436 *Macromolecules* 1993, *26*, 436–439

Organotitanium(IV) Compounds as Catalysts for the Polymerization of Isocyanates: The Polymerization of Isocyanates with Functionalized Side Chains

Timothy E. Patten and Bruce M. Novak*[1]

Department of Chemistry, University of California at Berkeley,
and Center for Advanced Materials, Materials Science Division,
Lawrence Berkeley Laboratories, Berkeley, California 94720

Received August 5, 1992; Revised Manuscript Received October 9, 1992

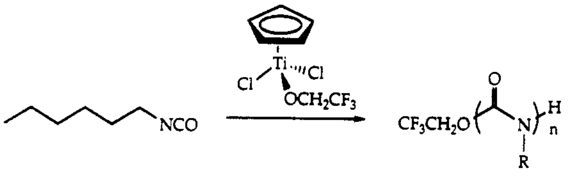
ABSTRACT: Catalysts of the form $CpTiCl_2X$, where X = $-OCH_2CF_3$, $-N(CH_3)_2$, or $-CH_3$ (IIa, IIb, IIc; Cp = η^5-cyclopentadienyl), $Cp^*TiCl_2OCH_2CF_3$ (III; Cp* = η^5-pentamethylcyclopentadienyl), and $Cp_2TiClOCH_2CF_3$ (IV) were used to polymerize a variety of isocyanates. Titanium–alkoxide, –amide, and –alkyl bonds were all found to be active in initiating the insertion of isocyanate monomer. An advantageous consequence of the lesser Lewis acidity of IIa–c relative to $TiCl_3OCH_2CF_3$ (I) is that the polymerization of highly functionalized monomers is possible using IIa–c and not I. 2-Isocyanatoethyl methacrylate (2IEM) was polymerized, using IIb, through the isocyanato group to a linear polymer; the resulting properties of this material were found to be quite different from what was reported by Graham et al.[12] 2IEM trimer was synthesized and subsequently cross-linked using a free-radical initiator, and it was found that the properties of this material matched those of the earlier report. The Diels–Alder adduct of 2IEM with cyclopentadiene, 2-((2-isocyanatoethoxy)carbonyl)-2-methylbicyclo[2.2.1]hept-5-ene (2IECMBH) was prepared and also polymerized using IIb. The use of cyclopentadienyltitanium trichloride derivatives also provides a general route through which a wide variety of end groups may be incorporated onto the end of the polyisocyanate chain.

Introduction

With the ongoing development of new well-controlled polymerization systems, chemists are beginning to look beyond the synthesis of conventional homo- and copolymers and toward the creation of synthetic macromolecules displaying higher order structures.[2] Such complex syntheses can be realized only with well-controlled polymerization techniques that display certain essential characteristics: The polymer produced displays a stable secondary structure. Monomers with high functional group density can be polymerized. The primary sequence of monomers along the backbone can be specified, and well-defined end groups can be placed on either end of the polymer chain. In our approach to this problem, we have focused our attention upon developing synthetic methods for polyisocyanates, since they maintain a helical conformation in solution for a very wide variety of side groups.[3] Recently, we reported the living polymerization of alkyl isocyanates catalyzed by $TiCl_3OCH_2CF_3$ (I);[4] those results prompted us to explore the effect of modifying the ligand sphere of the end group and the initiating ligand upon polymerization. We report here the polymerization of isocyanates with functionalized side chains. The catalysts used in this study were of the form $CpTiCl_2X$, where X = $-OR$, $-NR_2$, or $-CR_3$ (Cp = η^5-cyclopentadienyl), Cp^*TiCl_2OR (Cp* = η^5-pentamethylcyclopentadienyl), and $Cp_2TiClOR$. Polymerizations using $CpTiCl_2X$ were found to tolerate a wide variety of Lewis bases.

