Optically Active Polyisocyanates

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ABSTRACT: Optically active $poly(d-\beta-phenylpropyl isocyanate)$ has been synthesized. The optically active polymer has a negative optical rotation, opposite in sign to that of the monomer and of the model compound. but of greater magnitude. This enhanced optical activity shows that the polymer probably assumes a preferred conformation. A comparative circular dichroism (CD) study of this polymer and of a model compound indicates that dissymmetry in the polymer backbone and the aromatic side chains contribute to the CD spectrum of the optically active polymer. The nuclear magnetic resonance spectrum of the optically inactive polymer shows broad absorption bands while the spectrum of the optically active polymer has sharp peaks. This is consistent with our assumption that the optically active polymer possesses a preferred conformation. The optically active polymer is insoluble in most organic solvents. Chloroform represents a notable exception which may arise from a specific interaction between this solvent and the urea-like nature of the main chain.

rganic isocyanates have been known to cyclize to dimers and trimers in the presence of various basic reagents.^{2,3} Shashoua and coworkers⁴ first revealed that monoisocyanates could be homopolymerized by an anionic mechanism at low temperature to form linear, high molecular weight polymers which may be classified as N-substituted 1-nylons. Natta and associates⁵ reported that crystalline polymers can be obtained by the polymerization of phenyl and nbutyl isocyanates, using anionic catalysts such as lithium and sodium alkyls. Since there are no asymmetric atoms in the chain, a regularity of the chemical structure is sufficient to make the polymer, in principle, crystallizable.

Crystalline poly(n-butyl isocyanate) was also prepared by radiation-induced solid-state polymerization of the monomer at low temperature.⁶ The infrared spectrum of the polymer obtained by solid-state polymerization is guite similar to that obtained by Natta for the same crystalline polymer by catalytic liquidphase polymerization.

A number of monoisocyanates have been polymerized to high molecular weight polymers and the physical properties and chemical behavior of these materials investigated. Diffusion and sedimentation studies7 and dielectric measurements^{8,9} on poly(n-butyl isocyanate) led to the conclusion that the polymer is extremely rigid and may possess a helical conformation. Light scattering and viscosity studies¹⁰ on poly(nhexyl isocyanate) were consistent with a similar con-

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clusion. X-Ray studies¹¹ on crystalline poly(*n*-butyl isocyanate) showed that the polymer has a helical structure possessing a pseudohexagonal unit with an *a* axis of 13.3 Å and a *c* axis of 15.4 Å. The helical polymer has a translation of 1.94 Å and a rotation of 135° per monomeric unit (*i.e.*, the c axis corresponds to eight monomer residues in three helical turns). The osmotic second virial coefficient for poly(*n*-buty) isocyanate) was found to be independent of chain length and equal to the value predicted for a rodlike molecule.12 Electric dichroism of poly(n-butyl isocyanate) showed a quadratic dependence on field strength.¹³ Post-treatment (reprecipitation, annealing, and aging) of polyisocyanates tends to increase crystallinity.14 Aminolysis15 and thermal degradation16 of polyisocyanates converted the polymer to monomer and cyclic trimer. The present paper describes the synthesis of the first optically active polyisocyanate. poly(d- β -phenylpropyl isocyanate). The optically active polymer possesses a negative optical rotation, opposite to that of the monomer. Circular dichroism (CD) studies of this polymer have been carried out. In comparison with the model compound, dissymmetry of the optically active polymer chain contributes to the CD spectra. Attempts to prepare an optically active polyisocyanate from racemic monomer using a levorotatory optically active catalyst have had some success. Preliminary results show that the polymers obtained by this method are dextrorotatory.

Experimental Section

Synthesis of β -Phenylpropylamine. A. Reduction of α -Phenylpropionitrile to β -Phenylpropylamine. The method reported by Nystrom and Brown was adopted.¹⁷ Anhy-

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drous ether (700 ml) and lithium aluminum hydride (17.37 g, 0.45 mol) were placed into a 3-l., three-necked, roundbottomed flask fitted with a reflux condenser (and drying tube), a pressure-compensated dropping funnel, and a mechanical stirrer. α -Phenylpropionitrile (50 g, 0.38 mol) was introduced slowly through the dropping funnel. After the addition of nitrile was completed, water (10 ml) was added dropwise. Vigorous decomposition of the excess hydride occurred, and cooling was necessary to control the reaction. Afterward, a 20% solution of sodium potassium tartrate (500 ml) was added. After separating the ether layer, the chalky aqueous portion was extracted with ether several times. The combined ether extracts were dried over sodium sulfate. Distillation provided β -phenylpropylamine, 42 g, 84%, bp 69–70° (0.75 mm), η^{24} D 1.5268. The infrared spectrum showed strong NH absorption (3500 cm^{-1}) and no nitrile absorption (2250 cm^{-1}) .

