Synthesis and Characterization of Hyperbranched Polyurethanes Prepared from Blocked Isocyanate Monomers by Step-Growth Polymerization

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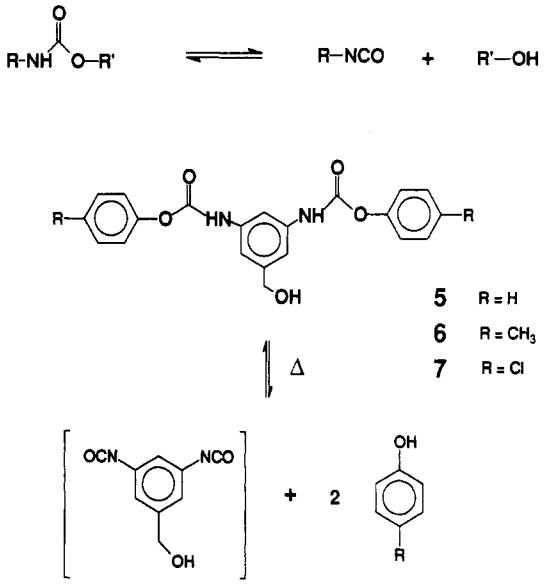
ABSTRACT: The step-growth polymerization of the AB_2 blocked isocyanate monomr 3,5-bis((benzoxycarbonyl)imino)benzyl alcohol at a monomer concentration of 1 M results in the formation of a hyperbranched polyurethane with M_W = 34 000. When the monomer concentration is increased to 2 M, a cross-linked polymer forms through the occurrence of a small amount of side reactions involving free isocyanate intermediates. Soluble polymers can be prepared, independent of the monomer concentration, when an end-capping alcohol is added at the start of the polymerization. The end-capping groups change the physical properties of the polymers such as T_g and solubility.

Introduction

Recent efforts toward the synthesis of highly branched macromolecules have followed two major pathways: one directed toward the synthesis of defect-free structures by a stepwise growth procedure[1-8] and the other aimed at less regular structures prepared by the one-pot polymerization of AB_x monomers.[9-15] Defect-free dentritic polymers, whether grown by the convergent[1-4] or the divergent procedure,[5-8] have been prepared with a number of different repeat structures, but the stepwise nature of their synthesis makes larger scale production difficult since the growth of a single generation requires several reaction and purification steps. The direct polymerization of an AB_x monomer permits the rapid preparation of highly branched polymers, known as hyperbranched polymers. In comparison to dendritic polymers, hyperbranched polymers have an irregular structure with a mixture of branched and linear repeat units. A wide variety of hyperbranched polymers have been prepared including poly(benzyl phenyl ethers),[9] polyesters,[10] polyamides,[11] polyphenylenes,[12] poly(siloxysilanes),[13] and poly(aryl ethers).[14] Some hyperbranched polymers have interesting physical properties with the formation of thermotropic[15] or lyotropic liquid crystalline phases,[11] and, in one case, the melt viscosity of polystyrene was reported to be dramatically reduced by the addition of 5% of a hyperbranched polyphenylene.[12] One important class of polymers which has not been explored as a hyperbranched structure is the polyurethanes.

