calorimetry curves of samples and components, and X-ray diffraction scan of sample II component 1 (29 pages). Ordering information is given on any current masthead page.

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(22) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13–18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

Unusual Anionic Desalting Oligomerization of Alkali Metal Salts of Bromo-Substituted Bicyclic Oxalactam

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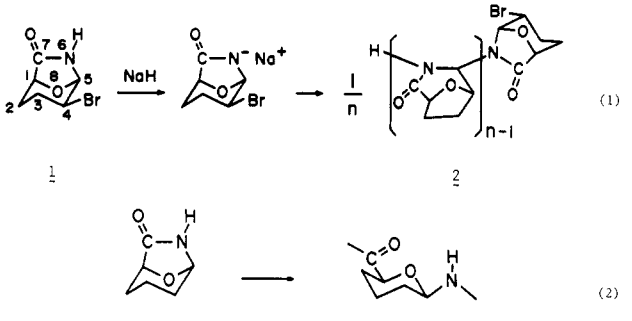
ABSTRACT: The oligomerization of sodium and potassium salts of a new bromo-substituted bicyclic oxalactam, 4(e)-bromo-8-oxa-6-azabicyclo[3.2.1]octan-7-one (**1**), proceeds in *N,N*-dimethylformamide or dimethyl sulfoxide at 0 or 25 °C with elimination of alkali metal bromide to give novel oligomers **2** having a bicyclic oxalactam ring in each monomer unit. Oligomers similarly obtained from mixtures of **1** with its sodium salt had lower average molecular weight. Two diastereomeric dimers and a trimer were isolated by fractional elution from a preparative silica gel column. Structural analyses indicate that the oligomerization proceeds with high enantiomeric selectivity and complete retention of the configuration of the bridgehead methine carbon atom adjacent to nitrogen. Possible mechanisms for this oligomerization are presented.

Introduction

The bicyclic oxalactam 8-oxa-6-azabicyclo[3.2.1]octan-7-one (**3**) can be polymerized anionically at room temperature and dimethyl sulfoxide (Me_2SO) to a high molecular weight polyamide, poly(tetrahydropyran-2(e),6(e)-diyliminocarbonyl) (**4**).[1,2] Polyamide **4** is easily cast to a hygroscopic membrane that has high permeability to water and high permselectivity for aqueous solutes.[1-6] The polyamide is also useful as a component of amphiphilic graft and block copolymers.[7-13] The facile polymerization of **3** must be related to its molecular structure.[1,2,14] The effect of a polar substituent on the reactivity of the bicyclic oxalactam, as in bicyclic acetals,[15-19] is of interest.



(1)

1 **2**

(2)

3 **4**

The anionic polymerization of common lactams generally proceeds through cleavage of the amide bond.[20-23] Recently, X-ray structural analysis of optically active **4** has shown that the anionic polymerization of **3** proceeds with no inversion of configuration of the methine carbon atoms adjacent to oxygen in **3**, indicating that **3** polymerizes through scission of the C–N amide bond. On the other hand, the cationic oligomerization of **3**, which has the structure –OCHNHCO–, proceeds by cleavage of the CH–NH bond,[25,26] while that of some bicyclic lactam ethers involves opening of the ether bond.[27,28] It was therefore of interest to determine whether a nucleophilic reaction of bicyclic oxalactam analogues with the ether–amide bond would involve cleavage of the amide bond.

We have made a preliminary report of the synthesis of a new bicyclic oxalactam, 4(e)-bromo-8-oxa-6-azabicyclo-[3.2.1]octan-7-one (**1**), and of the oligomerization of its sodium salt with elimination of sodium bromide.[29] We here report details of the anionic oligomerization of alkali metal salts of **1** and discuss the oligomerization mechanism as it relates to enantiomeric selectivity and retention of configuration.

Results and Discussion

Preparation of 1. Compound **1** was synthesized from sodium 3,4-dihydro-2*H*-pyran-2-carboxylate (**5**), which is also a starting material for the synthesis of **3** (Scheme I).[1,2]

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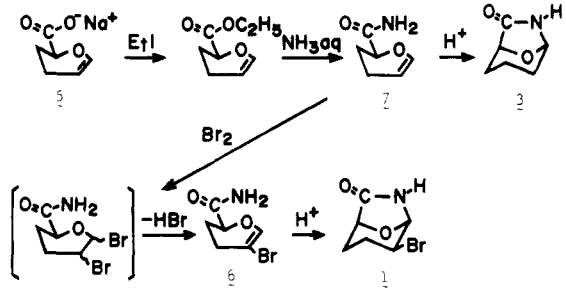
Table I
Anionic Desalting Oligomerization of the Sodium Salt of 4(e)-Bromo-8-oxa-6-azabicyclo[3.2.1]octan-7-one (1)

