Studies on the Initiation of a Free-Radical Condensation Hybrid Polymerization System

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ABSTRACT: Compositions of hexamethoxymethyl melamine (HMMM)–ether polyol and acrylate can be cured by a hybrid polymerization comprising condensation polymerization and free-radical polymerization, in the presence of a latent acid catalyst at high temperature. It was found that the initiating free radical was derived from the decomposition of hydroperoxides, which was formed by the oxidation of active methylene groups catalyzed by HMMM. It was also found that strong acid could accelerate the free-radical polymerization in the hybrid system. To make the formulations more flexible, the activities of different types of methylene groups were investigated and two compounds with more active methylene groups and hydroxyl were synthesized, characterized, and used as crosslinker–initiators in the hybrid polymerization system. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 1195–1200, 2001

Key words: hybrid polymerization; condensation polymerization; free-radical polymerization; crosslinker–initiators

INTRODUCTION

Hexamethoxymethyl melamine (HMMM) is a very important crosslinking agent widely used in coating formulations. Catalyzed by acid, HMMM can be reacted with polyol at high temperature by a transetherification mechanism. It was found that the cure rate of HMMM–ether polyol could be enhanced by acrylated resins, such as tetraethylene glycol diacrylate (T_4EGDA), in the presence of a latent acid catalyst. However, if hydroquinone as an inhibitor was added into the compositions, little or no enhancement was observed. Consequently, it was believed that besides the condensation polymerization of HMMM with polyol a free-radical polymerization of acrylated resins was involved.[1–4] Such a process containing two or more different mechanisms of polymerization or crosslinking, which occur at the same time, is referred to as a hybrid polymerization.[5]

It was also found that acrylated resins could improve the solvent resistance of cured films of HMMM–ether polyol. The property improvement probably results from the formation of an IPN structure. DSC investigation showed that the endothermic peak of condensation polymerization disappeared and the hybrid polymerization took place at a lower temperature, indicating there is an obvious synergetic effect in the hybrid polymerization system.[6]

Generally, a large amount of volatile organic solvent is needed to adjust the viscosity of HMMM–polyol, which is unfavorable to the environment. But in HMMM–polyol–acrylate hybrid compositions, the viscosity can be adjusted by acrylated resins. Therefore, the volatile organic solvent can be reduced. Because of these advantages, hybrid polymerization is a promising method for formulating a high cure rate, high solid content, and high-quality coating.[4,6] Further

Table I   Gel Times of HMMM–T$_3$EG–T$_4$EGDMA and Related Compositions

Composition (Weight Ratio)	Gel Times		
	80°C	90°C	100°C
HMMM (1.0)–T$_3$EG (0.6)[a]	319 min	143 min	49 min
HMMM (1.0)–T$_3$EG (0.6)–T$_4$EGDMA (1.6)[a]	33 min	16 min	9 min
T$_4$EGDMA[b]			8 h
HMMM (1.0)–T$_4$EGDMA (1.0)[b]			5 h
HMMM (1.0)–BD (0.6)[c]			108 min
HMMM (1.0)–BD (0.6)–BUDA (1.6)[c]			106 min

Latent acid catalyst: *trans*-2-hydroxycyclohexyl-*p*-toluenesulfonate (THCTS).
[a–c] Concentration of THCTS: [a]0.04 mol/L; [b]0 mol/L; [c]0.008 mol/L.

research into this hybrid polymerization system would be worthwhile.

In this article, the initiation was further investigated, including the effect of acid on the decomposition of hydroperoxides. To make the formulation more flexible, some compounds with more active methylene groups and hydroxyl were synthesized, characterized, and used as crosslinker–initiators in the hybrid polymerization system.

EXPERIMENTAL

Materials

Diethyl glycol, benzyl chloride, allyl chloride, and sodium were used as received. All solvents were purified before use by distillation. Triethylene glycol diacrylate (T$_3$EGDA), butanediol diacrylate (BUDA), trimethylolpropane triacrylate (TMPTA), tetraethylene glycol diacrylate (T$_4$EGDA), and tetraethylene glycol dimethacrylate (T$_4$EGDMA) were supplied by the agent of Sartomer Co. in Beijing. HMMM (Cy303, product of CYTEC Co.) was obtained from the Red Lion Coatings Co., Beijing, China.

