Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Copolymerization of Carbon Dioxide and Epoxide: Functionality of the Copolymer

Shohei Inoue[a]
[a] Department of Synthetic Chemistry Faculty of Engineering, University of Tokyo, Tokyo, Japan

To cite this Article Inoue, Shohei(1979) 'Copolymerization of Carbon Dioxide and Epoxide: Functionality of the Copolymer', Journal of Macromolecular Science, Part A, 13: 5, 651 — 664
To link to this Article: DOI: 10.1080/00222337908056679
URL: http://dx.doi.org/10.1080/00222337908056679

J. MACROMOL. SCI.–CHEM., A13(5), pp. 651-664 (1979)

Copolymerization of Carbon Dioxide and Epoxide: Functionality of the Copolymer

SHOHEI INOUE

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

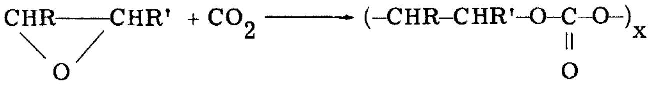
ABSTRACT

Carbon dioxide and epoxide copolymerize in the presence of some organometallic catalyst systems under moderate conditions to give aliphatic polycarbonates of high molecular weight. Some metalloporphyrins of aluminum and zinc were found to act as novel catalysts for the polymerization of epoxide and for the copolymerization of carbon dioxide and epoxide, though not alternating. The polymers are characterized by the narrow molecular weight distribution and the unusual stereoregularity. Starting from the copolymerization of carbon dioxide and trimethylsilyl glycidyl ether with diethylzinc-water catalyst system, a readily degradable polycarbonate having hydroxyl group was obtained.

INTRODUCTION

Chemical fixation of carbon dioxide is of much importance in connection with resource utilization. Recent interest in organic and bio-organic chemistry of carbon dioxide has led to the development of new synthetic reactions using carbon dioxide as a direct material, especially in the field of polymer synthesis.

We have been studying the alternating copolymerization of carbon dioxide and epoxide to form aliphatic polycarbonate with high molecular weight [1, 2]. The reaction proceeds under moderate conditions such as room temperature and atmospheric pressure by using some organometallic catalyst systems.



(1)

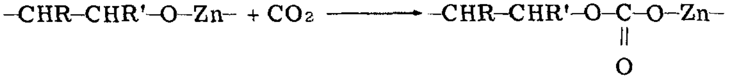
Among the catalyst systems so far examined, the systems based on diethylzinc, coupled with water [3, 4], primary amine [3, 4], dihydric phenol [5, 6], aromatic dicarboxylic acid [7], or aromatic hydroxycarboxylic acid [7], are effective. Diethylzinc–trihydric phenol or aminophenol systems were reported also to exhibit high catalytic activity [8-10]. Aging of diethylzinc-water [11] or -polyhydric phenol [10] system inthe presence of carbon dioxide enhances the catalytic activity of these systems. Although organoaluminum systems are known to be effective for the homopolymerization of epoxide, they tend to give homopolymer of epoxide even in the presence of carbon dioxide. Triethylaluminum-triphenylphosphine system gives the copolymer though not alternating [12]. Nonorganometallic catalysts such as zinc carbonate [3] and acetates of zinc or cobalt [13] are also effective to some extent.

The copolymerization reaction with organozinc catalyst systems is general for epoxides, substituted and unsubstituted. In the cases of ethylene oxide and propylene oxide, alternating copolymers with carbon dioxide having molecular weights of 50,000-150,000 may be obtained. On the other hand, four- and five-membered cyclic ethers, e. g., 3,3-bis(chloromethyl)-oxetane and tetrahydrofuran, do not copolymerize with carbon dioxide with the organozinc catalyst system. However, the triethylaluminum-water-acetylacetone system gave the copolymer of carbon dioxide and oxetane with carbonate as well as ether linkages [14].

