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Synthesis and Characterization of Wormlike Three-Arm Poly(*n*-hexyl isocyanate) Star Polymers

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ABSTRACT: We have previously reported the use of titanium alkoxide complexes as initiators for the living polymerization of isocyanates. In this paper, we present the synthesis of a trimetallic initiator, **2**, comprised of three titanium alkoxides connected to a central organic core and the use of this catalyst to form three-arm star polymers which contain rigid polyisocyanate arms. Kinetic and molecular weight experiments confirm that the trimetallic complex **2**, like its monometallic analogue, **6**, initiates the living polymerization of *n*-hexyl isocyanate and that the three-arm stars obtained from **2** are completely symmetrical. The number-average molecular weight of polymer obtained from **2** increases linearly with the monomer-to-catalyst ratio used, which indicates a lack of chain transfer during polymerization. A comparison of the rates of polymerization of *n*-hexyl isocyanate by **2** and **6** at fixed initial monomer and titanium concentrations ($k_2 = (3.99 \pm 0.2) \times 10^{-3}$ M min^{-1}, $k_6 = (3.84 \pm 0.1) \times 10^{-3}$ M min^{-1}) demonstrates that all three titanium centers in **2** are active and propagate independently of one another. The solution properties of these new three-arm star polymers were examined through tandem GPC/light scattering and solution viscometry experiments. Light scattering shows that there is a 55% reduction in the mean-square radius of gyration ($g = \langle R_G{}^2\rangle_{\text{star}}/\langle R_G{}^2\rangle_{\text{linear}} = 0.45 \pm 0.05$) of the three-arm star polyisocyanate from that of a linear polyisocyanate of the same molecular weight. The experimental value of *g* approaches the rod limit of *g* that indicates that the arms of the three-arm star can be construed as stiff, wormlike chains. Additionally, there is a 28% reduction in the intrinsic viscosity of three-arm polyisocyanate star from that of its linear equivalent. Finally, a 30% w/w solution of three-arm star polyisocyanate displays a nematic, lyotropic liquid crystalline mesophase.

Introduction

Multiarm star polymers have been the subject of a great deal of interest for the past few decades, with considerable attention given to the dilute solution properties of these materials.[1−3] Star polymers with up to 270 arms have been successfully produced.[4] Synthesis of these materials has been primarily through the addition of *p*-divinylbenzene or chlorosilanes to anionically polymerized styrene, butadiene, or isoprene, followed by fractionation.[1] Studies[1] on the properties of these macromolecules have included static light scattering, ultracentrifugation sedimentation, dilute solution viscometry, small-angle neutron scattering, rheometry, Monte Carlo and molecular dynamic simulations, and dynamic light scattering. However, much less is known regarding the properties of star polymers containing rodlike segments. Thus, we have been highly interested in developing star polymers that incorporate rigid, helical polyisocyanate arms. These types of polymers should show different dilute solution behavior than typical Gaussian coil star polymers due to the stiffness of the polymer arms (vide infra).[5−8]

Several researchers have been interested in the development of rodlike star polymers.[9−18] Recently, Mathias has synthesized a four-arm polyaramid star via a palladium-catalyzed carbonylation−condensation route.[9,10] The four-way directionality was enforced through use of a rigid, tetrafunctional adamantane core. However, solution studies of these polymers was hampered by the low solubility and molecular weight of the resultant polymer.

Much of the remaining work has focused on the formation of rodlike, helical polypeptide stars.[11−18] Branching was achieved through ring-opening polymerization of the *N*-carboxy anhydride of the corresponding peptide by polyamine initiators. However, due to incomplete consumption of the initiator, use of this synthetic technique produced polymers, which were nonsymmetric and polydisperse. Additionally, solution studies were complicated by aggregation.[12−15]

It is evident the main factor that has prevented a thorough investigation of the solution properties of rigid, multiarm star polymers has been the lack of well-controlled synthetic methodology. The living nature of titanium(IV) initiators toward the polymerization of *n*-hexyl isocyanate should provide excellent control over the architecture of multiarm star polymers. Polyisocyanates are a class of macromolecules which exhibit rodlike-to-wormlike solution characteristics,[19] with persistence lengths between 200 and 400 Å.[20] Additionally, they display a helical conformation in solution and the solid state,[21] chiral optical properties,[22] and liquid crystalline properties.[23] We have previously reported the use of $CpTiCl_2(OR)$ (Cp = η^5-cyclopentadienide), **1** (where OR′ can be a 1°, 2°, or 3° alkoxide), as initiators for the living polymerization of alkyl isocyanates at room temperature.[24−26] Initiation is proposed to occur through precoordination of the isocyanate to the titanium metal center, followed by migratory insertion of the isocyanate into the titanium alkoxide bond to form the propagating titanium amidate species (Scheme 1).

