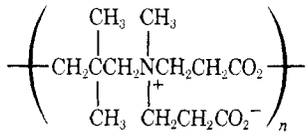
yield (>99%), which was identified as the 1:1 alternating copolymer of TMA and AA (**1**). This finding affords an additional support to the above scheme, *i.e.*, the reaction between **13** and TMA generated **10** which was the active species of the copolymerization.

The alternating copolymer **1** has the tertiary amine group in the main chain, which may possibly form a betaine **14** through a hydrogern transfer of AA as in the case of pyridine.[3] This type of betaine formation can give rise to the



14

chain branching like **14**. However, quaternary ammonium species have not been detected in the alternating copolymer prepared under the present reaction conditions of the 1:1 monomer feed. The copolymer **1** is of linear structure. This is due to the fact that TMA is by far the stronger nucleophile than the tertiary amine group in the copolymer chain;[5] *i.e.*, the interaction between TMA and AA is a rapid process. In accordance with these observations, a preliminary nmr survey of the copolymerization system revealed that the formation of the quaternary ammonium species such as **10** and **13** occurred fast, which was followed by the alternating copolymerization.

The present copolymerization provides a good method to prepare the amine-ester type copolymer. Mechanistic studies as well as the alternating copolymerization of TMA with βPL are currently undertaken in our laboratory.

References and Notes

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Takeo Saegusa,* Yoshiharu Kimura, Satoru Sawada, and Shiro Kobayashi

Department of Synthetic Chemistry
Faculty of Engineering
Kyoto University
Kyoto, Japan

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A New Route to Optically Active Linear Poly(propylenimine)

Preparation of optically active poly(propylenimine) has been achieved first by Price, *et al.*,[1] by the ring-opening polymerization of optically active propylenimine with acid catalysts. Our recent studies have resulted in the preparation of a linear and crystalline poly(ethylenimine) by the alkaline hydrolysis of poly(*N*-formylethylenimine) which was obtained by the isomerization polymerization of 2-oxazoline.[2] This new method was applied by us to the preparation of optically active poly(propylenimine) having an unequivocal linear structure. We report now a new synthesis of optically active linear poly(propylenimine) (**2**) by the alkaline hydrolysis of poly(*N*-formylpropylenimine) (**1**) which was prepared by the isomerization polymerization of optically active 4-methyl-2-oxazoline (4-MeOZO) with a cationic initiator.

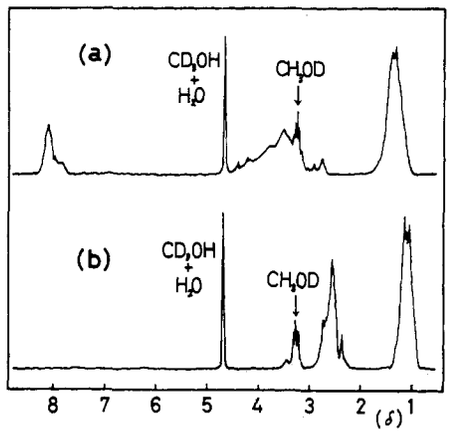
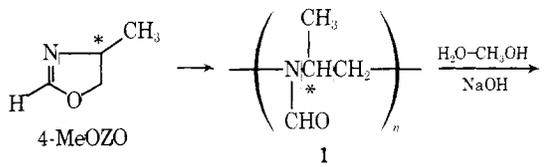
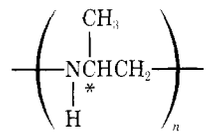


Figure 1. Nmr spectra of (a) poly(*N*-formylpropylenimine) and of (b) poly(propylenimine), both in CD_3OD.





