Polymerization of Ureidopyrimidinone-Functionalized Olefins by Using Late-Transition Metal Ziegler–Natta Catalysts: Synthesis of Thermoplastic Elastomeric Polyolefins**

Lee R. Rieth, Robert F. Eaton, and
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Many natural and synthetic polymers derive their unique functions and precise structures from hydrogen bonding. The double-helix conformation of DNA and the secondary structures of many proteins, both vital to the central mechanisms of living organisms, depend strongly upon the formation of specific hydrogen bonds. The amazing tensile strength and elasticity observed in spider silk results from strong intra- and intermolecular hydrogen bonds that stabilize the formation of helices and β-sheets.[1] Hydrogen bonding between polymer chains also dictates the mechanical properties of many synthetic polymers: the high tensile strength of aromatic polyamides[2] and the elastomeric properties of polyurethane block copolymers[3] arise from intermolecular hydrogen bonding.

The introduction of hydrogen bonding arrays into polyolefins is particularly attractive.[4] The nonpolar environment of the polyolefin matrix helps overcome the relative weakness of hydrogen bonds (compared to covalent bonds) and the entropic barrier to formation of hydrogen bond aggregates. Stadler et al. have shown that the hydrogen-bonding interactions of (4-carboxyphenyl)urazole moieties grafted onto polybutadiene significantly affect the properties of the bulk polymer due to the formation of a thermoreversible network.[5] This system relies on highly ordered urazole junction zones which phase separate from the amorphous polymer; the hydrogen-bonding interactions between urazole groups are, individually, fairly weak ($K_{\text{dimer}} < 10^2\,\text{M}^{-1}$ in chloroform for typical donor–acceptor dimers).[6]

Recent interest in the development of supramolecular polymers[7] has led to synthesis of complementary hydrogen bonding arrays with extremely high dimerization constants in nonpolar environments. Meijer, Sijbesma, and co-workers[8–10] and Zimmerman and Corbin[11] have developed heterocycles that dimerize strongly through an array of four hydrogen bonds arranged in a self-complementary donor-donor-acceptor-acceptor (DDAA) manner. For example, 2-ureido-4[1*H*]-pyrimidinones[12] structurally similar to the one pictured in Figure 1 exhibit the dimerization constant K_{dimer} of $6\times10^7\,\text{M}^{-1}$ (in chloroform) and $6\times10^8\,\text{M}^{-1}$ (in toluene) at 298 K.[9] Meijer, Sijbesma, and co-workers have demonstrated that telechelic oligomers with these 2-ureido-4[1*H*]-pyrimidinone endgroups self-assemble into supramolecular structures that behave like high molecular weight polymers;[8, 13–15] further stabilization by phase separation is not observed.[16]

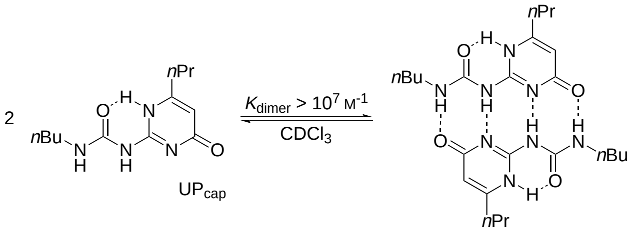

Figure 1. Quadruple hydrogen bonding of 2-ureido-4[1*H*]-pyrimidinones.

We are investigating the utility of 2-ureido-4[1*H*]-pyrimidinone derivatives as reversible crosslinks in polyolefin elastomers. Herein we report a simple method for randomly incorporating small percentages of olefinic 2-ureido-4[1*H*]-pyrimidinone (UP) derivatives within the main chain of amorphous polyolefins. The resulting pendant UP groups dimerize within the purified polymer matrix to form a reversible network,[8, 16] with properties strikingly different from those of comparable polyolefin homopolymers.

