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Size exclusion behavior of polymers in amide solvents

I. Elution characteristics of acrylonitrile polymers in *N, N*-dimethylformamide

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Summary

The abnormal behavior of acrylonitrile polymers shown by size exclusion chromatography (SEC) in N,N-dimethylformamide (DMF) was investigated by using model polymers having variable degrees of sulfonated moieties as electric charged groups. The unexpected small retention volume and very high UV absorption at 280 nm were observed in the case of the samples with ionic sulfonate groups even in very small amounts, as chain ends. The abnormal behavior was confirmed to be due to impurities of DMF decomposition which interact with charged groups in the polymers.

Introduction

Polyacrylonitrile (PAN) is one of the best precursors for carbon fibers. The determination of the molecular weight and the molecular weight distribution of PAN are essential to predict the performance of the final carbon fiber and can be obtained by size exclusion chromatography (SEC). Although N,N-dimethylformamide (DMF) is one of the best solvents for PAN, the SEC behavior in this eluent has shown several peculiarities(1-7).

Cha(1) was the first to report the unexpected elution characteristics studying SEC of PAN with pendant sulfonated groups (PAN-S) in DMF. The addition of LiBr to DMF resulted in remarkable changes in the shape of the SEC curve and retention volume. The previous multimodal profile became unimodal and an increase in the retention volume was observed. These effects were interpreted by Cha as a drastic decrease in the coil size due to the charge neutralisation of sulfonated groups along the chain.

Since then, several different interpretations for the abnormal SEC behavior of acrylonitrile polymers in DMF as well as the effect of LiBr have been published. Coppola et al(2) interpreted the small retention volume of the peaks as an intermolecular association of the sulfonated groups in the polymer (PAN-S). The addition of LiBr would cause the salting out of the polymer.

Acrylonitrile copolymers with vinyl ether and vinyl acetate were studied by Kenyon an Mottus(3,4). They suggested that peculiarities were due to intermolecular association

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between the dipoles of DMF and the nitrile groups in the polymer chain. The displacement of the curve by the addition of the electrolyte was interpreted as a result of the shielding effect of LiBr on the dipoles.

SEC anomalous curves of PAN-S over silica gel columns in DMF were also interpreted as due to ionic exclusion effects(6).

We have reported the SEC abnormal behavior of the acrylonitrile polymers having small amounts of ionic moieties which are pendant sulfonate groups (PAN-S) and sulfonate or sulfate end groups from the persulfate initiator (PAN) in DMF and 0.01M LiBr-DMF(7). In this paper, we discuss the influence of the treatment of DMF solvent and charged moieties on the SEC behavior of acrylonitrile polymers in comparison with the behavior of azo-bis-isobutyronitrile (AIBN) initiated PAN (PAN-A).

Experimental

Material

Acrylonitrile homopolymers were prepared by two procedures: azo-bis-isobutyronitrile (AIBN) initiated polymerization in DMF at 50°C (PAN-A) and potassium persulfate-sodium metabisulfite redox aqueous system at 40°C (PAN). Acrylonitrile-sodium methallyl sulfonate-methylmethacrylate terpolymer (PAN-S; sulfonate content, 0,6 mol%; MMA content, 1 mol%) was prepared by the same procedure as for PAN. Polymer samples were purified by precipitation of DMF polymer solution in 0.2% (w/v) NaCl aqueous solution. DMF was dried over magnesium sulfate and freshly distilled twice at 55°C/20 mmHg. Deionization was achieved by interposing cation exchange (Amberlite IR-120) and zeolite columns (molecular sieve, 3Å) between the pump and the sample injection bulb of the chomatograph.

SEC measurements

SEC measurements were carried out in a Toyo Soda HLC-803A equipped with a refractive index detector (JAI, model RI-2) and a UV detector (JASCO UVIDEC 100-II) set at 280 nm wave length. Toyo Soda TSK-GEL type GMH-6 (60cm x 7.5mm ID) columns packed with a mixture of polystyrene gel (porous diameter, 10^3-10^7Å; 23800 TP/columns) designed for DMF solvent were set in a constant temperature oven. The flow rate of eluents was 1.0 ml/min and recorder chart speed 0.5 cm/min.

