

Polymerizations of Ethylene and Propylene Initiated by Milled Metallic Oxides. II. Characterizations of the Mechanochemically Produced Polymers

SHIGERU MURAKAMI, MASAYOSHI TABATA,* and
JUNKICHI SOHMA, *Faculty of Engineering, Hokkaido University,
Sapporo 060, Japan*

Synopsis

Polyethylene was mechanochemically produced by milling of alumina powder at room temperature in the presence of ethylene monomer. Nearly 50% of the produced polyethylene was chemically bonded with the matrix of the alumina. The other 50% of the polymer was extracted by the organic solvents. The polyethylene extracted by the hot *n*-heptane was characterized as having a structure similar to that of the branched polyethylene of low density, and the toluene extracted polyethylene had a structure similar to that of the high density polyethylene. The molecular weights of the mechanochemically produced polyethylene were found to distribute from 10^2 to 10^6 by gel permeation chromatography. The weight average molecular weight was estimated as 260,000 after the 3 days milling. Mechanochemical polymerization of ethylene was also demonstrated by milling of silica in the presence of ethylene monomer. Polymerization of propylene by milling of alumina under propylene atmosphere was performed. The obtained polymer was found to be an atactic by IR measurement and the molecular weight of the extracted product was determined as ≈ 400 by the vapor pressure osmometer.

INTRODUCTION

Mechanochemical polymerizations initiated by fractured metallic oxides were found by Kargin and Plate¹ and Butyagin.² One of present authors (M.T.) also found that both ethylene and propylene were polymerized by the mechanochemical method on fractured metallic oxides, such as boron trioxide, alumina, and silica, and the preliminary results of this mechanochemical polymerization were published in our previous paper (I).³ In that paper (I), characterizations of the polymers were briefly described. The purpose of this paper (II) is to report the details of characterization of the polymers produced by the milling of metallic oxides.

EXPERIMENTAL

Samples. Both γ -alumina and silica used in the experiments were received from Merck Co., Ltd. The alumina and silica samples were pretreated under vacuum (ca. 10^{-4} Torr) for 20–30 min at around 700K for the purpose of removing adsorbing water and gases. Ethylene and propylene were supplied by Nippon Sanso Co., Ltd. and Seitetsu Chemical Co., Ltd., respectively. Mechanochemical

* To whom correspondence should be addressed.

polymerizations were carried out under an atmosphere of the monomer, either ethylene or propylene, at room temperature by using the ball-mill apparatus.³⁻⁵

Extraction of Polymers. Polymers produced by the milling were on the surfaces of fractured metallic oxides, as described in the previous paper.³ In order to characterize mechanochemically produced polymers, the polymers must be removed from the surface, on which they have been made. At first the metallic oxides covered with the mechanochemically produced polymers were washed with hot *n*-heptane agitating with glass balls at ca. 100°C for 2 h. By the treatment with *n*-heptane, polyethylene having lower molecular weights is preferentially dissolved. Polymer obtained by this treatment is called the heptane-extracted polymer in this paper. Although a fraction of the polymers formed on the surfaces of metallic oxides was removed by the dissolution with *n*-heptane, a large fraction of the polymers was still left on the surfaces. Then, the same samples were washed again with hot toluene (ca. 110°C) for 2 h. After separation of the metallic oxide from the polymer solution by filtration, the polymer was obtained by evaporation of toluene. The polymer sample extracted with hot toluene is named the toluene-extracted polymer hereafter.

¹³C-NMR spectrometer used was JEOL-FX 200 type. Gel permeation chromatographs were obtained by using GPC HLC-811 combined with the column GMH 6 × 2 made by Toyo Soda Manufacturing Co., Ltd. Average molecular weights of sample polymers were determined by a vapor pressure osmometer (VPO) made by Hitachi, Type 117, by which molecular weight is determined up to 2×10^4 using benzene as solvent.

RESULTS

Ethylene-Alumina

The simultaneous polymerization,³ which means polymerization caused by fracture of alumina in the presence of ethylene monomers, was performed at room temperature. Monomer gas was introduced into each glass ampoule up to ≈ 10 mmol, using a vacuum line. At the end of each run of the milling, the pressure of the monomer gas in the reaction ampoule was measured, and the gas consumption was estimated from the observed pressure drop. The monomer gas consumption is plotted against the milling time in Figure 1. The consumption of the monomer gas increases with the milling time but almost saturates at 5 days. The result means that ethylene monomers were almost converted into polyethylene after 5 days' milling at room temperature. In the same figure, yields of both the heptane-extracted and the toluene-extracted polyethylenes are plotted against the milling time. Yield of the heptane-extracted polyethylenes, which consists of a lower molecular weight, increases rapidly in the earlier stage but reaches a plateau. Yield of the toluene-extracted polyethylenes, which distributes in a wider range of molecular weight, increases slowly in proportion to the milling time and reaches to the plateau value.

