Synthesis and Polymerization of an Optically Active Bicyclic Oxalactam. A Novel Hydrophilic Polyamide Membrane Prepared from (+)-(1*R*,5*S*)-8-Oxa-6-azabicyclo[3.2.1]octan-7-one

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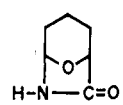
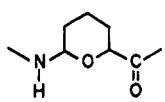
ABSTRACT: A novel optically active hydrophilic polyamide (referred to as (+)-poly(BOL), **2***) was prepared by the anionic ring-opening polymerization of an optically active bicyclic oxalactam, (+)-(1*R*,5*S*)-8-oxa-6-azabicyclo[3.2.1]octan-7-one (abbreviated as (+)-BOL, **1***), which was synthesized from sodium 3,4-dihydro-2*H*-pyran-2-carboxylate (**3**) through the optical resolution of its diastereomeric dehydroabietylammonium salt (**5**). Solution polymerization of **1*** in dimethyl sulfoxide proceeded readily at room temperature, leading to the high molecular weight stereoregular polyamide **2***. Thermal transitions due to fusion and decomposition of **2*** were observed at about 290–305 and 330 °C, respectively, which were higher than those for the polyamide prepared from racemic BOL. The hygroscopic properties of **2*** must result from some stereoregular arrangement of an amide linkage and a tetrahydropyran ring along the polymer chain, which may form polar hydrophilic microdomains surrounded by nonpolar hydrophobic microdomains. The hydrophilic membrane of **2*** was easily obtained by casting from a solution of the polymer in 2,2,2-trifluoroethanol–chloroform. The membrane exhibited better fractional solute rejection in its aqueous solution, together with high water permeability, than the membrane from racemic BOL.

Pioneering work by Hall[1,2] on the syntheses of a number of bicyclic lactams and their polymerizabilities is well-known. In preceding papers,[3,4] we have reported the anionic ring-opening polymerization at or below room temperature of a new class of racemic bicyclic oxalactam, 8-oxa-6-azabicyclo[3.2.1]octan-7-one (abbreviated as BOL, **1**), leading to a novel high molecular weight polyamide, poly(tetrahydropyran-2,6-diyliminocarbonyl) (poly(BOL), **2**). The markedly hydrophilic poly(BOL) membrane,



BOL, 1



Poly(BOL), 2

which was obtained easily by both "casting polymerization" and casting from the polymer solution in dimethyl sulfoxide (Me_2SO), has been characterized by the excellent permeability for water and permselectivity for alkali metal ions and solutes of various sizes in the aqueous solution.[5–8] Most of the characteristics of poly(BOL) have been presumed to result from some delicate alternating arrangement of polar hydrophilic and nonpolar hydrophobic microdomains, probably formed, even if partly, along and between the polymer chains. The steric microstructure of the polymer, however, may be altered in complexity when the polymer is prepared from racemic BOL 1.

The present paper is concerned with the synthesis and polymerization of an optically active BOL, (+)-(1*R*,5*S*)-8-oxa-6-azabicyclo[3.2.1]octan-7-one [(+)-BOL, **1***], to yield a novel optically active stereoregular polyamide [(+)-poly(BOL), **2***] and with characterizations of **2*** and its membrane compared with those of racemic poly(BOL) (**2**).

Experimental Section

Dehydroabietylammonium 3,4-Dihydro-2*H*-pyran-2-carboxylate (5* in Scheme I).[9] To an ice-cooled solution of 45 g of sodium 3,4-dihydro-2*H*-pyran-2-carboxylate (**3**) in 110 mL of water was added 50 mL of 6 N hydrochloric acid with stirring, and the resulting free carboxylic acid was salted out and extracted with 300 mL of ethyl ether followed by extraction with 100 mL of ethyl ether (2×) as quickly as possible. The ether extracts were then added to an ice-cooled ether solution of dehydroabietylamine (**4**) (about 500 mL) obtained from 104 g of purified dehydroabietylammonium acetate.[10] After the mixture was washed with ethyl ether, crude crystals of diastereomeric dehydroabietylammonium 3,4-dihydro-2*H*-pyran-2-carboxylate (**5***) were obtained in a yield of 97% (120 g). The crude crystals (414 g) were recrystallized from methanol four times to give 75 g of white needles: mp 173–176 °C; $[\alpha]^{23}_D$ +11.9° (ethanol *c* 1.0) [lit.:[9] mp 173–177 °C; $[\alpha]^{26}_D$ +10.7° (ethanol, *c* 1.05)].

