

## Aminobutadienes. XII. A Method for Modification of Polypropylene Fiber by Graft Copolymerization with 1-Phthalimido-1,3-butadiene by Thermal Mastication\*†

AKIRA TERADA, *Department of Industrial Chemistry, Kyushu Institute of Technology, Kitakyushu, Japan*

### Synopsis

The high reactivity of 1-phthalimido-1,3-butadiene for either homopolymerization or copolymerization was applied to prepare a graft copolymer with isotactic polypropylene using a roll mill. Five reaction systems containing the monomer 0, 1, 3, 5 and 10% in polypropylene were allowed to react at 175°C. under atmospheric pressure for 10 min. to give the graft copolymers. The resulting resin, tough and rigid, was melt-spun to give a single filament. This filament was extracted with 1,2-dichloroethane to remove the remaining monomer and homopolymer. The percentage of the grafted monomer against the feed was determined by ultraviolet spectroscopy. This modified method did not result in gel formation or decreased viscosity. Accordingly, spinning could be easily carried out. After fivefold stretching of the filament in hot water of 95°C., the tensile strength was almost identical to that of a sample obtained from the original polypropylene. However, a considerable decrease in elongation was observed. The filament can be dyed uniformly with some basic dyes at a rate proportional to the imidobutadiene contents. After hydrazinolysis, the filament acts as an anion-exchange fiber and imbibes acid dyes homogeneously throughout.

### INTRODUCTION

Such fibers as poly(vinyl chloride), poly(vinylidene chloride), polyethylene, and polypropylene contain no sites for dye absorption. Particularly, the conventional process for dyeing of isotactic polypropylene fiber encounters difficulties. Many processes to improve the dyeability have been tried, and some methods suitable for dyeing have been reported.<sup>3</sup> One plan consists of introducing dyeable functional groups such as amino, hydroxyl, and carboxyl groups by graft copolymerizations with monomers having such groups into polypropylene fiber. The procedures have been carried out by the use of catalyst, high energy irradiation, or by peroxidation. On the other hand, the method of graft and block copolymerization initiated by mechanochemical and thermoxidative degradation of high polymer which will be described here has often been used for the same purpose.

\* Paper presented at the Ōita Meeting of the Chemical Society of Japan, Ōita, Dec. 1965.

† For the preceding papers in this series, see Murata and Terada.<sup>1,2</sup>

It is well known that the tertiary carbon-hydrogen linkage which is existent in each monomer unit in a polypropylene molecule constitutes a weak point under heating, and the hydrogen bonded to such a tertiary carbon is more readily removed by hydrogen abstraction than those on secondary carbon. The tertiary carbon radical then affords the hydroperoxide under oxygen atmosphere, and its decomposition affords radicals initiating graft copolymerization.<sup>4</sup> Previously, we have found that 1-phthalimido-1,3-butadiene rapidly polymerized either radically or thermally to give the high polymer having a reduced viscosity of approximately 4, which preferentially contained the 1,4-configuration and approximately 20% of the 3,4-configuration.<sup>5</sup> This monomer also copolymerized well with other vinyl monomers such as acrylonitrile, methyl methacrylate, styrene, and *N*-vinylphthalimide, and gave the Alfrey-Price parameters as high as  $Q = 1.75$ , and  $e = +0.06$ .<sup>2</sup>

The enhanced reactivity of this monomer in copolymerization suggested use for the above-mentioned purpose. This paper will deal with a modification of isotactic polypropylene by graft copolymerization with 1-phthalimido-1,3-butadiene with the use of a roll mill.

## EXPERIMENTAL

### Materials

1-Phthalimido-1,3-butadiene (1-PB) was prepared as reported previously<sup>6</sup> and was obtained as yellow needles with a melting point of 114.5–116°C. Isotactic polypropylene (PP) pellets were obtained commercially [M.I., 6.0 g./10 min., 230°C. (ASTM D1238-52T); m.w.,  $22 \times 10^4$ ; m.p., 164–170°C.;  $D$ , 0.90 g./cc. (ASTM D792-50)].

