Waterborne Polymers for Use in Thermoset Coatings: A New Hydrolysis Resistant Monomer as a Replacement for Acetoacetoxyethyl Methacrylate

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INTRODUCTION

A primary concern of the modern paint industry is the reduction of volatile organic compound (VOCs) in the industry's products.[1,2] Thanks to relatively intense research efforts over the last two decades, there are several ways to accomplish this goal. Solvent-based paints with very high-solids levels, powder coatings, and waterborne materials are examples of low VOC systems. However, each of these is not without problems. In order to obtain very high-solid paints, relatively low molecular weight polymers must be used. Such polymers yield inferior films, generally speaking, if they are not crosslinked. However, while crosslinking does improve some film properties, low polymer molecular weight means high crosslink density and this can lead to brittle films. In addition, premature cures, i.e., short pot lives, can also be a problem in some systems. Powder coatings are near-zero VOC systems and can be relatively high in molecular weight, so even crosslinked films can have good flexibility. However, powder coatings are limited to application over substrates that can be heated so good flow and leveling can be obtained. Use of waterborne materials such as latexes, dispersions, and truly water soluble polymers is a very popular approach to lowering VOCs in paint. However, latexes and dispersions usually require the presence of an organic solvent in order to form good films. It is possible to greatly reduce the level of organic cosolvent required for a latex paint by synthesizing polymers with low T_gs. However, such polymers can produce films with inferior block resistances, less mar resistance, and increased dirt pickup. As mentioned previously, it is often necessary to crosslink films made from these polymers in order to obtain acceptable levels of performance. Crosslinking can be, and often is, effected by heating a film. However, in many applications heating the applied film would be impractical, so a film which cures at ambient temperatures after application is highly desirable. Therefore, we undertook the synthesis of a waterborne polymer that would yield films which cured at ambient temperature. We chose to concentrate on synthesizing polymers containing β-ketoester functionality. The β-ketoester functionality is known to react with a variety of species under mild conditions[3] and, at

In an effort to obtain waterborne polymers which would yield ambient temperature cured films, we synthesized several acetoacetoxyethyl methacrylate containing copolymers. While cured films could be obtained if the copolymers were used to make films soon after they were synthesized, a decline in film performance was noted which correlated with age of the copolymer solution/dispersion. Accordingly, we set out to synthesize a replacement for the acetoacetoxyethyl methacrylate. We decided on an amide type monomer which was synthesized in three steps from 3-isopropenyl-α,α-dimethylbenzyl isocyanate, with an overall yield of 65-70%. The new monomer did not homopolymerize but was found to copolymerize readily with styrene or n-butylacrylate. Films from polymers containing the new monomers had equal or better properties than films obtained from polymers containing acetoacetoxyethyl methacrylate. Analysis showed that the new monomer did not hydrolyze over a period of one year at ambient temperature.

the time this work was started, an acrylic monomer having β-ketoester functionality was newly available,[4] namely, acetoacetoxyethyl methacrylate (AAEM).
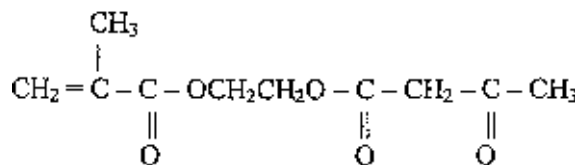
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Scheme 1—AAEM Hydrolysis
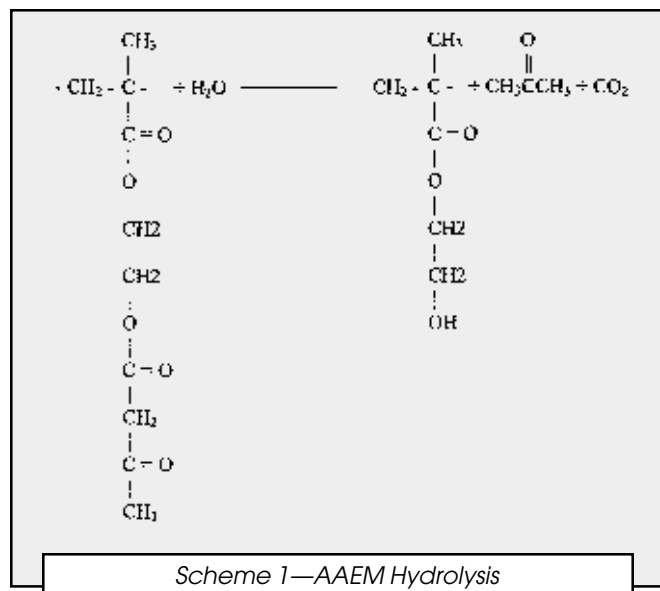
The AAEM copolymerized with facility and the co-polymers yielded films which were readily crosslinked at ambient temperature by reaction with multifunctional amines. The films obtained had good to excellent properties. However, as the aqueous polymer dispersions/solutions aged, the properties of films made from them began to erode. The cause was determined to be hydrolysis of the β-ketoester functionality of AAEM (*Scheme* 1).[5]