To synthesize these novel materials, we employ a coordination polymerization route utilizing catalyst precursor **1** (Figure 2), recently developed by Brookhart et al. for polymerization of α-olefins.[17–19] These catalysts undergo β-

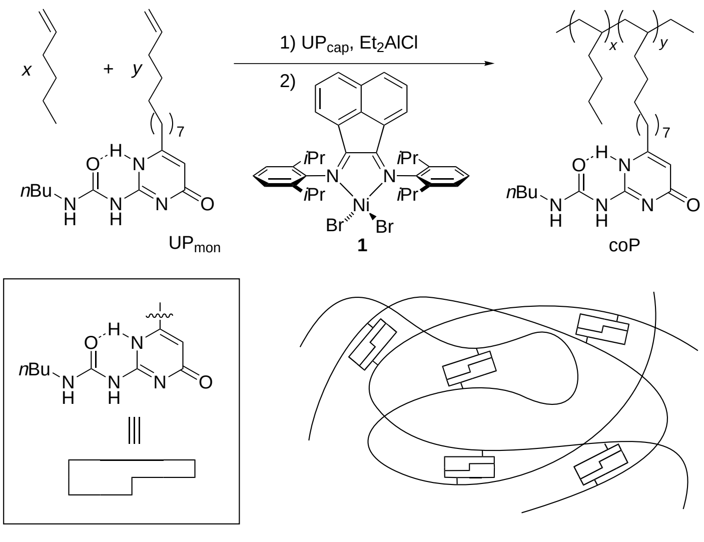

Figure 2. Synthesis and schematic drawing of 2-ureido-4[1*H*]-pyrimidinone-functionalized poly(1-hexene) (coP). The structure of the copolymer is more complicated than depicted due to chain-walking by the catalyst during polymerization, resulting in random branching in the main chain.

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hydride elimination followed by reinsertion (chain-walking) on a time scale faster than propagation, giving rise to unique, branched polyolefin architectures. Due to the low oxophilicity of nickel, they are also tolerant of functional Lewis basic groups, and are used here to copolymerize olefins with small amounts of UP_{mon} (typically 2%). Initial efforts have focused on 1-hexene as the primary comonomer. The relative rates of polymerization of 1-hexene and UP_{mon} are similar, ensuring that random copolymers are formed. Diethylaluminum chloride (Et_2AlCl) serves two purposes in this reaction. First, it activates the nickel catalyst precursor and serves as a weakly coordinating counteranion for the resultant cationic alkylnickel catalyst. Second, the aluminum reacts with UP derivatives, removing acidic hydrogens and protecting Lewis basic sites from reaction with the Ni center.[20] Initial efforts to copolymerize 1-hexene and UP_{mon} led to precipitation of the growing polymer during the reaction. We attribute this phenomenon to the ability of aluminum to coordinate more than one UP molecule, leading to formation of Al/UP clusters and an insoluble network. The presence of three equivalents of non-olefinic UP (UP_{cap}) during the polymerization prevents formation of an insoluble network and leads to a homogeneous solution throughout the reaction. Subsequent precipitation of the copolymer with acidic methanol displaces aluminum and returns the UP derivatives to their original state. UP_{cap} and aluminum remain in solution and are eliminated from the polymer.

To investigate the nature of the reaction between UP and the aluminum cocatalyst, UP_{cap} was stirred with Et_2AlCl overnight; the reaction was then quenched with HCl/H_2O. The resulting organic-soluble product, recovered in 85% yield, proved to be UP_{cap} (by ^1H NMR spectroscopy), thereby verifying that comonomer UP_{mon} returns to its original state after the acidic quench. In a similar experiment, the reaction is instead quenched with DCl/D_2O; ^1H NMR spectroscopy reveals a considerable decrease in the intensities of shifts of protons attached to the urea and pyrimidine nitrogen atoms. These sites, which pose the biggest threat to the activity of the Ni catalyst,[19] are apparently protected by aluminum during the polymerization.