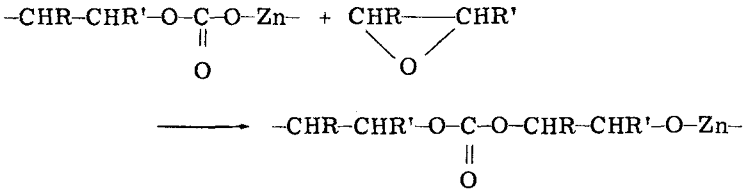
The ring-opening mode of epoxide in the copolymerization with carbon dioxide by the diethylzinc-water system has been studied in detail. Cyclohexene oxide(cis) when introduced into the copolymer chain is converted to trans-diol structure, indicating the inversion of configuration at the carbon atom where the ring opening takes place [15]. Ring opening of propylene oxide takes place predominantly at the methylene-oxygen bond [16], while styrene oxide ring is cleaved selectively at methine-oxygen linkage [17]. Cyclohexylethylene oxide [18] and benzylethylene oxide [19] behave similarly to propylene oxide.

The tacticity of the copolymer of carbon dioxide and racemic monosubstituted epoxide remains unknown. In the ternary copolymerization of carbon dioxide, (R)-propylene oxide and (R)- or (S)-styrene oxide, both enantiomers of styrene oxide, may be incorporated into the same copolymer chain with carbon dioxide and (R)-propylene oxide [20].

The copolymerization reaction is considered to proceed by the repetition of the attack of a zinc alkoxide towards carbon dioxide to form a zinc alkyl carbonate [Eq. (2)], followed by the reaction between the latter and epoxide to regenerate a zinc alkoxide [Eq. (3)].



$$\text{–CHR–CHR'–O–Zn–} + \text{CO}_2 \longrightarrow \text{–CHR–CHR'–O–}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{–O–Zn–} \qquad (2)$$



$$\text{–CHR–CHR'–O–}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{–O–Zn–} + \text{CHR–CHR'}(\text{–O–}) \longrightarrow \text{–CHR–CHR'–O–}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{–O–CHR–CHR'–O–Zn–} \qquad (3)$$

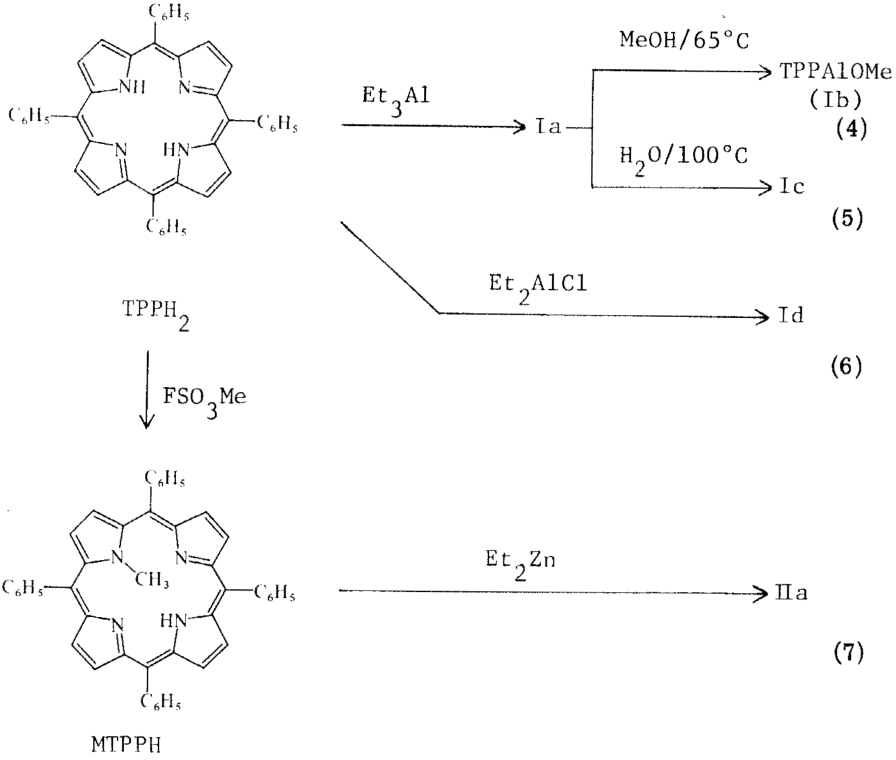
The possibility of the copolymer formation via cyclic carbonate may be excluded, since the latter does not polymerize under the relevant conditions.