In this paper, we present a simple modification of the catalyst to include not one, but three, titanium alkoxide groups attached to a central organic core, **2** (Scheme 2). Previously, this methodology was successfully employed to synthesize bimetallic titanium initiators, which pro-

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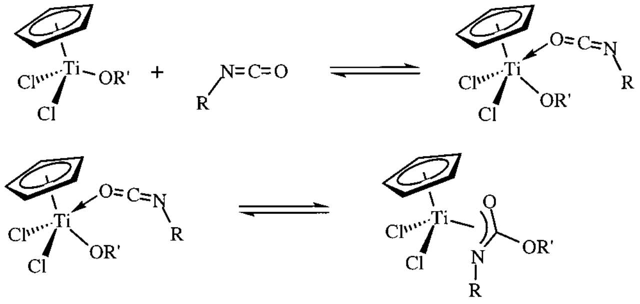
Scheme 1. Proposed Mechanism for the Polymerization of Isocyanates by Titanium(IV) Alkoxides



duced "once-broken" worms and triblock copolymers, respectively, containing rigid, polyisocyanate segments.[27] Use of the trimetallic catalyst, **2**, gives rise to well-defined three-arm star polyisocyanates.

Experimental Section

All manipulations involving air- and moisture-sensitive compounds were carried out under an argon atmosphere using standard Schlenk techniques. Solids and monomers were transferred in an argon- or nitrogen-filled Vacuum Atmospheres Inc. HE-432 drybox equipped with a HE 493 Dry Train or in a Braun Labmaster 100 drybox equipped with a Labmaster MB130 B-G inert gas system and an integrated SPS water−oxygen analyzer.

^{1}H and ^{13}C {^{1}H} NMR spectra were recorded on superconducting Fourier transform instruments maintained in the UC equipped with Cryomagnets, Inc., or Oxford/Spectrospin magnets. ^{13}C {^{1}H} NMR spectra were measured at 100 or 150 MHz on the UCB spectrometers. All NMR spectra were run in $CDCl_3$ unless otherwise indicated. Infrared spectra were obtained using a Perkin-Elmer 1600 series FTIR spectrometer and are uncalibrated. Unless otherwise indicated, solvents were removed with the aid of a rotary evaporator. $MgSO_4$ was used as a drying agent.

Gel permeation chromatography (GPC) was performed on a Hewlett/Packard 1050 series liquid chromatograph pump equipped with a HP model 1047 refractive index detector and HP model 3396A integrator. Separations were effected by 10^5, 10^4, 10^3, and 500 Å Waters Ultrastyragel columns run in series at room temperature and a flow rate of 1 mL/min. Tandem GPC/light scattering experiments were performed using a Wyatt Technology Dawn DSP model F 18-angle photometer utilizing THF as an eluent. Measurements of $d\eta/dc$ were performed using a Chromatics KMX-16 refractometer. Solution viscometry measurements were made with a Schött Geräte AVS 360 automated Ubbelohde viscometer with a thermostated water bath. Detailed procedures for polymerization kinetics, optical microscopy, solution viscometry, and tandem GPC/light scattering can be found in the Supporting Information.

Unless specifically noted, starting materials were obtained from commercial sources (Aldrich, unless otherwise noted) and used without additional purification. Tetrahydrofuran (THF), toluene, hexane, diethyl ether, d_8-THF, and d_6-benzene were distilled from sodium/benzophenone. Dichloromethane, triethylamine, and *n*-hexyl isocyanate was vacuum transferred from CaH_2 immediately before use. η^5-Cyclopentadienyltrichlorotitanium, $CpTiCl_3$, was synthesized by the modified method of Gorsich[28] devised by Patten and Novak.[26] Triethyl-*cis,cis*-1,3,5-cyclohexane tricarboxylate, **4**, was synthesized by the method of Nielsen.[29] *cis,cis*-1,3,5-Tris(hydroxymethyl)cyclohexane, **5**, was synthesized by the method of Galik.[30]

Trimetallic Catalyst, 2. To a solution of 1.2398 g (5.653×10^{-3} mol) of $CpTiCl_3$ in 40 mL of THF was added a solution of 0.3126 g (1.793×10^{-3} mol) of **7** and 1.40 mL (1.00×10^{-2} mol) of triethylamine in 20 mL of THF dropwise over 0.5 h. The reaction was stirred at room temperature 1 h after the addition was complete, and then the reaction was filtered through a Schlenk frit. The volatiles were removed in vacuo to yield an oily yellow solid. The solid was dissolved in a mixture of 20 mL of THF and 40 mL of toluene, and the solution was concentrated in vacuo until approximately half the original volume remained. The solution was cooled to 0 °C, and the resultant fine yellow precipitate was collected by filtration onto a medium Schlenk frit. The solid was then crystallized by diffusion of 20 mL of ethyl ether in a solution of the solid in 20 mL of THF at −40 °C over 3 days to yield 0.4701 g (36%) of yellow crystals. ^{1}H NMR (500 MHz, d_8-THF): δ 0.84 (q, 3H, $J = 12.27$), 1.79 (b, 3H), 1.93 (d, 3H, $J = 12.01$), 4.61 (d, 6H, $J = 5.96$), 6.78 (s, 15H); ^{13}C {^{1}H} NMR (500 MHz, d_8-THF): δ 32.45, 41.24, 90.92, 120.64. IR (KBr): 3104 (m), 2925 (m), 2849 (m), 1772 (w), 1671 (w), 1436 (m), 1368 (w), 1333 (w), 1262 (w), 1233 (w), 1067 (s), 1015 (sh), 922 (w), 906 (w), 825 (s), 693 (m), 693 (m), 664 (m), 583 (w), 528 (w) cm^{-1}. Anal. Calcd for $C_{24}H_{30}Cl_6O_3Ti_3$: C, 39.88; H, 4.18. Found: C, 40.22; H, 4.18.

