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Amphiphilic polyelectrolyte networks derived from 2-oxazolines

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Ionene graft copolymers and networks containing quaternary ammonium groups as linkages have been prepared by termination of living mono- and bifunctional poly(2-methyl-2-oxazoline) and poly(2-phenyl-2-oxazoline) with poly(dimethylaminoethyl methacrylate). Ionene networks of different density with p,p'-dichloroxylene and poly(2-alkyloxazoline)s as cross-linkers have been synthesized. The obtained graft and crosslinked copolymers are well defined and with controlled hydrophilic–hydrophobic balance. Viscosity examination and potentiometric titration of some of the products were carried out. Sorption ability towards Cu^{2+}, Ni^{2+}, Mn^{2+}, Fe^{3+} and anion-exchange capacity were investigated as well. The pH dependence of the sorption of metal ions was evaluated. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: poly(dimethylaminoethyl methacrylate)-g-poly(2-phenyl-2-oxazoline); poly(dimethylaminoethyl methacrylate)-*g*-poly(2-methyl-2-oxazoline))

INTRODUCTION

The synthesis of amphiphilic and reactive functionalized copolymers and networks based on polyoxazolines is of considerable interest in materials science[1–4]. The polyoxazolines have two advantages: (i) their polymerization is of a highly living nature and (ii) the polymers show hydrophilic, hydrophobic or amphiphilic properties, depending on the nature of the acyl groups. Because of their characteristic properties, they have been widely studied for various applications. Polymers containing quaternary ammonium groups are less studied, but they also have a variety of potential applications as chelating and ion-exchange resins, phase-transfer catalysts, disinfection and antibacterial agents.

Recently, we reported the synthesis of graft pEVA and poly(vinyl acetate) copolymers with poly(2-oxazoline)s (pROZO) and polyethyleneimine (pEI) branches, which exhibited wide variety of swelling and chelating properties[5].

The present paper describes the preparation of graft copolymers and networks containing quaternary ammonium groups by multicoupling reaction between water-soluble poly(dimethylaminoethyl methacrylate) and living mono- or bifunctional pROZO. The synthesis is based on the well-known Menschutkin reaction of tertiary diamines with dihalides, which has been used only for preparation of linear ionene polymers[6–8] and polyoxazoline macromonomer[9]. Most pEI networks investigated so far have been prepared by cross-linking with dihalogen derivatives[10–14] and diisocyanates[11,12].

Solution properties, chelating ability towards metal ions and anion-exchange capacity towards ferrocyanide and

rhodanide anions of the copolymers were investigated as well.

EXPERIMENTAL

Analytical

[1]H n.m.r. spectra were taken on a Bruker WM 250 Spectrometer at 25°C in $CDCl_3$ using TMS for reference. Mn values were determined on a Knauer vapour pressure osmometer in chloroform at 45°C with benzyl as standard. I.r. was recorded using a 'Karl Zeiss' spectrometer in films on KBr. Size exclusion chromatography (SEC) analyses were carried out in THF at 45°C on a Waters 244 apparatus equipped with a set of four 'UltraStyragel' columns (100 Å, 100 Å, 500 Å, 1000 Å). Polystyrene calibrations were applied. Some of the samples were measured in $ACN:H_2O = 20:80$ or $H_2O:MeOH = 80:20$ on the same apparatus and Linear 'Ultrahydrogel', 500 Å columns. PEG calibrations were applied.

The potentiometric measurements were performed on 'Präcitronic' pH meter. Viscosities were measured with 'Schott' viscometer (flow time of 110.5 s or 27.7 s) at 25 ± 0.1°C. The sorption ability of the copolymers towards metal ions was recorded using atom-absorption 'Pye Unicam SP 192' apparatus. The anion-exchange capacity was determined using a 'Specol 11' spectrometer.

To increase the surface of the graft copolymers and networks (measured in $m^2 g^{-1}$) in sorption and anion-exchange measurements, a kieselguhr carrier was used. The kinetic of sorption of the metal cations showed that equilibrium was reached in 1 h. The analysis of the supernatant solutions by an atom-absorption spectrophotometer were performed after 24 h.

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Table 1 Radical polymerization of DMAEM in 1,4-dioxane; 70°C; $[Mo] = 1.97\ mol\,l^{-1}$; benzoyl peroxide—$[In] = 1.2 \times 10^{-2}\ mol\,l^{-1}$

Polymer code	Time (h)	$\bar{M}_n$ SEC (THF)	$\dfrac{\bar{M}_n}{\bar{M}_n}$	Yield (%)
D_1	24	1600	1.9	70
D_2	48	4400^a	5.2	65
D_3	60	8500	2.2	55
D_4	72	17 000	1.5	54

^{a}In H_2O:MeOH (80:20)

Materials

Dimethylaminoethyl methacrylate (DMAEM) was distilled *in vacuo* and argon prior to use. Benzoyl peroxide (BPO) was precipitated from chloroform in methanol and dried *in vacuo* at room temperature in darkness. *p,p'*-Dichloroxylene was recrystallized from chloroform, filtered off and dried *in vacuo* at 35°C. 2-Phenyl-2-oxazoline (PhOZO) and 2-methyl-2-oxazoline (MeOZO) were purified as described previously[15]. Benzylchloride (BzCl) was distilled under reduced pressure and argon prior to use. Other reagents and solvents were purified in the usual way.

