

Gelation in the copolymerization of tetraallylammonium chloride with diallyldimethylammonium chloride and diallylammonium chloride

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Tetraallylammonium chloride (TAAC) was radically copolymerized with diallyldimethylammonium chloride (DADMAC) in water at 60°C. Gelation was delayed with an increase in the mole fraction of DADMAC in the monomer mixture. The precopolymer was easily incorporated into the gel at an initial stage of gelation, but a small amount of sol remained even at a late stage. The primary chain length increased with increasing DADMAC feed composition, while the discrepancy between the actual gel point and the theoretical one showed the opposite tendency, i.e. decreased. The swelling ratios of the resulting hydrogels were almost independent of the monomer composition up to 70 mol% of DADMAC. TAAC was then copolymerized with diallylammonium chloride; the actual gel points were compared with the theoretical ones and the swelling ratios of the resulting gels were observed. These results are discussed mainly in terms of the steric effect on intermolecular and intramolecular crosslinks arising from the bulkiness of both growing polymer radical and polymer chain having unreacted pendant double bonds.

(Keywords: tetraallylammonium chloride; diallyldimethylammonium chloride; diallylammonium chloride; hydrogel; copolymerization; gelation; crosslinking; steric effect; swelling ratio)

INTRODUCTION

Diverse applications are expected for hydrogels, especially in the fields of biochemistry and bioengineering. Moreover, the volume phase transition of hydrogels, discovered by Tanaka^{1,2}, is now one of the most attractive research subjects. Thus, the physical and mechanical properties of hydrogels are extensively discussed, but detailed molecular characterization of hydrogels is somewhat lacking, especially in connection with chemical network formation, although the elucidation of network formation processes seems to be important for the molecular design of useful hydrogels.

As an extension of our continuing studies concerned with gelation in the radical polymerization of water-insoluble polyvinyl monomers, the preceding article³ dealt with gelation in the polymerization of tetraallylammonium chloride (TAAC) as a water-soluble polyvinyl monomer. Thus gelation was quite delayed and the swelling ratios of the resulting gels were quite high compared with those of non-water-swollen gels^{4,5}, higher by more than one order, although the primary chain length is relatively long and the number of unreacted pendant double bonds is quite large, i.e. one or two allyl groups per structural unit in the initial polymers. Under the same circumstances, low gel-point conversion, microgel formation⁶ and low swelling ratio of the resulting gel would be expected for the gelation of water-insoluble polyvinyl monomers such as divinyl benzene and ethylene dimethacrylate in organic solvents.

In order to explore in more detail the gelation behaviour of water-soluble polyvinyl monomers, the previous discussion on TAAC gelation³ has been extended

to the copolymerization of TAAC with diallyldimethylammonium chloride (DADMAC) and diallylammonium chloride (DAAC). That is, the interesting gelation behaviour of TAAC may be ascribed to the electrostatic repulsion in the intermolecular and intramolecular crosslinking reactions between the polycationic growing radical and the allyl groups in the polycationic polymer chain, and furthermore to the steric effect on crosslinking arising from the bulkiness of both growing polymer radical and polymer chain having unreacted pendant double bonds. This paper mainly deals with the latter steric effect, which is reduced by the copolymerization with DADMAC or DAAC, although the former will be discussed elsewhere in terms of pH dependence and the effect of addition of salts.

EXPERIMENTAL

Materials

TAAC was prepared from the reaction of triallylamine with allyl chloride as described previously⁷.

A 67.1% aqueous solution of DADMAC, supplied by Dai-Ichi Kogyo Seiyaku Co. Ltd, was used without further purification.

DAAC was prepared from the reaction of diallylamine with hydrochloric acid in acetone under ice cooling and recrystallized from acetone.

4,4'-Azobis(4-cyanovaleric acid) (ACVA), supplied by Wako Pure Chemicals Ind. Ltd, was used after vacuum drying.

Distilled water as solvent was supplied from Wako Pure Chemicals Ind. Ltd.

