

Synthesis of Methyl Methacrylate-*n*-Butylacrylate Copolymers: Study of the Paint Properties

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ABSTRACT: A series of acrylic copolymer solutions were prepared by copolymerizing methyl methacrylate (MMA) with *n*-butylacrylate monomers in toluene to high conversion using dibenzoyl peroxide (0.5 wt %) as initiator. The various reaction parameters, such as MMA concentration and mode of addition of reactants to the reaction vessel, were changed to obtain an acceptable quality of the resins for the paint. The properties of the resins and the effect of MMA concentration on these properties (such as viscosity, drying time, hardness, and adhesion) were measured according to ASTM standard tests. A linear relation between final percentages of conversion and MMA concentration was observed. Drying time, hardness, and glass transition temperature of the samples were increased with MMA concentration; adhesion of the samples remained constant up to 50 wt % of MMA and then decreased significantly with a further increase in MMA concentration. These results led to the selection of resins with the properties that fulfill the requirement of a good quality traffic paint. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 367–372, 1998

Key words: acrylic resin; copolymer; methylmethacrylate; butylacrylate synthesis; solution; properties

INTRODUCTION

A considerable body of literature and patents concerned with the free radical copolymerization of the acrylic resins has been developed.^{1–4} The relative ease of copolymerization and the wide range of properties among the acrylic resins have led to the commercial production of many different resins suitable for a broad variety of applications.⁵ For example, these resins play a prominent role in the paint industry due to the unique combination of their properties.⁶ The properties of the synthesized resins are dependent not only on their average molecular weight, but also on their copolymer composition. Therefore, to achieve a

desired quality of the resin, it is necessary to control them by adjustment of the synthesis conditions and feed ratios.

The major factors that control the average molecular weight in a solution copolymerization are: initiator concentration, temperature, solvent, and monomer concentration. In our experiments, the temperature and solvent concentration are kept constant. By gradual addition of the monomers and initiator to the solvent in the reaction vessel, the heat of polymerization is controlled, and also lower molecular weight of the resins is obtained (rather than if all the monomers are charged). The reason for the use of this procedure is that acrylic copolymerizations are accompanied by the gel effect and the liberation of considerable heat; thus, the chances of a runaway reaction must be avoided.⁷

The aim of the present work is to synthesis a thermoplastic acrylic copolymer solution and to

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Table I Feed Policies for Copolymerization Experiments

Run	Reaction Vessel Heel	Addition Policy
1	116 g toluene, 87 g MMA, 87 g BA, 0.87 g BPO	No additional feeds, 4 h reaction time
2	116 g toluene, 0.87 g BPO added at reflux temperature	Mixture of 87 g MMA and 87 g BA, 8 intervals, 2 h
3	116 g toluene, 6.5 g MMA, 6.5 g BA, 0.065 g BPO (10 wt % precharge)	After 1 h: mixture of 80.5 g BA, 80.5 g MMA, and 0.805 g BPO, uniform rate, continuous, in 2 h
4	116 g toluene, 14.5 g BA, 14.5 g MMA, 0.145 g BPO (20 wt % precharge)	After 1 h: mixture of 72.5 g BA, 72.5 g MMA, and 0.725 g BPO, uniform rate, continuous, in 2 h
5	116 g toluene, 25 g MMA, 25 g BA, 0.25 g BPO (30 wt % precharge)	After 1 h: mixture of 62 g BA, 62 g MMA, and 0.860 g BPO, uniform rate, continuous, in 2 h

All reactions: at a reflux temperature of toluene, using 0.5 wt % initiator (based on monomers), weight of monomers to weight of toluene ratio, 60 : 40.

investigate the properties of the resins required for a good quality paint. Improvements in the paint properties by varying the polymer structure and synthesis of some acrylic terpolymers are under way in our laboratory.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) and *n*-butylacrylate (BA) were purchased from Nietacril Co. and Caldic Co., Ltd., Brazil, respectively, and were used as received. Toluene was supplied by Isfahan Petrochemical Complex (99.9% pure) and used without further purification. Dibenzoyl peroxide (BPO) was also obtained from Merck Chemical Co., Germany, and dried in a vacuum oven at 35°C for 6 h.