Results and Discussion

The series of compounds $CpTiCl_2X$ (where X = $-OCH_2CF_3$, $-N(CH_3)_2$, and $-CH_3$;[5], IIa, IIb, and IIc, respectively) were examined in order to identify active initiating ligands for these types of catalysts. Consistent with what has been reported in the literature,[6] titanium–alkoxide, –amide, and –alkyl bonds are active in initiating the insertion of isocyanate monomer: all three compounds showed identical activity in test polymerizations. Also, using purified oligomers of poly(*n*-hexyl isocyanate) prepared using IIa, we observed the trifluoroethoxy end group by ^{19}F NMR (δ −74.8 ppm) (eq 1). These compounds are easily prepared and isolated pure, so the use of derivatives synthesized from $CpTiCl_3$ provides a general route through which a wide variety of end groups may be incorporated onto the initiating end of the polyisocyanate chain. Also, experimental evidence indicates that the substitution of a chloride ligand with a Cp ligand (ie. I to IIa) does not affect the livingness of the titantium-based polymerizations of alkyl isocyanates.



(1)

^{19}F NMR: δ -74.8 ppm
(R = n-Hexyl)

We examined IIa, $Cp^*TiCl_2OCH_2CF_3$ (III), and $Cp_2TiClOCH_2CF_3$ (IV),[5] to determine how adding bulkier and more electron-donating ligands to the coordination sphere of the active titanium propagating center would affect the character of the polymerization. It is known that substitution of a chloride ligand with a Cp ligand decreases the Lewis acidity of a titanium complex relative to its parent compound. For example, $CpTiCl_3$ will not form stable complexes with monodentate Lewis bases,[7] whereas countless 1:2 Lewis acid/base complexes of $TiCl_4$ have been reported.[8] Also, the addition of Cp and Cp* to the end group adds increasing steric bulk at the metal center. Correspondingly, we found a decrease in the observed initial rate of the polymerization when polymerizations were conducted using catalysts I, IIa, and III, respectively (Table I). An advantageous consequence of the lesser Lewis acidity of IIa–c relative to I is that the polymerization of highly functionalized monomers is possible using IIa–c and not I. To illustrate this point, we report the first polymerization of 2-isocyanatoethyl methacrylate (2IEM) through the isocyanato group to a linear polymer (eq 2).

All attempts at polymerizing 2IEM using I failed to yield significant amounts of linear polymer; however, with

0024-9297/93/2226-0436$04.00/0 © 1993 American Chemical Society

Table I
Observed Initial Rates of Polymerization[a]

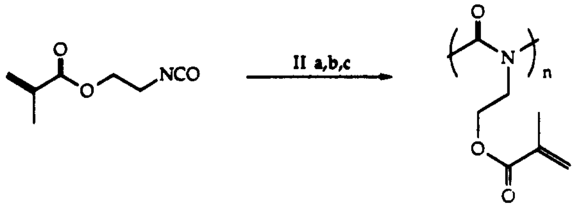
catalyst	10^2[catalyst]$_0$ (M)	[monomer]$_0$ (M)	k_{obs} (M s^{-1})
I	5.0	3.4	$1.8(5) \times 10^{-3}$
IIa	5.0	3.4	$8.0(5) \times 10^{-5}$
III	5.0	3.4	$9.5(5) \times 10^{-6}$
IV			

[a] Monomer = *n*-hexyl isocyanate; solvent = toluene. The rate was monitored for up to 50% completion of the polymerization. Note: polymerizations using IV were much too slow for the measurement of the rate of polymerization.

Table II
Yield and Molecular Weight Data from Polymerizations of *n*-Hexyl Isocyanate in the Presence of Added Lewis Bases[a]

lewis base	mon/in. ratio	yield (%)	M_n (GPC)	PDI
none	39	87	5700	1.22
ethyl trifluoroacetate	35	71	4600	1.22
THF	56	72	6700	1.40
methyl methacrylate	42	79	6200	1.27
acetonitrile	33	72	5400	1.29

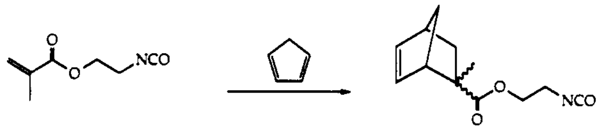
[a] Conditions: 0.250 mL of *n*-hexyl isocyanate, 1 equiv of Lewis base per monomer, 24-h reaction time, no solvent.



