JOURNAL OF APPLIED POLYMER SCIENCE VOL. 8, PP. 475–488 (1964)

Curing Relations of Hexakis(methoxymethyl)melamine and Its Combinations with Acrylic Polymers*

ROBERT SAXON and FIRMIN C. LESTIENNE, *American Cyanamid Company, Stamford, Connecticut*

Synopsis

The curing of hexakis(methoxymethyl)melamine (HMM) alone and in blends with functionally substituted acrylic polymers was monitored by means of torsional braid analysis, infrared spectroscopy, weight change, and analysis of the volatile by-products. HMM alone, when heated with a strong acid catalyst, forms thermoset condensation polymers which evidently have the same methylene-bridged structure as conventional melamine-formaldehyde resins; the major elimination product is methylal. When HMM is blended with an acrylic polymer containing methacrylic acid units, the acrylic chains are crosslinked by elimination of methanol and formation of methylene ester linkages between the acid groups and the melamine. The crosslinking reaction proceeds with or without strong acid catalysis and is many times faster than the self-condensation of HMM. Acrylic polymers containing primary hydroxyl groups (derived from 2-hydroxyethyl methacrylate) also undergo acid-catalyzed reaction with HMM, and at a rate so much faster than analogous carboxylated polymers, that storage stability of the catalyzed resin becomes a serious problem. If a weaker catalyst, such as phthalic anhydride, is used, the curing reaction is very much slower. In order to develop the maximum number of new linkages, according to any of the experimental criteria, all of these systems must be heated for longer times, or at higher temperatures, than are customarily used in thermosetting resin technology. Thus the known utility and durability of such acrylic/melamine resins are achieved with only a fraction of the total number of crosslinks which are potentially capable of formation.

Introduction

Hexakis(methoxymethyl)melamine[1] (HMM) is a versatile resin-forming material. Although the compound alone is thermally very stable, it is capable of reacting with a variety of functional groups, including carboxyl, hydroxyl, epoxide, acetal, and others. Where such groups are present on preformed linear polymers, HMM serves as a useful crosslinking agent. Technological applications of HMM have been referred to elsewhere,[2–4] but the chemical reactions involved have not been described in any detail. It is the purpose of the present paper to discuss some of the curing reactions of HMM with particular regard to rates and mechanisms.

Conventional procedures for assessing cure in resins are usually of an empirical nature. In surface coatings,[5,6] typical methods include solvent

---

* Paper presented before the Division of Organic Coatings and Plastics, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September 1962.

resistance, Sward hardness, and mandrel flexibility. In molding technology, freedom from blisters and water boil tests are commonly used criteria of acceptability. Such tests obviously do not define cure in chemical terms. In recent years, sensitive methods have been introduced for a more fundamental approach to this question. Among these are the attenuation and velocity of ultrasonic waves,[7] electrical resistivity changes,[8] dynamic mechanical measurements,[9,10] and infrared spectroscopy.[11] They have the advantage of providing more or less continuous monitoring of property change during a large part of the curing process, and in addition they may furnish information on specific chemical transformations which occur.

In the present study, a combination of techniques has been employed. These methods are (*a*) mechanical (a dynamic torsional measurement on the supported polymer[10,12]); (*b*) chemical (infrared spectroscopy); and (*c*) physical (weight loss due to evolution of volatiles during the condensation reaction in which crosslinks are formed). Where appropriate, the volatile products themselves were separated by vapor-phase chromatography and identified by mass spectroscopy.

EXPERIMENTAL

Materials

Two acrylic resins with pendant functional groups were prepared: a methyl methacrylate/methacrylic acid copolymer and a methyl methacrylate/2-hydroxyethyl methacrylate copolymer, each at 4/1 mole ratio. Poly(methyl methacrylate) was also prepared as a control. The polymers were made in methyl ketone by a semicontinuous method with the use of conventional benzoyl peroxide catalysis. To obtain the hexakis(methoxymethyl)melamine (HMM) for these studies, the commercial product (American Cyanamid Co.) was vacuum-distilled at 180°C./<0.1 mm. Hg. The distilled compound melted at 49.5–50°C. and was found by analysis to have a melamine/formaldehyde/methoxyl ratio of 1:6.0:5.8. Acid catalysts used in certain of the experiments were *p*-toluenesulfonic acid monohydrate (PTSA) (Eastman white label) and phthalic anhydride (American Cyanamid Co.). The latter was resublimed before use.

Methods

Dynamic mechanical measurements were carried out with a torsional braid apparatus.[10,12] The resin mixture, in methyl ethyl ketone, was brushed onto a glass yarn, which was suspended vertically from a pin vise, and fitted at the bottom with an inertial bar. The solution was allowed to air-dry overnight, then the dry yarn was fitted into a thermostatted apparatus as previously described, at either 100 or 150°C. in air. Measurements of torsional period *p* were taken on the yarn at frequent intervals, the experiment continuing as long as 72 hr. if necessary. Results were plotted in terms of apparent relative rigidity G', the relationship $G' = p_f^2/p^2$ being used, where p_f is the period measured at the end of the reaction. (This was done even in those few cases where equilibrium had not been attained in 72 hr.) The purpose of this transformation is to provide a function which is more nearly proportional (at least in the ideal case) to the number of crosslinks formed during curing.[13]

Infrared measurements were made by first applying a thin film of resin solution to a rock salt plate, air drying, and heating the plate in the torsional braid chamber (which served conveniently as an oven). The plate was removed at intervals and the absorption measured at 815 and 915 cm.$^{-1}$ for triazine and methoxyl groups, respectively. For each run duplicate plates were used, and the absorptions measured at two different spots on each plate; the four readings so obtained were then averaged.

