Kinetics of Microwave-Assisted Oxidative Degradation of Polystyrene in Solution

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The kinetics of the oxidative degradation of polystyrene in dichlorobenzene in the presence of benzoyl peroxide was studied in a microwave reactor. Solutions with peroxide concentration ranging from 15 to 40 kg/m^3 were irradiated by microwave of 700 W and frequency of 2.45 MHz with a different cycle heating period ranging from 20 to 45 s. The molecular-weight distributions were measured as a function of reaction time by gel permeation chromatography. Because the temperature of the system continuously varies with reaction time, a radical mechanism for oxidative degradation based on continuous distribution kinetics with time/temperature-dependent rate coefficients was proposed. The activation energy of 46.4 kJ/mol for the microwave-assisted oxidative degradation of polystyrene was obtained by nonlinearly regressing the experimental data.

Introduction

Microwave radiation has been found to enhance the rate of several processes, such as solid-state polymerization (Mallon and Ray, 1998), emulsion polymerization (Correa et al., 1998; Jacob et al., 1997), dissolution of polymers (Wang et al., 2002), and acid digestion (Kingsten and Haswell, 1997). Microwave radiation is different from thermal heating, because heat is generated in the material itself due to dielectric heating (Correa et al., 1998). The temperature profile of the heated material in a microwave depends on the dielectric properties, specific heats, and thermal conductivity of the material (Roussy and Pearce, 1995). There are also reports that show no enhancement in the reaction rate under both microwave and thermal methods at comparable temperatures (Mijovic and Wijaya, 1990; Mijovic et al., 1992; Raner and Stranus, 1992), suggesting simple dielectric heating of materials. Other investigations, however, show enhancement in reaction rates using microwave radiation over the thermal method (Marand et al., 1992; Bram et al., 1990; Berlan et al., 1991; Baghurst and Mingos, 1992), indicating a *specific microwave effect* other than *dielectric heating*. Microwaves are also found to increase the overall diffusion rate of a mass-transfer-limited process and decrease the activation energy for diffusion (Gibson et al., 1988). Whitaker and Mingos (1994) have published a review on microwave processes.

Oxidative degradation using peroxides in solution is more attractive, because the presence of the oxidizing agent initiates the reaction by free-radical generation, and the degradation rate increases nearly 400 times compared to nonoxidative thermal degradation (Kim and McCoy, 2000). The degradation rate can be controlled by the suitable use of oxidizing agents, solvents, and temperature (Jellinek, 1995).

Continuous distribution kinetics is an effective tool for modeling the time evolution of the molecular-weight distributions of polymers (Madras and McCoy, 1998; Madras et al., 1997) and coal pyrolysis (Wang et al., 1994). Recently, it was proposed for the oxidative degradation of polystyrene (Kim and McCoy, 2000). In this study, we show that microwave radiation considerably enhances oxidative degradation. To the best of our knowledge, this is the first study on microwave-assisted degradation of polymers in solution.

Experimental Studies

In the microwave, 2 kg/m^3 of polystyrene [number-average molecular weight $(M_n) - 172{,}000$; Poly dispersity index: 1.2] dissolved in dichlorobenzene was oxidatively degraded. Dichlorobenzene was distilled and filtered before use. The oxidizer (benzoyl peroxide) was purified to remove the water content by dissolving in chloroform and precipitating in a nonsolvent (methanol). The permittivities at 25°C of the

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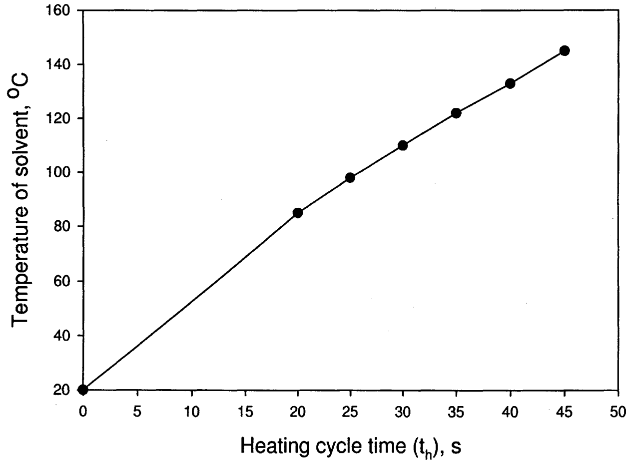

