

# Controlled Degradation of Polystyrene

SYOAKI IDE, TAICHI OGAWA,\* TAKESHI KUROKI,<sup>†</sup> and TADASHI IKEMURA, *Department of Industrial Chemistry, College of Science and Technology, Nihon University, 1-8 Kandasurugadai, Chiyoda-ku Tokyo 101, Japan*

## Synopsis

For the purpose of efficient utilization of waste polystyrene, the recovery method of a styrene oligomer having a molecular weight of 1000–3000 was studied. Thermal and catalytic degradations were carried out. It was impossible to obtain a styrene oligomer with a molecular weight less than 5000 by thermal degradation in the temperature range of 300–500°C. Catalytic degradation in the presence of silica–alumina catalyst in the temperature range of 190–230°C made it possible to control the decrease in molecular weight and to obtain a styrene oligomer having a molecular weight of 500–3000. Simultaneously, the molecular structures of the reaction products from thermal and catalytic degradations were determined by NMR analysis.

## INTRODUCTION

Since styrene oligomers are very useful as industrial additives and prepolymers, the method for their synthesis has been extensively studied.<sup>1,2</sup> Although specific conditions are generally required to synthesize these oligomers, no simple method has yet been found.

It is evident that styrene dimers and trimers are easily obtainable by the successive thermal degradation of polystyrene.<sup>3</sup> An attempt, however, to obtain a styrene oligomer having a molecular weight of 1000–3000 has not been carried out so far. A method for obtaining oligomers by degradation reactions makes it possible to control the degree of polymerization and terminal structures, thus should warrant attention.

A detailed investigation was made of a means for controlling the decrease in molecular weight during polystyrene degradation when synthesizing styrene oligomers. Reactions were carried out as one of a series of fundamental investigations<sup>4,5</sup> to recover useful constituents from waste polystyrene discarded by factories.

## EXPERIMENTAL

Two samples were used in the present work: one of them was styrene oligomer having a number average molecular weight ( $\bar{M}_n$ ) of about 3000 supplied by Tomoegawa Co., Ltd., and the other was polystyrene of an article on the market having an  $\bar{M}_n$  of about 93,300 supplied by Asahi Daw Co., Ltd. These samples were purified before use by several reprecipitations

\* Present address: Department of Chemistry, University of North Dakota, Grand Forks, ND 58202.

<sup>†</sup> Present address: 1-10-1 Shinmachi, Hoya-shi Tokyo 202, Japan.

from benzene solution by methanol and methylethylketone by methanol to exclude impurities.

The catalyst employed in the present work was supplied by Catalysts and Chemicals I.N.D. Co., Ltd. It contained 13% alumina and 87% silica. This catalyst was crushed to about 100-mesh size particles and calcinated in a stream of air at 540°C for 3 h before use.

Apparatus for the thermal degradation was a specific flow reactor, which was the same reported in the preceding paper.<sup>3</sup> That for the catalytic degradation was a Pyrex glass tube, as shown in Figure 1, which consisted of a reactor section and a trap section of the volatiles by liquid nitrogen. The procedure was as follows: Approximately 200 mg of a blend of the sample and catalyst, which were previously stirred and mixed, was enclosed in the Pyrex glass tube, and then the air in the reactor was evacuated by a vacuum pump, displaced with nitrogen to remove oxygen, and the system was shut at the end. And then a reactor was put into a metal bath which was kept at a constant temperature. The reaction conditions were temperature 190–220°C and reaction time 0.25–5 h, respectively. After the reaction was over, the residue in the reactor tube was dissolved in chloroform, and then the catalyst was filtered with a glass filter. Products collected in this way were used for the analysis.

Three instruments were mainly used for identifying the reaction products. In order to make an analysis of the volatiles, gas chromatography (Shimadzu, GC-6A) was used, with a column 3 mm × 3000 mm in length, with 15% Apiezon grease L supported on Chromosorb WAW (60–80 mesh). On the other hand, an analysis of the residue in the reactor was carried out using GPC (Toyo soda, HLC, 802 UR) and PFT-<sup>1</sup>H- and <sup>13</sup>C-NMR (Hitachi, Jeol, JNM-FX100). Conditions for the GPC and NMR (<sup>1</sup>H-) measurements for the analysis were as follows:

**GPC.** column, GMH<sub>6</sub> × 2 + G4000H<sub>8</sub>; column size, 7.5 mm I.D. × 600 mm; solvent, chloroform; flow rate, 1.2 mL/min; pressure, 5.6 kg/cm<sup>2</sup>; temperature, 41°C; detector, differential refractometer. The sample concentration was approximately 0.5% (w/v). The average molecular weight of the degraded polystyrene was determined according to the calibration curves obtained with some standard polystyrenes.

