Polymer Bulletin 44, 371–376 (2000)

Polymer Bulletin

Gelation kinetics of *N,N'*-diallyl malonamide/acrylamide system in pregel regime

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Received: 25 October 1998/Revised version: 2 May 1999/Accepted: 31 May 1999

Summary

Gelation kinetics of N,N' diallyl malonamide / acrylamide system is investigated by dilatometric technique. The effect of N,N'diallyl malonamide concentration on the gelation reaction at 60°C and at constant initiator concentration and the effect of temperature on the gelation reaction at constant crosslinker and initiator concentrations are investigated. Critical gelation times are determined in each case.

Introduction

Monofunctional allylamides give homopolymers of low molecular weight (1). In the case of radical initiation, monoallyls do not polymerize with benzoylperoxide but do polymerize with di-t-butyl peroxide. There is little work on polymerization of N,N' diallyl amides $R\text{-}CN(CH_2CH{=}CH_2)_2$. Most diallyl amides are solids. They polymerize very slowly with radical catalysts to give low molecular weight polymers. Even with di-t-butyl peroxide initiator and at 125°C homopolymerization of diallyls are very slow. On prolonged heating no change in refractive index and no crosslinking are recorded. Diallyl compounds are used as herbicides (diallyl chloracetamide), in sieving systems, in chromatography (N,N' diallyl tartaramide), in dyestuff and pharmaceutical field (diallyl thiourea), and these are some of the reported uses of diallyl compounds in industry.

On the other hand, gels derived from acrylamide and a bifunctional comonomer have wide applications (2). Their ability to absorb solvents 50 to 100 times more than their original weight and retain their durability enhances their use, especially in hydrolyzed form in holding aqueous solutions. Their uses extend from controlling humidity of soils to biomedical applications, in artificial organs and contact lenses and controlled drug release systems both for human and animal therapy.

Formation and properties of polyacrylamide gels and the gelation processes have been intensely studied. Baselga, Capek, Okay and many others can be cited among researchers who have worked in this field (3-9).

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N,N'diallyl malonamide (CH_2=CH-CH_2-NH-C(=O)-CH_2-C(=O)-NH-CH_2-CH=CH_2) is a new crosslinking agent. It is soluble in water and from this point of view it is a new candidate for hydrophylic systems instead of bisacrylamide. It has a great advantage over the N, N'

