Haloaldehyde Polymers. 55. Diastereomeric Bromal Unimers: Synthesis, Characterization, and Absolute Configuration†

Christoph Kratky,‡ Ulrike Wagner,‡ Koichi Ute,§ Koichi Hatada,§ William J. Simonsick, Jr.,∥ F. W. Hein Kruger,⊥ Fu Xi,⊥ and Otto Vogl*,⊥

Institute of Physical Chemistry, University of Graz, Graz, Austria, Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan, Marshall R&D Laboratory, E. I. du Pont de Nemours & Company, Philadelphia, Pennsylvania 19146, and Polytechnic University, 6 MetroTech Center, Brooklyn, New York 11201

Received September 26, 1991; Revised Manuscript Received December 27, 1991

ABSTRACT: Unimers of tribromoacetaldehyde (bromal) were prepared by the addition of equimolar amounts of lithium *tert*-butoxide or bornyl oxide to bromal followed by acetate end capping. This bornyl oxide-initiated unimer resulted in a crystalline mixture of the *R* and *S* diastereomers which had a melting range of 48–55 °C. Fractional crystallization from methanol gave compound A, mp = 83.5–84.0 °C, and compound B, mp = 82.0–82.5 °C. The optical rotation of A was $[\alpha]_D = -14.4°$; that of B was $[\alpha]_D = -29.7°$. A and B were characterized by single-crystal X-ray diffraction which determined their absolute configuration. All the unimers were also characterized by ^1H and ^{13}C NMR spectroscopy and potassium ion mass spectrometry of desorbed species (K+IDS).

Introduction

The study of the initiation and the embryonic state of polymerization has become an important tool in the investigation of the stereochemistry of the initial phase of addition polymerization, especially for those polymerizations that lead to helical polymers.[1,2]

The recent interest in the development of stereoregular polymers with bulky side groups (with the objective of forming polymers with an exclusive helical conformation) has led to an increased activity in the oligomerization of such monomers as chloral[3,4] and triphenylmethyl methacrylate.[5] The development of the stereostructure of methyl methacrylate oligomerization by the identification of individual oligomers[6–9] was also carefully investigated.

It was of great interest to establish and determine the relationship between the size of the side group and that of the initiating species with chloral as the prime example.[10] The insolubility of the resulting polymers and the development of stereospecificity as the polymerization proceeds in the gel phase also had to be considered.[11]

Chloral polymerization with *tert*-butoxide[4,12–14] and bornyl oxide[15] as the initiators has led to the isolation and identification of individual species of the unimers, dimers, trimers, and tetramers by ^1H NMR spectroscopy[16,17] and single-crystal X-ray analysis.[18–20] It was found that the addition of the first one or two monomer units is not stereospecific[16,17,21] but the addition of the third and fourth monomer unit becomes increasingly specific;[16–20] further addition of chloral units gave stereospecific isotactic polychloral with a helical conformation.

It was expected that bromal would give isotactic polymer even more readily. Bromal polymerization had been studied in a rather preliminary way[22] several years ago; the initiation of the polymerization was not clearly established, because the traditional initiators for chloral polymerization did not give efficient initiation for bromal polymerization. It was found that a still unidentified impurity in bromal interfered with the initiation. When both the monomer and the initiators were highly purified, the polymerization could readily be accomplished although only at very low temperature because of the low ceiling temperature of bromal polymerization.[22]

It was expected that the oligomerization of bromal should follow the same pattern as that of chloral with the one exception that the bulkier side group should more readily favor the formation of the helical conformation in the polybromal chain; this means that the meso configuration and the corresponding conformation would be more readily established.

It was the objective of this work to study the unimer formation of bromal with *tert*-butoxide and bornyl oxide, to isolate the individual unimers, and to characterize them by ^1H NMR spectroscopy[23,24] and K+IDS mass spectrometry. Where possible, it was the aim to isolate crystalline compounds and to determine their crystal structure by single-crystal X-ray analysis. This should establish their absolute configuration, and via a comparison with previously determined crystal structures of chloral derivatives,[20,24] it should permit an assessment of the conformational effect of a substitution of chlorine by bromine.

Experimental Part

A. Materials. Bromal (Aldrich Chemical Co.) was purified according to our previous work.[22]

(1*S*,2*R*,4*S*)-(−)-Borneol (99%), $[\alpha]^{25}_D = -35.6°$ (c = 5, C_2H_5OH), *n*-butyllithium (1.6 or 10.0 M, in hexane), *tert*-butanol and methylcyclohexane (anhydrous), and acetic anhydride (ACS reagent) were obtained from the Aldrich Chemical Co. All chemicals were used without further purification.

