The Grafting of Methyl Methacrylate onto Cotton by Tri-n-butylborane*

KUNIHARU KOJIMA, SUSUMU IWABUCHI, KUNIO MURAKAMI, KOICHI KOJIMA, and FUMIO ICHIKAWA, *Department of Applied Chemistry, Faculty of Engineering, Chiba University, Chiba, Japan*

Synopsis

Methyl methacrylate was grafted onto cotton by tri-n-butylborane in the presence of water. No graft was obtained in organic solvents, i.e., in the absence of water. The percentage of grafting increased with increases in reaction time, cotton amount, and initiator concentration. Pretreatment of cotton with pyridine also enhanced the percentage of grafting. Glycidyl methacrylate and ethyl acrylate were grafted onto cotton by tri-n-butylborane, while no grafting occurred when vinyl acetate and 4-vinyl pyridine were used. Usual radical initiators, such as azobisisobutyronitrile and benzoyl peroxide/dimethyl-p-toluidine, were not effective under the same conditions.

INTRODUCTION

The grafting of vinyl monomers onto natural and synthetic polymers has been studied in detail.[1-11] In most cases, the reaction is carried out at 60°C or higher by using ordinary radical initiators.[1-4] At room temperature, radiation and ceric ion methods as well as redox systems are applied to the grafting.[5-11] However, few authors have dealt with the grafting by alkylboranes,[12,13] although many studies on the polymerization of vinyl monomers with alkylborane initiators have appeared in the literature.[14-24]

In a previous paper,[13] we shortly reported the alkylborane-initiated graft copolymerization of methyl methacrylate (MMA) onto proteins and fibers. The main features revealed were: (1) tri-n-butylborane (Bu₃B) can initiate the grafting of MMA onto proteins (such as albumin and casein) and fibers (such as cotton, silk, and wool); (2) water is essential to the grafting, in other words, no grafting occurs in organic solvents; (3) MMA was grafted onto polymers containing hydrophilic groups (such as amino and hydroxy groups); and (4) so far as fibers are concerned, the efficiency of grafting (as defined in the experimental section) is in the following order:

$$\text{silk} > \text{wool} > \text{cotton} > \text{nylon} \gg \text{PP} \approx \text{PAN}$$

where PP = polypropylene and PAN = polyacrylonitrile.

In order to elucidate the alkylborane-initiated graft copolymerization of vinyl monomers onto fibers, we have investigated the grafting onto cotton in detail. Effects of reaction time, cotton amount, and initiator concentration on the grafting were studied. Pretreatment with pyridine was found to be effective. The purpose of this paper is to provide detailed information on the grafting of MMA onto cotton by Bu_3B.

EXPERIMENTAL

Materials

Commercial vinyl monomers and organic solvents were purified in the usual manner. Tri-*n*-butylborane (Bu_3B; Callery Chemical Co., U.S.A.) was distilled under nitrogen; bp 108–110°C (20 mm Hg). Commercial radical initiators were used without further treatment. Commercial cotton was dipped in boiling acetone for several hours, washed with methanol, and dried at 25°C in vacuo to constant weight.

Grafting

Typical Procedure. A mixture of 0.5 g cotton and 15 ml water was placed in a tapered joint glass tube of ca. 60-ml capacity and allowed to stand at room temperature for 15 hr. In another glass tube, we added 0.10 ml of Bu_3B to 5.0 ml MMA. This Bu_3B–MMA mixture was immediately poured into the first glass tube. Then the glass tube was shaken in a thermostatted shaking apparatus at 37°C for 2 hr. The grafting reaction was stopped by pouring the mixture into 200 ml methanol. The precipitate was filtered, washed with methanol, and dried at 60°C in vacuo to constant weight. The dry precipitate was extracted with acetone in a Soxhlet extractor for 50–80 hr. The acetone-soluble extract was reprecipitated with methanol to yield homopolymer. Both the acetone-insoluble residue (graft copolymer) and the homopolymer were dried at 50°C in vacuo to constant weight.