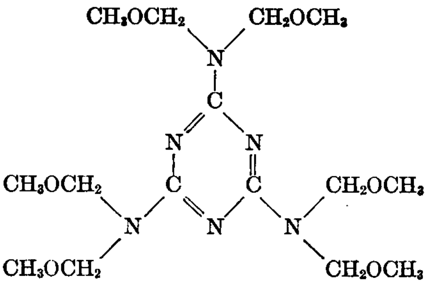
Weight loss experiments were carried out with small lengths of the glass yarn to which known weights of resin had been applied. As in the torsional runs, the glass/resin ratio was about 1:1 by weight. The weight loss yarns were likewise heated in the thermostatted torsional braid chamber. In the case of control experiments on HMM alone, when curing was sometimes slow or nonexistent, the resin was too fluid to remain on the heated braid; so weight loss trials were run in a small tared aluminum cup.

RESULTS AND DISCUSSION

Runs were carried out on HMM alone and on HMM blended with each of the reactive copolymers, using a mole ratio of 1 HMM for each 1.5 moles of methacrylic acid or 2-hydroxyethyl methacrylate in the copolymer. This ratio was shown earlier[14] to be a desirable value in carboxyl/HMM reactions, for esterifying all of the carboxyl groups under conditions typically used in the baking of thermosetting enamels. Various levels of catalyst based on HMM were used, and all runs were isothermal at either 100 or 150°C.

A. Hexakis(methoxymethyl)melamine Alone

Results of a typical experiment for all three methods are shown in Figure 1. This depicts the cure of HMM at 150°C. when catalyzed with 1% PTSA. There are several striking observations in this experiment. First, marked changes occur in all three parameters, so that crosslinks are undoubtedly being formed. Yet it is surprising, on organic chemical grounds, that this completely substituted melamine derivative can react at all, without some other compound being present in stoichiometric amount. Consideration of the structure (I) indicates that self-condensation cannot occur simply by loss of methanol. In weight loss experiments, exactly one-half of the original resin weight has disappeared at equilibrium, which corresponds to loss of the entire methoxyl content of the HMM. This is fortuitous, however, since infrared data indicate that



I

approximately 20–25% of the original methoxyl still remains. The actual course of the self-condensation reaction will be more fully discussed below.

Comparison of the rigidity studies on the one hand with the weight loss and infrared data on the other, indicates that attainment of mechanical equilibrium in this system is much more rapid than chemical equilibrium. The rigidity becomes constant in 2 hr. at 150°C., while methoxyls continue

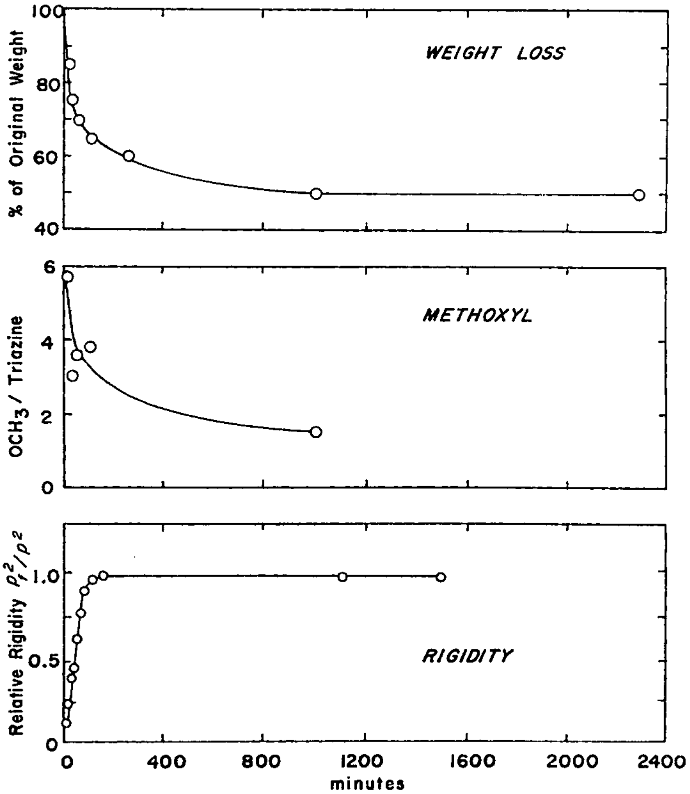


Fig. 1. Curing of HMM at 150°C. with 1% p-toluenesulfonic acid.

to disappear and volatiles continue to develop for some 18 hr. The theoretical analysis by Flory[13] indicates that for very long chains which undergo crosslinking the modulus should increase proportionately to the abundance of crosslinks. In his experiments with rubber vulcanization, the modulus actually increased more slowly than the theory predicted. Flory attributed this discrepancy to the fact that long chains are already entangled, and hence restrict molecular motion almost as much as true covalent crosslinks which might subsequently form between them. It would thus be possible to have chemical reaction continue with little change in rigidity. This is exactly the observation in the melamine curing reaction. To be sure, we are not dealing here with the crosslinking of