### Procedures

The mill used had chrome-plated rollers having the dimensions 7 cm. diameter and 15.0 cm. length. The roll speeds were 26 rpm (front) and 22 rpm (back). The rolls were electrically heated and the surface temperature as measured with a thermocouple was considered the reaction temperature. The samples were milled for 10 min. at 175°C.

The resulting graft copolymer was melted in a spinning cell at 275°C. under 4 kg./cm.<sup>2</sup> nitrogen pressure. The spinneret at the bottom of the cell, made from a copper alloy, had a hole 0.25 mm. in diameter. The filament emerging from the hole into air, traveled 1 m. downward vertically, and after worming through a cold water bath, another 1 m. horizontally, and then was wound up by a bobbin at a rate of 53 m./min.

### Extraction

The filament was subjected to Soxhlet extraction with 1,2-dichloroethane and then dried by the use of a drying pistol under 2 mm. Hg at the boiling point of methanol for 1 hr. This drying procedure was enough to give a constant weight.

### Hydrazinolysis

The filament extracted above (approximately 0.5 g.) was refluxed with 10 ml. of hydrazine hydrate for 20 hr. After washing several times with boiling water and boiling ethanol, the sample was dried under vacuum as above.

### Determination of Anion-Exchange Value

A dried sample obtained from the hydrazinolysis (approximately 0.5 g.) was weighed and immersed in 100 ml. of 1*N* sodium hydroxide at room temperature for 24 hr. and washed repeatedly with portions of boiling water until the washings became neutral. The sample was immersed in 100 ml. of 0.01*N* hydrochloric acid at room temperature for 24 hr., and the remaining acid was titrated with 0.01*N* sodium hydroxide.

### Spectroscopic Analysis

The absorption intensities were recorded on a Shimazu Model IR-27A infrared spectrophotometer and on a Shimazu ultraviolet spectrophotometer. For these measurements, the sample was melted between two photographic glass plates on a hot plate kept at 180°C. and pressed to give a thin, flat film of about 20  $\mu$  of thickness. The resulting film could easily be freed from the glass plates by briefly immersing in water. After air drying, the film thickness was measured by using a micrometer. The absorption intensities in the ultraviolet region were calculated by converting to 100  $\mu$  thickness of film by using the corresponding No. 1 sample as a compensative.

### Viscosity

The relative viscosity of the grafted copolymers and hydrazine-treated copolymers was determined as a 1% solution in 100% 1,2,3,4-tetrahydronaphthalene at 120°C. in an Ostwald viscometer.

## RESULTS AND DISCUSSION

The reaction was carried out for 10 min. under atmospheric pressure at 175°C., which is the melting point of isotactic polypropylene. The monomer content in the reaction mixture was limited to below 10%, because the use of more monomer results in a polypropylene fiber of less than optimal properties. A rapid disappearance of the strong yellow color of the monomer was observed during the first 5 min. of reaction.

The resin obtained as a tough, rigid plastic was melt-spun at 275°C. under 4 kg./cm.<sup>2</sup> nitrogen pressure into a single filament of 20  $\mu$  diameter. In order to remove the remaining monomer and the homopolymer, the filament was extracted with 1,2-dichloroethane (b.p. 83°C.) for 26 hr. with a Soxhlet extractor; the extraction was virtually completed after 20 hr. (Table I).\* 1,2-Dichloroethane was used here because it is a solvent for

\* Completeness of the extraction was shown by the fact that the absorption intensity at 1710 cm.<sup>-1</sup> was almost unchanged after two reprecipitations from the hot 1,2,3,4-tetrahydronaphthalene solution into a large amount of 1,2-dichloroethane.

TABLE I  
Product Analysis

Sample No.	1-PB used in PP, %	Grafted monomer, %, determined by <sup>a</sup>				Average values from UV		
		Weight loss by extraction, %		Solvent extraction	IR (1764 cm. <sup>-1</sup> )		UV	
		20 hr.	26 hr.				220 m $\mu$	295 m $\mu$
1	0	1.82	1.83	—	—	—		
2	1	2.34	2.39	48	57	54		
3	3	2.07	2.07	91	41	39		
4	5	2.44	2.44	85	58	56		
5	10	3.56	3.57	81	—	90		

<sup>a</sup> (Monomer grafted/monomer in feed)  $\times$  100.

