

NOTE

Preparation of a New Class of Telechelic Polyamides with Amino Groups from Bicyclic Oxalactam

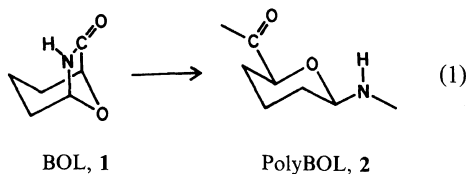
Kazuhiko HASHIMOTO and Hiroshi SUMITOMO

Faculty of Agriculture, Nagoya University,
Chikusa-ku, Nagoya 464, Japan

(Received February 12, 1983)

KEY WORDS Bicyclic Oxalactam / 8-Oxa-6-azabicyclo[3.2.1]octan-7-one / Ring-Opening Polymerization / Telechelic Amino Group / Polyamide / Macromer /

Bicyclic oxalactam, 8-oxa-6-azabicyclo[3.2.1]octan-7-one (abbreviated as BOL, **1**) is so highly polymerizable that at room temperature, its polymerization yields the high-molecular-weight polyamide.¹⁻⁵ Simultaneous film casting on a plate is also readily possible.^{2,3,6,7} The resulting hygroscopic polyamide membrane has excellent permeability forward water and allows for the permselectivity of solutes of various sizes in an aqueous solution.^{3,6-10}



Since the registered trademark of macromer (oligomer having polymerizable functional end-group(s)) was presented by Milkovich (1974),¹¹ several macromers have been prepared using the ring-opening polymerization method.¹²⁻¹⁷ Earlier telechelic prepolymers having various functional groups, by which condensation polymers can be formed, are also regarded as macromers. We wish to describe the synthesis of a new type of polyamide macromers having telechelic amino groups through the anionic polymerization of BOL.

EXPERIMENTAL

Reagents

BOL was prepared by the same procedure re-

ported earlier,^{2,3,6} and stored over phosphorus pentoxide *in vacuo* until use. Potassium pyrrolidone and *N*-acetyl-8-oxa-6-azabicyclo[3.2.1]octan-7-one (abbreviated as K-Pyrdn and *N*-acetyl BOL, respectively) were prepared as described in the literature.^{2,18,19} Dimethyl sulfoxide (Me₂SO) was dried over calcium hydride and distilled under reduced pressure. Toluene-2,4-diisocyanate (TDI) was distilled in high vacuum and stored in a closed vessel until use. Ethylenediamine (EDA) was dried over calcium hydride, distilled and stored in the same way as TDI.

Polymerization of BOL Followed by Amination of the Resulting Polyamide Chain Ends

Under a dry nitrogen atmosphere BOL, K-Pyrdn, and Me₂SO were placed in a flask and a Me₂SO solution of *N*-acetyl BOL was added to the mixture with stirring and kept at 25°C. After the polymerization an excess of EDA was directly added to the polymerization solution and the flask was allowed to stand in a constant-temperature bath. Volatile components were evacuated under reduced pressure and the residue was poured into a large amount of acetone. The resulting colorless polymer was collected on a glass filter, washed again with acetone, and dried *in vacuo*.

Characterization

¹H and ¹³C NMR spectra were recorded, respectively, on a JEOL JNM-MH-100 high-resolution spectrometer operating at 100 MHz at room temperature and a JNM-FX-100 Fourier

Table I. Estimation of the terminal structures of higher-molecular-weight polyBOL from the number of functional groups^a

Activator	mol%/BOL	Polymer yield	Functional group $\times 10^4$, mol g ⁻¹			M_n^d	Polymer structure
		%	Activator residue ^b	Amino group ^c	Carboxyl group ^c		
TDI	0.04	68	0.04 ₇	0.12 ₃	0.23 ₅	56,000	3+4
<i>N</i> -Acetyl BOL	0.02	50	0.03 ₁	0.19 ₇	0.22 ₃	44,000	3+5

^a Polymerization conditions: K-Pyrdn, 1 mol% to BOL; mole ratio of Me₂SO to BOL, 5.6; temperature, 25°C; time, 24 h; terminated with water.

^b Estimated from the initial amount of the activator and the polymer yield assuming that all the activator was consumed in initiating the polymerization.

^c Determined by volumetric titration.

^d Estimated from terminal group content.

Table II. Reaction of *N*-acetyl-BOL with ethylenediamine

Solvent	[<i>N</i> -Acetyl BOL]	[EDA]	Temp	Time	Conversion of EDA	Probability of attack of EDA on lactam carbonyl in <i>N</i> -acetyl BOL
	mol l ⁻¹	mol l ⁻¹	°C	min	%	
Me ₂ SO	0.60	0.26	27	10	45	—
Me ₂ SO	0.60	0.26	27	170	81	0.72
Me ₂ SO	0.60	0.26	27	1440	100	0.74
Me ₂ SO	0.67	0.21 ^a	27	<10	100	0.66

^a Sodium hydride was added to ethylenediamine by 4 mol%.

These results suggest that the growing chain ends were comprised of acyllactams during polymerization, as shown in eq 3.

The resulting polyBOL was so hygroscopic that its molecular weight could not be determined by vapor pressure osmometry, but was evaluated on the number of observed terminal end groups as shown in Table I.

