An Unexpected Chiral Spiro Tetramer Offers Mechanistic Insight into an Improved Sodium Cyanide Initiated Polymerization of *n*-Hexyl Isocyanate in Toluene

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Introduction

Poly(alkyl isocyanates)[1] are archetypical wormlike macromolecules which make them ideal experimental models for both dilute solution and lyotropic liquid crystal theoretical work.[2–4] Their dynamically racemic stiff helical backbone structure[5,6] has also stimulated studies of their optical activity properties which has revealed on extreme sensitivity of the helix sense ratio to tiny chiral perturbations.[7]

Aharoni[8] had originally used varying mixtures of DMF and toluene in the sodium cyanide initiated polymerization[1] of isocyanates to overcome the solubility problems of various aliphatic monomers in DMF. We report that the use of toluene as the overwhelming solvent gives also significant advantages in the nature of the polymerization process with high yields with some control of the molecular weight even at previously difficult to obtain low molecular weights.[1] Moreover we have discovered a strongly temperature-dependent unusual chain transfer produced tetramer structure which in concert with the long known trimer byproduct[1] acts to distort the relationship between the monomer to initiator ratio and the molecular weight. This modification of an easy to use method[1,2] may act as an adjunct to a recently developed living polymerization which requires somewhat specialized drybox techniques to prepare the initiator.[9]

Experimental Section

NMR and mass spectra were taken on JEOL GSX-270 and DX-303HF instruments, respectively. The molecular weight and the polydispersities of the poly(*n*-hexyl isocyanate) samples were determined using a Shodex R802.5 GPC and an A80M column or a Waters Model 6000 GPC with a series of Styragel columns in both cases calibrated against standard samples kindly supplied from the laboratory of Teramoto[3] and from a shear uncorrected single bulb intrinsic viscosity calibrated against the same samples.[3]

The polymerization of the *n*-hexyl isocyanate was carried out in a glass ampule under an atmosphere of dry nitrogen. See the exact amounts of monomer, initiator, and solvent in Table I. The *n*-hexyl isocyanate obtained from either Kantou Kagaku or Carbolabs Inc. was dried overnight over calcium hydride and distilled under vacuum (50 °C at 7 mm) just before use. Sodium cyanide was dried under vacuum and dissolved in dimethylformamide which was freshly distilled under vacuum from phosphorus pentoxide (45 °C at 10 mm). Dry syringes were used to transfer the monomer and solvent to the glass ampule through septum caps. After cooling to the designated temperature, the initiator solution was added with a syringe. In contrast to the classic system[1,10] no gel or precipitate was observed but only a slowly increasing viscosity of the solution. After several hours, or overnight, a small volume of methanol was added followed by a larger volume to precipitate the polymer. As usual, purification by precipitation from chloroform in methanol was followed by drying under vacuum.[10] Evaporation of the methanol yielded the low molecular weight materials discussed below.

Table I
Polymerization Data[a]

monomer	M/I	temp, °C	yield, %	M_w/M_n[d]	M	$[\alpha]_D$[i], deg
HIC	26[b]	−78	73	1.3	35000[e]	
	39[b]	−78	80	1.2	51000[e]	
	154[b]	−78	64	1.3	146000[e]	
	80[c]	−40	0			
	80[c]	−60	39	1.5	76000[f]	
	80[c]	−100	97	1.8	30000[f]	
	35[g]	−55	18	polymodal	38000[e]	
DMHI	200[h]	−78	70	1.8	178000[d]	−477
	100[h]	−78	98	1.8	135000[d]	−479
	50[h]	−78	99	1.8	72000[d]	−483
	13[h]	−78	89	2.8	35000[d]	−468

[a] See the Experimental Section; in toluene (except see footnote *g*) all using sodium cyanide dissolved in dimethylformamide as initiator; HIC (*n*-hexyl isocyanate); DMHI ((*R*)-2,6-dimethylheptyl isocyanate). [b] Via addition of the appropriately small volume of a solution of 120 mg of NaCN dissolved in 5 mL of DMF, to 0.5 g of monomer dissolved in 2.5 mL of toluene. [c] Same as *b* except from a stock solution of 60 mg of NaCN in 10 mL of DMF to 0.5 g of monomer in 5 mL of toluene. [d] Determined by GPC as described in the Experimental Section. [e] Viscosity-average molecular weight as described in the experimental Section. [f] Weight-average molecular weight via GPC calibration. For DMHI the appropriate monomer weight correction was made. [g] In dimethylformamide. [h] Initiator solution: 120 mg of NaCN in 20 mL of DMF; 0.26 g of monomer dissolved in 2.5 mL of toluene. [i] Measured for solution in chloroform at room temperature.