NMR spectroscopy and gel permeation chromatography (GPC) studies provide evidence that UP is incorporated into the polymer and forms reversible crosslinks in solution. The proton NMR spectrum of the copolymer shows the same peaks above $\delta = 2.0$ found in the spectrum of UP_{mon} (in its H-bonded dimer form), except the olefin peaks have disappeared. This suggests that UP_{mon} has been incorporated into the polymer, and the incorporated UP groups are dimerizing (i.e. forming crosslinks). Furthermore, the GPC's UV detector (254 nm) generates a signal at the same elution volume as the RI-detected polymer, demonstrating that the chromophoric UP moiety must be covalently attached to the polymer backbone. Poly(1-hexene) homopolymer, made by homopolymerization of 1-hexene under the same conditions, shows no significant UV absorption. NMR and GPC studies also verify the complete elimination of UP_{cap} from the copolymer after precipitation.

Viscosity experiments support our assertion that pendant UP groups dimerize strongly in solution. As expected, the viscosity of toluene solutions of homopolymer hP2 (Table 1) increases linearly with concentration (Figure 3). Solutions of coP2, however, show exponential increase in viscosity with increasing concentration. This phenomenon reveals the reversible nature of the UP crosslinks: at low copolymer concentrations, the equilibrium concentration of dimerized units is low, and the polymer behaves like the homopolymer. At higher copolymer concentration, the equilibrium concentration of dimerized units is high, and the effective molecular weight dramatically increases, leading to a large increase in viscosity. In fact, dissolving even higher concentrations of coP2 in toluene ($>20\,g\,L^{-1}$) leads to gelation.

Table 1. Homopolymers and UP-copolymers of 1-hexene prepared by using the Et_2AlCl-activated (α-diimino)$NiBr_2$ complex **1**.

Sample	% UP in polymer[a]	M_n[b]	M_w/M_n[b]
hP1	0	39000	1.6
hP2	0	104000	1.2
coP1	2.1	33000	1.4
coP2	1.9	74000	1.3
coP3	2.0	104000	1.2

[a] % mol of UP versus 1-hexene; determined by UV absorption. [b] Determined by using GPC versus monodisperse polystyrene standards.

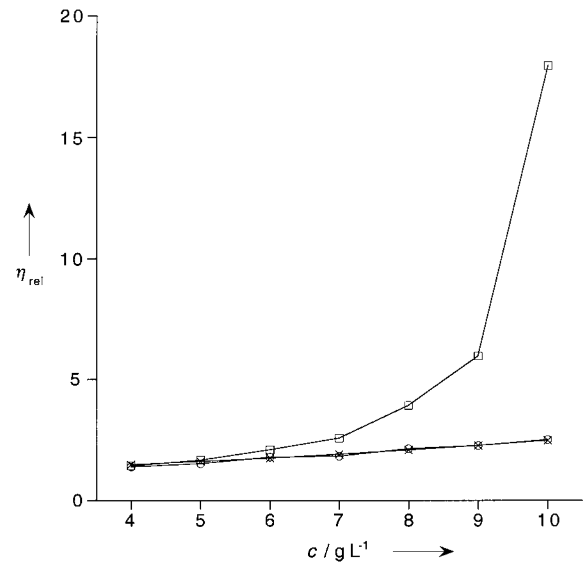

Figure 3. Relative viscosity (η_{rel}, versus pure toluene) of toluene solutions of homopolymer hP2 (×), copolymer coP2 (□), and coP2 with three molar equivalents of UP_{cap} (○) at various concentrations.

Addition of three equivalents of UP_{cap} to solutions of the copolymer coP2 completely eliminates the crosslinking effect of the attached UP groups. This solution displays a viscosity profile very similar to the homopolymer hP2 (Figure 3). The viscosity of an $8.0\,g\,L^{-1}$ solution of coP2 in toluene rapidly decreases as UP_{cap} is added, approaching near constant viscosity at $UP_{cap}/UP_{pol} = 1$. These experiments suggest that individual sets of hydrogen-bonded dimers are the predominant source of network formation—stacks or clusters of UP moieties would not be completely broken down by the presence of UP_{cap}, and must therefore not be a significant source of crosslinking.[8, 14, 15] The clear, colorless appearance of the bulk copolymer further supports this assessment.