Estimation of Percentage and Efficiency of Grafting. The percentage of grafting, the efficiency of grafting, and the total conversion were estimated as follows:

$$\text{percentage of grafting} = \frac{\text{weight of poly(MMA) grafted}}{\text{weight of MMA charged}} = \frac{\text{II}}{\text{I}}$$

$$\text{efficiency of grafting} = \frac{\text{weight of poly(MMA) grafted}}{\begin{array}{c}\text{weights of poly(MMA) grafted}\\\text{and homopolymer}\end{array}} = \frac{\text{II}}{\text{II} + \text{III}}$$

$$\text{total conversion} = \frac{\begin{array}{c}\text{weights of poly(MMA) grafted}\\\text{and homopolymer}\end{array}}{\text{weight of MMA charged}} = \frac{\text{II} + \text{III}}{\text{I}}$$

where I = weight of MMA charged, II = (weight of acetone-insoluble component) minus (weight of fiber), and III = weight of acetone-soluble component (homopolymer).

Measurements

Viscosities of the homopolymer were determined at 25°C in a Cannon-Fenske-type viscometer on chloroform solutions containing 5 g polymer per liter, and average molecular weights were estimated according to the equation[25]

$$[\eta] = 0.48 \times 10^{-4} \times M^{0.80} \qquad (dl/g, \ 25°C)$$

RESULTS AND DISCUSSION

Initiators Tested

The grafting of MMA onto cotton with various initiators was carried out at 37°C in the presence of water. Bu$_3$B was found to be capable of initiating the grafting, whereas the usual radical initiators, such as azobisisobutyronitrile (AIBN), benzoyl peroxide (BPO)/dimethyl-*p*-toluidine (DPT), and BPO/cobalt naphthenate (CoNaph), were not effective under the same conditions. These radical initiators yielded homopolymer only. The results are summarized in Table I.

TABLE I
Grafting of Methyl Methacrylate onto Cotton with Various Initiators[a]

Run no.	Initiators[b]	Cotton, g	Total yield, g	Conversion, %	Homopolymer, g	Graft, g	Per cent grafting, %	Efficiency of grafting, %
11	BPO/DPT	0.52	2.09	31.4	1.57	—	—	—
12	AIBN	0.52	0.52	—	—	—	—	—
13	Bu$_3$B	0.53	2.36	50.3	2.21	0.15	3.1	7.9
14	BPO/CoNaph	0.53	0.58	1.1	0.05	—	—	—

[a] Grafting conditions: methyl methacrylate, 5 ml; water, 15 ml; temperature, 37°C; swelling, 15 hr; grafting, 2 hr.

[b] BPO = benzoyl peroxide, 0.24 g; DPT = dimethyl-*p*-toluidine, 0.12 g; AIBN = azobisisobutyronitrile, 0.21 g; Bu$_3$B = tri-*n*-butylborane, 0.10 ml; CoNaph = cobalt naphthenate, 0.24 g.

Effects of Initiator Concentration

Figure 1 shows the effects of initiator concentration on the grafting of MMA by Bu$_3$B onto cotton. As the initiator concentration increased, the percentage of grafting and the total conversion were observed to increase. This would suggest that more grafting sites were generated by adding more initiator. The efficiency of grafting had a maximum point, which could be interpreted by assuming that initiator concentration influenced more the rate of homopolymerization than that of the grafting.
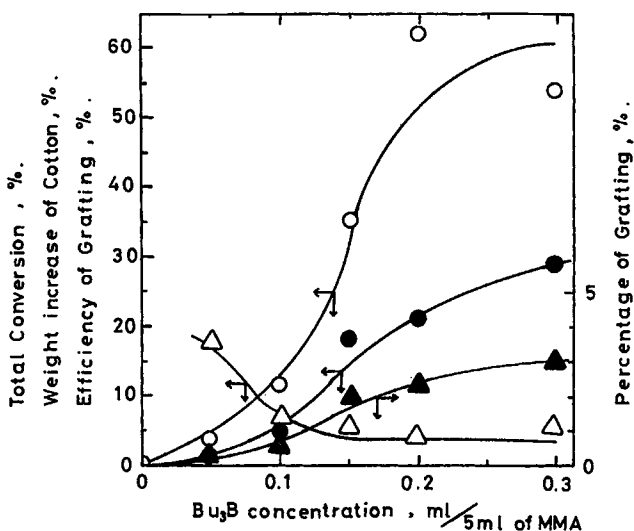
Fig. 1. Effects of initiator concentration: (O) total conversion; (●) weight increase of cotton; (▲) percentage of grafting; (△) efficiency of grafting. Cotton, 0.5 g; MMA, 5 ml; water, 15 ml; swelling, 24 hr; grafting, 2 hr; temperature, 37°C.