Molecular weight distributions of polyethylene extracted with *n*-heptane and toluene were investigated by gel permeation chromatography (GPC). GPC was taken for *o*-dichlorobenzene solution of the two samples, concentration of which was 0.2 w/v % at the column temperature of 120°C. A calibration curve for estimation of a molecular weight from an observed elution volume was made by

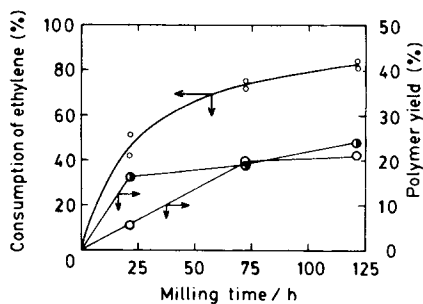


Fig. 1. Olefin gas consumption rate: small open circles, alumina-C₂H₄ at room temperature; (●) polyethylene yields extracted with hot *n*-heptane; (○) polyethylene yields extracted with hot toluene.

using standard polystyrenes with known molecular weights, and the calibration curve obtained for polystyrene was corrected for polyethylene by using the method developed by Williams and Ward.⁶ The molecular weight distributions of polyethylenes extracted with both solvents are shown in Figure 2. Apparently, the heptane-extracted polyethylene has a distribution in the range of lower molecular weights. It should be noticed that the distribution of the toluene-extracted polymer produced after 3 days milling has the wide distribution of the molecular weight curves shown in Figure 2, but no marked difference was observed in the characteristic shapes of distributions even for changing the milling time.

¹³C-NMR spectrum of the heptane-extracted polyethylene in a 1,2,4-trichlorobenzene solution was observed at 120°C using perdeuterated benzene as lock solvent. The spectrum is shown in Figure 3, and assignments of the peaks in the spectrum were made on the basis of Nishioka's assignment of low density polyethylene.⁷ The assignment of each peak is shown in the figure. The main peak, which scales out, is assigned naturally to CH₂ carbon in the main chain and other small peaks originate from the side chains and chain ends. The main character of the observed ¹³C-NMR spectrum quite resembles that of low density polyethylene.⁷ The resemblance convinces us that the heptane-extracted fraction of mechanochemically polymerized polyethylene has a structure similar to the low density polyethylene. In a striking contrast to the heptane extracted polyethylene, a ¹³C-NMR spectrum of the toluene-extracted polyethylene shows a single strong peak at 30 ppm, and other peaks were quite weak, as shown in Figure 4. This spectrum is the same to the high density polyethylene,⁸ and

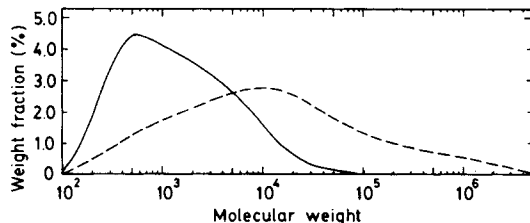


Fig. 2. Molecular weight distribution in the polyethylene extracted with hot *n*-heptane (—) and toluene (---), respectively.

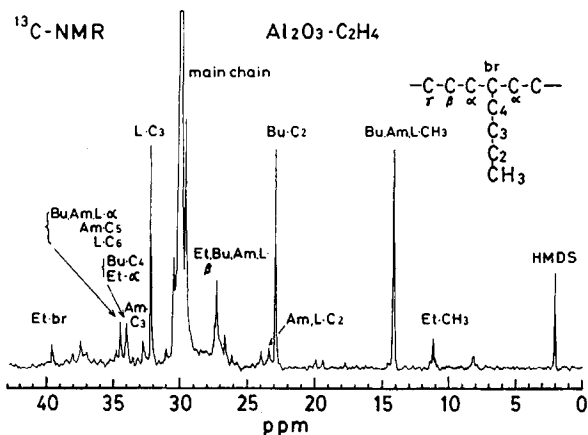


Fig. 3. ^{13}C -NMR spectrum of the low density polyethylene extracted with hot *n*-heptane. Hexamethyl disiloxan (HMDS) was used as internal standard (2.03 ppm vs. TMS). Solvent is 1,2,4-trichlorobenzene.

therefore the toluene-extracted fraction of the mechanochemically polymerized polyethylene is believed to be a high density polyethylene. By milling of alumina in the atmosphere of ethylene monomer, the two kinds of polyethylene were simultaneously produced by the mechanochemical polymerization: one was similar to the low density polyethylene of lower molecular weight having many branches and the other is the polyethylene, which has a wide distribution in molecular weight and whose branches are very few in number.