Ethyl (−)-(2*R*)-3,4-Dihydro-2*H*-pyran-2-carboxylate (6*).[9] The purified **5*** (192 g) and ethyl ether (100 mL) were added to a solution of 15 g of sodium hydroxide in 300 mL of water, and the heterogenous mixture was vigorously stirred. After all of the crystals had dissolved, the two layers were separated. After the aqueous layer was washed with ethyl ether for recovery of the released amine, the aqueous solution was condensed with a rotary evaporator below 50 °C. A white residue was dried under vacuum and then pulverized. The white powder was subsequently dissolved in 230 mL of dimethylformamide (DMF) in a 500-mL round-bottomed flask equipped with a stirrer, thermometer, and reflux condenser. To the mixture were added 111 g of ethyl iodide, 8 g of anhydrous sodium carbonate, and a trace amount of hydroquinone; then the contents of the flask was heated at 105–110 °C in an oil bath for 4.5 h with mechanical stirring. After the reaction mixture was cooled to room temperature, 200 mL of water and 450 mL of benzene were added. The aqueous layer was discarded and the benzene layer was washed with 200 mL of water three times, dried over anhydrous sodium sulfate, and filtered. The solvent was removed by fractional distillation, and the residue was distilled under reduced pressure to give 66 g (92%) of ethyl (−)-(2*R*)-3,4-dihydro-2*H*-pyran-2-carboxylate (**6***): bp 57 °C (3 mmHg), $[\alpha]^{25}_D$ −68.9° (ethanol, *c* 1.0) [lit.:[9] yield 68%; bp 57 °C (3 mmHg); $[\alpha]^{26}_D$ −69.3° (ethanol, *c* 1.53)].

(+)-(2*R*)-3,4-Dihydro-2*H*-pyran-2-carboxamide (7*). A mixture of 62.1 g of **6*** with 250 mL of 33% aqueous ammonia was stirred vigorously in a 1-L round-bottomed flask at about 35 °C for 1 h and heated at 60–65 °C on a water bath until the reaction mixture became homogeneous. When the solution was cooled in an ice bath, the amide crystallized out from the solution. It was washed with chilled water and dried under reduced pressure: yield 47 g (93%); mp 94–95 °C; $[\alpha]^{25}_D$ +20.8° (ethanol, *c* 1.0) (lit.[11] mp of racemic compound, 112–112.5 °C).

(+)-(1*R*,5*S*)-8-Oxa-6-azabicyclo[3.2.1]octan-7-one (1*). To an equal mixture of DMF and benzene (800 mL) in a 1-L three-necked, round-bottomed flask were added 47 g of **7*** and 3.5 g of *p*-toluenesulfonic acid; then the contents of the flask was stirred at 99–100 °C in an oil bath for 4.5 h. To the chilled reaction mixture was added 15 g of anhydrous sodium carbonate. After 30 min of stirring, the salt was filtered off and the solvents were removed by fractional distillation. The viscous residue was distilled under reduced pressure to give white crystals of (+)-(1*R*,5*S*)-8-oxa-6-azabicyclo[3.2.1]octan-7-one [(+)-BOL, **1***]: bp 103–105 °C (3 mmHg); yield 26 g (56%); $[\alpha]^{25}_D$ +98.7° (ethanol, *c* 1.0) [lit.:[4] bp of racemic compound, 114 °C (4 mmHg); yield

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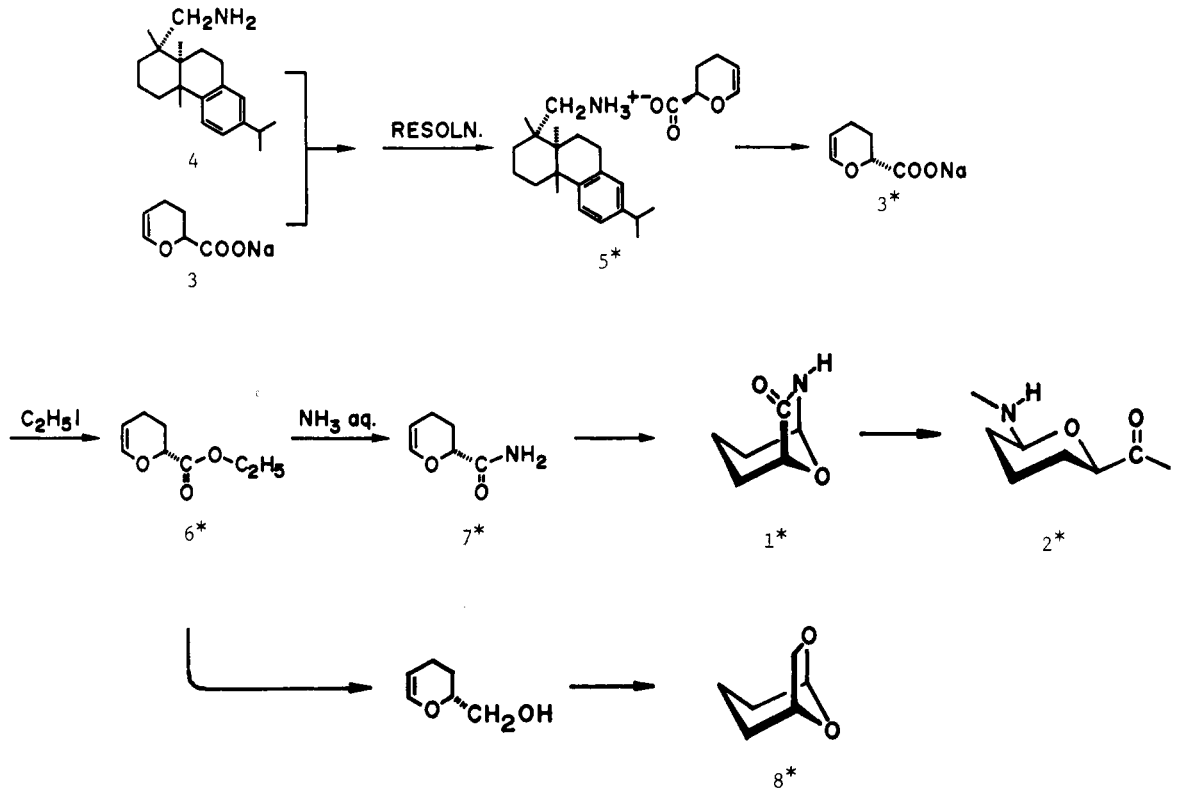
Scheme I



