Polymerization and Telomerization of Chiral Acrylamides

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The acrylamide derived from Oppolzer's camphor sultam was polymerized and the resulting polymer was converted to poly(allyl acetate) through a reduction-acetylation sequence. The poly(allyl acetate) thus obtained was analyzed by NMR and was compared with authentically prepared isotactic as well as atactic poly(allyl acetate). The ^{13}C NMR peaks were assigned at the tetrad level. It is concluded that the poly(allyl acetate) obtained from poly(camphor sultam acrylamide) has an isotacticity level as low as 54%. Telomerization studies indicated that this chiral auxiliary is unable to control stereochemistry for telomers with two or more monomers incorporated. A model is proposed to account for the low selectivity in these polymerizations.

Acyclic stereochemistry can be effectively controlled in free radical reactions using rationally designed chiral auxiliaries.[1] In addition to conventional organic synthesis,[2-5] the auxiliary approach can be used to control stereochemistry in iterative free radical additions, polymerizations,[6] and telomerizations.[2g,h,7] Curran has made good use of Oppolzer's camphor sultam in radical addition, cyclization, and transfer reactions. Thus, addition of radicals to the acrylamide 1 followed by transfer reactions to the prochiral radical generated α to the sultam gives products with good control of the configuration at the newly formed stereogenic center, see Scheme 1. Other auxiliary groups that give good selectivities[2g,h] in radical transfer reactions, when attached to appropriate monomers, produce polymers that are highly isotactic.[7] Oxazolidine acrylamides such as 2, R = t-Bu or i-Pr, give good selectivities in simple transfer reactions and 2, R = t-Bu or i-Pr, also polymerizes to give a highly isotactic polymer. Control of configuration of the newly formed stereogenic center is apparently exercised at every step in the polymerization. It is thus of interest to examine the polymerization and telomerization reactions of 1, with particular focus on the stereochemistry of products formed in multiple addition reactions. We report here results that suggest that whereas the camphor sultam gives good selectivities in simple allyl transfers, it does not control the stereochemistry of products formed in serial free radical addition reactions.

Results and Discussion

Synthesis and Characterization of Poly(sultam acrylamide). The less-expensive enantiomer, D-(-)-2,10-camphor sultam used in this study was purchased from Aldrich or prepared according to Oppolzer's procedure.[8] Acrylamide 1 was prepared as described in the literature by Curran and Heffner.[9] Due to the limited solubility of 1 in benzene, polymerizations were carried out using azobis(isobutyronitrile) (AIBN) as the initiator in dichloromethane at 60 °C in a sealed tube. After polymerization, the contents of the tube were usually poured into a large volume of pentane and the precipitate was separated, washed with pentane, and dried. The polymer 3 was isolated as an amorphous white solid. Poly(camphor sultam acrylamide) is moderately soluble in benzene and toluene, and it is very soluble in chloroform, dichloromethane, and THF.

The acrylamide appears to be somewhat resistant to homopolymerization.[10] Under polymerization conditions, 0.7 M 1 and 5% AIBN, the average molecular weight (M_p) of the polymer is about 9300 (dispersity = 1.3) as estimated from GPC.[11]

Conversion of the Poly(sultam acrylamide) to Known Polymers. Since both the ^1H and ^{13}C NMR spectra of 3 were complicated by the auxiliary, direct evaluation of polymer tacticity by NMR was impossible. Effort was then focused on removal of the chiral auxiliary and conversion of the polyacrylamide to a known polymer for the purpose of determining tacticity. Although acyl sultams are known to undergo hydrolysis under mild basic

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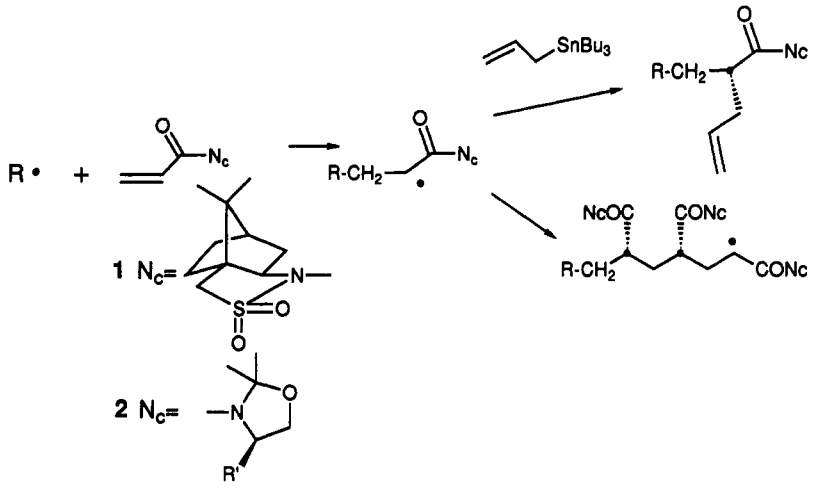
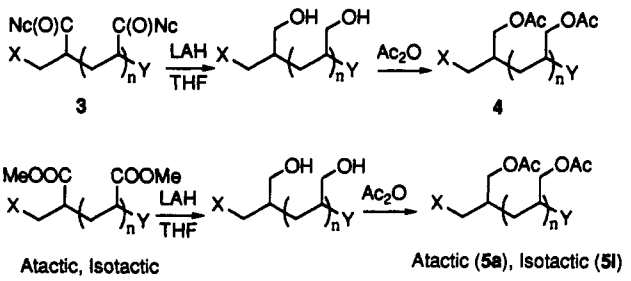
Scheme 1. Chain Transfer and Addition Reactions of Chiral Acrylamides



Scheme 2. Conversion of Poly(methyl acrylate) to Poly(allyl acetate)



conditions,[12] this polymer was very resistant to hydrolysis, even under drastic conditions. Lithium aluminum hydride was reported to cleave the carbonyl–sultam bond in small molecules reductively and this approach is effective for the polymer as well. However, the resulting poly(allyl alcohol) was difficult to purify due to complexation with aluminum salts and the good solubility of this polymer in water.[13] Thus, instead of converting the polyacrylamide to poly(allyl alcohol), whose NMR spectral data are known for both isotactic and syndiotactic sequences,[14] the polyacrylamide **3** was converted to poly(allyl acetate) (**4**), which is easier to purify. Thus, polyacrylamide **3** was reduced with LAH in THF, and the resulting poly(allyl alcohol) was acetylated *in situ* with acetic anhydride (Scheme 2).[13,15] The auxiliary released in the reduction step was also acetylated by acetic anhydride to give the sultam acetamide. Poly(allyl acetate) thus obtained can be purified by precipitation.

