

Preparation of Cationic Water-Absorbent Resin from PEI and PEO

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SYNOPSIS

Hydrophilic network copolymers containing poly(ethylene oxide) and polyethyleneimine blocks were prepared by cross-linking polyethyleneimine with poly(ethylene oxide) terminated at both ends with Br atoms in DMSO. The experimental results show that the network density of the copolymer and the water absorption power thereupon can be efficiently controlled by the change of the amount of DMSO in the reaction system. Further modification was obtained by converting these copolymers into quaternary ammonium salts. The resulting quaternary ammonium salts exhibit enormously enhanced water absorption power. The absorption power of these quaternary ammonium salts in several organic solvents and in aqueous solutions containing Na^+ , Ca^{2+} , Mg^{2+} , or Fe^{3+} was also examined.

INTRODUCTION

Although a wide variety of water-absorbent resins have been prepared in recent years, most of them are structurally based on negatively charged networks, many of which are formed of homogeneous carbon-carbon backbones. The counterion is usually Na^+ . Polymers of such all-carbon skeleton are difficult to degrade in nature, which would be a source of pollution when used as unrecoverable materials. Another problem is that their absorption power is not satisfactory in water containing Ca^{2+} , Mg^{2+} , or other heavy metal ions because of the ion-exchanging.

It would be of interest to prepare water-absorbent polymers that have positively charged networks with heteroatoms in the backbones. In present article, network copolymers with such characteristics were prepared by cross-linking polyethyleneimine with poly(ethylene oxide) terminated at both ends with Br atoms and then converting them into quaternary ammonium salts. The resulting polymers have positively charged networks with O and N^+ in the backbones. The counterion is Cl^- .

EXPERIMENTAL

Starting Materials

Poly(ethylene oxide) (PEO, $\bar{M}_n = 3000$, BASF) linear polymer was recrystallized in ethyl ether/ethanol (1 : 1). The recrystallized PEO was dissolved in dichloromethane and reprecipitated with ethyl ether, then dried to constant weight in vacuum at room temperature.

Polyethyleneimine (PEI, $\bar{M}_n = 1500$, BASF), supplied in 50% aqueous solution, was repeatedly mixed with anhydrous ethanol and distilled in a rotary evaporator at 70°C under reduced pressure to remove water, then dried to constant weight in vacuum at room temperature. The anhydrous PEI is a viscous liquid.

Tetrabromomethane, triphenylphosphine, and dimethyl sulfate, guaranteed reagent grade, were used as received. All solvents used were purified by conventional methods.

Bromination of Poly(ethylene oxide)

The preparation of poly(ethylene oxide) terminated at both ends with Br atoms (PEO- Br_2) was as follows^{1,2}: To a solution of 60.0 g PEO and 26.5 g

tetrabromomethane in 150 mL toluene was added a solution of 21.0 g triphenylphosphine in 40 mL toluene. The mixture was kept in the dark and shaken gently at room temperature for 48 h, then filtered to remove precipitated triphenylphosphine oxide, which was formed in the reaction. Ethyl ether was added to precipitate PEO-Br₂, which was further purified by recrystallization and reprecipitation in the same way as PEO. The yield of PEO-Br₂ was 58.9 g. Calculation from elemental analysis indicated that the conversion of OH groups is complete by using the method mentioned above, and both ends of each macromolecule are Br atoms.

Network Copolymer (PEO-PEI)

A flask charged with 5.0 g PEO-Br₂, a certain amount of PEI, and a certain amount of DMSO was flushed with argon to remove air and immersed in an oil bath thermostated at 120°C with a magnetic stirrer. After a few minutes, PEO-PEI was formed and the reaction system gelled; it was then kept in an oven thermostated at the same temperature as oil bath for a total of 5 h. The network copolymer gel was swelled in water, cut into small particles by quashing through a stainless-steel wire mesh, then washed with water thoroughly to remove all soluble substances. The dehydration of PEO-PEI particles was carried out by washing with ethanol, ethyl ether/ethanol (1 : 1), and ethyl ether in the given order and then dried to constant weight in vacuum at room temperature.