Polyurethanes are widely used in a number of important applications including foams, elastomers, coatings, adhesives, and the RIM process.[16] Because polyurethanes result from the reaction of an alcohol with an isocyanate, the preparation of a hyperbranched polyurethane would require the synthesis of an AB_2 monomer having both isocyanate and alcoholic moieties in the correct proportion within the same molecule. The high reactivity of isocyanates, either in self-condensation to form a dimer or with an alcohol functionality to form a carbamate, requires that the isocyanate moiety be protected during storage. The isocyanate protecting group should be selected for its ease of regeneration at the time of polymerization. Several methods have been developed for the protection of isocyanate groups including the widely used thermal dissociation of a carbamate moiety which releases an isocyanate and a hydroxyl compound (Scheme I).[17,18] The decomposition temperature of a carbamate (RNHCOOR') is dependent on the nature of the substituents R and R'. If both R and R' are alkyl groups, the decomposition temperature is close to 250 °C, while if both R and R' are aryl moieties the decomposition temperature is lowered to around 120 °C.[17] Furthermore, the decomposition temperature is dependent on several parameters such as the presence of a solvent or a catalyst and the presence of electron-withdrawing or -donating groups in the case of aryl carbamates.[17] This report describes the use of protected isocyanates, also known as blocked isocyanates, for the formation of hyperbranched polyurethanes by polymerization of 3,5-bis((benzoxycarbonyl)imino)benzyl alcohol (**5**).

Scheme I



Results and Discussion

Synthesis of Monomer. Scheme II outlines the synthetic strategy for the preparation of 3,5-bis((benzoxycarbonyl)imino)benzyl alcohol (**5**). The first step involves the protection of the alcohol moiety of 3,5-dinitrobenzyl alcohol (**1**) with a bulky *tert*-butyldiphenylsilyl ether group to prevent the conversion of the alcohol group to a benzyl chloride moiety during the subsequent phosgenation step. Attempts to use the less stable *tert*-butyldimethylsilyl group were not successful due to cleavage of the silyl ether

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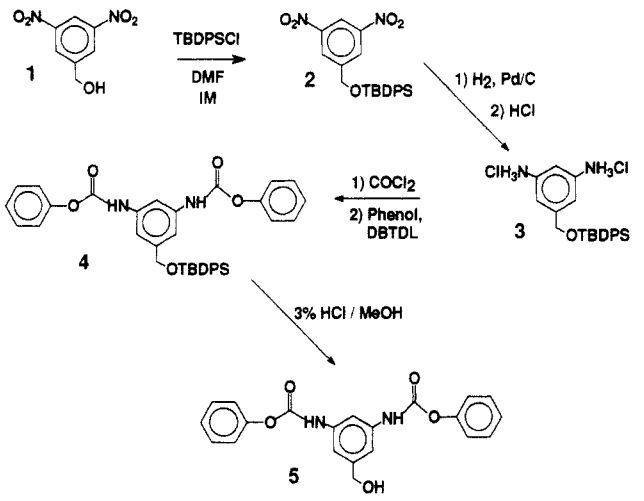
Scheme II



Scheme III

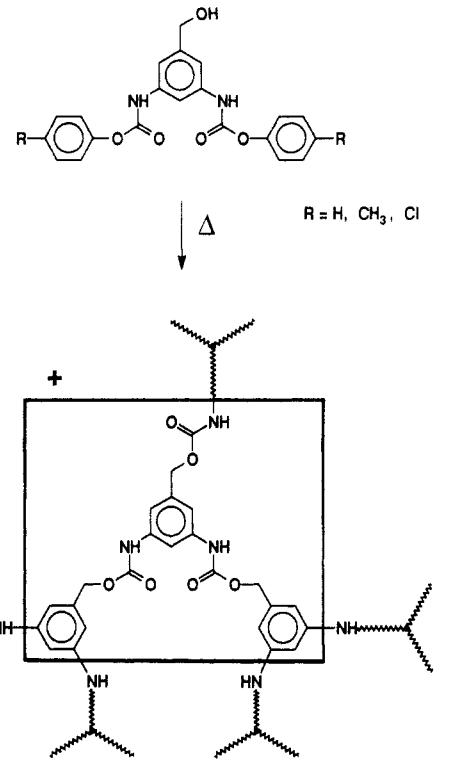


Table I. Polymerization of 5–7 in Refluxing THF Followed by End-Capping with *p*-Methoxybenzyl Alcohol

monomer	monomer concn (mol/L)	M_w	M_n	% yield
7	0.48	14000	7000	74
6	0.48	14000	7000	53
5	0.48	42000	7200	58
5	1.0	34000	11000	67
5	2.0	cross-linked		

