Mechanism and Kinetics of the Reaction of Acrylic Polyols with Hexa (Methoxymethyl) Melamine

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Synopsis

New procedures have been developed to study the mechanism and kinetics of the crosslinking of acrylic polyols with hexa (methoxymethyl) melamine. Both the rate of gel formation and alcohol release are found to be affected by the concentration and the nature of the catalyst and to be proportional to the hydrogen ion concentration. The rate of gel formation can be modeled by using the Miller and Macosko procedure with the input consisting of the polymer composition and the rate of release of reaction products. The correlation between calculated and experimentally determined quantity of gel formed is good when the reactions are slow, but becomes poor when gel formation is rapid, suggesting that the formation of large rings is favored by rapid reaction. The rate of gel formation shows much less variation among different polymer systems than does the rate of release of reaction products from the crosslinking reaction.

INTRODUCTION

The coatings industry has used melamine formaldehyde resins for over 40 years. During that time much effort has been expended in accumulating the information required to use these materials with confidence. Today, formulations having a very desirable balance of durability, mechanical properties, and application properties can be developed, and "melamine coatings" is a term connoting quality.

During this same period some of the work was aimed at unraveling the mechanism of the process, primarily with the partially formylated resins. Most recently Blank summarized the state of our understanding of these reactions.[1,2] The emphasis on reducing the emission of organic solvent from coatings has resulted in the widespread adoption of fully formylated, fully etherified products, such as hexa(methoxymethyl) melamine (HMMM). Blank has also described much of what is known about these materials and how they behave in coating systems. Much remains to be learned about the chemical behavior of the fully reacted systems.

Many of the standard techniques for studying chemical reactions are unsuitable for the study of curing systems because these systems crosslink and become insoluble and intractable during the curing process. Furthermore, the reacting groups are relatively dilute and often difficult to distinguish from similar, nonreacting species, so that interpretation of observed changes

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is often difficult. The conclusions drawn in many of these studies are based mostly on analysis of reaction products, isolated and analyzed after the

Model reactions have also been studied. Santer and Anderson[3] studied the stoichiometry of conventional melamines by using a monofunctional alcohol. Wicks and Hsin prepared a difunctional triazine derivative in order to be able to separate alcohol interchange from self-condensation. He also examined the kinetics of the reaction, but was unable to draw firm conclusions from his experimental data.

Bauer and co-workers[5] have used IR to investigate the reaction, the kinetics, and the correlation of film composition with film properties. Lazzara[6] has described an approach in which reaction products were determined continuously and the information was compared with ^{13}C NMR and FTIR measurements on the polymer. He showed that the various approaches give similar results and that relative rates of the chemical reactions can be studied readily. He did not measure changes in solubility or mechanical properties.
don,[11] when studying the free radical crosslinking of cotton fibers reacted

Attempts to measure the insoluble fractions of gel have been mentioned frequently, and some information has been published.[7] Other methods of studying crosslinking have included changes in modulus, swelling ratios or dielectric constants, and for coatings, such measurements as MEK rubs, hardness, or flexibility. Hardness has been a special favorite of many authors since it can be readily measured, and, if the starting material is a liquid, it gives an indication of the degree to which the film has reacted. Such measurements, however, have severe limitations when used as a measure of cure. Hardness is a complex phenomenon as shown by the fact that in some enamels a severe overbake can result in a decrease in hardness.

Recently we described an improved extraction technique that makes it possible to follow the course of insolubilization of thin films.[8] This allowed us to study the kinetics of the formation of insolubles (gel phase) during the course of heat curing of some acrylic/melamine compositions. We have also improved the method for measuring the rate of methanol formation. The panel oven described by Lazzara[6] needed a significant heat-up period (10 min) to reach the desired cure temperature; more detailed studies found that a significant degree of gas mixing occurred in the oven, so that the GPC data could not be used to determine the instantaneous extent of reaction.

EXPERIMENTAL

We developed a new technique that gives real time values for the quantity of methanol released, and provides quantitative rates rather than relative results.

The reactions in our system, both methanol generation and gel formation, proceeded very rapidly and were complete in less than 10 min. This is in line with the observations of Lazzara. The kinetics of the chemical reaction, as measured by the release of methanol, could be compared with the gel-forming reaction by means of a crosslinking model based on work of Miller and Macosko[9] (see also Bauer et al.). Finally, the effect of time and temperature on the physical and mechanical properties of films was also measured.

Enamel cure rate was determined by measuring the methanol liberated during the crosslinking reaction of pendant acrylic hydroxyl with the methoxy groups of melamine resins. In order to obtain this kinetic information, an apparatus capable of quantitatively measuring the instantaneous concentration of volatiles liberated as a function of time was developed.

The apparatus (shown schematically in Fig. 1) consisted of a 3 × ¼ in. stainless steel tube oven with minimal hold-up time as a reactor. This design gave virtually quantitative transfer of instantaneous volatiles and eliminated the irregular flow patterns associated with earlier models. A cutaway diagram is shown in Figure 2. The sample can be heated to a cure temperature of 121°C in less than 40 s. Temperature control of the oven is provided by a programmable ramp temperature controller with feedback from thermocouples implanted adjacent to the oven cavity.

Coating systems to be studied are coated on the inside of the tube. The viscosity of the formulated resin system was adjusted with an appropriate solvent and then flowed through the tube in order to obtain a continuous thin film 3–6 μm dry film thickness. The tubes are vacuum-dried at room temperature prior to analysis in order to remove solvents. The tube containing the resin film is placed in the tube oven at the desired temperature. The effluent is automatically sampled every 0.5 min during the first 10 min of the cure, when volatile evolution is at a maximum, and then every minute through the remainder of the 30-min cure cycle at 121°C. The gases were analyzed on a 6 ft, ⅛ in. carbowax 1500 on 80/100 Carbopak C column run isothermally at 80°C with a flow rate of 20 mL/min.

At the end of a cure cycle the gas chromatograph automatically transfers all essential peak information to a Minc II computer for data reduction. The output provides the percent conversion for each sampling, the kinetic rate constant and a concentration vs. time plot for each component. The versatility of these programs allows one to account for variations in reactant concentration when calculating rate data. The precision of the method as estimated from the difference between duplicate analysis gave 2 ± 0.40 mg over the range of 50–100 mg MeOH/g film. The coefficient of variation is 1.0%. Typical data are in Table I.

