

Graft Copolymerization of Methyl Methacrylate onto Polypropylene Oxidized with Ozone

JUN YAMAUCHI,^{1,*} AKIYOSHI YAMAOKA,² KUNJI IKEMOTO,² and TETSUJI MATSUI³

¹College of Liberal Arts and Sciences, Kyoto University, Kyoto 606, Japan, ²Himeji Institute of Technology, Shosha, Himeji 671-22, Japan, and ³Kobe City College of Technology, Maikodai, Tarumi-ku, Kobe 655, Japan

SYNOPSIS

After the reaction of polypropylene by ozone oxidation, methyl methacrylate was graft-copolymerized onto the polypropylene. The active species determined by ESR spectroscopy as a peroxy radical was converted to hydroperoxide, and the hydroperoxide was broken by heating, giving alkoxy and hydroxyl radicals, the former of which initiated graft copolymerization. The effect of the ozone-oxidation time and polymerization time on the graft copolymerization was investigated. At the constant polymerization time, the total conversion and the degree of the grafting increased with the ozone-oxidation time, while the graft efficiency decreased. On the other hand, at the constant oxidation time, the total conversion and the degree of grafting increased with the polymerization time, while the graft efficiency decreased. These results were compared with a polyethylene case. The mechanism of the ozone oxidation and the initiation of the graft copolymerization were also discussed.

INTRODUCTION

With graft copolymerization onto polypropylene or polyethylene, it has been found that when using benzoyl peroxide or azobisisobutyronitrile radical polymerization would not be initiated and, also, that the introduction of functional groups by means of a polymer reaction would be very difficult. It has been reported that the introduction of active species onto polymers by using radiation¹⁻⁵ or oxidation⁶⁻⁹ was very useful for this purpose. Since those methods using radiation are very expensive and not easy to handle, the introduction of the active species using the oxidation reaction is commercially hopeful. Moreover, the methods using oxidation have the merit that fewer homopolymers are produced, because the active species are formed on the trunk polymer in these methods. As one of the most advantageous methods, ozone oxidation would be applicable to graft copolymerization onto polyethylene or polypropylene.

Recently, we have reported graft copolymerization of methyl methacrylate onto polyethylene oxidized with ozone.¹⁰ The results were discussed in terms of the ozone-oxidation and polymerization times, and the oxidation mechanism was investigated. In the present paper, polypropylene was oxidized with ozone, followed by graft copolymerization with methyl methacrylate. The effect of the ozone-oxidation and polymerization times on the graft copolymerization was also investigated and compared with the polyethylene case. Previously, we have confirmed active species by ESR in the cases of polyethylene¹⁰ and polypropylene,¹¹ that is, peroxy radicals were formed on those polyolefins when they were treated with ozone.

EXPERIMENTAL

Materials

Powdered polypropylene (100 mesh-free) was used for copolymerization. Methyl methacrylate (MMA) was refined from a first-grade reagent with a conventional method.

* To whom correspondence should be addressed.

Ozone-Oxidation Method

Ozone was evolved using a silent discharge through an oxygen current. Polypropylene was oxidized through the ozone current (30 g/m^3) at 30°C for the prescribed hours.

Measurements of ESR Spectra

ESR measurements were carried out using an ME-3X spectrometer (Japan Electron & Optics Laboratory) at room temperature and at 77 K. The sample of fibrous polypropylene (100–200 mg) was put into a quartz tube, 10 mm in diameter, which was inserted into the ESR cavity. The ozone current was introduced into the quartz tube during the ESR measurement.

Determination of Hydroperoxide

The determination of hydroperoxide was made according to Chien et al.'s method.¹² The polypropylene oxidized with ozone (0.5 g) was immersed in benzene (5 mL) to swell for 60 min. Isopropyl alcohol (10 mL) containing acetic acid anhydride (0.5 mL) and potassium iodide (0.125 g) was added. Then, the solution was refluxed for 5 min and titrated with N/50 sodium thiosulfate. The content of hydroperoxide was calculated from the amount of isolated I_2 .

