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SIZE EXCLUSION BEHAVIOR OF POLYMERS IN AMIDE SOLVENTS—III. ELUTION CHARACTERISTICS OF ACRYLIC POLYMERS IN N,N-DIMETHYLFORMAMIDE

MARCOS L. DIAS,[a]* ELOISA B. MANO[a] and CHIAKI AZUMA[b]
[a]Instituto de Macromoléculas, Universidade Federal do Rio de Janeiro, C.P. 68525, 21945-970 Rio de Janeiro, RJ, Brazil
[b]The University of the Air, Japan 4-1-1, Shimouma, Setagaya-ku, Tokyo 154, Japan

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Abstract—Nonexclusion effects of acrylic polymers in the size exclusion chromatography using DMF as the mobile phase were investigated. A poly(methyl methacrylate) sample containing sulfate terminal end groups presented marked differences in the elution behavior when compared with the corresponding neutral sample, as in the case of polyacrylonitrile (PAN). It was observed that there is an unexpected small retention in the PS-DVB column and a large peak was detected by UV at 280 nm, which was not detected by the RI detector. The deionization of the DMF extinguished the peak detected by UV and shifted the retention volumes to higher values, but it did not affect the shape and position of the neutral polymer peak. A very strong adsorption effect was shown in the SEC of poly(acrylic acid) (PAA) in deionized DMF. The activity of the sites on the PS-DVB gel in deionized DMF was suppressed by saturation through successive injections of PAA. The elution peculiarities were ascribed to the electrostatic interaction between the charged polymer chains and the ionic species from DMF degradation. The addition of a small amount of LiBr to DMF inhibited the interactions completely. © 1997 Elsevier Science Ltd. All rights reserved

INTRODUCTION

DMF is a very attractive solvent to dissolve polar polymers, even those which are slightly soluble or practically insoluble in solvents such as THF. This is also a powerful solvent for SEC [1]. DMF has been used as the eluent in several SEC studies with a large variety of polar polymers [2–7]. However, problems have been observed with both active and neutral column packings. Abnormal small retention volumes and multimodal curves have been reported for polymers with relatively low molecular weights and expected Gaussian molecular weight distribution curves. Different and conflicting interpretations of these peculiar elution characteristics have been done.

We have systematically investigated the SEC behavior of several polymers in DMF. In previous papers [8, 9] we presented data on acrylonitrile polymers. We reported very small retention volumes and multimodal peaks for copolymers of acrylonitrile with a sulfonate-containing methallyl comonomer (PAN-S). Changes in the shape of the curves and retention volumes could be obtained by the deionization of DMF or by the addition of an electrolyte. The elution peculiarities observed were attributed to the interaction between ionic groups of the polymer chain and substances generated from DMF degradation. The effect was observed even in acrylonitrile homopolymers where the charges were present as end groups.

In this paper we discuss additional evidence of the electrostatic interaction between ionic macromolecules and ionic species in DMF and THF solutions of acrylic polymers containing charged moieties represented by sulfate end groups. The influence of nitrile groups on the peculiar SEC behavior of acrylonitrile polymers, previously reported, was elucidated.

EXPERIMENTAL

Samples and mobile phases

Poly(methyl methacrylate) samples were prepared by two procedures: azo-bis-isobutyronitrile (AIBN) initiated polymerization in DMF at 50° (PMMA-A) and potassium persulfate–sodium metabisulfite redox aqueous system at 40° (PMMA). Poly(acrylic acid) (PAA) was prepared according to the literature [10]. Lithium bromide (Fisher Laboratories) was used as received. DMF was dried over magnesium sulfate and freshly distilled twice at 55°/20 mmHG, using a column packed with steel helices. Deionization was achieved by interposing cation exchange (Amberlite IR-120) and zeolite (molecular seive, 3 Å) columns between the pump and the sample injection valve of the chromatograph.

Size exclusion chromatography

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 wavelength. Two types of Toyo Soda

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*To whom correspondence should be addressed.

