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Preparation and solution behaviour of graft copolymers with cationic groups in polyoxyethylene side chains

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Abstract

Novel, cationic graft copolymers with charged polyoxyethylene (PEO) side chains were prepared from the alternating copolymer poly(phthalimidoacrylate-*co*-styrene). Substitution of the good leaving phthalimido ester groups with α-trimethylammonioethyl-ω-amino-polyoxyethylene resulted in graft copolymers with PEO side chains end-functionalized with quaternary ammonium groups. In a two-step synthetic procedure the same precursor polymer was modified with 3-dimethylaminopropylamine. Then the tertiary amine groups were quaternized with α-methoxy-ω-bromopolyoxyethylene or with α-trimethylammonioethyl-ω-bromopolyoxyethylene to yield graft copolymers with cationic groups close to the backbone or bearing bifunctional side chains. The effect of ionic group location on the behaviour of the copolymers in a low-polarity and a polar solvent was studied by viscosity, GPC and static light scattering measurements. In a low-polarity solvent (tetrahydrofuran) the factors determining the solution properties of the cationic graft copolymers are the intramolecular side chain and ion-pair attractions which shrink the polymer chains. In a polar solvent (*N*,*N*-dimethylformamide) the behaviour of the graft copolymers with low degree of grafting is determined by the balance between the intramolecular side chain attraction and the electrostatic interactions of the dissociated ion-pairs. The ionic groups located at the end of the side chains cause polyelectrolyte behaviour. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

During the last few decades, a substantial research has been done to synthesize and characterize graft copolymers comprising hydrophobic backbone and polyoxyethylene (PEO) side chains. These materials are known for versatile applications such as emulsifiers, steric stabilizers, and surface modifiers. Their properties are function of the copolymer composition, the length of the PEO side chains and the degree of grafting. The copolymer behaviour in solid state and in solution may be controlled by introducing functionalities. Further, these functionalities can be reacted in a specific mode with polymer chains or with suitable molecules. The result is copolymers with desired characteristics.

Graft copolymers with well-defined side chains can be prepared by the macromonomer method or via grafting of preformed chains onto a functional backbone [1].

Water-soluble and micelle-forming PEO macromonomers were radically homopolymerized or copolymerized with suitable monomers to afford graft copolymers of variable composition [2–9]. The dispersion polymerization of vinyl monomers in the presence of PEO amphiphilic macromonomers resulted in graft copolymers that act as steric stabilizers for latex particles [10,11].

The "grafting onto" method involves reaction between end-functionalized PEO and a well characterised polyfunctional precursor. Anionic deactivation [12], transesterification [13], amidation [14] and urethane formation [15] produce amphiphilic graft copolymers with high degree of grafting.

Another method for the synthesis of graft copolymers is the activated ester method [16–18]. Its advantage is the specific interaction of polymeric activated esters with amine containing chains while the presence of other functionalities does not interfere with the leaving group substitution. The method also allows the preparation of polymeric reagents with functional groups at the end of pendant chains which can be used in further modifications [19].

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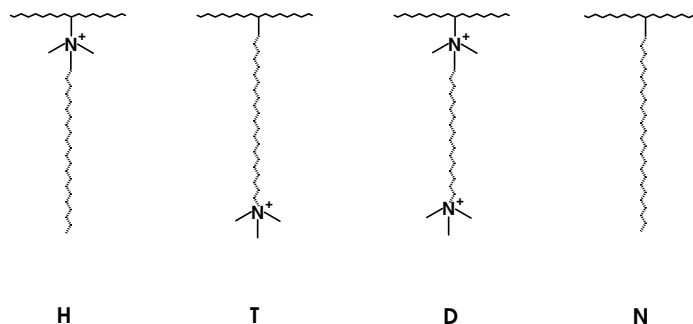*E-mail address:* ivberlin@polymer.bas.bg (I.V. Berlinova).

Fig. 1. Schematic structures of the graft copolymers; ⌇⌇⌇ stands for the backbone; ⌇⌇⌇ stands for the PEO side chains.

A way to influence the behaviour of polymeric materials is to introduce ionic groups at different sites of the component chains. Polymers of low charge density, known as ionomers, attract attention with their unusual properties [20,21]. The solution properties of ionomers are influenced by several parameters: solvent polarity, temperature, concentration, polymer structure and molar mass and ion content [22–34]. In non-polar solvents intramolecular dipole–dipole interactions cause a decrease in the dilute solution viscosity. Conversely, in dimethylformamide and dimethylsulfoxide ionomers with low percentage of charged groups and even monofunctional polymers end-capped with an ionic group show an upturn in reduced viscosity at low concentration, a typical polyelectrolyte behaviour [23,26–31].

