polymer

Polymer 40 (1999) 4965–4970

Polymer Communication

Nitration of polyethersulfone by ammonium nitrate and trifluoroacetic anhydride

András Botvay*, Árpád Máthé, László Pöppl

Institute of Chemistry, Eötvös Loránd University, P.O. Box 32, H-1518 Budapest 112, Hungary

Received 7 November 1998; accepted 1 December 1998

Abstract

Victrex polyethersulfone was nitrated efficiently and controllably on its deactivated aromatic ring with a mixture of ammonium nitrate and trifluoroacetic anhydride. The products were characterized by elemental analysis and IR spectroscopy, their thermal properties were investigated by TGA and DSC methods. A comparison is made between this procedure and the analogous nitration of Udel polysulfone.

Keywords: Polyethersulfone; Nitration; Thermal properties

1. Introduction and results

Polysulfones are important engineering polymers with excellent thermal, oxidative, and hydrolytic stability. The two best known types of them are illustrated in Fig. 1. Beyond several technical and medical applications, they are significant mainly as semipermeable membrane materials.

Chemical modification of the existing macromolecules enables us to produce specialty polymers with desirable chemical and physical properties. In recent years, there has been a dramatically growing research activity in the area of polymer analogous reactions. The variety of modified polymers, regarding both the backbone and the array of functionalities, as well as their applications have increased considerably, including ion exchange resins, chelating materials, polymeric reagents, protective groups and supports for solid phase synthesis, inert carriers for reactive substrates, and permselective materials for membrane separations. Focusing on the aromatic polymers, it can be established that the aromatic ring is usually a favourable structural portion for chemical modification, however, its reactivity is naturally influenced by its substituents. Polystyrene should be highlighted here as its rings can be easily functionalized (electrophilicly and by lithiation as well) and the main chain has enough stability to permit chemical transformations without chain scission. A notable part of work on functional group polymers in the past decades has been related to a multiplicity of polystyrene derivatives synthesized by chemical modification.

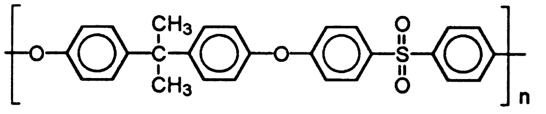
In contrast to polystyrene, where the hydrocarbon main chain activates the aromatic ring for electrophilic substitution, condensation polymers exhibit varying reactivity in these reactions depending on their linking units. For instance, the aryloxy groups, present in the backbone of many condensation polymers, facilitate the electrophilic attack in the *ortho* position while other groups, such as sulfone, deactivate the adjacent rings. Comparing the two types of polysulfones in Fig. 1, PSU seems to be more amenable to electrophilic elaboration on its bisphenol A moiety. Indeed, a variety of functional groups were introduced onto PSU by electrophilic substitutions such as sulfonation [1], bromination [2], halomethylation [3], nitration [4], and by further conversions of the primary derivatives. However, there appears little report on the chemical modification of PES as its rings are strongly deactivated by the electron withdrawing sulfone groups, and this impeding effect is just hardly decreased by the activating aryloxy groups. Recently, the bromination of PES was reported by our laboratory [5], using no polymer solvent in the reaction. (A more detailed survey of PSU modifications and reactivity comparison of PSU and PES are given in Ref. [5].)

Let us pay particular attention to nitration and nitrated polysulfones. Nitrated polymers are important mostly as intermediates for the amine derivatives, but introduction of the bulky and polar nitro group to the main chain affects the gas sorption and permeation properties, and hence, has significance in itself, too. However, the fuming HNO_3 or

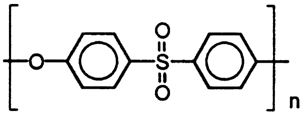
---

* Corresponding author.

0032-3861/99/$ - see front matter © 1999 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(98)00841-6



polysulfone, PSU (Udel)



polyethersulfone, PES (Victrex)

Fig. 1. The two best known types of polysulfones.