Figure 1. Experimental variation of solvent temperature with heating cycle time in the absence of peroxide.

dichlorobenzene, styrene, polystyrene, and benzoyl peroxide are 9.9, 2.4, 2.5, and 58.2, respectively. The permittivities decrease with an increase in temperature as the electrical storage capacity decreases with temperature. Samples of 50-mL volume were exactly placed below the magnetron in a top-heated microwave oven (Essentia, India, 700 W, 2.45 GHz). The duty cycle, defined as the irradiation period to the sum of irradiation period and dormant period (equal to 22 min), of the microwave-oven operation employed varied from 0.1 to 1. A duty cycle of 1 was employed in the present study, indicating that full power was supplied throughout the reaction time. The peroxide concentrations were varied from 15 kg/m^3 to 40 kg/m^3, and the heating-cycle times (t_h) were varied from 20 s to 45 s. The cyclic operation with a period of τ s consisted of heating the reactants for a set cycle time of t_h and cooling in an ice-cooled water bath to 20°C for 50 s (t_c). Each sample was irradiated for 10 cycles ($\tau = t_h + t_c$). For example, the total reaction time for 20-s heating cycle is 700 s with 200 s of microwave heating time. Similarly, for 25-, 30-, 35-, 40-, and 45-s heating cycles, the total reaction time was 750, 800, 850, 900, and 950 s, with an effective microwave exposure time of 250, 300, 350, 400, and 450 s. The temperature profile of the reactants in the microwave varies, as shown in Figure 1. The temperature gradient in the solution is negligibly small at low heating cycle times (~100 s) due to the natural convection of fluid in the top-heated microwave ovens (Ayappa et al., 1994). Although the temperature gradient in the top-heated microwave oven is negligible, the sample was rotated using a turntable to ensure the uniform mixing and temperature distribution.

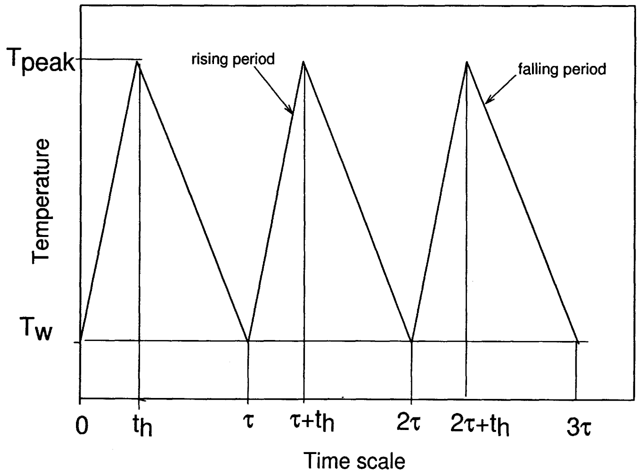

Figure 2. Theoretical temperature profile for each complete cycle, including heating and cooling.

The reactor consisted of a cylindrical vessel of ID 4.5 cm with height 7 cm. The temperature of the system was measured using a fluoroptic thermometer (Luxtron 790) with an accuracy of ±0.5°C. The cooling was accomplished by opening the oven and immersing the reaction vessel in the ice-cooled water bath maintained at 0°C (with vigorous stirring). By suitably adjusting the immersion, a linear cooling profile of 50 s was obtained. Thus, the rising and falling ramp constitutes the triangular temperature profile employed in the present study (Figure 2). The time evolution of the molecular-weight distribution was obtained by gel permeation chromatography (GPC) with THF as eluent at the rate of 1 mL/min. The details of the GPC were presented elsewhere (Sivalingam and Madras, 2002). All experiments were conducted in triplicate sets, and the rate coefficients determined had less than 2% standard deviation.