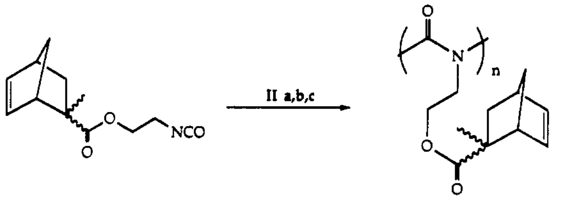
(2)

Poly(2IEM)

IIb, 2IEM was polymerized in bulk to yields of 91%. GPC (gel permeation chromatography) analysis[9] of all poly(2IEM) samples showed bimodal distributions of molecular weights (the elution volumes of both peaks were well before that of an independently synthesized sample of trimer). We conducted several polymerizations using 1 equiv of highly purified methyl methacrylate per equivalent of *n*-hexyl isocyanate (a 2IEM "substitute") as controls; we reasoned that this should determine whether the bimodal distribution arose from difficulty in purifying/drying the monomer or from a side reaction involving the methacrylate side group. The polymers isolated from these polymerizations consistently had narrow monomodal molecular weight distributions. Repeated distillation of 2IEM from CaH_2 (no impurities were detectable by NMR or IR spectroscopy each time) reduced the size of the lower of the two molecular weight peaks but did not eliminate it; therefore it appears that undetectable amounts of water/impurity in the monomer are sufficient to cause this bimodal molecular weight distribution. We also observe this behavior when using solvents which have not been rigorously dried. The tolerance of these polymerizations to added Lewis bases appears to be quite general. Polymerizations of *n*-hexyl isocyanate similar to the 2IEM control polymerization were conducted using ethyl trifluoroacetate, ethyl acetate, methyl methacrylate, acetonitrile, or THF (1 equiv of solvent/1 equiv of monomer), and only narrow monomodal distributions of molecular weights were observed (Table II). When polymerizations of *n*-hexyl isocyanate containing 1.5 M ethyl acetate or THF as the solvent were monitored by IR spectroscopy, no experimentally significant decrease in the observed rate of propagation was found. These results are significant in light of the fact that polymerizations using I will not proceed or will proceed only to low yields in the presence of Lewis bases, and also these results suggest that the polymerization of an even wider variety of functionalized isocyanates than those discussed here is possible using IIa–c.



(3.1)



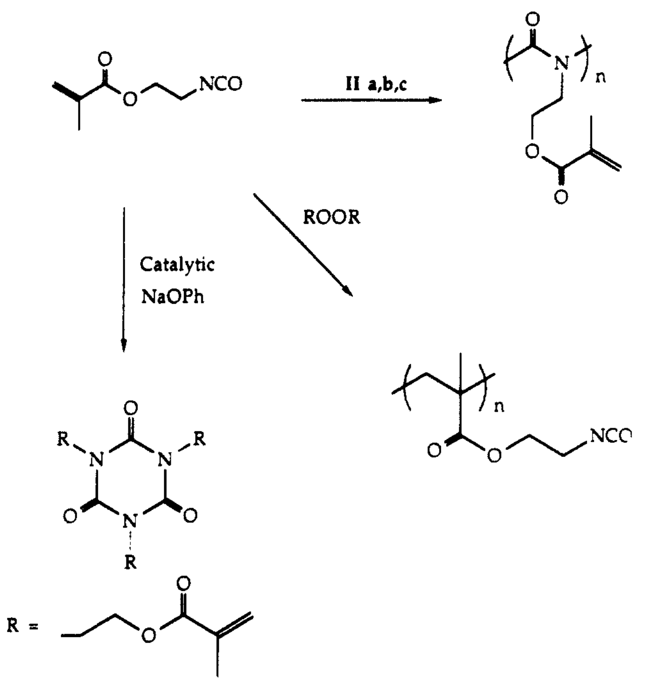
(3.2)

Poly(2IECMBH)

We also prepared the Diels–Alder adduct of 2IEM with cyclopentadiene, 2-((2-isocyanatoethoxy)carbonyl)-2-methylbicyclo[2.2.1]hept-5-ene (2IECMBH),[10] to increase the steric bulk next to the ester group (eq 3.1). The polymerization of 2IECMBH proceeded to high (~95% after workup) yields, and monomodal distributions of molecular weights were observed (eq 3.2). The presence of olefin groups in the side chain of the monomer also has no effect upon the polymerization, since IIa (and even I) will polymerize allyl isocyanate rapidly and to high yields. GPC traces of samples of poly(allyl isocyanate) showed monomodal and narrow distributions of molecular weights. Polymerizations using I and IIa are well-behaved and offer control over the molecular weight of the polymer formed; thus by conducting polymerizations with low monomer to initiator ratios, we have found that, in contrast to what Shashoua and Sweeney reported originally,[11] poly(allyl isocyanate) is actually soluble in chloroform and methylene chloride at low molecular weights (up to ~10^6 by GPC). Finally, ^{13}C{^{1}H} NMR spectra of poly(2IEM), poly(2IECMBH), and poly(allyl isocyanate) showed no extraneous methylene or methyne carbons that would indicate cross-linking or side reactions of the olefin groups.

