

Sorption and Polymerization of Methyl Isopropenyl Ketone in Low-Density Polyethylene

MINI AGARWAL and KYU YONG CHOI*

Department of Chemical Engineering, University of Maryland, College Park, Maryland 20742

SYNOPSIS

The polymerization of methyl isopropenyl ketone (MIPK) inside low-density polyethylene beads has been studied with lauroyl peroxide as the initiator. The reaction was carried out by first immersing the polymer beads in a liquid solution of MIPK monomer and initiator for 5 h at 55°C and then draining the excess liquid. The temperature of these monomer-soaked beads was increased to a reaction temperature (85°C) and the monomer was polymerized in the solid resins. The bulk polymerization of MIPK and the sorption characteristics of MIPK and initiator were also investigated through experimentation and model simulation. It has been observed that the monomer uptake in the solid polymer increased considerably in the presence of the lauroyl peroxide initiator in the liquid phase during the sorption stage. The differential scanning calorimetry study also indicated that some changes in the polymer morphology have occurred due to the incorporation of poly-MIPK into the polyethylene resins. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

With the rapidly growing environmental movement in recent years, society has become more aware of the problem of waste disposal and the environmental hazards that plastics pose to the land. The plastics industry is responding to this public outcry by the development of environmentally benign polymers. Both biodegradable and photodegradable polymers are being actively researched. Certain commercial polymers such as low-density polyethylene (LDPE), which are extensively used as packaging films, can be made partially photodegradable by incorporating photosensitive additives or comonomers into the polymer matrix. These light-sensitive materials or chromophores degrade upon exposure to ultraviolet radiation, causing the destruction of carbon-carbon bonds in high molecular weight molecules. However, the current technology for manufacturing commodity photodegradable polymers has some limitations in that the efficiency of ultraviolet light absorption is low and that they are expensive to manufacture. To improve the modification techniques for pro-

ducing photodegradable polymers, there is a need to understand the fundamental chemical and physical phenomena associated with the polymer modification process.

It has been reported in the literature that copolymers of polyethylene, polystyrene, poly(methyl acrylate), poly(methyl methacrylate), aliphatic polyesters, nitrile copolymers, and acrylonitrile and its copolymers with various ketone monomers degrade upon exposure to ultraviolet light.¹⁻⁵ For example, Alexandru and Guillet⁵ reported that fibers spun from specially prepared acrylonitrile copolymers containing small amounts of poly(methyl isopropenyl ketone) (poly-MIPK) lost most of their tensile strength and elongation after having been exposed to natural sunlight outdoors for several months, whereas the control samples that lacked this photosensitive additive retained their strength for much longer periods of time.

In this article, we investigated the polymerization of MIPK in low-density polyethylene beads. In an industrial polymer modification process, these virgin polymer beads are directly treated by MIPK and converted to photodegradable polymers. Thus, the main objective of this work was to study the synthesis of the MIPK polymer within LDPE beads with the aim of producing a photodegradable poly-

* To whom correspondence should be addressed.

mer. In our work, we utilized original beads of LDPE that are commercially available.

EXPERIMENTAL

Materials

Methyl isopropenyl ketone (MIPK) was supplied by RWE-DEA Aktiengesellschaft für Mineralöl und Chemie and was distilled under vacuum before use and its purity was confirmed by gas chromatographic analysis. Liquid hexane was provided by Exxon Company U.S.A. and was used as supplied. The initiator, lauroyl peroxide, was supplied by Atochem North America, Inc., and had an assay concentration of 98% as reported by the company. The low-density polyethylene (LDPE) beads were supplied by C & D Warehouse ($\rho = 0.92 \text{ g/cm}^3$).

Polymerization of MIPK in LDPE Beads

The polymerization of MIPK monomer in LDPE beads was carried out in two stages. First, monomer and initiator were sorbed into the PE beads during a 5 h soak period at a temperature of 55°C in a glass reactor fitted with a jacket through which oil from a temperature-controlled oil bath circulated. Then, the excess liquid not sorbed by the beads was drained from the bottom of the reactor, and the polymerization was carried out in the dry state at a temperature of about 85°C. Once the desired reaction time was over, the beads were immediately removed from the reactor. They were then dried *in vacuo* until all the unreacted monomer was expelled. Their final weight was noted. Since it is of interest to be able to predict the degree of MIPK polymerization within the beads, one must know the sorption characteristics of MIPK and lauroyl peroxide in the polyethylene beads and the extent of polymerization at the reaction conditions employed. In what follows, we report experimental results for the sorption of MIPK and lauroyl peroxide in LDPE and the bulk polymerization of this monomer.

Sorption Experiments

A known amount of LDPE beads were filled into a Pyrex test tube to which MIPK was then added. The test tube was sealed with a rubber septum and suspended in a constant temperature oil bath maintained at the desired temperature. The test tube was

periodically removed from the oil bath, the beads were quickly patted dry with a tissue, placed in a capped bottle, weighed, and then reinserted into the oil bath. In this way, the change in bead weight as a function of time was measured, allowing one to determine the time necessary to reach sorption equilibrium. One potential source of experimental error associated with this method (which cannot be eliminated) is that it was difficult to remove all the liquid from the bead surface. To measure the diffusivity of lauroyl peroxide (initiator) in the polyethylene beads, the same procedure was followed with some modifications. In this case, the beads were soaked in a solution of hexane and initiator of the desired initiator concentration (0.20 mol/L). Several samples were prepared. Periodically, a sample was removed, the beads were quickly patted dry with a tissue and weighed in a capped bottle, and then dried in the vacuum oven for several days at $\sim 40^\circ\text{C}$ to remove all the hexane present, leaving only the initiator behind. The bead weight after drying *in vacuo* was noted.

The diffusivity was determined from the weight gain data. The sorption and desorption kinetics for a spherical particle are given by the following relationship⁶:

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(\frac{-Dn^2\pi^2 t}{a^2}\right) \quad (1)$$

where t represents time; M_t is the mass of diffusant absorbed at time t ; M_∞ , the mass of diffusant absorbed at equilibrium; D , the diffusivity; and a , the sphere radius. However, before we could calculate the monomer diffusivity, the radius of these beads had to be determined. The beads used in this study were not all of the same shape or size, some of them being larger than others and somewhat cylindrical/spherical in shape. Therefore, the weight-equivalent radius, i.e., the radius of a spherical particle having the same weight as one polyethylene bead, was used. This value was determined using the following equality:

$$\text{Total sample weight} = N_{\text{beads}} \left(\frac{4}{3}\pi a^3\right) (\rho_{\text{PE}}) \quad (2)$$

where N_{beads} is the number of beads and a represents the weight-equivalent radius. For the polyethylene beads used in this study, the weight-equivalent radius was found to be 0.205 cm. Rosenbrock's optimal parameter search method was employed to estimate

the monomer diffusivity from the weight gain data. A good initial guess for D was calculated by using the following approximate solution to eq. (1) at $(M_t/M_\infty) = 0.5$ (Ref. 7):

$$D \cong \frac{0.00766d^2}{t_{1/2}} \text{ (cm}^2/\text{s)} \quad (3)$$

where $t_{1/2}$ is the diffusional half-time (s), and d , the sphere diameter (cm). To calculate the uptake of MIPK per gram of polyethylene, Y , the monomer concentration at each time τ is integrated according to the following equation:

$$Y = \frac{\left[\int_{r=0}^{r=a} 4\pi r^2 C(r) dr \right] (M_M)}{\frac{4}{3}\pi a^3 \rho_{PE}} \quad (4)$$

where M_M is the molecular weight of MIPK. For the integration of the monomer concentration profile, one needs to solve the dynamic diffusion equation and to specify the surface concentration of the monomer. The surface concentration of the monomer, C_s , is related to the concentration of the monomer in the bulk liquid phase, C_b , as follows:

$$C_s = \phi C_b \quad (5)$$

in which ϕ is the solubility coefficient measured from the sorption experiments.

