Organotitanium(IV)-Catalyzed Cyclopolymerizations of 1,2-Diisocyanates and Cyclocopolymerizations of Monoisocyanates with 1,2-Diisocyanates

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ABSTRACT: 1,2-Diisocyanates were cyclopolymerized using $CpTiCl_2N(CH_3)_2$. Treatment of 1,2-diisocyanatodecane with $CpTiCl_2N(CH_3)_2$ in THF effected its cyclopolymerization with stoichiometric control over molecular weight and with M_w/M_n ranging from 1.2 to 1.8. IR, ^1H NMR, and ^{13}C NMR spectra of the resulting polymers indicate that the monomer underwent complete cyclization. Studies of the solution properties of poly(1,2-diisocyanatodecane) showed that it maintains a smaller hydrodynamic volume than poly(*n*-hexyl isocyanate) at equivalent molecular weights. Living poly(*n*-hexyl isocyanate) was end-capped with blocks of poly(1,2-diisocyanatopropane) and poly(1,2-diisocyanatodecane). TGA and DSC studies of these block copolymers showed that the individual block segments decomposed at the same temperatures as their respective homopolymers. Random copolymerizations of *n*-hexyl isocyanate with 1,2-diisocyanatopropane and 1,2-diisocyanatodecane were conducted. TGA studies of these macromolecules showed that the decomposition temperature of the copolymer was a function of its 1,2-diisocyanate content, and the incorporation of a relatively high mole percent of the diisocyanate monomer was necessary to observe an increase in the decomposition onset of the copolymer.

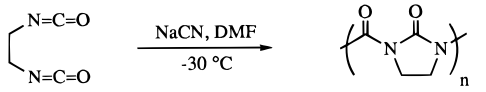
Introduction

In 1949, Butler and Bunch[3] reported the free-radical polymerization of diallyldiethylammonium bromide. The resulting polymeric material contained no unreacted double-bonds, yet it was soluble in water. This observation was unexpected, because it was generally assumed that the polymerization of polyfunctional monomers would yield insoluble cross-linked materials. Later,[4] this observation was explained by proposing the ring-forming polymerization mechanism currently known as cyclopolymerization.

Cyclopolymerizations are synthetically useful reactions, because they convert an acyclic monomer into a polymer containing monocyclic or polycyclic ring systems. These cyclic structures can impart a variety of properties upon the resulting polymer which differ greatly from those of its parent acyclic polymer: increased chain stiffness, increased thermal stability, stronger interchain interactions, and distinct chemical or biological properties.[5] Cyclopolymers are used commercially in wastewater treatment, in ion exchange processes (the “Sirotherm Process”), in resist technologies, as components of elastomers, and as paper and textile additives.[5]

The first example of a cyclopolymerization using diisocyanates was reported by Miller and Black in 1962.[6] In this work, 1,3-diisocyanatopropane was polymerized using sodium cyanide initiator in dimethylformamide solvent at −30 °C, and an oligomeric material soluble only in strong acids was obtained. This reaction was also the first example of a cyclopolymerization involving hetero double-bonds.

In 1964, Beaman[7] and King[8] reported the anionic polymerization of 1,2-diisocyanato derivatives of ethane, propane, and cyclohexane to produce soluble, linear polymers. Both authors found that the polymerization of 1,3-diisocyanates yielded insoluble polymers, which they attributed to the inability of such monomers to undergo exclusive cyclopolymerization. On the basis of IR spectra, they also concluded that 1,2-diisocyanates cyclopolymerize via alternating intermolecular/intramolecular carbon−nitrogen double-bond additions to yield a carbonyl-2-imidazolidone repeat unit structure (eq 1).



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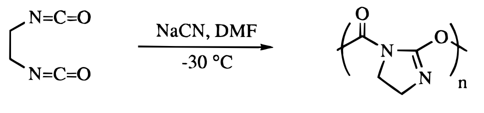
Diisocyanates with secondary centers, such as 1,2-diisocyanatopropane and *cis*-1,2-diisocyanatocyclohexane, also were found to cyclopolymerize readily under anionic conditions despite the fact that secondary monoisocyanates, such as isopropyl isocyanate and cyclohexyl isocyanate, do not homopolymerize.[9] Iwakura *et al.*[10] investigated the polymerization of a series of α,ω-diisocyanates and concluded from aminolysis reactions that 1,2-diisocyanates polymerize exclusively via alternating carbon−nitrogen/carbon−oxygen double-bond additions (not carbon−nitrogen/carbon−nitrogen double-bond additions) to yield a carbonylethyleneisourea repeat unit structure (eq 2). To date, no convincing case has been made for either regiochemistry of polymerization.



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In subsequent studies, several other diisocyanates were shown to undergo anionic cyclopolymerization: *cis*-1,3-diisocyanatocyclohexane,[11] *cis*-1,2-diisocyanatocyclopropane,[12] and both *cis*- and *trans*-1,3,5-triisocyanatocyclohexane (in these triisocyanates, only two of the three isocyanate units participate in the polymerization).[13] Multiisocyanates that have been cyclopolymerized include 1,2,3-triisocyanato derivatives[7,8] and poly(1-isocyanatoethylene), which yielded a ladder polymer.[14]

Our interest in the polymerization of 1,2-diisocyanates was twofold. First, we wanted to extend the living

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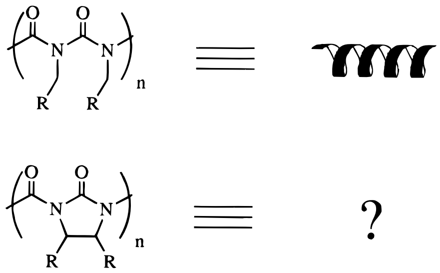
Scheme 1



organotitanium(IV) polymerization methodology developed for monoisocyanates to diisocyanates.[15] As seen in the organotitanium(IV)-catalyzed polymerization of monoisocyanates, the use of a living polymerization provided strict control over the polymer's molecular weight and polydispersity[15] and allowed for the design and synthesis of well-defined, architecturally interesting macromolecules not obtainable using the equivalent anionic procedure.[16]

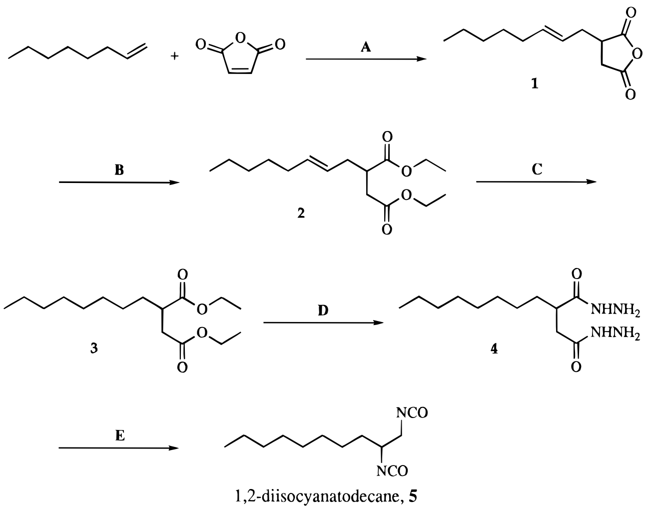
Second, we wanted to investigate the structure and properties of diisocyanate cyclopolymers, because little is actually known about these macromolecules. As mentioned above, the exact microstructure of these polymers has not been established, and no characterization of the polymers' conformational properties has been reported. In particular, we wanted to compare and contrast the solution properties of poly(monoisocyanate)s and poly(diisocyanate)s and to determine the impact of tethering together the side chains of two adjacent repeat units upon the conformational behavior of an isocyanate polymer backbone (Scheme 1).

Results and Discussion

1,2-Diisocyanate Monomer Synthesis. An inherent problem in studying diisocyanate cyclopolymers is their relative insolubility: they are either completely insoluble or only soluble in strong acids (sulfuric acid, phenols) and highly polar, deliquescent solvents (DMSO, DMF). Such solvents preclude the use of the reactive organotitanium(IV) catalysts, so it was necessary to design and synthesize diisocyanate cyclopolymers that were soluble in a wider range of organic solvents. A widely used strategy for increasing the solubility of a polymer in organic solvents is to attach long alkyl side chains to each repeat unit.[17] Poly(1,2-diisocyanatoethane) (P12DIE), as literature reports indicate[8] and our experience confirms, is an insoluble polymer. The simple addition of one methyl group to each repeat unit, as in poly(1,2-diisocyanatopropane) (P12DIP), dramatically increases the solubility of the polymer: P12DIP dissolves in dimethyl sulfoxide. Thus, further lengthening of this alkyl chain to six or more carbon units should render the polymer backbone soluble in even less polar organic solvents.

Our primary target monomer for these studies was 1,2-diisocyanatodecane, which would cyclopolymerize to yield a polymer with pendant *n*-octyl side chains. Because this compound and most aliphatic 1,2-diisocyanates are not commercially available, we devised a synthetic procedure for obtaining this class of compounds.

Scheme 2. Synthetic Sequence for 1,2-Diisocyanatodecane[a]



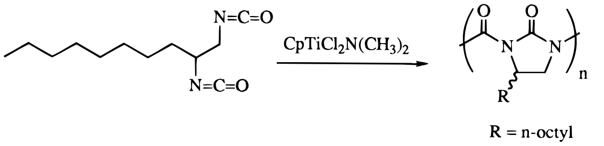
[a] (A) 160 °C, 7 days, 62% yield; (B) EtOH/cat. TsOH, Δ, 93% yield; (C) Pd/C, 60 psi H_2, 98% yield; (D) $N_2H_4 \cdot H_2O/H_2O/EtOH$, Δ, 95% yield; (E) (1) $NaNO_2/HCl$, H_2O/C_6H_6, 5 °C, (2) Δ, C_6H_6, 55% yield.

As shown in Scheme 2, 1,2-diisocyanatodecane was obtained in 30% overall yield, based on maleic anhydride starting material, in five steps. The thermal ene reaction of 1-octene and maleic anhydride yielded anhydride **1**, which contains the ten-carbon-atom backbone of the target molecule and a 1,2-dicarbonyl functionality that could be transformed into a diisocyanate. Anhydride **1** was converted to the diethyl ester, **2**, via esterification in absolute ethanol with a catalytic amount of *p*-toluenesulfonic acid monohydrate. The carbon–carbon double bond in diethyl ester **2** was then hydrogenated using palladium on activated carbon catalyst to yield the saturated diester, **3**. This step was necessary because olefins are not inert to nitrous acid, which was used in the last step of the synthesis. Conversion of both isomers of **2** to a saturated compound also greatly simplified the analysis of its NMR spectra and the assessment of the product's purity. Diethyl ester **3** was then converted into dihydrazide **4** by heating at reflux in an ethanol/water solution of hydrazine hydrate. Finally, dihydrazide **4** was converted into 1,2-diisocyanatodecane, **5**, using a modification of a two-step literature procedure.[8] First, the dihydrazide was oxidized to the corresponding diacyl azide using nitrous acid generated *in situ* at 5 °C, and then a benzene solution of this intermediate compound was heated at reflux to decompose the acyl azides. Careful isolation and distillation afforded monomer **5** as a clear, colorless, high-boiling liquid.

