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


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 Tgs. 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 and, at the time this work was started, an acrylic monomer having β-ketoester functionality was newly available, namely, acetoacetoxyethyl methacrylate (AAEM).
The AAEM copolymerized with facility and the copolymers 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 \[\text{3-ketoester functionality of AAEM} \] (Scheme 1). 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, copolymerized readily with common co-monomers 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.

**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 CDCl₃ 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 (3-45 wt%), methacrylic acid (12-24 wt%), chain transfer agent, isooctyl mercaptobutionate (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 1.25 hr. After the addition was complete, the reaction mixture was held at 80°C for 1.0 hr to ensure 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/dispersions 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-\(\alpha,\alpha\)-dimethylbenzyl Acetoacetamide**

3-\text{Isopropenyl-}\(\alpha,\alpha\)-\text{dimethylbenzyl Amin}e: 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 of 3-isopropenyl \(\alpha,\alpha\)-dimethylbenzyl isocyanate (m-TMI, Cytec) dissolved in 200 g of butyl cellulose. A solution of KOH (85 g) in 350 g of butyl cellulose 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.