

Homogeneous Graft Copolymerization of Styrene onto Cellulose in a Sulfur Dioxide–Diethylamine–Dimethyl Sulfoxide Cellulose Solvent*

MICHIKAZU TSUZUKI, IKUO HAGIWARA, NOBUO SHIRAISHI,
and TOKUO YOKOTA, *Department of Wood Science and Technology,
Faculty of Agriculture, Kyoto University, Sakyo-ku, Kyoto 606, Japan*

Synopsis

Graft copolymerization of styrene onto cellulose was studied in a homogeneous system (SO₂–DEA–DMSO medium) by γ -ray mutual irradiation technique. At the same time, homopolymerization of styrene was also examined separately in DMSO, SO₂–DMSO, DEA–DMSO, and SO₂–DEA–DMSO media by the same technique. Polymerization of styrene hardly occurs on concentrations above 10 mole SO₂–DEA complex per mole glucose unit. Maximum percent grafting was obtained in concentrations of 4 mole, after which it decreased rapidly. Total conversion and percent grafting increased with the irradiation time. The value (=0.55) of the slope of the total conversion rate plotted against the dose was only a little higher than the $\frac{1}{2}$ which was expected from normal kinetics. No retardation in homopolymerization of styrene in DMSO, SO₂–DMSO, and DEA–DMSO was evident, while the retardation of homopolymerization in the SO₂–DEA–DMSO medium was measurable. Sulfur atoms were detected in the polymers obtained in both of SO₂–DMSO and SO₂–DEA–DMSO solutions. All of the molecular weights of polymers obtained in the present experiment were very low (3.9×10^3 – 1.75×10^4).

INTRODUCTION

A large number of studies on graft copolymerization to cellulose have been reported on heterogeneous systems. It is well known that grafting occurs in amorphous regions of cellulose and not in crystalline regions. Generally speaking the number of branches per cellulose chain is almost less than one or far less than one.^{1–3} Although Stannett et al.⁴ and Yoshimura⁵ reported homogeneous graft copolymerization using cellulose derivatives such as cellulose acetate and allyl-cellulose, no attempt has been made to graft vinyl monomer onto cellulose in a homogeneous system owing to the unavailability of suitable media.

It has recently been reported that natural cellulose is soluble in liquid sulfur dioxide (SO₂) with the addition of amines such as diethylamine (DEA) and triethylamine.⁶ Furthermore, Yamazaki and Nakao⁷ found that cellulose is readily dissolved even in nonaqueous aprotic organic solvents such as dimethyl sulfoxide (DMSO) containing a little amount of SO₂ and various amines.

The purpose of the present investigation is to obtain a graft copolymer having numerous branches per unit cellulose chain. The present paper deals with the first half of the investigation and describes the graft copolymerization of styrene onto cellulose performed in a homogeneous system, a SO₂–DEA–DMSO system, under varying conditions by the γ -ray mutual irradiation technique.

* Presented in part at the 28th Annual Meeting of the Japan Wood Research Society, 4 April 1978, Nagoya, Japan.

EXPERIMENTAL

Material

Whatman cellulose powder CF-11 ($\overline{DP}_n = 228$) was used as a cellulose sample. The Whatman cellulose powder was extracted in a Soxhlet extraction apparatus with ethanol-benzene (1:1) mixture and then with acetone each for 10 hr, then the powder was washed thoroughly with distilled water and vacuum dried at 40°C. Styrene was purified by the conventional method.⁸

Grafting Procedure

Grafting was carried out in a 50-ml flask (Kjeldahl type, long neck). Cellulose (0.2 g) was placed in the flask, to which 20 ml of DMSO with a definite amount of sulfur dioxide, and an amount of DEA equivalent to sulfur dioxide were successively added. After the cellulose was dissolved thoroughly, styrene was added into the polymerization flask. A cycle of freezing, degassing, and melting was repeated three times to remove oxygen from the solution, and then the polymerization flask was sealed. The graft copolymerization was carried out as a homogeneous reaction utilizing a high energy irradiation method (mutual irradiation by ⁶⁰Co γ ray). The dose rate was 1.0×10^4 to 1.3×10^5 R/hr.