run	1, g	sodium salt of 1, g	mole ratio of 1 to its salt	solvent, mL	temp, °C	time, day	convn,[a] %
1	0	0.96	0	DMF, 10	0	3	87
2	0	0.61	0	Me_2SO, 2	25	1	66
3	0	1.01	0	DMF, 10	25	3	76
4[b]	0	0.90	0	DMF, 10	25	3	75
5	0	1.01	0	DMF, 10	25	7	94
6[c]	0.025	0.94	0.03	Me_2SO, 4	25	10	>95
7	0.52	1.14	0.5	DMF, 10	25	3	85
8	0.92	1.07	0.9	DMF, 15	25	3	82
9	0.81	0.088	9	DMF, 10	25	3	14
10	0.81	0.088	9	DMF, 10	25	7	15
11	0	0.43[d]	0	DMF, 10	25	3	>95
12	0	0.45[e]	0	DMF, 5	25	3	0

[a] Estimated by gel permeation chromatography of the reaction mixture. [b] *N*-Benzoyl derivative of 1 (2 mol %) was added to monomer. [c] In high vacuum. [d] Potassium salt of 1. [e] Sodium salt of 3.

Scheme I
Synthesis of 4(e)-Bromo-8-oxa-6-azabicyclo[3.2.1]octan-7-one (1)



5-Bromo-3,4-dihydro-2*H*-pyran-2-carboxamide (**6**) was prepared by bromination of amide **7** in DMF at low temperature, followed by dehydrobromination at room temperature. Since **1** should be formed by protic acid catalyzed intramolecular cyclization of **6**, we also heated the reaction mixture from the bromination of **7** to 110 °C without isolating **6** and obtained **1** in 40% yield. The bromine atom in **1** was judged to be equatorial to the tetrahydropyran ring from the coupling constants in its ^1H NMR spectrum, and this stereochemistry was confirmed by X-ray analysis of a crystal of **1**.[30]

Oligomerization. If the anionic polymerization of **1** occurred by the same mechanism as that for common lactams, the equatorial bromine atom should transfer to the axial position and be easily eliminated to give a dihydropyran ring. The base catalyst would be immediately consumed, and the reaction would stop. Accordingly, we chose to use the sodium and potassium salts of **1**, prepared by reaction of **1** with sodium and potassium hydrides, as monomers for the oligomerization of **1**.

When the sodium salt of **1** was kept in DMF or Me_2SO at 0 or 25 °C under nitrogen for 1–7 days, an oligomer mixture was formed in high conversion (Table I, runs 1–5, and Figure 1A).

A higher molecular weight oligomer was formed from the potassium salt of **1** (run 11 and Figure 1D). Similar treatment of mixtures of **1** with its sodium salt gave lower molecular weight oligomer. For example, the oligomer from **1** sodium salt was primarily trimer (run 3) whereas that from a roughly equimolar mixture of **1** and its sodium salt was primarily dimer (run 8). Higher ratios of **1** to sodium salt reduced conversion to the dimer (runs 9, 10). These results indicate that the alkali metal salt of **1** is the active monomer in the oligomerization.

Addition of the *N*-benzoyl derivative of **1** to the sodium salt did not accelerate the oligomerization, although *N*-benzoyl derivatives of common lactams are known to activate the anionic polymerization of these lactams.[20,21] Moreover, the sodium salt of the unsubstituted bicyclic lactam **3** did not oligomerize under our conditions, indicating that the bromine atom is essential to the oligomerization.

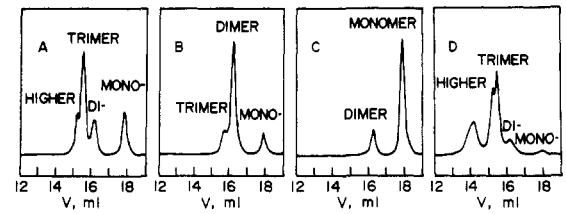


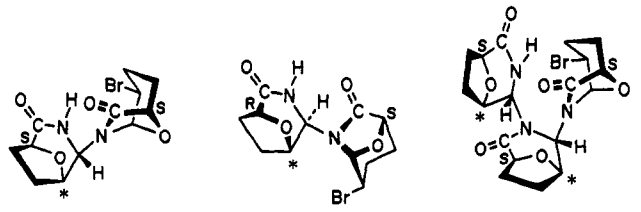
Figure 1. GPC curves for the reaction mixtures in anionic desalting oligomerization of alkali metal salts of 4(e)-bromo-8-oxa-6-azabicyclo[3.2.1]octan-7-one (**1**) in DMF at 25 °C for 3 days (Column, Shodex GPC KF-802, 8-mm i.d. × 600 mm; solvent, chloroform). Feed: (A), (B), and (C), sodium salt of **1**; D, potassium salt of **1**. Mole ratio of **1** to its salt: (A) 0; (B) 0.9; (C) 9; (D) 0.