TSK-GEL columns were used: Type GMH-6 (60 cm × 7.5 mm ID), comprising two columns packed with a mixture of polystyrene gel (porous diameter, 10^3–10^7 Å; 23,800 TP/columns) designed for DMF solvent; and Type H (30 cm × 7.5 mm ID), packed with a polystyrene gel (exclusion limit: 10^4, NTP = 21,600; and 4×10^5, NTP = 17,000) designed for THF solvent. Both were set in a constant temperature oven. The flow rate of eluents was 1.0 mL/min and the injection volume was 100 μL. Concentrations of 0.2% (w/v) were used as the ordinary condition; in concentration effect studies, a range from 0.1 to 0.8% (w/v) was used. Poly(ethylene oxide) (PEO) and polystyrene (PS) monodisperse standards from Toyo Soda were chosen to calibrate the DMF and THF columns, respectively.

RESULTS AND DISCUSSION

SEC in DMF

The retention volume (V_r) of PMMA prepared by redox persulfate initiation was very small when compared with PMMA-A samples prepared with AIBN. The curve was bimodal, as shown in Fig. 1. Redox initiation usually generates polymers with molecular weights (M_w) in the range 6×10^4 to 3×10^5. Therefore, the small value of V_r was rather unexpected. The same M_w range is shown in polymers obtained by initiation with AIBN in ordinary conditions. Taking PEO as standards, M_w values over 10^6 for PMMA and about 5×10^4 for PMMA-A were found.

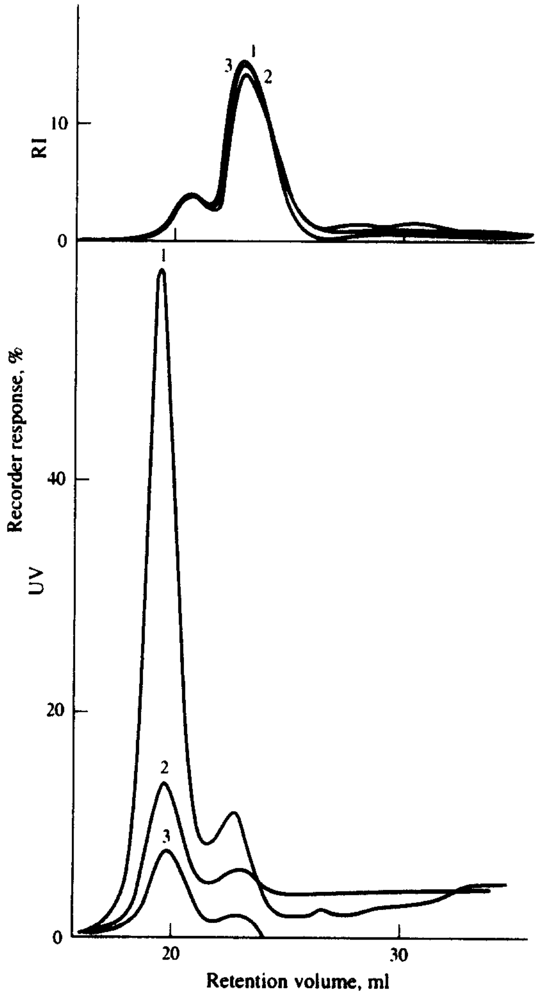

Fig. 1. SEC curves obtained by successive injections of PMMA in DMF at 30°. (1) First injection, (2) second injection and (3) third injection. Polymer concentration: 0.2%. Detector attenuation: RI, 8; UV, 0.02.

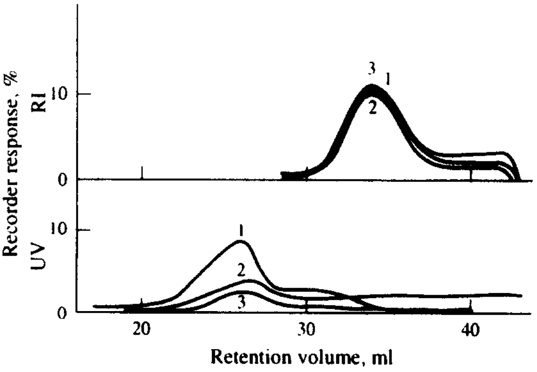

Fig. 2. SEC curves obtained by successive injections of PMMA-A in DMF at 30°. (1) First injection, (2) second injection and (3) third injection. Polymer concentration: 0.2%. Detector attenuation: RI, 8; UV, 0.02.