This paper deals with the synthesis of graft copolymers with PEO side chains bearing differently located quaternary ammonium groups: close to the backbone (H-type) or at the end of side chains (T-type) as illustrated in Fig. 1. A copolymer containing bifunctional side chains (D-type) was also prepared. The research aims at determining how the charge location in the side chain, the grafting degree and the polarity of the solvent affect the solution behaviour of the graft copolymers. Uncharged copolymers (N) were used for comparative studies.

2. Experimental

2.1. Materials

Styrene (S) was distilled and stored over CaH_2. Phthalimidoacrylate (IA) was synthesized as previously described [18]. 3-Dimethylaminopropylamine, *N,N*-dimethylethanolamine and thionyl bromide were distilled under reduced pressure prior to use. Triethylamine was distilled over potassium hydroxide prior to use. *N,N*-dimethylformamide (DMF) was dried over P_2O_5 and distilled under vacuum. Tetrahydrofuran (THF) was distilled over sodium–potassium alloy. Ethylene oxide was distilled at 0°C. Diazobicyclooctane (DABCO) was purified by sublimation. Methyliodide was distilled. α-Methoxypolyoxyethylene

(Fluka) of $M_n = 2000$ was dried by azeotropic distillation with toluene before use.

2.2. Precursor polymers

2.2.1. Poly(styrene-co-phthalimidoacrylate) (1)

S and IA were copolymerized at equimolar ratio in DMF solution at 60°C in the presence of AIBN. The composition of 1 was determined by ^{1}H NMR from the relative intensities of IA and S aromatic protons and by spectrophotometry in DMF solution from the absorption of the phthalimido units at 295 nm. The mole fraction of each monomer in the synthesized copolymer was equal to 0.5. The molar mass of the copolymer was $M_n = 41\,000$ g mol^{-1}, $M_w = 82\,000$ g mol^{-1} (determined by GPC analysis in THF using polystyrene standards).

2.2.2. Copolymers bearing tertiary amine groups in the side chains (2)

The preparation of 2 was adapted from that previously described [35]; the main change was the use of equimolar amounts of DABCO and 3-dimethylaminopropylamine in order to introduce a definite amount of tertiary amine groups in 1. In a typical reaction, a solution of required amounts of DABCO and 3-dimethylaminopropylamine in 10 ml of DMF was added dropwise under N_2 to a stirred solution of 1 (0.963 g, 3 mmol of ester groups) in 5 ml of DMF. The reaction was carried out at 95°C for 4 h. DMF was evaporated under vacuum. The workup depended on the degree of ester substitution: (a) polymers with degree of substitution up to 30 mol% were treated with ice and 0.5 N NaHCO₃. The solid was filtered off, washed with water and dried; (b) polymers with degree of substitution above 30 mol% were extracted with CHCl₃ in a Soxhlet extractor for 2 days and dried. Polymer yields were above 90%.

2.2.3. α-Methoxy-ω-bromopolyoxyethylene (3)

This compound was synthesized from α-methoxypolyoxyethylene of molar mass of 2000 and thionyl bromide according to the procedure given by Bückmann et al. [36]. The ^{1}H NMR spectrum of the product in DMSO-d₆ did not show the triplet at 4.56 ppm ascribable to the OH protons [37].

Table 1
Characteristics of the water insoluble fractions of the graft copolymers

Designation[a]	x[b]	Degree of grafting[c] (%)
T 2	39.0	2.5
T 5	18.0	5.6
T 19	5.5	18.6
H 4	24.0	4.2
H 8	13.0	7.8
H 33[d]	3.0	33.0
D 2	39.0	2.5
N 3	34.0	3.0
N 5	20.0	5.0

[a] The letter denoted the type of the copolymer and the accompanying number is equal to the degree of grafting.

[b] x is introduced in Eq. (1) and corresponds to the number of S units per PEO chain.

[c] Degree of grafting (%) is the mole ratio of PEO grafts to the repeating units in the backbone.

[d] Sample purified from unreacted PEO through dialysis in water.

2.2.4. α-Dimethylaminoethylpolyoxyethylene (4)

This compound was prepared by anionic polymerization of ethylene oxide in THF initiated by potassium alkoxide of *N,N*-dimethylethanolamine. The number average molar mass determined by ^{1}H NMR from the relative intensities of $-O-CH_2CH_2-O-$ and $(CH_3)_2N$-protons was $M_n = 2000$. Molecular mass data were also obtained from MALDI-TOF mass spectrum of **4** using 2,5-dihydroxybenzoic acid as a matrix: $M_n = 1973$, $M_w = 2081$.

