

Living Polymerization of Carbodiimides Initiated by Copper(I) and Copper(II) Amidinate Complexes

Koichi Shibayama, Scott W. Seidel, and Bruce M. Novak*

Department of Polymer Science and Engineering and the Materials Research Science and Engineering Center, University of Massachusetts at Amherst, Amherst, Massachusetts 01003

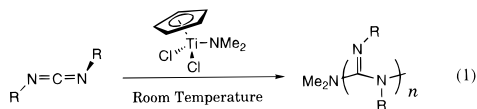
Received December 2, 1996; Revised Manuscript Received February 26, 1997

ABSTRACT: Various catalysts for the polymerization of carbodiimide have been investigated. In early studies, anionic polymerization techniques were employed, but the products obtained were low molecular weight oligomers. More recently, a living route using titanium(IV) complexes as initiators has been employed and the high molecular weight polymers obtained exhibit a well-ordered helical, extended-chain conformation. However, the titanium complexes are sensitive to high temperatures and the presence of oxygen or water. Herein, we report that more robust catalysts based on copper(I) and copper(II) complexes also initiate living carbodiimide polymerizations. The tolerance of these complexes to impurities is illustrated by the fact that they cleanly initiate the polymerization of carbodiimides under air and oxygen. They are even active in the presence of water, but both molecular weights and yields tend to be lower than in dry solvents. It has been shown that the catalytic activity of a copper(II) amidinate complex is almost equal that of reported titanium(IV) initiators. Analysis of these systems by gel permeation chromatography–light scattering measurements (GPC–LS) and preliminary kinetic analysis suggest this system to be living.

Introduction

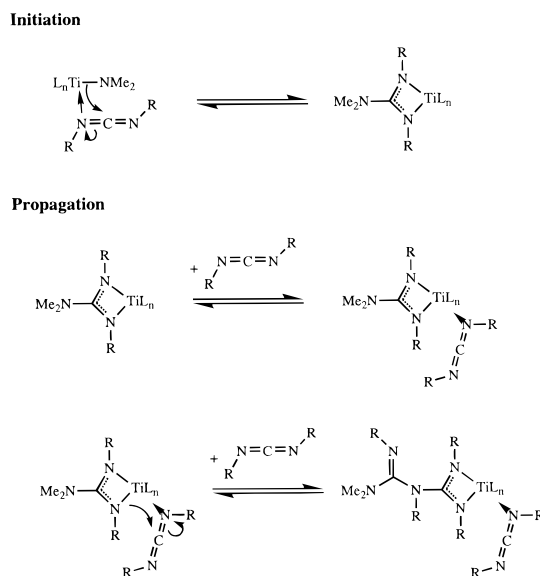
Polymers that adopt extended-chain structures often exhibit important properties including high modulus and strength^{1–3} and liquid crystallinity.⁴ Helical polymers, comprising a subset of extended-chain polymers, have the added feature of macromolecular chirality, which can endow these materials with a host of additional properties.⁵ To facilitate the synthesis of well-defined helical polymers with controlled molecular weights, narrow polydispersities, defined end groups, and supramolecular architectures, we have been interested in designing transition-metal complexes that initiate the living polymerization^{6–11} of prohelical monomers (i.e., monomers that when polymerized yield helical macromolecules). Recent examples from our laboratory include catalysts for the living polymerization of isocyanides,^{12,13} isocyanates,^{14,15} and carbodiimides.¹⁶

This report describes new air- and moisture-tolerant catalysts for the living polymerization of carbodiimides. Polycarbodiimides are a new class of macromolecules that adopt extended-chain, helical conformations.¹⁶ Data from X-ray scattering studies and molecular modeling indicate that polycarbodiimides display a 6/1 helix in the solid state, and viscometry and light scattering data indicate that this extended-chain conformation persists in solution. Living polymerization of carbodiimides can be carried out using titanium(IV) alkoxide, amidinate, or amide complexes. Of these, CpTiCl₂X (where X = –OR, –NR₂) offer the best control (eq 1). The mechanism for polymerization of carbodi-



imides by the Ti(IV) complexes has been shown to involve initiation by insertion of the monomer into the Ti–X bond to form an intermediate amidinate complex. Propagation then proceeds through monomer insertions into the metal–amidinate bond (Scheme 1). These steps

Scheme 1



are fully reversible, and the ceiling temperatures for monomers studied to date range from 80 °C (*N,N*-di-*n*-hexylcarbodiimide, **1**) to 156 °C (*(R/S)*-*N*-methyl-*N*-(α -phenylethyl)carbodiimide, **2**). Equilibrium considerations, therefore, favor running reactions either in the minimum amount of solvent or preferably in bulk.

