SHORT COMMUNICATIONS

Stabilization of Oligo(butyl isocyanate) by Acetyl End-Capping

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The chemical and thermal instability of polyisocyanates has been stated since the discovery of these polymers by Shashoua *et al.* When a solution of a polyisocyanate in *N,N*-dimethylformamide (DMF) is allowed to stand at room temperature in the presence of sodium cyanide, the polymer undergoes depolymerization forming cyclic trimers (isocyanurates).¹ The back-biting reaction has been suggested to be initiated by the abstraction of the proton at the -NH terminal of the polymer chain (eq 1), because a basic substance such as amines or DMF accelerates the depolymerization.²

As compared with high molecular-weight polyisocyanates, oligomers of isocyanates would be more susceptible to the depolymerization because they contain a larger amount of

the -NH terminal per weight. In fact, we found that each individual oligo(butyl isocyanate)s from tetramer to decamer (eq 2) degraded almost completely in 2-propanol/water at room temperature within 24 h after the fractionation by reversed-phase HPLC.*¹

In the present paper, we report the synthesis of the acetyl end-capped oligo(butyl isocyanate)s (eq 3 and 4) which are resistant to depolymerization during the chromatographic separation and the subsequent procedures.

We have recently studied a series of oligomers which assume helical structure in solution and/or in the crystalline state [isotactic oligomers of chloral,^{4,5} oligo(oxymethylene) diacetates⁶]. Each of the oligomers was isolated as a single compound that is uniform with respect to molecular weight and configuration,

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*1 Although Matsuda and his coworkers³ reported chromatographic separation of the oligo(*m*-methylphenyl isocyanate) with the -NH terminal, there was no mention of the depolymerization.

Figure 1. ^1H NMR spectra of the oligo(butyl isocyanate)s which were partially end-capped by acetylation (CDCl_3 , 30°C , 500 MHz); (a) $\text{TiCl}_3\text{OCH}_2\text{CF}_3$ -initiated, (b) $(\eta^5\text{-C}_5\text{H}_5)\text{TiCl}_2\text{CH}_3$ -initiated. The N-CH_2 resonance of the cyclic trimer are indicated by “*”.

and the uniformity of the oligomer samples enabled us to gain a better understanding of the helical chain structures by NMR and X-ray crystallographic techniques. The discovery of the living polymerization of isocyanates with organotitanium compounds^{7,8} has prompted us to prepare the low molecular weight homologues of polyisocyanates which are also known to exist in helical chain structure.^{9–12}

The oligomerization of butyl isocyanate was initiated with $\text{TiCl}_3\text{OCH}_2\text{CF}_3$ ⁷ ($[\text{BuNCO}]/[\text{Ti}]=4.5$ mol/mol) in benzene at 10°C . After 1 h, an excess of acetic anhydride ($[(\text{CH}_3\text{CO})_2\text{O}]/[\text{Ti}]=4.5$ mol/mol) was added, and the reaction mixture was allowed to stand for 4 h. The mixture was then poured into a large amount of methanol/water (80:20 v/v), and the insoluble part (yield = 35%, $\bar{M}_n = 3.06 \times 10^3$) was collected by centrifugation. This oligomer was fractionated by precipitation from chloroform with a 20-fold volume of methanol/water (95:5 v/v). Removal of solvent from the

Figure 2. HPLC curves of the $\text{TiCl}_3\text{OCH}_2\text{CF}_3$ -initiated oligo(butyl isocyanate) which was acetyl end-capped; (a) as prepared, (b) after the depolymerization of the -NH terminated oligomers. Chromatographic conditions: Chemcobond 5-ODS-H (1 cm i.d. $\times$ 30 cm); 2-propanol/water = 80/20 (initial), 90/10 (20 min), 100/0 (22 min); 1.5 mL min^{-1} ; 40°C .

soluble fraction afforded the oligo(butyl isocyanate) with an average degree of polymerization (DP) of 14.0. Figure 1a shows an ^1H NMR spectrum of the oligomer. Besides the strong signals due to the butyl groups, the signals due to the $\text{CF}_3\text{CH}_2\text{O-}$, -COCH_3 , and -NH terminals are observed at 4.52, 2.26, and 7.72 ppm, respectively. The quartet at 3.25 ppm is attributed to the methylene protons adjacent to the -NH terminal. From the relative intensity of the $\text{CF}_3\text{CH}_2\text{O-}$ and -COCH_3 resonances, it was determined that the acetyl end-group was introduced to 62% of the oligomer chains.^{*2} The oligomer components carrying the acetyl and -NH terminals could be partially resolved by HPLC (Figure 2a).