The materials required for this synthesis are readily available, inexpensive, and relatively nonhazardous, and the synthesis consists of simple reactions that give high yields. Consequently, this synthetic route provides rapid access to multigram quantities of monomer **5**. Also, this route provides access to a wide variety of derivatives simply by changing one or two of the starting materials instead of by developing a new synthesis for each new monomer. Other diisocyanate monomers that we have synthesized using this scheme, in part, include 1,2-diisocyanatoethane (starting material: dimethyl succinate), 1,2 diisocyanatopropane (starting material: diethyl methylsuccinate), *cis*-1,2-diisocyanatocyclohexane (starting material: *cis*-1,2-cyclohexanedicarboxylic anhydride), and 1,3-diisocyanatopropane (starting material: diethyl glutarate).

Polymerizations of 1,2-Diisocyanates. Addition of 1,2-diisocyanatodecane to a solution of $CpTiCl_2N(CH_3)_2$, **6**, in THF gave an orange solution. After 24 h the viscosity of the solution had increased notably, and excellent yields of polymer (85–95%) were isolated (eq

3). As expected, poly(1,2-diisocyanatodecane) (P12DID)



(3)

is soluble in a wide variety of solvents, such as chloroform, THF, benzene, and hexanes. Gel permeation chromatography (GPC) on the resulting polymers showed monomodal molecular weight distributions and a range of polydispersities (PDIs) ($M_w/M_n = 1.2-1.8$). A plot of the molecular weight of the polymer formed versus the initial monomer-to-initiator ratio ($[\text{monomer}]_0/[\text{initiator}]_0 = 50-500$) of the polymerization showed good linear correlation ($R^2 = 99.6\%$) and a slope (211 g mol^{-1}) very close to the molecular weight of the monomer (224 g mol^{-1}). The fact that the slope of the graph is, within experimental error, the same as the molecular weight of the monomer suggests that P12DID has the same hydrodynamic scaling properties as polystyrene, a random-coil polymer (confirmed by subsequent experiments). If so, then the elevated PDIs cannot be attributed to an extended polymer solution conformation and are due to either chain termination or the presence of multiple propagating species during the polymerization.[18] Because the attainable yield of these cyclopolymerizations decreased dramatically when the initial monomer-to-initiator ratio exceeded 1000, the former explanation seems more likely. The most obvious source for chain termination would have been hydrolysis of the monomer, but we eliminated this possibility when IR spectra of the monomer samples lacked the characteristic absorptions for a substituted ethyleneurea at 1786 and 1727 cm^{-1}. Upon exposure of the samples to ambient moisture, these signals appeared and increased with increasing exposure to the atmosphere. Nevertheless, small amounts of water present in the monomer would act as a terminating agent.

The qualitative properties of P12DID differ markedly from those of its acyclic analogue, poly(*n*-hexyl isocyanate) (PHIC). While PHIC can be precipitated from solution as either a powder (low molecular weight) or a waxy solid (high molecular weight), P12DID at any molecular weight synthesized thus far precipitated from a wide variety of solvents as a viscous oil. Out of necessity, P12DID was freeze-dried from benzene solutions in order to obtain it in a tractable solid form. Moreover, solutions of P12DID were noticeably less viscous than solutions of PHIC at the same concentration and GPC molecular weight. This qualitative comparison suggests that the chain-conformation characteristics of PHIC and P12DID are quite different (*vide infra*).

The polymerization of other 1,2-diisocyanates proceeded much like those of P12DID, yet a few interesting differences were noted. The polymerization of 1,2-diisocyanatopropane was very exothermic, and when bulk polymerizations of this monomer were attempted, the monomer boiled, and the polymer solution foamed vigorously. Poly(*cis*-1,2-diisocyanatocyclohexane) (P12DIC) was reported to be soluble only in DMSO,[8] but we had great difficulties in getting even modest amounts of the polymer to dissolve in this solvent. Instead, P12DIC was soluble in chloroform and moderately soluble in THF. Furthermore, *cis*-1,2-diisocyanatocyclohexane did not polymerize spontaneously, while 1,2-diisocyanatoethane, 1,2-diisocyanatopropane, and 1,2-diisocyanatodecane would polymerize spontaneously at unpredictable intervals after sitting under an inert atmosphere for days to weeks: generally, the longer or bulkier the alkyl side chain, the longer the time required to observe spontaneous polymerization.[19] These observations suggest that steric factors play an important role in the cyclopolymerization of 1,2-diisocyanates.

Table 1. Carbonyl IR Stretching Frequencies for Various 1,2-Diisocyanate Cyclopolymers and Model Compounds

polymer or compound	ν(C=O) inter-ring (cm^{-1})	ν(C=O) intra-ring (cm^{-1})	ref
P12DIE	1776 (5.63 μm)	1701 (5.88 μm)	a
	1773	1690	b
P12DIP	1773	1700	this work
	1776 (5.63 μm)	1701 (5.88 μm)	a
P12DIC	1771	1698	this work
	1776 (5.63 μm)	1701 (5.88 μm)	a
P12DID	1778	1698	this work
7	1757	1694	this work
	1745	1690	b
8		1670	this work

[a] Reference 8. [b] Reference 10.

The IR spectrum of P12DID showed two carbonyl absorptions at 1778 and 1698 cm^{-1} and no absorption at 2270 cm^{-1}, which would have indicated the presence of uncyclized isocyanate groups. These absorptions have been assigned in the literature as the inter-ring carbonyl and the intra-ring carbonyl stretching frequencies, respectively.[8,10] The IR carbonyl stretching frequencies for several 1,2-diisocyanate polymers are shown in Table 1. There is a very good correlation between the data obtained for cyclopolymers synthesized using organotitanium(IV) catalysts and those synthesized using the anionic procedure. The ^{1}H NMR spectrum of P12DID, and other cyclopolymers as well, was relatively uninformative, because the proton signals were so severely broadened that little information could be obtained from the spectrum. However, the ^{13}C spectrum of P12DID showed signals for all 12 carbons of the repeat unit. From these data, we conclude that the cyclopolymerization of 1,2-diisocyanates using organotitanium(IV) catalysts results in exclusive cyclization of the monomer and that the resulting polymers are identical, spectroscopically, to those obtained using the anionic procedure.

We also examined the polymerization of Iwakura's series of α,ω-diisocyanates containing two to four methylene units.[10] We were able to obtain IR spectra of poly(1,3-diisocyanatopropane) (P13DIP) and poly(1,4-diisocyanatobutane) (P14DIB), and our data are presented along with King's and Iwakura's in Table 2. Unfortunately, all of these polymers were insoluble in organic solvents, so we were unable to record NMR spectra. The IR spectrum of P13DIP showed two carbonyl absorptions at 1718 and 1685 cm^{-1}, which is consistent with a cyclic repeat unit structure containing a cyclic and an acyclic carbonyl. The IR spectrum of P14DIB, on the other hand, showed only a broad carbonyl absorption at 1700 cm^{-1}. Since the IR carbonyl absorption for poly(*n*-alkyl isocyanates) usually occurs between 1690 and 1700 cm^{-1}, this data suggests that little cyclization of the monomer had occurred and that a cross-linked monoisocyanate polymer backbone had formed. Soluble analogues of these polymers will be necessary to make definite conclusions about their cyclic repeat unit content.

One of our objectives in performing the spectroscopic characterizations was the determination of the poly-

Table 2. Carbonyl IR Stretching Frequencies for a Series of α,ω-Diisocyanate Cyclopolymers

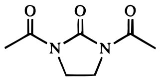
polymer	ν(C=O) inter-ring (cm^{-1})	ν(C=O) intra-ring (cm^{-1})	notes
P12DIE	1776 (5.63 μm)	1701 (5.88 μm)	*a*, *g*
	1773	1690	*b*, *h*
	N/A	N/A	*a*, *i*
P13DIP	1718	1685	*c*, *i*
	1720 (sh)	1685	*d*, *h*
		1686 (5.93 μm)	*c*, *g*
P14DIB		1700	*e*, *i*
	1716 (sh)	1688	*f*, *h*

[a] Reported insoluble in DMSO. [b] Reported soluble in DMSO. [c] Reported insoluble in phenol, *m*-cresol, and H_2SO_4. [d] Reported soluble in *m*-cresol and H_2SO_4. [e] Reported insoluble in dimethyl carbonate, and H_2SO_4. [f] Reported soluble in ethylene carbonate and H_2SO_4. [g] Reference 8. [h] Reference 10. [i] This work.

Table 3. $^{13}C\{^1H\}$ NMR Chemical Shifts for the Carbonyl-Carbon Signals of Various Cyclopolymers and Model Compounds

polymer or compound	inter-ring C=O δ (ppm)	intra-ring C=O δ (ppm)	NMR solvent
P12DIP	148.7	148.7	DMSO-d_6
P12DIC	150.5	149 (2 lines)	$CDCl_3$
P12DID	149.3	148.7	$CDCl_3$
7	170.6	151.84	$CDCl_3$
8		151.84	$CDCl_3$

mer's microstructure. In order to distinguish between the two possible microstructures, we used two repeat unit model compounds. The first model, *N*,*N'*-diacetyl-2-imidazolidone, **7**, has the core 2-imidazolidone ring structure with both nitrogen atoms derivitized with acetyl groups. The ring carbonyl in **7** has a very similar electronic environment to that of the polymer repeat unit as proposed by King (eq 1). Compound **7** showed two carbonyl absorptions in its IR spectrum at 1757 and 1694 cm^{-1}. The second model, *O*-*n*-butyl-*N*,*N'*-diisopropylisourea, **8**, has the same basic N−(C−O)=N structure as that of the repeat unit as proposed by Iwakura (eq 2). The IR spectrum of **8** showed a carbon−nitrogen double-bond stretching frequency at 1670 cm^{-1}, which was substantially different from the corresponding stretching frequencies of compound **7** and P12DID. Although the data supported the King repeat unit structure, the IR data alone were not sufficient to distinguish between the two possible microstructures, since **8** was not a perfect match for Iwakura's repeat unit and it has been argued that the addition of acyl groups to **8** could shift its C=N stretching frequency to a higher value.[10]



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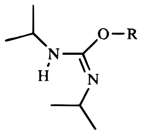


8: R = *n*-butyl

The $^{13}C\{^1H\}$ NMR spectrum of P12DID showed two carbonyl-carbon signals with chemical shifts at 149.30 and 148.66 ppm, and that of P12DIP showed one broad signal for the carbonyl carbons at 148.7 ppm (Table 3) Unfortunately, the carbonyl carbons of the two model compounds had identical chemical shifts at 151.84 ppm, so they were of little help in distinguishing between the two types of microstructures. Further refinement of compound **8** as a model for Iwakura's repeat unit may prove useful in determining the polymer microstructure, but since *O*-acetyl isoureas are known to be unstable, synthesizing an exact match may not be possible.