A limitation of these early-transition-metal catalysts is their high degree of sensitivity to ubiquitous impurities such as oxygen and water, as well as monomers bearing polar functional groups. As a minimum, hydrocarbon monomers must be vacuum distilled from CaH₂, and the solvents dried over sodium benzophenone ketyl. As in the case of anionic, cationic, and other coordination–insertion polymerizations, this initiator sensitivity limits the scope of these polymerizations. During experimental sorties directed at identifying alternative catalysts for carbodiimide polymerizations, it was discovered that select copper complexes are highly active in this regard. Furthermore, these late-

* Abstract published in *Advance ACS Abstracts*, April 1, 1997.

transition-metal complexes retain their activity and are living in the presence of oxygen and, to a lesser extent, water.

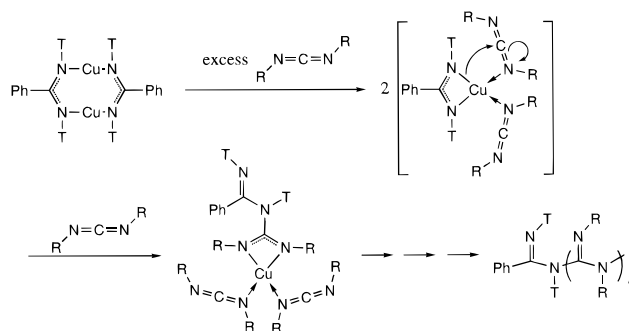
Results and Discussion

General Observations. In comparison to early-transition-metal complexes, late-transition-metal complexes are far less reactive with air and moisture. During our search for more robust catalysts, it was discovered that simple copper salts will initiate the polymerization of carbodiimides, albeit slowly, and in less than desirable yields. What was promising, however, was the fact that these reactions would proceed in wet organic solvents (e.g., toluene) under room atmosphere. Because it was shown that, in the Ti(IV)-catalyzed polymerizations, initiation involves insertion of monomer into a metal–alkoxide (amide) bond, we first investigated the use of copper alkoxides. Using Cu(O-*t*-Bu), it was found that **1** could be polymerized in 56% yield after 1 week at room temperature in toluene. Under an inert atmosphere (N₂ or argon) the reaction mixture remained colorless, indicative of a Cu(I) d¹⁰ complex. Essentially the same results were obtained using wet solvents, but the molecular weight of the polymer proved to be lower (*vide infra*). The identical reaction run under air or oxygen turned a dark emerald green, and the monomer was consumed at a faster rate. This color change is consistent with an air oxidation of the Cu(I) to Cu(II) d⁹ oxidation state. Because of solubility limitations with the alkoxide complex, direct evidence of this oxidation was obtained by ESR using copper chloride salts. The dark emerald green reaction solutions composed of CuCl₂ and **1** (monomer/initiator = 10/1) under either an inert atmosphere or oxygen showed a pronounced ESR signal consistent with the presence of the paramagnetic *S* = 1/2 spin state of Cu(II). Likewise, polymerization solutions of CuCl/**1** under oxygen showed an identical signal which became more pronounced with time and was accompanied by a color change from light yellow to the same dark green observed previously. In contrast, reaction solutions of CuCl under an inert atmosphere show no color change and no ESR signal. Polymer is obtained under all these conditions, indicating both Cu(I) and Cu(II) are active oxidation states, but detailed kinetics reveal that, of the two, Cu(II) is the more active (*vide infra*).

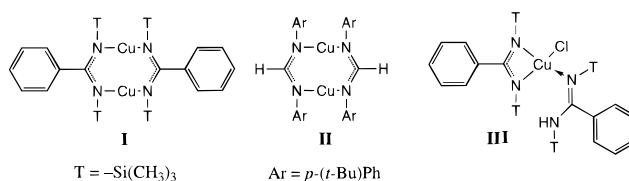
Attempts to synthesize a Cu(II) analogue, Cu(O-*t*-Bu)-Cl, proved futile due to its poor solubility. We were, however, able to synthesize the methoxy analogue, Cu(OCH₃)Cl,¹⁷ which, although highly insoluble in all common solvents, was found to be partially soluble in the carbodiimide monomers, thereby enabling their bulk polymerization albeit under heterogeneous conditions. Further attempts to solubilize this complex yielded mixed results. Addition of 2 equiv of P(CH₃)₃ per Cu center to the reaction mixtures successfully solubilized the catalyst, but unfortunately the resulting complex proved to be inert toward polymerizations. Replacing the strong donor phosphine with the weaker coordinating pyridine was more effective. A 50:50 mixture of toluene/pyridine was found to dissolve the catalyst in an active state and a 79% yield of polymer was obtained after 4 days. In summary, bulk heterogeneous polymerizations gave higher yields at slow rates, whereas homogeneous reactions in solution were faster but yields suffer because of monomer–polymer equilibrium constraints.