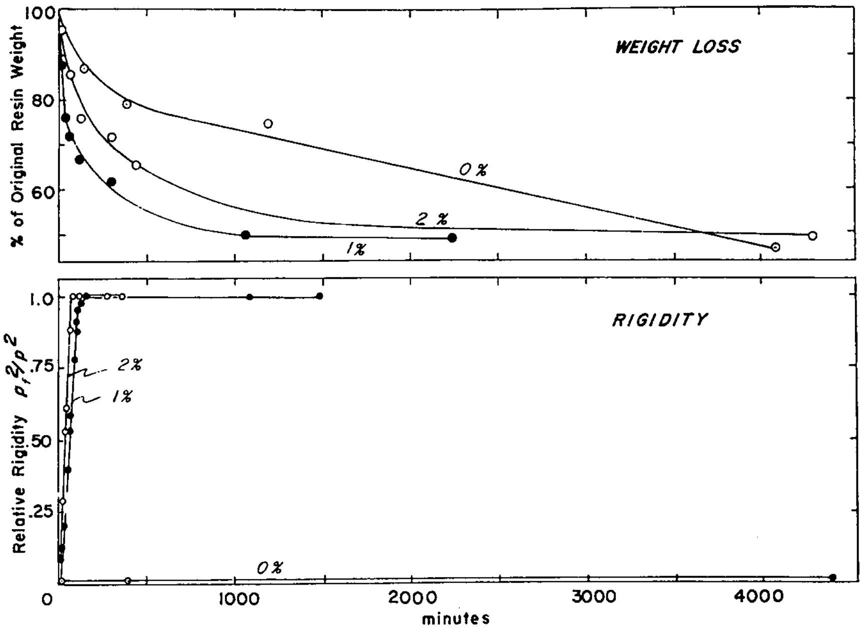


Fig. 2. Curing of HMM at 150°C. with various levels of *p*-toluenesulfonic acid.

linear chains, but rather with a ramification proceeding from individual monomeric units to an essentially random, three-dimensional network. Nevertheless, there must be a considerable amount of entanglement in a partially crosslinked melamine resin. It is therefore not surprising that any crosslinking which occurs in the later stages of the reaction makes very little contribution to the rigidity of the system. An alternate possibility can be envisioned, namely, that the chemical changes which occur after the resin reaches constant rigidity are not crosslinks at all, but instead represent some type of intramonomer reaction. However, the infrared spectrum of the cured resin gives no indication that any unusual structures of this type exist.

Figure 2 compares rigidity changes and weight loss values on curing the HMM resin alone at 150°C. with various levels of PTSA. (Infrared curves very closely parallel the weight loss in the catalyzed runs.) It is obvious that acid catalysis is required for the curing of the melamine as measured in terms of rigidity change. As for weight loss, even the uncatalyzed resin is affected appreciably on long heating, even though it is plainly not being cured. (Infrared spectra show no change in the methoxyl/triazine ratio in the absence of catalyst.) The weight loss in this case is attributed to the evaporation of the melamine ether. Loss due to evaporation is believed significant only where the curing reaction is extremely slow, since, if a major fraction of the HMM resinifies during the early stages of heating, it will obviously be bound in a nonvolatile form. In addition, the volume fraction of HMM in the acrylic blends is only about 0.3, which further reduces its tendency to volatilize. Nevertheless, the possibility of evaporation loss impairs, to some extent, the usefulness of the weight change data.

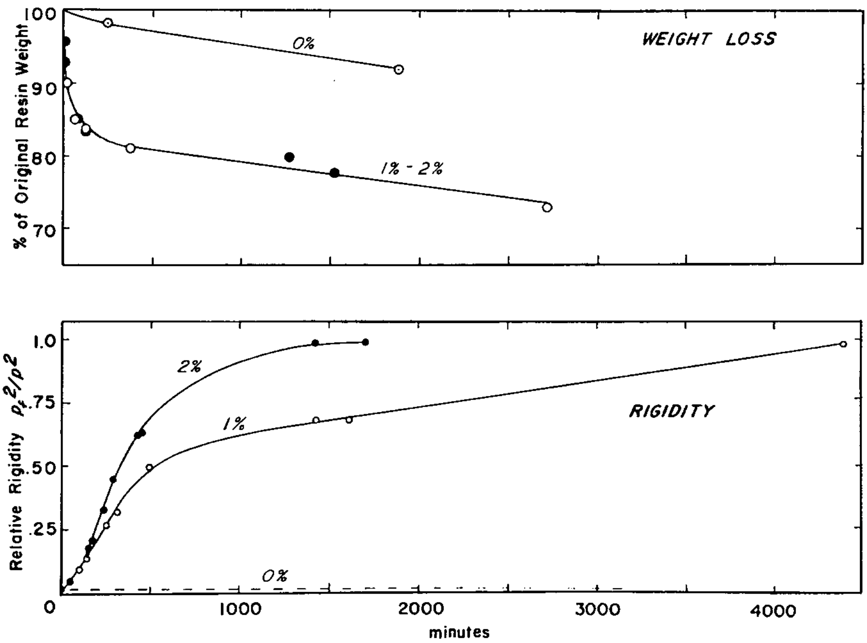


Fig. 3. Curing of HMM at 100°C. with various levels of *p*-toluenesulfonic acid.