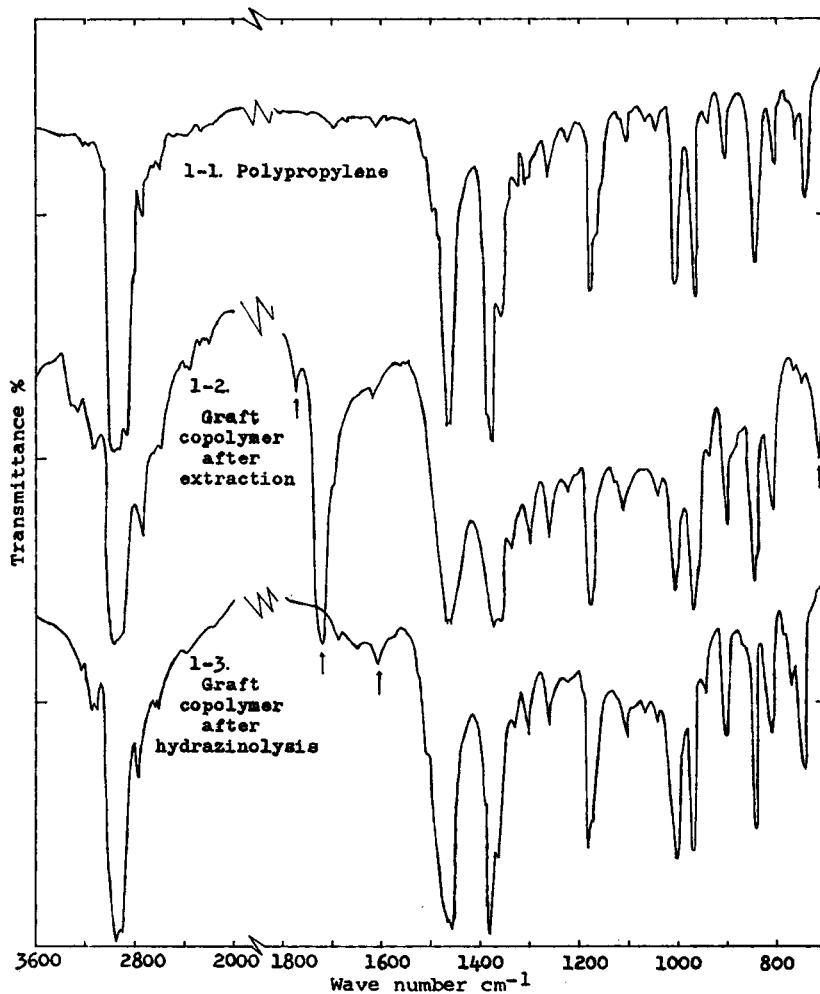


Fig. 1. Infrared spectra.

the monomer and homopolymer but not for isotactic polypropylene.<sup>5,8</sup> Even the standard sample prepared directly from the original polypropylene pellets, shows a weight loss of 1.83%. We suppose that this could come from the stabilizers present initially, while a few of soluble products should be formed by the thermal and oxidative decompositions of the polypropylene during mastication and melt-spinning processes, and furthermore the polypropylene filament itself may not be absolutely insoluble in this solvent under such extraction conditions. It seems reasonable that the first factor accounts for the extraction loss, however, since the loss was less than expected and commercial polypropylene generally contains approximately 1% of stabilizers.