Results And Discussion

Characterization of acrylonitrile polymers

Figure 1 shows the FTIR spectra of PAN-S, PAN and PAN-A. According to Yamada (8) PAN prepared by persulfate initiator exhibit a absorption at 1043 cm^{-1} attributed to axial stretching of S-O bonds in $-SO_3^-$ or $-SO_4^-$ terminal groups introduced in the polymer by the initiation process. We have observed this absorption in PAN-S and PAN. It is reported that the termination process of acrylonitrile polymerization is predominantly by radical recombination (9,10). So, PAN has sulfonate or sulfate groups only at the polymer chain ends. PAN-A has no sulfonate groups. The Scheme 1 shows the probable structure of the acrylonitrile polymers under investigation.

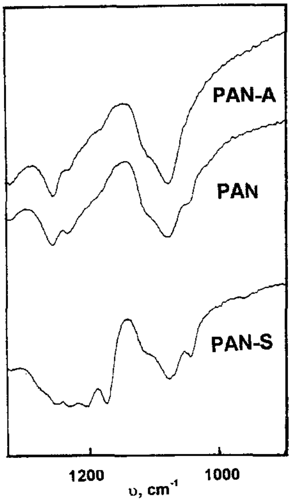
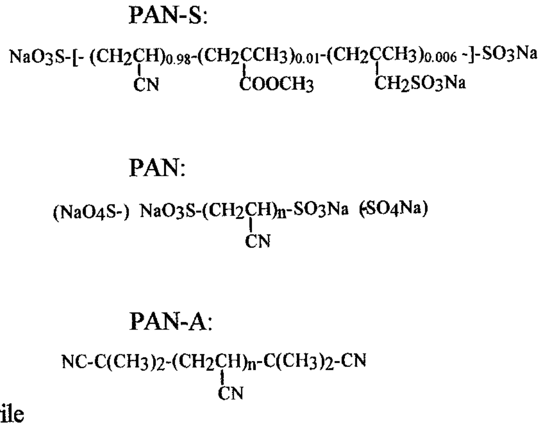


Figure 1. FTIR spectra of acrylonitrile polymers

Scheme 1:



PAN-S:

$NaO_3S\text{-}[\text{-}\ (CH_2\underset{CN}{C}H)_{0.98}\text{-}(CH_2\underset{COOCH_3}{C}CH_3)_{0.01}\text{-}(CH_2\underset{CH_2SO_3Na}{C}CH_3)_{0.006}\ \text{-}]\text{-}SO_3Na$

PAN:

$(NaO_4S\text{-})\ NaO_3S\text{-}(CH_2\underset{CN}{C}H)_n\text{-}SO_3Na\ (\text{-}SO_4Na)$

PAN-A:

$NC\text{-}C(CH_3)_2\text{-}(CH_2\underset{CN}{C}H)_n\text{-}C(CH_3)_2\text{-}CN$

SEC behavior of PAN-S and PAN in DMF

We previously reported that PAN containing pendant sulfonate groups (PAN-S) shows very peculiar SEC curves in DMF, as seen in the numbered chromatograms obtained by successive injections (7). The retention volume was abnormally small, with multimodal curve profiles. After several injections of the same fresh solution, the multimodal curve became nearly unimodal and the large peak detected by UV at 280 nm was greatly reduced. The largest peak detected by UV and the multimodality shown by RI were more intense in the first injection of the sample. This effect is more strongly observed through the shape of the UV and RI curves when the time intervals between two consecutive injections was longer (over one hour).

Although less intensely, the same PAN-S elution characteristics were also exhibited by PAN.

Abnormal behavior was remarkaby observed by UV detector. At 60°C PAN-S showed a bimodal curve with maximum at retention volumes 17 and 24 ml, respectively. The UV absorption of these two peaks was investigated. However, no UV absorption was observed on the eluent. So, the apparent high UV absorption maximum may be due to some UV radiation scattering originated by the presence of polymer complex as microparticles. The polymer complex seems to be formed by the interaction among ionic moieties in the polymer and some substances from DMF in the column.