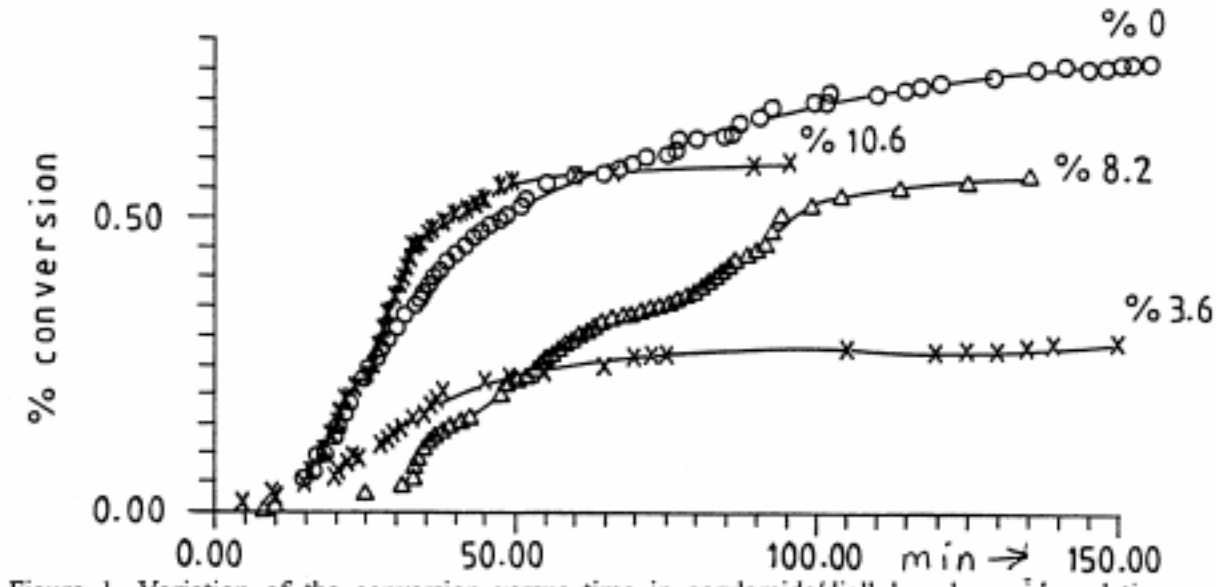

Figure 1. Variation of the conversion versus time in acrylamide/diallyl malonamide gelation. T=60°C. Initial monomer concentration is 0.49M.Concentrations of $K_2S_2O_8$, $NaHCO_3$ and $Na_2S_2O_3$ are $8.5x10^{-4}$, $1.0x10^{-3}$, $1.0x10^{-3}$. Diallyl concentrations are; 0; 3.6; 8.2; and 10.6 mol %.

methylene bisacrylamide since even in a slightly acidic medium the latter gives formaldehyde which is toxic.

In this work acrylamide monomer is crosslinked by diallyl malonamide by a free radical crosslinking copolymerization. Rate of polymerization is monitored by dilatometry at different temperatures and n,n'diallyl malonamide concentrations. Critical gelation times, t_{cr}, are determined in each case. From $\ln(t_{cr})$ vs. 1/T plots the overall activation energy is obtained by the equation.

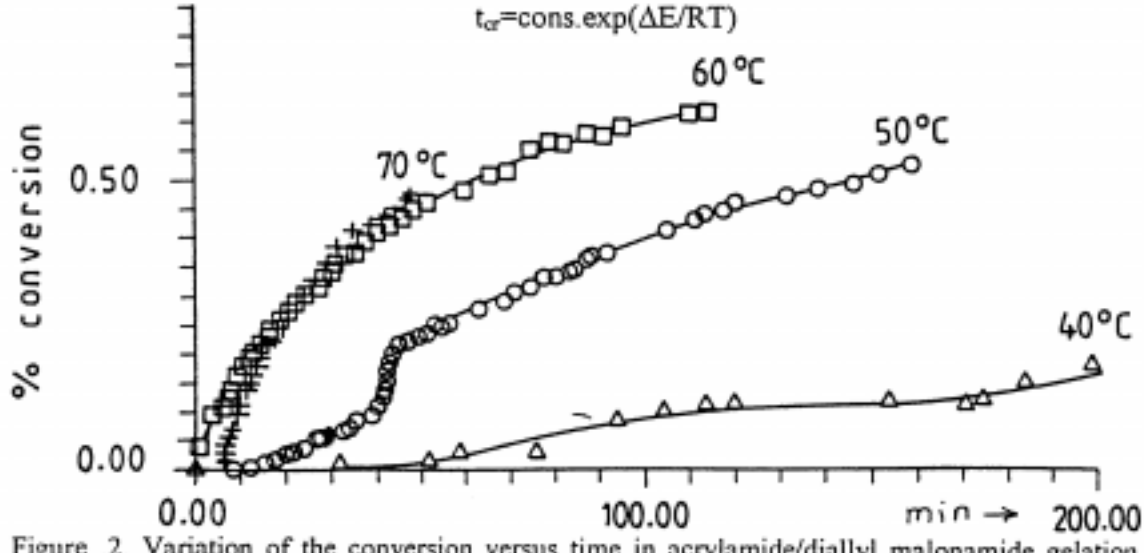

Figure .2. Variation of the conversion versus time in acrylamide/diallyl malonamide gelation at 40°C, 50°C, 60°C and 70°C. Initial monomer concentration is 0.49M.Concentrations of $K_2S_2O_8$, $NaHCO_3$ and $Na_2S_2O_3$ are $8.5x10^{-4}$, $1.0x10^{-3}$, $1.0x10^{-3}$. Diallyl concentration is 6.4 mol %.

Experimental

Synthesis of N,N' Diallyl malonamide (11): 15 g (.31 M) of diethyl malonate and 7 ml dioxane are placed in a two necked round bottom flask (250ml) which is equipped with a reflux condenser. While stirring 6 ml (0.63 M) allyl amine is added to the solution. The mixture is stirred for 24h at 55-60°C. After cooling the mixture is poured into 30 ml ether. The precipitated product is filtered and recrystallized from 30 ml of toluene. White. crystalline product is dried at 40°C for 24h. Acrylamide is supplied from industry and used after crystallization from methanol. Potasium persulphate (Merck), sodium thiosulphate (Merck) and sodium bicarbonate (Merck) are used as supplied.