Lithium *tert*-butoxide and lithium bornyl oxide were prepared in situ by treating equimolar amounts of the alcohol with *n*-butyllithium. The alkoxide solutions or suspensions were used immediately.

B. Measurements. Gas chromatographic analyses were carried out on a Varian 3300 gas chromatograph (column 0.5 m × 3 mm, packed with Chromosorb GHP 100/120, coated with 5% OV101). Heating rates of the *tert*-butoxide- and bornyl oxide-initiated unimers were 2.0 and 3.5 °C/min, respectively, and the initial column temperature was 110 °C in each case.

Optical rotation measurements were made on a Perkin-Elmer 241 polarimeter in a microcell (volume 1 mL; path length 100 mm) at 25 °C with the sodium D line using a sodium lamp.

† This paper is dedicated to Professor Otto Kratky on the occasion of his 90th birthday with our warmest wishes.
‡ University of Graz.
§ Osaka University.
∥ E. I. du Pont de Nemours & Co.
⊥ Polytechnic University.

0024-9297/92/2225-2319$03.00/0

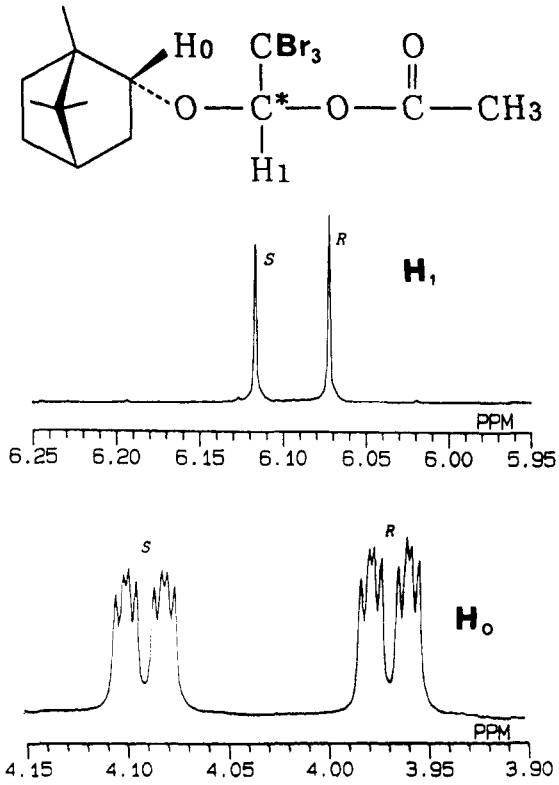
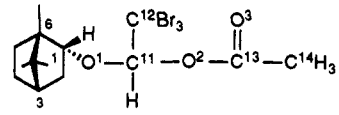


Figure 1. 500-MHz ^{1}H NMR spectra of the H_0 (2-position of the bornyloxy group) and the H_1 (acetal) proton region of the diastereomeric (*R*)- and (*S*)-BIABU.

Chart I
Numbering System for (*R*)- and (*S*)-BIABU



^{1}H NMR spectra were obtained on a Varian EM-390 (90-MHz) NMR spectrometer. More detailed spectra were recorded on a JEOL JNM-GX500 (500-MHz) spectrometer in chloroform-*d* at 35.0 °C.

K+IDS mass spectrometry was performed on a Finnigan 4615B quadrupole GC/MS system.[25-27] An EI source configuration was used in all K+IDS experiments. The ion source pressure (ion gauge) was $<10^{-6}$ Torr with a source temperature of 200 °C.

X-ray diffraction data were collected at low temperatures (liquid nitrogen) on an "in-house" modified STOE four-circle diffractometer (Mo Kα radiation, $\lambda = 0.710\ 69$ Å; graphite monochromator) equipped with a Nonius low-temperature attachment at about −170 °C.