Upon completion of the irradiation, the reaction solution was poured into an excess of cold methanol and the precipitate was filtered, washed with methanol, dried under reduced pressure at 40°C, and weighed. Then the sample was extracted with benzene in a Soxhlet extraction apparatus for 24 hr to remove homopolystyrene. After the extraction, the sample was vacuum dried at 40°C and weighed. The weight increase was considered to be due to grafted polystyrene.

Total conversion and percent grafting were calculated according to

$$\text{total conversion (\%)} = \frac{\text{weight of total polystyrene formed (g)}}{\text{weight of the monomer used (g)}} \times 100 \quad (1)$$

$$\text{percent grafting (\%)} = \frac{\text{weight increase after extraction (g)}}{\text{weight of starting cellulose (g)}} \times 100 \quad (2)$$

In the case of homopolymerization, the polymerization procedure was the same as the grafting procedure, except that cellulose was excluded from the reaction system. Conversion of monomer was calculated according to eq. (1).

Molecular Weight Determination

Simadzu GPC 700 was used to obtain molecular weights of the homopolymer. Seven columns packed with porous polystyrene gels having pore sizes of 10^2 , 10^3 , 10^4 , 10^4 , 10^5 , 10^6 , and 10^6 Å were used. The eluent was tetrahydrofuran and flow rate was ~ 1 ml/min.

RESULTS AND DISCUSSION

Figure 1 shows the effect of concentration of the SO_2 -DEA complex on the radiation grafting of styrene onto cellulose. It is well known that liquid sulfur dioxide behaves as an electron acceptor and forms charge-transfer-type complexes with donors such as amines and pyridine. Enomoto et al.⁹ found that polymerization of styrene was strongly retarded when comparable amounts of liquid sulfur dioxide and pyridine were present. The same phenomenon was found by Ishioroshi and Matsuda,¹⁰ when the polymerization of methyl methacrylate in the presence of liquid sulfur dioxide-triethylamine complex was examined. In Figure 1, it can be pointed out that total conversion decreases rapidly when the concentration of SO_2 -DEA complex per mole glucose unit exceeds the value of 4 mole. Polymerization of styrene hardly occurs in concentrations above 10 mole. Although DMSO was used as a diluent in the present experiment, this fact indicates that SO_2 -DEA complex also retards polymerization of styrene. It is also noteworthy from Figure 1 that total conversion in the presence of 3 mole of SO_2 -DEA complex is the same as in the absence of SO_2 -DEA complex. That is to say, it may be presumed that only SO_2 -DEA complexes which do not form ternary complexes⁵ with hydroxyl groups in cellulose participate in the retardation. On the other hand, a maximum percent grafting is obtained with the concentration of 4 mole SO_2 -DEA complex per mole glucose unit, after which it decreases rapidly. Whatman cellulose powder has a very high crystallinity. These crystalline regions are tightly and regularly hydrogen bonded and are consequently inaccessible to the diffusing monomer. Grafting can take place, therefore, only on the surface of these crystalline regions in addition to in the amorphous regions. Accordingly, percent grafting is very low in the absence of SO_2 -DEA complex, when cellulose is not dissolved. It has been well confirmed that the molecular weight of grafted polymer is similar in magnitude to that of homopolymer in a homogeneous graft copolymerization.^{11,12} In this experiment, therefore, the molecular weight of homopolymer is measured and taken as that of the grafted polymer. The molecular weight of the polymer decreases with increase of concentration of SO_2 -DEA complex as shown in Figure 1. This might explain the above-mentioned decrease in the percent grafting and the total conversion in SO_2 -DEA complex concentrations above 4 mole per mole glucose unit. That is, the combined effect of the increase of accessible regions by the