Syntheses

The solution copolymerization of MMA and BA were conducted in toluene solvent using BPO as the free radical initiator. The copolymers were synthesized in a 500-mL four-necked reaction vessel equipped with a mechanical stirrer, condenser, thermometer, and inlet-outlet valves for nitrogen purge. The reaction vessel was placed in an oil bath at 150°C and heated to the reflux temperature of the toluene. A series of the acrylic resins was synthesized.

The feed policies for each of the five different types of experiments are given in Table I. In lab-

oratory scale, run 1 was a batch reaction, and run 2 was a semibatch reaction with the addition of monomers in some intervals for 2 h to the solvent-containing initiator at reflux temperature in the reaction vessel. Runs 3–5 were semibatch, with the gradual addition of initiator and mixture of both monomers at a constant rate in 2 h time to the toluene containing a precharged monomer (i.e., 10%, 20%, and 30% by weight) at reflux temperature. The total reaction time for each experiment was about 4 h.

Using run 3 procedure, a number of resin samples were prepared by changing the MMA concentration in the addition policy (Table I). In all the experiments, the ratio of monomers to the solvent was 60 : 40 by weight.

The paint was prepared using a definite formulation shown in Table II. The ingredients were mixed in a special mixer for 24 h.

Table II Paint Formulation^a

Ingredients	Part Per Hundred (g)
Acrylic resin (60 wt %)	100
Titanium dioxide (pigment grade)	54.5
Baryte	15
Calcium carbonate	45.4
Talk	30.3
Dispersing agent	3
Anti-sediment	1
Toluene	60.6

^a Extenders were sand milled.

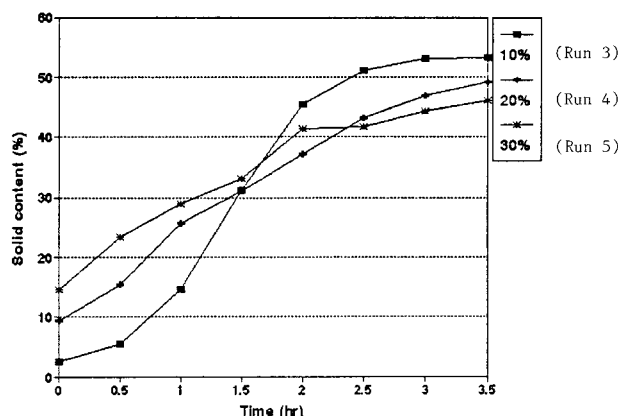


Figure 1 Effect of charge percent on variation of solid content percent *versus* reaction time during copolymerization of BA with MMA (feed ratio = 1).

Measurements

The percentages of solid content and conversion during copolymerization were measured by weighing the precipitated polymer. The polymer was precipitated by the addition of methanol and then vacuum-dried. Viscosity of the resins was measured by Ford viscosity cup no. 6, according to ASTM D 1200.

Drying time of the resin, adhesion (by tape test), and hardness of the paints were measured according to ASTM D 1640, D 3359, and D 3363, respectively.

The glass transition temperature of the resins was also measured using a DSC 1200 [Rheometric Scientific Ltd., England (previous co., Polymer Laboratory)].

RESULTS AND DISCUSSION

It was observed that run 1 reaction went out of control due to the Trommsdorf effect.⁷ Run 2 was conducted by adjustment of the interval periods of monomer addition; but, we were not able to run the reaction to a high conversion and not more than 65 wt % conversion was obtained. However, there was no problem in conducting runs 3 to 5 to a high conversion. Regarding ease of reaction, control of reaction, and the required properties of the resin for use as paint, run 3 reaction was selected among the runs 3–5.