C. Procedures. *tert*-Butoxide-Initiated, Acetate-End-Capped Bromal Unimer [TBIABU]. (1-*tert*-Butoxy-1-acetoxy-2,2,2-tribromoethane): An 80-mL polymerization tube, equipped with a Teflon-coated stirring bar, was flamed out and cooled under argon. Lithium *tert*-butoxide (50 mL, 0.037 mol) was prepared by adding 23 mL of a 1.6 M solution of *n*-butyllithium in hexanes to *tert*-butanol (3.5 mL, 2.75 g, 37 mmol) in methylcyclohexane (27 mL) with a dry syringe, which resulted in a 0.74 M solution. To this solution of lithium *tert*-butoxide was added at room temperature, slowly, over a period of 5 min, freshly purified bromal (10.5 g, 3.9 mL, 0.037 mol). The reaction mixture was allowed to stir for 40 min at room temperature. Acetic anhydride (3.6 mL, 0.037 mol) was added dropwise within 5 min, and the mixture was stirred for an additional 1 h. In a separatory funnel, the solution was washed with 5% aqueous sodium bicarbonate and then with water; the organic phase was separated and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the crude product (12.0 g, 81%) was purified by distillation under reduced pressure. TBIABU distilled at 92 °C (0.3 mmHg). GC showed TBIABU with a retention time of 12.9 min; the center cut of 4.6 g was >85% pure. Elem. anal. Calcd for $C_8H_{13}O_3Br_3$: C, 24.18; H, 3.27. Found: C, 23.77; H, 3.12.

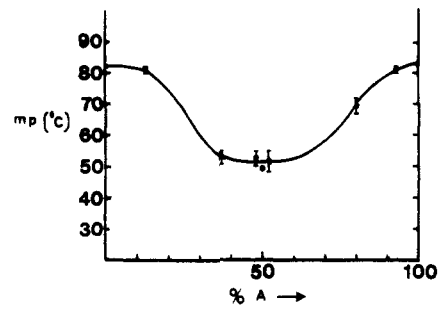


Figure 2. Melting points of mixtures of the diastereomeric (*R*)- and (*S*)-BIABU.

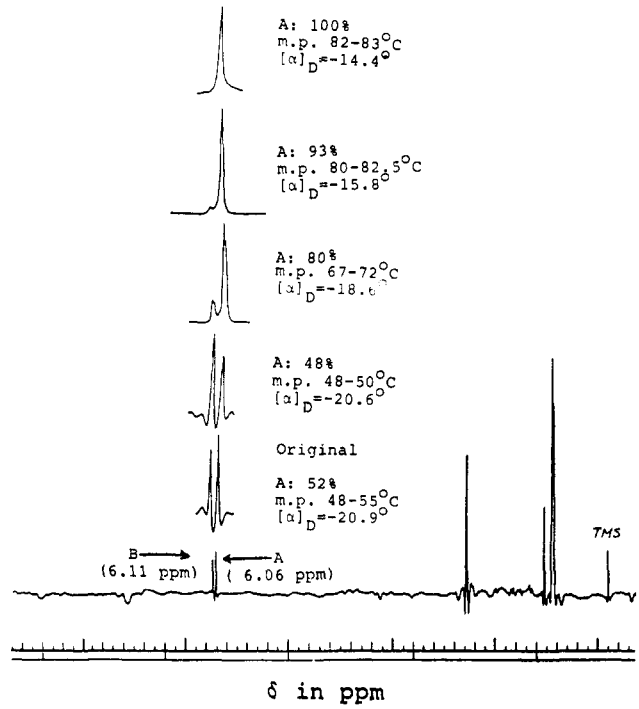


Figure 3. Composition of diastereomeric (*R*)- and (*S*)-BIABU mixtures determined from the H_1 (acetal) region of the 90-MHz ^{1}H NMR spectra.

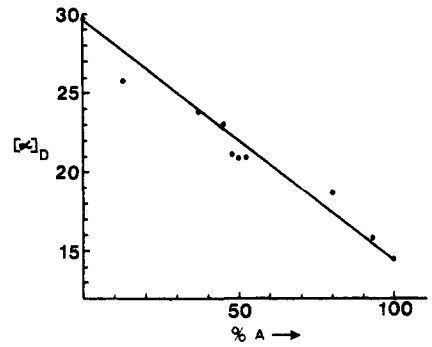


Figure 4. Optical rotations of mixtures of the (*R*)- and (*S*)-BIABU diastereomers.