There has been a previous report of a synthesis of poly(2IEM);[12] however, we note significant differences between the reported material's properties and the poly(2IEM) reported here. Poly(2IEM), in fact, is very soluble in chloroform and methylene chloride at all molecular weights we have prepared (up to ~10^6 by GPC). A thermal gravimetric analysis (TGA) trace of poly(2IEM) showed a decomposition onset within the characteristic range (170–200 °C) for polyisocyanates.[13] Considering that Graham et al. synthesized their material using refluxing hexane solvent, well above the measured ceiling temperature for isocyanate polymerizations (ca. 40 °C[4]), and that their catalyst system forms trimer in quantitative yield at room temperature, we believe that the material they characterized was a soluble fraction of cross-linked trimer. We therefore synthesized a sample of cross-linked 2IEM trimer by treating 2IEM with catalytic sodium phenoxide in THF to form the trimer and then treating the trimer with benzoyl peroxide in benzene at 90 °C. The cross-linked 2IEM trimer exhibited solubility, IR, and thermal properties identical with those of Graham's material.[14] ^{13}C{^{1}H} NMR was the most useful tool in differentiating between products: the signal for the carbonyl of the polymer backbone in polyisocyanates with aliphatic-like side chains is found at ~156 ppm ($CDCl_3$), whereas that for the trimer is found at ~149 ppm ($CDCl_3$). In general, 2IEM is a versatile bifunctional monomer, since several potentially useful materials can be synthesized from this compound: Polymerization exclusively through the iso-

Scheme I
Transformations of 2-Isocyanatoethyl Methacrylate



cyanato group can be accomplished using IIa–c. The trimer of 2IEM can be made using catalytic sodium phenoxide at room temperature,[15] and polymerization exclusively through the methacrylate group can be achieved using a free-radical initiator.[16]

Summary

We have shown that derivatives synthesized from CpTiCl$_3$ are very useful catalysts for the polymerization of isocyanates. They will polymerize monomers possessing a very high degree of functionality, such as 2IEM and 2IECMBH, and the wide variety of easily prepared organometallic derivatives of this type allows for the incorporation of many different types of end groups onto the initiating end of the polymer chain. These polymerizations are also tolerant toward the addition of Lewis bases, so a wide variety of well-defined polyisocyanates with interesting side chain and end group structures can be synthesized via this route.

Experimental Section

Methods and Materials. All syntheses and polymerizations were performed under argon or nitrogen atmospheres using Schlenk techniques or a Vacuum Atmospheres HE533 Dri Lab with attached HE493 Dri Train. Solvents were purified as follows: toluene, benzene, and tetrahydrofuran (THF) were distilled from Na/benzophenone; isocyanate monomers were distilled from CaH$_2$ and stored under an argon atmosphere; CH$_2$Cl$_2$, ethyl acetate, acetonitrile, and ethyl trifluoroacetate were distilled from CaH$_2$. Methyl methacrylate was distilled from CaH$_2$ and stored in a darkened container at −40 °C.

Gel permeation chromatography (GPC) was performed using a Hewlett/Packard 1050 series liquid chromatograph pump equipped with a HP Model 1047 refractive index detector and a HP Model 3396A integrator. Separations were effected by 10^5-, 10^4-, 10^3-, and 500-Å Waters Ultrastyragel columns, and molecular weights were calibrated relative to polystyrene standards (Scientific Polymer Products, Inc.). The mobile phase was CHCl$_3$, and the flow rate, 1 mL min^{-1}. ^{1}H, ^{13}C{^{1}H}, and ^{19}F{^{1}H} NMR spectra were determined at 400, 100, and 376 MHz, respectively, using a Bruker AM-400 FT spectrometer. Infrared spectra were determined using a Perkin-Elmer 1600 series FTIR. Thermal gravimetric analysis (TGA) was performed using a Perkin-Elmer PC Series TGA7: scanning rate = 20 °C min^{-1}, atmosphere = nitrogen. Melting points were determined using an Electrothermal capillary melting point apparatus and are uncorrected. Elemental analyses were performed by the Microanalytical Laboratory operated by the College of Chemistry, University of California, Berkeley, CA.