Theoretical Model

Continuous distribution models are developed to determine the kinetics of microwave-assisted oxidative degradation. This treatment is similar to Kim and McCoy (2000) and Madras and Chattopadhyay (2001) for the thermal oxidative degradation. However, since this study incorporates microwave radiation, the model accounts for the continuous variation of temperature with reaction time.

Modeling benzoyl peroxide dynamics

Consider the peroxide dissociation by homolytic cleavage into two radicals with a rate coefficient, k_p

$$C_2 \xrightarrow{k_p} 2C^* \tag{A}$$

The molar concentration of the peroxide is denoted by c_p, and the rate of disappearance of peroxide by dissociation is given by

$$\frac{dc_p}{dt} = -k_p c_p \tag{1}$$

The peroxide radicals formed in the preceding reaction get neutralized by the polymer to form tertiary radicals, $R^*(x)$, by abstracting hydrogen atoms from the polymer $P(x)$

$$C^* + P(x) \xrightarrow{k_d(x)} CH + R^*(x) \tag{B}$$

The rate of consumption of the peroxide radical can be obtained by the population balance as

$$\frac{dc(t)}{dt} = 2k_p c_p(t) - c(t)\int_0^\infty k_d(x')p(x',t)dx' \qquad (2)$$

The temperature of the sample in the microwave was experimentally measured and observed to increase linearly, as shown in Figure 1. The temperature profile for the entire cycle time is observed as a triangular function, as shown in Figure 2. Thus, the temperature profile for the cycle can be assumed to be

$$T = \begin{cases} T_w + \dfrac{T_{\text{peak}} - T_w}{t_h} t & \forall t \in (0, t_h) \\ T_{\text{peak}} - \dfrac{T_{\text{peak}} - T_w}{\tau - t_h}(t - t_h) & \forall t \in (t_h, \tau) \end{cases} \qquad (3)$$

where T_w is the temperature of the ice-cooled water bath (20°C), and T_{peak} is the maximum temperature reached at the end of the heating cycle. Arrhenius dependency of the rate coefficients was assumed for the present study. The thermal oxidative degradation models (Kim and McCoy, 2000; Madras and Chattopadhyay, 2001) solved Eqs. 1 and 2 directly, as the temperature of the operation was constant. In the present study, since the temperature varies with time, Eq. 3 is substituted in Eqs. 1 and 2, and the equations are solved simultaneously.

Time evolution of molecular-weight distribution of polymer

Polymers undergoing initiation and termination can be represented by a reversible reaction

$$P(x) \rightleftharpoons R^*(x') + R^*(x - x') \qquad (C)$$

These steps are infrequent compared with propagation and can be neglected in comparison with other steps (Kodera and McCoy, 1997). The reversible interchange of hydrogen by the abstraction by a polymer from a polymer radical can be represented by

$$P(x) \underset{k_H}{\overset{k_h}{\rightleftharpoons}} R^*(x) \qquad (D)$$

Then the propagation step by the irreversible β-scission of the polymers can be represented by

$$R^*(x) \xrightarrow{k_s} R^*(x') + P(x - x') \qquad (E)$$

The mass balance for the polymer and the radical can be represented by population balance equations as follows

$$\frac{\partial p(x,t)}{\partial t} = -k_d(x)c(t)p(x,t) - k_h(x)p(x,t) + k_H r(x,t) + \int_x^\infty k_s(x')r(x',t)\Omega(x,x')\,dx' \qquad (4)$$

$$\frac{\partial r(x,t)}{\partial t} = k_d(x)c(t)p(x,t) + k_h(x)p(x,t) - k_H r(x,t) - k_s(x)p(x,t) + \int_x^\infty k_s(x')r(x',t)\Omega(x,x')\,dx' \qquad (5)$$