linkage during the preparation of 3. Following reduction of the nitro groups of 2 by catalytic hydrogenation, the resulting diamine was converted to its hydrochloride salt, 3, for ease of handling and to prevent oxidation of the amino groups of 3. Some hydrolysis of the protecting group (ca. 2–6 mol % by ^{1}H NMR) occurs during addition of the hydrochloric acid, but the deprotected side product is removed easily during purification of 3. A slurry of the dihydrochloride salt, 3, in xylene was then allowed to react with phosgene at 110 °C to afford the diisocyanate, which was transformed into a carbamate without intermediate isolation by reaction with phenol, or a substituted phenol, in the presence of dibutyltin dilaurate (DBTDL). Monitoring of the carbamate formation was achieved by FT-IR using the disappearance of the isocyanate band at 2260 cm^{-1} as a diagnostic tool. Finally, the silyl protecting group of 4 was removed to give 5 in a 72% overall yield after purification.

Polymerization Studies. To explore the optimum conditions for the polymerization of 5, the reaction of a model compound, phenyl *N*-phenylcarbamate with *p*-methylbenzyl alcohol was studied. The reaction was found to proceed smoothly in refluxing THF with DBTDL as the catalyst.

The same reaction conditions were then employed for the polymerization of 5 (Table I). Time-dependent GPC studies of the polymerization showed that no significant increase in molecular weight was observed for polymerization times greater than 24 h. The polymers were isolated by precipitation into either methanol or diethyl ether, extracted in a Soxhlet apparatus to remove phenol and the catalyst, and then dried under vacuum to give a hyperbranched material that is stable to storage at ambient conditions. Thermal characterization of this polymer showed that it is not stable above 120 °C as the freely soluble polymer becomes cross-linked. The phenyl carbamate groups at the chain ends of the molecule were found to be reactive, as they were easily substituted by refluxing the polymer with an alcohol, such as *p*-methylbenzyl alcohol, in the presence of DBTDL. Alternately, a similar polymer with analogous properties can be prepared by refluxing the polycondensation product with an alcohol for an additional 24 h before isolation. As discussed earlier, the decomposition temperature of a phenolic-substituted carbamate is dependent on the substitution pattern of the aromatic ring.[17] In our polymerization studies, no difference in the degree of polymerization was found whether an electron-donating (methyl) or an electron-withdrawing (chloro) group was in the para position. The molecular weight of the polymer appears to depend on the initial concentration of the monomer since increasing the concentration from 0.5 to 1.0 M causes M_W to increase from 14 000 to 34 000. A further increase in the concentration of monomer to 2.0 M results in the formation of a cross-linked network which swells in THF, DMF, and DMSO. Refluxing the cross-linked polymer in the presence of an alcohol causes no further apparent change. It appears likely that the cross-linking reaction is associated with the formation of free isocyanate groups at the chain ends of the hyperbranched polymer during growth. A higher concentration of free isocyanate groups would inevitably result in the occurrence of the well-known side reactions (Scheme IV) that are characteristic of systems involving isocyanates.[19] One possibility would be the formation of isocyanate dimers. However, since these dimers can either be converted back to monomer thermally or are able to react with an alcohol to form a carbamate linkage, it appears that dimers are not the primary source of cross-linking sites. This conclusion is confirmed by the observation that the cross-linked polymer gel remains unchanged after refluxing with an alcohol. The presence of any adventitious H_2O in the system would cause the decomposition of some isocyanate groups to afford CO_2 and amines. These amine groups would then react further with 2 mol of isocyanate to give a biuret. Similarly, a free isocyanate functional group might react with a carbamate to form an allophanate. Lastly, cross-linking may result from the reaction of three isocyanate groups to form a thermally stable triisocyanurate. Despite our efforts, analysis of the cross-linked