Quaternary Ammonium Chloride of PEO-PEI

A flask charged with 2.0 g PEO-PEI particles was added to 12 mL dimethyl sulfate. After 10 min, 40 mL water was added and the pH of the mixture was

adjusted to 9–10 by adding drops of NaOH aqueous solution. The mixture was shaken gently at room temperature for 24 h, and its pH was kept in the above range constantly by adding NaOH aqueous solution. The particles were filtered, washed with water, then converted into quaternary ammonium chloride by pickling with HCl aqueous solution, and, finally, washed with water to neutrality. The dehydration and drying of the salt was similar to that of PEO-PEI particles.

Measurements

¹³C-NMR spectra were measured on a Bruker WM400 spectrometer, and elemental analysis was done with an elemental analyzer Model 1104 (Carlo Erba). The absorption power was determined by the so-called teabag test: A certain amount of polymer (0.1–1.0 g) was weighed into a teabag, which was then sealed and immersed in a test liquid at room temperature for a certain period of time. It was then taken out, and after 15 s, the teabag with the swelled polymer in it was weighed again. To deduct the weight of the wet teabag, a blank test was done. The absorption power was given by following equation:

Absorption power (g/g_p)

$$= \frac{\text{Total wt. of teabag} - \text{Wt. of wet teabag} - \text{Wt. of dry polymer}}{\text{Wt. of dry polymer}}$$

RESULTS AND DISCUSSION

Similar to PEO, PEO-Br₂ is a white crystal powder at room temperature, immiscible with PEI without solvent, even above its melting point. After the reaction takes place, a homogeneous mixture can be

Table I Effect of DMSO on Cross-Linking of PEI with PEO-Br₂

Sample	Before Reaction			Network Copolymer			Conversion (%)	
	PEO-Br ₂ (g)	PEI (g)	DMSO (mL)	Yield (g)	PEO : PEI (g : g) ^a	Absorption Power (g/g _p) ^b	PEO	PEI
5-1.75-0	5	1.75	0	5.40	82 : 18	8.0	88.6	55.5
5-1.75-8	5	1.75	8	5.90	78 : 22	18.0	92.0	74.2
5-1.75-14	5	1.75	14	5.90	76 : 24	25.4	89.7	80.9
5-1.75-30	5	1.75	30	5.80	76 : 24	30.2	88.1	79.5
5-1.75-40	5	1.75	40	5.70	76 : 24	69.0	86.6	78.2

^a Calculated from elemental analysis.

^b Tested in tap water; absorption time 100 min.

Table II Effect of the Ratio of PEI to PEO-Br₂ on Cross-Linking

Sample	Before Reaction			Network Copolymer			Conversion (%)	
	PEO-Br ₂ (g)	PEI (g)	DMSO (mL)	Yield (g)	PEO : PEI (g : g) ^a	Absorption Power (g/g _p) ^b	PEO	PEI
5-1.50-40	5	1.50	40	5.70	80 : 20	44.7	91.2	76.0
5-1.65-40	5	1.65	40	5.70	78 : 22	56.3	88.9	76.0
5-1.75-40	5	1.75	40	5.70	76 : 24	69.0	86.6	78.2
5-2.00-40	5	2.00	40	5.54	76 : 24	82.4	84.2	66.5
5-2.25-40	5	2.25	40	2.70	75 : 25	130.7	40.5	30.0

^a Calculated from elemental analysis.

^b Tested in tap water; absorption time 100 min.

formed in the reaction system of PEI with PEO-Br₂ and then gelled quickly. It is because PEO-Br₂ easily reacts with PEI to form PEO-PEI, which helps one phase to disperse into another phase. To make the cross-linking of PEI with PEO-Br₂ a real homogeneous reaction, DMSO, a common solvent both for PEI and PEO-Br₂, was used. When sufficient PEO-PEI was formed, the reaction system gelled. All the polymers in the system as well as DMSO were included in the gel.

