New, Strong Cationic Hydrogels: Preparation of N,N,N’,N’-Tetraallyl Piperazinium Dibromide and Its Copolymers with N,N-Diallyl Morpholinium Bromide

NIYAZI BİÇAK,1 BAHIRE FILİZ ŞENKAL,1 TUĞBA ŞİMANOĞLU,2 CEMAL ÖZEROĞLU2

1 Istanbul Technical University, Chemistry Department, Maslak 80626, Istanbul, Turkey
2 University of Istanbul, Department of Chemistry, Avcılar, Istanbul, Turkey

Received 7 June 1999; accepted 27 December 1999

ABSTRACT: N,N,N’,N’-tetraallyl piperazinium dibromide (TAP) has been prepared in high yields by quaternization of N,N’-diallyl piperazine with allyl bromide. Herein, we have described preparation of nonhydrolysable, strong, cationic hydrogels by copolymerization of TAP with N,N-diallyl morpholinium bromide (DAM) in the presence of t-butyl hydroperoxide as initiator in aqueous solutions. Because the monomer and crosslinker involved consist of quaternary amine functions, these hydrogels are fully cationic and do not carry hydrolysable groups. Contrary to expectations, the quaternary amine hydrogels presented do not show any super absorbency, instead dry gel particles in water undergo spontaneous disintegration with an audible bursting of the particles due to instantaneous, high osmotic pressure. Whereas, in KBr or HBr solutions, the swellings are relatively slow. © 2000 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 38: 1006–1013, 2000

Keywords: tetraallyl piperazinium dibromide; nonhydrolysable crosslinker; diallyl morpholinium bromide; strong cationic hydrogels

INTRODUCTION

Hydrogels have found many applications in various fields.1 In recent years, particular interest has been devoted to their phase transitions in response to changes in pH, temperature,2 and electrical field.3 Polyelectrolyte gels contain ionizable groups and show rapid swelling abilities. Because of strong Coulombic interactions, behaviors of polyelectrolyte gels are quite complicated in comparison to their nonionic counterparts.4 Another complication arises from their preparation using methylene bisacrylamide (MBA) as a crosslinking agent. MBA is the most common and commercially available comonomer for crosslinking of water-soluble polymers. But the main disadvantage of MBA is its hydrolytic instability because, even in dilute acid conditions, it undergoes hydrolysis to give a toxic compound, formaldehyde. On the other hand, crosslinking densities of the hydrogels constituting with MBA may decrease during processing in the acidic region of the pH. In order to overcome this drawback, trimethylol propane triacrylate has been proposed as a water-soluble crosslinker.5 In fact, this compound is not completely soluble in water and it is hydrolysable in nature.

In our previous study, a nonhydrolysable water-soluble crosslinker N,N,N’,N’-tetraallyl piperazinium dichloride has been demonstrated to be an efficient crosslinker in polymerization of acrylamide and acrylic acid.6 Its analogue N,N,N’,N’-tetraallyl piperazinium dibromide (TAP) is expected to exhibit similar efficiency as crosslinker.
Synthesis of this compound has been reported, first, as early as in 1949. Recently, Asrof Ali and coworkers obtained strong cationic hydrogels by copolymerization of tetraallyl piperazinium dichloride with N-formyl, N′-diallyl piperazinium dichloride. Presumably, that was the first report on synthesis of strong cationic hydrogels constituted with the monomer and crosslinker of both possessing quaternary ammonium groups. There are a few reports on the synthesis of strong cationic hydrogels based on quaternized polyvinyl pyridines and quaternized 2-amino ethyl methacrylate polymers. In these studies, common crosslinkers used were either divinyl benzene (DVB) or ethylene dimethacrylate (EDMA).