Scheme IV

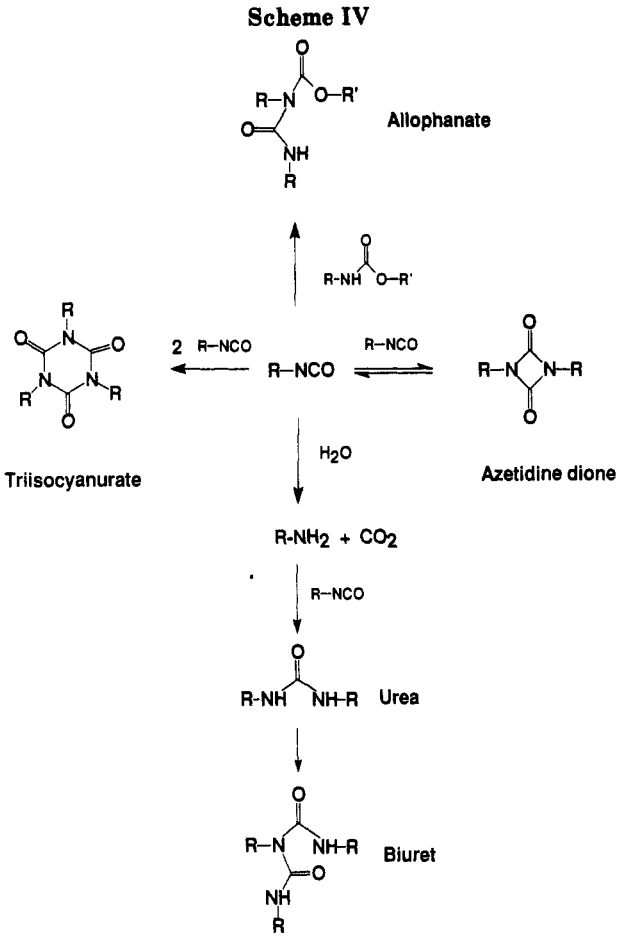


Table II. Polymerization of 5 with End-Capping Using an Equimolar Amount of Alcohol

capping group[a]	M_w	M_n	T_g (°C)	% yield	solubility
pMBA	10000	5000	119	28	THF, DMF, DMSO
pMBA	14000	5600	119	45	THF, DMF, DMSO
pNBA	5600	2600	111	83	THF, DMF, DMSO
hexanol	24000	11000	111	51	THF, DMF, DMSO
decanol	7400	5800	83	29	THF, DMF, DMSO, $CHCl_3$, Et_2O
MEE	9300	5000	57	79	THF, DMF, DMSO

[a] End-capping alcohols: pMBA = *p*-methoxybenzyl alcohol; pNBA = *p*-nitrobenzyl alcohol; MEE = (methoxyethoxy)ethanol.

polymer by ^1H and ^{13}C NMR spectroscopy as well as FTIR spectroscopy did not provide firm evidence to confirm the nature of the cross-linking sites.

Flory has shown that for a monomer such as **5**, polymerization leads to a branched polymer that contains $n + 1$ end groups, where n is the number of monomer repeat units in the polymer.[20] Therefore, a second way to prevent cross-linking is to add an equimolar amount of an alcohol at the start of the polymerization. While this procedure of end-capping during polymerization produces polymers with considerably lower M_W values (Table II), the polymerization can be performed at higher concentrations without any cross-linking being observed. The degree of polymerization is also concentration independent. Several different alcohols were used in these polymerization studies (Table II), and these examples illustrate the ease with which the species located at the chain ends can be varied. In all cases, the alcohol moieties added at the start of the polycondensation would react with **5** to form chain ends, thereby "decreasing" the amount of isocyanate available for side reactions. As expected,[9,12,15] the physical properties of the hyperbranched polyurethanes vary with the chains ends. As the end groups are changed from hexyl to decyl, T_g drops from 111 to 83 °C. A further decrease of T_g to 57 °C is seen for the (methoxyethoxy)ethanol-capped polymer. The hyperbranched, end-capped polyurethanes are also thermally stable up to 200 °C as shown by DSC and TGA measurements. This behavior is in contrast to that observed for polymers obtained without end-capping which are not stable above 120 °C. All of the polymers are soluble in THF, DMF, and DMSO, with the decyl-capped polymer also being soluble in diethyl ether–chloroform mixture.