Copper Amidinate Complexes. Based on these preliminary studies, three important catalyst design

Scheme 2



features emerged: (1) solubility of the initiator in the reaction medium (preferably neat carbodiimide); (2) accessing the paramagnetic Cu(II) oxidation state; (3) incorporation of a defined initiating group into the ligand sphere of the catalyst. Although not elucidated earlier, this last characteristic provides a mechanism for controlling the identity of the polymer end group. Additionally, initiation rates at least equal to the propagation rates are desirable for the formation of polymers with narrow polydispersities. One approach to matching these rates is to design initiators that are as structurally similar to the propagating species as possible. In so doing, the respective transition states for monomer insertions during initiation and propagation should also be of similar energy, and hence these kinetic steps should proceed with similar rates. With these criteria in mind and a mechanistic model based on our previous titanium work, we synthesized a series of copper amidinato complexes in both the +1 (complexes **I** and **II**) and +2 (complex **III**) oxidation states that should be structurally similar to the propagating chain end of these polymerizations.



Complexes **I**¹⁸–**III**¹⁹ were synthesized using modified literature procedures. The Cu(I) complexes, **I** and **II**, are isolated as dimers, while the Cu(II) complex, **III**, is isolated as a monomer with a hydrolyzed amidine coordinated to the copper center. The synthesis calls for use of a wet acetonitrile solvent which provides the necessary source of water. We have been unable to isolate any complexes that are either free of this hydrolyzed amidine or possess an amidine with the three TMS groups intact. We think the hydrolyzed amidine acts as a more competitive ligand for the vacant coordination site on the metal relative to its fully silylated analogue (steric considerations) or the acetonitrile solvent (stronger Lewis base).

True to our predictions, these copper amidinate complexes proved to be highly active toward the polymerization of carbodiimides. Polymerizations could be run in solution using organic solvents or in the bulk. The dimeric forms of complexes **I** and **II** found in the solid state are presumed to dissociate into monomeric forms upon treatment with the carbodiimide monomers (Scheme 2). Direct proof of the incorporation of the amidinate initiating group of **I** and **III** was obtained using ¹H NMR (–Si(CH₃)₃ singlet at 0.02 ppm). Molecular weight determination by this end-group analysis

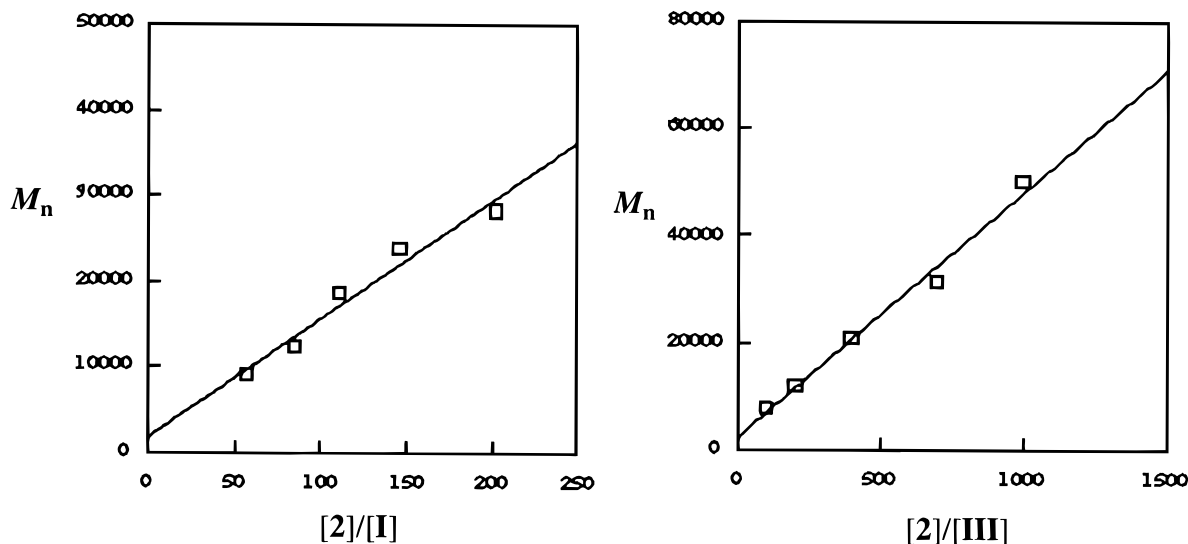


Figure 1. Plots of molecular weight as a function of monomer (2) to initiator ratio for amidinate initiators **I** and **III**.

was deemed unreliable because of the hydrolytic sensitivity of the TMS protecting groups.