The rate of hydrolysis was determined to be significant under all conditions tested. We therefore decided that a new monomer was needed. This new monomer should have a functionality capable of participating in crosslinking reactions at ambient temperatures, copoly-merized readily with common comonomers and, of course, the active moiety should be hydrolysis resistant. This paper reports the synthesis of such a monomer and the preliminary testing of crosslinked films from copolymers containing the monomer.

Figure 1—AAEM hydrolysis rate for the high acid resin.
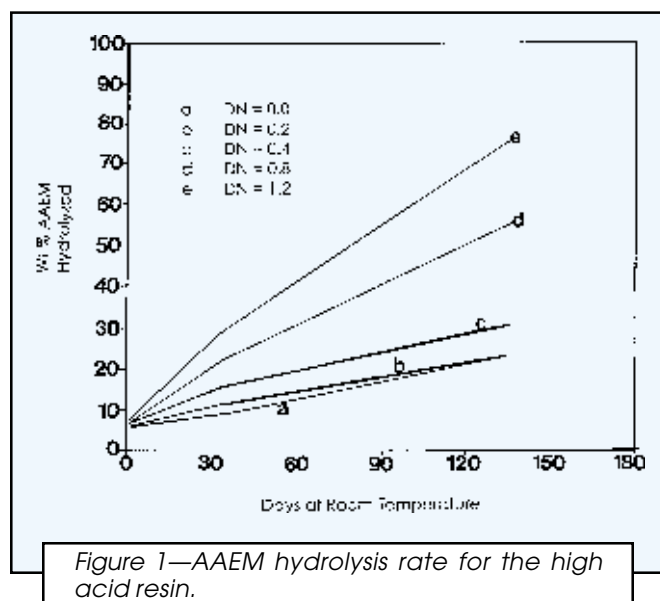
EXPERIMENTAL

All solvents and other chemicals used in this study were obtained from commercial sources and were used as received. Proton nmr spectra were obtained on $CDCl_3$ solutions of material at ambient temperature using a Varian Gemini 300 FT NMR. Molecular weights were measured using a GPC equipped with a Waters 510 pump and 410 RI detector and two Polymer Labs 30 cm columns. Numerical values for the molecular weights were obtained by comparison to a polystyrene calibration curve. Acetone levels were measured using an HP5890 GC. Degree of cure was estimated by measuring the number of methyl ethyl ketone double rubs required to break through a film to the substrate below. This test was performed with an Atlas AATCC crockmeter. All other film tests were performed according to the appropriate ASTM methodology.

Synthesis of Alkali Soluble Resins— General Procedure

Deionized water (540 g) was charged to a 1L flask equipped with a mechanical stirrer, reflux condenser, thermometer, and monomer inlet port. A surfactant (Sipex UB, 2.0 wt% based on total monomer weight) was added, the water was heated to 80°C and ammonium persulfate was then added. After a five-minute induction period, 230 g of a mixture consisting of methyl methacrylate (25-30 wt%), n-butyl acrylate (35-45 wt%), methacrylic acid (12-24 wt%), chain transfer agent, isooctyl mercaptopropionate (1.5-2.0 wt%), and the monomer with the crosslinking functionality (15-30%) was fed into the reaction flask by means of a metering pump over the course of 1-1.25 hr. After the addition was complete, the reaction mixture was held at 80°C for 1.0 hr to insure complete monomer conversion.

