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Synthesis and Polymerization of a New Class of Oligosaccharide- and Polyamide-Macromers Having a Styrene End-Group

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ABSTRACT

As an approach to synthesis of oligo- and polysaccharide-containing polymers, two types of polystyrenes having pendant carbohydrate groups were prepared. Their functions, especially amphiphilic behaviors in water, were revealed.

A new polyamide macromer having a vinylbenzyl group (M_n, 3000-3800) was prepared by the anionic polymerization of bicyclic oxalactam followed by the reaction with *p*-vinylbenzylamine. Another polyamide macromer telechelated with amino groups (M_n, 1400 and 4100) was also prepared by the similar method.

INTRODUCTION

Macromolecules forming hydrophilic and hydrophobic microdomains are of interest in connection with biomedical and membranous materials. This paper describes the synthesis of homo- and copolymers consisting of a hydrophobic polystyrene backbone and hydrophilic pendant saccharide or polyamide.

CARBOHYDRATE-CONTAINING POLYSTYRENES

Polymers that contain carbohydrate residues as side-group units are attracting an increasing amount of attention. We already

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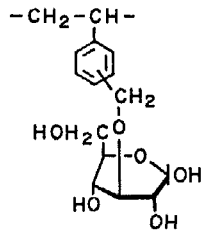

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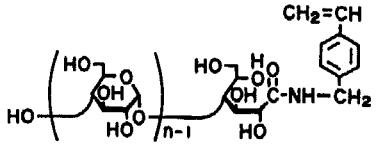

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reported synthesis and functions of homo- and copolymers having structural unit *1* [1-5]. Recently we have designed preparation and polymerization of styrene derivatives substituted with mono-, oligo-, and polysaccharides *2* [6]. This section first outlines functions of polymer *1*, then treats with polymerization of *N-p*-vinylbenzyl-D-gluconamide corresponding to n = 1 of *2*, and finally affords a prospect of polymers having pendant oligo- and polysaccharides.

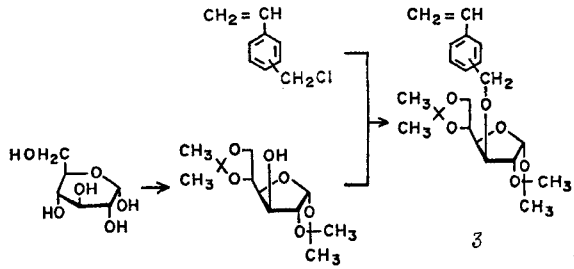
Carbohydrates comprise the most abundant group of natural compounds and are looked upon as prime biological substances. They serve as sources and stores of energy and as structural and supportive elements. Carbohydrates also play basic roles in information, recognition, and regulation of living organisms. Polymer-bound sugars are of interest as tools for the examination of bioorganic mechanisms, and for pharmacological applications [7,8]. In addition to biological functions, hydrophilicity and chirality of carbohydrates are available. Some sugar-polymers are valuable as reverse osmosis membranes [9], as selectively permeable membranes [4,5], and as potential chiral templates for the asymmetric synthesis and optical resolution of organic molecules [10,11]. They are also composites of petrochemicals and biomass chemicals, and may lead to the effective utilization of natural resources.

Amphiphilic Polymers *1*

The structural unit *1* has several chemical features. The oxygen atom in position 3 of a glucopyranose is covalently attached to a

vinylbenzyl residue by a *meta*- or *para*-benzyl ether linkage. The structural unit contains both a hydrophilic sugar and a hydrophobic vinylbenzyl moiety, and hence it is amphiphilic. The sugar moiety has a reducing end which is subject to various chemical modifications and biological interactions. A benzyl ether linkage is chemically stable even in acid and alkaline media.

This polymer structure was introduced by radical polymerization of 1,2:5,6-di-*O*-isopropylidene-3-*O*-vinylbenzyl-α-D-glucofuranose (*3*) followed by removal of the isopropylidene protecting groups. The monomer *3* was a product from commercial chloromethyl styrene and glucose as shown in Eq. 1. Homopolymers, styrene-copolymers (*4*), and acrylonitrile-copolymers (*5*) were prepared.