SEC of PAN-A in DMF

Polyacrylonitrile made by AIBN initiated solution polymerization in DMF presented a different SEC elution behavior. Figure 2 shows the influence of the sample concentration on the retention volume. PAN-A exhibited two peaks. Peak A, at higher retention volume, which did not show the abnormal SEC behavior and Peak B at smaller elution volume. It is interesting to observe that there is a curious change in the retention volume of Peak B with increasing concentration, not noticed in Peak A. Peak B behaves very similar to the samples containing ionic groups. This kind of effect suggested a different macromolecular composition of Peak B in relation to Peak A. The difference may be explained considering that chain transfer reactions to the DMF used in the preparation of PAN-A could have introduced terminal amide groups. These groups are susceptible to hidrolysis during the purification of the sample generating small amounts of ionic groups (Scheme 2). This type of displacement was also found in PAN-S chromatograms, as seen in Figure 3; the retention volume at the maximum of the curve increases significantly as the concentration of the polymer becomes higher. The same was observed for PAN. This behavior is quite common in aqueous solution of polyelectrolytes.

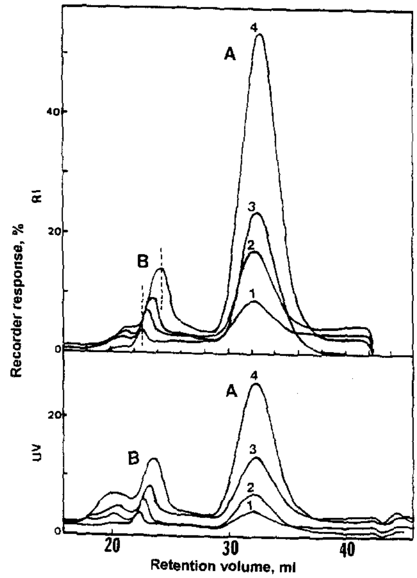


Figure 2. Influence of polymer concentration on the SEC curves of PAN-A in DMF at 30°C - Attenuation: RI, 8; UV, 0.08. (1) 0.1%; (2) 0.2%; (3) 0.4%; (4) 0.8%.

Scheme 2:

$$P_n^{\bullet} + HCON(CH_3)_2 \rightarrow P_n\text{-}H + {}^{\bullet}CO\ N(CH_3)_2 \xrightarrow{P_m^{\bullet}} P_m\text{-}CON(CH_3)_2 \xrightarrow{H_2O} P_m\text{-}COOH + HN(CH_3)_2$$

Peak B of PAN-A has also a very small retention volume. Taking into consideration the preparation process, it is not expected that the molecular weight of such a fraction could not be so much different. So, the small retention observed for PAN-A (Peak B), PAN-S and PAN seems to be related to some interaction which could cause an increasing in the hydrodynamic volume or a polymer/PS-DVB gel interaction. Hann (11) reported evidences that a quaternized polyurethane was adsorbed on PS-DVB gels, which are usually considered as being neutral, but display caracteristics of having anionic nature in DMF. From our results and considering the presence of negative sites over the gel, the small retention of the samples containing ionic moieties can be interpreted as ionic exclusion, since it is not expected that ionic end groups can contribute for such a high hidrodynamic volume expansion.

Influence of DMF solvent

When LiBr was added to DMF, normal SEC curves were found and the retention volume increased remarkably. For PAN-S, the peak position of the curves did not shift with the increase in concentration as shown in Figure 4. Deionized DMF as eluent also minimized the abnormality as seen in Figure 5. However, the peculiar SEC behavior is noticed again when the temperature was raised to 60°C. Thermal decomposition of DMF is reported to take place slowly at room temperature to generate dimethylamine and carbon monoxide(12). Therefore, the SEC peculiarity in DMF seems to be related to the existence of some substances, such as amines, generated by the decomposition of DMF at 60°C, since a cation exchange column preceding the injection device was effective in changing the position of the curve to a larger retention volume.