Hydrolysis Experiments

Ammonia was added in different amounts to the aqueous dispersions of the polymer synthesized as detailed earlier, depending on the degree of neutralization desired. The resulting polymer solutions/disperisions were then placed in tightly sealed containers which were pressure resistant and stored at ambient temperature or at elevated (50-60°C) temperature. Samples were removed by syringe periodically and analyzed for acetone levels via GC. By relating the measured acetone level to the initial quantity of AAEM in the polymer solution/dispersion (polymer and water), the percentage of AAEM hydrolyzed could be calculated.

Synthesis of 3-isopropenyl-α,α-dimethylbenzyl Acetoacetamide

3-ISOPROPENYL-α,α-DIMETHYLBENZYL AMINE[6]: A two-liter flask equipped with a mechanical stirrer, reflux condenser, and thermometer was charged with a solution of 200 g of the methyl urethane[7] of 3-isopropenyl-α,α-dimethylbenzyl isocyanate (m-TMI, Cytec) dissolved in 200 g of butyl cellusolve. A solution of KOH (85 g) in 350 g of butyl cellusolve was added and this reaction mixture was heated at reflux, with vigorous stirring, for 4.0 hr. The reaction mixture was allowed to cool to ambient temperature and 250 ml of water followed by 350 ml of 1,2-dichloroethane

was added. This mixture was stirred at ambient temperature for 12 hr and was then poured into a two-liter separatory funnel. The organic layer was separated and then washed with water (2×300 ml) and dried with anhydrous Na_2SO_4. The dichloroethane was removed under reduced pressure and the residue was subjected to vacuum distillation. The 3-isopropenyl-α,α-dimethylbenzyl amine (IDA) was distilled at 90-93°C/1.0 mm Hg. Yield=80.2%. ^{1}H-NMR, $CDCl_3$; δ7.63 (s.1H); δ7.36 (d.1H); δ7.25 (m.2H); δ5.05 (s.1H); δ2.15 (2.3H); δ1.59 (s.2H); δ1.40 (s.6H).

3-Isopropenyl-α,α-dimethylbenzyl Acetoacetamide[8]: A two-liter flask equipped with a mechanical stirrer, reflux condenser, Dean-Stark trap, pressure equalizing addition funnel, and thermometer was charged with 68.0 g of t-butyl acetoacetate and 300 ml of toluene. This solution was heated to 110°C and a solution of 75.22 g of IDA in 350 ml of toluene was added from the funnel over a period of one hour. During the course of the addition, t-butanol and toluene distilled out of the reaction mixture (~50% of the theoretical quantity of t-butanol). After the amine addition was complete, the reaction mixture was stirred at 110°C for 1.5 hr. During this time more t-butanol (~30% of theoretical) and toluene distilled out of the reaction mixture. The reaction mixture was cooled to ambient temperature and the flask was adapted for vacuum distillation. The remaining toluene and t-butanol were removed by distillation at 150 mm of Hg. The residue was a light yellow oil that crystallized to orange-white needles. The product was purified by recrystallization from ethanol/ water (70/30 v/v). Yield was 83.4%. ^{1}H-NMR, $CDCl_3$; δ7.79 (s.1H); δ7.50 (s.1H); δ7.25 (m.2H); δ5.40 (s.1H); δ5.05 (s.1H); δ3.10 (s.3H); δ2.18 (s.2H); δ2.03 (s.3H); δ1.59 (s.6H).

