# Synthesis and Polymerization of Alkyl $\alpha$ -(Phenoxymethyl)acrylates

# Robert W. Lenz,\* Keith Saunders, and T. Balakrishnan

Material Research Laboratory, Chemical Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003

### Koichi Hatada

Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan. Received December 26, 1978

ABSTRACT: Methyl and ethyl  $\alpha$ -(phenoxymethyl)acrylate were synthesized and polymerized by free-radical initiators at 60 and -50 °C. The polymers were of relatively low molecular weight, and analysis by NMR spectroscopy indicated that they were almost perfectly atactic in structure. There was little or no effect of polymerization temperature on yield, molecular weight, molecular weight distribution, or tacticity. As expected, the glass transition temperatures of the polymers were higher than those of the comparable methacrylate and  $\alpha$ -chloroacrylate polymers.

As part of a continuing program in this laboratory on the study of structure-property relationships in polymers from  $\alpha, \alpha$ -disubstituted ethylene monomers (principally acrylates),<sup>1</sup> we have initiated an investigation on the synthesis and controlled polymerization of methacrylate-type monomers containing substituents on the  $\alpha$ methyl position. The first such monomer investigated is that containing the phenoxy group, and the present report concerns the synthesis, preparation, structure, and properties of the methyl and ethyl ester derivatives of these  $\alpha$ -(phenoxymethyl)acrylates:



Reports of other monomers in this series will be made in the future.

#### **Monomer Preparation**

The monomers were prepared in good overall yield starting from the condensation of ethyl malonate with formaldehyde and reacting the bis(hydroxymethyl) derivative so formed with hydrogen bromide to generate a mixture containing approximately 75 mol % of the desired bis(bromomethyl) compound I and 25% of the interesting reactive monomer  $\alpha$ -(bromomethyl)acrylic acid as follows:

$$CH_{2}(COOC_{2}H_{s})_{2} + CH_{2}O \rightarrow (HOCH_{2})_{2}C(COOC_{2}H_{s})_{2} \xrightarrow{HBr} CH_{2}Br$$

$$CH_{2}=C' + (BrCH_{2})_{2}CHCOOH$$

$$I$$

$$I + ROH \rightarrow (BrCH_{2})_{2}CHCOOR \xrightarrow{C_{6}H_{s}OH} CH_{2}=C' \xrightarrow{CH_{2}OPh} CH_{2}CHCOR$$

$$I$$

$$I$$

Intermediate I could be readily esterified in alcoholic sulfuric acid solution, and the ester was converted directly to the desired monomer II by reaction with phenol in a solution of sodium hydroxide in methanol. Monomer structures were verified by NMR analysis.

### **Polymer Preparation and Properties**

In an attempt to prepare polymers of different tacticities, the methyl and ethyl ester derivatives of II were polymerized at two different temperatures, 60 and -50 °C, by free-radical initiators. For the former, azobis(isobutyronitrile) was used in toluene solution, while for the latter, irradiation of the monomer in tetrahydrofuran with ultraviolet light in the presence of benzoin was used. Polymer yields were approximately 10% in the former and 25% in the latter for both monomers. Results from the characterization of the methyl and ethyl ester polymers obtained from the high- and low-temperature polymerization reactions are collected in Table I, including both molecular weight measurements by gel-permeation chromatography and tacticity determinations by NMR.

The relatively low yields and molecular weights obtained are most likely a reflection of the low ceiling temperatures of polymerization to be expected for these sterically hindered monomers, although the molecular weights were not significantly affected by changes in polymerization reaction temperature. That is, a decrease in reaction temperature of 110 °C (from 60 to -50 °C) did not result in an increase in molecular weight for either ester monomer, although some increase in yield was obtained.

**Polymer Tacticity.** Quite remarkably, as shown by the data in Table I, no change in tacticity was observed for the polymers as a function of temperature of preparation. At both temperatures used, 60 and -50 °C, almost perfectly atactic polymers were obtained. It should be noted that the data in Table I are for the methyl ester polymer at 60 °C and the ethyl ester polymer at -50 °C. Tacticity analyses were not made for both polymers at both temperatures, so it is assumed that the results for one polymer prepared at one temperature apply equally well to the other at the same reaction temperature. The glass temperature data in Table I support this assumption, as discussed later.