Table II
Characterization of Oligomers Obtained by Anionic Desalting Oligomerization of Sodium Salt of 4(e)-Bromo-8-oxa-6-azabicyclo[3.2.1]octan-7-one (1)

	major dimer **8**	minor dimer **9**	trimer **10**
melting pt, °C	235.5–237.5	228–230	247–249
dec pt, °C	240–242	233.5–235	249–251
elem anal. found			
C, %	43.36	43.56	47.49
H, %	4.50	4.53	4.90
N, %	8.47	8.37	9.22
calcd for	$C_{12}H_{15}N_2O_4Br$	$C_{12}H_{15}N_2O_4Br$	$C_{18}H_{22}N_3O_6Br$
C, %	43.52	43.52	47.36
H, %	4.57	4.57	4.58
N, %	8.46	8.46	9.21
mol wt	331	331	456
m/e of parent peak in MS	330, 332	330, 332	455, 457
IR,[a] cm^{-1}	3396, ν_{N-H}	3390, ν_{N-H}	3390, ν_{N-H}
	1720, $\nu_{C=O}$	1723, $\nu_{C=O}$	1729, $\nu_{C=O}$
	1693, $\nu_{C=O}$	1692, $\nu_{C=O}$	1685, 1670, $\nu_{C=O}$

[a] In chloroform.

Characterization of the Dimers and Trimer. The oligomer mixture from run 8 (see GPC curve, Figure 1B) was fractionated in a preparative silica gel column with ethyl acetate–methanol eluant. Two dimers (**8** and **9**) and one trimer (**10**) were isolated in amounts of 0.77, 0.12, and 0.14 g, respectively. Their properties are listed in Table II. Molecular weights and elemental analyses indicate that one molecule of HBr was eliminated in the formation of



Major dimer, 8 Minor dimer, 9 Trimer, 10

Figure 2. Molecular structures of oligomers obtained from 4(e)-bromo-8-oxa-6-azabicyclo[3.2.1]octan-7-one.

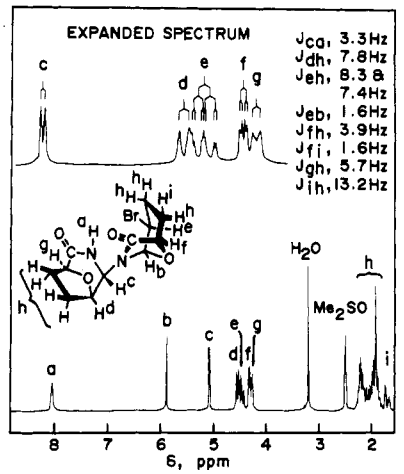


Figure 3. ^{1}H NMR spectrum of major dimer (8) (Me_2SO-d_6 solution, tetramethylsilane, 50 °C, 200 MHz).

each dimer and two molecules were eliminated in the formation of the trimer. These eliminations should result in the formation of either a double bond or a new ring, whereas the polymerizations of lactams usually involve ring opening.[20,21]

The IR spectra indicate that the oligomers contain no C–C or C–N unsaturation but do have two different amide carbonyl groups. The latter correspond to the five-membered and six-membered lactam rings in structures **8**, **9**, and **10**, which were determined by X-ray crystallographic analysis.[31,32]

The configurations of the methine carbon atoms adjacent to the carbonyl group indicate that **8** and **10** are formed from one or the other enantiomer of **1**, and that the minor dimer (**9**) is formed from both enantiomers. Dimers **8** and **9** are diastereomers, and their ratio (87:13) indicates significant enantiomeric selectivity in the oligomerization.

It is interesting that the configuration of only one methine carbon in the six-membered oxalactam ring of each monomer unit is inverted during the oligomerization (Figure 2, asterisks), while the configurations of the other methine carbons are unchanged.

The structures **8**–**10** are supported by ^{1}H and ^{13}C NMR analyses (Figures 3 and 4, Table III). The spectra of **10** were measured at 120 °C because some peaks were broadened below 100 °C. The rotation of monomer units about the C–N bonds joining them must be inhibited by steric interference of the neighboring bulky groups, particularly in **10**. Assignment of individual peaks is based on ^{1}H homodecoupling, ^{13}C{^{1}H} off-resonance decoupling, and ^{13}C{^{1}H} selective decoupling spectra.