The figure also shows the SEC curves obtained by successive injections of a fresh solution of PMMA. We observed a very marked difference in the curves with UV and RI type detectors. Using the RI detector we did not observe any change in the shape of the curve, while a decreasing peak was seen by the UV detector. These results were similar to those observed previously with acrylonitrile copolymers containing sulfonate moieties (PAN-S) and polyacrylonitrile with sulfate as terminal groups [8, 9]. PMMA is also expected to have a sulfate group only at the chain end.

Three successive injections of fresh solution of PMMA-A are shown in Fig. 2. Reproducible peaks were obtained by RI detection and no peak detected by UV was observed at the V_r range where the RI peaks appeared. PMMA-A is expected to have nitrile end groups introduced at the polymer chain by the AIBN initiator. Both carbonyl and nitrile chromophoric groups in PMMA-A did not have any detectable UV absorption at 280 nm, as seen in Fig. 2. Nevertheless, a small peak at lower V_r was observed only by the UV detector. The intensity of the peaks decreased in successive injections. This kind of behavior, which was also observed with PMMA, suggested that when the samples passed through the columns the macromolecules could interact with some substance adsorbed on PS-DVB gel. This substance probably comes from the degradation of DMF and is removed gradually from the column by the interaction with the polymer molecules. The interaction products are excluded from the highest size pore of the gel and do not completely transmit UV at 280 nm. It seems that only macromolecules containing ionic moieties can interact with this substance.

PMMA-A did not have any charged groups on the polymer chain. So, the peak detected by UV at the smaller V_r could be attributed to some chains containing ionic groups as impurities. As the sample was synthesized in DMF solution, some amide groups might have arose from chain transfer to solvent. These groups are susceptible to hydrolyze during the precipitation or during the process of dissolution in DMF. Probably chains containing these kinds of groups are present in a negligible amount that cannot be shown by the RI detector, but are recorded by the high sensitivity UV-type detector.

We have also investigated concentration effects on the elution characteristics of the samples in DMF. Figure 3 shows the influence of polymer concentration on their elution curves. The values of V_r correspond to the peak maximum. Curiously, the samples presented different behavior. PMMA showed increasing V_r with an increase of polymer concentration, while PMMA-A remains practically invariable. It seems that the presence of charged end groups in PMMA causes a coil contraction effect. This kind of behavior showed by PMMA is typical of polyelectrolytes in solvents of high dielectric constant. In the same figure it can be seen that the decrease in the hydrodynamic volume with increasing concentration is much more evident in the PAA solutions.

SEC in deionized DMF

Deionized DMF causes several modifications on the elution behavior of the PMMA samples under investigation. Both PMMA and PMMA-A did not show any peak detected by UV at 280 nm. The curve of PMMA was shifted to a higher V_r compared with the retention in nondeionized DMF and exhibited marked tailing. In the case of PMMA-A the curve remained symmetrical and practically no change in V_r was observed, as shown in Fig. 4.

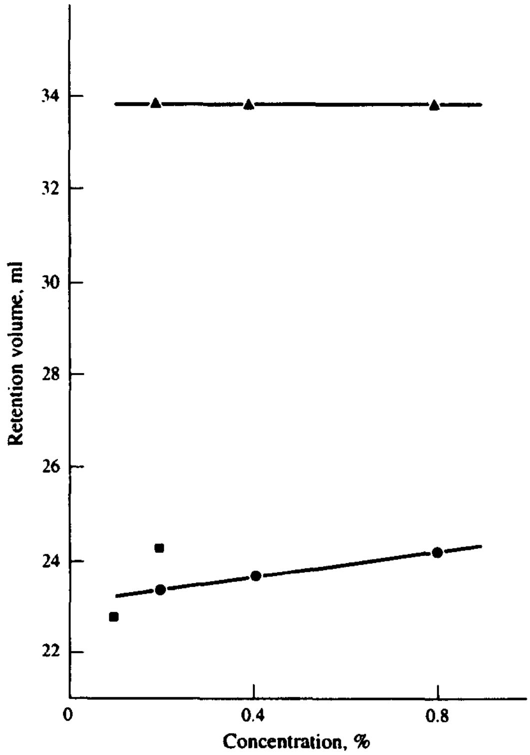

Fig. 3. Peak retention volume as function of concentration of acrylic polymers in DMF at 30°. (●) PMMA; (▲) PMMA-A; (■) PAA.

