terial.[34] Crystallographic calculations were performed on PDP11/44 and MicroVAX computers using the Enraf-Nonius Structure Determination Package (SDP 3.0). For all structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from ref 35.

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Supplementary Material Available: ORTEP diagrams showing the atom numbering schemes and tables of crystallographic data, atomic positional and thermal parameters, and bond lengths and angles for **2**, **4b**, **4c**, **5c**, **12b**, and **15c** (56 pages); tables of observed and calculated structure amplitudes (82 pages). Ordering information is given on any current masthead page.

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Chiral Auxiliary Control of Tacticity in Free Radical Polymerization

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Abstract: Chiral oxazolidine acrylamides undergo stereocontrolled free radical polymerization. Remarkably high degrees of tacticity have been demonstrated in the polymerization of acrylamides with these chiral auxiliaries that are derived from valine, phenylglycine, and *tert*-leucine. The polyacrylamides formed in these polymerizations can be converted to poly(acrylic acid), P(AA), and poly(methyl acrylate), P(MA), by hydrolysis and esterification. Tacticities as high as 92% have been measured for P(AA) and P(MA) resulting from these reactions. NMR studies of the microstructure of the polymers formed using chiral auxiliaries to control the stereochemistry of the reaction showed that the distribution of stereochemical sequences could be predicted by a statistical analysis based upon the mechanism of stereoselection. Specifically, these studies confirm that the stereocontrol is the result of facial selectivity in the addition of the monomer to the growing polymer radical. This face selectivity is thought to be the result of steric hindrance to approach of the monomer to one face of the radical caused by the chiral auxiliary. Further NMR studies were used to propose an analysis of the stereochemistry of P(MA) at the hexad level. Using HETCOR techniques, eight of the twenty hexads were conclusively identified, and a further six were narrowed to two possible choices.

Free radical polymerization of alkenes is an important method of making polymers. Control of the stereochemistry (i.e., the tacticity) in free radical polymerization reactions has been of interest since 1929 when Staudinger[1] pointed out that the tertiary carbons formed in vinyl polymerization reactions could have two different stereochemical arrangements. Significant stereocontrol of free radical polymerization reactions of vinyl monomers has never been achieved, with atactic polymers generally resulting from free radical polymerization. Important polymer bulk properties such as tensile strength, melting point, and solubility all have been shown to depend on the stereochemistry of the polymer,[2] and since free radical polymerization methods are convenient, the control of stereochemistry in free radical polymerization is a significant goal.

The degree of stereocontrol in a polymerization reaction is measured by the tacticity of the resulting polymer, where tacticity is defined by the relationship that adjacent stereocenters have to one another. In vinyl free radical polymerization, the difference between the activation barriers for the addition to the diastereotopic faces of the radical determines the selectivity of the polymerization, Figure 1. In a typical free radical polymerization, the stereoregulating effect results from a steric interaction between the incoming alkene and nearest stereocenter, but due to the conformational mobility of the chain, this effect is minimal. For example, the ratio of k_s/k_i for methyl acrylate is 1.1 at 0 °C.[3]

No systematic approach for controlling stereochemistry in acyclic radical reactions like those involved in polymerization had been undertaken prior to 1988. Since that time, work by several groups has employed chiral auxiliaries to control the stereochemistry of acyclic free radical addition reactions including telomerizations.[4-9] The use of groups such as pyrrolidine and

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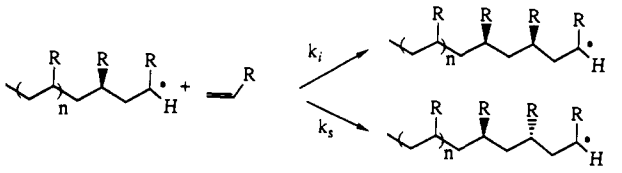


Figure 1. Stereocontrol in free radical polymerization.

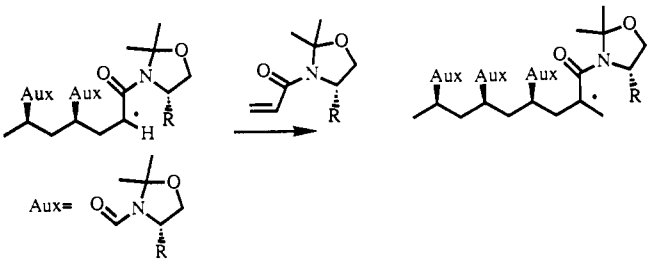


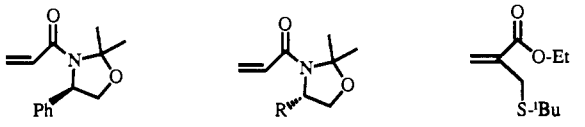
Figure 2. Chiral auxiliary controlled polymerization.

oxazolidine amides attached directly to radicals has allowed stereocontrol in addition reactions and has provided a framework of understanding for free radical acyclic stereocontrol. We report herein how chiral auxiliaries can be used to control tacticity in free radical polymerizations.

In contrast to typical free radical polymerization, the stereochemistry of stereogenic centers formed in addition reactions of chiral auxiliary controlled polymerization will not be dictated by the terminal stereocenter. Rather, we anticipated that the chiral auxiliary on the radical center will control the stereochemistry by exerting a steric influence on the diastereoface of the radical undergoing addition. Since each chiral auxiliary will direct the addition of the alkene to the same radical face, the resulting polymers should be predominantly isotactic. This strategy is presented in Figure 2, where an oxazolidine amide group is shown as the auxiliary attached to the radical center. Since this is a new approach for controlling free radical polymer tacticity, the nature of stereochemical defects and other aspects of the polymer microstructure were also examined by proton and carbon NMR.

Results and Discussion

Synthesis and Isolation of Isotactic Poly(acrylic acid) and Poly(methyl acrylate). Polymers were prepared using the acrylamides **1a–c** as monomers. It was anticipated that hydrolysis of the poly(acrylic oxazolidinide) resulting from **1a–c** would give



1a **1b**, R=t-Bu; **1c**, R=i-Pr

poly(acrylic acid) which has been previously characterized. There is literature precedent for measuring the tacticity of poly(acrylic acid) or poly(methyl acrylate) by NMR.[10-12] It should also be noted that isotactic poly(acrylic acid) and poly(methyl acrylate) can be obtained by low temperature anionic polymerization methods.[13] Thus, it should be possible to compare tacticities of free radical polymers made using chiral auxiliaries with tacticities of polymers made by anionic methods.

Polymerization of **1a–c** was initiated at 80 °C in benzene in degassed sealed tubes with AIBN with and without the chain transfer agent **2**. Without chain transfer agent, polymers with molecular weight >30 000 were obtained, whereas use of **2** gave smaller molecular weight polymers depending upon the relative amount of monomer and chain transfer agent that was present.[14] Polymer from **1a** was precipitated from methanol. The polymer collected in this manner is a powdery white solid which is soluble in aromatic solvents, such as benzene and *o*-dichlorobenzene, as well as in chlorinated solvents such as chloroform and methylene chloride. Proton NMR analysis of the **1a** polymer in $CDCl_3$ at room temperature gave a spectrum that was extremely broadened. Meaningful interpretation of spectra and any attempts to measure the tacticity of this polymer were fruitless, even at temperatures as high as 140 °C.