Peaks c, f, h, j, and l in the ^{13}C NMR spectra of each oligomer are assigned to the carbon atoms of the terminal unit having a five-membered oxalactam ring and a bromine atom (Table III) because their chemical shifts are similar to those in **1**. The other peaks d, e, g, i, and k, each of

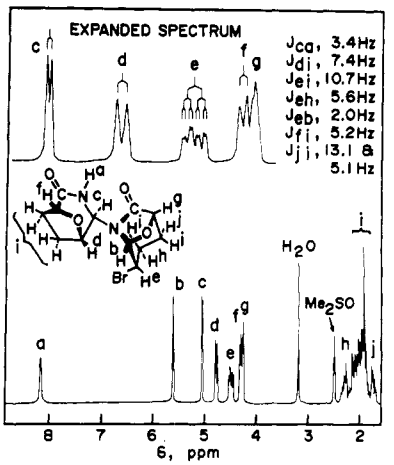
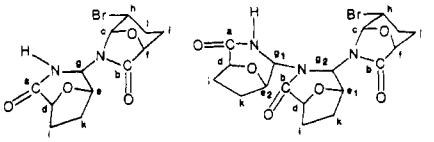


Figure 4. ^{1}H NMR spectrum of minor dimer (**9**) (Me_2SO-d_6 solution, tetramethylsilane, 50 °C, 200 MHz).

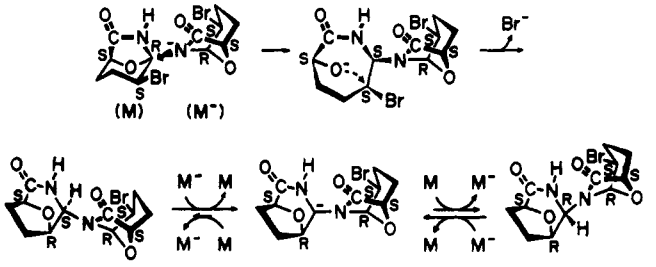
Table III
Chemical Shifts and Assignments of Peaks in the ^{13}C NMR Spectra of Oligomers of 4(e)-Bromo-8-oxa-6-azabicyclo[3.2.1]octan-7-one[a]

	major dimer 8, δ	minor dimer 9, δ	trimer 10, δ
carbonyl carbon	a 172.32	a 175.02	a 172.51
	b 169.48	b 170.23	b_1 170.96, b_2 169.75
methine carbon	c 88.81	c 86.65	c 91.50
	d 76.41	d 75.99	d_1 76.69, d_2 76.55
	e 75.60	e 74.56	e_1 78.15, e_2 73.90
	f 74.33	f 74.46	f 75.50
	g 61.63	g 63.99	g_1 65.33, g_2 65.11
	h 46.35	h 46.98	h 48.72
methylene carbon	i 29.48	i 29.52	i_1 30.35, i_2 29.96
	j 27.39	j 28.43	j 27.68
	k 26.42	k 26.07	k_1 26.61, k_2 25.10
	l 26.10	l 26.29	l 26.49

[a] Solvent, Me_2SO-d_6; reference, tetramethylsilane; temperature, 50 °C (dimers), 120 °C (trimer); 50 MHz.



Scheme II
Possible Mechanism of Formation of Major Dimer (8) by the Reaction of 1 and Its Anion

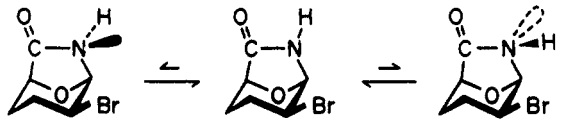


8

which is split in the trimer spectrum, are assigned to the carbon atoms in the monomer units having six-membered lactam rings. Peaks a and b are assigned to the carbonyl carbon atoms in the mono- and di-*N*-substituted amide groups, respectively.

The largest value of the three coupling constants of proton peak e in the ^{1}H NMR spectrum of **8** (8.3 Hz, Figure 3) is smaller than those of the corresponding peaks of **1** (10.4 Hz) and **9** (10.7 Hz, Figure 4). This fact suggests that the chair form of the tetrahydropyran ring in **8** is

Scheme III
Molecular Structure of 4(e)-Bromo-8-oxa-6-azabicyclo[3.2.1]octan-7-one



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significantly deformed in Me_2SO solution compared with the crystal.

Oligomerization Mechanism. The above results suggest a mechanism for the formation of the major dimer 8 (Scheme II). Even when the pure salt of 1 was used as the monomer, a trace of 1 should be present owing to hydrolysis of the salt by adventitious water in the reaction mixture. Nucleophilic attack of either enantiomer of 1 anion on a molecule of 1 at the methine carbon adjacent to nitrogen, which has the same configuration, cleaves the C5–O8 bond in the latter to form a seven-membered lactam ring. The alcoholate anion of this intermediate should undergo intramolecular reaction with the bromine-substituted methine carbon, eliminating bromide ion and forming a bicyclic skeleton with a six-membered oxalactam ring. Epimerization should proceed through abstraction of the active hydrogen between nitrogen atoms by another anion in order to relieve the steric hindrance around the C–N bond joining the two units, yielding the major dimer 8.