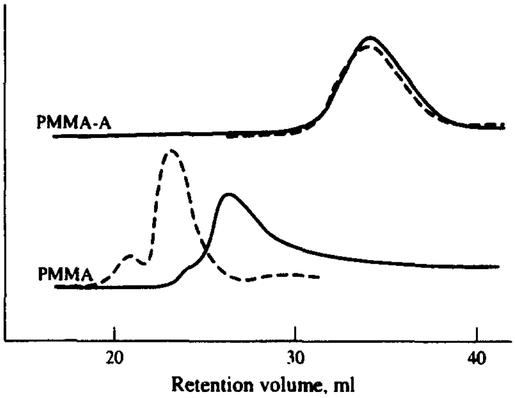

Fig. 4. SEC curves of PMMA samples at 30°. Influence of the deionization of DMF on retention volume and shape of the curves. (---) DMF, (——) deionized DMF. Polymer concentration: 0.2%. RI attenuation: 8.

It has been pointed out that in high molecular weight polymers the end groups have no effect on the solution properties. The main difference between the aforementioned polymers is the end groups. However, we observed a remarkable difference in the SEC elution behavior of the two samples.

For the deionization of DMF we have employed a set of two columns: Amberlite IR-120 and molecular sieve. It is known that DMF is very difficult to purify. Water and amines are the main impurities. DMF decomposes slowly by heating during distillation generating dimethylamine and carbon monoxide. If acidic or basic materials are present this decomposition is catalyzed and a considerable amount of dimethylamine may be produced at lower temperatures. Trace amounts of proton-releasing impurities can also be produced [11]. These kinds of protonic impurities have profound effects on conductimetric studies. Distillation using a steel helices column is a recommended procedure for good purification. However, the complete elimination of water is not possible by means of usual drying agents, which leaves about 0.001 to 0.1% of water in the final DMF [12]. There is even some evidence for an addition compound $DMF \cdot 2H_2O$ which may persist in appreciable concentration at room temperature. So, the presence of molecular sieve also increased DMF drying.

As a matter of fact, the deionization of DMF does not seem to influence the hydrodynamic volume of the samples as PMMA-A is not affected. On the other hand, the disappearance of the peak detected by UV suggests that the UV scattering species is not formed in deionized DMF. So, it seems that the treatment of DMF with the ion exchange and molecular sieve columns removes the chemical species responsible for the small V_r and high UV scattering of PMMA. The results also suggest that the small V_r observed for PMMA in nondeionized DMF can be due to some kind of association caused by electrostatic interaction between ionic species from DMF decomposition and polymer molecules.

We have also analyzed PAA in deionized DMF. The first injected sample was completely adsorbed onto the PS-DVB gel. After several successive injections we obtained peaks with a gradual intensity increase. When the nondeionized DMF was used again as eluent, PAA was not adsorbed by the gel. The result clearly indicates that PS-DVB gel is not a neutral column packing; it has active sites capable of retaining PAA molecules. In nondeionized DMF the active sites are probably nonactivated due to the adsorption of the ionic species that are generated by DMF degradation. We believe that these chemical species are kept adsorbed on the gel due to an equilibrium with the species of the same type in the DMF mobile phase. Deionization of the solvent reduces drastically the amount of these species in the mobile phase, destroying the equilibrium and activating the adsorption sites.