Different amounts of DMSO were used in the cross-linking reaction. From the data in Table I, it can be seen that the yield of PEO-PEI network copolymer, the content of PEI in the copolymer, and its absorption power increase by using DMSO. With further increasing of DMSO, the yield of copolymer

decreases slightly and the content of PEI in the copolymer remains unchanged, but its water absorption power increases continuously. From the above results, it could be deduced that DMSO acts not only as a solvent to make a real homogeneous reaction, but also as a diluent to decrease the network density of the copolymer, thus providing enhanced absorption power.

The effect of the ratio of PEI to PEO-Br₂ on the cross-linking was also investigated. The data in Table II show that as the amount of PEI increases the content of PEI in the copolymer increases and its water absorption power increases rapidly. The yield of the copolymer remains unchanged at first with the increase of PEI, but with a further increase of PEI, the yield of the copolymer drastically decreases. Obviously, a certain amount of PEO-Br₂ cannot be sufficient to cross-link too much PEI to form an insoluble network copolymer; some of the copolymer with insufficient cross-linking can be dissolved out. To both achieve enhanced water absorption power and not to drastically decrease the yield of the network copolymer, choosing a certain ratio of PEI to PEO-Br₂ and increasing the amount of DMSO would be preferable.

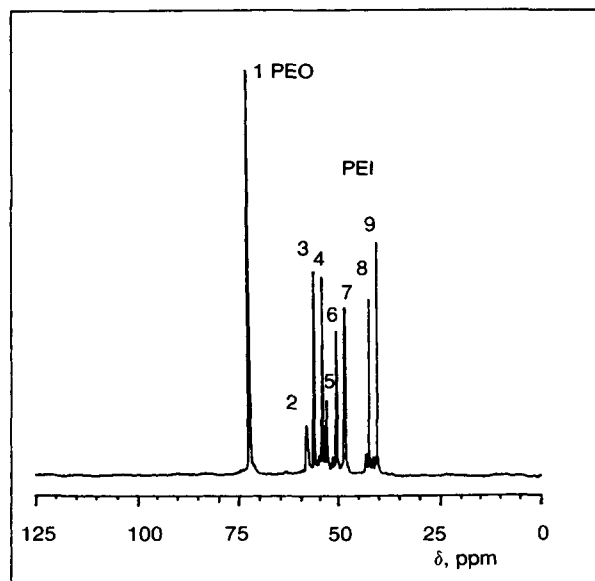


Figure 1 ¹³C-NMR spectrum of PEO-PEI in D₂O.

Table III Conversion of PEO-PEI into Quarternary Ammonium Chloride

Sample	Sample Weight (g)	
	Before Conversion	After Conversion
5-1.50-40	5.70	5.98
5-1.65-40	5.70	6.10
5-1.75-40	5.70	6.46
5-2.00-40	5.54	5.40

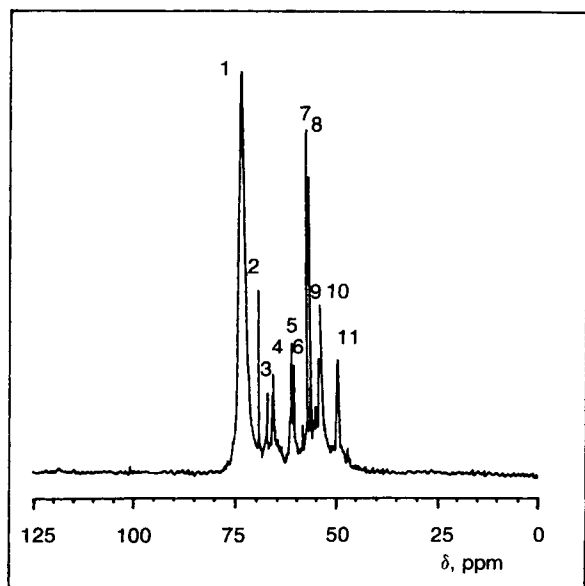
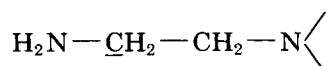
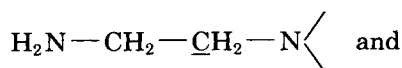


Figure 2 ^{13}C -NMR spectrum of quaternary ammonium chloride from PEO-PEI in D_2O .

