Free-Radical Polymerization and Copolymerization of Acrylimides: Homopolymers of Oxazolidinone Acrylimide and Control of 1,5-Stereochemistry in Copolymers Derived from Isobutylene and an Oxazolidinone Acrylimide

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Received September 13, 1999

The polymerization and copolymerization of *N*-acryloyl imides was investigated. Thus, Lewis acids were used to control the free-radical copolymerization of *N*-acryloyl imides derived from oxazolidinones and isobutylene. Complexation of an appropriate Lewis acid ($Sc(OTf)_3$) to acrylimides of achiral and chiral oxazolidinone auxiliaries allowed the preparation of alternating 1:1 copolymers as determined from integration of the copolymer ^1H NMR spectra. Highly isotactic copolymers were made when chiral oxazolidinones were used as starting material if Lewis acid was present in the reaction. NMR analysis (^1H and ^{13}C) of the copolymers showed that the *m*/*r* dyad ratio was in excess of 95:5 for some of the chiral acrylimides. Homopolymerization of the parent achiral acrylamide was also carried out. NMR analysis of the homopolymer showed a temperature-dependent preference for the *r* dyad with a *m*/*r* dyad ratio as low as 0.25 in polymerizations carried out at −78 °C.

Stereochemistry affects many of the important properties of polymers, such as solubility, melting point and glass transition temperature, and mechanical strength.[1] Free-radical polymerization of vinyl monomers is a commercially important method of polymer production, yet this reaction proceeds with little control of tacticity. Progress toward the goal of stereospecific polymerizations has been made with the use of chiral auxiliaries incorporated into the vinyl monomer (Scheme 1).[2] Oxazolidine acrylamides derived from chiral amino alcohols have been used to create highly isotactic polymers (*m*/*r* 92:8) that can be hydrolyzed to poly(acrylic acid) without epimerization. Conformational control of the amide auxiliary is accomplished by placing *gem*-dimethyl groups in the 2 position of the oxazolidine. Unfavorable steric interactions between the pseudoaxial methyl group and the hydrogen on the radical carbon bias rotamer population in favor of the indicated conformation. The R group (*tert*-butyl, isopropyl, or phenyl) shields one side of the radical from approach by an incoming monomer.

A similar approach toward controlling stereochemistry can be used with chiral oxazolidinones. Again, conformational control of the amide bond is required (Figure 1). Unfavorable dipole interactions between the oxazolidinone carbonyl and the acryloyl carbonyl bias rotamer population toward rotamer A, which places the shielding group away from the reactive center, providing little control of stereochemistry. Addition of an appropriate Lewis acid, however, locks the auxiliary in the preferred

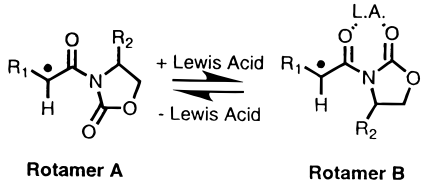
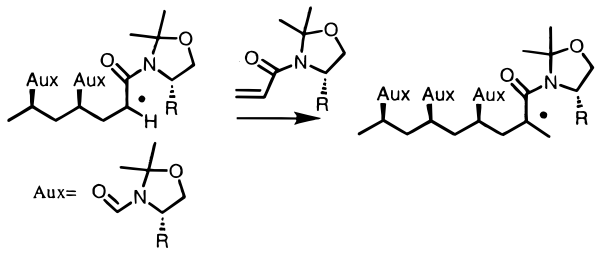


Figure 1. Rotamer control by bidentate chelation of oxazolidinone.

Scheme 1



conformation and diastereoselectivities in excess of 100:1 have been obtained in radical allyl transfer reactions.[3] Oxazolidinone auxiliaries have been used extensively in organic synthesis, and Sibi and his collaborators have made good use of these important substructures in free-radical transformations. Recently, we demonstrated unusually high threo selectivity in the telomers of the allyl transfer reactions of achiral oxazolidinone acrylamides **1a** (Scheme 2).[4] Selectivities as high as 93:7 in favor of threo $n = 2$ products, *threo*-**2**, were obtained in pentane. Selectivity also appeared to be dependent on solvent polarity with higher selectivities in solvents of lesser polarity. The $n = 2$ telomers from the allyl-transfer reaction of cyclododecyl iodide, **1a**, and allyltributylstan-

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(1) (a) Lenz, R. W. *Organic Chemistry of Synthetic High Polymers*; Wiley-Interscience: New York, 1967. (b) Seymour, R. B. *Polymer Chemistry: An Introduction*; M. Dekker: New York, 1988. (c) Stevens, M. P. *Polymer Chemistry: An Introduction*; Oxford University Press: New York, 1990. (d) Nicholson, J. W. *The Chemistry of Polymers*; Royal Society of Chemistry: Cambridge, 1991.

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(3) Sibi, M. P.; Ji, J. *J. Org. Chem.* **1996**, *61*, 6090.

