Gelation in the Copolymerization of Diallyldimethylammonium Chloride with Acrylamide

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ABSTRACT

Diallyldimethylammonium chloride (DADMAC) was free-radical co-polymerized with acrylamide (AA) in water at a total monomer concentration of 4 mol/L and 40°C with different monomer feed compositions. Gelation occurred only for 20/80 DADMAC/AA monomer feed although crosslinking was observed for all monomer feed compositions. The gel point was at 51% conversion, and the swelling ratios of the resulting gels were quite high, from 1400 to 700. Addition of 2-propanol as a chain-transfer reagent reduced crosslinking and prevented gelation. These results are mechanistically discussed in connection with the cyclopolymerizability of DADMAC, and significant allylic hydrogen abstraction by the growing polymer radical characteristic of allyl polymerization is proposed.

1475

INTRODUCTION

Since the pioneering work on radical polymerization of diallyl quaternary ammonium salts to yield water-soluble linear polymers, contrary to the expected formation of highly crosslinked resins [1, 2], a wide variety of nonconjugated dienes have been polymerized to give cyclopolymers, and the basic cyclopolymerization mechanism has been well established [3].

Furthermore, cyclopolymerization of diallyl quaternary ammonium salts led to the development of water-soluble cationic polyelectrolytes having marked utility in many applications [4, 5]. In particular, the copolymers of diallyldimethylammonium chloride (DADMAC) with acrylamide (AA) have been among the commercially most important polymers as cationic polyelectrolytes, outstandingly useful for flocculation applications. However, no detailed kinetic and mechanistic discussions of this copolymer system have been published.

During our investigation of the copolymerization of DADMAC with AA, monomer reactivity ratios for this copolymerization system were reported independently by Wandrey and Jaeger [6] and Tanaka [7] to give basic data about useful water-soluble cationic polyelectrolytes. However, we found that gelation occurs under the specified polymerization conditions. Thus, in this article we discuss gelation in the copolymerization of DADMAC with AA with consideration of the cyclopolymerization behavior of DADMAC.

EXPERIMENTAL

Aqueous solution (67.1%) of DADMAC, supplied by Dai-Ichi Kogyo Seiyaku Co., was used without further purification. AA, commercially available reagent, was recrystallized from acetone-chloroform. 2,2'-Azobis(isobutyramide) dihydrate (VA-088), supplied by Wako Pure Chemical Ind., was used without further purification.

Polymerization was carried out in ampules according to the conventional method. After the desired reaction time, the reaction mixture was poured into a large volume of acetone to precipitate the polymer. The gel fraction of the polymer samples obtained at conversions beyond the gel point was separated by using a phase transition phenomenon typical of hydrogel as follows: the polymer sample containing both sol and gel fractions was swollen in water, and then acetone was added until the gel fraction shrank drastically to give the precipitate, which was swollen again in water, followed by acetone addition, and this swell-shrink process was repeated twice.

The intrinsic viscosity of the polymer in 0.2 M sodium sulfate at 30°C was measured in an Ubbelohde viscometer.

GPC measurements were carried out with a Waters Associate ALC/GPC 501 apparatus at room temperature under the following conditions: Solvent, 0.2 M sodium sulfate; column combination, G3000PW, G5000PW, and G6000PW (TSK gel); polymer concentration, 0.5% (w/v); and flow rate, 1 mL/min. GPC curves monitored by a differential refractometer were analyzed by using the calibration curve obtained with standard samples of monodisperse poly(ethylene oxide) to estimate the molecular weight.

The swelling ratio of the gel was determined as follows: The required amount of gel (A g) was placed in a graduated centrifuge tube, and excess water was added to swell it completely. The tube was centrifuged to measure the volume of swollen gel (B mL). The swelling ratio was taken to be B/A by assuming the density of swollen gel as unity.