Poly[((2-(methacryloyloxy)ethyl)imino)carbonyl]. To a 25-mL Schlenk flask containing IIb (9.3 mg, 4.08 × 10^{-2} mmol) was added 0.250 mL (1.74 mmol) of 2IEM via syringe, and the catalyst dissolved to form an orange solution. (Note: 2IEM with inhibitor removed should be stored in the dark and at low temperatures. Cross-linking of the methacrylate side chains renders this polymer insoluble.) The Schlenk tube was covered with aluminum foil, and after approximately 1 h the polymerization solution had solidified. The polymerization was left for 24 h after which 5 mL of CH$_3$OH was added to terminate the active end groups. The mixture was filtered, and the polymer was washed with 20 mL of CH$_3$OH. Solvents were removed in vacuo. The polymer was reprecipitated from 10 mL of CHCl$_3$ with 50 mL of CH$_3$OH and isolated as described above, yielding 0.247 g (91%) of a white solid: ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 6.10–6.05 (broad, 1 H), 5.62–5.59 (broad, 1 H), 4.8–3.4 (overlapping group of broad signals, 4 H), 1.89 (broad, 3 H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ (ppm) 166.59, 155.34, 135.83, 126.15, 61.65, 47.27, 18.28; IR (thin film): 1719 (s, ν(C═O) methacrylate), 1701 (s, ν(C═O) polymer backbone), 1636 (m, ν(C═C)) cm^{-1}; TGA (onset temperatures) 190 °C (22% wt loss), 335 °C (remainder). Anal. Calcd for C$_7$H$_9$NO$_3$: C, 54.17; H, 5.85; N, 9.03. Found: C, 54.17; H, 6.05; N, 8.76.

Poly[1-((2-isocyanatoethoxy)carbonyl)-1-methylethylene]. Via syringe, 2IEM (1.00 mL, 6.96 mmol) was added to a stirred solution of 51.0 mg (0.211 mmol) of benzoyl peroxide in 10 mL of benzene. The polymerization was stirred and heated at 90 °C for 4 h and then allowed to cool. The solution was poured into 100 mL of petroleum ether, and a white precipitate formed which was filtered and washed with 50 mL of petroleum ether. Removal of solvent in vacuo afforded 0.886 g (82%) of a white powder: ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 4.10 (br, 2 H), 3.56 (br, 2 H), 2.10–1.4 (set of br signals, 2 H), 1.2–0.8 (set of br signals, 3 H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ (ppm) 177.0, 176.0, 128.28, 124.21, 64.04, 45.08, 44.91, 41.83, 41.73, 34.06, 22.27, 18.90, 17.18, 13.98; IR (thin film) 2275 (s, ν(NCO)), 1731 (s, ν(C═O)) cm^{-1}; TGA decomposition occurred steadily from 100 to 500 °C (95% wt loss). Anal. Calcd for C$_7$H$_9$NO$_3$: C, 54.17; H, 5.85; N, 9.03. Found: C, 54.48; H, 5.77; N, 8.68.