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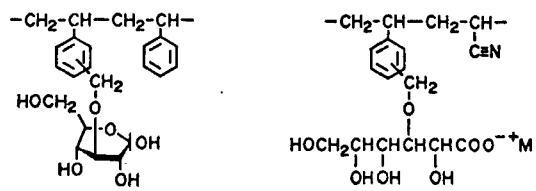


4 *5*

Homopolymers and styrene-copolymers exhibited amphiphilic characters depending upon the copolymer composition [1-3]. The polymers rich in sugar component were soluble in water, dimethyl sulfoxide (Me_2SO), and dimethylformamide (DMF). Behaviors of these polymers in water were peculiar. First, the intrinsic viscosities determined in Me_2SO were high, but those in water were remarkably low. Secondly, significant broadening of ^1H- and ^{13}C-NMR signals

was observed for the polymers measured in deuterium oxide. Thirdly, organic solutes such as methyl orange and magnesium 1-anilino-8-naphthalenesulfonate (ANS) were strongly bound to these polymers in water. These observation suggests that the polymers exist in a micelle-like conformation in water.

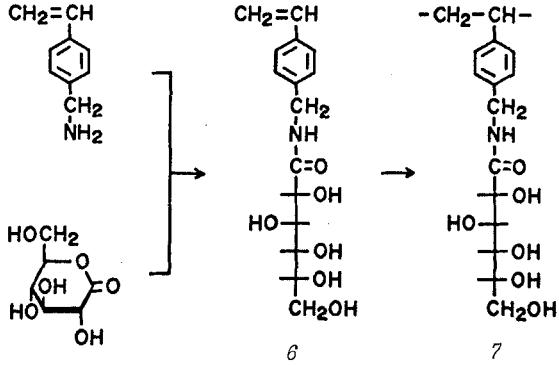
On the other hand, the copolymers rich in styrene unit were soluble in chloroform and dichloromethane. It was suggested from viscosity and NMR measurement that the copolymers in the chlorinated hydrocarbon solvents adopted a conformation similar to a reversed micelle.

We expected that the styrene-copolymers (*4*) may serve as a model of lignin-carbohydrate conjugate [3,12]. Lignins are complicated natural products of high molecular weight that are made of phenylpropane building units. They occur in woods and function as the structural support materials together with cellulose and hemicelluloses. Recently, it has been demonstrated that there exist chemical bonds between lignins and hemicelluloses [13]. We noted that the hybrid, termed as lignin carbohydrate conjugate (LCC), bears some similarities to the copolymer *4*. Thus, both are made of aromatics and sugar moieties, and exhibit amphiphilic characters. Some fractions are water-soluble and some are soluble in chloroform. The water-soluble fraction formed a micelle-like conformation in water [14]. Therefore, the copolymer *4* may make an approach to utilization of LCC, an enormous resource for biomass conversion in the future.

Functions of carbohydrates in polymer membranes were investigated with use of acrylonitrile copolymers [4,5]. A gluconate-containing polymer membrane *5* was prepared by the following three steps: (1) radical copolymerization between *3* and acrylonitrile, (2) casting membranes from a DMF solution, and (3) deprotection of isopropylidene group and subsequent oxidation of the glucopyranose reducing end. Selective permeation of Cu^{++} and Cd^{++} ions and active transport of Na^{+} ion against the concentration gradient were demonstrated.

Poly(*N*-*p*-vinylbenzyl-D-gluconamide) (*7*)

As a step of the approach to oligo- and polysaccharide-containing polymers, *N*-*p*-vinylbenzyl-D-gluconamide (*6*) corresponding to n = 1 of the structure *2* was prepared and polymerized (Eq. 2) [6].



(2)

6 *7*

p-Vinylbenzylamine was obtained from *p*-vinylbenzyl chloride according to the Gabriel synthesis. The coupling reaction of *p*-vinylbenzylamine with commercially available D-glucono-1,5-lactone was fast and the crystalline product *6* precipitated during the reaction. Yield, 92.4%; mp, 184°C; $[\alpha]_D^{25}$, +31.2° (c 1 in Me_2SO). Polymerization of *6* (8.0 mmol) was carried out with azobisisobutyronitrile (0.02 mmol) as the initiator in 5 ml of Me_2SO at 60°C for 4.5 h. A white powdery polymer was obtained in 44% yield. The specific rotation $[\alpha]_D^{25}$ in Me_2SO was +37.3°. It was soluble in water, glycerol, Me_2SO, DMF, and pyridine.