**NMR.** Solvent, chloroform-*d* (E. Merk, Uvasol, purity, 99.8% over); internal standard for chemical shifts, tetramethylsilane (TMS); sample concentration, about 10% (w/v); temperature, room temperature; spectral

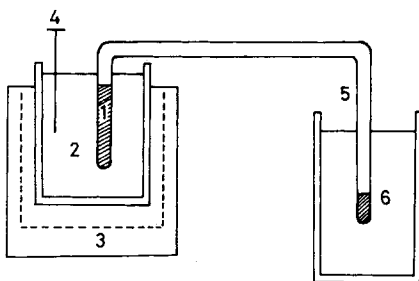


Fig. 1. Apparatus for the catalytic degradation of polystyrene: (1) reactor; (2) metal bath; (3) electric furnace; (4) thermocouple; (5) trap; (6) liquid nitrogen cooling bath.

width, 1 kHz; data points, 8192; pulse width, 8 s (a 45° pulse); pulse repetition, 10 s; number of transients, 2000–4000.

## RESULTS AND DISCUSSION

### Changes in Molecular Weight in the Thermal Degradation of Polystyrene

The thermal degradation of polystyrene generally occurs in two stages: in the first, a random scission takes place at "weak points"<sup>6,7</sup> in the main chain, and, in the second stage, formed short chains depolymerize, causing a loss in molecular weight. In the second stage, it is known that this decrease in molecular weight takes on a fixed value, since, after decreasing to a certain value, no further decrease can be detected.<sup>8–10</sup> During this process, many volatile products are formed, but the details of the reactions involved are not known. Since these reactions generally require considerable time, they are accompanied by complex secondary reactions, which make it impossible to know the initial process of each reaction.

However, we have developed a special flow reactor system for decomposing vinylic polymer and have used it to degrade polystyrene over a period of a few seconds and analyze the process of molecular weight decrease.<sup>11</sup> The process of the decrease in molecular weight in the thermal degradation of polystyrene in the range from 310°C to 390°C is shown in Figure 2. It can be seen from this figure that, with an increase in reaction temperature, the molecular weight of the degraded polystyrene tends to decrease. However, the decrease in molecular weight stopped at approximately 5000. As the reason for this, it is suggested that the intermolecular radical transfer of the polymer or small volatile radicals, formed during the molecular weight decrease, does not almost contribute to the  $\beta$ -scission of on-chain radicals. Another reason is that unzipping and backbiting reactions precede the intermolecular radical transfer of on-chain radicals in the later stage of reaction.

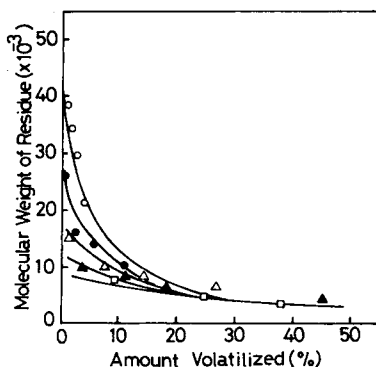


Fig. 2. Change in molecular weight in the thermal degradation of polystyrene: (○) 310°C; (●) 300°C; (△) 350°C; (▲) 370°C; (□) 390°C.

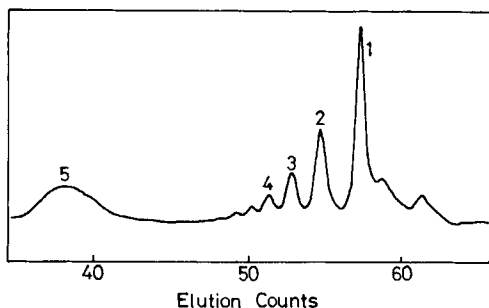
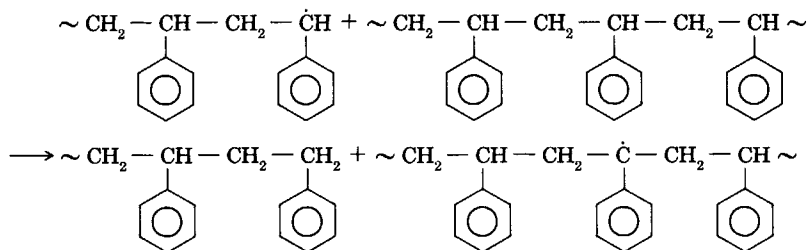