Polymerization of **1b** was carried out at 80 °C in benzene without chain transfer agent. After the reaction was complete, tubes were opened, and the reaction mixture was chipped out with a spatula since in the course of reaction the entire mixture had solidified. The polymer resulting from this reaction was purified by repeated washings with hexane followed by vacuum drying. This procedure effectively removed solvent and unreacted starting material. The polymer purified in this way is a fine white powder which is analytically pure and is apparently insoluble in any common solvent. Attempts to get an appreciable amount of this polymer to dissolve in any of several common solvents, including strong acid and base, were unsuccessful.

Polymerization of **1c** at 80 °C in benzene without chain transfer agent also gave a high molecular weight polymer. This polymer, which was insoluble in most common solvents, was purified by methanol precipitation. Proton NMR analysis of a smaller **1c** polymer formed using the chain transfer agent **2** gave a spectrum in $CDCl_3$ at room temperature that was extremely broadened. Meaningful interpretation of spectra and any attempts to measure the tacticity of this polymer were also fruitless.

Since direct NMR analysis of the polyacrylamides was impossible, attempts to hydrolyze the acrylamide polymer were made using dioxane/aqueous acid mixtures. Previous work[15] had shown that phenylglycinol-based amides could be hydrolyzed without loss of stereochemistry by refluxing the amide in a mixture of 1 N HCl and dioxane in 1:1 ratio, but hydrolysis of the polymer required more vigorous conditions. Attempts to hydrolyze the polymer with a range of acid concentrations and acid types showed that a minimum of 2 N HCl was required before the phenylglycinol could be removed. However, using 2 N HCl, the hydrolysis appeared to be complete as judged by weight of the recovered phenylglycinol. It should be noted, however, that a small amount of an unknown impurity was collected with the phenylglycinol. The *tert*-leucine-based and valine-based oxazolidine acrylamide polymers from **1b** and **1c** proved to require more vigorous hydrolysis conditions (12 N HCl:dioxane 1:1 at reflux). Recovery of *tert*-leucinol or valinol from the hydrolysis was nearly quantitative.

A number of different methods were employed in an effort to isolate the poly(acrylic acid) which resulted from the hydrolysis of the oxazolidine acrylamide polymers. The amino alcohol that resulted from hydrolysis (phenylglycinol, *tert*-leucinol, or valinol) could be removed by ether extraction of the hydrolysis mixture after the hydrolysis mixture had been basified. However, the isotactic poly(acrylic acid) was insoluble in nonaqueous solvents and could not be extracted from aqueous solution. In addition, attempts to separate the polymer from salts through precipitation using organic solvents were unsuccessful. Isotactic polymeric acid can, however, be isolated by pH-controlled precipitation. The isotactic poly(acrylic acid) can be precipitated by slowly decreasing the pH of the aqueous solution. At about pH 5, the polymer precipitates from solution and can be isolated either through centrifugation or filtration. Polymers isolated by this technique

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were found to be 88–92% isotactic as measured by ^{1}H NMR (see below for discussion of NMR analysis).

There was some concern that collecting the polymer through precipitation might artificially increase the tacticity of the polymer. That is, if only the more highly isotactic fractions of the polymer precipitated and the less highly isotactic fractions were left in solution, the tacticity measured would be higher than the tacticity actually achieved. To address this question, efforts were directed toward isolating the polymer resulting from the hydrolysis reactions using aqueous gel permeation chromatography (GPC). Using a pH 12 buffer as mobile phase, it was possible to collect poly(acrylic acid) using GPC. NMR measurements confirmed that the tacticity of the polymer was not affected by precipitation. However, GPC was a poor method for isolating the polymer in general, because it proved difficult to separate the polymer from the salts that were used to buffer the reaction. Having confirmed that the tacticity was not affected by precipitation, precipitation continued to be the method of choice for isolating poly(acrylic acid).

All three auxiliaries gave rise to poly(acrylic acid) which had impurities as determined by NMR. These NMR peaks indicated that there was apparently some amount of the auxiliary associated with the polymer. The impurity in polymers from the monomer based on valinol appears in the ^{1}H NMR spectrum as three poorly defined multiplets at 0.9, 3.8, and 3.9 ppm. If the multiplet at 0.9 ppm were to correspond to the six methyl protons from the isopropyl group, the relative area of this peak would indicate that approximately 3.5% of the auxiliary was still associated with the polymer. A similar analysis for the *tert*-leucine-based polymer (singlet at $\delta \sim 1.0$) indicates a comparable amount of impurity, while integration of the aromatic impurity from the phenyl glycinol-based auxiliary indicates substantially more phenyl associated with the product polymer ($\sim$10%).

There are three possibilities as to how the auxiliary might be associated with the polymer. First, it may be that the hydrolysis reactions are incomplete, and the auxiliaries are not completely removed. Second, it is possible that the auxiliary is removed but that the purification techniques do not completely separate it from the polymer, and thus it remains in the NMR spectrum. Finally, it is possible that the auxiliary is somehow incorporated into the polymer through some reaction such as polymer chain back-biting on the auxiliary.

The amount of the impurities did not seem to relate to the conditions of the hydrolysis reaction, suggesting that incomplete hydrolysis was not the problem. Thus, efforts to clean up the polymer focused on the other two possible sources of impurities. The polymer that was collected by precipitation was dissolved in a minimum of base and purified by dialysis against pure water or methanol in order to remove any lower molecular weight compounds. The product collected by this method was a clear plastic film after removal of the solvent and, as such, had the appearance of being much cleaner, probably due to the removal of small amounts of salt that were contaminating the original product. However, no difference was observed spectroscopically for this polymer after this treatment. We therefore conclude that auxiliary incorporation into the polymer by a covalent bond is the source of the auxiliary impurity. Attempts to elucidate the nature of this chemistry are ongoing, but for the purpose of our studies on polymer tacticity the level of polymer purity obtained with the leucinol and valinol auxiliaries is satisfactory.

In some cases, the poly(acrylic acid) polymer was converted to a poly(methyl acrylate) polymer by reaction with diazomethane in benzene. Previously,[16] isotactic poly(acrylic acid) had been converted to the methyl ester by treating a benzene solution of the polymer with diazomethane. This method was used with some success. An alternate method for generation of the same polymer is by treatment of the polyacrylamide with methanol/H_2SO_4 to give the polyester directly. Both the diazomethane and the methanolic acid procedures work best with smaller polymers, and compounds with molecular weight less than 10 000 were used in these procedures. The polyester that was isolated by this method was examined by NMR and was apparently a highly isotactic poly(methyl acrylate).

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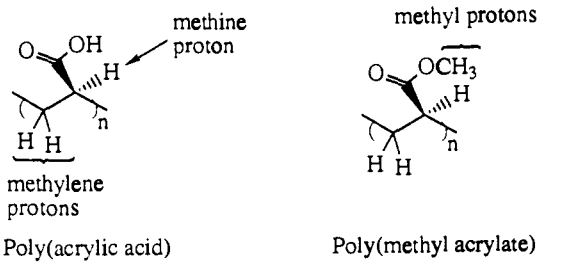

Figure 3. Substructure of poly(acrylic acid) and poly(methyl acrylate).