An opposite observation was reported previously [7] for the SEC of quaternized-amine polyester-based polyurethane in pure DMF. An indication of the interaction between the polymer and Styragel columns was evidenced by the large retention volumes and a very small peak in the first run of the sample. When successive runs of the same material were made, the intensity of the peak increased. According to the author, the PS-DVB columns exhibit charged nature in DMF and the active sites on the column must be negative. Based on this premise, cationic polymers are subjected to strong molecular adsorption effect while anionic polymers are repelled by the gel resulting in an ionic exclusion phenomenon. However, the results presented herein suggest that the ionic exclusion is not the only phenomenon in the case of PMMA. If so, the deionization of the solvent should not result in shifting of the peaks to higher V_r. We believe that in this case the absence of ionic impurities in the mobile phase reduces association effects.

The influence of the temperature on the elution behavior of PMMA samples in deionized DMF was also investigated. Figure 5 shows the SEC curves obtained with the column temperature set at 30 and 60°. When increasing column temperature, a reduction of V_r for both samples as a result of the decreasing DMF viscosity and the decreasing of liquid phase volume due to the expansion of polystyrene gel was observed. Nevertheless, the bimodality of PMMA is evidenced as temperature was raised. The appearance of a peak detected by UV only for PMMA was noticed as well. Increasing the column temperature accelerates the process of DMF degradation inside it. The higher concentration of the degraded species favors the association phenomenon with the polymer molecules containing ionic moieties.

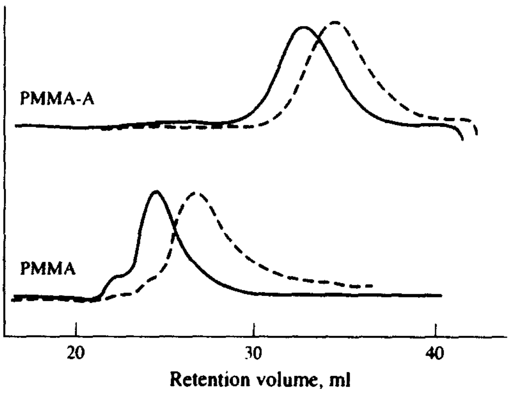

Fig. 5. SEC curves of PMMA samples in deionized DMF. Influence of the temperature on the retention volume and shape of the curves (– – –) 30°, (——) 60°. Polymer concentration: 0.2%. RI attenuation: 8.

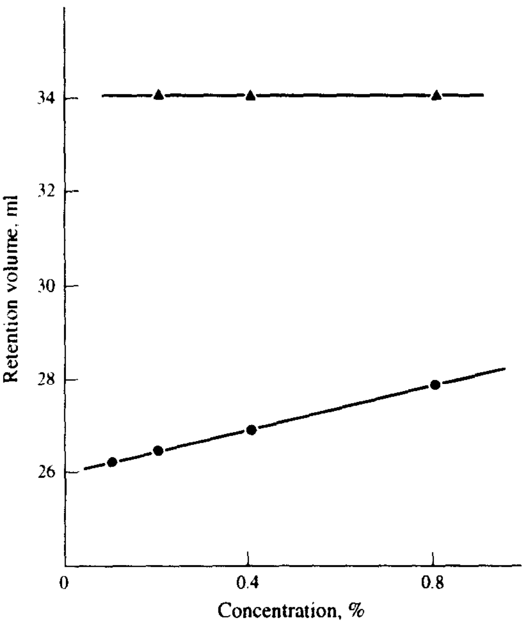

Fig. 6. Peak retention volume as function of concentration of acrylic polymers in deionized DMF at 30°. (●) PMMA; (▲) PMMA-A.

A further investigation on the effect of the polymer concentration on V_r is summarized in Fig. 6. The deionization of DMF did not cause any modification on the behavior of both samples, as previously reported for nondeionized DMF. Practically no change was observed for PMMA-A. However, the slope of the line corresponding to PMMA increased when compared with the nondeionized solvent. It means that although association was reduced, the polyelectrolyte characteristics of PMMA continued to be observed.