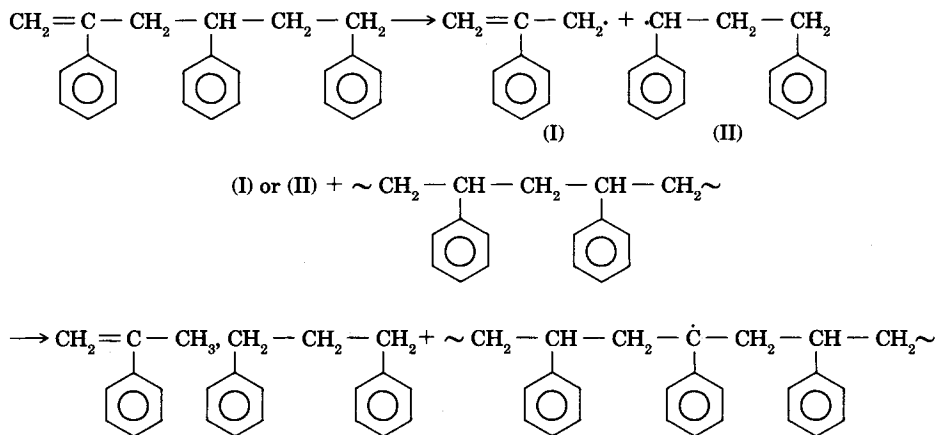
Fig. 3. GPC of the vacuum residues in the thermally degraded polystyrene: (1) trimer; (2) tetramer; (3) pentamer; (4) hexamer; (5) oligomers having a molecular weight of about 3000.

The results of the GPC analysis of the styrene oligomer from decomposed polystyrene are shown in Figure 3. The peaks of some of the styrene oligomers of lower molecular weight corresponding to 3–6 monomer units appear at elution counts from 50 to 60. Also, the peak of an oligomer having a molecular weight of 3000 appears near an elution count of 38. However, the total yield of these oligomers was 3% or less of all the degradation products.

Thus, it is impossible to obtain a styrene oligomer with a molecular weight less than 5000 by the thermal degradation of polystyrene. The reason why the decrease in molecular weight cannot be made to stop may possibly be that many volatile products are formed at the end of the polymer backbones, and the intermolecular radical transfer of the polymer or small volatile radicals, as indicated in the following scheme, does not contribute to scission of the main chain:



The volatile products formed consist primarily of the styrene monomer, dimer, and trimer which are stable constituents not having radicals and do not contribute to an intermolecular radical transfer.<sup>3</sup> However, as can be seen from Table I, the volatile products at 450°C and 500°C consisted of constituents such as toluene,  $\alpha$ -methylstyrene, and 1,3-diphenylpropane which are stabilized by the extraction of hydrogen radicals. From these findings, it follows that the concentration of small volatile radicals should increase. These radicals are stabilized only by intermolecular radical transfer. As Cameron indicated,<sup>12</sup> stabilization of small volatile radicals becomes possible primarily through the extraction of tertiary hydrogen in the polystyrene main chain as shown in the following scheme:



The successive occurrence of these reactions should result in a continual decrease in molecular weight. But actually, the molecular weight of polystyrene backbones does not decrease below 5000 as evident from Figure 2. Stabilization by intermolecular hydrogen extraction by small volatile radicals must contribute to the formation of internal olefins rather than the  $\beta$ -scission.

Thus, it is apparent that obtaining styrene oligomers of molecular weight less than 5000 by polystyrene thermal degradation is quite difficult.