Thermal degradation of carbon dioxide-ethylene oxide or carbon dioxide-propylene oxide copolymer at 170-180°C gives the corresponding cyclic carbonate in a high yield, while hydrolysis, e. g., in boiling water, takes place by random scission [21]. Carbon dioxide-ethylene oxide copolymer is degradable by enzyme pronase [22]. Some other physicochemical properties were reported [1, 21].

In the present paper are described some of the recent developments from our laboratories; (1) metalloporphyrins as a novel catalyst system for the polymerization of epoxide and the copolymerization with carbon dioxide, and (2) synthesis of a polycarbonate having hydroxyl group starting from carbon dioxide and epoxide as a functional polymer.

METALLOPORPHYRINS AS NOVEL CATALYST SYSTEM FOR CARBON DIOXIDE-EPOXIDE COPOLYMERIZATION

In the course of our studies on the reaction between carbon dioxide and organozinc [23] or organoaluminum [24] compounds, we have made a very interesting finding that $\alpha, \beta, \gamma, \delta$-tetraphenylporphinato(ethyl) aluminum (Ia) reacts with carbon dioxide in the presence of 1-methylimidazole only in visible light [25]. On the other hand, tetraphenylporphinatoaluminum methoxide (TPPAlOMe, Ib) reacts readily and reversibly with carbon dioxide in the presence of 1-methylimidazole even in the dark [26]. Carbon dioxide in this reaction product is activated enough to react readily with propylene oxide to give the corresponding cyclic carbonate as the main product. In the absence of 1-methylimidazole, the reaction of TPPAlOMe, carbon dioxide, and propylene oxide proceeds more slowly, the product being a copolymer containing both carbonate and ether linkages, but not cyclic carbonate. In this connection, some other metalloporphyrins have been examined as catalyst for the polymerization of propylene oxide and the copolymerization with carbon dioxide. The systems examined were prepared according to the reactions shown in Eqs. (4)-(7).



(4)

(5)

(6)

(7)

Among these, the main component of systems Ic, Id, and IIa are considered to be tetraphenylporphinatoaluminum hydroxide and chloride and N-methyltetraphenylporphinato(ethyl)zinc, respectively.

Molecular Weight Distribution

Metalloporphyrins examined exhibited catalytic activity for the copolymerization of carbon dioxide and propylene oxide, but in some cases only the homopolymer of the epoxide was formed even in the presence of carbon dioxide (Table 1). These sytems were also effective for the homopolymerization of the epoxide (Table 2).

Carbon dioxide–propylene oxide copolymer and the homopolymer of propylene oxide obtained with these catalyst systems are characterized by the very narrow molecular weight distribution as shown in Tables 1 and 2. For example, poly(propylene oxide) obtained with the system IIa had $\overline{M}_w/\overline{M}_n = 1.15$, whereas the polymer with diethylzinc-water (2:1) system has $\overline{M}_w/\overline{M}_n = 3$ [28]. The system Id gave the polymer with $\overline{M}_w/\overline{M}_n = 1.10$, while diethylaluminum chloride gave the polymer with $\overline{M}_w/\overline{M}_n = 1.70$.

Tacticity

Poly(propylene oxide) obtained with the metalloporphyrin catalysts have a much different tacticity from those by usual organometallic catalyst systems (Table 1). The diethylzinc-methanol (1:2) system is known to give a polymer rich in isotactic sequences, the tacticity being described in terms of "enantiomorphic catalyst site control" mechanism [29, 30]. In contrast, the system IIa gave a polymer rich in syndiotactic sequences, and the tacticity conforms rather to a "growing chain end control" mechanism. While diethylaluminum chloride gave polymer with head-to-tail as well as head-to-head (or tail-to-tail) linkages, the polymer obtained with the system Id is composed only of head-to-tail linkages (Fig. 1), and the tacticity conforms to the growing chain end control mechanism, although the polymer was rich in isotactic sequences.

The observed characteristics of these catalyst systems in the molecular weight distribution and the tacticity of the polymer are considered to be due to the reaction occurring on the metal isolated from others by a rigid planar porphyrin ring.