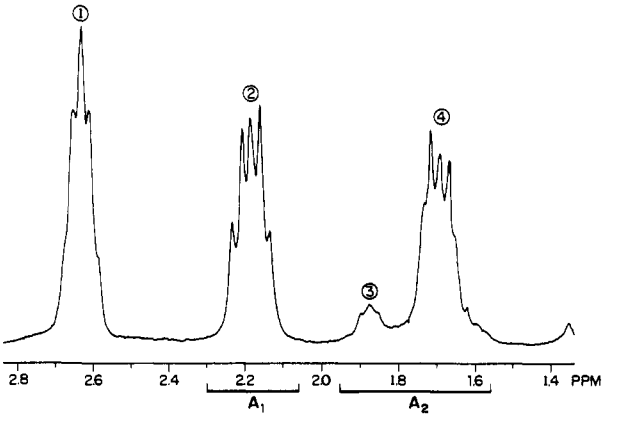

Figure 4. ^{1}H NMR spectrum of isotactic poly(methyl acrylate) prepared from oxazolidine **1b** at 75 °C in $CDCl_3$. Peaks 1–4 are defined in text.

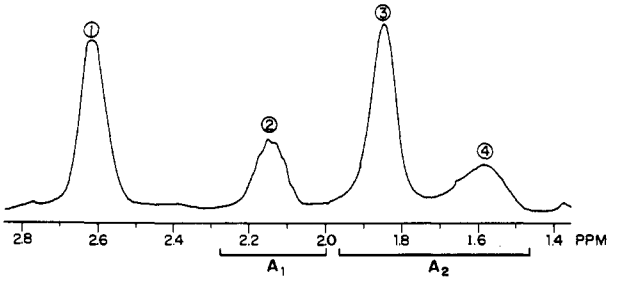

Figure 5. ^{1}H NMR spectrum of atactic poly(methyl acrylate) in $CDCl_3$ at ambient temperature.

^{1}H NMR: Tacticity Studies. For the purposes of studying the tacticity and microstructure of polymers that are formed in the auxiliary controlled polymerization reactions, four different polymers were used. For experiments with highly isotactic poly(acrylic acid), *i*P(AA), the high polymer made by the method described in the previous section was used. For the highly isotactic poly(methyl acrylate), *i*P(MA), a smaller polymer (MW about 4000 as calculated by GPC vs polystyrene standard) which was made by hydrolysis-esterification of the polymer made from monomer **1a–c** and the vinyl sulfide chain transfer agent[14] **2** was used. In addition, two atactic polymers were studied. Commercial poly(acrylic acid) (20 000 MW purchased from Fluka) was used as a standard poly(acrylic acid). Finally, for atactic poly(methyl acrylate), *a*P(MA), methyl acrylate polymerized under conditions identical to those used to make the acrylamide polymer were used.

The tacticity of the polymers used in the NMR experiments was calculated from the ^{1}H NMR spectra using the methods described by Matsuzaki[10] and Monjol.[11a] Spectra used to determine the tacticity of P(AA) were made in D_2O as solvent, and $CDCl_3$ was used as a solvent for P(MA) experiments. In ^{1}H NMR of both P(AA) and P(MA), the methylene (CH_2) protons are sensitive to diad stereochemistry. In contrast, the methine (CH) and methyl (CH_3) protons do not show any sensitivity to the stereochemical environment, Figure 3. The backbone protons, CH and CH_2, appear in the vicinity of 2 ppm for both P(AA)

and P(MA), and each of the four peaks that arise from the backbone protons has been previously identified,[12a,17,18] Figures 4 and 5. The most downfield of the peaks, peak 1, is the methine proton. Next upfield is one of the two methylene protons which is in an *m* (isotactic) diad, peak 2. The third peak, peak 3, is from methylene protons in an *r* (syndiotactic) diad, and the most upfield peak, peak 4, is the second of the two methylene protons which is in an *m* diad. Integration of the areas of the peaks that correspond to each of the stereochemical environments can be used to calculate the tacticity of the polymer. Using a 300 MHz spectrometer, the more downfield of the two isotactic methylene peaks is completely separated from the other peaks, but the syndiotactic protons and the upfield isotactic proton overlap somewhat, especially in the spectra of atactic polymers of P(AA). Thus, percent isotacticity (%i) was calculated by comparing the area of the downfield isotactic proton to the combined area of the syndiotactic protons and the upfield isotactic proton using the formula introduced by Monjol:[11a] $\%i = 2[A_1/(A_1 + A_2)]$ where A_1 is the area of the downfield isotactic proton and A_2 is the combined area of the syndiotactic protons and the upfield isotactic proton. In addition, the %i was calculated by comparing the area of the downfield isotactic proton to the area of the methine proton. This second method is less reliable because of the difficulties in comparing integrations of CH protons to CH_2 protons, but it nevertheless confirmed the results of the first method.

Using ^{1}H NMR, the tacticity of both the *i*P(AA) and *i*P(MA) was calculated to be 92% from both a *tert*-leucine-based and valinol-based polymer. Identical tacticities are expected for the acrylic acid and methyl acrylate polymers so long as no tacticity is lost in the esterification reaction. The tacticity of the two atactic polymers was also determined. Commercially available P(AA) was found to be 48% isotactic while the *a*P(MA) formed by free radical polymerization without stereocontrol was 49% isotactic. It was not surprising to find the "atactic" polymers slightly syndiotactic because there is a slight preference for uncontrolled free radical reactions to form syndiotactic diads because of 1,3 allylic strain.

These tacticity measurements show that the chiral auxiliaries impart a degree of stereocontrol to free radical polymerization that is unprecedented. Isotacticity of 92% represents the highest degree of stereocontrol ever reported for vinyl free radical polymerization reactions. There is, in fact, only one report of vinyl radical polymerization which results in polymers with greater than 60% isotacticity.[3,19,20] This reaction did not have the degree of stereoselectivity that is seen in the chiral auxiliary controlled reactions, and it does not represent a method which would be applicable to free radical polymerization in general. A greater degree of success has been achieved in stereocontrol of free radical reactions at very low temperatures to give syndiotactic polymers.[21] However, the selectivity in these reactions still does not equal that achieved with the chiral auxiliary controlled polymerizations. The fact that the chiral auxiliary controlled reactions were carried out at 80 °C makes these reactions even more impressive because it shows that high selectivity is possible even at elevated temperatures where selectivity might be expected to be low.

^{13}C NMR: The Nature of Stereochemical Defects. Using ^{13}C NMR, stereochemical information was obtained in both the methine and methylene regions of the spectrum, Figures 6 and 7. Visual comparison of the ^{13}C NMR spectra of the isotactic polymer to that of the atactic polymers reveals that the methine and methylene regions of the atactic polymer are much broader. The random distribution of the stereocenters in the atactic polymer results in the population of all of the possible stereosequences, and this is observed in the carbon spectrum. In contrast, the comparable regions of the isotactic polymers consisted of a single sharp peak representing the all isotactic stereosequences and a few smaller peaks which result from the small fraction of stereochemical defects in the polymer.