Effects of Monomer Concentration

Figure 2 illustrates the dependence of the grafting of MMA by Bu₃B onto cotton on the MMA concentration. The weight increase of cotton became higher with increase in MMA concentration and reached a plateau
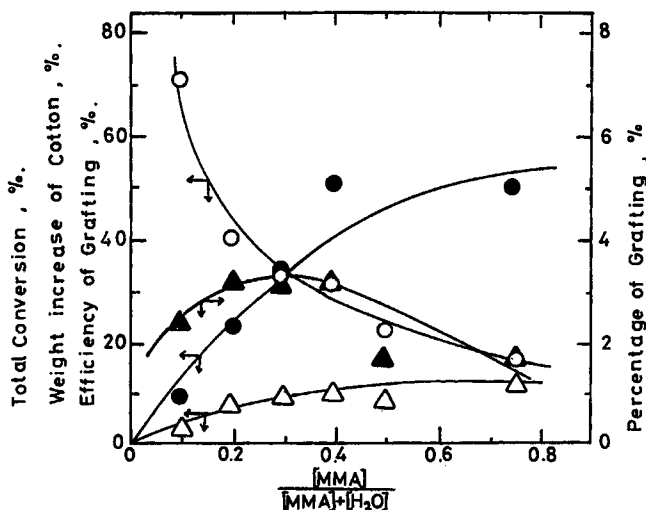

Fig. 2. Effects of monomer concentration: (O) total conversion; (●) weight increase of cotton; (▲) percentage of grafting; (△) efficiency of grafting. Cotton, 0.5 g; Bu₃B, 0.10 ml; (MMA + water), 20 ml; swelling, 24 hr; grafting, 2 hr; temperature, 37°C.

at ca. 3.7 moles/l.   The percentage of grafting also had a maximum point near 2.0 moles/l.   As the MMA concentration increased, the efficiency of grafting increased, while the total conversion decreased.   These results could be explained by assuming that MMA itself is incapable of generating grafting sites, although MMA participates in the generation.   Thus, an increase in the MMA concentration is effective in the grafting, so long as the ratios of MMA to the grafting site are small; and the increase becomes less effective when the MMA concentration is higher.

Reaction Time

Figure 3 presents the relationship between reaction time and the grafting.   As the reaction time became longer, the total conversion and the percentage of grafting increased, while the efficiency of grafting had a
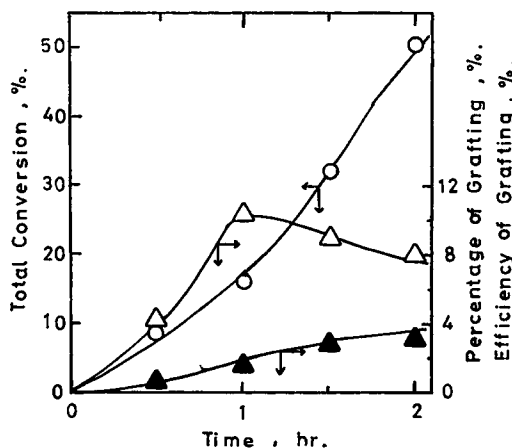

Fig. 3.   Effects of reaction time: (O) total conversion; (▲) percentage of grafting; (△) efficiency of grafting.   Cotton, 0.5 g; MMA, 5 ml; water, 15 ml; Bu₃B, 0.10 ml; swelling, 24 hr; temperature, 37°C.

maximum point at a reaction time of ca. 1 hr.   Reaction time seems to influence more the rate cf homopolymerization than the rate of grafting, as in the case of the effects of initiator concentration.

Reaction Temperature

As Figure 4 shows, reaction temperature positively influenced both the total conversion and the weight increase.   However, the percentage of grafting and the efficiency of grafting were practically constant with increase in reaction temperature.

Solvent Effects

When the grafting procedures were repeated in organic solvents, such as cyclohexanone, *n*-hexane, tetrahydrofuran, and toluene, no weight increase
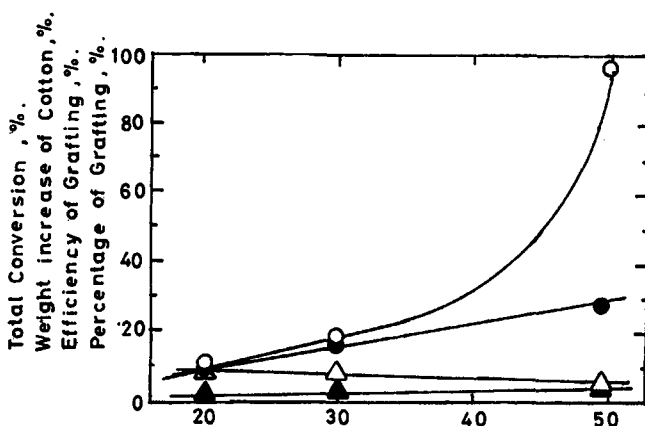
Fig. 4.   Effects of reaction temperature: (○) total conversion;   (●) weight increase of cotton;   (▲) percentage of grafting;   (△) efficiency of grafting.   Cotton, 0.5 g;   MMA, 5 ml;   water, 15 ml;   Bu₃B, 0.10 ml;   swelling, 24 hr;   grafting, 2 hr.

of cotton was observed.   This indicates that water is essential to the grafting.