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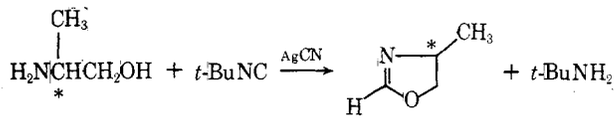
The monomer of L-4-methyl-2-oxazoline (L-4-MeOZO) was prepared by the cyclization reaction of L-alaninol ($[\alpha]^{29}D$ +21.7° (C_2H_5OH)) and *tert*-butyl isocyanide with silver catalyst, a method recently found in our laboratory.[3]



To a mixture of 15.5 mmol of L-4-MeOZO [$[\alpha]^{30}D$ −148° (C_2H_5OH)] and 1.5 ml of acetonitrile was added 0.46 mmol of ethyl trifluoromethanesulfonate. The reaction mixture was allowed to react at 80° for 50 hr. The mixture was diluted with methanol, poured into a large amount of diethyl ether to precipitate a white solid, and dried *in vacuo* to give 1.20 g (91% yield) of a solid polymer melting *ca.* 160°. It was shown to be partially crystalline by X-ray diffraction spectrum. The polymer structure was established by nmr and ir spectroscopy as well as elementary analysis to be poly(*N*-formylpropylenimine) (**1**). The nmr spectrum of **1** (Figure 1a) shows a broad singlet at δ 8.3–7.8 due to *N*-formyl proton (1 H), a broad signal at δ 4.5–3.1 due to methine (1 H) and methylene (2 H) protons, and a doublet-like peak centered at δ 1.30 due to methyl protons (3 H). The ir spectrum showed a characteristic band of amide group at 1660 cm^{-1} (>NCH=O). The molecular weight of **1** was 1330 by vapor pressure osmometry.

Anal. Calcd for $C_4H_7NO(H_2O)_{0.36}$: C, 52.50; H, 8.43; N, 15.31. Found: C, 52.87; H, 8.28; N, 15.09.

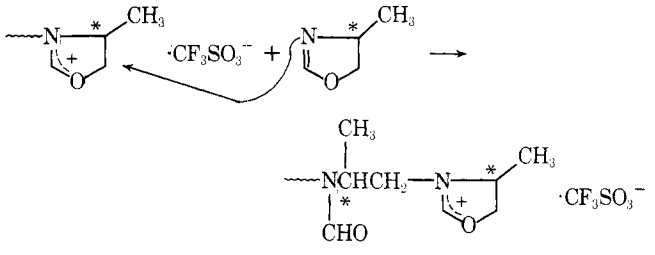
Polymer **1** is quite hygroscopic. To measure the optical activity of the polymer, the polymer content of the sample solution was first determined by nmr in CD_3OD on the basis of the relative intensities of two singlets at δ 8.0 due to N–CHO and at δ 7.3 due to C_6H_6 added as an internal standard. Then, the specific rotation of **1** was determined as $[\alpha]^{25}D$ +130° (CH_3OH).

The alkaline hydrolysis of **1** was carried out as follows.

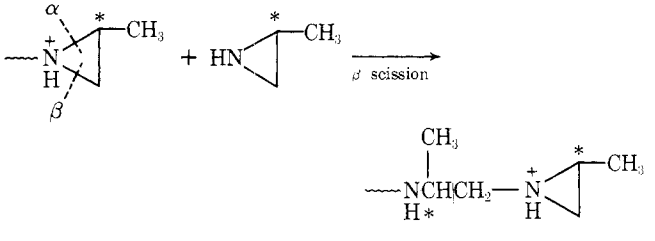
To a solution of 0.54 g of 1 in 6.2 ml of 50% aqueous methanol was added 0.44 g of NaOH. The homogeneous solution was kept at 100°. The reaction proceeded very slowly; *e.g.*, the extent of the reaction (followed by nmr) was 80% conversion after 68 hr and 95% after 160 hr. After a reaction time of 330 hr, the mixture was cooled to room temperature. The solvent was evaporated at reduced pressure. The residue was then extracted three times with cold chloroform and filtered and chloroform was evaporated. A waxy polymer was obtained in 84% yield. The nmr spectrum of the polymer (Figure 1b) supported the structure of poly(propylenimine) (**2**). A signal at δ 3.0–2.2 is ascribed to methylene (2 H) and methine (1 H) protons of **2**. A doublet centered at δ 1.1 is due to methyl protons (3 H) of **2**. It should be noted that the signal centered at δ 8.0 due to NCHO was completely absent, indicating that the alkaline hydrolysis had proceeded quantitatively.