The carbohydrate of polymer *7* is an open chain and connected to the *para*-substituted vinylbenzyl group by an amide linkage. Amphiphilic characters and micelle-like conformation in water was demonstrated as follows. The intrinsic viscosity determined in Me_2SO was high ([η] = 1.60 at 25°C), suggesting the polymer to be of high molecular weight. However, the intrinsic viscosity in water ([η] = 0.47 at 25°C) was about one third that in Me_2SO. It reflected a tightly-coiled conformation of *7* in water. ^1H- and ^{13}C-NMR spectra

were measured in Me_2SO-d_6 and deuterium oxide. In the latter solvent, the signals were observed to broaden, particularly the phenyl signals. Intense stacking of phenyl groups and small mobility of the main chains in water were suggested. Flexible membranes could be cast from a Me_2SO solution, but those cast from an aqueous solution were brittle.

Polymer *7* interacted ANS and methyl orange in water strongly. Fig. 1 depicts fluorescence emission spectra of ANS, a hydrophobic fluorescence probe, in the absence and presence of *7*. Fluorescence of ANS alone ($\lambda^F_{F,max}$, 525 nm) was negligible, but polymer *7* strikingly enhanced the fluorescence and blue-shifted the emission maximum to $\lambda^F_{B,max}$ = 477 nm. The blue-shift by about 50 nm indicates that the bound ANS remains in a hydrophobic microenvironment. Binding constants estimated from Benesi-Hildebrand and Klotz relationships are 120 and 110 M^{-1}, respectively. The corresponding binding

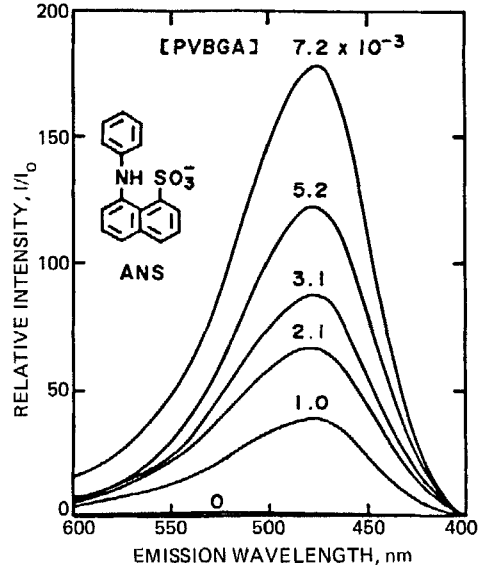


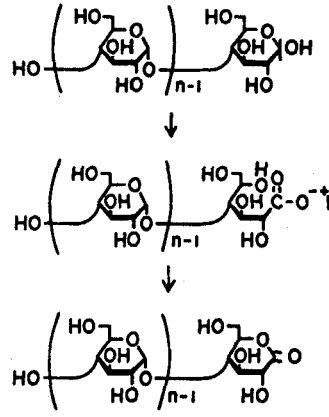
FIG. 1. Fluorescence emission spectra of ANS in the presence of polymer *7*. [ANS] = 5 × 10^{-5} M; [*7*] = 0 - 7.2 × 10^{-3} M; solvent, phosphate buffer (pH 6.88); excitation wavelength, 380 nm.

constants of methyl orange determined by difference absorption spectra were both 220 M^{-1}.

The strong affinity of *7* for organic solutes has thus been demonstrated. However, polymer *7* as well as polymer *1* carry no specific binding sites such as charged groups, long alkyl chains, inclusion cavities, and cross linking. In addition, monomer *6* exhibited no binding properties. Therefore we assumed the binding ability of *7* and *1* to be attributable to the polymer conformation induced by the amphiphilic structures. The vinylbenzyl residues aggregated to form hydrophobic regions surrounded by hydrated sugar residues. Organic solutes were held strongly in the hydrophobic regions in a micelle-like conformation.