The resultant polycarbodiimides from bulk polymerizations were isolated, after dissolving to toluene, by precipitation into excess methanol, and lyophilization from benzene, as a spongy white solid. Analysis of these polymers by gel permeation chromatography (GPC) (based on monodisperse polystyrene standards) erroneously indicated that the polymer was polydisperse ($M_w/M_n > 15$). On-line light scattering measurements (LS) of the effluent polymer demonstrated that very similar molecular weights were eluting over unusually large volumes. This phenomenon is also observed with polymers obtained when titanium(IV) initiators are used.¹⁶ The separation of polycarbodiimides does not appear to be based on size exclusion alone but rather is hindered by an affinity of these polymers for the GPC column substrate. Low polydispersities ($M_w/M_n \leq 1.25$) were obtained in the analysis of polymers using the tandem GPC/LS instrument.

Living Character: Absence of Chain-Transfer Steps. Proof of a living polymerization requires showing the kinetic insignificance of any chain termination and chain-transfer steps. The former is best demonstrated through kinetic experiments designed to show a constant number of active chains, whereas the latter can be demonstrated by experiments showing a constant number of chains. Counting chains can be done by a select number of methods including monitoring molecular weight as a function of the monomer to initiator ratio. The plots of molecular weight as a function of the monomer to initiator ratio are shown in Figure 1 for initiators **I** and **III**. Experiments were carried out under both oxygen and argon. In all cases, linear plots are obtained, which indicates that chain transfer does not occur from either the +1 or +2 oxidation states, in either the presence or absence of oxygen.

Living Character: Absence of Termination Steps. The kinetics of polymerization of four different copper catalysts were measured in order to evaluate the relative performance of these initiators and to elucidate the reaction mechanism and living nature of these catalysts. The kinetic runs for the bulk polymerization of the carbodiimides were measured using dilatometry techniques²⁰ wherein the reaction is followed by a decrease in volume associated with the conversion of

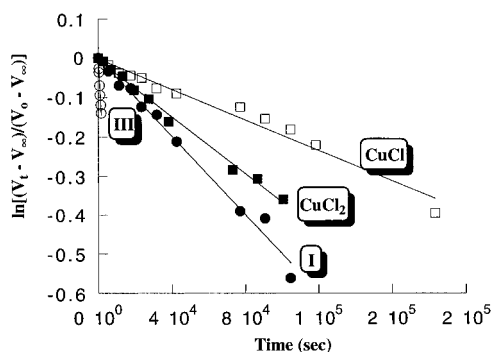


Figure 2. Kinetic performance of copper compounds in the bulk polymerization of (*R*)-*N*-methyl-*N*-(1-phenylethyl)carbodiimide (**2**).

monomer to polymer at 30.0 °C. The densities of monomer **2** (0.992 g/mL) and poly-**2** (1.170 ± 0.025 g/mL) were measured using a pycnometer. A comparison of the kinetic plots for the bulk polymerization of **2** using four different catalysts is shown in Figure 2. The polymerizations were all found to follow a reversible kinetic law with a pseudo-first-order rate dependence on monomer concentration. These rate constants of reaction were dependent on the catalyst used: $k(\text{CuCl}) = 5.4 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$, $k(\text{CuCl}_2) = 3 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$, $k(\text{I}) = 9 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$, $k(\text{III}) = 3 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$. The magnitude of these rate constants and the fit of the data to pseudo-first-order kinetic analysis must be taken in the context of the experimental conditions. Normally, kinetic data measured to 3–5 half-lives are required for high levels of confidence. Unfortunately, the bulk polymerizations used to produce these rodlike polymers become highly viscous at relatively early times, which precludes accurate data collection. Nevertheless, the relative trends observed and the order of magnitude differences in rates are accurate and provide valuable insights into these systems. Initiators **I**, **III**, and CuCl₂ were all soluble under the conditions employed, but the solubility of CuCl was limited such that the concentration of initiator in solution was not accurately known. The advantage of using the preformed initiators (e.g., compare **III** and CuCl₂) is evident by the 2 orders of magnitude increase in rate obtained. In fact, initiator **III** is nearly as active as our previously reported titanium(IV) catalyst, CpTiCl₂(N(CH₃)₂)₂.

Effect of Water. We noted earlier that polymerizations could be successfully run in wet organic solvents. More detailed studies, however, revealed that water actually acts as a mildly effective terminating agent. Polymerizations of **2** were run using **III** in wet and dry toluene but otherwise identical reaction conditions and times. The polymer from the reaction in wet solvents was obtained in lower yield (40% vs 51.6%), proved to be of lower molecular weight (1.0×10^4 vs 1.3×10^4), and had a slightly broader polydispersity (1.20 vs 1.13). All of these observations are consistent with a slow termination process by water.