1-Phthalimido-1,3-butadiene and its polymer have the characteristic

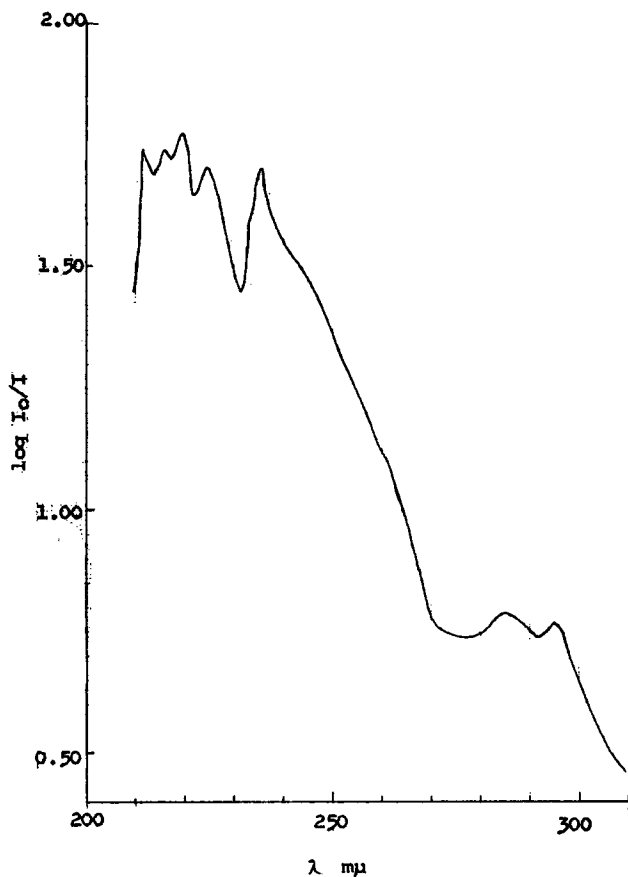


Fig. 2. Ultraviolet spectrum of 1-phthalimido-1,3-butadiene polymer on polypropylene film.

absorption peaks at 1710 and 1764  $\text{cm.}^{-1}$  assignable to the phthalimido carbonyl, and at 719  $\text{cm.}^{-1}$  from the *o*-disubstituted benzene (Fig. 1). The determination of 1-PB content in the copolymer by the infrared spectra was initially undertaken by using these key bands. However, these peaks are poorly defined at low 1-PB concentration. Also the gravimetric determination by extraction, as shown in Table I, gave increased errors at low 1-PB content. On the other hand, *N*-alkyl phthalimide in general and 1-PB polymer have some strong absorption peaks in the ultraviolet region (Fig. 2),\* while polypropylene was virtually transparent in this region. Consequently, the content of the 1-PB in the graft copolymer after extraction was determined by ultraviolet spectroscopy on comparison of the absorption intensity with that of a sample of known concentration before extraction (Table I, Figs. 2 and 3).

\*For example, *N*-allyl phthalimide in ethanol solution shows peaks at 219 and 295  $\text{m}\mu$  ( $\epsilon = 46,300$  and 2280, respectively).