Chiral chromatography was conducted on a cellulose tris[3,5-(dimethylphenyl)carbamate] HPLC column using a 90/10 mixture of *n*-hexane and 2-propanol as eleunt.

Results and Discussion

The results of the polymerization of *n*-hexyl isocyanate under various conditions of temperature and monomer to initiator ratio are summarized in Table I. Also included for comparison are four polymerization runs of (*R*)-2,6-dimethylheptyl isocyanate under similar conditions and with variable monomer to initiator ratios.

The last entry for HIC in Table I represents an attempt to prepare a moderate molecular weight of poly(*n*-hexyl isocyanate) by the classic procedure in dimethylformamide[1,11] with the typical result of very low yield and polymodal dispersity.[1,9] This certainly arises from the extremely fast propagation and the insolubility of the polymer product in the reaction medium and has caused even the extreme response of using acid degradation of high molecular weight polymer followed by fractionation to make available a wide range of molecular weights.[12]

The data in Table I demonstrate that retaining the initiator but simply changing the solvent from dimethylformamide to toluene[13] thereby allowing lower temperatures and solubility for the growing polyisocyanate chain makes a useful change in the yield, polydispersity, and control of the molecular weight. Although the system is clearly not living as indicated by the polydispersity and evidenced by the lack of an exact correspondence between the monomer to initiator ratio and the molecular weight (Table I), it is very simple to set up and is appropriate and inexpensive for scaling up.

Regarding the initiation, we have determined a rapid clouding, arising from the insolubility of sodium cyanide

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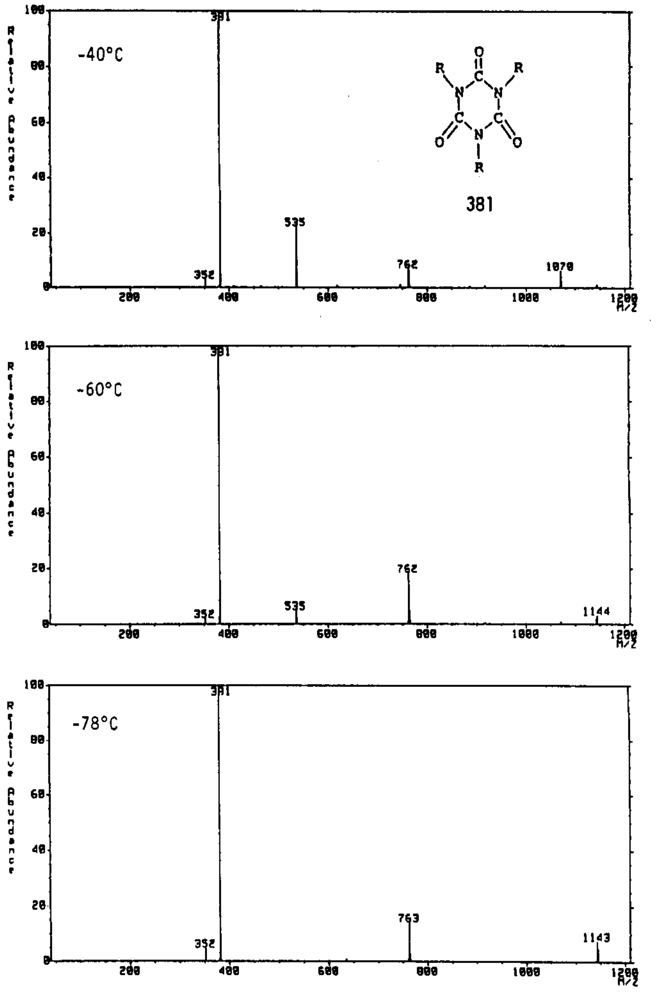