Formation of Linear and Cyclic Carbonates

The copolymerization of carbon dioxide and propylene oxide with organozinc catalyst systems is usually accompanied with the formation of cyclic carbonate. However, the correlation between these reactions remains yet unsolved.

TABLE 1. Copolymerization of Propylene Oxide (PO) and CO_2 at 20°C[a]

Catalyst	$\frac{[PO]}{[Cat]}$	Pressure of CO_2 (bar)	Time (hr)	Conversion (%)[b]	Content of oxycarbonyl units (mole-%)	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
Ib	730	1.0	430	98	15	c	-
	440	8.1	456	19	40	3900	1.15
Ic	700	1.0	152	>9	10	3700	1.10
Id	400	1.0	117	>18	~0	c	-
	400	8.1	168	10	~0	8500	1.08
IIa	380	1.0	45	~100	~0	c	-
	850	8.1	430	d	d	c	-

[a] Data of Takeda and Inoue [27].
[b] Based on PO.
[c] Not measured.
[d] Propylene carbonate was the sole product.

TABLE 2. Polymerization of Propylene Oxide (PO) at 20°C[a]

							Tacticity				
							Diad		Triad		
Catalyst	$\frac{[PO]}{[Cat]}$	Time (hr)	Conversion (%)	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	i	s	I	H	S
Id	420	0.4	38	8900	8100	1.10	69	31	47	43	10
$(C_2H_5)_2AlCl$	325	24	7.3	16500	9700	1.70					
IIa	2100	96	91	31000	27000	1.15	40	60	18	40	42
$(C_2H_5)_2Zn$-H_2O[b]	21		81			~3					
$(C_2H_5)_2Zn$-CH_3OH[c]	20	24					66	34	47	33	20

[a] Data of Takeda and Inoue [27].

[b] Mole ratio 2:1 [28].

[c] Mole ratio 1:2 [29].

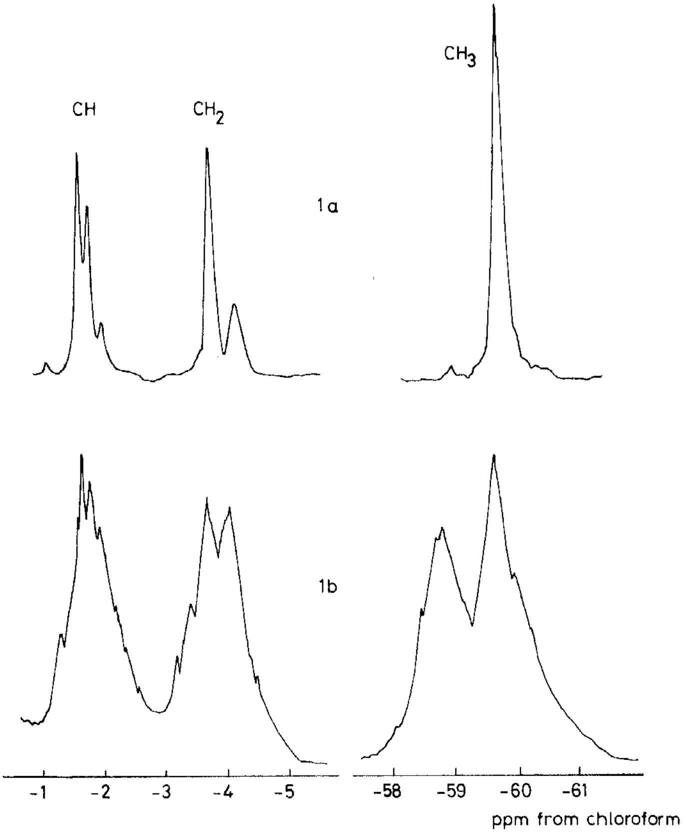


FIG. 1. ^{13}C-NMR spectra of poly(propylene oxides) obtained with the catalyst system (a) Id and (b) Et_2AlCl, in chloroform at 50°C [27].