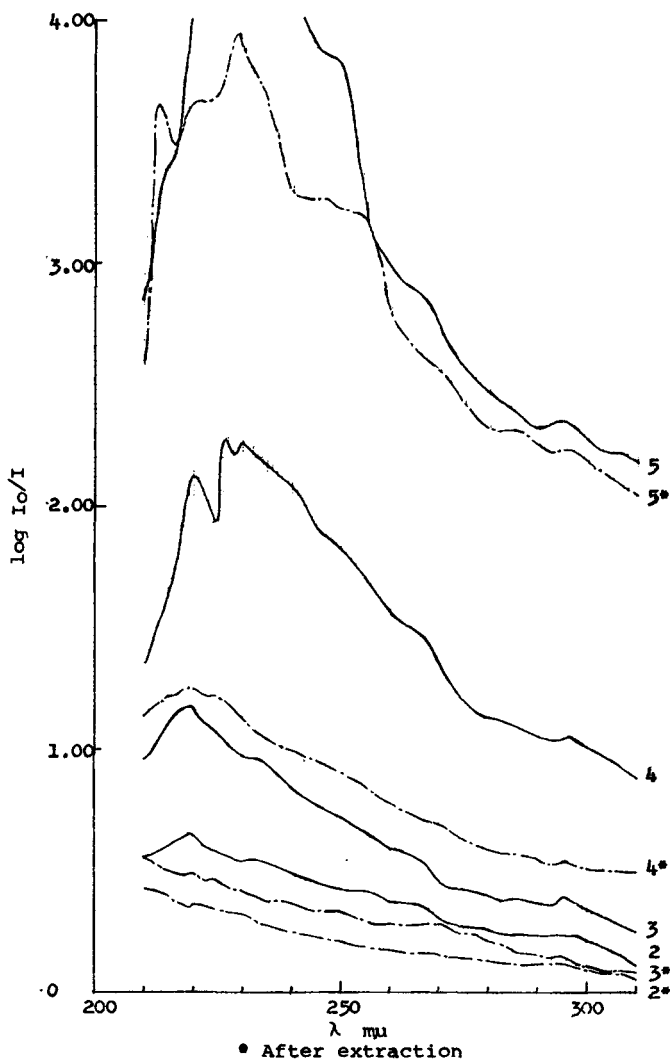


Fig. 3. Ultraviolet spectra of graft copolymers.

The monomer in cyclohexane solution exhibits the strongest absorption maximum at  $278.5 \text{ m}\mu$  ( $\epsilon = 35,400$ ).<sup>7</sup> Figure 3 shows no residual monomer in the filament samples as all of the curves lack any perceptible peak near this position.

Since this copolymerization was carried out in the melt and in the presence of oxygen, the initiation must come primarily from the tertiary carbon radical on the polypropylene backbone produced in thermal scission of the tertiary carbon-hydrogen bond rather than from the secondary carbon radical formed by main-chain scission on mastication. Graft copolymerization should therefore be favored over block copolymerization. This hypothesis can be supported by the results of viscosity measurement

TABLE II  
Viscosity

Sample no.	Treatment	$n_{sp}/c$
Standard <sup>a</sup>		1.307
1	Before extraction	1.330
1	After extraction with 1,2-dichloroethane	1.338
2		1.325
3		1.348
4		1.406
5		1.415
1	After hydrazinolysis	1.168
2		1.304
3		1.307
4		1.312
5		1.319

<sup>a</sup> Obtained directly from the original polypropylene pellets.

(Table II). There is no significant viscosity decrease which would accompany a drastic molecular scission. This modification method should be exempted from gel formation, because the initiation and copolymerization were carried out in the presence of monomer and of oxygen. In fact, the copolymer contained no gel and was homogeneously soluble in hot *sym*-tetrachloroethane, so that the melt-spinning process proceeded with ease and no thread breaking was observed.

The filaments obtained by this graft copolymerization process are easily dyed uniformly throughout the cross-section by using basic dyes and treatment similar to that used for wool. For example, Victoria Blue (conc.) satisfactorily dyed these filaments at a rate proportional to their 1-PB content. The dyed filaments resist boiling ethanol extraction for 30 min. and another soaping for 1 hr.

The phthalimido group in these filaments can also be converted into the free amino group on hydrazinolysis.<sup>9</sup> After treating with hydrazine, these filaments contain free amino groups and no amido and imido groups, as are shown in Figure 1. The weight loss of these filament samples after hydrazinolysis should be 65% of the original weight of grafted monomer, and the weight loss must be proportionally greater in the more grafted sample. However, the samples 2 and 3 in Table III showed weight decreases smaller than the expected values, compared with sample 1 which did not contain any grafted 1-PB. The sample 5, furthermore, showed a little increase. Also sample 1 in Table III, which must not have any amino group or any anion-exchange ability, shows a clear anion-exchange value of 0.0043 meq./g. These results suggest that these hydrazine-treated fibers contain hydrazine in such forms as, for example, hydrazones of some carbonyl compounds which may be formed by air oxidation of polypropylene chain. We would suppose that this also plays some role in the above weight increase. At present, however, we cannot prove the origin of weight increase and

