The Synthesis and Polymerization of β-Propiolactam and α-Phenyl-β-propiolactam

Bj Toshiyuki KODAIRA, Hideo MIYAKE*, Koichiro HAYASHI
and Seizo OKAMURA

(Received November 25, 1964)

There have been several reports concerning the polymerization of α,β-substituted[1] or *N*-substituted[2] β-propiolactam. In this note, the syntheses and polymerizations of unsubstituted β-propiolactam and α-phenyl-β-propiolactam will be reported. It was found by the present study that, in the presence of such anionic catalysts as butyl lithium, sodium methoxide or potassium hydroxide, β-propiolactam and α-phenyl-β-propiolactam polymerized easily in dimethyl sulfoxide (DMSO) under mild conditions, as is shown in Tables I and II. However, a cationic catalyst, boron trifluoride, was not effective for the polymerization. Further, it was observed that the polymerization of unsubstituted lactam took place rapidly in DMSO, but very slowly when it was polymerized in the solid state. The polymer yield was slightly influenced by the reaction temperature when polymerization was carried out in DMSO (Fig. 1 and Fig. 2).

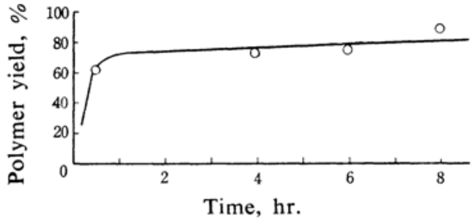

Fig. 1. Polymerization of 3-phenyl-β-propiolactam.
(M) : 3.16 mol./l.
(BuLi) : 4.3×10^{-3} mol./monomer mol.
Solvent : DMSO, Temp. : 25°C

The polymerizability of β-propiolactam was larger than that of α-phenyl-β-propiolactam because of the electron-donating character of the phenyl substituent.

The infrared spectra of both polymers had characteristic absorption bands attributable to NH linkage (3300 cm^{-1}) and to the poly-amide structure (1655 cm^{-1}). The infrared spectrum of poly-β-propiolactam agreed well with those

---

* Present address: Chalmers Tekniska Högskala Institutinen för Organisk Kemi, Gibraltargatan 5A, Göteborg S., Sweden.

[1] R. Graf, G. Lohaus, K. Börner, E. Schmidt and H. Bestian, *Angew. Chem.*, **74**, 523 (1962).

[2] T. Kagiya, H. Kishimoto, S. Narusawa, T. Sano and K. Fukui, The Symposium of Rubber and High Polymers, Nagoya, November, 1963.

TABLE I. POLYMERIZATION OF β-PROPIOLACTAM

No.	Cat.	Solvent	(M) mol./l.	(C) mol./mol.	Temp. °C	Polymerization time, min.	Conv. %
1	BuLi	DMSO	0.17	5.4×10^{-3}	30	20	35.7
2	BuLi	DMSO	0.18	5.3×10^{-3}	60	5	25.7
3	BuLi	Ether	0.071	4.3×10^{-3}	30	40	0.7
4*	BuLi	Ether	0.25	5.3×10^{-3}	30	40	0.6
5*	BuLi	Toluene	0.23	4.0×10^{-3}	30	40	0.5
6**	CH_3ONa	DMSO	0.23	9.5×10^{-2}	30	40	40.8
7**	KOH	DMSO	0.23	7.8×10^{-2}	30	40	36.8
8	BF_3OEt_2	CH_2Cl_2	2.25	5.0×10^{-2}	30	300	~0