2.2.5. α-Trimethylammonioethylpolyoxyethylene (5)

4 was quaternized with methyliodide. The reaction was carried out by dissolving **4** (3.3 mmol) in THF (100 ml) and adding an excess of methyliodide (6.6 mmol). Then the reaction mixture was refluxed for 2 days and concentrated on a rotary evaporator. The polymer was precipitated in diethyl ether and reprecipitated from chloroform/diethyl ether. The extent of quaternization ($>96\%$) was measured by ^{1}H NMR and elemental microanalysis. The ^{1}H NMR spectrum of **5** in DMSO-d_6 shows resonances for $(CH_3)_3N^+$ protons at 3.1 ppm and for OH proton at 4.6 ppm. The ratio of their integrated intensities was equal to 9. A resonance for dimethylamino protons at 2.13 ppm did not appear.

Anal. calcd for $C_{91}H_{186}INO_{44}$ (**5**): C, 51.44%; H, 8.76%; I, 5.98%; N, 0.66%; found: C, 52.60%; H, 9.06%, I, 5.75%; N, 0.72%.

2.2.6. α-Trimethylammonioethyl-ω-bromopolyoxyethylene (6)

5 (5 mmol) was dissolved in toluene (140 ml), followed by the addition of large excess of triethylamine (27 mmol). A solution of thionyl bromide (22.3 mmol) in 10 ml of toluene was added dropwise at 35°C. Then the mixture was stirred at 50°C overnight. The temperature was increased to 80°C, followed by filtration of the mixture through a thick layer of Hyflo Super Cel diatomaceous

earth. The filter cake was washed several times with hot toluene. The solvent was evaporated under vacuum, the residue was dissolved in chloroform and precipitated in ether. The crude product was recrystallized from 2-propanol to yield **6** (80%). The lack of OH triplet at 4.56 ppm in DMSO-d_6 suggested a complete substitution.

2.2.7. α-Trimethylammonioethyl-ω-aminopolyoxyethylene (7) and α-methoxy-ω-aminopolyoxyethylene (8)

5 and α-methoxypolyoxyethylene were end-functionalized with an amine group according to the three step procedure given by Zalipski et al. [38]. The functionality (mean number of amine groups per chain) was estimated by titration of the amine groups with 0.01 N HCl and elemental microanalysis.

Anal. calcd for $C_{91}H_{187}IN_2O_{43}$ (**7**): C, 51.46%; H, 8.81%; I, 5.98%; N, 1.32%; found: C, 52.80%; H, 9.21%, I, 6.12%; N, 1.18%; functionality = 0.9.

Anal. calcd for $C_{91}H_{185}NO_{45}$ (**8**): C, 54.30%; H, 9.20%; N, 0.70%; found: C, 54.15%; H, 9.00, N, 0.60%; functionality = 0.88.

2.3. Synthesis of graft copolymers

### 2.3.1. Synthesis of graft copolymers T and N

In a typical reaction, required equimolar amounts of **7** or **8** and triethylamine as 3% solution in DMF were added to a stirred solution of **1** (1 g, 3.11 mmol of ester groups) in 10 ml of DMF. Then the mixture was heated at 85°C for 3 days under N_2 atmosphere. After cooling to room temperature, the solution was filtered and DMF was evaporated under vacuum. The residue was treated with ice and 0.5 N NaHCO$_3$. The solid was filtered off, washed with water and dried.

2.3.2. Synthesis of graft copolymers H and D

In a typical reaction, **3** or **6** (0.5 mmol) dissolved in 10 ml of DMF was added to a solution of **2** (0.32 g, 0.5 mmol $(CH_3)_2N$-groups) in 5 ml of DMF. The reaction mixture was stirred under nitrogen atmosphere at 65°C for 14 days. Then the solution was concentrated on a rotary evaporator and the graft copolymer was precipitated in diethyl ether.

The products were purified from unreacted PEO by extraction with water. Two fractions: a water insoluble (Table 1, Samples H4, H8 and D2) and a water-soluble fraction were isolated. Only sample H33 was separated from the unreacted PEO derivative through dialysis in water for 2 weeks. A dialysis membrane (Spectrapor, Spectrum Medical Industries Inc., USA) with a cut-off value of 12 000– 14 000 was used.