B. Resolution of β -Phenylpropylamine. The resolution of racemic β -phenylpropylamine (300 g) was similar to the resolution of racemic α -phenylethylamine reported by Ingersoll.¹⁸ This method depends on the fractional crystallization of d- β -phenylpropylamine l-malate from water. The free amine was obtained by decomposing the pure malate with 1% excess 2 N sodium hydroxide. Distillation provided 30 g of *d*-amine, $[\alpha]^{25}D + 35.5^{\circ}$ (*c* 5, 95% ethanol).

Synthesis of the Monomer. *β*-Phenylpropylisocyanate was prepared by the method given by Rossi and coworkers.¹⁹ Concentrated hydrochloric acid (18.7 ml) was added to a suspension of β -phenylpropylamine (30 g, 0.222 mol) in 200 ml of water. The mixture was warmed to 80° and sodium cyanate (14.82 g) was added. The mixture was held at 80° for 15 min and then cooled to room temperature. Concentrated hydrochloric acid (44.2 ml) and benzene (100 ml) were added. After chilling to less than 10°, solution of sodium nitrate (15.59 g in 100 ml water) was added. When the addition was complete, the benzene layer was decanted, and the aqueous layer was extracted with 50 ml of benzene. The combined extract was dried over sodium sulfate. Benzene was evaporated under reduced pressure. The product (30.1 g) was obtained by distillation: bp 92–93° (1 mm); n^{24} D 1.5195; yield 84%. d- β -Phenylpropyl isocyanate showed $[\alpha]^{25}D + 35^{\circ}$ (c 5, 95% ethanol), $[M]^{25}D + 44.8^{\circ}$ (c 1.045, chloroform).

Anal. Calcd for C₁₀H₁₁NO: C, 74.53; H, 6.83; N, 8.69. Found: C, 74.62; H, 6.93; N, 8.88.

Polymerization by Anionic Catalysis. Polymerization was carried out in a serum-capped Pyrex glass tube. The tube was flamed while being swept with dry helium in order to ensure maximum dryness. (The helium was purified and dried by means of a train of alkaline pyrogallol, concentrated sulfuric acid, potassium hydroxide, calcium chloride, and Indicab, a carbon dioxide absorbent produced by the Fisher Scientific Co., before reaching the polymerization tube.) Dry N,N-dimethylformamide (2 ml) was added to the tube and cooled with Dry Ice-acetone. β -Phenylpropyl isocyanate (0.5 ml) was added. Afterward, a saturated solution of sodium cyanide in dry DMF (0.5 ml) was added dropwise from a syringe. The polymerization was terminated by adding methanol (4 ml). The polymer was isolated by filtration, washed with large amounts of methanol, and dried at 40° under vacuum.

Anal. Calcd for C₁₀H₁₁NO: C, 74.53; H, 6.83; N, 8.69. Found: C, 74.00; H, 6.96; N, 8.61.

Polymer prepared from d monomer initiated by sodium cyanide showed $[\alpha]^{25}D - 468.8^{\circ}$, $[M]^{25}D - 754.8^{\circ}$ (c 0.333, chloroform); polymer prepared from *dl* monomer initiated

by sodium *l*-borneolate showed $[\alpha]^{25}D + 18^{\circ}$, $[M]^{25}D + 29^{\circ}$ (c 1, chloroform); polymer prepared from dl monomer initiated by potassium *l*-mentholate showed $[\alpha]^{25}D + 60^{\circ}$, $[M]^{25}D + 96.6^{\circ} (c 1, chloroform).$

Synthesis of Model Compound, d-N,N-Diacetyl-\beta-phenylpropylamine. Synthesis of the model compound was accomplished by acetylation of d- β -phenylpropylamine with ketene by the method described by Dunbar and White,20 and Smirnova and coworkers.²¹ Ketene, generated by the pyrolysis of acetone, was introduced into a hexane solution (20 ml) of d- β -phenylpropylamine (1.454 g) at room temperature. The temperature of the mixture increased gradually as ketene was added. When the temperature started decreasing, the introduction of ketene was temporarily stopped. One drop of concentrated sulfuric acid was added at room temperature and the flow of ketene was resumed. The temperature rose again. When the temperature began falling off, the diacetylation was complete. The mixture was washed with saturated sodium bicarbonate solution and water until the washings showed neutrality. The product was dried over magnesium sulfate and distilled: bp 118° (0.5 mm); n^{24} D 1.5152; $[\alpha]^{25}$ D +118.4° (c 0.59, 95% ethanol); $[\alpha]^{25}D + 114.4^{\circ}$; $[M]^{25}D + 250.5^{\circ}$ (c 0.347, chloroform).

