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Poly(alkyl α-bromoacrylates). 2. Preparation and Properties of the Methyl, Ethyl, *n*-Propyl, Isopropyl, *n*-Butyl, and *n*-Pentyl Esters of Varied Tacticity[1]

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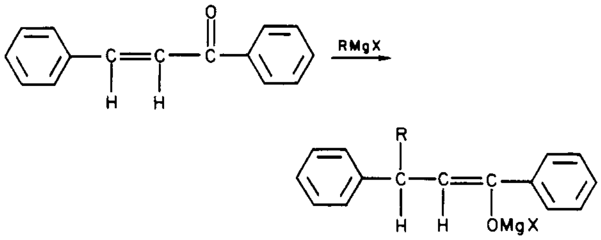
ABSTRACT: Polymers of widely ranging tacticities, from highly isotactic to highly syndiotactic, were synthesized from methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, and *n*-pentyl α-bromoacrylates. The isotactic polymers were synthesized with a modified Grignard complex consisting of the reaction product between a Grignard reagent and benzalacetophenone. A low-temperature, photolytically induced, free radical polymerization reaction was employed for the preparation of the syndiotactic polymers. Only atactic poly(*tert*-butyl α-bromoacrylate) could be synthesized because of its failure to polymerize with the modified Grignard complex or at temperatures below −20 °C. Polymer tacticity was determined by 19-MHz ^{13}C NMR spectroscopy. Complete assignments for the ten pentad peaks of the carbonyl carbon resonance were achieved for all but the isopropyl ester while a complete analysis of the tetrad tacticity for the backbone methylene carbon resonance was possible for all but the methyl ester. Because of insufficient peak separation of the quaternary carbon resonance, complete pentad assignments were not possible. The polymerization reaction mechanisms were discussed in terms of the propagation statistics which were calculated from the experimental tetrads and pentads.

Introduction

The principal motivation behind this investigation was to synthesize a series of high molecular weight, highly stereoregular poly(alkyl α-bromoacrylates) in which the influence of the steric structure on the glass transition temperature could be evaluated. Previous reports from this laboratory have been concerned with the synthesis,[2,3] characterization,[4,5] and properties[6,7] of the corresponding alkyl α-chloroacrylate polymers. These investigations revealed that the glass transition temperature differences for several isotactic–syndiotactic pairs of the poly(alkyl α-chloroacrylates) were somewhat lower than predicted by theory.[8] This result was attributed, at least in part, to the intermolecular forces arising from the polar chlorine atom.

The poly(alkyl α-bromoacrylate) series was studied next because of the lower polarity associated with the bromine atom as compared to the chlorine atom. However, during this investigation, the alkyl α-bromoacrylate polymers were found to undergo an internal cyclization reaction, producing butyrolactone groups along the polymer backbone. The formation of this five-membered lactone occurred at temperatures as low as 60 °C and, therefore, the precise evaluation of the glass transition temperatures was impossible by standard techniques. The effects of polymer tacticity on the degree of lactone formation will be reported in a forthcoming publication.

The synthesis of both highly isotactic and highly syndiotactic polymers was required to determine the effects of tacticity on physical properties. The isotactic samples were prepared by the method developed by Breslow and Kutner,[9] who synthesized the first highly isotactic, crystallizable poly(methyl α-chloroacrylate) of high molecular weight with a modified Grignard complex catalyst. Although numerous techniques and catalysts have been tried, none have come close to duplicating this result.[2,3,10–12] The complex, an addition product of a Grignard reagent of an α,β-unsaturated ketone such as benzalacetophenone, was presumed to have the structure[9] in eq 1, where RMgX represents the Grignard reagent. Typical Grignard reagents which have been found to be effective were ethylmagnesium chloride, isopropylmagnesium chloride and ethylmagnesium bromide, and catalyst activity was also observed with other α,β-unsaturated ketones like benzalacetone. It was reported[9] that the polymerizations could



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be carried out at temperatures from −30 to +68 °C with no change in polymer stereoregularity although NMR spectra were not offered as proof. However, it was found that excess benzalacetophenone decreased the catalyst efficiency but increased its stereospecificity. On the other hand, an excess of the Grignard reagent produced the desired catalyst complex as well as other catalytic species, which formed polymers with lower isotactic contents.

The catalyst structure proposed by Breslow and Kutner was substantiated by Uryu, Okaku, and Matsuzaki[12] by reacting benzalacetophenone with ethylmagnesium chloride and phenylmagnesium chloride under conditions identical with those used for catalyst preparation. After the reaction products were hydrolyzed with hydrochloric acid and purified, the melting points and infrared and NMR spectra confirmed the structures to be phenyl β-phenylbutyl ketone and β,β-diphenylethyl ketone, respectively. These compounds corresponded to those to be expected for the hydrolysis products of the catalyst species suggested by Breslow and Kutner.

An investigation concerning the effect of α,β-unsaturated ketones on the preparation of isotactic poly(ethyl α-chloroacrylate) revealed that compounds such as dibenzalacetone, benzalacetone, mesityl oxide, and methyl vinyl ketone were nearly as effective as benzalacetophenone.[12] Of all the ketones tried, benzalacetophenone produced the highest degree of isotactic units, 87% on a triad basis. Propiophenone and propylene oxide displayed no stereospecific activity and formed only atactic polymers. The catalyst structure prepared with ethylmagnesium chloride and either propiophenone or propylene oxide should have had a saturated alkoxide functional group, but the catalysts which were effective for forming stereoregular polymers should contain an unsaturated alkoxide function. Thus it seems reasonable to assume that the double bond exerted a controlling influence on the mechanism involved in isotactic placement. That is, the stereoregulating power of the catalyst complex required the presence of both a carbon–carbon double bond and an oxygen–magnesium alkoxide bond.

Dever and co-workers[3] successfully synthesized isotactic polymers of the methyl, ethyl, and isopropyl α-chloroacrylates with this polymerization catalyst. Triad tacticities of 68, 61, and 51% were achieved for the three esters, respectively. Ethylmagnesium chloride and benzalacetophenone were employed as the catalyst combination in all cases.