Experimental observations showed the mode of degradation to be a random chain scission whose stoichiometric kernel, $\Omega(x,x')$, is given by $1/x'$ (Kodera and McCoy, 1997). The rate coefficients, k_h, k_H, and k_s, are assumed to be linearly proportional to molecular weight, x. Applying the moment operation on Eqs. 4 and 5 results in

$$\frac{dp^{(j)}}{dt} = -k_d c(t)p^{(j+1)}(t) - k_h p^{(j+1)} + k_H r^{(j+1)} + \frac{k_s}{j+1} r^{(j+1)} \qquad (6)$$

$$\frac{dr^{(j)}}{dt} = k_d c(t)p^{(n+1)}(t) + k_h p^{(j+1)} - k_H r^{(j+1)} - k_s \frac{j}{j+1} r^{(j+1)} \qquad (7)$$

Since the radical species are highly active and are unstable, the quasi-steady-state approximation (QSSA) can be applied to Eq. 7. The radical concentration can be given by

$$r^{(j+1)} = (j+1)p^{(j+1)} \frac{k_d c(t) + k_h}{k_s j + (j+1)k_H} \qquad (8)$$

The simultaneous solution of Eqs. 6 and 8 yields the expression for the jth moment in terms of known quantities

$$\frac{dp^{(j)}}{dt} = -(j-1)k_s \frac{(k_d c(t) + k_h)}{jk_s + (j+1)k_H} \qquad (9)$$

The molar concentration of the polymer can be computed by setting $j = 0$ and Eq. 9 reduces to

$$\frac{dp^{(0)}}{dt} = k_o p^{(1)} \qquad (10)$$

where the overall rate coefficient, k_o, is given by $k_{\text{oxid}}c(t) + k_{th}$. The oxidative degradation rate coefficient, k_{oxid}, is $(k_d k_s)/k_H$ and the thermal degradation rate coefficient in the absence of peroxide, k_{th}, is $(k_h k_s)/k_H$. It was experimentally observed that there was no thermal degradation in the absence of peroxide. Hence, it is reasonable to neglect the contribution from thermal degradation toward overall degradation, leaving $k_o = k_{\text{oxid}}\, c(t)$. Thus, Eq. 10 reduces to

$$\frac{dp^{(0)}}{dt} = k_{\text{oxid}} c(t) p^{(1)} \qquad (11)$$

The mass concentration of the polymer, that is, the first moment, $j = 1$ in Eq. 9, gives $dp^{(1)}/dt = 0$, remains constant, confirming the mass conservation of polymer. Then the simultaneous solution of time-dependent Eq. 11 with Eqs. 1 and 2, along with their boundary conditions with temperature dependency from Eq. 3 gives the time evolution of the number-average molecular weight. The kinetic parameters for the peroxide decomposition, hydrogen abstraction, and oxidative random chain scission can be found by the nonlinear regression of the experimental data.

Results and Discussion

The microwave-assisted oxidative degradation of polystyrene was investigated at different microwave-cycle heating times ranging from 20 s to 45 s. The experiments were conducted with a peroxide concentration ranging from 15 kg/m^3 to 40 kg/m^3 by irradiating the reactants for the prescribed heating-cycle time, t_h, and then cooling the reaction mixture with the ice-cooled water bath for 50 s for 10 cycles. Figure 3 shows the rapid reduction in number-average molecular weight in the initial 6 min of effective microwave exposure, and thereafter slows down for a 25-s microwave heating cycle with 25 kg/m^3 peroxide. The abscissa used in Figure 3 represents the effective microwave heating time excluding the cooling time in between the heating cycles. This is consistent with the observation with thermal oxidative degradation of Madras and McCoy (1997), where a constant molecular weight was observed after 10 min. The polystyrene was also degraded in the absence of the microwave. The polymer with the peroxide was taken in a glass beaker (of the same dimension used for microwave experiments) and inserted directly into an oil bath, maintained at the maximum temperature (T_{peak}) achieved at the end of microwave heating cycle. No appreciable degradation was observed in these cases. This clearly shows that the enhancement in the molecular-weight reduction is due to the microwave effect rather than simple dielectric heating of materials. The enhanced degradation rates in the presence of microwave can be attributed to the enhanced decomposition of the peroxide, the stabilization of polymer radicals, and enhanced transport. In the present investigation, it is assumed that microwaves do not influence the decomposition of the peroxide, because the decomposition of peroxide is extremely fast. It is also unlikely that a microwave results in the stabilization of polymer radicals, because the simultaneous polymerization and depolymerization (Madras and Karmore, 2001) has been reported. It is most likely that enhanced transport and mixing influences the reaction.