The undecoupled <sup>1</sup>H-NMR spectrum of poly[ethy]  $\alpha$ -(phenoxymethyl)acrylate] was not sensitive to the stereoregularity of the polymer and gave no information on the tacticity, although this type of analysis was applied effectively for the methyl ester polymer. For the ethyl ester polymer, <sup>13</sup>C NMR analysis was effective for determining tacticity. The resonances of the carbonyl carbon in this polymer split into three peaks (Figure 1) and the <sup>13</sup>C spin-lattice relaxation time,  $T_1$ <sup>(13</sup>C), for these three peaks increased in the order of increasing magnetic field as shown in Table II. Previous investigations have revealed that the carbons in isotactic  $poly(\alpha$ -substituted acrylates) always show longer  $T_1$ 's than those in the corresponding syndiotactic ones; that is the  $T_1$  values should be in the order of isotactic > heterotactic > syndiotactic triads.<sup>2</sup> Hence, on this basis, it is possible to assign the carbonyl carbon peaks to syndiotactic, hete-

Table I Characterization of Methyl and Ethyl a. (Phenoxymethyl) acrylete Polymers

ester monomer	polym temp, °C	mol $wt^a$			tacticity, triad % <sup>b</sup>			
		M <sub>n</sub>	Mw	$M_{\rm w}/M_{\rm n}$	I	Н	S	$T_{g}$ , °C
methyl	60	4600	9400	2.04	23	49	28	114
	- 50	4400	9200	2.08				112
ethyl	60	5900	10400	1.75				86
	50	6200	10300	1.68	25	47	28	90

<sup>a</sup> As determined by GPC relative to polystyrene standards. <sup>b</sup> I = isotactic; H = heterotactic; S = syndiotactic triads.

Table II NMR Analysis of Methyl and Ethyl  $\alpha$ -(Phenoxymethyl)acrylate Polymers



**Figure 1.** <sup>13</sup>C-NMR spectra of carbonyl and C-1 (phenyl) carbons in (A) poly[methyl  $\alpha$ -(phenoxymethyl)acrylate] and (B) poly[ethyl  $\alpha$ -(phenoxymethyl)acrylate] measured in toluene- $d_8$  (1.0 mol/L) at 25 MHz and 110 °C: (A) 2000 scans, (B) 1700 scans.

rotactic, and isotactic triads with increasing magnetic field. The intensity measurement of the peaks indicated that the tacticity of the polymer is I 25%, H 47%, and S 28% (Table I). Because the polymers were almost perfectly atactic, with syndiotactic and isotactic triad contents being essentially identical, however, the assignment order made little difference as long as the heterotactic peak was selected as the central one.

The tacticity sequence of the chemical shifts of the carbonyl carbon atoms was the same as that observed in poly(methyl methacrylate)<sup>13</sup> but opposite to that in the poly( $\alpha$ -chloroacrylates);<sup>3</sup> that is, the sequence in the present case was syndiotactic < heterotactic < isotactic triads with increasing field strength.

The resonance of the C-1 carbon in phenyl ring also split

The <sup>1</sup>H-NMR spectrum of poly[methyl  $\alpha$ -(phenoxymethyl)acrylate] is shown in Figure 2. The methoxyl methyl protons show three peaks at 3.24, 3.12, and 2.98 ppm, which could be assigned to syndiotactic, heterotactic, and isotactic triads with increasing magnetic field by the comparison of the spectrum with the <sup>13</sup>C-NMR spectrum. The small splitting in the heterotactic peak should be due to the tactic pentad structures. The agreement of triad amount between the <sup>13</sup>C and <sup>1</sup>H measurements was within 3 to 4%.

peaks of the carbonyl carbon in the poly[ethyl  $\alpha$ -(phen-

oxymethyl)acrylate]. The three peaks in the C-1 carbon

resonance were well resolved and could be assigned to

syndiotactic, heterotactic, and isotactic triads in the order

of increasing magnetic field similarly to those in the

poly[ethyl  $\alpha$ -(phenoxymethyl)acrylate]. The polymer was

also completely atactic.