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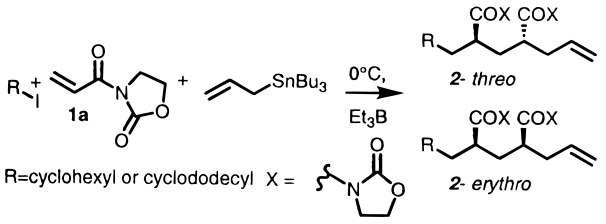
10.1021/jo9914420 CCC: $19.00
Published on Web 01/07/2000

Scheme 2



nane can be crystallized, and the X-ray crystal structure of the threo product (*threo*-**2**, R = cyclododecyl) shows the likely source of the high selectivities.[4] Carbonyls on adjacent auxiliaries align such that unfavorable dipolar interactions are minimized in this conformation which leads to the threo product.

Lewis acids have long been used in both polymerizations and copolymerizations to enhance the reactivities of monomers. Complexation of acrylates and acrylamides, for example, increases the electrophilicity of both the monomer and radical resulting from addition to the monomer. Often, the rate of polymerization can be increased simply by adding a Lewis acid.[5] In copolymerizations, this effect has been exploited to enhance alternation between a complexed electron-deficient monomer (e.g., methyl acrylate) and an electron-rich monomer (e.g., isobutylene).[6] These strategies may possibly be used with chiral Lewis acids to generate alternating copolymers with control of stereochemistry during addition to the complexed radical.

In this paper, we present the results of the copolymerization of **1a** and isobutylene using Lewis acids with chiral oxazolidinones as well as the results of homopolymerization of acrylamides such as **1a**. We focus particularly on the stereoselectivity of the derived polymers.

Diastereoselective Copolymerizations. The copolymerizations of 2-methyl-1-propene (isobutylene) and oxazolidinone acrylamides[7] **1a**−**f** were chosen to study the Lewis acid-promoted copolymerizations (Scheme 3). Although **1a**−**f** can be homopolymerized in the presence of Lewis acids, poor conversions are obtained except with **1a**. Presumably, complexation renders the radical and monomer too electron-deficient to react efficiently, although steric congestion around the radical in the homopolymerizations of **1b**−**f** could also contribute to the poor conversions. This increased electron deficiency, however, should enhance the reactivity of the complexed radical toward more electron-rich alkenes, and it has been observed to increase the alternating character of copolymers of isobutylene and methyl acrylate.[8] Isobutylene also is an ideal choice for a comonomer as it does not homopolymerize by radical pathways, and the analysis of the copolymer's tacticity is not complicated by additional stereocenters as would be the case with monosubstituted vinyl comonomers.

Scheme 3

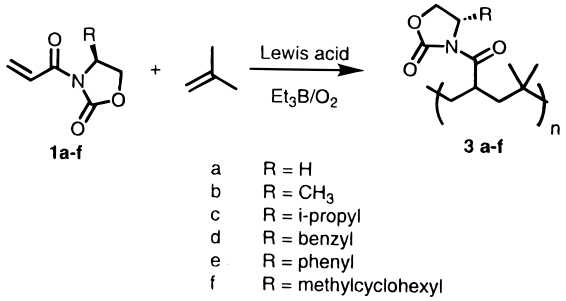


Table 1. Lewis Acid Effect on Degree of Alternation in 3a[a]

entry	Lewis acid	equiv of LA	solvent	*T* (°C)	A/IB[b]
1	$Zn(OTf)_2$	1.25	CH_2Cl_2	−78	66/34
2	$SnCl_4$	1.25	CH_2Cl_2	−78	NR
3	$Al(Et)_3$	1.0	CH_2Cl_2/pentane	−78	65/35
5	MgI_2	1.5	CH_2Cl_2	−78	NR
7	$La(OTf)_3$	1.25	CH_2Cl_2	−78	58/42
8	$Eu(OTf)_3$	1.25	CH_2Cl_2	−78	NR
9	$Sm(OTf)_3$	1.25	CH_2Cl_2	−78	NR
10a	$Yb(OTf)_3$	1.25	CH_2Cl_2	−78	NR
10b	$Sc(OTf)_3$	1.0	CH_2Cl_2	−40	65/35
11b	$Sc(OTf)_3$	2.0	ether	−78	50/50
11c	$Sc(OTf)_3$	1.5	ether	−78	51/49
11d	$Sc(OTf)_3$	1.0	ether	0	55/45
11e	$Sc(OTf)_3$	0.5	ether	0	57/43

[a] All reactions initiated with Et_3B/O_2. [b] Ratio of acylimide to isobutylene in the polymer.

The copolymerization of **1a** and isobutylene was attempted with a series of Lewis acids to determine which Lewis acids promote the formation of alternating, 1:1 copolymers (Table 1). A solution of **1a** and the Lewis acid was prepared and, cooled, and a large excess of isobutylene (approximately 20-fold) condensed into the solution. Initiation was performed with Et_3B/air. The resulting copolymer (**3a**) was precipitated from methanol or ethyl acetate after 3 h reaction to give a white powder that was partially soluble in $CHCl_3$ and dichloromethane, completely soluble in DMSO and DMF, and insoluble in all other common organic solvents and all aqueous solutions. Gel permeation chromatography analysis of **3a** relative to polystyrene standards gave an average M_w of 380 000. Analysis of the degree of alternation was performed by ^{1}H NMR at 95 °C in DMSO-d_6.

