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Catalytic Asymmetric Benzaldehyde Cyanohydrin Synthesis with Synthetic Optically Active Polymer.
III. *N*-Substituted Poly-(s)-isobutylethylenimine

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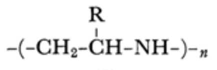
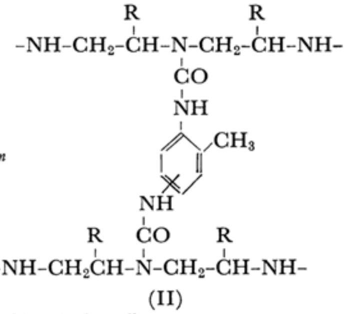
Asymmetric syntheses of benzaldehyde cyanohydrin in the presence of polymers of *N*-methyl-, *N*-ethyl- and *N*-benzyl-(s)-2-isobutylethylenimine as catalysts have been studied. The selectivity of these polymers was poor (optical yield of (−)-isomer obtained; 0—1%) compared with that of a non-*N*-substituted polymer (20%). It seems that the large difference in the optical yield can be ascribed to their conformation. As to the polymer being capable of promoting the reaction asymmetrically, it is assumed that the isobutyl group and a helical form are the responsible factors. On the basis of these findings, a model for the addition step has been suggested in order to explain the observed result.

In asymmetric syntheses of benzaldehyde cyanohydrin using poly-(s)-isobutylethylenimine (I) and its cross-linked polymer (II) as catalysts, the signs of the optical rotation of cyanohydrin produced were unexpectedly opposite to each other, though the two polymers are of the same configuration.[1,2] The cause of this was found to be due, not to the cross-linking of the polymer, but to the contribution of –NH–CO–N= group, for when linear and soluble polymers containing –NH–CO–N= group were used the (+)-isomer was obtained as well as when the insoluble polymer II was used. This suggests that the configuration of the product is not necessarily controlled by the configuration but rather by the conformation of the catalyst.



$$\text{-(-CH}_2\text{-}\overset{\text{R}}{\text{C}}\text{H-NH-)}_n$$

(I)



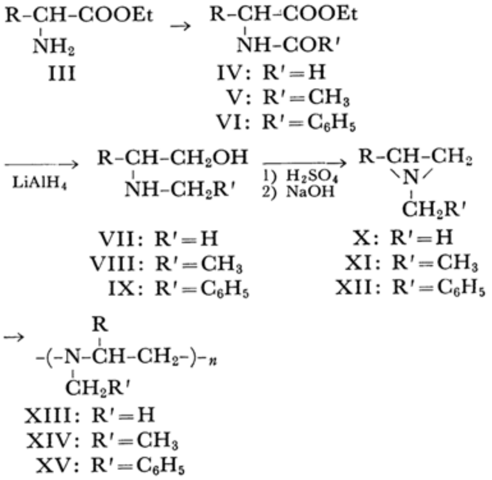
(II)

(R = Isobutyl)

This paper will describe the results of a similar asymmetric synthesis using *N*-substituted poly-(s)-isobutylethylenimine as the catalyst, it will attempt to elucidate in detail how the reactions proceed stereochemically.

The selectivity of the polymer I in the asymmetric reaction may be attributed to the steric effect of the regularly-arranged isobutyl group adjacent to the catalytic center and to the conformation effect of the polymer. For conformation of this, we have so far no data with which to draw any conclusion, yet if we assume a helical form for it, the reaction can be explained. In the *N*-substituted polymer, we can imagine that the pitch of the presumed helix becomes elongated by the steric hindrance of *N*-substituent and by the disappearance, in consequence of tertiarization, of hydrogen atom that might otherwise form hydrogen bonding between nitrogen atoms. Therefore, the said steric effect of the isobutyl group will be reduced by the unfavorable conformation, and a low selectivity may be expected.