Measurements of IR Spectra

Infrared spectrum of polypropylene film was obtained with a IR-27G spectrometer (Shimadzu Seisakusho Co.). The intensity of IR absorption was calculated using the usual base-line method.

Method of Graft Copolymerization

Powdered polypropylene (0.2 g) oxidized with ozone was weighed out accurately and placed in a test tube with MMA (2 mL), which was frozen in a dry ice/methanol bath. After air was replaced with nitrogen, the sample was enclosed in the test tube under reduced pressure. The test tube was placed into a water bath controlled at a given temperature and polymerized for the prescribed time. The polymer was precipitated by the addition of methyl alcohol, filtered with a glass filter, and dried for several days. This polymer's weight was defined as W_3 . The polymer was then boiled in acetone for 7 days, and homopolymer was removed. Acetone was replaced every day. Residues were filtered off and dried. We

regarded those residues as graft copolymer. This weight was defined as W_4 . The initial sample and monomer weights were defined as W_1 and W_2 , respectively. Then, total conversion (TC), degree of grafting (DG), and graft efficiency (GE) were calculated from the following equations:

$$TC = \frac{W_3 - W_1}{W_2} \times 100 (\%) \quad (1)$$

$$DG = \frac{W_4 - W_1}{W_1} \times 100 (\%) \quad (2)$$

$$GE = \frac{W_4 - W_1}{W_3 - W_1} \times 100 (\%) \quad (3)$$

Measurements of Molecular Weight by Means of Viscometry

1. Polypropylene trunk polymer: Viscosities were measured at 135°C by using an Ubbelode-type viscometer and decaline as a solvent. Intrinsic viscosities were given using Huggins' equation (Huggins' constant $k' = 0.36$). Molecular weight was calculated from Parrini's equation¹³:

$$[\eta] = 0.80 \times 10^{-4} \times M^{0.80} \quad (4)$$

2. Homopoly (methyl methacrylate): Viscosities were measured at 25°C by using an Ubbelode-type viscometer and methyl ethyl ketone as a solvent. Intrinsic viscosities were given using Huggins' equation (Huggins' constant $k' = 0.39$). Molecular weight was calculated from the following equation:

$$[\eta] = 0.79 \times 10^{-4} \times M^{0.72} \quad (5)$$

Calculation of Number of Branches

The number of branches (NB) was calculated from the mol ratio of the branch polymer to the trunk polymer.

RESULTS AND DISCUSSION

Ozone-Oxidation Mechanism and Effect of Ozone-Oxidation Time on Total Conversion, Degree of Grafting, and Graft Efficiency

Table I shows total conversion (TC), degree of grafting (DG), and graft efficiency (GE) when the

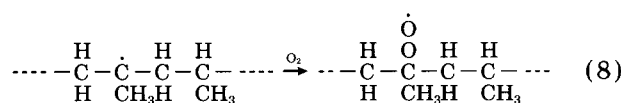
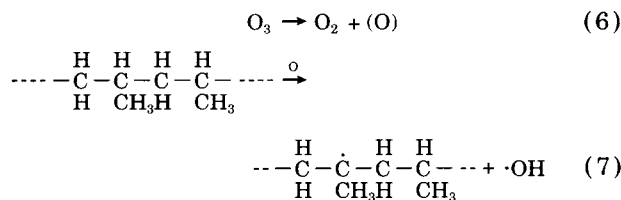
Table I Total Conversion (*TC*), Degree of Grafting (*DG*), and Graft Efficiency (*GE*) Depending on Oxidation Time

Oxidation Time (min)	<i>TC</i> (%)	<i>DG</i> (%)	<i>GE</i> (%)
30	29	203	73
60	40	232	63
90	46	240	54

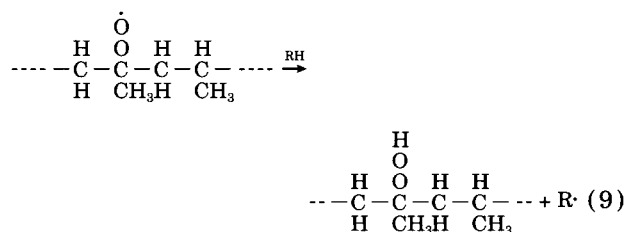
Sample: polypropylene oxidized with ozone; monomer: methyl methacrylate; polymerization conditions: 60°C, 60 min.

polypropylene oxidized with ozone for 30, 60, and 90 min was graft-copolymerized with MMA for 60 min. It is clear that the polypropylene that was not oxidized with ozone gave no graft copolymer, whereas the oxidized polypropylene was easily graft-copolymerized, and that *TC* and *DG* increased with the oxidation time.