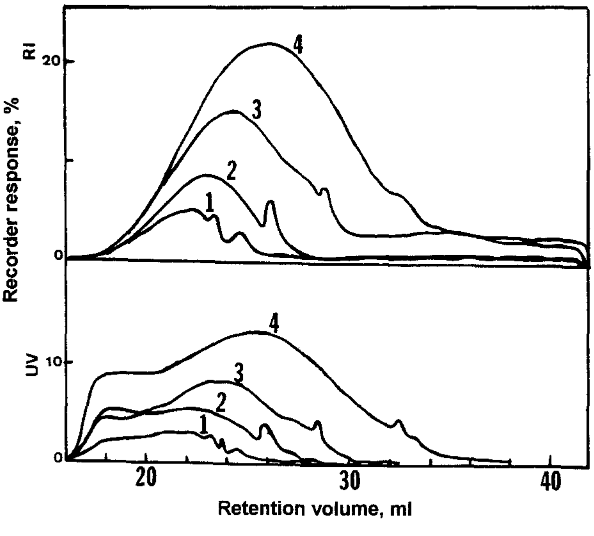


Figure 3. Influence of polymer concentration on the SEC curves of PAN-S in DMF at 30°C - Attenuation: RI, 8; UV,0.08. (1) 0.1%; (2) 0.2%; (3) 0.4%; (4) 0.8%.

Addition of LiBr to DMF and the deionization of the eluent did not influence the Peak A of PAN-A, as shown in Figure 6. However, Peak B was displaced to higher retention volume in deionized DMF and disappeared when electrolyte was added to the solvent.

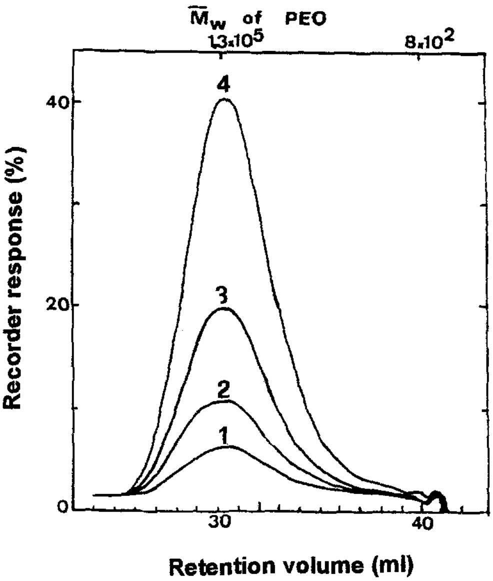


Figure 4. Influence of polymer concentration on the SEC curves of PAN-S in 0.01M LiBr-DMF at 60°C - Attenuation: RI, 8; UV,0.08. (1) 0.1%; (2) 0.2%; (3) 0.4%; (4) 0.8%.

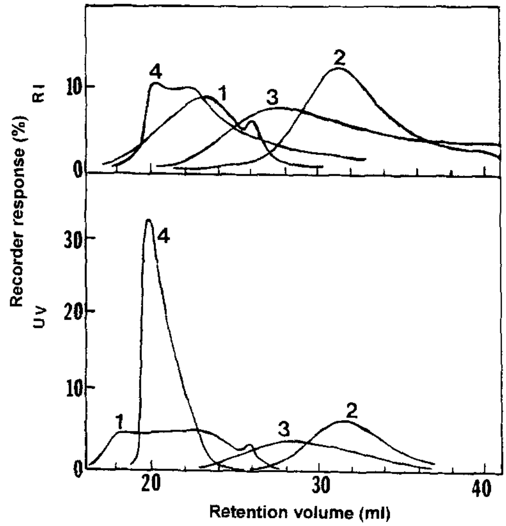


Figure 5. Influence of DMF eluents on the SEC curves of PAN-S at 30°C. (1) DMF; (2) 0.01M LiBr-DMF; (3) deionized DMF; (4) deionized DMF at 60°C. Polymer concentration: 0.2%.

Figures 7 and 8 show the influence of the polymer concentration on the retention volume of the SEC curves in DMF and deionized DMF. No change was observed in the case of PAN-A (Peak A), but in the case of PAN-S and PAN which contain ionic groups the retention volume increase with increasing concentrations. This effect is enhanced by increasing the amount of the charged groups on the polymer chain (PAN-S) and is observed in both solvents. The effect is remarkable in deionized DMF and could be interpreted taking into consideration the lower concentration of ionic impurities from DMF decomposition which cause a increasing in coil expansion.

