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Preparation of a New Polyamide Macromer Having a Vinylbenzyl Group from Bicyclic Oxalactam and Its Radical Copolymerization with Styrene

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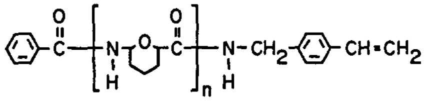
SUMMARY

A new polyamide macromer having a vinylbenzyl end group (*1*), of which molecular weight was 3700-3800, was prepared by the anionic polymerization of bicyclic oxalactam (*2*) followed by the reaction with *p*-vinylbenzylamine. Its radical copolymerization with styrene was conducted to obtain a novel graft copolymer consisting of a polystyrene stock-chain and hydrophilic polyamide branches.



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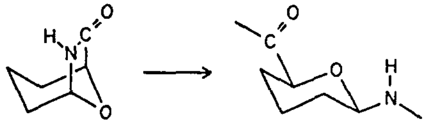
INTRODUCTION

In preceding papers we reported that the anionic polymerization of a bicyclic oxalactam, 8-oxa-6-azabicyclo[3.2.1]octan-7-one (abbreviated as BOL, *2*) proceeded in dimethyl sulfoxide (Me_2SO) at room temperature to give a high molecular weight polyamide (*3*) [1-5]. The hygroscopic membrane obtained from the resulting polyBOL is characteristic of the excellent permeability of water and permselectivity for solutes of various sizes in an aqueous solution [3,6-10]. The characteristics of the polymerization of BOL and the polyamide are expected to be utilized to open a new field in the macromolecular design.



2 *3*

(1)

Macromers (oligomers having polymerizable functional end groups), of which the trademark was proposed by Milkovich [11], are widely applicable to design composite materials comprising different polymer segments, because the length and distribution of the segment can be controlled beforehand [12]. Several macromers have been prepared using the ring-opening polymerization method [13-18]. We wish to describe the synthesis of a new polyamide macromer with a vinylbenzyl end group (*1*) through the anionic polymerization of BOL. The radical copolymerization of *1* with styrene is also mentioned.

EXPERIMENTAL

Reagents

BOL was prepared by the same procedure reported earlier [2,3,6], and stored over phosphorus pentoxide *in vacuo* until use. *N*-Benzoyl-8-oxa-6-azabicyclo[3.2.1]octan-7-one (*N*-BzBOL) was synthesized by the reaction of BOL (6.4 g) with benzoyl chloride (7.7 g) in pyridine (16 g) at 90°C for 2.5 hr and recrystallized from *n*-hexane: Yield, 9.8 g (84%); mp, 88-88.5°C. Elemental analysis. Calcd. for $C_{13}H_{13}NO_3$: C, 67.52; H, 5.67; N, 6.06%. Found: C, 67.22; H, 5.66; N, 5.93%. *N*-Acetyl-8-oxa-6-azabicyclo[3.2.1]octan-7-one (*N*-AcBOL) and potassium pyrrolidonate (K-Pyrdn) were prepared as described in the literature [2,19,20]. Me_2SO was dried over calcium hydride and distilled under reduced pressure. *p*-Vinylbenzylamine (VBA) was obtained through the Gabriel synthesis from *p*-vinylbenzyl chloride, which was prepared as reported in the literature [21]: Bp, 73 °C/3 mmHg (lit. 72-73°C/3 mmHg [22]). *N*-(*p*-Vinylbenzyl)acetamide was prepared by the reaction of VBA (0.47 g) and acetic anhydride (0.47 g) in ethyl acetate (10 ml) at room temperature for 1 hr and recrystallized from diethyl ether: Yield, 0.46 g (74%); mp, 103.5-104°C. Elemental analysis. Calcd. for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99%. Found: C, 75.70; H, 7.50; N, 7.91%. Styrene was distilled under reduced pressure after washing with an aqueous solution of potassium hydroxide and water followed by drying over anhydrous potassium carbonate. Azobisisobutyronitrile (AIBN) was recrystallized from ethanol.