Figure 3 compares weight loss and rigidity changes in the same system at 100°. At this temperature the reaction is, of course, very much slower. Constant rigidity with 1% PTSA is not attained even after 4400 min. (73 hr.). The macromolecular reaction is of too complex an order for rigorous kinetic analysis using the data thus far obtained, but a convenient means of comparing the various experiments is to consider the time re-

TABLE I
Time to Reach One-Half Final Rigidity in HMM Curing

	Time to reach one-half final rigidity, min.		
T, °C.	No PTSA	1% PTSA	2% PTSA
100	(∞)	>500	320
150	∞	65	35

quired to reach one-half of the final rigidity. A slight extrapolation is sometimes necessary. The values are shown in Table I.

Approximately a tenfold increase in reaction rate is observed for the 50°C. rise in temperature. By simple application of the Arrhenius equation, an activation energy of 14.5 kcal./mole is obtained. No data on activation energies in the formation of conventional amino resins appear to have been published, but the value may be compared with those for simple polycondensations (11.5–13 kcal./mole) determined by Flory[15] using acid–base titration.

In order to determine the chemical nature of the self-condensation of HMM, the pure compound plus 1% PTSA was dissolved in benzene and the dilute solution added to a flask filled with glass helices. On vacuum evaporation of the benzene at 25°C., the catalyzed HMM was deposited on the helices and the walls of the flask. The presence of the helices afforded a greatly increased surface area and hence facilitated evolution of volatiles on subsequent heating. The flask was held at 150°C. for 4 hrs., and the liberated gases were collected in a Dry Ice trap. The weight loss was 29% (cf. 37% on the torsional braid under similar conditions), prac-

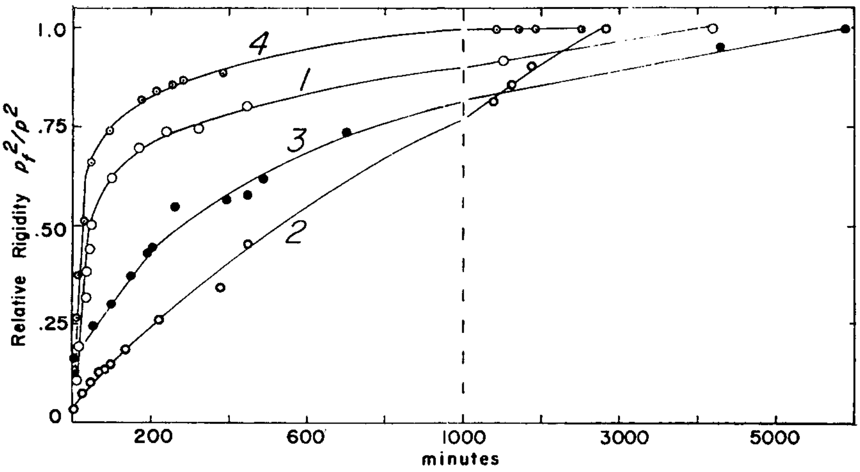
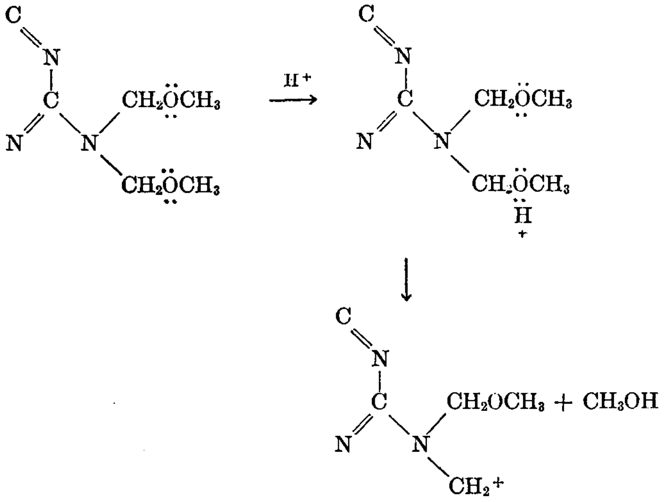


Fig. 4. Rigidity changes during cure at 150°C. in blends of HMM with (*1*) methyl methacrylate/methacrylic acid $^{4}/_{1}$ copolymer and 1% PTSA; (*2*) same copolymer with no catalyst; (*3*) methyl methacrylate homopolymer and 1% PTSA; (*4*) methyl methacrylate/2-hydroxyethyl methacrylate $^{4}/_{1}$ copolymer and 1% PTSA.

tically all of which was recovered in the trap. Analysis of the trap contents showed 83% methylal and 17% methanol.

