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Reactive Polyolefine

1. A New Crystalline Copolymer of Propylene with Methyl-1,4-hexadiene

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Summary

A new crystalline thermoplastic copolymer of propylene with methyl-1,4-hexadiene (MHD) was obtained with a conventional Ziegler-Natta catalyst. The copolymerization rate was not much depressed by the MHD monomer. Hydrogen was conveniently utilized to regulate the molecular weight of copolymer. In addition, hydrogen increased the copolymerization rate. The copolymer is characterized by chemical reactivity owing to the pendant unsaturation. Improved adhesion property of the copolymer has been shown, which implies useful applications.

Introduction

Polypropylene and copolymers of propylene with ethylene and with higher α-olefins have been utilized in various fields. These polymers, however, are inferior with respect to adherence , paintability and printability, because they are saturated hydrocarbons. No fundamental solution has been found yet.

We have expected that the introduction of carbon-carbon unsaturation to polypropylene would give a solution to the problems through chemical reaction due to the unsaturation.

Conjugated dienes such as butadiene and isoprene depress the copolymerization rate so much that they can not be used as comonomers.

EPDM is a typical unsaturated polyolefin. The copolymer of 1-hexene with methyl-1,4-hexadiene is known as a rubber(LAL and SANDSTROM, 1976). Homopolymer of 5-methyl-1,4-hexadiene is also known as a rubber(LAL and SANDSTROM, 1975). Ternary copolymer composed of ethylene, propylene and 4-methyl-1,4-hexadiene was produced in a form of colloid(HERCULES INC., 1972). All these unsaturated polyolefins are rubbers or rubber-like materials and the moleculer weight can not be regulated except EPDM.

In this paper, we wish to report the copolymerization of propylene with MHD, and some properties of the crystalline thermoplastic unsaturated copolymer obtained.

Experimental

Materials. Polymerization grade propylene was further purified by passing through molecular sieves. n-Heptane was degassed with argon and passed through molecular sieves. Methyl-1,4-hexadiene(MHD; 8:2 mixture of 4-methyl-1,4-hexadiene and 5-methyl-1,4- hexadiene) was degassed with argon, passed through alumina and then passed through molecular sieves. Activated δ-$TiCl_3$ was obtained commercially.

Copolymerization. A typical run is as follws: An 1-liter autoclave was charged with 370 ml of n-heptane and 130 ml of MHD. To the mixture were added 0.5 g of diethylaluminum chloride and 0.1 g of the activated spherical δ-$TiCl_3$. To this mixture was introduced 100 ml of hydrogen at standard conditions. Then, propylene was introduced under pressure maintaining the total pressure at 1 Kg/cm^2, while the system was kept at 17-20 °C for 15 minutes. Finally, the system was subjected to polymerization for 6 hours by maintaining the temperature at 60 °C and the total pressure at 6 Kg/cm^2 by introducing further propylene. The polymerization was stopped by addition of n-butanol. The yield of powdery solid copolymer was 210 g, while 0.9 g of amorphous polymer was recovered from the filtrate. The powdery solid copolymer showed the following properties: bulk density 0.52 g/ml; insoluble fraction after extraction with boiling n-heptane 97.1%; MHD content 3.7 mol%; and the melting point(DSC peak value) 153°C.

Measurement of crystallinity. The crystallinity of the copolymer was determined by X-ray diffraction analysis according to the method of NATTA et al.(1957).

Measurement of comonomer content. The comonomer content was determined by IR spectra.

Results and Discussion

The copolymerization of propylene with MHD proceeded at a high rate. The product copolymer containing a considerable amount of MHD unit was crystalline. The results are shown in

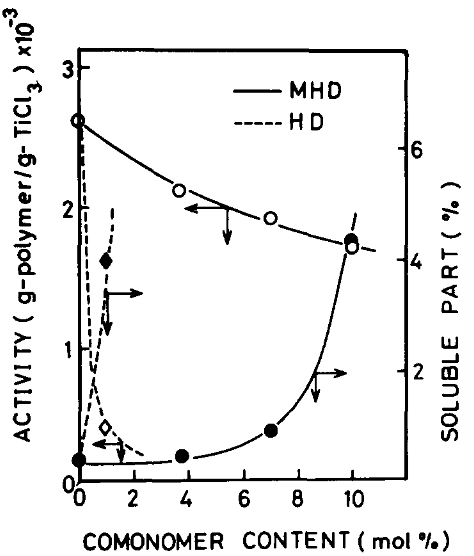

Fig. 1 Copolymerization of propylene with methyl-1,4-hexadiene(MHD) and 1,4-hexadiene(HD). Activity and n-heptane solubles

Fig. 1. The high activity is quite peculiar considering that 1,4-hexadiene(HD), an analogous comonomer, greatly supresses the terpolymerization involving ethylene, propylene and HD (GLADDING,1962). We have also found that HD reduces remarkably the copolymerization rate of propylene with HD. It is assumed that HD may coordinate tightly to the active center of the catalyst as a bidentate ligand and depresses the coordination of propylene. On the other hand, MHD did not bring about a big decrease of rate. This peculiar behavior of MHD may be explained by the sterically hindered structure of double bond of MHD which disturbs its strong coordination to the catalyst site. It is of interest to note in Fig. 1 that amorphous part of the copolymer is quite small.

