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Size exclusion behavior of polymers in amide solvents

IV. Elution characteristics of acrylonitrile polymers in *N*,*N*-dimethylacetamide

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Summary

The size exclusion chromatography of neutral polymers and polymers containing ionic groups was investigated using N,N-dimethylacetamide (DMA) as mobile phase. As reported previously for N,N-dimethylformamide (DMF), acrylonitrile polymers containing charges, even those at terminal end groups, showed markedly small retention volumes and multimodal peaks by refractive index and 280 nm UV detectors. In DMA containing small amounts of LiBr the peaks of the ionic polymers were shifted to small retention volumes while neutral polymers with analogous chemical structures did not show the same behavior. As in the case of DMF the peculiarities observed in DMA were attributed to the formation of supramolecular structures by the interaction of the ionic groups in the polymer and the ionic species from DMA decomposition.

INTRODUCTION

Amides are powerful solvents for several polymers. However, they have not been used frequently as systematic solvents for size exclusion chromatography (SEC) of macromolecules. Some authors report the use of N,N-dimethylformamide (DMF) in SEC (1-5). It is specially important in the analysis of polar polymers which are insoluble or partially soluble in THF, a common solvent employed in this technique (5). In previous papers (6-8), we have reported that polymers containing small amounts of charged groups showed some elution peculiarities in DMF. Multimodal peaks, very small retention volumes, and unexpected traces recorded by the UV detector were observed, whenever ionic moieties were present, even as chain end groups. When this solvent was deionized or LiBr was added, UV peaks disappeared and the

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peaks observed by refractive index detection were eluted at higher retention volumes. Experimental evidences indicate that in DMF the polystyrene gel is not an inert packing (9,10). It adsorbs cationic species resulting from DMF decomposition and these species can interact with anion containing polymer molecules forming complexes of larger hydrodynamic volumes. Deionization of DMF decreases the amount of the cationic species in the solvent, activates the adsorption sites on polystyrene gel, and modifies the elution behavior of anionic polymers.

We have also investigated the SEC of some neutral and ionic polar polymers in N,N-dimethylacetamide (DMA). In this paper, we report the results of SEC obtained with acrylonitrile polymers using DMA as mobile phase and double detection: UV and refractive index (RI).

EXPERIMENTAL

Samples and mobile phases

Acrylonitrile polymers 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). A commercial terpolymer of acrylonitrile-methylmethacrylate-sodium methallyl sulfonate (PAN-S) (MMA content: 1 mol %; sulfonate: 0.6 mol %) was prepared as PAN. They were purified by precipitation of DMF solution into water. Lithium bromide (Fisher Laboratories) and DMA (Wako Pure Chemicals) were used as received.

Size exclusion chromatography

SEC measurements were carried out by a Tosoh HPLC-8000 system with a RI detector (JAI, model RI-2) and a UV detector (JASCO UVIDEC 100-II) set at 280 nm. Two Toyo Soda TSK-GEL Type GMH-6 columns packed with polystyrene gel (60cm x 7.5mm ID, particle diameter: 10 μm, exclusion limit: 10^7, NTP= 23800/column) were used. The columns were supplied in acetone and were used after the solvent substitution for DMA. They were set in a constant temperature oven. The flow rate of eluents was 1.0 ml/min and the injection volume was 100 ml. Concentrations of 0.2% (w/v) were used as the ordinary condition except in concentration effect studies, where a range from 0.1 to 0.8% (w/v) was used. Monodisperse poly(ethylene oxide) (PEO) samples from Toyo Soda were calibrating standards.

RESULTS AND DISCUSSION

SEC in DMA

The peculiar elution behavior shown previously (6,7) using DMF as mobile phase lead us to check the generality of that effect for another N,N-disubstituted amide. N,N-dimethylacetamide, the simplest homologue of DMF was chosen. DMA has solvent characteristics very similar to DMF, being capable of easily dissolving acrylonitrile polymers.

Although the literature does not show any systematic study on the decomposition of DMA, the structural similarity between these two solvents made us to anticipate that the effect of the decomposition products could also influences the SEC analysis of these polymers.