Figures 4a and 4b represent the theoretical fit for the variation of the peroxide and radical concentration with the total reaction time for a heating cycle of 40 s with an initial peroxide concentration of 20 kg/m^3 (0.082 kmol/m^3). The figure parts are shown for 10 cycles of 40 s heating and 50 s cooling. Figure 4a shows that the peroxide concentration decreases rapidly during the heating cycle and decreases slowly in the cooling cycle. Figure 4b shows the variation of the peroxide radical concentration with time. The radical concentration is maximum at the end of each heating cycle, when the highest temperature is reached. Since the rate of degradation depends on the amount of peroxide radical in the system, the rate of the decrease in molecular weight is very rapid during the heating cycle, while the rate of decrease is slow during the cooling cycle, as shown in Figure 4c.

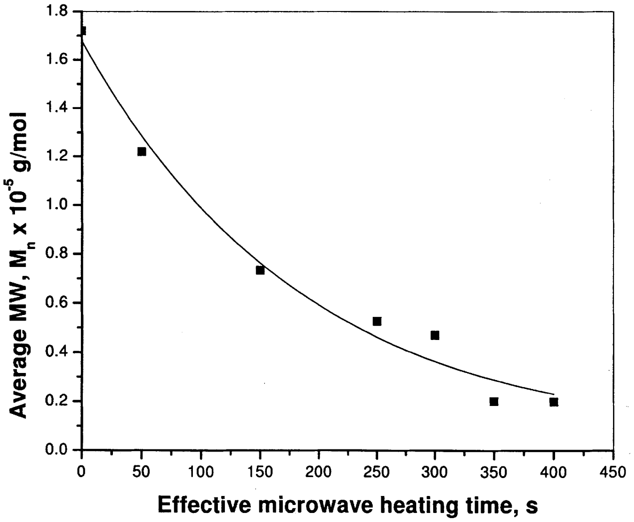

Figure 3. Variation of the number-average molecular weight of polystyrene with peroxide concentration of 25-kg/m^3 and 25-s heating cycle in the microwave.

The kinetic parameters can be determined by the nonlinear regression of the experimental data. The temperature dependency of the rate coefficients was assumed to be of the Arrhenius form. The temperature-dependent rate coefficients used were $k_p = k_{p0}\ \exp(-E_p/RT)$, $k_d = k_{d0}\ \exp(-E_d/RT)$, and $k_{\text{oxid}} = k_{\text{oxid}0}\ \exp(-E_{\text{oxid}}/RT)$. The temperatures in the preceding expressions were substituted as a function of time from Eq. 3. The rate coefficient for the homolytic cleavage of the peroxide, k_p, is given by $\ln k_p$ (in s^{-1}) $= 32.37 - 14{,}900/T$, where T is in K (Bandrup, 1975) and was assumed to be unaffected by the mode of heating. The kinetic parameters for the hydrogen abstraction and oxidative random chain scission were used as model-fitting parameters. Then the rate coefficients were substituted in the governing equations (Eqs. 1, 2, and 11), and were solved using Mathematica with boundary conditions $C_p(t = 0) = C_{po}$, $C(t = 0) = 0$, and $p^{(0)}(t = 0) = p_o^{(0)}$ to determine the polymer molar concentration at any time. The nonlinearly regressed values for k_d and k_{oxid} are $\ln k_d = 19.0 - 6{,}000/T$ and $\ln k_{\text{oxid}} = 12.5 - 5{,}600/T$. The experimental and theoretical predictions for various peroxide concentrations are in good agreement in a higher molecular-weight regime, and deviates slightly in the lower molecular-weight regime, as shown in Figure 5. The range of activation-energy values for the oxidative degradation of polymers like PVAc (Madras and Chattopadhyay, 2001) and PS (Madras et al., 1995) is around 83.7 kJ/mol. The microwave-assisted oxidative degradation of polystyrene is found to be 46.4 kJ/mol, suggesting that microwave radiation decreases the activation energy for the degradation of polystyrene. Figure 6 shows the variation in the polydispersity (ratio of weight-average to number-average molecular weights) as a function of peroxide concentration and the length of the heating cycle. It can be seen from the figure that the increase in the peroxide concentration reduces the