Bornyl Oxide-Initiated, Acetate-End-Capped Bromal Unimer [BIABU]. (1-(Bornyloxy)-1-acetoxy-2,2,2-tribromoethane): A 100-mL polymerization tube was equipped with a Teflon-coated stirring bar, flamed out, and cooled under dry argon. Freshly purified bromal (11.2 g, 4.1 mL, 0.04 mol) and lithium bornyl oxide reagent [prepared from borneol (6.2 g, 0.04 mol) in methylcyclohexane (60 mL) and 4.0 mL of a 10.0 M solution of *n*-butyllithium [which gave a 0.63 M solution]] were added with dry syringes in this sequence into the polymerization

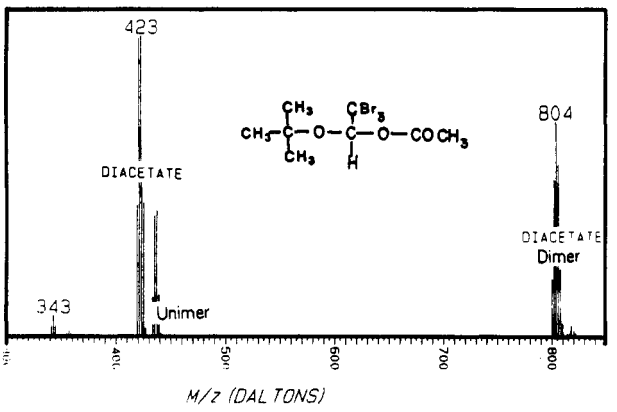


Figure 5. K + IDS mass spectrum of TBIABU.

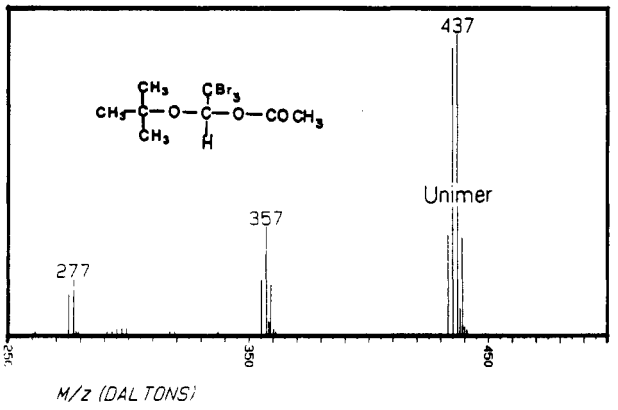


Figure 6. Degradation pattern of TBIABU, obtained from K + IDS analysis.

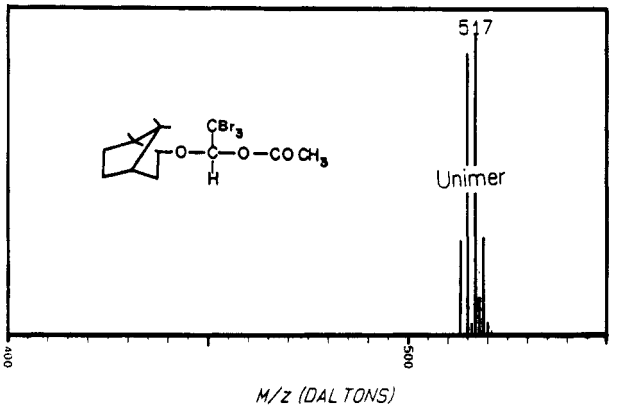


Figure 7. K + IDS mass spectrum of BIABU.

tube. After 30 min, acetic anhydride (4.1 mL, 0.044 mmol) was injected and allowed to react for 1 h. The resulting mixture was washed twice with 5% aqueous sodium bicarbonate and water and was dried over anhydrous sodium sulfate. After removal of the solvent, the residue (15.5 g, 87%) was distilled at 130 °C (0.3 mmHg) to yield 13.0 g (68%) of a yellowish, viscous liquid of mostly bornyl oxide-initiated acetate-end-capped bromal unimers. GC revealed that the product was 99% pure. The product crystallized on standing, with a melting range of 48–55 °C. Elem anal. Calcd for $C_{14}H_{21}O_3Br_3$: C, 35.22; H, 4.43. Found: C, 35.21; H, 4.43.

Results and Discussion

TBIABU and BIABU were synthesized as follows: *n*-butyllithium was allowed to react with an equimolar amount of *tert*-butanol or borneol in methylcyclohexane. Lithium *tert*-butoxide gave a clear solution, but lithium bornyl oxide precipitated from the mixture in the form of a fine suspension. The solution or the suspension was