Figure 1(a) shows the monomer uptake in the LDPE beads at a temperature of 55°C. It is observed that sorption equilibrium is attained after approximately 30 h and that the amount of MIPK sorbed into the polyethylene accounts for about 9% of the polymer weight at the equilibrium state. Similar experiments were performed using LDPE films made from the same beads and the results are shown in Figure 1(b). The rate of monomer sorption is much faster in the LDPE films than in the beads, as expected, and the equilibrium monomer uptake values are very close for both cases. The variations in these values is due to differences in the substrate morphology. These experiments with beads and films yielded close values of the monomer diffusivity.

The initiator diffusivity and solubility coefficient in the polyethylene pellets at 55°C were also estimated. In this case, the bulk concentration of the initiator at sorption equilibrium will be different from that at the start of the experiment due to the diffusion of initiator from the hexane solution into the beads. At equilibrium, the surface and bulk concentrations may be expressed as follows:

$$\frac{N_{eq}}{V_p} = \phi_{init} \left(\frac{N_{i0} - N_{eq}}{V_s} \right) \quad (6)$$

where N_{i0} is the initial amount of the initiator; N_{eq} , the amount of the initiator inside the beads at sorption equilibrium; V_s , the volume of the solvent in which the initiator is dissolved at equilibrium; and V_p , the volume of the polymer. Figure 2 shows the initiator uptake data. The value of N_{eq} is estimated from the experimental data, and V_s is given by the initial volume of hexane in which the initiator is dissolved minus the volume of hexane sorbed into the beads at equilibrium. The volume of hexane inside the beads at equilibrium was determined using the solubility of hexane in LDPE at 55°C (measured in a separate experiment). Substituting these values into eq. 6, the solubility coefficient of the initiator was determined to be 0.439. Rosenbrock's optimal parameter search method was then used to estimate a value for the initiator diffusivity such that the difference between the model-predicted value and the experimentally measured value of the uptake was minimized.

Bulk Polymerization of MIPK

The kinetics of the bulk polymerization of MIPK has been examined using lauroyl peroxide as the initiator. There is very little information in the literature regarding the bulk polymerization of MIPK. Polymerization experiments were conducted at temperatures of 80, 85, and 90°C using three different initial initiator concentrations of 0.10, 0.20, and 0.30 mol/L.

The polymerization experiments were carried out in Pyrex ampules. The reaction mixture of MIPK and lauroyl peroxide was filled into each of eight to 10 breakseal ampules. Each ampule was purged with nitrogen and degassed by many successive freeze-thaw cycles in a solution of dry ice and acetone until no bubbles were visible. Each ampule was then frozen in this solution of dry ice and acetone and sealed under vacuum using a flame torch. The ampules were then placed in an oil bath maintained at the desired reaction temperature to an accuracy of $\pm 0.1^\circ\text{C}$. An ampule was periodically removed and quenched in an ice-water bath. After cooling, the ampules were broken open and the samples were dissolved in toluene and the polymer was precipitated out by the addition of excess methanol. The samples were dried overnight *in vacuo* at approximately 40°C. This procedure of dissolution, precipitation, and drying was repeated several times to ensure that the un-

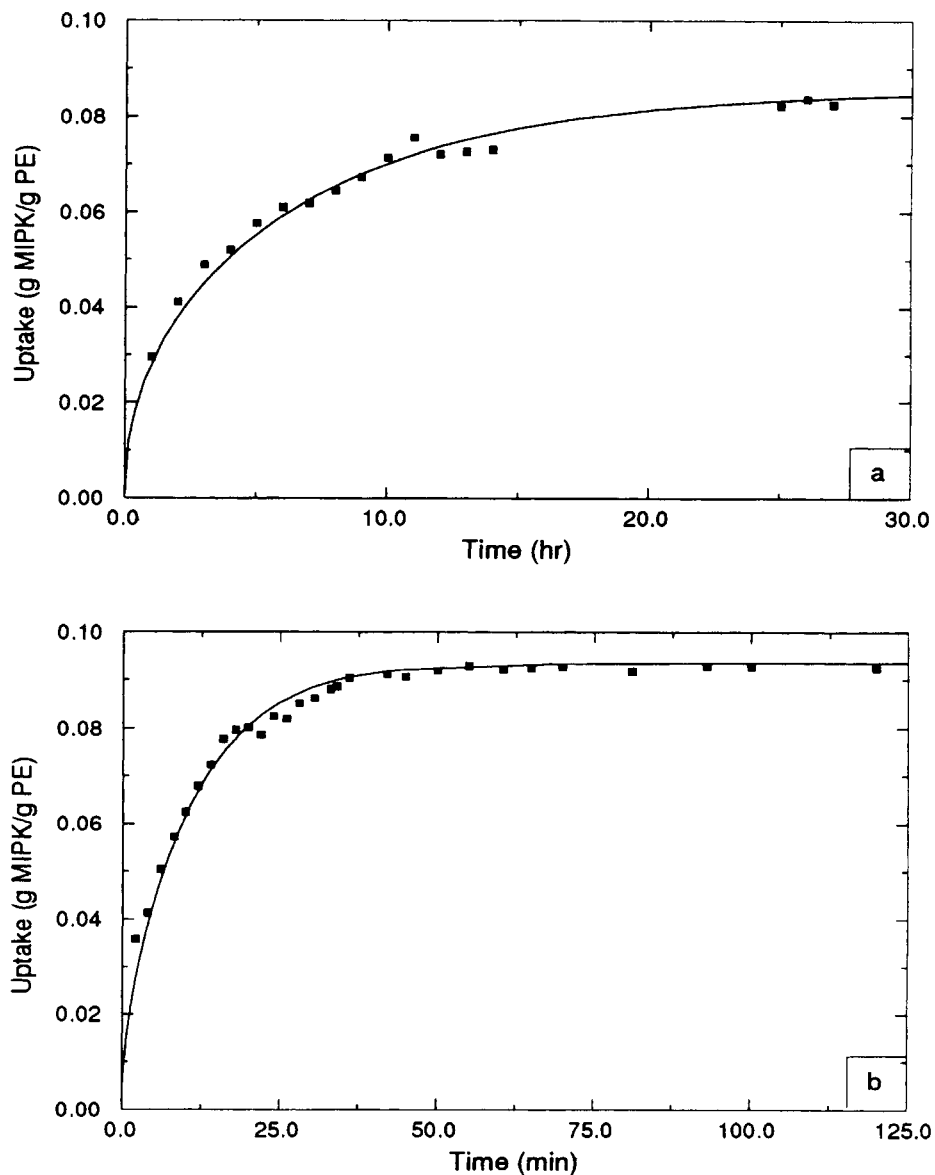
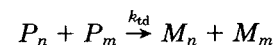
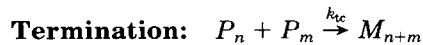
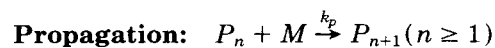
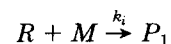
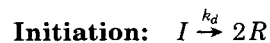


Figure 1 Sorption of MIPK at 55°C. (a) Beads: (—) model prediction for $D = 1.56 \times 10^{-7} \text{ cm}^2/\text{s}$ and $\phi = 0.091$. (b) Film: (—) model prediction for $D = 2.04 \times 10^{-7} \text{ cm}^2/\text{s}$ and $\phi = 0.101$.

reacted monomer was completely removed from the polymer. The monomer conversion was calculated by the gravimetric method.