Experimental Section

Alkyl 2,3-Dibromopropionate Synthesis. The primary and secondary esters of the poly(alkyl α-bromoacrylates) were prepared by the method of Marvel and Cowan initially developed for methyl α-bromoacrylate.[13] Only the methyl, ethyl, and *sec*-butyl esters had been previously prepared.[13,14] In this procedure the corresponding alkyl 2,3-dibromopropionates were used as intermediates. The synthesis consisted of three steps: esterification of acrylic acid, bromination of the vinyl ester to form the alkyl 2,3-dibromopropionate, and dehydrobromination. Quinoline, which was used to remove hydrogen bromide, abstracted exclusively the β bromine and the α hydrogen and produced the α-bromoacrylate monomer in a 70–85% yield.

Methyl 2,3-Dibromopropionate.[14] Methyl acrylate (86 g, 1 mol) was dissolved in 150 mL of distilled methanol in a 1-L, one-neck boiling flask. Cold bromine (60 mL, 2.3 mol) was added dropwise over a 1-h period with rapid magnetic stirring. The reaction temperature was maintained below 50 °C with an ice bath to minimize any possible thermal polymerization. Since a small excess of bromine was used in the reaction, the solution remained a light reddish color. After the reaction mixture was allowed to stand overnight, the methanol was distilled off and the product, a colorless liquid, was removed by vacuum distillation: yield 191.5 g (0.8 mol), 80%; bp 92–95 °C (20 mmHg).

Ethyl, *n*-Propyl, Isopropyl, *n*-Butyl, and *n*-Pentyl 2,3-Dibromopropionates. These compounds were prepared from acrylic acid but a modification of the synthetic procedure was developed so that the esterification and bromination reactions were effectively consolidated into one. Thus 72 g (1 mol) of acrylic acid was combined with 250 mL of the appropriate alcohol (distilled) in a 1-L, one-neck boiling flask followed by the addition of 60 mL (2.3 mol) of cold bromine. The reaction was left overnight, 75 mL of benzene was added, and an azeotropic distillation was conducted for 24–36 h to remove the esterification product, water. The propionate was removed under reduced pressure and yields in excess of 80% were achieved in most cases. Apparently, the formation of hydrobromic acid from bromine and water in the system provided an excellent catalyst for the esterification reaction.

Ethyl 2,3-dibromopropionate:[15] yield 190 g (0.75 mol), 75%; bp 80–82 °C (5 mmHg).

***n*-Propyl 2,3-dibromopropionate:**[16] yield 235 g (0.86 mol), 86%; bp 78–80 °C (2 mmHg).

Isopropyl 2,3-dibromopropionate:[17] yield 218 g (0.80 mol), 80%; bp 143–146 °C (60 mmHg).

***n*-Butyl 2,3-dibromopropionate:**[18] yield 245 g (0.85 mol), 85%; bp 120 °C (5 mmHg).

***n*-Pentyl 2,3-dibromopropionate**: yield 215 g (0.71 mol), 71%; bp 108–110 °C (1 mmHg).

Monomer Synthesis. In a 500-mL, one-neck boiling flask was placed 100 g (0.4 mol) of the alkyl 2,3-dibromopropionate. Following a 20-min purge with prepurified nitrogen, 65 g (0.5 mol) of freshly distilled quinoline was added slowly, with the formation of a reddish brown color. At this point, gentle heating was applied and a dark reddish brown precipitate materialized, presumably quinoline hydrobromide. The alkyl α-bromoacrylate, a colorless liquid, was immediately distilled from the reaction mixture under reduced pressure.

Methyl α-bromoacrylate: yield 55 g (0.33 mol), 83%; bp 80–82 °C (60) [lit.[13] bp 72–74 °C (78 mmHg)]; $d^{13} = 1.61$.

Ethyl α-bromoacrylate: yield 62 g (0.34 mol), 86%; bp 60–62 °C (20 mmHg) [lit.[14] bp 63.5–65 °C (15 mmHg)]; $d^{14} = 1.458$.

***n*-Propyl α-bromoacrylate**: yield 52 g (0.27 mol), 67%; bp 79–81 °C (22 mmHg); $d = 1.357$.

Isopropyl α-bromoacrylate: yield 49 g (0.25 mol), 63%; bp 73–75 °C (20 mmHg); $d = 1.296$.

***n*-Butyl α-bromoacrylate**: yield 61 g (0.30 mol), 74%; bp 94–96 °C (20 mmHg); $d = 1.321$.

***n*-Pentyl α-bromoacrylate**: yield 64 g (0.29 mol), 73%; bp 113–115 °C (20 mmHg); $d = 1.224$.

***tert*-Butyl α-Bromoacrylate Synthesis.** The preparation of this monomer could not be achieved by the previous technique due to the reactive nature of *tert*-butyl alcohol. *tert*-Butyl alcohol displayed a tendency toward dehydration in an acidic medium, and if hydrobromic acid was present, formation of *tert*-butyl bromide occurred. To avoid this problem, 2,3-dibromopropionyl chloride was used as the intermediate in the esterification. This compound exhibited a high reactivity toward the tertiary alcohol, which minimized the side reactions associated with conventional esterification. The reaction pathway first involved the preparation of 2,3-dibromopropionic acid from acrylic acid followed by treatment with thionyl chloride to form 2,3-dibromopropionyl chloride. *tert*-Butyl α-bromoacrylate was then obtained directly from the acid chloride and *tert*-butyl alcohol in the presence of quinoline.

2,3-Dibromopropionic Acid.[14] In a 1-L, one-neck boiling flask was placed 72 g (1 mol) of acrylic acid and 200 mL of diethyl ether. Cold bromine (60 mL) was added dropwise with rapid magnetic stirring. The temperature of the reaction mixture was controlled by both the rate of bromine addition and the diethyl ether solvent reflux. It was found that a solvent was necessary in this step due to the exothermic nature of the reaction. Without a solvent, localized heating resulted in large amounts of poly(acrylic acid). After the reaction was allowed to stir for approximately 24 h, the diethyl ether was distilled off and the product removed by vacuum distillation. The product was a white crystalline solid and had a boiling point of 110 °C (1 mmHg): mp 64–66 °C; yield 108 g (0.78 mol), 78%.

2,3-Dibromopropionyl Chloride.[14] A mixture of 80 g (0.35 mol) of 2,3-dibromopropionic acid was added to a 250-mL round-bottom flask and heated gently until it dissolved. Immediately, 80 g (1 mol) of thionyl chloride was added in a dropwise manner. At this point the reaction had not yet commenced since the liberation of hydrochloric acid was not observed. The reaction was left overnight with continuous stirring followed by 2 or 3 h of gentle reflux. Not long after the reflux began, the evolution of hydrochloric acid from the reaction mixture was detected. The excess thionyl chloride was removed by distillation and the product, a light yellow liquid, was removed under reduced pressure: yield 65 g (0.24 mol), 71%; bp 80–82 °C (20 mmHg).

