

Continuous Distribution Kinetics for the Thermal Degradation of LDPE in Solution

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ABSTRACT: Polymer degradation in solution has several advantages over melt pyrolysis. The degradation of low-density polyethylene (LDPE) occurs at much lower temperatures in solution (280–360°C) than in conventional melt pyrolysis (400–450°C). The thermal degradation kinetics of LDPE in solution was investigated in this work. LDPE was dissolved in liquid paraffin and degraded for 3 h at various temperatures (280–360°C). Samples were taken at specific times and analyzed with high-pressure liquid chromatography/gel permeation chromatography for the molecular weight distribution (MWD). The time evolution of the MWD was modeled with continuous distribution kinetics. Data indicated that LDPE followed random-chain-scission degradation. The rapid initial drop in molecular weight, observed up to 45 min, was attributed to the presence of weak links in the polymer. The rate coefficients for the breakage of weak and strong links were determined, and the corresponding average activation energies were calculated to be 88 and 24 kJ/mol, respectively. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 681–690, 2002; DOI 10.1002/app.2344

Key words: low-density polyethylene; degradation; continuous kinetics; solution; weak links

INTRODUCTION

The chemical recycling of waste plastic is becoming an increasingly attractive option to costly and unpopular landfill disposal methods.^{1,2} Melt-thermal and catalytic degradation of pure polymers has been the focus of such recycling research.³ These methods suffer from problems of high melt viscosity, severe heat-transfer resistance, complex degradation behavior, and undesirable by-product formation.⁴ The problems complicate reactor analysis, design, and scaleup.⁵

Degradation in solution offers an alternative by keeping all products in a single phase of much lower viscosity, enabling better heat transfer, enhanced reaction rates,⁶ improved residence time control, and a modified product profile.⁷ It can allow the introduction of plastic wastes into conventional cracking technology.⁸ The product distributions from the thermal and catalytic cracking of several plastic wastes (polypropylene, polystyrene, and polybutadiene) dissolved in refinery light cycle oil has been studied.⁹ Increased yields of aromatics and coke were reported for polystyrene-based plastics in laboratory-fluidized catalytic cracking units.¹⁰ High-density polyethylene (HDPE) has been catalytically cracked over HZSM-5 to produce valuable hydrocarbons in the C₃–C₅ range with a high olefinic content and a yield greater than 85%.¹¹ The conversion of low-density polyethylene (LDPE) to transportation fu-

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els in a fluidized catalytic cracking unit has been studied.¹² The catalytic decomposition of polyethylene in a tubular flow reactor has been used for gasification.¹³ A recent review of the kinetics of the low-temperature pyrolysis (<450°C) of polyethylene, polypropylene, and polystyrene found that there is considerable scatter in the reported kinetic data.¹

The controlled thermal degradation of polystyrene,¹⁴ poly(α -methylstyrene),¹⁵ poly(methyl methacrylate),¹⁶ and poly(styrene-allyl alcohol)¹⁷ in solution has recently been studied. Rate coefficients and activation energies have been obtained with continuous distribution kinetics. Solvent effects on the thermal degradation of polystyrene, poly(α -methylstyrene), and poly(*p*-methylstyrene) in solution have been studied.^{4,5} The conversion of polystyrene and poly(*p*-methylstyrene) to low molecular weight products depends markedly on the hydrogen-donating capability of the solvent used, whereas the conversion of poly(α -methylstyrene) is unaffected by the presence of a hydrogen donor. The various effects of hydrogen donors on degradation rates have been studied and explained in terms of the relative rates of various steps in the mechanism with Rice-Herzfeld kinetics.^{18,19}

There is not much fundamental information, however, on the solution degradation of polyethylene, the world's most important thermoplastic.²⁰ The effect of dilution by a solvent on the production of waxy polyethylenes by the thermolysis of HDPE has been studied recently at higher pressures (3–4 MPa).⁷ To our knowledge, no study on the degradation of LDPE in solution has been carried out.

The theoretical framework for an analysis of polymer degradation reactions is provided by continuous mixture kinetics. This is based on mass or population balance equations that govern the temporal-spatial behavior of a frequency distribution function.^{21,22} The advantage of such population balance models is that they provide straightforward procedures for deriving expressions for the moments of the frequency distributions. This allows us to construct the molecular weight distribution (MWD) as it evolves in time, thereby extracting more information on the rate coefficients. An unified approach to polymer degradation detailing random, chain-end, and mid-chain-scission models has been presented.²³ The kinetics of reversible polymer decomposition based on continuous mixtures has also been described in detail.²⁴ Continuous kinetics has been

applied to the melt pyrolysis of polyethylene,²⁵ but the random scission and repolymerization rate coefficients have not been determined. A random-chain-scission model, with a rate constant depending on the molecular weight, has been applied to HDPE liquefaction from the melt.²⁶ In our study, we determine the scission rate coefficients of weak links and strong links of LDPE in solution by assuming that the rate coefficients depends linearly on the molecular weight.