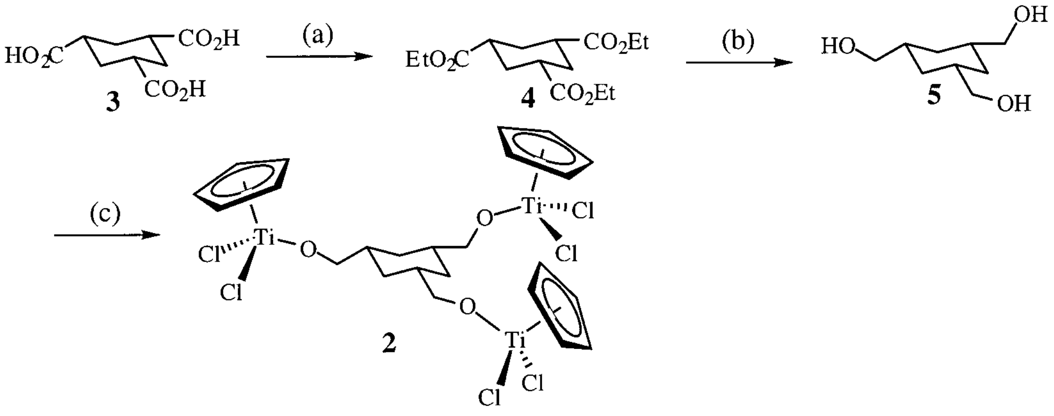
Dichloro-η^5-cyclopentadienylcyclohexylmethoxytitanium, 6. A solution of 0.5252 g (2.395×10^{-3} mol) of $CpTiCl_3$ in 30 mL of THF was treated with a solution of 0.250 mL (2.03×10^{-3} mol) of cyclohexylmethanol and 0.600 g (4.30×10^{-3} mol) of triethylamine in 10 mL of THF over 10 min. A white precipitate formed as the addition progressed. The reaction mixture was stirred for 1.5 h and then filtered, and the volatiles were removed in vacuo to give 0.5624 g (93%) of a orange-yellow solid. The product was crystallized from toluene/hexanes to give 0.4677 g (77%) of yellow crystals. Alternatively, the product could be sublimed at 70 °C (0.001 Torr). ^{1}H NMR (200 MHz, d_6-benzene): δ 0.83 (m, 2H), 2.06 (m, 2H), 1.32 (m, 1H), 1.58 (m, 2H), 3.93 (d, 2H, $J = 6.03$), 6.06 (s, 5H). ^{13}C {^{1}H} NMR (500 MHz, d_6-benzene): δ 25.92, 26.50, 29.38, 41.35, 90.86, 118.87. IR (KBr): 3105 (w), 2927 (m), 2844 (w), 1861 (w), 1772 (w), 1653 (w), 1437 (m), 1364 (m), 1263 (w), 1217 (w), 1178 (w), 1067 (s), 1017 (m), 894 (sh), 844 (sh), 821 (s), 672 (m), 589 (w), 556 (w) cm^{-1}. Anal. Calcd for $C_{12}H_{18}Cl_2OTi$: C, 48.52; H, 6.11. Found: C, 48.75; H, 6.06.

Typical Procedure for the Polymerization of *n*-Hexyl Isocyanate. Both *n*-hexyl isocyanate and dichloromethane were vacuum transferred from CaH_2. Use of *n*-hexyl isocyanate, which had been vacuum transferred and stored for longer than a day in a Schlenk storage tube, resulted in lower yields and wider molecular weight distributions. In the drybox, the catalyst was weighed into a 10 mL ampule, and a stir bar was added. The catalyst was then dissolved in dichloromethane measured with a syringe. With rapid stirring, a measured quantity of *n*-hexyl isocyanate was added via syringe, and a Schlenk line adapter was attached to the ampule. Typical monomer concentrations were 3.40 M and higher. The ampule was then removed from the drybox and frozen with liquid nitrogen, and the ampule was evacuated under dynamic vacuum. When the tube was completely evacuated, the stopcock was closed and the ampule sealed. The polymerization vessel was wrapped in aluminum foil to protect the catalyst end groups from ultraviolet light. When the polymerization was complete, the orange gel or solid was crushed with methanol to give a white solid. The resultant solid was then filtered or centrifuged. The solid was then redissolved in chloroform or THF, and the concentrated solution was added to a stirred flask of methanol. The precipitated white solid was then filtered or centrifuged. This procedure was repeated, and then the volatiles were removed in vacuo to give a powdery to waxy white solid.