For comparisons, authentic atactic poly(allyl acetate) (**5a**) and isotactic poly(allyl acetate) (**5i**) were prepared from atactic and isotactic poly(methyl acrylate), respectively, by the same reduction–acetylation method (Scheme 2). Isotactic poly(methyl acrylate) was prepared by n-butyllithium-catalyzed polymerization of methyl acrylate in toluene at −78 °C.[16] Its average molecular weight (M_p = 12700) and its dispersity (3.0) were estimated from GPC. This polymer was 90% isotactic by ^{1}H NMR. The commercial poly(methyl acrylate) from Aldrich, which has an average molecular weight about 30000, was used as an atactic standard material. By ^{1}H NMR, this polymer appears to be 50% isotactic.

NMR Studies. NMR is one of the most powerful techniques for the analysis of relative configurations of vinyl polymer chains.[17] The methylene protons of the backbone of a vinyl polymer are usually sensitive to stereochemistry of diad (a sequence of two monomer units). Figure 1 shows the ^{1}H NMR spectra and the peak assignments for polymers **4**, **5i**, and **5a**.[15a] As predicted, the spectrum of isotactic poly(ally acetate) (**5i**) clearly shows two branches around the backbone methylene region. The two branches of isotactic signals, however, are so close together that the syndiotactic signal is not well resolved from isotactic signals in the atactic poly(allyl acetate). Although it is impossible to extract quantitative information from the methylene region of this ^{1}H spectrum, it is clear by visual inspection that both **4** and **5a** contain a significant amount of syndiotactic diads. The side-chain ester methylene protons should be sensitive to the triad (three-monomer sequence) stereochemistry. Although the signals for each of the three triads are poorly resolved in the 300-MHz ^{1}H NMR spectrum, they are nevertheless visible in the methine-decoupled spectrum. They are better resolved on a 500-MHz NMR spectrometer, especially when the methine proton resonance is irradiated. Figure 2 shows the ester methylene region of the 500-MHz ^{1}H NMR spectrum. The peak assignments were determined by comparison of the spectrum with those for the isotactic and atactic polymers. Thus, the highest field doublet is due to the *mm* triad. In the *mm* triad, the methylene is presumably closer to the shielding cone of both neighboring acetate carbonyls. Following this argument, the center and the lowest field signals should be the *mr* and *rr* triads, respectively. The fact that the center signal in the atactic poly(allyl acetate) (**5a**) is the largest of the three signals supports this assignment since in a

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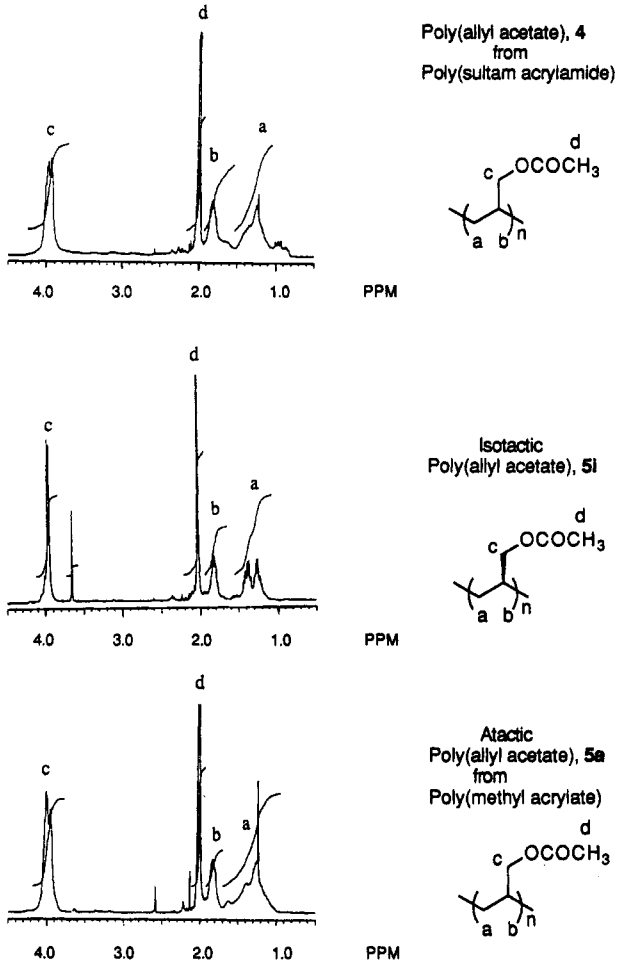


Figure 1. ^{1}H NMR spectra of poly(allyl acetate) **4**, **5i**, and **5a** at 70 °C ($CDCl_3$).

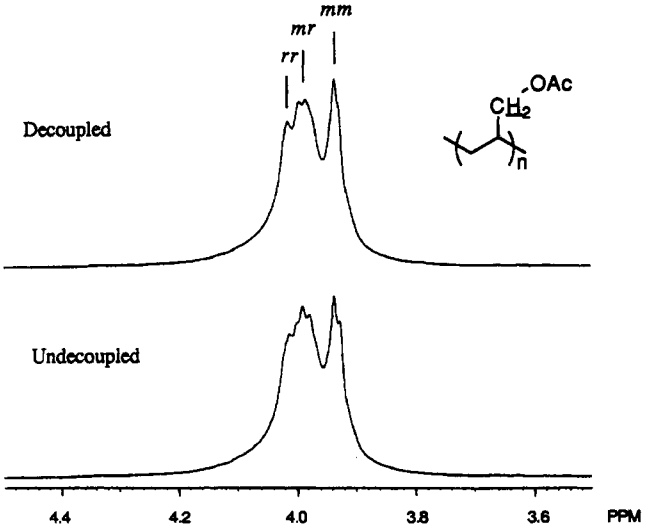


Figure 2. Ester methylene region of the 500-MHz ^{1}H NMR spectrum of the poly(allyl acetate) from poly(sultam acrylamide) at 70 °C.

random atactic polymer, the *mr* triad should be twice that of either the *mm* or *rr* triad. The *mr* signal shows two maxima even after decoupling because in the *mr* triad, the two protons are diastereotopic due to the absence of a symmetry plane which is present in the other two triads (Figure 3, R = CH_2OAc).