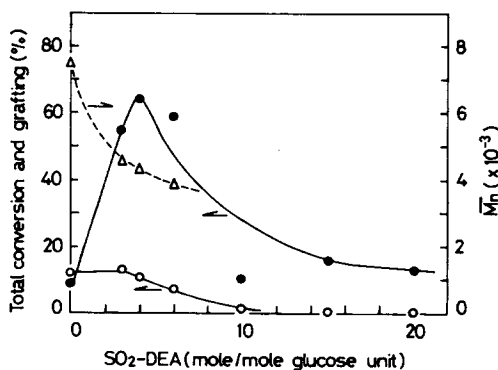


Fig. 1. Effect of SO_2 -DEA concentration on the graft copolymerization onto cellulose. Dose rate: 1.3×10^5 R/hr; irradiation time: 30 hr; styrene content: 20 vol %; (○) total conversion; (●) percent grafting; (Δ) molecular weight of polymer.

use of the SO_2 -DEA solute and the decrease of the molecular weight of the polymer formed with the concentration of SO_2 -DEA results in the maximum which appears in the percent grafting curve. All of the molecular weights of polymers obtained in this system are very low.

Figure 2 shows the effect of irradiation time on the graft copolymerization of styrene onto cellulose. An inflection point, showing a probable change of polymerization rate, appears on the plot of total conversion. This can be explained in terms of the retardation effect of SO_2 -DEA complexes on polymerization. As described above, free SO_2 -DEA complexes which do not associate with hydroxyl groups of cellulose probably retard polymerization of styrene up to the polymerization time of 40 hr. It is seen in Figure 2 that the percent grafting, except that corresponding to the polymerization time of 10 hr, increases linearly with the irradiation time and that the molecular weight of the polymer is kept approximately constant throughout the experimental period. From the fact that the molecular weight of grafted polymer remains constant regardless of irradiation time, the increase in percent grafting is considered to be due to the increase in the number of active sites, that is, the increase in the number of branches per cellulose molecule. The percent grafting is known to level off at high total radiation dose in a heterogeneous graft copolymerization to cellulose, but it is not the case in the present experiment. This is one of characteristic features of this homogeneous graft copolymerization.

The effect of dose rate on graft copolymerization onto cellulose was examined by varying the dose rate from 1.0×10^4 to 1.3×10^5 R/hr, keeping the other conditions constant. The results are shown in Figure 3. Total conversion of styrene decreases with increase in the dose rate. This result may be partly interpreted in terms of radical kinetics because the monomer consumption, i.e., the total conversion, is inversely proportional to the square root of the dose rate. The rate of polymerization or conversion increases with increase in the square root of the dose rate, since the rate of initiation is directly proportional to the dose rate. In practice, as shown in Figure 4, the value ($=0.55$) of the slope of the total conversion rate plotted against the dose rate on a log-log scale is only a little higher than the slope of $\frac{1}{2}$ which is expected from the normal kinetics of radical polymerization. In Figure 3, percent grafting decreases linearly from 130 to 64% with increase in the dose rate from 1.0×10^4 to 1.3×10^5 R/hr. Molecular weight

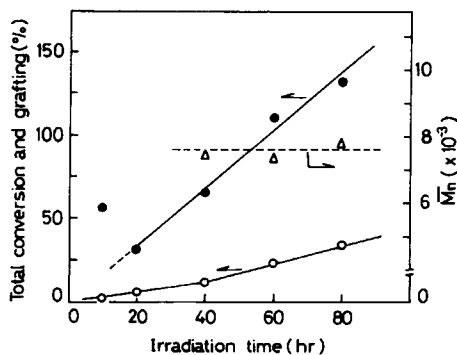


Fig. 2. Effect of irradiation time on the graft copolymerization onto cellulose. Dose rate: 1.0×10^5 R/hr; SO_2 -DEA concentration: 4 mole/mole glucose unit; styrene content: 33.3 vol %; (O) total conversion; (●) percent grafting; (Δ) molecular weight of polymer.