The composition of the graft copolymers was determined by ^{1}H NMR in DMSO-d_6 at 120°C from the relative intensities of styrene and oxyethylene protons. Eq. (1) gives the approximate number of S units (x) per grafted PEO chain. The degree of grafting defined as PEO moles per 100 mol
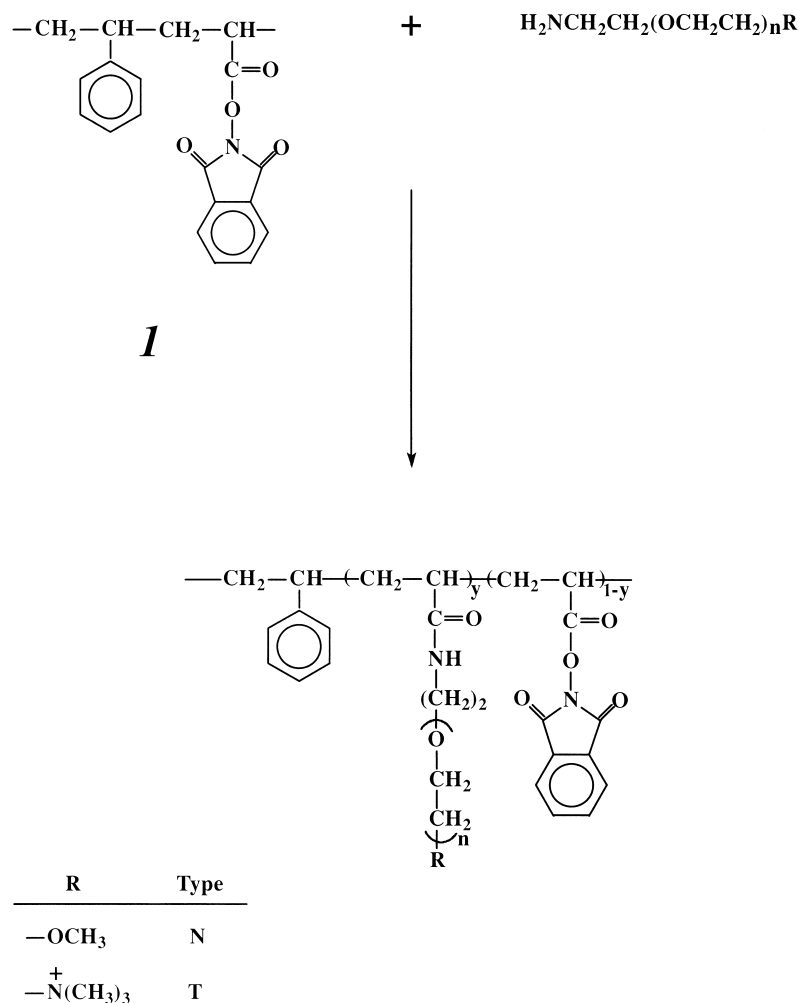
Scheme 1.

backbone repeating units was calculated from the x value

$$\frac{\text{Area of S protons at } \delta = 6.5 - 7.3}{\text{Area of PEO protons at } \delta = 3.56} = \frac{5x}{4\,DP_{\text{PEO}}} \quad (1)$$

The characteristics of the purified graft copolymers are listed in Table 1.

3. Characterization

3.1. Viscosity measurements

Solution viscosities were determined with an Ubbelohde viscometer at 25°C. Solvent flow time exceeded 250 s. Viscosity data were analysed using the Huggins [39] and Fuoss [40] equations:

$$\eta_{\text{sp}}/c = [\eta] + k_{\text{H}}[\eta]^2 c \quad (2)$$

$$c/\eta_{\text{sp}} = 1/A + Bc^{1/2}/A. \quad (3)$$

3.2. Light scattering measurements

Static light scattering measurements were conducted with a multi angle laser light scattering detector DAWN DSP Laser Photometer (Wyatt Technology Corporation) equipped with an argon laser emitting at a wavelength of 488 nm. Analyses were performed in a microbatch mode at 25°C. The specific refractive index increment, dn/dc, was measured at 25°C on an Optilab DSP Wyatt interferometric refractometer. The light scattering data were analysed by plotting the reciprocal reduced scattered intensity, Kc/R_0, against concentration c, where R_0 is the extrapolated to zero angle value of R_θ.

4. Results and discussion

4.1. Synthesis of graft copolymers

The radical polymerization of S and IA leads to a predominantly alternating copolymer 1. The substitution
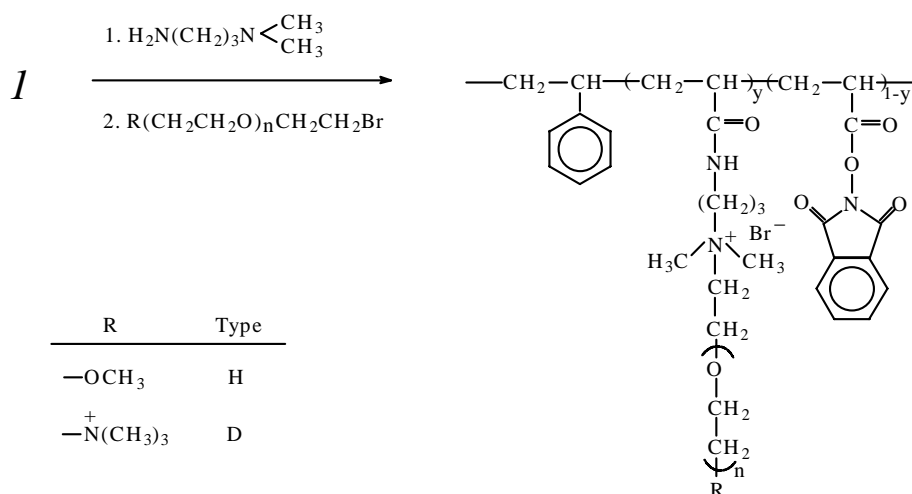
Scheme 2.