SEC in 0.01 M LiBr-DMF

Mobile phases containing dissolved electrolyte have been used to suppress nonexclusion effects in SEC. A small amount of LiBr was added to DMF to observe eventual changes in the elution behavior of PMMA samples. Figure 7 shows the SEC curves of PMMA and PMMA-A in 0.01 M LiBr–DMF at 60°. The addition of the electrolyte to DMF caused a marked change in the elution characteristics of the PMMA with ionic end groups. A large increase in the V_r and a broadening of the peak were observed. Slight modification in the value of V_r and in the curve profile were noticed for PMMA-A. On the other hand, no peak detected by UV at 280 nm is shown with both polymers. The results confirmed that the UV scattering of PMMA in nondeionized DMF did not come from some chemical group in the polymer chain, but arose from the mentioned electrostatic interaction between the macromolecules and impurities in the DMF. The addition of LiBr seems to prevent the formation of the polymer complex.

For both samples, no change in V_r values was observed as the concentration of the injected polymer solution was increased from *ca* 0.2 to 0.8% (w/v). So, the polyelectrolyte behavior shown by PMMA was completely eliminated.

It has been reported [13] that the excluded portion of a polymer sample begins to penetrate in the pores of the packing when the electrolyte concentration reaches 0.0125 M. In the present work it was possible to show that such peculiarities are completely eliminated with LiBr concentration of 0.01 M, as demonstrated by the absence of the peak detected by UV and the shifting of the PMMA peak to a higher V_r.

The effect of the electrolyte in suppressing nonexclusion effects in SEC when DMF is used as the mobile phase has been explained in several different ways. Cha [2] has investigated the SEC of PAN-S adding LiBr to the DMF to eliminate multiple peaks shown in pure DMF. He postulated that the electrolyte neutralizes the ionic groups, avoiding electrostatic repulsion between chain segments. The neutralization allowed the molecules to take on a smaller hydrodynamic volume. Coppola [3] has analyzed PAN polymers and concluded that, due to the highly polar groups, PAN tends to form agglomerates. The shielding of the dipoles on the polymer chain by the LiBr ions causes the association to be broken down. Also, Kenyon [4] related the association of polymers with the presence of nitrile groups in DMF. PMMA shows the peculiar SEC behavior, but has no nitrile group. Therefore, nitrile is not the cause of the abnormality reported. Our results show that LiBr interferes in the interaction between macromolecules containing ionic groups and the impurities present in DMF.

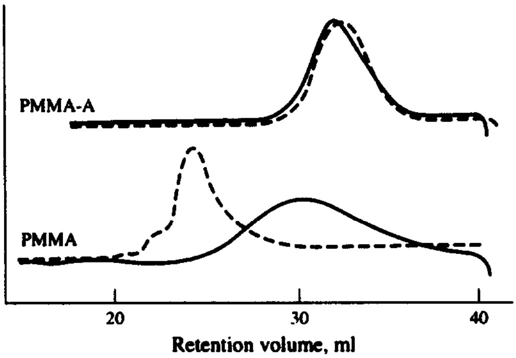

Fig. 7. SEC curves of PMMA samples at 60°. Influence of addition of LiBr to DMF on retention volume and shape of the curves. (---) DMF, (——) 0.01 M LiBr–DMF. Polymer concentration: 0.2%. RI attenuation: 8.