While the solution properties of the copolymer are intriguing, the primary motivation for this research was to demonstrate that the bulk copolymer forms an amorphous network with elastomeric properties. Consequently, tensile tests were performed on films of homopolymer and copolymer. Low molecular weight homopolymer hP1, a waxlike material, displayed tensile properties typical of a viscous liquid (Figure 4). After initial deformation associated with uncoiling the amorphous polymer chains, the stress required to continue elongation increased minimally. The lack of strong intermolecular forces allows the chains to freely reptate under low stresses. In contrast, coP1 displayed an elastomeric tensile profile: initial elongation again occurs at low stresses because the amorphous polymer chains can easily uncoil. However, crosslinks inhibit the chains from moving past each other. As a result, stresses required to continue deformation increase dramatically once chains have uncoiled; bond stretching and bond angle deformation become the principle routes to further elongation.[21] Thus, much higher stresses are observed at rupture. Higher molecular weight polymers hP2 and coP3 showed similar behavior under tension, except stresses and elongations were considerably higher at rupture, which we attribute to the increased intermolecular interactions of longer chains.

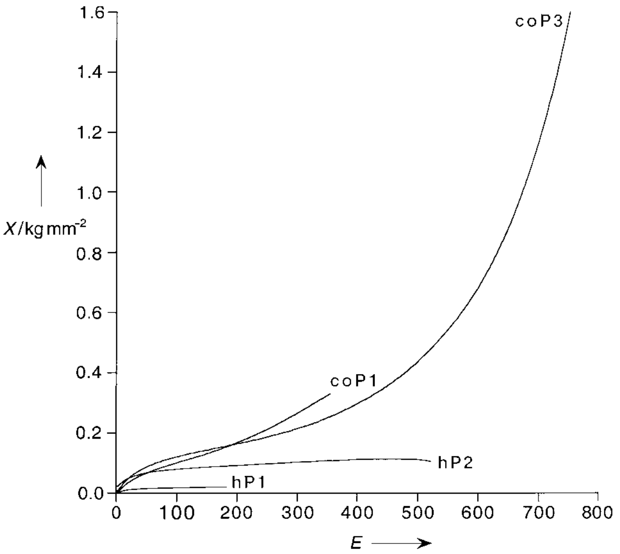

Figure 4. Stress–strain data for hP1, coP1, hP2, and coP3 (X = nominal stress; E = percent elongation).

In conclusion, we report a convenient, one-pot synthesis of a new polyolefin elastomer. The polymer utilizes strongly dimerizing hydrogen-bonding arrays to form noncovalent crosslinks within the polymer matrix. The bulk polymer displays elastomeric properties at room temperature, verifying the formation of a network. Viscosity tests show, however, that the crosslinks are reversible: the copolymers are soluble in chloroform and toluene, and addition of small amounts of endcapper leads to dramatic decreases in viscosity. Studies of the thermomechanical properties of the polymer are underway.