58%]. The extraction fractionation of crude (+)-BOL with boiling *n*-hexane followed by recrystallization yielded colorless, scale-shaped crystals: mp 124–125 °C; $[\alpha]^{25}_D$ +106.5° (ethanol, *c* 1.0) (lit.[4] mp of racemic compound, 91–92 °C).

Polymerization. (+)-BOL was dried and stored over phosphorus pentoxide in vacuo until use. Potassium pyrrolidonate (abbreviated as K Pyrdn) was prepared as described in the literature[12] and stored in an evacuated ampule at ca. −60 °C. α-Pyrrolidone was distilled under reduced pressure after azeotropic removal of water with xylene from the α-pyrrolidone–xylene mixture (1:3, v/v). *N*-Acetyl-8-oxa-6-azabicyclo[3.2.1]octan-7-one (abbreviated as *N*-acetyl-BOL) was prepared from BOL and an excess of acetic anhydride:[13] bp 85 °C (3 mmHg); yield 63%. Dimethyl sulfoxide (Me_2SO) was dried over calcium hydride and distilled under reduced pressure. (+)-BOL, K Pyrdn, and Me_2SO were placed, under a dry nitrogen atmosphere, in a glass ampule and an Me_2SO solution of *N*-acetyl-BOL was added to the mixture with stirring at room temperature. The sealed ampule was allowed to stand in a constant-temperature bath. After the polymerization was stopped by placing the contents of the ampule in a large amount of water, the product was minced and immersed repeatedly in fresh water to remove the residual monomer, catalyst, and solvent. The resulting white polymer was collected on a glass filter, washed again with water, and dried in vacuo at 100 °C.

Characterization. ^1H and ^{13}C NMR spectra were taken, respectively, with a Japan Electronics Model JNM-MH-100 high-resolution spectrometer operating at 100 MHz and a Model JNM-FX-100 Fourier transform spectrometer at 25 MHz. Tetramethylsilane was used as an internal standard. Thermal transitions were observed with a Perkin-Elmer Model DSC-2 differential scanning calorimeter. Optical rotations were measured in various solvents with JASCO Model DIP-4 and DIP-181 digital polarimeters. The X-ray diffraction data was recorded with a Rigaku Denki No. 2030/P Geigerflex diffractometer using Ni-filtered copper Kα radiation. Moisture sorption measurements were carried out gravimetrically at 20 °C; the relative humidity was controlled by varying the ratio of concentrated sulfuric acid to water. The water permeation rate through the polymer membranes at 25 °C under a pressure of 1–4 kg/cm^2 was determined by using a commerical ultrafiltration cell, of which the effective membrane area was 13.9 cm^2. The solute rejection test for the membranes was also conducted by using the ultrafiltration cell at 25 °C under a pressure of 3 kg/cm^2. The solute concentrations in permeating aqueous solutions were determined by means of UV spectrophotometry.

Results and Discussion

Optically Active Bicyclic Oxalactam. Recently the optically active bicyclic acetal (+)-6,8-dioxabicyclo-[3.2.1]octane (**8***) was synthesized in our laboratory from **3** through an optical resolution using **4** as a resolving reagent.[9] The optically active bicyclic oxalactam **1*** was also prepared from the sodium carboxylate **3***. After 4.5 h in DMF at 105–110 °C, it was esterified with an excess of ethyl iodide in 92% yield. The ammonolysis of the resulting ethyl ester **6*** with 33% aqueous ammonia proceeded almost quantitatively. Amide **7*** was cyclized in 1:1 DMF–benzene in the presence of *p*-toluenesulfonic acid as a catalyst.