In this study, we have described synthesis of tetraallyl piperazinium dibromide (TAP) and its new, strong, cationic hydrogels by its copolymerizations with N,N-diallyl morpholinium bromide (DAM) in concentrated aqueous solutions. Here the monomer DAM itself may be expected to form crosslinked polymers, likewise to diallyl esters, because of its dialkene functionality. However, diallylammonium monomers differ from other diallyl monomers in that they form linear polymers with five-membered repeating units in the main chain. This type of polymerization has been termed cyclopolymerization in which consecutive rings form during the polymerization. Although in earlier reports six-membered piperidinium ring structures, considered by careful 13C NMR spectroscopic analysis, revealed that cyclization to the five-membered pyrrolidinium ring structure is nearly quantitative. At moderate conversions about 2% residual allyl groups have been detected. Because pendant allyl groups are less reactive, these may cause branching at very high conversions. These polymers have found potential applications in sludge-dewatering and flocculation process.

In our recent study, we have demonstrated that polymerization of DAM in concentrated aqueous solutions by radical initiation gives a water-soluble homopolymer.

Not only quaternary diallyl ammonium monomers but also some other divinyl monomers such as diallyl sulfonamide and diallyl cyanamide can give cycopolymers with similar structures. However, there appears that one exception, N-alkyl diallylamine monomers, give insoluble crosslinked polymers under the same reaction conditions.

The goal of this study is to investigate swelling behavior of the crosslinked hydrogels constituting with DAM and TAP having nonhydrolysable linkages. In the study swelling characteristics of the gels with different crosslinking ratios have been investigated in water, salt (KBr), and acid (HBr) solutions.

**EXPERIMENTAL**

All the chemicals used were analytical grade commercial products: Allyl chloride (E. Merck), piperazine (Fluka), morpholine (Fluka), allyl bromide (Fluka). They were used as supplied. t-Butyl hydroperoxide was prepared from t-butanol according to the procedure given in the literature.

**Preparation of N,N-Diallyl Morpholinium Bromide (DAM)**

This was prepared from morpholine in two steps:

1. Condensation with allyl chloride to give N-allyl morpholine.
2. Quaternization with allyl bromide as described elsewhere.

**Preparation of N,N′-Diallyl Piperazin (DAP)**

Piperazine (43 g, 0.5 mol) was dissolved in 150 mL of methanol in a 1 L volume of canonical flask. The flask was placed in an ice bath. While stirring vigorously, 83 mL (1.02 mol) allyl chloride was added dropwise in about 40 min through a dropping funnel. After 1 h of stirring a white precipitate was observed. Stirring was continued for 13 h. The solution of 56 g (1.0 mol) KOH in 200 mL methanol was added portionwise to the mixture. The first portion 100 mL was added after 1 h and the remaining was divided in two equal portions and was added 3 and 5 h later. Stirring was continued overnight at room temperature. KCl was filtered and methanol was distilled off by a rotavapor. The liquor was transferred into 250 mL volume of distillation flask and distilled under diminished pressure. The fraction boiling at 108–111 °C/(1 mm) (lit8 213 °C, 760 mm) was collected.

Yield: 57 g (68 %). Elementary microanalysis: Calcd. for C10H18N2. Found: C, 72.3% (72.1); H, 10.8% (10.4); N, 16.9% (16.0).

1H NMR and FTIR spectra of the product are given in Figures 1 and 3(a), respectively.
Preparation of \(N,N,N^*\),\(N^*\)-Tetra Allyl Piperazinium Dibromide (TAP)

Under an efficient fume cupboard, 40 g (0.24 mol) \(N,N^*\)-diallyl piperazine was put into 250 mL volume flask in an ice bath. While stirring vigorously by a magnetic stirring bar, 63 mL (0.26 mol) allyl bromide was added to the flask dropwise in about 40 min. The mixture was stirred for 4 h. At that time, an oily phase was separated. Then the reaction content was left to stand for 5 days at room temperature. The hard crystalline product formed was filtered as quickly as possible and washed with ether. It was dried at 40 °C under vacuum for 24 h.

Yield: 96.2 g (98%). mp: 205 °C (lit\(^8\) 207 °C).

The quaternization product is very hygroscopic and very soluble in \(H_2O\) and DMF, insoluble in benzene and toluene, and slightly soluble in methanol.

Elementary microanalysis: Calcd. for \(C_{16}H_{28}\),\(N_2\)Br. Found: C, 47.0% (47.4); H, 6.86% (7.03); N, 6.86% (7.16).