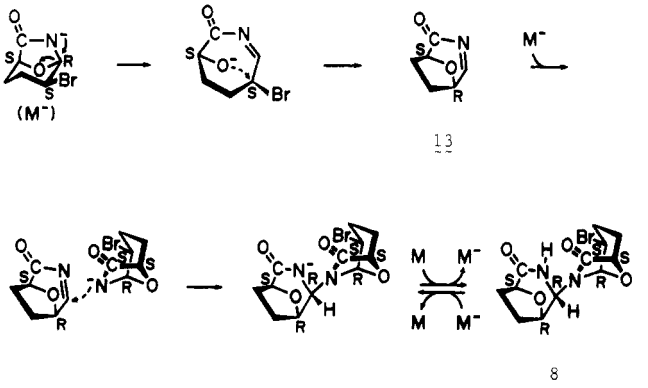
Reaction of either enantiomer of 1 anion with another molecule of 1 that has a different configuration should give the minor dimer **9**. The trimer **10** should be formed by reaction of either enantiomer of 1 anion with a molecule of 8 that has the same configuration as the anion. Other trimers have not been isolated.

The first step in this mechanism, cleavage of the ether bond by nucleophilic attack, generally proceeds readily only in three-membered cyclic ethers. However, tetrahydrofuran is known to be decomposed by strong bases such as *n*-butyllithium even at low temperature,[33] so it is reasonable that the C5–O8 bond can be weakened under our conditions. If stereoelectronic effects are involved,[34,35] the lobe of the lone electron pair in the amide nitrogen would be nearly antiperiplanar to the C5–O8 bond (**11**, Scheme III). The X-ray structural analysis of 1[30] indicates that the amide group is almost planar, so that its lone electron pair should be frequently in the p orbital perpendicular to the plane of the amide group. Nevertheless, the sp^3 hybrid orbital may also contribute significantly to the orbitals of the nitrogen atom (**11**, **12**) because of steric hindrance in the bicyclic skeleton.

In an alternative mechanism (Scheme IV), 1 anion is assumed to rearrange to the imino ketone **13** by cleavage of the C5–O8 bond, followed by intramolecular nucleophilic reaction with elimination of bromide ion. Since the lone electron pair on the nitrogen atom of 1 anion is nearly antiperiplanar to the C5–O8 bond, the ether bond could be weakened by stereoelectronic effects.[34,35] However, intermediate **13** has not been observed in the oligomer mixture. It is possible that the imino carbon atom in **13** is immediately attacked by another anion molecule to give the major dimer **8**. Such attack should be oriented by steric hindrance of the methylene groups in **13** with the nucleophile, and the configuration of the methine carbon in the C–N bond joining the two units would be retained.

The high enantiomeric selectivity in the oligomerization points to the mechanism of Scheme II as the more reasonable of the two. In Scheme II, interaction of the carbonyl group of 1 anion with the amide hydrogen of another molecule of 1 should control the direction of mutual approach (Scheme V).

Scheme IV
Possible Mechanism of Formation of Major Dimer (8) through the Imine 13



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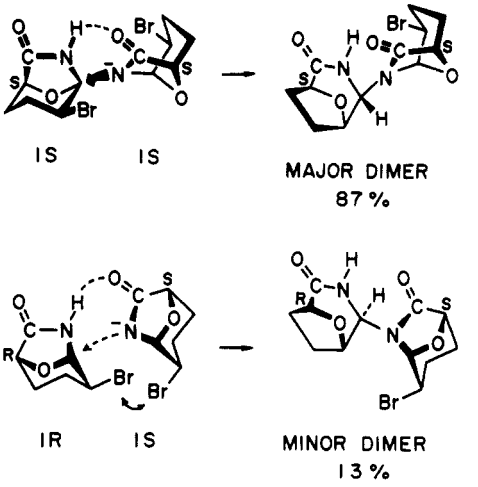
Scheme V
Enantiomer Selectivity in the Dimerization of Sodium Salt of 4(e)-Bromo-8-oxa-6-azabicyclo[3.2.1]octan-7-one (1)



In the formation of major dimer 8 there should be no interference between the two bulky bromine atoms as there should be in the formation of minor dimer 9. On the other hand, enantiomeric selectivity would not be expected in the mechanism of Scheme IV because the bromine atom in the anion is eliminated to give imine **13** before nucleophilic attack by another molecule of anion. Thus there would be little steric hindrance during this attack whichever enantiomer of the anion were the nucleophile.

In conclusion, the equatorial location of the bromine atom in 1 appears to be essential not only for the formation of the lactamate anion of 1 but also for the elimination of alkali bromide in the oligomerization.