Spectra

^{1}H-NMR spectra were recorded on a Bruker 250 MHz with CDCl$_3$ as a solvent and the chemical shifts were reported in ppm downfield relative to internal TMS. IR spectra were measured on a SHINADZU IR-408 infrared spectrometer.

Oxygen-absorption Experiments

The oxygen-absorption experiments were carried out in sealed containers with HMMM and T$_3$EG. The containers were immersed in a constant-temperature oil bath. The air samples were taken

with a syringe and the content of oxygen was determined by an oxygen assessor.

Synthesis

Diethylene Glycol Dibenzyl Ether[7]

A NaOH aqueous solution, 40 wt % (200 g), diethylene glycol (0.2 mol, 20 mL), and benzyl triethyl ammonium chloride were added to a three-necked flask equipped with mechanical stirrer. After intense stirring for 30 min, benzyl chloride (0.6 mol, 69.75 mL) was dropped in—this took 30 min. The mixture was heated at 50°C for 12 h. The organic portion was dried with anhydrous MgSO$_4$, and 38.5 g of a yellow liquid was obtained by distillation:

bp 214–215°C/11 mmHg. ^{1}H-NMR δ 3.60–3.69 (m, 8H), δ 4.55 (s, 4H), δ 7.26–7.33 (m, 10H); IR 3050, 1495, 1450, 1350, 1245, 1200, 1100, 1025, 735, 700 cm^{-1}.

Diethylene Glycol Diallyl Ether

A colorless liquid, 18.0 g, was prepared according to the method of synthesizing diethylene glycol dibenzyl ether:

bp 96–97°C/11 mmHg; ^{1}H–NMR δ 3.58–3.70 (m, 8H), δ 4.25 (d, 4H), δ 5.15–5.32 (m, 4H), δ 5.85–5.94 (m, 2H); IR 3075, 2750, 1645, 1420, 1345, 1100, 990, 920 cm^{-1}.

Diethylene Glycol Benzyl Ether[8]

1,4-Dioxane (50 mL) and diethyl glycol (0.3 mol, 28 mL) were added to a three-necked flask equipped with a mechanical stirrer and reacted with sodium (0.2 mol, 4.6 g) for 3 h. Then, benzyl chloride (0.2 mol, 23.2 mL) was added slowly. The temperature was increased slowly to about 110°C and the mixture was reacted for 8 h. After filtra-

tion, the residual solution was distilled and 21.8 g of a colorless liquid was obtained:

bp 158–159°C/11 mmHg; ^{1}H-NMR δ 3.52–3.69 (m, 8H), δ 4.53 (s, 2H), δ 3.45 (s, 1H), δ 7.24–7.33 (m, 5H); IR 3400, 3050, 2750, 1495, 1450, 1350, 1100, 885, 735, 700 cm^{-1}.

Diethylene Glycol Allyl Ether

A colorless liquid, 15.0 g, was prepared according to the method of synthesizing diethylene glycol benzyl ether:
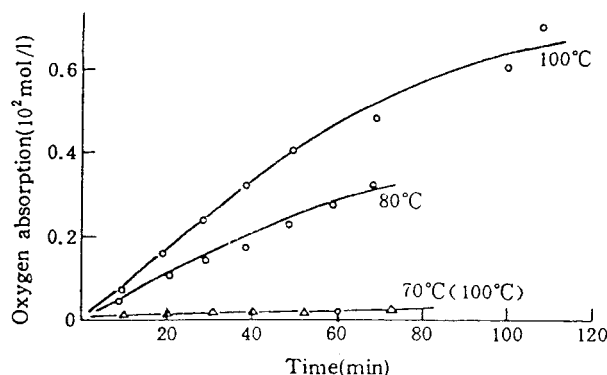
bp 106–108°C/11 mmHg; ^{1}H-NMR δ 3.59–3.75 (m, 8H), δ 4.02 (d, 2H), δ 3.17 (s, 1H), δ 5.16–5.33 (m, 2H), δ 5.85–5.94 (m, 1H); IR 3400, 3075, 2750, 1645, 1345, 1100, 990, 920, 885 cm^{-1}.
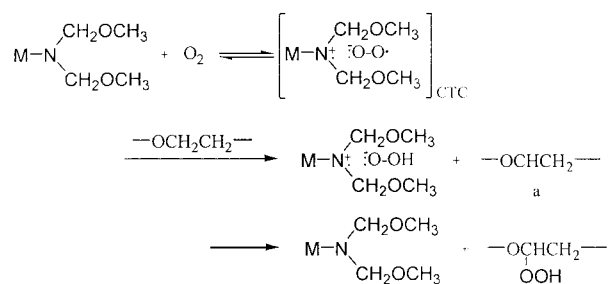
RESULTS AND DISCUSSION