Figure 1. FD-MS of methanol-soluble products obtained in the polymerization of HIC at −40, −60, and −78 °C in Table I.

in toluene, after addition of the initiator solution to toluene in the absence of monomer. The present polymerization results therefore indicate an initiation step which preempts the nucleation events which must precede precipitation of the sodium cyanide. If this competition plays a role in molecular weight control is uncertain but a rapid initiation by cyanide is consistent with polymerization in dimethylformamide[1,2] and with unpublished efforts on soluble alkylammonium cyanides in toluene.[14]

We have found the characteristics of the present system of use in our studies, and this system may therefore be a practical adjunct to the titanium-based living polymerization recently developed.[9]

In the course of these studies we examined the methanol-soluble products of the polymerization of HIC. The relative proportion of these materials increased with temperature, and at −40 °C (Table I) all the monomer was converted to these materials. To maximize these low molecular weight materials, a model reaction of *n*-hexyl isocyanate with NaCN was run under the conditions of toluene solvent in Table I but at 100 °C with a monomer to initiator ratio of 2.5. GPC analysis revealed that most of the product consisted of two oligomers produced in nearly equal amounts (I and II) and whose molecular weights were determined by field desorption mass spectrometry (FD-MS) to be 381 and 535, respectively. Note that the intensity of the FD-MS peaks does not correspond to the proportions of isolated materials. At lower temperatures I predominated over II with no II produced at −78 °C or below (Figure 1).

The molecular weight of oligomer I, 381, corresponds to that of the well-known and expected trimer isocyanurate structure, and this was confirmed by IR and NMR spectrometry. The molecular weight of oligomer II, 535, corresponds to the sum of the weights of four monomer units in addition to the cyanide initiator and a hydrogen atom. This could be a cyanide-initiated tetramer terminated by a proton except that the IR spectrum shows no nitrile group. The proton and carbon-13 NMR spectra of II show four distinct carbonyl and hexyl groups (see Figure 2). When II was treated with lithium *N,N*-diisopropylamide (LDA) in toluene followed by heavy water (D_2O), the NH proton of II was replaced by deuterium as evidenced by the FD-MS change in molecular weight. Although this is evidence for the formation of the nitrogen anion, addition of *n*-hexyl isocyanate under polymerization conditions at −78 °C caused no chain growth.

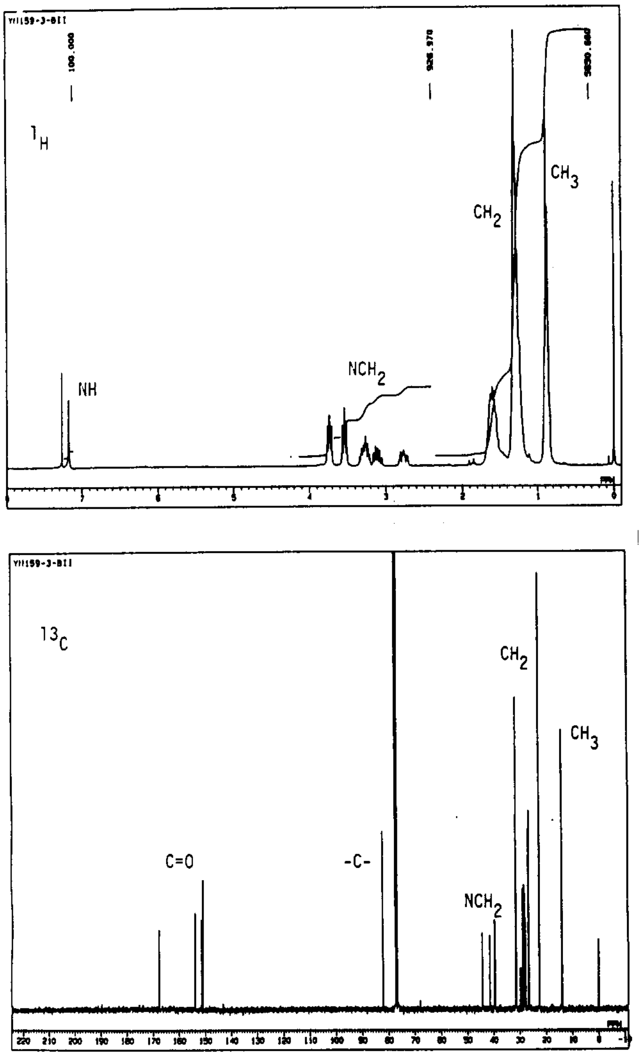

Figure 2. 270-MHz ^{1}H and 65-MHz ^{13}C NMR spectra of oligomer II ($CDCl_3$, 30 °C).