The titanium(IV) initiators described in our previous work are extremely sensitive to protic sources including monomers or solvents possessing enolizable protons. Although not an extensive list of functional monomers has been investigated, we have found that these copper catalysts tolerate a much larger array of functional groups and will polymerize carbodiimides in enolizable solvents such as acetone and ethyl acetate. The yields of polymer obtained are nearly identical with the yields obtained under the same conditions in toluene.

Conclusions. Our interest in structurally regular polymers has led us to develop a class of copper catalysts which initiate the living polymerization of carbodiimide monomers under conditions in which previous initiators would immediately deactivate (e.g., under oxygen (air) or in wet solvents). As a product of this quest, we have found that amidinate complexes of both Cu(I) and Cu(II) are highly active initiators for carbodiimide polymerizations. Mechanistic studies indicate that the carbodiimides insert into one of the copper–amidinate bonds, thus becoming the end group of the growing polymer chain. Both oxidation states are active, but Cu(II) complexes are more active in terms of rates of reaction. Regardless of the oxidation state of the initial complex, all polymerizations run in the presence of oxygen proceed through the Cu(II) oxidation state.

Experimental Section

General Procedures. Copper amidinate complexes **I** and **II**, Cu(OMe)Cl,¹⁷ were prepared according the literature procedures. When dried, acrylonitrile was stirred over powdered, activated molecular sieves (4 Å) for 56 h and was vacuum transferred. THF and Et₂O were distilled from sodium benzophenone ketal immediately prior to use. CH₂Cl₂ was deoxygenated by a series of freeze–pump–thaw cycles. All other materials were reagent grade and used without further purification.

Unless otherwise noted, all synthetic operations were carried out under inert gas (nitrogen or argon). Compounds were stored under an inert atmosphere in a Vacuum Atmospheres HE-533 Dri-Lab with attached HE-493 Dri Train. Solutions were concentrated via rotary evaporation unless otherwise specified. ¹H NMR spectra were recorded at 200 MHz on a Bruker AM-200 spectrometer or at 300, 400, or 500 MHz on Bruker AMX spectrometers. ¹³C NMR spectra were recorded at 121.5 MHz on a 300 MSL spectrometer. ¹H and ¹³C spectra are referenced to a residual resonance of the solvent employed. ¹H NMR data are tabulated by chemical shift, multiplicity, coupling constants in hertz, and number of protons. Infrared spectra were recorded on a Perkin Elmer 1600 Series Fourier transform infrared spectrometer. UV/vis spectra were acquired on a Hewlett-Packard 8452 Series ultraviolet/visible spectrophotometer. All ¹³C and ³¹P spectra are proton decoupled. Gel permeation chromatography was performed on a Hewlett-Packard 1050 Series pump with Waters ultrastaygel columns and THF as the eluant (1.0 mL/min). Light scattering was performed using the same GPC setup equipped with a Wyatt/Optilab Model 903 interferometric refractometer and an 18-angle Wyatt Dawn DSP-F laser photometer operat-

ing at 633 nm. GPC/LS data were analyzed using Wyatt ASTRA 1.2 or 1.4 software. Elemental analyses were performed on a Control Equipment Model 240XA elemental analyzer at the Microanalytical Laboratory Research Services, operated by the Graduate School, University of Massachusetts, Amherst, MA.

(*R*)-(+)-*N*-Methyl-*N*-(α -phenylethyl)urea. A 250-mL round-bottom flask was charged with 4.00 mL of methyl isocyanate (3.87 g, 67.8 mmol), a magnetic stir bar, and 100 mL of reagent-grade chloroform. [CAUTION! Methyl isocyanate is extremely toxic and is quite volatile. All operations should be carried out in an efficient fume hood.] The resulting solution was cooled to 0 °C by the use of an ice bath and covered with a septum to prevent evaporation of the methyl isocyanate and introduction of water. Over the next 30 min, 8.74 mL of neat (*R*)-(α -phenylethyl)amine (8.22 g, 67.8 mmol) was added to the cooled solution in 1 mL increments by temporary removal of the septa; constant stirring was provided by the use of a magnetic stirring plate. Additional CHCl₃ (20 mL) was used to ensure complete transfer of the (α -phenylethyl)amine. The resultant solution was stirred for an additional 20 min after the addition of the (α -phenylethyl)amine. Removal of the solvent by rotary evaporator at 60 °C yielded *N*-methyl-*N*-(α -phenylethyl)urea as a viscous, pale tan liquid which solidified, on standing at room temperature, to a white solid. The product of this reaction was of such purity that no further purification was necessary. Yield: 11.44 g (64.19 mmol, 95%). Mp: 100.7–101.0 °C. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 1.42 (d, 3H, CH₃, *J* = 6.81 Hz), 2.68 (s, 3H, CH₃), 4.45 (br s, 1H, urea H), 4.77 (m, 1H, benzylic H), 4.86 (br s, 1H, urea H), 7.23 (m, 1H, Ar), 7.32 (m, 4H, Ar). ¹³C-{¹H} (126 MHz, CDCl₃): δ (ppm) 23.37, 27.09, 50.24, 125.89, 127.25, 128.70, 144.23, 158.35. IR (CHCl₃): 3359 (m), 3031 (w), 3016 (m), 1632 (vs), 1570 (vs), 1493 (m), 1476 (m), 1450 (m), 1418 (w), 1376 (w), 1259 (m), 1165 (w), 1090 (w), 1012 (w) cm⁻¹. Anal. Calcd for C₁₀H₁₄N₂O: C, 67.39; H, 7.92; N, 15.72. Found: C, 67.42; H, 8.20; N, 15.68.