The objective of this work was to study the thermal degradation of LDPE in solution. We use continuous distribution kinetics, with a scission mechanism accounting for weak and strong links, to model the degradation and calculate the fundamental kinetic parameters. The degradation rate coefficients of the weak and strong links are determined. The activation energies are determined from the temperature dependence of the rate coefficients.

EXPERIMENTAL

Materials

Virgin LDPE (MFI 7) obtained from Indian Petrochemical Corp., Ltd. (Vandodara, India) was used as the starting material for degradation. The MWD of this polymer was obtained from high-pressure liquid chromatography (HPLC)/gel permeation chromatography [GPC; number-average molecular weight (M_n) = 200,000, polydispersity = 4.3]. Liquid paraffin (M_n = 400, polydispersity = 1.3) was used as the solvent in which the polymer was dissolved for degradation. Chlorobenzene (SD Fine Chemicals, Bangalore, India) was used as the diluent for samples and also as the eluent in GPC. Polystyrene standards with narrow MWDs (Waters and Tosoh, Milford, MA) were used for the calibration of the HPLC/GPC system. The calibration curve is shown in Figure 1.

Degradation Experiments

The degradation of LDPE was carried out in a three-necked, round-bottom flask with continuous stirring. The reactor was initially charged with 100 mL of liquid paraffin and heated to the desired reaction temperature (280, 300, 320, 340, or 360°C). The temperature was controlled within 1% of the set point with an on-off controller (Thermotherm Controls). The polymer (0.8 g) was added to the reactor when the desired reaction

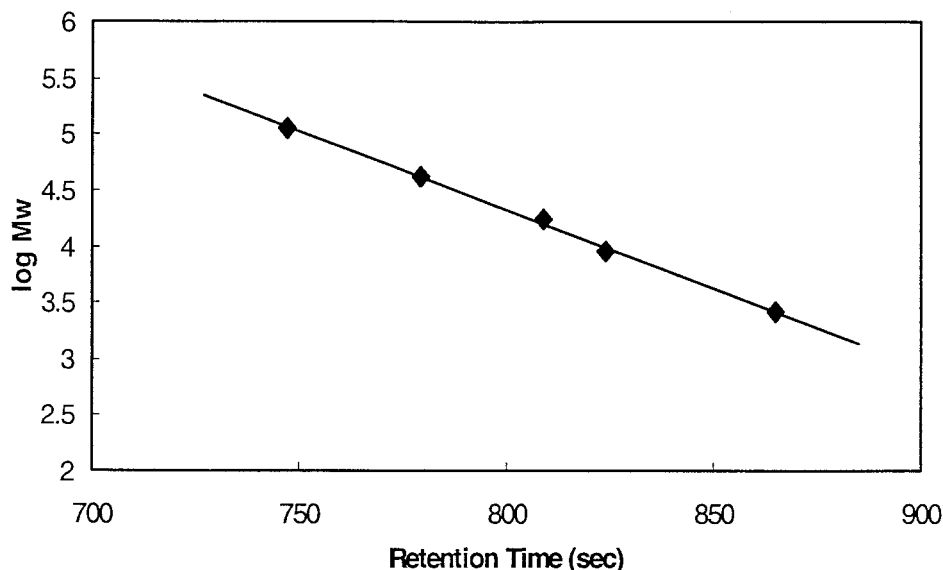


Figure 1 Calibration curve based on polystyrene: plot of $\log M_w$ [$-0.0140 \times$ retention time (s) + 15.5109] versus the elution time.

temperature was reached. The polymer dissolved completely within 15 min, and this was taken as the zero time for the reaction. Samples (1 mL) were taken at specific times (10, 20, 30, 60, 90, 120, 180, or 360 min). These samples, with a polymer concentration of 8 g/L, were diluted to 2 g/L with chlorobenzene for HPLC/GPC analysis.

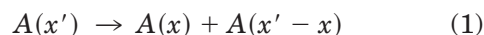
Analyses

The MWD of the degraded polymer was determined with an HPLC/GPC system (Waters). An HPLC pump (Waters 515) maintained the eluent (chlorobenzene) flow at 1 mL/min. Two Styragel columns (300 mm \times 7.8 mm ϕ ; Waters HR5E and HR1) were used for efficient separations. The columns and sample injection valve (Rheodyne 7725i) were maintained at 90°C with a column heater (Eldex 150). The sample (200 μ L) was injected, and the concentration was measured with a differential refractometer (Waters 2410) and transferred by a data-acquisition system to a computer. The chromatographs obtained were converted to MWDs, with the calibration curve (Fig. 1) adjusted to polyethylene with the Mark-Houwink constants ($K_{PS} = 2.32 \times 10^{-4}$, $\alpha_{PS} = 0.653$, $K_{PE} = 3.23 \times 10^{-4}$, $\alpha_{PE} = 0.735$).

