Polymerization of Bicyclic Oxalactam. A Novel Polyamide Poly(tetrahydropyran-2,6-diyliminocarbonyl)

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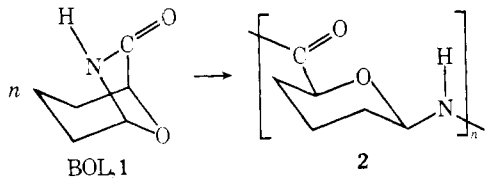
ABSTRACT: The anionic catalyzed polymerization of a new bicyclic oxalactam, 8-oxa-6-azabicyclo[3.2.1]octan-7-one (abbreviated as BOL), in tetrahydrofuran and dimethyl sulfoxide proceeded readily even at or below room temperatures without the addition of *N*-acetylated BOL as an activator, leading to a high molecular weight polyamide. Thus the room-temperature polymerization and simultaneous film casting on a plate can be easily attained ("casting polymerization"). Most of the resulting novel polyamide, poly(tetrahydropyran-2,6-diyliminocarbonyl), was soluble in formic acid, *m*-cresol, dimethyl sulfoxide, and even chloroform, while the polymer obtained in bulk at elevated temperatures at a high conversion was often insoluble even in *m*-cresol. Polymer characterization was carried out by means of IR and ^{1}H- and ^{13}C-NMR spectroscopies and DSC analysis. Thermal transitions appeared at about 130, 260–285, and 315 °C which may be due to glass transition, fusion, and decomposition, respectively. The observed uncommonly good solubility and distinguished hygroscopic properties of poly(BOL) may be accounted for by the occurrence, even if partly, of hydrophilic polar microdomains surrounded by hydrophobic nonpolar microdomains, which result from the alternating arrangement of an amide linkage and a tetrahydropyran ring along the chains.

Syntheses of a number of bicyclic lactams and their qualitative polymerizabilities were described by Hall[1,2] and others. It has also been known that the polymerization of some bicyclic lactam ethers was accompanied by the cleavage of the ether bond.[3,4] In a previous short communication[5] synthesis of a new class of bicyclic oxalactam, 8-oxa-6-azabicyclo-[3.2.1]octan-7-one (abbreviated as BOL, **1**), and a preliminary investigation on the polymerization by using sodium hydride as a catalyst were briefly reported.

The present paper is concerned with the monomer synthesis via an alternative route, polymerization of BOL under various conditions, especially at or below room temperatures, and the characterization of the resulting novel polyamide, poly(tetrahydropyran-2,6-diyliminocarbonyl) (**2**).

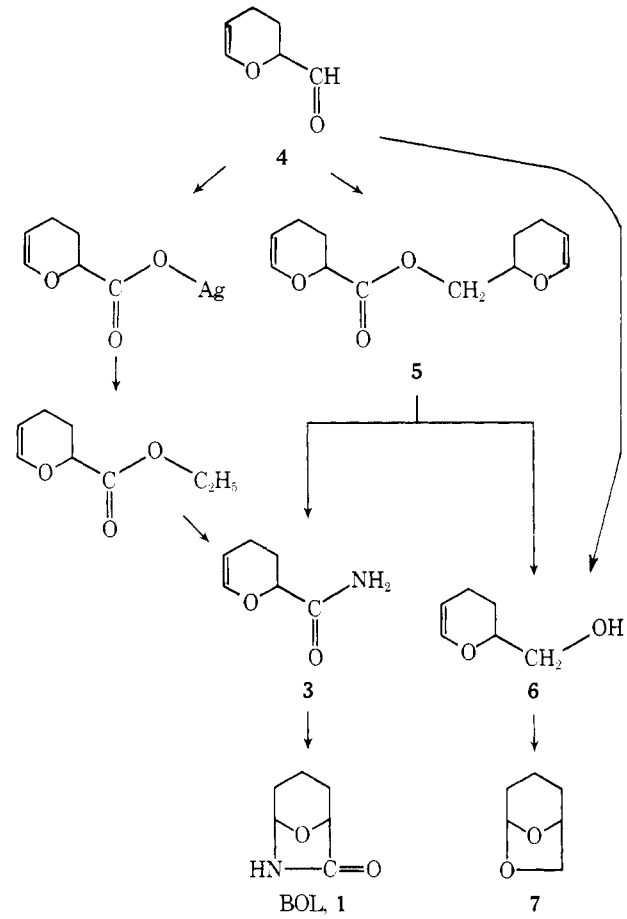


BOL, 1 2 (1)