***N,N*-Di-*n*-hexylurea.** The same procedure for the preparation of *N*-methyl-*N*-(α -phenylethyl)urea was employed. The quantities of reagents used were 10.0 mL of hexyl isocyanate (8.95 g, 70.3 mmol), 9.29 mL of 1-aminohexane (7.12 g, 70.3 mmol), and 150 mL of CHCl₃. Yield: 16.06 g (70.34 mmol, 100%). Mp: 74.2–74.8 °C. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 0.87 (t, 6H, CH₃, *J* = 6.87 Hz), 1.25 (m, 12H, CH₂CH₂CH₂), 1.47 (m, 4H, CH₂), 3.14 (m, 4H, CH₂N), 4.35 (br s, 2H, NH). ¹³C-{¹H} (125 MHz, CDCl₃): δ (ppm) 13.98 (CH₃), 22.55 (CH₂), 26.55 (CH₂), 30.18 (CH₂), 31.51 (CH₂), 40.62 (CH₂), 158.27 (C=O). IR (KBr pellet): 3334 (s), 2958 (s), 2931 (s), 2871 (s), 2857 (s), 1617 (vs), 1578 (vs), 1509 (w), 1478 (m), 1463 (m), 1299 (w), 1251 (m), 1222 (m). Anal. Calcd for C₁₀H₁₄N₂O: C, 68.37; H, 12.36; N, 12.27. Found: C, 68.27; H, 12.04; N, 12.53.

(*R*)-(+)-*N*-Methyl-*N*-(α -phenylethyl)carbodiimide. Most carbodiimides were prepared similarly with a slight modification of literature procedures.^{21,22} The following description of the preparation of (*R*)-(+)-*N*-methyl-*N*-(α -phenylethyl)carbodiimide serves as a typical example. A dry 500-mL round-bottom flask was charged with 250 mL of CH₂Cl₂, 18.74 g of triphenylphosphine (71.43 mmol, 25% excess), and a large egg-shaped stir bar. A dry pressure-equalizing addition funnel was charged with 30 mL of CH₂Cl₂ and 3.68 mL of bromine (11.4 g, 71.4 mmol, 25% excess) and was then placed on the 500-mL round-bottom flask. The whole apparatus was placed under a dry nitrogen atmosphere, and the triphenylphosphine solution was cooled by an ice bath and stirred vigorously with a magnetic stirring plate. The bromine solution was added dropwise over the course of 30 min, and the resulting solution was allowed to stir for an additional 10 min. The resulting suspension of dibromotriphenylphosphorane had 20.1 mL of triethylamine (14.6 g, 144 mmol, 26% excess) added to it by temporary removal of the nitrogen purge. In a similar fashion, 10.18 g of (*R*)-(+)-*N*-methyl-*N*-(α -phenylethyl)urea (57.1 mmol) was added in five equivalent portions to the 0 °C suspension over the next hour. One hour after the last addition of the urea, 100 mL of water was added to the round-bottom flask in order to extract the triethylammonium hydrochloride, and

Table 1. Efficiency of Copper Compounds as Catalysts for the Polymerization of Carbodiimides ($R_1-N=C=N-R_2$)

R_1, R_2 ($R_1-N=C=N-R_2$)	initiator	atmosphere	polymer yield (%)	note
methyl, 1-phenylethyl ^f	CuCl	Ar	88	a
methyl, 1-phenylethyl	CuCl ₂	Ar	81	a
methyl, 1-phenylethyl	Cu(OMe)Cl	Ar	91	a
methyl, 1-phenylethyl	I	Ar	82	a
methyl, 1-phenylethyl	II	Ar	86	a
methyl, 1-phenylethyl	I	O ₂	70	a
<i>n</i> -hexyl, <i>n</i> -hexyl	CuCl	air	96	b
<i>n</i> -hexyl, <i>n</i> -hexyl	CuCl ₂	air	100	c
<i>n</i> -hexyl, <i>n</i> -hexyl	Cu(OMe)Cl	air	99	d
<i>n</i> -hexyl, <i>n</i> -hexyl	III	N ₂	74	e

^a Typical conditions: carbodiimide/initiator ratio approximately 100:1. Neat (no solvent), reaction time 24 h, at room temperature.