RESULTS AND DISCUSSION

Cyclopolymerizability of DADMAC

Radical polymerization of diallyl quaternary ammonium salts has invariably been reported to yield water-soluble saturated polymers [1, 2]. Recently, Wandrey and coworkers [3] reported that poly(DADMAC) obtained by radical polymerization in water contains 0.1-3% double bonds as detected by radiochemical determination with [203]Hg acetate after thin-layer chromatographic separation of the hydroxymercurated products.
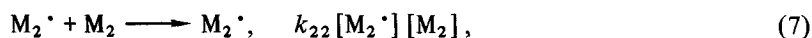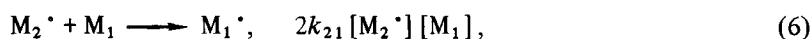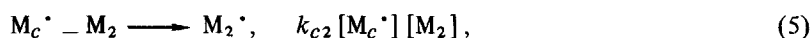
In this work the content of unreacted pendent double bonds of poly-(DADMAC), which had been synthesized with [M] 3 mol/L at 50°C and carefully reprecipitated three times from water-2-propanol, was checked by ^{1}H- and ^{13}C-NMR spectroscopy, but no double bonds were detected. In this connection, DADMAC was copolymerized with triallylmethylammonium chloride (TAMAC) to obtain poly(DADMAC-co-TAMAC) containing about 1% unreacted pendent double bonds. Its ^{13}C-NMR spectrum clearly showed the peaks assignable to vinylmethylene, and methyne carbons of allyl groups. Thus the content of the unreacted pendent double bond of poly(DADMAC) should be less than 1%, i.e., poly(DADMAC) should be a linear cyclopolymer. However, 1.17% unreacted double bonds were reported for poly(DADMAC) obtained with [M] 1.51 mol/L at 50°C, and the occurrence of branching was suggested for poly(DADMAC) obtained at high conversion [8]. In this connection, it was found that the dependence of the weight-average molecular weight clearly decreased with conversion according to the usual behavior of

monovinyl monomers, suggesting that no branching was present. This is in line with no detection of unreacted pendent double bond in the resultant poly(DADMAC).

Here it should be noted that nonconjugated 1,6-dienes, such as DADMAC, which can form five- or six-membered rings, are easily cyclopolymerized, but their cyclopolymerizability is still low compared to DADMAC. That is, the cyclization constant K_c, defined as the ratio of the rate constant of intramolecular cyclization to that of intermolecular propagation of uncyclized radicals, should be more than 600 mol/L for DADMAC, whereas K_c values less than 10 mol/L are usually estimated for nonconjugated 1,6-dienes [3], i.e., the polymers obtained at [M] 3 mol/L should contain more than 37.5% of unreacted pendent double bonds.

Cyclocopolymerization of DADMAC with AA

In the cyclocopolymerization of divinyl monomer (M_1) having two equivalent double bonds with monovinyl monomer (M_2), Reactions (1)-(7) represent the propagation reactions for copolymerization [9].

$$M_1 \cdot + M_1 \longrightarrow M_1 \cdot, \quad 2k_{11}[M_1\cdot][M], \tag{1}$$

$$M_1 \cdot + M_2 \longrightarrow M_2 \cdot, \quad k_{12}[M_1\cdot][M_2], \tag{2}$$

$$M_1 \cdot \longrightarrow M_c \cdot, \quad k_c[M_1\cdot], \tag{3}$$

$$M_c \cdot + M_1 \longrightarrow M_1 \cdot, \quad 2k_{c1}[M_c\cdot][M_1], \tag{4}$$

$$M_c \cdot \_ M_2 \longrightarrow M_2 \cdot, \quad k_{c2}[M_c\cdot][M_2], \tag{5}$$

$$M_2 \cdot + M_1 \longrightarrow M_1 \cdot, \quad 2k_{21}[M_2\cdot][M_1], \tag{6}$$

