

Polymerization of Ethylene and Propylene Initiated by Milled Alumina Powder

NORIO KUROKAWA, MASAYOSHI TABATA, and JUNKICHI SOHMA,
Faculty of Engineering, Hokkaido University, Sapporo 060 Japan

Synopsis

Generation of free radicals (mechano-radicals) by the milling of alumina powder at 77 K was demonstrated by ESR. After milling of alumina in the presence of ethylene (simultaneous milling) at 77 K, polyethylene-propagating radicals instead of the alumina mechano-radicals were detected by ESR. Also the contact of ethylene with the milled alumina converted alumina mechano-radicals into polyethylene propagating radicals at a temperature above the melting point of ethylene. The products extracted by hot toluene from the simultaneous milling were identified by IR to be polyethylene, and their molecular weights were roughly 10,000. The residues after the extraction were bonded with the alumina. Polypropylene was also produced by a similar method of milling of alumina in the presence of propylene. The obtained polypropylene was atactic, and its molecular weight was about 400.

INTRODUCTION

Kargin and Plate¹ initially found that some monomers were polymerized by mechanically fractured metallic oxides such as alumina and silicate. Similar polymerizations were reported by a few researchers.² The mechanically initiated polymerizations reported in the literature were all concerned with monomers that are known to be polymerized easily, for example, methyl methacrylate. An exhaustive review on mechano-chemically initiated reactions on polymers was published by Casale and Porter.³ To our knowledge, no report on polymerizations of ethylene and propylene initiated by fractured metallic oxides has been published. We found that polymerizations of ethylene and propylene were induced by milled metallic oxides such as TiO₂, SiO₂, and B₂O₃. In this paper the mechanical polymerizations of ethylene and propylene initiated by milled aluminum oxide is reported.

EXPERIMENTAL

Samples

Aluminum oxide (γ -Al₂O₃) manufactured by Merck Co. was used. Ethylene and propylene were supplied by Yokohama Chemical Co. and Mitsubishi Petrochemical Co., respectively. The alumina powder used in the experiments was heat treated under vacuum ($\sim 10^{-4}$ torr) for several hours at 363 K.

Milling

The ball-milling apparatus and the special ampoule used are described in detail in a previous paper.⁴ Ball milling was carried out at 77 K or room temperature. The ampoule containing the alumina was evacuated at several temperatures, and purified monomer gas was introduced to the degassed ampoule.

ESR spectra were obtained using a PE-1 X-band spectrometer (JEOL) with 100 KHz modulation. All observations were carried out at 77 K. IR spectra were obtained using an infrared spectrophotometer (Shimazu IR-430), with the KBr method, at room temperature.

RESULTS

Electron Spin Resonance

Ethylene

An ESR spectrum observed from the heat-treated γ -alumina powder milled at 77 K under vacuum ($\sim 10^{-4}$ torr) is shown in Figure 1. Appearance of ESR signals after the milling demonstrated a formation of magnetic centers, that is, generation of free radicals by mechanical action (mechano-radical formation). Ethylene gas was introduced into the glass ampoule containing the heat-treated γ - Al_2O_3 powder, and the alumina covered with frozen ethylene was milled (simultaneous milling) at 77 K by the ball-milling apparatus. ESR spectrum observed from this sample at 77 K after milling at 5 hr is shown in Figure 2(a). The observed spectrum after the milling of the mixtures of alumina and frozen ethylene was apparently different from that of the milled alumina alone. This spectrum is almost identical to the ESR spectrum, shown in Figure 2(b), of the propagating radical ($\sim \text{CH}_2\text{CH}_2\cdot$) of polyethylene.⁵

Ethylene gas was introduced into the sample tube containing the milled alumina, which was kept at 77 K. No changes in the ESR spectrum of the milled alumina was observed at 77 K even after the introduction ethylene to the milled alumina, as shown in Figure 3(a). The sample tube which contained milled alumina and ethylene was then warmed to 123 K and kept at this temperature for 5 min. After this treatment, ESR was observed at 77 K. By this heat treatment the line shape was changed. The observed spectrum is shown in Figure 3(b). New peaks in the observed spectrum correspond to the spectrum of the propagating radicals [Fig. 2(a)], and therefore the spectrum is the superposition of the spectra of the polyethylene radicals and the milled alumina. ESR spectra were observed after heat treatment at the various temperatures, and the

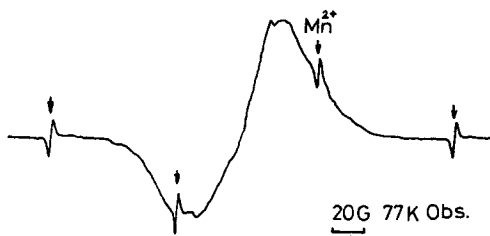


Fig. 1. ESR spectrum observed from milled alumina *in vacuo* at 77 K.