Preparation of Polyamide Macromer (*1*)

BOL, K-Pyrdn, and Me_2SO were placed under a dry nitrogen atmosphere in a flask and a Me_2SO solution of *N*-BzBOL was added to the mixture with stirring. After the polymerization at 25°C for 0.5 hr, an excess of VBA was directly added to the polymerization solution and the flask was allowed to stand in a constant-temperature bath. For the termination an excess of acetic acid was used, and volatile components were evacuated under reduced pressure after adding a trace amount of hydroquinone. 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*.

Radical Copolymerization of Macromer *1* with Styrene

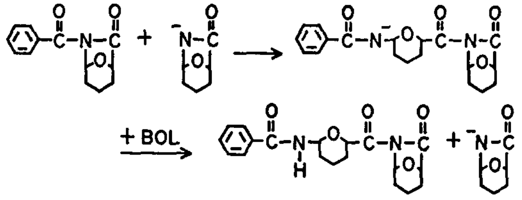
Polyamide macromer *1*, styrene, AIBN, and Me_2SO were mixed in an ampoule with stirring. After degassed four times in a cooling bath the ampoule was sealed and kept at 60°C for 1.5 day. The polymerization mixture was condensed under reduced pressure at about 30°C after addition of a trace amount of hydroquinone. The viscous residue was diluted with 10 ml of chloroform, and methanol (40 ml) was added drop by drop to the solution during 2 hr. The resulting copolymer was precipitated from the solution and collected on a glass filter. The unreacted macromer was recovered from the filtrate by the concentration and reprecipitation in a large amount of acetone.

Characterization

^1H- and ^{13}C-NMR spectra were taken with a JEOL JNM-FX-200 Foulier transform high resolution spectrometer operating at 200 MHz and 50 MHz, respectively. UV spectrum was recorded on a JASCO UVIDEC-1 spectrophotometer. Gel permeation chromatogram was measured with Hitachi Model 634A high performance liquid chromatograph (column, Shodex GPCA 80M, 8ϕ × 1000 mm; solvent, chloroform).

RESULTS AND DISCUSSION

In the anionic polymerization of BOL the initiation and propagation reactions activated with *N*-BzBOL can be shown in eqs. 2 and 3, the other side reaction may being relatively suppressed.



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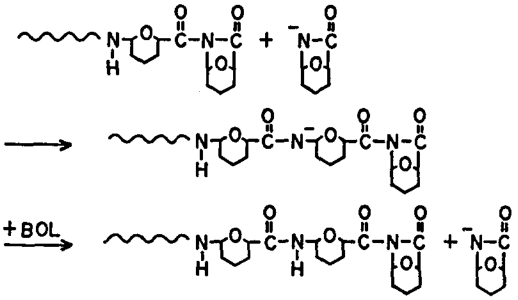
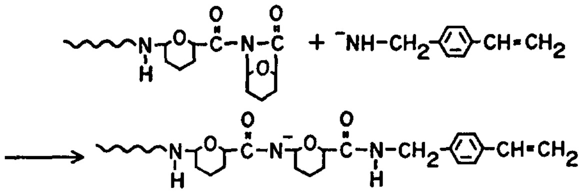


(3)

In order to obtain the polyamide macromer, VBA should be certainly reacted with the acyllactam type of growing species generated on the anionic polymerization of BOL (see eq. 4).



(4)

Usually the anionic polymerization of lactams is prevented by a trace amount of moisture, which should decrease the concentration of the monomer anion, whereas probably not destroy the acyllactam-type growing species. Therefore the reaction of the growing species with VBA will not be affected by the existence of a trace amount of water, as well as the reaction of the polymer chain ends with ethylenediamine [23].

Model Reaction of the Growing Species with *p*-Vinylbenzylamine

First the reaction of *N*-AcBOL, which can be regarded as a model compound of the growing chain end, with VBA in Me_2SO was followed by ^1H-NMR spectroscopy. All peaks in the spectrum were assigned in Figure 1, taking account of the variation of their intensity ratios with the reaction time. Although the amino group of VBA attacked either carbonyl group in *N*-AcBOL,