Initiation of Free-radical Polymerization[9,10]

As shown in Table I, in the presence of a latent acid catalyst, acrylated resins, such as T_4EGDMA, could enhance the cure rate of HMMM–T_3EG. However, if T_3EG and T_4EGDMA were replaced by butanediol (BD) and butanediol diacrylate (BUDA), respectively, no enhancement was observed (Table I). Free-radical polymerization of T_4EGDMA is considered to be initiated by hydroperoxides formed on the active methylene groups and the obvious difference of gel times between HMMM–T_3EG–T_4EGDMA and HMMM–BD–BUDA is ascribed to the absence of active methylene groups in BD and BUDA. This hypothesis was supported by further research.

It is well known that the methylene group of —OCH$_2$CH$_2$O— can be oxidized to form hy-

Scheme 1   Oxidation of active methylene groups in the presence of HMMM.

droperoxides, but the concentration is too low to initiate polymerization of acrylic resins. Therefore, the effect of HMMM on the oxidation of active methylene groups was investigated by oxygen-absorption experiments. The results are shown in Figure 1. From Figure 1, it can be seen that at low temperatures the oxygen absorption of the HMMM–T_3EG composition is not obvious. When the temperature is increased to above 80°C, the rate of oxygen absorption becomes obvious. However, without HMMM, T_3EG alone does not show oxygen absorption. On the other hand, if T_3EG is replaced by BD in the HMMM–T_3EG composition, there is also no oxygen absorption observed. Therefore, it is evident that HMMM is not only a crosslinking agent of polyol, but acts also as a catalyst of formation of the hydroperoxides on the active methylene groups as well.

According to the above experiments, the oxidation process was proposed as given in Scheme 1. The key step of catalysis of HMMM is the formation of a charge-transfer complex (CTC) between HMMM and oxygen, which will capture a hydrogen atom from —OCH$_2$CH$_2$O— and result in the formation of hydroperoxides.

Effect of Acid on the Decomposition of Hydroperoxide

It is well known that the decomposition active energy of hydroperoxide is very high (>130 kJ/

Figure 1   Oxygen absorption of HMMM–T_3EG composition. ○, HMMM–T_3EG; △, T_3EG.

Table II   Effect of Acid on Polymerization of Acrylated Resins

Composition	Gel Times
T_3EG^a–T_4EGDA	1 min 30 s
T_eEG^a–T_4EGDMA	2 min 10 s
T_3EG^b–T_4EGDA	>3 h
T_eEG^b–T_4EGDMA	>3 h

T_3EG: 0.6 g; T_4EGDA, T_4EGDMA: 1.6 g; T = 110°C.
[a,b] Toluenesulfonic acid: [a]10^{-4}/mol; [b]0 mol.

$$ROOH + 2HX \rightleftharpoons RO\overset{\overset{\text{H}}{|}}{O}H\cdots X^-\cdots$$
$$\longrightarrow RO\cdot + \cdot OH\cdots H^+X^-\cdots H-X$$
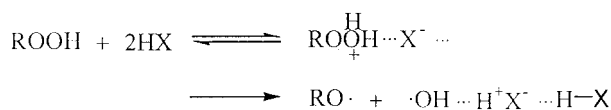
Scheme 2 Formation of free radical by reaction of hydroperoxides with strong acids.

mol). Even at high temperature, the initiation of hydroperoxide is very slow. It is inconsistent with the fact that the acrylated resins in the hybrid polymerization system can be free-radically polymerized quickly. It was found that the acid has an obvious effect on the decomposition of hydroperoxide into the initiating free radical. As shown in Table II, toluenesulfonic acid could improve the rate of free-radical polymerization of acrylated resins.