Synthesis of Polymer.—Polymers of *N*-methyl- (XIII), *N*-ethyl- (XIV) and *N*-benzyl-(s)-isobutylethylenimine (XV) were prepared by the following process:



$$\underset{\text{NH}_2}{\text{R-CH-COOEt}} \rightarrow \underset{\text{NH-COR}'}{\text{R-CH-COOEt}}$$

III

IV: $R'=H$
V: $R'=CH_3$
VI: $R'=C_6H_5$

$$\xrightarrow[\text{LiAlH}_4]{} \underset{\text{NH-CH}_2\text{R}'}{\text{R-CH-CH}_2\text{OH}} \xrightarrow[\text{1) H}_2\text{SO}_4 \;\; \text{2) NaOH}]{} \underset{\underset{\text{CH}_2\text{R}'}{\text{N}}}{\text{R-CH-CH}_2}$$

VII: $R'=H$
VIII: $R'=CH_3$
IX: $R'=C_6H_5$

X: $R'=H$
XI: $R'=CH_3$
XII: $R'=C_6H_5$

$$\rightarrow \text{-(-}\underset{\text{CH}_2\text{R}'}{\text{N}}\text{-}\overset{\text{R}}{\text{C}}\text{H-CH}_2\text{-)}_n$$

XIII: $R'=H$
XIV: $R'=CH_3$
XV: $R'=C_6H_5$

(R = Isobutyl)

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[1] S. Tsuboyama, This Bulletin, **35**, 1004 (1962).
[2] S. Tsuboyama, ibid., **38**, 354 (1965).

TABLE I. ASYMMETRIC SYNTHESIS OF BENZALDEHYDE CYANOHYDRIN WITH *N*-SUBSTITUTED POLY-(*s*)-ISOBUTYLETHYLENIMINE

Catalyst		Cyanohydrin			
Polymer	$[\alpha]_D$ of polymer*1 degree	Yield %	α_D, degree	$[\alpha]_D$*2, degree	P%
Original (I)	+59.70*3	50.0	−1.81	−7.07	16.1
Original (I)	+66.70	51.5	−2.28	−8.57	19.6
N-Methyl (XIII-1)	−46.03	82.0	−0.08	0	0
N-Methyl (XIII-2)	−10.60	61.1	−0.33	−1.01	2.3
N-Methyl (XIII)	−52.88*3	72.9	−0.04	0	0
N-Methyl (XIII)	−70.00	87.8	−0.09	0	0
N-Ethyl (XIV)	−144.8*3	64.2	0.00	0	0
N-Ethyl (XIV)	−207.4	91.2	0.00	0	0
N-Benzyl (XV)	−219.0	64.8	−0.20	−0.59	1.3

*1 *c* 0.5—2 in benzene. *2 *c* 1—5 in benzene.
*3 Lower molecular weight fraction. Molecular weight of polymer I: 1020, 5000.

Optically active *N*-substituted imine monomers, which were prepared from acylated amino acid esters through the corresponding amino alcohols, were polymerized by boron trifluoride-etherate under nitrogen. They became tacky low-molecular-weight polymers when heated at 100—120°C for a day or two; heating at higher temperatures causes thermal degradation.3) Several fractionations in acetone gave *N*-ethyl and *N*-benzyl polymers of a fairly high degree of crystallinity but with the low molecular weights of 1300—1600. For reference, the polymer I was treated with formaldehyde and formic acid (XIII-1) or methyl iodide (XIII-2) in order to introduce the *N*-methyl group into it. According to the analytical data and the infrared spectra, XIII-1 seemed to be partly acylated, and the amino groups of XIII-2 were partially quarternarized. In both cases, various treatments failed to remove the groups involved. The infrared spectra and optical rotatory dispersion curves of these polymers are shown in Figs. 1 and 2.

