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Novel ionenes with allyl pendant groups

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Summary

Novel ionenes with allyl pendant groups have been synthesized by condensation of N,N'- bisallylpiperazine with organic dihalides such as 1,4-dichlorobutane, 1,6-dibromohexane and 1,4-dichloromethylbenzene. The polymers are readily soluble in water and have low molecular weights. The structure of the ionenes has been identified by spectroscopic techniques. The concentrated aqueous solutions of the resulting ionenes can be crosslinked by t-butylhydroperoxide as a radical initiator to give transparent hydrogels. The ionenes also act as an crosslinking agent in copolymerization with high concentrations of acrylic acid in the presence of $K_2S_2O_8$ as a radical initiator in water at 65°C.

Introduction

Ionenes are ionic polymers containing onium groups (mostly quarternary ammonium groups) in the backbone. One of the most common way of preparing ionenes is Menschutkin reaction of ditertiary amines with organic dihalides. In this reaction, no polymer is formed when the number of carbon atoms between two amino groups is less than 3, due to cyclization (1).

The properties of ionenes depends strictly on the charge density. Ionenes with high charge density demonstrate strong ionic interactions in aqueous solutions. Whereas ionenes derived from dihalides with long alkyl chains have lower charge density and show many similarities to organic polymers (2).

Ionenes like other polyelectrolytes have found potential applications in flocculation (3) and preparation of symplex membranes for pervaporization (4). Principally all the ionenes are expected to have common usages of other cationic polyelectrolytes.

Recently, Wang et al synthesized the ionenes by reacting α,ω-dialkanediamines with α,ω-dibromoalkanes based on Menschutkin reaction(5). They found that by means of

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in-situ ^{13}C NMR the progress of aliphatic ionene polymerization was complex reaction.

In this study we have presented the synthesis of new ionenes with allyl pendant groups by quarternization of N,N'-diallylpiperazine with organic dihalides such as 1,4-dichlorobutane, 1,6-dibromohexane and 1,4-dichloromethylbenzene. The structures of the resulting ionenes have been identified by ^{1}H-NMR and FT-IR spectroscopic techniques.

The allyl pendant groups involving are expected to serve as crosslinker. Recently, Yokozawa and Takenoya have carried out the synthesis of polyethers with allyl side chains from dialdehydes, alkylene bis(trimethylsilyl)ethers and bis(trimethyl silyl)ethers(6). Allyl functional side chains are then reacted with 1,2-ethanedithiol in the presence of a radical initiator to yield a crosslinked polymer.

We also demonstrated that in the presence of the ionenes, free radical initiated copolymerization of acrylic acid gives transparent hydrogels which would be of interest in preparing of simplex membranes.

Experimental

All solvents and piperazine (Fluka), allylchloride (Fluka), acrylic acid (Fluka), 1,4-dichlorobutane (Merck), 1,6-dibromohexane (Merck), 1,4-dichloromethylbenzene (Fluka) and $K_0S_2O_8$ (Merck) were analytical grade and used as obtained. IR spectra were recorded on a Mattson 1000 FTIR spectrophotometer. ^{1}H NMR spectra were obtained with a Bruker AC 250 spectrometer.

Synthesis of Bisallyl piperazine (BAP):

It was prepared by condensation of piperazine with allylchloride as described in literature (7).

General procedure for the preparation of the ionenes:

3.32 g (20 mmol) of BAP and 5 mL of N-methyl-2-pyrrolidone (NMP) were placed in a 100 mL of flask which is mounted in an ice bath on a magnetic stirrer. 20 mmol 0f organic dihalide was added slowly to stirring solution. Stirring was continued for 4 hours at 0-5°C and 7 days at room temperature and then heated at 70°C for 3 hours. After cooling the mixture was poured into 30 mL of ether. The white precipitate was filtered and dried under vacuo at 40°C for 6 hours. All the products obtained are very hygroscopic.

Self-crosslinking polymerization of the ionenes:

In a typical procedure, 1.5 g of the ionene sample was dissolved in 1.5 mL of water. Nitrogen was flushed through the solution. The 0.1 mL of t-butylhydroperoxide was added and heated at 90 °C until gelation occurs. The gel formed was broken up and dispersed in 50 mL of water and filtered. It was then transferred into 20 mL of acetone and left to stand overnight. After filtration, it was dried at 40 °C under vacuo for 24 hours.