***tert*-Butyl α-Bromoacrylate.** Twenty-seven grams (0.1 mol) of the above 2,3-dibromopropionyl chloride was added to a 250-mL round-bottom flask containing 50 mL of dry (distilled from calcium hydride) *tert*-butyl alcohol. With rapid magnetic stirring, 35 mL (0.3 mol) of freshly distilled quinoline was added slowly and immediately the reaction mixture turned red and became progressively darker, almost brown, with subsequent additions. After all the quinoline had been added, the excess *tert*-butyl alcohol was distilled from the reaction mixture followed by the final product under reduced pressure. The monomer, as with the other monomers in the series, was collected at −78 °C to prevent polymerization. Quinoline was employed for two purposes in this reaction. One was to remove hydrogen bromide as in the previous reactions and the second was to complex the byproduct, hydrochloric acid, as it was liberated in the esterification reaction. In this way two steps were consolidated into one, thereby omitting the need for isolation of *tert*-butyl 2,3-dibromopropionate. Although this method was suitable for the preparation of all the esters, it was not the preferred technique due to the lower overall yields and the sensitive nature of the acid chloride. *tert*-Butyl α-bromoacrylate: yield 11 g (0.053 mol), 53%; bp 53–55 °C (1 mmHg).

It is necessary to point out that all of the above monomers were found to undergo polymerization within minutes in the bulk state at ambient temperature. This problem was alleviated by collecting the monomer at −78 °C as it distilled from the reaction mixture and storing it at this temperature in the crystalline state until immediately before use. Free radical inhibitors such as hydroquinone were found to be ineffective in preventing polymerization. The methyl and ethyl esters polymerized considerably faster than the other esters. Also, the monomers turned yellow after being exposed to light for a short period of time. When they were effectively shielded from the light, the monomers remained colorless and polymerized at a much slower rate.

Polymerization Techniques. Syndiotactic Polymers. The syndiotactic polymers were synthesized by a low-temperature free radical reaction in 40–60% by volume solutions in either toluene, benzene, or tetrahydrofuran. Reaction temperatures from −40 to −78 °C were employed although the majority of the experiments were performed at −40 °C. Ultraviolet radiation from a low-pressure mercury vapor lamp was used in conjunction with benzoin for initiation.

The experimental apparatus consisted of a quartz reaction tube, 25 mm in diameter and 30 cm in length, immersed in a large Dewar (20 cm in diameter) containing the mercury vapor lamp and a stirring device. A cooling coil and temperature probe connected to a refrigeration unit was used to achieve the required temperatures. Methanol served as an excellent cooling medium because of its minimal absorption in the ultraviolet region and because it remained in the liquid state to well below −78 °C. Initiator concentrations of 0.5 mol % and polymerization times of 18 h were used in most cases. Prepurified nitrogen was bubbled throughout the reaction, and it served both as an inert atmosphere and as a means of agitation.

A specified amount of the photosensitizer, benzoin, was added to the reaction tube followed by the addition of freshly distilled solvent. After the photosensitizer had dissolved, the reaction vessel was immersed into the thermostatically controlled bath and nitrogen was bubbled through for 30 min. After dropwise addition of the monomer, the nitrogen purge was continued for an additional 15 min, after which the mercury vapor lamp was switched on. The polymerization reaction was terminated by precipitating the reaction mixture into methanol, and the polymer was filtered and dried in a vacuum. The polymers were purified by repeated precipitation in methanol from a chloroform solution and were finally dried in a vacuum oven for 48 h.

Isotactic Polymers. A modified Grignard reagent consisting of the 1,4-addition product of a Grignard reagent and an unsaturated ketone, benzalacetophenone, was used for the preparation of the isotactic polymers. The polymerization reactions were carried out in a heptane–diethyl ether solvent mixture either under purified nitrogen or under vacuum at temperatures from 35 to 55 °C.

A technique was developed to achieve a stoichiometric equivalence between the two cocatalysts, regardless of the concentrations and quantities involved. The following is a description of the procedure for the preparation of 1 mol of the catalyst. The diethyl ether and *n*-heptane solvent were distilled directly into a two-neck reaction flask equipped with a reflux condenser and a rubber septum. With rapid stirring, 0.75 mol of a 0.25 M solution of benzalacetophenone in diethyl ether was added to the reaction vessel followed by the dropwise addition of 0.25 mol of methylmagnesium chloride, 3 M in tetrahydrofuran. The mixture, now an orange suspension, was transformed into a white precipitate after heating for 15 min at 90 °C. The remainder of the Grignard reagent, 0.75 mol, was added in 0.25-mol portions followed by heating each time as before. At this point the reaction mixture consisted of a white fluffy precipitate in a clear, colorless solvent. The 0.25 M benzalacetophenone solution was added dropwise until the orange color no longer developed and then was heated for a final 20 min. The solvent was light yellow, which indicated a slight excess of the benzalacetophenone. When the temperature of the reaction mixture reached the polymerization temperature (almost all of the polymerization reactions were run at 35 °C), the monomer was added dropwise from a syringe, and the reaction vessel was sealed off. Within minutes after monomer addition, a thick suspension developed, resulting from the onset of polymerization. Initiator concentrations of 1 mol % were utilized for the majority of the reactions. All additions were carried out through self-sealing rubber septums and the reactions were shielded from light for their duration. Termination of the polymerization reactions was achieved by the addition of a 10% solution of hydrochloric acid in methanol. Because of the limited solubility of the isotactic polymers at room temperature, they were purified by Soxhlet extraction with methanol for 2 weeks.

Atactic Polymers. A conventional free radical polymerization reaction was used for the preparation of the atactic esters. The reactions were carried out at 50 °C in either toluene, benzene, or tetrahydrofuran with decanoyl peroxide as the initiator. Reaction times of between 18 and 36 h and initiator concentrations of 0.1 and 1.0 mol % were used. All reactions were purged with purified nitrogen for a minimum of 30 min before and after addition of the monomer, after which the vessel was sealed under a nitrogen atmosphere. The resulting polymers were dissolved, filtered, and reprecipitated twice from methanol and dried at 30 °C in a vacuum for 48 h.