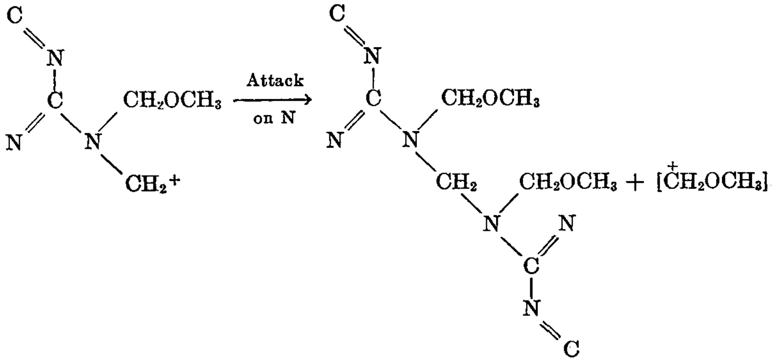
Evolution of methylal in a condensation reaction has not been reported in any previous work of which the present authors are aware. Only one mechanism for the HMM condensation process could be devised to account for this observation, the need for acid catalysis, and the fact that the resinous product has essentially the same linkages as a conventional melamine–formaldehyde polymer. The proposed mechanism is set forth in eqs. (1)–(3):

(*1*) *Initiation:*

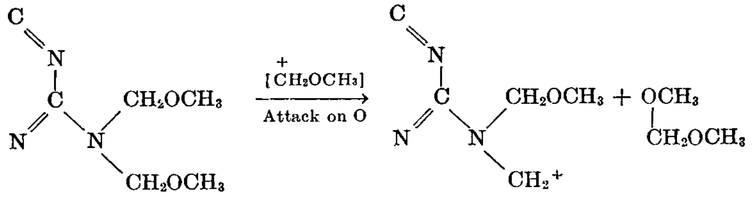


(1)

(*2*) *Propagation:*



(2)



(3)

According to this scheme, the reaction is initiated by protonation of the ether oxygen of one methoxymethyl group, evolution of methanol, and formation of a carbonium ion. Propagation involves alternate attack on nitrogen and on oxygen. The initial carbonium ion displaces a methoxymethyl group from the nitrogen of a second HMM molecule (to form the methylene crosslink characteristic for melamine resins); and the displaced methoxymethyl, by reaction with a third HMM, liberates methylal and regenerates a triazine carbonium ion to continue the reaction.

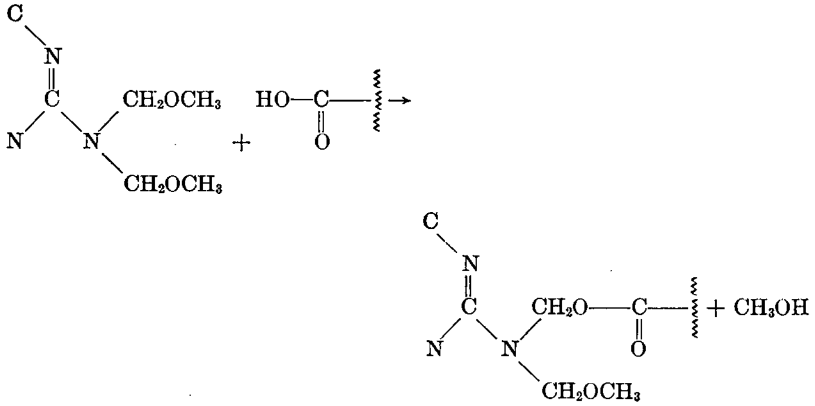
The methanol which was collected as a minor product of the reaction, is not adequately accounted for by the above mechanism. It is evidently a hydrolysis product, since along with its formation the cured resin develops a small new infrared absorption at 3300 cm.$^{-1}$ and a somewhat increased absorption at 1010 cm.$^{-1}$, both characteristic of OH groups. This suggests that the reaction

$$-\underset{|}{N}-CH_2OCH_3 + H_2O \rightarrow -\underset{|}{N}-CH_2OH + CH_3OH \qquad (4)$$

is occurring to some extent. The source of this water in a sufficient amount, however, remains unexplained.

B. Blends with Acrylic Polymers

1. Methacrylic Acid Copolymers. It was shown in an earlier paper[14] that HMM reacts with carboxyl-substituted acrylic polymers through displacement of the methoxyl with carboxyl according to (5):



(5)

The reaction is facilitated by the addition of strong acid, but even the acidity of the carboxyl group is sufficient for a practical degree of crosslinking.

Curves *1* and *2* of Figure 4 indicate the rigidity changes during this reaction with 0 and 1% PTSA at 150°C. Comparison with the curve for HMM alone (see Fig. 1) suggests that the HMM self-condensation is much faster than the crosslinking of the copolymer, and that the crosslinked system should contain a large proportion of melamine-to-melamine

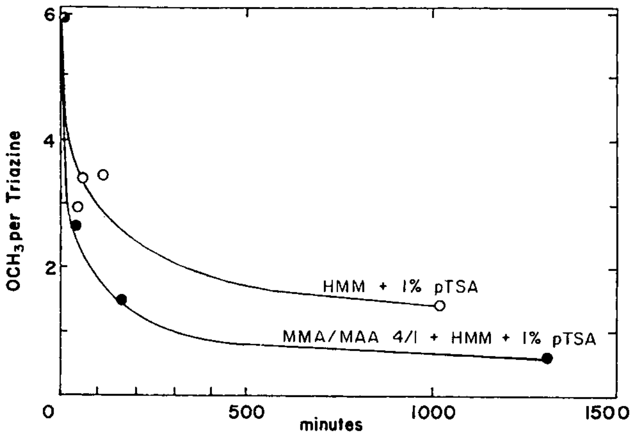


Fig. 5. Infrared changes during cure at 150°C.

linkages. That this is not in fact the case and that crosslinking dominates self-condensation of HMM, is demonstrated by two types of evidence.