THEORETICAL MODEL

Continuous distribution kinetics considers the polymer to be a mixture of a large number of

differently sized molecules with the molecular weight x as a continuous variable. $A(x)$ gives the MWD of the polymer. Polymer molecules can undergo binary fragmentation at random points along the chain:



Models are available for various types of degradation: combined random-chain scission, and chain-end scission,¹⁷ chain-end scission only,¹⁵ and random-chain scission and chain scission in the presence of weak links.¹⁴ LDPE was found to undergo primarily random-chain scission during thermal degradation. The presence of weak links in LDPE was inferred from the rapid initial drop in molecular weight followed by a comparatively slower change at longer times.

The presence of weak and strong links in the polymer can be accounted for by separate additive distributions:¹⁴

$$p(x,t) = p_s(x,t) + p_w(x,t) \quad (2)$$

where $p(x,t)$ is the time-dependent MWD of the polymer undergoing degradation. The molar concentration of the polymer is then the sum of the molar concentrations of the weak and strong links:¹⁴

$$p^{(0)}(t) = p_s^{(0)}(t) + p_w^{(0)}(t) \quad (3)$$

where $p^{(0)}(t)$ is the zero moment of $p(x,t)$. The M_n 's and weight-average molecular weights (M_w 's) for the total polymer can be expressed as

$$\begin{aligned} M_n &= p^{(1)}/p^{(0)} & M_{n0} &= p_0^{(1)}/p_0^{(0)} \\ M_w &= p^{(2)}/p^{(1)} & M_{w0} &= p_0^{(2)}/p_0^{(1)} \end{aligned} \quad (4)$$

where the subscript 0 indicates the initial value.

The balance equations for the stirred-batch reactor, if we assume first-order degradation, can be written in terms of the reaction time t ¹⁷ as

$$\begin{aligned} \partial p_w / \partial t &= -k_w(x)p_w(x,t) \\ &+ 2 \int_x^\infty k_w(x')p_w(x',t)\Omega(x,x') dx' \end{aligned} \quad (5a)$$

$$\begin{aligned} \partial p_s / \partial t &= -k_s(x)p_s(x,t) \\ &+ 2 \int_x^\infty k_s(x')p_s(x',t)\Omega(x,x') dx' \end{aligned} \quad (5b)$$

where the kernel $\Omega(x,x')$ determines the distribution of scission products and $k_w(x)$ and $k_s(x)$ are rate coefficients for weak-link and strong-link scission, respectively. For a random distribution of degradation products, $\Omega(x,x')$ is $(1/x')$.¹⁷

The effect of the MWD on the rates of the thermal degradation of polystyrene in solution has been studied.⁶ The rate coefficient for the random scission of the polymer chain was found to be a function of the molecular weight. The dependence of the rate coefficient on the molecular weight x can be represented as

$$k(x) = k_b x^b \quad (6)$$

Using eq. (6) for the rate coefficient with $b = 1$ in eq. (5b) gives

$$\partial p_s / \partial t = -k_s x p_s(x,t) + 2 \int_x^\infty k_s x' p_s(x',t) \Omega(x,x') dx' \quad (7)$$

The moment operation is defined by

$$p^{(n)}(t) = \int_0^\infty x^n p(x,t) dx \quad (8)$$

Applying the moment operation $\int_x^\infty x^n [] dx$ to eq. (7) with the initial condition $p_s(x,t=0) = p_{s0}(x)$ gives the n th moment for strong-link scission:

$$dp_s^{(n)}/dt = -((n-1)/(n+1))k_s p_s^{(1+n)} \quad (9)$$

The first-order differential equations for the zero and first moments are

$$dp_s^{(0)}/dt = k_s p_s^{(1)} \quad (10)$$

$$dp_s^{(1)}/dt = 0 \quad (11)$$

A similar analysis for weak links yields

$$dp_w^{(0)}/dt = k_w p_w^{(1)} \quad (12)$$

$$dp_w^{(1)}/dt = 0 \quad (13)$$

The addition of eqs. (11) and (13) shows that the total polymer mass is constant. Equations (10) and (12) can be solved with the initial conditions $p_s^{(0)}(t=0) = p_{s0}^{(0)}$ and $p_w^{(0)}(t=0) = p_{w0}^{(0)}$, respectively, to yield

