

Viscometric Behavior of Quaternized Polysulfones

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ABSTRACT: The effects of the quaternary ammonium group size and the solvent nature and composition on the viscometric behavior of several quaternized polysulfones (PSFs) were investigated. The solution viscosity of the cationic PSFs was determined over a wide concentration range in *N,N*-dimethylformamide (DMF). The experimental data were plotted in the terms of the Fedors equation. It was found that the intrinsic viscosity values were strongly dependent on the size of quaternary ammonium groups. The viscosity of PSF quaternized with *N,N*-dimethylbutylamine (PSF-DMBA) was also measured in the mixed solvents consisting of DMF/methanol and DMF/diethylether. Polyelec-

trolyte behavior was observed for PSF-DMBA in the mixtures of DMF/methanol for all compositions employed and in the mixtures of DMF/diethylether with the diethylether content as high as 25 vol %. The viscosity decrease and precipitation in the polymer solution with increasing diethylether content was attributed to the dipole–dipole attraction between ion pairs formed in a less polar medium. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 465–469, 2003

Key words: quaternized polysulfones; solution viscosity; mixed solvent; conformational change

INTRODUCTION

Polysulfones (PSFs) and their derivatives have shown many interesting properties that have led to a wide spectrum of industrial and environmental applications.^{1–7} The PSFs functionalized with ammonium and pyridinium groups are particularly effective for chelating of heavy metals, the removal of viruses from water by filtration, or fabrication of membranes.^{8,9} This type of polymer combines both the characteristics of PSF (good thermal and chemical stability, mechanical strength) and those of the polyelectrolytes. It is well known that polyelectrolytes are polymers with ionizable groups that dissociate in polar solvents into charges bound to the chain and counterions in solution. The presence of charged groups in hydrophobic PSFs may have serious effects on their solution properties. From theoretical and experimental viewpoints it is of interest to consider dilute quaternized PSF solutions in order to find the factors that affect the polymer conformation. Viscometry is the method of choice to study the conformational changes of polymers in various solvents.¹⁰ The viscosity depends on many parameters such as the chemical structure of the macroion and its size and charge density, the ionic strength of the solution, and the solvent polarity.^{11–13} Reports on the viscometric behavior of PSFs are very scarce.^{14,15} This article deals with the influences of the

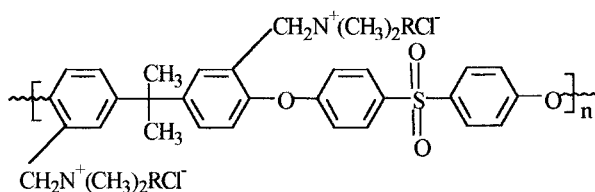
quaternary ammonium group's size and the solvent nature and composition on the viscometric behavior of some quaternized PSFs in order to obtain information about their chain conformation in the salt-free organic solvents *N,N*-dimethylformamide (DMF), methanol, and diethylether and in the mixed solvents DMF/methanol and DMF/diethylether. The viscometric behavior of this kind of quaternized PSF solution has not been investigated so far.

EXPERIMENTAL

Materials

Quaternized PSFs were synthesized by reacting chloromethylated PSF (PSF-CM) with *N,N*-dimethylalkylamines having different alkyl chain lengths: *N,N*-dimethylbutylamine–polymer (PSF-DMBA), *N,N*-dimethyloctylamine–polymer (PSF-DMOA), and *N,N*-dimethylhexadecylamine–polymer (PSF-DMHA). PSF-CM was synthesized, purified, and characterized as described previously.¹⁶ Starting from a PSF-CM with a weight-average molar weight (M_w) of 39,500 and a polydispersity (M_w/M_n) of 2.863, three cationic polymers were obtained that possess different size quaternary ammonium groups. The quaternization reaction was performed in DMF at 80°C using a PSF-CM/tertiary amine molar ratio of 1:1.2. Their general structure is presented in Scheme 1. The quaternary polymers were isolated from the reaction medium by precipitation in diethylether, washed 3 times with diethylether, and dried for 48 h under a vacuum at room temperature. Polycations were characterized by the content in ionic chlorine (Cl_i ; determined by potenti-

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R=(CH₂)₃CH₃, polycation PSF-DMBA; R=(CH₂)₇CH₃, polycation PSF-DMOA;
R=(CH₂)₁₅CH₃, polycation PSF-DMHA

Scheme 1 The general structure of the polycations.

metric titration with 0.02 aqueous AgNO₃ solution): Cl_i = 6.71% for PSF-DMBA, Cl_i = 6.09% for PSF-DMOA, and Cl_i = 4.97% for PSF-DMHA.