Radical polymerization of DMAEM

Appropriate amount of DMAEM was dissolved in dry 1,4-dioxane in glass ampoules. The ampoules were blown out with argon. After addition of BPO the ampoules were connected to a high vacuum line and degassed several times using liquid nitrogen. The sealed ampoules were kept at 70°C (*Table 1*). The polymer was precipitated in petroleum ether, reprecipitated, filtered off and dried under reduced pressure, in darkness at 35°C.

Cationic polymerization of MeOZO and PhOZO using BzCl or p,p'-dichloroxylene as initiators

An appropriate amount of BzCl or *p,p'*-dichloroxylene was dissolved in dry acetonitrile, KJ for counterion exchange and PhOZO or MeOZO were added in reactor closed with septum under argon. The reactor was kept at 80°C (*Table 2*). Aliquots of the reaction mixture sampled out were precipitated in diethyl ether, reprecipitated twice

from chloroform in diethyl ether, dried under reduced pressure at 35°C and used for analysis. The rest of the living polymer without isolation was used for grafting or cross-linking of poly(dimethylaminoethyl methacrylate) (pDMAEM).

Grafting and crosslinking procedures

An appropriate amount of dry pDMAEM was dissolved in dry acetonitrile in a reactor closed with septum. A calculated volume of the reaction mixture of mono- or bifunctional poly(2-methyl-2-oxazoline) (pMeOZO) or poly(2-phenyl-2-oxazoline) (pPhOZO) was added through a syringe at room temperature (*Table 3*; *Table 5*). The reactor was closed and kept at 80°C until an increasing of the viscosity or gellation was observed. All manipulations were carried out under argon. The graft copolymers were precipitated in diethyl ether and twice reprecipitated from chloroform in diethyl ether and dried.

The networks were carefully washed up with ACN (the network of pDMAEM and pMeOZO with water) and dried under reduced pressure at 35°C.

Preparation of a graft copolymer on to carrier

A typical run was as follows: 0.5 g of the graft copolymer was dissolved in 12 ml acetonitrile and 0.6 g kieselguhr was added under stirring. The sample was precipitated slowly in diethyl ether under vigorous stirring, filtered off and dried.

Preparation of a network on to carrier

The procedure was carried out during the crosslinking. For example: 1.1 g of well dried carrier was added to the solution of 0.7 g pDMAEM in 5 ml acetonitrile following by addition of the bifunctional poly(2-methyl-2-oxazoline) (pMeOZO) or poly(2-phenyl-2-oxazoline) (pPhOZO). The other steps were the same as described above in accordance with the procedure for crosslinking of pDMAEM.

Swelling properties

The equilibrium degree of swelling of the polymer networks was determined in distilled water and chloroform. Dried samples were weighed into a tarred columns with a

Table 2 Ring-opening polymerization of 2-alkyloxazolines at 80°C in CH_3CN

Sample code	Monomer	$[M_o]$ (mol l^{-1})	Initiator	$[In]$ (10^{-3} mol)	$\dfrac{[M_o]}{[In]}$	$\bar{M}_n$ (VPO)	$\bar{M}_n$ (n.m.r.)	$\bar{M}_n$ (SEC)	$\dfrac{\bar{M}_w}{\bar{M}_n}$ (SEC)	F (n.m.r.)
pPhOZO-J	PhOZO	1.7	Benzylchloride	2.2	8	1500	1000	900	1.13	1.03
J-pPhOZO-J-I	PhOZO	1.7	*p,p'*-Dichloroxylene	3.68	5	800	720	800	1.3	1.95
J-pPhOZO-J-II	PhOZO	2.04	*p,p'*-Dichloroxylene	1.67	12	1600	—	1200	1.21	1.93
pMeOZO-J	MeOZO	2.95	Benzylchloride	3.73	8	800	1070	—	1.17	0.92
J-pMeOZO-J	MeOZO	2.95	*p,p'*-Dichloroxylene	1.54	19	1800	1900	—	1.49	1.94

Table 3 Grafting of phenyl- and methyloxazoline on to poly(dimethylaminoethyl methacrylate) at 80°C in CH_3CN

pDMAEM (M_1)				Grafting agent (M$_2$)			Graft copolymers			Degree of grafting (%)		Sample code
Sample code	$\bar{M}_n$ (SEC)	M_1 (g)	$[M_1]$ (g l^{-1})	Sample code	M_2 (g)	$\bar{M}_n$ (VPO)	$\bar{M}_n$ (n.m.r.)	$\bar{M}_n$ (SEC)	$\dfrac{\bar{M}_w}{\bar{M}_n}$	Feed	N.m.r.	
D_1	1600	0.65	162.5	pPhOZO-J 1.9		1500	6700	7500^a	1.0	30	~30	pD_1-*g*-pPh
D_2	4400	0.7	140	pMeOZO-J 2.0		800	9300	$12\,000^b$	1.3	50	~50	pD_2-*g*-pMe