$$p_s^{(0)} - p_{s0}^{(0)} = k_s p_s^{(1)} t \quad (14)$$

$$p_w^{(0)} - p_{w0}^{(0)} = k_w p_w^{(1)} t \quad (15)$$

Equations (14) and (15) can be summed to give

$$p^{(0)} - p_0^{(0)} = (k_s p_s^{(1)} + k_w p_w^{(1)}) t \quad (16)$$

RESULTS AND DISCUSSION

We examined the thermal degradation rates of LDPE in solution by analyzing the time dependence of the MWDs. Figure 2 shows the variation of M_n as a function of t for different temperatures. There is a rapid decrease in M_n at times less than 30 min. Figure 3 shows a plot of $p^{(0)}/p_0^{(0)}$ versus t , where $p^{(0)}$ is the molar concentration of the polymer as a function of time and $p_0^{(0)}$ is the initial molar concentration. The rapid increase in the zero moment up to 30 min is evident from the expanded plot of $p^{(0)}/p_0^{(0)}$ versus t shown in Figure 4. For all temperatures, the slope is less after 30 min, indicating a decreased degradation rate. This behavior of rapid initial degradation followed by slower chain breakage has also been observed for HDPE in solution,⁷ HDPE in bulk,²⁶

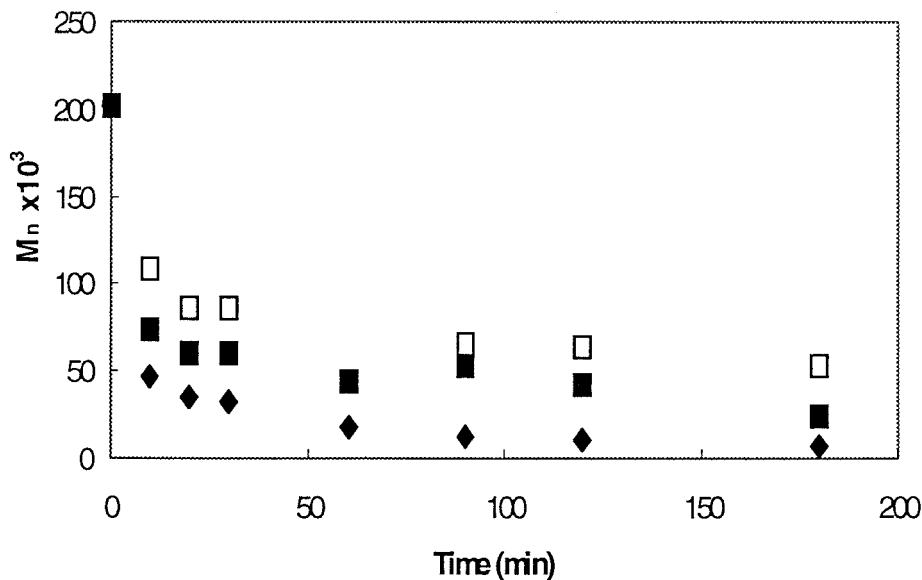


Figure 2 Plot of M_n against t at three different temperatures [(\blacklozenge) 360, (\blacksquare) 340, and (\square) 280°C].

polypropylene in bulk by thermogravimetric analysis (TGA),²⁷⁻²⁹ and polystyrene in solution.¹⁴

The high initial rate of chain breakage is generally attributed to the presence of weak links randomly distributed along the polymer chain.²⁹ Branching sites on the polymer are such potential weak spots.²⁶ The branch sites can undergo scission at a faster rate. This would split the chain rapidly into several small fragments, which

would then degrade slowly. The presence of oxidized moieties along the chain as weak spots has also been suggested.²⁸

Because the concentration of the weak links is much smaller than that of strong links,^{14,30} we consider that all the fast-reacting weak links have been exhausted by time t_f , so that the molar concentration of the weak-link scission products remains constant for $t \geq t_f$. The concentration of