of the good leaving phthalimido groups by **8** has been shown to be an appropriate method for the synthesis of amphiphilic graft copolymers with PEO side chains (type N, Scheme 1) [18]. Now changing **7** for **8** we succeeded in the preparation of graft copolymers with PEO side chains end-functionalized with quaternary ammonium groups (type **T**, Scheme 1). The two-step approach presented in Scheme 2 enabled the preparation of graft copolymers with cationic groups close to the backbone (type H) and with bifunctional side chains (type D). Water-insoluble fractions were isolated from samples prepared at low molar ratio of PEO to the main chain ester groups. Since their degree of grafting is low, they can be considered as random ionomers with regard to the ion distribution along the main chain.

4.2. Solution behaviour

4.2.1. Solution behaviour in THF

Only copolymers of N and H type dissolve in THF. GPC analyses of unfractionated H copolymers show that the hydrodynamic volume and the dispersity of the copolymers decrease with increasing the degree of grafting (Fig. 2). We have already shown [18] that the elution volumes of uncharged copolymers with degree of grafting >10% are between those of the backbone polymer and **8**. This effect was attributed to the ability of PEO side chains to interact and form organized structures in solution [7,41]. GPC in THF is not an appropriate method for analysis of ionomers on account of their adsorption on the column packing [42]. However, the elution of H copolymers proceeded like that of uncharged graft copolymers. This can be explained by the
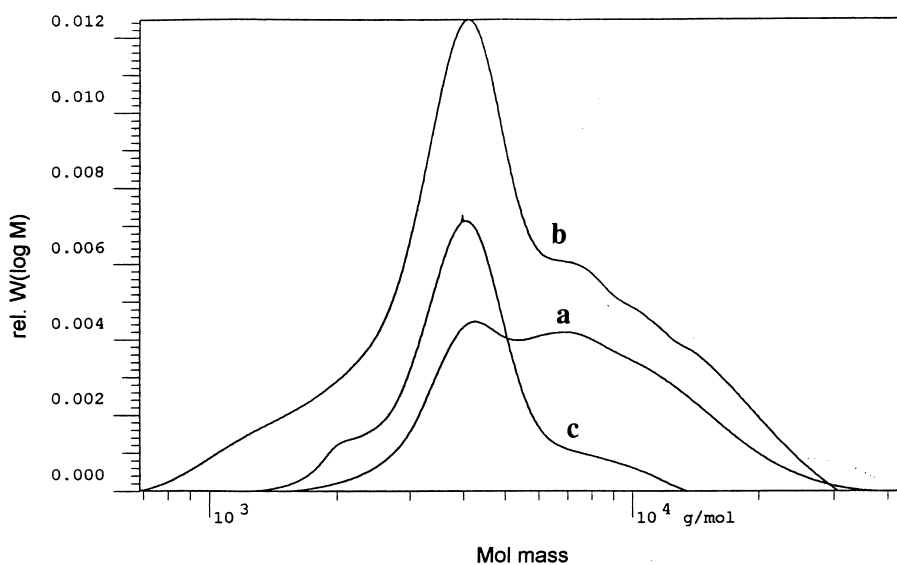
Fig. 2. GPC curves of unfractionated samples of H type with different degree of grafting: (a) 10%; (b) 15%; and (c) 20%.
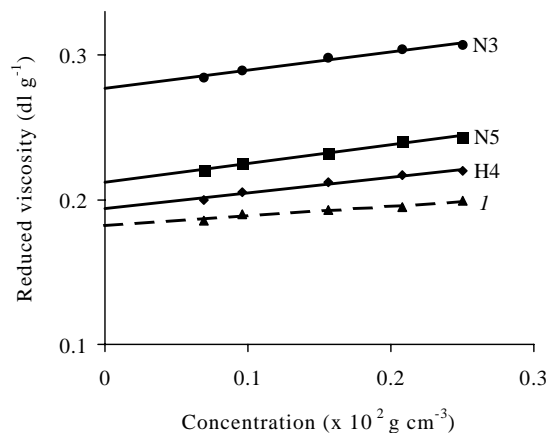
Fig. 3. Concentration dependence of reduced viscosity for graft copolymers of H and N type and for the main chain copolymers in THF at 25°C.