The mechanochemically produced polyethylene on the alumina surfaces were extracted two times by using either *n*-heptane or toluene at higher temperatures, but not all of the products were removed from the surfaces. From the IR spectrum of the alumina after extraction twice with hot heptane and toluene, it was found that nearly 50% of the initially produced polyethylene was still on the alumina surfaces. Polyethylene undissolved with hot toluene is believed to be chemically bonded with alumina matrix, as discussed in the previous paper.³ It may be hard to characterize polyethylene chemically bonded to the matrix of alumina at the present stage.

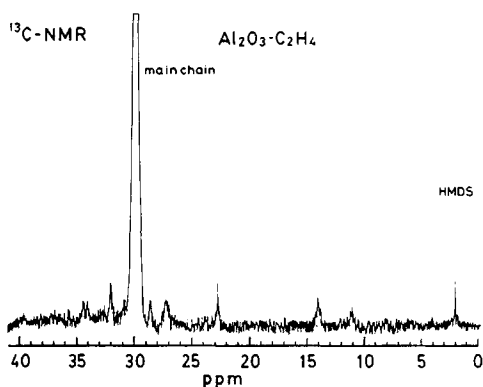


Fig. 4. ^{13}C -NMR spectrum of the high density polyethylene extracted with hot toluene. Chemical shifts are determined using HMDS and TMS. Solvent is 1,2,4-trichlorobenzene.

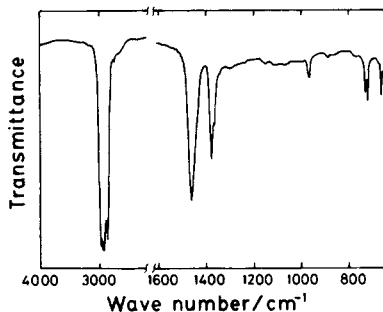


Fig. 5. IR spectrum of heptane-extracted polyethylene obtained after milling silica with ethylene monomer.

Ethylene-Silica

The simultaneous polymerization of the ethylene-silica system was performed at room temperature. Polymers were extracted by hot heptane from surfaces of the milled oxide. The observed IR spectrum (Fig. 5) of the heptane-extracted polymers indicated that the extracted polymers were polyethylene. GPCs of *o*-dichlorobenzene solution of the heptane-extracted polyethylene from those produced by the milling are shown in Figure 6, and no marked difference exists between those obtained after 3 and 5 days' milling. For comparison the GPC curve of the polyethylene extracted with heptane in the alumina-ethylene system is also displayed by a dotted line. Obviously, the molecular weight of polyethylene produced by the mechanochemical polymerization of the silica-ethylene system is much smaller than that of the alumina-ethylene system. The ¹³C-NMR spectrum (Fig. 7) of the heptane-extracted polyethylene is almost similar to that of Figure 3. These results demonstrate that the polyethylene mechanochemically produced by fracture of the silica is highly branched as low density and lower molecular polyethylene. Extraction of polymer by hot toluene after the heptane extraction was tried by the same procedure for the ethylene-alumina system; but no toluene solution was filtered, and separation of the solvent from the silica-polymer system failed because of an emulsion formation. After the extraction with hot heptane, the IR spectrum was observed from the milled silica.

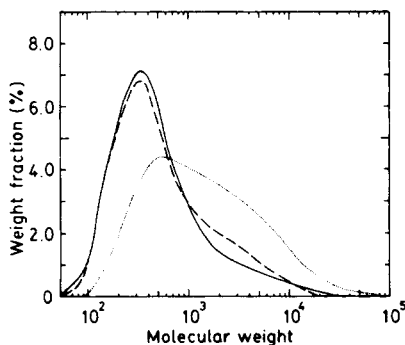


Fig. 6. Molecular weight distributions of polyethylene extracted with hot *n*-heptane from products obtained after ball milling of silica for 3 days (—), alumina for 3 days (---), and silica for 5 days (· · ·).

TABLE I

Metallic oxides	Al ₂ O ₃	SiO ₂	
Solvent for extraction	<i>n</i> -Heptane	Toluene	<i>n</i> -Heptane
Molecular weight	10 ² -10 ⁵	10 ² -10 ⁶	10 ² -10 ⁴
¹³ C-NMR			
Branch point (ppm)			
Ethyl (11.2)	7	1 2	10
<i>n</i> -Bu + ethyl (34.0)	9	1 2	9
<i>n</i> -Am + long (23.4)	5	0	4
Other branch type			
(8.1)	3	0	0
(19.6)	2	0	4
(20.2)	2	0	
	LDPE	HDPE (<i>d</i> ≈ 0.96)	LDPE

The C—H stretching band (2900 cm⁻¹) superposed with the broad band of silica itself appears clearly even after the extraction. By comparison of the intensity of the C—H stretching band before and after the extraction nearly 20% of the produced polymers were extracted. This proves that the majority of the produced polyethylene are chemically bonded to the matrix of silica. The conclusions derived from the mechanopolymerized polyethylene are summarized and compared in Table I.

