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# Synthesis and Free Radical Polymerization of Methyl α-Benzylacrylate

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ABSTRACT: Methyl α-benzylacrylate was synthesized from dimethyl malonate following well-known organic reactions. The purified monomer was polymerized by a free radical mechanism in benzene, using 2,2′-azobis(isobutyronitrile) as initiator, at several temperatures ranging from 40 to 80 °C. The absence of polymeric species at polymerization temperatures of 70 and 80 °C, together with the low molecular weight of the polymers obtained, seems to indicate that a ceiling temperature between 60 and 70 °C may be expected. The application of results obtained to known kinetic treatments gives a ceiling temperature of 67 ± 2 °C under the experimental conditions used in this work.

## Introduction

Polymerization of methyl and other alkyl methacrylates has been reported by many authors; however, little attention has been paid to the free radical polymerization of α-alkyl- or α-arylacrylates. Attempts to initiate the polymerization of α-alkyl- or α-arylacrylic esters resulted in either low molecular weight polymers or no polymer at all,[1,2] which was attributed to the strong interfering effect exerted on free-radical polymerization by the α-substituent group.

From a thermodynamic point of view, the free energy of polymerization mainly depends on the enthalpy of polymerization, since the entropy of polymerization presents values relatively constant or with little variation in a narrow range and is less sensitive than the enthalpy of polymerization to the chemical structure of monomers. As it is well-known, the enthalpy of polymerization is low for α,α-disubstituted monomers and therefore free energy of polymerization is less negative and the polymerization reaction more difficult.[3] Thus, free-radical polymerization of methacrylate monomers containing phenoxy groups as substituents on the α-methyl position with relative low yield and molecular weights has been reported by Lenz et al.[4] and the results have been attributed to the low ceiling temperatures of polymerization expected for these sterically hindered monomers. However, in our knowledge, no ceiling temperatures for this family of monomers have been reported and it may be interesting to know this parameter in order to gain more information about the reactivity of this kind of vinyl monomers. The present report is concerned with the synthesis, free-radical polymerization, and ceiling temperature determination of methyl α-benzylacrylate.

## Experimental Section

**Synthesis of Monomer.** The synthesis of monomer involved three steps and well-characterized organic reactions were used in all of them.[5,6]

**Step 1.** Dimethyl benzylmalonate was prepared from dimethyl malonate (0.95 mol) and sodium methoxide (0.87 mol) in 1450 mL of methanol and benzyl chloride (0.91 mol). The reaction mixture was warmed until neutralization. The product was fractionated under vacuum and collected at 118-122 °C at 2 mmHg. A 42.2% yield was obtained.

**Step 2. Monomethyl Ester of Benzylmalonic Acid.** To a solution of potassium hydroxide (0.425 mol) in 145 mL of methanol was added 0.425 mol of dimethyl benzylmalonate in 560 mL of dried methanol. After standing for about 24 h, the solution was acidified with 25 mL of HCl (35%) and the monoester was extracted with ether. A 91.3% yield was obtained.

**Step 3. Methyl α-Benzylacrylate.** Diethylamine (0.37 mol) was added to monomethyl ester of benzylmalonic acid (0.37 mol) and the mixture was kept in an ice bath with stirring while 38 mL of formaldehyde (35% in methanol-water solution) was slowly

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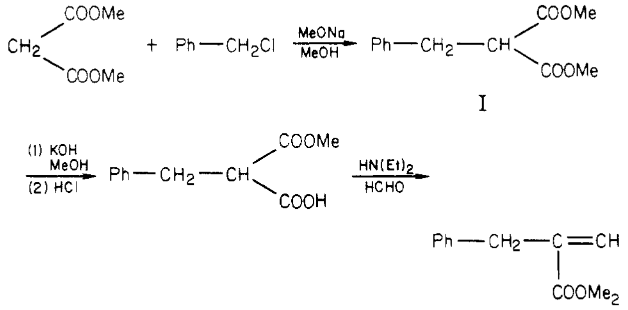
added. The reaction mixture was kept without stirring in an ice bath and after about 24 h two distinct layers had separated. The upper organic layer was fractionated under vacuum and methyl α-benzylacrylate was collected at 82–84 °C at 2 mmHg. An 87.3% yield was obtained.