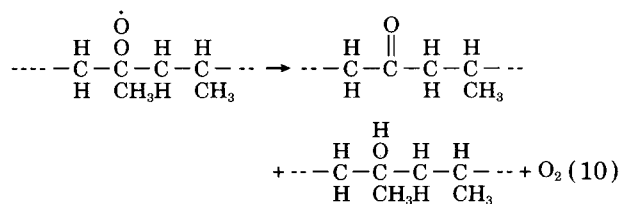
The results of Table I, together with IR and ESR data discussed later, would suggest the following reaction mechanism: When polypropylene is oxidized with ozone, carbon and hydroxyl radicals are made from the active oxygen atom formed upon decomposition of ozone. The carbon radical reacts immediately with an oxygen molecule, giving a peroxy radical:



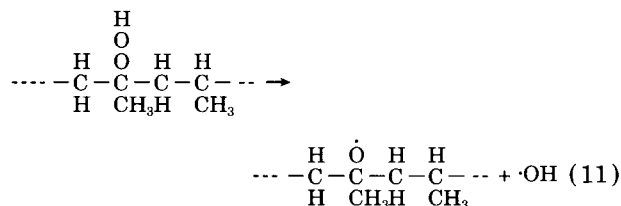
A part of the peroxy radicals gives hydroperoxide by pulling out the hydrogen atom of polypropylene:



Another part of the peroxy radicals gives inert substances such as alcohol or ketone by recombination:



The O—O bond of the hydroperoxide given in reaction (9) is broken by heating, and thus the hydroperoxide gives alkoxy and hydroxyl radicals as follows:



The alkoxy radical and the hydroxyl radical thus obtained would initiate polymerization as active sites and give graft copolymer and homopolymer, respectively.

The presumed mechanism mentioned above would be supported by the determination of hydroperoxide and the measurements of IR and ESR spectra. Figure 1 shows that the concentration of hydroperoxide increased linearly with the oxidation time. This result surely supports reactions (7)–(10). Because the alkoxy radical formed in reaction (11) is proportional to the ozone-oxidation time, both *TC* and *DG* increased with the oxidation time. Figures 2 and 3 exhibit variations of IR spectra of poly-

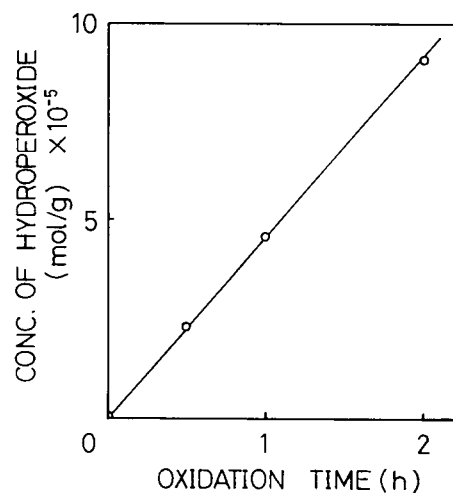


Figure 1 Relationship between oxidation time and concentration of hydroperoxide in polypropylene oxidized with ozone.