#### Catalytic Degradation of Polystyrene in the Presence of a Silica-Alumina Catalyst

Figure 4 shows the results of the catalytic degradation of polystyrene with a silica-alumina catalyst at 190°C to 200°C. In this case, it is assumed that the melted polystyrene does not come into sufficient contact with the

TABLE I  
Data on Thermal Degradation of Polystyrene by Using a Flow Reactor System

Reaction temp (°C)	350	400	450	500
Residence time (s)	4	4	4	4
Process period (min)	65	72	72	74
Sample feed rate (g/min)	0.27	0.23	0.23	0.21
Products yield (wt % polystyrene)				
Gaseous products	—	—	0.1	0.1
Toluene	—	—	0.7	0.9
Ethylbenzene	—	—	0.2	0.4
Styrene	35.4	50.1	58.5	64.5
$\alpha$ -Methylstyrene	—	—	1.7	1.8
Diphenylmethane	—	—	0.5	1.5
1,2-Diphenylethane	—	—	0.5	1.3
1,3-Diphenylpropane	—	—	0.6	0.9
2,4-Diphenyl-1-butene	12.3	9.5	8.8	7.2
1,3-Diphenyl-2-butene	—	—	1.5	1.6
2,4,6-Triphenyl-1-hexene	24.9	18.2	5.3	2.0
Isomeric trimer	—	—	1.4	—
Residue <sup>a</sup>	11.6	9.3	10.5	7.8
Reactor residue and weight losses	15.8	12.9	9.7	10.0

<sup>a</sup> Retained in the GLC column.

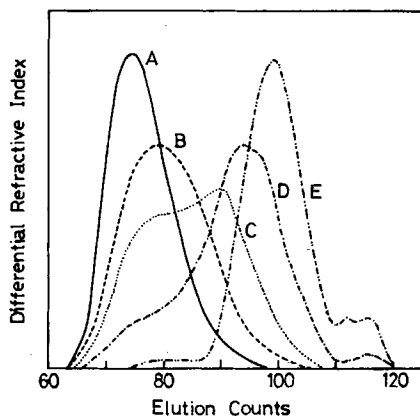


Fig. 4. GPC of the catalytic degraded polystyrene: (A) original; (B) 190°C; (C) 200°C; (D) 210°C; (E) 220°C.

catalyst. But, as indicated in Figure 4, the molecular weight distribution of degraded polystyrene undergoes much change. The yield of the volatile products was less than 20 wt % regardless of the reaction conditions. Thus, scission of the main chain takes place more than volatile product formation in catalytic degradation. The molecular weight shown by the GPC curves for each reaction temperature decreases rapidly in the high temperature region accompanied by the formation of numerous volatile products. Curves C, D, and E show some of the features of the molecular weight distribution. For instance, curve C is particularly broad and seems to have two peaks. But at a high reaction temperature and long reaction time, the long chains in the high molecular weight region gradually crack into oligomers of fixed low molecular weight. The volatile products formed at this time are mainly benzene and indan derivatives substituted by methyl groups. The number average molecular weight ( $\bar{M}_n$ ) calculated from the calibration curve is approximately 3000 at 210°C and 1000 at 220°C. From these results, it is evident that, although the decrease in molecular weight cannot be controlled in the thermal degradation of polystyrene, it can be done by catalytic degradation.

Furthermore, the molecular weight decrease of styrene oligomers of about 3000 in molecular weight could be observed in detail. In Figure 5, degradation through only heat causes a virtually undetectable decrease in molecular weight. But, in catalytic degradation throughout the temperature region from 190°C to 220°C, the decrease in molecular weight is remarkable, particularly at high temperatures. This was also observed by a change in molecular weight distribution. In particular, the low molecular weight oligomers ranged from about 100 to 1000 in this region accompanied by an increase in distribution. The number average molecular weight over a period of 3 h at 220°C was approximately 500. This is a very low molecular weight compared with that for the long chain molecules in Figure 4. The effect of reaction time on the change in molecular weight distribution is shown in Figure 6. This figure also shows that the molecular weight distribution curve of catalytic degraded polystyrene shifts with very small changes in form, toward a low molecular weight distribution side with rising

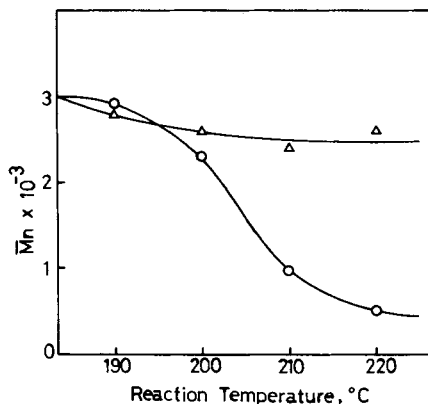


Fig. 5. Comparison of the molecular weight decrease between thermal and catalytic degradation of styrene oligomer (reaction time, for 3 h): ( $\Delta$ ) thermal degradation; ( $\circ$ ) catalytic degradation.

temperature. However, the change in the distribution of degraded styrene oligomers by catalytic degradation was different at the beginning and end of the reactions. That is, the change was less with reaction time, probably because of deactivation of the catalyst itself.

