

Synthesis of Polyethylene Using Ultrasonic Energy with a Metallocene Catalyst

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ABSTRACT: Ethylene polymer was synthesized by the treatment of a metallocene catalyst $Zr(CP)_2Cl_2$ solution with ultrasonic energy. Ultrasonic energy irradiation was used to change the polymer structure of the formed polymer. Different ultrasonic energy irradiation times were applied to the metallocene catalyst solution. The ultrasonic energy had an effect on the average molecular weight, molecular weight distribution, and polymer productivity. A lower average molecular weight and a narrower molecular weight distribution

were produced with a longer ultrasonic irradiation time. The polymer productivity was almost constant when the metallocene catalyst was treated with ultrasonic energy. Finer polyethylene particles were produced with longer ultrasonic irradiation times. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 756–759, 2006

Key words: catalysts; metallocene catalysts; polyethylene (PE)

INTRODUCTION

Polyethylene (PE) is a very important polymer in the plastic industry. The PE industry has a multibillion-dollar-per-year turnout, with a world-wide production in excess of 160 billion pounds.¹ PE has excellent electrical properties, good clarity, high impact strength, good chemical resistance, and excellent processability. The PE industry is one of the major industries that require catalysts for its production.

Ultrasonic energy can be applied to ethylene polymerization. Ultrasonic energy plays an important role in controlling the polymer structure of the polymer produced with organometallic reagents and a metallocene catalyst. Ultrasonic energy has shown an effect on polymers produced by emulsion ultrasonic polymerization.^{2–4} The high temperature created as a result of bubble collapse (cavitation phenomenon or hot spot theory) is responsible for the initiation of free-radical emulsion polymerization.² This hot spot is estimated to have radii smaller than 299 nm with a lifetime of less than 2 μ s. On solid surfaces, asymmetric bubble collapse will lead to liquid microjets directed toward the surfaces with a velocity estimated to be as high as 100 m/S. This action by ultrasonic energy will increase the collisions between the particles, erosion, solid breakage, and well-known mixing. In the vicinity of a solid surface, ultrasonic streaming

produces strong convective currents that cause a reduction of the thickness of diffusion layers, thereby enhancing diffusion-controlled processes.⁵

A recent work in material chemistry has been the preparation of ultrafine particles.⁶ Sonochemical decomposition experiments of organometallic compounds have provided very interesting results.⁷ One of the advantages of sonochemical synthesis is that various results of nanophase materials can be generated by a change of the reaction medium. For example,⁷ when a metal precursor is sonicated in high-boiling alkanes such as decane, nanostructure powders are formed. However, when a polymeric ligand such as polyvinylpyrrolidone is used with a metal precursor, nanophase metal colloids are obtained, or when inorganic supports such as silica are used, nanostructured supported metal catalysts are generated with very interesting catalytic activity.

EXPERIMENTAL

Apparatus

A Sonics and Materials (Newtown, CT) model VCX-750 20-kHz ultrasonic generator with a 13-mm solid probe standard titanium horn was used. The oscillator power ranged from 0 to 100%, and the acoustic energy² was set at 50% (corresponding to 10 W/cm²). A three-necked, 50-mL Suslick reaction vessel was used to carry out ultrasonic irradiation with bushing, an O-ring, and an adapter to be connected to the ultrasonic probe.

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Reagents and materials

Toluene and 10% methylaluminoxane (MAO) in toluene were obtained from Aldrich (Gillingham, United Kingdom). The catalyst $Zr(Cp)_2Cl_2$ was obtained from Aldrich, and 2.5×10^{-5} mol was prepared in the solvent toluene.

Polymerization procedure

Different polymerization conditions were studied with ultrasonic irradiation and metallocene catalysts. The polymerizations were performed in a Fischer bottle reactor (Washington, DC). The ingredients for the polymerization were 5 mL of 10% MAO in toluene and 44 mL of toluene. These were added to a 50-mL Suslick reaction vessel. To this, 1 mL of 2.5×10^{-5} mol of a metallocene catalyst was also added. The Suslick vessel was connected to an ultrasonic probe inside a glove drybox and taken to the VCX-750 ultrasonic generator at different times for ultrasonic energy irradiation. The temperature was controlled with cold water to keep the temperature at $25 \pm 2^\circ C$. The top of the Suslick vessel was covered with a stopper. The tip of the horn was placed in the Suslick vessel at 1.0 cm from the bottom of the vessel. The solution was transferred into a Fischer 250-mL bottle reactor inside a glove drybox; then, the reactor was taken out, and 99.99% ethylene gas was purged under 60 psi. The stirring was performed with a magnetic bar at 500 rpm at room temperature. The polymerization was quenched with methanol. The polymers were separated by filtration, washed with methanol, and dried *in vacuo*.

Density measurements

The density of the polymer particles was measured with a AccuPyc (Norcross, GA) 1330 pycnometer model analyzer.