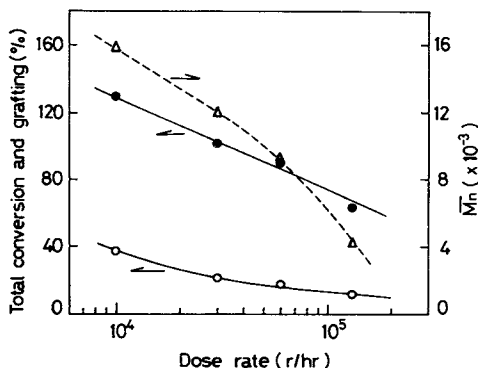


Fig. 3. Effect of dose rate on the graft copolymerization onto cellulose. Total dose: 3.9×10^6 R; SO_2 -DEA concentration: 4 mole/mole glucose unit; styrene content: 20 vol %; (○) total conversion; (●) percent grafting; (Δ) molecular weight of polymer.

of polymer also decreases considerably from 1.6×10^4 to 4.4×10^3 with an increase in dose rate. This result can be also interpreted in terms of radical kinetics in which molecular weight of the polymer is inversely proportional to the square root of the dose rate. In other words, the remarkable decrease of the molecular weight of the polymer can be explained in terms of recombination of shorter growing chain radicals which are generated in large quantities during definite time intervals at high dose rates. Consequently, it is probable that the decrease of percent grafting is mainly attributable to the molecular weight of grafted polymer.

Figure 5 shows the effect of the styrene content on the radiation grafting of styrene onto cellulose. The total conversion is kept almost constant in regions containing more than 20 vol % of styrene. The molecular weight of the polymer increases almost linearly with the styrene content, which can be understood in terms of a kinetic viewpoint. In spite of the increase in the molecular weight of the polymer with the styrene content, the value of percent grafting under these conditions slightly decreases, having a maximum around styrene content of 20 vol %, in contrast with the results of the percent grafting shown in Figure 3. This is due to the decrease in the number of branches per one graft copolymer. In other words, the existence of styrene in large quantities in the reaction system weakens the effect of the SO_2 -DEA complex retarding the polymerization of

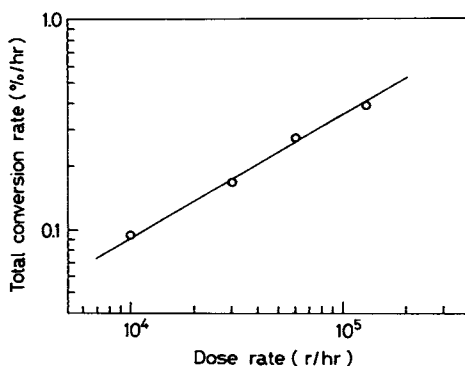


Fig. 4. Influence of dose rate on the total conversion rate of styrene in the graft copolymerization onto cellulose.

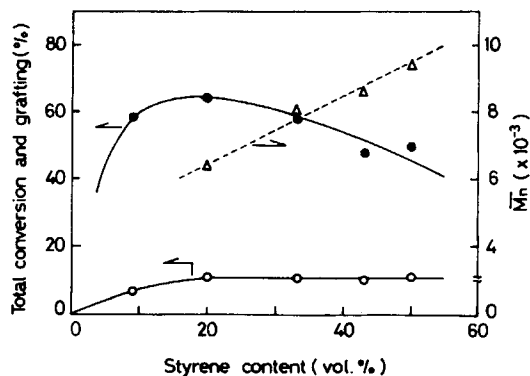


Fig. 5. Effect of styrene content on the graft copolymerization onto cellulose. Dose rate: 1.3×10^5 R/hr; irradiation time: 30 hr; SO_2 -DEA concentration: 4 mole/mole glucose unit; (○) total conversion; (●) percent grafting; (Δ) molecular weight of polymer.

styrene and at the same time generating more active sites on the cellulose chain, which results in an increase in the number of branches per unit cellulose chain.

