

NOTE

Morphology of Polyethylene Produced by Alumina-Supported Zirconium Tetrabenzyl

INTRODUCTION

The morphology of the beads of polymer produced by polymerization of ethylene with an alumina-supported zirconium tetrabenzyl catalyst has been studied as a function of conversion, and it was concluded that the development of the structure was dependent upon the ratio of polymerization to monomer diffusion rate.¹ In this work, the effect of more rapid polymerization rate to the morphology was studied.

RESULTS AND DISCUSSION

The initial monomer concentration at 8 atm pressure is four times higher ($\sim 0.712 \text{ mol L}^{-1} \text{ atm}^{-1}$) than in the previous work.^{1,2} On the other hand, the 25°C rise in temperature during the polymerization results in about a five times higher polymerization rate since activation energy was reported³ to be 16 kcal mol⁻¹. The overall polymerization rate could be considered about 20 times higher than the rate of the system described in the early publication.¹

Aggregates of polymer subparticles, which consist of disintegrated alumina granules and shish-kebab type crystals, were obtained (Fig. 1). At higher magnification, the shish and kebabs can be seen early.

The results of DSC studies were similar to those for slower polymerization.^{1,2} The initial melting peak temperature was about 140°C and remelting after cooling was at 133°C (heating and cooling rate = 8°C min⁻¹). On cooling there was also a shoulder on the high temperature side of crystallization exotherm. This was due to some retained order in the molten polymer, which was able to initiate crystallization. This shoulder disappeared rapidly on annealing the sample above its melting point (at 177°C for 1 min) or exposure to fuming nitric acid (Figs. 2 and 3). The effect of heating rate on the first melting is shown in Figure 4. At low heating rates annealing behavior and at high heating rates superheating behavior seem to be present. After 8 h oxidation, superheating behavior disappears completely (Fig. 5). This is a typical behavior of shish-kebabs, oriented crystalline fibers.

It was observed with an optical microscope that the aggregates remain visibly intact throughout the crystalline melting process and only collapse when they reach a temperature of about 180°C. One-hour-oxidized samples collapse at 140°C. DSC observations together with electron microscope pictures of the sample and optical microscope studies clearly show that the initial granules disintegrate and polyethylene crystallizes mainly in the form of shish-kebabs when the initial rate of polymerization is so high that the polyethylene chains may not find enough time to crystallize during formation. Therefore, at the beginning of the polymerization, polyethylene fills the pores of alumina granules so fast that it causes the granules to disintegrate.

From these results, it can be concluded that high initial rate of polymerization cause the granules to disintegrate during polymerization to give morphology different from, but about the same melting behavior as, those in the previous work.

EXPERIMENTAL

Preparation and characterization of the catalyst was carried out in a similar way described before.¹ The alumina used for supporting the catalyst was Ketjen grade B, which consist of spherical particles of 20–70 μm diameter. It was dehydrated at 500°C and treated with zirconium tetrabenzyl. Polymerization of ethylene was carried out in a stainless-steel reactor using toluene

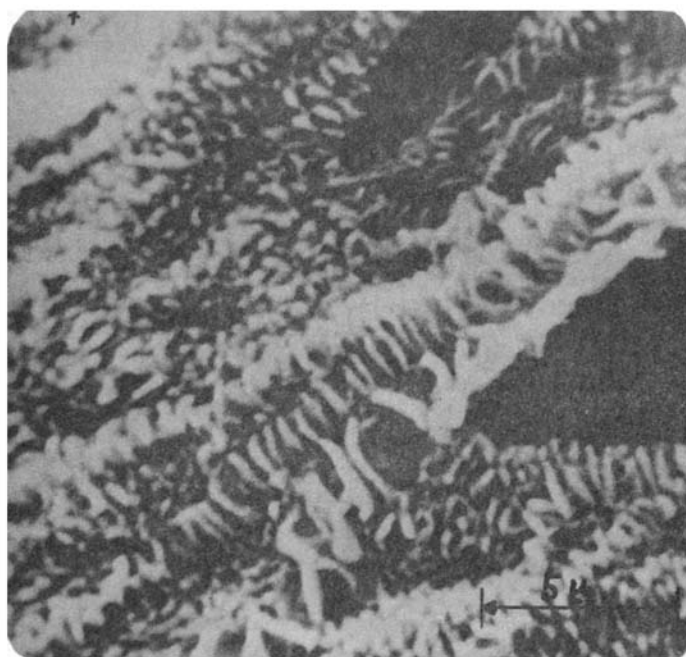
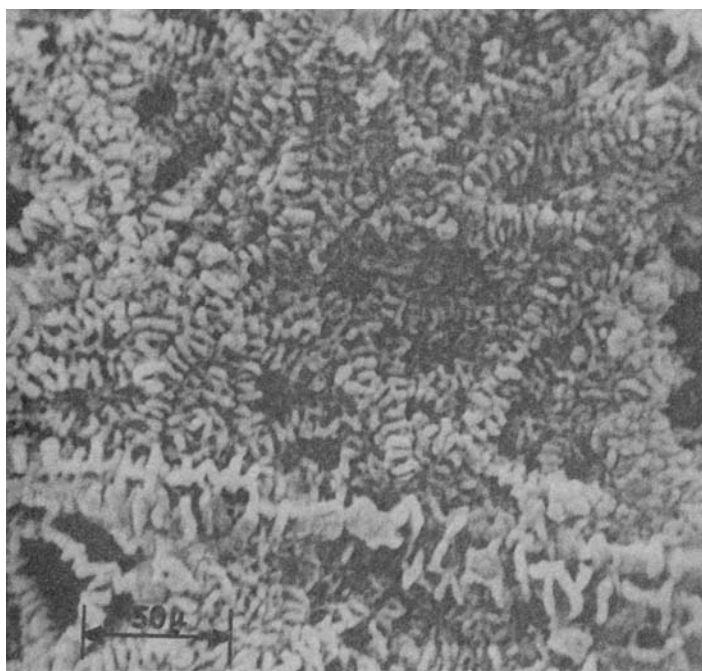


Fig. 1.