Molecular weight analysis

The average molecular weights were measured by gel permeation chromatography (GPC) with mixed-bed B columns (300×7.8 mm i.d., 10- μ m particle size) sup-

plied by Polymer Labs (Amherst, MA) with Cirrus software version 2.0 and a Hamielec calibration (linear) model for the evaluation. The flow rate was 0.9 mL/min, trichlorobenzene was used as the eluting solvent, and the measurement was performed at $150^\circ C$. Four calibration broad-molecular-weight PE standards were used.

RESULTS AND DISCUSSION

Ultrasound by itself has no measurable action on chemical bonds. Indeed, under the usual conditions of most sonochemical experiments, the energy density⁵ of an acoustic field is only about 10^{-10} eV per atom ($1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$). Because no direct interaction is possible between the wave and the matter, an indirect phenomenon must act as a relay to induce a reaction. This phenomenon is called cavitation. Cavitation is a description of bubble formation in a liquid as the wave propagates. After an expansion forced by the acoustic field, the bubble undergoes a violent collapse during compression, which focuses mechanically the low energy density of the sound field by more than 11 orders of magnitude. There are two possible mechanisms by which an enhanced chemical reaction occurs with ultrasonic energy. First, a high local temperature produced during the compression phase of bubble collapse will result in the dissociation of the molecules in the system. Second, shear stresses and shock waves will cause the movement of solvent molecules around the bubble and produce intense field flows of solvent molecules toward the bubble. This can also enhance a chemical reaction by a mechanical degradation process.

Ultrasonic energy has been used in organometallic synthesis and in syntheses involving organometallic reagents. Price⁸ used a Ziegler–Natta catalyst: high-density PE, polypropylene, and other polyolefins were produced with a mixed metal catalyst containing a vacant coordination site, such as alkyl aluminum with titanium tetrachloride. Styrene polymer was synthesized with a Ziegler–Natta catalyst with the support of ultrasonic energy. He showed that the reaction was sped up because of an enhanced transfer of the monomer to the active sites on the catalyst, which had

TABLE I
Effect of Different Ultrasonic Irradiation Times on the Molecular Weight of PE

Time of ultrasonic irradiation (min)	Number-average molecular weight	Weight-average molecular weight	Polydispersity
0.0	93,107	297,367	3.2
10	45,251	239,267	5.3
15	16,828	99,619	4.7
20	5,045	27,212	3.0

The results are the averages of two measurements.

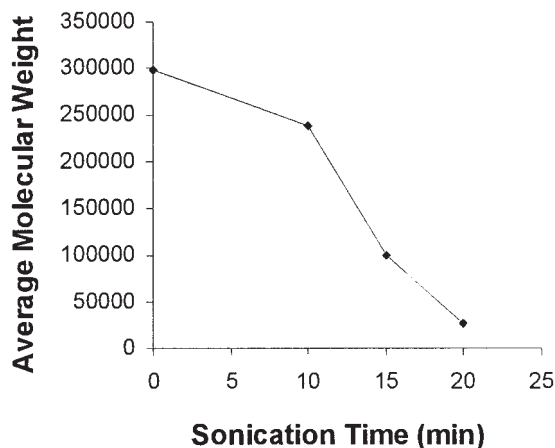


Figure 1 Average molecular weight of PE at different irradiation times.

dramatic effects on the molecular weights while high stereoselectivity was maintained. The molecular weight showed a broader distribution in the absence of ultrasonic energy irradiation. The polymerization of ethylene⁹ by either the classical heterogeneous Ziegler–Natta catalyst or a homogeneous metallocene catalyst usually gives highly linear polymers (i.e., high-density PE). The production of branched PE requires copolymerization with another monomer such as 1-butene, 1-hexene, or 1-octene or with a nickel-type catalyst¹ to produce branched PE. In this study, Ultrasonic energy has been used to synthesize PE with a metallocene catalyst.

Effect of ultrasonic energy on the molecular weight and molecular weight distribution of PE

The molecular weight and molecular weight distribution are very important characteristics of any kind of

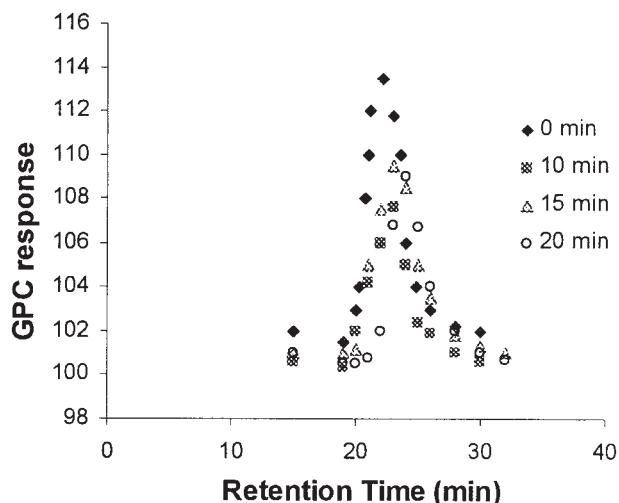


Figure 2 Average molecular weight and molecular weight distribution of PE at different irradiation times.