Figure 1. ^1H NMR spectrum of a hyperbranched polyurethane prepared by adding (methoxyethoxy)ethanol at the start of the polymerization.

Figure 1 shows the ^1H NMR spectrum of a hyperbranched polyurethane that was prepared by adding (methoxyethoxy)ethanol at the start of the polymerization. The presence of two types of carbamate groups is shown by the two separate resonances of the carbamate NH group at 9.84 and 9.79 ppm. The aromatic (7.64 and 7.15 ppm), benzyl carbamate (5.01 ppm), and the end-capping groups (4.15, 3.52, 3.41, and 3.21 ppm) resonances all integrate to give the expected structure. The resonance at 4.38 ppm is assigned to the single OH group from the benzyl alcohol focal[1] group. A comparison of the integrated peak area for this single hydroxyl resonance with those of the other protons can be used to estimate M_n. Table III reports the M_n values obtained by ^1H NMR and the values obtained by GPC for the polymers obtained by end-capping of the polymer during the polymerization. The correlation is reasonably good except for the two polymers that are capped by straight-chain alkyl alcohols, where the values obtained by NMR are significantly lower than the GPC figures.

These experiments show the versatility of preparing hyperbranched polyurethanes by the polymerization of an AB_2 monomer. The ability to tailor easily the surface

Table III. Comparison of Molecular Weights by NMR and GPC Measurements for End-Capped Hyperbranched Polyurethanes

end-capping group[a]	M_n(NMR)	M_w(GPC)
p-methoxybenzyl alcohol	6600	5600
p-nitrobenzyl alcohol	2500	3300
(methoxyethoxy)ethanol	3800	4900
hexanol	5900	11000
decanol	2600	5700

properties of the hyperbranched polyurethanes by adding an alcohol is a very attractive feature of this procedure.

Experimental Section

General Procedures. Infrared spectra were recorded on a Nicolet IR/44 spectrometer either as thin films on a KBr plate or as KBr pellets. Dimethylformamide was used as received. Tetrahydrofuran was distilled from benzophenone ketyl under a N_2 atmosphere. Xylene was distilled from CaH_2 under a N_2 atmosphere. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Bruker WM300 instrument using the solvent signal as an internal reference. Differential scanning calorimetry and thermogravimetric analysis were performed on Mettler instruments. Size exclusion chromatography was performed with five 10-μm PL-gel GPC/SEC columns (200 to 3×10^6 exclusion limits) with THF as the solvent. Columns were calibrated using narrow dispersity polystyrene standards (Polymer Laboratories). Melting points are reported as the uncorrected values.

3,5-Dinitrobenzyl *tert*-Butyldiphenylsilyl Ether (2). 3,5-Dinitrobenzyl alcohol (1) (10.00 g, 50.5 mmol) and *tert*-butyldiphenylsilyl chloride (22.82 g, 83.0 mmol) were added to a three-neck flask under a positive pressure of N_2. The starting materials were dissolved in DMF, and then imidazole (9.96 g, 146 mmol) was added slowly to the reaction mixture. After the mixture was stirred overnight, TLC monitoring confirmed that the reaction was complete. The product was precipitated into H_2O and then extracted with diethyl ether. After the organic layer was washed with H_2O, the solvent was removed to give a yellow solid that was purified by flash chromatography (17% Et_2O in hexanes) to afford 19.25 g (44.1 mmol, 87% yield) of **2** as an off-white solid: mp 90–2 °C; ^1H NMR ($CDCl_3$) δ 8.94 (t, ArH, 1H), 8.49 (d, ArH, 2H), 7.69–7.38 (m, Ph, 10H), 4.89 (s, CH_2, 2H), 1.13 (s, CH_3, 9H); ^{13}C NMR ($CDCl_3$) δ 148.4, 145.7, 135.5, 132.3, 130.2, 128.0, 126.1, 117.4, 63.9, 26.8, 19.2. Anal. Calcd for $C_{23}H_{24}N_2O_5Si$: C, 63.28; H, 5.54; N, 6.42. Found: C, 63.48; H, 5.66; N, 6.57.