Anal. Calcd for C13H17NO2: C, 71.23; H, 7.76; N, 6.39. Found: C, 71.04; H, 7.78; N, 6.39.

Synthesis of Optically Active Catalysts, Sodium /-Borneolate and Potassium l-Mentholate. Synthesis of these two alkoxides is similar to that reported by Leffler and Calkins.22 The optically active alcohol, *l*-borneol (20 g, 0.129 mol) or l-menthol (20 g, 0.128 mol), was allowed to react with excess sodium (5 g, 0.218 g-atom) or potassium (8 g, 0.205 g-atom) in a 250-ml, three-necked, round-bottomed flask fitted with a reflux condenser (and drying tube), a gas-inlet tube, and a stainless-steel Hershberg stirrer. The reaction was carried out in refluxing toluene (50 ml) and under dry nitrogen. After 15 hr, most of the metal had disappeared. After filtering to remove the excess metal, the alkoxide was isolated by evaporating the solvent.

Measurements. Circular dichroism spectra were carried out on a Cary 60 spectropolarimeter equipped with a Cary CD attachment. A 450-W Osram Xenon lamp was used as the light source. Spectra were obtained at room temperature with 1.00- and 0.2-mm fused silica cells. Nuclear magnetic resonance spectra were obtained with a Varian HR-220 spectrometer. Infrared spectra were obtained with a Perkin-Elmer 521 infrared spectrometer.

Ultraviolet measurements were run on a Cary 14 spectrophotometer. Optical rotations were measured with a Perkin-Elmer 141 polarimeter. Viscosity determinations were carried out at 30° in chloroform by using an Ubbelohde dilution-type viscometer and it was found that the optically active polymer from the d monomer had an intrinsic viscosity of 0.73 dl/g.

Results and Discussion

We first attempted to polymerize α -phenylethyl isocyanate; however, no polymer was obtained. This agrees with Shashoua's observation that the steric factors which influence the polymerizability of a given isocyanate appear to be associated with the α -carbon atoms. When the isocyanate group is attached to a primary aliphatic carbon atom, polymerization occurs

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Figure 1. 220-MHz nuclear magnetic resonance spectra: (A) optically active polymer, $poly(d-\beta-phenylpropyl iso$ cyanate); (B) racemic polymer, $poly(dl-\beta-phenylpropyl iso$ cyanate); both polymers are in deuteriochloroform at 75°.

readily. Attachment to a secondary carbon atom prevents polymerization.

We therefore synthesized and resolved β -phenylpropylamine. The monoisocyanate from this amine polymerizes at low temperature (-78°) in DMF using anionic initiator, sodium cyanide.

The formation of the 1-nylon structure is shown by the appearance of the amide I band at 1695 cm⁻¹ and the disappearance of the isocyanates band at 2250 cm^{-1} in the infrared spectrum. The presence of the intense carbonyl absorption band suggests that the polyisocyanate has the structure

$$O$$

 $(N-C)$

the same as the N-substituted 1-nylons prepared by Shashoua⁴ and Natta.⁵ The infrared spectra of the optically active and the racemic polyisocyanates are essentially the same. However, the polyisocyanate polymer, which possesses a urea-like backbone, has a carbonyl absorption higher than those of the substituted ureas. Tetramethylurea exhibits carbonyl absorption at 1668 cm⁻¹ while tetraethylurea absorbs at 1661 cm^{-1,23} Iwakura and coworkers²⁴ reported that the carbonyl absorption of imidazolidone-2 occurs at 1660 cm⁻¹ and the same characteristic absorption band appears at 1751 cm⁻¹ in N-acetylimidazolidone-2. Apparently, acylation of the NH group in the cyclic urea shifts the carbonyl absorption to a substantially higher frequency.