As described above, the reaction of TPPAlOMe (Ib), carbon dioxide, and propylene oxide gave a copolymer having carbonate as well as ether linkages. In this case, however, the formation of cyclic carbonate was not observed, as indicated by the absence of the corresponding band (1805 cm^{-1}) in the infrared spectrum of the reaction mixture (Fig. 2A).

After the removal of unreacted carbon dioxide and epoxide from the reaction mixture, followed by the addition of 1-methylimidazole, linear carbonate linkage of the copolymer (1750 cm^{-1}) was converted gradually to cyclic carbonate (Fig. 2B).

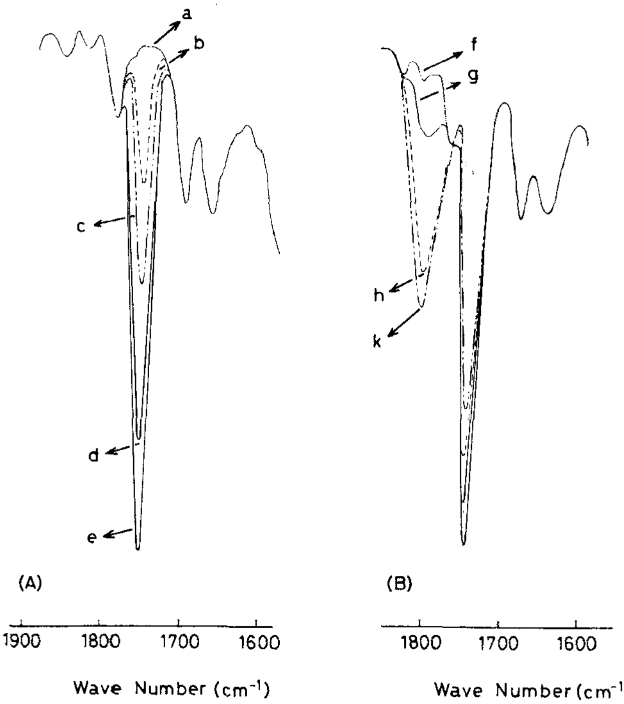


FIG. 2. Infrared spectra of the reaction mixture of TPPAlOMe (Ib), CO_2, and propylene oxide: (A) a-e, increase of linear carbonate; (B) f-k, increase of cyclic carbonate at the expense of linear carbonate, when 1-methylimidazole was added after removal of CO_2 and epoxide.

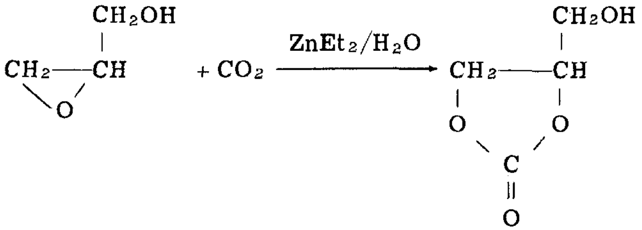
Therefore, in other catalyst systems as well, there is the possibility that cyclic carbonate as the by-product be formed, at least partly, via the copolymer.

SYNTHESIS AND PROPERTIES OF POLYCARBONATES WITH HYDROXYL GROUP

With high concentration of carbonate linkage along the main chain, carbon dioxide-epoxide copolymer is considered to have potential use as a functional polymer.

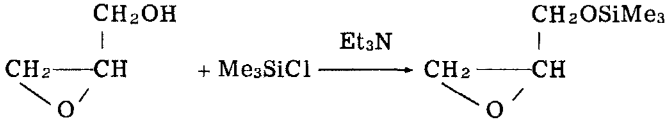
Although the possibility of enzymatic degradation of carbon dioxide-ethylene oxide copolymer was indicated [22], the extent of water absorption of carbon dioxide-ethylene oxide or carbon dioxide-propylene oxide copolymer is low [1, 21], and the synthesis of more hydrophilic copolymer is desirable.

Although the copolymerization of carbon dioxide and glycidol was attempted by use of the diethylzinc-water system as catalyst, only cyclic carbonate was obtained [Eq. (8)].