^{a}Determined in THF
^{b}Determined in CH_3CN:$H_2O = 20$:80
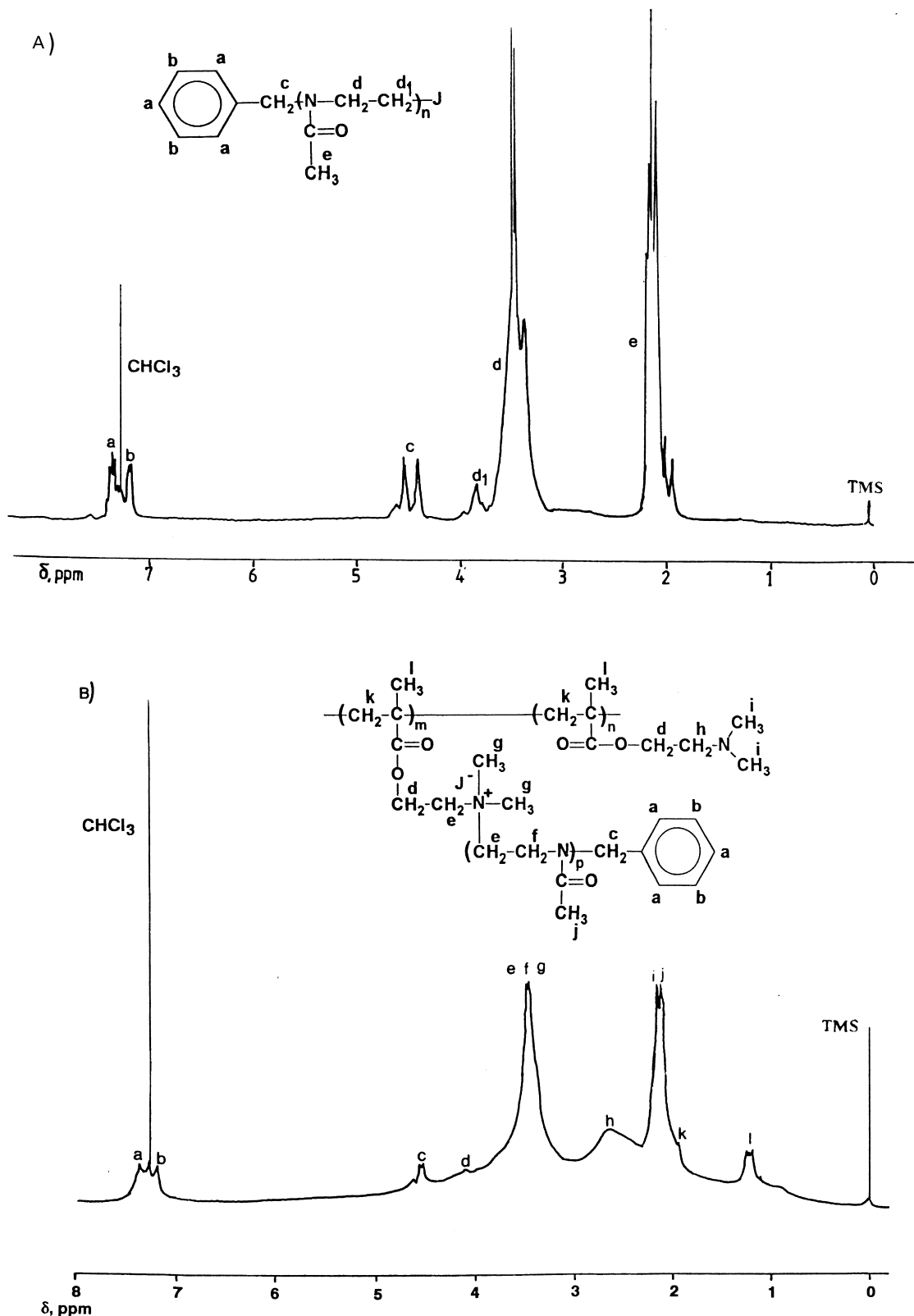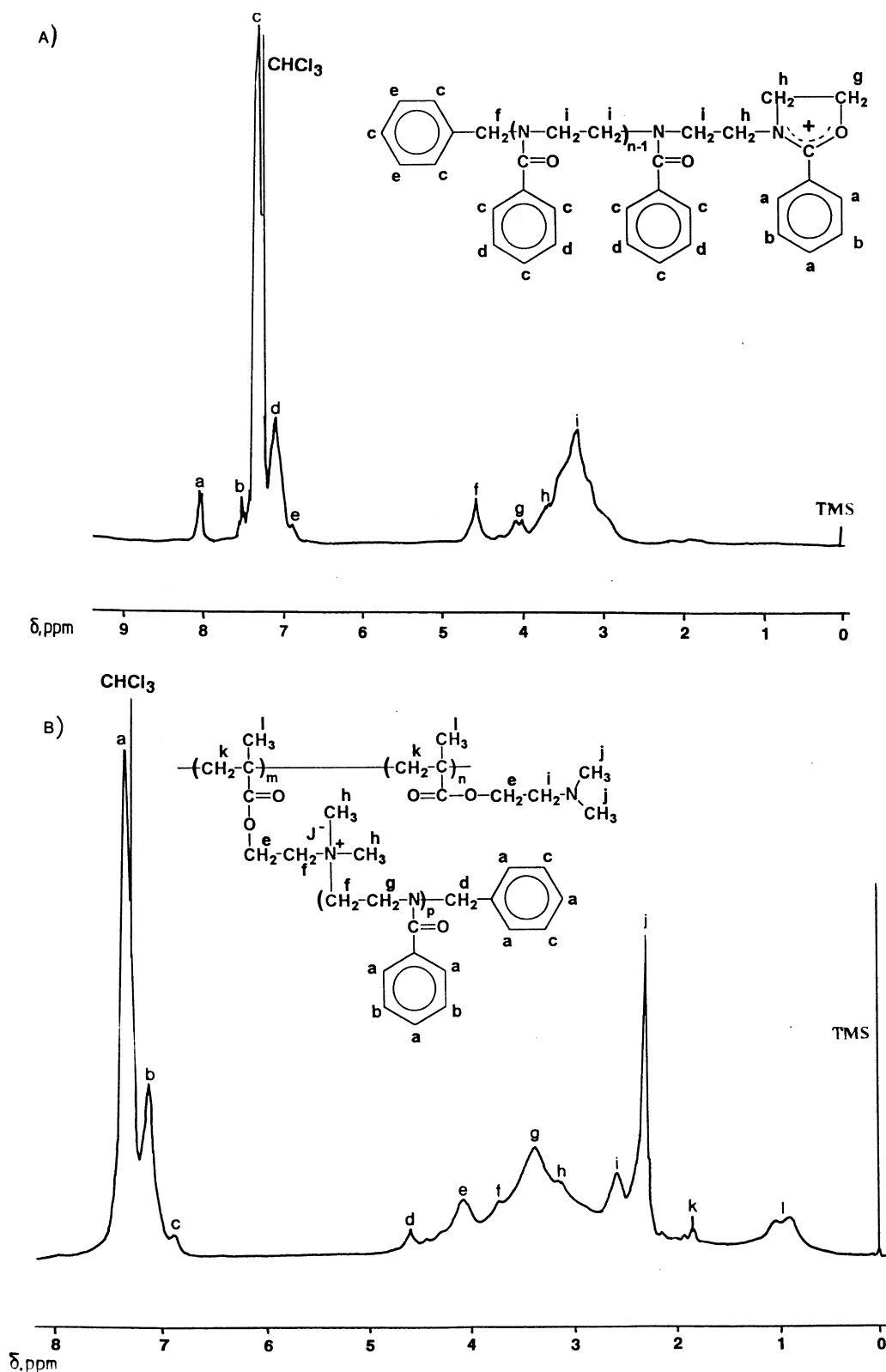
A)