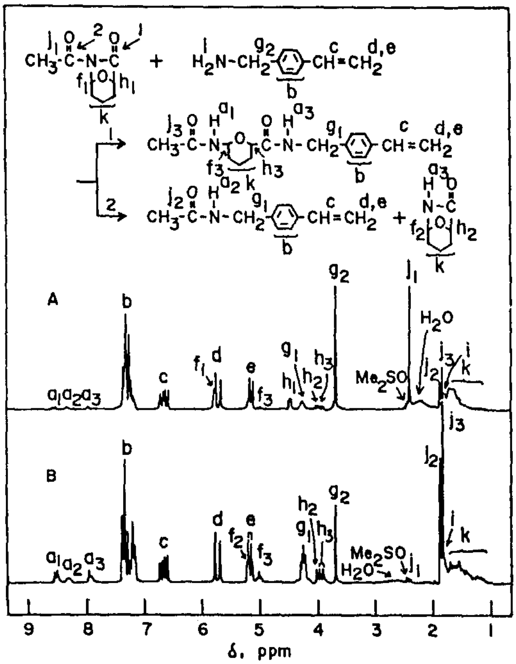


Fig. 1. ^1H-NMR spectra of reaction mixtures of *N*-AcBOL with *p*-vinylbenzylamine in Me_2SO-d_6 at 27°C. Mole ratio of *N*-AcBOL to VBA, 0.78; reaction time: A, 0.3 hr; B, 28 hr.

Table 1
Reaction of *N*-Acetyl BOL with *p*-Vinylbenzylamine[a]

[*N*-AcBOL], mol/l	[VBA], mol/l	Time, hr	Conversion of *N*-AcBOL, %	Probability of attack of VBA to lactam carbonyl in *N*-AcBOL
0.83	1.06	0.3	40	0.59
0.83	1.06	2	77	0.60
0.83	1.06	28	>98	0.66
0.94	1.40[b]	0.3	93	-
0.94	1.40[b]	2	100	-

[a] Solvent, Me_2SO-d_6; temperature, 27°C.
[b] K-Pyrdn of 14 mol% was added to VBA.

the reaction proceeded quantitatively at room temperature, and was accelerated by the addition of a base to VBA as indicated in Table 1. From these results we expected that the reaction of the acyllactam-type growing species with VBA as shown in eq. 4 was useful for the introduction of a vinylbenzyl group at the end of the polyamide chain.

Synthesis of Polyamide Macromer *1*

After BOL was anionically polymerized in Me_2SO using *N*-BzBOL as an activator at 25°C for 0.5 hr, an excess of VBA was directly added to the solution under the condition shown in Table 2. The residual base in the solution must accelerate this coupling reaction.

Table 2
Anionic Polymerization of BOL
Followed by Reaction with *p*-Vinylbenzylamine

Reaction time of VBA,[b] hr	Acetone insoluble polymer,[c] g	Terminal group × 10^4, mol/g			M_n[f]	$\frac{M_w}{M_n}$[g]
		Benzamide[d]	Vinylbenzyl[d]	Vinylbenzyl[e]		
6	1.88	2.6	2.5	2.4	3800	1.2_5
24	1.86	2.7	2.9	2.9	3700	1.3_0

[a] BOL, 2.54 g; K-Pyrdn, 1 mol%/BOL; *N*-BzBOL, 5 mol%/BOL; Me_2SO, 7.8 g; polymerization temperature, 25°C; polymerization time, 0.5 hr.
[b] Mole ratio of VBA to *N*-BzBOL, 2; temperature, 25°C.
[c] Terminated by ^1H-NMR spectroscopy.
[d] Determined by UV spectroscopy using *N*-(*p*-vinylbenzyl)acetamide as a model compound.
[f] Estimated from the amount of benzamide in the polyamide.
[g] Determined by gel permeation chromatography.

In the ^1H-NMR spectrum of the resulting polymer as shown in Figure 2 were detected not only the proton peaks due to the polyBOL segment but also the characteristic peaks assignable to the protons of benzamide, which was the activator residue, and the vinylbenzyl groups. Their concentrations were determined from the peak ratios in the expanded spectrum, which were in fair agreement with each other as summarized in Table 2. The content of the vinylbenzyl group was measured also by UV spectroscopy using *N*-(*p*-vinylbenzyl)acetamide as a model compound (ε_{max}, 1220 at 284 nm in chloroform), which agreed closely with that determined by ^1H-NMR spectroscopy. In the ^{13}C-NMR spectrum of the polyamide, both characteristic peaks assigned to the activator residue and the vinylbenzyl group were detected, but no peak was observed at the range from 173 to 185 ppm where the carbonyl carbon peak due to the aliphatic carboxylic acid appears usually.