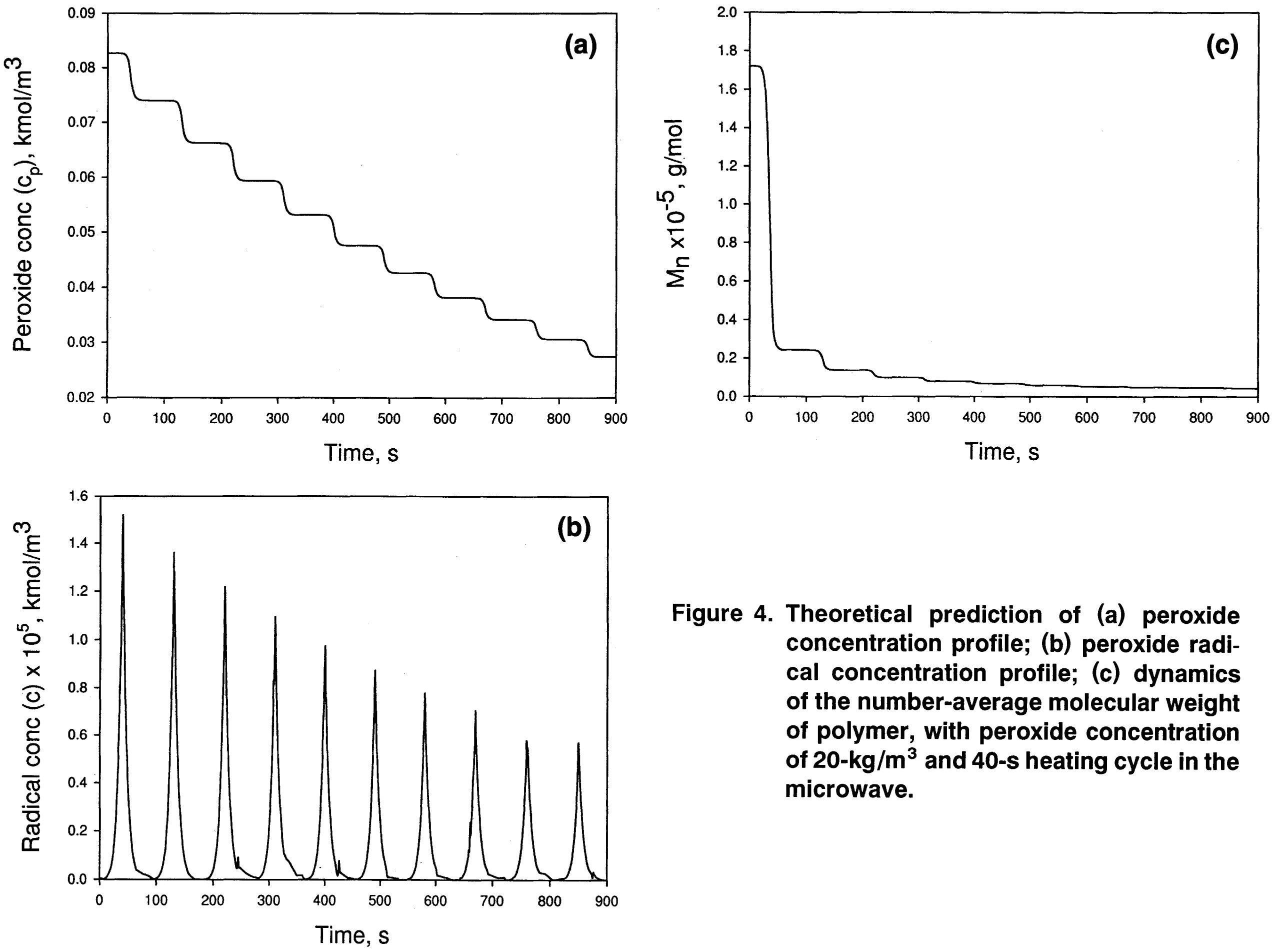

Figure 4. **Theoretical prediction of (a) peroxide concentration profile; (b) peroxide radical concentration profile; (c) dynamics of the number-average molecular weight of polymer, with peroxide concentration of 20-kg/m^3 and 40-s heating cycle in the microwave.**

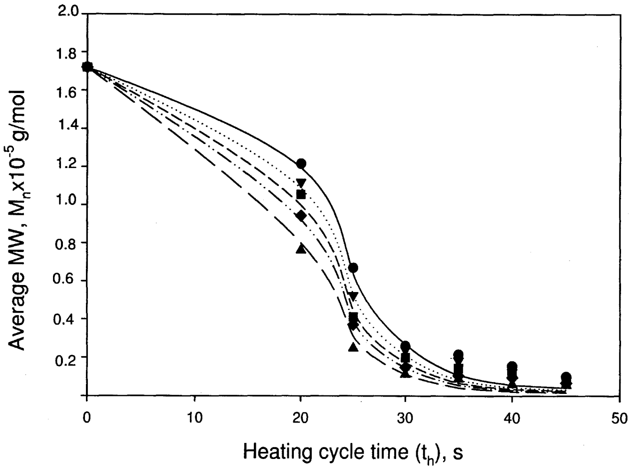

Figure 5. **Variation of number-average MW for different heating-cycle times at various peroxide concentrations.**

Legend: ●, 15 kg/m^3; ▼, 20 kg/m^3; ■, 25 kg/m^3; ◆, 30 kg/m^3; ▲, 40 kg/m^3. —— Model fit.

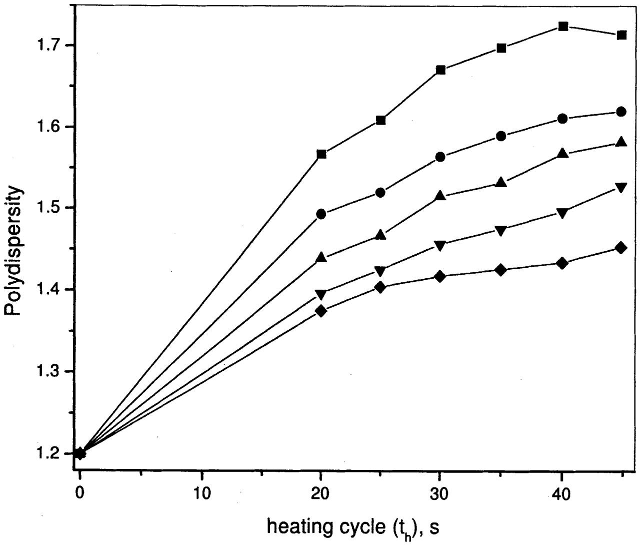

Figure 6. **Experimental variation of the polydispersity as a function of peroxide concentration and heating-cycle times.**

Legend: ■, 15 kg/m^3; ●, 20 kg/m^3; ▲, 25 kg/m^3; ▼, 30 kg/m^3; ◆, 40 kg/m^3.

polydispersity, while polydispersity increases with the length of the heating cycle.

Conclusions

The oxidative degradation of polystyrene was studied with microwave irradiation with different heating cycles and reaction times by varying the concentration of peroxide in the solution. The microwave oxidative degradation is found to be more efficient than the thermal-assisted process. A model was developed based on continuous distribution kinetics with time/temperature dependent rate coefficients. The rate coefficient and the activation energy for the degradation were determined.

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