^{b,c} Approximately 1 M monomer solution in toluene. ^d Approximately 1 M monomer solution in toluene; reaction time 120 h.

^e Approximately 1 M monomer solution in toluene; reaction time 96 h. ^f (*R*)-(+)-*N*-Methyl-*N*-(α -phenylethyl)carbodiimide.

the organic and aqueous phases were separated using a separatory funnel. The dichloromethane solution, after drying over sodium sulfate, was reduced to approximately 50 mL by the use of a rotary evaporator. Addition of 300 mL of pentane to the viscous, dark brown oil served to precipitate the triphenylphosphine oxide as a loose slurry. The slurry, 0.1 g of CaH₂, and an additional 100 mL of pentane (to ensure complete transfer of the slurry) were placed in a Soxhlet extractor which was attached to a 500-mL round-bottom flask. A reflux condenser was attached, and the slurry was extracted overnight (12 h) with pentanes. The following day, most of the pentane was removed by a rotary evaporator, and the crude product was filtered in order to remove the small quantity of triphenylphosphine oxide that had been extracted with the product. Distillation of the extracts from CaH₂ using a short path distillation head at 53–54 °C and 0.8 Torr afforded (*R*)-(+)-*N*-methyl-*N*-(α -phenylethyl)carbodiimide as a clear, colorless liquid. Yield: 6.40 g (39.9 mmol, 70%). ¹H NMR (500 MHz, acetone-*d*₆): δ (ppm) 1.48 (d, 3H, CH₃, *J* = 6.69 Hz), 2.89 (s, 3H, CH₃N), 4.62 (q, 1H, benzylic H, *J* = 6.71 Hz), 7.25 (m, 1H, aromatic), 7.35 (m, 4H, aromatic). ¹³C{¹H} (125 MHz, acetone-*d*₆): δ (ppm) 25.49 (CH₃), 32.62 (CH₃), 56.93 (CHCH₃), 126.64 (CH), 127.93 (CH), 129.21 (CH), 141.41 (N=C=N), 145.28 (aromatic C). IR (neat): 3055 (m), 2908 (s), 2935 (s), 2124 (vs), 1492 (s), 1452 (s), 1421 (s), 1372 (m), 1356 (m), 1304 (m), 1289 (m), 1213 (w), 1123 (w), 1067 (s), 1039 (m), 1005 (m), 1002 (m) cm⁻¹. LRMS (*m/z*+) = 160. Anal. Calcd for C₁₀H₁₂N₂: C, 74.97; H, 7.55; N, 17.48. Found: C, 74.85; H, 7.84; N, 17.35. [α]_D²⁵ = +25.8° (*c* = 2.436 g/dL, toluene).

***N*-Methyl-*N*-(α -phenylethyl)carbodiimide.** The same procedure for the preparation of (*R*)-(+)-*N*-methyl-*N*-(α -phenylethyl)carbodiimide was employed. The quantities of reagents used were 21.04 g of triphenylphosphine (80.23 mmol, 25% excess), 4.13 mL of bromine (12.8 g, 80.2 mmol, 25% excess), 250 + 50 mL of CH₂Cl₂, 22.5 mL of triethylamine (16.4 g, 162 mmol, 26% excess), 11.44 g of *N*-methyl-*N*-(α -phenylethyl)urea (64.19 mmol), and 350 + 50 mL of pentanes. Yield: 8.42 g (52.5 mmol, 82%). Bp: 75–78 °C (0.5 Torr). This compound displayed identical spectral characteristics to the enantiomerically pure (*R*)-(+)-*N*-methyl-*N*-(α -phenylethyl)carbodiimide.