Oligomerization of butyl isocyanate with $(\eta^5\text{-C}_5\text{H}_5)\text{TiCl}_2\text{CH}_3$ ⁸ was carried out in a

^{*2} After we got some preliminary results of the acetylation, we were informed that the reaction of acetyl chloride with an organotitanium-initiated living polyisocyanate introduced the acetyl end-group to about 80% of the polyisocyanate chains.¹³

Figure 3. HPLC curves of the $(\eta^5\text{-C}_5\text{H}_5)\text{TiCl}_2\text{CH}_3$ -initiated oligo(butyl isocyanate) which was acetyl end-capped; (a) as prepared, (b) after the depolymerization of the -NH terminated oligomers (*). See Figure 2 for chromatographic conditions.

similar manner as described above ($[\text{BuNCO}]/[\text{Ti}]=7.3$ mol/mol, oligomerization time = 4 h). In this case, acetyl chloride was used instead of acetic anhydride. The reaction between the living oligo(butyl isocyanate) and acetyl chloride was allowed to proceed for 18 h. The resultant oligomer consisted of the acetyl-initiated, -NH terminated oligomer (83%) and the symmetrical oligomer having an acetyl group at both terminals (eq 4, 17%) (cf. Figure 1b). An HPLC trace of the oligomer mixture is shown in Figure 3a.

Though the acetylation of living oligo(butyl isocyanate) was incomplete in both cases using $\text{TiCl}_3\text{OCH}_2\text{CF}_3$ or $(\eta^5\text{-C}_5\text{H}_5)\text{TiCl}_2\text{CH}_3$ as an initiator, the -NH terminated oligomers were removable from the oligomer mixtures by their selective depolymerization. The aforementioned oligo(butyl isocyanate) whose HPLC curve is shown in Figure 2a was dissolved in 2-propanol containing 0.15% NaOH and stirred at 20°C for 15 min. The solution was diluted with toluene, and washed with 1% hydrochloric acid and water. The oligomer recovered by evaporation of solvent contained *ca.* 65 wt% of depolymerization

Figure 4. Supercritical fluid chromatogram of the $\text{CF}_3\text{CH}_2\text{O}$ -initiated, acetyl-terminated oligo(butyl isocyanate). The authentic sample of the 15mer was added to the oligomer as an internal standard. Chromatographic conditions: Develosil 100-5 (1 cm i.d. $\times$ 25 cm); $\text{CO}_2/\text{C}_2\text{H}_5\text{OH}=85/15$ (initial), 70/30 (25 min); 10 mL min^{-1} ; 90°C ; 20 MPa.

products (mainly the cyclic trimer). The depolymerization products were eliminated from the mixture with preparative GPC. Figure 2b shows the chromatogram of the remaining oligomer. The satellite peaks indicated by "*" in Figure 2a are not found in Figure 2b, showing that the -NH terminated oligomers were completely removed. The removal was also evidenced by ^1H NMR. The symmetrical oligo(butyl isocyanate) having the structure of eq 4 was obtained in a similar manner (Figure 3b).

It is clear from the results described above that the stability of oligo(butyl isocyanate) is significantly enhanced by acetyl end-capping. In order to evaluate the stabilizing effect, we followed the decomposition of the oligo(butyl isocyanate)s with and without acetyl end-capping in methanol- d_4 by ^1H NMR spectroscopy. The initial rate of decomposition obeyed first-order kinetics. The rate constant for the -NH terminated oligomer ($DP=20.4$) was $3.8 \times 10^{-6}\text{ s}^{-1}$ at 50°C , while that for the acetyl end-capped oligomer ($DP=22.8$) was $4.7 \times 10^{-7}\text{ s}^{-1}$ at 60°C . This indicates that the rate of decomposition is reduced to *ca.* 1/20 by the acetyl end-capping. It is well

known that low molecular-weight polyacetal (*para*-formaldehyde) can be stabilized by chemical modification of the end-groups.¹⁴ The present results demonstrate that a similar approach is effective for the stabilization of oligoisocyanates.

A sample of the poly(butyl isocyanate) having the structure of eq 3 ($\bar{M}_n = 3.97 \times 10^3$, $\bar{M}_w/\bar{M}_n = 1.20$) was separated into the individual homologues from 15 mer to 65 mer by means of supercritical fluid chromatography (SFC) using CO₂/ethanol as a mobile phase at 90°C and 20 MPa (Figure 4). Under these conditions, the acetyl end-capped polyisocyanate was resistant to depolymerization. Figure 4 also shows an SFC trace of the uniform 30 mer (C₁₅₄H₂₇₅O₃₂N₃₀F₃ = 3116.1) obtained by the fractionation. The 30 mer gave a single peak in the chromatogram (besides the peak of the authentic 15 mer added), demonstrating its uniformity with respect to *DP*.

These samples of uniform polyisocyanates would be useful for the detailed structural determination by NMR and X-ray crystallographic techniques. The molecular weight dependence of their characteristics such as liquid crystalline properties and induced optical activities is also the question to be answered by the studies of the uniform poly-

isocyanates. This has become possible by the controlled synthesis of stable polyisocyanates and subsequent fractionation with SFC.

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