Structure of PEO-PEI

^{13}C -NMR spectra of the PEO-PEI copolymer were measured to explore the structure. A representative spectrum is shown in Figure 1. All the signals in the spectrum can be found in the spectra of PEI and PEO used in the research except for signals 2 and 9. Signal 2 (58.05 ppm) and signal 9 (40.29 ppm) are attributed to



respectively.^{3,4} Therefore, it could be concluded that the PEO chain is combined with the last N but one in the PEI chain. Because PEI is a highly branched polymer,³ it can react with PEO- Br_2 to form a network copolymer. This conclusion has been further confirmed by the fact that the reaction of PEO- Br_2 with a linear molecule, e.g., triethylenetetramine and tetraethylenepentamine, cannot form a gel, but, rather, will form linear copolymers.

Quaternary Ammonium Chloride of PEO-PEI

Further modification of PEO-PEI was carried out by conversion into quaternary ammonium chloride. The results are listed in Table III. Figure 2 shows the ^{13}C -NMR spectrum of the quaternary ammonium chloride from PEO-PEI. Signals 5 (60.29 ppm), 9 (54.18 ppm), 10 (53.70 ppm), and 11 (49.30 ppm) are attributed to

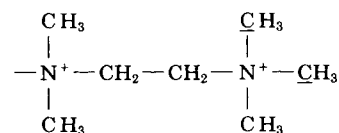
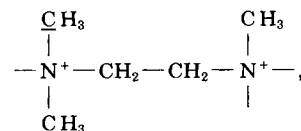
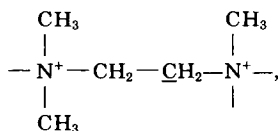


Table IV Comparison of Absorption Power between PEO-PEI and Quaternary Ammonium Chloride

Sample	Absorption Power (g/g _p)			
	Salt-Free Water		0.9% NaCl Aqueous Solution	
	Before Conversion	After Conversion	Before Conversion	After Conversion
5-1.50-40	83.5	375	47.5	51.0
5-1.65-40	88.0	450	52.4	60.0
5-1.75-40	95.0	550	62.5	61.5
5-2.00-40	105.0	645	64.5	76.5
Luquasorb HC9797		480		60.0

^a Absorption time 100 min.

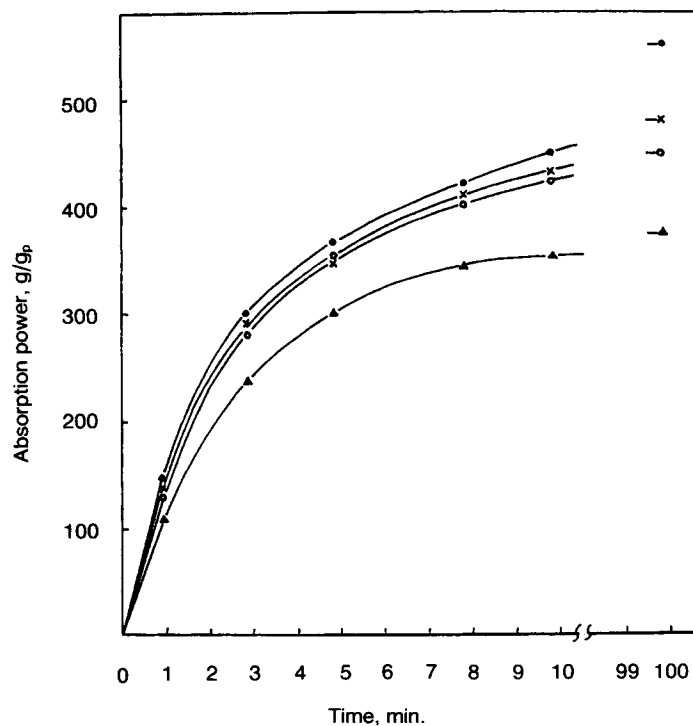
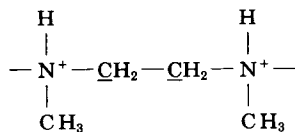