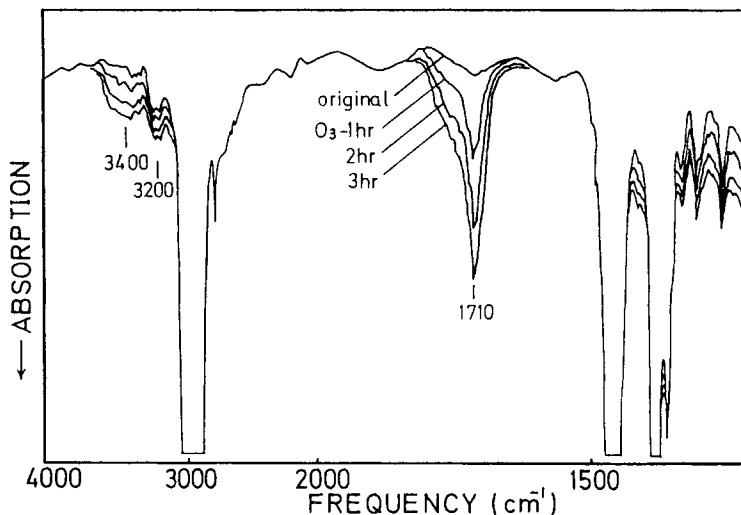


Figure 2 Variation of infrared spectrum of polypropylene with oxidation time.

propylene with oxidation time and the intensity change of the carbonyl group, respectively. The intensity also increased with the oxidation time. This result suggests that reaction (10) progressed very smoothly. Figure 4 compares two ESR spectra of polyethylene and polypropylene oxidized with ozone. Spectra B and C show temperature variations typically found in polypropylene as a peroxy radical.¹¹ From spectrum C, $g_{\parallel} = 2.034$ and $g_{\perp} = 2.008$ were obtained. One line of spectrum A is due to motional narrowing because of the higher flexibility of polyethylene. The intensity of ESR spectrum B of polypropylene, which is expressed as a peak area, increased rapidly for the first 10 min after the intro-

duction of ozone; then, the rate increased gradually and linearly. As soon as the ozone current was stopped, the intensity dropped rapidly. After a few minutes, it decreased gradually and remained for a long time. Therefore, reactions (7) and (8) might be concluded. Here it must be noted that some of the peroxy radicals, though it is a very small amount, persists in the polypropylene oxidized with ozone.

Table II shows a relationship between the molecular weight of polypropylene and the ozone-oxidation time. As the ozone oxidation proceeds, the molecular weight of polypropylene decreases, indicating that the polymer chains were broken by the ozone oxidation. This result suggests the following reaction:

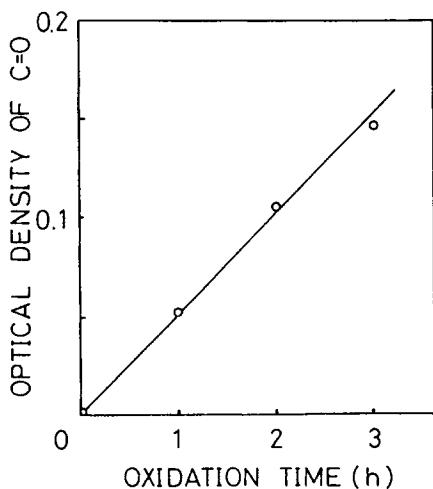


Figure 3 Relationship between oxidation time and optical density of carbonyl group in polypropylene oxidized with ozone.

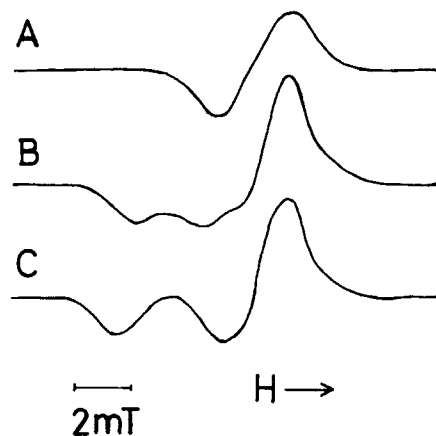
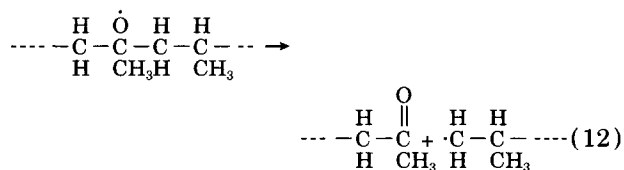


Figure 4 ESR spectra of polyethylene and polypropylene oxidized with ozone: (A) PE 293 K; (B) PP 293 K; (C) PP 77 K.