The nuclear magnetic resonance (nmr) spectra of the optically active polymer (from d monomer) and of the optically inactive polymer (from dl monomer) in deuteriochloroform taken with a Varian HR-220 MHz instrument at 75° show some interesting differences and are illustrated in Figure 1. The absorption from the phenyl protons appears as two bands in the optically active polymer. The δ values for these protons relative to tetramethylsilane are 7.15 and 7.37 ppm. The areas under these absorption bands have a ratio of approximately 3:2. The band appearing at 7.37 ppm probably arises from the ortho protons. The resolution of phenyl protons has also been observed by Bovey and coworkers²⁵ in polystyrene. In the optically inactive polymer, no such resolution is observed with the Varian HR-220.

Integration of the spectral bands shows areas under these absorption bands in the ratio of 5:3:3, indicating that the methinyl proton signal is combined with the methylene proton signal in both the optically active polymer and the optically inactive polymer. In the optically active polymer, however, the methinylmethylene proton absorption bands are distinguishable and can be assigned approximate δ values of 3.57 and 3.48 ppm, respectively. The δ values for the methyl protons are 1.32 ppm in the optically active polymer, and 1.37 ppm in the racemic polymer. Although the chemical shifts of all nmr bands in both polymers are similar, the widths of the bands of the racemic polymer are broader than those of the optically active polymer.

In general, either higher segmental mobility or a smaller number of conformational states tends to narrow nmr bands. The narrower nmr bands in the spectrum of the optically active polymer cannot arise from higher segmental mobility. A better explanation is that the optically active polymer should have fewer allowed conformational states than the racemic polymer.

X-Ray diffraction shows that the optically active polymer has a crystalline structure, while the racemic polymer is amorphous. Neither polymer forms a fiber.

The softening point of the optically active polymer is about 230°. This is about 20° higher than that of the racemic polymer, as expected.

A solution of the optically active polymer from dmonomer in concentrated sulfuric acid has ultraviolet absorption peaks at 312, 273, and 266 nm and a shoulder at 262 nm. The model compound absorbs at 301, 273, and 267 nm and has a shoulder at 262 nm. Although the uv spectra are similar for the polymer and the model compound, their circular dichroism spectra are significantly different. Plots of molar ellipticity vs. wavelength are shown in Figure 2. The polymer exhibits two positive dichroic peaks at 275 and 267 nm which can be attributed to the symmetry-forbidden $\pi \rightarrow \pi^*$ transitions of the phenyl chromophore. A monosubstituted benzene chromophore exhibits three major transitions in the accessible isotropic absorption region; one of them is a weak band termed ${}^{1}L_{b}$ in the Platt notation²⁶ in the 255-275-nm region corresponding to a symmetry-forbidden $\pi \rightarrow \pi^*$ transition. The extinction coefficient of benzene varies over an enormous range.²⁷ If the 183-nm transition with ϵ approaching 50,000 is a normal, allowed transition, then the bands near 250 nm must be "partially forbidden," while those at 330 nm are "highly forbidden."

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The CD spectrum of the model compound shows a broad unsymmetric band with a trough at 341 nm and two positive bands at 293 and 267 nm, followed by a region of positive dichroism below 254 nm.

The change from a protonating solvent to an aprotic solvent shows interesting results in the CD spectra of both the polymer and the model compound. The results for chloroform are shown in Figure 3. The polymer in chloroform shows a broad positive circular dichroism band between 274 and 290 nm. In contrast, the long-wavelength region of the spectrum in sulfuric acid shows two well-resolved peaks. Below this retion, the polymer in chloroform produces a strong negative circular dichroism, as in sulfuric acid. This negative dichroism has a molar ellipticity of -28,000deg cm²/dmol in chloroform, 18 times larger than the value observed in sulfuric acid. The polymer also shows a region of positive dichroism emerging below 234 nm. The strong negative dichroism in the polymer is red-shifted from 248 nm in sulfuric acid to 252 nm in chloroform, and the ellipticity is greatly enhanced.

For the model compound in the chloroform (Figure 3) the circular dichroism results show a broad unsymmetric band with a trough at 243 nm. This negative dichroic band also appears in sulfuric acid (Figure 2), but at longer wavelength with reduced ellipticity. The model compound also shows a region of positive dichroism below 232 nm.

The facts that in chloroform the $n \rightarrow \pi^*$ transition of the amide chromophore is shifted to a longer wavelength and an enhanced ellipticity is observed suggest that chloroform and sulfuric acid have different solvating effects on the polymer.