Polymer Characterization. 90-MHz ^{1}H NMR. A Perkin-Elmer R-32 nuclear magnetic resonance spectrometer was used for analysis. Measurements were carried out at temperatures from 35 to 120 °C, with tetramethylsilane or hexamethyldisiloxane as an internal standard. The polymer spectra were measured on 5–10% (w/v) solutions in tetrachloroethane.

^{13}C NMR. A Varian CFT-20 NMR spectrometer was used for the determination of polymer tacticity. The spectra were obtained on polymers dissolved in either deuterated chloroform or a mixture of tetrachloroethane and deuterated chloroform at 35 °C with 10–40% (w/v) solutions. In general, good spectra were produced by using 10 000–50 000 transients, a pulse width of 15 s, a 1-s acquisition time, and a delay time of 1 s. An internal deuterium lock and a tetramethylsilane reference were used.

Molecular Weight. The molecular weights and molecular weight distributions were determined in tetrahydrofuran solutions with a Waters gel permeation chromatograph Model 501. Concentrations of 0.1–0.3% (w/v) were employed for all measurements. The molecular weight calibration curve was obtained with narrow molecular weight polystyrene standards under identical conditions.

Elemental Analysis. The elemental analyses of the compounds prepared in this investigation were carried out by the microanalytical laboratory of the University of Massachusetts.

Differential Scanning Calorimetry. Measurements were made on a Perkin-Elmer differential scanning calorimeter, Model 2-B, using 5–20-mg samples and scanning rates from 20–80 °C/min. Crystalline melting points and glass transition temperatures were not measurable because of the low thermal stability of the polymers. Even heating to temperatures just above room temperature resulted in the formation of lactone rings along the polymer backbone, making quantitative thermal measurements impossible.

Results and Discussion

Preparation of Isotactic Polymers. All of the polymerization reactions involving the use of the modified Grignard complex were carried out with benzalacetophenone as the unsaturated ketone and, almost exclusively, with methylmagnesium chloride as the Grignard reagent. Tables I–VII list the experimental conditions utilized in the preparation of the polymers. Ethylmagnesium chloride was used in the polymerization of both methyl α-bromoacrylate and ethyl α-bromoacrylate, but the yields were considerably lower than those from methylmagnesium chloride, and accordingly, its use was discontinued. Quantitative measurements of tacticity were not carried out on the polymers prepared from ethylmagnesium chloride but qualitatively they appeared to be less isotactic.

It was discovered that the concentration of diethyl ether had a significant effect on the yield of the polymerization reactions. When only small amounts of diethyl ether were present (<5%), the yields were always below 10%, while with diethyl ether concentrations of 10–20% the yields were generally in excess of 30%. In addition, it was found that if diethyl ether was absent from the system, the resulting polymer was severely deficient in bromine content, usually by 10–15%. The bromine contents were close to the theoretical amount as long as the ether was present in excess of about 2 vol %. Breslow and Kutner[9] briefly suggested the need for a complexing agent such as diethyl ether but stated nothing further.

The need for an exact 1:1 ratio between the two cocatalysts was pointed out previously[3,9] because evidence for a two-state propagation mechanism was observed when the Grignard reagent was present in an excess. In that case, the product could be fractionated into two types of polymers, one composed of highly isotactic units and the other composed of atactic units.

With this previous result in mind, the stereoregular polymerization reactions were carried out by employing several different ratios of the two cocatalysts in order to determine the effects of an excess of either of the cocatalysts on polymer tacticity and molecular weight. Tables I and II show the results of using different cocatalyst ratios and polymerization conditions for the preparation of poly(methyl α-bromoacrylate) and poly(ethyl α-bromoacrylate), respectively. Samples 2 and 13 were synthesized with a twofold excess of methylmagnesium chloride, and both displayed exceptionally broad molecular weight distributions with $\bar{M}_w$ to $\bar{M}_n$ ratios of 11.6 for the methyl ester and 7.89 for the ethyl ester, as shown in Table VIII. The molecular weight curves, as obtained by gel permeation chromatography, were resolved into two peaks, one for a relatively high molecular weight fraction and one for a low molecular weight fraction. Formation of a low molecular weight fraction was typical of previous results with the poly(alkyl α-chloroacrylates) initiated by Grignard reagents.[2,3,12]

A technique was developed to achieve a stoichiometric equivalence between the two cocatalysts, regardless of the concentrations and quantities involved. This preparative technique, which is described in the Experimental Section, was employed for all of the polymerization reactions using the Grignard catalysts that were prepared with an excess of benzalacetophenone (see Tables I–VI and Table VIII). The molecular weights obtained were invariably higher in those cases, and the molecular weight distributions were unimodal and displayed $\bar{M}_w/\bar{M}_n$ ratios close to 3.0.

The triad tacticities calculated from both the pentad tacticity of the carbonyl carbon resonance and the tetrad tacticity of the backbone methylene carbon resonance are listed in Table IX. The tetrad and pentad tacticities were determined by 19-MHz ^{13}C NMR spectroscopy.[19] The great increase in isotactic content as the [methylmagnesium chloride]:[benzalacetophenone] ratio was decreased illustrated the need for an equivalence between the two cocatalysts. In the cases where the catalyst ratio was equal to 1 or slightly less, the isotactic triad contents were consistent and ranged from 0.60 to 0.74. The polymers of low isotactic content could be fractionated into samples of higher and lower stereoregularity, but the tacticity of the highly isotactic polymers was not significantly improved by this technique.

Preparation of Syndiotactic Polymers. Predominantly syndiotactic polymers can be synthesized at low temperatures because of the difference in activation energies associated with iostactic and syndiotactic placement.[20] In most cases, the formation of a syndiotactic repeat unit requires slightly less activation energy than the formation of the corresponding isotactic unit, presumably due to a lower degree of steric repulsion in the formation of the syndiotactic configuration. In that case, a decrease in the polymerization temperature will produce more syndiotactic units relative to isotactic units.

In the present investigation several different polymerization solvents, including toluene, methylene chloride, and tetrahydrofuran, were used, but the best yields were achieved with toluene because of better initiator and polymer solubility at the low polymerization temperatures. The results from these polymerization reactions are compiled in Tables I–VII. Only the methyl ester monomer polymerized at −78 °C, and the only other monomer that polymerized below −50 °C was ethyl α-bromoacrylate. At −40 °C only *tert*-butyl α-bromoacrylate would not polymerize, and even at −20 °C polymer formation was not possible with this monomer.