***N,N*-Di-*n*-hexylcarbodiimide.** The same procedure for the preparation of (*R*)-(+)-*N*-methyl-*N*-(α -phenylethyl)carbodiimide was employed. The quantities of reagents used were 20.59 g of triphenylphosphine (78.49 mmol, 25% excess), 4.04

mL of bromine (12.5 g, 78.5 mmol, 25% excess), 250 + 50 mL of CH₂Cl₂, 22.1 mL of triethylamine (16.0 g, 158 mmol, 26% excess), 14.34 g of *N,N*-di-*n*-hexylurea (62.80 mmol), and 350 + 50 mL of pentanes. Yield: 9.17 g (43.6 mmol, 69%). Bp: 76–81 (0.2 Torr). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 0.82 (t, 6H, CH₃, *J* = 6.65 Hz), 1.23 (br m, 12H, CH₂CH₂CH₂), 1.50 (tt, 4H, CH₂CH₂N, *J*₁ = 7.29 Hz, *J*₂ = 6.79 Hz), 3.14 (t, 4H, CH₂N, *J* = 6.50 Hz). ¹³C{¹H} (100 MHz, CDCl₃): δ (ppm) 13.93, 22.51, 26.44, 31.23, 31.34, 41.06, 46.09, 144.40, 157.90. IR (neat): 2958 (s), 2932 (s), 2859 (s), 2131 (vs), 1467 (m), 1342 (m) cm⁻¹. LRMS (*m/z*+) = 210. Anal. Calcd for C₁₃H₂₆N₂: C, 74.23; H, 12.46; N, 13.32. Found: C, 74.40; H, 12.24; N, 13.38.

Polymerizations. Polymerizations were carried out at room temperature or 30 °C at a monomer/catalyst ratio of 100:1. Polymerizations were run either neat or in a toluene solution. Yields ranged from 70 to 100% depending on monomers and catalysts used as shown in Table 1. Reaction times ranged from 8 to 96 h depending on catalyst used.

Kinetic Studies. Kinetics of polymerization were studied with CuCl, CuCl₂, **I**, and **III** as initiators with monomer **2**. Data were best obtained by dilatometry¹¹ as polymerization with some of the copper initiators is relatively slow. The rate of reaction was followed by observing the gradual volume decrease as monomer converts to polymer at 30.0 °C.

Acknowledgment. We gratefully acknowledge support of this work from the NSF Materials Research Science & Engineering Center at the University of Massachusetts (NSF Chemistry Division) and Sekisui Chemical Co. Ltd.

References and Notes

- (1) Farris, R.; Allen, S. R.; Thomas, E. L. *J. Mater. Sci.* **1985**, *20*, 4583.
- (2) Farris, R.; Allen, S. R.; Thomas, E. L. *J. Mater. Sci.* **1985**, *20*, 2727.
- (3) Zachariades, A. E.; Porter, R. S., Eds. *The Strength and Stiffness of Polymers*; Marcel Dekker: New York, 1983.
- (4) Ciferri, A., Ed. *Liquid Crystallinity in Polymers*; VCH Publishers: New York, 1991.
- (5) Farina, M. *Top. Stereochem.* **1987**, *17*, 1–111.
- (6) Quirk, R. P.; Lee, B. *Polym. Int.* **1992**, *27*, 359.
- (7) Webster, O. W. *Science* **1991**, *251*, 887.
- (8) Flory, P. J. *J. Am. Chem. Soc.* **1940**, *62*, 1561.
- (9) Szwarc, M. *Nature* **1956**, *178*, 1168.
- (10) Szwarc, M.; Levy, M.; Milkovich, R. *J. Am. Chem. Soc.* **1956**, *78*, 2656.
- (11) Fetters, L. J. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overburger, C. G., Menges, G., Eds.; Wiley-Interscience: New York, 1987; Vol. 10; p 19.
- (12) Deming, T. J.; Novak, B. M. *Macromolecules* **1991**, *24*, 6043.
- (13) Deming, T. J.; Novak, B. M. *J. Am. Chem. Soc.* **1993**, *115*, 9101.
- (14) Patten, T. E.; Novak, B. M. *J. Am. Chem. Soc.* **1991**, *113*, 5065.
- (15) Patten, T. E.; Novak, B. M. *J. Am. Chem. Soc.* **1996**, *118*, 1906.
- (16) Goodwin, A. A. *Macromolecules* **1994**, *27*, 5520.
- (17) Brubaker, J. *Inorg. Nucl. Chem.* **1965**, *27*, 5962.
- (18) Maier, S.; Hiller, W.; Strahle, J. *Z. Naturforsch. B* **1988**, *43*, 1628.
- (19) Hey, E.; Ergezinger, C.; Dehnicke, K. *Z. Naturforsch. B* **1988**, *43*, 1679.
- (20) Odian, G. C. *Principles of Polymerization*, 2nd ed.; Wiley-Interscience: New York, 1981; p 192.
- (21) Bestmann, H. J.; Lienert, J.; Mott, L. *Liebigs Ann. Chem.* **1968**, *718*, 24.
- (22) Palomo, C.; Mestres, R. *Synthesis* **1981**, 373.

MA961750P