Only scandium trifluoromethanesulfonate gave alternating 1:1 copolymerizations. Lewis acids such as MgI_2, $MgBr_2$, and $Yb(OTf)_3$, which all give good yields in allyltransfer reactions with oxazolidinone acrylamides,[9] either showed poor alternating characteristics (excess of acrylamide units) or no reaction at all. It is not entirely clear why scandium triflate gave the best results in this study. We note, however, that scandium has a small atomic radius and bears a charge of +3 and that the triflate salt shows good solubility in ether in the presence of acrylamides **1a**−**f**. We suggest that solubility and Lewis acid

(5) E.g.: Seno, M.; Matsumura, N.; Nakamura, H.; Sato, T. J. *Appl. Polym. Sci.* **1997**, *63*, 1361.

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(7) **1b**−**f** were synthesized from the appropriate oxazolidone by the procedure of Pikul and Corey (*Organic Synthesis* **1993**, *71*, 31) and their spectra compared to literature reports. The oxazolidones were either purchased from Aldrich or synthesized from the commercially available amino alcohols following the procedure of Evans and Gage (*Organic Synthesis*, **1990**, *68*, 77).

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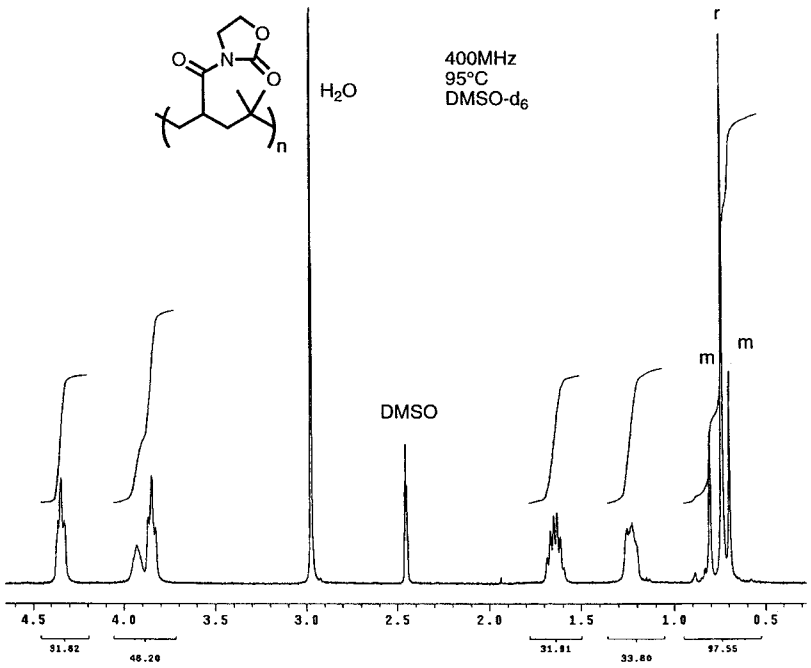


Figure 2. ^{1}H NMR spectrum of **3a**.

strength are therefore the critical factors that favor scandium triflate as the Lewis acid of choice in these studies. Complexation of scandium with the acrylimides makes the complex more reactive to addition of carbon radicals, and the radical generated, being complexed to scandium, is more electrophilic and therefore more reactive in the addition with isobutylene.

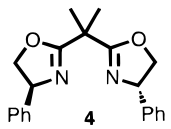
With a suitable Lewis acid (scandium triflate) in hand, **1b**−**f** were copolymerized with isobutylene in the hopes of obtaining highly isotactic copolymers. The copolymers **3b**−**d** were isolated by precipitation from ether. All three copolymers were white powders that were partially or completely soluble in most polar organic solvents. Copolymer **3e** resisted solubilization in nearly every solvent, with the exception of DMF at elevated temperatures, and even then, the copolymer would precipitate from solution upon standing overnight. Copolymer **3f** was completely insoluble in all solvents, exhibiting only swelling but never going into solution regardless of prolonged heating, stirring, or other physical efforts to solubilize the copolymer.

Determination of tacticity was performed by ^{1}H or ^{13}C NMR analysis of the copolymers. Initially, it was hoped that the copolymers could be derivatized by converting the oxazolidinone auxiliaries to methyl esters by hydrolysis and esterification as the NMR assignments in both ^{1}H and ^{13}C NMR have been made for *m* and *r* dyad signals from the geminal CH_3 groups in the methyl acrylate/isobutylene copolymer.[8a] Unfortunately, while the oxazolidinone auxiliary can be removed under very mild conditions in small organic molecules, all attempts to derivatize **3a**−**e** failed at the hydrolysis step—only completely insoluble material was recovered regardless of the method of hydrolysis. Attempts to derivatize the oxazolidinones by reduction followed by acetylation also failed.