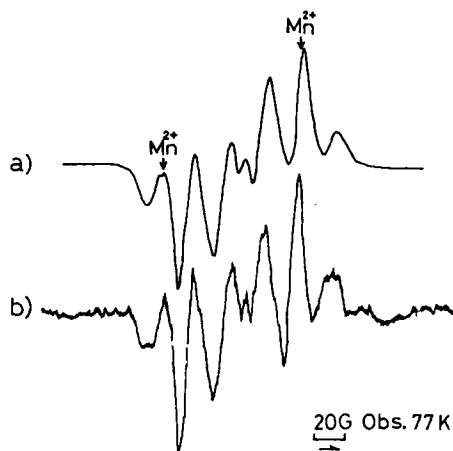
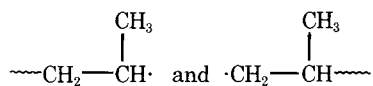


Fig. 2. ESR spectra observed after milling at 77 K: (a) alumina and ethylene; (b) polyethylene *in vacuo*.

relative intensities of the spectra were plotted against the temperatures of the heat treatment. This plot was termed the decay curve and is shown in Figure 4. The decay curves of the spectra shown in Figures 1, 2(a), and 2(b) are represented by squares, open circles, and filled circles, respectively. A sharp decay of polyethylene propagating radicals was observed at the lower temperature in comparison with the decay of the alumina mechano-radical.

Propylene

The ESR spectrum observed at 77 K from the alumina powder covered with frozen propylene, after milling at 77 K, is shown in Figure 5(a). The observed spectrum was quite different from that of the alumina mechano-radicals but equivalent to that of polypropylene mechano-radicals, shown in Figure 5(b). It was identified as the superimposed spectrum of two radical species generated by the scission of polypropylene main chain,⁶



Gas Consumption

Monomer gas consumption, as well as room temperature, for both cases of ethylene and propylene, was observed on milling at 77 K. The experiment was carried out by using a special glass ampoule having a few arms with breakable seals. The pressure of the monomer gas was monitored by a mercury manometer connected to the special glass ampoule after milling. The consumption of the monomer gas was calculated from the observed pressure drop and the known volume of the ampoule. The millimoles of consumed monomer per gram alumina in the ampoule are plotted against the milling time in Figure 6. The gas consumption was roughly proportional to milling time for both ethylene and pro-

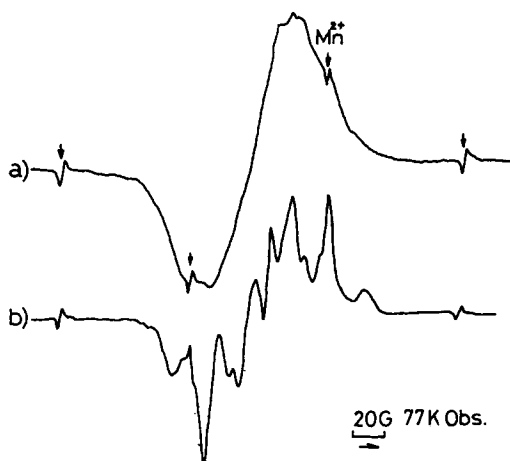


Fig. 3. ESR spectra observed by postpolymerization with ethylene: (a) spectrum from alumina mechano-radical obtained after contact of ethylene at 77 K; (b) after heat treatment at 123 K for 5 min.

pylene. Similar behavior was found for the alumina that had been annealed at 1073 K. The effect of differences in the alumina species was examined. Instead of γ -alumina, α -alumina was used and milled in the ethylene atmosphere at room

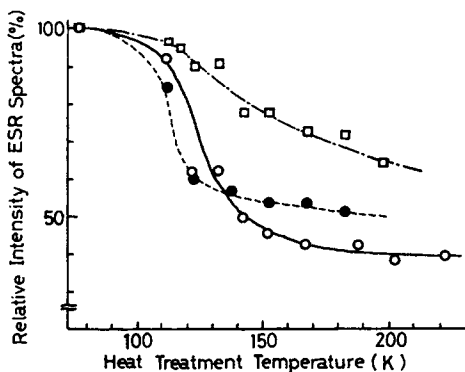


Fig. 4. Decay curves. Open circles are for $Al_2O_3-C_2H_4$; filled circles are for polyethylene mechano-radical; squares are for Al_2O_3 mechano-radical.