The decoupled 500-MHz ^{1}H NMR spectrum of **4** was deconvoluted based on Lorentzian line shape analysis into four individual components (Figure 4). The broadest

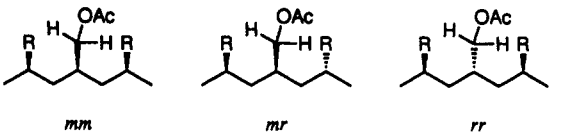


Figure 3. Symmetry considerations in triads.

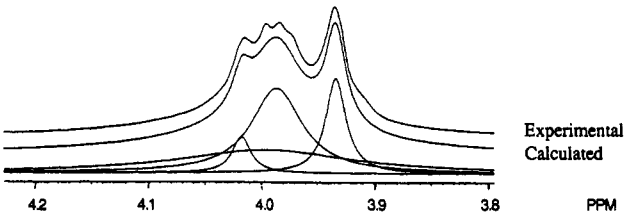


Figure 4. Deconvolution of the decoupled 500-MHz ^{1}H NMR spectrum of poly(allyl acetate) **4**.

component which reflects variations in baseline is discarded and the *mr* triad signal is simulated as a single peak. Integration of the three peaks gives a ratio of the three triads, *mm*:*mr*:*rr* = 2.7:6.3:1. This ratio indicates that the diad tacticity of this polymer is only (2.7 + 6.3 × 0.5)/(2.7 + 6.3 + 1) = 58% isotactic.

The ^{13}C NMR spectra of the three poly(allyl acetate)'s were also analyzed. All three polymers show a single carbonyl peak at 170.65 ppm. Figure 5 shows the aliphatic regions of the three ^{13}C spectra, and the backbone regions are expanded and inserted into each spectrum. Peaks are assigned by comparisons of ^{13}C, DEPT, and HETCOR spectra (not shown) in addition to statistical considerations. The acetate methyl ^{13}C shows only one peak for all three polymers. While the methine ^{13}C signal shows some sensitivity to pentad tacticities, without tacticity information from the ^{1}H NMR, it is only possible to assign the *mmmm* pentad peak by comparison with the isotactic polymer **5i**. The ester methylene region for both polymer **4** and **5a** shows three poorly resolved peaks resulting from the *mm*, *mr*, and *rr* triads. Three triads are assigned by comparison of the ^{13}C spectra of the three polymers and HETCOR spectra of **4** and **5i**. The backbone methylene ^{13}C is sensitive to tetrad tacticities and there is enough information in the HETCOR spectrum to allow assignments for all six tetrads. The *mmm* and *rrr* tetrads are identified with certainty by comparison of the ^{13}C NMR and HETCOR spectra. The *mmr* peak is assigned knowing that it is the next to the most abundant tetrad in the isotactic polymer **5i**. The HETCOR spectrum of **4** indicates that there is an *r*-centered tetrad underneath the *mmr* peak which is assigned to *mrm*. Since both *mrr* and *mmr* should be double intensity in the random atactic polymer **5a**, the downfield shoulder of the *mmr* peak is assigned to the *mrr* tetrad based on the HETCOR spectrum of **4** and the ^{13}C NMR spectrum of **5a**. The peak next to the *rrr* peak is assigned to the *rmr* tetrad based on the HETCOR spectrum of **4**.

Telomerization of Camphor Sultam Acrylamide. Although various attempts to fit the NMR data of polymer **4** to a statistical model[18] were unsuccessful largely due to poorly resolved peaks, it is clear that the diad tacticity level is very low (53–58% isotactic by various estimations). This result is surprising given the excellent selectivity observed for simple allyl transfer reactions of radicals bearing this auxiliary.[4] To understand better the camphor sultam auxiliary as a stereocontrol element, a telomerization study of monomer **1** was carried out. An addition-

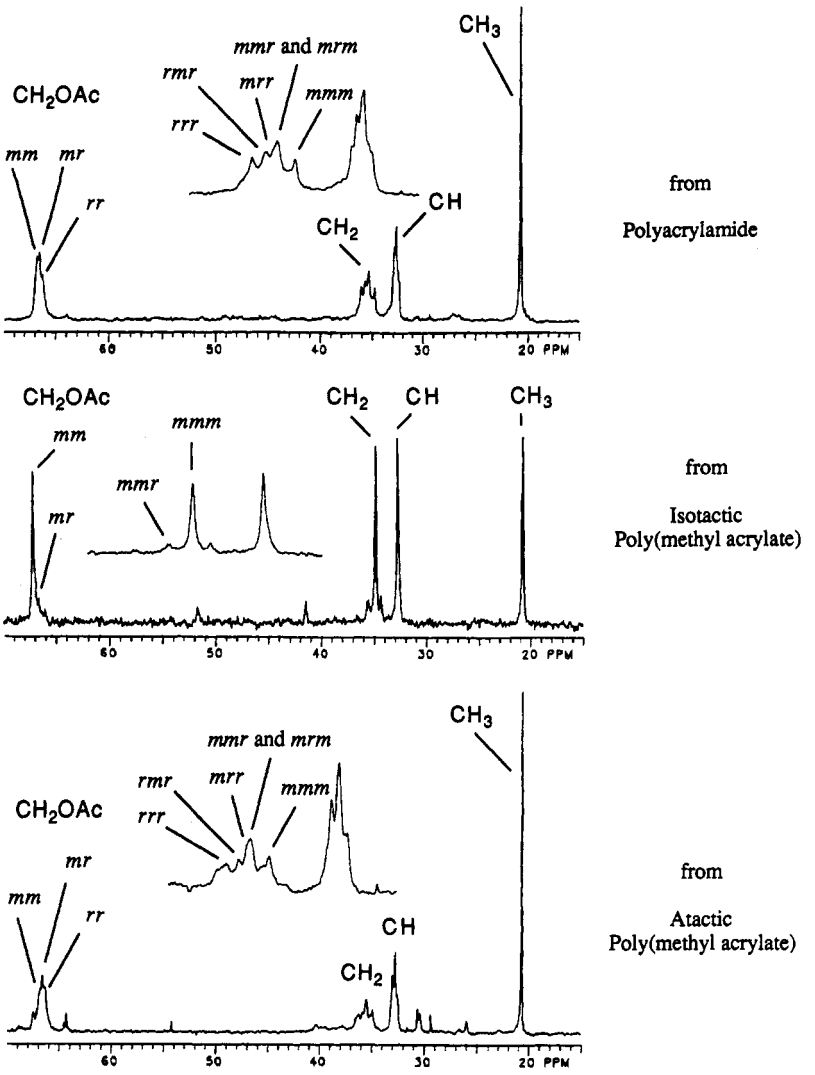
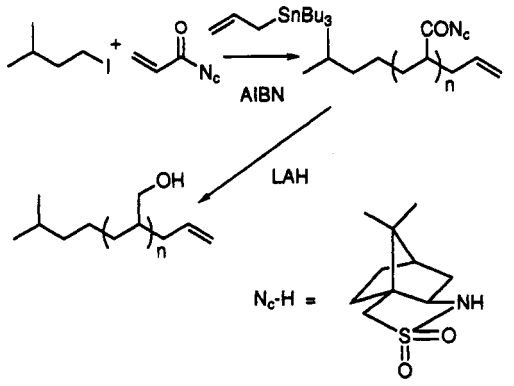