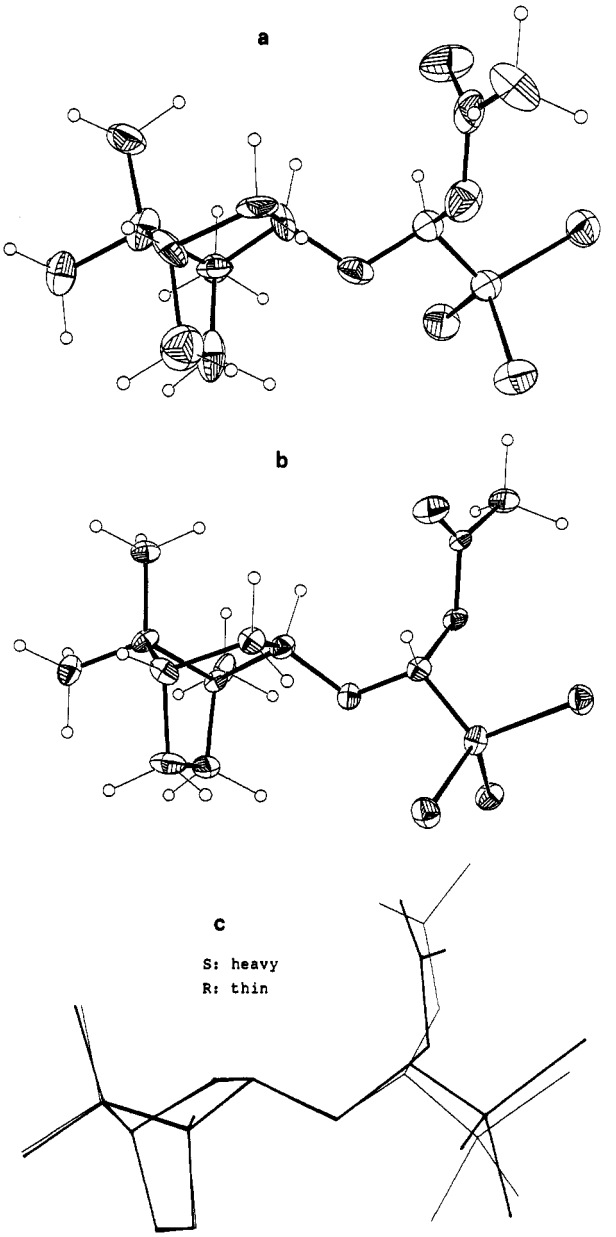


Figure 8. Results of the crystal structure determination of the *R* and *S* diastereomers of the bornyl oxide-initiated, acetate-end-capped bromal unimer (BIABU). (A) ORTEP drawing (50% probability) of (*S*)-BIABU; three atoms with nonzero definite adp's have been drawn without shading. (B) ORTEP drawing of (*R*)-BIABU. (C) Superposition of the two structures (matching of the atoms of the bornyl group); the *S* diastereomer is represented by a heavier line.

allowed to react with bromal in approximately equal molar amounts at room temperature. In the case of the bornyl oxide initiation, the reaction of the suspension of lithium bornyl oxide with bromal was manifested by the formation of a clear solution. Each solution was treated with acetic anhydride to acetylate the bromal-terminated alkoxides, to yield TBIABU or BIABU. The latter consisted of a mixture of the *R* and *S* diastereoisomers (see Chart I).

The bromal unimers could be identified by GC. TBIABU gave a single peak, but BIABU showed the double peak. The first peak in the gas chromatogram of BIABU at a retention time of 19.2 min is the (1*S*,2*R*,4*S*)-bornyl-(*R*)-bromal unimer (A) as determined by NMR spectroscopy; the second peak at a retention time of 19.8 min is the (1*S*,2*R*,4*S*)-bornyl-(*S*)-bromal unimer (B).

TBIABU showed the ^{1}H NMR signals of the *tert*-butyl protons at 1.37 ppm, the acetal proton at 6.25 ppm, and

