

Preparation of an Open-Chain Polyimide

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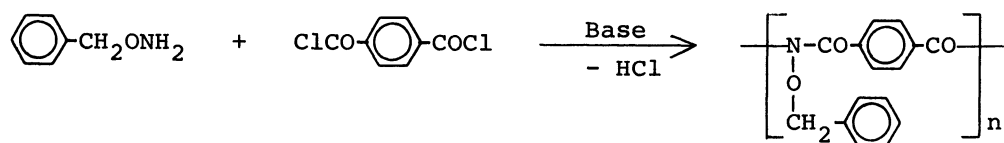
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A high molecular weight open-chain polyimide was prepared for the first time from benzyloxyamine and terephthaloyl chloride. It showed high solubility in contrast to the conventional polyimides.

Polyimides are rated highest among high performance organic materials owing to the excellent heat- and electrical-resistivity in spite of the poor fabricability.¹⁾ They all have cyclic imides as connecting blocks, and no polyimide having open-chain structure has been synthesized. This is ascribable partly to the difficulty in preparing open-chain imides in quantitative yield necessary for the formation of high polymers. In view of developing a novel type of tractable polyimides, open-chain polyimides are quite attractive.

Although ordinary amines are rather reluctant in imidization, O-substituted hydroxylamines were expected to be diacylated more easily on account of the high electronegativity of the oxygen atom. Benzyloxyamine was thus subjected to the model reactions with acetic anhydride and benzoyl chloride in the presence of bases. The expected imides proved extremely soluble, but were isolated in up to around 70% yield depending on the conditions, indicating this type of amine to have high possibility in imide synthesis. A detailed further study for the reaction was done with terephthaloyl chloride, and the polymerization conditions were evaluated in terms of the molecular weight of the resulting polymer.

A mixture of equimolar amounts of the monomers and a given amount of bases in DMAC was stirred under nitrogen at 0 °C for 1 h and then at 25 °C for 23 h.



The polymer was isolated in ethanol as a white fibrous material and purified by repeated reprecipitation using tetrahydrofuran and ethanol. With an equimolar amount of triethylamine, both the yield and molecular weight were very low. The polymerization was then attempted with various kinds of acid acceptor systems including pyridine and mixtures of these amines.²⁾ As a result, a mixture of an equimolar amount of triethylamine and a half molar amount of pyridine was confirmed to be the most appropriate. The effects of polymerization solvents were also examined, and DMAc appeared to be superior to other common aprotic polar solvents. A smaller amount of solvent resulted in a higher molecular weight, and a value as high as 12530 was achieved in 1.5 ml of DMAc, the minimum amount to enable stirring. Some typical results are summarized in Table 1.

The resulting open-chain polyimides showed very high solubility in ordinary solvents such as acetone, chloroform, tetrahydrofuran, and dioxane in addition to polar solvents. This is in remarkable contrast to the poor solubility of the conventional polyimides. The thermooxidative stability was examined by thermogravimetry at a heating rate of 5 °C·min⁻¹ in air; the temperatures of weight loss commencement and 10% weight loss were 191 and 245 °C, respectively. These values are somewhat lower than those of the conventional wholly aromatic polyimides as expected from the open-chain structure.

Consequently, a new type of high molecular weight polyimide having open-chain imide structure could be synthesized utilizing an oxyamine as a difunctional monomer and was characterized by the much improved solubility.

Table 1. Synthesis of the Polyimide^{a)}

DMAc cm ³	Acid acceptor		Yield %	\overline{M}_n ^{b)}
	Triethylamine (mmol)	Pyridine (mmol)		
4	4	0	17.2	920
4	6	0	52.0	4570
4	4	2	74.3	6480
4	2	4	39.8	2550
1.5	4	2	87.3	12530

a) Monomers; 2 mmol each.

b) Determined by GPC with polystyrene standards.

References

- 1) H.-G. Elias and F. Vohwinkel, "New Commercial Polymers 2," Gordon and Breach Science Publishers, New York (1986).
- 2) T. Suzuki and K. Mitsuhashi, *Nippon Kagaku Kaishi*, **1979**, 631.

(Received September 11, 1987)