Figure 5. ^{13}C-NMR spectra of poly(allyl acetate) **4**, **5i**, and **5a** at 60 °C in $CDCl_3$.

Scheme 3. Telomerization of Camphor Sultam Acrylamide



chain transfer sequence similar to that used by Curran[4] was employed in this telomerization reaction (Scheme 3). Isopentyl iodide was used[19] as the alkyl iodide and appropriate conditions were chosen so that the resulting telomers were usually composed of mostly $n = 1$ and $n = 2$ telomers. Thus, 40 mM of acrylamide , 10 equiv of isopentyl iodide, and 1 equiv of allyltributyltin were used in a typical telomerization reaction.

The diastereomers of $n = 1$ telomer **6** were formed in ~7:1 ratio by GC analysis. Three major $n = 2$ telomers **7** were isolated by HPLC. NMR analysis suggest that one of them, the third eluting $n = 2$ telomer on HPLC, is a rearranged product (**7R**). Apparently, the radical resulting from addition of isopentyl to the sultam acrylamide is so electrophilic that a 1,5 hydrogen shift from the electron-rich tertiary C–H bond to the radical becomes competitive to allyl transfer and the second addition (Scheme 4).[20] The isotactic $n = 2$ telomer **7i** was crystalline and its stereochemistry was confirmed by X-ray crystallographic analysis (Figure 6, see supplementary material for details). Reduction of $n = 2$ telomers **7i**, **7s**, and **7R** gives diols, **8i**, **8s**, and **8R**, respectively.

Analysis of the $n = 2$ telomers directly was difficult due to complications from minor diastereomers and the fact none of the $n = 2$ telomers are readily eluted through GC columns. In order to obtain quantitative information about the $n = 2$ telomers, the crude telomer mixture (excess reagent and tin byproducts were removed by a simple vacuum distillation) was reduced with LAH in THF directly. The reduction mixture was analyzed by HPLC (50% ethyl acetate/hexane). A typical analytical HPLC gives a product ratio of the three diols, **8i**:**8s**:**8R** = 1.2:1:1. If the polymerization reaction is just a repetition of this telomerization, the calculated isotacticity would be 1.2/(1 + 1.2) = 54% which falls in the tacticity range (53–58%

(20) For rate constants of allyl chain transfer reactions, see: Curran, D. P.; van Elburg, P. A.; Giese, B.; Gilges, S. *Tetrahedron Lett.* **1990**, *31*, 2861.

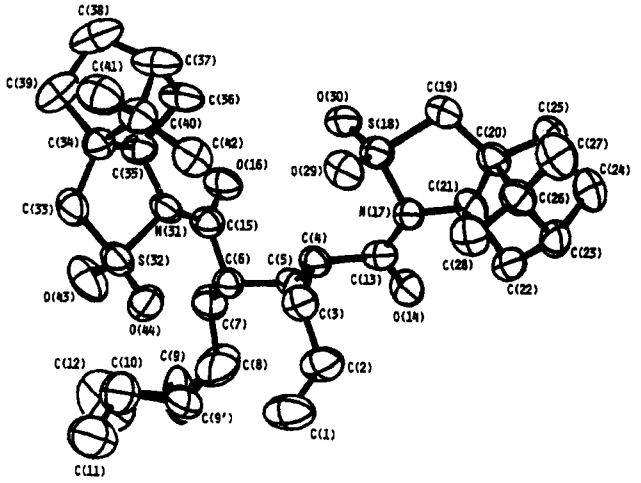
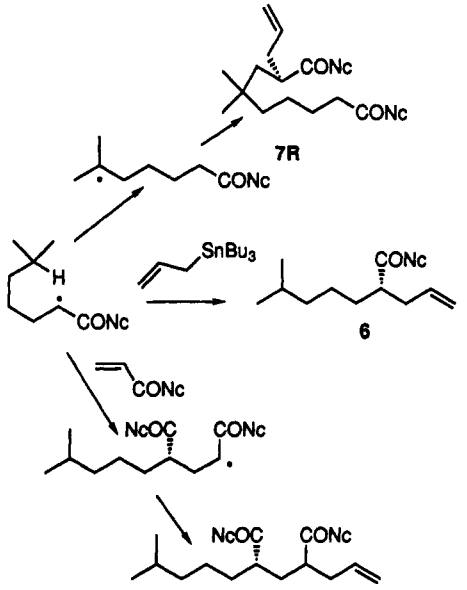


Figure 6. ORTEP diagram (40% probability ellipsoids) showing the crystallographic atom numbering scheme and solid-state conformation of isotactic $n = 2$ telomer **7i**. C(9) is disordered over two positions [C(9) and C(9′)]. Hydrogen atoms have been omitted for clarity.

Scheme 4. Reaction Pathways of the Monoaddition Radical



7i: *isotactic* **7s**: *syndiotactic*

isotactic) estimated from the NMR studies of poly(allyl acetate) **4** derived from polymer **3**.

Stereoselection in Polymerizations of Chiral Acrylamides. The results of polymerization of the acrylamides **1** and **2** are striking. While both acrylamides give rise to high selectivities in simple allyl transfer reactions, **1** gives an atactic polymer while **2** gives a highly isotactic polymer. While tertiary polymer structure may be the cause of this selectivity, the telomerization studies reported here suggest another cause. A working model that describes the stereoselectivity of polymerization of camphor sultam acrylamide **1** is presented in Figure 7.