The curves obtained by 3 successive injections of a fresh solution of PAN-S in DMA is shown in Fig. 1. The UV detector shows bimodal peaks. In the first injection (Fig. 1a), the fraction eluted at 5.6 ml was higher in concentration, decreasing gradually in the second and third runs (Figs. 1b and 1c). The fraction eluted at about 8 ml remained practically invariable in height from the second injection. However, the appearance of the peaks by RI detection was quite different from that obtained by UV. They were monomodals and the only difference among the three curves was the higher amount of low retention volume fractions in the chromatogram of the first injected sample, as indicated by the arrow.

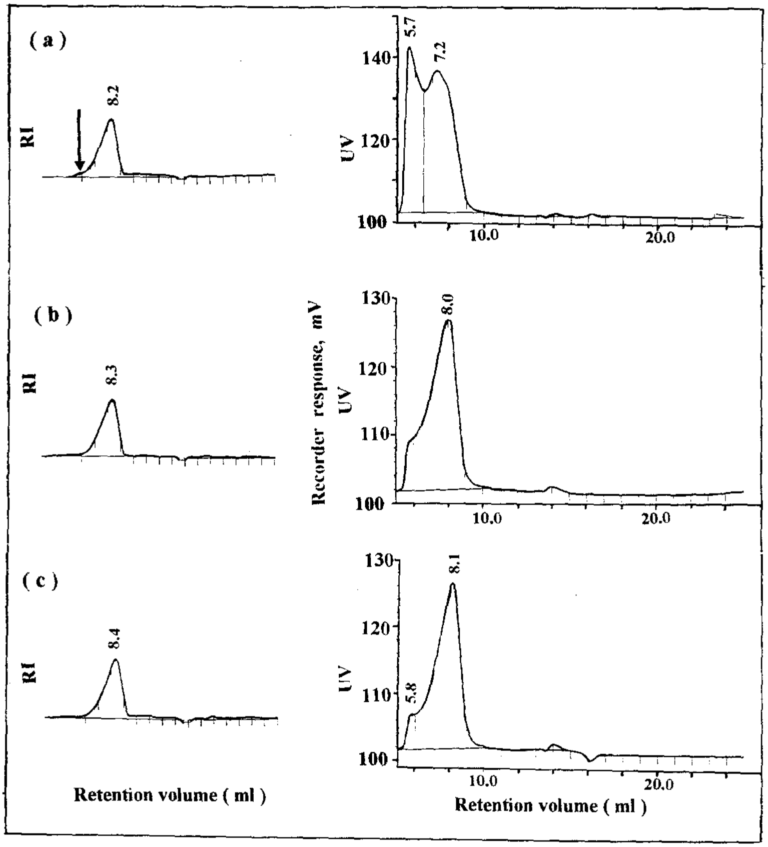

Figure 1. SEC curves obtained by three successive injections of PAN-S in DMA at 30°C. (a) first injection; (b) second injection; (c) third injection. Polymer concentration: 0.2%. Detector attenuation: RI, 8 ; UV, 0.02.

It is interesting to observe that the same behavior was seen for PAN and PAN-A when successive injections were performed, as presented in Figures 2 and 3. In both samples, the UV detection showed multimodal peaks.

Fig. 2 shows the SEC curves obtained in three successive injections of PAN. No change can be seen by RI detection, however, multimodal peaks appeared by UV detection. A polymer fraction with peak maximum around 5.9 ml was eluted earlier and its height also decreased in the second and third injections. It is evident that the concentration of that species, detected only by the more sensitive UV detector, is small as compared to the fraction eluted at 8.4-8.5 ml, detected by both devices. The peak at 8.4 ml did not practically change in height and form from the second injection. Another fraction near 9 ml also decreased with successive injections.