2-Isocyanatoethyl Methacrylate Trimer. Via syringe, 2IEM (1.00 mL, 6.96 mmol) was added to a stirred solution of NaOPh (6.1 mg, 5.3 × 10^{-2} mmol) in 5 mL of THF. The solution was stirred overnight and subsequently poured into 100 mL of petroleum ether. A cloudy suspension formed which was removed by filtration through a 0.2-μm Nylon filter, yielding 0.158 g (15%) of a white solid. Most of this material would not dissolve in CHCl$_3$; a ^{1}H NMR spectrum (CDCl$_3$) of an extraction showed that the soluble material was 2IEM trimer. The insoluble material shows properties identical with those of the cross-linked trimer. The petroleum ether filtrate was cooled to 0 °C, and colorless crystals formed. These were collected, and residual solvents were removed in vacuo. Yield: 0.612 g (57%) of colorless crystals. Mp: 82–84 °C (lit.:[15] 83–85 °C). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 6.05 (s, 1 H), 5.54 (s, 1 H), 4.34 (t, 2 H, J = 5.3 Hz), 4.21 (t, 2 H, J = 5.2 Hz), 1.88 (s, 3 H) [lit.[15] (CDCl$_3$ and acetone-d_6): 6.07, 5.56, 4.35, 4.23, 1.90]. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ (ppm) 167.10, 148.83, 135.81, 126.17, 61.23, 41.86, 18.17 [lit.[15] (acetone-d_6): 167.17, 148.90, 135.90, 126.14, 61.29, 41.93, 18.20]. IR (thin film): 1718 (s, ν(C═O) methacrylate), 1696 (s, ν(C═O) ring), 1637 (m, ν(C═C)) cm^{-1} (lit.:[15] 1720, 1693, 1638). TGA (onset temperature): 380 °C (90% wt loss) (lit.:[15] 250 °C). Anal. Calcd for C$_{21}$H$_{27}$N$_3$O$_9$: C, 54.17; H, 5.85; N, 9.03. Found: C, 54.23; H, 5.69; N, 8.68.

Cross-Linking of 2-Isocyanatoethyl Methacrylate Trimer. 2IEM trimer (0.206 g) and benzoyl peroxide (55.0 mg) were dissolved in 10 mL of benzene. The solution was stirred and heated at 90 °C for 4 h under an argon atmosphere. After an initial 15 min of heating a white solid began to precipitate from solution. After 4 h the solution was cooled and filtered. The white product was washed with a large amount of hexane to remove unreacted trimer and then dried in vacuo. Yield: 0.162

g (79%) of a white solid which was insoluble in chloroform. Like the material Graham reported,[12] this solid had a limited solubility in phenol. An IR spectrum of this product (KBr pellet) showed a band at 1636 cm^{-1}, indicating that some methacrylate groups remained unreacted. A TGA trace of the solid showed an onset decomposition temperature at 260 °C (89% wt loss), similar to Graham's material.

2-((2-Isocyanatoethoxy)carbonyl)-2-methylbicyclo[2.2.1]hept-5-ene (2IECMBH). In a 100-mL round-bottom flask 5.00 mL (34.8 mmol) of 2IEM, 20.0 mL (0.298 mol) of freshly cracked cyclopentadiene, and 5.0 mg (2.3×10^{-2} mmol) of 2,6-di-*tert*-butyl-*p*-cresol were stirred. The reaction was monitored by ^{1}H NMR and after 10 days it was judged to be at >70% completion. Cyclopentadiene was removed from the reaction by distillation of the mixture at reduced pressure (T = 35 °C). Afterward the heat applied to the distillation was increased and the product fraction was collected at 63–64 °C and 0.01 Torr, yielding 5.35 g (69%) of a colorless liquid: ^{1}H NMR-selected resonances (400 MHz, CDCl$_3$) δ (ppm) 6.20, 6.13, 6.06, and 6.02 (olefin protons, 2 H, endo/exo), 3.03 and 2.81 (bridgehead protons, 2 H), 1.43, and 1.11 (methyl protons, 3 H, endo/exo); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ (ppm) 178.36, 177.01, 138.64, 138.03, 134.98, 133.35, 63.49, 63.19, 50.86, 50.32, 50.02, 49.59, 48.92, 46.83, 42.76, 42.51, 42.18, 37.76, 37.52, 30.21, 26.22, 24.07; IR (neat liquid) 2270 (s, ν(NCO)), 2229 (sh), 1730 (s, ν(C=O)) cm^{-1}; Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83; N, 6.33. Found: C, 65.14; H, 7.09; N, 6.42.