B)

Figure 1 ^{1}H NMR spectra (300 MHz) in CDCl$_3$ (25°C) of: (A) poly(2-methyl-2-oxazoline); (B) poly(dimethylaminoethyl methacrylate)-*g*-poly(2-methyl-2-oxazoline)

fritted bottom. It was then soaked at room temperature (25°C) in the solvent. The weight of the swollen gels was measured periodically after removing the excess liquid by centrifugation for 10 min at 1100*g*. The measurements were continued to constant weights.

The degree of swelling was calculated by the following expression

$$S_w = (W - W_o)/W_o \qquad (1)$$

where W_o is the initial weight of the swollen gel, and W is the weight of the swollen gel.

Experiments were carried out using three

Figure 2 ^{1}H NMR spectra (300 MHz) in CDCl$_3$ (25°C) of: (A) poly(2-phenyl-2-oxazoline); (B) poly(dimethylaminoethyl methacrylate)-*g*-poly(2-phenyl-2-oxazoline)

replicates and the swelling degrees reported are average values.

RESULTS AND DISCUSSION

Synthesis

pDMAEMs with different molecular weights were prepared by radical polymerization with benzoyl peroxide

in 1,4-dioxane at 70°C (*Table 1*). They were used as backbone polymers in the synthesis of graft and crosslinked copolymers.

Table 2 summarizes the results of the ring-opening polymerization of methyl- and phenyloxazolines. All living pROZOs were prepared in quantitative yields. The molecular weights were controlled by the feed ratio of the monomer to the initiator and were determined by several
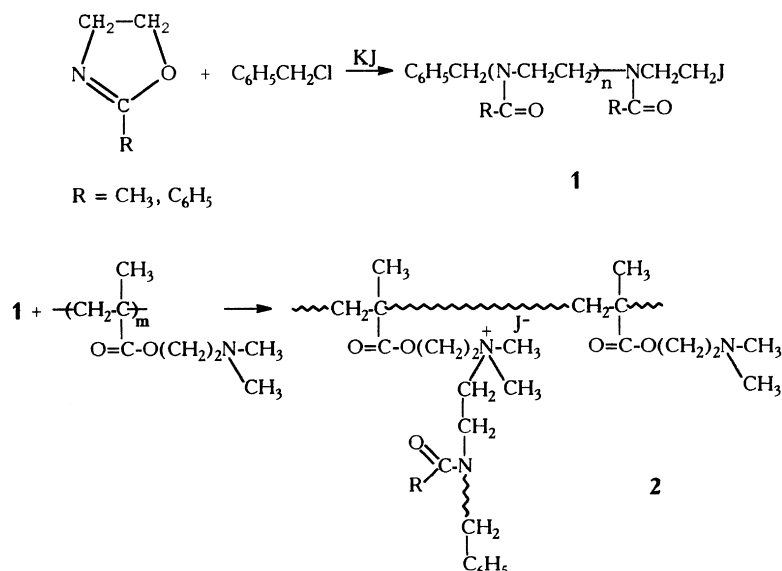
Scheme 1

Table 4 Solubility of pDMAEM-*g*-pROZO

R	H_2O	CH_3OH	THF	1,4-Dioxane	ACN	$CHCl_3$
Me	+	+	−	−	+	+
Ph	−	−	+	+	+	+
			under heating	under heating		