Results and Discussion

Catalyst Synthesis. In designing an appropriate core for synthesis of our trimetallic catalyst, we were bound by a number of criteria. First, the catalyst had to be soluble in a noncoordinating solvent, since coordinating solvents such as tetrahydrofuran have a detrimental effect upon the polymerization of isocyanates. Second, good steric and electronic separation of the

Scheme 2. Synthesis of Trimetallic Catalyst, 2



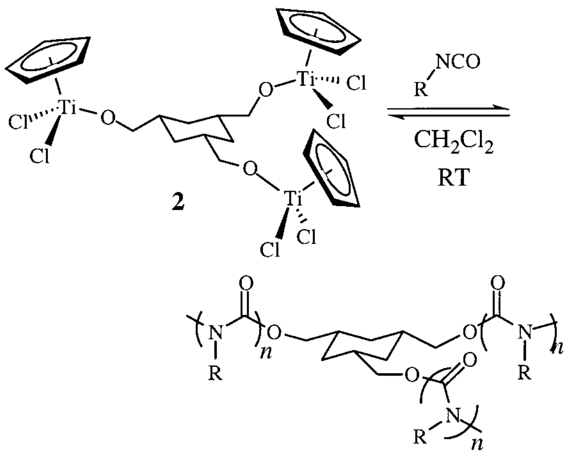
(a) EtOH, HCl (b) $LiAlH_4$ (c) $CpTiCl_3$, Et_3N

titanium centers was necessary to ensure that there would be no intramolecular chelation of one titanium center and no competition between the titanium centers for isocyanate, which would lead to incomplete initiation.

Thus, *cis,cis*-1,3,5-trihydroxymethylcyclohexane, **5**, can be synthesized in two steps starting from the commercially available *cis,cis*-1,3,5-cyclohexanetricarboxylic acid, **3**.[23,24] Esterification of **3** gives the ethyl ester, **4**,[29] in 56% yield. Subsequent hydrogenation of **4** with lithium aluminum hydride results in the desired triol, **5**,[30] in 27% yield. Addition of **5** to 3 equiv of $CpTiCl_3$ in tetrahydrofuran in the presence of triethylamine produces the trimetallic catalyst, **2**, in 36% yield. The catalyst is soluble in dichloromethane, a good solvent for the polymerization of isocyanates.

The ^1H and ^{13}C $\{^1H\}$ NMR spectra of **2** show resonances of 4.63 and 90.92 ppm due to the methylene adjacent to the alkoxide group (Supporting Information). The downfield shifts are characteristic of the highly deshielding nature of the coordinating titanium metal.[31] A singlet at 6.78 and 120.64 ppm in the ^1H and ^{13}C-$\{^1H\}$ NMR, respectively, are typical of a cyclopentadienide ligand attached to a titanium metal center.[31]

Polymer Synthesis. Complex **2** polymerizes *n*-hexyl isocyanate (HIC) in dichloromethane at room temperature with yields ranging from 65 to 88%,[32] depending on the time elapsed before quenching the polymerization with methanol (eq 1). The degree of polymerization varies from 100 to 1400, with polydispersities ranging from 1.02 to 1.16,[32] as obtained from tandem GPC/light scattering (Supporting Information). The monomodal, narrow molecular weight distributions support the lack of other bimetallic or monometallic impurities during the polymerization.



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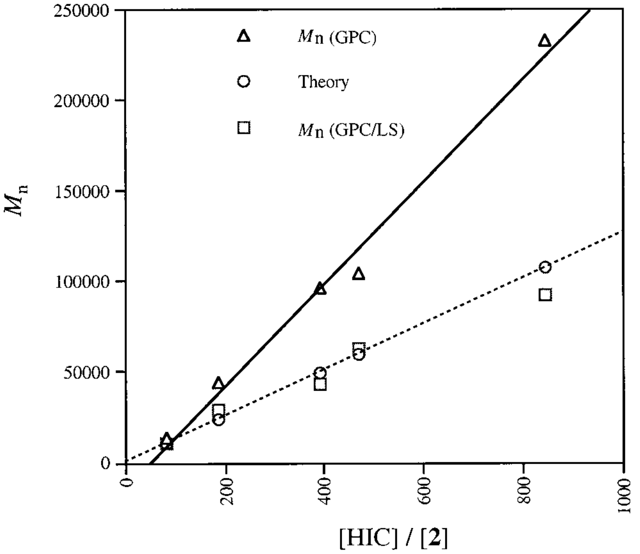


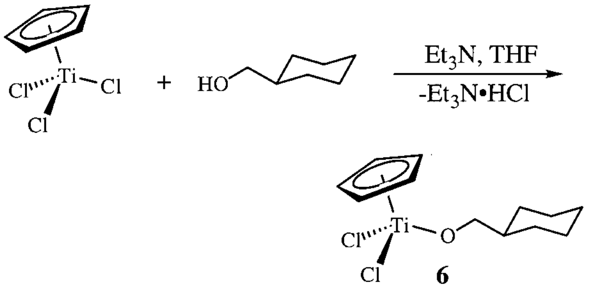
Figure 1. Molecular weight vs monomer-to-catalyst ratio for trimetallic catalyst, **2** (monomer-to-catalyst ratio corrected for the percent yield).