Interactions between amides and sulfuric acid result in protonation. Evidence from cryoscopic measurements by Fraenkel and Franconi²⁸ showed that several simple amides such as N,N-dimethylformamide, N,Ndimethylacetamide, N-methylacetamide, and acetamide were monoprotonated in 100% sulfuric acid predominantly on oxygen. Berger and associates²⁹ studied the protonation of N-methylacetamide in acidic solutions using an nmr technique. They also concluded that amides protonate mainly on oxygen. The protonated amide resonance forms can be depicted as



We believe that polyisocyanates are substantially pro-

62 (1959).



Figure 2. Circular dichroism spectra of the optically active polymer, $poly(d-\beta-phenylpropyl isocyanate)$, and of the model compound, d-N,N-diacetyl- β -phenylpropylamine, in sulfuric acid.



Figure 3. Circular dichroism spectra of the optically active polymer, $poly(d-\beta-phenylpropyl isocyanate)$, and of the model compound, *d*-N,N-diacetyl- β -phenylpropylamine, in chloroform.

tonated and as a result, the polymer is extended as a polyelectrolyte.

In chloroform, the interaction between the polymer and the weakly acidic solvent may result in dipoledipole interactions. The following structure is illustrative of solvation that can occur between chloroform and the polymer backbone



Here the chloroform molecule interacts with a unit including two carbonyls and the nitrogen as the electron-rich center. The bulkiness of this chloroform solvate may prevent another chloroform molecule from solvating an adjacent imide unit. Such solvation may restrict the possible conformations of the polymer. Chloroform, however, is a relatively small molecule, spherical in shape. It could, therefore, interact with more imide units in the backbone than most other solvents. This model may also explain the specific solvent effect of chloroform.

Pino and associates³⁰ synthesized an (R)-3,7dimethyl-1-octene-styrene copolymer and a model compound, (3S,9S)-3,9-dimethyl-6-phenylundecane. The dimethyl ether extractable fractions of the copolymer and the model compound in chloroform show multiple circular dichroism Cotton effects in the 260nm spectral region. The authors attributed these Cotton effects to $\pi \rightarrow \pi^*$ transitions of the phenyl chromophore.

In Pino's copolymer, the asymmetric carbon atoms of the side chains are far removed from the phenyl groups as can be seen in the representative partial sequence shown.



In polyisocyanates, the macromolecular sequence can be represented as



Here the phenyl groups are attached to the asymmetric carbon atoms. We expect and find a large

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TABLE I ROTATORY PROPERTIES OF POLYMERS AND THEIR MODEL COMPOUNDS

	[α]²5D, deg	CD bands, in chloroform	
	(in chloro- form)	λ _{max} , nm	Molar ellipticity
Polyisocyanate	- 468.8	280 252	+1,000 -28,000
<i>d</i> -N,N-Diacetyl-β-phenyl- propylamine, model com- pound	+114.4	243	-9,100
(<i>R</i>)-3,7-Dimethyl-1-octene– styrene copolymer	-83	262	- 990
(3 <i>S</i> ,9 <i>S</i>)-3,9-Dimethyl-6- phenylundecane, model compound	+14.2	262	+56

aromatic group contribution to the rotational strength in both the polymer and its model compound. However, the polymer exhibits substantially enhanced rotatory properties (*cf.* Table I).

The α -olefin-styrene copolymer also has a higher rotational strength than that of its model compound. Pino, *et al.*, attributed this observation to the greater conformational rigidity of the phenylethylene groups in the copolymer. Table I illustrates the salient features of these two polymer systems.

We can combine the findings from polyisocyanates, the (*R*)-3,7-dimethyl-1-octene-styrene copolymer, and their model compounds. Enhancements of $[\alpha]_D$ for the polymers as compared to their model compounds are explained by conformational selections and preferences induced by optically active side chains on the main chains. The differences in CD patterns between the polyisocyanates and the N,N-diacetyl- β -phenylpropylamine are indicative that both aromatic and the urea-like main-chain chromophores contribute to the CD bands. It is reasonable therefore to suggest that the optically active polyisocyanates assume an ordered structure in chloroform solution.

Synthesis of optically active polyisocyanates by optically active catalysts was also carried out. Optically active alcohols such as *l*-borneol and *l*-menthol were allowed to react with sodium or potassium to make optically active alkoxide initiators. Optically active alcohols with steric hindrance near the hydroxyl group should be effective for stereoelection. At a 5 mol % initiator level, we were able to polymerize the racemic β -phenylpropyl isocyanate. The CD spectra of the resulting polymers follow the pattern of the optically active polymer prepared from the *d* monomer but with much lower optical rotatory intensity.

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