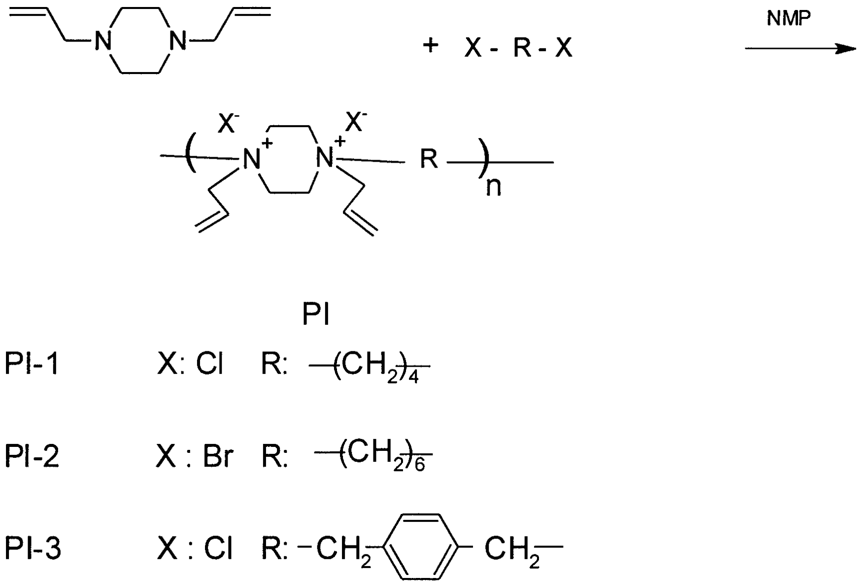
Copolymerization of the ionenes with acrylic acid:

In order to test crosslinking ability of the ionenes, 10 mL of aqueous solutions of 1 mmol (based on repeating unit) the ionene and 3.6 mL (50 mmol) of acrylic acid were simply copolymerized under N_2 atmosphere with $K_2S_2O_8$ initiator at 65°C. Gelation times were monitored and listed in Table I.

Results and Discussion

Synthesis and characterization of the ionenes:

Quarternization of N,N'-bisallylpiperazine with organic dihalides in NMP solution gives the corresponding ionenes with allyl pendant groups in low to high yields depending on the organic dihalides employed (Scheme 1).



Scheme 1

^{1}H NMR spectrum of ionene (PI-2) shows signals appeared in 5.05-5.98 ppm and 3.95-4.25 ppm range corresponding to six olefinic and four methylenic protons of two allylic groups, respectively (Fig. 1). Eight methylenic protons of piperazine group are observed at 3.48 ppm as a broad singlet. Remaining twelve protons of hexyl group are assigned as multiplet peaks between 1.2-3.17 ppm range.

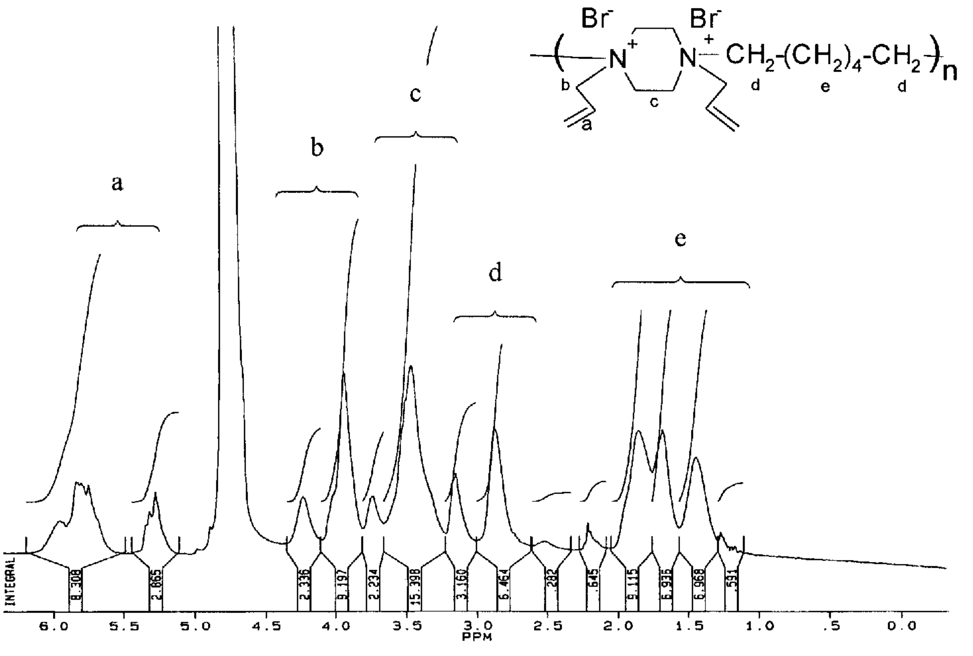


Figure 1. ^{1}H NMR spectrum of the ionene (PI-2) in D_2O.