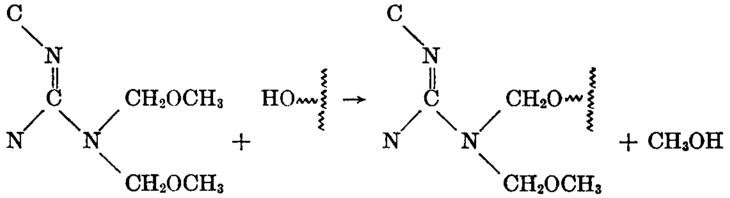
(*1*) When acid-catalyzed HMM is diluted with the homopolymer of methyl methacrylate, in the same weight ratio as used with the MMA/MAA copolymer, the self-condensation is slowed to a great degree. This reaction is shown as curve *3* of Figure 4. In this blend the HMM comprises 35% of the total weight, and the time to reach half of the final rigidity is 280 min.; while in the undiluted reaction, the half-time was 60 min. For the crosslinking system, represented by curve *1* of Figure 4, HMM again is 35% of the overall composition, but the half-time is only 45 min.

(*2*) Since the volatile product of the self-condensation contains 83% methylal, and the crosslinking reaction gives rise only to methanol, the relative rates can be estimated by analysis of the actual mixture obtained. Using the same general procedure as described above, the crosslinking acrylic/HMM blend underwent a 16% weight loss in 205 min. at 150°C. (cf. 19% on the torsional braid); the volatile products collected were methanol 88, methylal 4, and methyl methacrylate 8%. The formation of monomer by thermal "unzipping" of the methacrylate chains proceeds in this system to almost the same extent as observed with MMA homopolymer.[16] From the ratio of the other products, it may be concluded that crosslinking of the acrylic polymer is about 20 times as rapid as HMM self-condensation under the selected experimental conditions.

Figure 5 compares the infrared changes observed during the course of the bulk self-condensation and the crosslinking reactions. These data contain a curious anomaly. From the weight and analysis of the volatiles lost from the catalyzed HMM, the methoxyl/triazine ratio remaining after 240 min. should be about 2.0, in good agreement with the value found by infrared. In the case of the acrylic/melamine blend, however, a similar calculation indicates an expected residual methoxyl (after 205 min.) of 1.9 per triazine, which is significantly more than the 1.2 groups found by infrared spectroscopy. From the stoichiometry of this blend, furthermore, only enough carboxyls are present (1.5 mole/mole of HMM) to displace 25% of the available methoxyls, and to cause a weight loss of 6–7%. No explanation can be advanced for the additional methoxyl groups which are evidently being lost in the acrylic/melamine blend. There is no straightforward reaction scheme by which methanol could be generated from the MMA units in the acrylic polymer.

One final point deserves mention. In practical acrylic/melamine formulations, a typical cure calls for 30 min. heating at 150°C. with 1% of a strong acid catalyst. It is now seen that changes—mechanical, chemical, and physical—continue to occur for much longer periods of time with the same temperature and catalyst. Nevertheless, exceedingly useful resins for coatings and other applications have been devised, largely on an empirical basis, using the mild conditions of cure.[2] It is apparent that more effective curing conditions could be utilized, which would presumably lead to still more serviceable resinous products.

2. Hydroxylated Acrylic Polymers. The reaction between polymers containing pendant hydroxyl groups, as in 2-hydroxyethyl methacrylate (HEMA), and HMM is a transesterification. This reaction proceeds readily when any higher alcohol, particularly a primary alcohol, is heated with HMM and an acidic catalyst.[17] Methanol is liberated:


(6)

The rate of this reaction was shown by qualitative experiment to be much faster than that of carboxylated polymers with HMM. When a copolymer of HEMA and methyl methacrylate in methyl ethyl ketone was blended with HMM in the same proportions as described above for the methacrylic acid copolymer, the blend was stable indefinitely at room temperature; but on addition of 1% PTSA, it gelled in about 10 min. The carboxyl formulation, similarly catalyzed, did not gel in several months. The gelation of the hydroxyl system made it difficult to carry out experiments comparable to those performed with the methacrylic acid copolymer. By working rapidly, it was possible to apply the catalyzed resin blend to the torsional braid before gelation occurred, and thus to obtain the rigidity plot shown as curve *4* in Figure 4. As would be expected from the behavior of the blend at room temperature, the curing at 150°C. is very rapid, with a rigidity half-time of 30 min.; this is less than for either the carboxylated system (45 min.) or HMM alone (280 min.).