Experimental Section

Monomer Synthetic Scheme. In a previous communication[5] it was described that BOL (**1**) was synthesized by the intramolecular cyclization of 3,4-dihydro-2*H*-pyran-2-carboxamide (**3**) prepared according to Whetstone and Ballard,[6] starting from 3,4-dihydro-2*H*-pyran-2-carbaldehyde (acrolein dimer) (**4**). The precursor **3** can also be obtained by an alternative route via 2-(3,4-dihydro-2*H*-pyranyl)methyl 3,4-dihydro-2*H*-pyran-2-carboxylate (**5**), accompanied by the equimolar formation of 2-hydroxymethyl-3,4-dihydro-2*H*-pyran (**6**). The compound **6**, which of course can be obtained also directly from **4**, is a precursor for 6,8-dioxabicyclo[3.2.1]octane (**7**) and 6,8-dioxabicyclo[3.2.1]oct-3-ene, from which polysaccharide-type polymers have been synthesized in our laboratory.[7–10] The synthetic routes described above are illustrated in Scheme I.

Scheme I



2-(3,4-Dihydro-2*H*-pyranyl)methyl 3,4-Dihydro-2*H*-pyran-2-carboxylate (5). The Tishchenko reaction[11] of **4** was carried out as follows: To 224 g of **4** placed in a 500 mL round-bottomed flask equipped with stirrer and thermometer, 5.6 g of aluminum isopropoxide was added in small amounts with stirring at room temperature. In order to avoid a violent exothermic reaction the reaction mixture was cooled below 35 °C with ice-cold water and then allowed to stand overnight at room temperature. A colorless liquid ester **5** was isolated by distillation: bp 125–127 °C (2 mm) (lit.[11] 115–125 °C (0.5 mm)); yield 166 g (74%).[12]

3,4-Dihydro-2*H*-pyran-2-carboxamide (3) and 2-Hydroxymethyl-3,4-dihydro-2*H*-pyran (6). A mixture of 165 *g* of **5** and 300 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 60–70 °C on a water bath until the reaction mixture became homogeneous. Upon cooling in an ice bath, the amide **3** crystallized out of solution. It was washed with chilled water and dried under reduced pressure: yield 78 g (83%); mp 112–113 °C (lit.[6] 112–112.5 °C). The mother liquid was subjected to salting out and extraction with methylene chloride. After removal of the solvent, distillation under a reduced pressure gave 66 g (79%) of **6**: bp 50–52 °C (3 mm) (lit.[13] 100–103 °C (47 mm)).

8-Oxa-6-azabicyclo[3.2.1]octan-7-one (BOL) (1). To 380 mL of an equivalent mixture of DMF and benzene in a 1-L three-necked round-bottomed flask equipped with stirrer, thermometer, and reflux condenser, 25.5 g of **3** and 1.9 g of *p*-toluenesulfonic acid were added and then stirred at 100 °C in an oil bath for 4 h. The reaction was stopped by the addition of 8 g of anhydrous sodium carbonate to the chilled reaction mixture followed by stirring for 0.5 h. After removing

the residual sodium carbonate and recovering the solvents, distillation under reduced pressure yielded a white waxy solid of 1: bp 114 °C (4 mm); yield 14.8 g (58%). Recrystallization from *n*-hexane yielded colorless fine needle-shaped crystals, mp 91–92 °C, which were stored over phosphorus pentoxide in vacuo until use.

Catalysts and Activator. Potassium pyrrolidonate (abbreviated as K Pyrdn) was prepared as described in the literature[14] and stored in an evacuated ampule at ca. −60 °C. Triethylamine was dried over sodium hydroxide. *n*-Butyllithium–hexane solution and sodium hydride–oil dispersion were commercial reagents. *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 by the conventional acylation method:[15] bp 85 °C (2 mm); yield 63%.

Materials. α-Pyrrolidone was distilled under reduced pressure after azeotropic removal of water with xylene from the α-pyrrolidone–xylene (1:3 volume) mixture. ε-Caprolactam was recrystallized from cyclohexane and dried over phosphorus pentoxide under vacuum. Tetrahydrofuran, *n*-hexane, benzene, and xylene were refluxed over and distilled from sodium metal. DMF and DMSO were dried over anhydrous magnesium sulfate and calcium hydride, respectively, and distilled under reduced pressure before use. *m*-Cresol was distilled under reduced pressure. Commercial aluminum isopropoxide was used as it is.