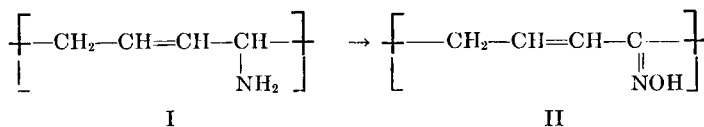


TABLE III  
Weight Changes of the Filaments on Hydrazinolysis

Sample no.	Sample wt., mg.		Wt. change	
	Initial	After hydrazinolysis	mg.	%
1	493.03	489.71	-3.32	-0.67
2	451.30	450.10	-1.20	-0.27
3	492.05	491.00	-1.05	-0.21
4	494.08	493.76	-0.32	-0.06
5	482.94	486.40	+3.46	+0.76

hydrazone formation. Because the formation of a carbonyl group must accompany the backbone scission of polypropylene molecule, this disagrees with the viscosity data (Table II). The weight increase is accountable for, in part, by the oxygen absorption on oxidation of the grafted polymer.

The ultraviolet spectrum of each of the hydrazinolized samples shows a strong absorption maximum at  $232.5 \text{ m}\mu$  (Fig. 4). Also, in the infrared spectrum (Fig. 1), a peak of  $1610 \text{ cm.}^{-1}$  becomes moderately strong. The peaks in the ultraviolet region are conspicuous, while the intensity of the peak in the infrared region is still weak. These facts suggest the existence of a conjugated oxime structure,<sup>10,11a</sup>  $-\text{C}=\text{C}-\text{C}=\text{NOH}$  (in general,  $\lambda_{\text{max}} = 236 \pm 6.5 \text{ m}\mu$ ,  $\epsilon = 12,000\text{--}23,000$ ).<sup>10</sup> Previously, we observed in some polyvinylamine derivatives that free polyvinylamine was rapidly oxidized in air with color darkening.<sup>12,13</sup> Since this hydrazine-treated filament has an allylic amine structure (I), it might be easily oxidized by oxygen or by some peroxides produced on the polymer molecule itself to conjugated oxime (II).<sup>11b,14</sup>



This filament acts as an anion-exchange fiber (Table IV) and, as a matter of course, could be dyed with acid dyes such as Naphthol Yellow S at a rate proportional to its amine content. The resulting dyed sample also resists soaping for 30 min.

Table V shows the results of the physical tests of these filaments. All of the samples, before test, were drawn  $5\times$  in hot water bath at  $95^\circ\text{C}$ . and had a circular cross section  $9 \mu$  diameter. These results indicate that the present procedure for graft copolymerization does not greatly decrease the tensile strength of polypropylene but results in considerable decrease in elongation compared with those of the standard sample as found in Table V, for a reason not presently understood. The former conclusion also supports our prior hypothesis obtained from the viscosity data that scission of the polymer backbone virtually does not occur. However, these results