The methanol, DMF, and diethylether solvents were analysis reagents and were used without further purification.

Measurements

The PSF-CM molar mass was determined by GPC with a chromatograph PL-EMD950 evaporative mass detector using polystyrene standards.

The viscosity measurements of the quaternized PSFs in DMF, methanol, and solvent mixtures of DMF/methanol and DMF/diethylether were carried out at 25°C with an Ubbelohde viscometer with internal dilution in a thermostated bath; the viscometer allows a reproduction of the flow times with an accuracy of 0.03 s. The solution was maintained about 10 min prior to the measurements for temperature equilibration. All viscosity measurements were repeated at least in duplicate. The reproducibility of the data was within ±3%.

RESULTS AND DISCUSSION

The incorporation of charges in PSFs has a number of affects on their solution properties. In addition to attractive hydrophobic interactions, one expects another contribution arising from repulsive electrostatic interactions. Figure 1 shows the viscosity behavior of the quaternized PSFs in DMF, together with the original PSF-CM.

Three major comments are appropriate. First, a slight linear decrease of the reduced viscosity values (η_{sp}/C) occurred with dilution in the case of PSF-CM, as expected for a neutral polymer. Second, all quaternized PSFs demonstrated polyelectrolyte behavior, that is, the η_{sp}/C values increased with decreasing polymer concentration. This typical polyelectrolyte behavior occurs because the ionizable groups on the polymer side chain can dissociate in the solvent, which has a modest polarity. Thus, the intramolecular repulsive interactions between charged groups along

the chain increase and the expansion of the polymer chain consequently takes place. Third, PSF-DMBA exhibits higher reduced viscosity values than the other polymers under study, indicating a more expanded chain in the case of this polyelectrolyte. A remarkable decrease of the η_{sp}/C values is also noticed in the case of PSF-DMOA and PSF-DMHA. A longer alkyl substituent of quaternary ammonium groups brought about an intensification of hydrophobic interactions between side chains. At a low polyion concentration where intramolecular associations prevail over the intermolecular ones, the hydrophobic interactions determined the decrease of the dimension of the polymeric coil and consequently the reduced viscosity.

Obviously it is not possible to extrapolate the reduced viscosity to zero concentration in order to determine the intrinsic viscosity ($[\eta]$). This problem can be solved either by addition of low molar mass electrolyte or by means of empirical equations, like the

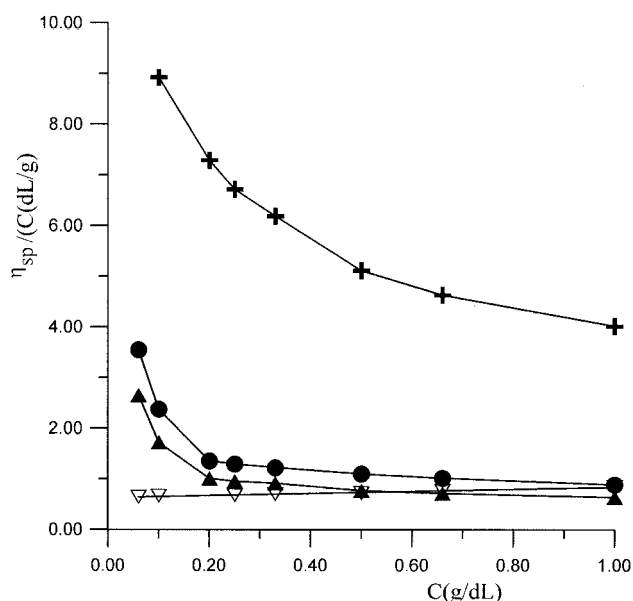


Figure 1 The variation of the reduced viscosity (η_{sp}/C) versus the concentration (C) of PSFs in DMF at 25°C: (+) PSF-DMBA, (●) PSF-DMOA, (▲) PSF-DMHA, and (▽) PSF-CM.