Copolymerizations for Reactivity Ratio Determination

The desired amount of each comonomer was weighed into a clean, dry, thick walled vial. 1,2-Dichlorobenzene (5 ml of 99%) was then added followed by 1.0 wt% AIBN. The solution was sparged with dry N_2 while cold and the vials were then tightly capped with Teflon lined screw caps. The vials were then placed in a thermostated oil bath at 80°C for the desired length of time. The vials were removed from the bath, cooled to ambient temperature and methanol or n-heptane was added to the vial to precipitate the copolymer. The copolymers were purified by two reprecipitations from $CHCl_3$ solution into either methanol or n-heptane. The copolymers were then dried in vacuo to a constant weight and conversions were determined gravimetrically.

Coating Formulations

To 100 g of resin solution/dispersion (30 wt% solids) 3.0 g of butyl cellusolve was added. To this thoroughly mixed solution, a stoichiometric quantity of 1,6-hexamethylene diamine (as a 50 wt% aqueous solution) was added with vigorous stirring. Films were made by drawing this mixture over aluminum (Alodine) panels or Lenetta cards with a #32 wire wound drawdown rod. The films were allowed to cure at ambient temperature and constant humidity (70%) for three days and were then evaluated for property development.
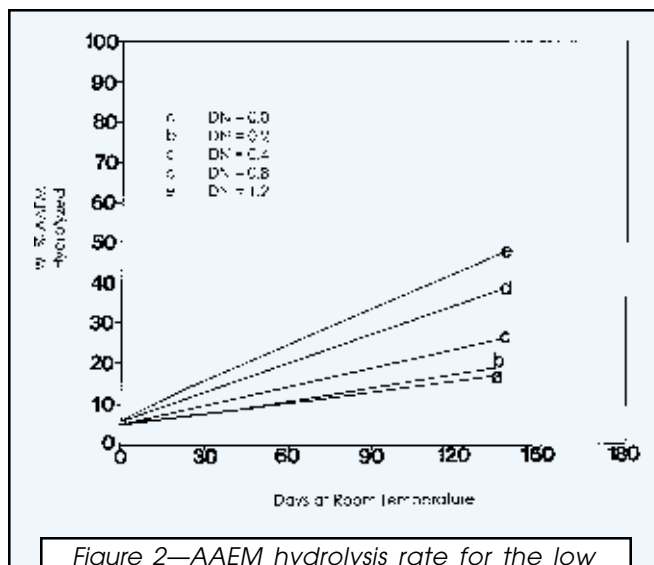

Figure 2—AAEM hydrolysis rate for the low acid resin.

RESULTS AND DISCUSSION

The results of the hydrolysis experiments are shown in *Figures* 1 and 2. *Figure* 1 shows a high acid resin (24 wt% methacrylic acid in the feed), while *Figure* 2 shows the curves obtained for a low-acid (12 wt% methacrylic acid in the feed) resin. The curves in the figures represent the mole percent of acetoacetoxyethyl methacrylate (AAEM) β-ketoester functionality lost to hydrolysis over certain periods of time. The differences in the lines represent different degrees of neutralization (DN) of the carboxylic acid groups of the polymer; for example, a DN = 0.8 means that 80 mol% of the available carboxylic acid groups have been neutralized with ammonia. Throughout this paper we have referred to these copolymer-water mixtures as solutions/dispersions. In order to determine if the mixtures were true solutions particle size measurements using Capillary Hydrodynamic Fractionation (CHDF) were
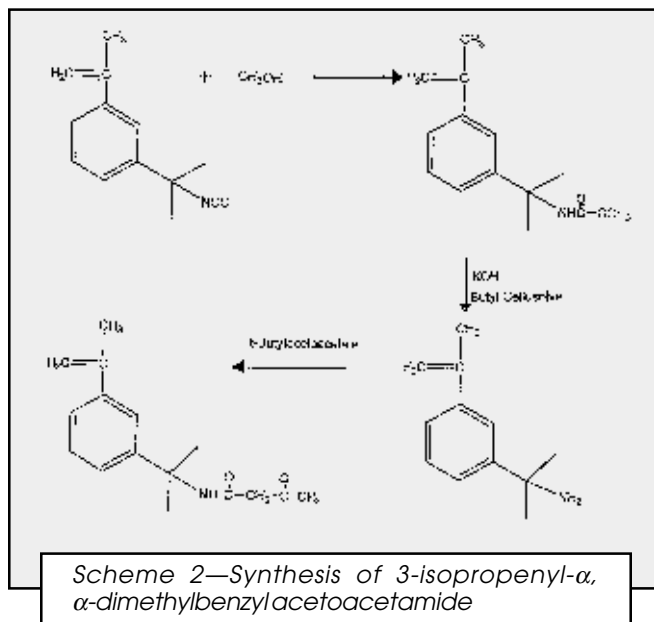