3,5-Diaminobenzyl *tert*-Butyldiphenylsilyl Ether Dihydrochloride (3). A pressure bottle was charged with **2** (6.64 g, 15.2 mmol), 10% Pd/C (350 mg), and 125 mL of 95% ethanol. Compound **2** is only slightly soluble in 95% ethanol but as the reaction progresses, the solution clears. After the pressure bottle was purged and evacuated three times, the bottle was brought to 40 psi and shaken until TLC showed that the reaction had gone to completion (ca. 5 h). The solution was filtered through a bed of Celite and then acidified with an ethanolic HCl solution (2.5 mL of HCl or 30 mmol in 50 mL of 95% ethanol) added dropwise under a positive pressure of N_2. The solvent was removed to afford a light brown solid (6.47 g, 14.6 mmol, 96% yield) which was stored in a N_2-filled glovebox. ^1H NMR showed that up to 6% of the silyl ether groups were hydrolyzed during the addition of the acid, but since this impurity is easily removed during the purification of the final monomer **5**, no further purification of **3** was attempted. ^1H NMR (DMSO-d_6) δ 7.65–7.43 (m, SiArH, 10H), 6.94 (s, ArH, 2H), 6.88 (s, ArH, 1H), 4.71 (s, $ArCH_2$, 2H), 1.03 (s, *t*-Bu, 9H).

3,5-Bis((benzoxycarbonyl)imino)benzyl Alcohol (5). Compound **3** (4.639 g, 10.3 mmol) was weighed into a three-neck flask inside a N_2-filled glovebox. The stoppered flask was then placed under a positive pressure of argon, and freshly distilled xylene (from CaH_2, 35 mL) was added to the flask. Phosgene was then introduced into the stirred slurry via a sintered frit while the mixture was heated to 110 °C. After ca. 30 min, the solid had dissolved and the flow of phosgene was continued for an additional 15 min while the reaction was kept at 110 °C for 1 h. The solution was sparged with N_2 for 1 h to remove HCl and the excess phosgene which was captured in a series of neutralizing alkaline baths. When the reaction mixture had cooled to room temperature, 1.94 g of phenol (20.6 mmol) and 50 μL of dibutyltin dilaurate (84 μmol) were added. After 12 h of stirring at room temperature, TLC and FTIR monitoring of the reaction suggested that it had gone to completion. The solvent was removed under vacuum to give a brown solid which was then passed through a short silica column to remove the catalyst. The recovered solid was redissolved in a minimum of ethyl acetate, and then the solution was added dropwise to 100 mL of 3% HCl in methanol to remove the silyl ether protecting group. After 3 h TLC indicated that the reaction had gone to completion. The product was precipitated into H_2O and extracted into ethyl acetate. The amber solid was purified by flash chromatography (eluting with 1:1.75 hexanes/ethyl acetate) to give 3.14 g (83.0 mmol, 80% yield) of a white solid: mp 85–7 °C; ^1H NMR (acetone-d_6) δ 9.18 (s, NH, 2H), 7.77 (t, ArH, 1H), 7.43–7.19 (m, ArH + phenyl, 12H), 4.60 (d, $ArCH_2$, 2H), 4.27 (t, OH, 1H); ^{13}C NMR (acetone-d_6) δ 152.5, 152.0, 145.3, 130.0, 126.1, 122.6, 112.5, 108.5, 64.6. Anal. Calcd for $C_{21}H_{18}N_2O_5$: C, 66.66; H, 4.79; N, 7.40. Found: C, 66.10; H, 5.05; N, 7.39.