Table I
Experimental Data of the Crystal Structure of (*R*)- and (*S*)-BIABU

	(*S*)-BIABU	(*R*)-BIABU
crystallzn conditions	methanol (room temp)	water/acetone (room temp)
space group (*Z*)	$P2_12_12_1$ (4)	$P2_1$ (2)
cell dimens		
a, Å	7.794 (0.007)	6.679 (0.013)
b, Å	11.047 (0.009)	13.216 (0.021)
c, Å	19.482 (0.026)	9.994 (0.020)
β, deg	90	105.04 (0.15)
V, Å^3	1677.5 (1.0)	851.8 (1.0)
calcd from no. of reflections	18	58
in the range of	$7.5° < 2\theta < 23°$	$10° < 2\theta < 18°$
absorption coefficient μ, cm^{-1}	71.5	70.4
calcd density, g/cm^3	1.89	1.86
crystal size, mm	0.25 × 0.25 × 0.25	0.3 × 0.3 × 0.25
scan type	ω/θ	ω
scan width, deg	0.8	1.6
temp of experiment, K	94.0 ± 0.5	103.0 ± 0.5
reflections		
measured	2572	3974
independent	2467	3647
significant [$F > 4\sigma(F)$]	1187	2451
2θ range	$5.5° < 2\theta < 60°$	$5.5° < 2\theta < 70°$
residual factor *R* (unit weights)	0.067	0.045
no. of observations	1186	2450
no. of parameters	202	202
highest/lowest peak in last ΔF Fourier synthesis, e Å^{-3}	1.08/−1.07	1.03/−1.18

the methyl protons of the acetyl group at 2.17 ppm. The ^{13}C NMR signals appear at 28.17 ppm (*tert*-butylmethyl), 78.78 ppm (quaternary), 45.21 ppm (tribromomethyl), 94.29 ppm (methine), 169.82 ppm (carbonyl), and 21.33 ppm (acetylmethyl).[28]

The quantitative ^1H NMR spectrum measured at 500 MHz of the mixture of the isomers A and B showed an isomer ratio of 53:47 (Figure 1). The chemical shift value for the H_0 proton (the 2-position of the bornyloxy group) of A is at 3.97 ppm, and that of the H_1 proton (the acetal protons) is 6.07 ppm. The chemical shift value for the H_0 proton of B is 4.09 ppm, and that of the H_1 proton is 6.12 ppm. The ^1H NMR spectra were measured in deuteriochloroform at 35 °C and 500 MHz and related to the ^1H NMR spectra of the corresponding chloral unimers whose absolute configuration of the *R* isomer was determined by single-crystal X-ray analysis.[20,24]

The differences between the chemical shifts for the H_0 protons of the two BIABU diastereomers are 0.12 ppm and for the H_1 protons 0.05 ppm, with the values for the *R* diastereomer at higher field.[24] The *R* diastereomer of BIACU is the key compound in these studies, because for this compound the absolute configuration had been determined by single-crystal X-ray crystallography.[20] For the BIACU diastereomers, the difference is still 0.07 ppm for the H_0 protons and 0.04 ppm for the H_1 protons, with the *R* diastereomer at a higher field in both cases.[20,24]

The difference in the shift values for the H_0 protons (0.02 ppm) and the H_1 protons (0.02 ppm) of (1*S*,2*R*,4*S*)-bornylfluoral unimer (BIAFU) is much smaller but clearly distinguishable. When the spectra were measured with a 500-MHz spectrometer,[24] the *R* diastereomers also showed the acetal protons at a higher field.

The mixture of the two diastereomers BIABU A and B (A:B ratio 53:47), which crystallized on standing, showed a melting range of 48–55 °C and an optical rotation $[\alpha]_D$ of −20.7°. A and B were separated by fractional crystallization from methanol. The change of the melting points of the A and B mixtures is shown in Figure 2. The compositions of the mixtures and the purity of the individual compounds were judged by the relationship of the acetal protons (Figure 3). The change of the optical rotation was also recorded and is shown to have a linear relationship (Figure 4). The pure isomer A had a mp of 83.5–84.0 °C and an optical rotation $[\alpha]_D$ of −14.4°; the B isomer had a mp of 82.0–82.5 °C and an optical rotation $[\alpha]_D$ of −29.7°.

TBIABU and the diastereomeric unimers BIABU were analyzed by potassium ionization mass spectrometry of desorbed species (K+IDS) (Figures 5–7). K+IDS affords a pseudomolecular ion in the form of $[M]K^+$. The details of the method are published elsewhere.[25] Figure 5 shows the K+IDS mass spectrum of a TBIABU/bromal diacetate mixture showing a $[M]K^+$ of 437 Da which corresponds to the potassiated unimer. The distribution around the 437 Da ion arises from the natural isotopes of bromine. A detailed explanation is given in ref 29. The bromal diacetate can be seen at a $[M]K^+$ of 423 Da and a fragmentation ion at 343 Da which we attribute to a loss of HBr (80 Da). Furthermore, the cluster seen at 343 Da gives a pattern characteristic of two bromine atoms. A small amount of the potassium-bound bromal diacetate dimer at 805 Da is also noticeable. This pattern seen at 805 Da corresponds to a six bromine atom isotope distribution.