The optical purity of crude **1*** obtained by the distillation under reduced pressure ($[\alpha]^{25}_D$ +98.7° in ethanol) may be similar to that of **8*** derived from the optically active ethyl ester **6*** (97%).[9] Repetition of the extraction fractionation for this crude **1*** with boiling *n*-hexane followed by recrystallization increased the specific rotation from +98.7 to +106.5° in ethanol. Such purification may be due not only to the preferential extraction of the unreacted amide **7*** but also to that of the contaminating racemic BOL, in view of the results of the extraction fractionation test for an equal mixture of racemic BOL and (+)-BOL, as summarized in Table I. As a result, the optical purity of (+)-BOL purified as described above can be regarded to be about 100%.

The absolute configuration of the monomer **1*** can be decided with (+)-(1*R*,5*S*)-8-oxa-6-azabicyclo[3.2.1]octan-7-one, taking into account that **8*** obtained from the precursor ester **6*** has the opposite absolute configuration to that obtained from D-glucose.[9,14]

Although ^1H and ^{13}C NMR spectra of **1*** obtained here were the same as those of the racemic compound, their

Table I
Extraction Fractionation Test for Crude Optically Active 8-Oxa-6-azabicyclo[3.2.1]octan-7-one with Boiling *n*-Hexane Followed by Recrystallization

fraction no.	amt of *n*-hexane, g	boiling time, h	recovd BOL, g	$[\alpha]^{25}_D$, deg	optical purity, %
unfractionated[a]			1.057	+50.5	47.5
1	30.4	2	0.204[b]	+13.5	12.7
			0.287[c]	+4.2	3.9
2	31.8	3	0.116[b]	+106.3	99.8
			0.017[c]		
3	62.8	2.5	0.271[c]	+106.7	100
4	31.9	1.5	0.072[c]	+106.5	100

[a] Equal mixture of racemic BOL (0.528 g) and (+)-BOL (0.529 g, $[\alpha]^{25}_D$ +101° in ethanol). [b] Recrystallized at 25 °C from the *n*-hexane solution used for extraction. [c] Recrystallized at 5 °C from the solution after removal of BOL deposited at 25 °C.

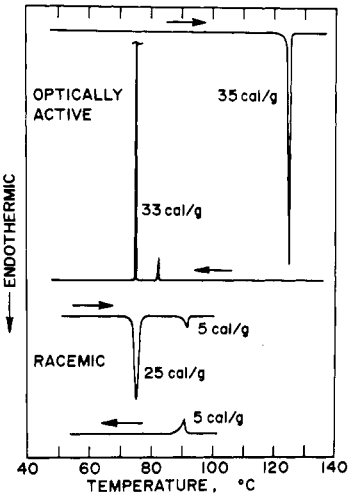


Figure 1. DSC thermograms of 8-oxa-6-azabicyclo[3.2.1]octan-7-one (heating rate and cooling rate, 2.5 °C/min).

X-ray diffraction diagrams were clearly distinguishable from each other. As shown in Figure 1, the scale-shaped crystals of **1*** melted at a higher temperature than the needle-shaped crystals of racemic BOL, and the former were recrystallized more easily than the latter. In addition, the solubility of **1*** in boiling *n*-hexane (0.4 g/100 g) was found to be less than one sixth of that of racemic BOL (2.6 g/100 g). Racemic BOL, therefore, is not a conglomerate, but a racemate.[15]

Polymerization of (+)-BOL. In a previous study[4] the anionic polymerization of racemic BOL has been shown to proceed easily in Me_2SO, even at room temperature, without the addition of *N*-acetyl-BOL as an activator, in contrast with ε-caprolactam and α-pyrrolidone. The optically active BOL was also polymerized in Me_2SO in the presence of K Pyrdn at 25 °C to yield a high molecular weight optically active polyamide (**2***), although the use of the activator was necessary (Table II). While the polymerization of racemic BOL proceeded in a homogeneous phase, the polymerization system of **1*** became turbid and formed a gel after a long time. The viscosity number of the resulting (+)-poly(BOL) (**2***) in *m*-cresol was nevertheless very high. It can be said that the very high molecular weight optically active polyamide was obtained by the polymerization of **1*** in the presence of a slight amount of *N*-acetyl-BOL as an activator.

Thermal Analysis of (+)-Poly(BOL). As presented in Figure 2, the results of the differential scanning calorimetry showed thermal transitions by the fusion and decomposition of **2*** at 290–305 and 330 °C, respectively, higher than those of racemic poly(BOL).[16] The specific gravity of **2*** (d^{25}_4 1.407) was higher than that of racemic poly(BOL) (d^{25}_4 1.362). These facts may reflect that intermolecular cohesive forces of **2*** are stronger than those of racemic polymer.