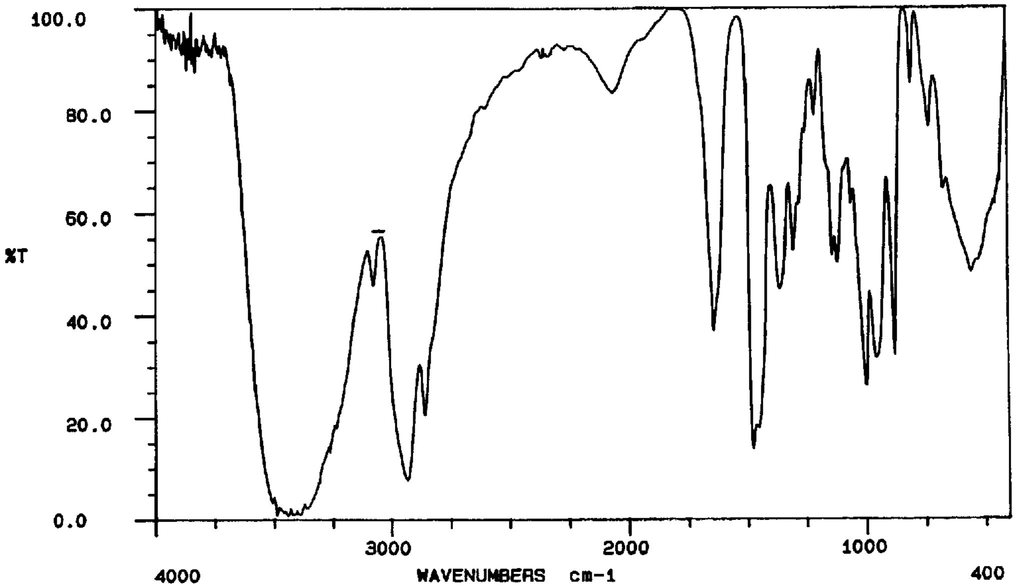


Figure 2. IR spectrum of the ionene (PI-2) obtained from KBr disc.

IR spectrum of the ionene (PI-2) shows characteristic peaks of allylic groups, C=C and C-H stretching vibration bands at 1680 cm^{-1} and 3050 cm^{-1}, respectively, and C-H stretching vibrations of alkyl groups at 2850-2960 cm^{-1} (Fig. 2).