Figure 3 Absorption power of quaternary ammonium chloride vs. time in salt-free water: (\blacktriangle) from sample 5-1.50-40; (\circ) from sample 5-1.65-40; (\bullet) from sample 5-1.75-40; (\times) Luquasorb HC9797.

and



respectively.⁴ Table IV shows the comparison of absorption power between PEO-PEI and quaternary ammonium chloride, both in salt-free water and in 0.9% NaCl aqueous solution. For reference, the absorption power of Luquasorb HC9797 (a commercial water-absorbent resin, BASF) was tested and the results are also listed in Table IV. The enhanced water-absorption power of quaternary ammonium chloride of PEO-PEI is notable, especially that in salt-free water.

Absorption Power of Quaternary Ammonium Chloride

Figure 3 shows the absorption behavior of quaternary ammonium chloride in salt-free water. The absorption behavior of the quaternary ammonium chloride from the PEO-PEI sample 5-1.65-40 is

similar to that of Luquasorb HC9797, and the quaternary ammonium chloride from sample 5-1.75-40 is better.

Table V shows the absorption power of the quaternary ammonium chloride in organic solvents. Table VI shows their absorption power in aqueous solutions containing Ca^{2+} , Mg^{2+} , and Fe^{3+} . It can

Table V Absorption Power of Quaternary Ammonium Chloride in Organic Solvents

Sample	Sample ^b		
	5-1.50-40	5-1.75-40	5-2.00-40
Ethanol	60	110	170
Toluene	12	11	12
Dichloromethane	7.5	9.0	8.5
Trichloromethane	5.5	5.7	5.7
Tetrachloromethane	3.2	3.3	3.2
Trichloroethylene	5.7	5.7	5.6

^a Absorption time 100 min.

^b Quaternary ammonium chloride from corresponding PEO-PEI.

Table VI Absorption Power of Quaternary Ammonium Chloride in Aqueous Solutions Containing Metal Ions

Aqueous Solution	Sample ^a	Absorption Time (min)					
		1	2	4	10	20	30
0.9% CaCl ₂	5-1.75-40	24.0	28.4	33.2	36.0	36.8	36.8
	Luquasorb HC9797	4.0	4.0	4.1	4.1	4.3	4.3
0.9% MgCl ₂	5-1.75-40	24.8	31.2	33.2	36.4	36.8	36.8
	Luquasorb HC9797	5.0	5.2	5.2	5.2	5.1	5.2
0.9% FeCl ₃	5-1.75-40	16.2	27.0	29.2	34.0	34.8	34.8
	Luquasorb HC9797	4.0	4.4	4.8	4.8	4.8	4.8

^a Quaternary ammonium chloride from PEO-PEI sample 5-1.75-40.

be seen that even in such aqueous solutions the quaternary ammonium chloride exhibits better absorption power.

CONCLUSIONS

Hydrophilic network copolymers containing poly(ethylene oxide) and polyethyleneimine blocks can be prepared by cross-linking polyethyleneimine with poly(ethylene oxide) terminated at both ends with Br atoms in DMSO. The network density of the copolymer can be efficiently controlled by changing the amount of DMSO in the reaction system. Further modification can be obtained by converting the copolymer into quaternary ammonium chloride. The resulting quaternary ammonium chloride exhibits enhanced water absorption power and better absorption power in aqueous solutions containing Ca²⁺, Mg²⁺, and Fe³⁺.

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