^{1}H NMR and ^{13}C NMR spectra of **3a**−**e** proved helpful. As in the case of the methyl ester/isobutylene copolymer, the geminal CH_3 groups of the oxazolidinone copolymers (derived from isobutylene) gave both ^{1}H and ^{13}C signals from which dyad stereochemistry could be determined. Three separate signals were seen in both the ^{1}H spectra (Figure 2) and ^{13}C spectra (Figure 3). Just as in the copolymer of methyl acrylate with isobutylene, the meso signals were the most upfield and downfield while the racemic dyad signals were the middle of the three. COSY spectra confirmed coupling between the *m* dyad peaks, and HMQC experiments confirmed assignments of the *gem*-CH_3 *m* and *r* dyad signals in the ^{13}C spectra. Copolymer **3a** exhibits *gem*-CH_3 signals in both the ^{1}H and ^{13}C spectra in an almost 1:2:1 ratio that is expected for a predominantly atactic polymer. Copolymers **3b**−**e** show a preponderance of meso dyad signals. With these assignments, the *m*/*r* ratios were determined as well as selectivity at each step of the polymerization (Table 2).

As expected, auxiliaries with larger shielding groups (benzyl and phenyl) have higher selectivities than the smaller alkyl shielding groups (methyl and isopropyl). Still, in all four cases, selectivities were quite high.

Enantioselective Copolymerizations. Recently, catalytic control of enantioselectivity in acyclic radical additions to achiral *N*-acrylyl-2-oxazolidinone, **1a**, complexed by Lewis acids and chiral bisoxazolines has been demonstrated.[10] In this case, an achiral oxazolidinone acrylamide is used as the monomer, and stereocontrol is exerted by steric shielding of one face of the radical by a complexed chiral Lewis acid. The copolymerization of **1a** with isobutylene in the presence of a Lewis acid and ligand **4** was therefore chosen to study enantioselective copolymerizations. A variety of Lewis acids were assayed in combination with ligand **4** to determine if alternating 1:1 copolymers could be synthesized (Table 3).



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Selectivity for entry 8c was 68:32 in favor of *m* dyads (80% selectivity at each step), somewhat lower than the

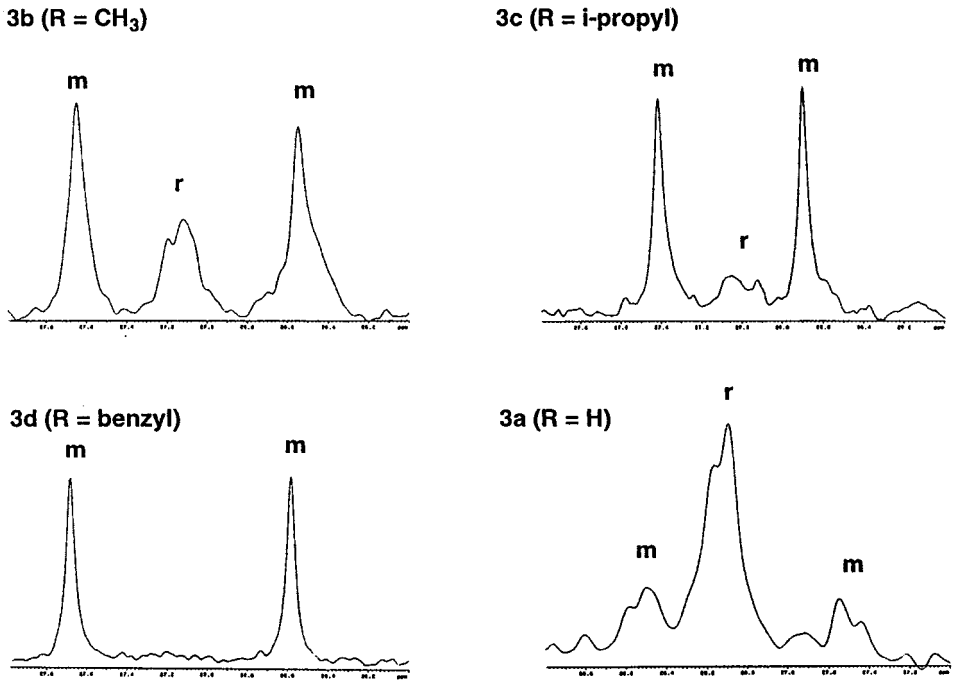


Figure 3. ^{13}C NMR of *gem*-CH_3 region of **3a**−**d**.

Table 2. Copolymer Tacticities for 3b−e[a]

R	equiv of Sc	*m*/*r*	selectivity
CH_3	2.5	80:20	10:1
i-Pr	2.0	90:10	20:1
phenyl	2.5	>95:5	>30:1
benzyl	2.0	>95:5	>30:1

[a] All reactions at −40 °C with Et_3B/O_2 initiation.