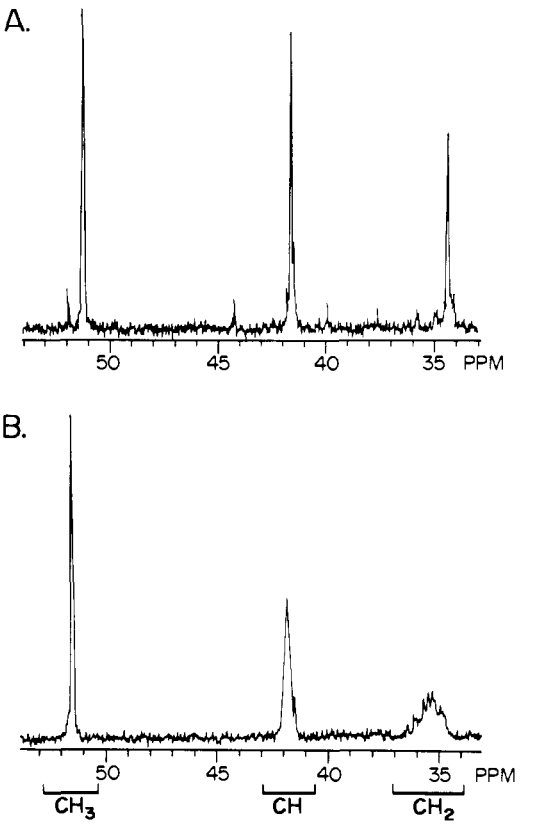

Figure 6. ^{13}C NMR spectrum of poly(methyl acrylate) at ambient temperature in $CDCl_3$. Under similar conditions of concentration and spectrum acquisition: (a) isotactic, (b) atactic.

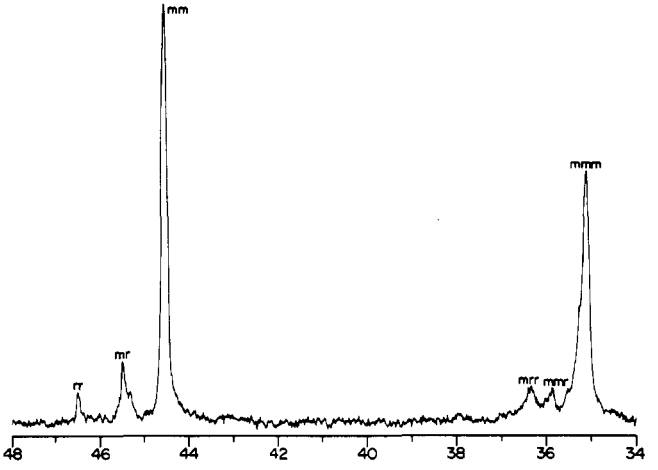

Figure 7. ^{13}C NMR spectrum of isotactic poly(acrylic acid) at 80 °C in D_2O at pH 12.

Because of the novelty of this approach to controlling the stereochemistry in free radical polymerization, it was of interest to examine the microstructural defects of the polymer in order to show that the stereocontrol was resulting from the chiral auxiliary. In addition, through the use of 300 MHz NMR and modern NMR techniques, specifically HETCOR, we are able to propose an analysis of the stereochemistry of P(MA) at the hexad level. Previously, analysis had only been possible at the tetrad level,[12b] and this only for *m*-centered tetrads. The analysis of P(AA) has been reported at the pentad level.[17] It is important to be able to carry out the analysis of the polymers using as large a stereosequence as possible because more detail about the microstructure of the polymers can be discerned from longer ster-

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(21) Bovey, F. A. *J. Polym. Sci.* **1960**, *46*, 59.

eosequences. Thus, NMR was used to study the microstructure of the isotactic polymers that had been made using chiral auxiliaries to control the stereochemistry.

One way of using the microstructure of a polymer to confirm the mechanism of stereocontrol is to compare the observed stereosequences to those predicted by the model for stereocontrol.[22] In a normal free radical polymerization reaction, the stereochemistry of each newly formed stereogenic center is influenced only by the previous stereogenic center. For this type of polymerization, the stereosequences of the polymer are described by Bernoullian statistics.[23] In Bernoullian statistics, the probability that a given stereosequence will be the same as the one before it (forming an *m* diad) is defined as P_m. Since the chance of forming all possible diads is 1, the probability of forming an *r* diad, P_r, is $1 - P_m$. Thus, by knowing overall tacticity of a polymer, it is possible to calculate the relative amounts of each stereosequence that should be present if the polymer were polymerized under Bernoullian conditions.

The other commonly used statistical model for polymerization tacticity is first-order Markov statistics. In first-order Markov statistics the probability of a given diad forming is dependent not on the previous stereogenic center but rather on the stereochemistry of the previous diad. This gives rise to four different probabilities. If the last stereosequence in a growing polymer is *m*, then the there are two possibilities. The new monomer could make an *mm* or it could make an *mr* sequence. Thus there are two probabilities that result that must be considered, $P_{m/m}$ and $P_{m/r}$, which are the probabilities of the *m* diad giving rise to *mm* and *mr* stereosequences, respectively. Similarly, $P_{r/m}$ and $P_{r/r}$ are the probabilities that an *rm* or an *rr* stereosequence would result from an *r* diad. These probabilities can be used to calculate the distribution of stereosequences in polymers that are formed under first-order Markov conditions just as P_m and P_r are used in Bernoullian statistics.

For polymerization in which the stereochemistry is controlled by a chiral auxiliary, neither Bernoullian nor first-order Markov statistics would appear to be appropriate because the stereochemistry of each new center is presumably independent of the previous stereogenic centers. In the chiral auxiliary model, there is a probability that a newly formed stereogenic center will have one configuration (P_1), and the probability that the stereogenic center will have the opposite stereochemistry (P_0) is $1 - P_1$. The stereoselectivity of the polymerization, which is determined by P_1, depends on the effectiveness of the chiral auxiliary. The facial selectivity imparted by the auxiliary, when expressed as the ratio of the addition of monomer to the favored side of the radical compared to the addition to the unfavored side, is equal to P_1/P_0.

Because the stereochemistry of each stereogenic center is independent of other centers, P_1 is the same for every stereogenic center. It is therefore possible to predict the distribution of the stereosequences based on P_1 and P_0. The most convenient method for calculating probabilities using chiral auxiliary statistics is to introduce the notation of 1,0 where 1 indicates a monomeric unit with one configuration (arbitrarily the one favored by the chiral auxiliary), and 0 indicates the opposite configuration.[23] Using this notation, there are 2^n possible configurations for a stereosequence incorporating *n* monomeric units (an "*n*-ad"). The probability of a given configuration is then the product of the probabilities of each monomeric unit having the correct conformation. For example, the probability of 10 is P_1P_0 and the probability of 11 is P_1^2. Using this notation, there are four (2^2) possible diads. These are 11, 10, 01, and 00, but because only relative configuration can be detected using NMR, there are only two distinct diads which can be measured. These diads are *m*, which results from 11 and 00, and *r*, which results from 10 and 01. Using chiral auxiliary statistics, the probability of a given relative configuration being formed is simply the sum of the probabilities of each of the configurations that have relative configuration being formed. Thus, the probability of an *m* diad is $P_1^2 + P_0^2$, and the probability of an *r* diad is $2P_1P_0$.

Table I. Statistical Calculation of the Distribution of Triads

stereosequence	triad	*B* prob	*CA* prob
111	*mm*	P_m^2	$P_1^3 + P_0^3$
000	*mm*		
110	*mr*	$2P_mP_r$	$2P_1^2P_0 + 2P_0^2P_1$
001	*mr*		
100	*mr*		
011	*mr*		
101	*rr*	P_r^2	$P_1^2P_0 + P_0^2P_1$
010	*rr*		

%i	statistical model[a]	*mm*	*mr*	*rr*
50	B	1	2	1
	CA	1	2	1
88	B	54	7.3	1
	CA[b]	13.7	2	1

[a] a_B = Bernoullian statistics, CA = chiral auxiliary statistics. [b] P_1 and P_0 are calculated from *%i* using eq 1.