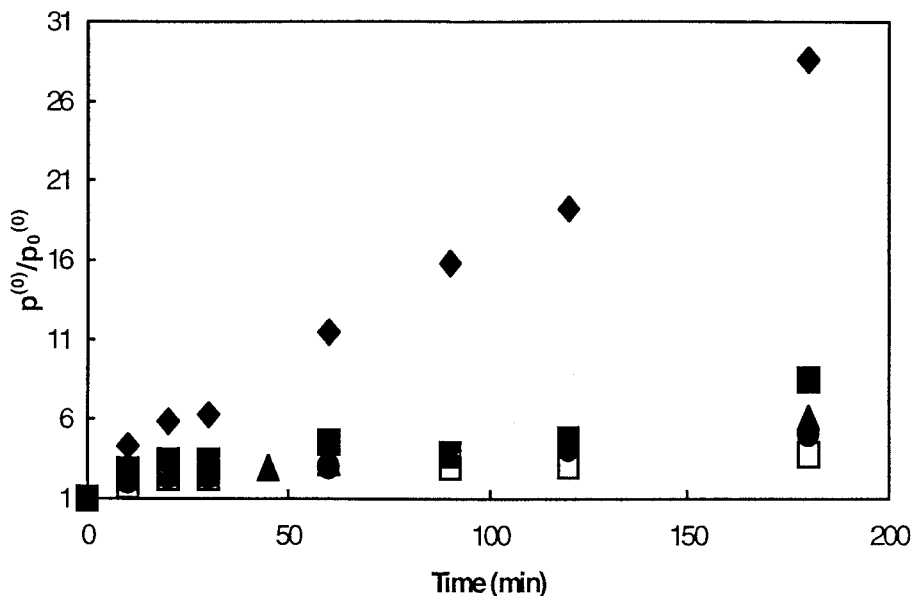


Figure 3 Plot of $p^{(0)}/p_0^{(0)}$ against t [(\blacklozenge) 360, (\blacksquare) 340, (\blacktriangle) 320, (\bullet) 300, and (\square) 280°C].

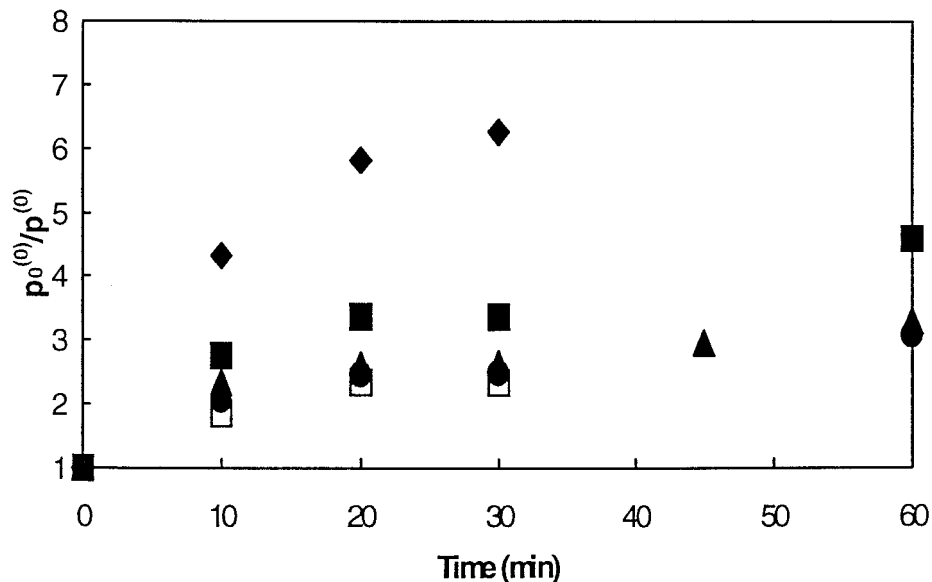


Figure 4 Expanded plot of Figure 3 [(♦) 360, (■) 340, (▲) 320, (●) 300, and (□) 280°C].

the random scission products is the sum of weak-link and strong-link scission products, and so eq. (16) can be rewritten as follows. For $t \leq t_f$

$$(p^{(0)}/p_0^{(0)}) - 1 = (k'_s + k'_w)t \quad (17)$$

For $t \geq t_f$

$$(p^{(0)}/p_0^{(0)}) - 1 = k'_s t + k'_w t_f \quad (18)$$

where $k'_s = k_s p_s^{(1)}/p_0^{(0)}$ and $k'_w = k_w p_w^{(1)}/p_0^{(0)}$. We infer from Figures 2–4 that the weak links are completely depleted after 30 min. Figure 5 shows a plot of the experimental data of $(p^{(0)}/p_0^{(0)}) - 1$ versus t for $t > 30$ min, and this has an intercept.