On the basis of the findings presented above, it is evident that the decrease in molecular weight can be controlled through the proper choice of catalyst.

### NMR Analysis of Reaction Products from Thermal and Catalytic Degradation

To study the molecular structure of the styrene oligomers obtained from thermal and catalytic degradation, the NMR spectra of the reaction products were measured. Figures 7 and 8 show the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of the reaction products. The main resonances were assigned on the basis of the data of Inoue et al.<sup>13</sup> as follows:  $^1\text{H}$ -NMR: 1.48 ppm, methylene proton; 1.82 ppm, methin proton; 6.58 ppm, ortho-position proton of phenyl groups;

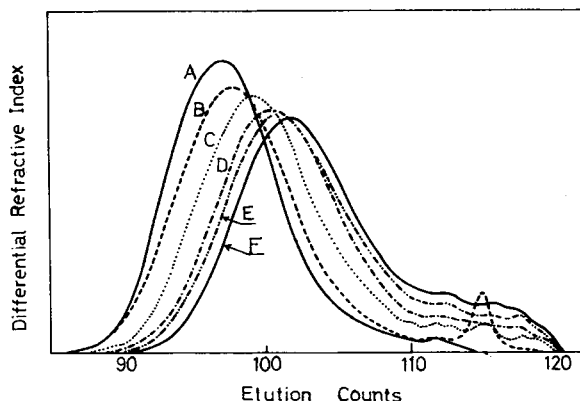


Fig. 6. Change in GPC curves of the catalytic degraded styrene oligomer with reaction time: (A) original; (B) 1 h; (C) 2 h; (D) 3 h; (E) 4 h; (F) 5 h.

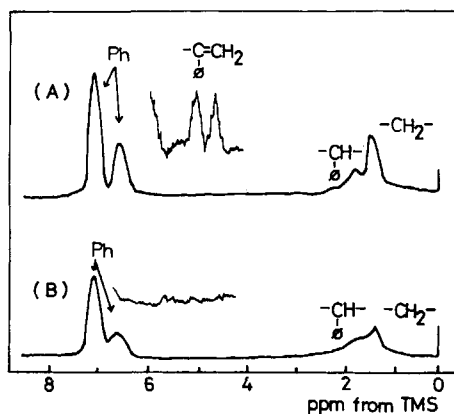


Fig. 7. <sup>1</sup>H-NMR spectra of the thermally degraded polystyrene (A) and the catalytic degraded polystyrene (B).

7.07 ppm, meta- and para- position protons of phenyl groups. <sup>13</sup>C-NMR: 40.3 ppm, methin carbon; 43.5 ppm, methylene carbon; 125.6 ppm, para-position carbon of phenyl groups; 127.8 ppm, ortho- and meta-position carbon of phenyl groups; 145.2 ppm, quarternary carbon of phenyl groups.

In the <sup>1</sup>H-NMR spectra, two multiplet signals were detected near 4.73 and 5.08 ppm in the spectrum of the thermal degradation products shown in Figure 7(A). These resonances were assigned to the terminal vinylidene type olefins on the basis of a comparison of the chemical shifts of styrene oligomers (2,4-diphenyl-1-butene, 2,4,6-triphenyl-1-hexene, etc.) as model compounds. The terminal olefin appeared as two unequivalent proton resonances due to the influence of neighboring methylene and phenyl groups, and was formed through either an intramolecular or intermolecular radical