$$M_2 \cdot + M_2 \longrightarrow M_2 \cdot, \quad k_{22}[M_2\cdot][M_2], \tag{7}$$
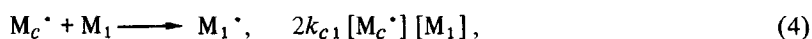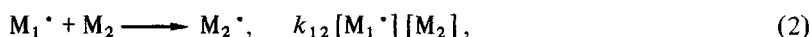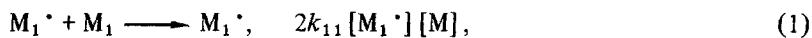
By assuming steady-state conditions, the following copolymer composition equation was derived [9]:

$$\frac{d[M_1]}{d[M_2]} = \frac{2[M_1]}{[M_2]} \cdot \frac{2r_1[M_1] + [M_2] + K_c'}{2[M_1] + r_2[M_2] + K_c'(2[M_1] + r_2[M_2])/2r_c[M_1] + [M_2])}, \tag{8}$$

where $r_1 = k_{11}/k_{12}$, $r_c = k_{c1}/k_{c2}$, $r_2 = k_{22}/k_{21}$, $K_c = k_c/k_{11}$, and $K_c' = k_c/k_{12}$.

The cyclopolymerizability of DADMAC is extremely high compared to common 1,6-dienes, as described above. The unreacted pendent double bonds of the resultant copolymers, which may be formed through Eqs. (1) and (2), were checked tentatively by ^{13}C-NMR spectroscopy. Although no peaks assignable to vinylmethylene and methyne carbons of allyl groups were detected for poly(DADMAC), the copolymer obtained at a monomer feed of [DADMAC]/[AA] = 70/30 and a total monomer concentration of 2 mol/L showed slight peaks only in a highly magnified spectrum, suggesting the presence of a trace amount of uncyclized DADMAC units in the copolymer.

Then Eq. (8) would be replaced by Eq. (9) under the present polymerization conditions where the intermolecular propagation of the uncyclized radical, i.e., Eqs. (1) and (2), may be negligible.

$$\frac{d[M_1]}{d[M_2]} = \frac{2[M_1]}{[M_2]} \cdot \frac{2r_c[M_1] + [M_2]}{2[M_1] + r_2[M_2]} \tag{9}$$

or

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{R_1[M_1] + [M_2]}{[M_1] + R_2[M_2]}, \tag{10}$$

where $R_1 = 2r_c$ and $R_2 = r_2/2$.

Here the r_c and r_2 values are responsible for one allyl group of DADMAC monomer and the R_1 and R_2 values for DADMAC monomer. The latter were estimated to be 0.12 and 6.2, respectively, for $[M_1 + M_2] = 2$ mol/L and 40°C although the copolymer composition was determined from the analysis of both IR- and UV-monitored GPC curves [10]. Wandrey and Jaeger [6] reported that R_1 and R_2 depend on the content of DADMAC in the feed and the total monomer concentration, facts which are explained by association of the cationic monomer and by electrostatic interactions. This is not the case in our results for [M] = 2 mol/L, a concentration which is lower than their cases (3 and 4 mol/L). Our R_1 and R_2 values are in reasonable agreement with their values. Calculation from Q and e, with 1.12 and 1.19 for AA [11] and 0.029 and 0.04 for one allyl group of diallyl phthalate [12], respectively, yields R_1 and R_2 of 0.054 and 6.1, respectively, quite close to our results. Quite a high R_1 (0.58) was reported by Tanaka [7], although his R_2 value of 6.7 is reasonably in line with our results.

Crosslinkability: Conversion Dependence of Intrinsic Viscosity

As discussed above, the cyclopolymerizability of DADMAC is extremely high to give primarily water-soluble, cyclic poly(DADMAC) and poly-(DADMAC-co-AA). However, it seemed that the quite high reactivity of AA, compared to DADMAC, demonstrates the possibility of leaving uncyclized DADMAC units in the copolymer, i.e., the uncyclized units would be introduced into the copolymer chain through a fast intermolecular $M_1{}^\bullet + M_2$ reaction (Eq. 2), and the content of uncyclized units may be increased by increasing the mole fraction of AA and the total monomer concentration in the feed. The unreacted pendent allyl group in the uncyclized DADMAC unit could then react with a growing polymer radical, accompanied by the forma-