RATE OF GEL FORMATION

The extent of crosslinking was determined by measuring the quantity of material soluble in 2-butanone after curing for a given period of time and temperature. The extraction was carried out by supporting the coating on a coil of aluminum window screening and then placing the coil in a Soxhlet extraction thimble for removal of solubles. The residue was dried, and the weight of the insolubles determined. All samples were run in duplicate, but the individual values were used in determining standard deviations. In experiments designed to measure the composition of the soluble fractions, duplicate samples were combined and concentrated. The composition of the soluble fraction was determined by using the ratio of the styrene aromatic absorption at 720 cm^{-1} to the triazine absorption at 830 cm^{-1}.

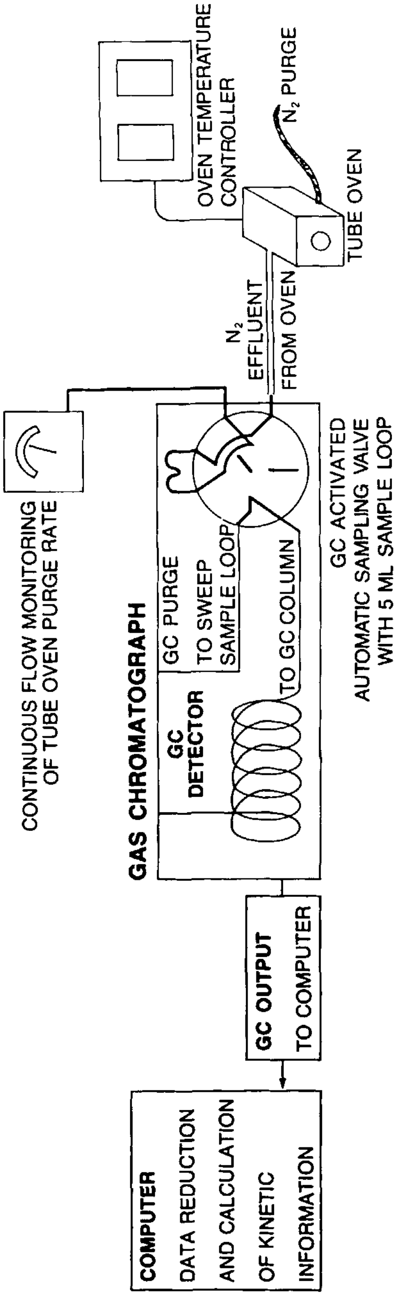

Fig. 1. Tube oven gas chromatography apparatus for determining enamel cure rates.

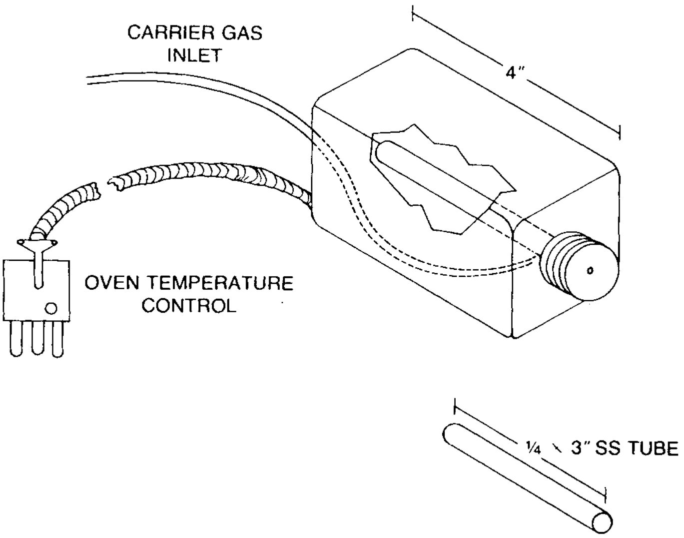

Fig. 2. Tube oven apparatus for studying cure kinetics.

TABLE I
GPC Kinetic Data[a]

Time (min)	% Conversion	2nd-order K ($\times 10^2$)
0.5[b]	10.45	4.90
1.0[b]	27.48	7.42
1.5[b]	40.99	8.40
2.0	51.31	8.86
2.5	58.87	8.96
3.0	64.81	8.96
3.5	69.69	8.94
4.0	73.98	8.98
4.5	77.58	9.01
5.0	80.64	9.04
5.5	83.25	9.06
6.0	85.49	9.08
6.5	87.44	9.12
7.0	89.22	9.19
7.5	90.79	9.28
8.0	92.23	9.43
8.5	93.44	9.56
9.0	94.62	9.78
10.0	95.60	9.50
12.0	96.93	8.97
14.0	97.72	8.44
16.0	98.31	8.05
18.0	98.95	8.09
20.0	99.40	8.27

[a] HEA Copolymer Cymel 303 70/30 1.05×10^{-3} m/g PTSA salt; 121°C.

[b] Distorted by noninstantaneous heating rate.

SWELLING

Swelling ratios were determined by a simple technique that requires only one measurement before and one after swelling. A 1 mm i.d. hypodermic needle was cut to a flat tip which was then machined to a sharp edge. When pressed into a free film, this cut a circular disk whose diameter was readily measured in a microscope. Since the disk was uniform in size, only one measurement was required to measure the ratio of diameters before and after swelling, and, making the assumption that swelling was isotropic, the increase in volume was calculated by taking the cube of the ratio of the diameters.

MATERIALS USED

We used two acrylic polymers and one melamine resin for this study. One polymer, a styrene/acrylic copolymer, $M_n = 2\text{–}3 \times 10^3$, $M_w = 6\text{–}7 \times 10^3$, containing 30% by weight of hydroxyethyl acrylate, is identified as the hydroxyethyl acrylate copolymer (HEA). The other polymer, of similar molecular weight, contained 40% hydroxypropyl acrylate and is identified as the HPA copolymer. The hydroxypropyl acrylate contained about ⅓ 2-acryloxy-1-propanol and ⅔ 1-acryloxy-2-propanol. All monomers were commercial grade, used without further purification. The hydroxy acrylate monomers contained about 0.8% acrylic acid and 0.4% diacrylate.

The melamine resin used was Cymel 303 (American Cyanamid Co.), which for purposes of kinetic calculations of the release of methanol was assumed to be pure hexa(methoxymethyl) melamine. Blank reports that this product may contain as much as 70% dimer, which would mean an average DP of 1.7.[2]

Catalysts used were dodecylbenzene sulfonic acid (DBSA) and *p*-toluene sulfonic acid (PTSA) and their dimethyloxazolidine (DMO) salts.

MECHANISM STUDIES

The primary chemical reaction is the release of methanol and occurs regardless of stoichiometry, oligomer molecular weight, or functionality. The physical phenomena of gelation involves network formation through methylene bridges and occurs only if the stoichiometry and functionality are in the appropriate limits.