Other techniques, such as ^{15}N NMR or ^{13}C NMR of cyclopolymers synthesized using C_2-symmetric monomers should provide more insight.[20]

Thermal Characterization of 1,2-Diisocyanate Cyclopolymers. Beaman[7] and King[8] conducted simple melting point studies on vicinal diisocyanate cyclopolymers and found that they decompose at significantly higher temperatures than monoisocyanate polymers. Thermal gravimetric analysis (TGA) of P12DID, P12DIC, and P12DIP showed onset of decomposition temperatures at 276, 300, and 320 °C, respectively. PHIC, for reference, showed an onset of decomposition temperature at 180 °C. These results were consistent with Beaman's and King's observations.

It is known that PHIC thermally decomposes to cyclic trimer and that the thermodynamic stability of this product is presumably a large driving force for the decomposition of the polymer.[21] This cyclic trimerization pathway, however, is not available for diisocyanate cyclopolymers, because the cyclic trimer formed from such a process would have the nitrogen atoms of the planar ring linked via a two-carbon-atom chain, and consequently the trimer would have a very large strain energy. Therefore, 1,2-diisocyanate cyclopolymers must decompose via another pathway that presumably has a higher activation barrier relative to that for monoisocyanate polymers. Beaman[7] has noted that P12DIP thermally depolymerizes to monomer.

Differential scanning calorimetry (DSC) thermograms of P12DID were featureless except for a large exotherm which began at approximately the same temperature that decomposition was observed in TGA measurements. The absence of a glass transition temperature (T_g) or a melt temperature (T_m) in this DSC experiment does not signify that the polymer does not exhibit a T_g or T_m, because the change in heat capacity during these transitions may be smaller than detectable using that particular instrument. Previous reports[8] of T_ms for diisocyanate cyclopolymers near their decomposition temperature may have been due to plasticization by monomer formed via thermal decomposition.[7]

Solution Characterization of 1,2-Diisocyanate Cyclopolymers. As mentioned above, qualitative results suggested that 1,2-diisocyanate cyclopolymers have a less extended conformation in solution than monoisocyanate polymers. Tandem GPC/light-scattering studies were conducted on P12DID and PHIC in THF. Plots of absolute polymer molecular weight (M_w) versus elution volume, which is proportional to hydrodynamic volume, showed that at equivalent molecular weights PHIC adopts a larger hydrodynamic volume than P12DID (Figure 1).

This experiment indicates that tethering two adjacent amide units in poly(monoisocyanate)s to form a five-membered ring prevents the polymer backbone from adopting a helical, extended conformation. Most likely, ring formation reduces or eliminates the side-group-to-backbone steric interactions responsible for driving the monoisocyanate polymer backbone into a helical conformation. Also, the lack of flexibility inherent in the five-membered ring prevents the carbon−nitrogen bonds along the polymer backbone from rotating to attain the proper dihedral angles, Ψ and Φ, for the helical conformation.[22] The different steric requirements for the conformation of 1,2-diisocyanate cyclopolymers versus monoisocyanate polymers explain why diisocyanates

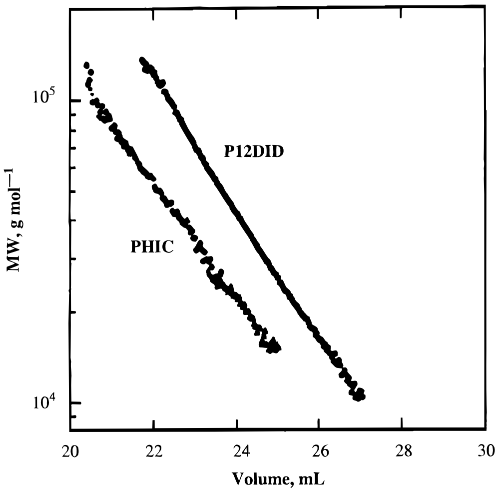


Figure 1. Plots of absolute molecular weight (M_w) versus elution volume in THF for PHIC and P12DID from tandem GPC/light-scattering experiments.

with secondary centers, such as *cis*-1,2-diisocyanatocyclohexane, readily polymerize while secondary monoisocyanates, such as cyclohexyl isocyanate, do not homopolymerize. Previous statements[8] asserting that ring formation is a powerful thermodynamic driving force for cyclopolymerization of isocyanates appear, at best, to be irrelevant in light of the apparent difference in the conformations of these two types of isocyanate polymers and in light of the fact that five-membered rings generally contain a nonnegligible amount of strain energy.[23] Further studies into the hydrodynamic properties of 1,2-diisocyanate cyclopolymers will help elucidate the differences between these two types of isocyanate polymers.

Block Copolymers of *n*-Hexyl Isocyanate with 1,2-Diisocyanates. A major difficulty associated with applications for poly(monoisocyanate)s is their low thermal stability ($T_{\mathrm{decomposition}} = 180-200$ °C).[24] 1,2-Diisocyanate cyclopolymers are significantly more thermally stable than monoisocyanate polymers but do not possess the unique optical and conformational properties of poly(monoisocyanate)s.[25] Because *n*-hexyl isocyanate is an inexpensive, commercially available monomer and because PHIC is a well-studied, well-understood polymer, the thermal stabilization of PHIC remains an important goal in polymer chemistry.

The base-catalyzed degradation of PHIC in solution has been studied,[26] and the main decomposition product identified was cyclic trimer. Because the intrinsic viscosity of the polymer remained approximately constant until complete conversion to trimer, it was concluded that the base-catalyzed solution degradation of PHIC was initiated by abstraction of the acidic proton from the polymer chain end. The amidate anion formed backbites into the polymer chain and degrades the polymer at room temperature into the more thermodynamically stable cyclic trimer. The thermal degradation of PHIC has also been studied and is less understood.[27] The main decomposition product observed was also cyclic trimer; however, the exact mechanism of thermal decomposition remains unknown. It has been assumed that the mechanism of the base-catalyzed solution degradation of PHIC can be extrapolated to describe its thermal degradation process.[28]

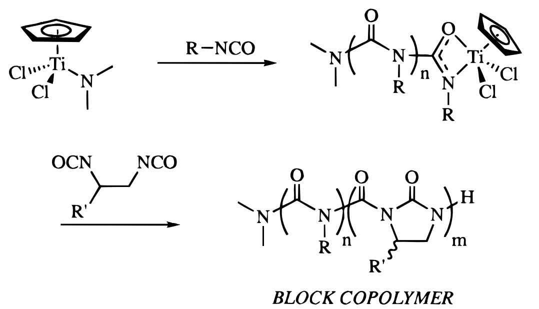
Several other polymers that have low ceiling temperatures, such as polyformaldehyde ($T_c = 116$ °C), thermally decompose to monomer by a chain-end-initiated process, and these polymers can be stabilized using a variety of methods.[29] One strategy is to replace the acidic hydroxy proton at the polymer chain end with an acetyl or alkyl group. This substitution in polyformaldehyde prevents the formation of an alkoxide anion and blocks the initiation of decomposition. The stabilization of polyformaldehyde can also be effected by copolymerizing formaldehyde with small amounts of an epoxide, which act as degradation "stops." When decomposition of a copolymer chain is initiated, depolymerization proceeds until a ring-opened epoxide unit is reached and then ceases due to the high energetic barrier for the depolymerization of the epoxide unit. Stabilization by either of these methods converts polyformaldehyde from a useless, low-temperature polymer that decomposes into a toxic, carcinogenic compound into a commercially useful polymer that can be compression molded at 180–220 °C into tough, translucent objects. The historical success in stabilizing polymers such as polyformaldehyde prompted us to apply these methods toward the stabilization of PHIC.

Previously,[15b] we demonstrated that PHIC prepared using organotitanium catalysts can be end-capped quantitatively using carboxylic acid anhydrides. These end-capped polymers displayed TGA decomposition onset temperatures ($\sim$200 °C) that were within the range found for un-end-capped polyisocyanates. Hatada and co-workers[30] investigated the end-capping of poly(*n*-butyl isocyanate) (PBIC), prepared using organotitanium catalysts, with carboxylic acid anhydrides and found that end-capping reduces that rate of solution depolymerization by an order of magnitude relative to uncapped PBIC. The lack of increased thermal stability of end-capped PHIC may have been due to several factors. The trifluoroacetyl end-cap might be a very unstable moiety, or perhaps a small fraction of the chains were left uncapped, and the thermal activation of these chains resulted in the catalytic degradation of the whole sample. A third explanation for this result is that polyisocyanates thermally degrade by a process other than a chain-end-initiated mechanism.

We surmised that the first two of the aforementioned possibilities could be tested by studying the thermal stability of PHIC end-capped with a block of a 1,2-diisocyanate cyclopolymer. Poly(1,2-diisocyanates) show good thermal stability, and the presence of small amounts of uncapped PHIC chains could be detected more easily using GPC and solubility techniques. Also, block copolymers with a random-coil segment and a helical segment would be interesting materials in their own right. There have been only a few examples of the preparation block,[16,31] random,[32] and alternating[33] copolymers of monoisocyanates with other monomers.

Two isocyanate/1,2-diisocyanate block copolymers were prepared (Scheme 3). First, an oligomerization of *n*-hexyl isocyanate was conducted using **6**. The active oligomer (GPC $M_n = 6790$) was dissolved in THF and treated with 1,2-diisocyanatodecane. Polymerization of the diisocyanate ensued, and the molecular weight of the resulting polymer increased (GPC $M_n = 9960$) while the PDI remained approximately the same (M_w/M_n increased from 1.1 to 1.2). The increase in molecular weight may actually be significantly larger than measured, because the hydrodynamic scaling properties of PHIC blocked with a more flexible polymer are most certainly different from that of PHIC alone. No refractive index signal was observed in the GPC chromatogram at the elution volume of the PHIC block. A second

Scheme 3



R = *n*-hexyl
R' = methyl, *n*-octyl

block copolymer was prepared in a likewise manner using *n*-hexyl isocyanate and 1,2-diisocyanatopropane. In this case, solubility difference tests were conducted, because PHIC is soluble in both chloroform and hexanes while P12DIP is not. The resulting copolymer was soluble in chloroform and insoluble in hexanes, and hexanes extracts of the copolymer contained no PHIC. $^{13}C\{^1H\}$ NMR spectra of both copolymers showed three carbonyl signals at the same chemicals shifts found for the homopolymers (PHIC at 157 ppm and P12DIP at 149 and 148.5 ppm), which lends support to a block structure for the copolymer. Elemental analyses of the copolymers matched the expected elemental composition based upon the quantities of the monomers used in the synthesis. The above characterization data indicate that the polymers prepared from these syntheses are block type in structure and not a mixture of homopolymers.