Figure 6 shows the K+IDS mass spectrum run under slightly more severe conditions. It shows not only the molecular peak of TBIABU at a $[M]K^+$ of 437 Da but also degradation peaks at $[M]K^+$ of 357 Da corresponding to the loss of one molecule of HBr and a peak $[M]K^+$ at 277 Da resulting from the loss of two HBr molecules.

K+IDS mass spectral analysis of BIABU shows the molecular peak of $[M]K^+$ at 517 Da (Figure 7) with the expected three bromine atom isotope pattern. All K+IDS mass spectra of the bromal unimers are in full agreement with the expected molecular masses; in addition, they show the typical composite peaks of the bromine isotope distribution. A careful analysis of the isotope distribution of the bromal unimers and higher oligomers will be presented elsewhere.[29]

Experimental conditions and a selection of crystallographic data are listed in Table I. Both structures of the two diastereomeric isomers of the *R* and *S* configurations of the bornyl oxide-initiated, acetate-end-capped bromal

Table II
Torsion Angles (deg) around the Bromyl Group for (*R*)- and (*S*)-BIABU Compared to the Values Observed for (*R*)-1-(Bornyloxy)-1-acetoxy-2,2,2-trichloroethane (*R*)-BIACU[17]

torsion angle	(*R*)-BIABU	(*S*)-BIABU	(*R*)-BIACU
C1–O1–C11–O2	−86.7	81.8	−88
C11–O2–C13–O3	−5.8	0.9	−5
O1–C11–O2–C13	112.2	−118.6	118

unimers were solved with direct methods using SHELXS.[30] An empirical absorption correction was applied with all non-hydrogen atoms of the molecule included.[31] The absolute configuration of both structures was assigned by refining both enantiomeric configurations and subsequently comparing the crystallographic *R* values. For the (1*S*,2*R*,4*S*)-bornyl-(*R*)-bromal unimer ((*R*)-BIABU) the two residual factors had a ratio of $R_s/R_r = 0.0395/0.0375$. For the (1*S*,2*R*,4*S*)-bornyl-(*S*)-bromal unimer ((*S*)-BIABU) the R_s/R_r ratio was 0.0671/0.0709. In either case the difference allows an unambiguous assignment of the absolute configuration purely on the basis of the crystallographic data, which agrees with the known (1*S*,2*R*,4*S*) configuration of the bornyl residue. In the last cycles of the refinement, all non-hydrogen atoms were refined with anisotropic atomic displacement parameters (adp). Hydrogens were included at the calculated positions, but only an isotropic adp was refined for each. Atomic coordinates, bond length and angles, and atomic displacement parameters have been deposited at the Cambridge Crystallographic Data Centre. Other programs used were SHELX[32] and ORTEP.[33]

The absolute configuration for the two diastereomeric bromal unimers as determined by X-ray crystallographic investigation is shown in parts a–c of Figure 8. The *R*/*S* assignment for the bromal unimers is in complete agreement with the assignment of the absolute configuration of the diastereomeric unimers based on the chemical shift values obtained from the ^{1}H NMR spectrum of the bromal unimers. The chemical shift values and their positions are based on and related to the data of the single-crystal X-ray analysis for the *R* diastereomer of the chloral unimer. Table II lists relevant torsion angles for the two diastereomeric bromal unimers plus the corresponding (*R*)-chloral derivative. The data points show a striking conformational similarity of the two *R* diastereomers, in spite of the fact that the two crystal structures are not isomorphous.

Acknowledgment. This work was supported by the Herman F. Mark Chair of Polytechnic University and by the National Science Foundation (Grant No. DMR 8617788). We are grateful to J. Bartus for his suggestions and his assistance in preparing this manuscript.