Gelation in the blend of HEMA and HMM can be delayed, although not prevented, by decreasing the amount of strong acid catalyst. For reasonable solution stability, however, a weaker acid must be employed. Phthalic anhydride is a convenient source of acidity; it reacts with a few of the hydroxyl groups to form polymeric half-esterified phthalates:

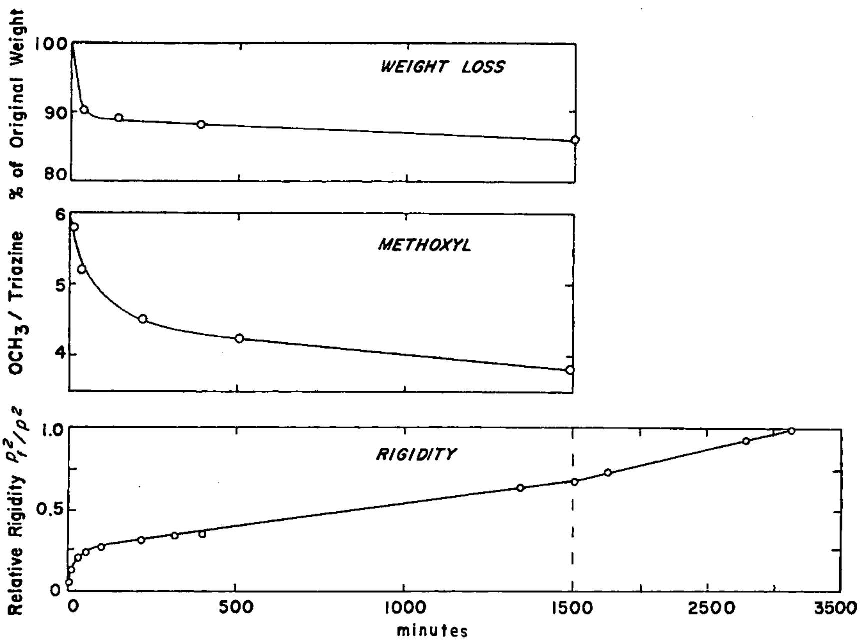
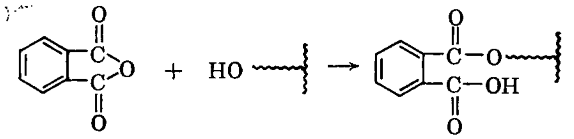


Fig. 6. Curing of MMA/HEMA 4/1 copolymer and HMM at 150°C. with 1.5% phthalic anhydride.



(7)

Figure 6 gives plots of curing for a methyl methacrylate/HEMA copolymer blended with HMM and 1.5% phthalic anhydride (based on HMM content) at 150°C. In comparison, HMM and 1.5% phthalic anhydride alone gave *no* evidence of curing. Test films cast from these combinations and baked for 30 min. at 150°C. were, in the case of the blend, hard, clear, and solvent-resistant, while in the case of phthalic-catalyzed HMM alone, the film was as soft and waxy after heating as before. Furthermore, an uncatalyzed copolymer/HMM blend remains soluble after heating, so that acidic catalysis of some type is essential.

The HEMA system shown in Figure 6, like the methacrylic acid system described earlier, continues to develop crosslinks on very prolonged heating —for several hundred minutes at least—although from a practical point of view about 30 min. is adequate to give films from such resins which exhibit good durability.[18] Thus, once more the coatings technologist is dealing with only partially crosslinked polymers. What the ultimate level of crosslinking might be is difficult to estimate. The same problem in the interpretation of the infrared results as was encountered in the MAA-containing system is found here as well. From the quantities of the respective components present, loss of only 1.5 methoxyls per triazine should result when all of the available pendant hydroxyl groups have been etherified. Yet, from the infrared data, approximately 35% of the initial methoxyls, or 1.9 per triazine, are consumed after 1500 min. and the reaction is slowly continuing. It is possible that a very small amount of melamine self-condensation accompanies the true crosslinking. However, this can be no more important, under the conditions studied, than during the reaction of carboxylated polymers with HMM.

Microanalyses were carried out by the Research Service Dept. of these laboratories. Mr. J. P. Falzone and Dr. R. B. Hannan performed the infrared determinations and the separation and identification of the volatile reaction products. Valuable assistance in the design and interpretation of the torsional braid experiments was given by Drs. J. K. Gillham and A. F. Lewis.

References

1. Gams, A., G. Widmer, and W. Fisch, *Helv. Chim. Acta*, **24E**, 302 (1941).
2. *CYMEL 300 Hexamethoxymethylmelamine*, American Cyanamid Co., Wallingford, Conn., 1962.
3. Daniel, J. H., U. S. Pat. 2,906,724 (to American Cyanamid Co.), Sept. 29, 1959.
4. Frazier, C., and L. E. Cadwell, U. S. Pat. 2,681,897 (to American Cyanamid Co.), June 22, 1954.
5. Werner, H. M., *Offic. Dig. Federation Soc. Paint Technol.*, **33**, 948 (1961).
6. Robinson, A. K., *Brit. Plastics*, **35**, No. 2, 80 (1962).
7. Dietz, A. G. H., et al., *Ind. Eng. Chem.*, **48**, 75 (1956).
8. Warfield, R. W., and M. C. Petree, *SPE Trans.*, **1**, 1 (1961).
9. Drumm, M. F., C. W. H. Dodge, and L. E. Nielsen, *Ind. Eng. Chem.*, **48**, 76 (1956).
10. Lewis, A. F., and J. K. Gillham, *J. Appl. Polymer Sci.*, **6**, 422 (1962).
11. Dannenberg, H., J. W. Forbes, and A. C. Jones, *Anal. Chem.*, **32**, 365 (1960).
12. Gillham, J. K., and A. F. Lewis, paper presented to Division of Organic Coatings and Plastics, 142nd National Meeting, American Chemical Society, Atlantic City, September 1962; *J. Appl. Polymer Sci.*, **7**, 685 (1963).
13. Flory, P. J., *Ind. Eng. Chem.*, **38**, 417 (1946); *Chem. Revs.*, **35**, 51 (1944).
14. Saxon, R., and J. H. Daniel, Jr., *J. Appl. Polymer Sci.*, to be published.
15. Flory, P. J., *J. Am. Chem. Soc.*, **61**, 3337 (1939); *ibid.*, **62**, 2259 (1940).
16. Jones, C. E. R., A. F. Moyles, and G. E. J. Reynolds, in *High Temperature Resistance and Thermal Degradation of Polymers*, Society of Chemical Industry, London, 1961, p. 132.
17. Magrane, J. K., and R. E. Layman, U. S. Pat. 3,020,255 (to American Cyanamid Co.), Feb. 6, 1962.
18. Petropoulos, J. C., C. Frazier, and L. E. Cadwell, *Ind. Eng. Chem.*, **53**, 466 (1961).

