Studies on Reactions of Polypropylene. VII. The Modification of Polypropylene by Making Use of Oxidation and Treatment with Toluylene Diisocyanate

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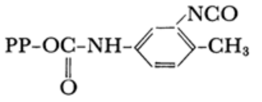
It is well-known that there are a few drawbacks in the practical use of polypropylene, including its poor dyeability and its susceptibility to oxidation. In this work, the latter drawback was utilized in order to improve the former. Namely, polypropylene (PP) was oxidized in order to introduce the hydroperoxide group[1,2] or the carbonyl group,[3] and then these groups were reduced to the hydroxyl group.

$$\text{PP} \xrightarrow{\text{air}} \text{PP-OOH} \xrightarrow{\text{AlEt}_3} \text{PP-OH} \xrightarrow{\text{TDI}}$$



(PP-TDI)

When PP–OH prepared is dipped in toluylene diisocyanate (TDI), one of the two isocyanate groups of TDI may react with the hydroxyl group of PP–OH and TDI may be fixed to the polypropylene chain. The other isocyanate group may still be reactive and may react with a dye in the dyeing process. The film of PP–OH was dipped in TDI at room temperature for 8 days; then the film of PP-TDI was washed with dry acetone untill no TDI was detected in acetone. Absorption bands were detected at 4.5 μ and 5.9—6.7 μ in the infrared spectrum of this film (Fig. 1). On the other hand, these bands were not detected in the spectrum of the film of PP similarly treated.

From the fact that the film of PP-TDI was perfectly soluble in hot *p*-xylene and that the isocyanate group was present in the film, as is indicated by the absorption band at 4.5 μ, it is clear that, while one of two isocyanate groups of TDI reacted with the hydroxyl group on the polypropylene chain, the other group remained reactive. The band at 4.5 μ disappeared when the film was treated with dry methanol, but it could survive the dipping of the film in water for two days, although the film then became a cloudy white. It seems likely that the isocyanate group is protected from water by the water-repelling property of polypropylene. As the removal of TDI soaked in the polymer was not needed practically, the TDI content of the PP-TDI film was weighed without any special treatment other than wiping of TDI on the surface of the film with a filter paper. The results are shown in Table I.

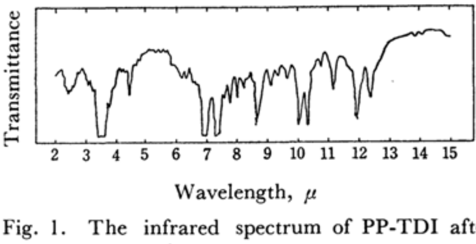


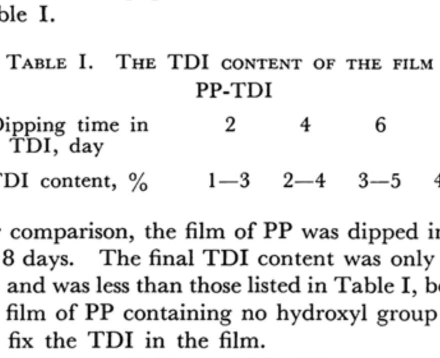
Fig. 1. The infrared spectrum of PP-TDI after acetone-extraction.

TABLE I. THE TDI CONTENT OF THE FILM OF PP-TDI

Dipping time in TDI, day	2	4	6	8
TDI content, %	1—3	2—4	3—5	4—7

For comparison, the film of PP was dipped in TDI for 8 days. The final TDI content was only about 1% and was less than those listed in Table I, because the film of PP containing no hydroxyl group could not fix the TDI in the film.

The films and fibers of PP–OH were dipped in TDI for 8 days, washed quickly with dry acetone, and dyed by the ordinary method with such dispersed dyes as Duranol Red X3B, Celliton Blue Extra, and Estrol Fast Violet B. They were dyed deeply, clearly, and homogeneously to the inner part (Photo 1).



The dyed fiber was not decolored by extraction with acetone. This was evidence of the perfect fixation of the dye in the fiber, as had been elucidated by

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[1] K. S. Minsker, I. Z. Shapiro and G. A. Razuvayev, *Polym. Sci. U. S. S. R.*, **4**, 112 (1963).

[2] G. Natta, E. Beati and F. Severini, *J. Polym. Sci.*, **34**, 685 (1959).

[3] S. S. Stivala, R. Reich and P. G. Kelleher, *Makromol. Chem.*, **59**, 28 (1963).

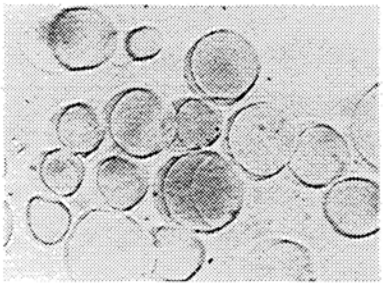

Photo. 1. The microphotograph of the cross-section of the dyed fiber.
Magnification: 250

Kubota et al.⁴⁾ Since the isocyanate group is protected from water, as has been described above, and since it reacts with amino groups more rapidly than with water,⁵⁾ the addition reaction between the isocyanate group and amino groups of the dyes should occur in the dyeing process. When the film of PP-TDI was treated with dry methanol, the isocyanate group in the film was killed. Accordingly, this film was dyeable with the dispersed dye, but it was easily decolored by acetone.

PP–OH could be prepared also by the relatively severe oxidation of polypropylene to introduce the carbonyl group and then by reduction with lithium aluminum hydride. The film thus treated acted in a manner similar to that of the film described above, except that the film became partially insoluble in hot *p*-xylene when dipped in TDI at room temperature for 7 days. This can be explained as resulting from the crosslinking behavior of TDI and the much greater content of the hydroxyl group in the film.

Experimental

Materials.—The powdery polypropylene used contained no stabilizer and its properties were as follows: melt index (at 230°C, load: 2.16 kg./cm.^{2}): 2.5, and specific gravity (at 23°C): 0.912. The film about 0.2 mm. thick was molded under a nitrogen atmosphere, and the fiber was spun at 270°C under a nitrogen atmosphere by the use of a spinneret 0.5 mm. in diameter.

The Preparation of PP-OH.—(1) The powdery sample was oxidized at 70°C for 7 hr. under air in order to introduce the hydroperoxide group. The oxidized sample (4 g.) was dipped in a 2% *n*-heptane solution of aluminum triethyl (70 cc.) at 20°C for 24 hr., then hydrolyzed with a 0.1 N aqueous solution of hydrochloric acid, and washed with water. The hydroxyl group to be introduced was limited to be about 0.3%.¹⁾ (2) The powdery sample was oxidized at 125°C for 2 hr. under air in order to introduce the carbonyl group. The oxidized sample (1 g.) was refluxed for 4 hr. in an ether solution of lithium aluminum hydride (1.9 g./200 cc.) under a nitrogen atmosphere, then washed with methanol, a 15% aqueous solution of sodium hydroxide and water.

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4) M. Kubota, M. Katayama and O. Ishizuka, *J. Chem. Soc. Japan Ind. Chem. Sect. (Kogyo Kagaku Zasshi)*, **66**, 725 (1965).

5) J. H. Saunders and K. C. Frisch, "Polyurethanes, Chemistry and Technology Part I Chemistry," Interscience Publishers, New York (1962), p. 181.