Table II Relationship between Molecular Weight of Polypropylene and Oxidation Time

Oxidation Time (min)	Molecular Weight ($\times 10^4$)
0	19.78
30	8.82
60	6.59
90	5.88
120	5.08
180	4.20



On the other hand, the fact that the values of GE were kept comparatively large (Table I) may suggest that only a small amount of homopolymer was generated. Table I also indicates that GE decreased with the ozone-oxidation time. This may be because the ozone oxidation proceeds from the surface to the inside. The hydroperoxide, therefore, is made on the surface of the polymer at the relatively early stage of oxidation, so that the alkoxy radical can react readily with the monomer that is present near the surface, thus producing graft copolymer. With a long oxidation time, however, the ozone oxidation may proceed to inside the polymer and the alkoxy radical produced later from hydroperoxide inside the poly-

mer has little chance to react, because monomers cannot easily diffuse inside the polymer. On the other hand, the hydroxyl radical produced inside the polymer at the same time can diffuse to outside the polymer more easily than can monomers. Thus, the hydroxyl radical can react with the monomer smoothly, resulting in a large amount of homopolymer.

Several properties of graft copolymerization of MMA onto polypropylene and polyethylene were compared in Figures 5 and 6. The graft efficiency shown in Figure 5 is almost the same between polypropylene and polyethylene, whereas the degree of grafting is higher with polypropylene and the molecular weight change against the oxidation time (Fig. 6) is larger with polyethylene. These facts may be explained by taking into account the stability of the active sites, that is, the active sites of polypropylene are more stable than are those of polyethylene and less reactive in such a cleavage reaction as (12).

Effect of Polymerization Time on Total Conversion, Degree of Grafting, and Graft Efficiency

Table III shows TC , DG , and GE values when polypropylene oxidized with ozone for 30 min was graft copolymerized with MMA for 30, 60, and 90 min. Both TC and DG increased with the polymerization time, while GE decreased. These results indicate that the graft copolymer fixed at one end cannot diffuse readily as compared with the homopolymer, and the graft copolymer surrounded by the reaction mixtures

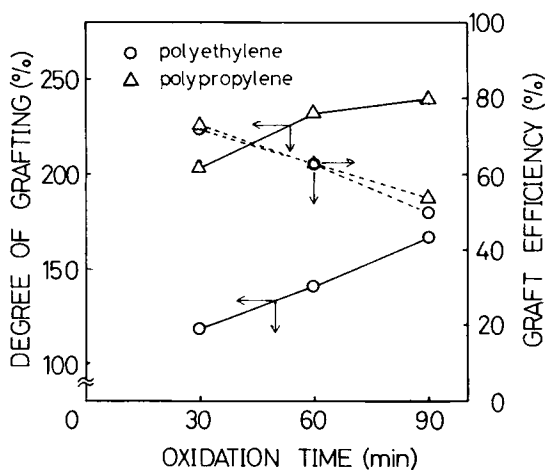
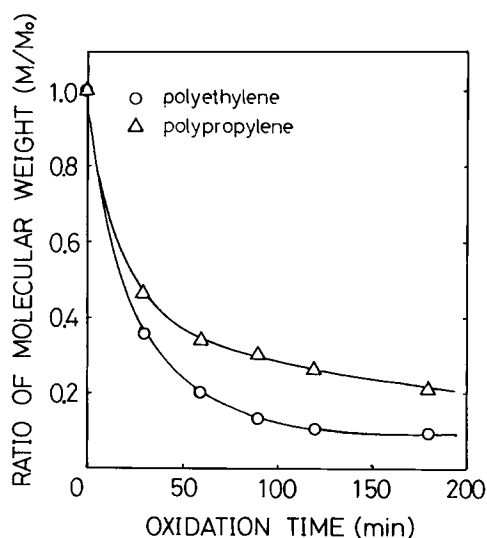
**Figure 5** Plot of degree of grafting (DG) and graft efficiency (GE) vs. oxidation time in polyethylene and polypropylene.**Figure 6** Plot of ratio of molecular weight (M/M_0) vs. oxidation time in polyethylene and polypropylene.