\(^1\)H NMR and FTIR spectra of the product are given in Figures 2 and 3(b), respectively.
Copolymerization with N,N-Diallyl Morpholinium Bromide

The copolymerization was carried out in concentrated (60%) aqueous solutions at 85 °C using TBH as radical initiator. Using different monomer–comonomer combinations, the copolymerization was conducted until gelation occurred.

A typical procedure is as follows: 2.23 g (9.0 mmol) DAM and 0.4 g (1.0 mmol) TAP are placed in a 50 mL volume of a two-necked flask attached to a reflux condenser. The flask is mounted in an oil bath of which the temperature is adjusted by a contact thermometer. Then 1.8 mL water is added to the flask and heated at 50 °C until a clear solution is observed. While stirring, the solution is purged with nitrogen and 0.05 mL TBH is added by means of a micropipette. The temperature is raised up to 85 °C and the stirring is continued at this temperature until gelation occurs (34 min). The clear hydrogel formed is broken up by a glass rod and transferred into a sintered glass funnel. The gel is washed with excess of water and dried at 60 °C for 24 h under vacuum. Yield: 2.1 g (80.0%). The gel obtained is sticky and this causes inevitable mechanical losses in handling.

Determination of the Residual Unsaturation in the Copolymers

The residual unsaturations were estimated roughly by comparison of C—H stretching vibrations of the polymers and monomers, observed at 3080 cm\(^{-1}\), as described in the literature.\(^{21}\) The bromine addition method was also considered to determine unreacted allyl groups in the polymer. But this method seemed not to be satisfactory due to slow diffusion of the bromine into the crosslinked polymer matrix and its probable substitution on the morpholine ring.

In the procedure, 4.08 mg (10\(^{-5}\) mol) TAP and 4.8 mg (10\(^{-4}\) mol) DAM were mixed in a mortar quickly and 1 mg, 2 mg, 3 mg, and 5 mg samples were weighed and each mixed separately with 300 mg of dry KBr samples. These were mixed homogeneously by grinding and their pellets were prepared as usual. A calibration curve of unsaturation was prepared based on the intensities of the IR bands at 3080 cm\(^{-1}\). Using band intensities of the copolymers at some frequency, the residual unsaturations per gram were found by the calibration curve. The results found were tabulated in Table I.

Swelling Experiments

After synthesis, the dry hydrogels were placed in synerider glass funnels, which were immersed in distilled water, KBr, and HBr solutions. The swellings of the hydrogels were monitored by mass measurements every 10 min; approximately 1 h was enough to reach equilibrium swelling. Once equilibrium was attained, the hydrogels were weighed, dried at 60 °C in vacuum for 24 h, and re-weighed. The swelling ratio is defined as the mass ratio of swollen hydrogel to dry hydrogel.
(W/W$_0$). The relevant graphics, given in Figures 5 and 6 have been pictured based on mean average values of the swelling ratios obtained by three different measurements.

RESULTS AND DISCUSSION

Preparation of the Ionic Crosslinker

The reaction of piperazine with two equivalents of allyl chloride gives rise to N,N'-diallyl piperazine (DAP) as shown in Scheme 1. The reaction proceeds smoothly in methanol solution. Equivalent amounts of KOH is added portionwise to avoid any probable isomerization of the allyl groups. The yield of pure liquid product, after distillation, is 68%. Quaternization of DAP with allyl bromide gives N,N,N',N'-tetraallyl piperazinium dibromide as a very higroscopic solid. Best yields are obtained by direct interaction of the reagents at 0 °C. However, when the reaction is performed at room temperature, violent explosions occur in about 10 min of contacting times. To avoid explosions, in this study, we have also tried to use solvents as described in the original procedure of Butler. However, these experiments with or without heating always gave low yields (20–40%) in our hands.