Table 3. Lewis Acid/Ligand Effect on Degree of Alternation in 3a[a]

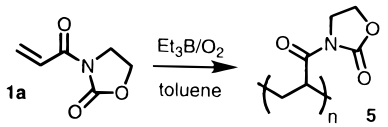
entry	Lewis acid	equiv of LA	equiv of **4**	solvent	A/IB
1	$SnCl_4$	1.25	1.35	CH_2Cl_2	60/40
2	$TiCl_4$	1.25	1.35	CH_2Cl_2	NR
3	$La(OTf)_3$	1.25	1.35	CH_2Cl_2	63/37
4a	$Eu(OTf)_3$	1.25	1.35	CH_2Cl_2	53/47
4b	$Eu(OTf)_3$	1.25	1.35	ether	NR
5a	$Sm(OTf)_3$	1.25	1.35	CH_2Cl_2	53/47
5b	$Sm(OTf)_3$	1.25	1.35	ether	NR
6	$Yb(OTf)_3$	1.25	1.35	CH_2Cl_2	NR
7	$Sc(OTf)_3$	1.25	1.35	ether	67/33
8a	$Zn(OTf)_2$	0.50	0.55	CH_2Cl_2	70/30
8b	$Zn(OTf)_2$	1.25	1.35	CH_2Cl_2	56/44
8c	$Zn(OTf)_2$	3.75	4.05	CH_2Cl_2	50/50

[a] All reactions performed at −78 °C with Et_3B/O_2 initiation.

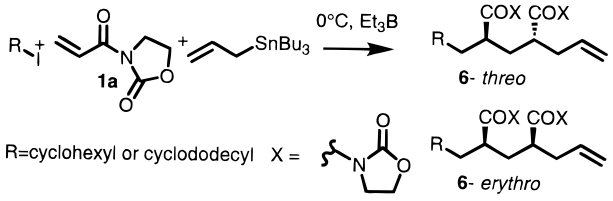
typical enantiomeric excesses seen in allyl transfer reactions (93% selectivity under identical reaction conditions). This low selectivity can be explained in part by the presence of background copolymerization that can occur when only $Zn(OTf)_2$ is present. In the allyl-transfer reactions, conversion does not occur without the presence of both $Zn(OTf)_2$ and ligand **4**.

$Sc(OTf)_3$, which performs well in the absence of ligand, does not effectively promote copolymerizations in the presence of **4**. Only with large excesses of $Zn(OTf)_2$ and ligand could 1:1 copolymers be obtained. Not surprisingly, this combination of substrate and chiral Lewis acid has proved to be the most effective for generating enantioselectivity in allyl-transfer reactions.[11]

Scheme 4



Scheme 5. *Threo*-selective n = Telomerization with 1a



The necessity for large stoichiometric excesses of $Zn(OTf)_2$ and **4** as compared to the substoichiometric amounts possible in the allyl-transfer reactions can be explained in part by the differing reactivities of the alkene. Allyltributylstannane is a more reactive alkene.

Homopolymers. Monomer **1a** was polymerized in the course of studies of the copolymerization, and NMR analysis of the homopolymer was undertaken. The monomer polymerized rapidly in the presence of initiators (Scheme 4), and the homopolymer was isolated by precipitation from methanol to give a white powder. Conversion of monomer was in excess of 90%. Both polymers were insoluble in aqueous solvents as well as all common organic solvents except DMSO and DMF. Analysis of molecular weight by gel permeation chromatography by comparison to polystyrene standards gave a "weight average" molecular weight in excess of 200 000 with the broad molecular weight distribution typical of free radical polymerizations. Attempts to polymerize acrylimides **1b**−**f** under conditions identical to those used

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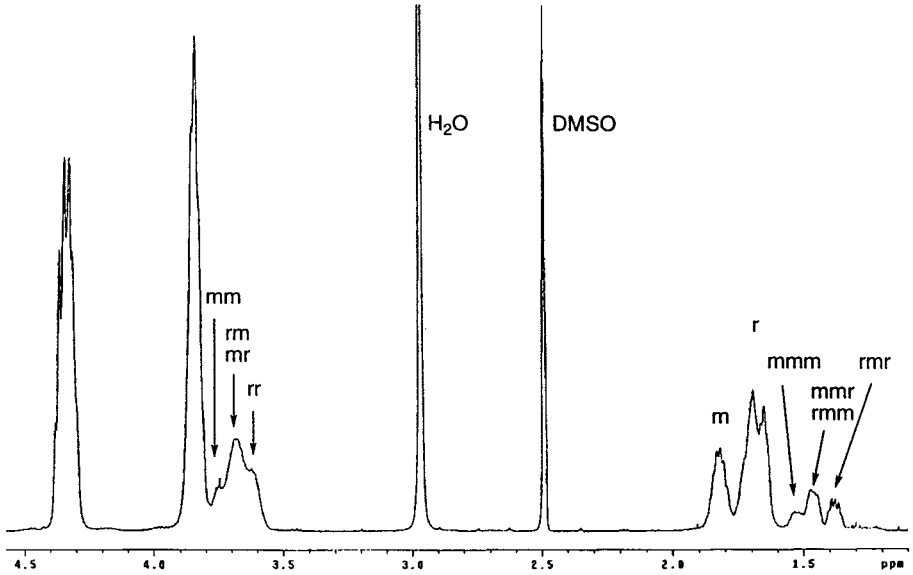

Figure 4. ^{1}H NMR of **5** at 100 °C with dyad, triad, and tetrad assignments.

in the homopolymerization of **1a** resulted in poor yields of homopolymer. The reason for the poor performance of monomers **1b**−**f** is not entirely clear, but it is reasonable to suggest that the resulting polymers would be sterically crowded and therefore form with difficulty.