The polymer yields decreased as the polymerization temperature decreased and as the ester group increased. For example, within the series of ester monomers studied at a polymerization temperature of −40 °C, the yields decreased in a continuous pattern from 9% for the methyl monomer to 1% for the *n*-pentyl monomer. This trend was believed to be a consequence of steric effects which became increasingly important as the size of the ester alkyl group increased. The failure of *tert*-butyl α-bromoacrylate to polymerize, even at −20 °C, further substantiated this rationale.

The syndiotactic triad tacticities for the samples polymerized at −40 °C ranged from 0.60 to 0.66 as shown in Table X. The fraction of syndiotactic triads for poly(methyl α-bromoacrylate) increased from 0.66 to 0.77 with a decrease in the polymerization temperature from −40 to −78 °C. This result was consistent with the expectation that a syndiotactic placement had a slightly lower enthalpy of activation than an isotactic placement.[20]

The difference in activation enthalpies and entropies for isotactic and syndiotactic propagation steps can be expressed by the following relationship if Bernoullian configurational statistics are obeyed:[21]

$$\Delta S_m^{\ddagger} - \Delta S_r^{\ddagger} = R \ln [P_m/(1 - P_m)] + (\Delta H_m^{\ddagger} - \Delta H_r^{\ddagger})/T$$

Table I
Reaction Conditions for the Synthesis of the Poly(methyl α-bromoacrylates)

		reaction conditions					polymer properties			
sample	initiator (I)	% I[a]	solvent[b]	temp, °C	time, h	polymer yield, %	$\overline{M}_n$[c]	$\overline{M}_w/\overline{M}_n$[c]	% C[d]	% Br[d]
1	EtMgCl-benzalacetophenone, 2-fold excess of EtMgCl	2	heptane–ether	35	15	4	3 500			
2	MeMgCl-benzalacetophenone, 2-fold excess of MeMgCl	2	heptane–ether	55	15	10	3 000	11.6	31.29	46.25
3	MeMgCl-benzalacetophenone, slight excess of benzalacetophenone	1	heptane–ether	35	18	8	31 000	3.35	30.14	47.48
4	decanoyl peroxide	1	toluene	50	42	49	33 000	2.12	29.35	48.59
5	decanoyl peroxide	0.1	toluene	50	42	18	28 000	3.01	28.93	47.95
6	decanoyl peroxide	0.1	benzene	50	42	11	24 000			
7	decanoyl peroxide	0.1	THF	50	42	10	31 500			
8	benzoin	0.5	toluene	−40	18	9	29 500	2.10	30.15	48.57
9	benzoin	1	THF	−78	20	1	26 000	2.06	29.10	48.32
10	none	0	none	35	30 days	90	13 000			

[a] Mole percent initiator to monomer. [b] 50 vol % monomer. [c] By gel permeation chromatography. [d] Theoretical analysis: C, 29.12; Br, 48.43.

Table II
Reaction Conditions for the Synthesis of the Poly(ethyl α-bromoacrylates)

		reaction conditions					polymer properties			
sample	initiator (I)	% I[a]	solvent[b]	temp, °C	time, h	polymer yield, %	$\overline{M}_n$[c]	$\overline{M}_w/\overline{M}_n$[c]	% C[d]	% Br[d]
11	EtMgCl-benzalacetophenone, 1.25-fold excess of EtMgCl	2	heptane–ether	35	18	14	12 000			
12	MeMgCl-benzalacetophenone, 1.25-fold excess of MeMgCl	2	heptane–ether	35	18	20	14 000			
13	MeMgCl-benzalacetophenone, 2-fold excess of MeMgCl	2	heptane–ether	35	18	8	9 000	7.89	34.19	43.11
14	MeMgCl-benzalacetophenone, slight excess of benzalacetophenone	1	heptane–ether	35	18	15	37 000	3.09	34.30	43.81
15	MeMgCl-benzalacetophenone, slight excess of benzalacetophenone	1	heptane	35	18	7	6 500			
16	decanoyl peroxide	1	toluene	50	42	56	21 000	2.58	34.87	42.42
17	decanoyl peroxide	0.1	toluene	50	42	10	40 000	3.20	34.36	42.25
18	benzoin	1	THF	−78	18	0				
19	benzoin	1	toluene	−78	18	0				
20	benzoin	1	toluene	−50	18	3	38 500			
21	benzoin	0.5	toluene	−45	18	5	37 000			
22	benzoin	0.5	toluene	−40	18	7	42 000	2.17	33.81	44.01

[a] Mole percent initiator to monomer. [b] 50 vol % monomer. [c] By gel permeation chromatography. [d] Theoretical analysis: C, 33.54; Br, 44.64.

Table III
Reaction Conditions for the Synthesis of the Poly(*n*-propyl α-bromoacrylates)

		reaction conditions					polymer properties			
sample	initiator (I)	% I[a]	solvent[b]	temp, °C	time, h	polymer yield, %	$\overline{M}_n$[c]	$\overline{M}_w/\overline{M}_n$[c]	% C[c]	% Br[d]
23	MeMgCl–benzalacetophenone[e]	1	heptane–ether	35	18	33	34 500	3.12	38.48	40.80
24	decanoyl peroxide	1	toluene	50	24	46	8 000	3.44	37.16	40.81
25	decanoyl peroxide	0.1	toluene	50	24	5	14 500	1.73	37.63	41.06
26	decanoyl peroxide	1	toluene	60	15	46	6 500			
27	benzoin	1	THF	−78	24	0				
28	benzoin	1	dichloromethane	−78	24	0				
29	benzoin	0.5	toluene	−78	24	0				
30	benzoin	0.5	toluene	−40	18	7	44 000	2.15	38.58	41.34

[a] Mole percent initiator to monomer. [b] 50 vol % monomer. [c] By gel permeation chromatography. [d] Theoretical analysis: C, 37.33; Br, 41.39. [e] Using slight excess of benzalacetophenone.