Dilatometric experiments: Acrylamide and N,N'diallyl malonamide copolymerizations are carried out in water with $K_2S_2O_8$ / $Na_2S_2O_3$ redox initiator system with $NaHCO_3$ buffer. O_2 is removed from the system by N_2 bubbling for 30 mins. At constant diallyl concentration (6.4 %mol)the % conversion is followed dilatometrically at different temperatures (40, 50, 60 and 70°C). At 60°C the time conversion plots are determined for various diallyl concentrations. The dilatometer used is a round bottomed glass bulb with 30 ml volume, connected to a 30cm length of 1.5mm diameter capillary tubing with a ground glass joint. The meniscus is read with millimetric paper to 0.5mm. During the copolymerization reaction the mixture is stirred continuously with a magnetic stirrer and the critical gelation point is determined from the point when the magnet slowed down.

Percent conversion values have been calculated from the following equation. Here d_m and

$$\% x = (- \pi r^2 d_m / M_{top})(1-d_m/d_p)^{-1} \Delta h$$

d_p are density of monomer and polymer , M_{top} is the total amount of monomer at the beginning, r is the radius of capillary tube and Δh is cm shrikage. The density values of the acrylamide/bisacrylamide system are used throughout the study (3-8).

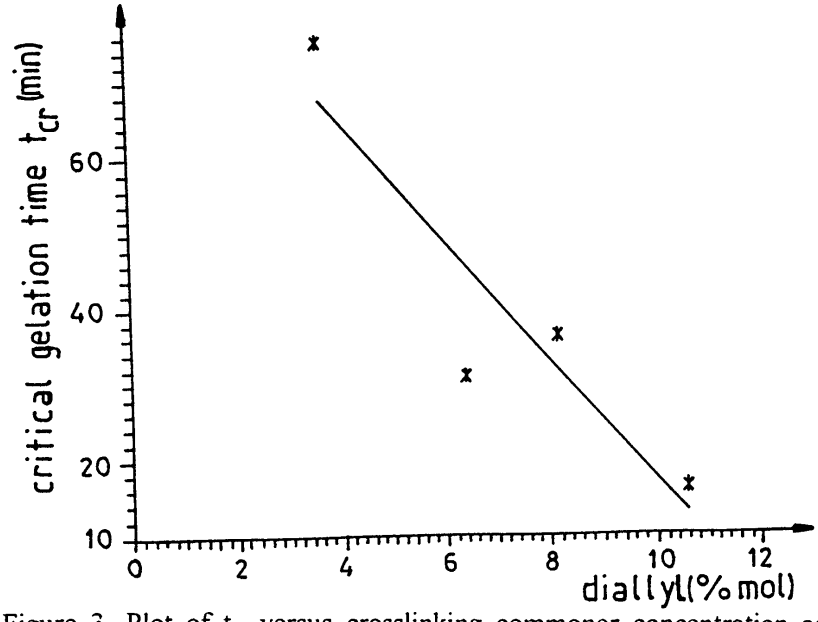

Figure 3. Plot of t_{cr} versus crosslinking commoner concentration as % mol during acrylamide diallyl malonamide gelation for $[I]_0 = 8.5x10^{-4}$ mol/lt $[diallyl]_0$=0.49 mol/lt $[acrylamide]_0$= 0.0336 mol/lt

Results

At constant temperature (60°C), the time conversion plots for different diallyl percents are given in Fig.1. Even though the conversion seems to have leveled off especially at %3.6 and %10.6, this is not the case, conversion is increasing extremely slowly after the critical gelation time. Time conversion plots at constant diallyl concentration for different temperatures are given in Fig.2. The induction period at the beginning of the reaction shows the presence of the dissolved oxygen at present conditions. Keeping everything constant in all experiments, including the N_2 bubbling period, a slight dependence of induction period on the crosslinker concentration is observed as in Fig.1, as the amount of crosslinker decreases the induction period increases. In Fig.2, induction period increases as the temperature decreases.The critical gelation time versus diallyl concentration are given in Fig.3. From Fig.3 a decrease in critical gelation time is observed as diallyl content is increased.

The maximum rates have been calculated by fitting polynomial to the points in Fig.1 and Fig.2 Continous lines shown in figures represent the polynomial. In Fig.1 a high initial rate is observed at zero diallyl concentration namely for acrylamide homopolymerization. The presence of the diallyl comonomer reduced the initial rate in copolymer and increased the viscosity of the medium and reduced the rate of reaction.