$^1$H NMR spectra of DAP and TAP in Figures 1 and 2 confirm the structures proposed. $^1$H NMR spectra of DAP in Figure 1 show four different proton signals as expected. Piperazine ring protons of the DAP are observed at 2.6 ppm as a sharp singlet. The protons of the allylic carbon give a doublet at 3.1 ppm. The multiples at 5.3 and 5.9 ppm indicate protons of CH$_2$ and CH groups, respectively. In the NMR spectra of TAP (Fig. 2) all the proton signals shift to lower fields because of quaternization. In this case, the singlet of the piperazine ring protons shifts to 4.1 ppm and the doublet of the protons of allylic groups appears at 4.4 ppm. Slight down shifts are observed for the olephinic-proton signals after quaternization and these are observed at 6.0 and 6.2 ppm, respectively.

These transformations can also be followed by their FTIR spectra shown in Figure 3(a, b). In both spectra, characteristic C–C and C–H stretching vibrations are observed at about 1680 and 3080 cm$^{-1}$, respectively. In the FTIR spectra of DAP (Fig. 3(a)) C–N stretching vibrations represent intense band at 1100 cm$^{-1}$. Whereas, for the case of TAP, this band [Fig. 3(b)] is observed at 1150 cm$^{-1}$ because of quaternization.

Copolymerization with N,N-Diallyl Morpholinium Bromide (DAM)

Homopolymerization of TAP and its copolymerization with DAM in concentrated aqueous solutions (60%) with t-butyl hydroperoxide initiator at 85 °C give transparent hydrogels in high yields. No precipitation and any heterogeneity is observed in the polymerizations. The rigid gels obtained are completely homogeneous and transparent. The structures of the crosslinked polymer gels can be depicted as shown in Scheme 2. Low yields are obtained, however, in more dilute solutions because of strong Coulombic repulsion between the monomers as has been demonstrated for the polymerization of some quaternary diallyl ammonium monomers. Indeed, with 10% of total monomer concentrations, no gels were obtained even after 8 h of reaction times. When the total monomer concentration was raised to 20%, the dry gel yields were about 10–20%. In the reaction condition studied, as the ratio of the crosslinker, TAP to the DAM, is increased, the gelation time reduces significantly (Table I).

In the FTIR spectra of these gels [Fig. 3(d)] the olephinic C–H stretching vibrations of the monomers, at 3080 cm$^{-1}$ do not disappear completely, which imply some residual unsaturations. Intensities of these bands are in accordance with the crosslinker ratios. In the case for 5% of the crosslinker ratio only a weak band is observed for the homopolymer of the crosslinker, TAP. The surface area of this band is about 8.3% of its monomer. Obviously, these residual unsaturations can be ascribed to the unreacted allyl groups of the crosslinker. Interestingly, after a successive washing of the homopolymer of TAP, intensity of this band becomes somewhat weaker than its original. This reveals that some of the unreacted monomer remain entrapped in the gel ma-
trix and washing presumably causes its extraction to some extent.

**Swelling Characteristic of the Gels**

Not having hydrolysable groups, investigation of the swelling behaviors of the gels constituted with fully ionizable quaternary ammonium groups seemed to be very exciting because combination of nonhydrolysability and full ionizability was considered to be extremely beneficial for examination of the swelling characteristics in drastic conditions. According to our present knowledge, these gels are expected to show high swelling, as high as those for superabsorbents and rapid water sorptions.

Indeed swelling of the gels is very interesting. The dried gel samples when soaked in water disintegrate with an audible cracking sounds of particles. The sounds continue for about 50 min and the gel samples turn into suspended small transparent particles. Obviously, this behavior can be ascribed to the high osmotic pressure due to strong ionic groups inside the gels. According to the network theory outlined by Flory and by other authors, polymer–solvent interaction, polymer elasticity, and ionic effects govern swelling of the gels, as has been stated by Praustnitz; polymer–solvent interaction can be neglected when ionic charge density is high enough. As a result, in these gels, there is a competition of high osmotic pressure with the polymer elasticity. Since, in our case, the ammonium groups in the gels are close to each other, the ionic effect is far more superior to the elasticity and the polymer elasticity will not be able to hold the polymer in swollen state. As a result, excess osmotic pressure yields disintegration of the gel particles. In other words, in order to obtain gels of quaternary ammonium polymers with high swelling ability elastic segments must be incorporated by copolymerization or by other means.