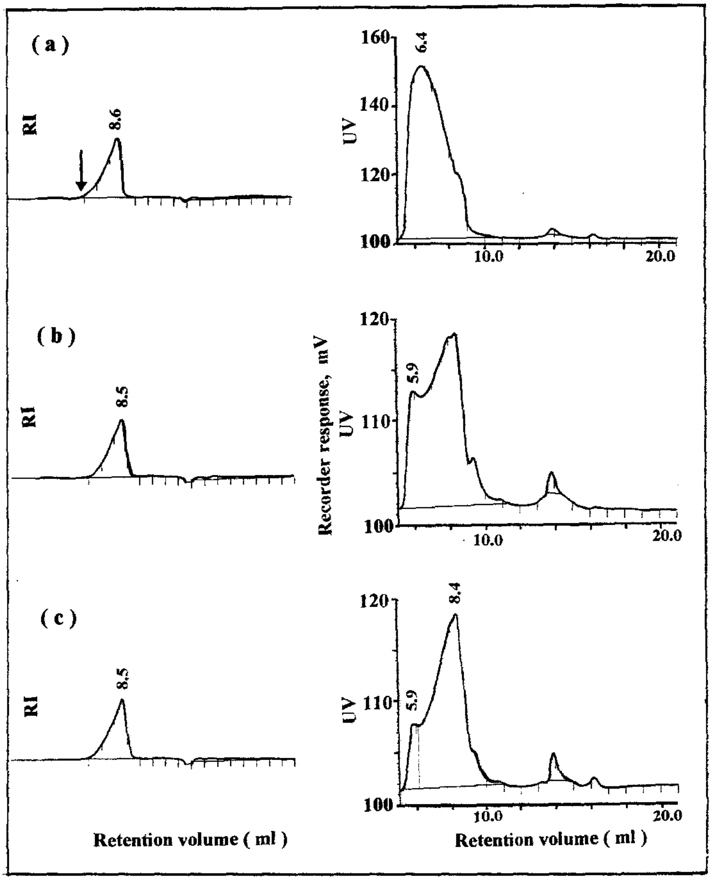

Figure 2. SEC curves obtained by three successive injections of PAN in DMA at 30°C. (a) first injection; (b) second injection; (c) third injection. Polymer concentration: 0.2%. Detector attenuation: RI, 8 ; UV, 0.02.

Fig. 3 reports the SEC curves of PAN-A. For this polymer, multimodal peaks are seen with both detectors. Injecting the sample successively, no change of the curve profile was seen by RI while the curve recorded by UV changed markedly from the first to the second injection, becoming practically unchanged from this injection on. Also for this polymer a small retention volume fraction around 7.4 ml appeared, besides a higher retention volume fraction eluted at 10.1 ml.

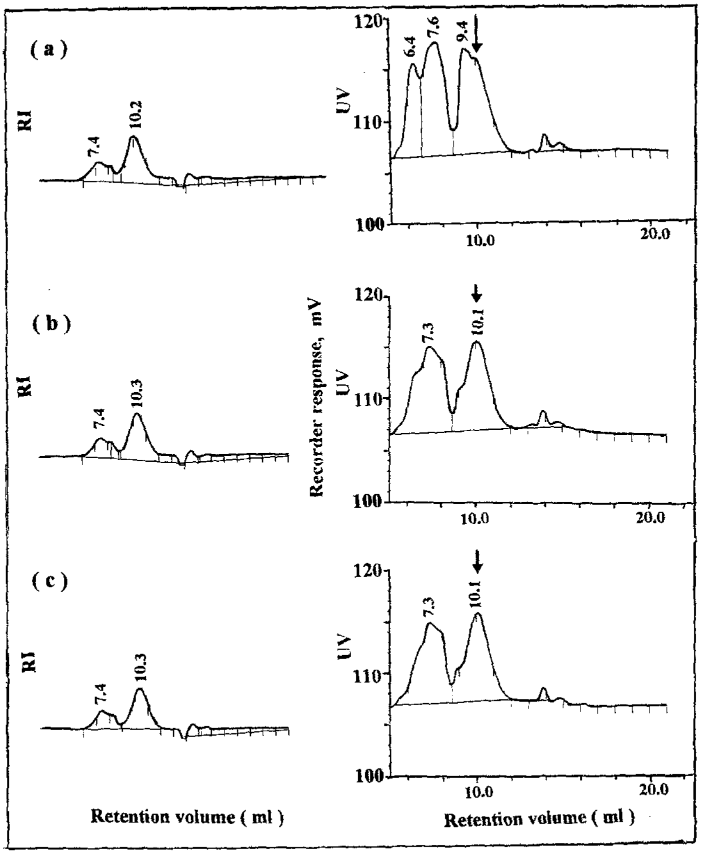

Figure 3. SEC curves obtained by successive injections of PAN-A in DMA at 30°C. (a) first injection; (b) second injection; (c) third injection. Polymer concentration: 0.2%. Detector attenuation: RI, 8; UV, 0.02.