Fig. 2 shows the relative rate of copolymerization when hydrogen is used as the molecular weight regulator. As the amount of hydrogen increased, an increase in the relative rate was observed in the copolymerization of propylene with MHD.

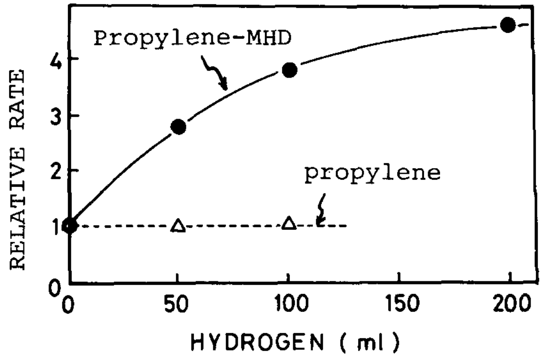

Fig. 2 Amount of hydrogen and relative rate

This finding constitutes a sharp contrast to the fact that hydrogen does not bring about an increase of propylene homopolymerization rate. Hydrogen may act as a hydride ligand to the catalyst to depress the chelate coordination of MHD, leading MHD to act like a monoolefin.

In Fig. 3 is shown the regulation of the melt flow rate (MFR) by hydrogen. Addition of hydrogen moderately raised the MFR of the propylene-MHD copolymer. In the copolymerization of propylene with HD, on the other hand, the MFR change was very big with much depressed rate of copolymerization. The results indicate that the regulation of MFR of the propylene-MHD copolymer is much easier than that of propylene-HD copolymer.

The propylene-MHD copolymer has characteristic infrared absorption bands at 1670 cm^{-1} and 770 cm^{-1}(Fig. 4). In addition to the characteristic absorption band of isotactic polypropylene segment, the band at 1670 cm^{-1} can be assigned to $\nu_{C=C}$. The band at 770 cm^{-1} may be assigned to δ_{CH}. These two bands are based on the tri-substituted pendant olefin groups derived from MHD.

In Table 1 are summarized some properties of propylene-

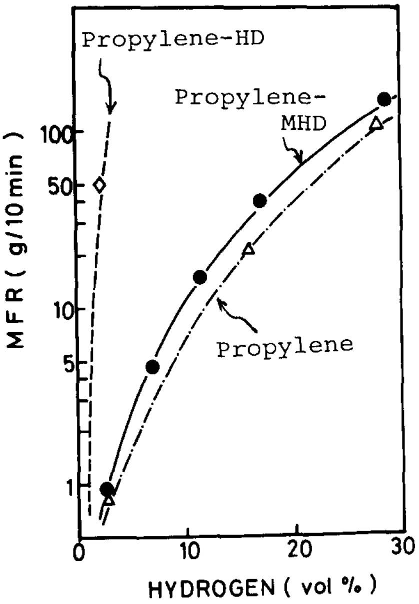

Fig. 3 Amount of hydrogen and melt flow rate(MFR)

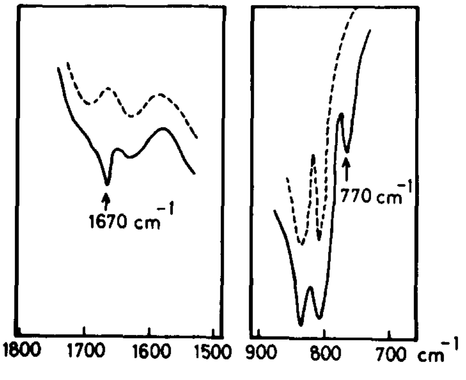

Fig. 4 IR spectra of propylene-MHD copolymer(———) and propylene homopolymer(------)

MHD copolymer. The copolymer has high bulk density and high crystallinity even at 8.5 mol% of the MHD content. Increasing content of MHD tends to decrease the tensile modulus. These properties of the copolymer are thought to be correlated to the structure of the copolymer. The detailed structure remains open.

When the test pieces of the propylene-MHD copolymer were treated with an aqueous $KMnO_4$ solution at 15°C for a minute,

TABLE 1

Properties of propylene-MHD copolymer

MHD content (mol%)	Bulk density (g/ml)	Crystallinity (%)	Melting point (DSC peak ; °C)	Tensile modulus (Kg/cm^2)
0	0.52	51	165	5,600
1.2	0.51	49	158	5,400
3.9	0.52	47	153	5,300
8.5	0.50	42	152	3,900

they adhered tightly to each other with an epoxy-resin adhesive. The adhesive strength was higher than that of the copolymer itself, i.e., excess shear causes the break of the test piece but not of the adhesion layer. On the other hand, propylene homopolymer did not adhere. This shows that propylene-MHD copolymer can be chemically modified easily.

The copolymer has other chemical reactivities owing to the reactive pendant double bond, e.g., paintability and cross-linking etc. These properties will be reported later.

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