Table IV
Reaction Conditions for the Synthesis of the Poly(isopropyl α-bromoacrylates)

		reaction conditions					polymer properties			
sample	initiator (I)	% I[a]	solvent[b]	temp, °C	time, h	polymer yield, %	$\overline{M}_n$[c]	$\overline{M}_w/\overline{M}_n$[c]	% C[d]	% Br[d]
31	MeMgCl–benzalacetophenone[e]	1	heptane–ether	35	20	7	90 000	3.24	37.93	41.02
32	decanoyl peroxide	1	toluene	50	42	15	26 000	2.46	38.38	38.48
33	decanoyl peroxide	0.1	toluene	50	24	3	35 000	3.07	38.06	38.24
34	decanoyl peroxide	1	toluene	60	12	28	19 000			
35	benzoin	1	toluene	−78	18	0				
36	benzoin	0.5	toluene	−40	18	4	45 000			
37	decanoyl peroxide	0.1	none	50	24	0				

[a] Mole percent initiator to monomer. [b] 50 vol % monomer. [c] By gel permeation chromatography. [d] Theoretical analysis: C, 37.33; Br, 41.39. [e] Using slight excess of benzalacetophenone.

Table V
Reaction Conditions for the Synthesis of the Poly(*n*-butyl α-bromoacrylates)

		reaction conditions					polymer properties			
sample	initiator (I)	% I[a]	solvent[b]	temp, °C	time, h	polymer yield, %	$\overline{M}_n$[c]	$\overline{M}_w/\overline{M}_n$[c]	% C[d]	% Br[d]
38	MeMgCl–benzalacetophenone[e]	1	heptane	35	20	2	19 000			
39	MeMgCl–benzalacetophenone[f]	1	heptane–ether	35	15	18	93 000	2.99	40.52	38.77
40	decanoyl peroxide	1	toluene	50	42	51	25 500	2.61	40.13	37.66
41	decanoyl peroxide	0.1	toluene	50	24	5	20 500	2.89	39.44	37.62
42	benzoin	1	toluene	−78	18	0				
43	benzoin	0.5	toluene	−40	18	2	48 000	1.84	39.98	40.88

[a] Mole percent initiator to monomer. [b] 50 vol % monomer. [c] By gel permeation chromatography. [d] Theoretical analysis: C, 40.60; Br, 38.59. [e] 2-fold excess of MeMgCl. [f] Using slight excess of benzalacetophenone.

Table VI
Reaction Conditions for the Synthesis of the Poly(n-pentyl α-bromoacrylates)

		reaction conditions						polymer properties		
sample	initiator (I)	% I[a]	solvent[b]	temp, °C	time, h	polymer yield, %	$\overline{M}_n$[c]	$\overline{M}_w/\overline{M}_n$[c]	% C[d]	% Br[d]
44	MeMgCl-benzalacetophenone[e]	1	heptane-ether	35	20	16	89 000	3.18	44.01	36.20
45	decanoyl peroxide	1	toluene	50	42	29	33 000	2.96	43.93	34.20
46	decanoyl peroxide	0.1	toluene	50	24	9	44 000	3.12	43.71	35.09
47	benzoin	0.5	toluene	−40	18	1	63 000	2.04	44.04	37.08
48	decanoyl peroxide	0.1	none	50	18	1	16 000			

[a] Mole percent initiator to monomer. [b] 50 vol % monomer. [c] By gel permeation chromatography. [d] Theoretical analysis: C, 43.46; Br, 36.14. [e] Using slight excess of benzalacetophenone.

These statistics are almost always obeyed in free radical propagation processes. The probability that a monomer unit will add to the polymer chain in the same configuration as the last unit on its growing end is represented by the quantity $P_m = 1 - S^{1/2}$, where S is the proportion of syndiotactic triads. Since methyl α-bromoacrylate was the only monomer to be polymerized free radically at more than two temperatures, only data for this monomer are presented. The triad values used for the calculation of P_m are listed in Tables X and XI. From a plot of ln $[P_m/(1 - P_m)]$ vs. $1/T$, values of 1.2 kcal for $\Delta H_m^{*} - \Delta H_r^{*}$ and 0.2 eu for $\Delta S_m^{*} - \Delta S_r^{*}$ were obtained from the slope and y intercept, respectively. Thus the preference for syndiotactic placement can be attributed to the lower enthalpy of activation for the syndiotactic propagation step as compared to the isotactic propagation step. Isotactic placement is slightly favored by the entropy of activation. The preference for syndiotactic placement in the free radical polymerization of methyl methacrylate was demonstrated by the similar enthalpies of activation of 0.78 kcal reported by Bovey[21] and 1.07 kcal reported by Fox and Schnecko.[22]

Preparation of Atactic Polymers. The atactic polymers were prepared at 50 °C, employing a conventional free radical polymerization initiator. Initially, the polymerization reactions were carried out at 60 °C, but this temperature was found to be too high because of the thermal instability of the polymers. Decanoyl peroxide was chosen as the initiator because higher yields were possible at a lower temperature with this initiator than with either benzoyl peroxide or azobis(isobutyronitrile).

Table XI lists the triad tacticities of the polymers polymerized with 1% decanoyl peroxide at 50 °C. The values were very typical of atactic polymers in general. A comparison of the data in Table X and XI revealed that as the temperature was increased from −40 to +50 °C, the performance of isotactic units in the polymers increased significantly, and it is conceivable that at a high enough temperature, a purely heterotactic polymer could be synthesized.[23] The effects of the polymerization mechanism on the polymer tacticity will be discussed in detail in the next section.

The preparation of poly(*tert*-butyl α-bromoacrylate) was achieved only in bulk at 50 °C. The reactions carried out in solution failed to form polymers. A similar behavior was obsered with the other α-bromoacrylate monomers, and each would polymerize in bulk at room temperature in the absence of any initiator but not if solvent was present. This phenomenon was observed in a variety of solvents, including toluene, benzene, tetrahydrofuran, and chloroform.

Tacticity Determination from ^{1}H NMR Spectra. The quantitative determination of tacticity by 90-MHz ^{1}H NMR spectroscopy was not possible for any of the polymers in this investigation, although qualitative information was obtainable from the backbone methylene protons at chemical shifts between 3.1 and 3.8 ppm downfield from tetramethylsilane (Me_4Si). That is, the polymers prepared with the modified Grignard complex catalyst exhibited a nearly perfect AB quartet for the backbone protons, which indicated a high degree of isotacticity.