**Polymerization.** Polymerization was initiated by 2,2′-azobis(isobutyronitrile) (AIBN) in benzene, purified as reported elsewhere.[7,8] The solutions prepared were placed in Pyrex glass ampules and sealed under high vacuum. The reaction temperature was regulated between 40 and 80 °C with a thermostatic bath in which the temperature precision was ±0.05 °C. Polymers were isolated and purified by pouring the reaction product into vigorously agitated methanol. The swollen solid was washed and redissolved in benzene and the solution was filtered. The polymer was reprecipitated by pouring the solution into methanol, and finally it was washed and dried to constant weight. The polymerization of methyl methacrylate was carried out in a similar way.

**Characterization.** Monomer and polymer were analyzed by IR (Perkin-Elmer 457) and $^1$H NMR (Varian EM-390, 90 MHz) spectroscopies. The number-average molecular weight of the polymer was determined with a Knauer vapor pressure osmometer.

## Results and Discussion

**Monomer Preparation.** The monomer was prepared through the following scheme:



Monomer structure was verified by IR and NMR analyses. The IR spectrum showed strong absorption bands at 1720 and 1630 cm$^{-1}$ corresponding to α,β-unsaturated carbonyl and C=C groups, respectively. The NMR spectrum showed five signals: two doublets at 5.3 and 6.2 ppm from $Me_4Si$, assigned to the resonance of the two nonequivalent protons ($H_A$ and $H_B$) of the β-carbon. The signal at 3.7 ppm corresponds to the methoxyl methyl protons, a singlet for the methylene protons at 3.5 ppm and a singlet for the phenyl protons at 7.1 ppm. The boiling point of monomer was 82–84 °C/2 mmHg and its purity tested by gas–liquid chromatography was higher than 99.5%.

**Polymer Preparation and Ceiling Temperature.** Methyl α-benzylacrylate was polymerized in a 5 mol/L benzene solution, with $1.5 \times 10^{-2}$ mol/L of AIBN as initiator, at temperatures between 40 and 80 °C. For comparison, methyl methacrylate was also polymerized between 40 and 60 °C in similar experimental conditions.

The absence of polymer after 10 days of polymerization at 70 and 80 °C is noteworthy. The conversion–time plots at 40, 50, 60, and 64 °C are shown in Figure 1. Analysis of the results indicates that, within experimental error, the polymerization reaction is first order with respect to monomer concentration. The constant conversion obtained at 60 °C after 6 days of polymerization could be explained taking into consideration that the concentration of initiator [I] will decay exponentially with time according to eq 1

$$[I] = [I]_0 \exp(-k_d t) \qquad (1)$$

where $[I]_0$ is the initial concentration of initiator, $t$ the reaction time, and $k_d$ the rate constant for the initiator decomposition. Taking into consideration the $k_d$ values obtained by Tobolsky et al.,[9] initiator concentration decreases 150 times after 6 days and near 800 times after 8 days of polymerization, whereas at 50 and 40 °C the decreases of initiator concentration are 5 and 2 times after 8 and 16 days of polymerization, respectively.

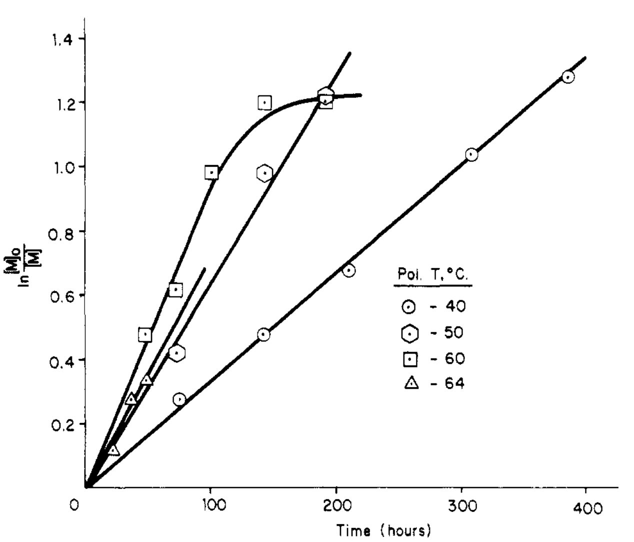


**Figure 1.** Conversion–time diagrams for the free-radical polymerization of methyl α-benzylacrylate in benzene at different temperatures.