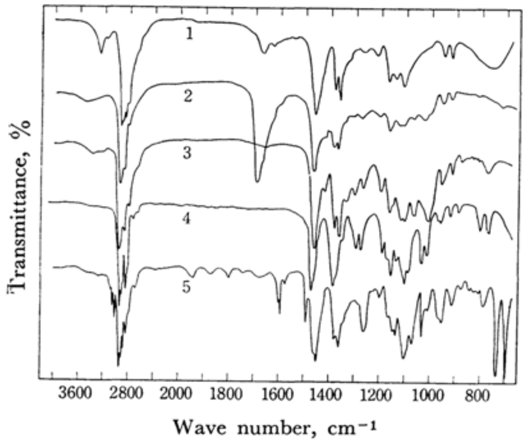

Fig. 1. Infrared absorption spectra.
1. polymer I; 2. polymer XIII-1 (*N*-methyl); 3. polymer XIII (*N*-methyl); 4. polymer XIV (*N*-ethyl); 5. polymer XV (*N*-benzyl).

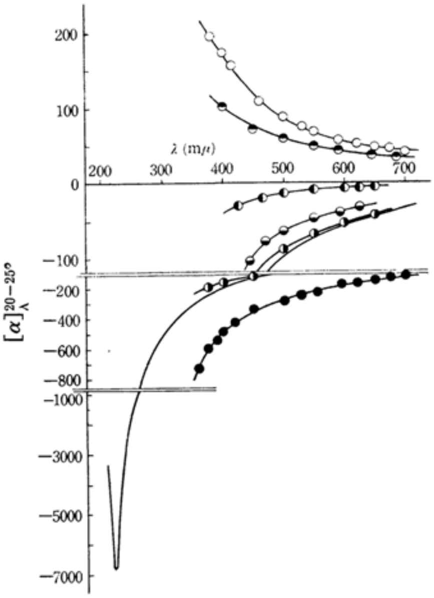

Fig. 2. Optical rotatory dispersion curves.
○, polymer I in benzene; ◓, polymer I in dioxane; ◐, polymer XIII-2 (*N*-methyl) in benzene; ◒, polymer XIII-1 (*N*-methyl) in dioxane; ◑, polymer XIII (*N*-methyl) in dioxane; ●, polymer XIV (*N*-ethyl) in benzene; —, polymer XV (*N*-benzyl) in isooctane

Asymmetric Synthesis.—The asymmetric synthesis and analysis of the product were carried out in the manner described in a previous paper.1) The results are summarized in Table I.

The selectivity of these polymers for the asymmetric reaction was quite low or non-existent and was independent of their molecular weight. As regards the *N*-methyl polymer XIII-2, NH group capable of promoting the asymmetric reaction

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3) W. G. Barb, *J. Chem. Soc.*, **1955**, 2577.

seemed still to remain in it. The rates of cyanohydrin formation with the polymers XIII and XIV indicated that the reactions did not proceed asymmetrically from the beginning (Fig. 3). These findings justify the expectation mentioned above; nevertheless, some other causes might produce a similar result. For instance, if the racemization rate of cyanohydrin is faster than the rate of formation during the reaction, the selectivity of the reaction will become hardly observable. In confirmation of this, the racemization of optically active cyanohydrin in the presence of the polymer XIV was examined; we thus found that the optical rotation of cyanohydrin is not affected by the presence of the polymer.