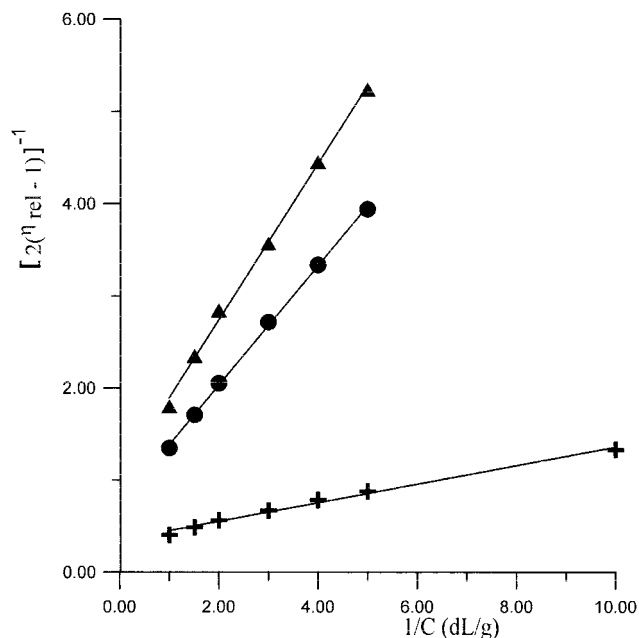


Figure 2 The representation of the Fedors equation for (+) PSF-DMBA, (●) PSF-DMOA, and (▲) PSF-DMHA.

Fuoss¹⁷ and Fedors equations.¹⁸ The curves shown in Figure 1 were linearized applying Fedors equation:

$$1/[2(\eta_r^{1/2} - 1)] = 1/[\eta] \times C - 1/[\eta] \times Cm \quad (1)$$

where *Cm* is a polymer concentration parameter.

As can be observed in Figure 2, the straight lines are obtained for all polycations in the concentration range we used, allowing us to calculate $[\eta]$. The applicability of the Fedors equation to describe the viscosity of the polymer solution was also found in the case of other polyelectrolytes.^{19,20}

The variation of the $[\eta]$ value with the length of the alkyl chains of quaternized units is illustrated in Figure 3. One can see the greatest $[\eta]$ value decrease occurred when increasing the size of the alkyl chain from PSF-DMBA to PSF-DMOA; the lower $[\eta]$ values in the case of the latter two polycations confirms that the macroion coils assume more compact conformations in the case of the greater size of the quaternary ammonium groups.

We also studied the viscometric behavior of the PSF-DMBA polycation in the mixtures of DMF/methanol and DMF/diethylether in order to observe the conformation changes of the macroion when changing the solvent composition. In a polyelectrolyte solution, the solvent quality is determined by both the affinity of the solvent to the neutral polymer and the solvation of the ionic species. As can be seen in Figure 4, PSF-DMBA shows polyelectrolyte behavior both in methanol and in the mixed solvent DMF/methanol at all employed compositions. According to Figures 1 and 4, the reduced viscosity values are higher in DMF than in

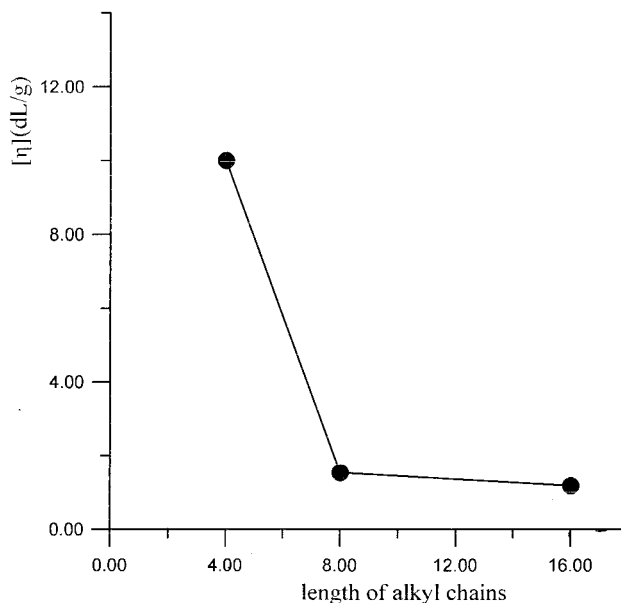


Figure 3 The variation of the intrinsic viscosity ($[\eta]$) with the length of the alkyl chains of quaternized units.