Past studies of polyol/melamine systems on high molecular weight systems in which the number of functional groups per polymer chain is large (usually >15) have used the chemical reaction as a measure of the crosslinking reaction. With the advent of low molecular weight systems, in which the functionality per chain can approach values as low as 2, this approach may no longer be valid. It is necessary to study both the chemical reaction and the physical change to an insoluble gel to understand how the system crosslinks and to correlate the chemical reaction with the film properties.

RATE OF METHANOL FORMATION

The formation of methanol from the HEA copolymer followed simple second order rate law to >90% conversion of the polymer hydroxyl groups according to the equation

$$d/[\mathrm{ROH}]/dt = k[\mathrm{ROH}][\mathrm{Mel{-}OCH_3}]$$

This is shown in Figure 3.

The single straight line observed for the HEA copolymer with no change in slope implies that the increasing density of crosslinking has very little or no effect on the reaction rate constant. The first data points are already beyond the initial gel state for the polymer, as calculated by the Miller–Macosko theory; however, there is no indication that the line does not pass through the origin or very close to it.

This means that the chemical reaction is not affected by the increase in gel content or by the increase in the glass transition temperature. These reactions are carried out at 121°C which is well above the glass transition temperature of the initial polymer and unquestionably in the rubbery region of the final film. The lack of change of the rate constant is unexpected, as it is generally assumed that gel formation decreases reaction rates.

Figure 4 shows the results for the HPA copolymer. In this case, the reaction shows a rapid linear rate followed by a region of slowly decreasing rate. This is consistent with the presence of both a primary and a secondary

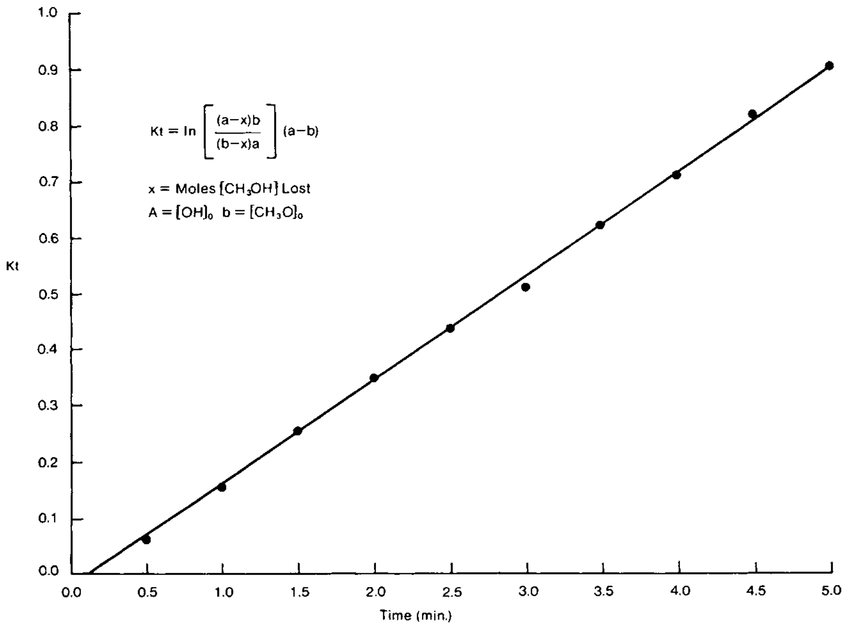

Fig. 3. Kinetics of methanol formation: HEA copolymer/Cymel 303 70/30 (1.05×10^{-3} m/g PTSA salt; 121°C).

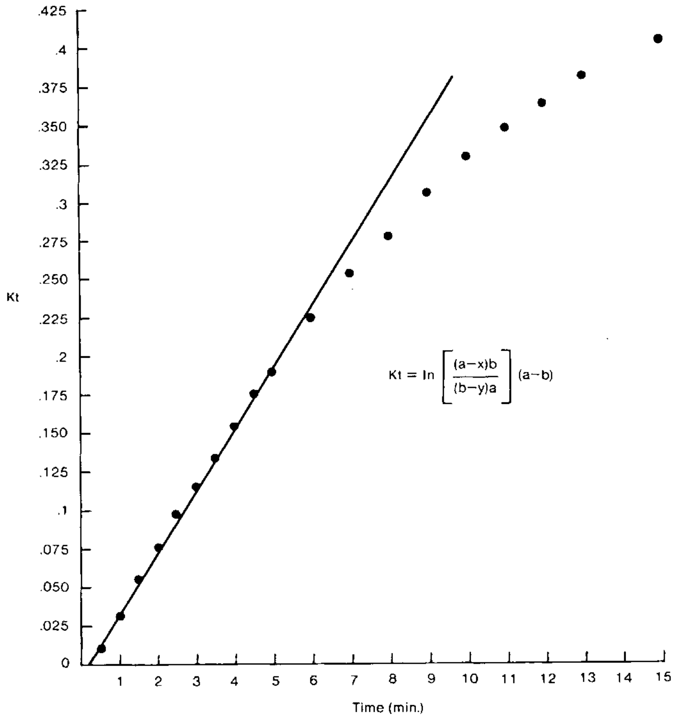

Fig. 4. Kinetics of methanol formation: HPA copolymer/Cymel 303 70/30 (1.05 × 10^{-3} m/g PTSA salt; 121°C).

hydroxyl. The ratio of the rate constants for the secondary/primary hydroxyl was found to be 0.03/1; this is quite comparable to the relative reactivity reported for SN_2 substitution of secondary vs primary hydroxyls.

GEL FORMATION

The apparent rate of crosslinking was calculated from the ratio of the gelled to ungelled or soluble material as determined in the extraction experiments. A second order reaction was assumed so that the rate constant could be calculated from

$$kt = 1/a\,(a-x) \tag{1}$$

in which x = weight fraction of insoluble material ($x=0$ at $t=0$) and a = the weight fraction of soluble material ($a=1.0$ at $t=0$). We also used the simplifying assumption that the reactants are at equal concentration. While this is obviously not rigorously true, it is reasonable in view of the nature of the reaction since the technique measures only how fast individual molecules are incorporated into the network.