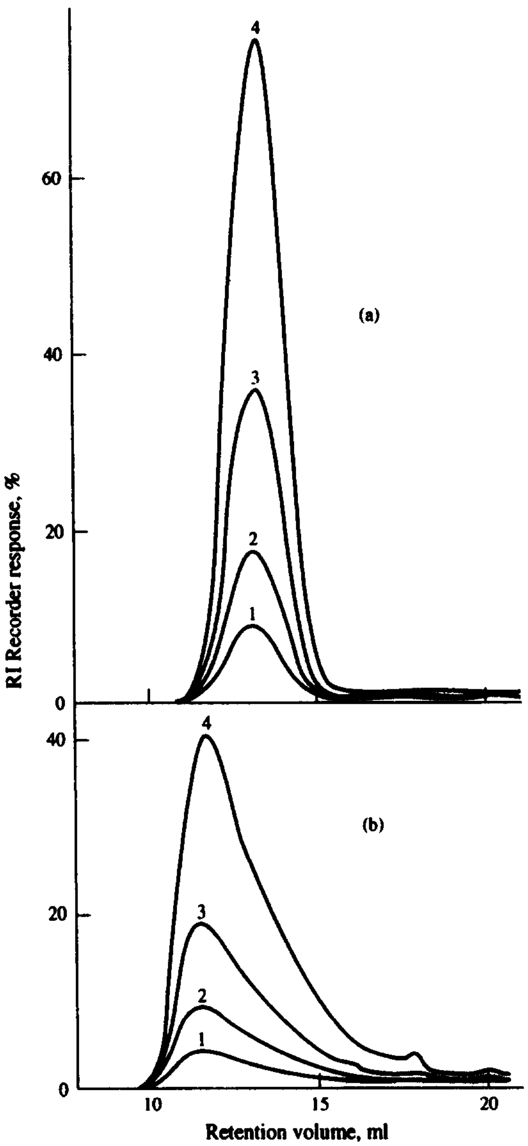

Fig. 8. SEC curves of PMMA samples in THF at 30°. (a) PMMA-A and (b) PMMA. Influence of polymer concentration on retention volume and shape of the curves. (1) 0.1%; (2) 0.2%; (3) 0.4%; (4) 0.8%. RI attenuation: 8.

SEC in THF

In order to confirm the influence of the type of eluent on the previously observed behavior in amide solvents, we studied PMMA samples in THF solution. Both samples presented M_W and distribution curves in the expected range taking into consideration the polymer preparation conditions. Figure 8 shows the curves of PMMA and PMMA-A injected in different concentrations. Changes in the maximum retention volume were small and probably due to overload effects. THF has a lower dielectric constant than DMF. The ionic end groups are less solvated than in DMF and the polyelectrolyte behavior is not so evident. The high V_r of PMMA in THF indicates that the small retention shown in nondeionized DMF is related with the Solvent type and is not controlled by the polymer M_W. This means that the small PMMA retention shown in DMF originates from the formation of polymer complex involving impurities in DMF.

The peculiarities of the SEC can be summarized as:

(1) quaternary ammonium polycations are attracted and adsorbed in DMF [7];

(2) polyacrylic acid and polymers containing carboxyl groups are adsorbed in deionized DMF (this paper) and THF [14];

(3) polymers containing $SO_3^-Na^+$ or $SO_4^-Na^+$ groups, even as chain ends, are eluted earlier [8, 9];

(4) Polyacrylic acid and polymers containing carboxyl groups are eluted earlier in nondeionized DMF.

These peculiarities may be interpreted by considering the existence of divalent or multivalent species generated from DMF decomposition. The mechanism may be speculated as

(i) Formation of possible impurities.

$$HCON(CH_3)_2 \rightarrow CO + HN(CH_3)_2$$

$$HCON(CH_3)_2 \rightarrow HCO^{\cdot} + {}^{\cdot}N(CH_3)_2$$

$$\rightarrow HCO—COH + (CH_3)_2N—N(CH_3)_2$$

$$2HCO^{\cdot} \rightarrow HCO—COH$$

$$HCO—COH + O_2 \rightarrow HOOC—COOH$$

$${}^{\cdot}N(CH_3)_2 \rightarrow HN(CH_3)CH_2^{\cdot}$$

$$2HN(CH_3)CH_2^{\cdot} \rightarrow HN(CH_3)CH_2CH_2(CH_3)NH$$

$$HOOC—COOH + HN(CH_3)CH_2CH_2(CH_3)NH$$

$$\rightarrow {}^-OOC—COO^- + {}^+NH_2(CH_3)CH_2CH_2(CH_3)H_2N^+$$

Divalent quaternary cation

(ii) Adsorption of the cation on nucleophylic polystyrene gel, the counter anion being a free ion.

(iii) Exchange reaction between the ionic impurities from DMF (A^+B^-) adsorbed on PS-DVB gel and the polymer with ionic moieties.

$$(PS\text{-}DVB)A^+B^- + C^+D^- \rightarrow (PS\text{-}DVB)A^+D^- + C^+B^-$$

or

$$(PS\text{-}DVB)C^+B^- + A^+D^-$$

where, C^+D^- = polymer molecules containing ionic groups.