Bulk Polymerization. BOL and catalyst were added to THF in an ampule equipped with three-way stopcock under dry nitrogen atmosphere. In some cases a small amount of *N*-acety-BOL was also used. After rapid removal of the solvent under reduced pressure, the ampule was allowed to stand at a fixed temperature. Polymerization was terminated by addition of a large amount of water. The resulting white polymer was minced, immersed repeatedly in fresh water to remove the residual monomer and catalyst, collected on a glass filter, washed again with water, and dried in vacuo at 100 °C.

Solution Polymerization. Solution of BOL in THF or DMSO, including catalyst and if necessary activator, was placed in an ampule or spread over a glass or a metal plate under a nitrogen atmosphere and allowed to stand at a fixed temperature. Termination and polymer purification were made analogously as mentioned above.

Characterization. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on Japan Electronics Model JNM-MH-100 operating at 100 MHz and Model JNM-FX-100 Fourier transform high-resolution spectrometers at 25 MHz, respectively, at room temperature. Tetramethylsilane was used as an internal standard. IR spectra were taken with a Japan Optics Model IR-G spectrophotometer. Thermal transitions were observed with a Perkin-Elmer Model DSC-2 differential scanning calorimeter. Viscosities were determined in *m*-cresol with a Ubbelohde viscometer at 25 ± 0.05 °C. 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.

Results and Discussion

Characterization of BOL. BOL was characterized by infrared, NMR, and elemental analysis. Infrared (in CCl_4) 3180 and 3090 (ν(NH)), 2955, 2920, 1721 (ν(C=O)), 1468, 1420, 1330, 1280, 1248, 1077, 1068, 1034, 984, and 882 cm^{-1}; ^{1}H-NMR (in CCl_4) δ 8.39 (1 H, -N*H*C(=O)-), 5.29 (1 H, -O-C*H*-N-C(=O)-), 4.10 (1 H, -O-C*H*C(=O)N-), and 1.83 ppm (6H, -C*H*$_2$-); ^{13}C-NMR (in $CDCl_3$) δ 177.5 (-NHC(=O)-), 85.9 (-OCHNH-), 75.5 (-OCHC(=O)-), 27.8, 24.4, and 15.7 ppm (-CH_2-); mass spectrum (*m/e*) 127 (M^+).

Anal. Calcd for $C_6H_9NO_2$: C, 56.68; H, 7.14; N, 11.01. Found: C, 56.28; H, 7.19; N, 10.99.

It may be noted that BOL obtained here was found to show some unexplainable thermal behavior. As shown in Figure 1, a fine needle crystal sample of BOL gave two thermal transition points in the DSC thermogram: at 62 and at 91–92 °C. The BOL sample, ground in an agate mortar with a pestle, however, had a sharp endothermic peak at 74–75 °C (at this temperature most of the sample had melted as observed with a melting point measuring microscope), and a small peak again at 91–92 °C (at which temperature the rest melted). This thermal behavior may be attributed to some extent of hygroscopicity and the spherical nature of the molecule which begins to spin before the crystal lattice collapses, and/or to the chiral structure of BOL having two asymmetric carbons, and must be the subject of future investigation.

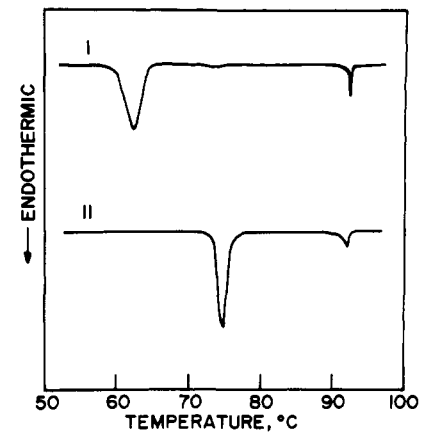


Figure 1. DSC thermograms of 8-oxa-6-azabicyclo[3.2.1]octan-7-one. Heating rate, 2.5 °C/min; (I) needle crystal; (II) after grinding I in agate mortar with pestle.