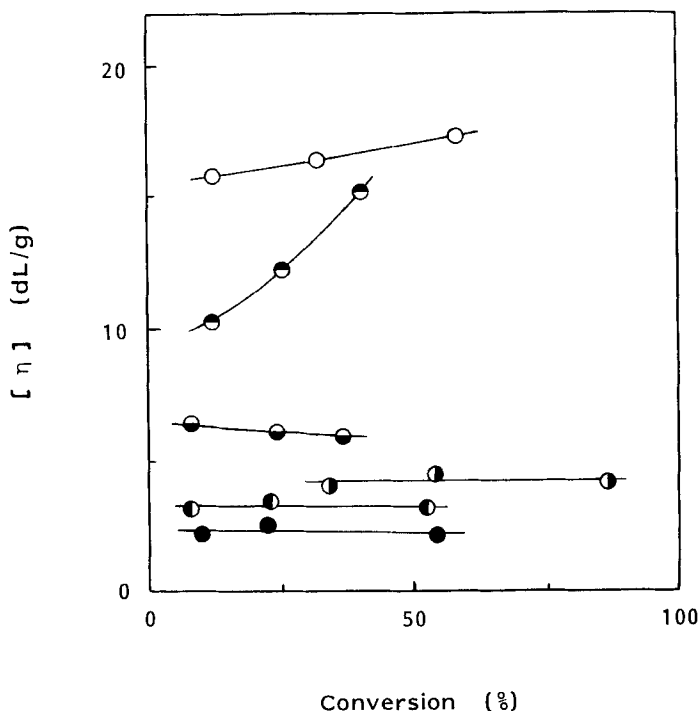

FIG. 1. Dependence of intrinsic viscosity [η] on conversion in the aqueous copolymerization of DADMAC with AA: feed molar ratio [DADMAC]/[AA]: (○) 10/90, (◔) 20/80, (◐) 30/70, (◖) 50/50, (○) 75/25, and (●) 87.5/12.5. Conditions: VA-088, 0.01 mol/L; [M], 4.0 mol/L; 40°C.

tion of crosslinks, the probability of which would increase with conversion, eventually leading to gel formation at high conversion. The crosslinkability was therefore followed by measurement of intrinsic viscosities of the resulting copolymers at different conversions.

Figure 1 shows the dependence of intrinsic viscosity on the conversion. A clearly increasing tendency was observed only in the DADMAC/AA (20/80) copolymerization system, eventually to give gel, suggesting the occurrence of crosslinking. In general, the molecular weight of the resulting copolymer was too high for GPC measurement, except in the case of 87.5 mol% DADMAC. As the conversion rises, the GPC curves in Fig. 2 become wider toward lower elution volume, i.e., the higher molecular weight range broadens, indicating more crosslinking at higher conversion. It should be recalled that the copolymerizability of AA is quite high compared to DADMAC. Thus AA is largely consumed during the early stages of polymerization and therefore, at the later stages, DADMAC participates predominantly in the copolymerization. As a
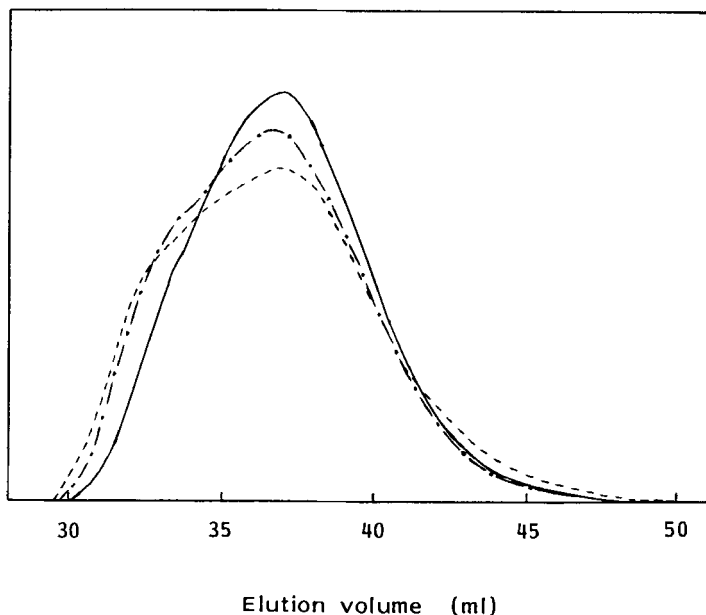
Elution volume   (ml)