TGA performed on each of the copolymer samples showed that their thermal decomposition followed a step function, where each of the decomposition onset temperatures corresponded with the onset found for the individual homopolymers (Figures 2 and 3). Differential scanning calorimetry (DSC) thermograms of both materials showed an exotherm at the decomposition temperature for the PHIC block and a large endotherm at a temperature corresponding to the decomposition and volatilization of the cyclopolymer block. In an experiment using a separate sample, the DSC temperature was ramped to 200 °C and then cooled back to 25 °C. Upon ramping the temperature for a second time, no exotherm was observed at 180 °C, indicating that this feature was due to the decomposition of the PHIC block. The two-step weight loss in the TGAs and the DSC results for these block copolymers are consistent with a decomposition process in which the two blocks decompose independently of one another. The fact that quantitative end-capping of PHIC with either a small molecule or a block of a more stable polymer does not alter its decomposition temperature strongly suggests that the thermal decomposition of PHIC does not occur by a chain-end-initiated mechanism and that poly(monoisocyanate)s cannot be stabilized to thermal degradation by end-capping methods.

Random Copolymers of *n*-Hexyl Isocyanate with 1,2-Diisocyanates. Because end-capping was ineffective for the stabilization of polyisocyanates, we focused our studies upon using the copolymerization method that had proven successful for polyformaldehyde. The monomers used as the "degradation stop" in these experiments were 1,2-diisocyanates, because the resulting 2-imidazolidone repeat unit depolymerizes at a significantly higher temperature than that for PHIC. The five-membered ring structure also cannot be incorporated into a cyclic trimer, because it would increase the ring strain of the trimer.

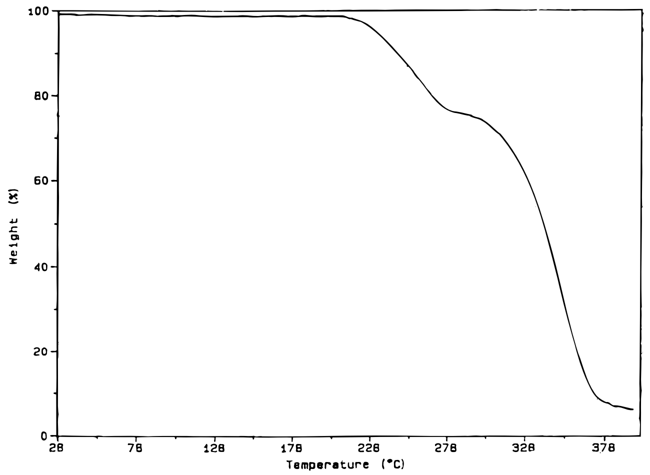


Figure 2. TGA thermogram of the block copolymer of *n*-hexyl isocyanate with 1,2-diisocyanatopropane. Onsets = 200 and 320 °C.

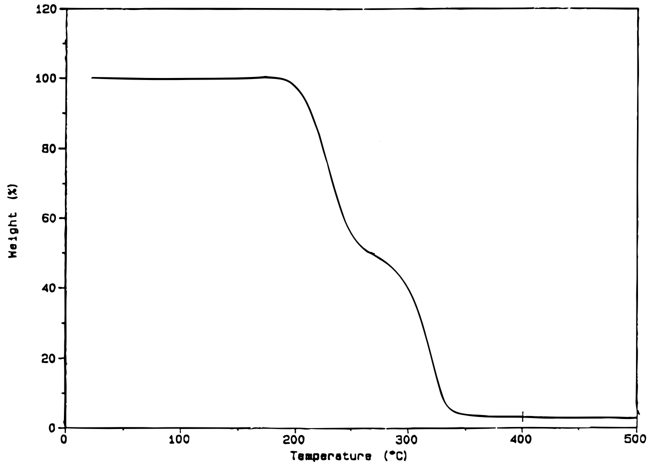
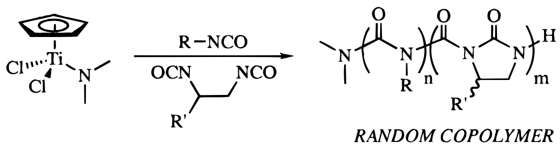


Figure 3. TGA thermogram of the block copolymer of *n*-hexyl isocyanate with 1,2-diisocyanatodecane. Onsets = 200 and 290 °C.

Several copolymerizations of *n*-hexyl isocyanate with 1,2-diisocyanatodecane or 1,2-diisocyanatopropane in various proportions were prepared using **6** (eq 4). The resulting copolymers were isolated in good yield, and the feed ratios were closely reflected in the experimentally determined incorporation ratios. $^{13}C\{^1H\}$ NMR spectra of both types of 50% copolymers showed one broad two maxima signal at 150 ppm for the backbone carbonyls. No signal at 158 ppm, which would have indicated the presence of large segments of PHIC, was observed.



(4)

R = *n*-hexyl
R' = methyl, *n*-octyl

TGA was performed on each of the copolymer samples, and in every case, the step-function degradation curve characteristic of the corresponding block copolymers was not observed. The position and sharpness of the co-

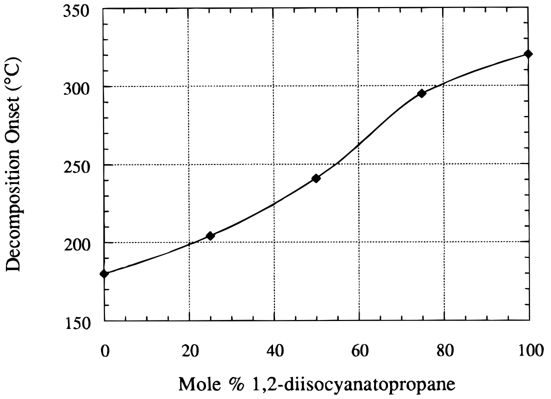


Figure 4. Plot of the thermal decomposition onset temperature versus mole percentage composition of 1,2-diisocyanate for the random copolymers of *n*-hexyl isocyanate with 1,2-diisocyanatopropane.

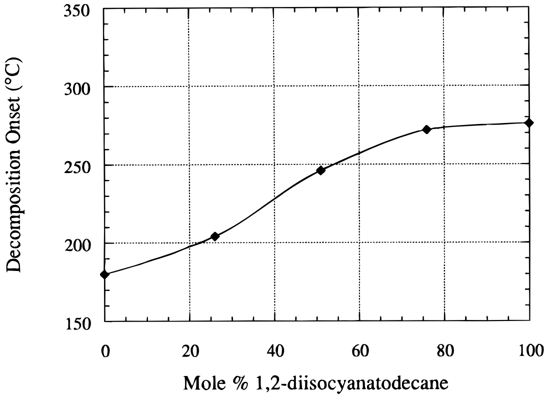


Figure 5. Plot of the thermal decomposition onset temperature versus mole percentage composition of 1,2-diisocyanate for the random copolymers of *n*-hexyl isocyanate with 1,2-diisocyanatodecane.

polymer decomposition onset temperature displayed a marked dependence upon the amount of 1,2-diisocyanate monomer in the copolymer composition. Plots of the decomposition onset temperature versus composition (Figures 4 and 5) showed that the thermal stability of these copolymers was a function of the content of 1,2-diisocyanate in the copolymer, with an increase in 1,2-diisocyanate composition translating into greater thermal stability for the copolymer. The fact that the addition of up to 25 mol % of a 1,2-diisocyanate results in only a small increase in thermal stability of the copolymer suggests that the segments of PHIC are inherently unstable at 180−200 °C.

Conclusion

1,2-Diisocyanatodecane was synthesized and polymerized with stoichiometric control over molecular weight using $CpTiCl_2N(CH_3)_2$, **6**. Other monomers that were polymerized in a likewise manner include 1,2-diisocyanatoethane, 1,2-diisocyanatopropane, and *cis*-1,2-diisocyanatocyclohexane. IR, ^1H NMR, and ^{13}C NMR spectra of the resulting polymers indicate that complete cyclization of the monomers occurred, although the question concerning the exact structure of the repeat unit remains unresolved. The solution properties of one soluble cyclopolymer, P12DID, was investigated using tandem GPC/light scattering, and it was shown that this cyclopolymer has a smaller hydrodynamic volume at equivalent molecular weights than the stiffer, helical PHIC. Investigations into stabilizing PHIC to thermal degradation were conducted. End-capped PHIC showed the identical thermal properties as PHIC terminated using protic sources. Living PHIC was also end-capped with blocks of P12DIP and P12DID. TGA and DSC studies of these block copolymers showed that the individual block segments decomposed at the same temperatures as their respective homopolymers. Random copolymers of *n*-hexyl isocyanate with 1,2-diisocyanatopropane and 1,2-diisocyanatodecane were prepared, and TGA studies of these copolymers showed that the decomposition onset temperature of the copolymer was a function of its 1,2-diisocyanate content. The thermal studies on the block and random copolymers suggest that the thermal degradation of PHIC does not occur by a chain-end-initiated degradation mechanism.

Experimental Section

General Procedures and Characterizations. All manipulations involving air- and moisture-sensitive compounds were carried out under atmospheres of argon using standard Schlenk techniques. Solids and monomers were transferred in an argon-filled Vacuum Atmospheres HE533 Dri Lab with attached HE493 Dri Train.

^1H and $^{13}C\{^1H\}$ NMR spectra were determined at 400 and 100 MHz, respectively, using a Bruker AM-400 or an AMX-400 FT NMR spectrometer at 500 and 125 MHz, respectively, using a Bruker AM-500 FT NMR spectrometer. Chemical shifts for ^1H spectra are reported in units of δ (ppm), positive values indicating shifts downfield of tetramethylsilane, and are referenced to a selected residual proton signal of the solvent: $CDCl_3$, 7.25 ppm, singlet; DMSO-d_6, 2.49 ppm, broad. Significant ^1H NMR data are tabulated in the order multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broadened signal), coupling constant(s) in hertz, and number of protons. Chemical shifts for $^{13}C\{^1H\}$ spectra are reported in units of δ (ppm), positive values indicating shifts downfield of tetramethylsilane, and are referenced to a selected carbon resonance of the solvent employed: $CDCl_3$, 77.0 ppm, triplet; DMSO-d_6, 39.5 ppm, septet. Infrared spectra were determined using a Perkin-Elmer 1600 series FTIR. 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.

Polymer Characterizations. 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.) Mobile phase: $CHCl_3$ or THF; flow rate: 1 mL min^{-1}. Light scattering in the tandem GPC/light-scattering experiments was performed using a Wyatt Technology Dawn DSP Model F multiangle photometer. Measurements of $(\delta n/\delta c)_{T,P}$ were performed using a Chromatix KMX-16 refractometer. Thermal gravimetric analysis (TGA) was performed using a Perkin-Elmer PC Series TGA7: scanning rate = 10 °C min^{-1}, atmosphere = nitrogen. Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer PC series DSC.