Polymerization and isolation of polymer

Polymerization was carried out at 60°C in ampoules. The pH value of the aqueous reaction mixture was adjusted to 2 by the addition of HCl; this will eliminate the effect of free amine even if a trace amount of free amine remained in the monomer, although the rate of polymerization of TAAC homopolymerization was substantially unchanged by the addition of HCl⁷. After a definite reaction time, the aqueous reaction mixture was poured into around 15-fold volume of acetone containing a trace amount of hydroquinone as inhibitor. The polymer thus obtained, which contains some amount of unreacted monomer, was then reprecipitated from an appropriate solvent-precipitant system; the selection of precipitant was done by using g.p.c., a typical example being shown for the TAAC-DADMAC (5/95) copolymer in Figure 1, and water was always used as the solvent. That is, the use of methanol or 2-propanol as precipitant evidently lost some amount of low-molecular-weight polymer, while the unreacted monomer still remained by the use of acetone or 2-propanol-acetone mixture. Thus the methanol-acetone mixture was chosen as the precipitant. For TAAC-DADMAC (30/70 and 60/40) and TAAC-DAAC copolymers, the 2-propanol-acetone and methanol-acetone mixtures were used, respectively.

Sol-gel separation and characterization

The gel fraction of polymer samples obtained at a conversion beyond the gel point was separated by extracting the sol fraction with methanol.

G.p.c. measurements to determine the molecular weight of the sol and the determination of the swelling ratio of the gel were done as described previously³.

RESULTS AND DISCUSSION

Copolymerization of TAAC with DADMAC

In our previous article⁷, the cyclopolymerizability of TAAC was estimated kinetically as the ability of five-membered monocyclic radical to form a bicyclic ring,

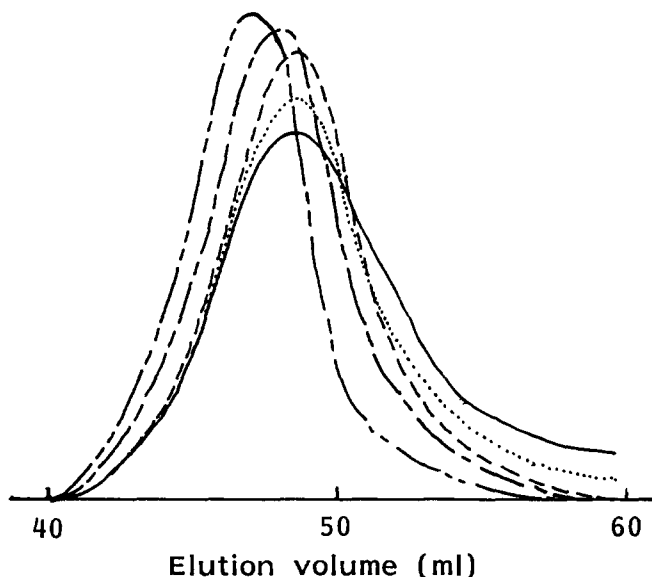
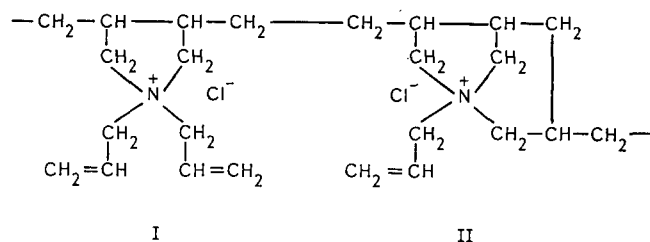