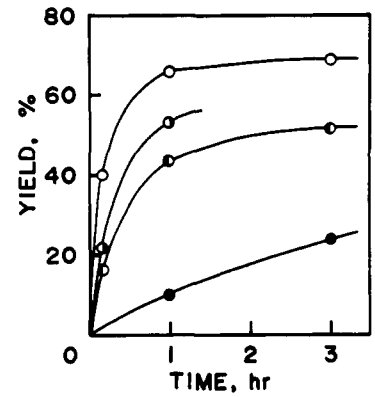


Figure 2. Time–conversion curves for the bulk polymerization of 8-oxa-6-azabicyclo[3.2.1]octan-7-one: (○) 100 °C; (◑) 80 °C; (◐) 70 °C; (●) 60 °C.

Bulk Polymerization. The results of bulk polymerization of BOL by using different catalysts are summarized in Table I. BOL was easily polymerized in the presence of alkali metal compounds above 60 °C. The polymerization at 150 °C was too fast to be controlled. The yield and the viscosity number, η_{sp}/c, of the resulting polyamide increased with the reaction time. The initial rate of the polymerization became higher with the size of the countercation, in analogy to the case of anionic polymerization of ε-caprolactam.[16] The rate increased also with raising temperature as shown in Figure 2 and Table II.

Polymerization of BOL virtually does not take place in bulk below about 60 °C, being due to the initial solidification of the polymerization system. It is well known that the anionic polymerization of lactams in general is markedly facilitated by the addition of *N*-acetylated lactams.[17–19] The polymerization of BOL was also accelerated by the addition of *N*-acetyl-BOL (Tables I and II).

Solution Polymerization. The anionic polymerization of BOL is characterized by a rapid conversion in THF and DMSO, even at or below room temperatures, as indicated in Table III.

In THF the reaction system became turbid and set to gel as the polymerization proceeded. In DMSO it proceeded in a homogeneous phase. It is also worth noting that BOL was able to polymerize in these solvents without *N*-acetyl-BOL. The prolonged polymerization resulted in the formation of sufficiently high molecular weight polymer. These facts indicate that the BOL anion, produced by proton exchange

Table I
Bulk Polymerization of 8-Oxa-6-azabicyclo[3.2.1]octan-7-one

BOL, g	Catalyst	Catalyst, mol %/monomer	*N*-Acetyl-BOL, mol %/monomer	Temp, °C	Time, min	Yield, %	η_{sp}/c [a]
0.64	K Pyrdn	1	0	100	10	40	0.61
0.64	K Pyrdn	1	0	100	180	68	1.1
0.64	K Pyrdn	1	0	100	360	82	*b*
0.64	K Pyrdn	1	0	70	10	16	0.50
0.64	K Pyrdn	1	0	70	60	44	0.77
4.65	K Pyrdn	1	0.2	70	10	72	0.51
0.64	K Pyrdn	1	0	60	60	10	0.40
0.64	K Pyrdn	1	0	50	60	~0	
0.64	K Pyrdn	1	0.2	50	60	1.4	
2.80	NaH	1	0.2	70	10	62	0.43
1.27	*n*-BuLi	1	0.2	70	60	32	0.26
0.63	NEt_3	10	1	100	720	0	

[a] In *m*-cresol, c = 0.2 g/100 mL, 25 °C. [b] Insoluble in *m*-cresol.

Table II
Initial Rate of Polymerization of 8-Oxa-6-azabicyclo[3.2.1]octan-7-one[a]

Temp, °C	*N*-Acetyl-BOL, mol %/monomer	Rp, %/min
70	0	1.6
70	0.2	3.6
60	0	0.17
60	0.2	0.25
50	0	0
50	0.2	0.02

[a] K Pyrdn, 1 mol %/monomer.

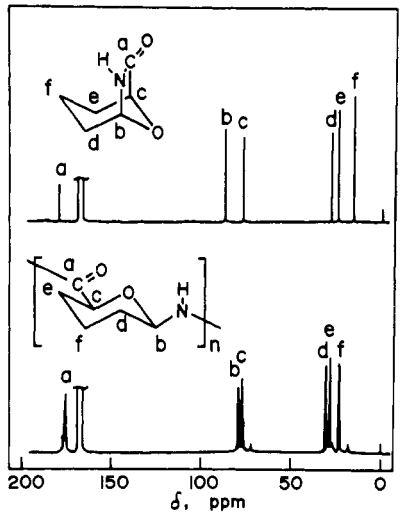
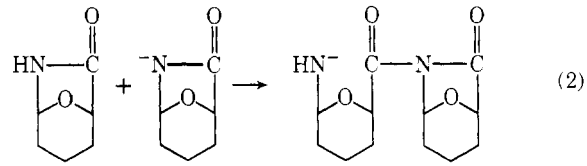