To determine the presence of chain transfer during polymerization, the number-average molecular weight, M_n, was measured as a function of the monomer-to-catalyst ratio used (Figure 1). The bottom dotted line in Figure 1 represents the calculated M_n that should be theoretically obtained from the monomer-to-catalyst ratio used. Since this is an equilibrium polymerization, the monomer-to-catalyst ratio was corrected for the polymer yield. As can be seen, the absolute M_n obtained from tandem GPC/light scattering increases linearly with the monomer-to-catalyst ratio used in the polymerization and concurs well with the theoretical molecular weight. Thus, we can conclude that there is no chain transfer during the polymerization. The upper line in Figure 1 represents linear increase in the relative M_n from GPC vs polystyrene standards as a function of the monomer-to-catalyst ratio used. As would be expected for a rigid chain polymer, there is a large inflation in molecular weight between that obtained via size exclusion chromatography vs polystyrene standards and the absolute molecular weight.[33]

Table 1. Weight-Average Molecular Weights, Intrinsic Viscosities, and Polydispersities of Three-Arm Star PHICs

sample no.	M_w	$[\eta]$ (dL g^{-1})	PDI
SIV124DD	12 000	0.2270	1.07
SIV119	31 000	0.6230	1.06
SIV205	44 300		1.02
SIV123	64 800	1.7544	1.03
SV18A	93 500		1.02
SIV125AA	102 300	3.0138	1.16
SIV147A	126 200	2.9455	1.09
SIV147B	177 000	4.6601	1.16

Kinetics of Polymerization. To verify the activity of all three centers in the trimetallic catalyst toward the polymerization, the rates of polymerization of HIC were studied using **2** and the analogous monometallic catalyst, **6**. Complex **6** may be synthesized by addition of cyclohexylmethanol to 1 equiv of $CpTiCl_3$ in the presence of triethylamine (eq 2). With **6** in hand, we then determined the relative initial rate of propagation for **2** and **6**.



6 (2)

The rate of disappearance of HIC was measured by IR kinetics at 25 °C at identical initial monomer concentrations for both **2** and **6** and so that the concentration of **6** was 3 times that of **2**. Under these conditions, the concentrations of titanium centers in the reactions initiated using **2** and **6** were identical. From the slope of a linear plot of $[HIC] - [HIC]_0$ vs time, pseudo-zero-order rate constants were determined for the polymerization of HIC by **2** and **6** (Supporting Information). The pseudo-zero-order rate constant for the trimetallic catalyst, **2**, $k_2 = (3.99 \pm 0.2) \times 10^{-3}$ M min^{-1}, is the same within experimental error as that for the monometallic catalyst, **6**, $k_6 = (3.84 \pm 0.1) \times 10^{-3}$ M min^{-1}. Hence, we conclude that all three titanium centers in **2** are active, and furthermore their activities are neither attenuated nor enhanced by the presence of the proximal titanium center.

On the basis of the polymerization kinetics, narrow polydispersities, and stoichiometric molecular weight control, we can conclude that the polymerization is living and that the polymers formed using **2** are symmetrical three-armed stars. We were next interested in the properties displayed by these new macromolecules. To study the solution behavior of these macromolecules, several samples of the three-arm star poly(*n*-hexyl isocyanate) (PHIC) of different molecular weights were synthesized using **2**. Additionally, linear samples of PHIC were synthesized using catalysts such as **6**. Tables 1 and 2 show the weight-average molecular weights, polydispersities, and intrinsic viscosities for the three-arm and linear PHICs.

Table 2. Molecular Weight, Intrinsic Viscosity, and Polydispersity for Linear PHIC's

sample no.	M_w	$[\eta]$ (dL g^{-1})	PDI
SIV89	10 750	0.1916	1.05
SIV85	28 700	0.7767	1.06
T129	25 000	0.9799	
SIV97	45 900	1.5743	1.12
T258	50 000	1.8124	
SIV93	60 450	1.9296	1.14
T386	71 000	2.6543	
T515	82 000	3.1625	
SIV98	120 500	3.5882	1.35

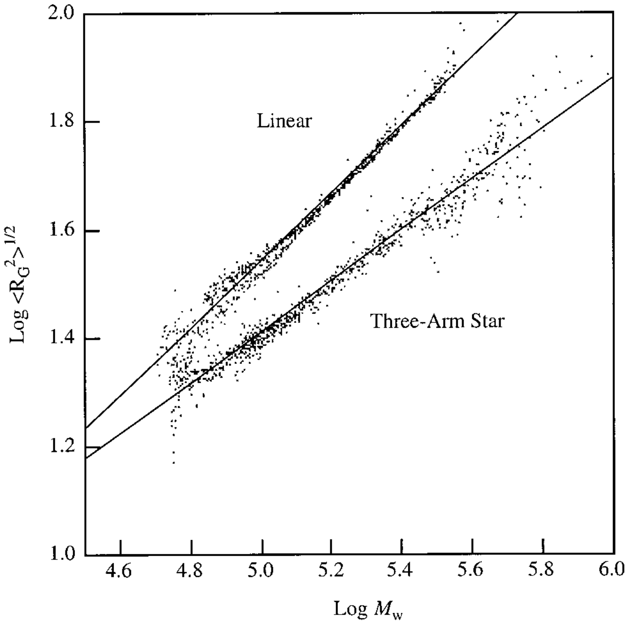


Figure 2. Logarithm of the root-mean-square radius of gyration vs the logarithm of the weight-average molecular weight of the linear and three-arm star PHIC (data obtained via tandem GPC/light scattering in THF).