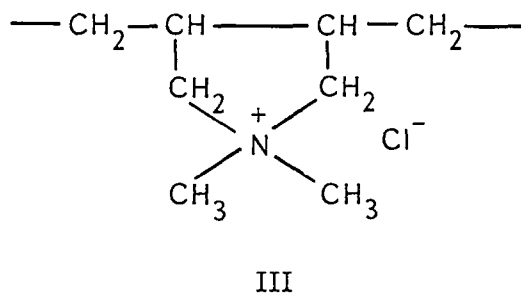
Figure 1 G.p.c. curves of the TAAC-DADMAC (5/95) copolymer recovered from different reprecipitation systems, with water used as the solvent and with various precipitants: (—) acetone; (.....) 2-propanol-acetone mixture; (---) methanol-acetone mixture; (— — —) 2-propanol; (— · — ·) methanol

giving the cyclization constant of 21 mol l⁻¹ at [M] = 2 mol l⁻¹. That is, the polymer obtained at an initial stage of polymerization where crosslinking is negligible consisted of 16% of monocyclic (I) and of 84% of bicyclic (II) structural units as follows:



Thus a quite rigid polymer chain is formed and the steric effect on the intermolecular and intramolecular crosslinking reactions between the growing polymer radical and the unreacted pendant allyl group in the polymer chain seems to be significant, leading to delayed gelation and the high swelling ratio of the resulting gel³.

On the other hand, it is well known that the radical polymerization of diallyl quaternary ammonium salts yielded water-soluble, saturated polymers^{8,9}, suggesting a quite high cyclopolymerizability of DADMAC. In this connection, we have estimated the cyclization constant K_c , defined as the ratio of the rate constant of intramolecular cyclization to that of intermolecular propagation of uncyclized radical, to be more than 600 mol l⁻¹ for DADMAC¹⁰. That is, substantially no uncyclized units having unreacted pendant allyl group are formed under the polymerization conditions in this work. Furthermore, the cyclic structures (III) of poly-(DADMAC) consist predominantly of five-membered rings¹² as follows:



Thus DADMAC monomer would act just like a monovinyl monomer in place of divinyl monomer in the copolymerization with TAAC. In addition, the incorporation of less-bulky five-membered DADMAC units (III) into the copolymer chain reduces the steric effect in the homopolymerization of TAAC. On the other hand, TAAC monomer, whose incorporation into the copolymer chain offers one or two unreacted pendant double bonds responsible for crosslinking, would act just like a divinyl monomer in place of tetravinyl monomer; although two double bonds in the monocyclic structural unit (I) have the possibility of making two crosslinks, they would be used for the formation of only one crosslink by considering steric crowding of the crosslinked site. The copolymerization of TAAC with DADMAC may be, therefore, regarded as a pseudo-monovinyl-divinyl copolymerization system.

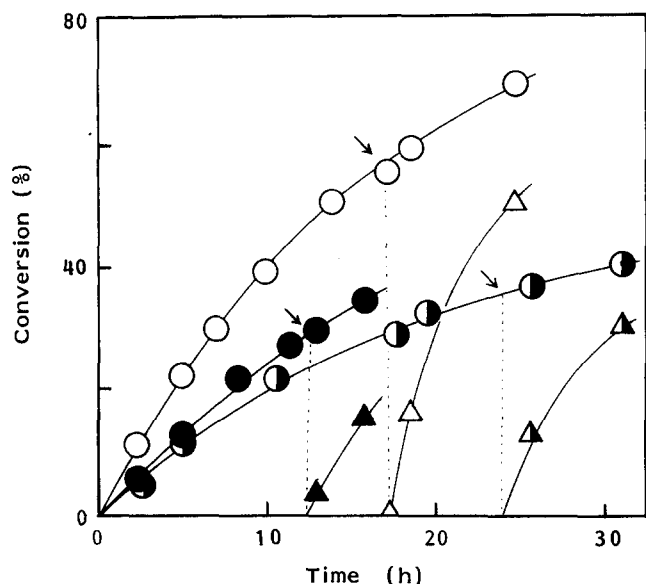


Figure 2 Determination of the gel point in the copolymerization of TAAC with DADMAC at $[M]=2\text{ mol l}^{-1}$, $[\text{TAAC}]/[\text{DADMAC}]=100/0$ (full symbols); $30/70$ (half-full symbols); $5/95$ (open symbols). Circles and triangles correspond to total and gel polymers, respectively