+ Soluble; − insoluble

Table 5 Crosslinking of pDMAEM with pROZO-J or *p,p'*-dichloroxylene

pDMAEM				Crosslinking agent				Crosslinked copolymer		
Sample code	$\bar{M}_n$ SEC	M_1 (g)	$[M_1]$ (g l^{-1})	Sample code	M_2 (g)	Solvent	$\bar{M}_n$ VPO	$\dfrac{-\mathrm{N(CH_3)_2}}{-\mathrm{CH_2J}}{}^a$ (mol mol^{-1})	Yield^b (%)	Sample code
D_1	1600	0.65	162.5	J-pPhOZO-J-I	1.9	ACN	800	1	97	D_1-Ph-I
D_2	4400	0.7	140	J-pMeOZO-J	2	ACN	1800	2	86	D_2-Me
D_3	8500	0.79	158	J-pPhOZO-J-II	1.2	ACN	1600	3	96	D_3-Ph-II
D_3	8500	1.0	125	*p,p'*-dichloroxylene	0.6	ACN	174	1	87	D_3-X
D_4	17 000	0.7	35	*p,p'*-dichloroxylene	0.6	THF	174	1	88	D_4-X

^{a}Calculated from the feed
^{b}Isolated yield after extraction

methods. The values calculated from ^{1}H n.m.r. spectra (*Figure 1a* and *Figure 2a*) and those determined by VPO and SEC are in a good agreement with the theoretical ones. The ^{1}H n.m.r. analysis indicated that the functionality (*F*) of the products is very close to 1.00 or 2.00, depending on the initiator used.

Scheme 1 illustrates the synthesis of α-benzyl-ω-iodide poly(N-acylethyleneimine) and the termination reaction with pDMAEM, which results in formation of graft copolymer through quaternary ammonium groups.

The structure of the prepared graft copolymers was investigated by IR and ^{1}H n.m.r. spectra. Their IR spectra show absorption bands at 1630 cm^{-1} (ν C=O amide), at 1730 cm^{-1} (ν C=O ester) and at 1580 cm^{-1} and 720 cm^{-1} (C_6H_5-, pPhOZO). The overall composition, the average molecular weight and the degree of grafting were calculated from ^{1}H n.m.r. spectra using the intensity ratios of peaks free from overlapping (*Table 3*; *Figure 1b* and *Figure 2b*). The peak ratios at δ 2.15–2.28 [$-$N(CH$_3$)$_2$] to δ 2.1 (CH$_3$-pMeOZO amide) or δ 7.1–7.4 (Ar from In end groups) (*Figure 1b*) and at δ 1.18–1.24 (CH$_3-$, pDMAEM) to δ 6.9–7.33 (C$_6$H$_5-$, pPhOZO or C$_6$H$_5$ − CH$_2$) (*Figure 2b*) were used in the calculations for pPhOZO and pMeOZO, respectively. The degree of grafting is very close to that calculated by the feed ratio. The solubility data also indicate formation of graft copolymers (*Table 4*). The results suggest that the Menschutkin reaction could be successfully applied for grafting and probably for crosslinking using polyoxazolinium iodides as halides and pDMAEM as tertiary amines.

The high efficiency of the grafting reaction was a reason to expect successful synthesis of networks by interaction of α,ω-diiodide of pROZO with pDMAEM (*Scheme 2*).

$$R = CH_3, C_6H_5 ; \quad R_1 = CH_2C_6H_4CH_2$$
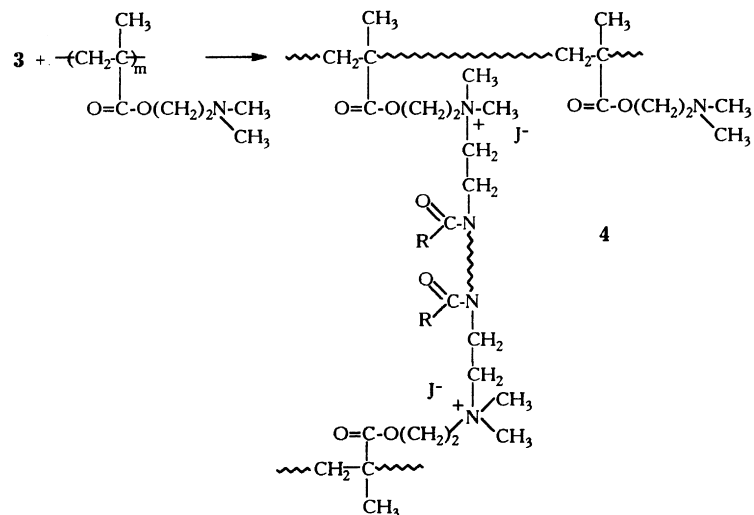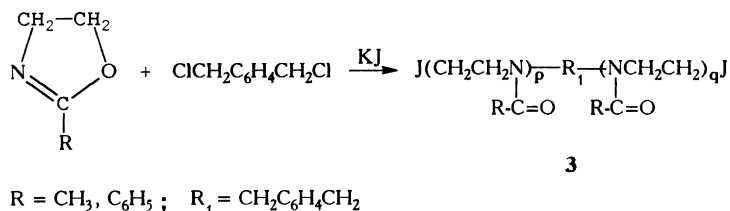
Scheme 2

The crosslinking reaction was carried out at 80°C by three types of cross-linkers until gel was formed (*Table 5*). All products were obtained in high yields, which allowed the assumption that the average density of the network could be controlled by the ratio $-N(CH_3)_2/-CH_2J$ and by the molecular weight of the bridge. Naturally, it is possible for some molecules of the cross-linker to react only with one of their ends or/and with a single backbone chain producing closed loops. The structure of the obtained networks was confirmed by their i.r. spectra and solution properties. The i.r. spectra showed absorption bands attributed both to pDMAEM and to pROZO: at 1640 cm^{-1} (ν C=O amide), at 1730 cm^{-1} (ν C=O ester) and at 1580 cm^{-1} and 720 cm^{-1} (Ar– from pPhOZO).