Of course, crosslinking density and salt effect are common effects on swelling. In Figure 4 swelling rates of DAM/TAP copolymers are in accordance with their crosslinking densities. But homopolymer of the crosslinker (TAP) itself differs from the others in that its swelling rate is higher than those of DAM-TAP (20%) copolymer in the first 20 min from the beginning.

The difference can be ascribed to the charge densities. In the DAM-TAP copolymers the density of quaternary amine functions is in 4.1–4.28 mmol g\(^{-1}\) range, whereas it is 4.9 mmol g\(^{-1}\) for the homopolymer. So about 0.6 mmol of charge difference per gram must be responsible for the high swelling rate of the latter.

Moreover, Peppas kinetic swelling formula \(W/W_\infty = kt^n\) (where \(W_\infty\) is weight of the gel at the equilibrium and \(W\) is the weight at time \(t\), \(k\) and \(n\) are constants) gives 0.87–1.04 values for the \(n\) exponent, which is characteristic for ionic hydrogels. This formula is valid in the swelling ratio less than 60%. Using this criteria the exponents, \(n\), are obtained from the slope of the logarithmic plots \(\log (W/W_0)\) versus \(\log t\) as usual. Figure 5 shows salt effect on the swelling behaviors. As might be expected, the swelling rates and equilibrium swelling degrees become lower than in pure water. No disintegration is observed in the salt solutions. Also, HBr solution has the same effect with those of the KBr solutions (cf. bottom curve in Fig. 4). In other words, acid solutions do not impose additional effect other than the salt effect, which is common for polyelectrolytes. Although no remarkable effect is observed in dilute alkaline solutions at room temperature, the hydrogels become light yellow in color when boiled in 1M NaOH solution for 30 min. Most probably the colorination is because of the overall HBr elimi-
nation so called Hofmann’s exhaustive methylation yielding vinyl residues.

**Ion Exchange in Concentrated Acid Solutions**

Some transition metal ions are known to be capable of anionic chloro complexes in concentrated HCl solutions. Because the hydrogels obtained are nonhydrolysable and quite stable in acid solutions, these were considered to be efficient for the ion exchange with anionic chloro complexes of some transition metal ions.

In a preliminary study we have investigated exchange capabilities of Fe (III), Zn (II) and Cr (III) ions forming FeCl$_4^{-}$, Zn Cl$_4^{-}$ and Cr Cl$_4^{-}$ ions in concentrated HCl solutions. For this purpose the gel with the 10% crosslinker was simply mixed with each of the above metal ions in HCl solutions with various concentrations.

\[
\text{N}^+ \text{Br}^- + \text{FeCl}_4^- \rightleftharpoons \text{N}^+ \text{FeCl}_4^- + \text{Br}^-
\]

By analysis of the metal contents (AA) of residual acid solutions the exchange capacities were calculated and pictured as a function of the acid concentrations. Figure 6 represents that the gel sample has 0.23 mmol g$^{-1}$ exchange capacity FeCl$_4^{-}$ ions in 7 M HCl solutions. In this concentration, exchange of FeCl$_4^{-}$ ions is somewhat selective in comparison to ZnCl$_4^{2-}$ and CrCl$_4^{2-}$ ions.

![Swelling kinetics of the hydrogel with 10% crosslinker in H$_2$O (---); KBr (0.1 M) (- - -); KBr (1.0 M) (· · ·); HBr (1M) solutions (—).](image)

**Figure 5.** Swelling kinetics of the hydrogel with 10% crosslinker in H$_2$O (---); KBr (0.1 M) (- - -); KBr (1.0 M) (· · ·); HBr (1M) solutions (—).

Of course this subject needs further study. However, in light of the preliminary study, the nonhydrolysable hydrogels can be regard as promising materials for removal of Fe(III) and possibly some other metal ion in acid-leaching solutions.

In conclusion, the hydrogels with quaternary amine functions are nonhydrolysable in nature and suitable for exploiting in concentrated acid solutions. Moreover, since the monomer and the crosslinker are both consisting of quaternary amine functions these can be regard as model hydrogels to examine pure Coulombic effects.

**REFERENCES AND NOTES**