### Table I
### Decomposition Rate Constants for AIBN and Overall Polymerization Rates of Methyl Methacrylate and Methyl α-Benzylacrylate at Several Temperatures[a]

| temp, °C | $10^6 k_d$, s$^{-1}$ | $10^5 R_p$*, mol L$^{-1}$ s$^{-1}$ | $10^8 R_p$**, mol L$^{-1}$ s$^{-1}$ | $R_p$*/ $R_p$** |
|---|---|---|---|---|
| 40 | 0.49 | 2.93 | 4.65 | 630 |
| 50 | 2.28 | 7.41 | 9.00 | 823 |
| 60 | 9.63 | 19.25 | 13.90 | 1384 |
| 64 | 16.74 | | 10.60 | |

[a] $R_p$* is the overall rate of methyl methacrylate polymerization, and $R_p$** is the overall rate of methyl α-benzylacrylate polymerization.

Overall rates of polymerization were determined from the diagrams represented in Figure 1 and the corresponding values, together with those obtained for the polymerization of methyl methacrylate in the same experimental conditions, are shown in Table I. Values of the ratio between overall rates of polymerization of methyl methacrylates and methyl α-benzylacrylate, quoted in the fifth column of Table I, seem to indicate a higher value of the termination rate constant for methyl α-benzylacrylate than for methyl methacrylate, since differences between the propagation rate constant of methyl methacrylate and the apparent propagation rate constant of methyl α-benzylacrylate would not satisfactorily account for the values obtained. In this connection values of 26 and 176 mol L$^{-1}$ s$^{-1}$ for propagation rate constants at 60 °C of α-methylstyrene and styrene, respectively, have been reported;[10,11] however, the termination rate constant at this temperature for α-methylstyrene is $10^3$ greater than that of the termination rate constant of styrene.[12] Number-average molecular weights of the polymers obtained do not change with the polymerization temperature and have values of 5400 g/mol at 40, 50, and 60 °C. The decrease of the apparent propagation rate constant of methyl α-benzylacrylate as the polymerization temperature approaches the ceiling temperature as well as the increase of the rate constant for AIBN dissociation and the high values expected for the termination rate constant of methyl α-benzylacrylate would give rise to similar molecular

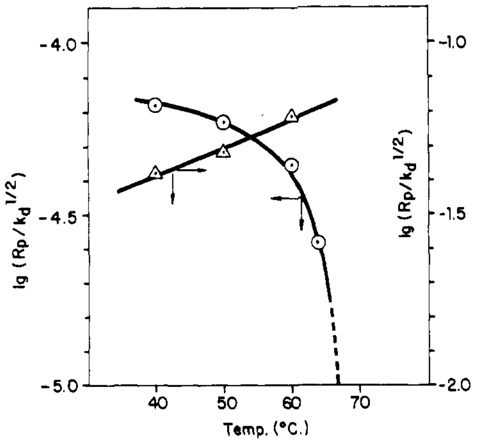


**Figure 2.** Relationship between log $(R_p/k_d^{1/2})$ and polymerization temperature in the radical polymerization of (⊙) methyl α-benzylacrylate and (△) methyl methacrylate.

weights. Similar results have been reported by Lenz et al.,[4] who did not find significant differences in both number- and weight-average molecular weights for polymers prepared from methyl or ethyl α-(phenoxymethyl)acrylates by irradiation of monomers in tetrahydrofuran with ultraviolet light in the presence of benzoin at −50 °C and in toluene solution at 60 °C, using AIBN as initiator.

The low conversion in the interval of temperatures between 40 and 64 °C and the absence of precipitate species at 70 and 80 °C, together with the low molecular weight of the polymers obtained, seem to indicate that for this sterically hindered monomer a ceiling temperature of polymerization between 60 and 70 °C could be expected in our experimental conditions.

Since the average lifetime of growing radicals is too short to reach the polymer–monomer equilibrium, the ceiling temperature in free-radical polymerization experiments is usually determined by the extrapolation to $R_p = 0$ of the diagram obtained by plotting the overall rate of polymerization ($R_p$) against the polymerization temperature. In order to avoid the effect of initiation rate on the observed overall polymerization rate, Yamada et al.[13] suggested the use of diagrams resulting from the representation of log $(R_p/k_d^{0.5})$ against polymerization temperature and in a more elaborated treatment, Yamada et al.[14] found that the representation of log $(k_p'/k_t^{0.5})$ (where $k_t$ denotes the rate constant for the termination reaction and $k_p'$ the overall rate constant for the propagation–depropagation equilibrium reaction) as a function of the reciprocal of the polymerization temperature gives a curve with a slope that approaches infinity at the ceiling temperature. In this paper we have used both treatments for the determination of the corresponding ceiling temperature.