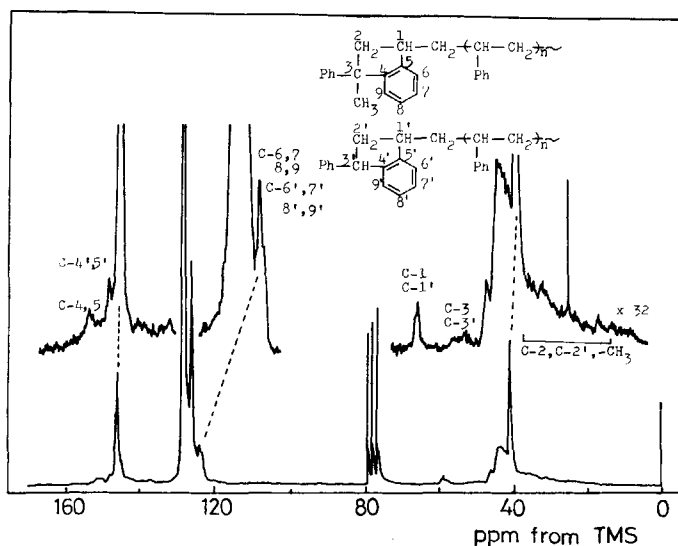
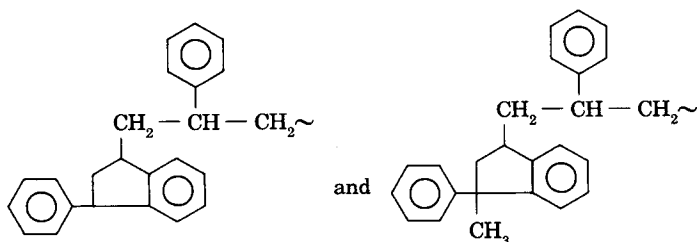


Fig. 8. <sup>13</sup>C-NMR spectra of the catalytic degraded polystyrene.



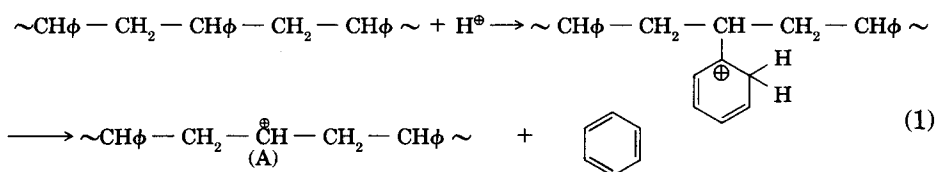
transfer followed by a  $\beta$ -scission of the main chains in the propagation reaction.<sup>14</sup>

But as can be seen from Figure 7(B), the spectrum of the catalytic degradation products did not have these proton resonances of the terminal olefin. In the <sup>13</sup>C-NMR spectrum shown in Figure 8, specific resonances were detected at 49.8, 58.1, 123.5, 147.5, and 150.9 ppm, but could not be detected in the spectrum of the original polystyrene and the thermally degraded polystyrene. These resonances were assigned according to changes in the volatile product composition (the main products were indan derivatives substituted by methyl groups) and a comparison of the chemical shifts of styrene oligomers and certain indan substituted by methyl and phenyl groups as model compounds. From these results, the catalytically degraded terminal structures were determined as the following:

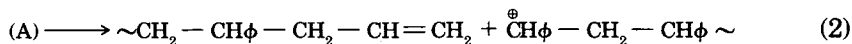


These indan skeletons at the ends of the main chains must be in intramolecular rearrangement reaction of on-chain carbonium ions produced during catalytic degradation of polystyrene. The formation of these indan skeletons is to be proceeded by an ionic reaction mechanism.

Most possible catalytic degradation routes of polystyrene in the presence of silica-alumina catalyst are considered to be the following. The reaction is initiated by the proton addition reaction to the phenyl groups of the side chain.<sup>15</sup> The reaction mechanism involving this reaction is indicated by



An on-chain carbonium ion produced by an elimination reaction of a phenyl group is stabilized mainly by the  $\beta$ -scission of the main chains as shown by



It is suggested that methylindan derivatives of main volatile products are formed by way of an intramolecular rearrangement reaction of a carbonium ion formed at the chain end as shown by eq. (2). Schematic reactions for the formation of methylindan derivatives are indicated as shown in the following equations:



10. G. G. Cameron and J. R. MacCallum, *Review in Macromolecular Chemistry*, G. B. Butler et al., Eds., Marcel Dekker, New York, 1967.
11. T. Kuroki, T. Ikemura, T. Ogawa, and Y. Sekiguchi, *Polymer*, **23**, 1091 (1982).
12. G. G. Cameron, *Makromol. Chem.*, **100**, 255 (1967).
13. Y. Inoue, A. Nishioka, and R. Chujo, *Makromol. Chem.*, **156**, 207 (1972).
14. L. A. Wall and J. H. Flynn, *Rubber Chem. Tech.*, **35**, 1157 (1967).
15. S. Ide, H. Nanbu, T. Kuroki, and T. Ikemura, *J. Chem. Soc. Jpn.*, **1983**, 1657.

Received July 20, 1983

Accepted December 23, 1983