TABLE II
Some Physical Properties of the Produced PE

Time of ultrasonic irradiation (min)	T_m (°C)	Density (g/cm ³)	Yield (g)	Polymer productivity (kg/mmol)
0.0	117.5	0.99	10.5	25.1
10	117.5	0.98	9.4	24.5
15	114.6	0.98	7.2	22.8
20	109.4	0.96	7.4	23.6

The results are the averages of two measurements.

polymer.¹ Many methods¹⁰ have been used to control the molecular weight. The nature of the ligands and the stereochemistry of these ligands^{10,11} in catalyst compounds are very important for controlling the molecular weight and molecular weight distribution. The temperature and pressure¹⁰ are also important factors for controlling the molecular weight. Price⁸ found that ultrasound has an effect on the molecular weight of polystyrene produced with a Ziegler–Natta catalyst and ultrasonic irradiation. A narrower peak distribution of polystyrene was produced with a longer time of sonication irradiation. In this work, ultrasonic energy was applied to a metallocene catalyst solution, and the polymerization of ethylene gas was applied to produce PE. The polydispersity decreased with an increasing sonication time, as shown in Table I. Lower molecular weight PE was produced with a longer time of sonication irradiation, as shown in Table I and Figures 1 and 2. As explained previously, a possible explanation for this reaction is that shear stress and shock waves as a result of bubble collapse during irradiation with ultrasonic energy cause a movement of solvent molecules around the bubble and produce intense field flows of solvent molecules toward the

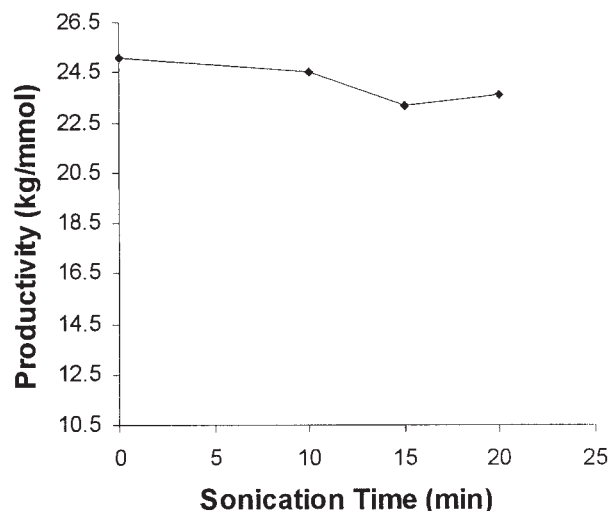


Figure 3 Polymer productivity of PE at different irradiation times.

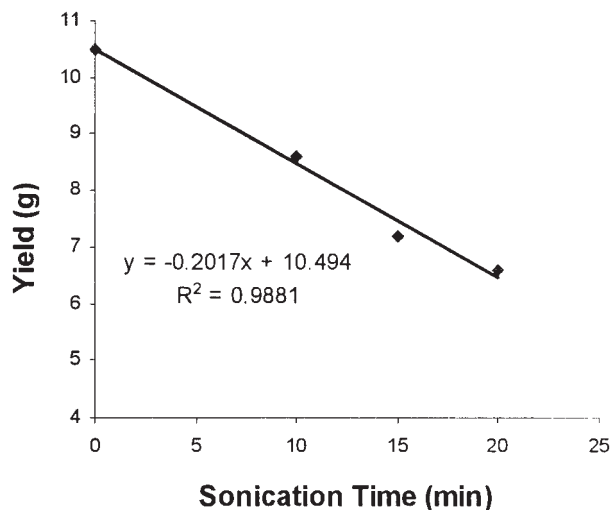


Figure 4 Yield of PE at different irradiation times.

bubble. This action may enhance the chemical reaction by creating more active catalyst, which will lead to the changes in the molecular weight and molecular weight distribution

Effect of ultrasonic energy irradiation on the polymer production and yield

The polymer productivity was almost constant when a metallocene catalyst was treated with ultrasonic energy, as shown in Table II and Figure 3. The yield of PE decreased with longer ultrasonic irradiation. The yield showed linear propagation with the ultrasonic irradiation time, as shown in Figure 4. The stereochemistry of the ligand is a very important factor for determining the reactivity of the polymer produced because the ligand controls how much monomer will

enter the center metal to build up the polymer. Ultrasonic energy can displace the ligand to let more monomers enter the center metal.

CONCLUSIONS

Ultrasonic energy is a good technique for controlling the PE structure. Ultrasonic energy has an effect on the average molecular weight and molecular weight distribution. A lower average molecular weight and a narrower molecular weight distribution of PE are produced with a longer sonication time. Almost constant polymer reactivity is produced when a metallocene catalyst is treated with ultrasonic energy. Finer PE particles are produced with longer ultrasonic irradiation times.

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