Fig. 5. Concentration dependence of reduced viscosity for T copolymers in DMF at 25°C.

assumption that the associated PEO chains shield the ion pairs located close to the backbone from the surrounding environment.

The viscosity data for fractionated H and N copolymers with low degree of grafting are shown in Fig. 3. The concentration dependence of the reduced viscosities is linear. However, the reduced and intrinsic viscosities for H copolymer are lower than those of similar uncharged copolymers. Two types of interactions contribute to the increased compactness of the charged graft copolymers: (a) dipole–dipole interactions of the contact ion pairs; and (b) interaction of the electron donating carbonyl groups along the backbone with the quaternary ammonium groups, as has been proposed by Hamid and Sherrington [43].

4.2.2. Solution behaviour in DMF

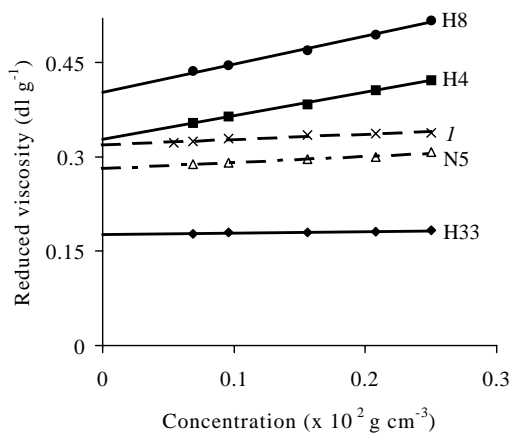DMF is a good solvent for all charged graft copolymers. The major factor determining their behaviour is the

dissociation of the ion pairs which creates cationic charges at different positions of the PEO side chains.

The viscosity data for H and N copolymers are shown in Fig. 4. The concentration dependence of the reduced viscosities is linear but the viscosities of H copolymers are higher than those of the uncharged copolymers unlike their behaviour in THF.

The viscosity behaviour of H copolymers in DMF is controlled by two opposite effects: (a) the cationic charges close to the backbone increase its rigidity and hence the reduced and intrinsic viscosities of the copolymers also increase; and (b) the intramolecular association of PEO side chains causes shrinkage of the copolymer coil and the viscosity decreases. The former effect prevails at low degrees of grafting and results in higher viscosities when compared to those of N copolymers. In contrast, PEO association is dominant at high degrees of grafting and this is the reason for the low viscosity of H33.

T copolymers in DMF solutions show a polyelectrolyte behaviour, characterized by a η_{red} increase when decreasing

Fig. 4. Concentration dependence of reduced viscosity for graft copolymers of H and N type and for the main chain copolymer in DMF at 25°C.

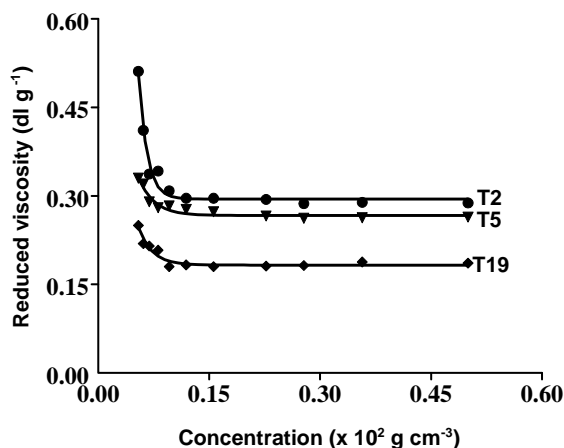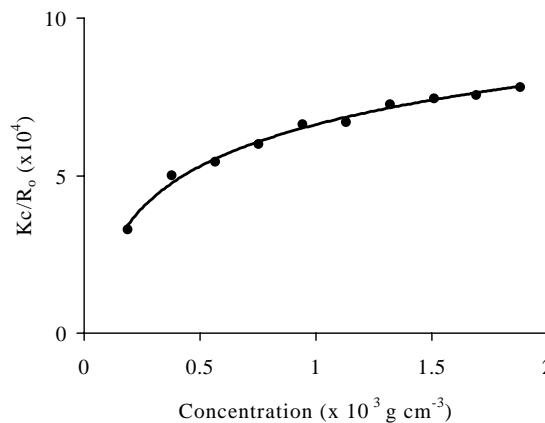Fig. 6. Reciprocal of reduced scattering intensity vs concentration for T2 copolymer in DMF.
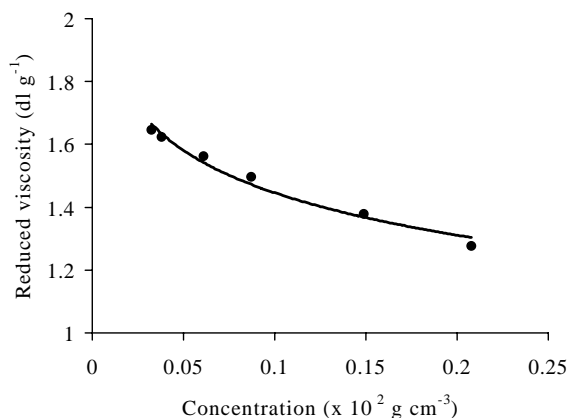
Fig. 7. Concentration dependence of reduced viscosity for D2 copolymer in DMF at 25°C.