3,5-Bis(((*p*-methylbenzoxy)carbonyl)imino)benzyl Alcohol (6). Compound **3** (1.50 g, 3.34 mmol) was weighed into a three-neck flask inside a N_2-filled glovebox. The stoppered flask was transferred out of the glovebox and placed under a positive pressure of Ar. Freshly distilled xylene (from CaH_2, 35 mL) was added to the flask, and phosgene was introduced into the stirred slurry via a sintered frit while the mixture was heated to 110 °C. After ca. 30 min, the solid had dissolved and the flow of phosgene was continued for an additional 15 min while the reaction was kept at 110 °C for 1 h. The solution was sparged with N_2 for 1 h to remove HCl and the excess phosgene. When the reaction mixture had cooled to room temperature, 722 mg of phenol (6.68 mmol) and 50 μL of dibutyltin dilaurate (84 μmol) were added. After 12 h of stirring at room temperature, TLC and FTIR monitoring of the reaction suggested that it had gone to completion. The solvent was removed under vacuum to give a brown solid which was then passed through a short silica column to remove the catalyst. The recovered solid was redissolved in a minimum of ethyl acetate, and then the solution was added dropwise to 100 mL of 3% HCl in methanol to remove the silyl ether protecting group. In 3 h the reaction had gone to completion (TLC). The product was precipitated into H_2O and extracted into ethyl acetate. The amber solid was purified by flash chromatography (eluting with 1:1.75 hexanes/ethyl acetate) to give 936 mg (2.30 mmol, 69% yield) of a white solid: ^1H NMR (CD_2Cl_2) δ 7.48 (s, NH, 2H), 7.19–7.08 (m, ArH, 11H), 4.60 (s, CH_2, 2H), 2.32 (s, CH_3, 6H); ^{13}C NMR (CD_2Cl_2) δ 152.7, 149.8, 145.1, 140.2, 135.5, 130.4, 122.4, 112.5, 108.5, 64.6, 20.7; mp 140–2 °C. Anal. Calcd for $C_{23}H_{22}N_2O_5$: C, 67.97; H, 5.46; N, 6.89. Found.

3,5-Bis(((*p*-chlorobenzoxy)carbonyl)imino)benzyl alcohol (7). Compound **3** (1.844 g, 4.10 mmol) was weighed into a three-neck flask inside a N_2-filled glovebox. The stoppered flask was transferred out of the glovebox and placed under a positive pressure of Ar. Freshly distilled xylene (from CaH_2, 35 mL) was added to the flask, and phosgene was introduced into the stirred slurry via a sintered frit while the mixture was heated to 110 °C. After ca. 30 min, the solid had dissolved and the flow of phosgene was continued for an additional 15 min while the reaction was kept at 110 °C for 1 h. The solution was sparged with N_2 for 1 h to remove HCl and the excess phosgene. When the reaction mixture had cooled to room temperature, 1.05 g of *p*-chlorophenol (8.21 mmol) and 50 μL of dibutyltin dilaurate (84 μmol) were added. After 12 h of stirring at room temperature, TLC and FTIR monitoring of the reaction suggested that it had gone to completion. The solvent was removed under vacuum to give a brown solid which was then passed through a short silica column to remove the catalyst. The recovered solid was redissolved in a minimum of ethyl acetate, and then the solution was added dropwise to 100 mL of a 3% HCl solution in methanol to remove the silyl ether protecting group. In 3 h the reaction had gone to completion (TLC). The product was precipitated into H_2O and extracted into ethyl acetate. The amber solid was purified by flash chromatography (eluting with 1:1.75 hexanes/ethyl acetate) to give 1.126 g (2.50 mmol, 61% yield) of a white solid: ^1H NMR (acetone-d_6) δ 9.26 (s, NH, 2H), 7.76 (t, ArH, 1H), 7.46–7.24 (m, ArH, 10H), 4.60 (d, $ArCH_2$, 2H), 4.31 (t, OH, 1H); ^{13}C NMR