PROPERTIES

Swelling

The structure of the crosslinked products, although not precisely defined, assumes high charge-density of ionic groups. The networks are polyfunctional and contain both strong-base (quaternary ammonium) and weak-base (tertiary amine) groups of two different amino-containing polymers. They were expected to behave as hydrogels and amphigels, since the backbone is hydrophilic and the bridges could be hydrophilic or hydrophobic, depending on the oxazoline acyl group. Further modification by conversion of the free tertiary amine groups into the quaternary ammonium salt form is possible as well.

It is well known, that swelling is a main property predicting the characteristic behaviour of gels, chelating resins, etc., and is determined by their hydrophilic–hydrophobic balance. We investigated the swelling of the networks in water and chloroform changing the nature and the length of the cross-linkers and the average molecular weight of pDMAEM segments between the nearest bridges.
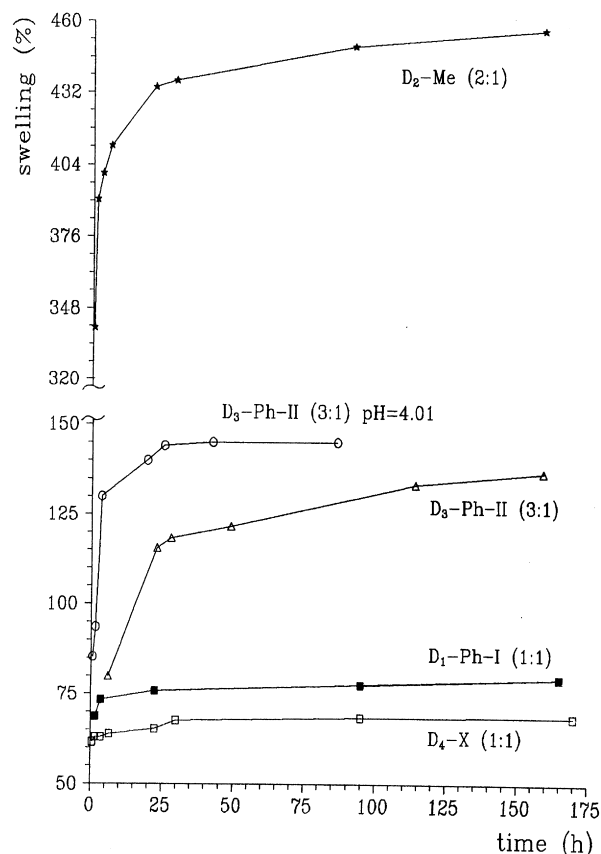

Figure 3 Swelling of polymer networks in distilled water, 25°C

Increasing the length of the pPhOZO bridges and of the segments between two crosslinking points (between nearest bridges), the water uptake increase from 80% for D_1-Ph-I (1:1) to 140% for D_3-Ph-II (3:1) (*Figure 3*). It was expected
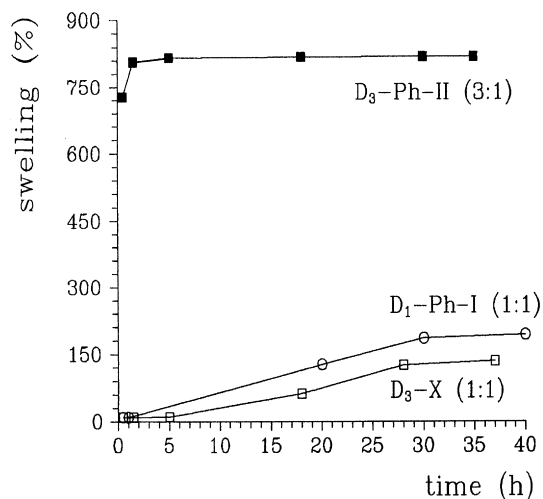
Figure 4 Swelling of polymer networks in chloroform, 25°C

Figure 5 Reduced viscosity–concentration relationship of pDMAEM-g-pMeOZO (curve 1); Fuoss–Strauss plot according $\eta_{sp}/c = A(1 + B.c^{1/2})$—curve 2; $A = 10.63$ dl g^{-1}, $B = 2.32$ dl$^{1/2}$ g$^{-1/2}$

that in acidic water (at pH $= 4.01$) the gel would absorb water to a much higher extent. However, the equilibrium swelling is only about 10–15% higher. Probably, the diffusion of water into the hydrophobic area of the shrunken pPhOZO chains is hampered (*Figure 3*). The higher rate of swelling and the small increase in the degree of swelling is caused by protonation of the remaining tertiary amine groups in pDMAEM improving the diffusion in the hydrophilic area. The polymer samples based on pMeOZO (D$_2$-Me) display typical hydrogel properties with water uptake about 460% (*Figure 3*). The swelling of the amphiphilic networks in chloroform (common solvent for the building polymers) confirms the assumption that swelling depends on the solubility of the blocks comprising the network and the diffusion of the solvent, determined by the density of the network (*Figure 4*). The equilibrium swelling of D$_3$-Ph-II (*Figure 4*) drastically increased compared with that of D$_1$-Ph-I (*Figure 4*) because of the decrease in crosslinking density. D$_3$-Ph-II absorbs about 800% chloroform. Comparing the swelling degrees of D$_3$-X (*Figure 4*) and D$_1$-Ph-I (*Figure 4*) as well as D$_4$-X (*Figure 3*) and D$_1$-Ph-I (*Figure 3*), it is seen that the molecular weight of the main chain has no effect. The swelling equilibrium was reproducible within experimental error, which showed that the networks were stable and swelling changes took place without disintegration. The results suggest that the swelling of the products based on pDMAEM and pROZO could be controlled by the molecular weight of the crosslinking agent and the distance between the cross points–N(CH$_3$)$_2$/CH$_2$J ratio.