Experimental results for the HEA copolymer are shown in Figure 5. Figure 5(a) shows the gel formation vs. time; Figure 5(b) shows the same data

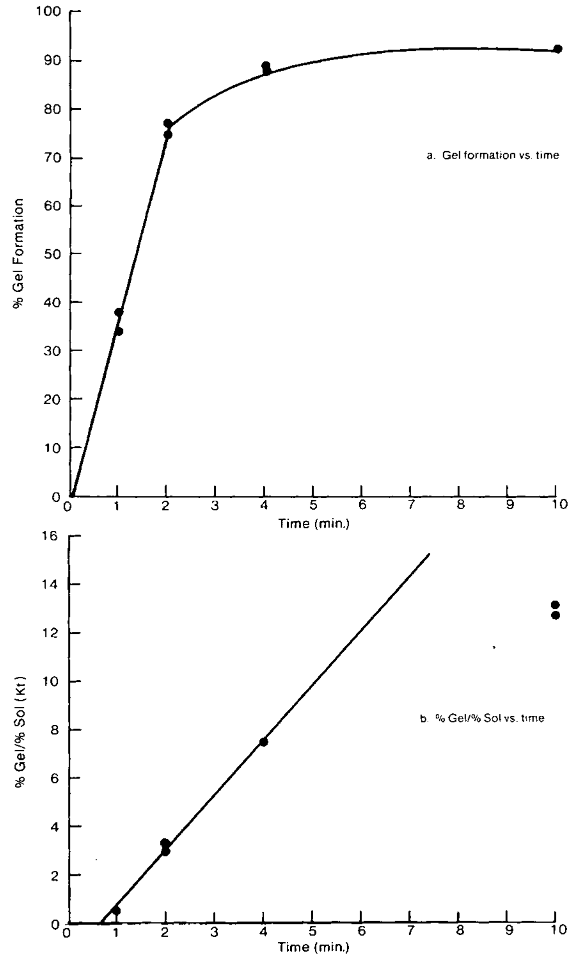

Fig. 5. HEA copolymer/Cymel 303 70/30, 121°C.

plotted according to eq. 1, from which the rate constant for gelation is obtained.

The intercept with the abcissa indicates the time at which gel or insoluble material first forms and can be taken as the gel point. The rate of gel formation eventually slows down because the crosslinked matrix reduces the probability of further reaction faster than the reduction in concentration. However, as shown in Figure 5(b), the data are linear to over 80% conversion to gel. In most cases, the rate constants can be determined to a standard deviation of ±25% or less.

The rate of gel formation according to eq. (1) can also be calculated using the gelation model to be described later. This is shown in Figure 6, where the rate according to eq. (1) is plotted vs. the extent of chemical reaction as determined experimentally from methanol evolution. A straight line results in this case, even though the actual stoichiometry is used so that there are no assumptions about equal concentrations.

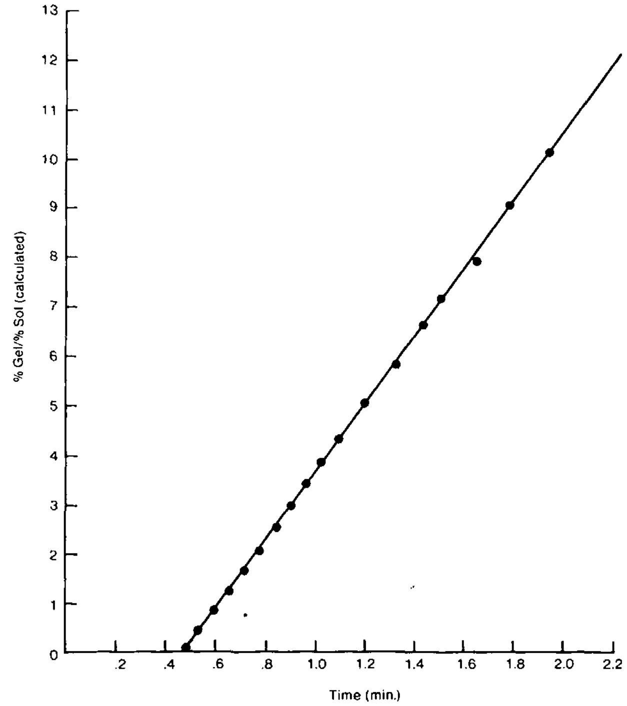

Fig. 6. Calculated rate curve for gel formation HPA copolymer.

EFFECT OF CATALYST ON GELATION

The effect of the catalyst on gelation was examined using *p*-toluene sulfonic acid (PTSA) and dodecyl benzene sulfonic acid (DDBSA), as well as their salts with dimethyl oxazolidine.

The results are summarized in Table II for the HEA copolymer. Both acids gave similar rates of gelation. Figure 7 shows a plot of the gelation rate vs.

TABLE II
Rate Constants for Gel Formation (121°C)[a]

Run no.	Catalyst[b] (mol × 10/100 g)	k (min^{-1})	t_0 (min)[c]
191	1.05	2.32 ± 0.22	0.5
183	1.05	1.94 ± 0.26	0.5
180	1.05	2.31 ± 0.39	0.6
123	1.05	2.36 ± 0.17	0.7
54	1.05	2.0 ± 0.18	1.0
86	0.35	1.44 ± 0.13	0.2
113	0.176	0.74 ± 0.14	1.6
114	0.176	0.82 ± 0.18	1.8

[a] HEA copolymer/Cymel 303 70/30.
[b] Oxazolidine salt of PTSA.
[c] Extrapolated time for gel formation.

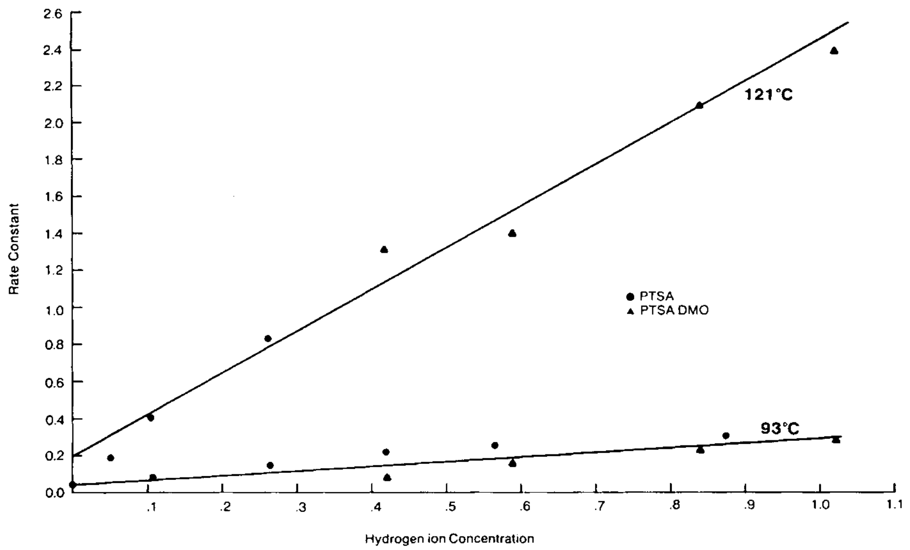

Fig. 7. Rate constant for gel formation as a function of hydrogen ion concentration: (●) PTSA; (▲) PTSA/DMO.

the catalyst concentration at 121° and 93°C. An excellent linear relationship is obtained at both temperatures, indicating first-order dependence on free acid.