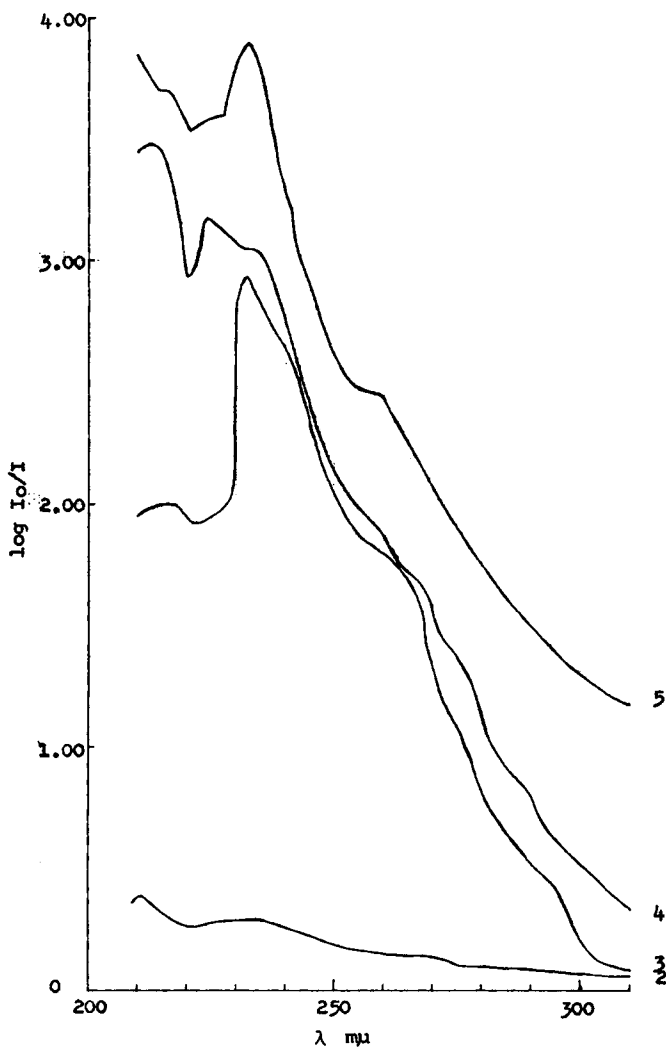


Fig. 4. Ultraviolet spectra of graft copolymers after hydrazinolysis.

TABLE IV  
Anion-Exchange Values of the Filaments

Sample no. <sup>a</sup>	Anion-exchange value, meq./g.
1	0.0043
2	0.0052
3	0.0110
4	0.0164
5	0.0282

<sup>a</sup> After hydrazinolysis.

TABLE V  
Tensile Strength and Elongation of Filaments at 25°C.<sup>a</sup>

Sample no.	Treatment	Ultimate strength <sup>b</sup>		Elongation at break, % <sup>c</sup>
		g.	%	
Standard <sup>c</sup>		35.8	100	100
1	After extraction with 1,2-dichloroethane	35.4	99	70
2		42.0	117	30
3		38.6	108	40
4		33.4	93	80
5	After hydrazinolysis	30.6	85	50
1		49.2	137	100
2		36.2	101	40
3		45.2	126	60
4		35.0	98	50
5		31.0	87	40

<sup>a</sup> Determined by an Instron tensile tester. Filaments of  $9 \pm 0.2 \mu$  in diameter were selected.

<sup>b</sup> Average value of five filaments.

<sup>c</sup> Obtained directly from the original polypropylene pellets.

suggest to us that the use of more than 10% monomer may produce a polymer with less than the optimal properties of polypropylene fiber.

Inspection of the filaments through a microscope (400 $\times$  magnification with a stage micrometer) indicated that they had excellent circular cross-section and the diameter was almost uniform, and that the filaments, after solvent extraction, had many tubercular processes on the face and holes inside. That is, they were very porous, again suggesting ease of dyeability. The drawing of the filament made the surface very smooth and the fiber white, because of many striped patterns formed by drawing, especially in the hydrazinolized filament.

The author is much indebted for skilled technical assistance of Messrs. Masao Egami, Takahiro Muraoka, Shigeru Oda, and Nobuyuki Yoshida. Also he wishes to thank the Government Industrial Research Institute, Osaka, for the use of the roll mill.

### References

1. K. Murata and A. Terada, *J. Polymer Sci. A-1*, **4**, 2989 (1966) (Part VI).
2. K. Murata and A. Terada, *Bull. Chem. Soc. Japan*, **39**, 2494 (1966) (Part VII).
3. D. J. Angier, in *Chemical Reactions of Polymers*, E. M. Fettes, Ed., Interscience, New York, 1964, p. 1099.
4. W. L. Hawkins and F. H. Winslow, in *Chemical Reactions of Polymers*, E. M. Fettes, Ed., Interscience, New York, 1964, p. 1055.
5. A. Terada and K. Murata, *J. Polymer Sci. A-1*, **5**, 2219 (1967).
6. A. Terada and K. Murata, *Nippon Kagaku Zasshi*, **83**, 490 (1962) (Part III).
7. A. Terada, *Nippon Kagaku Zasshi*, **81**, 1773 (1960) (Part I).
8. I. Inoue and S. Kawakami, *Polypropylene*, Nikkan Kogyo Shinbunsha, Tokyo, 1962, p. 31.
9. A. Terada and K. Murata, Japanese Pat. 468,683 (1966).
10. L. K. Evans and A. E. Gillam, *J. Chem. Soc.*, **1943**, 565.