Reagents. Solvents and reagents for air-sensitive reactions were purified as follows: toluene, benzene, and tetrahydrofuran (THF) were distilled from Na/benzophenone, degassed, and stored under argon. Aniline was distilled from CaH_2. $CpTiCl_2NMe_2$[15b] was prepared as described previously, and 1,4-diisocyanatobutane was distilled from CaH_2 before use. All diisocyanate monomers were stored under an argon atmosphere in a drybox due to their extreme sensitivity to moisture. Unless specified otherwise, all other reagents were obtained from Aldrich Chemical Co. and used without further purification.

Mono- or dianiline derivatives of diisocyanate monomers were prepared by adding a toluene solution of the diisocyanate to a solution of 2 equiv of aniline in toluene and then stirring the solution overnight. The precipitate was filtered and washed with toluene. Volatile materials were removed under vacuum, and then the melting point of the material was measured.

***cis/trans*-(2-Octenyl)succinic Anhydride (1).** In a 500 mL three-necked round-bottom flask with a magnetic stirrer, thermometer adapter, high-temperature thermometer, and spiral reflux condenser, 36.5 g (0.372 mol) of maleic anhydride, 105 mL (75.1 g, 0.669 mol) of 1-octene, and 15.0 mL of THF were stirred in 150 mL of 1,2,4-trichlorobenzene. The flask was placed in a heating mantle sand bath, and the solution was brought to reflux at approximately 135 °C. Over the course of 1 week, the solution was stirred and heated at reflux, and the temperature of the solution rose to approximately 145 °C. The solution was cooled, and the thermometer adapter and reflux condenser were removed. A short-path distillation head was attached, and the volatile components of the solution (mainly 1-octene) were removed under vacuum. Then the 1,2,4-trichlorobenzene was removed by vacuum distillation to leave a discolored oil. This oil was transferred to a round-bottom flask and was distilled in a Kugelrhor apparatus at 70 °C and 0.02 Torr to give a colorless oil. Yield 42.7 g (55%). Note: In the oil some white precipitate forms which settles out over time and, as best as can be determined, is not an impurity. The whole sample, white precipitate and all, can be used in the next step with no detriment to the reaction. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 5.57 (m, 1H), 5.26 (m, 1H), 3.17 (m, 1H), 2.99 (dd, $J_1 = 9.8$ Hz, $J_2 = 18.8$ Hz [values are for *trans* isomer], 1H), 2.69 (dd, $J_1 = 5.9$ Hz, $J_2 = 18.8$ Hz [values are for *trans* isomer], 1H), 2.47 (m, 2H), 1.97 (m, 2H), 1.26 (m, 6H), 0.85, (t, $J = 6.7$ Hz [value is for *trans* isomer], 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 173.4, 170.1, 136.8, 135.5, 122.8, 122.2, 40.5, 33.4, 33.1, 32.9, 32.3, 31.3, 31.2, 29.0, 28.7, 27.8, 27.3, 22.4, 22.3, 13.9; IR (neat) 2956 (m), 2927 (m), 2857 (m), 1863 (m), 1783 (vs), 1459 (w), 1437 (w), 1412 (w), 1379 (w), 1308 (w), 1229 (m), 1067 (m), 976 (w), 920 (m), 724 (w) cm^{-1}.

Diethyl *cis/trans*-(2-Octenyl)succinate (2). To a 250 mL round-bottom flask equipped with a magnetic stir bar and a reflux condenser were added 42.7 g (0.203 mol) of *cis/trans*-(2-octenyl)succinic anhydride, 75.0 mL of absolute ethanol (58.9 g, 1.28 mol), and 0.348 g (1.83 mmol) of *p*-toluenesulfonic acid monohydrate. The solution was heated at reflux under a dry atmosphere overnight. The next day the reflux condenser was removed, 75 mL of toluene was added to the solution, and a distillation head was attached. The flask was heated until the ethanol/water/toluene azeotrope began to distill at 78 °C, and the heating was kept constant until the temperature of the distillate dropped to approximately 70 °C. Then 75 mL of ethanol was added to the solution, the reflux condenser was replaced, and the above reflux/azeotropic distillation procedure was repeated. The solution was extracted with 100 mL of ether, and the ether extract was washed with 2 × 100 mL of 5% aqueous Na_2CO_3. The aqueous solutions were combined and extracted with 2 × 100 mL ether. The ether layers were combined and dried over $MgSO_4$. Ether was removed with a rotary evaporator, leaving a colorless oil, which was purified by vacuum distillation (130 °C, 0.02 Torr) to yield 6.06 g (71%) of a clear, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 5.45 (m, 1H), 5.27 (m, 1H), 4.11 (m, 4H), 2.84 (m, 1H), 2.64 (dd, $J_1 = 9.4$ Hz, $J_2 = 16.6$ Hz [values are for *trans* isomer], 1H), 2.40 (dd, $J_1 = 5.1$ Hz, $J_2 = 16.6$ Hz [values are for *trans* isomer], 1H), 2.33 (m, 1H), 2.19 (m, 1H), 1.94 (m, 2H), 1.25 (m, 12H), 0.85, (t, $J = 6.7$ Hz [value is for *trans* isomer], 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 174.35, 172.02, 134.15, 133.08, 125.50, 124.98, 60.56, 60.47, 60.46, 41.29, 41.25, 35.19, 34.85, 32.41, 31.45, 31.30, 29.27, 29.18, 28.99, 27.17, 22.49, 22.45, 14.17, 14.11, 13.98; IR (neat) 2958 (s), 2928 (s), 2856 (s), 1735 (vs), 1466 (m), 1445 (m), 1374 (m), 1160 (s), 1097 (m), 1032 (s), 972 (m), 857 (w) cm^{-1}.

Diethyl *n*-Octylsuccinate (3). A glass Parr shaker bottle was charged with 53.8 g (0.189 mol) of diethyl *cis/trans*-(2-octenyl)succinate and 0.501 g of palladium on activated carbon. The bottle was attached to a Parr shaker hydrogenation apparatus, and the system was purged with dihydrogen. The apparatus was charged with dihydrogen to a pressure of 60 psi, and the reaction mixture was shaken overnight. The reaction mixture was taken up in 100 mL of diethyl ether and filtered through 3 cm of diatomaceous earth. The solids were washed with 3 × 100 mL of diethyl ether. Diethyl ether was removed from the filtrate with a rotary evaporator, and the remaining oil was distilled at 135 °C and 0.02 Torr to yield 53.1 g (98%) of a clear, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 4.09 (m, 4H), 2.78 (m, 1H), 2.66 (dd, $J_1 = 9.3$ Hz, $J_2 = 16.3$ Hz, 1H), 2.37 (dd, $J_1 = 5.1$ Hz, $J_2 = 16.3$ Hz, 1H), 1.59 (m, 1H), 1.47 (m, 1H), 1.22 (m, 18H), 0.84 (t, $J = 6.7$ Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 174.97, 171.96, 60.44, 60.39, 41.23, 36.09, 31.91, 31.77, 29.37, 29.30, 29.13, 26.83, 22.58, 14.15, 14.10, 14.00; IR (neat) 2927 (s), 2856 (s), 1734 (vs), 1465 (m), 1412 (w), 1374 (m), 1342 (w), 1257 (s), 1160 (s), 1096 (w), 1031 (s), 858 (w) cm^{-1}.

***n*-Octylsuccinic Dihydrazide (4).** To a 500 mL round-bottom flask equipped with a magnetic stir bar and a reflux condenser were added 53.1 g (0.185 mol) of diethyl *n*-octylsuccinate, 42.0 mL (43.2 g, 0.863 mol) of hydrazine hydrate, 41.5 mL (41.5 g, 2.30 mol) of water, and 150 mL of ethanol. The solution was stirred and heated at reflux under a N_2 atmosphere for 24 h. Heating and stirring were discontinued, and upon cooling, crystals began to form in the solution. After complete cooling, the reaction mixture had completely solidified. The solid was isolated using suction filtration with enough diethyl ether to help transfer and wash the solid. Volatile materials were removed from the solid under vacuum. Yield 45.5 g (95%), mp 150−153 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 9.05 (s, 1H), 8.95 (s, 1H), 4.18 (s, broad, 4H), 2.17 (dd, $J_1 = 6.5$ Hz, $J_2 = 14.4$ Hz, 1H), 2.06 (dd, $J_1 = 8.0$ Hz, $J_2 = 14.5$ Hz, 1H), 1.36 (m, 1H), 1.21 (m, 14H), 0.84 (t, $J = 6.6$ Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ (ppm) 173.40, 169.95, 40.04, 36.23, 31.75, 31.22, 29.00, 28.88, 28.61, 26.65, 22.04, 13.89; IR (KBr pellet) 3282 (vs), 3182 (m), 3048 (m), 2917 (s), 2850 (m), 1629 (vs), 1534 (s), 1458 (m), 1364 (m), 1479 (m), 1191 (m), 1126 (w), 1079 (w), 1043 (w), 1024 (m), 956 (m), 910 (w), 770 (w), 692 (m), 630 (m), 496 (w) cm^{-1}.

1,2-Diisocyanatodecane (5). The following apparatus was assembled: a 250 mL three-necked flask with a glass stopper, a pressure-equalizing addition funnel, a thermometer adapter with a low-temperature thermometer, and a magnetic stirbar. The flask was charged with 10.3 g (39.9 mmol) of *n*-octylsuccinic dihydrazide and 56.0 mL (97.9 mmol) of a 1.748 M aqueous HCl solution, and the mixture was stirred until all the solid had dissolved. The addition funnel was charged with a solution of 5.83 g (84.5 mmol) of $NaNO_2$ in 27 mL of water. The flask was cooled to 5 °C with the aid of a NaCl/ice bath, and as soon as this temperature was reached, the addition of the $NaNO_2$ solution was started; otherwise crystals would form in the solution. The $NaNO_2$ solution was added at such a rate that the reaction temperature never exceeded 8 °C, and rapid increases in the reaction temperature were moderated by the addition of a few pieces of ice. During this addition, the reaction solution bubbled and turned slightly yellow and opaque. At the halfway point of the addition of the $NaNO_2$ solution, 60 mL of benzene cooled to approximately 5 °C using an ice bath was added to the reaction mixture. After complete addition, the ice bath was removed, and the reaction mixture was allowed to stir and warm to room temperature for 15 min. The benzene layer was separated, and the aqueous layer was extracted with 3 × 100 mL of benzene. The benzene layers were combined and dried over P_2O_5 for 2 h. [*Warning*: This is a solution of an acyl azide! This should be handled in dilute solutions in order to dissipate the heat produced from the slow decomposition to isocyanate and N_2 which occurs at room temperature and in order to prevent vigorous spontaneous decomposition.] The solution was then gravity filtered into an oven-dried 500 mL round-bottom flask with a magnetic stirbar and reflux condenser. The solution was stirred under a flow of dry nitrogen, and its temperature was ramped to the boiling point of benzene at a moderate rate. The solution was heated at reflux for 1 h, and a large amount of gas evolved. After the solution had cooled, benzene was removed with a rotary evaporator. [Note: 1,2-diisocyanates are very moisture sensitive, so contact time with ambient atmosphere at this point should be kept to a minimum.] The remaining oil was distilled using a short-path distillation apparatus at 102−104 °C and 0.04 Torr. The distillation was repeated to yield 4.84 g (54%) of a clear, colorless oil: ^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm) 3.47 (m, 1H), 3.41 (dd, $J_1 = 4.2$ Hz, $J_2 = 13.1$ Hz, 1H), 3.34 (dd, $J_1 = 6.6$ Hz, $J_2 = 13.1$ Hz, 1H), 1.55 (m, 2H), 1.43 (m, 1H), 1.27 (m, 11H), 0.87 (t, $J = 6.6$ Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ (ppm) 124.0, 123.7, 56.3, 48.1, 33.9, 31.8, 29.3, 29.1, 29.0, 25.8, 22.6, 14.0; IR (neat) 2960 (s), 2927 (m), 2857 (m), 2270 (vs), 1456 (m), 1350 (m), 1260 (m), 1077 (m), 875 (m), 797 (m) cm^{-1}. Anal. Calcd for $C_{12}H_{20}N_2O_2$: C, 64.26; H, 8.99; N, 12.49. Found: C, 64.81; H, 8.85; N, 12.12.