The molecular weight of the poly-MIPK samples was measured by gel permeation chromatography. Since the Mark-Houwink constants are not known, nor are standards for this polymer available, the molecular weights reported here are the polystyrene-equivalent molecular weights. Figures 3 and 4 show the experimental results.

The following free-radical mechanism of initiation, propagation, and termination was used to model the polymerization kinetics:



For this kinetic scheme, the rate of monomer consumption is expressed as

$$-\frac{dM}{dt} = k_p M \left(\frac{2f_i k_d I}{k_{tc} + k_{td}} \right)^{1/2} \quad (7)$$

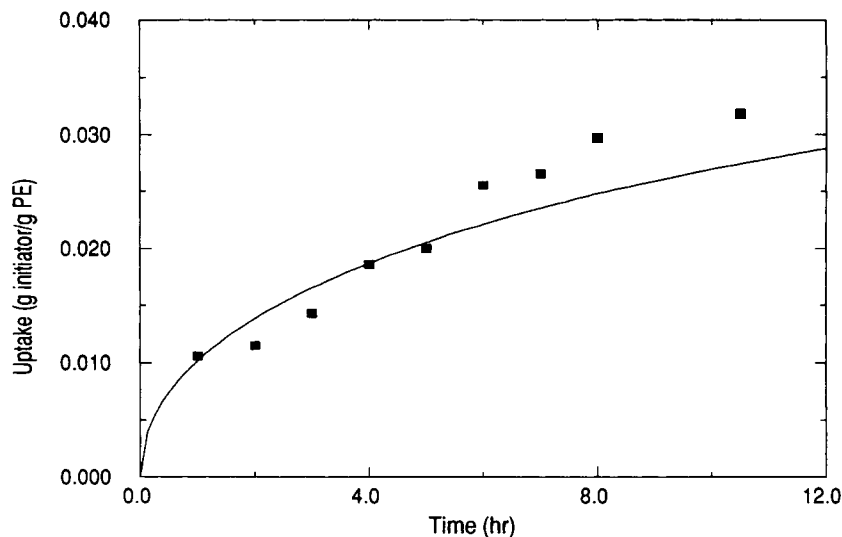


Figure 2 Sorption of a solution of hexane and lauroyl peroxide in polyethylene beads at 55°C. (—) Model prediction for $D = 9.29 \times 10^{-8}$ cm²/s and $\phi = 0.439$.

where f_i is the initiator efficiency factor. The method of moments was employed in this work to calculate the polymer molecular weight averages. The k -th moment of the live polymer species is given by

$$\lambda_k^l = \sum_{n=1}^{\infty} n^k P_n \quad (8)$$

and the dead polymer moments are given by

$$\lambda_k^d = \sum_{n=2}^{\infty} n^k M_n \quad (9)$$

Then, the polymer molecular weight moments for the live and dead polymers take the following form:

Live polymers:

$$\frac{d\lambda_0^l}{dt} = k_i RM - (k_{tc} + k_{td})P^2 \quad (10)$$

$$\frac{d\lambda_1^l}{dt} = k_i RM + k_p MP - (k_{tc} + k_{td})P\lambda_1^l \quad (11)$$

$$\begin{aligned} \frac{d\lambda_2^l}{dt} = & k_i RM + k_p M(P + 2\lambda_1^l) \\ & - (k_{tc} + k_{td})P\lambda_2^l \quad (12) \end{aligned}$$

Dead polymers:

$$\frac{d\lambda_0^d}{dt} = k_{td}\alpha P^2 + \frac{1}{2} k_{tc} P^2 \quad (13)$$

$$\frac{d\lambda_1^d}{dt} = k_{td}P(\lambda_1^l - P_1) + k_{tc}\lambda_0^l\lambda_1^l \quad (14)$$

$$\frac{d\lambda_2^d}{dt} = k_{td}P(\lambda_2^l - P_1) + k_{tc}(\lambda_0^l\lambda_2^l + \lambda_1^{l2}) \quad (15)$$

where P represents the total polymer radical concentration defined as

$$P = \left(\frac{2f_i k_d I}{k_{tc} + k_{td}} \right)^{1/2} \quad (16)$$

and α is the propability of propagation given by

$$\alpha = \frac{k_p M}{k_p M + (k_{tc} + k_{td})P} \quad (17)$$

It may be noted that the zeroth live polymer moment equation is equivalent to the total polymer radical concentration, i.e., $\lambda_0^l = P$. Applying the QSSA to the first and second live polymer moments, one obtains

$$\lambda_1^l = \frac{P}{1 - \alpha} \quad (18)$$

$$\lambda_2^l = \frac{P(1 + \alpha)}{(1 - \alpha)^2} \quad (19)$$

Substituting these expressions for the live polymer moments, the dead polymer moment equations are then reduced to the following:

$$\frac{d\lambda_0^d}{dt} = k_{td}\alpha P^2 + \frac{1}{2} k_{tc} P^2 \quad (20)$$