It has so far been found that polymerization of styrene in the presence of sulfur dioxide yields polysulfone (styrene-sulfur dioxide copolymer).^{13,14} Therefore, it is predictable even at low sulfur dioxide concentrations, such as in the present experiment, that sulfur dioxide is copolymerized and included in the branch and homopolymer. The IR spectra of pure polystyrene and the polymers obtained by the present experiment are representatively shown in Figure 6. Both of the IR spectra for the polymer obtained by the present experiment have clear key bands at 1312 and 1126 cm^{-1} , which do not appear in the spectrum of pure polystyrene and are attributable to stretching vibrations of S—O group. In fact, chemical analyses show that the samples B and C in Figure 6 have 3.7 and 11.9 sulfur atoms per one polymer chain, respectively.

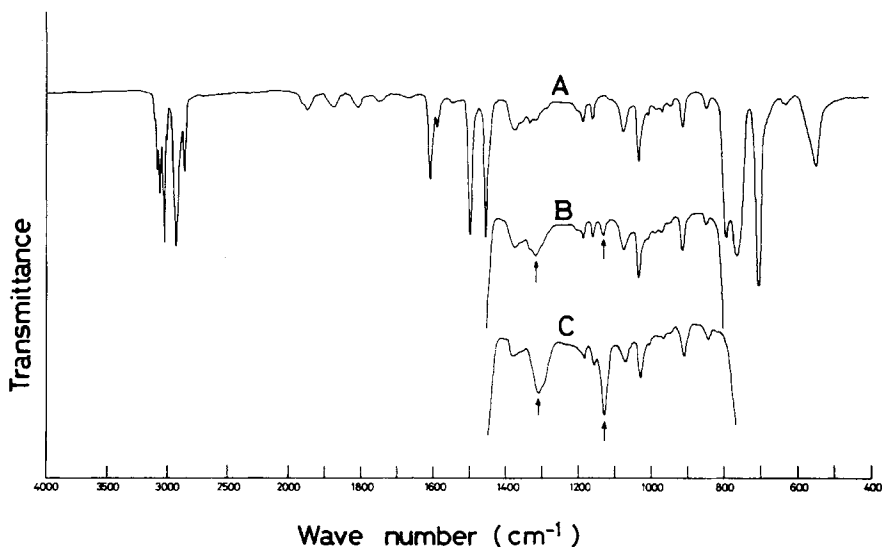


Fig. 6. IR spectra of pure polystyrene (A) and polystyrenes containing sulfur [(B) and (C)]. The number of sulfur atoms per one polymer: (B) = 3.7, (C) = 11.9.

TABLE I
Change of Number of Sulfur Atom per One Polymer Chain Obtained in the Graft Copolymerization^a

Sample code	SO ₂ -DEA concentration ^b	C%	H%	S%	O%	NSP ^c
Calculated value	—	92.31	7.96	—	—	0
CS-0	0	92.18	7.73	0	0.09	0
CS-3	3	87.80	7.54	1.98	2.68	2.1
CS-4	4	87.00	7.48	2.54	2.98	3.1
CS-6	6	84.86	7.41	3.15	4.58	3.8

^a Dose Rate: 1.3×10^5 R/hr; irradiation time: 30 hr; styrene content: 20 vol %.

^b Mole/mole glucose unit.

^c NSP: number of sulfur atoms per one polymer chain.

The effect of the concentration of SO₂-DEA complex on the number of sulfur atoms taken up per unit polymer chain was examined next. The results of the elementary analyses are summarized in Table I. DMSO does not participate in the formation of the sulfur-combined polymer. This is evidenced by the fact that no sulfur atoms were detected in the product formed in the absence of SO₂-DEA complex (sample code: CS-0). However, it is seen that sulfur included in the polymer obtained in the presence of the complex (sample code: CS-3, CS-4, and CS-6) and the number of sulfur atoms per one polymer chain increases slightly with the concentration of the complex. In contrast, nitrogen atoms were never detected in the polymers obtained under various conditions.