Poly[((2-(((2-methylbicyclo[2.2.1]hept-5-en-2-yl)carbonyl)oxy)ethyl)imino)carbonyl]. To a 25-mL Schlenk flask containing $CpTiCl_2N(CH_2CH_3)_2$ (9.4 mg, 3.7×10^{-2} mmol) dissolved in toluene (0.250 mL) was added 1.00 mL (1.12 g, 5.06 mmol) of 2IECMBH via syringe. The polymerization was stirred for 24 h after which the polymerization mixture was a clear orange solid. CH_3OH (10 mL) was added to terminate the active end groups. The mixture was filtered, and the polymer was washed with 20 mL of CH_3OH. Solvents were removed in vacuo. The polymer was reprecipitated from 10 mL of $CHCl_3$ with 50 mL of CH_3OH and isolated as described above; this purification procedure was repeated once more, yielding 1.04 g (93%) of a white solid: ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 6.21, 6.06, and 5.90 (olefin protons, broad, 2 H, endo/exo), 3.10–2.60 (bridgehead protons, several broad signals, 2 H), 1.57 and 1.05 (methyl protons, broad, 3 H, endo/exo); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ (ppm) 178.1, 156 (br signal), 138.9, 133.2, 62 (br signal), 50.91 and 50.21, 48.96, 46.76, 42.79 and 42.70, 37.57 and 37.20, 26.11 and 25.82, 24.02 (due to broadening, not all of the signals could be resolved into endo/exo signals.); IR (thin film) 1727 (s, ν(C=O) side group), 1703 (s, ν(C=O) polymer backbone) cm^{-1}; TGA (onset temperatures) 180 °C (60% wt loss), 370 °C (remainder). Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83; N, 6.33. Found: C, 64.19; H, 6.89; N, 6.26.

Poly[(2-propenylimino)carbonyl]. To a 25-mL Schlenk flask containing IIa (15.7 mg, 5.55×10^{-2} mmol) dissolved in toluene (0.050 mL) was added 0.500 mL (5.66 mmol) of allyl isocyanate via syringe. The polymerization was stirred for 24 h after which the polymerization mixture was an orange solid. CH_3OH (10 mL) was added to terminate the active end groups. The mixture was filtered and the polymer was washed with 20 mL of CH_3OH. Solvents were removed in vacuo. The polymer was reprecipitated from 10 mL of $CHCl_3$ with 50 mL of CH_3OH and isolated as described above, yielding 0.393 g (84%) of a white solid: ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 5.8–5.7 (broad, 1 H), 5.25, 5.21, 5.15, and 5.12 (broad signals, 2 H), 4.30–4.17 (very broad, 2 H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ (ppm) 148.45, 130.86, 119.04, 44.94; IR (thin film) 1705 (s, ν C=O), 1647 (sh, ν C=C) cm^{-1}; TGA (onset temperature) 170 °C (79% wt loss). Anal. Calcd for C_4H_5NO: C, 57.82; H, 6.07; N, 16.86. Found: C, 57.53; H, 6.02; N, 16.67.

Kinetic Measurements. Kinetic analysis of polymerizations was performed by diluting timed samples of a polymerization (thermostated at 25.0 ± 0.2 °C) 80 to 1 using HPLC grade chloroform and then determining the percent transmittance of these solutions at 2271 cm^{-1} via FTIR spectroscopy. Experiments showed that the effect of depolymerization by active catalyst end groups upon monomer concentration was negligible for up to 1 h after the dilution was performed. Concentrations of the monomer were determined using a Beer's law plot. The initial rate of the polymerization was determined by a linear fit of the data (concentration vs time) for the initial (~50% conversion) part of the polymerization.

Acknowledgment. This work was supported by the following sources: UC Berkeley, U.S. National Science Foundation Presidential Young Investigator Program, Alfred P. Sloan Foundation, and generous contributions from E.I. du Pont de Nemours and Co., Exxon, Amoco, and Chevron. T.E.P. gratefully acknowledges the U.S. Department of Defense for a NDSEG Fellowship. We also acknowledge the Waymouth group at Stanford University for the use of their TGA equipment, Anne-Lise Mogstad for help in acquiring the TGA data, and Dow Chemicals for their generous gift of 2IEM.

References and Notes

(1) NSF Presidental Young Investigator 1991–1996; Alfred P. Sloan Foundation Fellow 1991–1993.