The methoxy ester protons in poly(methyl α-bromoacrylate) appeared as a weak triplet centered at 3.8 ppm downfield from Me_4Si. The downfield peak was assigned to the isotactic triads, the upfield peak to the syndiotactic triads, and the intermediate peak to the heterotactic triads. These assignments were in agreement with those for the methoxy protons of poly(methyl α-chloroacrylate)[3,11,12] and for the α-methyl protons of poly(methyl methacrylate).[24,25]

Table VII
Reaction Conditions for the Synthesis of Poly(*tert*-butyl α-bromoacrylate)

sample	initiator (I)	reaction conditions				polymer yield, %	polymer properties			
		% I[a]	solvent[b]	temp, °C	time, h		$\overline{M}_n$[c]	$\overline{M}_w/\overline{M}_n$[c]	% C[d]	% Br[d]
49	MeMgCl-benzalacetophenone[e]	1	heptane-ether	35	18	0				
50	MeMgCl-benzalacetophenone[e]	2	heptane-ether	35	18	0				
51	decanoyl peroxide	1	toluene	50	18	0				
52	decanoyl peroxide	2	toluene	50	24	0				
53	decanoyl peroxide	0.5	none	50	24	40	208 000	2.27	40.05	37.82
54	benzoin	1	toluene	−20	−20	15				

[a] Mole percent initiator to monomer. [b] 50 vol % monomer. [c] By gel permeation chromatography. [d] Theoretical analysis: C, 40.60; Br, 38.59. [e] Using slight excess of benzalacetophenone.

Table VIII
Effect of Excess Methylmagnesium Chloride on the Molecular Weight and Molecular Weight Distribution in the Synthesis of Poly(methyl α-bromoacrylate) and Poly(ethyl α-bromoacrylate)

sample	ester	peak	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
2[a]	methyl	A + B[b]	3 000	33 500	11.6
2[a]	methyl	A	21 500	57 000	2.68
2[a]	methyl	B	1 500	3 000	2.33
3[c]	methyl	total[d]	31 000	105 000	3.35
13[a]	ethyl	A + B[b]	9 000	70 000	7.89
13[a]	ethyl	A	31 500	87 000	2.77
13[a]	ethyl	B	2 500	4 000	1.72
14[c]	ethyl	total[d]	37 000	114 500	3.09

[a] 2-fold excess of methylmagnesium chloride. [b] The molecular weight distribution was bimodal. [c] Slight excess of benzalacetophenone. [d] The molecular weight distribution was unimodal.

Unfortunately, a quantitative comparison of the three methoxy proton peaks was not possible for any of the isotactic polymers because of peak overlap with the backbone protons. In addition, a quantitative analysis based on the ester peaks for the higher ester polymers was not possible because of insufficient peak resolution at 90 MHz. For example, the methyl peak from the ester group of poly(ethyl α-bromoacrylate) should have consisted of three triplets corresponding to the isotactic, heterotactic, and syndiotactic contributions, but only one triplet was observed. A similar lack of peak separation or peak overlap was observed for the other polymers in this series.

Configurational Statistics and Polymerization Mechanism. The first publication in the present series reported on the determination of pentad tacticity for isotactic and syndiotactic poly(methyl α-bromoacrylate) and poly(n-propyl α-bromoacrylate).[1] Because of incomplete pentad assignments for the isotactic samples, the calculation of their corresponding triad tacticities was not possible. The triad tacticities reported in Tables IX–XI were calculated from both the tetrad and pentad tacticities, which will be presented in a forthcoming publication.[19]

Calculated values for isotactic, $P_{m/m}$, syndiotactic, $P_{r/r}$, and heterotactic, $P_{m/r}$ and $P_{r/m}$, triad configurational probabilities are collected in Tables XII–XIV. In addition, these tables give the specific persistence ratio, $\rho = 2(m)(r)/mr$, which expresses the tendency of the r and m units to propagate themselves preferentially.[26,27] When $\rho > 1$, the lengths of the m or r sequences are longer than those in equivalent polymers in which the propagation reactions follow Bernoullian statistics, and a value of $\rho < 1$ indicates that the lengths of the m or r sequences will be shorter than for Bernoullian growth. The former case generally represents a stereoblock polymer while the latter indicates an alternating stereosequencing in the polymer.

All of the samples in Table XII were polymerized anionically by the complexed Grignard catalyst and all displayed the features expected for an isotactic-like polymer. That is, the $P_{m/r}$ value was considerably less than 0.5 and the $P_{r/m}$ value was very high. The value of ρ was slightly greater than 1, again demonstrating the tendency for m units to exist in a blocky arrangement, and the fact that ρ exceeded 1 only slightly indicated that the r units were placed in a random manner. Both results confirmed that the isotactic polymers did not conform in structure to that expected for Bernoullian growth statistics.

The data in Table XIII for the atactic polymers and in Table XIV for the syndiotactic polymers show that both of these types of polymers followed Bernoullian statistics in their growth. In all cases ρ and $\sum P$ were very close to

Table IX
Calculated Triad Tacticities for the Isotactic Polymers

ester	sample	[MeMgCl]/ benzalacetophenone	from tetrads[a]			from pentads[b]		
			rr	mr	mm	rr	mr	mm
methyl	2	2				0.29	0.39	0.32
methyl	3	1				0.06	0.26	0.68
ethyl	13	2	0.27	0.42	0.31	0.26	0.40	0.34
ethyl	14	1	0.08	0.24	0.68	0.07	0.27	0.66
n-propyl	23	1	0.04	0.19	0.77	0.05	0.21	0.74
isopropyl	31	1	0.08	0.28	0.64	0.10	0.30	0.60
n-butyl	39	1	0.06	0.26	0.68	0.07	0.29	0.64
n-pentyl	44	1	0.04	0.22	0.74	0.05	0.25	0.70

[a] Determined by ^{13}C NMR analysis of the backbone methylene carbon resonance. [b] Determined by ^{13}C NMR analysis of the carbonyl carbon resonance.

Table X
Calculated Triad Tacticities for the Syndiotactic Polymers

ester	sample[c]	from tetrads[a]			from pentads[b]		
		rr	mr	mm	rr	mr	mm
methyl	8				0.66	0.31	0.03
methyl	9[d]				0.77	0.22	0.01
ethyl	22	0.64	0.32	0.04	0.64	0.33	0.03
n-propyl	30	0.61	0.35	0.04	0.62	0.34	0.04
isopropyl	36	0.58	0.36	0.06	0.60	0.35	0.05
n-butyl	43	0.60	0.35	0.05	0.61	0.35	0.04
n-pentyl	47	0.61	0.35	0.04	0.64	0.33	0.03

[a] Determined by ^{13}C NMR analysis of the backbone methylene carbon resonance. [b] Determined by ^{13}C NMR analysis of the carbonyl carbon resonance. [c] Polymerized at −40 °C except as indicated. [d] Polymerized at −78 °C.