* Solid state polymerization ** Heterogeneous catalyst

TABLE II. POLYMERIZATION OF 3-PHENYL-β-PROPIOLACTAM

No.	Cat.	Solvent	(M) mol./l.	(C) mol./mol.	Temp. °C	Polymerization time, min.	Conv. %
9	BuLi	DMSO	0.23	1.22×10^{-2}	30	80	20.6
10	BuLi	DMSO	3.16	4.3×10^{-3}	30	20	70.2
11	BuLi	DMSO	0.23	1.22×10^{-2}	60	5	6.5
12*	BuLi	Ether	0.23	1.22×10^{-2}	30	40	1.0
13*	BuLi	*n*-Hexane	0.23	1.22×10^{-2}	30	20	0.5
14*	BuLi	Toluene	0.23	1.22×10^{-2}	30	40	0.3
15**	CH_3ONa	DMSO	0.23	9.1×10^{-2}	30	40	71.4
16**	KOH	DMSO	0.23	12.9×10^{-2}	30	40	42.5
17	BF_3OEt_2	CH_2Cl_2	1.87	5.0×10^{-2}	30	300	~0

* Solid state polymerization ** Heterogeneous catalyst

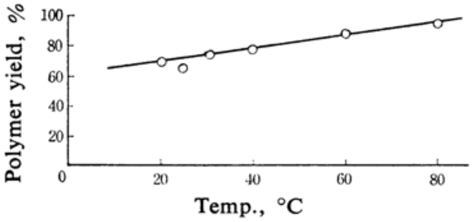

Fig. 2. Polymerization of 3-phenyl-β-propiolactam, influence of polymerization temperature.
(M) : 3.16 mol./l.
(BuLi) : 4.3×10^{-3} mol./monomer mol.
Solvent : DMSO, Polym. time : 20 min.

of the polymer obtained from the polycondensation reaction of dithiocarbonylethoxy-dicarbonyl-β-alanine.³⁾ Further, the polymers had higher melting points (>300°C) and larger viscosities (the [η] values were 0.7—1.0 in a 0.5% dichloroacetic acid solution at 35°C) than those of the polymers obtained by poly-condensation³⁾ or by the hydrogen-transfer polymerization of acryl-amide.⁴⁾

The results of the X-ray diffraction diagram show that the poly-β-propiolactam has a higher crystalline structure (2θ : 18°46′, 26°26′, 28°40′ and 32°6′), while poly-α-phenyl-β-propiolactam has a lower one, because of the bulky substituent of the phenyl group.

Experimental

The Synthesis of β-Propiolactam. — β-Alanine-ethyl ester hydrochloride (I) was prepared from β-alanine by a method similar to that used for the synthesis of α-alanine-ethyl ester hydrochloride.⁵⁾ It was recrystallized from a chloroform-ether mixture.⁶⁾ Yield 93%, m. p. 64—65°C. The β-Alanine-ethyl ester was prepared from I by a procedure similar to that used for the glycine derivative.⁷⁾ Yield 32%, b. p. 58°C/14 mmHg. β-Propiolactam (m. p. 74—75°C) was synthesized by the method of Holley.⁸⁾ The synthesis of 3-phenyl-β-propiolactam (m. p. 119—120°C) followed the method of Testa.⁹⁾

The polymerizations were carried out under a dry nitrogen stream, and the polymers obtained were precipitated in methanol.

Department of Polymer Chemistry
Faculty of Engineering
Kyoto University
Sakyo-ku, Kyoto

---

3) H. Kato, K. Suzuoki, T. Higashimura and S. Okamura, unpublished results.

4) N. Ogata, This Bulletin, 33, 906 (1960), *Makromol. Chem.*, 40, 55 (1960).

5) S. D. Brewer and R. M. Herbst, *J. Org. Chem.*, **6**, 870 (1941).

6) W. J. Hale and E. M. Honan, *J. Am. Chem. Soc.*, **41**, 774 (1919).

7) E. Fischer, *Ber.*, **34**, 436 (1901).

8) W. Holley and Am. D. Holley, *J. Am. Chem. Soc.*, **71**, 2129 (1949).

9) E. Testa, F. Fava and L. F. Liebig, *Ann. Chem.*, **614**, 167 (1958).