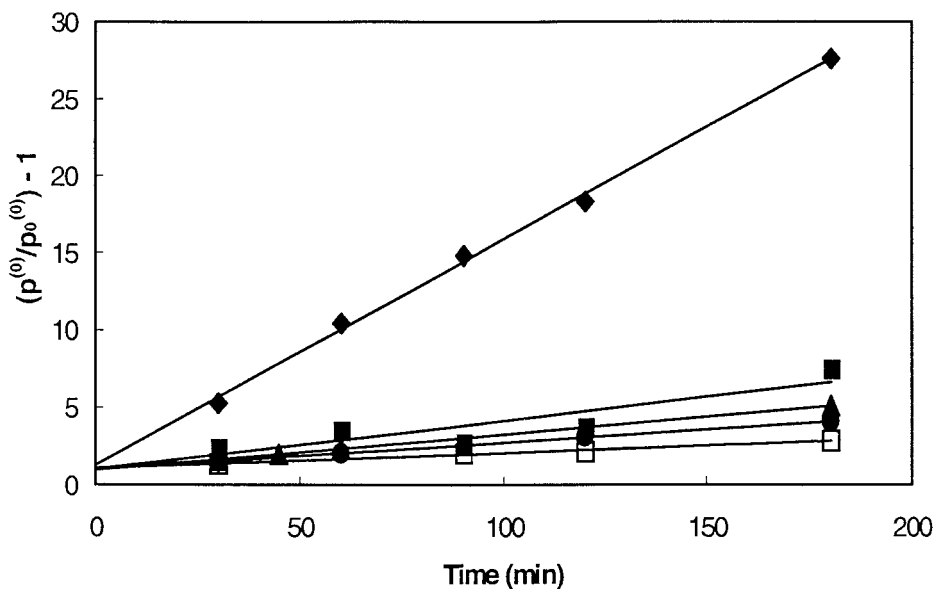


Figure 5 Plot of $(p^{(0)}/p_0^{(0)}) - 1$ against t for times greater than 30 min [(♦) 360, (■) 340, (▲) 320, (●) 300, and (□) 280°C].

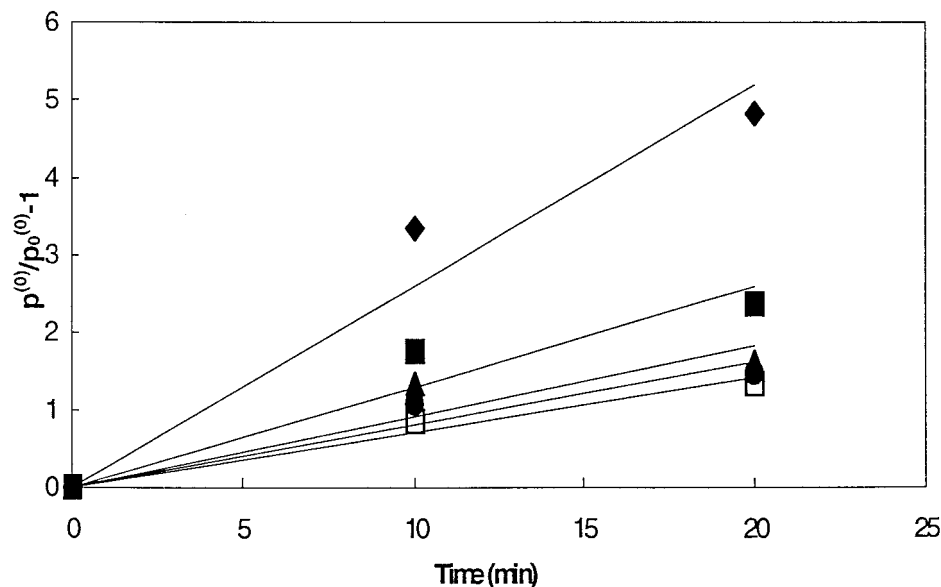


Figure 6 Plot of $(p^{(0)}/p_0^{(0)}) - 1$ against time t for times up to 30 min [(\blacklozenge) 360, (\blacksquare) 340, (\blacktriangle) 320, (\bullet) 300, and (\square) 280°C].

By eq. (18), this intercept corresponds to $k'_w t_f$ and the slope is equal to k'_s . The intercept is nearly the same for all temperatures, and the observation that $k'_w t_f$ is nearly constant is consistent with the results observed by Madras et al.¹⁴ The slopes of the lines in Figure 5 give us the value of k'_s at each temperature. The value of the rate coefficient k'_s varies from 0.0096 to 0.1461 $\text{min}^{-1} \text{g mol}^{-1}$.

Figure 6 shows a plot of $[(p^{(0)}/p_0^{(0)}) - 1]$ against

t for times up to 30 min. By eq. (17), the slope corresponds to $k'_w + k'_s$. Thus, k'_w is obtained from the slopes and is in the range 0.06–0.11 $\text{min}^{-1} \text{g mol}^{-1}$.

To find the rate coefficients k_s and k_w , we need to know the mass concentrations of the weak and strong links individually. The total mass concentration $p^{(1)}$ is the sum of the mass concentrations of strong links $p_s^{(1)}$ and the mass concentration of weak links $p_w^{(1)}$, so that