Figure 3. ^{13}C-NMR spectra of 8-oxa-6-azabicyclo[3.2.1]octan-7-one and its polymer (7% in formic acid). Polymerization: at 70 °C for 10 min in 72% yield; η_{sp}/c 0.51 (in *m*-cresol, 0.2 g/100 mL, 25 °C).

between a BOL monomer and pyrrolidonate anion from the catalyst, can also attack easily the amide group of another BOL monomer as well as the imide group of *N*-acetyl-BOL as shown in eq 2 and 3.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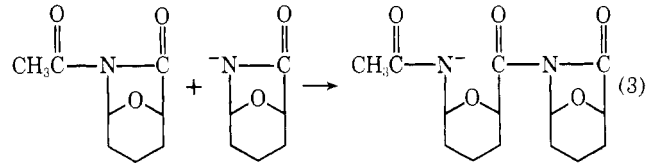
(3)

From the kinetic viewpoint the polymerizability of BOL is considered to be higher than that of ϵ-caprolactam, which is polymerized[20,21] usually at temperatures above 135 °C. Thermodynamically, the polymerization of BOL appears to be more favored than that of α-pyrrolidone, for which no polymerization is observed in THF.[20-22] The higher polymerizability of BOL may be attributed not only to its highly strained bicyclic structure but also to the activation of the BOL anion by the separation of the countercation from the amidate anion, under the influence of possible interaction of the cation with the ring ether oxygen. Thus room-temperature polymerization and simultaneous film casting on a glass or a metal plate appear feasible ("casting polymerization").

Solubility of Poly(BOL). Most samples of the resulting poly(BOL) were soluble in formic acid, *m*-cresol, DMSO, and even chloroform, while the polymer prepared in bulk at elevated temperatures at a high conversion was often insoluble

Table III
Solution Polymerization of 8-Oxa-6-azabicyclo[3.2.1]octan-7-one[a]

BOL, g	Solvent	S/M[b]	*N*-Acetyl-BOL, mol %/monomer	Temp, °C	Time, h	Yield, %	η_{sp}/c [c]
1.31	THF	4.9	0	50	1	20	0.80
1.30	THF	4.9	0.2	25	1	67	0.53
1.36	THF	4.9	0.2	0	1	15	0.26
1.00	DMSO	2.8	0	50	1	61	0.99
1.39	DMSO	2.8	0.2	50	1	79	0.59
2.65	DMSO	5.6	0	25	2	28	1.70
2.24	DMSO	5.6	0.2	25	1	92	0.64
5.92	DMSO	5.6	0	19	72	56	1.97

[a] K Pyrdn, 1 mol %/monomer. [b] Molar ratio of solvent to monomer. [c] In *m*-cresol, 0.2 g/100 mL, 25 °C.

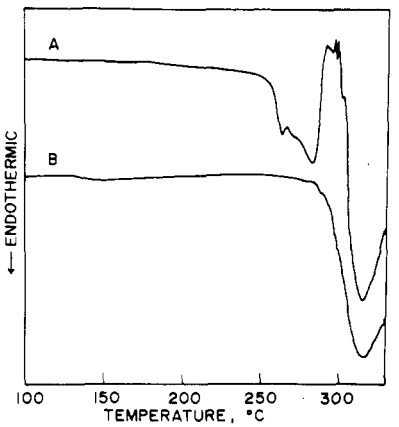

Figure 4. DSC thermograms of poly(tetrahydropyran-2,6-diyliminocarbonyl) prepared in DMSO at 19 °C for 72 h in 56% yield. Heating rate, 10 °C/min: (A) original scanning; (B) rescanning after scanning up to 290 °C.

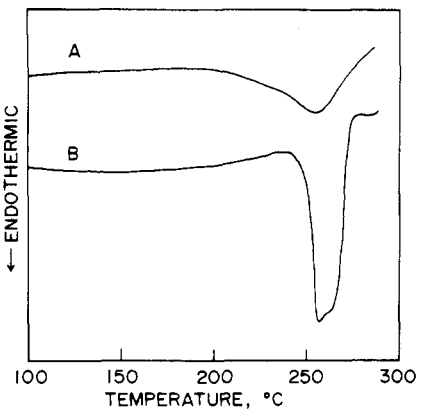

Figure 5. DSC thermograms of polyamide prepared by bulk polymerization of 8-oxa-6-azabicyclo[3.2.1]octan-7-one. Heating rate, 10 °C/min. Polymerization: (A) at 100 °C for 6 h in 82% yield; (B) at 70 °C for 3 h in 52% yield.