Résumé

La vulcanisation de l'hexakis(méthoxyméthyl)mélamine (HMM) seul et en mélange avec des polymères acryliques avec des fonctions substituéees se fait au moyen de l'analyse par la tresse tordue, la spectroscopie infra-rouge, le changement de poids et au moyen de l'analyse des produits volatils secondaires. HMM seul, lorsqu'il est chauffé avec un acide fort comme catalyseur, forme des polymères de condensation thermodurcissables lesquels sont évidemment de même structure à pont-méthylénique que les résines mélamine-formaldéhyde conventionnelles; le produit majeur d'élimination est le formaldéhyde. Lorsque HMM est mélangé avec un polymère acrylique contenant des unités d'acide méthacrylique, les chaînes acryliques sont pontées par élimination de méthanol et par formation de liaisons ester-méthylène entre les groupes acides et le mélamine. La réaction de pontage a lieu avec ou sans acide fort comme catalyseur et est beaucoup plus rapide que l'auto-condensation de HMM. Les polymères acryliques contenant des groupes hydroxyles primaires (dérivés du méthacrylate de 2-hydroxyéthyle) subissent aussi la réaction de catalyse acide avec HMM à une vitesse plus rapide que celle des polymères carboxylés analogues, de sorte que leur stabilité au cours de leur conservation devient un sérieux problème. Si un catalyseur plus faible, tel que l'anhydride phtalique est employé, la réaction de vulcanisation est beaucoup plus lente. Afin de développer au maximum le nombre de nouvelles liaisons, en accord avec plusieurs critères expérimentaux, tous ces systèmes doivent être chauffés plus longtemps, ou à plus hautes températures qu'il n'est habituellement d'usage dans la technologie des résines thermodurcissables. L'utilité et la durabilité connues de telles résines acrylique/mélamine sont acquises avec seulement une fraction du nombre total de ramifications qui sont potentiellement capables d'être formées.

Zusammenfassung

Die Härtung von Hexakis(methoxymethyl)melamin (HMM) allein und in Mischung mit funktionnell substituierten Acrylpolymeren wurde durch Torsionsgeflechtanalyse, Infrarotspektroskopie, Gewichtsänderung und Analyse der flüchtigen Nebenprodukte verfolgt. HMM allein bildet beim Erhitzen mit einer starken Säure als Katalysator wärmehärtende Kondensationspolymere, welche offenbar die gleiche Methylenbrückenstruktur wie konventionelle Melamin-Formaldehydharze besitzen; das Haupteliminierungsprodukt ist Methylal. In Gemischen von HMM mit einem Acrylpolymeren mit Methacrylsäurebausteinen, werden die Acrylketten durch Eliminierung von Methanol und Bildung von Methylenesterbrücken zwischen Säuregruppen und Melamin vernetzt. Die Vernetzungsreaktion verläuft mit und ohne Katalyse durch starke Säuren und ist vielmals rascher als die Selbstkondensation von HMM. Acrylpolymere mit primären Hydroxylgruppen (abgeleitet von 2-Hydroxyäthylmethacrylat) gehen ebenfalls eine säure-katalysierte Reaktion mit HMM ein, deren Geschwindigkeit um so viel grösser als die der analogen karboxylgruppen-hältigen Polymeren ist, dass die Lagerfähigkeit des katalysierten Harzes ein ernstes Problem wird. Bei Verwendung eines schwächeren Katalysators, wie Phthalsäureanhydrid, verläuft die Härtungsreaktion sehr viel langsamer. Zur Ausbildung der maximalen Zahl neuer Bindungen müssen, nach Aussage aller experimentellen Kriterien, alle diese Systeme durch längere Zeit oder auf höhere Temperaturen erhitzt werden, als es sonst in der Technologie wärmehärtender Harze üblich ist. Es wird daher die bekannte Verwendbarkeit und Beständigkeit solcher Acryl-Melaminharze mit nur einem Bruchteil der gesamt-möglichen Vernetzungsbildung erreicht.

Received October 26, 1962