Considering the above exchange reaction, the four aforementioned cases can be explained according to the following schemes:

(a) $(PS\text{-}DVB)A^+B^- + P\text{-}NR_3^+X^-$

$$\rightarrow [(PS\text{-}DVB)A^+B^-][P\text{-}NR_3^+X^-]$$

(b) $(PS\text{-}DVB)A^+B^- + P\text{-}COOH$

$$\rightarrow [(PS\text{-}DVB)A^+B^-][P\text{-}COO^-H^+]$$

(c) $(PS\text{-}DVB)A^+B^- + P\text{-}SO_3^-Na^+$

$$\rightarrow (PS\text{-}DVB)Na^+B^- + P\text{-}SO_3^-A^+$$

(d) $P\text{-}COO^-H^+ + HN(CH_3)_2$

$$\rightarrow [P\text{-}COO^-][{}^+NH_2(CH_3)_2]\,(PS\text{-}DVB)A^+B^-$$

$$+ [P\text{-}COO^-][{}^+NH_2(CH_3)_2]$$

$$\rightarrow (PS\text{-}DVB)\,[NH_2(CH_3)_2]^+B^- + [P\text{-}COO^-]A^+$$

where, P = polymer chain.

If A^+ is a divalent cation, $[P\text{-}SO_3^-]A^+$ and $[P\text{-}COO^-]A^+$ of (c) and (d) give rise to high hydrodynamic volume associated species that are excluded from the largest pore of the column.

CONCLUSIONS

The polyelectrolyte effect is observed even in acrylic polymers containing only ionic end groups in DMF, as shown by the results reported in this paper. DMF degradation products interact electrostatically with ionic groups in the polymer, causing a peculiar SEC elution behavior. These products are generated inside the columns along with the time even at room temperature and remain adsorbed on the PS-DVB gels. The removal of such products from the columns by the polymer is an indication that PS-DVB gels are not an inert packing in the case of DMF. Polymers with ionic moieties in the chain show small retention volumes and multimodal curves resulting in erroneous molecular weight determinations. The deionization of DMF modifies the shape and position of the peaks. The interaction effects are completely suppressed by the addition of a small amount of a strong electrolyte such as LiBr to DMF.

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REFERENCES

1. Dubin, P. L., Koontz, S. and Wright, K. L., *J. Polym. Sci., Polym. Chem. Ed.*, 1977, **15**, 2047.
2. Cha, C. Y., *J. Polym. Sci.* 1969, **B7**, 343.
3. Coppola, G., Fabri, P., Pallesi, B. and Bianchi, U., *J. Appl. Polym. Sci.*, 1972, **16**, 2839 (1972).
4. Kenyon, A. S., and Mottus, E. H., *Appl. Polym. Symp.*, 1974, **25**, 57.
5. Mori, S., *Anal. Chem.*, 1983, **55**, 2414.
6. Domard, A., Rinaudo, M. and Rochas, C., *J. Appl. Polym. Sci., Polym. Phys.*, 1979, **17**, 673.
7. Hann, N. D., *J. Polym. Sci., Polym. Chem. Ed.*, 1977, **15**, 1331.
8. Azuma, C., Dias, M. L. and Mano, E. B., *Macromol. Chem., Macromol. Symp.*, 1986, **2**, 169.
9. Azuma, C., Dias, M. L. and Mano, E. B., *Polym. Bull.*, 1995, **34**, 585.
10. Bugni, E. A., Lachtermacher, M. G., Monteiro, E. E. C., Mano, E. B. and Overberger, C. G., *J. Polym. Sci., Polym. Chem. Ed.*, 1986, **24**, 1463.
11. Thomas, A. B., and Rochow, E. G., *J. Am. Chem. Soc.*, 1957, **79**, 5, 1843.
12. Perrin, D. D., Armarego, W. L. F. and Perrin, D. R., *Purification of Laboratory Chemicals*, p. 224. Pergamon Press, Oxford 1980.
13. Scheuing, D. R., *J. Appl. Polym. Sci.*, 1984, **29**, 2819.
14. Bugni, E. A., *Master Thesis*, Instituto de Macromoléculas, Universidade Federal do Rio de Janeiro, Rio de Janeiro, 1985.