Table II
Anionic Polymerization of Optically Active 8-Oxa-6-azabicyclo[3.2.1]octan-7-one[a]

amt of (+)-BOL,[b] g	amt of *N*-acetyl-BOL, mol %/monomer	time, h	yield, %	$[\eta]$[c]	$[\alpha]^{25}_D$,[d] deg
1.65	0	72	3		
1.85	0.01	72	25	3.5_0	+169
16.0	0.02	24	15	2.3_4	+173
5.94	0.05	48	56	4.6_3	+177
1.57	0.2	18	86	1.9_6	+172
1.67	0.2	24	95	1.8_2	+170
5.92[e]	0	72	56	1.9_7[f]	
20.0[e]	0.01	24	73	2.1_3	
2.24[e]	0.2	1	92	0.6_4[f]	

[a] K Pyrdn, 1 mol %/monomer; molar ratio of Me_2SO to monomer, 5.6; temperature, 25 °C. [b] $[\alpha]^{25}_D$ +106.5° (ethanol, *c* 1.0). [c] In *m*-cresol at 25 °C. [d] In 1:1 2,2,2-trifluoroethanol-chloroform (w/w) mixed solvent. [e] Racemic BOL. [f] η_{sp}/c, *c* 0.2 g/100 mL.

Table III
Qualitative Solubilities of Various Polyamides[a]

solvent	(+)-poly-(BOL)	poly-(BOL)	nylon 6	nylon 4
m-cresol	s	s	s	s
TFE[b]	x	s	s	s
TFE-CH_3Cl[c]	s	s	s	s
Me_2SO	x	s	i	i
CH_3Cl	x	x	i	i
CH_3Cl-CH_3OH[d]	i	s	i	i

[a] Room temperature; concentration, 10 mg/mL; s = soluble, i = insoluble, x = swollen. [b] 2,2,2-Trifluoroethanol. [c] Mixing ratio (wt), 4:1-1:4. [d] Mixing ratio (wt), 25:1-2.7:1.

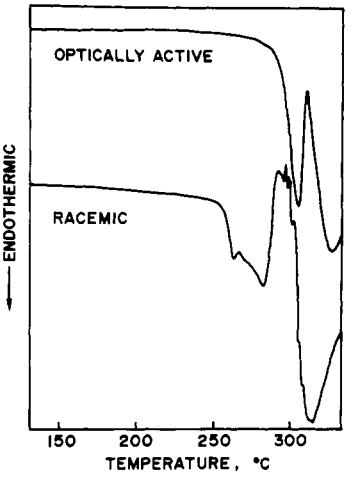


Figure 2. DSC thermograms of poly(tetrahydropyran-2,6-diyliminocarbonyl) (heating rate, 10 °C/min).

Solubility. Qualitative solubilities of various polyamides at room temperature are listed in Table III. The unusually good solubilities of racemic poly(BOL) are thought to be mainly due to weakening of the hydrogen bonds between amide groups resulting from steric hin-

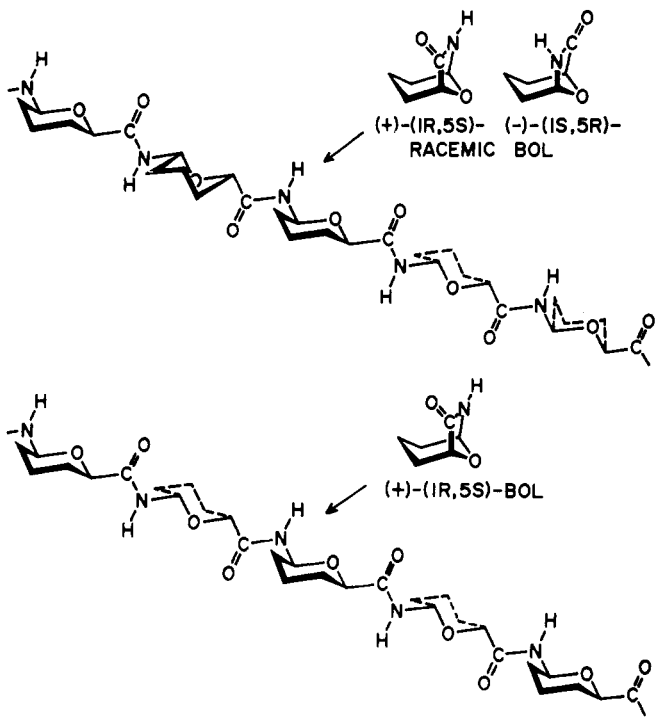


Figure 3. Schematic representation of configurations of the polyamide chains prepared from racemic BOL and optically active BOL.