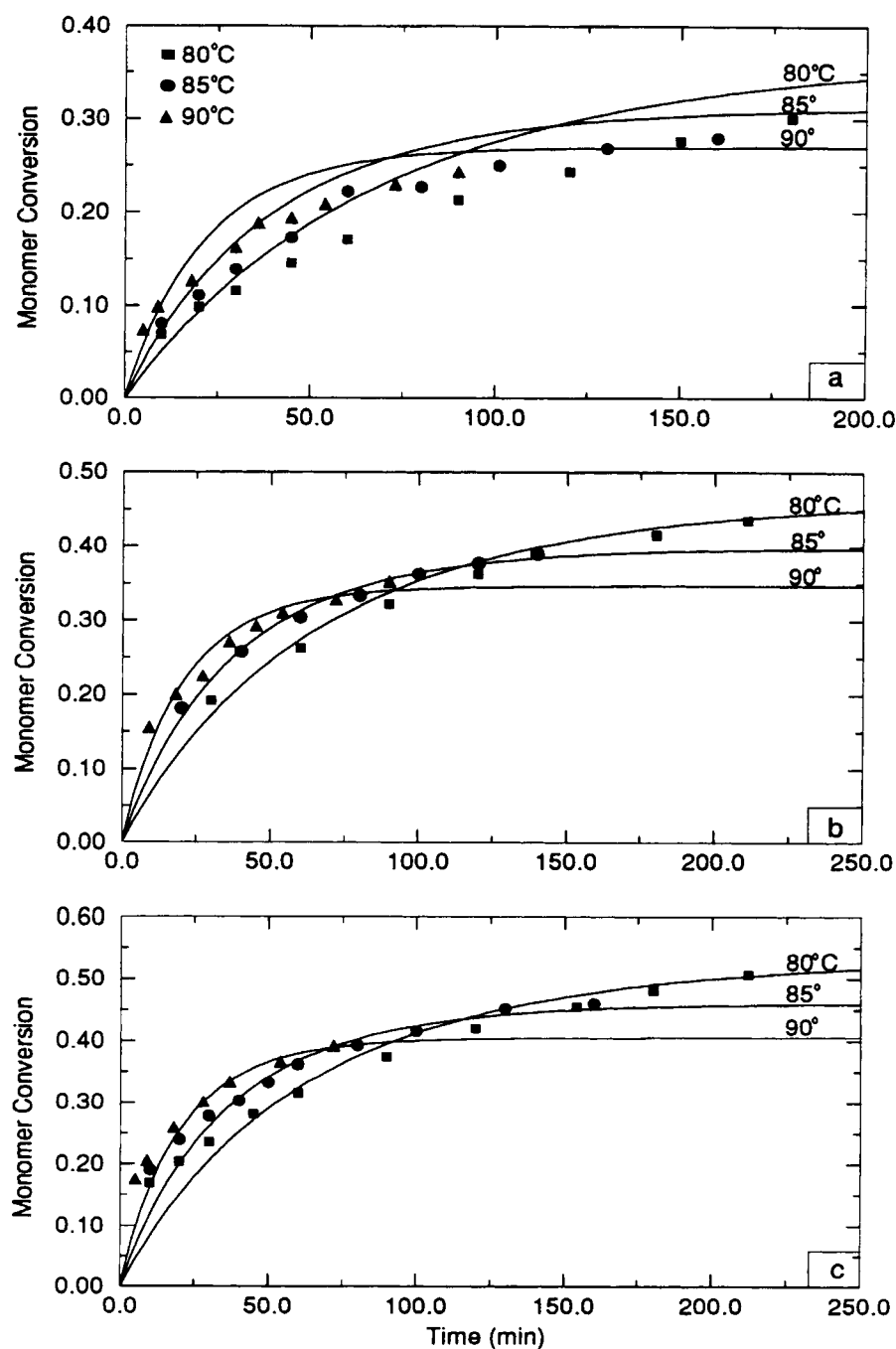


Figure 3 Effect of temperature and initiator concentration on monomer conversion: (a) $I_0 = 0.10$ mol/L; (b) $I_0 = 0.20$ mol/L; (c) $I_0 = 0.30$ mol/L. (—) Model prediction.

$$\frac{d\lambda_1^d}{dt} = k_{td} \left(\frac{P^2}{1-\alpha} \right) \alpha(2-\alpha) + k_{tc} \left(\frac{P^2}{1-\alpha} \right) \quad (21)$$

$$\frac{d\lambda_2^d}{dt} = k_{td} P^2 \alpha \left[\frac{\alpha^2 - 3\alpha + 4}{(1-\alpha)^2} \right] + k_{tc} P^2 \left[\frac{2+\alpha}{(1-\alpha)^2} \right] \quad (22)$$

It is not known whether this polymer terminates exclusively by disproportionation or combination termination. However, to solve the dead polymer moment equations to obtain the molecular weight distribution, one must assume that one of these two mechanisms dominates over the other since the individual values of k_{tc} and k_{td} cannot be determined at this time. In this work, we assumed that termi-

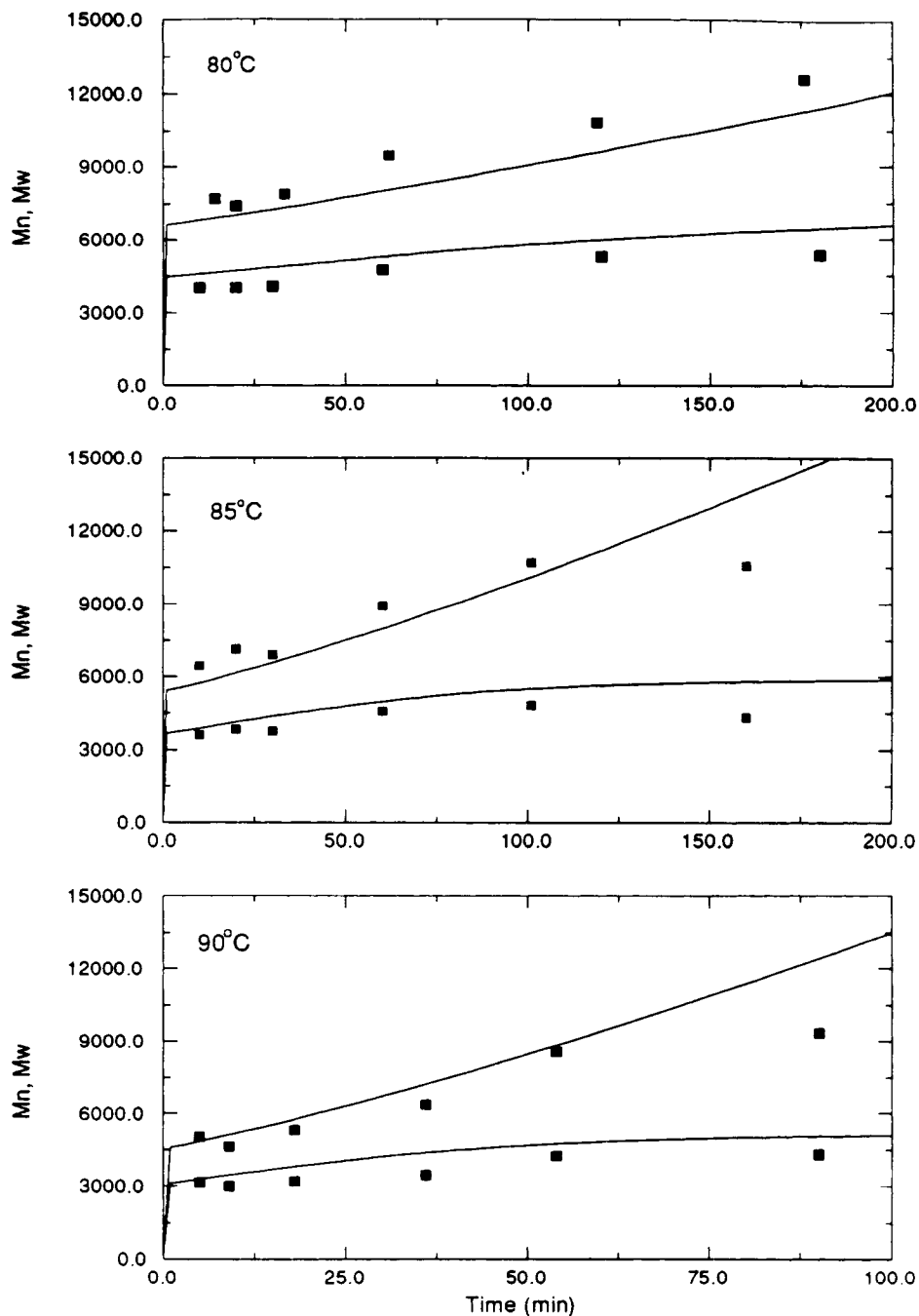


Figure 4 (a) Effect of temperature on polymer molecular weight for $I_0 = 0.10$ mol/L. (—) Model prediction. (b) Effect of temperature on polymer molecular weight for $I_0 = 0.20$ mol/L. (—) Model prediction. (c) Effect of temperature on polymer molecular weight for $I_0 = 0.30$ mol/L. (—) Model prediction.

nation occurs via combination only. To solve the kinetic modeling equations, it is necessary to find the values of $k_p/k_t^{1/2}$ and the initiator efficiency factor f_i . These two parameters were estimated using Rosenbrock's optimal parameter search method with the following objective function:

$$F = \sum_{i=1}^n w_n \left(\frac{M_{n,\text{exp}} - \hat{M}_n}{M_{n,\text{exp}}} \right)^2 + w_w \left(\frac{M_{w,\text{exp}} - \hat{M}_w}{M_{w,\text{exp}}} \right)^2 + w_x \left(\frac{x_{\text{exp}} - \hat{x}}{x_{\text{exp}}} \right)^2 \quad (23)$$