It is possible to calculate P_1 and P_0 from the percent isotacticity of the polymer using the relationships derived in the previous paragraph.[22] Because %i is equal to the probability of an *m* diad being formed, $\%i = P_1^2 + P_0^2$. This can be rewritten as $\%i = P_1^2 + (1 - P_1)^2$, which can be solved for P_1 using the quadratic equation resulting in eq 1. It is also possible to calculate P_1 and

$$P_1 = \frac{2 \pm (-4 + 8\ (\%i))^{1/2}}{4} \qquad (1)$$

P_0 from %r or the ratios of larger configurations such as triads and tetrads. For a polymer of isotacticity of 92%, P_0 is calculated to be 0.042. This corresponds to a selectivity $(P_1/P_0) = \sim 23{:}1$ in the radical addition reaction for both the *tert*-leucine and valine-based polymers.

In isospecific Ziegler–Natta polymerizations, it has been postulated that the chirality of the catalyst is the main stereoregulating factor.[2,23,24] If this is the case, then the distribution of stereosequences in these template polymers would be the same as that predicted using chiral auxiliary statistics. In this case, P_1 and P_0 would result from the selectivity imparted by the catalyst template as opposed to a chiral auxiliary as is the case in the present work. Investigators have shown that the distribution of stereosequences in Ziegler–Natta polymers is in agreement with this type of model.[2,23,25] Studies of some Ziegler–Natta polymerization may be hampered by the fact that multiple polymerization mechanisms may operate during any given polymerization using some catalysts.

In order to show that the stereocontrol of the chiral auxiliary controlled polymerizations was taking place following the predicted model, we calculated the distributions of the stereosequences in the polymers studied in this work using both the Bernoullian model and the chiral auxiliary model, Tables I and II. By comparing the experimental results with the predicted distributions, it was possible to show that the chiral auxiliary statistics model accurately describes stereochemistry of the polymers reported here. In contrast, there are significant discrepancies between the experimental results and the distribution calculated by the Bernoullian model.

The assignment of stereochemical configuration in the ^{13}C NMR spectrum of P(AA) up to the pentad level has been reported by St. Pierre.[12a] The relative areas of predominate peaks in the spectrum of the *i*P(AA) were compared by integration of these peaks. The three possible triads are well-resolved in the methine region of the P(AA), Figure 7, and thus the relative areas of these three peaks were compared. Chiral auxiliary statistics requires

(22) Randal, J. C. *Polymer Sequence Determination: Carbon-13 Method*; Academic Press: New York, 1977.

(23) (a) Bovey, F. A. *High Resolution NMR of Macromolecules*; Academic Press: New York, 1972. (b) Bovey, F. A. *Chain Structure and Conformation of Macromolecules*; Academic Press: New York, 1982. See page 78 for a discussion of propagation errors in isospecific Ziegler–Natta polymerization.

(24) Pino, P. *Adv. Polym. Sci.* **1965**, *4*, 393.

(25) Wolfsgruber, C.; Zannoni, G.; Rigamonti, E.; Zambelli, A. *Makromol. Chem.* **1975**, *176*, 2765.

Table II. Statistical Calculation of the Distribution of Tetrads

stereosequences	tetrad	B prob	CA prob
1111	*mmm*	P_m^3	$P_1^4 + P_0^4$
0000	*mmm*		
1110	*mmr*	$2P_m^2P_r$	$2P_1^3P_0 + 2P_0^3P_1$
0001	*mmr*		
0111	*mmr*		
1000	*mmr*		
1001	*rmr*	$P_mP_r^2$	$2P_1^2P_0^2$
0110	*rmr*		
1100	*mrm*	$P_m^2P_r$	$2P_1^2P_0^2$
0011	*mrm*		
1101	*mrr*	$2P_mP_r^2$	$2P_1^3P_0 + 2P_2^3P_1$
0010	*mrr*		
1011	*mrr*		
0100	*mrr*		
1010	*rrr*	P_r^3	$2P_1^2P_0^2$
0101	*rrr*		

%i	statistical model[a]	*mmm*	*mmr*	*rmr*	*mrm*	*mrr*	*rrr*
50	B	1	2	1	1	2	1
	CA	1	2	1	1	2	1
88	B	394	54	7	54	7	1
	CA[b]	106.5	14.6	1	1	14.6	1

[a] B = Bernoullian statistics, CA = chiral auxiliary statistics. [b] P_1 and P_0 are calculated from %*i* using eq 1.

that there will be a 2:1 ratio of the *mr* and *rr* triads, while Bernoullian statistics suggest that for a polymer which is 88% isotactic, the ratio of these peaks will be 15:1. The observed ratio of 2.6:1 clearly shows that the chiral auxiliary statistics model supports the experimental data. The observed ratio of *rr* to *mm* of 1:15 is close to the 1:13.7 predicted by chiral auxiliary statistics, while the 1:54 predicted by Bernoullian statistics clearly is not in agreement with the observed ratio. In addition, the *mmm*, *mmr*, and *mrr* tetrads are prominent in the methylene region, and these were also compared. Chiral auxiliary statistics predicts that the *mmr* and *mrr* tetrads will be in a 1:1 ratio, and the observed ratio of 1:1.02 clearly is in agreement, while Bernoullian statistics predicts a 7:3 ratio for these two tetrads. In addition, chiral auxiliary statistics predicts that the *mmr* and *mrr* tetrads will be in a 7.3:1 ratio to *mmm*. This is in line with the observed 8:1 ratio, while Bernoullian statistics predicts ratios of 3.6:1 and 26.9:1.

These calculations clearly show that the observed distribution of the stereochemical configurations of the chiral auxiliary controlled polymer is in good agreement with those predicted by the chiral auxiliary statistics model. The slight discrepancies between the observed ratios and the predicted ratios, with the exception of the *rr* to *mr* ratio, can all be explained in terms of small errors in measuring the tacticity of the polymer. An error of ±1 in the calculation of the %i would lead to the differences between the observed and calculated values. In fact, if the polymer that was used for the reported measurements were 89%i and not 88%i, as calculated by ^{1}H NMR, the differences would be significantly less than the limits on the measurement imposed by error in integration on the NMR peaks. The agreement between the observed and calculated distribution is compelling evidence that the stereocontrol in the free radical polymerization of acrylamides with chiral auxiliaries is the result of the face selectivity imparted by the auxiliaries.

We expect that defects in chiral auxiliary controlled polymerization will result in a pair of *r* diads, as is also the case in isospecific Ziegler–Natta systems. In normal isotactic polymerization, if an addition takes place in the wrong sense, the newly formed stereogenic center will direct future addition to have the same configuration, and the polymer will be made up of a blocks of monomeric units which have the same absolute configuration. Thus, defects in this type of polymerization will generally appear as isolated *r* diads. However, in chiral auxiliary controlled polymerization, the chiral auxiliaries direct each of the new stereogenic centers to have the same absolute configuration. Thus if a "wrong" addition takes place, the next stereogenic center will return to the preferred conformation, and a pair of *r* diads will

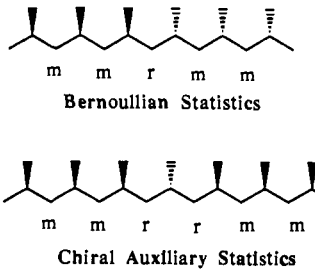

Figure 8. Predicted defects for an isotactic polymer.