There still remains the problem of the stereoregularity of these polymers. Though there is no suitable method for the direct determination of the regularity, it seems likely that, in acid-catalyzed polymerization, a preferential break in the cyclic imine ring at CH_2–N bond occurs independently of the asymmetric carbon, giving rise to polymers with an unaffected asymmetry.4–6) Consequently, the configuration of the asymmetric atoms in the polymer must be identical to those of the monomer. This matter will be discussed in another paper on the ring-opening orientation of (R) (+)-ethylethylenimine. Furthermore, the optical rotatory dispersion data may account for the configurational regularity, though the following is not necessarily a proper comparison because it contains an involved group, as has been described above. As is shown in Fig. 2, the curve of the polymer I is positive, whereas when the polymer is *N*-methylated, the curve becomes negative, similar to that found in the case of the polymer XIII prepared from monomers already containing *N*-methyl groups. Therefore, the regularity of these polymers may be considered to be similar despite the large difference in selectivity. This again seems to suggest that the variances in the contributions of these polymers to asymmetric synthesis as catalysts are ascribable, not to their configurational regularity, but to their overall molecular arrangement—conformation. As regards the *N*-benzyl polymer, it may be different from *N*-alkylated polymers with a slight selectivity as a result of a favorable conformation resulting from interaction between aromatic rings in the side chain of the polymer.

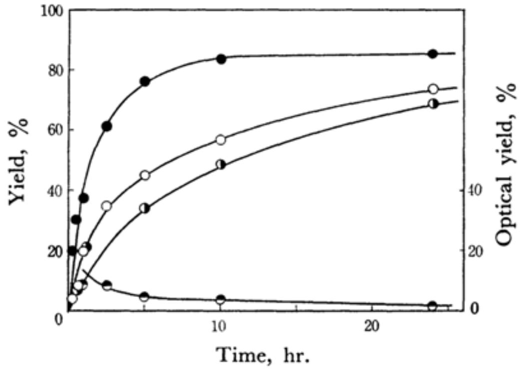

Fig. 3. Time dependence of cyanohydrin formation and its optical yield: ○, polymer XIII (*N*-methyl); ●, polymer XIV (*N*-ethyl); ◑, polymer XV (*N*-benzyl); ◓, optical yield with polymer XV.

Previously it was postulated that the amine catalyst in this asymmetric synthesis should have not only one steric group in a monomeric unit, but also one more obstructive factor with regard to the mobile catalytic center. However effective the steric group may be, because of the ability of trivalent nitrogen to undergo rapid inversion,7) and since the catalytic center in a monomeric unit may also be converted into their conformers and since asymmetric reactions occur on two sides of the conformer, the products that arise there are enantiomers of equal amounts; hence, there will be no optical rotation. Therefore, only when the accessibilities of the reagent to the catalytic center are different on the two sides of the amine does an asymmetric reaction become possible. In the polymer I, the isobutyl group and the helical conformation are likely to be responsible for the asymmetric reaction. In the *N*-substituted polymer, however, the contribution of the conformation to the reaction is smaller than in the polymer I; this will cause the reagent to approach the active site equivalently, and therefore the optical yield will be lowered.

In the early stage of the reaction, the carbonyl reagent and the amine catalyst form a stereospecific transition complex, to which cyanide ion is then added.8) Accordingly, the conformation of the transition intermediate should be the most important factor in controlling the steric course of the reaction. In the model of the polymer I shown in Fig. 4, it is assumed that the conformation is helical, even in such a solvent. The isobutyl group will be found on the outside of the helix, with its axis perpendicular to the plane of the paper. In the transition state, the carbonyl reagent will approach the least-hindered site of the conformation of the catalyst as a result of the

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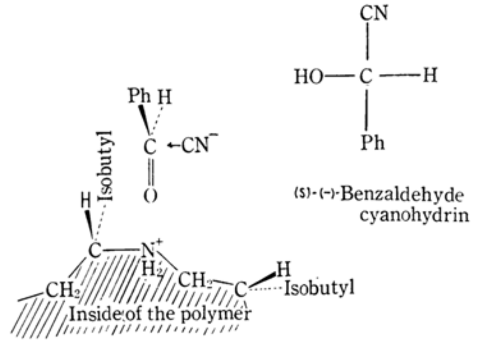
4) J. D. Jones, A. Langsjoen, M. M. C. Neumann and J. Zomlefer, *J. Org. Chem.*, **9**, 125 (1944); J. D. Jones, ibid., **9**, 484 (1944).