A comparison of copolymerizations in runs 3–5 are shown in Figure 1. In this figure, solid content percent *versus* reaction time is observed. Although one would initially expect them to be sim-

ilar (before reflux temperature), the rate of copolymerization in runs 4 and 5 is higher because an increase in precharged monomers means higher reactivity in the medium leading to higher rate of copolymerization. Based on run 3, the copolymer composition is changed by varying the MMA concentration in the feed, keeping the ratio of monomer weight to solvent weight 60 : 40. Figure 2 shows the effect of MMA concentration on solid content during the copolymerizations. Increase in MMA concentration caused a lower amount of solid content up to 2.5 h of the reaction. Higher solid content is observed with an increase in MMA concentration from 2.5 h to the end of the reaction. In Figures 1 and 2, start time for solid content measurements is the beginning of reflux temperature of the solution.

The ability of the monomers to become involved in a copolymerization process is controlled by the reactivity ratio of the monomers.⁸ The reactivity ratio of MMA monomer provides information about the rate of addition of the MMA to the BA radical. The reactivity of BA is lower than that of MMA monomer during copolymerization.⁹ By referring to these statements, a contradiction is seen in Figure 2. But, data in this figure may be explained by the effect of inhibitors (in the monomers and oxygen) on MMA macroradicals. The inhibitors present in 10 wt % precharged monomers are consumed by the free radicals formed from the decomposition of the initiator molecules during the period in which the reaction reaches the refluxing temperature of the solution. As the monomers containing inhibitor and initiator are

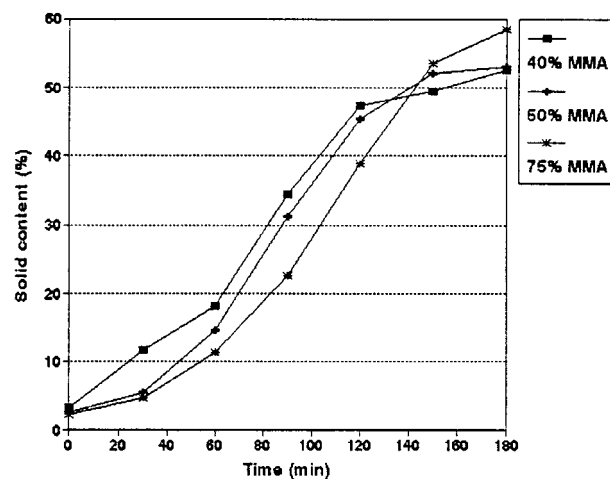


Figure 2 Effect of MMA concentration on variation of solid content percent *versus* reaction time during copolymerization of BA with MMA.

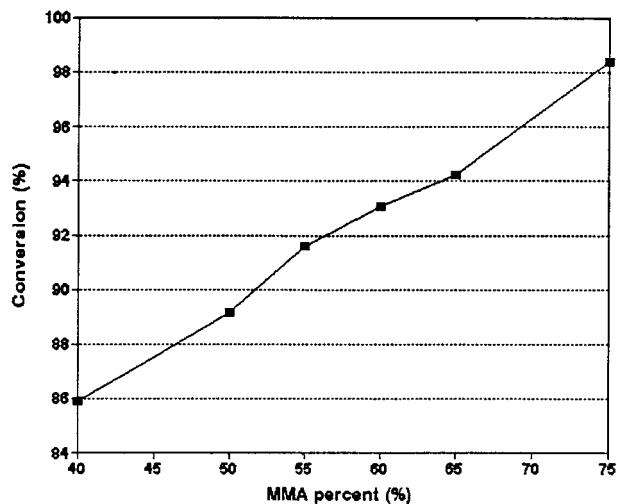


Figure 3 Variation of conversion *versus* MMA concentration during copolymerization of BA with MMA.

gradually added to the medium, a percentage of the free radicals, including MMA radicals, is trapped by the inhibitor molecules. This gives a chance for BA to present a higher activity in this condition. Also, a linear relation between the final conversion and MMA concentration is observed (Figure 3). The reason may be the increase in propagation rate.