Solution properties

It is well established that the introduction of relatively small amounts of ionic groups into a polymer modifies its solution properties. The viscosity behaviour of water-soluble pDMAEM grafted with poly(2-methyl-2-oxazoline) chains (pDMAEM–graft-pMeOZO) was investigated in order to illustrate the successful formation of graft and crosslinked polyelectrolytes by Menschutkin reaction. The reduced viscosity increases considerably with decreasing concentration of the polymer and does not obey the Huggins relation (*Figure 5*, curve 1). However, it fits very well the Fuoss–Strauss equation[7] for the reduced viscosity of solutions containing flexible polyelectrolytes, indicating the dissociation of the polyelectrolyte in H$_2$O (*Figure 5*,
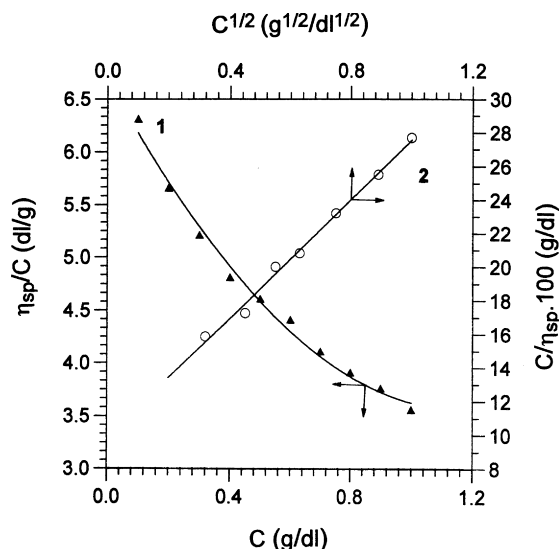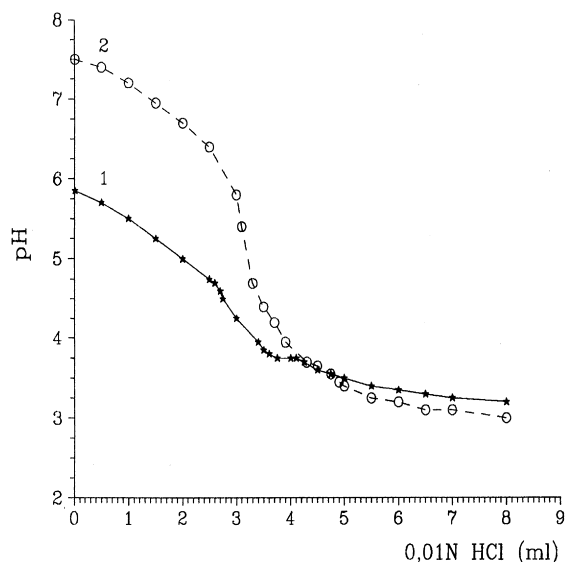

Figure 6 Potentiometric titration curves of pDMAEM-g-pMeOZO [2 g l^{-1}] with HCl [0.01N]: 1—in distilled water; 2—$\mu = 0.1$ mol l^{-1} (KCl)

curve 2). Constants A and B are characteristic for the copolymer and the A value of 10.63 dl g^{-1} suggests that the polymer is highly expanded in water.

The polybase nature of the water-soluble graft copolymer is best demonstrated by the potentiometric titration. The titration extends over a very wide pH range and the titration curves markedly differ from simple type curves (*Figure 6*). In salt-free water the profile of the curve is similar to that of intermediate polybase electrolytes with two steps at pH 4.65 and pH 3.70 (*Figure 6*, curve 1). The curve obtained by titration of solution with constant ionic strength $\mu = 0.1$ mol l^{-1} (KCl) is more steep, but it also has two steps weekly expressed (*Figure 6*, curve 2). Probably, the second step is due to the hardly accessible amino groups from pDMAEM.

The effect of the neighbouring ammonium groups on the dissociation and pK_a were determined by means of potentiometric titration using a modified Henderson–Hasselbalch

Table 6 Sorption and distribution coefficient, K_d, of metal ions on pDMAEM–pROZO in water solutions at pH 7[a]

Copolymer	Fe^{3+}		Mn^{2+}		Cu^{2+}		Ni^{2+}	
	(%)	$K_d \times 10^{-2}$ (ml g^{-1})	(%)	$K_d \times 10^{-2}$ (ml g^{-1})	(%)	$K_d \times 10^{-2}$ (ml g^{-1})	(%)	$K_d \times 10^{-2}$ (ml g^{-1})
pD$_1$-g-pPh	13.55	1.08	12.65	1.01	21.50	1.72	29.20	2.34
D$_3$-Ph-II	5.50	0.44	15.04	1.20	17.50	1.40	16.60	1.33
D$_2$-Me	6.65	0.53	15.20	1.22	28.50	2.28	18.70	1.50