Although it is well-known that the chemical structure and concentration of monomer modify the initiator efficiency,[3] values of $f$ for AIBN reported by Brooks in the polymerization of methyl methacrylate[15] have been used in this work and the possible variation of $f$ with the polymerization temperature has not been considered, since it is reasonable to assume that in the interval of temperatures considered changes in $f$ will not have significant effects on the overall rate of polymerization.

The values of $k_d$ quoted in Table I were calculated according to the Arrhenius equation for decomposition of AIBN reported by Tobolsky et al.[9]

Plots of treatments described by Yamada et al.,[13,14] together with the results obtained for the polymerization of methyl methacrylate, are shown in Figures 2 and 3. As can be seen, while the values of log $(R_p/k_d^{0.5})$ and log $(k_p'/k_d^{0.5})$ increase with the reaction temperature for the polymerization of methyl methacrylate, those obtained for the polymerization of methyl α-benzylacrylate decrease and the extrapolated values for the ceiling temperature are in both cases equal to 67 ± 2 °C.

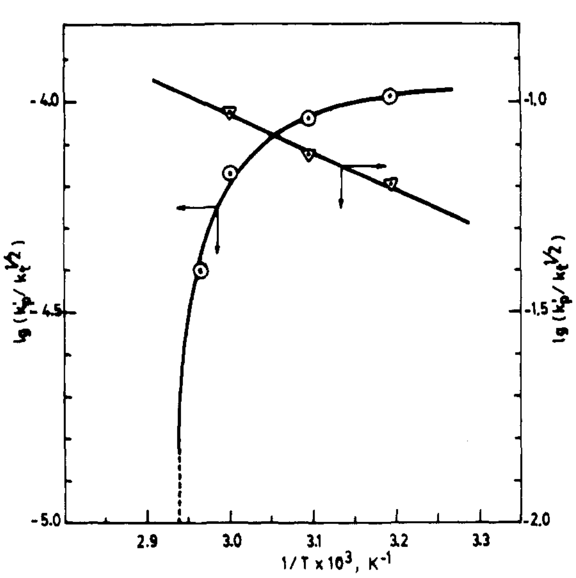


**Figure 3.** Plots of log $(k_p'/k_t^{1/2})$ against $1/T$ for (⊙) methyl α-benzylacrylate and (△) methyl methacrylate.

Only a few values on the temperature interval expected for the ceiling temperature of several α,α-disubstituted acrylic monomers have been reported in the literature. Thus, ceiling temperatures higher than 60 °C have been estimated for the free-radical homopolymerization of methyl and ethyl α-(phenoxymethyl)acrylates,[4] whereas anionic homopolymerization data indicate ceiling temperatures between 0 and −20 °C for methyl α-phenylacrylate[16] and between 0 and 30 °C for methyl α-ethylacrylate.[17] The differences in the expected ceiling temperatures for methyl α-phenylacrylate[16] and methyl α-ethylacrylate[17] could arise from the higher steric strain of the phenyl group in comparison with the ethyl group. However, the differences in ceiling temperatures expected for methacrylate-type monomers containing substituents on the α-methyl position, i.e., methyl α-ethylacrylate,[17] methyl and ethyl α-(phenoxymethyl)acrylates,[14] and methyl α-benzylacrylate, could be related to both steric strain and resonance stabilization differences.

From a structural point of view, the influence of substituent R on the steric strain of acrylic derivatives ($CH_2{=}CR{-}COOCH_3$) may be in the order R = α-benzyl > α-phenoxymethyl > α-ethyl. However, no additional conjugative effects could be expected on the methacrylate-type monomers for the considered substituents on the α-methyl position, although the radical stabilization is affected by the chemical structure of substituents. Thus, while the α-ethyl substituent only could contribute through hyperconjugative effects to the stabilization of poly(methyl α-ethylacrylate) radicals, poly(methyl or ethyl α-(phenoxymethyl)acrylates) and poly(methyl α-benzylacrylate) radicals could be stabilized by the conjugative effect of oxygen electrons and for the π electrons of the aromatic ring, respectively. In this way, the stability of radicals could be in the order methyl α-benzylacrylate > methyl or ethyl α-(phenoxymethyl)acrylates > methyl α-ethylacrylate.