According to the elution volume peak of acrylonitrile polymers against poly(ethylene oxide)(PEO) standards, the molecular weight is over one million. However, the molecular weight determined previously for these samples (8) is in the range of 3.4×10^4 - 2.5×10^5. Thus, all the samples studied had peaks eluting earlier than expected. As reported in our previous paper (7), PAN-S and PAN contain ionic moieties in the polymer. In the case of PAN the ionic groups are present as terminal groups introduced by the initiator (11,12). Thus, it is probable that the characteristic elution behavior reported herein is related to the charged nature of these polymers. Nevertheless, considering the ionic nature of the polymers, it is difficult to explain the multimodality and curve profile modifications of PAN-A. As this polymer was prepared by AIBN in DMF solution, no ionic group in the chain was expected. On the other hand, some amide groups might have been introduced by chain transfer to the solvent. These groups are susceptible to hydrolysis during purification, which could introduce charges. Although ionic groups are present probably in a very small number of chains, these molecules behave like PAN-S and PAN. By interaction with the SEC system, PAN-A can give rise to different chemical species capable of been separated by the column set. Certainly, neutral chains are also present. Indeed, we made a similar observation for the SEC of PAN-A in DMF (7).

From the results it is evident that the peculiar elution behavior of ionic polymers previously observed in DMF is also shown in other N,N-dimethyl substituted amides like DMA. Although the heat decomposition of DMA is not reported in the literature, it is possible that solvent hydrolysis has occurred and the reaction products have become adsorbed on the polystyrene gel particles. In contact with polymers containing ionic groups, electrostatic interactions with the impurities occur, generating polymer complexes able to promote UV absorption. Successive injections clean the polystyrene gel particles by the polymer, which decreases the polymer complex concentration and consequently, the UV peak.

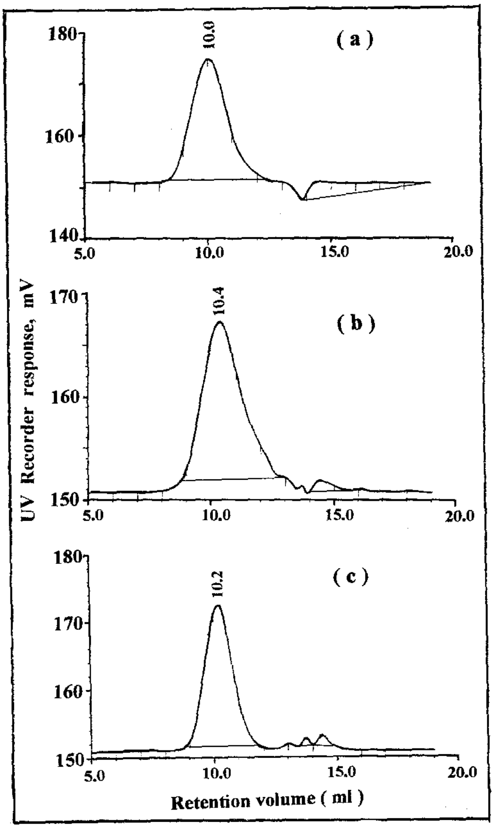

Figure 4. SEC curves in 0.01M LiBr-DMA at 30°C. (a) PAN-S; (b) PAN; (c) PAN-A . Detector attenuation: UV, 0.02.

SEC in 0.01M LiBr-DMA

The effect of electrolyte addition to the solvent on the elution characteristics of acrylonitrile polymers is shown in Fig. 4. In 0.01M LiBr-DMA solution at 30°C, the multimodal peaks disappeared completely and all samples became gaussian. The peaks of PAN-S and PAN were shifted about 2 ml to lower retention volumes as compared to the elution in pure DMA. However, in the case of PAN-A the peak eluted at 10.1 ml in pure DMA did not change the position in the electrolyte containing solvent. This peak was ascribed to neutral molecules. It means that, as expected, the addition of LiBr modified the retention volumes of the charged polymer chains, but did not affect the neutral ones. The same behavior was observed in DMF (7-10). The changes in retention can be understood as an interference on the electrostatic interaction between charged chains and the anionic sites on polystyrene gel, that could cause ionic exclusion phenomena.

CONCLUSION

As in the case of DMF, DMA as eluent turns SEC very sensitive to the presence of charged groups in the chain. Adequate SEC results in amide solvents require much attention to impurities in polymers and solvents. Even trace amounts of ionic groups in the polymer may cause a drastic change in the SEC elution curves.

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