Pretreatment

As previously reported,[26] pyridine and its derivatives show cocatalytic effects on the Bu₃B-initiated polymerization of MMA.   In order to enhance the efficiency of grafting, we tried to graft MMA onto cotton after dipping cotton into aqueous solutions of pyridine.   The results are summarized in Table II, which shows that the pretreatment was effective. Similar treatment of cotton with acids, such as hydrochloric and phosphoric acids, was ineffective.   However, when the typical grafting procedures were done after adding pyridine to MMA, no cocatalytic effect was observed, although more homopolymer was obtained.

TABLE II
Effects of Pretreatment with Pyridine on the Grafting of Methyl Methacrylate onto Cotton by Bu₃B[a]

Pyridine, %	Cotton, g	Total yield, g	Total conversion, %	Graft, g	Per cent grafting, %	Efficiency of grafting, %
0	0.52	1.77	26.7	0.11	2.4	8.9
5	0.53	1.88	28.9	0.16	3.4	11.7
10	0.51	1.95	30.4	0.19	4.0	13.0
20	0.50	2.64	45.8	0.27	5.7	12.5

[a] Pretreatment, 24 hr;   MMA, 5 ml;   Bu₃B, 0.10 ml;   water, 20 ml;   grafting, 2 hr; temperature, 37°C.

Grafting of Other Vinyl Monomers

The grafting of other vinyl monomers by Bu₃B onto cotton was also investigated under the same conditions.   The results are given in Table

III.   It was found that ethyl acrylate and glycidyl methacrylate were grafted, while practically no grafting occurred when styrene, vinyl acetate, and vinyl pyridine were used.   This order,

$$\text{glycidyl methacrylate} > \text{MMA} \gg \text{vinyl acetate}$$

was also observed in our study on the grafting of vinyl monomers by Bu_3B onto solid blood components.[27]

TABLE III
The Grafting of Vinyl Monomers onto Cotton by Bu_3B[a]

Vinyl monomers	Total yield, g	Total conversion, %	Graft, g	Per cent grafting, %	Efficiency of grafting, %
Methyl methacrylate[b]	2.10	34.1	0.13	2.8	8.3
Glycidyl methacrylate[b]	3.40	53.8	1.77	32.9	61.0
Vinyl acetate[c]	4.90	52.6	—	—	—
Ethyl acrylate[b]	1.09	12.7	0.56	12.1	95.2
4-Vinylpyridine[b]	1.05	10.6	—	—	—

[a] Cotton, 0.50 g; swelling, 15 hr; grafting, 2 hr; temperature, 37°C.
[b] Monomer, 5 ml; Bu_3B, 0.10 ml.
[c] Monomer, 10 ml; Bu_3B; 0.06 ml.

Reaction Mechanism

It is well known that the alkylborane-initiated polymerization of vinyl monomers in the presence of oxygen proceeds via radical mechanism.[14-24] Since the Bu_3B-initiated grafting was carried out in the presence of oxygen and water, the grafting may be assumed to involve free radicals.   This assumption would be quite acceptable, because free-radical polymerization is less sensitive to water than ionic polymerization in general.

It could be possible that grafting sites were generated on cotton by the chain transfer reaction between cotton and active growing chains.   In order to clarify this, the polymerization of MMA by Bu_3B was carried out in the presence of glucose, the monomeric unit of cellulose.   As listed in Table IV, glucose had no influence on the average molecular weights of poly(MMA) within the limit of experimental errors.   This suggests that the generation of grafting sites on cotton is independent of the chain transfer.   As mentioned above, the addition of pyridine to MMA did not promote the grafting, although more homopolymer was obtained.   Since an increase in the number of active species was observed in the polymerization of MMA by Bu_3B–pyridine system[28] (Table V), effects of the chain transfer were assumed to be negligibly small.   The usual radical initiators, such as AIBN, BPO/DPT, and BPO/CoNaph, were ineffective in the grafting (Table I); they initiated the homopolymerization only.   This also suggests that grafting has nothing to do with chain transfer.