Experimental Section

4(e)-Bromo-8-oxa-6-azabicyclo[3.2.1]octan-7-one (1).[29] To a solution of 12.7 g of 3,4-dihydro-2*H*-pyran-2-carboxamide (**7**) in 125 mL of DMF was added a solution of 16 g of bromine in 20 mL of DMF dropwise with stirring below −25 °C for 0.5 h. After the reaction mixture was kept in air for 2 h, it was poured into a solution of 13.5 g of potassium *tert*-butoxide in 60 mL of DMF with stirring at −25 °C. After evaporation of the organic solvent, 70 mL of water was added to the residue and it was extracted with 200-mL portions of chloroform more than seven times. The chloroform phase was dried over anhydrous sodium carbonate for 1 day. After removal of the solvent, yellowish crystals were obtained. The crude 5-bromo-3,4-dihydro-2*H*-pyran-2-carbox-

amide (6) was recrystallized from chloroform; yield 13.3 g (65%); mp 161–162 °C; dec 172–173 °C. Anal. Calcd for $C_6H_8NO_2Br$: C, 34.98; H, 3.91; N, 6.80. Found: C, 35.03; H, 3.89; N, 6.62. Molecular weight, 206 (*m/e* of parent peaks in mass spectrum, 205 and 207). IR (KBr disk) 3398 and 3196 (ν_{N-H}, amide), 1665 ($\nu_{C=O}$, amide), 1645 ($\nu_{C=C}$), 1221 (ν_{C-O}), 603 and 550 (ν_{C-Br}) cm^{-1}. ^1H NMR (Me_2SO-d_6, room temperature) δ 7.39 and 7.37 (s, 2 H, amide), 6.75 (dd, $J(^6CH^4CH)$ = 2.2 and 1.7 Hz, 1 H, ^6CH), 4.32 (dd, $J(^2CH^3CH)$ = 8.0 and 3.4 Hz, 1 H, ^2CH), 2.45–2.15 (m, 2 H, $^4CH_2$), 2.15–1.85 (m, 2 H, $^3CH_2$) ppm. ^{13}C NMR (Me_2SO-d_6, room temperature) δ 170.94 (C=O), 141.22 (^6C), 99.03 (^5C), 73.07 (^2C), 27.82 (^4C), 25.37 (^3C).

In order to prepare 4(e)-bromo-8-oxa-6-azabicyclo[3.2.1]octan-7-one (1) from 7 without isolating the intermediate 6, the reaction mixture from the bromination was heated at 110 °C for 1 h. After the addition of 5 g of anhydrous sodium carbonate for quenching, excess carbonate was filtered off and the organic solvent evaporated. The residue was added to 80 mL of water and extracted with 4 × 400 mL of chloroform. After it was dried over anhydrous sodium carbonate the organic phase was condensed and fractionated through a preparative silica gel column, using ethyl acetate as eluant. Crude 1 was obtained in 40% of yield (8.3 g). After recrystallization from ethyl acetate, 1 was characterized as follows: mp 146–147 °C, 183–186 °C dec. Anal. Calcd for $C_6H_8NO_2Br$: C, 34.98; H, 3.91; N, 6.80. Found: C, 35.01; H, 3.85; N, 6.68. Molecular weight, 206 (*m/e* of parent peaks in mass spectrum, 205 and 207); IR (KBr disk) 3444 and 3088 (ν_{N-H}, amide), 1736 and 1725 ($\nu_{C=O}$, amide), 1238 (ν_{C-O}), 583 (ν_{C-Br}) cm^{-1}; ^1H NMR (Me_2SO-d_6, 60 °C) δ 8.22 (s, 1 H, amide), 5.28 (br s, 1 H, ^5CH), 4.36 (ddd, $J(^4CH_{ax}{-}^3CH_{ax})$ = 10.4, $J(^4CH_{ax}{-}^3CH_{eq})$ = 5.8, $J(^4CH_{ax}{-}^5CH)$ = 1.9 Hz, 1 H, $^4CH_{ax}$), 4.06 (m, 1 H, ^1CH), 2.30 (m, 1 H, $^3CH_{eq}$), 2.16–1.80 (m, 2 H, $^2CH_{ax}$ and $^3CH_{ax}$), 1.72 (m, $J(^2CH_{eq}{-}^2CH_{ax})$ = 13.1, $J(^2CH_{eq}{-}^3CH_{ax})$ = 5.7 Hz, 1 H, $^2CH_{eq}$); ^{13}C NMR (Me_2SO-d_6, 60 °C) δ 174.17 (C=O), 86.23 (^5C), 73.37 (^1C), 48.34 (^4C), 27.63 (^3C), 26.27 (^2C).