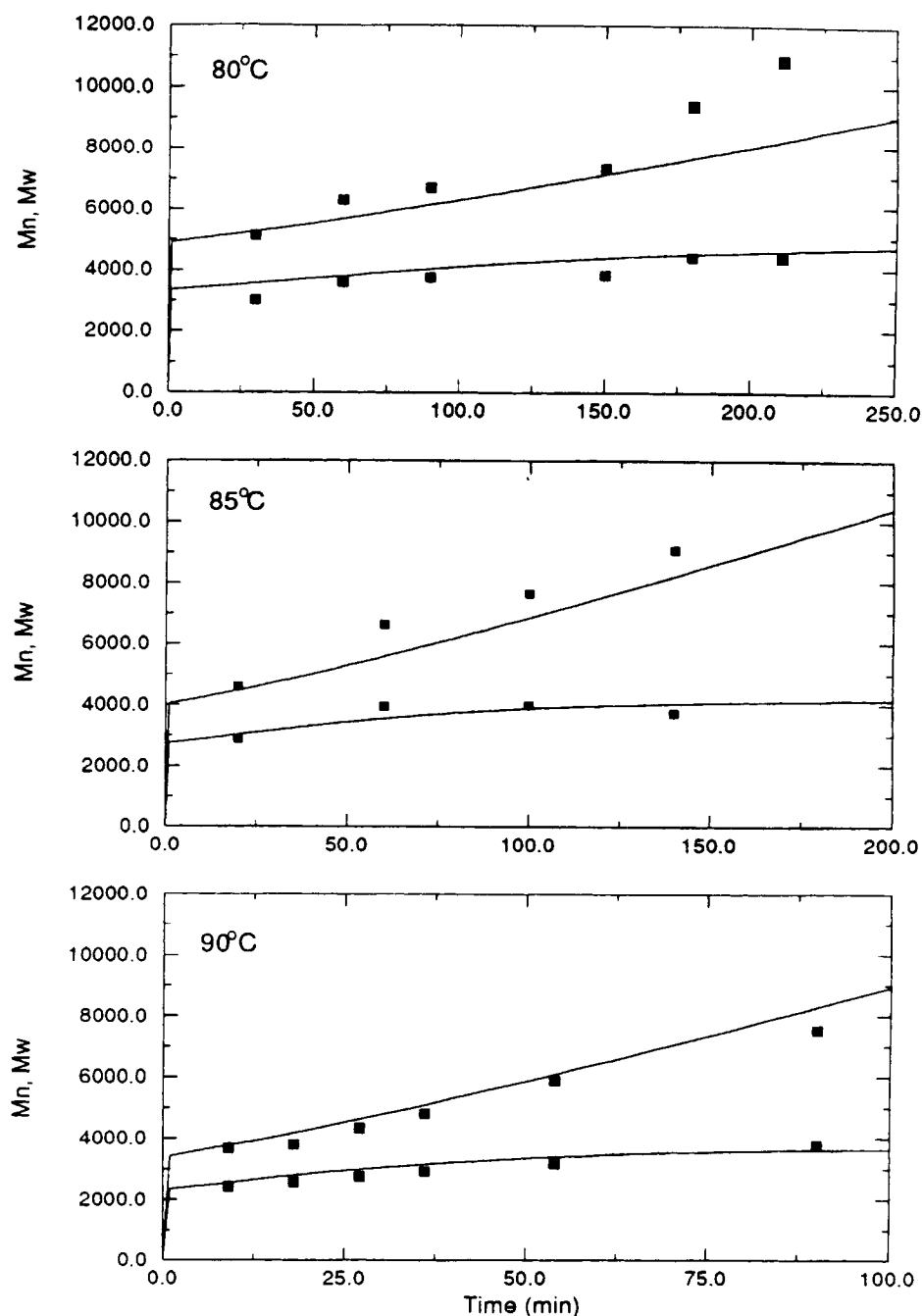


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where n is the number of data points, w_j are the weighting factors, and $(\hat{\cdot})$ represent the model-predicted value. Equal values were assumed for the three weights. Table I lists the average values of the overall rate constants at each reaction temperature obtained by this method (the n -weighted standard deviation is included in parentheses). The average values of the initiator efficiency factors obtained by the optimal parameter search method are given in Table II (again the n -weighted standard deviation

is included in parentheses). Notice that the initiator efficiency factor tends to decrease slightly as the initiator concentration is increased. Similar observations were reported by Kim et al.⁸

The solid lines in Figures 3 and 4(a)–(c) represent the model predictions using the kinetic parameters listed in Tables I and II. It is observed that predictions of the monomer conversion are quite good for all the experiments. However, some discrepancies are seen between the experimentally

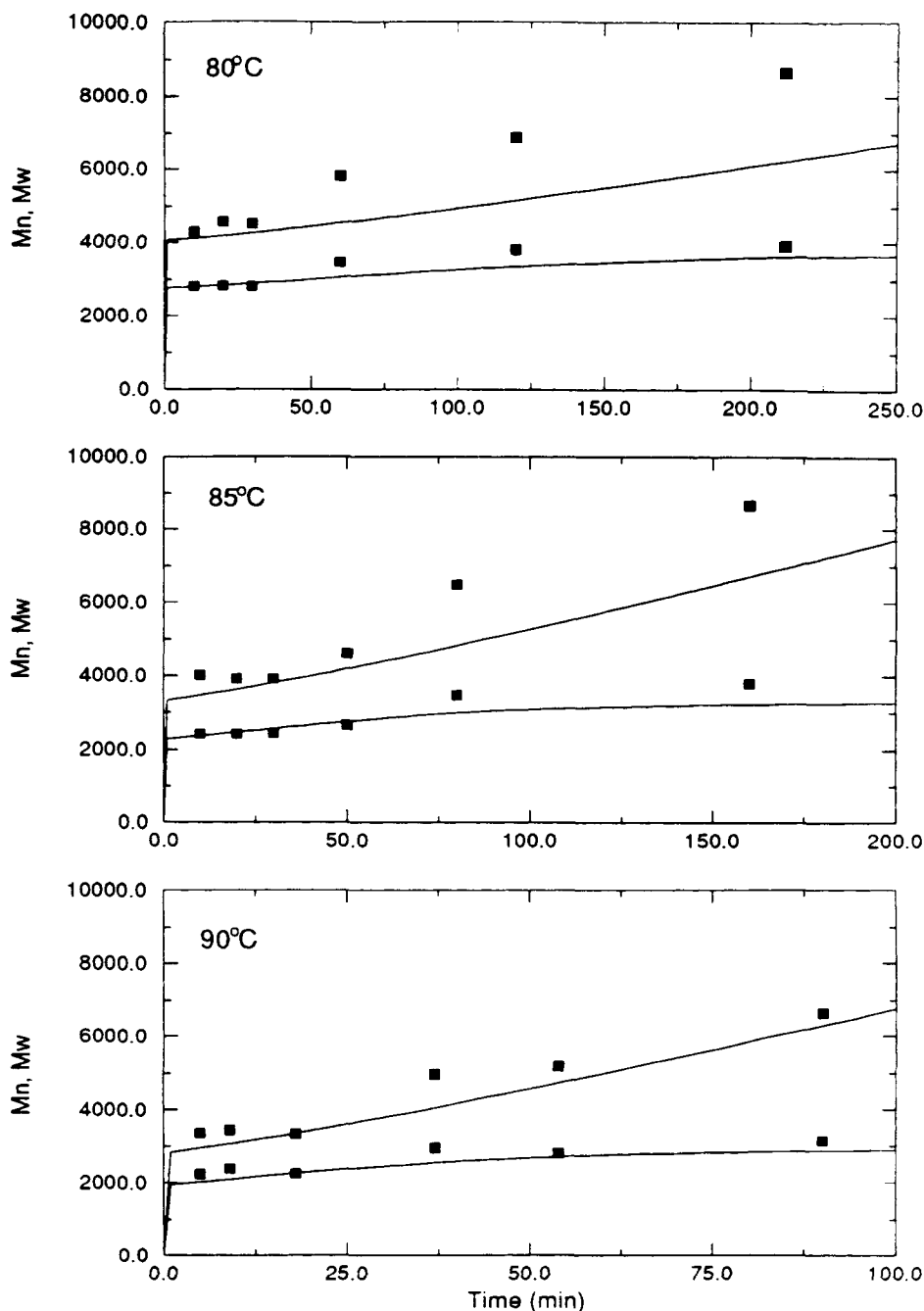


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measured and model-predicted number- and weight-average molecular weights. The proper trend of the number-average molecular weight is predicted by the model for all the experiments, whereas the agreement between the model and experimental results for the weight-average molecular weight tends to improve as the temperature is increased for fixed initiator concentration. These discrepancies may be due to some other reactions such as chain transfer to initiator and/or monomer that have not been in-

