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Size exclusion behavior of polymers in amide solvents

II. Molecular weight determination of acrylonitrile polymers in *N,N*-dimethylformamide

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Summary

Size exclusion chromatography (SEC) procedure for the determination of molecular weight and molecular weight distribution of acrylonitrile polymers (PAN) is described. The Mark-Houwink-Sakurada parameters of PAN polymers in DMF and 0.01M LiBr-DMF at 60°C were estimated. The values of a parameters obtained by us for PAN prepared both by persulfate-metabisulfite aqueous system (PAN), and azo-bis-isobutyronitrile in DMF solution (PAN-A) were the same, while for PAN sample containing small amounts of sulfonated pendant groups (PAN-S) was higher. The addition of inorganic salt, such as LiBr, to DMF suppressed the abnormal SEC elution behavior observed in the solvent without the electrolyte although SEC of PAN-A showed almost the same results as in DMF with electrolyte. The universal calibration using monodisperse poly(ethylene oxide) standards as well as application of the Mark-Houwink-Sakurada parameters were satisfactory for the determination of the molecular weights.

Introduction

One of the best solvents for polyacrylonitrile (PAN) is N,N-dimethylformamide. However, the determination of molecular weight and its distribution by size exclusion chromatography (SEC) has been described as difficult since abnormal small retention volumes and multimodal curves are usually obtained(1-4). This peculiar elution behavior in DMF has been also reported for other polymers(5-8). The addition of inorganic electrolytes such as LiBr has been the approach used to eliminate these peculiarities. Although some authors accept the universal calibration method(9) for SEC using DMF as eluent(10), the presence of salt in DMF is not considered valid by other investigators(2,3).

We have recently reported that the peculiar elution behavior of PAN polymers in DMF is related to the interaction between ionic groups in the polymer molecule and ionic substances originated from DMF degradation(11,12). This paper presents a procedure for the universal calibration of SEC column systems for analysis of acrylonitrile polymers in 0.01M LiBr-DMF. The sample were prepared by both persulfate-metabisulfite aqueous system (PAN) and azo-bis-isobutyronitrile initiation in DMF solution (PAN-A). Industrial samples of polyacrylonitrile containing small amount of sulfonate groups (PAN-S) were also investigated.

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Experimental

Acrylonitrile polymers (PAN, PAN-A and PAN-S) were prepared as reported elsewhere(12). PAN and PAN-A were fractionated by using n-heptane and DMF at 60°C. SEC equipment and columns were described previously(11-12). DMF was freshly distilled twice at 55°C/20mmHg after drying over magnesium sulfate. Deionization of DMF was achieved by the same method as reported previously(12). Polystyrene (PS) and poly(ethylene oxide)(PEO) standards with narrow molecular weight distribution ($\overline{M}_w/\overline{M}_n$= 1.01-1.02 for PS; $\overline{M}_w/\overline{M}_n$= 1.02-1.14 for PEO) from Toyo Soda Co. were used to calibrate the column system. Intrinsic viscosities [η] were measured using an Ubbelohde type capillary viscometer.

Results and discussion

Mark-Houwink-Sakurada parameters are needed for SEC universal calibration of acrylonitrile polymers. Cleland and Stockmayer(13) had established the parameters for polyacrylonitrile prepared with AIBN initiator (PAN-A) at 25 C in DMF as follows:

$$[\eta]^{\mathrm{DMF}/25^\circ\mathrm{C}} = 2.43 \times 10^{-4}\, \overline{M}_v^{0.75} \qquad (1)$$

Viscosity average molecular weight M_v is expressed by the following equation:

$$\overline{M}_v = (\,\Sigma\, w_i\, M_i^{a}\,)^{1/a} \qquad (2)$$

where w_i denotes weight fractions of the polymer. Therefore, $\overline{M}_v$ obtained from Equation 1 cannot be applied to determine the parameters for acrylonitrile polymers in other conditions, such as 0.01M LiBr-DMF at 60°C, unless a value is the same as in DMF at 25 C. In addition, the following ratio:

$$[\eta]^{\mathrm{LiBr\text{-}DMF}/60^\circ\mathrm{C}} \;/\; [\eta]^{\mathrm{DMF}/25^\circ\mathrm{C}} \qquad (3)$$

becomes constant, when both a values are the same. The Kramer constant K" in the following relationship:

$$\ln \eta_r/c = [\eta] + K''\,[\eta]^2\, c \qquad (4)$$

can be also a good indication of the similarity of a values in two different conditions(14). Table 1 summarises the intrinsic viscosities and Kramer constant for acrylonitrile polymers under investigation. The decimal digit in the sample identification means successive fractions of the crude sample. For all samples, the viscosities did not change in DMF and 0.01M LiBr-DMF at 60°C; K" values were also similar for PAN-A and PAN. Therefore, the solution properties for PAN seem to be the same as for PAN-A. Addition of a small amount of LiBr to DMF does not cause substantial change in coil size in the acrylonitrile polymers, so that a value for PAN may be considered to be the same as for PAN-A. The Kramer constant for PAN-S was different from those of PAN and PAN-A, suggesting also a different a value. The ratio (3) was constant as presented in Table 2 and represents the ratio between K parameters in 0.01M LiBr-DMF and DMF at 60°C and in DMF at 25°C. Therefore, a parameter for PAN and PAN-A was taken as 0.75.

The viscosity-molecular weight relationship for the standards, PEO and PS, was:

$$[\eta_{PEO}]^{LiBr\text{-}DMF/60°C} = 5.50 \times 10^{-4}\, \bar{M}_v^{0.643} \qquad (5)$$

$$[\eta_{PEO}]^{DMF/60°C} = 3.59 \times 10^{-4}\, \bar{M}_v^{0.673} \qquad (6)$$

$$[\eta_{PS}]^{LiBr\text{-}DMF/60°C} = 1.30 \times 10^{-4}\, \bar{M}_v^{0.662} \qquad (7)$$

Table 1. Intrinsic Viscosities and Kramer's Constants of acrylonitrile Polymers in DMF

Polymer	Sample	DMF/25°C		DMF/60°C		0.01MLiBr-DMF/60°C	
		[η]	k"	[η]	k"	[η]	k"
	1	1.46	-0.185	1.30	-0.186	1.27	-0.185
	2	1.48	- 0.185	-	-	1.29	-0.186
PAN-S	3	1.49	-0.185	-	-	1.31	-0.183
	4	1.55	-0.185	1.36	-0.187	1.34	-0.187
	average	-	-0.185	-	-0.187	-	-0.185
	1.0[a]	2.49	-0.140	2.17	-0.138	2.18	-0.138
	1.0[b]	2.45	-0.140	2.17	-0.138	-	-
PAN	1.1[c]	3.15	-	2.77	-	2.72	-0.124
	1.2[c]	2.07	-	1.77	-	1.83	-0.126
	1.3[c]	1.05	-	0.920	-	0.920	-0.145
	average	-	-	-	-	-	-0.133
	2.0	1.25	-0.138	1.09	-0.139	1.06	-0.141
PAN-A	3.0[a]	0.880	-0.140	0.750	-0.140	0.735	-0.140
	3.4[c]	0.790	-0.140	0.645	-0.140	0.640	-0.134
	average	-	-0.140	-	-0.140	-	-0.138

a) Unfractionated
b) In deionized DMF
c) Polymers fractionated by using n-heptane and DMF at 60°C.

As the addition of very small amounts of LiBr to DMF eliminate completely the peculiar elution behavior of acrylonitrile polymers as described previously (11,12), 0.01M

LiBr-DMF solution was used preferentially as eluent for the construction of the universal calibration curve. The use of PS and PEO standards leads to different curves(11). This may be due to adsorption effects of PS over the polystyrene gel in the column as a result of the poor solubility in DMF. The universal calibration curve with PEO standards was used. Table 3 summarises SEC data; the intrinsic viscosities were measured in an Ubbelohde capillary viscometer. Data were calculated according to the equations proposed by Weis and Cohn-Ginsberg(15). The intrinsic viscosities obtained for PAN and PAN-A from SEC results by the universal calibration using PEO standards and the viscosity parameters of Table 2 agreed with those measured by solution viscosity. Therefore, the SEC universal calibration method for determining molecular weight of acrylonitrile polymers using PEO as standards and 0.01M LiBr-DMF solution as eluent is valid for PAN and PAN-A. As for PAN-S, the viscosity parameters were calculated by iterative method from SEC in 0.01M LiBr-DMF at 60°C and found to be $K=2.717 \times 10^{-5}$ and $a=0.90$.