5) L. B. Clapp, *J. Am. Chem. Soc.*, **70**, 184 (1948).

6) Y. Minoura, M. Takebayashi and C. C. Price, ibid., **81**, 4689 (1959).

7) J. Meisenheimer, L. Angermann, O. Finn and E. Veiweg, *Ber.*, **57**, 1747 (1924); A. T. Bottini and J. D. Roberts, *J. Am. Chem. Soc.*, **80**, 5203 (1958).

8) V. Prelog and M. Wilhelm, *Helv. Chim. Acta*, **37**, 1634 (1954).



(S)-(-)-Benzaldehyde cyanohydrin

Fig. 4. Asymmetric synthesis of benzaldehyde cyanohydrin with polymer I.

steric group. Hence, the product may be expected to be of the s-configuration. Cyanohydrin was found by observation to be negative in sign, which means that it has the s-configuration and that the assumption of a steric course is justified. For the cross-linked polymer II, some other model must be constructed.

Experimental

***N*-Formyl-L-leucine Ethyl Ester (IV).** — The procedure proposed by du Vegneaud and Meyer for the formylation of phenylalanine[9] was used with a slight modification. To a solution of L-leucine ethyl ester (III) (32 g., 0.2 mol.) in 88% formic acid (360 g., 7 mol.) was added dropwise acetic anhydride (122 g., 1.2 mol.) at room temperature with vigorous stirring. The reaction mixture was then kept at 70°C for 15 min. After the excess of the reagents had been removed in vacuo, the residual liquid was distilled under reduced pressure to give 36 g. (96%) of a colorless liquid, b. p. 124—125°C/3 mmHg, n^{27}_{D} 1.4459, $[\alpha]^{27}_{D}$ $-31.90°$ (*c* 2.539, ethanol).

Found: C, 57.72; H, 8.99; N, 7.32. Calcd. for $C_9H_{17}NO_3$: C, 57.73; H, 9.15; N, 7.48%.

***N*-Acetyl-L-leucine Ethyl Ester (V).**—This was prepared according to the method of the literature.[10] The acetylated ester V was obtained in 94% yield, b. p. 138—139°C/6 mmHg, n^{20}_{D} 1.4470, $[\alpha]^{20}_{D}$ $-42.07°$ (*c* 2.686, ethanol). (Found: C, 59.62; H, 9.19; N, 6.87%.)

***N*-Benzoyl-L-leucine Ethyl Ester (VI).**—The ester was prepared by the method given by Bergmann and Zervas.[11] Recrystallization from petroleum ether afforded 25 g. (95%) of fine needle crystals (from 16 g., 0.1 mol. of ester), m. p. 66.5—67.5°C, $[\alpha]^{25}_{D}$ $-22.47°$ (*c* 1.112, ethanol). (Found: C, 68.18; H, 8.03; N, 5.24%)

***N*-Methyl-L-leucinol (VII).**—The amino alcohol was obtained from IV (18.7 g., 0.1 mol.) by refluxing with lithium aluminum hydride for 24 hr. in ether. The yield of VII was 10.6 g. (81%), and it had b. p. 84.5—85°C/8 mmHg, n^{27}_{D} 1.4425, $[\alpha]^{23}_{D}$ $+47.33°$ (*c* 1.627, ethanol).

Found: C, 64.08; H, 13.46; N, 10.93. Calcd. for $C_7H_{17}NO$: C, 64.07; H, 13.06; N, 1.68%.

Monooxalate: crystallized from ethanol in needles, m. p. 143—143.5°C, $[\alpha]^{30}_{D}$ $+12.45°$ (*c*, 0.964, ethanol).

Found: C, 48.68; H, 8.49; N, 6.22. Calcd. for $C_9H_{19}NO_5$: C, 48.85; H, 8.66; N, 6.33%.