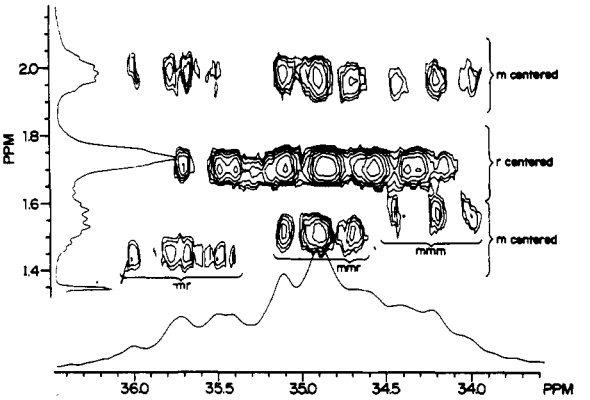

Figure 9. Methylene region of HETCOR NMR experiment for atactic poly(methyl acrylate) at ambient temperature in $CDCl_3$.

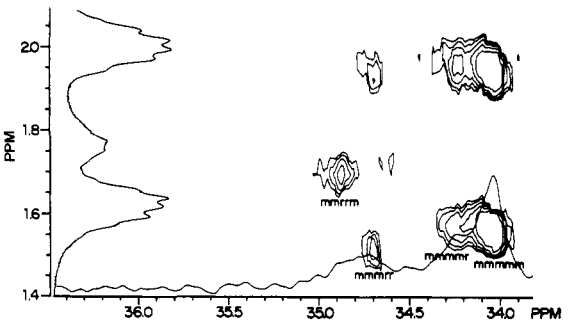

Figure 10. Methylene region of HETCOR NMR experiment for isotactic poly(methyl acrylate) at ambient temperature in $CDCl_3$.

be formed, Figure 8. These defect patterns are predicted by the statistical analysis that is applied. For example, using chiral auxiliary statistics, the *mmr* and *mrr* tetrads are equally likely to be formed, while with Bernoullian statistics the *mmr* tetrad is increasingly preferred at higher P_m.

Preliminary NMR experiments with P(MA) indicated that sensitivity to the hexad stereochemistry was seen in the methylene region of the ^{13}C NMR. Thus, efforts were made to analyze the P(MA) at the hexad level. In order to do this, HETCOR experiments were carried out using both isotactic and atactic P(MA). The spectra that resulted from these experiments are presented in Figures 9 and 10. The twenty different hexads could be identified in the spectrum of atactic P(MA). The ten *m*-centered hexads appear above and below the ten *r*-centered hexads. Furthermore, the lower *m*-centered hexads (upfield in the ^{1}H NMR spectrum) are clearly divided into three groups. Previous work had shown that decoupling of the ^{1}H NMR spectrum of the P(MA) split the upfield isotactic spectrum into the three *m*-centered tetrads. These tetrads correspond to the three groups that are seen in the HETCOR of atactic P(MA). The most upfield of these tetrads is the *mmm*-centered tetrad, followed by the *mmr* tetrad, and the *rmr* tetrad is the most downfield of the three.

In the HETCOR of the *i*P(MA), only four of the twenty possible hexads are seen. However, a statistical analysis of distribution of these hexads allows them to be unambiguously assigned. These four hexads are the *mmmmm*, *mmmmr*, *mmmrr*,

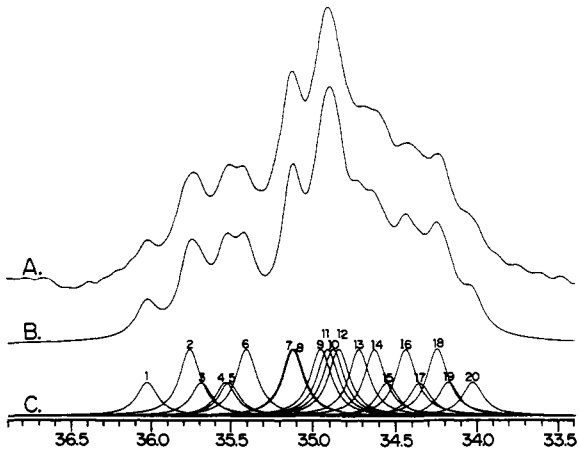

Figure 11. Methylene region of ^{13}C NMR spectrum of atactic poly(methyl acrylate): (A) Experimental; (B) simulation; (C) twenty hexads used in the simulation. Peak assignment (where a = one of *mmmrm*, *rmmrm*, *rmmrr*, *mmrrr*, *rmrr*): 1, *rrmrr* or *mrmrm*; 2, *mrmrr*; 3, *rrrr* or *mrrrm*; 4, *rrmrr* or *mrmrm*; 5, *rrrrr* or *mrrrm*; 6, *mrrrr*; 7, a; 8, a; 9, a; 10, a; 11, a; 12, *mmrrm*; 13, *mmmmrr*; 14, a; 15, *rmmmr*; 16, *mmrmr*; 17, *mmrmm* or *rmrmr*; 18, *mmmmr*; 19, *mmrmm* or *rmrmr*; 20, *mmmmm*.

and *mmrrm* hexads. These are the hexads which result from purely isotactic sequences and those that result from a single *rr* defect. For assigning the other sixteen hexads in the atactic P(MA), the ^{13}C NMR spectrum was deconvoluted into the twenty hexads following the method of St. Pierre,[12a] Figure 11. The area of each of the peaks was assigned on the basis of the expected distributions of an atactic polymer. That is, the unsymmetrical hexads were given double weighting. In addition, the peaks were aligned with the known hexads from the HETCOR spectrum. This gave rise to a simulated spectrum which differed from the experimental spectrum by much less than a root mean square error of 1%. This allowed four additional hexads to be unambiguously assigned. The *rmmmr* hexad was identified because it was the only one of the three *mmm*-centered hexads which had not previously been assigned, thus it must be the remaining peak by default. The three unsymmetrical hexads which were based on even tetrads could also be assigned because they were the doubly weighted peaks in groups of hexads which are in a ratio of 1:2:1. These are *mrrrr*, *mrmrr*, and *mmrmr*. Thus eight of the twenty hexads could be unambigiously assigned. The six remaining symmetrical hexads could not be unambiguously assigned but could be grouped in pairs. For example, peaks 1 and 4 in the deconvoluted spectrum are *rrmrr* and *mrmrm*. The last six hexads are the hexads based on unsymmetrical tetrads. These could not be more specifically assigned. However, they all fall in a limited area in the center of the spectrum and make up only three distinct peaks in the ^{13}C NMR spectrum. These assignments are an almost complete assignment of the hexads that make up the ^{13}C NMR spectrum of P(MA). It would be possible to definitively assign the remaining hexads if a polymer could be made which was less isotactic than the polymers used in this study.

Literature reports suggested that the stereosensitivity of the P(AA) was affected by the pH of the solution in which the NMR was measured.[12b] Thus, the NMR of the P(AA) was taken in several solutions across a wide pH range. It was only at low pH (pH ~2) that it was possible to measure tacticity using ^1H NMR. In contrast, St. Pierre reported that tacticity measurement of P(AA) using ^{13}C NMR was only possible at high pH (pH ~12). Thus, it was not possible to assign the peaks of P(AA) using HETCOR techniques because there was no solvent in which both proton and carbon stereochemistry could be measured simultaneously.