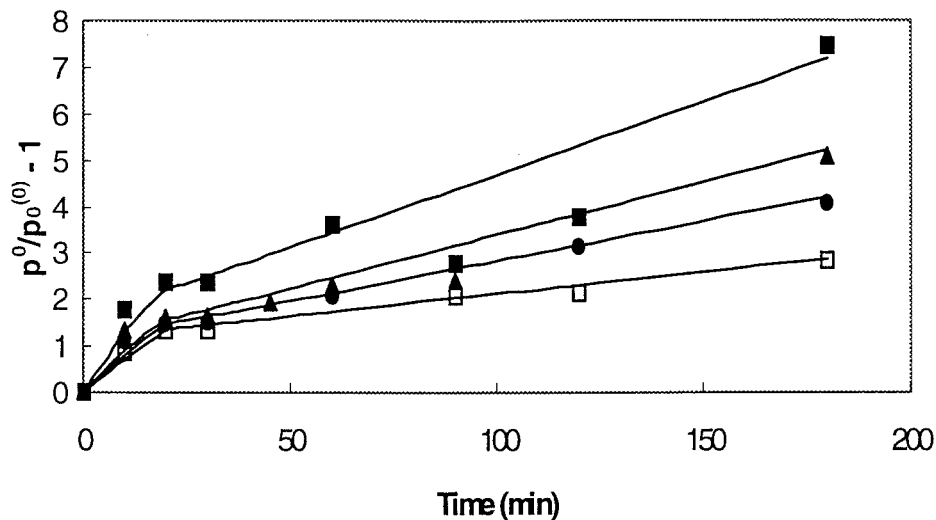


Figure 7 Model fit of $(p^{(0)}/p_0^{(0)}) - 1$ against t [(\blacksquare) 340, (\blacktriangle) 320, (\bullet) 300, and (\square) 280°C]. Symbols indicate data points, and solid lines indicate fits with eq. (20).

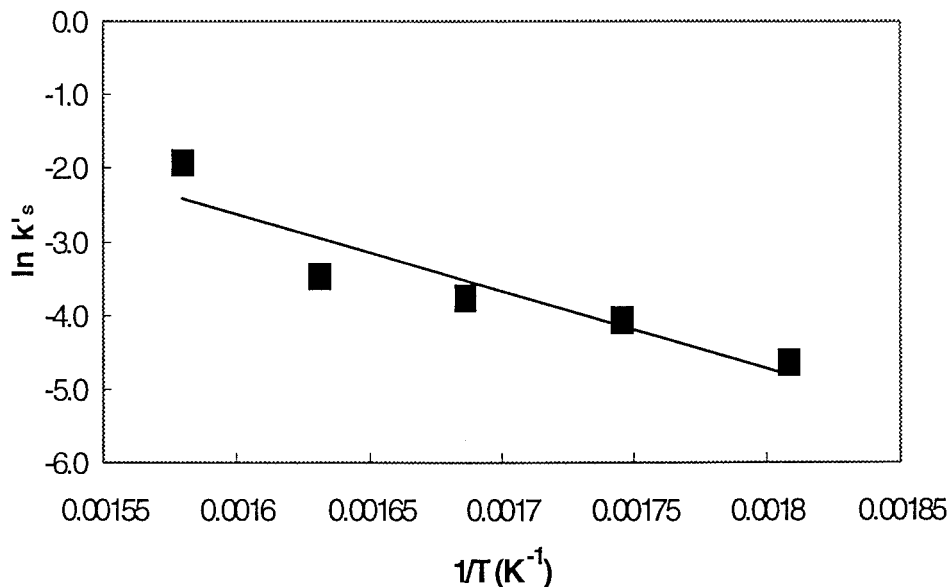


Figure 8 Arrhenius plot of the variation of k'_s with T . Symbols indicate data points, and solid line indicates linear fit.

$$p_s^{(1)}/p^{(1)} + p_w^{(1)}/p^{(1)} = 1 \quad (19)$$

If we denote with $f = p_s^{(1)}/p^{(1)}$ the weight fraction of strongly linked polymer and note that the mass concentration is constant, eqs. (17) and (18) can be written as follows. For $t \leq t_f$,

$$(p^{(0)}/p_0^{(0)}) - 1 = (k_s f + k_w(1 - f))M_{n0}t \quad (20)$$

For $t \geq t_f$,

$$(p^{(0)}/p_0^{(0)}) - 1 = k_s f M_{n0}t + k_w(1 - f)M_{n0}t_f \quad (21)$$

Knowing f , we can find k_s from the slopes in Figure 5 from eq. (18). The fraction of weak links is not known a priori. LDPE has around 20 branch points per 1000 atoms.²⁶ These weak spots are thus about 2–3% of the total. Choosing a value of $f = 0.98$, we found k_s to be between 4.9×10^{-8} and $74 \times 10^{-7} \text{ min}^{-1}$. The range of k_w calculated from eq. (21) was 1.5×10^{-5} to $2.8 \times 10^{-5} \text{ min}^{-1}$. The weak-link scission rate coefficients are 2 orders of magnitude larger than the strong-link rate coefficients. We used these values to find t_f from eq. (21). The calculated values in the range 11–17 min correspond well to values of 12–19 min fitted to the data and reported earlier for polystyrene degradation.¹⁴ The model fits for eq. (20) are shown in Figure 7.