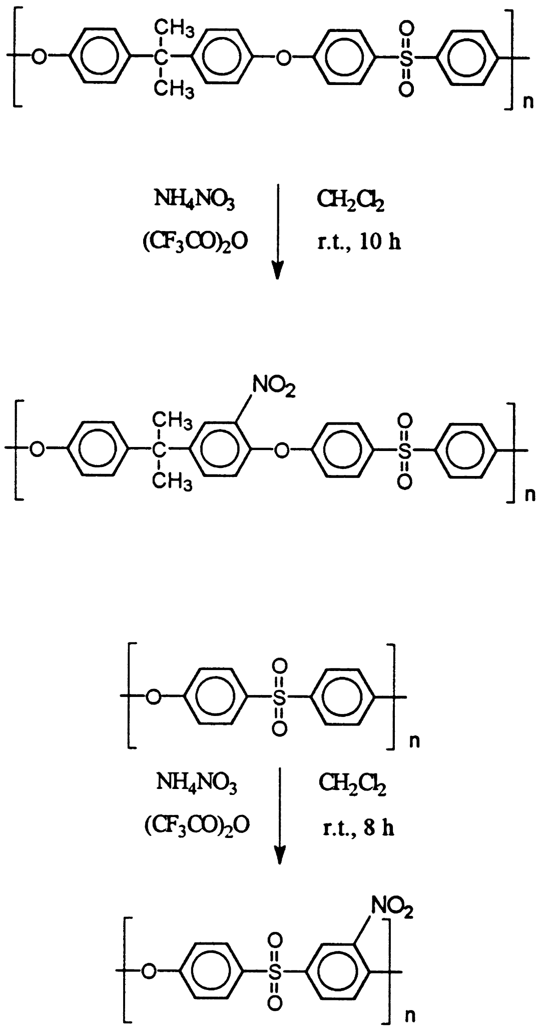
$HNO_3 + H_2SO_4$/oleum mixture, extensively used for the nitration of aromatic compounds, tend to degrade condensation polymers. Crivello [6] described an alternative mild – or at least milder – nitration method, especially for polymers, employing ammonium nitrate (AN) and trifluoroacetic anhydride (TFAA) to generate NO_2^+ cations. This electrophilic substitution route was effective for polystyrene, poly(phenylene oxide)s and polycarbonate (with slight degradation), and later it was utilized by Daly et al. [4] to nitrate polysulfone (Udel type) relatively mildly, but efficiently. The NO_2 groups occupy the *ortho* ether position in the bisphenol A moiety of the repeat unit (as expected and confirmed by NMR [7]). The degree of substitution (DS), i.e., the average number of substituents on a repeat unit can range from 0 to 2; however, it appeared that the reasonable upper limit of the DS is only about 1 as severe degradation occurs at higher DS [8]. The chain scission is promoted by trifluoroacetic acid which is produced during the reaction. (The same was observed when poly(2,6-dimethyl phenylene oxide), PPO, was nitrated by this method, even at lower DS, i.e., above 0.15 [7].) These facts indicate the bounds of this procedure. The phenylsulfone part of the Udel repeat unit was inert in this reaction (and generally in other electrophilic substitutions, too). A nitrated polysulfone containing NO_2 groups *meta* to the sulfone linkage (DS = 1.92) could be prepared only by nitrating 4-chlorophenyl sulfone and then condensing the product with bisphenol A [8]. It was difficult to reduce nitrated polysulfones to amine; after all, stannous chloride and hydrochloric acid proved to be effective agents.

Ghosal et al. [7,8] studied the gas permeability, solubility and diffusivity of unmodified and nitrated polysulfones for CO_2, CH_4, O_2 and N_2. They found that the permeability and diffusivity decreased for all gases as the DS increased and hence, fractional free volume of the polymer and torsional mobility of the chain decreased. These results suggest that NO_2 groups fill free space between the chains. The polar substituent enhances polymer cohesive energy density and, in turn, packing efficiency. However, the permselectivity for both O_2/N_2 and CO_2/CH_4 gas pairs increased as did solubility selectivity and diffusivity selectivity for the latter one.

Naik et al. [9] reported that a 60% polyetherethersulfone/40% polyethersulfone (PEES/PES) copolymer had been nitrated solely on the hydroquinone moiety employing a mixture of nitric acid and sulfuric acid in nitrobenzene solution. The DS ranged from 0 to 1 (i.e., the –OPhO– part was mononitrated in the latter case). Only sodium dithionite was found to be suitable for reducing the nitro compounds to the corresponding amines which were further converted to crosslinkable derivatives. The PES unit of the polymer remained unchanged during nitration as it would be expected from the calculated relative rates of reaction for the two different repeat units: there is a 2×10^5 factor in favour of the hydroquinone unit.