**Glass-Transition Temperature.** Glass-transition temperatures,  $T_{g}$ , as determined by differential scanning calorimetry, DSC, for the two different ester polymers, are

collected in Table I. The  $T_g$  values were essentially identical within each ester polymer for the polymers prepared either at high or low temperatures because the polymers did not vary in molecular weight or tacticity as a function of polymerization temperature.<sup>1</sup> As expected, the  $T_{\rm g}$  values of the methyl ester polymer were considerably higher (even at lower molecular weights) than those of the related ethyl ester polymers because of the generally observed increasing internal plasticization by the ester group with increasing size of the alkyl group.<sup>4</sup>

# Conclusions

Polymers with almost perfectly atactic structures are uncommon, but such structures have been reported for the free-radical polymerizations of methyl acrylate,<sup>5</sup> ethyl acrylate,<sup>6</sup> vinyl chloride,<sup>7</sup> acrylonitrile,<sup>8</sup> and vinyl acetate.<sup>9</sup> Trimethylsilyl acrylate also gave atactic polymers at higher polymerization temperatures.<sup>6</sup> In the free-radical polymerization of  $\alpha$ , $\alpha$ -disubstituted olefin monomers, such as methyl methacrylate<sup>10</sup> and  $\alpha$ -methylstyrene,<sup>11</sup> syndiotactic polymers are usually obtained, although the fractions of heterotactic triads in these products generally increase with increasing polymerization temperatures.

Large substituents at the  $\alpha$  position of acrylate monomers have been shown to favor the formation of atactic polymer, and, as shown by one of us, methyl  $\alpha$ -phenylacrylate gave an almost perfectly atactic polymer by free-radical as well as by anionic polymerization.<sup>12</sup> As discussed previously, the formation of an atactic polymer indicates that the steric and polar interactions of the two  $\alpha$  substituents are nearly equal in the stereoregulating step, that is, in the formation of the new tetrahedral center on addition to the next monomer unit.<sup>12</sup> In the present case, the insensitivity of tacticity to polymerization temperature specifically indicates that the activation energies of syndiotactic and isotactic addition were the same and were independent of ester type.

As expected for the presence of the large  $\alpha$ -phenyl substituent, the glass temperatures of these polymers were quite high and were higher than those of either methacrylate or chloroacrylate polymers. For example, at comparable molecular weights, the glass temperature of poly(ethyl  $\alpha$ -chloroacrylate) having a triad tacticity distribution of 31% I, 44% H, and 25% S was 70  $^{\circ}C^{1}$ compared to 90 °C for poly[ethyl  $\alpha$ -(phenoxymethyl)acrylate] of 25% I, 47% H, and 28% S.

Atactic poly[methyl  $\alpha$ -(phenoxymethyl)acrylate] and poly(methyl  $\alpha$ -phenylacrylate) had glass temperatures of 117 and 118 °C, respectively, but the latter polymer may have been of higher molecular weight.<sup>12</sup> In contrast, poly(methyl  $\alpha$ -benzylacrylate) was observed to have essentially the same glass temperature, approximately 45 °C, as poly(methyl methacrylate) at a similar tacticity and molecular weight. Unfortunately, both tacticity and molecular weight have a very strong effect on this property, and more careful comparisons of samples of different polymers with identical structural characteristics must be made.

#### **Experimental Section**

Dimethyl Bis(hydroxymethyl)malonate. In a 1-L beaker, 90 g (3 mol) of formaldehyde was combined with 8 g of  $K_2CO_3$ , followed by the addition of 160 g (1 mol) of diethyl malonate while maintaining the temperature below 20 °C to prevent polymerization of formaldehyde. After being stirred for 1 h, the reaction contents were transferred to a separatory funnel containing 320 mL of a saturated ammonium sulfate solution and shaken well. To this mixture was added 320 mL of diethyl ether, the ether layer was separated and dried over 20 g of anhydrous  $Na_2SO_4$ , ether and excess formaldehyde were distilled off, and the residual liquid was placed in an ice-bath until the product crystallized (2-3 h). Isopropyl ether (500 mL) was added and the mixture was warmed to 50 °C until the product dissolved. The solution was transferred to a flask, stirred in an ice-bath until a thick suspension of crystals formed, and left there for an additional 2 h. After the white product was filtered and dried under vacuum for 24 h, a melting point of 48-50 °C was observed. The yield was 165 g or 75%. Recrystallization from isopropyl ether gave a product melting at 50-51 °C.

 $\beta$ , $\beta'$ -Dibromoisobutyric Acid. One mole (220 g) of the product from above and 800 mL (7 mol) of a 48% hydrobromic acid solution were combined in a 2-L, one-neck boiling flask and heated until ethyl bromide began to distill from the reaction mixture. After this liquid ceased to distill, the reaction mixture was refluxed for 6 h. Subsequently, the product was crystallized from solution in an ice-bath for 3 h. The solid was filtered, washed with ice water, and dried as before. A second fraction of crystals was obtained by removing approximately 400 mL of liquid from the filtrate and repeating the crystallization. Crops of 120 and 50 g resulted in a combined yield of 70%, with a melting point of 101-103 °C.