A different relation was found with the salts. In this case the rate of gelation was proportional to the square root of the catalyst concentration. This is to be expected if H^+ is the active catalyst since the free acid concentration will be a function of the square root of the salt concentration. The rate constants for the salts fall on the same line as the acid when adjusted to equal hydrogen ion concentration (see Fig. 7).

The activation energy for gelation of the amine-neutralized catalyst is substantially greater than for unneutralized acid; from the data in Table III $k_{121}/k_{93} = 5.5$ for the acid and 8.7 for salt. This difference is even greater when the rate at 121°C is compared with room temperature. At 121°C both systems gel in less than 2 min; at room temperature, in the presence of free acid gelation occurs in a few hours, but in the presence of the amine salt the system is stable for many months.

TABLE III
Rate Constant for Gel Formation at Equal Hydrogen Ion Concentration[a]

Catalyst	93°C	121°C
PTSA	0.6 ± 0.2[b]	3.0 ± 0.2[b]
PTSA · DMO[d]	0.3 ± 0.1[c]	2.5 ± 0.3[c]
DBSA · DMO[e]	0.38 ± .14[c]	2.0 ± 0.5[c]

[a] HEA copolymer/Cymel 303 (70/30).

[b] Experimental rate constant/[catalyst concn].

[c] Experimental rate constant/$\sqrt{\text{(catalyst concn)}}$.

[d] Oxazolidine salt of PTSA.

[e] Oxazolidine salt of DBSA.

TABLE IV
Effect of CH_3O/OH Ratio on Rate of Gel Formation[a]

CH_3O/OH[b]	$k_{121°C}$	$k_{93°C}$
0.81	2.20 ± 0.68	0.33 ± 0.09
1.49	2.24 ± 0.62	0.20 ± 0.015
1.90	2.21 ± 0.41	0.23 ± 0.02
2.55	2.32 ± 0.22	0.20 ± 0.03
4.44	1.72 ± 0.11	0.24 ± 0.03
5.95	1.30 ± 0.22	0.11 ± 0.01

[a] HEA copolymer/Cymel 303 1.05 × 10^{-3} m/g PTSA salt.
[b] Assuming an equivalent weight/CH_3O in Cymel 303 of 65.

EFFECT OF STOICHIOMETRY ON GELATION

Within fairly broad limits the stoichiometric ratio of methoxymethyl to hydroxy does not affect the rate of gel formation of the HEA copolymer. Rate constants for gel formation (see Table IV) are almost unaffected as the CH_3O/OH ratio increased from 0.8 to 3, but decreased substantially at ratios >6. Similarly, as shown in Table V, the fraction remaining soluble after a 30-min cure does not change appreciably until the CH_3O/OH ratio exceeds a value of about 2.5; then the soluble fraction increases rapidly up to a CH_3O/OH ratio of 6.

GEL FORMATION AND METHANOL RELEASE

The rate of methanol release does not have the same relationship to catalyst concentration as does the rate of gel formation. Figure 8 shows the

TABLE V
Effect of CH_3O/HO Ratio on Extractable Melamine

A/M[a]	CH_3O/HO[b]	% Soluble[c]	% Mel. in sol.	% Mel. soluble[d]
50/50	5.95	17.11	82.5	28.3
50/50	5.95	15.64	84.1	26.1
60/40	4.44	10.73	72.7	19.5
60/40	4.44	9.73	77.1	18.8
70/30	2.55	7.6	52.5	13.3
70/30	2.55	6.7	48.8	11.0
75/25	1.98	6.99	31.0	8.7
75/25	1.98	5.09	29.9	6.1
80/20	1.49	6.35	16.5	5.2
80/20	1.49	3.52	11.0	1.9
85/15	1.05	7.99	7.4	3.8
85/15	1.05	4.63	4.8	1.8

[a] HEA copolymer/Cymel 303 at 121°C; 1.05 × 10^{-3} m/g PTSA·DMO.
[b] Assuming pure HMMM.
[c] After 95% conversion of —OH.
[d] Based on quantity of melamine in film originally.

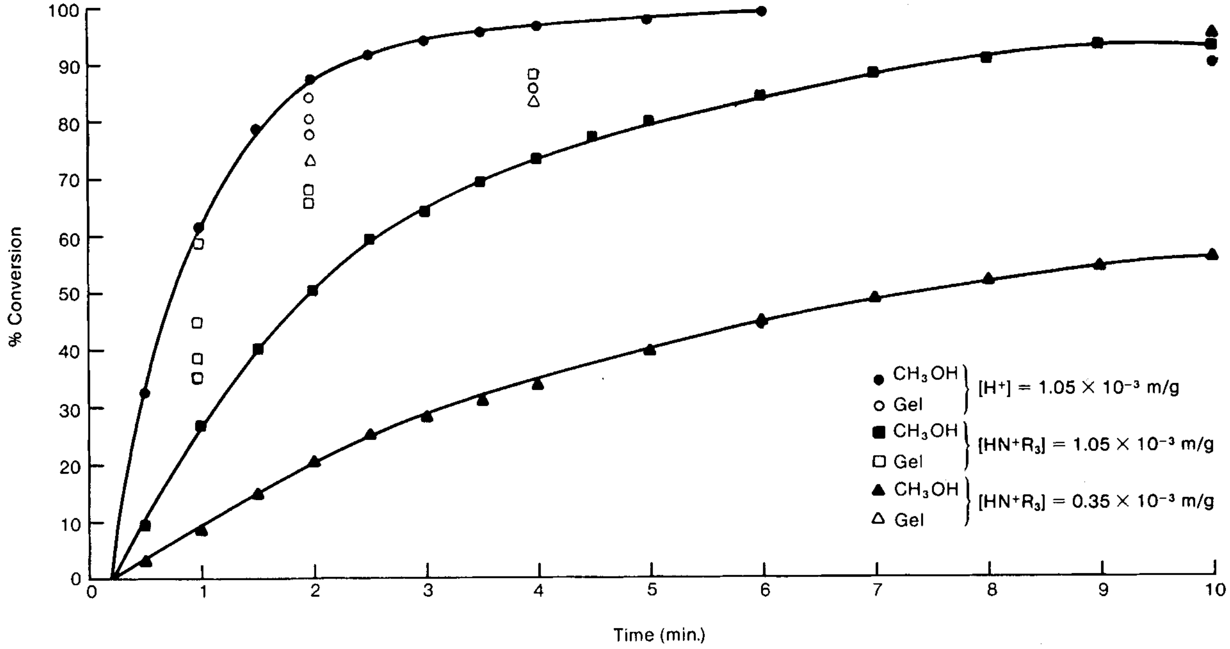

Fig. 8. Conversion vs. time, HEA copolymer/Cymel 303 70/30; 121°C. Comparison of effect of changes in catalyst on CH_3OH and gel formation: (●) CH_3OH and (○) gel, $[H^+] = 1.05 \times 10^{-3}$ m/g; (■) CH_3OH and (□) gel, $[HN^+R_3] = 1.05 \times 10^{-3}$ m/g; (▲) CH_3OH and (△) gel $[HN^+R_3] = 0.35 \times 10^{-3}$ m/g.

evolution of methanol and gel formation as a function time for three different catalyst systems. The resins consist of the HEA copolymer blended 70/30 w/w with Cymel 303. The catalysts consist of 0.2% PTSA, the same neutralized with DMO, and 0.067% PTSA neutralized with DMO. The release of methanol is clearly a strong function of the hydrogen ion concentration; the gel formation varies much less, and all systems are close to the same conversion after 4 min.