methanol. Comparing the dielectric constants of DMF ($\epsilon = 36.7$) and methanol ($\epsilon = 32.7$), we observe that there is only a small difference in their values and thus assume that the ionic dissociation and consequently the electrostatic repulsive interactions between the ionized groups are similar in the two solvents. The higher reduced viscosity values for PSF-DMBA in DMF than methanol may be ascribed to the better affinity of the former solvent for the neutral polymer. The strong polymer-solvent interaction is also sus-

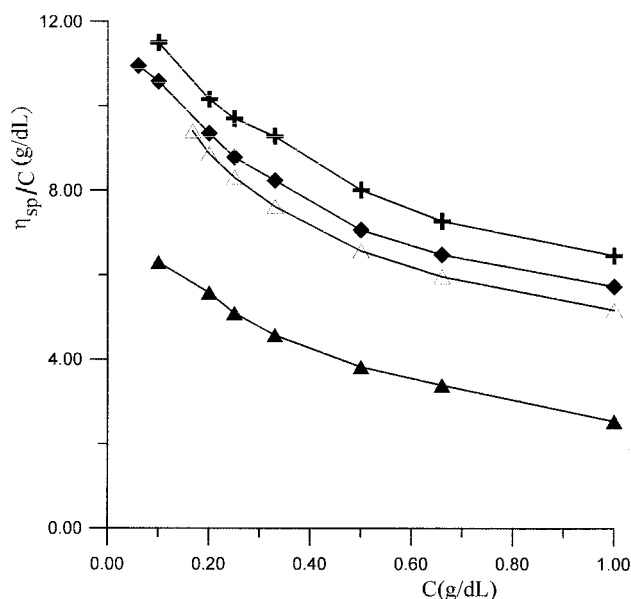


Figure 4 The variation of the reduced viscosity (η_{sp}/C) versus the concentration (*C*) of PSF-DMBA in DMF/methanol mixtures: (▲) methanol, (Δ) 25/75, and (◆) 75/25, and (+) 50/50.

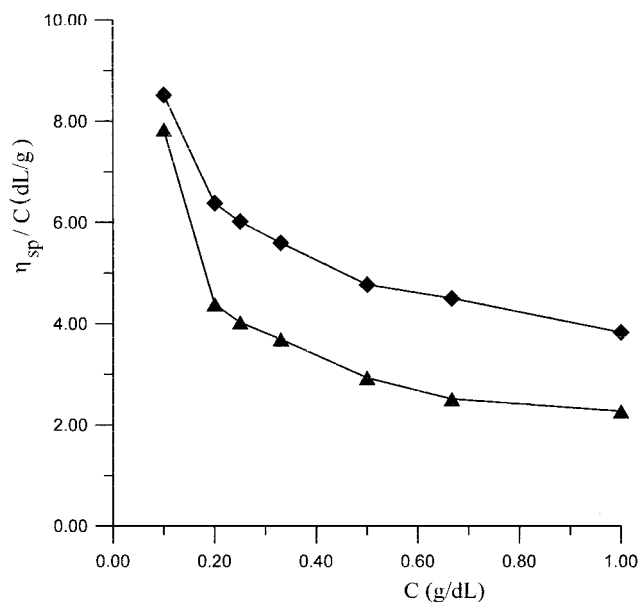


Figure 5 The variation of the reduced viscosity (η_{sp}/C) versus the concentration (C) of PSF-DMBA in DMF/diethylether mixtures: (\blacklozenge) 90/10 and (\blacktriangle) 75/25.

tained by the low value of the Huggins constant ($k_H = 0.222$) as obtained in PSF-CM in DMF (cf. Fig. 1). The greater reduced viscosity values for polyelectrolytes in mixtures of methanol/DMF reflect the greater solvation power of the mixed solvents for the PSF-DMBA than the solvents alone. Among the mixed solvents, the 50/50 DMF/methanol mixture is the best solvent for polyion chains. The increase of either the methanol or DMF content in the mixture led to the decrease of the reduced viscosity values as the solvent composition approaches that of the pure solvent.

Next we show the variation of the reduced viscosity as a function of the polymer concentration in the mixtures of DMF/diethylether (Fig. 5). Because diethylether is a nonsolvent for this polymer, measurements were performed to determine the diethylether content in the mixture for which the precipitation of the polyelectrolyte takes place. One can notice the polyelectrolyte behavior of PSF-DMBA in DMF/diethylether with a diethylether content as high as 25 vol %. When the diethylether content is increased in the mixture, a loss in viscosity is seen as the solvent gets poorer and the chains form more compact conformations. The precipitation of PSF-DMBA was observed when the diethylether content in the DMF/diethylether mixture was raised beyond 25 vol %; the precipitation in the polymer solution with increasing diethylether content can be attributed to the dipole-dipole attraction between ion pairs formed in the less polar medium ($\epsilon_{\text{diethylether}} = 4.2$).