corporated into the model at this time due to a lack of information. Overall, however, it is seen that this simple model gives reasonable predictions of the monomer conversion and polymer molecular weight averages.

Polymerization of MIPK in LDPE Beads

The percent weight increase of the beads (based upon the initial weight of the virgin polyethylene

Table I Average Values of $(k_p/k_t^{1/2})$

Temperature (°C)	$\frac{k_p}{k_t^{1/2}} \left(\frac{L^{1/2}}{\text{mol}^{1/2} \text{ min}^{1/2}} \right)$
80	$1.18 \times 10^{-1} (\pm 1.01 \times 10^{-2})$
85	$1.31 \times 10^{-1} (\pm 1.08 \times 10^{-2})$
90	$1.50 \times 10^{-1} (\pm 1.52 \times 10^{-2})$

pellets) after the polymerization of MIPK are shown in Figure 5. The reaction time cited is the duration of time spent at 85°C after a 30 min startup period in which the temperature was raised from 55 to 85°C. Figure 5 shows that the bead weight increases as much as 13% after 4 h of reaction in the solid phase. It was observed that, during the course of the reaction period, some of the beads melted a bit and stuck to the reactor walls and sometimes even formed a thin layer on the reactor walls. Also, sometimes, there was breakup of the pellets while stirring. An attempt to recover as much material as possible was made but some loss of material was inevitable, leading to inaccuracies in the weight measurement. Some reactor runs were repeated and the results varied by as much as $\sim 2.5\%$.

According to the sorption experiment with pure MIPK in the absence of lauroyl peroxide, the head weight increased only by about 6% after soaking for 5 h at 55°C [Fig. 1 (a)]. Thus, the maximum percent weight increase was expected not to exceed 6%. If MIPK is polymerized in bulk with an initiator concentration of 0.20 mol/L at 85°C, the experimental result shown in Figure 3(b) indicates that the monomer conversion is only about 40% after 4 h of reaction. Therefore, the 13% weight increase observed in our experiment poses a question of what has happened during the sorption period in the presence of lauroyl peroxide. One obvious possibility is that the MIPK monomer polymerizes in the polymer beads during the sorption period at 55°C. Thus, we performed sorption experiments at 55°C using a solution of monomer and initiator ($I_0 = 0.20$ mol/L).

Measured amounts of polyethylene beads were placed in several Pyrex test tubes to which the mixture of MIPK and lauroyl peroxide was added. The test tubes were then suspended in a constant temperature oil bath maintained at 55°C. A test tube was periodically removed from the oil bath, the beads were quickly removed and patted dry with a tissue, weighed in a capped bottle, and then dried *in vacuo* for several days. Their weight after drying was noted. Data for the first 5 h of this experiment were taken twice and the reproducibility was excellent. Figure

6 shows the results of this experiment. In this case, the label "before drying" refers to the weight of the beads immediately after soaking them in the liquid solution. "After drying" is the bead weight increase after they were completely dried in the vacuum oven for several days. First, it is observed that the weight gain continues to increase during the measurement time period and is far from sorption equilibrium after 8 h. Surprisingly, the percent weight increase before drying was about 19% after 5 h and the corresponding percent weight increase after drying was about 12%. Recall that when pure MIPK was sorbed into the polyethylene beads at 55°C for 5 h, only about 6% increase in bead weight was found even before drying. Therefore, the experimental observations from Figures 1 (a) and 6 suggest that the presence of lauroyl peroxide in the liquid monomer may have caused the additional monomer incorporation into the polyethylene beads.

We can speculate that one possible cause for the enhanced monomer sorption in the presence of lauroyl peroxide is the formation of poly-MIPK in the polyethylene beads, i.e., as MIPK is consumed by the polymerization reaction, more monomer diffuses into the polyethylene beads. To examine the effect of polymer formation within the beads during the sorption period, we solved a model for diffusion and polymerization of MIPK in polyethylene beads. Assuming constant diffusivities for the initiator and monomer, one can derive the following mass balance equations for both the initiator and monomer:

$$\frac{\partial I_i}{\partial t} = D_I \left(\frac{\partial^2 I_i}{\partial r^2} + \frac{2}{r} \frac{\partial I_i}{\partial r} \right) - k_d I_i \quad (24)$$

$$\frac{\partial M_i}{\partial t} = D_M \left(\frac{\partial^2 M_i}{\partial r^2} + \frac{2}{r} \frac{\partial M_i}{\partial r} \right) - k_p M_i \left(\frac{2 f_i k_d I_i}{k_t} \right)^{1/2} \quad (25)$$

$$@ t = 0, 0 < r < a, I_i = 0, M_i = 0$$

$$@ r = 0, t > 0, (\partial I_i / \partial r) = 0, (\partial M_i / \partial r) = 0$$

$$@ r = a, t > 0, I_i = I_s, M_i = M_s$$

Table II Average Values of f_i

I_0 (mol/L)	f_i
0.10	0.460 (± 0.025)
0.20	0.422 (± 0.020)
0.30	0.417 (± 0.008)

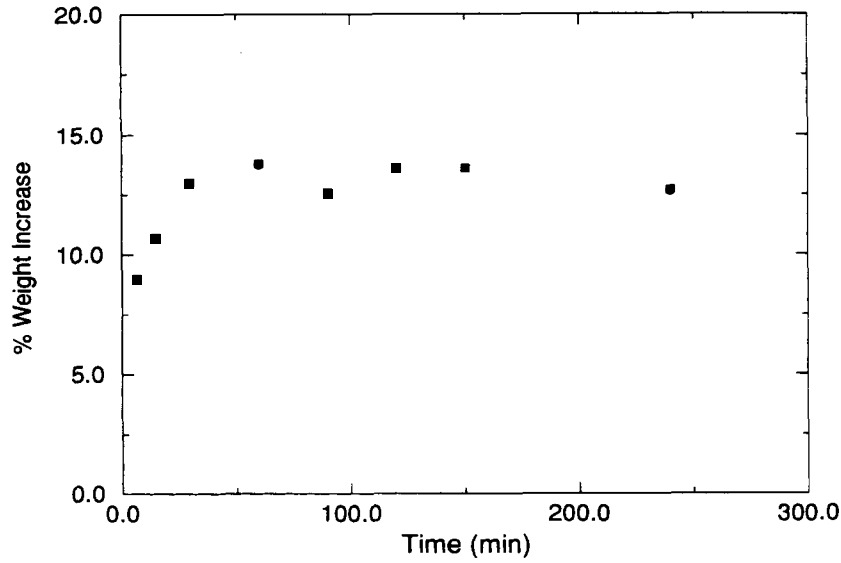


Figure 5 Experimental results for reactor runs at 85°C to synthesize poly-MIPK inside the polyethylene beads.