the concentration (Fig. 5). With increasing the degree of grafting the reduced viscosity decreases but the upturn of its concentration dependence is clearly observed.

Besides viscometrically the polyelectrolyte behaviour of T copolymers was also detected by static light-scattering technique through determination of the dependence Kc/R_0 vs concentration (Fig. 6). The observed curvature is indicative of polyelectrolyte behaviour and suggests a considerable increase in the polymer size at lower concentrations. Similar behaviour was also reported for random [27,28] and telehelic ionomers [30,32] in polar solvents.

Of particular interest are the viscometric properties of D2. Despite the very low degree of grafting of bifunctional side chains the reduced and intrinsic viscosities of D2 are considerably higher than those of similar T and N copolymers. Since D2 revealed a polyelectrolyte behaviour in the whole concentration range studied (Fig. 7), $[\eta]$ was determined by applying the Fuoss equation (Fig. 8). $[\eta] = 2.04$ dl/g.

The polyelectrolyte effect is usually interpreted in terms of the repulsive electrostatic interactions among the fixed charges in the polymer chain. However, it is not plausible that repulsive interactions between the cationic groups located at the end of remote PEO side chains may cause
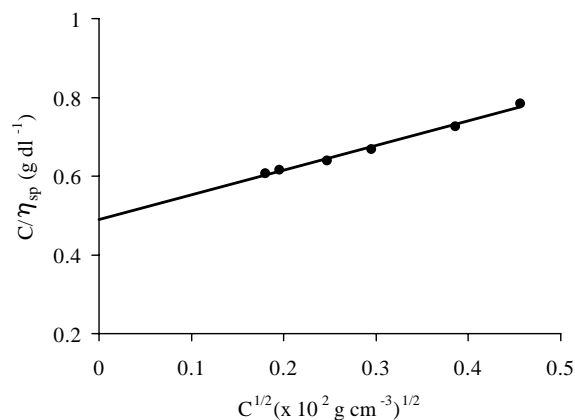

Fig. 8. Fuoss plot for D2 copolymer in DMF at 25°C.

chain expansion of D and T copolymers being of low degree of grafting. One can assume that the solution behaviour of these copolymers in DMF is dominated by intermolecular electrostatic interactions as already suggested by Hara et al. [29,30] to explain the viscosity and light scattering data for telehelic ionomers in a polar solvent.

In solutions of T copolymers in DMF the intermolecular electrostatic interactions compete with the intramolecular side chain attraction. The decrease in the reduced viscosity with increasing the degree of grafting reflects the enhancing role of the intramolecular PEO association which causes a shrinkage of the copolymer chain.

The charges located both at the end of the side chains and close to the backbone of copolymer D2 are those determining its viscosity behaviour. The effect is a considerable increase in the reduced and intrinsic viscosities and is in favour of the suggestion that the charge location and the balance between intra- and inter-molecular interactions determine the size of the charged graft copolymers in a polar solvent.

5. Conclusions

The location of cationic groups at different positions in the PEO side chains of graft copolymers has a pronounced effect on their solution properties. In THF dipole–dipole interactions of the ion pairs contribute to the intramolecular side chain interactions and cause a greater decrease of the hydrodynamic volume compared to that of uncharged copolymers. In DMF the behaviour of the cationic graft copolymers is determined by the balance between the electrostatic interactions of the dissociated ion pairs and the intramolecular side chain association. The copolymers bearing charges at the end of the side chains display typical polyelectrolyte effect arising from intermolecular interactions of the end cationic groups. When the charges are located close to the backbone they cause its stiffening and the viscosities of the copolymer solutions in DMF are higher than those of the uncharged copolymers with the same degree of grafting. Cationic graft copolymers with low level of bifunctional side chains show the greatest viscosity increase. It is rationalized on the basis of both effects, the stiffening of the backbone and the intermolecular interaction of charges.