Consider a growing polymer radical **9** that may adopt two conformations **9a** and **9b** of bonds near the stereogenic center that was formed from the previous chain extension addition reaction. Carbon C-2 should be *Z* to the carbonyl oxygen based upon radical conformational arguments,[1] and the *anti* conformation should be favored along the single C1–C2 bond. Auxiliary control would lead to

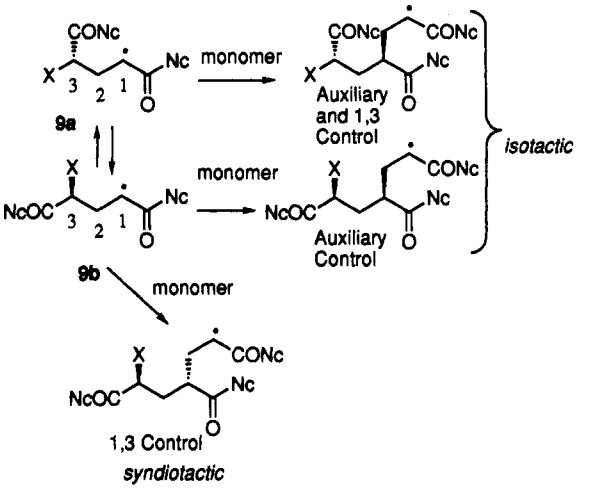


Figure 7. Origins of the stereoselectivity in polymerization of chiral acrylamides. N_c = chiral amide.

formation of an isotactic diad for reaction from either conformation **9a** or **9b**. The auxiliary controls the configuration of the new stereogenic center. On the other hand, the 1,3 interaction between the polymer stereogenic center at C-3 and the incoming acrylamide would favor the formation of an isotactic diad if the favored transition state for addition looks like **9a** while a syndiotactic diad would be formed if the transition state for addition was analogous to **9b** (and if 1,3 control is dominant). In **9a**, auxiliary and 1,3 control elements are "matched" while in **9b**, auxiliary and 1,3 control elements are "mismatched".

The results of polymerization and telomerization studies reported here suggest that 1,3 stereocontrol is exerted in competition with auxiliary control for polymerization of the sultam acrylamide **1**. The transition state for addition must resemble conformer **9b**, and substrate control (1,3 interactions in the growing polymer chain) and auxiliary control are "mismatched". The result is a polymer with a nearly 50:50 isotactic:syndiotactic diad ratio. This view is consistent with the fact that formation of the first stereogenic center occurs with substantial control of stereochemistry while subsequent centers are formed without control. In the first addition reaction, no 1,3 stereocontrol element is present while in subsequent additions, this effect comes into play.

Polymerization and allyl transfer reactions of the oxazolidine acrylamide **2** give products with a different stereochemical pattern than does the sultam acrylamide **1**.[7] The acrylamide **2**, R′ = *tert*-butyl, gives allyl transfer products with a selectivity of 23:1 at 80°, see Scheme 1. Consistent with this result, polymers formed from **2**, *R* = *tert*-butyl, are highly isotactic with an m:r diad ratio of 92:8. This diad ratio corresponds to a selectivity for each addition reaction of about 22:1.[7] For the acrylamide **2** with R′ = isopropyl, allyl transfer selectivity is only 4:1 at 80°, but the polymer is still formed with an *m:r* diad ratio of 92:8.[7] There is no diminution of the isotactic diad in the polymer even though the auxiliary group with R′ = isopropyl is less selective in the single-step allyl transfer reaction than is the case for the auxiliary with R′ = *tert*-butyl.

We now suggest, based upon the analysis presented in Figure 7, that the growing polymer obtained from monomer **2** has a "matched" selectivity for auxiliary and 1,3 control. The "less effective" auxiliary **2**, R′ = isopropyl, in single allyl transfer reactions can be used to exert a high level

of control of configuration in the multiple addition sequence since 1,3-stereocontrol supplements normal auxiliary control for this auxiliary.

It is not clear what elements are critical in determining whether auxiliary control and 1,3 stereocontrol are "matched" or "mismatched" for a particular auxiliary group. We have discussed,[2h] in detail, the conformational preferences of products formed from oxazolidine-derived auxiliaries like 2, but we have little information on products of sultam-derived acrylamide 1 to provide a reasonable comparison. A more-detailed analysis will benefit from model studies that focus on the 1,3-stereocontrol suggested in Figure 7. We emphasize again that polymer tertiary structure may be important in determining tacticity, and model studies will also provide information on this important question.

Experimental Section

Tetrahydrofuran was freshly distilled from sodium/benzophenone. Dichloromethane was distilled from calcium hydride and stored over molecular sieves. Benzene and toluene were distilled from sodium/benzophenone and stored over molecular sieves. Gas chromatography was performed on a Hewlett-Packard 5890A gas chromatograph with a flame ionization detector coupled to a Hewlett-Packard 3393A integrator (conditions: 15-m, 0.32-mm i.d. SPB-1 column, 5 psi, 3 min at 100 °C to 280 °C at 15 °C/min). NMR spectra were run on either a Varian XL-300 or a General Electric QE-300 at 300 MHz for ^{1}H and 75 MHz for ^{13}C. The 500-MHz ^{1}H NMR was performed on a Varian Unity-500 spectrometer. High-temperature NMR spectra were obtained using degassed and sealed sample tubes. Chemical shifts are reported in ppm downfield from TMS with residual solvent as an internal standard (for ^{1}H NMR, $CHCl_3$: δ 7.25 ppm; for ^{13}C NMR, $CDCl_3$: δ 77 ppm). Mass spectra were obtained on a Hewlett-Packard 5988A gas chromatograph/mass spectrometer. Chemical ionization was performed under 2×10^{-4} atm CH_4/NH_3. Flash chromatography was performed using 35–70 μm silica gel. Analytical HPLC was performed using a Waters M6000 pump, tandem Beckman Ultrasphere Si-4.6 mm × 25 cm columns, and a Waters R401 differential refractometer. Preparative HPLC was performed using an Isco 2350 pump, a Dynamax 60 A Si 83-121-C5 silica column, and a Waters R401 differential refractometer. GPC was conducted using THF as the eluting solvent with a Waters 600E pump, Waters Ultrastyragel 100-Å and 500-Å columns in series, and a Waters R401 differential refractometer. Melting points and boiling points are uncorrected.