where I_i and M_i represent the initiator and monomer concentrations inside the polyethylene bead, respectively; D_I (9.29×10^{-8} cm²/s) and D_M (1.56×10^{-7} cm²/s) are the initiator and monomer diffusivities at 55°C, respectively; and I_s and M_s are the surface concentrations of initiator and monomer, respectively. These equations have been solved numerically. The amount of poly-MIPK Y_p , produced was calculated as follows:

$$Y_p = \frac{\left[\int_{t=0}^{t=t_f} \int_{r=0}^{r=a} 4\pi r^2 R_p(t, r) dr dt \right] (M_M)}{\frac{4}{3}\pi a^3 \rho_{PE}} \quad (26)$$

where R_p is the rate of polymerization. Solution of this model led to the curve given in Figure 7, which indicates that the amount of poly-MIPK formed during the 5 h soak period at 55°C is minimal and

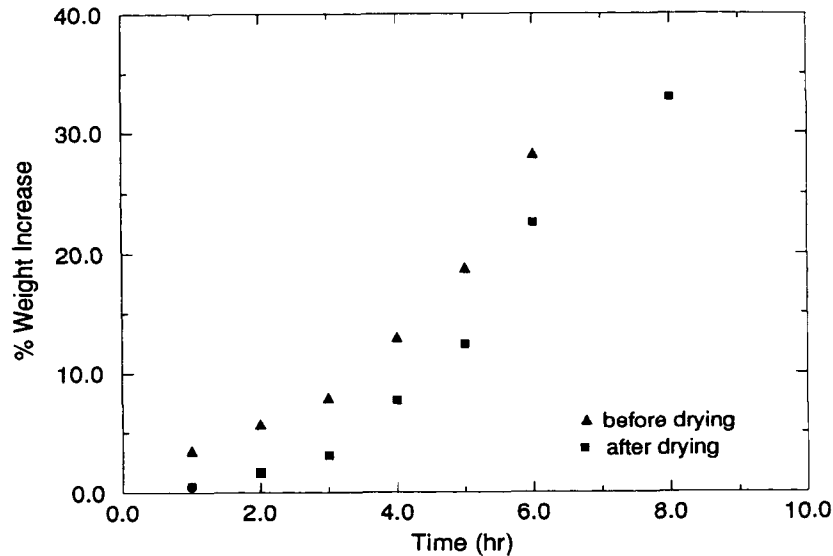


Figure 6 Experimental results for polyethylene beads immersed in a solution of MIPK and initiator at 55°C.

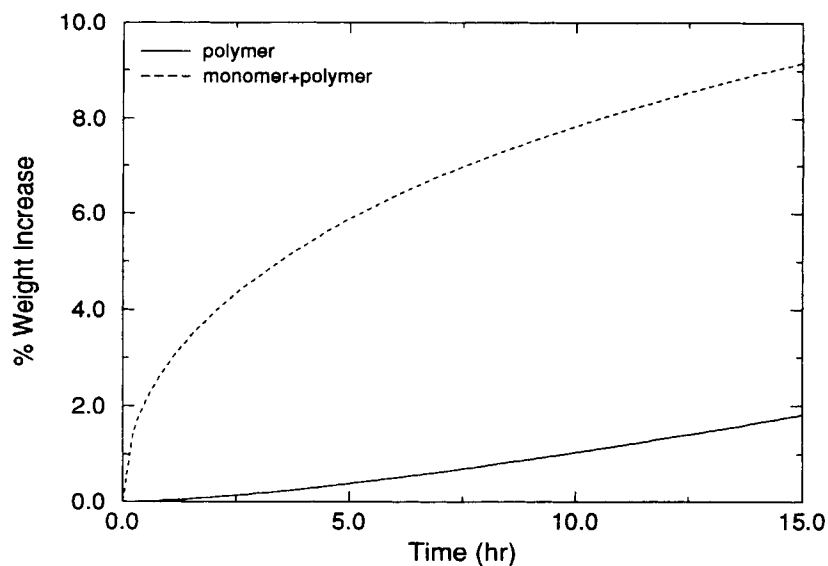


Figure 7 Model prediction of the percent weight increase due to the synthesis of poly-MIPK at 55°C.

the total weight increase is far smaller than experimentally observed. However, the upward trend of the curve (solid line) shown in Figure 7 is very similar to that of the experimental results.

There are several possible reasons to explain these results. For one, it is believed that the polyethylene containing poly-MIPK has a greater affinity for monomer than does pure polyethylene, i.e., the solubility of the monomer in the polyethylene containing poly-MIPK could be higher. Therefore, as more poly-MIPK is synthesized, the solubility of the monomer in the resulting polymer will increase. In addition, the overall rate constant ($k_p/k_t^{1/2}$) for the reaction taking place within the amorphous regions may be much higher than that for the homopolymerization of the monomer, because within these amorphous regions in which the polymerization of the monomer occurs, chain termination may be less, leading to an increased overall polymerization rate. Due to the lack of additional data, we were not able to incorporate this possibility into our reaction model. Another possibility may be that the heat of polymerization may increase the temperature within the amorphous regions, leading to an acceleration in the reaction rate. Last, but not least, it is likely that the diffusion coefficients are not constant throughout the course of the polymerization reaction but decrease as the amount of polymer synthesized increases. On a physical level, this can simply be explained as due to a decrease in the free volume, for the monomer and initiator to diffuse into, as more polymer is produced.

Similar observations have been made by other researchers.^{9,10} Fels and Huang⁹ found that the diffusivities and solubilities of benzene and hexane in polyethylene-*g*-polystyrene copolymers were a function of the percent grafting. They observed that the solubility of benzene in the 26% graft was 50–90% higher than for (low density) polyethylene and that the diffusion coefficient of each liquid decreased as the amount of grafting increased. Odian and co-workers¹⁰ performed radiation-induced grafting of styrene to LDPE at room temperature. They determined that the value of the overall rate constant was three times larger for the grafting reaction than for the homopolymerization of styrene and attributed this to the higher viscosity of the reaction medium. They also found that the solubility of styrene increased as the percent grafting to polyethylene increased.

Analysis of the Treated Pellets

The treated pellets were analyzed using different analytical means to determine any changes in the polymer properties. Soxhlet extractions were performed on the reacted pellets using toluene as the solvent, to determine whether the poly-MIPK synthesized within was permanently grafted onto the polyethylene backbone. The Soxhlet extractions with the treated LDPE pellets were conducted twice for each reactor run (one reactor run for each reaction time), initially for 48 h and then for 24 h after it became evident that any conclusions could

not be drawn from the first set of results. These additional experiments, however, were also inconclusive regarding a good estimate of the relative amounts of possibly grafted polymer and homopolymer since, for the same reactor run, one sample when extracted for 24 h would reveal, for instance, a 8% decrease in weight, whereas when extracted for 48 h, the weight would decrease by 3%. Also, in some cases, a sample of reacted pellets from the same reactor run would dissolve to some extent during one extraction and form one large solid mass at the end of the extraction, whereas for another extraction, the beads would remain in the whole form, separate from one another. In fact, in one extreme case, the pellets almost completely dissolved and the decrease in weight was many times larger than was the increase in weight due to the reaction. Essentially, no distinct trend in the extent of grafting, or solid proof of grafting, could be observed from the results of the extractions. Therefore, the weight percentage increases cited in Figure 5 are the sum of the homopolymer and *possibly* grafted poly-MIPK. There are some problems associated with this method. For one, there may be removal of low molecular weight substrate material by such extractions in addition to the dissolution and removal of the homopolymer of poly-MIPK, thus masking the actual amount of the grafted polymer. Also, if the second polymer is not grafted onto the substrate material but rather forms a semi-interpenetrating network, this method cannot clearly distinguish between these two cases.