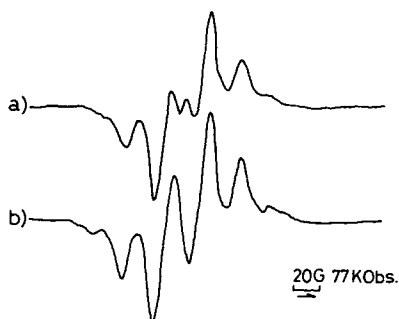


Fig. 5. ESR spectra observed after milling at 77 K: (a) alumina and propylene; (b) polypropylene *in vacuo*.

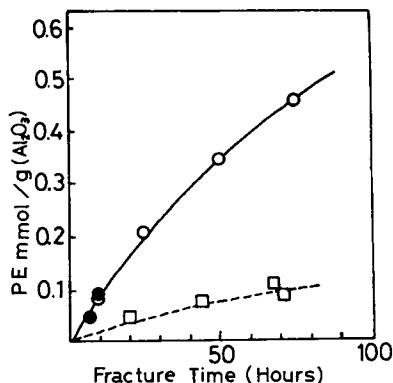


Fig. 6. Monomer gas consumption rate. Open circles are for $\text{Al}_2\text{O}_3\text{-C}_2\text{H}_4$ at room temperature; filled circles are for $\text{Al}_2\text{O}_3\text{-C}_2\text{H}_4$ at 77 K; squares are for $\text{Al}_2\text{O}_3\text{-C}_3\text{H}_6$ at room temperature.

temperature, and gas consumption was measured. The results obtained with α -alumina were almost the same as those obtained with γ -alumina.

Infrared Spectroscopic and Gravimetric Measurements

IR spectra observed from the alumina and ethylene after the milling is shown in Figure 7(a). Absorption peaks at the C-H stretching band (2900 cm^{-1}) and methylene deformation band (1470 cm^{-1}), both marked with arrows in the figure, appeared clearly. The milled sample was then washed thoroughly with hot toluene and the IR spectrum of the washed sample was observed [Fig. 7(b)]. Absorption peaks at both 2900 and 1470 cm^{-1} remained even after the extraction. After drying, the extract was also checked by IR measurement; this spectrum is shown in Figure 8(a). The IR spectrum of high-density polyethylene (Sholex 6050) is shown in Figure 8(b) for comparison. The similarity between the spectra proves that the extract was polyethylene.

Absorption at 2900 cm^{-1} was noted in the spectrum obtained from the Al_2O_3 milled in propylene atmosphere at room temperature. The extract obtained with ethyl ether was not solid but was very viscous and oily even after evaporation

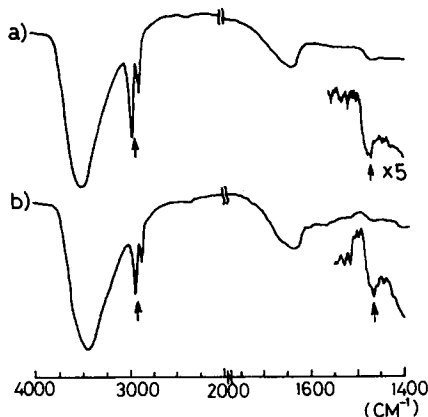


Fig. 7. IR spectra: (a) after milling alumina and ethylene; (b) spectrum from sample washed with hot toluene.

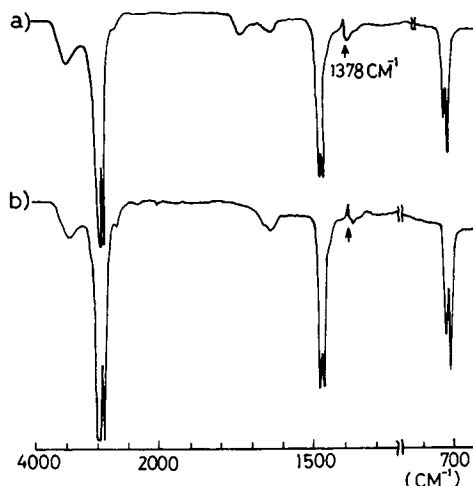


Fig. 8. IR spectra: (a) spectrum of extract from milled sample; (b) high-density polyethylene (Sholex 6050). Arrows indicate 1378 cm^{-1} .

of the ethyl ether. After extraction with ethyl ether, no material was obtained from the alumina-propylene system by washing with hot toluene. This result suggested strongly that no isotactic polypropylene was extracted. The extract was identified as atactic polypropylene by comparison of its infrared spectrum with that of a standard polypropylene sample.