Sodium Salt of 1. Tetrahydrofuran (THF) used for a solvent was distilled after refluxing over sodium metal. To a mixture of 0.48 g of 50% sodium hydride dispersion in oil with 50 mL of THF in a 200-mL round-bottomed flask equipped with stirrer and thermometer was added dropwise a solution of 2.47 g of 1 in 50 mL of THF with stirring at room temperature under dry nitrogen. The reaction mixture was stirred for 1 h after the evolution of hydrogen gas was completed. The resulting white precipitate was collected on a glass filter and washed with fresh THF in a drybox filled with dry nitrogen. The white powder was dried in vacuo, sealed in a glass ampule, and kept in a refrigerator until used. The purity of the salt determined by volumetric titration with 0.1 N hydrochloric acid solution was 99%. The potassium salt of 1 was prepared by using potassium hydride instead of sodium hydride by the same procedure.

***N*-Benzoyl-4(e)-bromo-8-oxa-6-azabicyclo[3.2.1]octan-7-one.** To the THF solution of the salt of 1 prepared as above, a solution of 1.40 g of benzoyl chloride in 50 mL of THF was added at 10 °C under dry nitrogen. After evaporation of the solvent, 50 mL of water was added to the residue and extracted with 3 × 100 mL of chloroform. After it was dried over magnesium sulfate, the chloroform phase was condensed with a rotary evaporator. The resulting colorless crystals were recrystallized from ethyl acetate: yield 1.5 g (49%); mp 121–124 °C. Anal. Calcd for $C_{13}H_{12}NO_3Br$: C, 50.36; H, 3.90; N, 4.52. Found: C, 50.36; H, 3.99; N, 4.42. Molecular weight, 310 (*m/e* of parent peaks in mass spectrum, 309 and 311); IR (KBr disk) 1760 and 1660 ($\nu_{C=O}$), 1580 ($\nu_{C=C}$), 1080 (ν_{C-O}), 580 (ν_{C-Br}) cm^{-1}; ^1H NMR (Me_2SO-d_6, 60 °C) δ 7.80–7.42 (m, 5 H, Ar), 6.40 (d, $J(^5CH{-}^4CH_{ax})$ = 2.2 Hz, 1 H, ^5CH), 4.68 (ddd, $J(^4CH_{ax}{-}^3CH_{ax})$ = 10.3, $J(^4CH_{ax}{-}^3CH_{eq})$ = 5.7, $J(^4CH_{ax}{-}^5CH)$ = 2.2 Hz, 1 H, $^4CH_{ax}$), 4.62 (m, 1 H, ^1CH), 2.52–2.45 (m, 1 H, $^3CH_{eq}$), 2.45–2.25 (m, 1 H, $^3CH_{ax}$), 2.25–2.00 (m, 1 H, $^2CH_{ax}$), 2.00–1.85 (m, 1 H, $^2CH_{eq}$); ^{13}C NMR (Me_2SO-d_6, 60 °C) δ 170.60 (endo-carbonyl), 166.25 (exo-carbonyl), 132.77 (Ar quarternary), 132.43 (Ar para), 128.94 (Ar ortho), 127.77 (Ar meta), 87.28 (^5C), 76.23 (^1C), 46.73 (^4C), 28.09 (^3C), 27.04 (^2C).

Oligomerization. DMF and Me_2SO were dried over anhydrous magnesium sulfate and calcium hydride, respectively, and distilled under reduced pressure. Under dry nitrogen certain amounts of 1 and its alkali metal salt were dissolved in purified DMF or Me_2SO in a 20-mL round-bottomed flask equipped with stirrer and three-way stopcock and kept at 0 or 25 °C. After the oligomerization was halted by the addition of a small amount of acetic acid, the mixture was concentrated by evaporation of organic solvents and the residue was dried in vacuo. Conversion to the oligomer was determined by gel permeation chromatography.

Isolation of Dimers and Trimer. The reaction mixture from the oligomerization (run 8) was fractionated through a preparative silica gel column (Fuji Davison, Silica Gel BW-820MH, 100 g), eluting with 500 mL of ethyl acetate and 750 mL of ethyl acetate–methanol (20:1 vol). The eluent was taken in more than 100 portions, which were qualitatively analyzed by thin layer chromatography (Merck, TLC plates Silica Gel 60 F_{254}). After removal of the solvents, three kinds of colorless crystals were isolated in yields of 0.12, 0.77, and 0.14 g in order of elution.

Characterization. Gel permeation chromatograms were developed on a Hitachi Model 634A high-performance liquid chromatograph with a Shodex GPC KF-802 (8-mm i.d. × 600 mm), using chloroform as eluant. ^1H and ^{13}C NMR spectra were obtained with a JEOL JNM-FX-200 Fourier transform high-resolution spectrometer at 200 and 50 MHz, respectively. The mass and infrared spectra were recorded on a JEOL JMS-D100 mass spectrometer and a JASCO A-3 spectrophotometer, respectively. The DSC thermogram was taken with a Perkin-Elmer Model DSC-2 differential scanning calorimeter.