Viscosity (equivalent to flow time) of the resins increases with MMA concentration (Figure 4). It has been shown that instantaneous changes in monomer concentration with time during copolymerization is proportional to the square root of vis-

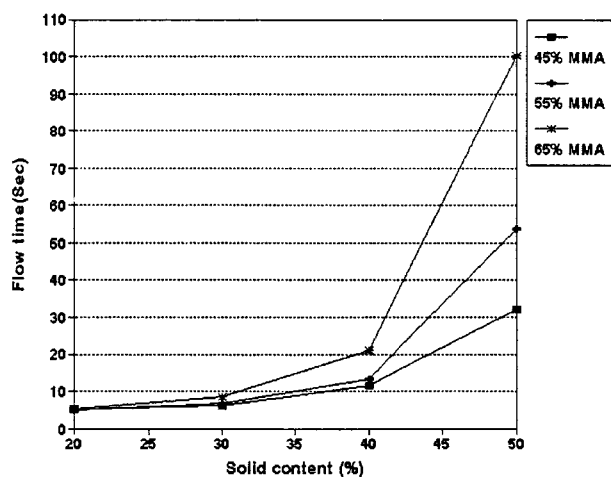


Figure 4 Variation of flow time *versus* solid content percent during copolymerization of BA and MMA: effect of MMA concentration (0.5% BPO).

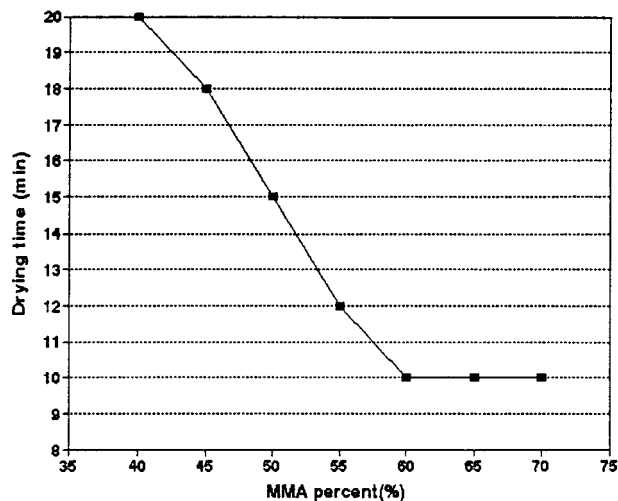


Figure 5 Effect of MMA concentration on drying time of the acrylic copolymer resins.

cosity.¹⁰ Because viscosity is proportional to average molecular weight, the thermoplastic acrylic resin solution having a definite range of viscosity should be synthesized for paint production. Also, a higher amount of solvent should be used for the higher viscosity resins in paint preparation, which is more beneficial to producers (not consumers and environmentalists). If the viscosity of the resin is lower than a certain level, the properties of the paint, made from it, will not be acceptable.¹¹

Figure 5 shows the effect of MMA concentration on drying time of the film resins. A high rate of reduction in drying time of the samples is observed up to 60 wt % of MMA and then remains constant by a further increase in MMA concentration. This is explained by an increase in the glass transition temperature (T_g) of the resin samples, with an increase in MMA concentration.¹² To confirm this statement, T_g measurements of the resins synthesized with different concentrations of MMA are presented in Table III.

Hardness of the paint films shows a high rate of increase with MMA concentration up to 55 wt % and then remains constant at 4H (Fig. 6). This may also be attributed to the effect of MMA methyl groups in the copolymers.^{12,13}

Figure 7 shows a variation of adhesion of paint film samples with MMA concentration in the feed.

Table III T_g of MMA-BA Copolymers

MMA (wt %)	60	65	70	75
T_g (°C)	35.5	42.2	48.8	61.5

The measurements conducted with the tape adhesion test. Using this test, adhesion of the samples remained constant up to 50 wt % of MMA at 2B and then decreases to 0B with 60 wt % of MMA.