Figure 9 compares the gel formation vs. methanol release for the HEA and HPA copolymer. While the actual rates of gel formation are quite similar for these two systems, methanol evolution is slower from the HPA copolymer. This means that the HPA copolymer is actually more efficient at forming the gelled network than the HEA system for a given level of chemical reaction. This is contrary to general expectations and may relate to differences in the ease of intramolecular reactions which do not contribute effective crosslinks.

GELATION MODEL

The development of a mathematical model of the crosslinking reaction could offer substantial benefits in terms of both understanding the reaction and for predicting the effect of changes in variables.

We have used the statistical approach developed by Miller and Macosko[9] and modified by Bauer et al.[5] In this model the fraction of insoluble material is calculated as a function of the extent of the crosslinking reaction, which is determined by the methanol formed. Since we have independently measured the rate of this methanol formation, we can use the model to calculate

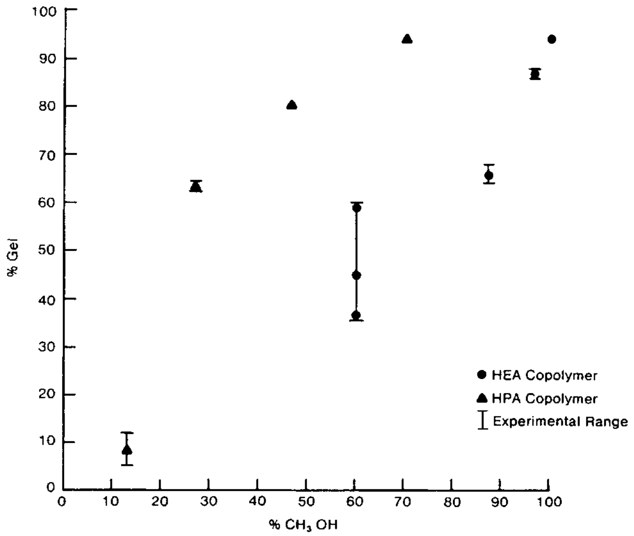

Fig. 9. Experimental data: % gel as a function of % CH_3OH formed for HEA and HPA copolymers (Acrylic/melamine 70/30; 121°C; 1.05 × 10^{-3} m/g PTSA salt).

the rate of gelation and compare with the actual experimental results. The equations were solved by standard numerical techniques using the ratio of OH to OCH_3, the distribution of functionality of the polyol, and the distribution of functionality of the melamine resin. The functionality distribution of the polyol was calculated from the individual exclusion chromatography curves for the HEA and HPA copolymers, making the assumption that the copolymers have a random monomer distribution. This assumption is reasonable in view of the synthesis of the copolymers, which were prepared by a "high-conversion" process that prevented the accumulation of slower reacting monomers.

For the melamine, we used functionalities of 6 and 9; this corresponds to the presence of 0% dimer and 70% dimer which is the value reported by Blank.[2] The dimer has little effect on the methoxymethyl concentration, but will have a small but real effect on the rate of gelation.

COMPARISON OF EXPERIMENTAL AND CALCULATED RATES OF GELATION

The calculated curves and experimental data for the HEA copolymer at two different catalyst concentrations are shown in Figure 10 (1.05×10^{-3} m/g of PTSA salt), and in Figure 11 (0.35×10^{-3} mg/g PTSA salt). The results for the HPA copolymer catalyzed by 1.05×10^{-3} m/g of the PTSA salt are shown in Figure 12. Finally, Figure 13 shows the results for the HEA copolymer catalyzed by free PTSA. The best agreement between the experimental results and those predicted by the model is obtained with the slowest reaction in Figure 11. At higher catalyst concentrations or with the free acid, greater deviations from the model are observed.

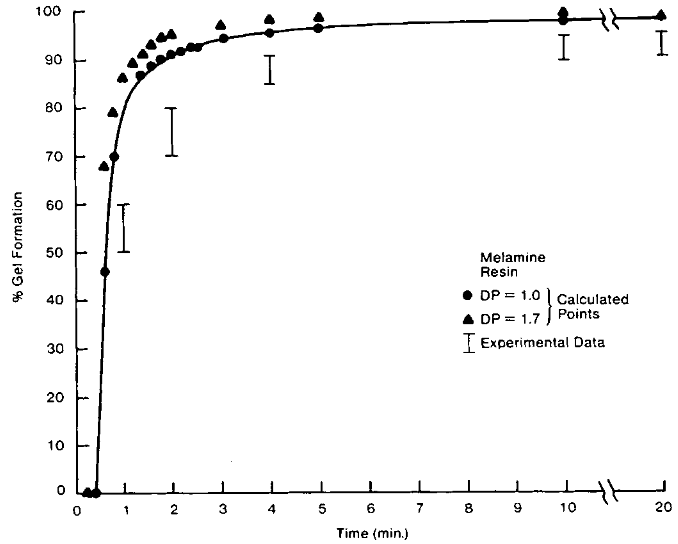

Fig. 10. Calculated and experimental values for % gel formation vs. time (HEA copolymer/Cymel 303 70/30; 121°C; 1.05×10^{-3} m/g PTSA salt). Melamine resin: (●) DP = 1.0 and (▲) DP = 1.7, calculated points; (I) experimental data.