Acknowledgements

References

[1] Dreyfuss P, Quirk RP. In: Mark H, Bikales N, Overberger C, Menges G, editors. 2nd ed. Encyclopedia of polymer science and engineering, vol. 7. New York: Wiley, 1987. p. 551.

[2] Suzuki T, Tomono T. J Polym Sci, Part A: Polym Chem 1984;22:2829.

[3] Rempp P, Lutz P, Masson P, Chaumont P, Franta E. Makromol Chem Suppl 1985;13:47.

[4] Chao D, Itsano S, Ito K. Polym J 1991;23:1045.

[5] Ito K, Tanaka K, Tanaka H, Iwai G, Kawaguchi S, Itsano S. Macromolecules 1991;24:2348.

[6] Ito K, Tomi Y, Kawaguchi S. Macromolecules 1992;25:1534.

[7] Geetha B, Mandal AB, Ramasami T. Macromolecules 1993;26:4083.

[8] Liu J, Chew CH, Gan LM. J Macromol Sci Chem A 1996;33:337.

[9] Liu J, Chew CH, Wong SY, Gan LM. J Macromol Sci Chem A 1996;33:1181.

[10] Capek J, Riza M, Akashi M. Eur Polym J 1995;31:895.

[11] Kawaguchi S, Winnik MA, Ito K. Macromolecules 1996;29:4465.

[12] Berlinova IV, Amzil A, Panayotov IM. J Macromol Sci Chem A 1992;29:975.

[13] Wesslen B, Wesslen KB. J Polym Sci: Polym Chem Ed 1989;27:3915.

[14] Eckert AR, Webber SE. Macromolecules 1996;29:560.

[15] Berlinova IV, Dimitrov IV, Gitsov I. J Polym Sci A: Polym Chem 1997;35:673.

[16] Ashrady R. Makromol Chem Rapid Commun 1990;11:193.

[17] Berlinova IV, Amzil A, Tsvetkova S, Panayotov IM. J Polym Sci: Part A; Polym Chem 1994;32:1523.

[18] Berlinova IV, Amzil A, Vladimirov NG. J Polym Sci: Part A; Polym Chem Ed 1995;33:1751.

[19] Arshady R, Fallah F. J Polym Sci: Part A; Polym Chem 1992;30:1705.

[20] MacKnight J, Earnest TR. J Polym Sci: Macromol Rev 1981;16:41.

[21] Fitzgerald JJ, Weiss RA. J Macromol Sci—Rev C 1988;28:98.

[22] Lundberg RD, Makowski HS. J Polym Sci: Polym Phys 1980;18:1821.

[23] Lundberg RD, Phillips RR. J Polym Sci: Polym Phys 1982;20:1143.

[24] Agarwal PK, Garner RT, Graesseley WW. J Polym Sci: Polym Phys Ed 1987;25:2095.

[25] Hara M, Lee AH, Wu J. J Polym Sci: Part B; Polym Phys 1987;25:1407.

[26] Hara M, Wu J. Macromolecules 1986;19:2887.

[27] Lantman CW, MacKnight WJ, Peiffer DG, Sinha SK, Lundberg RD. Macromolecules 1987;20:1096.

[28] Hara M, Wu J. Macromolecules 1988;21:402.

[29] Hara M, Wu J, Lee AH. Macromolecules 1988;21:2214.

[30] Hara M, Wu J, Jerome RJ, Granville M. Macromolecules 1988;21:3330.

[31] Charlier P, Jerome R, Teyssie P. Polymer 1993;34:369.

[32] Wu J, Wang Y, Hara M, Granville M, Jerome RJ. Macromolecules 1994;27:1195.

[33] Young M, Garcia R, Higgins JS, Timbo AM, Peiffer DG. Polymer 1998;39:1525.

[34] Young AM, Brigault G, Heenan R, Higgins JS, Peiffer DG. Polymer 1998;39:6685.

[35] Berlinova IV, Dimitrov IV, Kalinova RG, Vladimirov NG. Polymer 2000;41:831.

[36] Bückmann AF, Morr M. Makromol Chem 1981;182:1379.

[37] Dust JM, Fang Z, Harris JM. Macromolecules 1990;23:3742.

[38] Zalipsky S, Gilon C, Zilkha A. Eur Polym J 1983;19:1177.

[39] Huggins ML. J Am Chem Soc 1942;64:2716.

[40] Fuoss RM, Cathers GI. J Polym Sci 1949;4:97.

[41] Gramain Ph, Frere J. Makromol Chem 1987;188:593.

[42] Žagar E, Žigon M. Polymer 1999;40:2727.

[43] Hamid S, Sherrington D. Polymer 1987;28:325.