Poly(propylenimine) (**2**) is also very hygroscopic. The ir spectrum of **2** showed strong absorption bands at 3400 and 1630 cm^{-1} due to H_2O. Therefore, the band of ν_{N-H} of **2** overlapped at a region of 3400 cm^{-1}. The optical activity was measured after the net content of polymer **2** in solution was determined also by nmr similarly to the measurement of **1** with C_6H_6 as internal standard. The specific rotation of **2** was found to be $[\alpha]^{26}D$ +105° (CH_3OH).

The present study provides a new route to optically active poly(propylenimine). It was established by nmr[4] that the polymerization proceeds *via* an SN2 reaction between oxazolinium trifluoromethanesulfonate and monomer, in which the attack at the asymmetric carbon atom is never



involved in the propagation. In the cationic polymerization of propylenimine, on the other hand, the possibility of the inversion or racemization at the chiral carbon atom in propagation (α scission) cannot be ruled out, although Price, *et al.*,[1] claimed that β scission took place exclusively.



As an additional consideration for the structure of Price's poly(propylenimine), considerable branching must be unavoidable in the cationic ring-opening polymerization of the aziridine ring.[5]

The obtained value of $[\alpha]D$ +105° in our present study is close to the highest values of the polymers prepared by the polymerization of L-propylenimine.[1] The molecular weight of the sample polymer of the present study is low. Therefore, higher values of specific rotation will be obtained when the molecular weight of **2** is increased. Preparation of higher molecular weight polymers of **2** as well as kinetic studies are now being undertaken.

References and Notes

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Takeo Saegusa,* Shiro Kobayashi, and Michihiro Ishiguro
Department of Synthetic Chemistry
Faculty of Engineering
Kyoto University
Kyoto, Japan

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Direct Measurement of Polymer Dimensions in Concentrated Solutions by Small-Angle X-Ray Scattering

During the last 20 years the concentration dependence of polymer chain dimensions has been predicted by several authors theoretically[1-5] and by computer simulation.[6] To our knowledge, however, no experimental evaluation has been published, though molecular dimensions in bulk polymers have been estimated by a few authors.[7-9] Here we would like to report a new method for the direct measurement of polymer dimensions in concentrated solution and in bulk, as well as some preliminary results.

In X-ray scattering, polymers with heavy atom labels at both ends (end-tagged polymer)[7,10] have usually been employed for this purpose. In this case, however, the difference between the scattered intensity of tagged polymer and that of untagged polymer is rather small, because the number of heavy atoms is not sufficiently large. The higher the molecular weight, the smaller the difference, so that the application of this method may be limited to polymers of relatively low molecular weight, as has been pointed out by Ballard, *et al.*[9]

It is true that neutron scattering is a powerful technique, but it does not lie ready to everyone's hands. So we intend to improve the tagged polymer method in the X-ray scattering using random copolymers of styrene and *p*-iodostyrene synthesized by iodination of polystyrene.[11] These copolymers are assumed to be "randomly tagged polymers," which have heavy atom labels (iodine) along the molecular chains. Using this copolymer, we can expect stronger scattered intensity than that for end-tagged polymer, but the iodine atoms attached to the chain may give rise to conformational changes in the chain, the effect of which must be eliminated by an appropriate method.

As a sample, monodisperse polystyrene (batch no. 4b, Pressure Chemicals Ltd.), whose nominal molecular weight was 110,000 and $M_W/M_N < 1.06$, was used. The iodine content of copolymer was determined by argentometry.[12] As solvent, spectral grade toluene, which is a good solvent for polystyrene, was used without further purification.

Random copolymers of styrene and *p*-iodostyrene with various compositions were synthesized by iodination of polystyrene. Solutions of polystyrene and of a mixture of polystyrene and a small amount of tagged polystyrene (copolymer), both of which had the same total concentration, were studied by small-angle X-ray scattering with a Kratky camera.[13] The fluctuation of the intensity of the primary beam of the Kratky camera was smaller than 0.2% during the measurement. The temperature of the sample was maintained at 25 ± 0.1°.