylvinylpyridine-vinyl acetate-acrylonitrile, prepared by suspension polymerization, was carefully fractionated by the same method. The polymer was shown to have a double-peak molecular weight distribution in agreement with the earlier suggestion that acrylonitrile in aqueous suspension polymerizes by two simultaneous mechanisms: (1) homogeneous polymerization of single radicals in solution, and (2) heterogeneous growth of radicals present in stable suspended polymer particles. The above conclusion was further supported by methylvinylpyridine analysis on secondary fractions. It was found that the low molecular weight fractions contained appreciably more of the water-soluble monomer (M.V.P.), than the high molecular weight fractions.

Résumé

Le mécanisme de précipitation de polymères de l'acrylonitrile a été étudié en employant différents non-solvants. L'effet de la constante diélectrique et la polarité de liaisons individuelles dans la molécule du précipitant est discuté brièvement. Un copolymère méthacrylate de méthyle-acrylonitrile a été fractionné avec succès à partir d'une solution dans le diméthylformamide, en employant une technique de fractionnement en deux étapes, et un mélange de (2 parties de *n*-hexane + 1 partie d'éther) comme précipitant. Les distributions du poids moléculaire des fractions primaires sont penchées sur la gauche et se recouvrent l'une l'autre. Un grand échantillon (100 g.) du même copolymère était séparé en huit fractions primaires lesquelles, par refractionnement, donnent un résultat essentiellement le même que celui obtenu par l'expérience à petite échelle. Un terpolymère expérimental de la méthylevinylpyridine-acétate de vinyle-acrylonitrile,

préparé par polymérisation en suspension était soigneusement fractionné par la même méthode. On a montré que ce polymère avait un double pic pour la distribution des poids moléculaires en accord avec l'hypothèse antérieure que l'acrylonitrile en suspension aqueuse polymérise par deux mécanismes simultanés: 1) polymérisation homogène de simples radicaux en solutions, et 2) croissance hétérogène de radicaux présents dans une suspension stable de particules de polymères. La conclusion ci-dessus fut vérifiée ultérieurement par l'analyse de la méthylevinylpyridine sur les fractions secondaires. Il a été trouvé que les fractions de bas poids moléculaires contenaient appréciablement plus de monomères solubles dans l'eau (MVP) que les fractions de poids moléculaires élevés.

Zusammenfassung

Der Fällungsmechanismus von Polyacrylnitril mit verschiedenen Fällungsmitteln wurde untersucht. Der Einfluss der Dielektrizitätskonstanten und der Polarität individueller Bindungen im Molekül des Fällungsmittels wird kurz diskutiert. Ein Methylmethacrylat-Acrylnitrilcopolymeres wurde erfolgreich aus Dimethylformamidlösung nach einem zweistufigen Fraktionierungsverfahren mit einer Mischung aus 2 Teilen *n*-Hexan und einem Teil Äther als Fällungsmittel fraktioniert. Die Molekulargewichtsverteilungen der Primärfractionen waren nach links abgescrängt und überlappten sich gegenseitig. Eine grosse, 100 g-Probe des gleichen Polymeren wurde in acht Primärfractionen zerlegt, die bei der Refraktionierung ein im wesentlichen gleiches Ergebnis wie der Versuch in kleinem Massstab lieferten. Ein durch Suspensionspolymerisation hergestelltes Versuchsterpolymeres aus Methylvinylpyridin, Vinylacetat und Acrylnitril wurde nach der gleichen Methode sorgfältig fraktioniert. Das Polymere wies eine Molekulargewichtsverteilung mit zwei Maxima auf. Das stimmt mit der schon früher geässerten Anschauung überein, dass Acrylnitrile in wässriger Suspension nach zwei Simultanmechanismen polymerisiert: (1) homogene Polymerisation einzelner Radikale in Lösung und (2) heterogenes Wachstum der in stabilen suspendierten Polymerpartikeln vorhandenen Radikale. Eine weitere Stütze für diese Ansicht lieferte die Methylvinylpyridinbestimmung in Sekundärfractionen. Es zeigte sich, dass die niedermolekularen Fractionen beträchtlich mehr von dem wasserlöslichen Monomeren (MVP) enthalten als die hochmolekularen Fractionen.

Received August 7, 1962