Polymerization of Camphor Sultam Acrylamide, 1. A solution of acrylamide **1**, (2 g, 7.4 mmol) and AIBN (60 mg, 0.36 mmol) in 10 mL of dichloromethane was placed in a glass tube and degassed by three freeze-pump-thaw cycles. The tube was sealed under vacuum and then immersed in a oil bath whose temperature was held at 60 ± 0.1 °C. After 21.5 h, the tube was opened and the contents were analyzed by GC and then precipitated in pentane. The GC of the crude mixture indicated that a small amount of the acrylamide was still present. The precipitate was collected, washed with pentane, and dried under vacuum. The polymer (**3**, 1.81 g, 90% yield) was obtained as a white solid. The molecular weight (M_p = 8200) and dispersity (1.3) were estimated from GPC. Anal. Calcd for $C_{13}H_{19}NO_3S$: C, 57.97; H, 7.11; N, 5.20; S, 11.90. Found: C, 58.02; H, 7.13; N, 5.17; S, 11.84.

Conversion of Poly(camphor sultam acrylamide) to Poly(allyl acetate). Polymer **3** (1.5 g, 5.6 mmol of monomer) was dissolved in 100 mL of THF and added dropwise over 30 min to a refluxing suspension of LAH (1 g, 26 mmol) in 100 mL of THF. This mixture was refluxed for 3 h and then cooled to room temperature. Acetic anhydride (100 mL) was added cautiously. This mixture was heated slowly with stirring, and THF was allowed to distill until the internal temperature reached 110 °C. The mixture was heated at 110 °C for 3 h. At one point, the mixture was very thick, but after 20 min more heating, it became fluid again. The mixture was cooled to room temperature and filtered, and the filter cake was washed thoroughly with acetone. Volatiles were removed from the combined washings and the residue was redissolved in acetone and then precipitated in ether. Polymer **4** (268 mg, 48% yield) was obtained as a brownish solid. NMR of the evaporated ether phase indicated that there is some polymer lost in the mother liquor. The ^{1}H and ^{13}C NMR spectra of polymer **4** are presented in Figures 1 and 5, respectively.

Camphor Sultam Acetamide. During the above conversion of poly(camphor sultam acrylamide) to poly(allyl acetate), the auxiliary was acetylated to give camphor sultam acetamide. This byproduct (1.21 g, 84% yield) was isolated as a white solid from the ether mother liquor by flash column chromatography (50% ethyl acetate/hexane): mp 128–131 °C; GC/CIMS MH^+ = 258, $M + NH_4^+$ = 275; ^{1}H NMR ($CDCl_3$) δ 3.84 (dd, J_1 = 5.1, J_2 = 7.5 Hz, 1H), 3.46 (m, 2H), 2.39 (s, 3H), 2.11 (m, 2H), 1.87 (m, 3H), 1.36 (m, 2H), 1.14 (s, 3H), 0.96 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 168.49, 65.05, 52.65, 48.28, 47.66, 44.52, 38.29, 32.71, 26.34, 23.11, 20.73, 19.80. Anal. Calcd for $C_{12}H_{19}NO_3S$: C, 56.01; H, 7.44; N, 5.44; S, 12.46. Found: C, 55.88; H, 7.38; N, 5.38; S, 12.40.

Preparation of Isotactic Poly(methyl acrylate). Methyl acrylate (20 mL) was dissolved in 100 mL of toluene and cooled to −78 °C. Butyllithium (5 mL, 2.5 M in hexanes) was added slowly via a syringe and the mixture was stirred at −78 °C for 9 h. The cold solution was poured into MeOH resulting in formation of a gummy precipitate. The precipitate was collected and redissolved in acetone then reprecipitated in MeOH. This dissolution–precipitation procedure was repeated and the final precipitate was collected and dried under vacuum. The polymer (3 g gummy white solid) showed a clean NMR which was identical to that reported in literature. NMR analysis suggested that the diad isotacticity of this poly(methyl acrylate) was ~90%. Its average molecular weight (M_p = 14400) and dispersity (3.0) were estimated from GPC, based on polystyrene as a standard.

Conversion of Poly(methyl acrylate) to Poly(allyl acetate). The reduction and acetylation procedure for poly(camphor sultam acrylamide) was used. The isotactic poly(allyl acetate) (**5i**) was prepared in 46% yield from isotactic poly(methyl acrylate) while the atactic polymer **5a** was prepared in 86% yield from commercial atactic poly(methyl acrylate). The ^{1}H and ^{13}C (for **5i**) NMR spectra are presented in Figures 1 and 5, respectively. The sharp lineshape of the ^{13}C NMR spectrum of isotactic poly(allyl acetate) (**5i**) allows measurement of C–H coupling constants by off-resonance decoupling of the proton frequency. Thus, ^{13}C NMR ($CDCl_3$) δ 170.65 (s), 67.29 (t, J = 145 Hz), 34.94 (t, 125 Hz), 32.85 (t, J = 133 Hz), 20.64 (q, J = 130 Hz).

Telomerization of Camphor Sultam Acrylamide. A solution of the acrylamide (2 g, 7.4 mmol), isopentyl iodide (8 mL, 61 mmol), allyltributyltin (2.8 mL, 9 mmol), and AIBN (120 mg, 0.73 mmol) in 200 mL of benzene was purged with argon for 15 min and then refluxed for 9 h. Solvent was removed under reduced pressure and the residue was vacuum-distilled while the pot temperature was kept below 180 °C. The residue was subjected to separation by flash column chromatography (gradient elution: 15–50% ethyl acetate/hexane) to give the n = 1 telomer and a mixture of n = 2 telomers. The n = 2 telomers were further separated by preparative HPLC (25% ethyl acetate/hexane).