drance of a bulky tetrahydropyran ring and the diversity of the configuration as shown in Figure 3. Solubilities of **2***, on the other hand, were generally poorer than those of nylon 6 and nylon 4, which may be caused by the stiffness and the stereoregularity of the polymer chain. It is noteworthy that optically active poly(BOL) can be dissolved in 2,2,2-trifluoroethanol (TFE)–chloroform, despite the poor solubilities in either solvent alone, as well as that racemic poly(BOL) is soluble in Me_2SO, TFE, TFE–chloroform, and chloroform–methanol; it seems that poly(BOL) is more or less amphiphatic. These facts may also support our previously mentioned concept[4] that the alternating sequence of a polar amide linkage and a nonpolar bulky tetrahydropyran ring in the poly(BOL) chain results in the occurrence, even if partly, of polar hydrophilic microdomains surrounded by nonpolar hydrophobic microdomains along and between the polymer chains. It is also interesting that 1:1 TFE–chloroform (w/w) mixed solvent is separated into two phases at 5 °C, but the same solvent with dissolved (+)-poly(BOL) remains homogeneous at that temperature, which differs from the behavior with racemic poly(BOL).

^{13}C NMR Analysis. As shown in Figure 4, peaks a and b emerge as sharp singlets in the ^{13}C NMR spectrum of **2*** in TFE–chloroform, while they are either broad or slightly split in the spectrum of racemic poly(BOL), probably owing to the different dyads. In the former spectrum half-widths of methylene peaks d–f are larger than the half-width of carbonyl peak a, which may suggest that molecular motions of the trimethylene group in the bulky tetrahydropyran ring are comparatively suppressed in this solvent.

Moisture Sorption. The results of an elemental analysis of dried (+)-poly(BOL) suggest that about 5% water was retained in the polymer. The water would be absorbed in the polymer in the course of the analytical process, even if the dried (+)-poly(BOL) had been freed from water. Moisture sorption isotherms of various polyamides determined at 20 °C on the coarsely ground

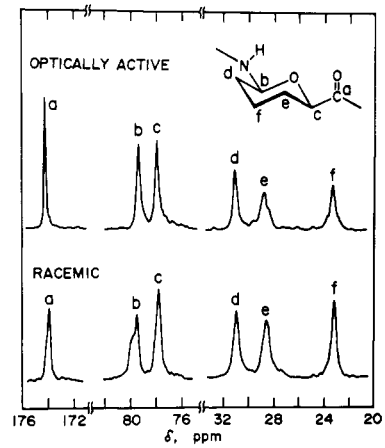


Figure 4. 25-MHz ^{13}C NMR spectra of poly(tetrahydropyran-2,6-diyliminocarbonyl) (solvent, 2:1 2,2,2-trifluoroethanol–chloroform (w/w); temperature, 60 °C).

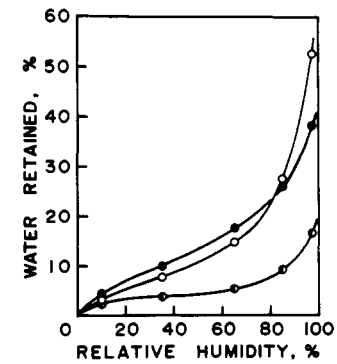


Figure 5. Moisture sorption isotherms of various polyamides at 20 °C: (○) (+)-poly(BOL); (●) poly(BOL); (◐) nylon 6.

samples indicate, as shown in Figure 5, that optically active poly(BOL), as well as racemic poly(BOL), is much more hygroscopic than nylon 6. It should also be noted that the amount of water retained in (+)-poly(BOL) exceeds that in racemic poly(BOL) at 80% relative humidity or above. The greater capacity of the latter for moisture sorption at low humidity may come from the presence of a large number of relatively weak polar sites, including amide and ether linkages throughout the relaxed polymer structure.[7] On the other hand, the (+)-poly(BOL) structure having a more stereoregular arrangement of hydrophilic and hydrophobic microdomains may be inferred to absorb a much larger amount of water at higher humidity.

Water Permeability of (+)-Poly(BOL) Membranes. Optically active poly(BOL) membranes were easily cast from the 5% solutions in 1:1 TFE–chloroform (w/w) under the following conditions: (A) immersed in water after casting from the polymer solution and keeping in air at 20 °C for 20 min (apparent polymer concentration on immersion, 8.6%); (B) immersed in water after casting from the polymer solution and keeping in a large closed vessel at room temperature for 3 h (apparent polymer concentration on immersion, 17%); (C) drying at room temperature after casting from the polymer solution.