Monoaniline derivative: mp 158−159 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 9.87 (s, 1H), 7.48 (d, $J = 7.62$ Hz, 2H), 7.29 (dd, $J_1 = 7.62$ Hz, $J_2 = 7.41$ Hz, 2H), 7.05 (t, $J = 7.41$ Hz, 1H), 6.21 (s, 1H), 4.09 (dd, $J_1 = 9.09$ Hz, $J_2 = 10.35$ Hz, 1H), 3.73 (m, 1H), 3.62 (dd, $J_1 = 10.48$ Hz, $J_2 = 6.18$ Hz, 1H), 1.57 (m, 2H), 1.28 (m, 12H), 0.86 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ (ppm) 158.19, 150.76, 137.83, 128.88, 123.52, 119.66, 48.67, 47.87, 36.01, 31.73, 31.73, 29.40, 29.29, 29.12, 25.14, 22.57, 14.01; IR (thin film) 3228 (m), 2927 (m), 2853 (m), 1723 (s), 1689 (m), 1601 (m), 1559 (m), 1484 (w), 1467 (w), 1448 (w), 1419 (m), 1292 (w), 1264 (w), 1242 (m), 1164 (w), 1077 (w), 754 (s), 692 (w), 669 (w) cm^{-1}.

Succinic Dihydrazide. The same procedure as for the synthesis of *n*-octylsuccinic dihydrazide was followed. The quantities of reagents used were 25.0 mL of diethyl succinate (26.2 g, 0.150 mol), 400 mL of absolute ethanol, 30.0 mL of hydrazine hydrate (30.9 g, 0.617 mol), and 60 mL of water. After the reaction mixture had cooled to room temperature, solvents were removed by vacuum distillation, leaving about 50 mL of a thick oil. When this oil cooled, crystals formed, which were collected on a Buchner funnel and washed with THF. Volatile materials were removed under vacuum, leaving 12.1 g (55%) of an off-white crystalline solid: mp 169−171 °C (lit. mp 164−166 °C);[8] ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 8.95 (s, br, 2H), 4.21 (s, br, 4H), 2.23 (s, 4H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ (ppm) 170.99, 29.05; IR (KBr pellet) 3304 (vs), 3181 (s), 3043 (m), 2875 (w), 1626 (vs), 1534 (s), 1458 (s), 1352 (s), 1241 (m), 1182 (m), 1125 (w), 1014 (s), 950 (m), 800 (w), 751 (m), 663 (m), 639 (s), 465 (m) cm^{-1}.

Methylsuccinic Dihydrazide. The same procedure as for the synthesis of *n*-octylsuccinic dihydrazide was followed. The quantities of reagents used were 40.0 mL (43.0 g, 0.269 mol) of dimethyl methylsuccinate, 200 mL of absolute ethanol, 57.0 mL (58.7 g, 1.17 mol) of hydrazine hydrate, and 50.0 mL of water. After the reaction mixture cooled to room temperature, 24.9 g of colorless crystals was collected by suction filtration. The product was washed with diethyl ether, and solvents were removed under vacuum. The filtrate was cooled using an ice/water bath, and another crop of crystals formed. The crystals were isolated as previously described, yielding another 8.51 g of product. The volume of filtrate from this crystallization was reduced to about 100 mL with a rotary evaporator, and then 100 mL of absolute ethanol was added. This flask was closed and placed in a −40 °C freezer overnight, and another crop of crystals formed. The crystals were isolated as previously described, resulting in another 5.20 g of product. The overall yield for this procedure was 38.6 g (90%): mp 168−170 °C (lit. mp 160−162 °C);[8] ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 8.95 (s, 1H), 8.90 (s, 1H), 4.14 (s, br, 4H), 2.60 (m, 1H), 2.22 (dd, $J_1 = 6.36$ Hz, $J_2 = 14.43$ Hz, 1H), 2.03 (dd, $J_1 = 6.36$ Hz, $J_2 = 14.46$ Hz, 1H), 0.93 (d, $J = 6.92$ Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ (ppm) 174.43, 170.19, 37.25, 34.57, 17.59; IR (KBr pellet) 3308 (vs), 3184 (s), 3050 (m), 2971 (m), 2920 (w), 1626 (vs), 1535 (s), 1459 (m), 1438 (m), 1376 (m), 1358 (s), 1243 (m), 1211 (m), 1130 (w), 1108 (w), 1076 (w), 1052 (m), 1011 (s), 987 (s), 935 (m), 779 (w), 683 (m), 653 (m), 608 (w), 508 (w) cm^{-1}.

Glutaric Dihydrazide. The same procedure as for the synthesis and isolation of succinic dihydrazide was followed. The quantities of reagents used were 10.0 mL (10.2 g, 54.3 mmol) of diethyl glutarate, 80 mL of absolute ethanol, 13.0 mL (13.4 g, 267 mmol) of hydrazine hydrate, and 20 mL of water. Yield 6.72 g (77%) of colorless crystals; mp 210−212 °C (lit. mp 174−176 °C);[8] ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 8.90 (s, 2H), 4.13 (s, 4H), 1.98 (t, $J = 7.50$ Hz, 4H), 1.68 (quintet, $J = 7.4$ Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ (ppm) 171.17, 32.86, 21.47; IR (KBr pellet) 3209 (m), 3043 (m), 2981 (w), 2944 (m), 2902 (w), 1662 (vs), 1545 (s), 1416 (m), 1363 (m), 1274 (m), 1242 (m), 1211 (m), 1164 (m), 1117 (w), 1023 (w), 935 (w), 882 (w), 855 (w), 802 (w), 625 (w), 597 (w), 569 (w), 495 (w) cm^{-1}.

1,2-Diisocyanatoethane. The same procedure as for the synthesis of 1,2-diisocyanatodecane was followed. The quantities of reagents used were 7.85 g (53.7 mmol) of succinic dihydrazide, 60.4 mL (106 mmol) of 1.748 M aqueous HCl, 7.71 g (112 mmol) of NaNO$_2$, 15.0 mL of water, and 50 mL of benzene. Yield 2.81 g (47%) of a clear liquid which spontaneously polymerized completely upon sitting for 1 week in a drybox; mp (dianiline adduct) 185−187 °C (lit. mp 164−166 °C);[8] ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 3.48 (s); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ (ppm) 123.77, 43.83; IR (neat) 2962 (s), 2905 (m), 2286 (s), 1446 (m), 1412 (m), 1352 (m), 1267 (s), 1235 (s), 1076 (s), 1007 (s), 967 (s), 864 (s), 798 (s) cm^{-1}.

1,2-Diisocyanatopropane. The same procedure as for the synthesis of 1,2-diisocyanatodecane was followed. The quantities of reagents used were 10.0 g (62.4 mmol) of methylsuccinic dihydrazide, 9.54 g (138 mmol) of NaNO$_2$, 86.0 mL (150 mmol) of a 1.748 M aqueous HCl solution, 30 mL of water, and 100 mL of benzene. The product was distilled under dynamic vacuum twice, yielding 4.75 g (60%) of a colorless liquid. This compound spontaneously polymerized after a few weeks of sitting in a drybox: mp (dianiline adduct) 232−234 °C (lit. mp 160-162 °C);[8] ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 3.75 (m, 1H), 3.38 (dd, $J_1 = 4.40$ Hz, $J_2 = 13.12$ Hz, 1H), 3.31 (dd, $J_1 = 6.49$ Hz, $J_2 = 13.13$ Hz, 1H), 1.32 (d, $J = 6.53$ Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ (ppm) 124.11, 123.81, 51.62, 49.27, 20.13; IR (neat) 3672 (w), 2958 (s), 2905 (m), 2266 (vs), 1446 (m), 1414 (m), 1385 (m), 1357 (m), 1340 (m), 1299 (m), 1253 (s), 1134 (s), 1100 (s), 1059 (s), 996 (m), 936 (w), 868 (s), 800 (m), 661 (m), 581 (m) cm^{-1}.

1,3-Diisocyanatopropane. The same procedure as for the synthesis of 1,2-diisocyanatodecane was followed. The quantities of reagents used were 6.72 g (41.8 mmol) of glutaric dihydrazide, 48.0 mL (83.9 mmol) of a 1.748 M aqueous HCl solution, 5.96 g (86.4 mmol) of NaNO$_2$, 15 mL of water, and 50 mL of benzene. The product was vacuum distilled, yielding 1.96 g (37%) of a colorless liquid. This compound spontaneously polymerized after several weeks of sitting in a drybox: mp (dianiline adduct) 225−227 °C (lit. mp 174−176 °C);[8] ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 3.47 (t, $J = 6.32$ Hz, 4H), 1.83 (quintet, $J = 6.32$ Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ (ppm) 122.22, 39.85, 31.85; IR (neat) 3687 (m), 2966 (s), 2903 (m), 2268 (vs), 1634 (w), 1528 (w), 1463 (w), 1428 (w), 1370 (w), 1342 (m), 1318 (w), 1280 (w), 1255 (m), 1231 (m), 1211 (w), 1098 (m), 1015 (s), 893 (w), 852 (s), 823 (w), 801 (w), 751 (w), 708 (w), 660 (w), 574 (m) cm^{-1}.