(8)

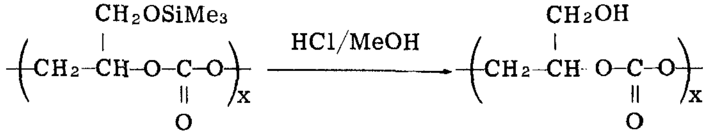
The hydroxyl group of glycidol was next protected with the trimethylsilyl group [31] [Eq. (9)].



(9)

The protected monomer, trimethylsilyl glycidyl ether, could be copolymerized with carbon dioxide to give alternating copolymer of high molecular weight (Table 3).

The removal of trimethylsilyl group from the copolymer may be carried out by the addition of HCl/methanol to a benzene solution of the copolymer [Eq. (10)].



$$\left(-CH_2-\overset{\displaystyle CH_2OSiMe_3}{\overset{|}{CH}}-O-\underset{\displaystyle O}{\underset{\|}{C}}-O-\right)_x \xrightarrow{HCl/MeOH} \left(-CH_2-\overset{\displaystyle CH_2OH}{\overset{|}{CH}}-O-\underset{\displaystyle O}{\underset{\|}{C}}-O-\right)_x \qquad (10)$$

III

The benzene-insoluble product III dissolves in water, methanol, and pyridine, but dissolution is accompanied by degradation to cyclic carbonate (Fig. 3). The degradation took place also in the solid state in moist atmosphere, as indicated by the appearance of infrared

TABLE 3. Copolymerization of Carbon Dioxide, Trimethylsilyl Glycidyl Ether (TMSGE), and Propylene Oxide (PO)[a]

Monomer					Copolymer	
TMSGE (g)	PO (g)	Mole ratio	Time (days)	Yield (g)	TMSGE:PO (mole ratio)	$[\eta]$ (dl/g)[b]
14.6	-	-	7.8	0.47	-	2.0
14.6	-	-	7.9	0.57	-	3.55
3.7	4.4	1:3	3.8	0.93	1:18	1.46
7.3	2.9	1:1	6.9	4.06	1:3	2.41
11.0	1.5	3:1	9.8	1.89	1:1.5	1.44

[a] Conditions: CO_2, 40-55 kg/cm^2; in dioxane; Et_2Zn-H_2O (1:0.9) catalyst; 35°C.

[b] In benzene, 30°C.

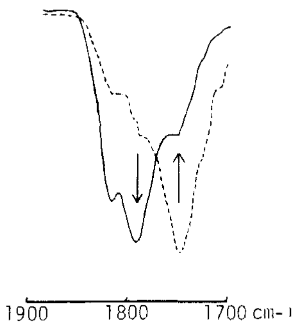
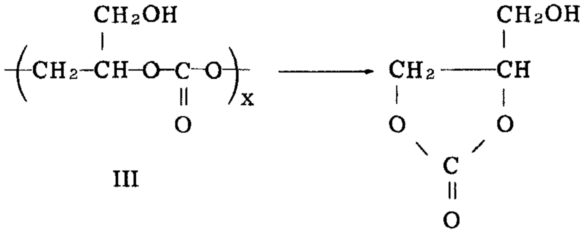


FIG. 3. Infrared spectra of polycarbonate III containing hydroxyl groups in methanol.

absorption at about 1800 cm^{-1} at the expense of that at 1750 cm^{-1}. Upon heating III at about 80°C, a similar degradation was observed [Eq. (11)].



(11)

Much easier degradation of III compared to carbon dioxide-ethylene oxide or carbon dioxide-propylene oxide copolymer may be due to intramolecular attack of the pendant hydroxyl group towards the carbonate linkage.

In order to obtain polycarbonate with various amounts of hydroxyl group, the ternary copolymerization of carbon dioxide, trimethylsilyl glycidyl ether, and propylene oxide was carried out. As shown in Table 3, ternary copolymer of high molecular weight could be obtained, though the reactivity of trimethylsilyl glycidyl ether was lower than that of propylene oxide.

The treatment of the ternary copolymers with HCl/methanol gave the copolymers with various amounts of hydroxyl group. Preliminary examination has revealed that the materials of various degradative properties may be obtained by such a procedure. Since various functional groups may be introduced at the hydroxyl group (or by the direct reaction with trimethylsilyloxy group), these products would be useful as biodegradable, functional polymer.