Conclusions

This work has shown that it is possible to use chiral auxiliaries to control the stereochemistry of free radical polymerizations. Remarkably high degrees of tacticity have been demonstrated in the polymerization of acrylamides with these chiral auxiliaries. Tacticities as high as 92% have been measured for P(AA) and P(MA) resulting from these reactions. In fact, it was somewhat surprising that the polymerizations were this selective. Work done with these acrylamides had shown that the selectivity in the addition reactions of the valinol-based acrylamide at room temperature that took place under telomerization conditions was only 7:1.[15] However, selectivity as high as 23:1 (as was calculated from P_1/P_0) was observed in the polymerization reactions. Why the polymerization reactions are more selective than are the simple addition reactions of analogous radicals is not understood. One can speculate that this might be the result of a secondary selectivity effect in which the auxiliary group orientation of the stereogenic centers which have been formed earlier in the polymerization increases the selectivity of the addition. It is known, for example, that polymer formed from polymerization of trityl methacrylate has a helical shape which imparts a high degree of isotacticity to the polymerization.[26] However, there is no experimental evidence to either confirm or disprove this speculation with regard to the chiral auxiliary controlled polymerizations.

Experimental Section

Materials. Benzene was distilled from sodium/benzophenone and stored over molecular sieves. Methylene chloride was distilled from calcium hydride and stored over molecular sieves. Tetrahydrofuran was freshly distilled from sodium/benzophenone. *p*-Dioxane, acryloyl chloride, and *N*-methylmorpholine were freshly distilled. Water was deionized and filtered using a Millipore system. AIBN was recrystalized from ethanol. All other solvents and reagents were used as received without further purification.

Gel Permeation Chromatography (GPC) Experiments. GPC of unhydrolyzed polymers and poly(methyl acrylate) was done using a Waters 600E gradient system with two Waters ultrastyrogel columns in tandem (8 m, 500 Å, 100 Å, 7.8 × 300 mm). UV or refractive index detection was used, and tetrahydrofuran at a flow rate of 1 mL/min was used as the mobile phase. GPC of poly(acrylic acid)s was done using an Isco Model 2350 pump with a Waters precolumn filter, Waters ultrahydrogel column (250 Å, 7.8 × 300 mm), and refractive index detector. A 0.05 M solution of tribasic potassium phosphate (ca. pH 12) at a flow rate of 0.8 mL/min was used as the mobile phase.

NMR Experiments. Routine NMR experiments of monomers and their synthetic intermediates were done at ambient temperature in deuteriochloroform using a Varian XL-300 spectrometer. NMR measurements of polymers were measured using either a Varian XL-300 or a General Electric QE-300 spectrometer. Experiments at elevated temperature and experiments with poly(acrylic acid) were made using the Varian XL-300, while 2-D experiments and deconvolution experiments were made using the General Electric QE-300. ^1H NMR spectra of poly(acrylic acid) were measured at 80 °C in deuterium oxide (D_2O) to which aliquots of 37% DCl in D_2O were added until the pH of the solution was 2 as measured using a Corning Model 109 pH meter. Typically, ^1H NMR experiments were short term experiments involving 16 or 32 acquisitions. ^{13}C NMR experiments were carried out at 80 °C in D_2O to which aliquots of 0.05 M tribasic potassium phosphate in D_2O were added until the pH of the solution was 12. Dioxane was used as an internal standard (66.5 ppm relative to TMS). A pulse angle of 67° (13 ms), sweep width of ±7575 Hz, and 16K data points were used. A delay time of 5 s was used. Thus, the repetition rate was at least 10 times the longest spin-relaxation time (T_1) calculated by St. Pierre.[12a] In addition, for experiments which were used to calculate the relative stereochemical distribution, the decoupler was only activated during the acquisition phase of the pulse sequence. ^{13}C NMR data were collected for 9.5 h, during which time between 7000 and 12000 acquisitions were accumulated. ^1H and ^{13}C NMR spectra of poly(methyl acrylate) were measured in deuteriochloroform at ambient temperature (some experiments with high MW P(MA) were done at 75 °C). HETCOR experiments were carried out under conditions identical to the 1-D experiments except that narrow sweep widths were used so that digitization was increased sufficiently for the peaks of interest that resolution was acceptable. Deconvolution of the experimental spectra was accomplished using the CHRCAP simulation program provided by the GE software using completely lorenzian line shapes.

Synthesis of Monomers. (*S*)-2-Amino-3,3-dimethylbutanol. To a flame dried 500-mL three-necked flask equipped with a condenser and an argon line was added 150 mL of anhydrous diethyl ether. This so-

(26) Nakano, T.; Okamoto, Y.; Hatada, K. *J. Am. Chem. Soc.* **1992**, *114*, 1318.

lution was cooled to 0 °C with an ice bath, and 2.9 g of lithium aluminum hydride was washed into the flask with 50 mL of ether. Over a period of 30 min, 5 g of L-*tert*-leucine was added. The ice bath was removed, and the reaction mixture was stirred for 30 min at room temperature before being refluxed for 6 h. The reaction mixture was then left to stir at room temperature for an additional 10 h. The reaction was cooled to 0 °C and quenched by the consecutive addition of 3 mL of water, 9 mL of 10% sodium hydroxide, and 3 mL of water. The reaction mixture was stirred for 30 min and then filtered. The filtrate was washed with additional ether, and the combined ether fractions were dried with sodium sulfate. After the solvent was removed under reduced pressure, a slightly yellow oil was isolated. This was used immediately in the synthesis of acrylic 2,2-dimethyl-5(*S*)-*tert*-butyl-1,3-oxazolidinide (**1b**) without further purification.

General Procedure for Acrylic 2,2-Dimethyl-5-alkyl-1,3-oxazolidinides 1a–c. The appropriate amino alcohol (from 1 to 10 g gave similar yield and purity) was added to 10 equiv of reagent grade acetone, and sufficient magnesium sulfate was added so that the $MgSO_4$ was free flowing. This was stirred for 2 h and filtered. After the solvent was removed under reduced pressure, the material was dissolved in methylene chloride (20 mL/g of starting amino alcohol). This was cooled to 0 °C in an ice bath and 1.1 equiv of *N*-methylmorpholine was added dropwise followed by dropwise addition of 1.1 equiv of acryloyl chloride. After 30 min the ice bath was removed, and the reaction was stirred at room temperature for an additional 4 h.

Acrylic 2,2-Dimethyl-5(*R*)-phenyl-1,3-oxazolidinide (1a). Starting with (*R*)-phenylglycinol, a crystalline white solid was isolated in 74% yield following recrystallization from a small volume of ethyl acetate: mp 81.0–82.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–7.25 (m, 5 H), 6.28 (dd, J = 2.02, 16.63 Hz, 1 H), 6.08 (dd, J = 10.14, 16.65 Hz, 1 H), 5.45 (dd, J = 2.01, 10.15 Hz, 1 H), 5.00 (dd, J = 2.26, 6.46 Hz, 1 H), 4.38 (dd, J = 6.53, 8.91 Hz, 1 H), 3.92 (dd, J = 2.38, 8.92 Hz, 1 H), 1.87 (s, 3 H), 1.68 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.3, 141.4, 129.7, 128.9, 127.8, 127.8, 125.8, 96.2, 71.3, 61.1, 25.2, 23.2; $[\alpha]^{23}_D$ = −85.8°; MS (CI, isobutane) MH^+ = 232. Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.50; H, 7.34; N, 6.01.