Diethyl *cis*-1,2-Cyclohexanedicarboxylate. The same procedure as for the synthesis of diethyl *cis*/*trans*-(2-octenyl)-succinate was followed. The quantities of reagents used were 20.6 g (0.134 mol) of *cis*-1,2-cyclohexanedicarboxylic anhydride, 50.0 (39.5 g, 0.856 mol) + 50.0 mL of absolute ethanol, 0.238 g (1.25 mmol) of *p*-toluenesulfonic acid monohydrate, and 50 + 50 mL of toluene. The product was distilled at 70 °C and 0.02 Torr, yielding 23.5 g (77%) of a colorless oil: ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 4.07 (q, $J = 7.1$ Hz, 4H), 2.75 (m, 2H), 1.93 (m, 2H), 1.71 (m, 2H), 1.45 (m, 2H), 1.35 (m, 2H), 1.18 (t, $J = 7.1$ Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ (ppm) 173.5, 60.1, 42.5, 26.2, 23.6, 14.0; IR (neat) 2980 (m), 2936 (s), 2859 (m), 1730 (vs), 1450 (m), 1370 (m), 1340 (w), 1302 (m), 1178 (s), 1129 (m), 1098 (w), 1072 (w), 1040 (m), 930 (w), 896 (w), 862 (w), 760 (w) cm^{-1}.

***cis*-1,2-Cyclohexanedicarboxylic Dihydrazide.** The same procedure as for the synthesis and isolation of methylsuccinic dihydrazide was followed. The quantities of reagents used were 10.0 g (43.8 mmol) of diethyl *cis*-1,2-cyclohexanedicarboxylate, 10.0 mL (10.3 g, 206 mmol) of hydrazine hydrate, 10.0 mL of water, and 38 mL of absolute ethanol. Yield 5.90 g (67%) of colorless crystals; mp 236−238 °C (lit. mp 230−231 °C);[8] ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 8.96 (br s) and 8.76 (br s) (2H total), 3.88 (broad, 4H), 2.45 (m, 2H), 1.95 (m, 1H), 1.57 (m, 3H), 1.26 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ (ppm) 173.62, 173.05, 43.41, 41.38, 29.78, 26.69, 25.05, 23.15; IR (KBr pellet) 3415 (s), 3296 (vs), 3050 (s), 2922 (s), 2858 (m), 1620 (vs), 1528 (s), 1438 (m), 1388 (m), 1328 (m), 1274 (m), 1229 (m), 1199 (w), 1127 (w), 1098 (w), 1040 (w), 1020 (m), 965 (m), 864 (w), 846 (w), 806 (w), 735 (w), 676 (m) cm^{-1}.

***cis*-1,2-Diisocyanatocyclohexane.** The same procedure as for the synthesis of 1,2-diisocyanatodecane was followed. The quantities of reagents used were 4.40 g (30.0 mmol) of *cis*-1,2-cyclohexanedicarboxylic dihydrazide, 32.0 mL (55.9 mmol) of a 1.748 M aqueous HCl solution, 3.27 g (47.4 mmol) of $NaNO_2$, 15 mL of water, and 30 mL of benzene. The product was distilled at 50 °C and 0.01 Torr, yielding 1.81 g (50%) of a colorless oil. This compound did not spontaneously polymerize even after several weeks of sitting in a drybox: ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 3.33 (m, 2H), 2.04 (m, 2H), 1.70 (m, 2H), 1.40 (m, 2H), 1.26 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 123.80, 59.34, 33.14, 23.58; IR (neat) 2958 (s), 2905 (m), 2865 (m), 2270 (vs), 1449 (m), 1414 (m), 1368 (m), 1350 (m), 1247 (s), 1179 (m), 1129 (m), 1045 (m), 1016 (s), 953 (m), 874 (m), 847 (m), 825 (s), 780 (m), 660 (m) cm^{-1}.

Dianiline derivative: mp 278−280 °C (lit. mp 230−231 °C);[8] ^1H NMR (400 MHz, DMSO-d_6) δ (ppm) 8.49 (s, 2H), 7.35 (d, J = 7.89 Hz, 4H), 7.17 (dd, J_1 = 7.89 Hz, J_2 = 7.33 Hz, 4H), 6.84 (t, J = 7.33 Hz, 2H), 6.08 (d, 2H), 3.41 (m, 2H), 1.96 (m, 2H), 1.63 (m, 2H), 1.24 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ (ppm) 155.07, 140.47, 128.54, 120.90, 117.62, 52.48, 32.89, 24.34; IR (KBr) 3369 (m), 3301 (w), 3289 (w), 3178 (w), 3036 (w), 2941 (w), 2851 (w), 1647 (vs), 1596 (s), 1565 (vs), 1499 (m), 1443 (m), 1316 (m), 1258 (w), 1230 (w), 756 (m), 696 (m), 516 (w) cm^{-1}.

Poly(1,2-diisocyanatodecane). In a drybox, an oven-dried 25 mL Schlenk tube with a magnetic stirbar was charged with 2.6 mg (1.14 × 10^{-2} mmol) of $CpTiCl_2NMe_2$. THF (0.500 mL) was added, and the mixture was stirred until all of the catalyst had dissolved. Then 0.534 g (2.38 mmol, M/I = 209) of 1,2-diisocyanatodecane was added. The color of the solution changed from red-orange to orange. After 40 h (less time is required for lower monomer to initiator ratios), the solution was viscous, so this was dissolved in 20 mL of a 10% $CH_3OH/CHCl_3$ (v/v) solution. The solution was poured into 150 mL of vigorously stirred CH_3OH, and a white preciptate formed. The precipitate was isolated using a centrifuge. The oily solid was dissolved in 25 mL of benzene and transferred to a 25 mL round-bottom flask. The flask was attached to a vacuum line and immersed in a liquid nitrogen bath. After the solution was completely frozen, the flask was placed under vacuum, and the liquid nitrogen bath was removed. After all of the benzene had sublimed, a foamy, white solid remained. Yield 0.463 g (87%); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) [4.21 (br), 3.90 (br), 3.49 (br)] total = 3H, [1.98 (br), 1.49 (br)] total = 2H, 1.18 (br, 12H), 0.80 (br, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 149.3, 148.7, 52.7 (br), 46.6 (br), 31.6, 31.7 (br), 29.0 (br), 24.2 (br), 22.4, 13.8; IR (thin film) 2955 (m), 2925 (s), 2855 (m), 1778 (vs), 1698 (vs), 1466 (w), 1360 (m), 1246 (s), 1202 (s), 1094 (w), 725 (w), 693 (w) cm^{-1}. Anal. Calcd for $(C_{12}H_{20}N_2O_2)_n$: C, 64.26; H, 8.99; N, 12.49. Found: C, 63.78; H, 8.99; N, 12.53.

Poly(1,2-diisocyanatopropane). The same procedure used for the synthesis of poly(1,2-diisocyanatodecane) was followed (polymerization time = 24 h). [Note: These polymerizations are highly exothermic! If small amounts of solvent are to be used, then during the addition of the monomer the flask should be kept in an ice bath; otherwise the solution will get very hot, the solvent and monomer will reflux, and the solution will foam vigorously.] To isolate and purify the polymer, the solid polymerization mixture was dissolved in hot DMSO, and a large amount of CH_3OH was added. A white precipitate formed which was isolated by filtration, and volatile materials were removed under vacuum. The amounts of reagents used were 11.9 mg (5.22 × 10^{-2} mmol) of $CpTiCl_2NMe_2$, 1.00 mL of THF, and 0.547 g (4.34 mmol, M/I = 83) of 1,2-diisocyanatopropane. Yield 0.505 g (92%) of a white solid, TGA (onset temperature) = 320 °C (lit. mp 287 °C);[8] ^1H NMR (400 MHz, DMSO-d_6) δ (ppm) 4.27 (br, 1H), 3.96 (br, 1H), 3.43 (br, 1H), 1.30 (br, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6) δ (ppm) 148.7 (br), 49 (br, 2 maxima), 18.1 (br); IR (KBr pellet) 2981 (m), 2937 (w), 2910 (w), 1773 (vs), 1700 (vs), 1477 (m), 1387 (s), 1342 (s), 1252 (s), 1202 (s), 1124 (m), 1095 (m), 998 (w), 943 (m), 739 (m), 689 (m) cm^{-1}. Anal. Calcd for $(C_5H_6N_2O_2)_n$: C, 47.62; H, 4.80; N, 22.21. Found: C, 45.63; H, 5.12; N, 21.22.

Poly(*cis*-1,2-diisocyanatocyclohexane). The same procedure used for the synthesis and isolation of poly(1,2-diisocyanatodecane) was followed (polymerization time = 24 h). The amounts of reagents used were 21.5 mg (9.43 × 10^{-2} mmol) of $CpTiCl_2NMe_2$, 0.100 mL of THF, and 0.499 g (3.00 mmol, M/I = 32) of *cis*-1,2-diisocyanatocyclohexane. Yield 0.411 g (82%) of a white solid, TGA (onset temperature) = 300 °C (lit. mp 303 °C);[8] ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 3.5, 2.25, 2.25, 2.05, 1.8, 1.25 (all broad signals); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 150.5, 149 (2-line signal), 60.7 (multiline signal), 29.37, 26.85, 23.70; IR (thin film) 2985 (m), 2941 (s), 2865 (m), 1771 (vs), 1698 (vs), 1448 (m), 1329 (s), 1238 (s), 1213 (m), 1150 (m), 1132 (m), 1108 (m), 1078 (m), 1047 (m), 937 (w), 735 (w), 686 (m), 632 (w) cm^{-1}. Anal. Calcd for $(C_8H_{10}N_2O_2)_n$: C, 57.82; H, 6.07; N, 16.86. Found: C, 56.84; H, 6.18; N, 16.66.

Poly(1,2-diisocyanatoethane). Immediately upon distillation, 1,2-diisocyanatoethane began to polymerize spontaneously, as evidenced by the formation of copious amounts of white precipitate in the clear, liquid monomer. This process continued for about 12 h until a solid white mass remained. This material was insoluble in boiling DMSO and difficult to break apart or grind, so no characterization was attempted.

Poly(1,3-diisocyanatopropane). The same procedure used for the synthesis of poly(1,2-diisocyanatodecane) was followed. As the polymerization proceeded, the color of the solution changed from orange to yellow, and a precipitate formed. The solution never became viscous. After 24 h, CH_3OH (20 mL) was added, and the white precipitate was isolated by filtration. Volatile materials were removed under vacuum. This solid was insoluble in hot DMSO, THF, or $CHCl_3$, so no further purification was possible. The amounts of reagents used were 9.9 mg (4.34 × 10^{-2} mmol) of $CpTiCl_2NMe_2$, 1.00 mL of THF, and 0.438 g (3.47 mmol, M/I = 80) of 1,3-diisocyanatopropane. Yield 0.175 g (40%), TGA (onset temperature) = 275 °C (lit. mp 338 °C);[8] IR (KBr pellet) 2968 (m), 2909 (w), 2877 (w), 1718 (vs), 1685 (vs), 1478 (s), 1411 (s), 1315 (s), 1267 (s), 1196 (s), 1148 (s), 1099 (s), 1041 (w), 945 (w), 776 (m), 670 (m), 505 (w) cm^{-1}.