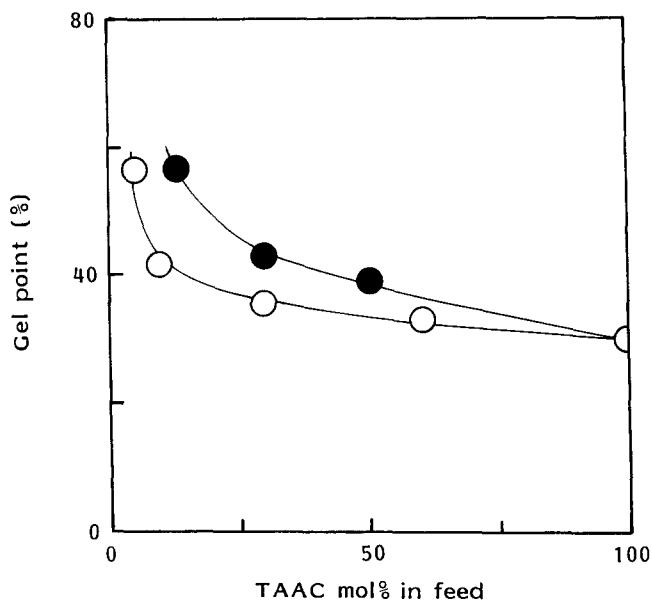


Figure 3 Relationships between gel point and monomer composition in the copolymerization of TAAC with DADMAC (○) and DAAC (●) at 60°C

Figure 2 shows the time-conversion curves in the copolymerization of TAAC with DADMAC at 60°C in water using 0.05 mol l^{-1} of ACVA at $[M]=2\text{ mol l}^{-1}$ as examples, along with TAAC homopolymerization. The percentage of gel polymer obtained by sol-gel separation was also plotted against time in *Figure 2*. The gel point was estimated to be the conversion at the time at which the gel starts to form. The gel points thus obtained were plotted against the monomer composition in *Figure 3*; gelation was delayed with an increase in the mole fraction of DADMAC in the monomer mixture, although the rather gradual delaying tendency became abrupt beyond 90 mol% of DADMAC. *Figure 4* shows the plots of gel fraction versus conversion; in all cases, the prepolymer was easily incorporated into the gel at an initial stage of gelation, and the sol fraction at a late stage of gelation

tended to increase with increasing DADMAC content in the feed monomer. The former result may be relevant to the high swelling ratios of the resulting gels as shown later in *Figure 6* and the latter may be due to the fast consumption of TAAC compared to DADMAC, leading to the formation of a copolymer having a small amount of unreacted pendant double bonds at a high conversion.

Figure 5 shows the dependence of weight-average molecular weight \bar{M}_w on conversion before gelation; \bar{M}_w increased with conversion as a reflection of intermolecular crosslinking. The molecular weight $\bar{M}_{w,0}$ of the initial copolymer was estimated by extrapolating the conversion

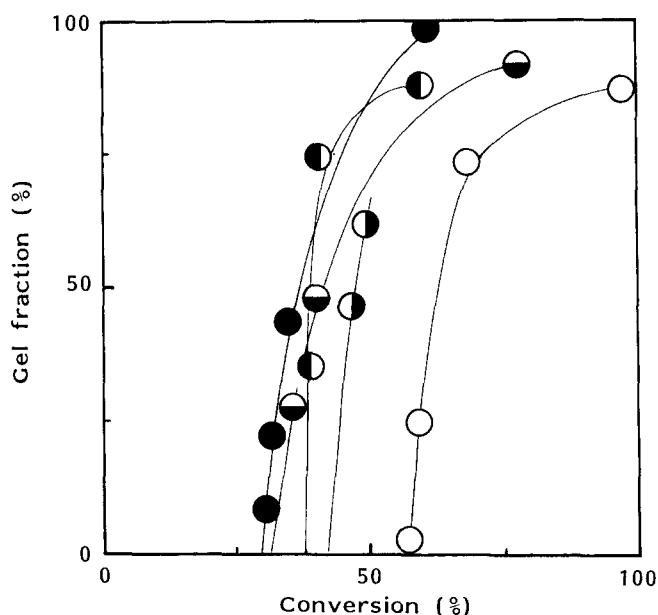


Figure 4 Dependence of the gel fraction on conversion in the copolymerization of TAAC with DADMAC. $[\text{TAAC}]/[\text{DADMAC}]=100/0$ (●); $60/40$ (◐); $30/70$ (○); $10/90$ (●); $5/95$ (○)