***N*-Ethyl-L-leucinol (VIII).**—The amino alcohol was prepared in 77% yield (8.3 g.) from V (15 g., 0.075 mol.) according to the procedure described above. The product had b. p. 82—83°C/6 mmHg, m. p. 38—39°C, $[\alpha]^{18}_{D}$ $+48.01°$ (*c* 2.084, ethanol).

Found: C, 66.11; H, 13.10; N, 9.50. Calcd. for $C_8H_{19}NO$: C, 66.15; H, 13.19; N, 9.64%.

***N*-Benzyl-L-leucinol (IX).**—This compound also was prepared from VI (17 g., 0.064 mol.) and lithium aluminum hydride in tetrahydrofuran. The solution of the ester was refluxed for 3 hr. A silky crystal (10.9 g., 81%) was obtained by recrystallization from petroleum ether, m. p. 73—74°C, $[\alpha]^{26}_{D}$ $+23.44°$ (*c* 1.024, benzene).

Found: C, 75.46; H, 10.19; N, 6.66. Calcd. for $C_{13}H_{21}NO$: C, 75.31; H, 10.21; N, 6.76%.

***N*-Methyl-(s)-isobutylethylenimine (X).** — The procedure followed was Leighton's method.[12] Redistillation over sodium gave 4.5 g. (40%) of a volatile liquid which odored of imine from VII (13 g., 0.1 mol.), b. p. 116—117°C, $n^{31.5}_{D}$ 1.4063, $[\alpha]^{31.5}_{D}$ $+30.18°$ (*c* 0.994, benzene). The infrared specturm showed the presence of an imine ring (3050 cm^{-1}) and of the N–CH_3 group (2785 cm^{-1}).

Found: C, 73.85; H, 13.11; N, 12.43. Calcd. for $C_7H_{15}N$: C, 74.27; H, 13.36; N, 12.37%.

The reaction product of X with hydrogen chloride in ether was recrystallized from ether-ethanol, m. p. 149—150°C, $[\alpha]^{21}_{D}$ $+23.32°$ (*c* 2.745, ethanol). It is probably 1-chloro-4-methyl-2-methylaminopentane hydrochloride.

Found: C, 45.11; H, 9.08; N, 7.33; Cl, 38.65. Calcd. for $C_7H_{17}NCl_2$: C, 45.17; H, 9.21; N, 7.53; Cl, 38.10%.

***N*-Ethyl-(s)-isobutylethylenimine (XI).**—This also was prepared by Leighton's method. From VIII (18 g., 0.12 mol.), the imine was obtained as a colorless liquid (7.5 g., 48%), b. p. 135—136°C, n^{20}_{D} 1.4161, $[\alpha]^{20}_{D}$ $+22.67°$ (*c* 1.147, benzene). The infrared spectrum showed the presence of an imine ring at 3060 cm^{-1}.

Found: C, 75.41; H, 13.23; N, 10.98. Calcd. for $C_8H_{17}N$: C, 75.52; H, 13.47; N, 11.01%.

The reaction product of XI with hydrogen chloride in ether was white flakes and had m. p. 141—142.5°C, $[\alpha]^{25}_{D}$ 0.00° (*c* 0.2132, ethanol), after several recrystallizations from ether-ethanol.

Found: C, 48.17; H, 9.28; N, 6.75; Cl, 35.61. Calcd. for $C_8H_{19}NCl_2$: C, 48.01; H, 9.57; N, 7.00; Cl, 35.43%.

From the mother liquor another crystal was obtained, m. p. 204—205°C, $[\alpha]^{28}_{D}$ $+8.48°$ (*c* 1.061, ethanol).

Found: C, 48.20; H, 9.37; N, 7.23; Cl, 35.11. Calcd. for $C_8H_{19}NCl_2$: C, 48.01; H, 9.57; N, 7.00; Cl, 35.43%.