The values of hydraulic permeability through the membranes, K_w, as well as the water flux, J_w, given by the relationship in eq 1, where $\Delta p/\Delta x$ is a pressure gradient,[18,19] much depended upon the casting conditions as shown in Table IV. The (+)-poly(BOL) membrane having a high degree of hydration, which was prepared by immersion in water after casting, permeated a large amount

$$J_w = K_w \Delta p / \Delta x \quad (1)$$

Table IV
Water Permeation through Optically Active Poly(BOL) Membranes at 25 °C under a Pressure of 3 kg/cm²

membrane no.	casting condition[a]	deg of hydration[b]	thickness,[c] mm	permeation rate, L/(m²·h)	$10^9 K_w$, mol/(cm·s·atm)
M-5-2	A	0.61	0.10	1.6	8.6
M-3-8	B	0.52	0.17	0.10	0.86
M-5-1	C	0.44	0.040	0.18	0.37
Cell[d]		0.69	0.032	3.9	6.5

[a] A, immersed in water after casting from a 2,2,2-trifluoroethanol–chloroform solution of (+)-poly(BOL) and keeping in air for 20 min; B, immersed in water after casting from the polymer solution and keeping in a closed large vessel for 3 h; C, dried after casting from the polymer solution. [b] Volume fraction of water in membrane. [c] In wet state. [d] Cross-linked cellulose (data of Kawaguchi et al.[17]).

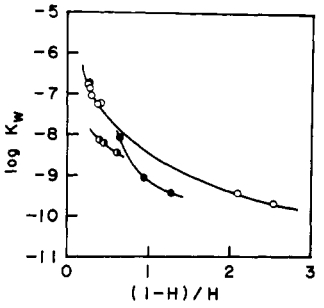


Figure 6. Dependence of hydraulic permeability of various membranes on their degree of hydration H at 25 °C: (○) poly(BOL); (●) (+)-poly(BOL); (◑) cross-linked cellulose.

of water. Even the membrane prepared by drying after casting showed a relatively high degree of hydration and high water permeability, probably owing to the inherent hygroscopicity of (+)-poly(BOL).

The hydraulic permeability through the membranes tends, in general, to increase with the water content as shown in Figure 6. In comparison with the racemic poly(BOL) membrane of the same degree of hydration, the (+)-poly(BOL) membrane exhibited a relatively low water permeability, although its permeability seemed to be still higher than that through a cross-linked cellulose membrane.[17] This fact suggests that the water molecules absorbed in the (+)-poly(BOL) membrane are bound to polar amide and ether group sites in hydrophilic microdomains more tightly than those in the racemic poly(BOL) membrane having the same water content. Such an inference is supported by the fact that the former membrane contains a larger amount of nonfreezing water than the latter membrane.[20]

As shown in Figure 7, the linear relationship between J_w and reciprocal absolute temperature for the (+)-poly(BOL) membranes show points of inflection at about 34 or 39 °C. These temperatures are higher than the temperature for the racemic poly(BOL) membrane (27 °C) described in the previous report.[8] At the above-mentioned temperatures, some variation of a participation mode of water molecules to polar amide and ether group sites in the polymer chains, including removal of various types of intercatenary water molecules, is assumed to take place discontinuously.[8]

Solute Rejection. The results of a solute rejection test for (+)-poly(BOL) membranes are summarized in Table V. The (+)-poly(BOL) membrane prepared by immersion in water after casting (membrane no. M-5-2) rejected 96% of albumin (MW 67 000) from its aqueous solution, without

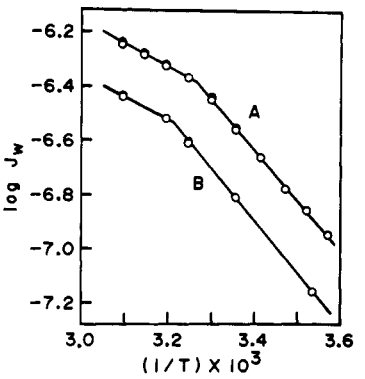


Figure 7. Temperature dependence of water flux through optically active poly(BOL) membranes (pressure, 3 kg/cm²): (A) membrane no. M-5-1 (degree of hydration, 0.44; thickness, 0.040 mm); (B) membrane no. M-3-8 (degree of hydration, 0.52; thickness, 0.17 mm).

Table V
Solute Rejection from Its Aqueous Solution by Various Poly(BOL) Membranes[a]

		solute rejection, %			
		optically active		racemic	
solute	mol wt	M-5-2[b]	M-5-1[c]	R-3[d]	R-6[e]
creatinine	113	3	2	3	28
vitamin B_{12}	1355	16	85	78	42
albumin[f]	67000	96	93	94	94

[a] Pressure, 3 kg/cm²; temperature, 25 °C. [b] (+)-Poly(BOL) membrane (immersed in water after casting); degree of hydration, 0.61; thickness, 0.10 mm; permeation rate, 1.6 L/(m₂·h). [c] (+)-Poly(BOL) membrane (dried after casting); degree of hydration, 0.44; thickness, 0.040 mm; permeation rate, 0.18 L/(m²·h). [d] Poly(BOL) membrane (casting polymerization); degree of hydration, 0.73; thickness, 0.58 mm; permeation rate, 1.9 L/(m²·h). [e] Poly(BOL) membrane (dried after casting); degree of hydration, 0.27; thickness, 0.035 mm; permeation rate, 0.11 L/(m²·h). [f] Bovine serum.