FIG. 2. Variation of GPC curves with conversion for the DADMAC/AA (87.5/12.5) copolymerization system. Conversion (%): (——) 2.7, (– • –) 2.18, and (- - -) 53.5.
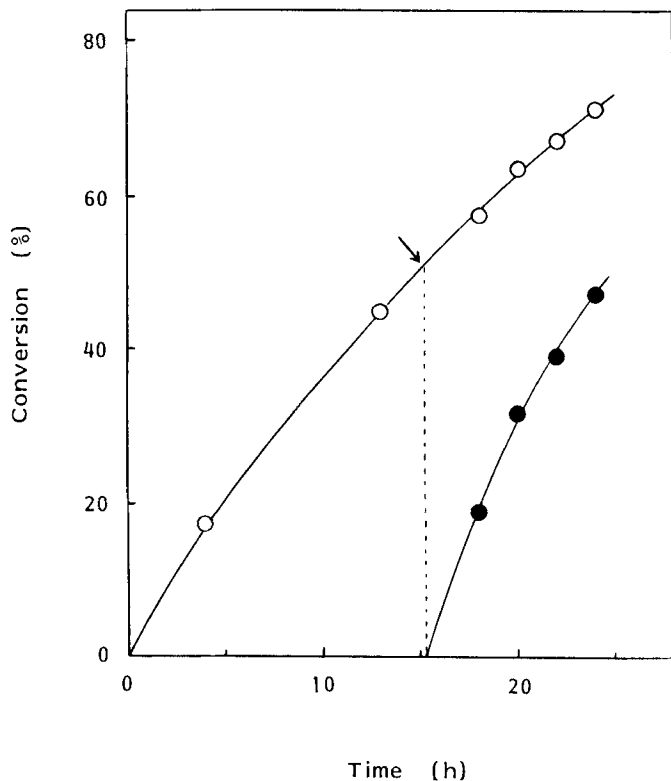
FIG. 3. Time–conversion curve for DADMAC/AA (20/80) copolymeriza-
tion. (O) Total polymer, (●) gel polymer, (↓) gel point. Conditions: VA-088,
0.01 mol/L; [M], 4.0 mol/L; 40°C.

result, the intrinsic viscosity should decrease with conversion when no cross-
linking occurs. Thus the results shown in Fig. 1 demonstrate the occurrence
of crosslinking in all copolymerization systems. In this connection, the homo-
polymerization of DADMAC was conducted under the same polymerization
conditions. The molecular weight increased slightly with conversion, as
opposed to the result at [M] 3 mol/L, although the unreacted pendent allyl
group was again not detected by ^{13}C-NMR spectroscopy.

Gelation in the DADMAC/AA (20/80) Copolymerization

Figure 3 shows the time versus conversion curve for the solution copolymer-
ization of DADMAC with AA as well as the percentage of gel polymer obtained
by the sol-gel separation. The gel point, i.e., the conversion at the time at
which gel starts to form, was determined to be 51%.