The viscometric data of PSF-DMBA in DMF/methanol and DMF/diethylether fits well with the Fedors equation (Figs. 6, 7).

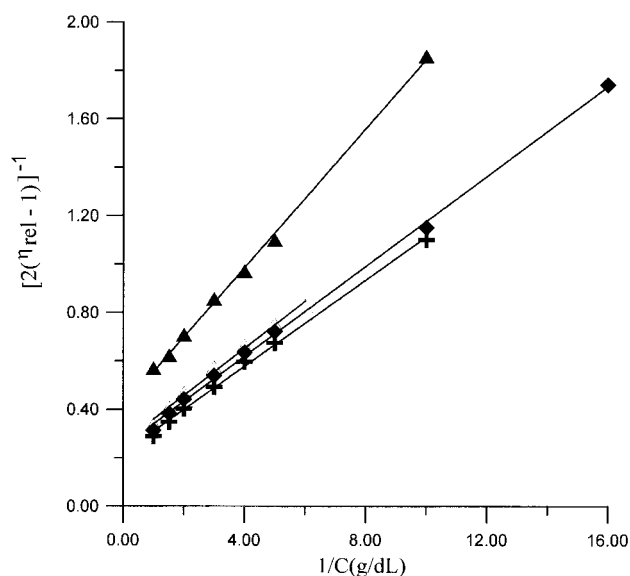


Figure 6 The representation of the Fedors equation for PSF-DMBA in DMF/methanol mixtures: (\blacktriangle) methanol, (\triangle) 25/75, (\blacklozenge) 75/25, and ($+$) 50/50.

It is a well-known fact that polyelectrolyte solutions reach the semidilute regime even at low concentration because of the large expansion of the macroions. The overlap concentration values (c^*) that separate the semidilute/dilute regimes²¹ was determined both experimentally, as the concentration for which the vis-

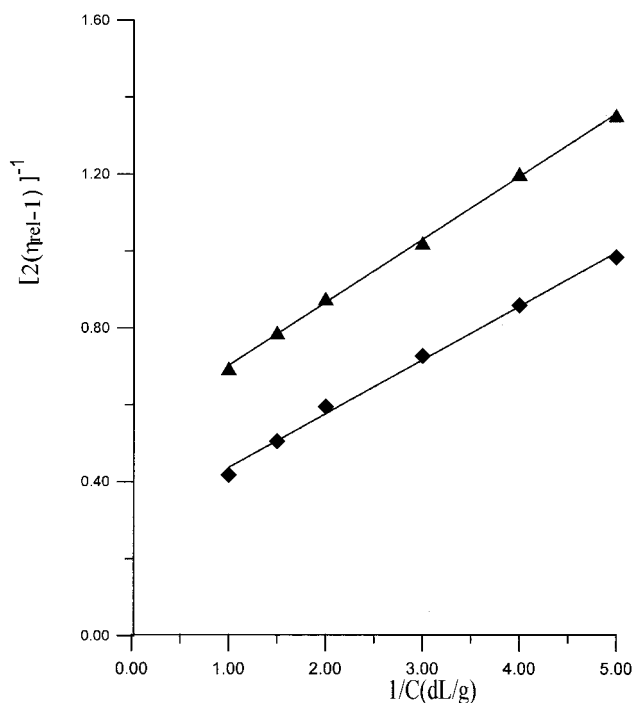


Figure 7 The representation of the Fedors equation for PSF-DMBA in DMF/diethylether mixtures: (\blacklozenge) 90/10 and (\blacktriangle) 75/25.