Conningham et al. [10] could have performed the nitration/reduction procedure on PES by dissolving first the polymer in 98% sulfuric acid (H_2SO_4 neither sulfonates nor degrades the polymer in itself), then nitrating it with potassium nitrate (dissolved in H_2SO_4 as well) or fuming nitric acid (less effectively), finally reducing the nitro derivative (PES-NO_2) with dithionite or hydrogen in the presence of Raney Ni. Degrees of nitration as high as 1.6 (calculated from N%; see table 2 in Ref. [10]) were reached by employing excess KNO_3, however, the reaction was accompanied by chain fission, more and more with increasing DS. One nitration was carried out without any acids, in sulfolane medium using nitronium tetrafluoroborate, but this method turned out to be even more degradative. The authors suggested a three-step degradation mechanism involving the *ipso* attack of NO_2^+ at C–S chain linkages which would yield *p*-NO_2- and *p*-SO_2OH-ended entities. Nonetheless, this mechanism has not been verified. The reduction was also problematic. An alternative polycondensation procedure using 2-amino-4-chlorophenyl sulfone (partly replacing 4-chlorophenyl sulfone) and 4-hydroxyphenyl sulfone gave only polymers with low inherent viscosity, probably because of the reactivity-reducing effect of the amino groups *meta* to the chlorine. The position of the NO_2 groups on the aromatic rings in the electrophilic substitution was not determined in this contribution, but we have shown that bromination of PES takes place *ortho* to the ether linkage [5], as supported by calculations, too, so the same would be expected during nitration. Accordingly, the polycondensation method mentioned earlier gives the isomeric amine, as the NH_2 group is placed *ortho* to the sulfone bridge in that.

We tried to utilize the Crivello–Daly procedure to nitrate Victrex polyethersulfone, having each *ortho* ether site in the deactivated phenylsulfone portion, and the result was surprisingly successful (considering the difficulties in other electrophilic substitutions [5]). We had to find a solvent other than chloroform for this reaction because PES is not well soluble in it. The first choice was tetrachloroethane, but it is not miscible with TFAA, so the reaction took place in emulsion (under stirring). The DS was 0.41 in this experiment. After this, dichloromethane (DCM) was found to be the appropriate medium for the reaction in



Scheme 1. Nitration of PSU and PES.

which the DS attained 0.80. (DCM is miscible with TFAA and a good solvent for PES.) Unlike the previous experiment, AN was not dissolved in TFAA in advance, but it was suspended in the polymer solution and TFAA was added dropwise to this system while cooling. We could avoid the boiling of the reagent solution by this means. Interestingly, the nitrated polymer could not be recovered from the DCM solution by precipitation into methanol because only a milk-like emulsion was produced in this case. However, water proved to be appropriate non-solvent to separate PES-NO_2 from the reaction mixture. We have nitrated Udel polysulfone under the same conditions and got PSU-NO_2 with a DS of 1.10; methanol was suitable for precipitation here while water was not. It can be seen that the difference between the reactivity of the two polymers in this reaction is much smaller than expected. The nitrations are illustrated in Scheme 1. Besides the mentioned examples, we have prepared several nitrated derivatives of both polymers with differing DS by varying the reaction conditions.

Table 1
DSC data for PSU, PES, and their nitrated derivatives

Polymer	T_g(°C)	$\Delta T = T_{end} - T_{ons}$ (°C)	ΔC_p (J/(gK))
PSU	187.3	6.4	0.24
PSU-NO_2 (DS = 0.52)	189.1	6.6	0.27
PES	225.0	4.4	0.24
PES-NO_2 (DS = 0.53)	226.9	10.0	0.45

Elemental analysis was used to determine the nitrogen content of the products from which the DS was calculated. IR spectroscopy was applied to prove the presence of the aromatic NO_2 group in the polymer samples: the characteristic antisymmetric stretch ($\nu_{as}NO_2$) could be easily identified at 1537 (PES-NO_2) and at 1534 cm^{-1} (PSU-NO_2), respectively. Literature data: PES-NO_2: 1540 cm^{-1} [10]; PSU-NO_2: 1535 cm^{-1} [7,8] (and 1550 cm^{-1} [4], however, this latter one is presumably wrong or simply an erratum). The symmetrical stretch ($\nu_s NO_2$) is less pronounced and is assigned only in the spectrum of PSU-NO_2 at 1360 cm^{-1} [4,7,8]; in the case of PES-NO_2 this peak appeared only as a shoulder on the doublet (1299 and 1325 cm^{-1}) resulting from the asymmetric stretching of the sulfone group [1]. The spectra of our PES-NO_2 samples were very similar to that of Conningham et al. [10].