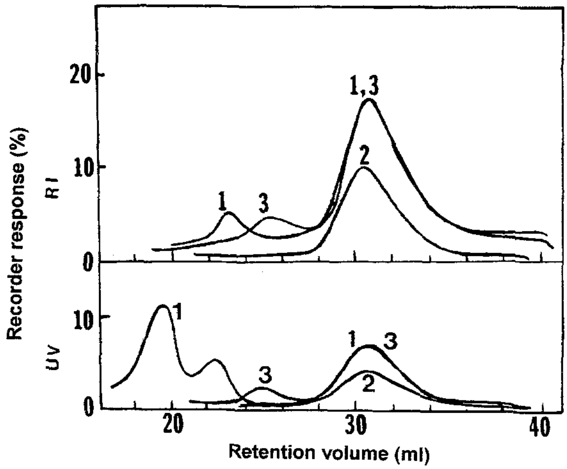


Figure 6. Influence of DMF eluents on the SEC curves of PAN-A at 30°C. (1) DMF (polymer concentration, 0.2%); (2) 0.01M LiBr-DMF (polymer concentration, 0.1%); (3) deionized DMF (polymer concentration: 0.2%).

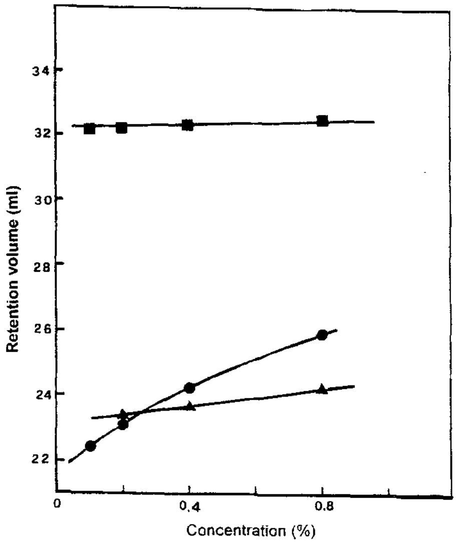


Figure 7. Influence of polymer concentration on retention volume. DMF; 30°C; (●) PAN-S; (▲) PAN; (■) PAN-A (Peak B).

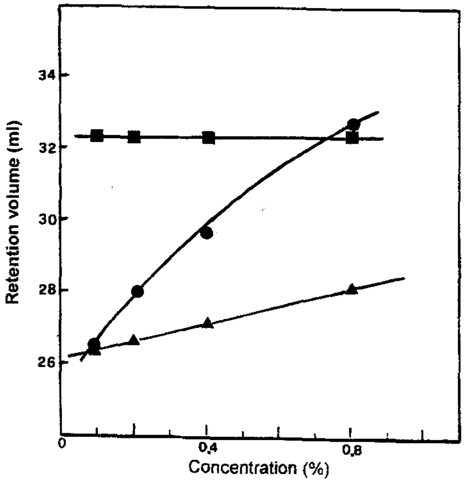


Figure 8. Influence of polymer concentration on retention volume. Deionized DMF; 30°C; (●) PAN-S; (▲) PAN; (■) PAN-A (Peak B).

As a conclusion, we noticed that there are two phenomena for the peculiarities on the SEC of acrylonitrile polymers: UV scattering due to the formation of polymer complex as microparticles by the electrostactic interaction among some ionic impurities in the column and the polymers containing ionic moieties; and abnormally small retention volume which may be cause by ionic repulsion between the polymers containing anionic groups and anionic sites on the polystyrene gel. The first phenomenum is responsible for the deformed shapes of the SEC curves, detected specially by UV detector but also by RI at inicial injections run, and the high apparent UV absorption. These phenomena are caused by some impurities from DMF decomposition. We do not know what are the impurities from DMF decomposition. Deionization of DMF and addition of LiBr could interfere in both types of interaction decreasing or eliminating completely these peculiarities.

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