Table XI
Calculated Triad Tacticities for the Atactic Polymers

ester	sample[c]	from tetrads[a]			from pentads[b]		
		rr	mr	mm	rr	mr	mm
methyl	4				0.46	0.44	0.10
ethyl	16	0.44	0.45	0.11	0.43	0.46	0.11
n-propyl	24	0.43	0.45	0.12	0.44	0.47	0.09
isopropyl	32	0.43	0.46	0.11	0.46	0.43	0.11
n-butyl	40	0.45	0.45	0.10	0.45	0.46	0.09
n-pentyl	45	0.45	0.45	0.10	0.46	0.44	0.10

[a] Determined by ^{13}C NMR analysis of the backbone methylene carbon resonance. [b] Determined by ^{13}C NMR analysis of the carbonyl carbon resonance. [c] Polymerized at −40 °C.

unity, with the deviations never in excess of 6%. Both the atactic and syndiotactic polymers were synthesized with free radical initiators and, therefore, both were expected to obey Bernoullian growth statistics.[3,25]

The effect of the polymerization temperature on the relative formation of m and r units was indicated very well by the two polymerization probabilities $P_{m/r}$ and $P_{r/m}$. For example, the atactic polymers, which were polymerized at higher temperatures, had $P_{m/r}$ values between 0.66 and 0.72 as compared to 0.78–0.85 for the syndiotactic polymers.

The experimental propagation statistics of all the isotactic poly(alkyl α-bromoacrylates) were generated fairly well by a first-order Markov process as shown in Table XV. According to Bovey,[25] the criteria for applicability of first-order Markovian statistics is that four of the six tetrad values calculated from the $P_{m/r}$ and $P_{r/m}$ probabilities must agree, within experimental error, with the experimentally determined tetrads. For the five esters listed in Table XV, the experimental rrr, rmr, rrm, and mrm tetrads agreed with those generated by the nonrandom first-order Markov process. The values for the remaining two tetrads, mmr and mmm, were not as close as the other four but were still reasonably close, usually within 5%. In addition, the sum of the mmr and mmm experimental values was very close to the sum of the mmr and mmm calculated values. Considering the experimental error resulting from the lack of detail in some of the ^{13}C NMR spectra, an error of 5% was reasonable. Furthermore, the value of ρ (see Table XII) was equivalent to $1/\sum P$, which is an additional requirement for Markovian statistics.

Table XII
Configurational Statistics[a] of the Isotactic Poly(alkyl α-bromoacrylates)[b]

ester	sample	m	r	$P_{m/r}$	$P_{r/m}$	ρ	ΣP	polymer type
methyl	3	0.81	0.19	0.16	0.68	1.18	0.84	isotactic-like
ethyl	14	0.79	0.21	0.17	0.66	1.23	0.83	isotactic-like
n-propyl	23	0.84	0.16	0.12	0.63	1.34	0.75	isotactic-like
isopropyl	31	0.75	0.25	0.20	0.60	1.25	0.80	isotactic-like
n-butyl	39	0.79	0.21	0.18	0.67	1.14	0.85	isotactic-like
n-pentyl	44	0.83	0.17	0.15	0.71	1.13	0.86	isotactic-like

[a] Based on the carbonyl carbon resonance. [b] Synthesized with the modified Grignard complex.

Table XIII
Configurational Statistics[a] of the Atactic Poly(alkyl α-bromoacrylates)[b]

ester	sample	m	r	$P_{m/r}$	$P_{r/m}$	ρ	ΣP	polymer type
methyl	4	0.32	0.68	0.69	0.33	0.99	1.02	syndiotactic-like
ethyl	16	0.34	0.66	0.68	0.35	0.98	1.03	syndiotactic-like
n-propyl	24	0.33	0.67	0.72	0.34	0.94	1.06	syndiotactic-like
isopropyl	32	0.33	0.67	0.66	0.32	1.02	0.98	syndiotactic-like
n-butyl	40	0.32	0.68	0.72	0.33	0.95	1.05	syndiotactic-like
n-pentyl	45	0.32	0.68	0.69	0.33	0.99	1.02	syndiotactic-like

[a] Based on the carbonyl carbon resonance. [b] Synthesized with decanoyl peroxide at 50 °C.

Table XIV
Configurational Statistics[a] of the Syndiotactic Poly(alkyl α-bromoacrylates)[b]

ester	sample	m	r	$P_{m/r}$	$P_{r/m}$	ρ	ΣP	polymer type
methyl	8	0.18	0.82	0.84	0.19	0.95	1.03	syndiotactic-like
ethyl	22	0.20	0.80	0.85	0.21	0.94	1.06	syndiotactic-like
n-propyl	30	0.21	0.79	0.81	0.22	0.98	1.03	syndiotactic-like
isopropyl	36	0.22	0.78	0.78	0.23	0.98	1.01	syndiotactic-like
n-butyl	43	0.21	0.79	0.81	0.22	0.95	1.03	syndiotactic-like
n-pentyl	47	0.19	0.81	0.85	0.20	0.94	1.05	syndiotactic-like

[a] Based on the carbonyl carbon resonance. [b] Synthesized with benzoin at −40 °C.

Table XV
Calculated First-Order Markov Tetrads vs. Experimental Tetrads for the Isotactic Poly(alkyl α-bromoacrylates)

		tetrads					
ester	method	rrr	rmr	rrm	mmr	mrm	mmm
ethyl	exptl	0.04	0.04	0.06	0.17	0.09	0.60
	calcd	0.03	0.03	0.07	0.22	0.10	0.55
n-propyl	exptl	0.02	0.02	0.05	0.15	0.06	0.70
	calcd	0.02	0.02	0.06	0.18	0.07	0.65
isopropyl	exptl	0.03	0.03	0.10	0.20	0.10	0.54
	calcd	0.03	0.03	0.11	0.24	0.09	0.50
n-butyl	exptl	0.02	0.03	0.08	0.19	0.09	0.59
	calcd	0.02	0.03	0.09	0.23	0.10	0.53
n-pentyl	exptl	0.01	0.02	0.07	0.17	0.08	0.65
	calcd	0.01	0.02	0.07	0.21	0.09	0.60

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