Model Reaction of the Growing Chain End with EDA

The reaction of *N*-acetyl BOL, which can be regarded as a model compound of the growing chain end, with EDA in Me₂SO was followed by ¹H NMR spectroscopy. The spectra showed that the amino group of EDA attacked either carbonyl group in *N*-acetyl BOL.

As for the reaction with the growing ends of the higher-molecular-weight polyBOL (eq 4), however, both attacks should give rise essentially to the same polyamide molecules telechelated with amino

groups. More noteworthy are the facts that this reaction proceeds quantitatively and is accelerated by the addition of a small amount of base on EDA as shown in Table II.

Preparation of Telechelic PolyBOL with Amino Groups

After BOL was anionically polymerized in Me₂SO at 25°C using TDI as an activator, excess EDA was directly added to the solution under various conditions as shown in Table III.

In the ¹³C NMR spectrum of the resulting polyBOL were found the peaks assigned to the activator residue and terminal amino groups as shown in Figure 1. In addition peaks *h*₁ and *i*₂ show that their groups are linked to the internal and terminal repeating units in the polyBOL chain (6) respectively.

Table III. Anionic polymerization of BOL followed by reaction with ethylenediamine^a

TDI mol%	Polymerization time h	Reaction with EDA ^b		Acetone insoluble polymer		Functional group $\times 10^4$, mol g ⁻¹			M_n^c	Aminolysis ^f
		Temp °C	Time day	g	(%)	Activator residue ^c	Amino group ^d	Carboxyl group ^d		
4	1	25	5	1.97	(77)	3.48 (3.64)	8.43	<0.02	2,370	0.21
1.8	3	40	1	1.87	(74)	1.85 (1.93)	12.4	<0.02	1,610	2.3
0.04	24	60	0.25	2.14	(84)	— (0.037)	31.9	<0.02	630	109
0.04	24	—	—	1.73 ^e	(68)	— (0.047)	0.12 ₃	0.23 ₅	56,000	—

^a BOL, 2.54 g; K-Pyrdn, 1 mol% to BOL; Me₂SO, 16.9 g; polymerization temperature, 25°C.

^b Mole ratio of EDA to BOL, 3—4.

^c Determined by UV spectroscopy. The molecular extinction coefficient of 2,4-bis(*N'*-propylureido)toluene was used for that of the activator residue. The figure in parenthesis was estimated from the amount of activator used.

^d Determined by volumetric titration.

^e Estimated from the content of terminal groups.

^f Frequency of aminolysis during the reaction with EDA.

^g Water insoluble polymer.

Consequently amino groups may be introduced directly and quantitatively onto the ends of the polyBOL molecules by reacting with EDA following polymerization.

Acknowledgement. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

REFERENCES

1. H. Sumitomo, K. Hashimoto, and M. Ando, *J. Polym. Sci., Polym. Lett. Ed.*, **11**, 635 (1973).
2. H. Sumitomo and K. Hashimoto, *Macromolecules*, **10**, 1327 (1977).
3. K. Hashimoto and H. Sumitomo, *Macromolecules*, **13**, 786 (1980).
4. K. Hashimoto and H. Sumitomo, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 397 (1983).
5. H. Sumitomo, K. Hashimoto, and Y. Betsuda, *Kobunshi Ronbunshu*, **39**, 807 (1982).
6. H. Sumitomo and K. Hashimoto, *Kobunshi Ronbunshu*, **34**, 747 (1977).
7. H. Sumitomo, K. Hashimoto, and T. Ohyama, *Polym. Bull.*, **1**, 133 (1978).
8. T. Matsukura, T. Kinoshita, A. Takizawa, Y. Tsujita, H. Sumitomo, and K. Hashimoto, *Kobunshi Ronbunshu*, **35**, 803 (1978).
9. H. Sumitomo, K. Hashimoto, and T. Ohyama, *Polym. Bull.*, **1**, 635 (1979).
10. H. Sumitomo and K. Hashimoto, "Contemporary Topics in Polymer Science," Vol. 4, W. J. Bailey and T. Tsuruta Ed., Plenum, New York, in press.
11. R. Milkovich, "Anionic Polymerization. Kinetics, Mechanism, and Synthesis," J. E. McGrath Ed., *ACS Symp. Ser.*, **166**, 41 (1981) and references therein.
12. E. J. Goethals and M. A. Vlegels, *Polym. Bull.*, **4**, 521 (1981).
13. J. Sierra-Vargas, P. Masson, G. Beinert, P. Rempp, and E. Franta, *Polym. Bull.*, **7**, 277 (1982).
14. M. Takaki, R. Asami, and T. Kuwabara, *Polym. Bull.*, **7**, 521 (1982).
15. M. Maeda and S. Inoue, *Makromol. Chem., Rapid Commun.*, **2**, 537 (1981).
16. T. Yasuda, T. Aida, and S. Inoue, *Polym. Prepr. Jpn.*, **31**, 1221 (1982).
17. Y. Kawakami, Y. Miki, T. Tsuda, R. A. Murthy, and Y. Yamashita, *Polym. J.*, **14**, 913 (1982).
18. H. Sekiguchi, *Bull. Soc. Chim. Fr.*, 1827 (1960).
19. H. K. Hall, Jr., M. K. Brandt, and R. M. Mason, *J. Am. Chem. Soc.*, **80**, 6420 (1958).
20. M. Sela and A. Berger, *J. Am. Chem. Soc.*, **77**, 1893 (1955).