Scheme 2—Synthesis of 3-isopropenyl-α, α-dimethylbenzyl acetoacetamide

Table 1—Copolymerization Results

Polymer	M₁	M₂	M_f M₁ in Feed[a]	M_f M₂ in Feed	Pzn Time (min.)	Wt% Conv.	M_f of M₁ Copolymer	M_f of M₂ Copolymer	M_n	M_w
1	IDAA	Styrene	0.031	0.969	75	25.5	0.040	0.960	13000	23000
2	IDAA	Styrene	0.060	0.940	75	29.8	0.060	0.940	8700	14600
3	IDAA	Styrene	0.200	0.900	75	23.7	0.20	0.900	9800	16200
4	IDAA	Styrene	0.160	0.840	75	15.9	0.130	0.870	9200	14500
5	IDAA	Styrene	0.410	0.480	300	5.8	0.350	0.650	8100	14600
6	IDAA	nBA	0.074	0.926	75	3.5	0.180	0.820	1600	3100
7	IDAA	nBA	0.210	0.790	75	25.0	0.310	0.690	9500	24600
8	IDAA	nBA	0.440	0.560	120	3.5	0.430	0.570	8800	8800
9	IDAA	nBA	0.590	0.410	120	7.7	0.500	0.500	6800	6800

(a) M_f = mole fraction.

made. Since, within the limits of detection of the instrument (MATEC 2000), no particles were detected, we concluded that the copolymer-water mixtures were solutions. However, it is possible that the mixtures contain very small particles which we could not detect, hence our use of the term solution/dispersion. The results show that high levels of acid in the resin lead to greater hydrolysis rates. It also seems that after a DN of 0.2 the rate of hydrolysis increases significantly. This data shows that at ambient temperature a significant (as good as 80 mol%) portion of the active functionality of AAEM is lost in as little as 140 days. Temperature exacerbates this problem, at 60°C virtually 100 mol% of the active functionality is lost after 30 days when DN ~ 0.8. If one is attempting to formulate an ambient cure, one-pack paint/coating or any paint or coating for that matter, long-term storage stability without loss of performance is usually required. Because our data indicated that AAEM containing copolymers in aqueous media would not have stability and the performance of films made from aged resin samples was significantly less than films made from fresh samples, and because the β-ketoester moiety did provide copolymers curable at ambient temperature, we decided to attempt the synthesis of a hydrolytically stable analog of AAEM. The approach we took is outlined in *Scheme* 2.

We reasoned that since amide linkages are more stable to hydrolysis than ester linkages and that sterically hindered amide linkages are even more stable,[9,10] than an acetoacetamide based on a molecule such as m-TMI should be stable enough to provide polymers with a hydrolysis resistant, ambiently reactive functionality. The 3-isopropenyl-α,α-dimethylbenzyl aceto-acetamide (IDAA) was readily synthesized in three steps from m-TMI. The yield from each step was relatively high so a good overall yield of IDAA was obtained (65-70% based on m-TMI).

As the IDAA is a substituted α-methylstyrene derivative it was not homopolymerizable via free radical initiation at the temperatures and pressures normally employed for such polymerizations. However, the IDAA should be copolymerizable with a variety of standard monomers. To

show that this was indeed the case we chose two representative comonomers, styrene and n-butyl acrylate, and conducted copolymerization experiments. The results of these experiments are summarized in *Table* 1.

The conversions obtained for some of the copolymerizations made the use of the Kelen-Tudos high conversion method for calculating reactivity ratios necessary.[11] The calculated reactivity ratios are listed in *Table* 2.