TABLE I
Intrinsic Viscosity and Overlap Concentration for PSF-DMBA in DMF/Methanol Mixtures

DMF/Methanol (vol 1%)	$[\eta]_{\text{Fed}}$ (dL/g)	$C^* = 1/[\eta]_{\text{Fed}}$ (g/dL)	C^*_{exp} (g/dL)
0	6.98	0.1430	0.1520
25	10.27	0.0973	0.0971
50	11.23	0.0890	0.0940
75	10.77	0.0928	0.0901
100	10.00	0.1000	0.1080

cosity is twice the solvent viscosity,²² and by means of the following equation²³:

$$c^* = 1/[\eta] \quad (2)$$

Table I presents the $[\eta]$ and c^* values for PSF-DMBA in various mixtures of DMF/methanol. The decrease of $[\eta]$ and the anticipated increase of c^* confirm the reduction of the hydrodynamic dimension of the macromolecular coils as the solvent quality becomes poorer. It is also important to note the agreement between the c^* values obtained (cf. Dobrynin et al.²² and Reed et al.²³).

CONCLUSIONS

The viscosity of some quaternized PSFs in DMF was determined. All solutions of polymers showed polyelectrolyte behavior, that is, a typical upturn of the $\eta_{\text{sp}}/C = f(C)$ plots at low concentration. The reduced viscosity values decreased with the increase of the size of alkyl chains because of the intensification of the intramolecular interactions of hydrophobic side chains. Polyelectrolyte behavior was also found for PSF-DMBA in the mixtures of DMF/methanol for all compositions employed and in the mixtures of DMF/diethylether with a diethylether content as high as 25 vol %. A further increase in the diethylether content

brought about phase separation in the solution of PSF-DMBA. The η values decreased as the solvent quality became poorer. The agreement between the c^* values obtained (cf. Dobrynin et al.²² and Reed et al.²³) was noted for PSF-DMBA in the mixtures of DMF/methanol.

References

- Kahana, N.; Arad-Yellin, R.; Deshe, A.; Warshawsky, A. *J Polym Sci Polym Chem Ed* 1990, 28, 3303.
- Airinei, A.; Butuc, E.; Cozan, V.; Ardeleanu, R. *Appl Organometal Chem* 1998, 12, 485.
- Tanaka, N.; Iijima, T.; Fukuda, W.; Tomoi, M. *Polymer Int* 1997, 42, 95.
- Ueda, M.; Toyota, H.; Ouchi, T.; Sugiyama, J.-I.; Yonetake, K.; Masuko, T.; Teramoto, T. *J Polym Sci Polym Chem Ed* 1993, 31, 853.
- Schult, K. A.; Paul, D. R. *J Polym Sci Polym Phys Ed* 1996, 34, 2805.
- Ting, Y.-P. R.; Hancock, L. F. *Macromolecules* 1996, 29, 2619.
- Hancock, L. F. *J Appl Polym Sci* 1997, 66, 1353.
- (a) Hyun, J.-H.; Jeon, J.-Y.; Tak, T.-M. *Membrein* 1996, 6, 79; (b) Hyun, J.-H.; Jeon, J.-Y.; Tak, T.-M. *Chem Abstr* 1996, 125, 7.
- Summers, G. J.; Ndawuni, M. P.; Summers, C. A. *Polymer* 2001, 42, 397.
- Forster, S.; Schmidt, M. *Adv Polym Sci* 1995, 120, 51.
- McCormick, C. L.; Salazar, L. C. *J Polym Sci Polym Chem Ed* 1993, 31, 1099.
- Ise, N. *Proc Jpn Acad* 1998, 74, 192.
- Ohtani, N.; Inoue, Y.; Kanero, Y.; Okumara, S. *J Polym Sci Polym Chem Ed* 1995, 33, 2449.
- Allen, G.; McAinsh, J.; Strazielle, C. *Eur Polym J* 1969, 5, 319.
- Maes, C.; Godard, P.; Daoust, D.; Legras, R. *Macromol Chem Phys* 1995, 196, 1523.
- Avram, E. *Polym Plast Technol Eng* 2001, 40, 275.
- Fuoss, R. M.; Strauss, U. P. *J Polym Sci* 1948, 3, 246.
- Fedors, R. F. *Polymer* 1979, 20, 225.
- Ghimici, L.; Popescu, F. *Eur Polym J* 1998, 34, 13.
- Dragan, S.; Ghimici, L. *Polymer* 2001, 42, 2887.
- Mattoussi, H.; O'Donohue, S.; Karasz, F. E. *Macromolecules* 1992, 25, 743.
- Dobrynin, V. A.; Colby, R. H.; Rubinstein, M. *Macromolecules* 1995, 28, 1859.
- Reed, W. F.; Ghosh, S.; Medjahdi, G.; Francois, J. *Macromolecules* 1991, 24, 6189.