Tandem GPC/Light Scattering. The weight-average molecular weights and polydispersities of the samples were measured by static light scattering in tandem with gel permeation chromatography on a Wyatt Technologies model F 18-angle laser photometer (Tables 1 and 2). Additionally, the radius of gyration as a function of the weight-average molecular weight was determined by tandem GPC/light scattering in THF for several samples in Tables 1 and 2. The logarithm of the root-mean-square radius of gyration for the combined data is plotted vs the logarithm of the molecular weight for both the three-arm star and the linear polyisocyanate (Figure 2). It is clear from Figure 2 that the three-arm star occupies a much smaller volume than a linear polymer of the same molecular weight.

The effect of branching on the molecular dimensions of a star polymer may be expressed as *g*, the ratio of the mean-square radius of gyration of the star and linear polymer at the same molecular weight:[6] $g = \langle R_G{}^2\rangle_{\text{branched}}/\langle R_G{}^2\rangle_{\text{linear}}$. To calculate *g*, the mean-square radius of gyration of the star and linear polymer were compared at the same molecular weight. When the polymers were of the same molecular weight, the mean-square radius of gyration of the three-arm star PHIC was divided by that of the linear polymer to give values of *g* at a given molecular weight; the remaining data points were discarded. Figure 3 shows *g* as a function of the degree of polymerization. Theoretically, we would expect *g* to increase with the degree of polymerization.[7,8,34] However, Figure 3 shows *g* to gradually decreases from a value of 0.50 ± 0.1 at a degree of

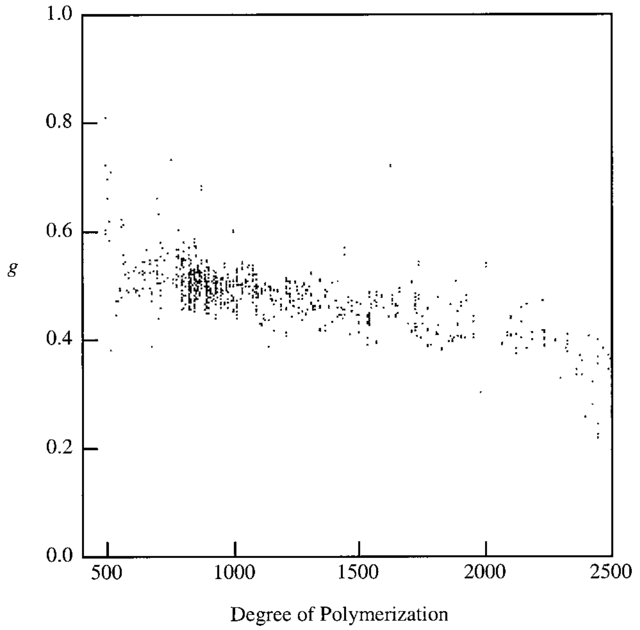


Figure 3. Values of *g* vs the degree of polymerization for linear and three-arm PHICs.

polymerization of 500 to a value of 0.40 ± 0.1 at a degree of polymerization of 2500, which corresponds to an average value of *g* of 0.45 ± 0.1. The deviation of the slope may be due to the narrow molecular weight range examined as well as the increased scatter in the radius of gyration at the lowest and highest degrees of polymerization, since these data points were determined at very low concentrations.

Values of *g* scale differently depending on the rigidity of the linear polymer and the arms of the star polymer. Thus, expressions may be derived for *g* at the rod and Gaussian coil limits, where *f* is the number of polymer arms:[6,7]

$$g_{\mathrm{Gaussian}} = (3f - 2)/f^2 \tag{3}$$

$$g_{\mathrm{rod}} = 4/f^2 \tag{4}$$

For a three-arm star, *g* is calculated to be 0.44 at the rod limit and 0.78 at the Gaussian coil limit. The average value of *g* of 0.45 for the three-arm polyisocyanate falls close to the rod limit of 0.44 calculated from Mansfield and Stockmayer's theory of wormlike stars.[7] Thus, the polymer arms may be construed as stiff, wormlike chains, as would be expected for rigid PHIC stars.

The magnitude of the decrease in the radius of gyration of the three-arm star polyisocyanate is best emphasized by comparison to multiarm Gaussian coil star polymers such as polystyrene. For example, a three-arm polystyrene star has a *g* of 0.79, while a four-arm polystyrene star has a *g* of 0.61 in a good solvent.[35] The same reduction in the radius of gyration is only achieved by a six-arm polystyrene star, which has a value of *g* of 0.45.[35]

Solution Viscometry. We next examined the effect of branching on chain dimensions through solution viscometry. The intrinsic viscosities of several samples of the three-arm star and linear PHIC were measured using an automated Ubbelohde viscometer in toluene at 25 °C (Tables 1 and 2). Linear fitting of the viscosity data (Supporting Information) gives Mark–Houwink constants for the three-arm star PHIC of $K = (5.17 \pm 0.05) \times 10^{-6}$ and $a = 1.14 \pm 0.05$. Similarly, values of *K* and *a* of $(3.09 \pm 0.06) \times 10^{-6}$ and 1.22 ± 0.1 were derived for the linear PHIC. These constants for linear PHIC are nearly identical to those found by Teramoto and Aharoni for linear PHIC in the same solvent and temperature ($K = 2.99 \times 10^{-6}$, $a = 1.20$).[36] The coefficient, *a*, for the three-arm star is similar to that of the linear polymer. This is to be expected because the arms of the star polyisocyanate and the linear polyisocyanate should have the same persistence length.

