Fuming nitric acid treatment of isotactic polypropylene film

I. Effects of selective oxidation on proton spin-lattice and spin-spin relaxation times

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Abstract: Fuming nitric acid treatment has been made on a melt-quenched and an annealed isotactic polypropylene film. The treated samples were characterized by measurements of weight loss, density, molecular weight, spin-lattice, $T_1$, and spin-spin, $T_2$, relaxation times. Concurrent with the increases in weight loss, density and a decrease in molecular weight, increases in $T_{10}$ and $F_a$, a fraction of crystalline region, and decreases in $T_{2a}$ and $F_a$, a fraction of amorphous region, were observed as a consequence of the decrease in an amount of noncrystalline portions. However, unexpected fall in $T_{10}$ was also observed after about 2–3 hr of treatment time. These observations were discussed by the structural changes that took place during acid etching.

Key words: Fuming Nitric Acid, Isotactic Polypropylene, Proton Magnetic Relaxation, Spin-Lattice Relaxation Time, Spin-Spin Relaxation Time.

Introduction

A selective oxidative degradation technique with fuming nitric acid has been extensively used for the investigation of the polymer morphology since Palmer and Cobbold [1] have successfully utilized this technique in the structural study of bulk polyethylene. A great deal of works using this technique have been made mainly on polyethylene [1–51] and a few papers have described the morphological study of ethylene-propylene [53–55], ethylene-butene [52–55], and other copolymers [56] and isotactic polypropylene [57–60]. There are also few papers which describe the structural study of the single crystals [6, 10] and the bulk polyethylene [14, 21], using the nuclear magnetic resonance, treated with fuming nitric acid. In the present study a description was given of the effects of the fuming nitric acid treatment on the proton spin-lattice and spin-spin relaxation times of the isotactic polypropylene film. Concurrent with the measurement of these relaxation times, the changes in density, weight loss, and molecular weight were also measured as a function of treatment time. These data are expected to provide useful information on the structural changes that take place during fuming nitric acid treatment.

Experimental

Material

The material used in this study was an isotactic polypropylene film about 0.85 mm thickness and was characterized by the $M_n = 45,000$, $M_w = 270,000$, and $M_w/M_n = 6.0$. Tacticity which was determined by extraction with boiling $n$-heptane was 94.4%.

Preparation of sample film

Two series of samples were prepared as follows.

1. A piece of the parent sample film was melt-pressed in a hot press at 230 °C for 5 min at about 40 kg/cm² between thin chrome-coated plates followed by quenching in ice water. The thickness of the film was about 0.30 mm. Hereafter the sample film prepared by this procedure is referred to as a "melt-quenched sample".

2. The melt-quenched sample was annealed in a poly(ethylene glycol) bath at 155 °C for 1 hr and then quenched in ice water. Hereafter the sample film prepared by this procedure is referred to as an "annealed sample".

Fuming nitric acid treatment

Both the melt-quenched and the annealed samples, 8 cm in length, 2 cm in width, and about 0.30 mm in thickness, were employed for the fuming nitric acid treatment. The sample film was placed in a large glass tube and 100 ml of fuming nitric acid was poured into the glass tube. Then the glass tube was immersed into a poly(ethylene glycol) bath thermostatted at 70 °C. After treatment for desired time the glass tube was transferred to water and cooled to room temperature. Then the sample film was taken out from the glass tube, rinsed by water and finally extracted with acetone using a Soxhlet extractor for 6 hr and dried in an air oven at 60 °C for 4 hr.

Weight loss measurement

Weight loss of a sample was determined from the change in weight of the sample before and after treatment.

weight loss (%) = \((W_0 - W)/W_0 \times 100\)
where \( W_0 \) and \( W \) refer to weight of the sample before and after treatment, respectively.

**Density measurement**

The densities of the samples were measured in a density gradient column prepared with \( \pi \)-propyl alcohol and water at 23 °C.

**Molecular weight measurement**

The measurements of the \( M_w \) and \( M_n \) of the sample were carried out with a Waters Associates GPC 150C.

**Measurement of relaxation times**

Spin-lattice and spin-spin relaxation times were measured using a Bruker P 20 wide line pulse spectrometer operating at 19.8 MHz at 40 °C. A spin-lattice relaxation time, \( T_1 \), was obtained from 180°-t-90° pulse sequences and a spin-spin relaxation time, \( T_2 \), was obtained from a free induction decay (FID) following a 90° pulse. The mobile (amorphous), intermediate and rigid (crystalline) fractions of the sample were also determined from the FID curve using the method reported by Fujimoto et al. \[61\], as well as \( T_2 \). An accumulation of FID signals were carried out with a Transient Memory M 100E and an averager TMC 600 of Kawasaki Electronics Co., Ltd. and resulted in considerable improvement in S/N ratio.

**Results and discussion**

Figure 1 shows the weight loss plotted as a function of time of exposure to fuming nitric acid. There is a more considerable increase in weight loss for the melt-quenched sample than for the annealed sample as the melt-quenched sample contains larger amounts of noncrystalline portions which are susceptible to acid attack. It is also expected that the crystalline portions are gradually attacked by the acid upon further treatment \[57, 58\].

Density is plotted as a function of treatment time in figure 2. As is similar to the situation in the weight loss, the change in density is also more pronounced for the melt-quenched sample than for the annealed one and the values of density for both samples become approximately equal after treatment time of 3.5 hr - 4 hr, suggesting that the major parts of the noncrystalline portions are removed by the preferential oxidation. The density of the sample treated longer than 3.5 hr exceeds the theoretical value of the crystalline density, 0.936 g/cm³ \[62\], owing to the addition of the heavy nitro- and carboxyl-groups at the end of the chain \[57, 58\]. Therefore, the treatment time which yields the value of crystalline density, i.e., about 3.5 hr, is not necessarily the time at which all the noncrystalline portions are removed. Considering the change in slope of the curve, it is expected that the noncrystalline portions of the sample are almost completely removed after treatment time of 4 hr.

Fig. 1. Weight loss plotted as a function of treatment time. ◆ melt-quenched sample, ○ annealed sample

Fig. 2. Density plotted against treatment time. ◆ melt-quenched sample, ○ annealed sample