Ghosal et al. [7,8] reported the glass transition temperatures (T_g) of unmodified and nitrated polysulfones. They found that T_g did not change upon addition of a single NO_2 group (remained 190°C), but rose to 206°C when the DS was 1.92. However, the T_g of PPO went up from 207°C to 233°C on only 15% nitration (i.e., when the DS was 0.15). This is owing to an increase in the rotational energy barrier and in inter-chain attraction occasioned by the polar nitro group. However, contrary to the repeat unit of PPO which contains merely one substituted phenoxy group, the repeat unit of PSU consists of many segments rendering diverse local motions possible. The glass transition arises from cooperative segmental motions which are not hindered substantially in the case of PSU by introducing one NO_2 group per repeat unit. But at high DS (1.92), the increase in T_g indicates the stiffening of large scale polymer backbone motion and restriction of chain torsional mobility (cf. with the gas transport properties). These observations are in keeping with those of Naik et al. [9] who have described that the T_g of nitrated PEES/PES copolymers augmented only very slightly with growing DS (from 207°C to 210°C upon monosubstitution of the hydroquinone moiety).

We have determined the T_g of PSU and PSU-NO_2 (DS = 0.52) by differential scanning calorimetry (DSC) and got values similar to that of Ghosal et al. [7,8]. In Table 1, the thermal data for PES and PES-NO_2 (DS = 0.53) are also summarized; it can be seen that nitration of both polymers does not increase the glass transition temperature considerably. It means that PES behaves like the PEES/PES copolymer or PSU upon nitration (though has a shorter repeat unit) and not like PPO.

The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of nitrated PSU and PES have not been