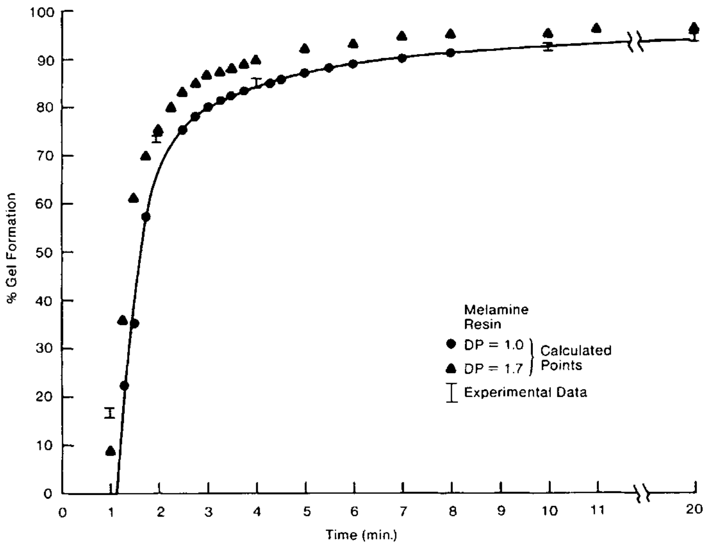

Fig. 11. Calculated and experimental values for % gel formation vs. time (HEA copolymer/Cymel 303 70/30; 121°C; 0.35 × 10^{-3} m/g PTSA salt). Melamine resin: (●) DP = 1.0 and (▲) DP = 1.7, calculated points; (I) experimental data.

The discrepancy between the model and the results may be due to experimental errors in the measurement of the gel content or the methanol evolution, particularly at short reaction times. However, it is more likely due to a neglect of intramolecular cyclization as a reaction path which will lead to methanol formation but will not contribute to effective crosslinking and

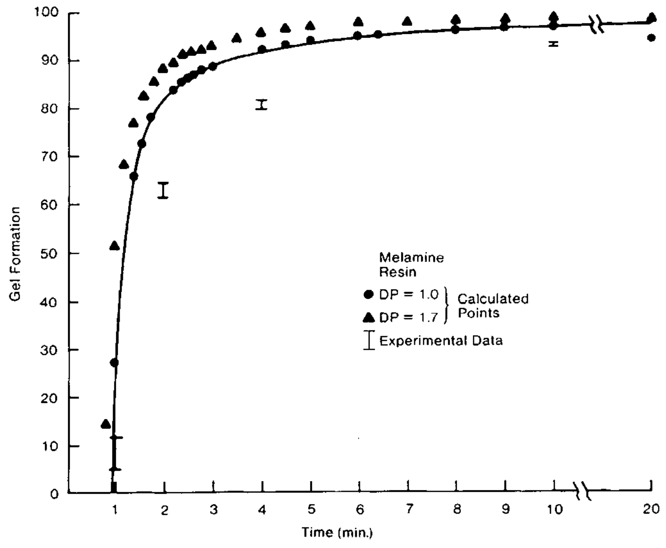

Fig. 12. Calculated and experimental values for % gel formation vs. time (HPA copolymer/Cymel 303 70/30; 121°C; 1.05 × 10^{-3} m/g PTSA salt). Melamine resin: (●) DP = 1.0 and (▲) DP = 1.7, calculated points; (I) experimental data.

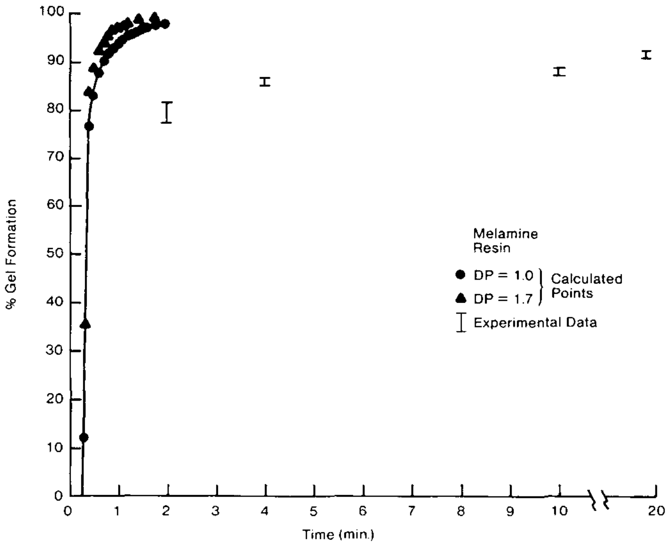

Fig. 13. Calculated and experimental values for % gel formation vs. time (HEA copolymer/Cymel 303 70/30; 121°C; 1.05 × 10^{-3} m/g PTSA). Melamine resin: (●) DP = 1.0 and (▲) DP = 1.7, calculated points; (I) experimental data.

gelation. The fact that the HPA copolymer contains a larger fraction of gel than the HEA copolymer at a comparable extent of reaction clearly indicates that some systems form gel more efficiently than others. While fully alkylated melamines are not expected to self-condense under our reaction conditions, the spatial restrictions that develop once the bulky melamine moiety has reacted with the acrylic chain favors some intramolecular reaction.

One measure of such a reaction is the amount of unreacted melamine; the amount of this will be a function of the acrylic/melamine ratio, the functionality of the melamine, and relative rates of the intramolecular and intermolecular reactions.

Professor K. F. O'Driscoll suggested and wrote a computer program to simulate the effect of such competitive reactions on the level of unreacted melamine. The model considers the relative rate of the addition (A) of the melamine to the acrylic chain to the rate of crosslinking (X) to form an effective crosslink, and to the rate of cyclization (C) to form an ineffective crosslink. The program provides the fraction of unreacted melamine at any conversion for assumed values of the ratios of C/A and X/A.

Table VI shows the effect of such variations on the calculated percent of the original melamine which is unreacted after 95% conversion of OH. This value was chosen because 3–5% of soluble material was always found in extraction experiments. Table VII compares the empirical data (from Table VI) with results calculated assuming that the ratio of crosslinking to addition is 0.1, that the ratio of cyclization to addition is 0.5, and that the melamine has an average functionality of 5. This implies that a substantial amount of cyclization occurs, reducing the true rate of crosslinking. Gardon,[11] when studying the free radical crosslinking of cotton fibers reacted

TABLE VI
Computer Simulation of Effect of Relative Rates of Addition, Crosslinking, and Cyclization on % Unreacted Melamine

Acrylic/ melamine, OH/MeOH	F(M)	Relative rates[a]							
		0.1/0.1	0.1/0.5	0.3/0.3	0.3/0.5	1/0	1/1	1/2	0.2/0.2
85/15	6	0		3			0		
	5								
	4			0			0		
80/20	6		0		0	0		15	13
	5								
	4		0		0			0	
75/25	6			8			26		
	5		2						
	4			1			8		
70/30	6	0		12	14	33	33	41	
	5		4						
	4			6				28	
60/40	6	11		38					
	5		20					44	
	4								
50/50	6	33		29	45	52	59	56	
	5		33	44					
	4			39			47		

[a] $\frac{X}{A}\Big/\frac{C}{A}$, where X = crosslinking, C = cyclization, A = addition. See text.

with acrylmidomethyl groups, found evidence for intramolecular reaction, the extent of which increased as the concentration of polymerizable groups on the cellulose chain increased. Also simulations of gelation by Leung and Eichinger[12] show that a substantial amount of cyclization can occur even in simple model systems involving narrow molecular weight distributions and ideal functionalities of 2.0. A fast reaction in terms of the release of methanol is certain to lead to rapid gelation and to the rapid attainment of a high degree of crosslinking. A slower formation of methanol does not signify slower gelation nor less complete insolubilization.