ACKNOWLEDGMENT

The author is grateful to Professor Teiji Tsuruta for constant encouragement, and to Dr. Norikazu Takeda, and Messrs. Yasuhiko Yoshida, Shigeru Morita, and Shigeto Fukushima for their collaboration.

REFERENCES

[1] S. Inoue, Chemtech, 6, 588 (1976).
[2] S. Inoue, Progr. Polym. Sci. Japan, 8, 1 (1975).
[3] S. Inoue, H. Koinuma, and T. Tsuruta, Makromol. Chem., 130, 210 (1969).
[4] S. Inoue, M. Kobayashi, H. Koinuma, T. Tsuruta, Makromol. Chem., 155, 61 (1972).
[5] M. Kobayashi, S. Inoue, and T. Tsuruta, Macromolecules, 4, 658 (1971).
[6] M. Kobayashi, Y.-L. Tang, T. Tsuruta, and S. Inoue, Makromol. Chem., 169, 69 (1973).
[7] M. Kobayashi, S. Inoue, and T. Tsuruta, J. Polym. Sci. Polym. Chem. Ed., 11, 2383 (1973).
[8] W. Kuran, S. Pasynkiewicz, J. Skupinska, and A. Rokicki, Makromol. Chem., 177, 11 (1976).
[9] W. Kuran, S. Pasynkiewicz, and J. Skupinska, Makromol. Chem., 177, 1283 (1976).
[10] W. Kuran, S. Pasynkiewicz, and J. Skupinska, Makromol. Chem., 178, 2149 (1977).
[11] M. Rätzsch and W. Haubold, Faserforsch. Textiltech., 28, 15 (1977).
[12] H. Koinuma and H. Hirai, Makromol. Chem., 178, 1283 (1977).
[13] K. Soga, K. Uenishi, S. Hosoda, and S. Ikeda, Makromol. Chem., 178, 893 (1977).
[14] H. Koinuma and H. Hirai, Makromol. Chem., 178, 241 (1977).
[15] S. Inoue, H. Koinuma, Y. Yokoo, and T. Tsuruta, Makromol. Chem., 143, 97 (1971).
[16] S. Inoue, H. Koinuma, and T. Tsuruta, Polym. J., 2, 220 (1971).
[17] T. Hirano, S. Inoue, and T. Tsuruta, Makromol. Chem., 176, 1913 (1975).
[18] T. Hirano, S. Inoue, and T. Tsuruta, Makromol. Chem., 177, 3237 (1976).

[19] T. Hirano, S. Inoue, and T. Tsuruta, Makromol. Chem., 177, 3245 (1976).
[20] S. Inoue, T. Hirano, and T. Tsuruta, Polym. J., 9, 101 (1977).
[21] S. Inoue, T. Tsuruta, T. Takada, N. Miyazaki, M. Kambe, and T. Takaoka, J. Appl. Polym. Sci. Polym. Symp. Ed., 26, 257 (1975).
[22] Y. Imai, K. Kojima, A. Watanabe, and E. Masuhara, Jinkō Zōki, 3, (Suppl.) 212 (1974).
[23] S. Inoue and Y. Yokoo, J. Organometal. Chem., 39, 11 (1972).
[24] S. Inoue and Y. Yokoo, Bull. Chem. Soc. Japan, 45, 3651 (1972).
[25] S. Inoue and N. Takeda, Bull. Chem. Soc. Japan, 50, 984 (1977).
[26] S. Inoue and N. Takeda paper presented at 8th Int. Conf. Organometal. Chem., 1977, Kyoto; Abstracts, p. 195.
[27] N. Takeda and S. Inoue, Makromol. Chem., 179, 1377 (1978).
[28] C. Booth, W. C. Higginson, and E. Powell, Polymer, 5, 479 (1964).
[29] M. Ishimori, K. Tsukigawa, T. Nakada, and T. Tsuruta, J. Macromol. Sci.–Chem., 11, 379 (1977).
[30] T. Tsuruta, J. Polym. Sci. D, 6, 179 (1972).
[31] A. Wende and D. Joel, Plaste Kautschuk, 9, 343 (1962).