TABLE IV

The Polymerization of MMA by Bu_3B in the Presence of Water and Glucose[a]

Run no.	Glucose, g	Poly(MMA)		
		Yield, g	$[\eta]$[b]	$M_v \times 10^{-5}$[b]
90	—	1.18	0.65	1.46
91	0.103	0.80	0.67	1.54
92	0.200	1.33	0.63	1.40
93	0.396	1.30	0.68	1.54
94	0.800	1.54	0.65	1.46
95	1.600	1.48	0.63	1.41

[a] MMA, 10 ml; water, 10 ml; Bu_3B, 0.10 ml; reaction, 2 hr; 37°C.
[b] Determined in chloroform at 25°C (see experimental section).

TABLE V

Cocatalytic Effects of Nitrogen-Containing Compounds on the
Polymerization of MMA by Bu_3B[a,b]

Run no.	Catalytic systems[c]	Yield, %	$[\eta]$	$\bar{M} \times 10^{-5}$
410	Bu_3B	9.2	0.93	2.3
425	Bu_3B/AIBN	8.9	0.92	2.2
426	Bu_3B/DMPT	8.7	0.83	2.0
427	Bu_3B/TEA	5.8	1.28	3.4
428	Bu_3B/Aniline	8.4	0.91	2.2
429	Bu_3B/Pyridine	20.9	0.51	1.1

[a] Ref. 28.
[b] MMA, 3.75 mole/l.; Bu_3B, 8×10^{-3} mole/l.; cocatalyst; 2.4×10^{-2} mole/l.; solvent, cyclohexanone; reaction, 3 hr; temperature, 30°C.
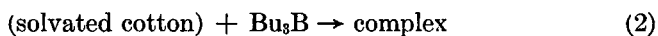[c] AIBN = azobisisobutyronitrile; DMPT = dimethyl-p-toluidine; TEA = triethylamine.

It is interesting to point out again that the presence of water is essential to the grafting, while water reacts with trialkylboranes to form less active hydroxy derivatives (e.g., R_2BOH[14,29]) and finally inert boric acid.[30] No grafting occurred in the usual organic solvents, such as cyclohexanone, n-hexane, tetrahydrofuran, and toluene, although trialkylboranes can initiate polymerization of vinyl monomers in the presence of oxygen in these organic solvents.[14-24] This discrepancy could be interpreted by assuming the following reaction steps:
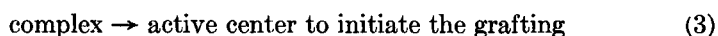Solvation:

$$\text{cotton} + n \cdot H_2O \rightarrow \text{(solvated cotton)} \qquad (1)$$

Formation of the complex:

$$\text{(solvated cotton)} + Bu_3B \rightarrow \text{complex} \qquad (2)$$
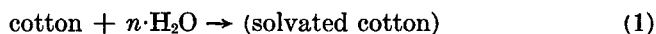
Formation of the active center:

$$\text{complex} \rightarrow \text{active center to initiate the grafting} \qquad (3)$$

Step 1 could be supported by the fact that MMA was grafted onto cotton in the presence of water only.   When cellulose triacetate was treated similarly, no grafting occurred.   The pretreatment of cotton with pyridine seems to promote the solvation.

In step 2, the solvated cotton is assumed to behave as an electron donor. As previously reported,[13,27,31] MMA was found to be grafted onto polymers which contain hydrophilic groups, such as amino and hydroxyl groups.   These polymers are fibers (e.g., silk and wool[13]), hemoglobin,[31] proteins (e.g., albumin and casein[13]), solid blood components,[27] etc.   Participation of vinyl monomers in the formation of the complex could be possible.

As already discussed above, step 3 is assumed to involve free radicals.

Further studies on the reaction mechanism and the grafting are now in progress.