Major n = 1 telomer **6**: 477 mg, 17% yield; mp 77–80 °C; ^{1}H NMR ($CDCl_3$) δ 5.78 (m, 1H), 5.00 (m, 2H), 3.89 (t, J = 6.0 Hz, 1H), 3.50 (m, 2H), 3.11 (m, 1H), 2.34 (m, 2H), 2.02 (m, 2H), 1.87 (m, 3H), 1.70 (m, 1H), 1.50 (m, 1H), 1.35 (m, 5H), 1.14 (s, 3H), 1.12 (m, 2H), 0.95 (s, 3H), 0.83 (d, J = 6.6 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 175.12, 135.11, 117.15, 65.28, 53.25, 48.08, 47.68, 45.02, 44.60, 38.94, 38.49, 38.06, 32.86, 31.02, 27.73, 26.43, 24.94, 22.63, 22.54, 20.83, 19.91. Anal. Calcd for $C_{21}H_{35}NO_3S$: C, 66.10; H, 9.25; N, 3.67; S, 8.40. Found: C, 66.17; H, 9.19; N, 3.70; S, 8.30.

Major syndiotactic n = 2 telomer **7s**: 164 mg, 7% yield; first eluting on HPLC; ^{1}H NMR ($CDCl_3$) δ 5.70 (m, 1H), 5.05 (m, 2H), 3.85 (m, 2H), 3.45 (m, 4H), 3.17 (m, 1H), 3.07 (m, 1H), 2.50 (m, 1H), 2.23 (m, 2H), 1.90 (m, 10H), 1.05–1.55 (m, 12 H), 1.22 (s, 6H), 0.95 (s, 6H), 0.81 (d, J = 6.6 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 174.68, 173.97, 135.18, 117.30, 65.33, 65.25, 53.10, 53.08, 48.19, 48.17, 47.73, 44.58, 44.56, 43.01, 42.32, 38.81, 38.25, 34.85, 34.26, 32.87, 32.82, 30.38, 27.70, 26.48, 26.41, 25.01, 22.71, 22.45, 22.43, 20.71, 19.98, 19.93, 19.89.

Major isotactic $n = 2$ telomer **7i**: 255 mg, 11% yield; second eluting on HPLC; mp 200–201 °C. The crystal structure is presented in Figure 6. ^{1}H NMR ($CDCl_3$) δ 5.68 (m, 1H), 5.00 (m, 2H), 3.88 (m, 2H), 3.42 (m, 4H), 3.03 (m, 2H), 2.60 (m, 1H), 2.30 (m, 2H), 1.05–2.15 (m, 12 H), 1.19 (s, 3H), 1.11 (s, 3H), 0.94 (s, 3H), 0.93 (s, 3H), 0.818 (d, J = 6.6 Hz, 6H), 0.816 (d, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 174.94, 174.23, 134.38, 117.55, 65.46, 65.27, 53.21, 53.05, 48.10, 48.07, 47.69, 47.60, 44.64, 42.29, 42.21, 38.75, 38.52, 38.39, 36.48, 33.46, 32.91, 32.88, 32.38, 27.68, 26.49, 26.33, 24.62, 22.56, 21.10, 21.08, 20.91, 20.88, 20.84, 19.86. Anal. Calcd for $C_{34}H_{54}N_2O_6S_2$: C, 62.74; H, 8.36; N, 4.30; S, 9.85. Found: C, 62.68; H, 8.27; N, 4.31; S, 9.75.

Major rearranged $n = 2$ telomer **7R**: 261 mg, 11% yield; mp 82–84 °C; ^{1}H NMR ($CDCl_3$) δ 5.72 (m, 1H), 5.00 (m, 2H), 3.85 (m, 2H), 3.45 (m, 4H), 3.05 (m, 1H), 2.68 (m, 2H), 2.35 (m, 1H), 2.20 (m, 1H), 2.03 (m, 4H), 1.85 (m, 6H), 1.60 (m, 2H), 1.05–1.50 (m, 10 H), 1.13 (s, 6H), 0.94 (s, 6H), 0.79 (s, 3H), 0.76 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 174.52, 172.05, 134.99, 117.57, 65.44, 65.14, 53.14, 52.92, 48.31, 48.21, 47.71, 47.67, 44.65, 44.59, 44.52, 42.04, 40.72, 40.61, 39.48, 38.51, 35.59, 32.92, 32.79, 32.72, 26.87, 26.82, 26.65, 26.42, 26.37, 25.31, 23.46, 20.84, 19.89, 19.84. Anal. Calcd for $C_{34}H_{54}N_2O_6S_2$: C, 62.74; H, 8.36; N, 4.30; S, 9.85. Found: C, 62.56; H, 8.44; N, 4.25; S, 9.84.

Reduction of the Telomers with LAH. The above purified telomers were reduced separately to the corresponding alcohols. Generally, the telomer is dissolved in THF and excess LAH is added cautiously. The reaction mixture is usually allowed to stir at room temperature for at least 2 h, diluted with ether, and then worked up with the standard 1:1:3 water–15% NaOH–water procedure. This mixture is usually dried directly with 1:1 Na_2SO_4–$MgSO_4$. Upon filtration and evaporation, the residue is purified by flash column chromatography (for the $n = 1$ product: 10% ethyl acetate/hexane; for the diols: 50% ethyl acetate/hexane).

The $n = 1$ telomer: clear oil; 92% yield; ^{1}H NMR ($CDCl_3$) δ 5.81 (m, 1H), 5.02 (m, 2H), 3.55 (m, 2H), 2.11 (m, 2H), 1.56 (m, 3H), 1.28 (m, 4H), 1.16 (m, 2H), 0.85 (d, J = 6.6 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 137.16, 116.13, 65.56, 40.38, 39.23, 35.81, 30.82, 27.90, 24.65, 22.61. Anal. Calcd for $C_{11}H_{22}O$: C, 77.60; H, 13.02. Found: C, 77.32; H, 12.97.

Syndiotactic $n = 2$ telomer **8s**: clear oil; 76% yield; ^{1}H NMR ($CDCl_3$) δ 5.80 (m, 1H), 5.05 (m, 2H), 3.52 (m, 4H), 2.06 (m, 4H), 1.74 (m, 1H), 1.60 (m, 1H), 1.50 (m, 1H), 1.28 (m, 6H), 1.14 (m, 2H), 0.85 (d, J = 6.6 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 136.91, 116.41, 65.88, 39.31, 37.77, 37.55, 36.44, 32.78, 31.77, 27.90, 24.66, 22.61; GC/CIMS: M + H$^+$ = 229, M + NH_4^+ = 246. Anal. Calcd for $C_{14}H_{28}O_2$: C, 73.63; H, 12.36. Found: C, 73.46; H, 12.47.