References and Notes

(1) Vogl, O.; Kratky, C.; Simonsick, W. J., Jr.; Hatada, K. *Makromol. Chem., Suppl.*, in press.
(2) Vogl, O.; Jaycox, G. D. *Polymer* **1987**, *28* (13), 2179.
(3) Vogl, O. *Chemist* **1985**, *62* (9), 16.
(4) Zhang, J.; Jaycox, G. D.; Vogl, O. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1985**, *26* (1), 156.
(5) Okamoto, Y.; Suzuki, K.; Ohta, K.; Hatada, K.; Yuki, H. *J. Am. Chem. Soc.* **1979**, *101*, 4763.
(6) Ute, K.; Nishimura, T.; Matsuura, Y.; Hatada, K.; *Polym. J.* **1989**, *21*, 231.
(7) Hatada, K.; Ute, K.; Kitayama, T.; Tanaka, K.; Imanari, M.; Fujii, N. *Polym. J.* **1989**, *21*, 447.
(8) Ute, K.; Nishimura, T.; Hatada, K. *Polym. J.* **1989**, *21*, 1027.
(9) Kitayama, T.; Ute K.; Hatada, K. *Br. Polym. J.* **1990**, *23*, 5.
(10) Lipp, D. W.; Vogl, O. In *Ring Opening Polymerization*; Saegusa, T., Goethals, E., Eds.; ACS Symposium Series 59; American Chemical Society: Washington, DC, 1977; p 111.
(11) Corley, L. S.; Kubisa, P.; Yamada, B.; Vogl, O. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1980**, *21* (1), 205.
(12) Corley, L. S.; Jaycox, G. D.; Vogl, O. *J. Macromol. Sci., Chem. (U.S.—Japan Symp.)* **1988**, *A25* (5–7), 519.
(13) Zhang, J.; Jaycox, G. D.; Vogl, O. *Polymer* **1988**, *29* (4), 707.
(14) Vogl, O.; Bartus, J.; Murdoch, J. R. In *Frontiers of Macromolecular Science*, 32nd IUPAC International Symposium on Macromolecules, Kyoto, Japan, Aug 1–5, 1988; Saegusa, T., Higashimura, T., Abe, A., Eds.; Blackwell Scientific Publishers: Brookline Village, MA, 1989; p 31.
(15) Zhang, J.; Jaycox, G. D.; Vogl, O. *Polym. J.* **1987**, *19* (5), 603.
(16) Jaycox, G. D.; Xi, F.; Vogl, O.; Hatada, K.; Ute, K.; Nishimura, T. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30* (2), 167.
(17) Hatada, K.; Ute, K.; Nakano, T.; Vass, F.; Vogl, O. *Makromol. Chem.* **1989**, *190*, 2217.
(18) Vogl, O.; Xi, F.; Vass, F.; Ute, K.; Nishimura, T.; Hatada, K. *Macromolecules* **1989**, *22*, 4658.
(19) Ute, K.; Nishimura, T.; Hatada, K.; Xi, F.; Vass, F.; Vogl, O. *Makromol. Chem.* **1990**, *191*, 557.
(20) Ute, K.; Kashiyama, M.; Oka, K.; Hatada, K.; Vogl, O. *Makromol. Chem.* **1990**, *11*, 31.
(21) Abe, A.; Tasaki, K.; Inomata, K.; Vogl, O. *Macromolecules* **1986**, *19*, 2707.
(22) Lipp, D. W.; Vogl, O. *Polymer* **1977**, *18*, 1051.
(23) Jaycox, G. D.; Hatada, K.; Xi, F.; Vogl, O. *Pac. Polym. Prepr.* **1989**, *1*, 267.
(24) Hatada, K.; Ute, K.; Nishimura, T.; Xi, F.; Vogl, O. *Bull. Soc. Chim. Belg.* **1990**, *99* (11/12), 903.
(25) Simonsick, W. J., Jr. *J. Appl. Polym. Sci.: Appl. Polym. Symp.* **1989**, *43*, 257.
(26) Simonsick, W. J., Jr.; Fulginiti, M.; Xi, F.; Vogl, O. *Pac. Polym. Prepr.* **1989**, *1*, 269.
(27) Simonsick, W. J., Jr.; Xi, F.; Hatada, K.; Vogl, O. *Macromolecules* **1990**, *23*, 4720.
(28) Blom, K.; Simonsick, W. J., Jr.; Hatada, K.; Vogl, O., in preparation.
(29) Ute, K.; Sakaki, T.; Hatada, K.; Xi, F.; Vogl, O., in press.
(30) Sheldrick, G. M. *SHELXS-86, a Computer Program for Crystal Structures Solution*; University of Gottingen: Gottingen, FRG, 1986.
(31) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.
(32) Sheldrick, G. M. *SHELX-76, a Computer Program for Crystal Structure Determination*; University of Cambridge: Cambridge, U.K., 1976.
(33) Johnson, C. K. ORTEP. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

Registry No. TBIABU, 136760-22-0; (*R*)-BIABU, 139657-06-0; (*S*)-BIABU, 139657-05-9; Br_3CCHO, 115-17-3; LiOBu-*t*, 1907-33-1; AcOAc, 108-24-7; lithium bornyl oxide, 129646-58-8.