(2) (a) Green, M. M.; Ringsdorf, H.; Wagner, J.; Wustfeld, R. *Angew. Chem., Int. Ed. Eng.* 1990, *29*, 1478. (b) Percec, V.; Heck, J.; Ungar, G. *Macromolecules* 1991, *24*, 4957. (c) Percec, V.; Heck, J.; Ungar, G. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1992, *33* (1), 152. (d) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A. *Angew. Chem., Int. Ed. Eng.* 1990, *29*, 138. (e) Hawker, C. J.; Frechet, J. M. J. *J. Chem. Soc., Chem. Commun.* 1990, 1010. (f) Hawker, C. J.; Frechet, J. M. J. *J. Am. Chem. Soc.* 1990, *112*, 7638. (g) Ashton, P. R.; Douglas, P.; Spencer, N.; Stoddart, J. F. *Makromol. Chem., Macromol. Symp.* 1992, *54/55*, 441 and references therein.

(3) For examples see: (a) Goodman, M.; Chen. S. *Macromolecules* 1971, *4*, 625. (b) Green, M. M.; Reidy, M. P.; Johnson, R. J.; Darling, G.; O'Leary, D. J.; Wilson, G. *J. Am. Chem. Soc.* 1989, *111*, 6452.

(4) Patten, T. E.; Novak, B. M. *J. Am. Chem. Soc.* 1991, *113*, 5065.

(5) Patten, T. E.; Hoff, S. M.; Novak, B. M. Manuscript in preparation. Experimental material included for review with the submission of this article.

(6) (a) Meth-Cohn, O.; Thorpe, D.; Twitchett, H. J. *J. Chem. Soc. C* 1970, 132. (b) Chandra, G.; Lappert, M. F. *Inorg. Nucl. Chem. Lett.* 1965, *1*, 83. (c) Chandra, G.; Jenkins, A. D.; Lappert, M. F.; Srivastava, R. C. *J. Chem. Soc. A* 1970, 2550. (d) Clark, R. J. H.; Stockwell, J. A.; Wilkins, J. D. *J. Chem. Soc., Dalton Trans.* 1976, 120.

(7) See ref 6d.

(8) The number of such complexes is too great to be covered here. For an introduction into this area see: Feld, R.; Cowe, P. L. *The Organic Chemistry of Titanium*; Butterworths: Washington, DC, 1965; pp 114–128.

(9) Note: It has been shown that GPC is not a useful tool for the determination of absolute molecular weights of rigid polymers. However, it is the only molecular weight characterization technique that gives information (and it is a valid tool in this respect for polyisocyanates) on the relative distribution of molecular weights within a polymer sample. Since K and α have not been determined for the polymers discussed in this paper (except poly(n-hexyl isocyanate)), we must rely on GPC for molecular weight information with the caveat that MWs and PDIs are higher than the true values. See: Dubin, P. L.; Principi, J. M. *Macromolecules* 1989, *22*, 1891.

(10) von Brachel, H.; Bayer, O. U.S. Pat. 3 222 387, 1965.

(11) (a) Shashoua, V. E. *J. Am. Chem. Soc.* 1959, *81*, 3156. (b) Shashoua, V. E.; Sweeney, W.; Tietz, R. *J. Am. Chem. Soc.* 1960, *82*, 866.

(12) Graham, J. C.; Xu, X.; Jones, L.; Orticochea, M. *J. Polym. Sci., Part A: Polym. Chem.* 1990, *28*, 1179.

(13) (a) Aharoni, S. M. *J. Polym. Sci., Polym. Phys. Ed.* 1980, *18*, 1303. (b) Durairaj, B.; Dimcock, A. W.; Samulski, E. T.; Shaw, M. T. *J. Polym. Sci., Part A: Polym. Chem.* 1989, *27*, 3211.

(14) Properties of the material reported in ref 12: Slightly soluble in phenol, insoluble in $CHCl_3$; ^{1}H NMR (phenol-d_6) δ 6.09, 5.39, 4.30, 4.07, 1.81; ^{13}C{^{1}H} NMR (phenol-d_6) δ 154? (obscured by solvent signal), 149.20, 135.49, 127.22, 62.06, 42.17, 17.70; IR 1725, 1703, 1638 cm^{-1}; TGA T_d = 250 °C.

(15) See also: Graham, J. C.; Xu, X.; Orticochea, M. *Catal. Lett.* 1989, *3*, 413.

(16) Francis, C. V.; Heilmann, S. M.; Krepski, L. R.; Rasmussen, J. K. U.S. Pat. 4 952 640, 1990.