Table III Total Conversion (TC), Degree of Grafting (DG), and Graft Efficiency (GE) Depending on Polymerization Time

Polymerization Time (min)	TC (%)	DG (%)	GE (%)
30	7	47	70
60	29	203	73
90	41	264	66

Sample: polypropylene oxidized with ozone; monomer: methyl methacrylate; oxidation time: 30 min; polymerization temperature: 60°C.

may lose a chance to react with the monomer. These results were also compared with those of polyethylene in Figure 7. The difference in degree of grafting versus polymerization time seems to be understood on the basis of the stability of the active sites, as discussed in the above section.

Molecular Weight of the Branch Polymer and Number of Branches

To obtain information on the branch polymer, the molecular weight of the homopolymer was determined. It is usually difficult to isolate branch polymer from graft copolymer and to know the molecular weight directly. Nevertheless, there were several reports¹⁴⁻¹⁷ in which branch polymers were isolated and their molecular weights were determined in natural rubber and cellulose. These reports mentioned that the molecular weight of the branch polymer was equal to that of the homopolymer or was slightly larger in the graft copolymerization of the

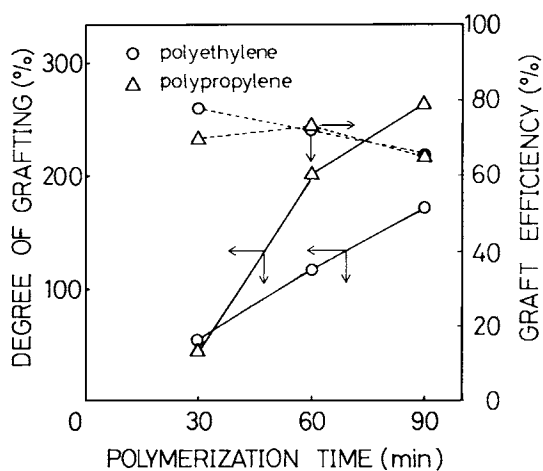


Figure 7 Plot of degree of grafting (DG) and graft efficiency (GE) vs. polymerization time in polyethylene and polypropylene.

heterogeneous system. If one assumes an equal molecular weight of branch polymer to that of homopolymer, the number of branches can be estimated.

Table IV shows the molecular weight of the homopolymer and the number of branches. The value of the molecular weight of the homopolymer was found to be of the order of 10^6 and increased with the polymerization time at the constant oxidation time (30 min). The molecular weight of the homopolymer slightly decreased with the ozone-oxidation time at the constant polymerization time (60 min). Considering that the concentrations of the alkoxy and hydroxyl radicals increase with the ozone-oxidation time at the constant polymerization time, these results lead to the conclusion that the quantity of the monomer that reacts per unit time and unit polymer molecule decreases, causing a low molecular weight.

According to Table IV, the following two facts are concluded: (1) the number of branches increases with the polymerization time at the constant ozone-oxidation time (30 min), and (2) the number of branches slightly increases with the ozone-oxidation time at the constant polymerization time (60 min). In either case, the variation is of the order of 10^{-2} . These results suggest that the graft copolymer has several branches with high molecular weight per 100 trunk polymer chains.