Application to Synthesis of Polymers Having Pendant Oligo- and Polysaccharides

Polymers containing oligo- and polysaccharides as side-group units are also of interest, but no simple synthetic method has been reported so far. The monomer synthetic reaction of Eq. 2 proved a convenient, high yield procedure for preparing the vinyl compound containing carbohydrate moiety. Only mixing of the two reactants gave the product in a quantitative yield. An advantage is that the reactant lactone needs no protection of hydroxyl groups. Mono-, oligo-, and polysaccharides having a reducing terminal can be converted to lactones by oxidation as shown in a representative

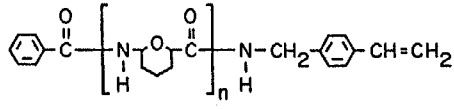


(3)

reaction scheme (Eq. 3) [15,16]. Therefore, the present method has a bright prospect of developing a new field of polymers having pendant oligo- and polysaccharides.

POLYAMIDE MACROMERS PREPARED FROM BICYCLIC OXALACTAM

Now we wish to describe the preparation of new classes of polyamide macromers having a *p*-vinylbenzyl group *8* and telechelic amino groups *9* through the anionic polymerization of bicyclic oxalactam, 8-oxa-6-azabicyclo[3.2.1]octan-7-one (abbreviated as BOL, *10*) [17,18].



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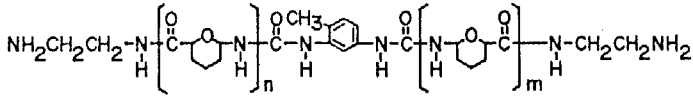

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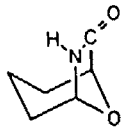
Anionic solution polymerization of BOL *10* proceeds in dimethyl sulfoxide (Me_2SO) at room temperature to give the high molecular weight polyamide *11* [19,20].



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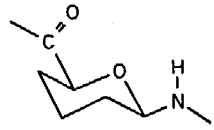

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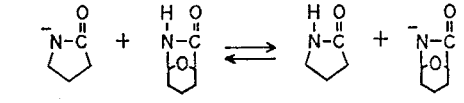
The water sorption capacity of polyBOL was much higher than those of nylon 6 and nylon 4 at any relative humidity, and roughly speaking, comparable to natural fibers, wool and silk. The hygroscopic poly-BOL membranes, which were obtained easily by both casting from the resulting polymer solution and "casting polymerization (the room-temperature polymerization and simultaneous casting on a plate)", exhibited a high water permeability as well as the permselectivity of solutes of various sizes in aqueous solution [20-22]. These

conspicuous behaviors may result from some delicate arrangement of polar hydrophilic and nonpolar hydrophobic microdomains probably found along and between the polymer chains [19,20,23]. Such a novel polyamide may be used as a valuable component in the composite materials.

Macromers can be widely applied to composite materials comprising different polymer segments, of which the length and the distribution were easily controlled beforehand. Since the registered trademark was proposed by Milkovich [24], several macromers have been prepared using the ring-opening polymerization method [25-31]. Earlier various telechelic prepolymers with functional groups, from which condensation polymers can be derived, are also regarded as macromers.

Principle for Preparation of Polyamide Macromer

The anionic polymerization of BOL *10* using potassium pyrrolidonate and *N*-benzoyl BOL as a catalyst and an activator, respectively, proceeds at the growing end of *N*-acyllactam as shown in Eqs. 4-6.



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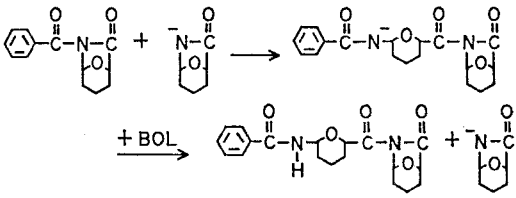