NMR Analysis of 5. Although **5** has been reported in the literature,[12] its tacticity has never been examined. Surprisingly, the ^{1}H spectrum of **5** provided more information about tacticity than the ^{13}C spectrum. The ^{1}H NMR analysis at 100 °C in DMSO-d_6 showed the best overall resolution while analysis at 140 °C provided better resolution of the racemic methylene chain protons at the expense of resolution of the methine protons. Figure 4 shows the spectrum of **5** at 100 °C in DMSO-d_6 along with assignments of dyad, triad, and *m*-centered tetrad signals.

^{1}H,^{1}H−COSY spectroscopy allows assignment of the methylene signals to meso and racemic dyads. The most upfield and downfield sets show cross-peaks in the COSY and integrate for equal amounts and are assigned to the meso dyad protons. The middle set of signals belongs to the racemic dyad protons. This pattern of *m*/*r*/*m* signals is common in many polymers of monosubstituted alkenes. In addition to sensitivity to meso and racemic dyad stereochemistry, the ^{1}H spectrum also suggests that longer range stereosequences can be determined. COSY spectra and the analysis of the spectra are presented in the Supporting Information, Figures S6 and S7.

Additional evidence supporting these assignments comes from examining the methylene and methine regions of **5** formed in the presence of a Lewis acid, scandium trifluoromethanesulfonate ($Sc(OTf)_3$). Scandium complexes with the carbonyls of **1a** should prevent them from forming the energetically favorable dipole−dipole alignments between adjacent auxiliaries (for a discussion of Lewis acid complexation in free-radical transformations, see ref 13). As a result, polymer formed with scandium triflate present should be less syndiotactic than that formed without scandium. Comparison of the methine and methylene regions respectively of **5** made

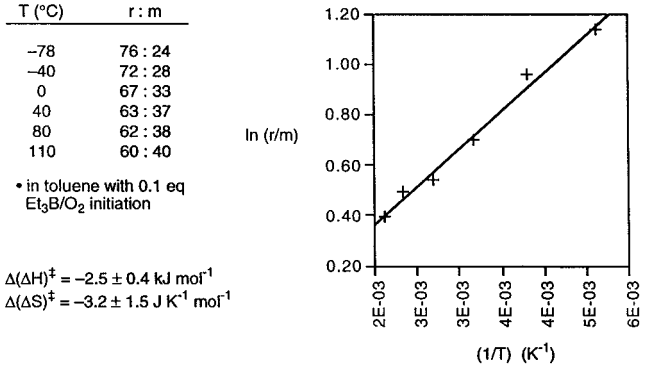

Figure 5. Temperature dependence of *r*/*m* selectivity and Eyring plot for **5**.

with and without $Sc(OTf)_3$ under identical conditions (25 °C, dichloroethane solvent) indicates that polymer formed without $Sc(OTf)_3$ contains greater amounts of signals from triads and tetrads containing *r* dyad sequences than the polymer formed in the presence of $Sc(OTf)_3$.

With the assignments of stereochemistry outlined above, *r*/*m* ratios can be determined by direct integration of the methylene region. Examination of *r*/*m* ratios of **5** synthesized under different temperature conditions shows a strong temperature dependence. Eyring analysis (Figure 5) shows an enthalpic preference for racemic arrangements, while the entropic term favors meso stereochemistry.

Although polymerization of **1a** does give polymers enriched in *r* dyads, it is of interest to compare the

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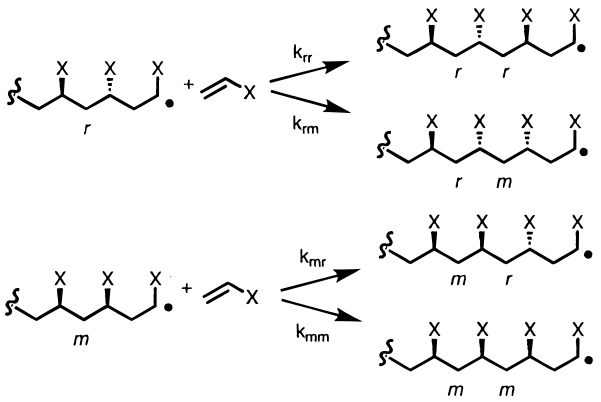

Figure 6. *r:m* selectivity depending on identity of previous dyad.

polymer with smaller telomers obtained from trapping the growing polymer chain with allyltributylstannane (see Scheme 2). The X-ray crystal structure of threo $n =$ 2 product (*threo*-**2**) shows that the two oxazolidinone rings are nearly parallel (within 18°) and the distance between opposed carbonyls is just under 3.5 Å. In addition, ^{1}H NMR signals of the two chiral methine protons show a strong downfield shift that is consistent with the proposed orientation seen in the X-ray structure, supporting the notion that the solution-state conformation is similar to the solid state. This conformation permits dipole−dipole stabilization of the carbonyls and favors the formation of the threo product in the telomer or the *r* dyad in the polymer.