Radical species capable of initiating free-radical polymerization can be formed by the interaction of hydroperoxides with strong acids as shown in Scheme 2.[11] To investigate the effect of acid on the decomposition of hydroperoxides quantitatively, the apparent active energy, E_a, of the polymerization of methyl methacrylate (MMA), initiated by butyl hydroperoxide, was measured.[12] The rate of polymerization was determined by a dilatometer from 50 to 70°C. The relationship between ln R_p and $1/T$ is shown in Figure 2. According to the Arrhenius equation, it can be calculated that E_a of the polymerization of MMA without the catalysis of acid is 86.96 kJ/mol, but it decreases to only 62.36 kJ/mol if toluenesulfonic acid (1:1 relative to butyl hydroperoxide) is added to the system. From the equation $E_a = (E_p - E_t/2) + E_d$, where E_p is the active energy of propagating and E_t is the active energy of termination, the active energy of decomposition of the initiator, E_d, can be calculated.[10] It is 83.8 kJ/mol in the presence of toluenesulfonic acid and 133.0 kJ/mol without the acid. Therefore, the acid acts not only as the catalyst of condensation polymerization, but also as the catalyst of decomposition of hydroperoxides as well.
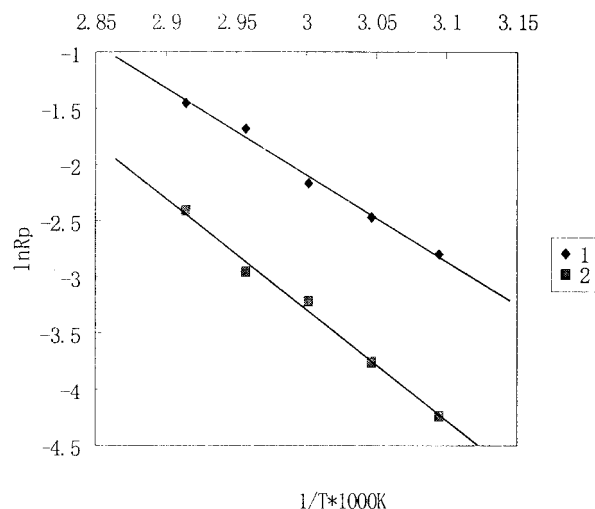
Figure 2 ln R_p versus $1/T$ plots for the polymerization of MMA: (1) catalyzed by toluenesulfonic acid; (2) without acid.

In the hybrid polymerization system, a latent acid catalyst is used. Only at high temperature can strong acid be released and there is no acid at low temperature. Therefore, at room temperature, the hybrid polymerization system is very stable. However, at high temperature, owing to the release of strong acid and the catalysis of acid, the hybrid polymerization system becomes very active.

Design and Synthesis of Crosslinker–initiators of Hybrid Polymerization System

As discussed in the section Initiation of Free-radical Polymerization, it is necessary that the components of hybrid polymerization should have active methylene groups, such as ether polyol and poly[(ethylene glycol) di(meth)acrylate]. Otherwise, the acrylated resins could not be free-radically polymerized in a hybrid system. An effective way to solve this problem is to add some free-radical initiators. If initiators such as AIBN and

Table III Investigation of Activities of Different Types of Active Methylene Groups

Composition		Gel Times
T$_3$EG	T$_3$EGDA	21 min
Diethylene glycol diallyl ether	T$_3$EGDA	3 min 20 s
Diethtylene glycol dibenzyl ether	T$_3$EGDA	4 min 40 s

Toluenesulfonic acid: 10^{-4} mol; T$_3$EG, diallyl ether, and dibenzyl ether: each 10^{-3} mol; T$_3$EGDA: 2.0 g; $T = 110$°C.