Acrylic 2,2-Dimethyl-5(*S*)-*tert*-butyl-1,3-oxazolidinide (1b). Starting with (*S*)-2-amino-3,3-dimethylbutanol, a slightly yellow solid was isolated in 76% yield following column chromatography (3:1 hexane:ethyl acetate): mp 56–58 °C; ^{1}H NMR ($CDCl_3$) δ 6.51 (dd, J = 10.07, 16.55 Hz, 1 H), 6.34 (dd, J = 16.55, 2.06 Hz, 1 H), 5.62 (dd, J = 10.07, 2.06 Hz, 1 H), 4.01 (m, 1 H), 3.92 (m, 1 H), 3.76 (m, 1 H), 2.00 (m, 1 H), 1.74 (s, 3 H), 1.52 (s, 3 H), 0.92 (s, 9 H); ^{13}C NMR δ 166.18, 130.6, 127.2, 96.3, 65.0, 64.9, 35.7, 27.6, 26.4, 22.9; R_f = 0.46 (50% EtOAc in hexane). Anal. Calcd for $C_{12}H_{21}NO_2$: C, 68.21; H, 10.02; N, 6.63. Found: C, 68.27; H, 10.05; N, 6.63.

Acrylic 2,2-Dimethyl-5(*S*)-isopropyl-1,3-oxazolidinide (1c). Starting with (*S*)-valinol, a yellow oil was isolated in 81% yield following column chromatography (3:1 hexane:ethyl acetate): ^{1}H NMR ($CDCl_3$) δ 6.39 (d, J = 5.4 Hz, 2 H), 5.66 (m, 1 H), 3.93 (m, 2 H), 3.77 (m, 1 H), 2.00 (m, 1 H), 1.70 (s, 3 H), 1.54 (s, 3 H), 0.93 (m, 6 H); ^{13}C NMR δ 162.96, 129.64, 127.80, 95.48, 64.31, 62.13, 31.96, 25.87, 22.86, 19.76, 17.14. Anal. Calcd for $C_{11}H_{19}NO_2$: C, 66.97; H, 9.71; N, 7.10. Found: C, 66.79; H, 9.74; N, 7.01.

Synthesis of Polymers. General Polymerization Method. The appropriate amount of monomer (0.1–2.0 g was used with equal facility) was dissolved in benzene (solutions were made 3 M in monomer). This was then added to a vessel appropriate for sealing containing an equal volume of benzene in which an amount of AIBN equal to 1% (molar ratio) of the monomer had been dissolved. This was degassed by taking the solvent through three freeze–pump–thaw cycles, following which the reaction vessel was sealed. The sealed tube was wrapped in aluminum foil and immersed in a oil bath held at a constant temperature of 80 °C. After reaction (typically overnight although experiments showed that the reaction was 97% complete after 30 min) the vessel was removed, cooled to 0 °C, and broken open. The polymer was washed with hexane and filtered, following which the residual solvents were removed by drying under vacuum.

Poly(acrylic 2,2-dimethyl-5(*R*)-phenyl-1,3-oxazolidinide). The monomer was polymerized following the general method, except that the reaction was carried out in a round bottom flask equipped with a reflux condenser rather than a sealed tube; thus no attempt was made to degas the reaction mixture. In addition, the polymer was purified by precipitation of the reaction mixture by adding it to 10 times the volume of methanol. A powdery white solid was isolated in 99% yield. Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 71.73; H, 7.39; N, 6.02.

Poly(acrylic 2,2-dimethyl-5(*S*)-*tert*-butyl-1,3-oxazolidinide). The monomer was polymerized following the general polymerization method. A powdery white solid was isolated in 99% yield. Anal. Calcd for $C_{12}H_{21}NO_2$: C, 68.21; H, 10.02; N, 6.63. Found: C, 68.06; H, 10.00; N, 6.62.

Poly(acrylic 2,2-dimethyl-5(*S*)-isopropyl-1,3-oxazolidinide). The monomer was polymerized following the general polymerization method. A powdery white solid was isolated in 100% yield. Anal. Calcd for $C_{11}H_{19}NO_2$: C, 66.97; H, 9.71; N, 7.10. Found: C, 66.71; H, 9.57; N, 6.91.

Atactic Poly(methyl acrylate). Methyl acrylate (500 mg) and vinyl sulfide **2** (0.5 equiv) were polymerized following the general polymerization method except that the benzene-soluble polymer was isolated using GPC: ^{1}H NMR ($CDCl_3$) δ 3.4 (s, CH_3, 3 H), 2.6 (m, CH, 1 H), 2.2 (m, mCH_2, 0.5 H), 1.8 (m, rCH_2, 1 H), 1.6 (m, mCH_2, 0.5 H); ^{13}C NMR δ 174.88, 51.46, 41.77, *m*36.5–33.5.

Isotactic Poly(acrylic acid). To a 25-mL round bottom flask equipped with a reflux condenser was added 1 g of poly(valinol acrylamide) and 4 mL each of dioxane and 12 N hydrochloric acid. This was heated to reflux in a 110 °C oil bath and left for 9 h, during which time the solid polymer slowly dissolved and the solution became increasingly less viscous. The reaction was left to cool to room temperature, at which time the reaction was basified by the addition of saturated sodium hydroxide solution until the reaction mixture was pH 12 as measured with pH paper. Hydrolyzed valinol was extracted by washing the reaction mixture four times with 25-mL portions of diethyl ether. The poly(acrylic acid) was then collected by slowly adding 6 N HCl until the polymer precipitated. The polymer was further purified by dialysis of a basic solution of the polymer against pure water for 24 h using 3500 MW exclusion dialysis tubing: ^{1}H NMR (D_2O, pH 2) δ 2.5 (m, CH, 1 H), 2.0 (m, mCH_2, 0.9 H), 1.8 (m, rCH_2, 0.2 H), 1.7 (m, mCH_2, 0.9 H); ^{13}C NMR (D_2O pH 12) δ 184.86, *m*47.0–45.0, *m*37.0–33.0.

Isotactic Poly(methyl acrylate). Isotactic poly(methyl acrylate) was prepared starting from isotactic poly(acrylic acid) as described above with the following exceptions. Vinyl sulfide chain transfer agent **2** was included in the polymerization reaction (0.5 equiv), and rather than precipitating the poly(acrylic acid) the polymer was isolated by removing the solvent under vacuum. This poly(acrylic acid) was dissolved in a small amount of benzene. An ethereal solution of diazomethane made using a mini diazald kit was added dropwise to the benzene solution until the yellow color persisted. This was stirred for 2 h, following which argon was passed over the solution until the yellow color faded. The solvent was removed and the poly(methyl acrylate) was isolated using GPC: ^{1}H NMR ($CDCl_3$) δ 3.6 (s, CH_3, 3 H), 2.3 (m, CH, 1 H), 1.9 (m, mCH_2, 0.9 H), 1.7 (m, rCH_2, 0.2 H), 1.5 (m, mCH_2, 0.9 H); ^{13}C NMR δ 174.88, 51.87, 41.21, *m*35.5–33.5.

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