In the homopolymerization of **1a**, the selectivity is not as high as that seen in the $n = 2$ telomerizations under identical conditions. The Eyring analyses also show slightly different results. In both cases, enthalpic considerations favor threo or racemic arrangements. However, in the polymerization reaction, there is a definite entropic term that favors meso dyads (erythro stereochemistry). It is possible that in the polymerization reaction, once two dipoles are aligned by the 1,3-dipolar effect, the next incoming monomer "sees" a dipole in the ultimate oxazolidinone auxiliary that has been masked by the one in the penultimate position. This would manifest itself in a difference in *r*/*m* selectivity depending on whether a racemic dyad or a meso dyad precedes the newly forming dyad (Figure 6).

If this hypothesis is correct, k_{rr}/k_{rm} should be less than k_{mr}/k_{mm}. This could be easily determined if tetrad populations were known accurately. Unfortunately, line-shape deconvolution does not provide precise enough information to make this determination. However, some evidence of this effect can be seen if one examines not only the $n = 2$ telomer products (compounds *threo*- and *erythro*-**2** in Scheme 2**)** but also the $n = 3$ products as well (Table 4).[14]

Although the $n = 3$ telomer stereochemistry has not been rigorously determined, if one assumes that the major $n = 3$ is the *rr* product, the minor $n = 3$ is the *mm* product, and the two other $n = 3$ telomers are the *mr* and *rm* products, then the *r*/*m* ratio from the $n = 3$ products is lower than that found in the $n = 2$ products. Additionally, in all cases, the amount of *rr* $n = 3$ product seen is lower than that predicted from the $n = 2$ *r*/*m* ratios. It is likely that stereoselectivity suffers as more acrylamide units are added to a growing chain.

(14) Radinov, R. Unpublished work.

Table 4. Ratios of r:m Stereosequences from $n = 2$ Telomers and Calculated from $n = 3$ Telomers in Telomerization of 1a[a]

	% total $n = 2$ telomer		% total $n = 3$ telomer				*r*/*m* calcd
solvent	*r*	*m*	*rr*	*mr*?	*rm*?	*mm*	from $n = 3$
benzene	83.9	16.1	64.8	18.2	14.0	3.0	79.7:20.3
toluene	84.8	15.2	63.4	19.5	14.6	2.5	83.3:16.7
pentane	87.0	13.0	68.7	18.5	10.4	2.4	83.1:16.9

[a] All 0 °C warmed to 25 °C and 0.1 equiv of Et_3B/O_2 initiation.

Experimental Section

General Procedures. ^{1}H NMR spectra were obtained on a Varian Unity 400 MHz spectrometer at 25 °C in $CDCl_3$ unless otherwise noted. All Lewis acids were used as received from Aldrich.

Typical Copolymerization Reaction for 1a−f. In a three-necked 50 mL round-bottom flask, 15 mL of ether, 50 mg of **1a**, and 2 equiv of $Sc(OTf)_3$ were stirred for 15 min and then cooled to 0 °C. Approximately 20 equiv of isobutylene was condensed into the solution utilizing a dry ice/acetone condenser. The flask was capped with a drying tube, 0.5 equiv of Et_3B (1 N solution in hexanes) was added, and the solution was stirred for 3 h. The copolymer was precipitated from an equal volume of ethyl acetate and collected by filtration. Trace volatiles were removed by placing the copolymer on a high vacuum line overnight.

(2-Oxazolidone)acrylamide coisobutylene (3a): ^{1}H NMR (95 °C, DMSO-d_6) δ 4.35 (t, 2H), 3.95 (m, 1H), 3.80 (t, 2H), 1.65 (m, 2H), 1.25 (m, 2H), 0.80 (s, *m*CH_3, 1.5H), 0.75 (s, *r*CH_3, 3H), 0.70 (s, *m*CH_3, 1.5H); ^{13}C NMR (95 °C, DMSO-d_6) δ 179.5, 154.7, 63.5, 49.9. 44.7, 35.7, 35.3, 28.5 (*m*CH_3), 28.1 (*r*CH_3), 27.5 (*m*CH_3). Anal. Calcd for $C_{10}H_{15}NO_3$: C, 60.90; H, 7.67; N, 7.10. Found: C, 59.41; H, 7.30; N, 6.95.

(5(*R*)-Methyl-2-oxazolidone)acrylamide coisobutylene (3b): ^{1}H NMR (95 °C, 500 MHz, DMSO-d_6) δ 4.45 (m, 2H), 4.00 (m, 1H), 3.95 (m, CH, 1H), 1.65 (m, CH_2, 2H), 1.30 (m, 3H), 1.25 (m, CH_2, 2H), 0.85 (s, *m*CH_3, 2.4H), 0.80 (m, *r*CH_3, 1.2H), 0.75 (m, *m*CH_3, 2.4H); ^{13}C NMR δ 178.3, 153.4, 69.2, 51.4, 49.3, 49.1, 34.9, 34.6, 27.6 (*m*CH_3), 27.1 (*r*CH_3), 26.5 (*m*CH_3), 18.6. Anal. Calcd for $C_{11}H_{17}NO_3$: C, 62.54; H, 8.11; N, 6.63. Found: C, 61.80; H, 7.95; N, 6.02.