Propylene-Alumina and Propylene-Silica

Either alumina or silica was milled in the presence of propylene monomer at room temperature, and the simultaneous polymerizations of propylene were observed for both cases. The heptane-extracted polymers gave the same IR spectrum as that of atactic polypropylene, as shown in Figure 8. Molecular weight of the heptane extracted were determined ca. 400 by VPO method, and therefore the heptane-extracted polymers were oligomers of propylene having atactic structure. IR spectra of both alumina and silica covered with the products were observed after the heptane extraction, and the C—H stretching band (2900 cm⁻¹) was observed after the extraction. This fact indicates that either polymers or oligomers of propylene were chemically bonded to the matrix of either alumina or silica.

DISCUSSION

Ethylene-Alumina. As shown in Figure 1 the fraction of lower molecular weight, which is extracted by *n*-heptane, is more produced than the fraction of higher molecular weight in the early stage of mechanochemical polymerization. Moreover, nearly half of the mechanochemically produced polyethylene was extracted by the organic solvents, and the other half was not. This fact means that half of the mechanochemically produced polyethylene is chemically bonded to the matrix of alumina, presumably in either both of the two chemical bonds, —C—Al or —C—O—Al. Mechanical actions initiate polymerization and monomers propagate under mechanical agitation,³ although mechanism of the

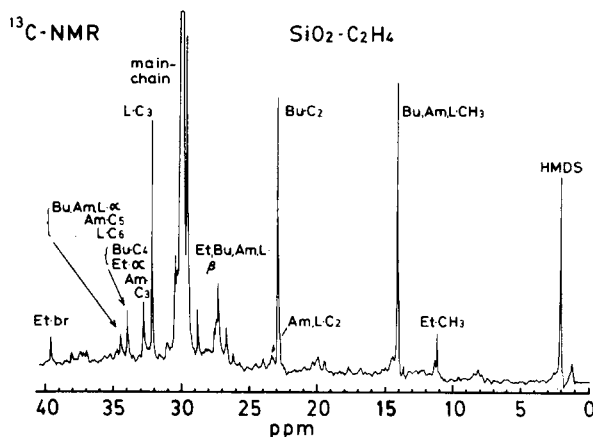


Fig. 7. ^{13}C -NMR spectrum of the low density polyethylene extracted with hot *n*-heptane from silica-ethylene product.

mechanochemical polymerizations is still open to question. It is quite reasonable to assume that polymerization proceeds with the milling time, and therefore the fact is understood that the major fraction of the produced polymers were low molecular weight in the early stage of the mechanochemical polymerization.

Ethylene-Silica. Formation of the bonded polyethylene was evidenced by IR data in this case, too. The heptane extracted polyethylene in this case showed distributions, which resemble that of the heptane-extracted polyethylene of the ethylene-alumina case, although mean-molecular weights in this case is a little smaller than the other case.

Propylene-Alumina. In this system the mechanochemical reaction produced no polymers of propylene but merely the oligomers as far as the heptane-extracted products are concerned. Although the formation of the propylene polymers bonded to alumina was proved by IR data, there was no positive evidence to determine whether or not these are polymers. If polypropylene were actually produced in this case, the broken fragments of polypropylenes could be produced and be dissolved in the organic solvent. But this is not the case.

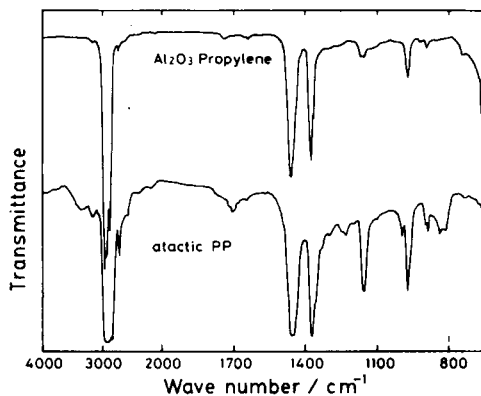


Fig. 8. IR spectra of the commercial atactic polypropylene above and mechanochemically produced atactic polypropylene below.

The consideration combined with the observed fact induces us to believe that no polymers are presumably produced by the mechanochemical method in this case. This makes a remarkable contrast between ethylene and propylene. At present stage the mechanism of mechanochemical polymerization is not clearly understood.

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