Homopolymerization of styrene was carried out in DMSO, SO₂-DMSO, DEA-DMSO, and SO₂-DEA-DMSO systems, separately, keeping the other

TABLE II
Composition of Styrene and Sulfur Dioxide in Polymer Obtained in the Homopolymerization^a

Sample code	Radiation time (hr)	C%	H%	S%	O%	\bar{M}_n ($\times 10^{-3}$)	MSP ^b	St:SO ₂ in polymer
H series (DMSO medium)								
H-1	10	92.06	7.70	—	—	17.6	—	—
H-3	40	92.32	7.73	—	—	20.2	—	—
H-5	80	92.08	7.72	—	—	18.3	—	—
HSO series (SO ₂ -DMSO medium)								
HSO-1	10	83.86	7.21	4.28	4.65	17.5	23.4	6:1
HSO-2	20	84.82	7.19	3.96	4.03	17.3	21.3	7:1
HSO-3	40	86.86	7.35	2.96	2.83	16.3	15.1	10:1
HSO-4	60	86.90	7.46	2.70	2.94	14.1	11.9	11:1
HSO-5	80	88.04	7.40	2.09	2.47	9.6	6.2	14:1
HA series (SO ₂ -DEA-DMSO medium)								
HA-2	20	85.87	7.42	2.61	4.10	6.1	4.9	11:1
HA-3	40	87.83	7.43	1.92	2.82	5.8	3.5	15:1
HA-4	60	89.09	7.47	1.70	1.74	6.9	3.7	18:1
HA-5	80	89.44	7.58	1.42	1.56	7.6	3.4	21:1

^a Dose Rate: 1.0×10^5 R/hr; SO₂ or SO₂-DEA complex: 4 mole/mole glucose unit; styrene content: 33.3 vol %.

^b MSP: number of sulfur atom per one polymer chain.

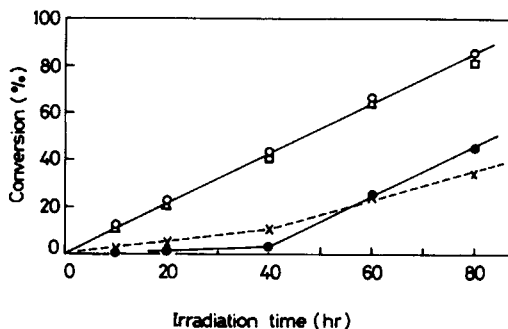


Fig. 7. Time-conversion curves of styrene for graft copolymerization (×) and for homopolymerization in DMSO (○), SO₂-DMSO (△), DEA-DMSO (□), and SO₂-DEA-DMSO (●). Dose rate: 1.3×10^5 R/hr; SO₂-DEA concentration: 4 mole/mole glucose unit; ratio of styrene/DMSO: 10/20 (ml).