(acetone-d_6) δ 152.2, 150.7, 145.2, 140.0, 130.8, 130.0, 124.4, 112.7, 108.5, 64.5; mp 152–4 °C. Anal. Calcd for $C_{21}H_{16}Cl_2N_2O_5$: C, 56.39; H, 3.60; N, 6.26. Found.

Polymerization of 5 with End-Capping after Polymerization. To a flame-dried Schlenk flask were added 5 (378 mg, 1.00 mmol), DBTDL (10 μL, 17 μmol), and 1 mL of freshly distilled THF. The flask was connected to a reflux condenser and the reaction mixture was kept under an atmosphere of Ar. After the mixture was refluxed for 24 h and then cooled to room temperature, *p*-methylbenzyl alcohol (122 mg, 1.00 mmol) was added to the polymer solution. The reaction was brought back to reflux for an additional 24 h. After precipitation into methanol, the solid polymer was collected by centrifugation, extracted for 24 h with diethyl ether in a Soxhlet apparatus, and dried to afford 209 mg (67% yield) of an off-white polymer: ^{1}H NMR (DMSO-d_6) δ 9.64 and 9.77 (s, NH, 2H), 7.65 (s, ArH para to benzyl, 1H), 7.25 and 7.15 (s, ArH ortho to benzyl + ArH on *p*-methylbenzyl alcohol, 6H), 5.05 and 5.00 (s, CH_2, 4H), 2.25 (s, CH_3, 3H); ^{13}C NMR (DMSO-d_6) δ 153.3, 153.2, 139.6, 137.6, 137.3, 133.6, 128.9, 128.1, 112.2, 108.1, 65.5, 20.7; GPC (polystyrene standard) M_W = 34 000; M_n = 11 000.

A cross-linked polymer was formed when compound 5 (756 mg, 2.00 mmol) was added to a flame-dried Schlenk flask along with 1 mL of freshly distilled THF and 13 μL of DBTDL and the reaction mixture was brought to reflux. After 16 h of refluxing, the reaction mixture had solidified and the polymer only swelled in THF and did not change its physical properties after refluxing with 244 mg (2.00 mmol) of *p*-methylbenzyl alcohol.

Polymerization of 5 with End-Capping at the Start of the Polymerization. To a flame-dried Schlenk flask were added 5 (500 mg, 1.32 mmol), (methoxyethoxy)ethanol (0.16 mL, 1.32 mmol), DBTDL (10 μL, 17 μmol), and 1.3 mL of freshly distilled THF. The reaction was performed as described above except that after 24 h of refluxing, the polymer was precipitated from diethyl ether, collected by filtration, extracted with diethyl ether for 24 h (Soxhlet), and dried to give 323 mg (79% yield) of an off-white polymer: ^{1}H NMR (DMSO-d_6) δ 9.84 and 9.79 (s, NH, 2H), 7.64 (s, ArH, 1H), 7.15 (s, ArH, 2H), 5.01 (s, $ArCH_2$, 2H), 4.38 (d, OH, 0.15H), 4.15 (s, CH_2, 2H), 3.52 (s, CH_2, 2H), 3.41 (s, CH_2, 2H), 3.21 (s, CH_3, 3H); ^{13}C NMR (DMSO-d_6) δ 153.4, 153.2, 139.6, 137.5, 112.1, 108.2, 71.2, 69.5, 68.6, 65.7, 63.5, 58.0.

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