CONCLUSIONS

When polypropylene was oxidized with ozone, the graft copolymerization with MMA onto it became possible. The hydroperoxide that plays an important role as active sites was formed by the ozone-oxidation, and its decomposed radical by heating initiated the graft copolymerization. At the constant poly-

Table IV Molecular Weight of Homopoly(methyl methacrylate) in Graft Copolymer on Polypropylene and Number of Branches

Oxidation Time (min)	Polymerization Time (min)	Molecular Weight of Homo-PMMA ($\times 10^6$)	Number of Branches ($\times 10^{-2}$)
30	30	2.44	1.70
30	60	4.24	4.22
30	90	4.93	4.72
60	60	3.77	4.06
90	60	3.56	3.96

Polymerization temperature 60°C.

merization time, the active sites increased with the ozone-oxidation time and the degree of grafting increased, but the graft efficiency decreased. At the constant ozone-oxidation time, both total conversion and degree of grafting increased with the polymerization time, but the graft efficiency decreased. Assuming that the molecular weight of the branch polymer is equal to that of the homopolymer, the number of branches was estimated. The molecular weight of the branch polymer was of the order of 10^6 , and it was fairly large. At the constant ozone-oxidation time, the branch polymer grew with an increase in polymerization time, and the number of the branches became bigger as well. At the constant polymerization time, however, the molecular weight of the branch polymer became smaller, and the number of branches decreased somewhat with the ozone-oxidation time. The number of the branches was of the order of 10^{-2} , and this means that the graft copolymer had several branches per unit of 100 trunk polymer chains.

Finally, comparisons between polypropylene and polyethylene graft copolymerizations show quite similar results. This would promise universal application of ozone oxidation to graft polymerization. However, small but interesting differences in polypropylene and polyethylene were found and these may be due to the stability of the active sites produced in both olefins.

REFERENCES

1. Y. Shinohara and K. Tomioka, *J. Polym. Sci.*, **44**, 195 (1960).
2. T. Matsuda, J. Hayakawa, K. Nunome, and K. Kawase, *Koubunshi Kagaku (Polym. Chem.)*, **18**, 634 (1961).
3. M. H. Rao, K. N. Rao, M. D. Teli, A. D. Jog, and H. T. Lokhande, *J. Appl. Polym. Sci.*, **33**, 2743 (1987).
4. M. H. Rao, K. N. Rao, H. T. Lokhande, M. D. Teli, and A. D. Jog, *J. Appl. Polym. Sci.*, **33**, 2707 (1987).
5. A. K. Mukherjee and B. D. Gupta, *J. Appl. Polym. Sci.*, **30**, 4455 (1985).
6. M. Imoto, T. Ohtsu, and K. Yamada, *Kogyokagaku Zasshi (J. Chem. Soc. Jpn. Ind. Chem.)*, **65**, 1875 (1962).
7. S. Kawamatsu and M. Miura, *Koubunshi Kagaku (Polym. Chem.)*, **21**, 652 (1964).
8. T. Ikeda, *Sen'i Gakkaishi (J. Polym. Soc. Jpn.)*, **29**, 396 (1973).
9. A. Narebska and Z. Bukowski, *Makromol. Chem.*, **186**, 1411 (1985).
10. A. Yamaoka, K. Ikemoto, T. Matsui, and J. Yamauchi, *Nippon Kagaku Kaishi (J. Chem. Soc. Jpn. Chem. & Ind. Chem.)*, 1919 (1989).
11. J. Yamauchi, K. Ikemoto, and A. Yamaoka, *Makromol. Chem.*, **178**, 2483 (1977).
12. J. C. W. Chien, E. J. Vanderberg, and H. Jabloner, *J. Polym. Sci., A-1*, 381 (1968).
13. P. Parrini, *Makromol. Chem.*, **38**, 27 (1960).
14. F. Ide, *Kogyokagaku Zasshi (J. Chem. Soc. Jpn. Ind. Chem.)*, **64**, 1489 (1961).
15. Y. Mori and Y. Minoura, *Kogyokagaku Zasshi (J. Chem. Soc. Jpn. Ind. Chem.)*, **61**, 109 (1958).
16. Y. Ogata, N. Yasumoto, S. Fujine, Y. Minoura, and M. Imoto, *Kogyokagaku Zasshi (J. Chem. Soc. Jpn. Ind. Chem.)*, **65**, 1136 (1963).
17. W. Cooper, G. Baughan, and R. W. Madden, *J. Appl. Polym. Sci.*, **1**, 329 (1959).

Received March 12, 1990

Accepted December 20, 1990