It is probable that the former is 2-chloro-1-ethylamino-4-methylpentane hydrochloride and that the latter is 1-chloro-2-ethylamino-4-methylpentane hydrochloride, because the latter, which has an optical activity, seems to be produced by breaking at the primary

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9) V. du Vigneaud and C. E. Meyer, *J. Biol. Chem.*, **98**, 295 (1932).

10) E. Fischer, *Ber.*, **34**, 433 (1901).

11) M. Bergmann and L. Zervas, *J. Biol. Chem.*, **133**, 341 (1936).

12) P. A. Leighton, *J. Am. Chem. Soc.*, **69**, 1540 (1947).

carbon of the cyclic imine ring, regardless of the asymmetric carbon, and so the asymmetry is maintained.

***N*-Benzyl-(s)-isobutylethylenimine (XII).**—The imine was produced in 46% yield (3.1 g.) from IX (7 g., 0.034 mol.) by the procedure described above. The product had b. p. 98.5—99.5°C/6 mmHg, n_D^{23} 1.4975, $[\alpha]_D^{23}$ $+9.74°$ (*c* 1.129, benzene). The infrared spectrum indicated an imine band at 3030 cm^{-1}.

Found: C, 82.35; H, 9.93; N, 7.97. Calcd. for $C_{13}H_{19}N$: C, 82.48; H, 10.12; N, 7.40%.

Poly-(s)-*N*-methylisobutylethylenimine (XIII).—The polymerization of the imine was carried out as described previously,[1] and the product obtained was refined by fractionation in cold acetone. The product was a light-yellow tacky solid which was soluble in common organic solvents but insoluble in water, and which exhibited no crystallinity. The infrared specturm of film evaporated from a benzene solution showed an $N-CH_3$ band at 2785 cm^{-1}, while the band at 3050 cm^{-1} disappeared; $[\alpha]_D^{20}$ $-70.00°$ (*c* 1.000, benzene), molecular weight, 1330 (cryoscopic method with benzene).

Found: C, 72.44; H, 13.13; N, 12.15. Calcd. for $(C_7H_{15}N)_n$: C, 74.27; H, 13.36; N, 12.37%.

Poly-(s)-*N*-ethylisobutylethylenimine (XIV). — After fractionation using acetone, the precipitate was freeze-dried to give a white powder, m. p. 146°C, $[\alpha]_D^{15}$ $-207.4°$ (*c* 1.176, benzene), molecular weight, 1340; it had a high crystallinity.

Found: C, 75.71; H, 13.19; N, 10.99. Calcd. for $(C_8H_{17}N)_n$: C, 75.52; H, 13.47; N, 11.01%.

Poly-(s)-*N*-benzylisobutylethylenimine (XV). — The polymer obtained had m. p. 118—121°C, $[\alpha]_D^{22}$ $-219.0°$ (*c* 0.950, benzene), molecular weight, 1645. Although the infrared spectrum still showed the band near 3050 cm^{-1} despite treatment several times with various methods, it seems not to be the absorption band of the imine ring but that of the C–H stretching of the aromatic ring. An X-ray examination of the polymer showed a fairly high degree of orientation.

Found: C, 82.12; H, 10.16; N, 7.30. Calcd. for $(C_{13}H_{19}N)_n$: C, 82.48; H, 10.12; N, 7.40%.

***N*-Methylation of Polymer I.**—*By Eschweiler-Clarke's Method (XIII-1)*.—Attempts to prepare a product which had no carbonyl group were unsuccessful. The polymer I (200 mg.) was added to a solution of 35% formaldehyde (1 g.) and 88% formic acid (0.25 g.) with a slight warming. The mixture was heated gently until the evolution of carbon dioxide ceased, and then it was refluxed on a steam bath for 5 hr. The solution obtained was cooled and saturated with solid potassium hydroxide. The organic layer was separated, diluted with benzene, and washed with water until it was neutral. After freeze-drying, the benzene solution gave 170 mg. of a pale yellow powder, m. p. 132—140°C, $[\alpha]_D^{25}$ $-46.03°$ (*c* 1.035, benzene). In the infrared specturm, the band of the $N-CH_3$ group is observed instead of the disapperance of the N–H band near 3285 cm^{-1}. Besides, a strong peak near 1700 cm^{-1} appears even after various purifications. It perhaps indicates a carbonyl group coming from alkylating agents.