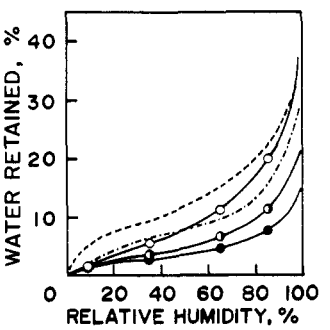

Figure 6. Sorption isotherms of different polyamides. At 20 °C: (○) poly(BOL); (◑) nylon-4; (●) nylon-6; (- - -) wool; (- · -) silk.

even in *m*-cresol. These solubility behaviors reflect a linear structure of the former and a cross-linked structure of the latter. The uncommonly good solubility of this polyamide in such aprotic solvents as DMSO and chloroform suggests that the hydrogen bonds between amide groups are loosened by the interference from bulky tetrahydropyran rings.

IR and NMR Analyses. The infrared spectrum of poly(BOL) in chloroform shows absorptions at 3400 and 3500 (ν(NH)), 3000, 2950, 2920, 2860, 1678 (ν(C=O)), 1528 (δ(NH)), 1440, 1300, 1193, 1145, 1092, 1068, 1030, and 919 cm^{-1} and indicates that the cyclic amide linkage in the monomer was transformed to the linear amide group. The ^{13}C-NMR (Figure 3) and ^{1}H-NMR spectra also support that the polymer ob-

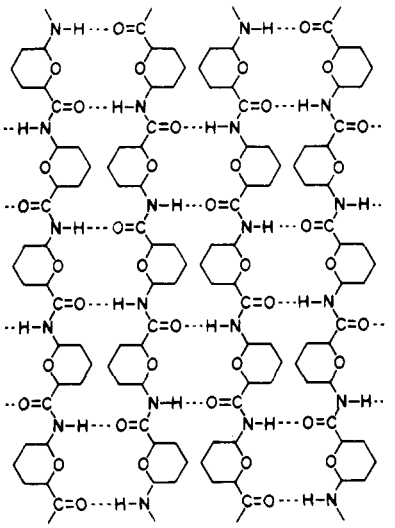

Figure 7. Possible planar arrangements of poly(tetrahydropyran-2,6-diyliminocarbonyl) molecules provided all hydrogen bonds are ideally regularly formed between the chains.

tained here is a novel polyamide, poly(tetrahydropyran-2,6-diyliminocarbonyl) (**2**). The chemical shift of peak f in the ^{13}C-NMR spectrum of poly(BOL) is lower by 7 ppm than that of BOL monomer which shifts to the higher magnetic field because of the steric effect of the axial substituents on the tetrahydropyran ring. In addition, the chemical shift of peak b in the spectrum of poly(BOL) is higher by 8 ppm than that of the monomer which shifts to the lower magnetic field due to the magnetic anisotropic effect of the ring carbonyl group. These shifts indicate that the amide group is located in the axial position to the tetrahydropyran ring in BOL and in the equatorial one in the polymer. In addition to the six main peaks, there appear some small peaks in the spectrum, which may result from stereoisomerism of the repeating unit or branched structures.

Thermal Analysis. The DSC thermogram of poly(BOL) prepared in DMSO at 19 °C has two endothermic peaks at 260–285 and 315 °C due to the fusion and decomposition, respectively, as shown in Figure 4. Another transition appeared at about 130 °C on the rescanning after rapid cooling of the molten polyamide. It seems probably to be a glass transition point. The polyamide prepared in bulk at 70 °C also melted sharply at 250–260 °C. On the other hand the cross-linked poly(BOL), which was prepared in bulk at 100 °C in a high conversion, has nothing but a broad endothermic curve up to near 300 °C as shown in Figure 5.