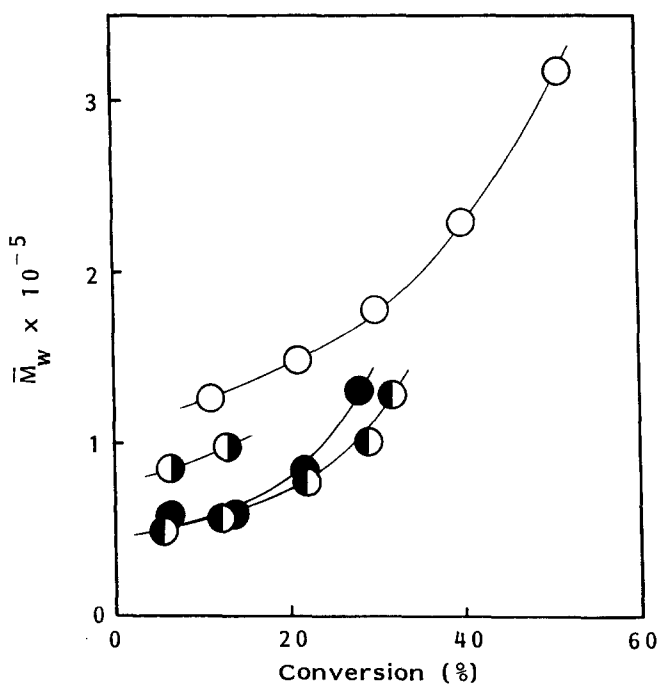


Figure 5 Dependence of \bar{M}_w on conversion in the copolymerization of TAAC with DADMAC. $[\text{TAAC}]/[\text{DADMAC}]=100/0$ (●); $30/70$ (◐); $10/90$ (○); $5/95$ (○)

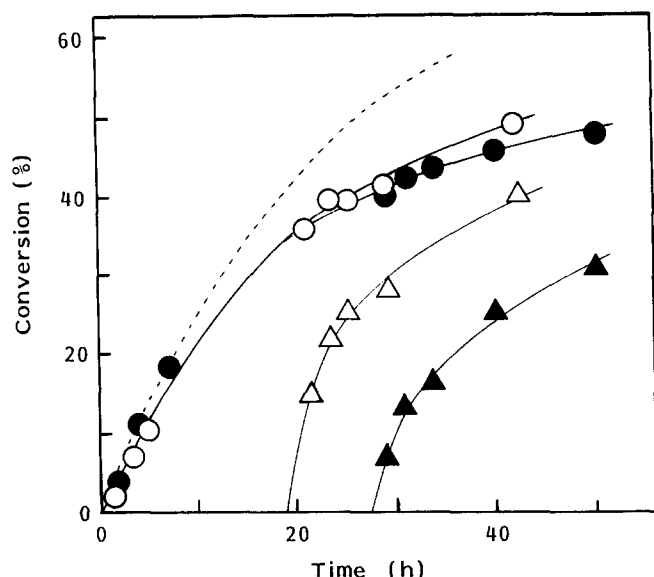


Figure 7 Time-conversion curves in the copolymerization of TAAC with DAAC in water using 0.05 mol l^{-1} of ACVA at $[M]=2 \text{ mol l}^{-1}$ and at 60°C . $[\text{TAAC}]/[\text{DAAC}]=100/0$ (-----); 50/50 (○, △); 30/70 (●, ▲). Circles and triangles correspond to total and gel polymers, respectively

Table 2 Deviation of actual gel point from theoretical one in the copolymerization of TAAC with DAAC