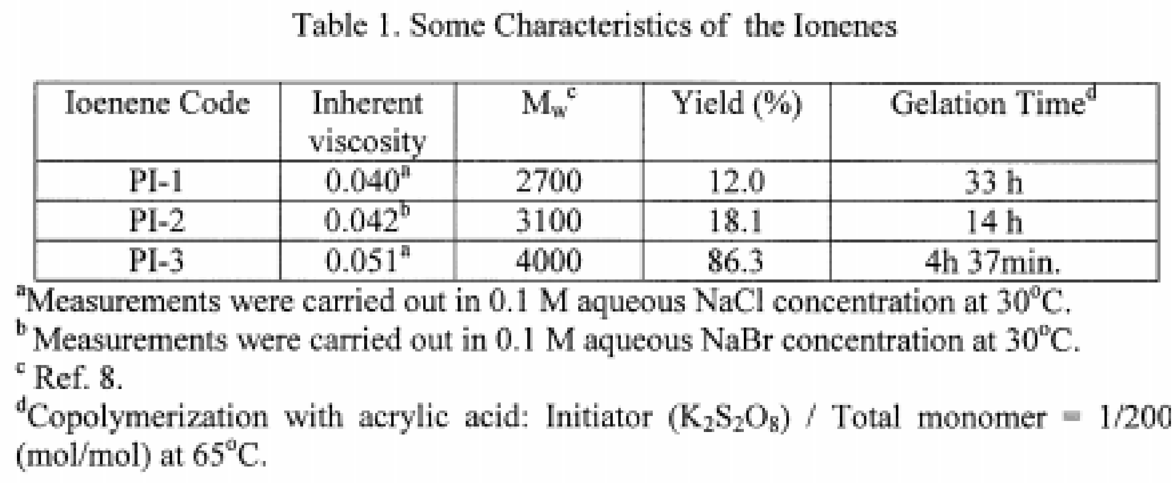


Table 1. Some Characteristics of the Ionenes

Ioenene Code	Inherent viscosity	M_w[c]	Yield (%)	Gelation Time[d]
PI-1	0.040[a]	2700	12.0	33 h
PI-2	0.042[b]	3100	18.1	14 h
PI-3	0.051[a]	4000	86.3	4h 37min.

[a] Measurements were carried out in 0.1 M aqueous NaCl concentration at 30°C.

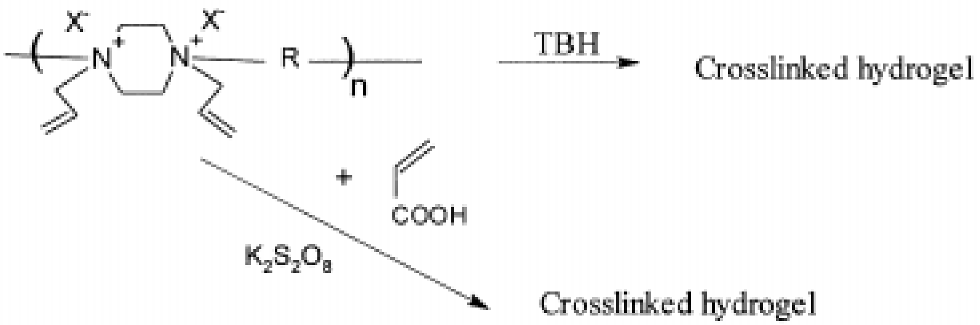
[b] Measurements were carried out in 0.1 M aqueous NaBr concentration at 30°C.

[c] Ref. 8.

[d] Copolymerization with acrylic acid: Initiator ($K_2S_2O_8$) / Total monomer = 1/200 (mol/mol) at 65°C.

The properties of the ionenes:

The ionenes show substantially low viscosities indicating low molecular weights (Table 1). Molecular weights of the ionenes were calculated as 2700-4000 daltons corresponding to 8-9 repeating units by using the average values of Mark-Houwink parameters ($K=1.4 \times 10^{-4}$ and $a = 0.71$) derived for polycations (8).



Scheme 2

The ionenes obtained do not undergo crosslinking in moderate concentrations with t-butylhydroperoxide (Scheme 2). Gel formation only occurs in highly concentrated solutions of the ionenes, ie. 50% (w/w). No gelation was observed by employing $K_2S_2O_8$ initiator. This behaviour similar to those of common allyl monomers in which the allyl groups are less susceptible to form high molecular weight polymers, most probably because of the well known allylic effect. It is interesting to note that 1,2-ethanedithiol does not cause any crosslinking when mixing for 7 hours even in the high concentrations of the ionenes. Obviously this must be because of the strong repulsion between fully ionized quarternary ammonium groups in the structure. Crosslinking copolymerization of the ionenes with acrylic acid in the presence of $K_2S_2O_8$ takes place at relatively longer reaction periods (Table 1). However low gel yields are obtained under the conditions studied. Because at high concentrations, the gels formed contain soluble fragments which are washed away with excess amount of water.

The ionenes (PI-1 and 2) are obtained in low yields (Table 1). In order to attain high yields we have tried higher temperatures. An optimum temperature around 60°C has been suggested for the quarternization reaction by Wang et al (5). However at 70°C for long reaction periods, the resulting products especially from dichlorobutane were somewhat colored indicating HX elimination as a side reaction. This was not observed when 1,4-dichloromethylbenzene having no alpha hydrogen was used. To avoid side reactions a mixing 7 days at room temperature followed by 3 hours at 70°C was found to be suitable for the quarternization.

Another interesting behaviour of the ionenes, is that the addition of aqueous sodium or potassium perchlorate solution to the aqueous solutions of the ionenes causes rapid precipitation, which can be explained in terms of affinity of quarternary salts towards heavy anions.

Further modifications through pendant allyl groups such as epoxidation may be of interest to obtain water soluble epoxides, which will be subject of next study.

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