The effect of branching upon the intrinsic viscosity of a star polymer can be expressed as g', the ratio of the intrinsic viscosities of the branched polymer to that of its linear equivalent of the same molecular weight (eq 5):[6]

$$g' = [\eta]_{\mathrm{star}}/[\eta]_{\mathrm{linear}} \tag{5}$$

Values of g' as a function of the degree of polymerization were thus derived. Factor g' decreases from 0.78 at a degree of polymerization of 100 to 0.66 at a degree of polymerization of 1000. The apparent decrease in g' is a function of the variation in *a* for the linear and branched polyisocyanates; however, on the basis of chain stiffness, we would expect the lines to be parallel. Compensating for the error in *a*, g' is equal on average to approximately 0.72 ± 0.06, which corresponds to a 28% reduction in the intrinsic viscosity from that of the linear polymer. It is useful to compare this value of g' for a rigid-arm polymer to that of a Gaussian coil–arm polymer in a good solvent. Thus, a three-arm polystyrene star was found to have a value of g' of 0.84, which is significantly higher than that obtained for the three-arm polyisocyanate star.[35]

While theories for the mean-square radius of gyration of star polymers are relatively well-defined, the effect of branching upon the intrinsic viscosity is much less understood. The Flory–Fox relationship expresses the intrinsic viscosity as a function of the radius of gyration:[37]

$$[\eta] = 6^{3/2}\Phi_0\alpha_\eta^{\,3}[\langle R_G^{\,2}\rangle_0^{\,3/2}/M] \tag{6}$$

Thus, it is expected that g' should be equal to $g^{3/2}$, since Φ_0 and α_h are constants at a given molecular weight:

$$g' = [\eta]_{\mathrm{star}}/[\eta]_{\mathrm{linear}} = \langle R_G^{\,2}\rangle_{\mathrm{star}}^{\,3/2}/\langle R_G^{\,2}\rangle_{\mathrm{linear}}^{\,3/2} = g^{3/2} \tag{7}$$

In fact, however, this relationship has failed for several branched systems.[38] More recently, Zimm and Kilb have studied the intrinsic viscosity of branched polymers by the *spring and bead model*.[39] The *spring and bead model* defines a polymer as a chain of $(n + 1)$ segments or beads with a friction coefficient, ζ, joined together with a Hooke's law spring. Zimm and Kilb extended this model to derive an expression for the ratio of the intrinsic viscosity of branched and linear chains of the same number of segments or beads:

$$[\eta]_{\mathrm{star}}/[\eta]_{\mathrm{linear}} = (2/f)^{3/2}[0.390(f - 1) + 0.196]/0.586 \tag{8}$$

Through comparison of the numerical values of this expression and the factor *g*, they found that

$$g' = g^{1/2} \tag{9}$$

This expression has been found to hold true for a number of experimental polymers, and the authors propose that it should be valid for many different branched systems.[39]

In our system, because the intrinsic viscosity and tandem GPC/light scattering measurements were performed in different solvents, we may not directly compare the experimental values of g and g'. However, from eqs 4 and 5, values of g at the rod and Gaussian coil limits for a three-arm star may be calculated of 0.444 and 0.778, respectively. Using these limits of g, values of g' for the rod and Gaussian coil limits of 0.296 and 0.686, respectively, are calculated using eq 8. However, when eq 9 is used, the values of g' for the rod and Gaussian coil limits become 0.667 and 0.882. Given that the experimental value of g for the three-arm star PHIC falls close to the rod limit, g' would be expected to do the same. Clearly, the experimental value of g' of 0.72 is outside the range for g' calculated from eq 8. However, the experimental value of 0.72 approaches the rod limit of g' of 0.67 derived from eq 9. Thus, we conclude that Zimm and Kilb's[39] theory describes the relationship between the radius of gyration and intrinsic viscosity more accurately than does that derived from the Flory–Fox relationship.[37] However, this result should be viewed with caution due the inexact nature of the relationship between chain dimensions and the intrinsic viscosity.

Liquid Crystalline Properties. In 1979, Aharoni first observed that poly(alkyl isocyanates) such as PHIC would form lyotropic, nematic liquid crystals, in a variety of hydrocarbon and chlorinated solvents above concentrations of 15–35% v/v.[23,40] It was interesting to consider what the effect of branching would have on the nematic liquid crystalline state of poly(*n*-hexyl isocyanate). Would the branch point preclude alignment of the polymer rods or effect the type of morphology observed for the three-arm polyisocyanates? To answer these questions, the liquid crystalline state of the three-arm star PHIC was studied in toluene at room temperature.

Solutions of the three-arm star PHIC ($M_n = 43\,400$) and linear PHIC ($M_n = 53\,800$) were made in toluene at concentrations of 15, 20, 25, 30, and 35 wt %. The solutions were transferred into glass cells of 1.00 mm thickness and observed through cross-polarizers. Solutions of the linear PHIC displayed birefringence at 25% w/w and greater. No birefringence was observed for the three-arm star up to 25% w/w in toluene. However, solutions of the three-arm star PHIC displayed birefringence at 30% w/w and higher. The lack of birefringence of the three-arm star PHIC at 25% w/w would seem to indicate that the branch point necessitates a higher critical concentration in order to form the liquid crystalline state.