Found: C, 72.35; H, 12.04; N, 10.46. Calcd. for $(C_7H_{15}N)_n$: C, 74.27; H, 13.36; N, 12.37%.

By Methyl Iodide (XIII-2).—The polymer I (300 mg.) was dissolved in 10 g. of methyl iodide and then allowed to stand at 50°C for 48 hr. After the excess of the reagent had been removed, the residue was added to benzene and washed by alcoholic potash, 3 N potassium nitrate, N sodium chloride, N sodium hydroxide solution, and water successively. A yellow, powdery polymer was obtained by freeze-drying. The yield was 310 mg., $[\alpha]_D^{31}$ $-6.20°$ (*c* 1.000, benzene). Although the reaction and treatment were repeated, the alkylation of the polymer was not sufficient and no halogene could be removed: $[\alpha]_{30}^{D}$ $-10.62°$ (*c* 2.730, benzene).

Found: C, 68.20; H, 12.05 N, 11.78; Halogene as iodide, 6.86. Calcd. for $(C_9H_{19}NO)_n$: C, 66.15; H, 13.19; N, 11.02%.

A similar polymer was obtained by the quaternarization of polymer XIII with methyl iodide, but it was more difficult to obtain it in a pure state than in the case of XIII-2.

Asymmetric Synthesis.—A catalyst polymer (0.5 mmol.) in benzene was added to a solution of refined benzaldehyde (5 ml.) and anhydrous hydrogen cyanide (2 ml.) in benzene at 20°C; then the mixture was made up to 25 ml. with benzene. After this solution had been allowed to stand at 20°C for 20 hr., the reaction mixture was quenched by 10% sulfuric acid solution; the unchanged hydrogen cyanide was then removed in vacuo in the presence of one drop of phosphoric acid. The residue was decanted or filtered off, and the resulting solution was again made up to 25 ml. with benzene. The optical rotation of the solution was measured in a 2 dm. tube. Whenever the rotatory power was very small, distillation was carried out and the optical rotation was checked by a photoelectric instrument. The concentration of the solution was determined by titration with 0.1 N silver nitrate solution by a method described previously.[1]

Rate of Cyanohydrin Formation.—A polymer was dissolved in a mixture of benzene and 20 ml. of refined benzaldehyde. To the solution, hydrogen cyanide (8 ml.) was then added, and the mixture was made up to 100 ml. with benzene at 20°C. The solution was kept at 20°C. At intervals, 5 ml. portions were withdrawn and treated in a way similar to that described above except that the sample was made up to 10 ml.

Racemization of Cyanohydrin by Polymer XIV.—The polymer XIV (63.6 mg.) was added to (+)-cyanohydrin ($[\alpha]_D^{25}$ $+1.49°$, *c* 9.340) benzene solution at 20°C. The mixture was then kept at 20°C for 105 min. Distillation gave (+)-isomer with $[\alpha]_D^{25}$ $+1.47°$ (*c* 20.400, benzene). When the distillation was carried out in the presence of the polymer XIV and one drop of phosphoric acid, no racemization of the cyanohydrin occurred. Before distillation, $[\alpha]_D^{25}$ $-0.52°$ (*c* 21.24, benzene); after distillation, $[\alpha]_D^{25}$ $-0.52°$ (*c* 3.09, benzene).

Optical Rotatory Dispersion.—This was measured by Rudolph spectro-polarimeter. Model 200-S-80 and Nihon Bunko, Jasco ORD/UV-5 type.

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