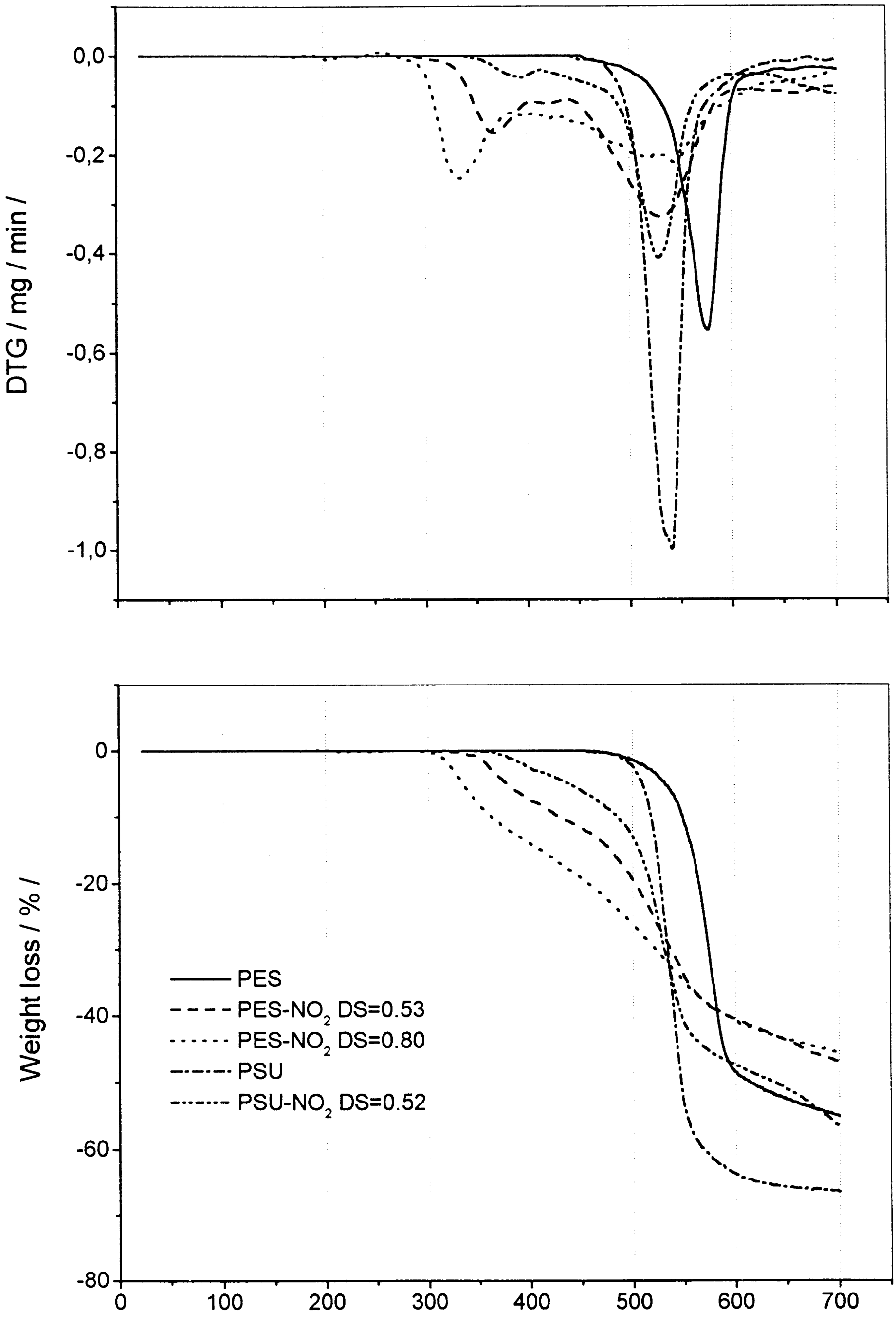


Fig. 2. T.g. (below) and d.t.g. (above) curves of unmodified and nitrated polymers.

reported. We found that both the nitro derivatives exhibit two-step degradation profile, shown in Fig. 2, comparing with the unmodified polymers. While PSU has a lower onset temperature than PES, PSU-NO_2 starts to decompose at a higher temperature than nitrated polyethersulfones. In the case of PES-NO_2, the onset temperature decreases with an increase in DS. We believe that the first-step weight losses originate from the release of NO_2. The two-stage degradation is characteristic of some other derivatives of polysulfone as well, e.g., PSU-COOH [11] ($-CO_2$), PSU-N_3 [12] ($-N_2$) or PSU-CH_2X^3, where X = Cl or Br. However, PSU-Br [2] and PES-Br [5] displayed one-step degradation, occurring at lower temperature compared to that of the unsubstituted polymers, without initial loss of bromine. Aminated polysulfones (PSU-NH_2) showed similarly simple degradation profiles [13].

Summing up, we demonstrated a new method for the nitration of PES using AN and TFAA which is held to be milder than the conventional nitrating procedures. Comparisons were drawn between the nitration of PSU and PES. The success of the reactions was proved by nitrogen analysis and IR spectroscopy. DSC and TG measurements were also performed. We shall later report on the properties of the nitrated polymers more circumstantially and investigate the further transformations of these materials.

2. Experimental

The polymers were Victrex PES 4800 (ICI) and Udel P-1700 (Amoco Performance Products, Inc.). The solvents used were laboratory grade obtained from commercial sources and were dried over anhydrous sodium sulphate. TFAA was 97% pure grade (Fluka). AN was analytically pure grade (Reanal).

IR spectra were recorded with a Bruker IFS55 FTIR spectrometer; the samples were dispersed in KBr pellets.

DSC measurements were carried out using a Netzsch DSC 200 differential scanning calorimeter equipped with MITAS data acquisition and evaluation system. The samples weighing 4–7 mg were heated to a temperature 30°C–50°C higher than T_g at 10°C/min, quenched to the liquid nitrogen temperature, and the T_g was taken as the midpoint of the heat capacity change from the second heating at the same heating rate. Experiments were executed under pure nitrogen at a flow rate of 80 ml/min. The temperature and heat flow response of the calorimeter were calibrated using high purity indium and zinc. The time lag correction was also performed.

To determine the thermal stability of derivatives, a Mettler TA-1 Thermoanalyser or a Derivatograph PC was used. Experiments were carried out on 5–10 mg of sample under pure nitrogen at a flow rate of 110 ml/min, at a heating rate of 10°C/min.