(5(*S*)-Isopropyl-2-oxazolidone)acrylamide coisobutylene (3c): ^{1}H NMR (95 °C, 500 MHz, DMSO-d_6) δ 4.35 (m, 2H), 4.30 (m, 1H), 4.00 (m, CH, 1H), 2.20 (m, 1H), 1.65 (m, CH_2, 2H), 1.25 (m, CH_2, 2H), 0.90 (d, 3H), 0.85 (s, *m*CH_3, 2.7H), 0.80 (d, 3H), 0.80 (s, *r*CH_3, 0.6H), 0.75 (s, *m*CH_3, 2.7H); ^{13}C NMR δ 178.3, 154.1, 63.6, 59.5, 49.3, 48.8, 34.9, 34.5, 28.8, 27.4 (*m*CH_3), 27.0 (*r*CH_3), 26.7 (*m*CH_3), 18.1, 15.2. Anal. Calcd for $C_{14}H_{25}NO_3$: C, 65.85; H, 9.87; N, 5.49. Found: C, 65.11; H, 9.80; N, 5.31.

(5(*S*)-Benzyl-2-oxazolidone)acrylamide coisobutylene (3d); ^{1}H NMR (95 °C, 500 MHz, DMSO-d_6) δ 7.25 (m, 5H), 4.60 (m, 1H), 4.25 (m, 1H), 4.10 (m, 1H), 4.0 (m, CH, 1H), 3.20 (m, 1H), 2.75 (m, 1H), 1.75 (m, CH_2, 2H), 1.30 (m, CH_2, 2H), 0.90 (s, *m*CH_3, 3H), 0.80 (s, *m*CH_3, 3H); ^{13}C NMR (95 °C, 125 MHz, DMSO-d_6) δ 178.5, 153.4, 136.4, 129.7, 129.0, 127.2, 66.4, 56.1, 49.2, 48.8, 37.5, 35.0, 34.7, 27.7 (*m*CH_3), 26.6 (*m*CH_3). Anal. Calcd for $C_{18}H_{25}NO_3$: C, 71.26; H, 8.31; N, 4.62. Found: C, 70.78; H, 8.21; N, 4.42.

(5(*S*)-Phenyl-2-oxazolidone)acrylamide coisobutylene (3e): ^{1}H NMR (DMF-d_7) δ 7.4 (m, 5H), 5.6 (m, 1H), 4.8 (m, 1H), 4.4 (m, 1H), 4.1 (m, 1H), 1.8 (m, 1H), 1.6 (m, 1H), 1.3 (m, 2H), 0.9 (s, *m*CH_3, 3H), 0.7 (s, *m*CH_3, 3H).

Typical Telomerization of Cyclohexyl Iodide, 1a, and Allyltributylstannane. In a 25 mL round-bottom flask, 8.7 mL of benzene, 190 mg of **1a**, 1.3 mL of allyltributylstannane, and 140 μL of cyclohexyl iodide were stirred under argon at 80 °C. Approximately 10 mg of AIBN was added, the mixture

was stirred for 45 min, another 10 mg of AIBN was added, and the mixture was stirred for an additional 90 min. The solvent was removed by rotary evaporation, and the sample was diluted in 80 mL of ether and stirred with 80 mL of 10% potassium fluoride solution overnight. The ether layer was separated, filtered, dried with anhydrous magnesium sulfate, filtered, and concentrated. The resulting oil was chromatographed on silica with 200 mL of 50% ethyl acetate in hexanes, 200 mL of 75% ethyl acetate in hexanes, and then 400 mL of pure ethyl acetate. The fractions containing the $n = 1$ telomer were concentrated and then further purified by normal-phase HPLC with 50% ethyl acetate in hexanes on a semipreparative scale column (flow 10 mL/min, differential refractometer detector). The fractions containing the $n = 2$ telomers were concentrated, and then the $n = 2$ diastereomers were separated (if possible) by normal-phase HPLC with 100% ethyl acetate on a semipreparative scale column (flow 10 mL/min, differential refractometer detector).

Typical Polymerization of 1a. In a 25 mL round-bottom flask, 75 mg of the acrylamide was mixed with 5 mL of toluene. The polymerization was initiated by 0.1 equiv of Et_3B (1 N solution in hexanes) and the reaction stirred for 3 h. The polymer was collected by precipitation from organic solvent (methanol or hexanes).

Poly(2-oxazolidone)acrylamide: ^{1}H NMR (500 MHz, 100 °C, DMSO-d_6) δ 4.37 (m, 2H), 3.77 (m, 2H), 3.75 (m, *mm*CH), 3.68 (m, *rm*/*mr*CH), 3.61 (m, *rr*CH), 1.86 (m, *m*CH_2), 1.76 (m, *mrm*CH_2), 1.73 (m, *rrm*/*mrr*CH_2), 1.68 (m, *rrr*CH_2), 1.56 (*mmm*CH_2), 1.49 (m, *rmm*/*mmr*CH_2), 1.41 (m, *rmr*CH_2); ^{13}C NMR (125 MHz, 100 °C, DMSO-d_6) δ 175, 153, 62, 43, 37. 35.

Acknowledgment. Support of this research from an NSF (CHE-9996188) grant is gratefully acknowledged.

Supporting Information Available: Discussion of NMR polymer stereochemistry assignments and NMR COSY analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

JO9914420