FTIR analysis was performed using a Perkin-Elmer 1600 Series spectrophotometer. Analysis of the virgin polyethylene pellets revealed a very small carbonyl absorption at 1740 cm^{-1} and a small peak at 1129 cm^{-1} , which is most likely due to oxidation when molding the pellets to produce film for the analysis or the absorption of oxygen by the beads simply upon being exposed to the air. This is a common observation that has been made by others for LDPE.¹¹ The IR spectra of a sample of the reacted beads (before extracting with toluene) and of a sample of the beads immersed in a solution of monomer and initiator at 55°C , both showed a very strong carbonyl absorption at 1700 cm^{-1} , clear evidence of the $\text{C}=\text{O}$ group, indicating the presence of poly-MIPK. After extracting a sample of reacted pellets for 48 h, the IR spectrum of the sample again exhibited a strong $\text{C}=\text{O}$ stretch at 1700 cm^{-1} , indicating that there may be some grafted poly-MIPK present. However, it is felt that further analysis is required to truly verify the presence of grafted polymer.

Lastly, the melting temperature, T_m , and crystallinity of the reacted beads was measured by DSC analysis that was performed using a Perkin-Elmer DSC-7 calorimeter. The DSC curves for a sample of virgin polyethylene beads and of a sample of reacted beads are shown in Figure 8. Looking at the top curve in this figure for the virgin pellets, it is seen that there is one predominant material giving rise to a single endotherm. The behavior of a sample of reacted beads is, however, quite different. For the reacted pellets, there appears to be a "bimodal endotherm." Similar observations have been made for irradiated polyethylene,^{12,13} and this bimodal endotherm is the result of changes in the surface free energy of the polyethylene crystals due to the synthesis of poly-MIPK. The DSC analysis revealed a small decrease in crystallinity and lowering of the melting temperature for the treated pellets. This decrease in crystallinity is expected because the synthesis of a second polymer within the polyethylene matrix disrupts the regularity of this matrix, and the melting point will correspondingly be lower.¹⁴

CONCLUDING REMARKS

In this work, the sorption and polymerization of MIPK in solid LDPE beads have been investigated. For the production of photodegradable polyethylene, it is important to incorporate an optimal amount of MIPK polymer in the polyethylene substrate. To do so, there is a need to understand the physical and chemical processes involved in the manufacturing of the polyethylene masterbatch. As the first step in developing more efficient photodegradable polyethylene, our work reported in this article has been aimed at quantifying the sorption and polymerization kinetics. Using both original beads and thin films, we measured the equilibrium solubility in the polymer. The monomer diffusivity was also estimated using the experimental sorption data and a diffusion model. It has been observed that the monomer uptake in the polymer beads at 55°C for 5 h in the presence of the lauroyl peroxide initiator was much larger ($\sim 20\%$) than that in the absence of lauroyl peroxide ($\sim 6\%$). As a result, when the solid phase polymerization of MIPK was carried out at 85°C for 4 h, the total weight increase was as large as 13%. The model simulation indicates that at the sorption temperature (55°C) the amount of MIPK polymerized in the solid resin is quite small. This implies that the poly-MIPK formed during the sorption period is not solely responsible for the en-

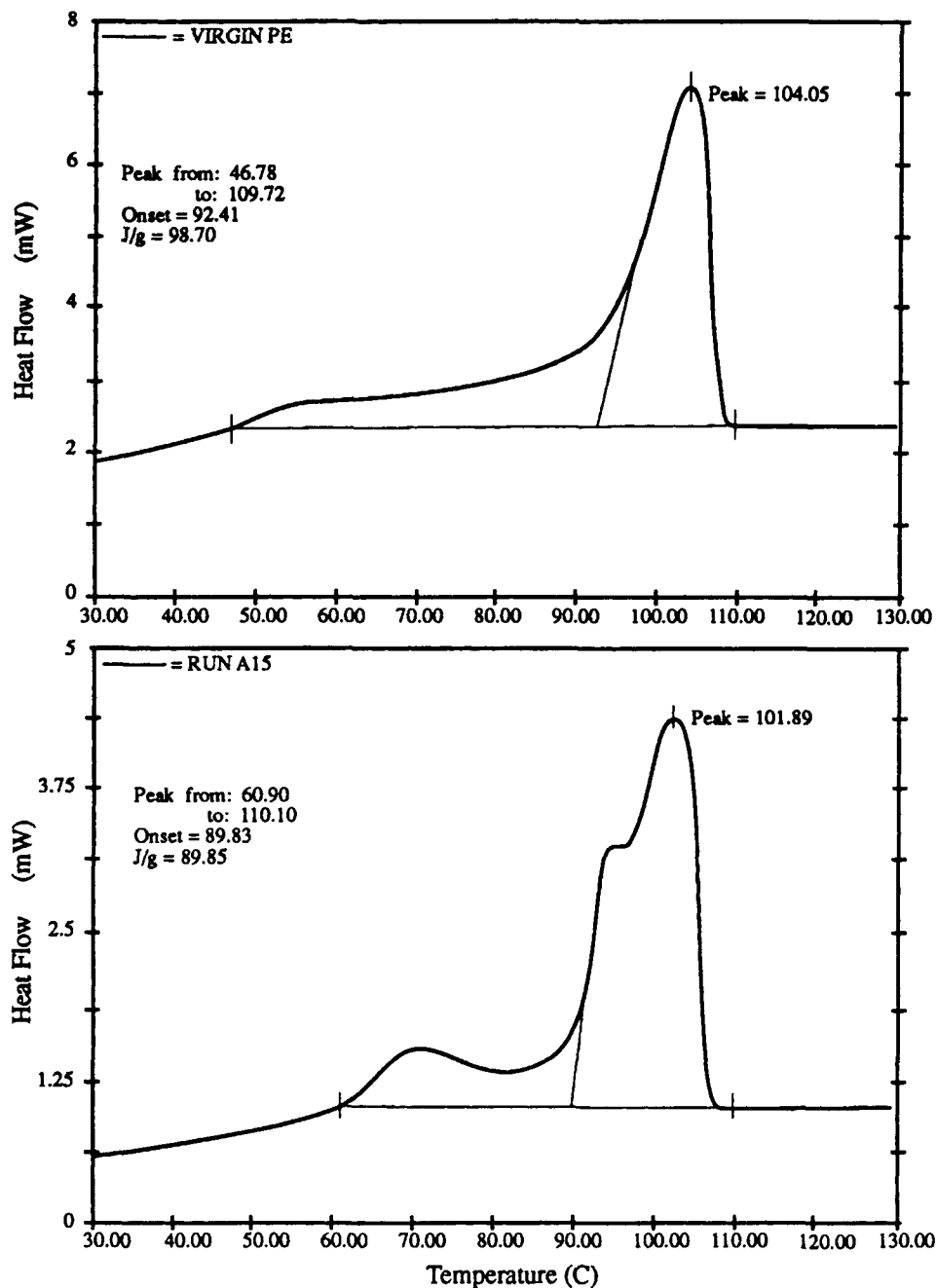


Figure 8 DSC results for the virgin polyethylene beads (top) and the reacted beads (bottom).

hancement of monomer uptake in the presence of initiator. More study is needed to elucidate the effect of various physical and chemical effects on the monomer uptake and subsequent polymerization in the solid phase.

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