Registry No. (±)-1, 107041-46-3; (±)-1·Na, 107041-47-4; (±)-1·Na (homopolymer), 110774-12-4; (±)-1·K, 110774-10-2; (±)-1·K (homopolymer), 110774-13-5; (±)-1 (*N*-benzoyl), 110774-09-9; (±)-6, 110774-11-3; (±)-7, 110849-59-7; (±)-8, 107041-49-6; (±)-9, 107081-11-8; (±)-10, 107041-48-5; C_6H_5COCl, 98-88-4.

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Glass Transition and Melting Behavior of Poly(thio-1,4-phenylene)

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ABSTRACT: Thermal properties of poly(thio-1,4-phenylene) (PPS) have been determined by differential scanning calorimetry. The solid heat capacity was measured from 220 to 350 K and the liquid heat capacity from 540 to 600 K. A detailed description of the glass transition at 363 K, its increase in heat capacity of 29.9 J/(K mol), broadness, and hysteresis effects, is reported. Three parts of the heat of fusion are identified. Their corresponding crystallinities are w^c(H), contributed by a higher melting peak; w^c(L), contributed by a lower melting peak; and w^c(C), developed on cooling after isothermal crystallization. A rigid amorphous fraction above the glass transition is needed to explain the failure of the two-phase model. Recrystallization, perfection, and reorganization of crystals are identified. The width of the melting range was found to be about 150 K. There is considerable similarity in the glass transition and melting behavior of PPS and PEEK.

Introduction

Poly(thio-1,4-phenylene) (PPS) is one of the thermoplastic polymers considered recently as a high-temperature engineering matrix material in composites. The polymer has good thermal stability and high physical strength and is easily processed.[1-4] In addition, PPS has recently generated interest as being the first melt and solution processable polymer that can be rendered electrically conductive.[5,6] From the scientific point of view, engineering processing is closely related to crystal structure, crystal morphology, crystallization kinetics, and thermal properties.

The crystal structure of PPS has been reported by Tabor et al.[7] Brady[8] has discussed in depth the effects of processing conditions on crystallinity. The growth of single crystals of PPS, as well as polycrystalline aggregates from solution,[9] the determination of morphological characteristics of melt-grown samples, including unique thin-film morphologies,[10] and the examination of structure and morphological changes accompanying doping with conductivity enhancing materials[11] have been studied widely. Crystallization kinetics of PPS, as a resin sample, has been carried out by Lovinger et al.[12] and with carbon fiber, as a matrix material, by Jog et al.[13]

Compared with those previous studies of the structure, morphology, and crystallization kinetics of PPS, the thermal properties of PPS are less well established so far. The calculation of solid heat capacity of PPS has been completed recently.[14] The glass transition temperature, T_g, of PPS varies with the measuring conditions, and lies in the range from 357 to 365 K. The absence of liquid heat capacity data of PPS made it impossible to assess the increase of heat capacity, ΔC_p, at the glass transition temperature. The equilibrium melting temperature of PPS, $T_m°$, is still uncertain. The only report of $T_m°$ for low to intermediate molecular mass PPS was between 576 and 588 K, based on $T_m - T_c$ extrapolation.[12] The heat of fusion was claimed to be 8.65 kJ/mol per repeating unit for 100% crystalline PPS.[8]

In this paper, we focus on the thermal analysis of various semicrystalline PPS samples. Both the solid and liquid heat capacities have been measured which now permits the determination of ΔC_p at T_g. The crystallinity and micromorphology dependence of ΔC_p as well as T_g are discussed. The concept of a "rigid amorphous" polymer is introduced for PPS. It is the cause of lower heat capacity of semicrystalline PPS above T_g, i.e., the rigid amorphous fraction does not contribute to the increase in heat capacity at T_g but unfreezes only at a higher temperature. Similar behavior was found, for example, for poly(aryl ether ether ketone) (PEEK).[15] The overall "rigid fraction, f_r", is computed from C_p by setting

$$f_r = 1 - [\Delta C_p(m)/\Delta C_p(a)] \qquad [\Delta C_p \text{ in J/(K mol)}] \qquad (1)$$

where ΔC_p(m) is the measured heat capacity increase at T_g for semicrystalline PPS and ΔC_p(a) applies to totally amorphous PPS. The crystallinity, in turn, is determined by

$$w^c = \Delta H_f(m)/\Delta H_f \qquad (\Delta H_f \text{ in kJ/mol}) \qquad (2)$$

where ΔH_f(m) is the measured heat of fusion of the semicrystalline sample and ΔH_f the heat of fusion of a 100% crystalline sample. If the two-phase crystallinity model is valid, f_r is equal to w^c. If not, one finds $f_r > w^c$ and a rigid amorphous fraction exists between T_g and T_m. The case of $f_r < w^c$ has not been observed.

Semicrystalline PPS shows irreversible melting. Below the main melting peak premelting peaks are found that

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