A fascinating clue to the structure of II arises by chiral chromatography.[15] A resolution was affected with a large separation between oppositely rotating fractions (Figure 3). This experiment demands that II is a chiral structure, although produced as a racemic mixture under the polymerization conditions.

A structure for II which would fit the facts above in addition to a flow scheme for the formation of I and II and polymer is shown in Figure 4. The formation of the low molecular weight materials I and II as well as other byproducts associated with the unassigned peaks in the FD-MS in Figure 1 may be arising from termination events in early chain growth. One cannot though exclude backbiting mechanisms in long chains where active end

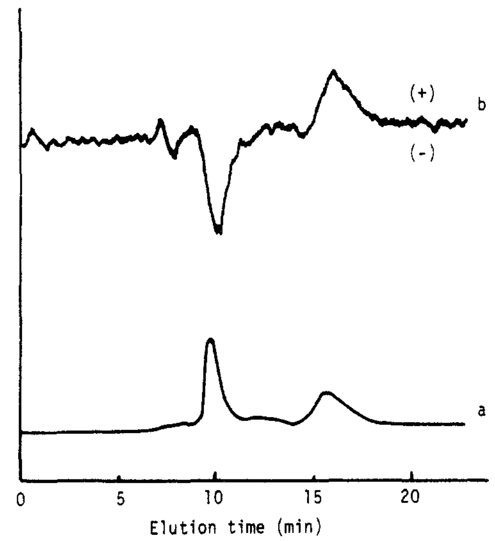

Figure 3. Chromatographic optical resolution of oligomer II by HPLC using cellulose tris[(3,5-dimethylphenyl)carbamate] as the chiral stationary phase [column, 25 × 0.46 (i.d.) cm; eluent, hexane–2-propanol (97:3, 0.5 mL/min); detector, (a) UV and (b) polarimeter].

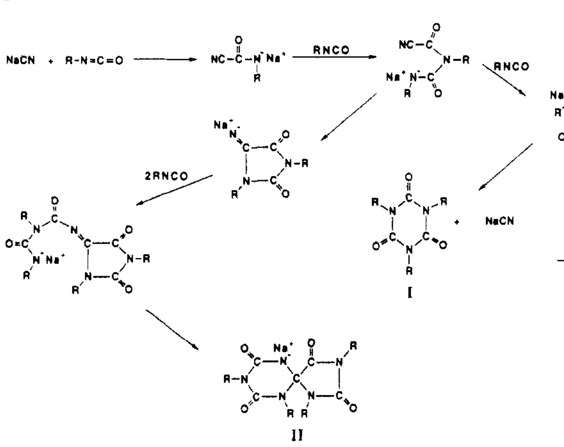

Figure 4. Mechanism of the polymerization of hexyl isocyanate with NaCN.

groups, perhaps starved for monomer, act to cleave the chain. These fragments arising in the early stages of the polymerization, in reducing the number of chains, must contribute to an observed degree of polymerization higher than the monomer to initiator ratio (Table I). Apparently in toluene at −40 °C these events entirely preclude chain growth since the ceiling temperature even at these monomer concentrations is far higher.[9,16]

The last four entries in Table I for the optically active branched monomer DMHI demonstrate the applicability of this method for other alkyl monomers and, from the optical activity, that the helical structure and physical properties are identical to the product of this polymerization in DMF.[17]

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Registry No. I, 1248-39-1; II, 143144-56-3; $C_6H_5CH_3$, 108-88-3; $CH_3(CH_2)_5NCO$, 2525-62-4; $CH_3(CH_2)_5NCO$ (homopolymer), 26746-07-6; NaCN, 143-33-9; Me_2NCHO, 68-12-2; (*R*)-2,6-dimethylheptyl isocyanate (homopolymer), 122093-50-9.