From this point of view and taking into consideration the experimental data, the differences in ceiling temperatures for methacrylate-type monomers containing substituents on the α-methyl position seem to arise from energetic differences between stabilization of monomers and radicals more so than differences on steric strain, but more experimental data would be necessary to give definitive conclusions.

**Registry No.** Methyl α-benzylacrylate, 3070-71-1; dimethyl malonate, 108-59-8; dimethyl benzylmalonate, 49769-78-0; benzyl chloride, 100-44-7; monomethyl benzylmalonate, 54561-75-0; formaldehyde, 50-00-0.

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# Substitution Reaction of Poly((chloromethyl)styrene) with Salts of Various Nucleophilic Reagents Using Phase-Transfer Catalysts

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ABSTRACT: The substitution reactions of poly((chloromethyl)styrene) (polymer 1) with various nucleophilic reagents were studied by using phase-transfer catalysts (PTCs) such as tetrabutylammonium bromide (TBAB), tetrabutylphosphonium bromide (TBPB), dicyclohexyl-18-crown-6 (DCHC), 18-crown-6 (CR6), and 15-crown-5 (CR5) in solid–liquid and liquid–liquid two-phase reaction systems. From these studies, the following was found. The quaternary salts TBAB and TBPB were more effective than the crown ethers DCHC, CR6, and CR5 in the reaction of the chloromethyl group in polymer 1 with the salts of O-anions such as carboxylate and phenolate. On the other hand, the lipophilic crown ether DCHC showed higher catalytic activity than the quaternary salts in the reaction of the chloromethyl group in the polymer with the salts of S-anions. Also, the catalytic activity of the PTCs in the reaction of polymer 1 with salts of N-anions lies between those in the reactions of polymer 1 with salts of S-anions and O-anions. Generally, the solid–liquid two-phase system gives a polymer with a higher degree of substitution than does the liquid–liquid two-phase system. However, when lipophilic PTCs such as DCHC and lipophilic reagents such as S-anions are used, polymers with high degrees of substitution can be obtained by employing the liquid–liquid two-phase system.

## Introduction

The substitution reactions of the pendant chloromethyl groups in the polymers with some nucleophilic reagents have been investigated[1] in aprotic polar solvents such as hexamethylphosphorus triamide, *N,N*-dimethylformamide (DMF), dimethyl sulfoxide and *N*-methyl-2-pyrrolidone, and the effect of the polymer skeletons on the reactivity of the pendant chloromethyl groups and the solvent effect in the reactions have been determined. Also, it was elucidated that the addition of the quaternary salts or crown ethers to these reaction systems accelerated[1c,e] the reaction of the pendant chloromethyl group in the polymer with the nucleophilic reagents. Recently, the substitution reactions of the pendant chloromethyl groups in the polymers with nucleophilic reagents have been studied[2] by using phase-transfer catalysts (PTCs) in nonpolar solvents such as toluene, chlorobenzene, diglyme, and others. This simple and economical method is very important for the modifications of the commercial polymers and the syntheses of the functional polymers such as polymer supports, polymeric reagents, polymeric catalysts, and polymeric carriers. Also the reactions of the active alkyl halide and alkyl sulfonates with nucleophilic reagents were carried out[3] with a great number of quaternary salts and crown ethers as PTCs in organic chemistry. The catalytic effect in each reaction, the reactivity of alkyl halides with nucleophilic reagents, and the solvent effect were studied from those results. However, the relationship between the catalytic activity of PTCs and the reactivity of haloalkyl groups with nucleophilic reagents has not been reported on the reactions of pendant chloromethyl groups contained in the polymers and the alkyl halides with nucleophilic reagents using PTC so far.

In an earlier article,[4] we have established the relationship between the catalytic activity of PTCs and the reactivity of chloromethyl group with the nucleophilic reagents in the solid–liquid two-phase reactions of poly((chloromethyl)styrene) (polymer 1) with potassium acetate and potassium thioacetate using quaternary salts and crown ethers as a PTC under mild conditions.

In this article, we wish to describe the catalytic effect of PTCs in the substitution reaction of polymer 1 with

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