Experimental Section

Synthesis: Catalyst **1**,[17] monomer UP$_{\mathrm{mon}}$,[15] and UP$_{\mathrm{cap}}$[10] were synthesized by using modifications of literature preparations. Diethylaluminum chloride (1.8 M in toluene) was purchased from Aldrich. Toluene and 1-hexene were distilled from sodium benzophenone ketyl and 4 Å molecular sieves, respectively, and degassed by three freeze/pump/thaw cycles prior to use. All polymerizations were conducted under nitrogen using glovebox and Schlenk techniques. Reaction conditions: UP$_{\mathrm{mon}}$ (0.30 g, 0.80 mmol) and UP$_{\mathrm{cap}}$ (0.60 g, 2.4 mmol) were dissolved in toluene (75 mL). 1.8 M Et_2AlCl (10.0 mL) was added, and the resulting solution was stirred for 15 min. 1-Hexene (5.0 mL, 40.0 mmol) was added, followed by Ni catalyst (20 mg) dissolved in toluene (25 mL). The reaction mixture was stirred at 0°C (high molecular weight) or room temperature (lower molecular weight) for 20 h. The reaction was then quenched by slowly adding acidic methanol (100 mL; 1% HCl v/v), which caused the polymer to precipitate. The polymer was isolated (by decanting), washed with methanol, and dried in vacuo at 80°C overnight. Residual aluminum was removed by redissolving the polymer in toluene (200 mL) and refluxing overnight with acidic methanol (20 mL; 5% HCl); then the polymer was reisolated by concentrating in vacuo and precipitating with excess methanol. Yields ranged between 75% and 80%.

Characterization of coP1–3: ^{1}H NMR (300 MHz, [D$_8$]toluene): $\delta = 13.4$ (s, 1H; NH), 12.3 (s, 1H; NH), 10.9 (s, 1H; NH), 5.7 (s, 1H; =CH), 3.4 (t, 2H; $CH_2NHC(=O)$), 0.8–1.8 (m; aliphatic CH, CH_2, CH_3). Molecular weights and molecular weight distributions were determined by gel permeation chromatography using THF solution versus polystyrene standards. Incorporation of UP monomer was determined by UV absorption at 245 nm in chloroform. Elemental analysis for residual aluminum (< 0.02%) was performed by Desert Analytics. Viscosity measurements were performed by using a Canon 0B C202 Ubbelohde viscometer at 30.0°C. Toluene solutions of the compounds were filtered through glass wool prior to testing. Relative viscosities are based on pure toluene. Tensile measurements were performed at an extension rate of 100 mm min^{-1}. Films were prepared by solvent evaporation from chloroform solutions, and samples were subsequently cut into strips (typical cross sections = 5.0 mm × 0.20 mm; clamp distance = 25.0 mm).

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Base-Assisted Formation of Organozirconium Oxides with the $[Zr_6(\mu_6\text{-}O)(\mu_3\text{-}O)_8]$ Core Structure[**]

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Mathias Noltemeyer, and Hans-Georg Schmidt

Dedicated to Professor Dieter Sellmann
on the occasion of his 60th birthday

Zirconium oxides have long-been used as catalysts for the hydrogenation of carbon monoxide[1] and ethylene,[2] the highly selective isomerization of 1-butene and the formation of 1-butene from 2-butanol or 2-butanamine,[3] and the selective oxidation of hydroxy-containing organic compounds.[4] In general, complete hydrolysis of zirconium chlorides leading to zirconium oxides without an appreciable amount of chloride and hydroxide is difficult to achieve and only possible at very high temperatures. ZrO_2 is prepared by treating $[ZrOCl_2\cdot 8\,H_2O]$ at 1000 °C[5] or by calcining zirconium hydroxide in O_2 at 500 °C.[1g, 3a] Base-assisted hydrolysis of organozirconium chlorides results in the formation of organozirconium oxide complexes containing chloride or hydroxide ligands, such as $[(Cp_2ZrCl)_2(\mu\text{-}O)]$,[6] $[\{(Cp^*ZrCl)(\mu\text{-}OH)\}_3(\mu_3\text{-}OH)(\mu_3\text{-}O)]\cdot 2\,THF$,[7] $[\{(Cp^*ZrCl)(\mu\text{-}OH)\}_3(\mu_3\text{-}O)(\mu\text{-}Cl)]$.[8] To the best of our knowledge so far no larger aggregate of an organozirconium oxide has been isolated or detected.