Rearranged $n = 2$ telomer **8R**: white solid; 66% yield; ^{1}H NMR ($CDCl_3$) δ 5.80 (m, 1H), 5.02 (m, 2H), 3.61 (t, J = 6.6 Hz, 2H), 3.53 (dd, J_1 =4.7 Hz, J_2 = 10.7 Hz, 1H), 3.42 (dd, J_1 = 6.9 Hz, J_2 = 10.8 Hz, 1H), 2.13 (m, 2H), 1.60 (m, 5H), 1.20 (m, 8H), 0.83 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 137.18, 116.32, 66.84, 62.89, 42.56, 42.05, 38.13, 36.21, 33.30, 32.71, 27.26, 27.21, 26.58, 23.79. The HETCOR and COSY NMR spectra were consistent with structure. GC/CIMS: M + H$^+$ = 229, M + NH_4^+ = 246. Anal. Calcd for $C_{14}H_{28}O_2$: C, 73.63; H, 12.36. Found: C, 73.44; H, 12.41.

Isotactic $n = 2$ telomer **8i**: clear oil; 87% yield; ^{1}H NMR ($CDCl_3$) δ 5.80 (m, 1H), 5.02 (m, 2H), 3.61 (dd, J_1 = 4.7 Hz, J_2 = 10.7 Hz, 2H), 3.43 (m, 2H), 2.90 (br s, 2H), 2.07 (t, J = 6.8 Hz, 2H), 1.64 (m, 1H), 1.50 (m, 3H), 1.20 (m, 7H), 0.84 (d, J = 6.6 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 136.86, 116.33, 65.54, 65.21, 39.29, 38.07, 38.03, 36.64, 32.56, 32.27, 27.91, 24.65, 22.61; GC/CIMS: M + H$^+$ = 229, M + NH_4^+ = 246. Anal. Calcd for $C_{14}H_{28}O_2$: C, 73.63; H, 12.36. Found: C, 73.38; H, 12.28.

Quantitative Analysis of the Telomers. A solution of camphor sultam acrylamide (500 mg, 1.8 mmol), isopentyl iodide (2.5 mL, 19 mmol), allyltributyltin (0.7 mL, 2.2 mmol), and AIBN (30 mg, 0.18 mmol) in 50 mL of benzene was purged with argon for 15 min and then refluxed for 6.5 h. This mixture was concentrated and vacuum-distilled to remove excess reagents and tin byproducts. The residue was dissolved in 40 mL of THF and stirred with LAH (650 mg, 17 mmol) at room temperature overnight. This mixture was diluted with ether and worked up with 1 mL of water followed by 1 mL of 15% NaOH and then 3 mL of water. This mixture was stirred at room temperature until the color turned from gray to white. A 1:1 mixture of Na_2SO_4 and $MgSO_4$ was added and this mixture was stirred for 30 min. Upon filtration and concentration, the residue was dissolved in ethyl acetate and analyzed on HPLC (50% ethyl acetate/hexane). The peaks were collected and their identities were checked by GC and NMR. The syndiotactic and isotactic diols were shown to coelute on GC. GC/MS suggested that $n = 3$ telomers were also formed. The ratios of the three $n = 2$ telomers were measured by cut-and-weigh method.

X-ray Crystal Structure Analysis of 7i.[21,22] Crystal data: $C_{34}H_{54}N_2O_6S_2$, M = 650.95, orthorhombic, space group $P2_12_12_1$-(D_2^4) – No. 19, a = 15.464(2) Å, b = 30.823(3) Å, c = 7.441(1) Å (from 25 accurately-centered reflections, 30° < θ < 35°, widely separated in reciprocal space), V = 3547(1) Å^3, Z = 4, D_{calcd} = 1.219 g cm^{-3}, μ(Cu Kα radiation, λ = 1.5418 Å) = 16.7 cm^{-1}; crystal dimensions: 0.03 × 0.06 × 0.80 mm. Preliminary unit-cell parameters and space group information were derived from oscillation and Weissenberg photographs. The space group $P2_12_12_1$ was defined uniquely by the systematic absences: $h00$ when $h \neq 2n$, $0k0$ when $k \neq 2n$, $00l$ when $l \neq 2n$. Intensity data ($+h,+k,+l$, 3579 nonequivalent reflections) were recorded on an Enraf-Nonius CAD-4 diffractometer [Cu Kα radiation, graphite monochromator; ω–2θ scans, scan width (0.70 + 0.14 tan θ)°]. The intensities of four reference reflections, remeasured every 2 h during data collection, showed no significant variation (<2%). Corrections for the usual Lorentz and polarization effects were applied to the data. The crystal structure was solved by direct methods (MULTAN 11/82). Approximate coordinates for the sulfur and its bonded oxygen and nitrogen atoms were derived from an E-map. The remaining non-hydrogen atoms were located in a series of weighted F_o Fourier syntheses phased successively by an increasing number of atoms. Positional and thermal parameters of all non-hydrogen atoms (at first isotropic and then anisotropic) were adjusted by means of several rounds of full-matrix least-squares calculations [minimizing $\Sigma w\Delta^2$; $w = 1/\sigma^2$-($|F_o|$), $\Delta = (|F_o| - |F_c|)$]. During the course of these iterations, the anisotropic thermal parameters of C(9) and the bonding geometry associated with this atom indicated that it was disordered over two positions. In the final iterations, hydrogen atoms, except those of C(8), C(9) and C(10), were incorporated at their calculated positions, and an extinction correction (g) was included as a variable. The parameter refinement converged (max shift:esd = 0.03) at R = 0.047 (R_w = 0.062, GOF = 1.27, g = 1.1(1) × 10^{-6}) over 1531 reflections with $I > 3.0\sigma(I)$. A final difference Fourier synthesis contained no unusual features [$\Delta\rho$(e/Å^3); max, 0.16; min, –0.17]. Crystallographic calculations were performed on PDP11/44 and MicroVAX computers by use of the Enraf-Nonius Structure Determination Package (SDP). For all structure factor calculations, neutral-atom scattering factors and their anomalous dispersion corrections were taken from ref 21.

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Supplementary Material Available: Tables of atomic positional and thermal parameters, bond lengths, bond angles, and torsion angles for **7i** and a discussion of NMR assignments for the polymer are presented (15 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(21) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U. K., 1974; Vol. IV.

(22) The authors have deposited atomic coordinates for **7i** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.