Moisture Sorption. The results of an elemental analysis of poly(BOL), dried at 100 °C until a constant weight was reached, showed a discrepancy from the calculated values, suggesting that water persisted in the polymer. Poly(BOL) film is flexible in water but more or less hard on drying at room temperature. Figure 6 represents the moisture sorption isotherms determined at 20 °C on the coarsely ground samples of different polyamides, together with the curves for wool and silk fibers cited from the literature.[23] The amount adsorbed on poly(BOL) is always much larger than that of either poly(α-pyrrolidone) or poly(ϵ-caprolactam) at any relative humidity and is, roughly speaking, comparable to wool and silk. The observed moisture sorption of 42% at 99% relative humidity corresponds to the sorption of more than three molecules of water per BOL monomer unit in the polymer chain. Such a distinguished hygroscopic property of poly(BOL) may be accounted for by the occurrence, even if partly, of hydrophilic polar microdomains surrounded by hydrophobic nonpolar microdomains, which result from the alternating arrangement

of an amide linkage and a tetrahydropyran ring along the chains. Possible molecular arrangements providing all hydrogen bonds are ideally regularly formed between polymer chains are illustrated in Figure 7. In the presence of water hydrogen bond interactions must exist between the water molecules and the amide groups. The ring ether oxygens may also interact with the water molecules.

Poly(BOL) film has been found to exhibit some extent of permeability and permselectivity for alkali metal ions in water. Further work is in progress on the properties of poly(BOL) and will be published in the near future.

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Preparation and Characterization of Head-to-Head Polymers. 5. Head-to-Head Polystyrene[1]

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ABSTRACT: Head-to-head (H-H) polystyrene was obtained by radical 1,4-polymerization of 2,3-diphenylbutadiene followed by selective hydrogenation with potassium and ethanol. The chemical, physical, and thermal properties of H-H polystyrene were studied and compared with those of both atactic and isotactic head-to-tail (H-T) polystyrene. The T_g of the H-H polymer was found to be nearly the same as the T_g of the atactic H-T polymer. The degradation behavior of H-H and H-T polystyrene was also very similar indicating that both types of linkages are of comparable stability.

In our earlier work we discussed the synthesis and characterization of head-to-head (H-H) poly(methyl cinnamate),[2a,4] H-H poly(methyl acrylate),[2b,4] and H-H poly(methyl crotonate).[3,4] It was found that the H-H polymers behaved differently from the head-to-tail (H-T) polymers. The glass transition temperatures of the H-H polymers as determined by differential scanning calorimetry or thermomechanical studies were 30 to 50 °C higher than those of the corresponding H-T polymers.

On the other hand, it was found to our surprise that H-H poly(methyl acrylate) showed the same thermal degradation spectrum as did the H-T polymer. Also the degradation behavior and the maximum rate degradation temperatures of both polymers were essentially identical. This result was not surprising if one considered Grassie's[5] earlier work on the thermal degradation of polystyrene where he suggested that the breakage of the H-T linkage in polystyrene does not require more energy than that of the H-H linkage. However, Grassie compared the degradation behavior of polystyrene with that of styrene–stilbene copolymers of low stilbene content. Therefore it was of interest to synthesize and investigate pure H-H polystyrene and compare its properties to those of the normal H-T polystyrene.

Several unsuccessful attempts have been made to prepare pure H-H polystyrene. Richards[6–9] used a step growth polymerization with the styrene dimer dianion as the starting material and obtained polymers of relatively low molecular weight and with a structure that did not contain entirely H-H linkages. Thus the more or less direct preparation did not seem to be feasible at this time.

An indirect preparation of H-H polystyrene was reported in a preprint by Asami[10] who studied the hydrogenation of poly(1,2-diphenylbutadiene) and poly(2,3-diphenylbutadiene). A complete paper has not appeared which would allow the verification of the data. Also, a polymer claimed to be H-H polystyrene of high molecular weight prepared by reduction of poly(2,3-diphenylbutadiene) with sodium and aniline has been investigated by light scattering, dilatometry, and stress relaxation methods.[11]

It was the purpose of our work to prepare pure H-H polystyrene by hydrogenation of 1,4-poly(2,3-diphenylbutadiene) and compare its chemical, physical, and thermal properties with those of atactic and isotactic H-T polystyrene.

Experimental Section

Materials. The following materials were obtained from Eastman Kodak Co.: benzene, tetrahydrofuran, ethanol, *n*-heptane, azobis(isobutyronitrile) (AIBN), and *p*-toluene sulfonhydrazide.

Benzene was dried over calcium chloride and distilled from sodium metal prior to its use.