loss of the high water permeability, whereas the rejection percent of vitamin B_{12} (MW 1355) was only 16%. On the other hand, the thin membrane having relatively low water content (membrane no. M-5-1) rejected 85% of vitamin B_{12} from its aqueous solution. In any event, it is evident that (+)-poly(BOL) membranes exhibit an excellent fractional solute rejection behavior in the aqueous solution and that a boundary region, which is observed fairly sharply in the relationship between the molecular weight of solutes and the rejection percent,[6] shifts with the casting conditions from MW in the hundreds to MW in the thousands.

As mentioned above, the characteristic solubilities and hygroscopicity of the present novel polyamide, poly(tetrahydropyran-2,6-diyliminocarbonyl), and the high water permeability of the membrane should be considered to result from the inherent polymer structure having an alternating arrangement of a polar amide linkage and a nonpolar bulky tetrahydropyran ring along the polymer chains, which may form polar hydrophilic microdomains surrounded by nonpolar hydrophobic microdomains along and between the polymer chains. In addition, the high stereoregularity brought about by the polymerization of the optically active monomer may result in a delicate distribution of stereoregular microdomain structures in an aggregate state of the polymer. It is likely that the stereoregular microdomain structures enhance both hydrophilic and hydrophobic intermolecular interactions, leading to the improvement of the properties and functions

of the hydrophilic poly(BOL) membrane.

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Step Polymerization with Unequal Reactivities of Functional Groups

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ABSTRACT: The effect of the nonequivalent reactivity of the two functional groups in a difunctional monomer on the kinetics of step polymerization with a symmetric monomer and the molecular weight distribution of the product was calculated by using a combination of kinetic and probabilistic arguments. The model involves four rate constants. It was shown that the usually assumed maximum value of 2 for the polydispersity index is wrong if the monomer possessing unequal reactivity reacts slower than the oligomers and if it is present in excess of or in exact stoichiometric proportion with the symmetric monomer. When such conditions are obtained, $\bar{M}_n$ is unaffected while $\bar{M}_w$ is increased (causing the polydispersity index to be greater than 2) considerably.

Recently we[1] considered the step polymerization of two kinds of difunctional monomers—one in which the reactive functional groups have unequal reactivities and the other for which the monomeric functional groups react at a rate that is different from those that are present as chain ends. These may be referred to as asymmetry and induced asymmetry, respectively. Symmetric diisocyanates are known[2] to exhibit induced asymmetry. The polymerization of cyclic monomers such as anhydrides turned out to be[1] mathematically equivalent to the monomers with induced asymmetry. For these cases we[1] obtained the molecular weight distribution (MWD) as a function of the extent of reaction or time. It has also been shown that the polydispersity index (PDI) shows discontinuities and can be much greater than the usual maximum value of 2 and that this is due to the contribution of the unreacted monomer. A modified polydispersity index (MPDI) obtained by defining the number and weight average molecular weights excluding the monomer contributions showed no discontinuities and had a maximum value of 2.

Many of the monomers, however, can exhibit a more complicated behavior than simple asymmetry or induced asymmetry. Thus Peebles[3] proposed that asymmetric monomers, such as 2,4-tolylene diisocyanate, can exhibit asymmetry and induced asymmetry simultaneously. Here we wish to obtain the kinetics of and MWD in step polymerization of such monomers and examine the necessity and usefulness of MPDI. We will consider an ideal batch or plug flow reactor.

Model and Kinetics of Polymerization

Let A_1A_2 be a difunctional monomer showing asymmetry and induced asymmetry simultaneously. Let it react with a monomer BB which has neither asymmetry nor induced asymmetry. The reactions can be represented as

$$A_2A_1 + BB\sim \xrightarrow{k_1} A_2A_1BB\sim \quad (1)$$

$$A_1A_2 + BB\sim \xrightarrow{k_2} A_1A_2BB\sim \quad (2)$$

$$\sim A_2A_1 + BB\sim \xrightarrow{k_1^*} \sim A_2A_1BB\sim \quad (3)$$

$$\sim A_1A_2 + BB\sim \xrightarrow{k_2^*} \sim A_1A_2BB\sim \quad (4)$$

where $\sim$ represents a chain. Reactions 1 and 2 or 3 and 4 characterize asymmetry while reactions 1 and 3 or 2 and 4 characterize induced asymmetry.

From reactions 1–4 it is clear that the A_1 and A_2 groups belonging to the monomer have to be distinguished from the A_1 and A_2 groups which are present as chain ends. To make this distinction clear and to facilitate understanding,

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