Methyl  $\beta_{,\beta'}$ -Dibromoisobutyrate. This esterication reaction was carried out by combining 246 g (1 mol) of the acid from above, 250 mL of methanol, and 2 mL of concentrated sulfuric acid in a round-bottom flask. After 12 h of reflux, the reaction mixture was extracted with 100 mL of water. The nonaqueous layer was dried over anhydrous sodium sulfate, filtered, and subjected to distillation to remove the alcohol. The remaining liquid was distilled under a reduced pressure of 5 mm Hg, giving a colorless liquid boiling at 70-72 °C in a 70% yield.

Methyl  $\alpha$ -(Phenoxymethyl)acrylate. The previous product (0.5 mol) was added slowly to a solution of sodium hydroxide (1 mol) and phenol (1 mol) in 200 mL of methanol. After 6 h of stirring at room temperature, methanol was removed by normal distillation. The residual liquid was extracted with 200 mL of diethyl ether, washed with 50 mL of 10% sodium hydroxide solution and 50 mL of water, and dried over anhydrous magnesium sulfate. Removal of the ether after filtration left a colorless liquid in 85% yield, boiling point 85 °C/2 mm. The boiling point of the ethyl ester was 94 °C (2 mm Hz). Elemental analyses of the two esters were as follows: Calcd for methyl ester: C, 68.73; H, 6.30. Found: C, 67.69; H, 6.54. Calcd for ethyl ester: C, 69.88; H, 6.84. Found: C, 67.88; H, 7.18.

Acknowledgment. The authors are grateful to UNESCO for the fellowship provided to T.B. and to the NSF-sponsored Materials Research Laboratory at the University of Massachusetts for the use of their facilities and financial support. The measurements of the tacticity and spin-lattice relaxation times were carried out by Mr. T. Kitayama at Osaka University in his Doctoral thesis research program.

#### **References and Notes**

- (1) G. R. Dever, F. E. Karasz, W. J. MacKnight, and R. W. Lenz,
- K. Hatada, T. Kitayama, Y. Okamoto, K. Ohta, Y. Umemura, and H. Yuki, *Makromol. Chem.*, **179**, 485 (1978); J. R. Lyerla, Jr., T. T. Horikawa, and D. E. Johnson, J. Am. Chem. Soc., 99, 2463 (1977); K. Hatada, T. Kitayama, and R. W. Lenz, Polym. Prepr., Jpn., 27, 503 (1978); K. Hatada, T. Kitayama, K. Ohta,
- Y. Ókamoto, H. Yuki, and R. W. Lenz, *ibid.*, 27, 1632 (1978).
   K. Hatada, T. Kitayama, and R. W. Lenz, *Makromol. Chem.*, 179, 1951 (1978)
- (4) F. A. Karasz and W. J. MacKnight, Macromolecules, 1, 537 (1968).
- (5) K. Matsuzaki, T. Uryu, A. Ishida, T. Ohki, and M. J. Takeuchi, J. Polym. Sci., Part A 1, 5, 2167 (1967).
- (6) T. Uryu, H. Shiroki, M. Okada, K. Hosonuma, and K. Matsuzaki, J. Polym. Sci., Part A-1, 9, 2335 (1971).
- (7) F. A. Bovey, Acc. Chem. Res., 1, 175 (1968).
   (8) K. Matsuzaki, M. Okada, and T. Uryu, J. Polym. Sci., Part A-1, 9.1701 (1971)
- (9) S. Murahashi, S. Nozakura, M. Sumi, H. Yuki, and K. Hatada,
- (9) S. Murahashi, S. Nozakura, M. Sumi, H. Yuki, and K. Hatada, J. Polym. Sci., Polym. Lett. Ed., 4, 65 (1966).
  (10) R. C. Ferguson, Macromolecules, 2, 237 (1969).
  (11) S. Brownstein, S. Bywater, and D. J. Worsfold, Makromol. Chem., 48, 127 (1969).
  (12) H. Yuki, K. Hatada, T. Niinomi, M. Hashimoto, and J. Oshima, Polym. J., 2, 629 (1971).
- (13) Y. Inoue, A. Nishioka, and R. Chujo, Polym. J., 2, 535 (1971).