The reactivity ratio values show that IDAA is readily incorporated into the copolymer backbones. Copolymerization with styrene is more facile, but this is to be expected as IDAA and styrene are more similar in structure then IDAA and n-butyl acrylate. The styrene-IDAA copolymers tend to have a more random morphology while the n-butyl acrylate-IDAA copolymers tend toward alteration (r_1r_2 is low).

Having established that IDAA readily enters copolymer chains we investigated the film performance of IDAA copolymers. Alkali soluble resins were synthesized as described above. Resins containing AAEM or IDAA at approximately the same level were synthesized: 7.0 mol% for AAEM, 60 mol% for IDAA. These mole percents correspond to ~ 15 wt% for each monomer. The molecular weight for each resin was nearly the same (M_n = 9000 ± 600) and the solids level was ~ 30 wt% for both resins. 1,6-Hexamethylene diamine (stoichiometric amount) was added and drawdowns were made as previously described. The films were allowed to cure at ambient temperature for three days and were then evaluated for property development. The results obtained are summarized in *Table* 3.

The aged samples were alkali soluble resins stored at ambient temperature for a period of 140 days. The resins were formulated into coatings mixtures as described earlier and drawdowns over aluminum were made. The results show that the AAEM containing resins erode in terms of resistance properties with age. This decrease in performance directly reflects the hydrolysis of the β-ketoester moiety of the AAEM. With the decrease in the concentration of active functionality, the crosslink density of the films is lower, resulting in decreased performance of the films. In contrast, alkali soluble resins containing IDAA exhibit no decrease in film performance with age. This result indicates no hydrolysis of the acetoacetamide moiety of IDAA. Additionally, monitoring of the IDAA resin solutions by GC revealed no evolution of a decomposition product (acetone or any other

Table 2—Reactivity Ratios

M₁	M₂	r_1	r_2	r_1r_2
IDAA	Styrene	0.50 ± .06	0.98 ± .10	0.490
IDAA	nBA	0.10 ± .02	0.28 ± .08	0.028

Table 3—Film Results

	Crosslinking		MEK Double	50% Ethanol[d]			5%NaOH			70% Isopropanol			Water		
Resin	Monomer	Crosslinker[b]	Rubs	C	G	S	C	G	S	C	G	S	C	G	S
1	AAEM	1,6 HMDA	56	4.5	4.5	1.5	1.5	2.5	1.0	3.0	3.0	3.0	3.0	3.0	2.0
2	IDAA	1,6 HMDA	90	5.0	4.5	2.5	2.0	2.5	1.0	3.5	3.0	3.0	3.5	3.5	2.5
1A[a]	AAEM	1,6 HMDA	27	2.4	2.4	0.5	0.0	.0.0	0.0	0.0	0.0	0.0	3.0	3.5	3.0
2A[a]	IDAA	1,6 HMDA	100	5.0	4.0	2.5	2.5	2.5	1.0	3.5	3.0	3.0	3.5	2.5	3.0

(a) 1A, 2A = aged samples.
(b) 1,6 HMDA = 1,6-hexamethylene diamine.
(c) MEK = methyl ethyl ketone.
(d) C = Cracking, G = Gloss, S = Softening.
Scale = 0-4 with 4 = best.

small molecule) over the course of one year at ambient temperature.

CONCLUSIONS

The results of this study show that AEEM hydrolyzes significantly in aqueous dispersions/solutions at ambient temperature. The hydrolysis results in films with inferior properties being obtained. In an attempt to make resins that yield films curable at ambient temperature which were resistant to hydrolysis; we synthesized a new monomer, IDAA, from a commercially available material, m-TMI. The new monomer was obtained in good overall yield and the synthetic route employed was straightforward. The new monomer was not homopolymerizable by free radical means, but readily entered into copolymerization reactions. The alkali soluble resins containing the new monomer gave films that cured at ambient temperature and aqueous solutions/dispersions of these resins proved hydrolytically stable for extended periods of time.

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