11. P. A. S. Smith, *Open-Chain Nitrogen Compounds*, Benjamin, New York, 1966, (a) Vol. II, p. 31; (b) Vol. I, p. 49.  
 12. T. Yoshida and A. Terada, *Kogyo Kagaku Zasshi*, **54**, 783 (1951).  
 13. T. Yoshida and A. Terada, *Kogyo Kagaku Zasshi*, **55**, 27 (1952).  
 14. I. T. Millar and H. D. Springall, *Sidgwick's Organic Chemistry of Nitrogen*, 3rd Ed., Oxford Univ. Press, Oxford, 1966, p. 112.

### Résumé

La réactivité élevée du 1-phthalimido-1,3-butadiène à l'égard soit de l'homopolymérisation, ou de la copolymérisation, a été appliquée en vue de fabriquer des copolymères greffés avec le polypropylène isotactique en utilisant un laminoir. Cinq systèmes de réaction contenant du monomère dans le polypropylène dans l'ordre 0, 1, 2, 3, 5 et 10% ont été soumis à réaction à 175°C sous pression atmosphérique durant 10 minutes en vue de former des copolymères greffés. La résine résultante, dure et rigide, était filée à l'état fondu pour fournir un filament unique. Ce filament était extrait avec du 1,2-dichloroéthane en vue d'éliminer le monomère résiduel et le homopolymère. Le pourcentage de monomère greffé en fonction du mélange de départ a été déterminé par spectroscopie ultraviolette. Cette méthode de modification n'entraîne pas la formation de gels, ni de diminution de viscosité. De même le processus de filature peut être facilement appliqué. Après un étirement quintuple du filament dans l'eau chaude à 95°C, la force de tension est pratiquement identique à celle d'échantillons obtenus au départ de propylène de départ. Toutefois, une diminution considérable d'élongation a été observée. Ce filament peut être teint uniformément même à l'intérieur du filament avec certains colorants basiques à une vitesse proportionnelle à la teneur en imidobutadiène. Après hydrazinolyse, le filament agit comme fibre échangeur d'anions et absorbe certains colorants acides de façon homogène à travers toute la section transversale du filament.

### Zusammenfassung

Die grosse Reaktionsfähigkeit von 1-Phthalimido-1,3-butadien sowohl bei Homopolymerisation als auch bei Copolymerisation wurde dazu verwendet, um Pfropfcopolymere mit isotaktischem Polypropylen in einem Walzwerk herzustellen. Man liess die fünf Reaktionssysteme, die der Reihe nach 0, 1, 2, 3, 5 und 10% des Monomeren in Polypropylen enthielten, bei 175°C unter Atmosphärendruck 10 min reagieren, um die Pfropfcopolymeren zu erhalten. Das entstandene Harz, das zäh und hart war, wurde aus der Schmelze zu einem unendlichen Faden versponnen. Dieser Faden wurde zur Entfernung des restlichen Monomeren und Homopolymeren mit 1,2-Dichloräthan extrahiert. Der auf die eingesetzte Menge bezogene Prozentsatz an aufgepfropftem Monomeren wurde mittels Ultraviolett-Spektroskopie bestimmt. Diese Modifizierung bewirkte weder Gelbildung, noch eine Abnahme der Viskosität. Demgemäss war das Spinnverfahren leicht durchzuführen. Nach einer Dehnung des Fadens in heissem Wasser von 95°C auf das Fünffache war die Zugfestigkeit nahezu identisch mit der einer aus dem ursprünglichen Polypropylen erhaltenen Probe. Es wurde jedoch eine beträchtliche Abnahme der Elongation festgestellt. Diesen Faden kann man einheitlich bis ins Innere mit einigen basischen Farbstoffen färben, mit einer Geschwindigkeit, die dem Imidobutadien-Gehalt proportional ist. Nach Hydrazinolyse wirkt der Faden wie eine Anionenaustauscher-Faser und nimmt einige saure Farbstoffe homogen über den gesamten Querschnitt auf.

Received April 12, 1967

Revised May 22, 1967

Prod. No. 1666