The values of the rate constants are comparable to those determined for the degradation of HDPE in phenylether solution.⁷ The degradation of HDPE in phenylether was, however, carried out at a higher temperature range and higher pressure. The values of k_s in this study were 0.49×10^{-7} , 15×10^{-7} , and $74 \times 10^{-7} \text{ min}^{-1}$ at 280, 340, and 360°C, respectively. The reported values⁷ for HDPE in solution at 370, 390, and 400°C were 9.42×10^{-6} , 43.1×10^{-6} , and $95.4 \times 10^{-6} \text{ min}^{-1}$, respectively. These values are for the overall rate coefficient without accounting for weak and strong links. The rate coefficients for the melt pyrolysis of HDPE have been reported in the temperature range 440–490°C.²⁶ An initial high degradation rate [$16 \times 10^{-4} \text{ min}^{-1} (\text{g/g mol})^{-0.58}$] followed by a much lower rate [$1.4 \times 10^{-4} \text{ min}^{-1} (\text{g/g mol})^{-0.85}$] was reported. If we account for the initial number-average molecular weight (M_{n0}), the rate coefficients for melt pyrolysis are 0.16 and 0.12 min^{-1} for initial and later stages of degradation, respectively. The melt pyrolysis study was carried out for only 30 min and gave changes in M_{n0}/M_n of around 3. In our work, the overall change in M_{n0}/M_n was around 28 at 360°C and 3 at 280°C. The larger changes in M_n were possible at lower temperatures than for bulk pyrolysis because of better heat-transfer rates and the dilution effect observed in solution degradation.

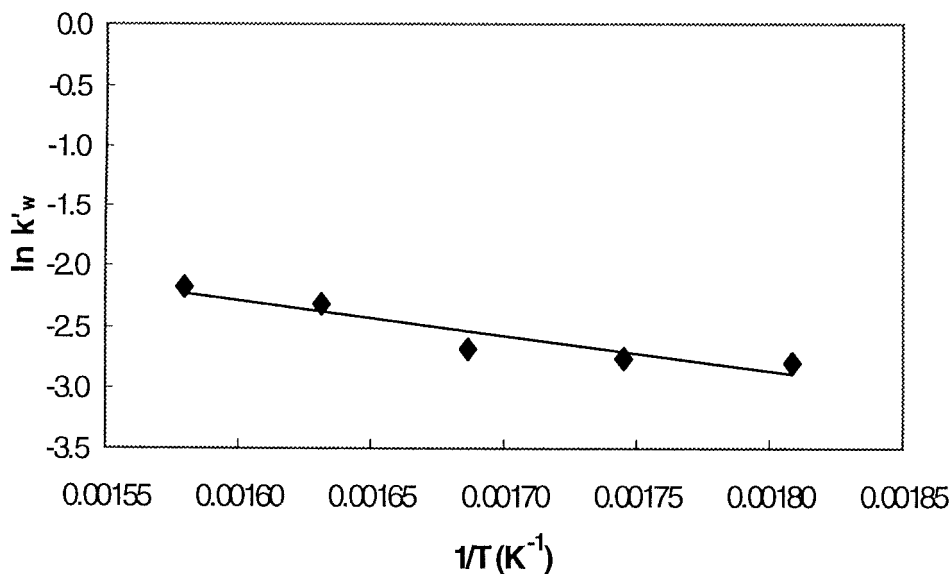


Figure 9 Arrhenius plot of k'_w with T for the determination of the activation energy. Symbols indicate data points, and solid line indicates linear fit.

Figure 8 shows the temperature dependence of k'_s . On an Arrhenius plot of $1/T$ versus $\ln k'_s$, all data fall on a straight line. The overall activation energy over the entire temperature range (280–360°C) for the breakage of strong links is 88 kJ/mol. These activation energies are comparable to the activation energies observed in a TGA study of polypropylene degradation,²⁸ where the activation energy was 98 kJ/mol at 404–421°C.

Figure 9 is an Arrhenius plot of the temperature and k'_w . The overall activation energy for weak links for the entire range is determined from the slope of the line and found to be 24 kJ/mol. These activation energies for weak links are comparable to the activation energy (28 kJ/mol) for weak links of polystyrene degradation reported by Chiantore et al.³¹

CONCLUSIONS

This work provides fundamental information about the degradation of LDPE in solution. Continuous kinetics provides the theoretical basis for evaluating the degradation rate coefficients. The thermal degradation of LDPE occurs at much lower temperatures for degradation in solution (280–360°C) compared with conventional melt pyrolysis (400–500°C). Weak links are present in LDPE that cause a rapid decrease in the molecular weight at low reaction times. On the depletion

of weak links, the degradation proceeds at a much slower rate. The corresponding activation energies show a large difference, with the activation energy for weak links being nearly one-fourth of the value of the activation energy for strong links.

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