DAAC (mol%)	$\bar{P}_{w,0}$	Gel point		Actual GP
		Actual	Theoretical	Theoretical GP
0	245	30.2	0.41	73.7
50	188	36.2	0.80	45.2
70	217	40.7	1.00	40.6 (47.2) ^a

^a TAAC-DADMAC copolymerization

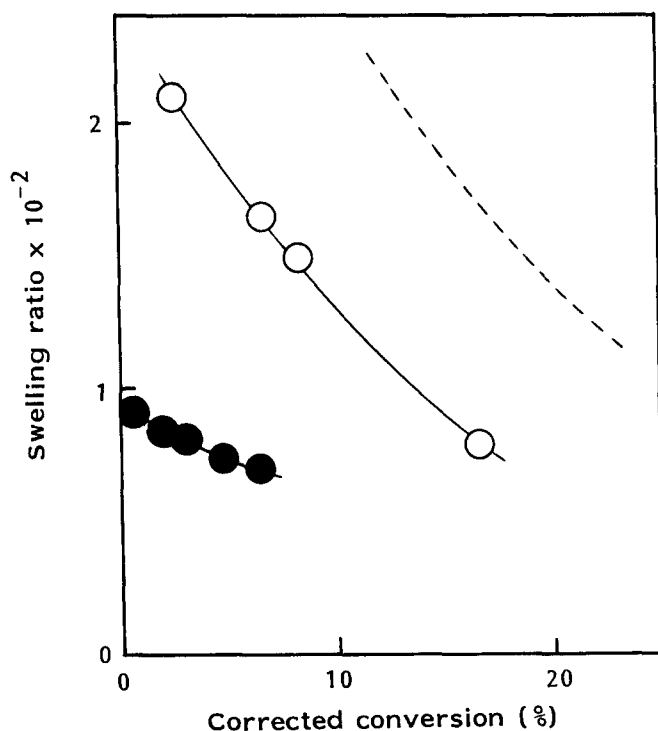


Figure 8 Decrease of swelling ratio with the progress of gelation beyond the gel point conversion. $[\text{TAAC}]/[\text{DAAC}]=100/0$ (-----); 50/50 (○); 30/70 (●). Conversion (on abscissa) is corrected such that the corresponding gel points are 0% of conversion

TAAC-DAAC copolymerization may be ascribed mainly to the shorter primary chain length as compared to TAAC-DADMAC copolymerization.

The swelling ratios of the resulting gels are shown in Figure 8; they decreased with the progress of gelation, and it is noted that they were quite reduced with increasing mole fraction of DAAC in the feed, a different result from Figure 6. These results suggest the much enhanced occurrence of intramolecular crosslinking through much less-bulky DAAC growing radical as compared to DADMAC growing radical. In addition, the incorporation of cyclic DAAC units (IV) into the copolymer chain would afford the flexibility of the polymer backbone, being another reason to undergo easily intramolecular crosslinking. In other words, this suggests that the steric effect on crosslinking that arises from the bulkiness of both growing polymer radical and polymer chain having unreacted pendant double bonds is a significant factor in the understanding of the interesting gelation behaviour in TAAC polymerization³.

Here it should be recalled that, in the copolymerization of diallyl terephthalate with allyl benzoate, the discrepancy of the actual gel point from the theoretical one was quite reduced with increasing molar fraction of allyl benzoate in the feed, being similar to the cases of the copolymerization of TAAC with DADMAC or DAAC, but the degree of discrepancy was less than one-fifth, especially one-tenth at 90 mol% of monovinyl monomer¹³, as compared to those of TAAC-DADMAC or TAAC-DAAC copolymerizations. Also, the swelling ratios of TAAC-DADMAC or TAAC-DAAC gels were more than one order higher as compared to those of non-water-swollen gels. That is, the great discrepancy between the actual and theoretical gel points and the high swelling ratio of the resulting gel in TAAC-DADMAC or TAAC-DAAC copolymerization suggests the importance of electrostatic repulsion in the intermolecular and intramolecular crosslinking reactions between the polycationic growing radical and allyl groups in the polycationic polymer chain in addition to the steric factor mentioned above.

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