Figure 4 shows the dependence of swelling ratios of the resulting gels on
conversion beyond the gel point. Gel with a remarkably high swelling ratio
of about 1400 was obtained just beyond the gel point, and the swelling ratio
decreased with the progress of gelation although, even at the highest conversion,
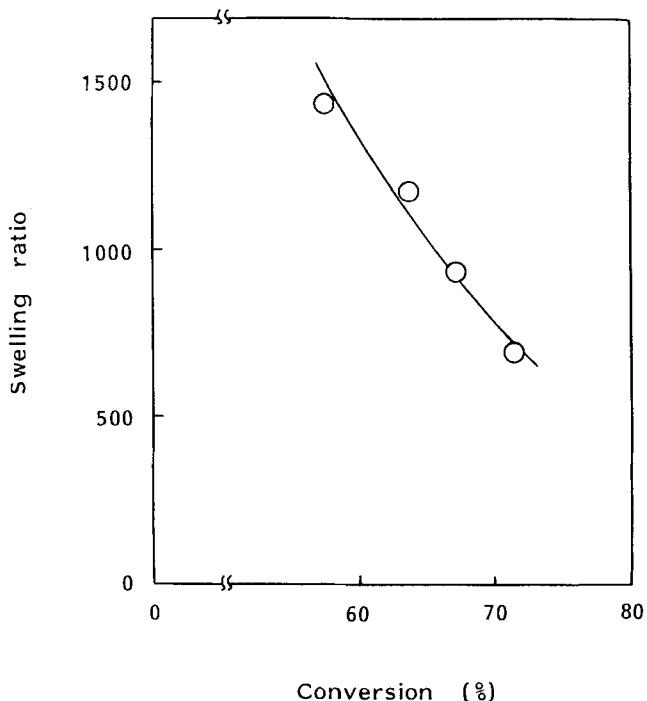the swelling ratio was about 700.

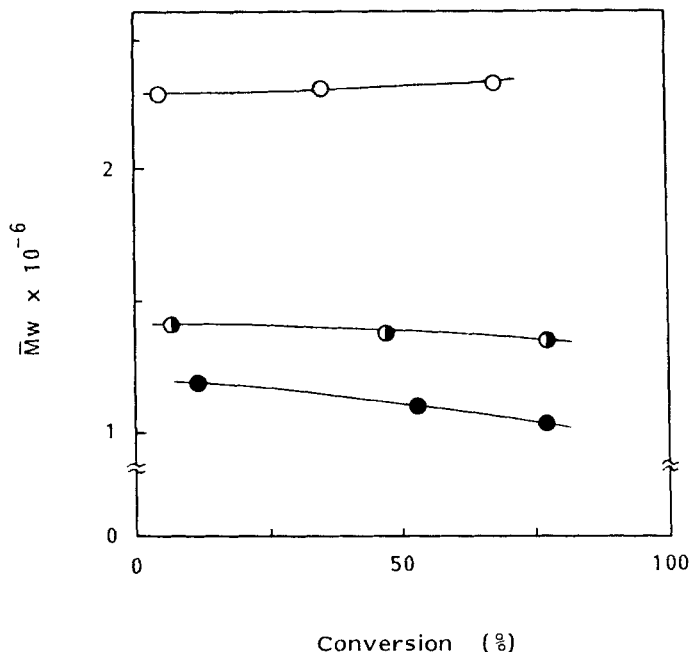FIG. 4. Dependence of swelling ratio on conversion.

FIG. 5. Dependence of weight-average molecular weight, $\bar{M}_w$, on conversion for DADMAC/AA (20/80) copolymerization in the presence of (○) 3.3, (◐) 6.7, and (●) 10 vol% 2-propanol.