The weights of milled alumina covered with the polymers were measured before and after burning of the sample in an electric furnace. Weight losses were obtained for the alumina-ethylene and alumina-propylene samples, and the results were listed in Table I. Similar weight loss measurements were carried out for the Al_2O_3 -ethylene and Al_2O_3 -propylene samples after washing, and the results were listed as the extracted sample. The weight loss indicates that polypropylene chemically bonded with alumina was produced by the mechanical polymerization. This was reconfirmed by IR measurements of the Al_2O_3 -propylene sample after washing.

DISCUSSION

Al_2O_3 -Ethylene

The asymmetric broad singlet (Fig. 1) of the milled γ -alumina was not assigned to any radical species because of the poor resolution of the spectrum. On the other hand, the radical species produced by milling of the ethylene-coated alumina at 77 K was identified as a propagating radical of polyethylene. From the

TABLE I
Weight Loss of Alumina-Ethylene and Alumina-Propylene after Burning the Samples

| Sample | Weight loss, % | |
|-----------|--|--|
| | $\text{Al}_2\text{O}_3 + \text{C}_2\text{H}_4$ | $\text{Al}_2\text{O}_3 + \text{C}_3\text{H}_6$ |
| Milled | 7.8 | 3.9 |
| Extracted | 3.6 | 2.3 |

contact of ethylene with milled alumina, the superposition of the spectrum of the propagating radicals was observed, as shown in Figure 3(b). These results demonstrate that Al_2O_3 mechano-radicals were converted into polyethylene propagating radicals. This radical conversion indicates that ethylene polymerization was initiated by the alumina mechano-radicals prior to propagation. The ethylene polymerization occurred at 77 K in the case of simultaneous milling of the alumina and solid ethylene in contact with the milled alumina.

An ESR spectrum was not detected from the alumina-ethylene system after milling at room temperature. However, consumption of monomer gas, which was nearly linear with milling time, was observed. The most reasonable interpretation of this consumption of monomer gas is that a phase change of ethylene from the gas to the solid occurred. Therefore, this experimental result suggests strongly that polymerization of ethylene was initiated at room temperature by the milled alumina and propagated to consume nearly two-thirds of the initial amount of the monomer gas. The last but most direct evidence for the polymerization is the observed IR spectra. Peaks characteristic of methylene in the simultaneous milling of alumina-ethylene are present. The spectrum of the extract was the same as that of polyethylene. Mechanisms of the initiation of polymerization by the alumina mechano-radical and of the propagation step have not yet been elucidated.

No marked difference was observed in the polymerization even when α -alumina was used instead of γ - Al_2O_3 , although the specific surface area of α - Al_2O_3 is much smaller than that of γ - Al_2O_3 . These facts indicate that polymerization was not influenced by the intrinsic nature of the alumina, which differs for the α -type and the γ -type, but was determined by the mechanical action. The molecular weight of the polyethylene produced by this mechano-polymerization, determined by the viscosity⁷ of decalin solution at 408 K, was found to be about 10,000. More branching in the mechanically polymerized polyethylene than the high-density polyethylene standard was also found from comparison of the methyl peaks at 1378 cm^{-1} in the observed spectra.⁸ The mechanically produced polyethylene had 10–20 branches per 1000 carbons, and the crystallinity of the mechanically produced polyethylene was estimated to be 60–70% from IR measurement at 720 and 730 cm^{-1} .^{9,10}

After extraction by hot toluene, the weights of the milled alumina were measured before and after the burning of the sample. According to these results, 40–50% polyethylene remained in the sample, as shown in Table I. This suggests that some (40–50%) of the mechanically produced polyethylene molecules were chemically bonded to the alumina.

Al_2O_3 -Propylene

Polymerization of polypropylene by the alumina mechano-radicals was concluded from the experimental results, which were similar to the changes in ESR spectra and, monomer consumption observed with alumina-ethylene. Most of the polypropylene produced by this mechanical method at room temperature was extracted by ethyl ether. The observed IR spectrum of the extract was identical to that of atactic polypropylene, and therefore we conclude that atactic polypropylene was produced by the milling of Al_2O_3 and propylene. The molecular weight of this atactic polypropylene was estimated by means of the vapor pressure method to be about 300–500.

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