2.1. Nitration of Victrex polyethersulfone 1

A solution of AN (0.57 g, 7 mmol) in TFAA (6 ml, 43 mmol) was added to PES (1.63 g, 7 mmol), dissolved in 1,1,2,2-tetrachloroethane (15 ml). (*Caution*: AN dissolves slowly in TFAA, but this is an exothermic process that finally leads to the boiling of the solution because the boiling point of TFAA is just 40°C. The boiling solution was quickly added to the polymer solution stirred magnetically in a flask. If TFAA was cooled, AN did not dissolve in it.) The reaction mixture was white in the beginning, later (after 2 h) it turned into bright yellow and was not translucent. Stopping the stirrer the system formed two phases, but it was an emulsion when stirred. After stirring for 25 h at room temperature, the polymer was precipitated into methanol (100 ml), then the product was filtered and washed successively with methanol, saturated aqueous $NaHCO_3$, water, and finally methanol again. After drying in a vacuum oven 1.54 g of nitrated polyethersulfone was obtained. Found: N%:2.29; 2.30; DS = 0.41. The polymer recovery was 88%. IR: 1537 cm^{-1} ($\nu_{as}NO_2$).

2.2. Nitration of Victrex polyethersulfone 2

Unlike the previous experiment, AN was not dissolved in TFAA, but was suspended in the polymer solution and TFAA was added dropwise to this system while cooling. Thus, PES (2.99 g, 13 mmol) was dissolved in dichloromethane (45 ml), AN (1.05 g, 13 mmol) was suspended in the solution, then TFAA (12.4 ml, 88 mmol) was dropped into the flask (cooled with an iced water bath). (Less TFAA was not enough to dissolve AN, so the TFAA : AN ratio had to be somewhat higher than in the preceding case.) The amber-coloured, limpid reaction mixture was stirred for 8 h, then precipitated by dropping into water, the product was separated by filtration, washed with water, saturated aqueous $NaHCO_3$, water again, and finally, with methanol to aid drying in a vacuum oven. 2.32 g of PES-NO_2 was obtained. N%: 4.18, 4.19; DS = 0.80.

2.3. Nitration of Udel polysulfone (modification of the Crivello-Daly procedure)

In the solution of PSU (5.69 g, 13 mmol) with DCM (45 ml) was suspended AN (1.03 g, 13 mmol), and TFAA (12.8 ml, 90 mmol) was added dropwise during cooling and magnetic stirring to dissolve AN completely. The golden, limpid reaction mixture was stirred at room temperature for 10 h, then the polymer was recovered by precipitating the solution dropwise into methanol (300 ml). The white flakes obtained were separated by filtration and washed sequentially with methanol, saturated aqueous $NaHCO_3$, water, and finally again with methanol. After drying in a vacuum oven, 5.91 g of nitrated polysulfone was obtained (N%: 3.08, 3.17; DS = 1.10; recovery: 92%). The product was white with a shade of yellow in it, IR: 1534 cm^{-1} ($\nu_{as}NO_2$).

Acknowledgements

We thank Dr H. Medzihradszky-Schweiger for nitrogen analyses and G. Magyarfalvi for IR measurements.

References

[1] Noshay A, Robeson LM. J Appl Polym Sci 1976;20:1885.
[2] Guiver MD, Kutowy O, ApSimon JW. Polymer 1989;30:1137.
[3] Warshawsky A, Kahana N, Deshe A, Gottlieb HE, Arad-Yellin R. J. Polym Sci, Polym Chem Edn 1990;28:2885.
[4] Daly WH, Lee S, Rungaroonthaikul C. In: Benham JL, Kinstle JF, editors. Chemical Reactions on Polymers. ACS Symp Ser 1988, vol. 364, p. 4.
[5] Botvay A, Máthé Á, Pöppl L, Rohonczy J, Kubatovics F. J Appl Polym Sci, to appear.
[6] Crivello JV. J Org Chem 1981;46:3056.
[7] Ghosal K, Chern RT. J Membr Sci 1992;72:91.
[8] Ghosal K, Chern RT, Freeman BD, Savariar R. J Polym Sci, Polym Phys Edn 1995;33:657.

[9] Naik H, Parsons IW, McGrail PT, MacKenzie PD. Polymer 1991;32:140.
[10] Conningham P, Roach RJ, Rose JB, McGrail PT. Polymer 1992;33:3951.
[11] Guiver MD, Croteau S, Hazlett JD, Kutowy O. Br Polym J 1990;23:29.
[12] Guiver MD, Robertson GP. Macromolecules 1995;28:294.
[13] Guiver MD, Robertson GP, Foley S. Macromolecules 1995;28:7612.