Effect of Addition of 2-Propanol in the DADMAC/AA (20/80) Copolymerization

As described above, gelation was clearly observed in the DADMAC/AA (20/80) copolymerization but the molecular weight of the copolymer, even at a low conversion, was too high for GPC measurement. In order to explore the gelation behavior in more detail, we tried to reduce the molecular weight of the resulting copolymer by adding 2-propanol as a chain transfer reagent. Figure 5 shows that the molecular weight increased slightly with conversion in the presence of 3.3 vol% 2-propanol, but 10 vol% 2-propanol induced a decreasing tendency of the molecular weight with conversion (see Figs. 5 and 6). No gelation was observed in any of the copolymerizations in the presence of 2-propanol, probably because of the decrease of the molecular weight, i.e., the decrease of the number of crosslinking points per polymer chain.
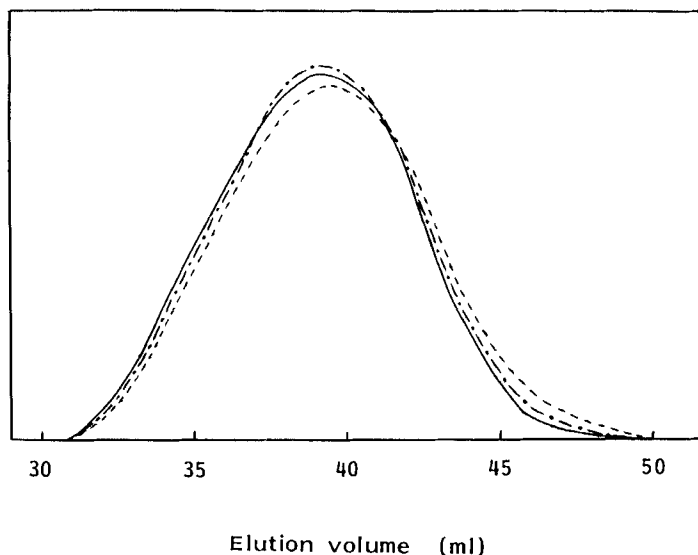
Elution volume (ml)

FIG. 6. Variation of GPC curves with conversion for DADMAC/AA (20/80) copolymerization in the presence of 10 vol% 2-propanol. Conversion (%): (——) 11.3, (- • -) 53.7, and (- - -) 77.7.

Tetraallyl ammonium chloride (TAAC) was then added as a crosslinker to increase the crosslinking points per polymer chain in the presence of 10 vol% 2-propanol, even though the cyclopolymerization of TAAC has been shown in detail in our previous article [13] to yield cyclopolymer consisting of mono-cyclic and/or bicyclic structural units with more than one unreacted allyl group per structural unit. The addition of 2 mol% of TAAC caused production of gel at about 10% conversion.

Mechanistic Discussion

As is evident from the above data, crosslinking occurred in the copolymeriza-tion of DADMAC with AA and, eventually, gel was formed at the molar ratio [DADMAC]/[AA] = 20/80 in the feed. First, it was thought that the un-cyclized DADMAC units would be introduced into the copolymer chain through a fast intermolecular M_1 • + M_2 reaction, and the resulting unreacted pendent allyl groups would react with a growing polymer radical. However, this is not in agreement with the following facts: (1) almost no pendent allyl

groups were detected in the copolymers by ^{13}C-NMR spectroscopy, and (2) no crosslinking occurred in the DADMAC/AA (20/80) copolymerization in the presence of 10% 2-propanol.

In the polymerization of allyl compounds, chain transfer of the growing polymer radical to the monomer called "degradative chain transfer," becomes very important compared to normal vinyl polymerizations [13]. Thus, in the present allylic copolymerization system the following two types of chain transfer reactions could be important: 1) intermolecular chain transfer of the growing cyclized DADMAC radical to DADMAC monomer to produce a monomeric allyl radical (M*') and 2) intramolecular chain transfer accompanying abstraction of an allylic hydrogen from a pendent allyl group by the uncyclized DADMAC radical to produce the polymeric allyl radical (P*'), as has been observed in the polymerization of diallyl aromatic dicarboxylates [14-16]. When M*' and P*' reinitiate a new chain or couple with the growing polymer radical, two or one carbon-carbon double bond would be introduced into the polymer chain end or the central portion of the polymer chain, respectively. The crosslinking reaction may proceed through direct addition to carbon-carbon double bonds or allylic hydrogen abstraction and subsequent reinitiation by a growing polymer radical, perhaps mainly by a growing AA radical. Thus the crosslink density of the resulting polymer would be very low. This may be the reason why the swelling ratio of the resulting gel was so very high.

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