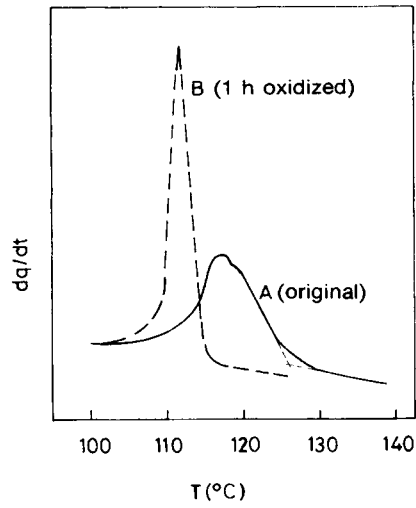


Fig. 2.

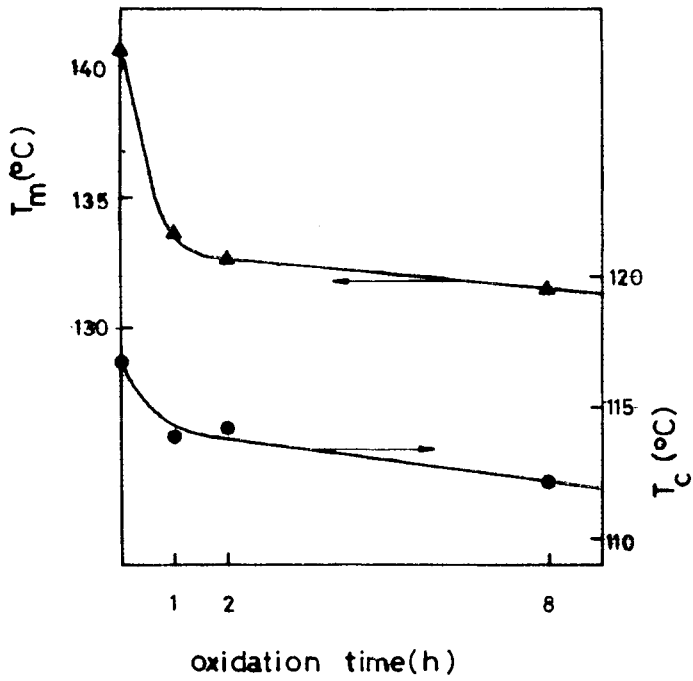


Fig. 3.

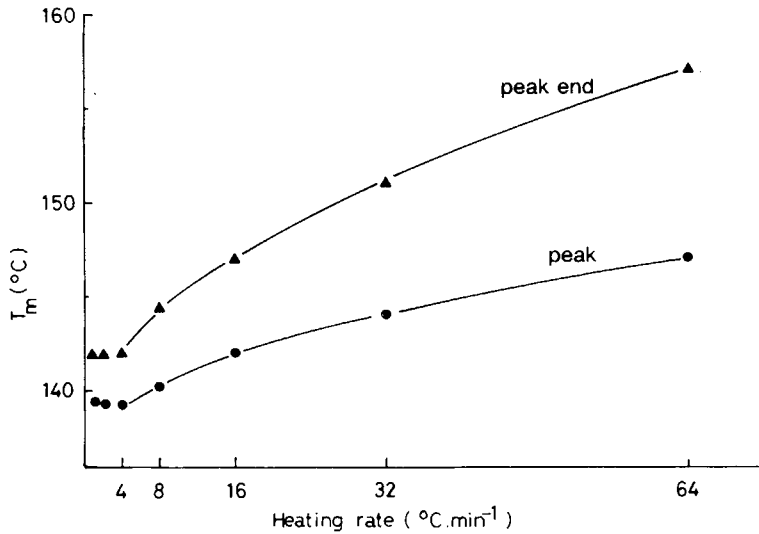


Fig. 4.

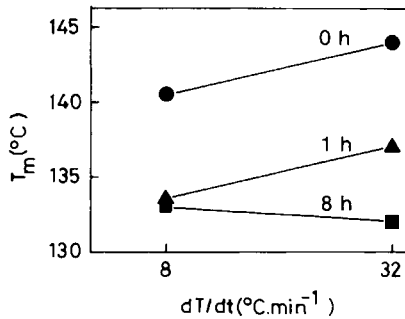


Fig. 5.

as the suspension medium. The polymerization vessel was pressurized with ethylene to a pressure of 8 atm at 55°C and the mixture continuously stirred. The temperature rose from 55 to 80°C during the polymerization due to low heat transfer from the reactor to the cooling media. After about 15 min, the polymerization was terminated by addition of methanol and the polymer recovered by filtration. Yield: 100 g/g alumina. Differential scanning calorimetry was performed using a Perkin-Elmer DSC-1.

References

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