[a] $[Me^{n+}] = 20 \, mg \, l^{-1}$ as $Me^{n+}(NO_3)_n$; copolymer $[C] = 1.25 \, g \, l^{-1}$ on kieselguhr with $S_{sp} = 1 \, m^2 \, g^{-1}$

$$K_d = \frac{\text{metal ions in polymer}}{\text{metal ions in solution}} \times \frac{\text{volume of solution (ml)}}{\text{weight of polymer (g)}}$$
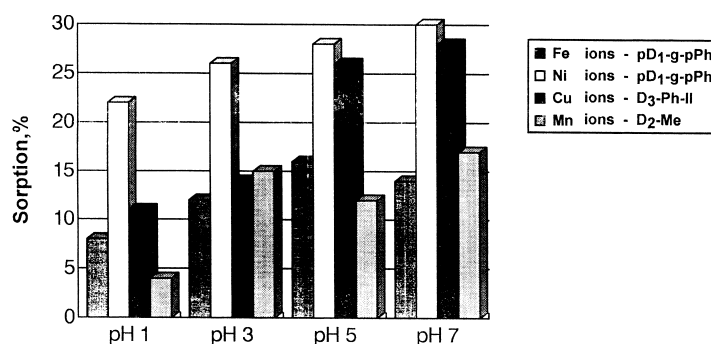
Figure 7 pH dependence of metal ions sorption on graft copolymers and polymer networks

equation[16]

$$pH = pK_a - m \log \frac{1-\alpha}{\alpha} \qquad (2)$$

where α is the degree of neutralization, pK_a is the average dissociation constant and m is a measure of the effect of neighbouring ammonium groups on dissociation of the quaternary ammonium groups. The constants pK_a and m were obtained at the half-neutralization point ($\alpha = 0.5$) and from the slope of the straight line of pH *versus* log $(1 - \alpha)/\alpha$ plot, i.e. at $\alpha = 0.2$. They were determined to be $pK_a = 5.21$ and $m = 0.54$. The equation is valid in the range of values between 0.2 and 0.5. The value $pK_a = 5.21$ suggests that there is a polycation in the solution.

Sorption of metal ions

The network's bridge chains contain weak-base tertiary amino groups and are known to exhibit sorption capacity for metal ions, although not high[5]. The sorption of Cu^{2+}, Mn^{2+}, Ni^{2+} and Fe^{3+} from aqueous solutions of the corresponding nitrates was measured by atom absorption spectrophotometry. The products were studied both in the swollen state and supported on kieselguhr. The distribution coefficient and the quantity of metal ions sorbed from their aqueous solutions are presented in *Table 6*.

The effect of pH on the sorption is given in *Figure 7*. These relationships are of certain importance in explaining the nature of the interaction as well as for the recycling of the polymer sorbents. Contrary to some data[13,17] we find that polyoxazoline chains interact with some bivalent metal ions. As *Figure 7* shows, sorption of metal ions occurs even after protonation of all free tertiary amino groups from pDMAEM (at pH = 4 to pH = 7).

Anion-exchange properties

The polyelectrolyte amphiphilic copolymers and networks contained high concentration of ammonium groups. The networks were studied for anion-exchange of ferrocyanide and rhodanide ions. These complex anions are
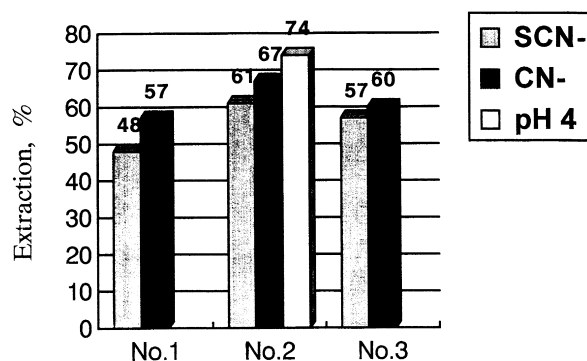
Figure 8 Sorption of $Fe(CNS)_3$ and $Fe_4[Fe(CN)_6]_3$ on polymer networks. pDMAEM: Mn = 1600 (No. 1); Mn = 1600 (on kieselguhr) (No. 2); Mn = 8500 (on kieselguhr) (No. 3). pPhOZO: Mn = 800 (No. 1); Mn = 800 (on kieselguhr) (No. 2); Mn = 174 (on kieselguhr) (No. 3)(*p,p'*-dichloroxylene)

characteristic with their intensive colour and are often used in analytical chemistry.

The anion-exchange capacity was determined by spectral methods on kieselguhr-supported samples and on pieces of the networks swollen in aqueous solutions of $Fe(CNS)_3$ and $Fe_4[Fe(CN)_6]_3$. The results obtained are given in *Figure 8*. It can be seen that over 60% of the ions are extracted from the solution in the gel phase. The polymer products exchange ferrocyanide ions better. When the network is kieselguhr supported, the extraction degree increases and reaches 70%. The results show that the high charge-density of the ammonium groups is the most important factor for the anion-exchange, while the diffusion has a negligible effect. The maximum anion-exchange is at pH 4. It is due to the additional quaternization of the free tertiary amino groups in pDMAEM.

CONCLUSION

Novel polyelectrolyte graft copolymers and networks have been synthesized using the quaternization reaction between

poly(dimethylaminoethyl methacrylate) and mono- and bifunctional polyoxazolinium iodides. The method allows the length of the grafts or crosslinking blocks, the charge-density of ammonium groups and the density of the network to be controlled. Depending on structure of the polymer and the nature of the polyoxazoline segments, the products obtained exhibit swelling properties of the hydrogels or amphigels.

The copolymers and networks show the solution properties of polyelectrolytes. Because of the high ammonium charge-density, they exhibit good anion-exchange capacity which could be controlled by the synthesis methods. The polyoxazoline chains interact also with some bivalent metal cations.

ACKNOWLEDGEMENTS

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