We are interested in studying the products formed by the reaction of early transition metal compounds in the liquid ammonia/toluene two-phase system. Recently we reported on the reaction of $[L_2TiCl_2]$ ($L = p\text{-}MeC_6H_4C(NSiMe_3)_2$) with $NaNH_2$ in liquid ammonia and toluene[9] to yield $[(LTi)_6(\mu_3\text{-}N)_2(\mu_3\text{-}NH)_6]\cdot 6\,(C_7H_8)$, and on the formation of $[\{(MeC_5H_4)Zr\}_5(\mu_5\text{-}N)(\mu_3\text{-}NH)_4(\mu\text{-}NH_2)_4]$ from the reaction of $[(MeC_5H_4)_2ZrCl_2]$ with K in liquid ammonia and toluene.[10] The imido-bridged dinuclear zirconium complex $[\{(\eta^3\text{-}L')Zr(\mu\text{-}NH)\}_2]$ ($L' = (tBuNP)_2(tBuN)_2$) was obtained by treating $[L'ZrCl_2]$ with KH in liquid ammonia and toluene.[11] These results prompted us to attempt the complete hydrolysis of metal chlorides, which is difficult to achieve under base-assisted conditions at low temperatures.

Herein we report on the reaction of $[(EtMe_4C_5)ZrCl_3]$ (**1**) with H_2O (1:1.5 molar ratio) in toluene at room temperature with successive treatment by KH (1:3 molar ratio) in liquid ammonia and toluene at −78 °C. The strong basic reagent KH affords the complete removal of chloride and the formation of the organozirconium oxide **2** [Eq. (1)]. The influence of the solvent on the solid-state structure of **2** was demonstrated by recrystallization of **2** from mesitylene which gave cluster **3** [Eq. (2)].

$$\underset{\mathbf{1}}{6\,[(EtMe_4C_5)ZrCl_3]} + 9\,H_2O \xrightarrow{\substack{\text{1. toluene, RT, 2 h}\\ \text{2. 18 KH, liq. NH}_3,\\ \text{toluene, }-78\,^\circ\text{C.}}} \underset{\mathbf{2}}{[\{(EtMe_4C_5)Zr\}_6(\mu_6\text{-}O)(\mu_3\text{-}O)_8]\cdot C_7H_8 + 18\,KCl + 18\,H_2} \qquad (1)$$

$$\underset{\mathbf{2}}{[\{(EtMe_4C_5)Zr\}_6(\mu_6\text{-}O)(\mu_3\text{-}O)_8]\cdot C_7H_8} \xrightarrow[\text{−toluene}]{\text{mesitylene}} \underset{\mathbf{3}}{[\{(EtMe_4C_5)Zr\}_6(\mu_6\text{-}O)(\mu_3\text{-}O)_8]\cdot C_9H_{12}} \qquad (2)$$

A proposed mechanism for the formation of **2** is given in Equations (3)–(8) ($Cp' = EtMe_4C_5$; X = Cl, NH_2, or OH). The first step of the reaction involves the formation of the water adduct **4** [Eq. (3)]. The acidic nature of the hydrogen atoms of the coordinated H_2O results in hydrogen chloride elimination under formation of ammonium chloride in the presence of NH_3 [Eq. (4)]. We were unable to isolate **2** from the reaction of **1** with H_2O in liquid ammonia and toluene. Excess of ammonia does not result in a complete hydrolysis of **1**. Partial hydrolysis and ammonolysis have been also observed in the base-assisted hydrolysis of $[Cp^*ZrCl_3]$[7, 8] and the ammonolysis of ZrX_4 (X = Cl, Br) in liquid NH_3.[12] In the presence of KH, NH_4Cl is converted to KCl and hydrogen [Eq. (5)]. On the other hand KH reacts with ammonia under formation of KNH_2 and hydrogen [Eq. (6)].[13] Moreover, we have shown that KNH_2 reacts with a compound containing a Zr–Cl bond to yield the amide [Eq. (7)].[10] Due to the Lewis acidity of the Zr^{IV} center, the OH group functions as an acid

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