References

1. H. A. J. Battaerd and G. W. Tregear, *Graft Copolymers*, Interscience, New York, 1967.

2. G. Natta, F. Severini, M. Pegoraro, and C. Tavazzani, *Makromol. Chem.*, **119**, 201 (1968).

3. M. Imoto, Y. Iki, Y. Kawabata, and M. Kinoshita, *Makromol. Chem.*, **140**, 281 (1970).

4. Y. Sakaguchi, K. Tamaki, H. Kosaka, and J. Nishino, *Kobunshi Kagaku* (*Chem. High Polym.*), **27**, 741 (1970).

5. Y. Nakamura, O.Hinojosa, and J. C. Arthur, Jr., *J. Appl. Polym. Sci.*, **15**, 391 (1971).

6. I. Sakurada, Y. Ikada, and H. Horii, *Makromol. Chem.*, **139**, 171 (1970).

7. Y. Imai, E. Masuhara, and Y. Iwakura, *J. Polym. Sci. B*, **8**, 75 (1970).

8. G. F. Fanta, R. C. Burr, C. R. Russel, and C. E. Rist, *J. Appl. Polym. Sci.*, **14**, 2601 (1970).

9. G. Odian, R. L. Kruse, and J. H. T. Kho, *J. Polym. Sci. A-1*, **9**, 91 (1971).

10. A. Kantouch, A. Hebeish, and M. H.-Raffie, *J. Appl. Polym. Sci.*, **15**, 1007 (1971).

11. Y. Ogiwara and H. Kubota, *J. Appl. Polym. Sci.*, **14**, 2611, 2879 (1970).

12. E. Masuhara, K. Kojima, N. Tarumi, and Y. Higuchi, *Reports of Research Institute of Dental Materials, Tokyo Medical and Dental University*, Tokyo, Japan, **2**, 788 (1966).

13. K. Kojima, S. Iwabuchi, K. Kojima, and N. Tarumi, *J. Polym. Sci. B*, **9**, 25 (1971).

14. J. Furukawa, T. Tsuruta, and S. Inoue, *J. Polym. Sci.*, **26**, 234 (1957); *ibid.*, **28**, 227 (1958); *ibid.*, **40**, 237 (1959); *ibid.*, *Makromol. Chem.*, **31**, 122 (1959).

15. G. S. Kolesnikov and N. V. Klimentova, *Izvest. Akad. Nauk.*, USSR, 652 (1957); *C.A.*, **51**, 15458 (1957).

16. K. Fujii, T. Eguchi, J. Ukeda, and M. Matsumoto, *Kobunshi Kagaku* (*Chem. High Polym.*), **16**, 519 (1959).

17. C. H. E. Bawn, D. Margerison, and N. M. Richardson, *Proc. Chem. Soc.*, 397 (1959).

18. G. Talamini and G. Vidotto, *Makromol. Chem.*, **50**, 129 (1961).

19. F. J. Welch, *J. Polym. Sci.*, **61**, 243 (1962).

20. E. Masuhara, K. Kojima, and T. Kimura, *Reports of Research Institute of Denta Materials, Tokyo Medical and Dental Univ.*, Tokyo, Japan, **2**, 368 (1962).

21. E. Masuhara, K. Kojima, T. Hirasawa, N. Tarumi, and T. Kimura, *Reports of Research Institute of Dental Materials, Tokyo Medical and Dental University*, Tokyo, Japan, **2**, 457 (1963).

22. F. S. Arimoto, *J. Polym. Sci. A-1*, **4**, 275 (1966).

23. J. Grotewald, E. A. Lissi, and A. E. Villa, *Chem. Commun.*, 21 (1965); *J. Polym. Sci. A-1*, **6**, 3157 (1968); *ibid.*, **7**, 3430 (1969).

24. L. Reich and A. Schindler, *Polymerization by Organometallic Compounds*, Interscience, New York, 1966, p. 431.

25. J. Bischoff and V. Desreux, *J. Polym. Sci.*, **10**, 437 (1953).

26. K. Kojima, Y. Iwata, M. Nagayama, and S. Iwabuchi, *J. Polym. Sci. B*, **8**, 541 (1970).

27. K. Kojima, S. Iwabuchi, K. Kojima, and N. Tarumi, *J. Polym. Sci. B*, **9**, 453 (1971); *ibid., A-1*, **9**, 3213 (1971).

28. K. Kojima, S. Iwabuchi, E. Asami, and Y. Iwata, *J. Faculty of Engineering, Chiba University*, Japan, **22**, 47 (1971).

29. B. M. Mikhailov, V. A. Vaver, and Y. N. Bubnov, *Dokl. Akad. Nauk. SSSR*, **126**, 575 (1959); *C.A.*, **54**, 261e (1960).

30. K. Kojima, Chiba University, unpublished data.

31. K. Kojima, S. Iwabuchi, K. Kojima, and N. Tarumi, *Bull. Chem. Soc. Japan*, **44**, 1891 (1971).