Polarizing micrographs of the linear and three-arm PHIC were taken of 30% and 35% w/w toluene solutions, respectively, between two glass slides. Figure 4 shows the textures of the linear and three-arm PHICs observed through cross-polarizers, after shearing between the two glass slides. Both the linear and three-arm star show a typical Schlieren texture with four intersecting disinclination lines, which is very characteristic of a nematic mesophase.[41] The fact that the three-arm star forms a nematic liquid crystal may be a function of the flexibility of carbamate bonds, which can allow rotation of one arm of the star to lie parallel to a second arm. In this way, a rodlike arrangement of the star polymer is possible at a high critical concentration.

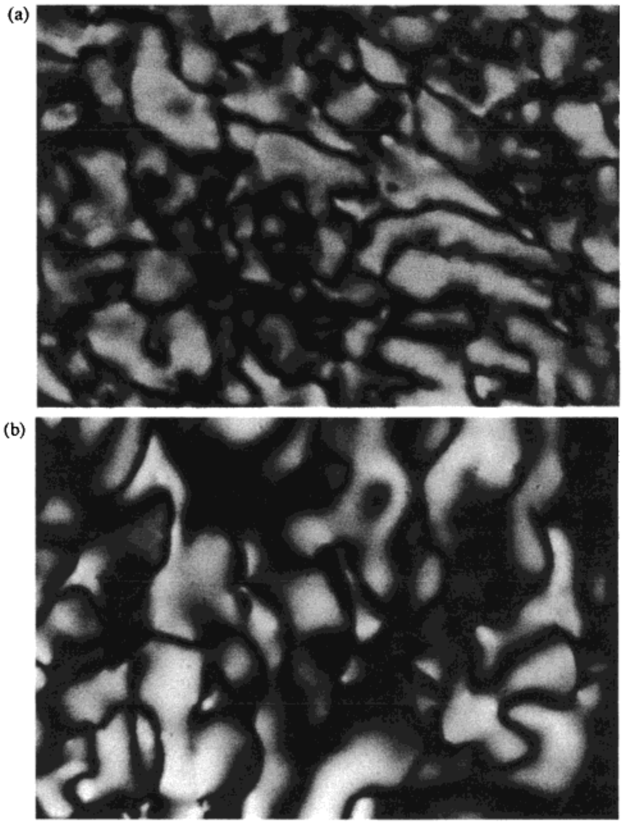


Figure 4. Cross-polarized optical micrograph of (a) linear PHIC, 30% w/w in toluene, and (b) three-arm PHIC, 35% w/w in toluene.

The sheared 35% w/w solution of the three-arm star was heated to 70 °C on a hot stage and observed between cross-polarizers. The Schlieren texture relaxed giving a nearly uniform anisotropic phase at 70 °C. The 30% w/w solution of the linear polymer was also heated to 70 °C. However, unlike the three-arm star, the texture of the linear polymer remained fairly stable up to this temperature. Additionally, the sheared 35% w/w solution of the three-arm star was allowed to stand at room temperature and was then observed between cross-polarizers. The same relaxation of the Schlieren texture that was seen on heating the solution was observed at room temperature, albeit at a slower rate.

Conclusions

We have been able to synthesize a trimetallic titanium(IV) alkoxide catalyst, **2**, which polymerizes *n*-hexyl isocyanate in a living manner to give three-arm polyisocyanates. Initial rate kinetics on **2** and an analogous monometallic catalyst, **6**, has shown that all three centers in the trimetallic catalysts are active toward the polymerization of *n*-hexyl isocyanate. Therefore, we can conclude that the three-arm stars formed by **2** are completely symmetrical and that the arms are of equal length.

Light scattering studies of the three-arm star and the linear polyisocyanates reveal that there is a 55% reduction in the mean-square radius of gyration from that of the linear polymer of the same molecular weight. This decrease is comparable to the change in the mean-square radius of gyration of a six-arm polystyrene star. Additionally, there is a 28% reduction in the intrinsic viscosity of three-arm polyisocyanate star from that of its linear equivalent.

A 30% w/w solution of three-arm star polyisocyanate was found to display a nematic, lyotropic liquid crystalline mesophase. While a linear PHIC was found to be birefringent at 25% w/w, a 25% w/w solution of the three-arm star of the same molecular weight was found to display no birefringence at all. This indicates that the branch point has a significant effect upon the liquid crystalline alignment of the rods in that it necessitates a higher critical concentration in order to form the liquid crystalline state.

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Supporting Information Available: Detailed procedures for polymerization kinetics, optical microscopy, solution viscometry, and tandem GPC/light scattering; ^{1}H and ^{13}C {^{1}H} NMR spectra of the trimetallic initiator, **2**; representative GPC trace of the three-arm star PHIC; pseudo-zero-order kinetic plots for the trimetallic initiators, **2** and **6**, respectively; and log−log plot of intrinsic viscosity vs M_w for linear and three-arm star PHIC samples. This material is available free of charge via the Internet at http://pubs.asc.org.

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