Poly(1,4-diisocyanatobutane). The same procedure used for the synthesis of poly(1,2-diisocyanatodecane) was followed. As the polymerization proceeded, the color of the solution changed from orange to yellow. After 24 h, the solution had become a gel. [Note: when smaller amounts of solvent are used in the polymerization, a hard, unbreakable, clear solid is formed, which prevents isolation or purification of the polymer.] CH_3OH (20 mL) was added, and the gel was broken apart using a spatula. The mixture was stirred until all of the material had lost all of its color. The solid was isolated by filtation, and volatile materials were removed under vacuum. The resulting material was insoluble in hot DMSO, THF, $CHCl_3$, phenol, or dimethyl carbonate, so no further purification was possible. The amounts of reagents used were 12.0 mg (5.26 × 10^{-2} mmol) of $CpTiCl_2NMe_2$, 2.50 mL of toluene, and 0.538 g (3.84 mmol, M/I = 73) of 1,4-diisocyanatobutane. Yield 0.175 g (40%); TGA (onset temperature) = 275 °C (lit. mp > 350 °C);[10] IR (KBr pellet) 2940 (m), 2864 (w), 1700 (very broad, s), 1560 (w), 1543 (w), 1459 (m), 1400 (m), 1340 (m), 1260 (m), 1235 (s), 1136 (s), 1078 (m), 1021 (m), 967 (s), 869 (w), 765 (w), 647 (w) cm^{-1}.

Block Copolymerization/Cyclopolymerization of *n*-Hexyl Isocyanate with 1,2-Diisocyanatopropane. To a 10 mL Schlenk flask with a magnetic stirbar were added 19.3 mg (8.47 × 10^{-2} mmol) of $CpTiCl_2NMe_2$ and 0.10 mL of THF. After all of the catalyst had dissolved, 0.600 mL (0.519 g, 4.08 mmol) of *n*-hexyl isocyanate was added. The solution was stirred, and after 24 h it was an orange solid. Of this solid, 20.3 mg was removed for GPC analysis. GPC (THF): M_n = 7280, PDI = 1.11. The remaining solid was added to 1.00 mL of rapidly stirring THF. Immediately after all the polymer had dissolved, 0.557 g (4.42 mmol) of 1,2-diisocyanatopropane was added. Over the next 10 min, the viscosity of the solution increased until it gelled. The polymerization was left overnight. The next day, the solid was dissolved in 10 mL of 5% (v/v) CH_3OH in $CHCl_3$, and this solution was poured into stirring CH_3OH. A white solid precipitated which was collected by filtration, and volatile materials were removed under vacuum. The resulting solid was very soluble in $CHCl_3$ and CH_2Cl_2, somewhat soluble in THF, and insoluble in hexane and CH_3OH. Yield 0.954 g (90%); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 4.30 (br), 3.93−3.75 (br, 4 maxima), 3.45 (br), 1.91 (br), 1.56 (br), 1.40 (br), 1.25 (br), 0.84 (br); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 156.66, 149.32, 148.58, 48.44 (sharp signal overlapping a broad signal), 31.38, 28.30, 26.11, 22.43, 18.00 (br), 13.83; IR (thin film, $CHCl_3$) 2956 (s), 2930 (s), 2858 (m), 1770 (vs), 1694 (vs), 1462 (m), 1383 (sh), 1347 (s), 1284 (sh), 1247 (s), 1205 (s), 1183 (sh), 1123 (w), 1094 (m), 1026 (w), 999 (w), 942 (w), 890 (w), 733 (m) cm^{-1}. Anal. Calcd for $[(C_7H_{13}NO)_1(C_5H_6N_2O_2)_{1.13}]$: C, 56.35; H, 7.40; N, 16.92. Found: C, 55.31; H, 7.01; N, 17.27.

Block Copolymerization/Cyclopolymerization of *n*-Hexyl Isocyanate with 1,2-Diisocyanatodecane. The same procedure employed for the block copolymerization/cyclopolymerization of *n*-hexyl isocyanate with 1,2-diisocyanatopropane was used. The amounts of reagents used were 21.3 mg (9.34×10^{-2} mmol) of $CpTiCl_2NMe_2$ and 0.600 mL (0.519 g, 4.08 mmol) of *n*-hexyl isocyanate (of the resulting solid, 21.8 mg was removed for GPC analysis; GPC (THF): $M_n = 6790$, PDI = 1.09), 0.500 mL of THF, and 0.308 g (1.37 mmol) of 1,2-diisocyanatodecane. Yield 0.627 g (76%); GPC (THF) $M_n = 9960$, PDI = 1.24; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 4.2−3.0 (v br), 2.2−1.5 (v br), 1.0−1.5 (br), 0.8−1.0 (br); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 156.71, 149.0, 53 (br), 48.50, 46.6 (br), 31.76, 31.42, 29.15, 28.35, 26.15, 25 (br), 22.59, 22.47, 14.00, 13.86; IR (thin film, $CHCl_3$) 2956 (s), 2925 (s), 2857 (s), 1770 (s), 1698 (vs), 1538 (w), 1463 (m), 1348 (s), 1296 (m), 1245 (m), 1182 (s), 1093 (m), 999 (w), 890 (w), 787 (w), 756 (w), 730 (w) cm^{-1}. Anal. Calcd for $[(C_7H_{13}NO)_{2.85}(C_{12}H_{20}N_2O_2)_1]$: C, 65.40; H, 9.80; N, 11.58. Found: C, 65.41; H, 9.49; N, 11.73.

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References and Notes

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(2) University of Massachusetts, Amherst.
(3) Butler, G. B.; Bunch, R. L. *J. Am. Chem. Soc.* **1949**, *71*, 3120.
(4) Butler, G. B.; Angelo, R. J. *J. Am. Chem. Soc.* **1957**, *79*, 3128.
(5) Butler, G. B. *Cyclopolymerization and Cyclocopolymerization*; Marcel Dekker: New York, 1992; Chapter 12.
(6) Miller, W. L.; Black, W. B. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1962**, *3*(2), 345.
(7) Beaman, R. G. U.S. Patent 3,048,566, 1962 (Aug 7).
(8) King, C. *J. Am. Chem. Soc.* **1964**, *86*, 437.
(9) Shashoua, V. E.; Sweeny, W.; Tietz, R. *J. Am. Chem. Soc.* **1960**, *82*, 866.
(10) Iwakura, Y.; Uno, K.; Ichikawa, K. *J. Polym. Sci., Part A: Polym. Chem.* **1964**, *2*, 3387.
(11) Corfield, G. C.; Crawshaw, A. *J. Chem. Soc., Chem. Commun.* **1966**, 85.
(12) Oku, A.; Shono, T.; Oda, R. *Makromol. Chem.* **1967**, *100*, 224.
(13) Butler, G. B.; Corfield, G. C. *J. Macromol. Sci., Macromol. Chem.* **1971**, *5*, 37.
(14) (a) Overberger, C. G.; Ozaki, S.; Mukamal, H. *J. Polym. Sci., Polym. Lett. Ed.* **1964**, *2*, 627. (b) Schulz, R. C.; Stenner, R. *Makromol. Chem.* **1964**, *57*, 202.
(15) (a) Patten, T. E.; Novak, B. M. *J. Am. Chem. Soc.* **1991**, *113*, 5065. (b) Patten, T. E.; Novak, B. M. *J. Am. Chem. Soc.* **1996**, *118*, 1906.
(16) Hoff, S. M.; Novak, B. M. *Macromolecules* **1993**, *26*, 4067.
(17) (a) Rodriguez-Parada, J. M.; Duran, R.; Wegner, G. *Macromolecules* **1989**, *22*, 2507. (b) Ballauff, M.; Schmidt, G. F. *Mol. Cryst. Liq. Cryst.* **1987**, *147*, 163. (c) Wenzel, M.; Ballauff, M.; Wegner, G. *Makromol. Chem.* **1987**, *188*, 2865.
(18) Quirk, R. P.; Lee, B. *Polym. Int.* **1992**, *27*, 359.
(19) Spontaneous polymerization may be the result of trace amounts of water or other nucleophiles in the monomer sample. To date, we do not know the source of initiation.
(20) Novak, B. M.; Jones, N., manuscript in preparation.
(21) Durairaj, B.; Dimcock, A. W.; Samulski, E. T.; Shaw, M. T. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 3211.
(22) Lifson, S.; Felder, C.; Green, M. M. *Macromolecules* **1992**, *25*, 4142.
(23) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper and Row: New York, 1987; Chapter 2.
(24) Aharoni, S. M. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1303.
(25) Green, M. M.; Peterson, N. C.; Sato, T.; Teramoto, A.; Cook, R.; Lifson, S. *Science*, **1995**, *268*, 1860.
(26) Iwakura, Y.; Uno, K.; Kobayashi, N. *J. Polym. Sci., Part A-1: Polym. Chem.* **1968**, *6*, 1087.
(27) Durairaj, B.; Dimcock, A. W.; Samulski, E. T.; Shaw, M. T. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 3211.
(28) Green, M. M.; Reidy, M. P.; Johnson, R. J.; Darling, G.; O'Leary, D. J.; Wilson, G. *J. Am. Chem. Soc.* **1988**, *111*, 6452.
(29) Allcock, H. R.; Lampe, F. W. *Contemporary Polymer Chemistry*; Prentice-Hall: Englewood Cliffs, NJ, 1990; pp 90, 123 and references therein.
(30) Ute, K.; Asai, T.; Fukunishi, Y.; Hatada, K. *Polym. J. (Tokyo)* **1995**, *27*, 445.
(31) (a) Godfrey, R. A; Miller, G. W. *J. Polym. Sci., Part A-1: Polym. Chem.* **1969**, *7*, 2387. (b) Baker, W. P. U.S. Patent 3,225,119, 1965.
(32) (a) Furukawa, J.; Yamashita, S.; Maruhashi, M.; Harada, K. *Makromol. Chem.* **1965**, *85*, 80. (b) Harada, K.; Deguchi, D.; Furukawa, J.; Yamashita, S. *Makromol. Chem.* **1970**, *132*, 281. (c) Harada, K.; Furukawa, J.; Yamashita, S. *Makromol. Chem.* **1971**, *131*, 185. (d) Raes, M. C.; Karabinos, J. V.; Dietrich, H. J. *J. Polym. Sci., Part A-1: Polym. Chem.* **1968**, *6*, 1067. (e) Odian, G.; Hiraoka, L. S. *J. Polym. Sci., Part A-1: Polym. Chem.* **1970**, *8*, 1309. (f) Odian, G.; Hiraoka, L. S. *J. Macromol. Sci., Macromol. Chem.* **1972**, *A6*, 109.
(33) Kitahama, Y.; Ohama, H.; Kobayashi, H. *J. Polym. Sci., Part A-1: Polym. Chem.* **1969**, *7*, 935.

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