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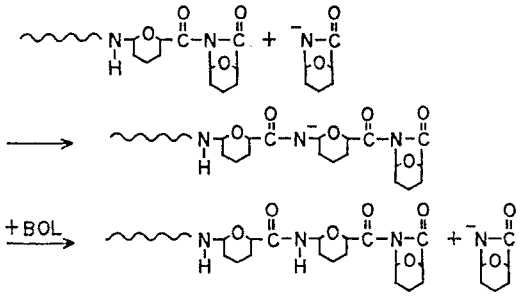
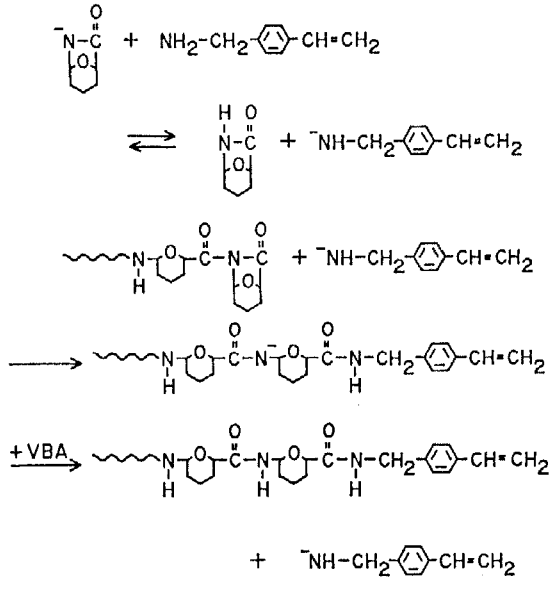


(6)

Such a growing species should react with *p*-vinylbenzylamine (VBA) after the polymerization (Eqs. 7 and 8), leading to produce the new polyamide macromer having a vinylbenzyl group.



(7)

(8)

First the reaction of *N*-acetyl BOL, which can be regarded as a model compound of the growing chain end, with *p*-vinylbenzylamine in Me_2SO was followed by ^1H-NMR spectroscopy. This reaction was found to proceed quantitatively at room temperature and be accelerated by the addition of a small amount of a base to *p*-vinylbenzylamine.

Preparation of Polyamide Macromer *8*

Under a dry nitrogen atmosphere a Me_2SO solution of *N*-benzoyl BOL was poured into a mixture of BOL, K-Pyrdn, and Me_2SO in a flask with stirring, which was kept at 25°C for 0.5 h. Then an excess of *p*-vinylbenzylamine was directly added to the polymerization solution. The residual base in the solution must accelerate this coupling reaction. The reaction conditions in the preparation of the polyamide macromer and the results are summarized in Table 1.

Table 1
Anionic Polymerization of BOL Followed by Reaction with *p*-Vinylbenzylamine[a]

VBA,[b] mole ratio to *N*-benzoyl BOL	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]		
2	0.90	3.1	3.1	2.7	3300	1.24
10	0.86	3.3	3.5	3.3	3000	1.16

[a] BOL, 1.27 g; K-Pyrdn, 1 mol%/BOL; *N*-benzoyl BOL, 5 mol%/BOL; Me_2SO, 3.9g; polymerization temperature, 25°C; polymerizaton time, 0.5 h.
[b] Reaction temperature, 25°C; reaction time, 1 day.
[c] Terminated with acetic anhydride.
[d] Determined by ^{1}H-NMR spectroscopy.
[e] 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.

The resulting acetone insoluble polymer was isolated as a white powder after the termination with acetic anhydride. Acetic acid can be also used as the terminator [17].

In the ^{13}C-NMR (see Figure 2) and ^{1}H-NMR spectra of the resulting polyamide were detected not only the peaks due to the polyBOL segment but also both characteristic peaks assignable to the benzamide, which was the activator residue, and the vinylbenzyl groups. But no peak was observed at the range from 173 to 185 ppm in the former spectrum, where the carbonyl carbon peak of the aliphatic carboxylic acid appears usually. The contents of the activator residue and the vinylbenzyl group in the polyBOL were determined from the peak ratios in the expanded ^{1}H-NMR spectrum, which were in fair agreement with each other. The latter concentration was measured also by UV spectroscopy.

From these results a new type of polyamide macromer having a vinylbenzyl group was confirmed to be prepared by the reaction of *p*-vinylbenzylamine with the growing species coming from the anionically polymerized BOL.