TABLE VII
% Melamine Extracted as a Function of Acrylic/Melamine Ratio[a]

Acrylic/melamine	Calculated[b]	Found
85/15	0	3
80/20	0	4
75/25	2	7
70/30	4	12
60/40	20	19
50/50	33	27

[a] HEA copolymer/Cymel 303.

[b] Calculated for Kx/Ka = 0.1 and Kc/Ka = 0.5 and for melamine functionality = 5 (see Table VI).

TABLE VIII
Film Properties vs. Bake Time[a]

Bake time (min, 121°C)	4	10	20	30
Tensile strength (kpsi)	1.2 ± 0.2	3.8 ± 0.2	2.7 ± 0.2	3.4 ± 0.6
% Elongation	41.7 ± 3.4	5.3 ± 0.0	3.4 ± 0.3	3.9 ± 0.6
Modulus (kpsi)	10.8 ± 3.7	41.2 ± 9.0	40.7 ± 6.0	41.0 ± 0.9
Swelling in CH_2Cl_2[b]				
Linear	1.265	1.201	1.200	1.192
Volume	2.025	1.732	1.720	1.693

[a] HEA polymer/Cymel 303 70/30; PTSA·DMO 1.05 × 10^{-3} m/g.
[b] See text for procedure.

TABLE IX
Effect of Catalyst Concentration on Coating Properties[a]

% Catalyst PTSA salt	20° Gloss	DOI[b]	Hardness	
			Tukon	Persoz
0.2	91.0 ± 2.0	82.4 ± 1.2	9.3	280
0.1	88.0 ± 2.0	80.1 ± 1.3	7.7	250
0.03	81.6 ± 1.8	56.4 ± 4.3	0.6	51

[a] HEA copolymer/Cymel 303 70/30; 30 min at 121°C.
[b] Definition of image.

FILM PROPERTIES

The effect of baking time on the properties of the films is shown in Table VIII. There are no significant changes in the mechanical properties of free films of the HEA copolymer system catalyzed by 0.2% PTSA salt after a 10-min bake. The swelling data in Table VIII, however, show that the film continues to crosslink throughout the reaction.

The effect of catalyst concentration on hardness, gloss and definition of image (DOI) was measured after a 30-min bake (Table IX). The catalyst concentration affects the appearance. The DOI and hardness drop with decreasing catalyst concentration. Lower hardness would be expected, but the lower DOI was not. This may reflect efficient gel formation at a point at which a considerable quantity of reaction products still has to form and leave the film. The shrinkage this causes could reduce the surface smoothness.

SUMMARY

The crosslinking reaction of acrylic polyols with hexa(methoxymethyl) melamine consists of a complex set of reactions. The release of methanol is first order in both OH and CH_3O— concentrations, and proportional to the hydrogen ion concentration. The release of methanol is not a suitable indicator for gelation. The gelation is a function of the acrylic molecular weight and functionality, distribution of functionality, ratio of reactants, and the efficiency of the crosslinking reaction. The latter refers to the number of chains that are incorporated into the gel network per unit of methanol released. This number seems to be inversely proportional to the rate of which methanol is evolved. While rapid evolution of methanol correlates with rapid gelation, a slower evolution of methanol does not signify slower gelation.

In summary then, the reaction of HMMM with a hydroxyl containing acrylic polymer appears to be second order with respect to the reacting species, first order with respect to alcohol, and first order with respect to methoxymethyl. The reaction is also proportional to the concentration of available hydrogen ions. Thus one can speculate that the rate-controlling state is a complex of the three species involved, or that a sequence of two reactions closely following on top of each other is involved.

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References

1. W. Blank, *J. Coat. Technol.*, **51** (656), 61–70 (1979).
2. W. Blank, *J. Coat. Technol.*, **54** (687), 26–41 (1982).
3. O. J. Santer and G. J. Anderson, *J. Coating Technol.*, **52** (667), 33 (1980).
4. Z. W. Wicks, Jr. and D. Y. Y. Hsin, *J. Coat. Technol.*, **55** (707), 29 (1983).
5. (a) D. R. Bauer and R. A. Dickie, *J. Polym. Sci., Poly. Phys.* Ed., **18**, 1997 (1980); (b) **18**, 2015 (1980); (c) D. R. Bauer and G. F. Budde, *Ind. Eng. Chem, Prod. Res. Dev.*, **20**, 674 (1981); (d) D. R. Bauer, *J. Appl. Polym. Sci.*, **27**, 3651 (1982); (e) D. R. Bauer, and G. F. Budde, *J. Appl. Polym. Sci.*, **28**, 253 (1983); (f) D. R. Bauer, *Prepr., Am. Chem. Soc., Div. Orga. Coatings Appl. Polym. Sci.*, **47**, 737 (1982).
6. M. G. Lazzara, *J. Coat. Technol.*, **56** (710), 19 (1984).
7. (a) P. M. James, et al., *J. Macromol. Sci. Chem.* **A8**, 135 (1974); (b) R. A. Brett, *J. O. C. C. A.*, **47**, 767 (1964).
8. W. Zimmt, M. Lazzara, C. Senkler, and J. Collette, *Organic Coatings Science and Technology,* Dekker, New York, 1984, p. 41.
9. (a) C. W. Macosko and D. R. Miller, *Macromolecules,* **9**, 199 (1976); (b) D. R. Miller and C. W. Macosko, *ibid.*, 206 (1976); (c) D. R. Miller, E. M. Valles, and C. W. Macosko, *Polym. Eng. Sci.*, **19**, 272 (1979).
10. C. K. Ingold, *Structure and Mechanism in Organic Chemistry,* Cornell Univ. Press, Ithaca, NY, 1969.
11. J. Gardon, *J. Polym. Sci., Part A,* **2**, 2657 (1964).
12. (a) Y. K. Leung and B. E. Eichinger, *Prepr., Am. Chem. Soc., Div. Org. Coatings Appl. Polym. Sci.*, **48**, 400 (1983); (b) L. Y. Shy, Y. K. Leung, and B. E. Eichinger, *Prepr., Am. Chem. Soc., Div. Polym. Sci.*, **25**(1) 248 (1984).

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