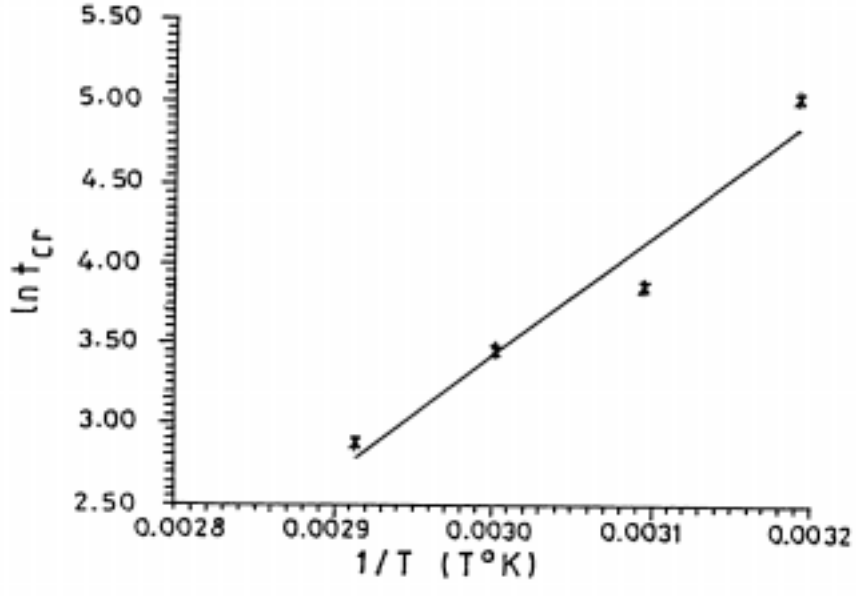

Figure 4. Plot of ln (t_{cr}) versus 1/T during acrylamide diallyl malonamide gelation for $[I]_0$ = $8.5x10^{-4}$ mol/lt $[diallyl]_0$=0.49 mol/lt $[acrylamide]_0$=0.0336 mol/lt

The maximum rates, $(dx/dt)_{max}$, are given in Tab.1 for different initial diallyl contents at 60°C. The rate first decreased and then increased as diallyl content is increased. It should be noted that the rate at "0" diallyl is comparable to that of the % 10 diallyl concentration. The maximum rates at a constant diallyl concentration at 40, 50, 60, and 70°C temperatures are shown in Tab. 2. As expected the maximum rate increased as the temperature is increased.

Table 1. Maximum rate dx/dt for different diallyl malonamide concentrations, at T=60°C. Initial monomer concentration is 0.49M. $K_2S_2O_8$, $NaHCO_3$ and $Na_2S_2O_3$ concentrations are $8.5x10^{-4}$, $1.0x10^{-3}$, $1.0x10^{-3}$ respectively.

% mol allyl	dx/dt
0	0.0194
3.6	0.0027
6.4	0.0020
8.2	0.0028
10.6	0.0193

Table 2. Maximum rate dx/dt at different temperatures. Diallyl concentration=6.4 % mol. Initial monomer concentration =0.49M. Concentrations of $K_2S_2O_8$, $NaHCO_3$ and $Na_2S_2O_3$ are $8.5x10^{-4}$, $1.0x10^{-3}$, $1.0x10^{-3}$.

T°C	dx/dt
40	0.0017
50	0.0087
60	0.020
70	0.025

In Fig.4. the plot of ln (t_{σ}) versus 1/T is shown (σ =0.2). If one assumes that this plot is linear, an average value of the activation energy may be obtained which is equal to 15 Kcal for the present reaction conditions. This activation energy is high compared to the value found for the bisacrylamide/acrylamide system which is found as 10 Kcal (10, 12), for the same conditions, indicating the slowness of crosslinking reaction in diallyl case.

The latter result is another promising point in the use of diallyl malonamide in acrylamide gels. It is known that the bisacrylamide gels are inhomogeneous and this inhomogeneity causes their properties to change on swelling (8-10). The slow forming clear diallyl gel might result in a more homogeneous structure.

Acknowledgement : We express our thanks to Mrs. Guia Kaslowski from Organik Kimya AŞ. for supplying the acrylamide monomer.

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