The main reason for the strong adhesion of acrylate polymers is their low T_g .¹¹ Because adhesion of the samples depends on the copolymer composition, as the content of BA in the copolymer of MMA-BA increases, adhesion increases and vice-versa. By using the tape adhesion test, the decrease in adhesion with an increase in MMA concentration up to 50 wt % is not recognizable on this scale.

Regarding the role of toluene during copolymerization, not only the transfer reaction to toluene occurs (which reduces the average molecular weight of the resins), but also it decreases the overall rate constant of copolymerization according to either the theory of hot radical or the so-called electron-donating and accepting complex theory.^{14,15} These theories make the chain propagation step responsible for the toluene dependence of the overall rate constant. Also, by an increase in the viscosity of solution copolymerization, especially at the final stage of the reaction, the toluene dependence of polymerization is described by the diffusion theory wherein chain termination is diffusion-controlled.^{16,17}

CONCLUSIONS

The following conclusions are drawn:

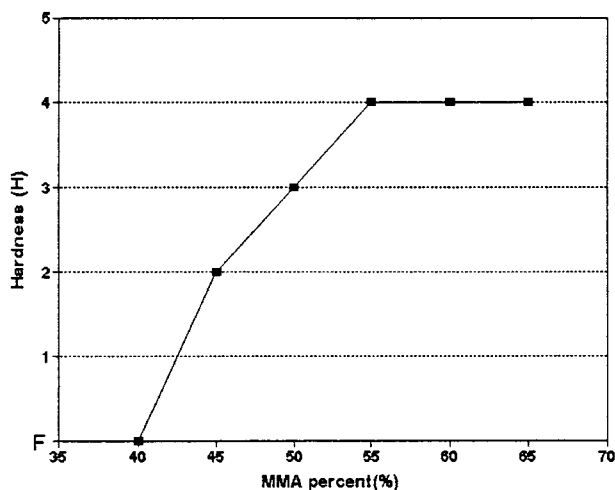


Figure 6 Effect of MMA concentration on the hardness of synthesized copolymers.

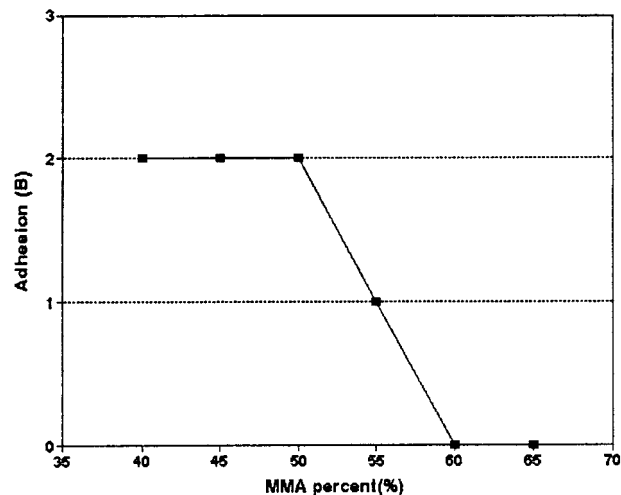


Figure 7 Variation of adhesion versus MMA concentration of acrylic copolymer.

1. The synthesis parameters, such as amount of reactants, mode of addition to the toluene, reaction time, and temperature are adjusted to obtain the copolymer resins with high conversion.
2. By referring to the synthesis condition and measurement of the resin properties, thermoplastic acrylic resins suitable for paint use are obtained.
3. BA shows contradictory reactivity with MMA during the copolymerizations due to the MMA macroradical trapping by the inhibitors that are present in the monomers.
4. Drying time of the resins is decreased with MMA concentration in the feed, which is directly related to the T_g of the resin.
5. Hardness and adhesion measurements of the paints, made from the resins, indicate that using a limited range of MMA concentration (50–55%) in the feed will fulfill the resin requirements for paint.

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