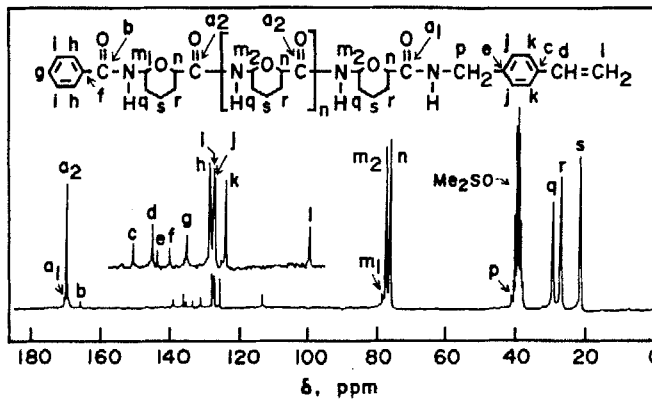


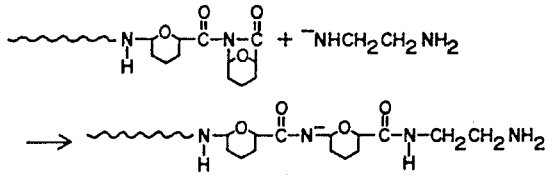
FIG. 2. ^{13}C-NMR spectrum of polyamide macromer obtained by anionic polymerization of BOL followed by reaction with *p*-vinylbenzylamine (M_n, 3800; 9.5% Me_2SO-d_6 solution; 45°C; 50 MHz; TMS).

The radical copolymerization of the polyamide macromer (M_n, 3800; 1.09 g) with styrene (1.07 g) (mole fraction of macromer in feed, 0.027) using azobisisobutyronitrile (2.7 mg) as a catalyst proceeded almost homogeneously in Me_2SO (6.0 g) at 60°C for 1.5 day, although the homopolystyrene is insoluble in Me_2SO. The resulting graft copolymer consisting of the polystyrene and polyamide segments (0.55 g), of which weight fractions (and mole fractions) were 0.74 (0.99) and 0.26 (0.010), respectively, was easily isolated from the reaction mixture by the fractional precipitation, while the unreacted macromer was also recovered. The conversions of the macromer *8* and styrene were calculated from the above data to be 13% and 38%, respectively. The number average molecular weight of the copolymer was estimated to be about 78,000 by gel permeation chromatography using a standard polystyrene.

Preparation of Polyamide Macromer *9*

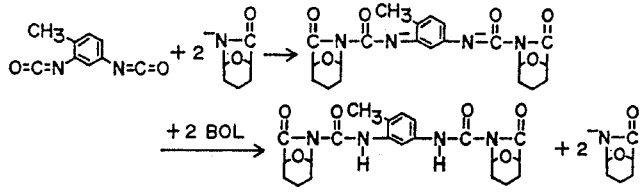
Another polyamide macromer telechelated with amino groups *9* was also prepared by the similar reaction of the acyllactam-type

growing species with ethylenediamine (EDA), after the anionic polymerization of BOL (see Eq. 9) [18]. In order to introduce the amino



(9)

groups at both polymer ends, tolylene-2,4-diisocyanate was used as an activator in the polymerization (see Eq. 10) and large excess of ethylenediamine by 100 times to the amount of the used activator was added to the polymerization mixture.



(10)

After keeping at 25°C volatile compounds were evacuated under reduced pressure and the residue was poured into a large amount of acetone. No carboxyl group was found by the volumetric titration to enter in the resulting polyamide. The amount of amino groups in the polyamide was estimated to be about twice that of the activator residue determined by UV spectroscopy using 2,4-bis(*N'*-propylureido)-toluene as a model compound. Consequently the polyamide macromer telechelated with amino groups (M_n, 1400 and 4100) was prepared in this method.

In any event, the anionic polymerization of lactam is usually prevented by a trace amount of moisture, which should decrease the concentration of the monomer anion, while does probably not destroy the acyllactam-type growing species. Therefore, the reactions of the growing species with amines should not be affected by the existence of a trace amount of water. In addition any side reactions can be easily suppressed in the anionic polymerization of

BOL under a relatively mild condition. As a result the acyllactam-type growing species can be remained in the polymerization system even after the polymerization and react almost completely with such amines as *p*-vinylbenzylamine and ethylenediamine.

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