Table 2. Viscosity Parameters for Acrylonitrile Polymers

Polymer	DMF/60°C			0.01M LiBr-DMF/60°C		
	$\frac{[\eta]_{\mathrm{DMF/60^{\circ}C}}}{[\eta]_{\mathrm{DMF/25^{\circ}C}}}$	K^c	a	$\frac{[\eta]_{\mathrm{LiBr\text{-}DMF/60^{\circ}C}}}{[\eta]_{\mathrm{DMF/25^{\circ}C}}}$	K^c	a
PAN-S [a]	-	-	-	0.872	$2.72\mathrm{x}10^{-5}$	0.900
PAN [b]	0.870	$2.11\mathrm{x}10^{-4}$	0.750	0.875	$2.12\mathrm{x}10^{-4}$	0.750
PAN-A [b]	0.847	$2.06\mathrm{x}10^{-4}$	0.750	0.838	$2.04\mathrm{x}10^{-4}$	0.750

a) Obtained from SEC data.

b) Calculated by using $a= 0.75$, $K=2.43\mathrm{x}10^{-4}$ for PAN-A in DMF at 25°C, obtained by Cleland and Stockmayer(13).

c) 100 ml/g.

The Mark-Houwink-Sakurada parameters estimated by iterative method on PAN-S seem to be acceptable because the a value was almost the same as the value (0.897) which was obtained by Mori resulting from SEC experimental data and molecular weight determined by light scattering method(4). However, the K value ($2{,}72 \times 10^{-5}$) was about the double of that (1.46×10^{-5}).

The lack of validity of the universal calibration as previously reported(2,3) may be due to erroneous MW results for acrylonitrile polymers. As a matter of fact, the inherent difficulties in the application of light scattering, osmometry and sedimentation velocity to acrylonitrile polymers in DMF has already been pointed out by Krigbaum and Kotliar(16).

Table 3. Molecular Weights, Polydispersity and Intrinsic Viscosities of Acrylonitrile Polymers

Polymer	Sample	$\bar{M}_w x10^{-4}$	$\bar{M}_n x10^{-4}$	$\bar{M}_w/\bar{M}_n$	$[\eta]$ (100ml/g)		Remark
					SEC	viscometry	
PAN-S	1	16.01	5.562	2.88	1.27	1.27	0.01M LiBr-DMF a=0.90 K=2.72x10^{-5} 60°C
	2	15.59	5.813	2.70	1.25	1.29	
	3	16.94	6.175	2.74	1.34	1.31	
	4	16.87	6.052	2.79	1.34	1.34	
	5	15.57	6.055	2.57	1.24	1.24	
	6	15.10	6.726	2.25	1.21	1.23	
	7	15.51	6.478	2.39	1.24	1.25	
PAN	1.0 [a]	25.16	6.242	4.03	2.17	2.18	0.01 M LiBr-DMF a=0.75 K=2.12x10^{-4} 60°C
	1.1 [b]	32.09	11.93	2.69	2.67	2.72	
	1.2 [b]	20.05	8.247	2.43	1.87	1.83	
	1.3 [b]	8.002	3.042	2.63	0.943	0.920	
PAN-A	2.0 [a]	9.896	4.327	2.29	1.07	1.06	0.01 M LiBr-DMF a=0.75 K=2.04x10^{-4} 60°C
	3.0 [a]	6.132	2.864	2.14	0.754	0.735	
	3.1 [b]	8.706	4.903	1.78	0.989	0.937	
	3.2 [b]	7.587	4.459	1.70	0.894	0.880	
	3.4 [b]	5.054	2.552	1.98	0.652	0.640	
PAN-A	2.0 [a]	11.04	4.746	2.33	1.16	1.09	DMF a=0.75 K=2.06x10^{-4} 60°C
	3.0 [a]	6.417	3.016	2.13	0.745	0.750	
	3.1 [b]	7.986	4.595	1.74	0.939	0.980	
	3.2 [b]	7.078	4.010	1.77	0.855	0.900	
	3.4 [b]	3.413	2.069	1.65	0.591	0.645	
PAN-A	3.0 [a]	6.195	2.983	2.08	0.743	0.750	Deionized DMF a=0.75 K=2.06x10^{-4} 60°C
	3.1 [b]	8.105	4.646	1.74	0.949	0.980	
	3.2 [b]	7.180	4.142	1.73	0.865	0.900	

a) Unfractionated.

b) Polymer fractionated by using n-heptane and DMF at 60°C.

As the result of our investigation, on the contrary of what has been reported, we suggested that SEC universal calibration using electrolyte-DMF eluents may be accepted as a valid method for the determination of MW of polymers containing ionic groups since eventual ionic interaction effects are suppressed. Also, in the case of PAN-A which does not have ionic moieties, SEC in DMF and deionized DMF showed almost the same results as in 0.01M LiBr-DMF.

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