From these analyses the acyllactam-type growing ends were estimated to have still remained in the polymerization system

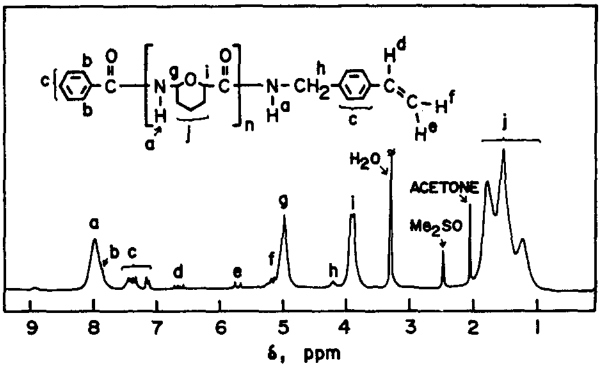


Fig. 2. ^{1}H-NMR spectrum of polyamide macromer obtained by anionic polymerization of BOL followed by reaction with VBA (M_n, 3800; 9.5% Me$_2$SO-d_6 solution; 27°C; TMS; 200 MHz).

after the polymerization reaction at 25°C for 0.5 hr, and to react almost completely with VBA at 25°C for more than 6 hr.

In fact a new type of polyamide macromer having a vinylbenzyl group, of which molecular weight was 3700-3800, was confirmed to be prepared by the reaction of VBA with the growing species coming from the anionic polymerization of BOL.

Radical Copolymerization of Macromer *1* with Styrene

The radical copolymerization of the polyamide macromer *1* with styrene in Me$_2$SO proceeded almost homogeneously under the condition shown in Table 3, although homopolystyrene is insoluble in Me$_2$SO. The resulting copolymer consisting of both segments of polystyrene and polyamide, of which weight fractions were 0.74 and 0.26, respectively, was easily isolated from the polymerization mixture by the fractional precipitation as shown in Figure 3. The unreacted macromer was also recovered from the filtrate. The number average molecular weight of the

Table 3
Radical Copolymerization of Polyamide Macromer (M_1) with Styrene (M_2)[a]

M_1,[b] g	M_2, g	Mole fractn. of M_1	Polymer yield,[c] g	Mole fractn. of M_1 in copolymer[d]	Mole fractn. of BOL unit in polymer[d]	$M_n \times 10^{-4}$[e]
1.09	1.07	0.027	0.55[f]	0.010	0.22	7.8

[a] AIBN, 2.7 mg; Me$_2$SO, 6.0 g; temperature, 60°C; time, 1.5 day.
[b] M_n, 3800.
[c] Insoluble in methanol-chloroform (4:1 v/v) mixture.
[d] Determined by ^{1}H-NMR spectroscopy.
[e] Determined by gel permeation chromatography.
[f] Conversion of M_1, 13%; conversion of M_2, 38%.

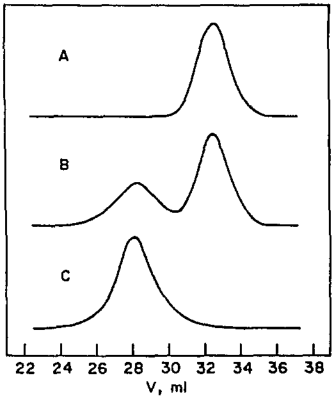


Fig. 3. GPC curves of polymers. A, polyamide macromer (M_n, 3800); B, reaction mixture obtained by radical copolymerization of macromer with styrene; C, copolymer isolated by fractional precipitation from the reaction mixture.

copolymer was estimated to be about 78,000 by gel permeation chromatography using a standard polystyrene. It is suggested from the results of the radical copolymerization that the polyamide macromer presented in this note may be employed effectively for the design of a new type of well-defined graft copolymers.

ACKNOWLEDGEMENT

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