conditions constant, i.e., the ratio of styrene/DMSO was fixed at 10/10 ml and the dose rate was 1.0×10^5 R/hr. The results are illustrated with that of graft copolymerization in Figure 7. No retardation in homopolymerization of styrene in the media of DMSO (○), SO₂-DMSO (△), and DEA-DMSO (□) is recognized, while the retardation of homopolymerization in SO₂-DEA-DMSO (●) is evident. An inflection point can be seen on the plot of conversion versus irradiation time for homopolymerization in the presence of SO₂-DEA-DMSO at 40 hr. The appearance of the inflection point is pronounced in comparison with the case of corresponding graft copolymerization shown in Figure 2. It is clear from these results that only the SO₂-DEA complex retards polymerization of styrene and the retardation of polymerization is not caused by SO₂ or DEA alone in DMSO. It should be noted that the slope of the conversion curve obtained for the SO₂-DEA-DMSO system is identical to those obtained in other systems after irradiation time of 40 hr. In comparing the data for homopolymerization with those for graft copolymerization in Figure 7, it can be pointed out that the retardation effect of SO₂-DEA complex on homopolymerization is stronger than that on graft copolymerization up to 40 hr, after which the relationship reverses. In the case of graft copolymerization, the amount of SO₂-DEA complex that is free from the direct involvement in the formation of the complex with cellulose and is considered to be able to take part in strong retardation of polymerization of styrene is equivalent to 1 mole per mole glucose unit, because the other 3 mole equivalents of the complexes have associated with the cellulose thereby dissolving it. We have no evidence that the SO₂-DEA complex forming ternary complex with hydroxyl groups of cellulose does not work as a retardant for the graft copolymerization. However, the results shown in Figure 7 mentioned above reveal that at least the two kinds of the SO₂-DEA complex which exist in the reaction system with or without direct interaction with cellulose act differently as the retardant for grafting.

The results of elementary analysis for the products obtained by the homopolymerization in Figure 7 are summarized in Table II. No sulfur was detected in the polymer obtained by means of polymerization of styrene in DMSO alone (H series). Large quantities of sulfur were recognized in the polymer obtained by utilizing SO₂-DMSO medium (HSO series). It should be noteworthy that in all cases the styrene content in the polymer for HA series is higher (about 1.5

times) than that for HSO series. This fact indicates that the presence of DEA which forms a complex with SO_2 reduces the tendency of styrene polysulfone generation. No sulfur and nitrogen were detected in the polymer obtained in DEA-DMSO. As shown in Table II, molecular weights of the polymer for HA series are much lower than those for the other series. This result shows that the SO_2 -DEA complex also acts as a kind of chain transfer agent and retards polymerization of styrene in the present graft copolymerization. In both of the HSO and HA series, the molecular weight and the contents of sulfur and oxygen are known to decrease with an increase in the radiation time. These facts might indicate a degradation character of styrene polysulfone by γ -ray irradiation as well as a consumption of effective nonassociated SO_2 -DEA complexes during the course of the irradiation grafting.

References

1. R. Y. M. Huang and P. Chandramouli, *J. Appl. Polym. Sci.*, **12**, 2549 (1968).
2. I. Sakurada, Y. Ikada, and Y. Nishizaki, *J. Polym. Sci., Part C*, **37**, 265 (1972).
3. T. Taga and H. Inagaki, *Angew. Makromol. Chem.*, **33**, 129 (1973).
4. H. A. Ende and V. T. Stannett, *J. Polym. Sci., Part A*, **2**, 4047 (1964).
5. S. Yoshimura, *Sen I Gakkaishi*, **21**, 359 (1965).
6. K. Hata and K. Yokota, *Sen I Gakkaishi*, **22**, 96 (1966).
7. S. Yamazaki and O. Nakao, *Sen I Gakkaishi*, **30**, 234 (1974).
8. T. Yokota, T. Nakagami, S. Ito, and N. Tsujimoto, *Mokuzai Gakkaishi*, **18**, 307 (1972).
9. T. Enomoto, M. Iino, M. Matsuda, and N. Tokura, *Bull. Chem. Soc. Jpn.*, **44**, 3140 (1971).
10. Y. Ishioroshi and M. Matsuda, Nineteenth Polymer Symposium, Kyoto, 1970, 20B08.
11. V. T. Stannett, J. D. Wellons, and H. Yasuda, *J. Polym. Sci., Part C*, **4**, 551 (1965).
12. K. Matsuzaki, S. Nakamura, and H. Tsukamoto, *Sen I Gakkaishi*, **26**, 560 (1970).
13. W. G. Barb, *Proc. R. Soc. London, Ser. A*, **212**, 66, 177 (1952).
14. M. Matsuda and M. Iino, *Macromolecules*, **2**, 216 (1969).

Received November 29, 1979

Accepted April 4, 1980