Table IV   Effect of Crosslinker Initiators on the Hybrid Polymerization

Composition (Weight Ratio)	Gel Times
HMMM(1.0)–T_3EG(0.6)–T_3EGDA(1.6)	7 min 20 s
HMMM(1.0)–BD(0.6)–TMPTA(1.6)	67 min
HMMM(1.0)–BD(0.6)–TMPTA(1.6)–ally ether(0.5)	4 min
HMMM(1.0)–BD(0.6)–TMPTA(1.6)–benzyl ether(0.5)	2 min 40 s

$T = 100°C$. Toluenesulfonic acid: 10^{-4} mol.

BPO, which are commonly used in free-radical polymerization, are added, the shelf time of the hybrid polymerization system will be shortened due to the relatively low decomposition active energies of these free-radical initiators.

Another way is to add some compounds containing more active methylene groups. Therefore, the activities of different types of methylene groups were investigated. It is well known that the activities of methylene groups differ from each other due to the influence of different adjacent groups. To investigate the effect of adjacent groups, diethylene glycol diallyl ether and diethylene dibenzyl ether were synthesized and characterized. The comparison of activities was carried out by gel-times investigation. The results in Table III show that the polymerization of acrylated resins initiated by dially ether or dibenzyl ether is much faster than that initiated by T_3EG, indicating that hydroperoxides can be formed on —OCH_2CH=CH_2 or —OCH_2Ph more easily than on —OCH_2CH_2O—, which is due to the resonance of adjacent —CH=CH_2 and —Ph groups, which make the radical a (Scheme 1) more stable and easier to be formed, resulting in the quick formation of the corresponding hydroperoxides.

Based on the above results, diethylene glycol ally ether and diethylene glycol benzyl ether were designed and synthesized to make the formula-

tion more flexible. The results in Table IV show that they also have high activities and can shorten the gel times of HMMM–BD–TMPTA greatly. The enhancement of the cure rate is again observed and the polyol and acrylated resins can be selected freely to meet different demands. On the other hand, the hydroxyl group of diethylene glycol benzyl ether or diethylene glycol ally ether may be reacted with HMMM at high temperature in the presence of an acid. Thus, a bridge between the network of free-radical polymerization and the network of condensation polymerization will be formed (Scheme 3). Further research is being continued in our lab.

CONCLUSIONS

Compositions of HMMM–polyol–acrylate can be cured by hybrid polymerization comprising free-radical polymerization and condensation polymerization in the presence of acid at high temperature. HMMM is not only the crosslinking agent of polyol, but also acts as the catalyst of formation of hydroperoxides formed on active methylene groups, which initiate the free-radical polymerization of acrylate efficiently. It was also found that strong acid could decrease the decomposition active energy of hydroperoxides. To make the for-
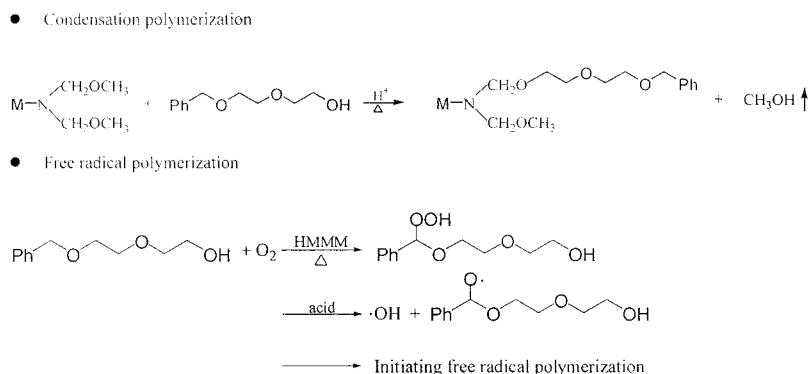
Scheme 3   Proposed reactions of crosslinker–initiators.

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