Enhancement of Solid-State Polymerization with Microwave Energy

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ABSTRACT: This work reports on using microwave energy to increase the rate of solid-state polymerization for PET and nylon 66. Theoretical analysis and experimental evidence show that the increase in polymerization rate is not due to an increase in the bulk temperature. Instead, the effect is consistent with directed heating of the condensate leading to enhanced diffusion rates. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 1203–1212, 1998

Key words: enhanced solid state polymerization; microwave enhanced diffusion

INTRODUCTION

Solid-state polymerization of PET (polyethylene terephthalate) and nylon is limited by the diffusion rate of small molecules. This idea is reflected in the many patents for enhancing solid-state polymerization rates by increasing mass transport rates.[1–6]

There have been many reports of microwave assisted desorption and diffusion in the literature.[7–14] Many of the published reports show only enhanced desorption of a small molecule without distinguishing the microscopic details. Particularly, microwaves might provide the heat for desorption or heat the matrix. Gibson et al.[8] controlled the temperature in their reactor with infrared thermometry. Although the microwaves increased the overall diffusion rate, the activation energy for diffusion was found to decrease with the application of microwaves.

In this work, the knowledge of the diffusion limited nature of solid-state polymerization will be combined with the finding that microwaves can enhance diffusion rates in polymers. By enhancing the diffusion rate in PET and nylon 66, the solid-state reaction rates will increase without any significant thermal increase.

EXPERIMENTAL

The apparatus for the experiment is shown in Figure 1. The thermocouple inside the microwave oven was removed prior to experiments to avoid arcing; actual temperature control was done by manipulating the inlet gas temperature. In the apparatus, the field strength was continuously varied by manipulating a length of polypropylene tubing with water inside. The more water inside the polypropylene tube, the greater the rate of microwave absorption and the lower the overall field strength inside the microwave oven. Table I summarizes the operating characteristics of the microwave oven in the experiments.

The conditions of Table II are the base case for the PET experiments reported in the text; all deviations from these conditions are noted.

For each polymerization, the reactor was charged with pellets. The bed was purged with high-purity nitrogen for 2 min (flow rate was approximately 3 L/min). The temperature was increased in steps to precrystallize the PET to avoid
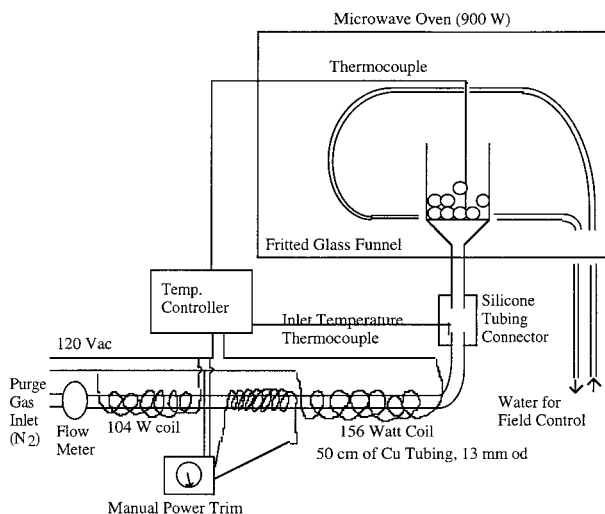
Figure 1 Microwave reactor setup.

sticking at reaction temperature. After purging, the external gas heaters were turned on, the inlet temperature setpoint set at 132°C, and the flow rate was increased to 17 L/min. This first crystallization step was allotted 8 min. Next, the temperature setpoint was raised to 190°C for 10 min (the second crystallization step). Finally, the temperature set point was raised to the reaction temperature. When the temperature settled to within 5°C of the set point, the experiment was considered to have begun, i.e., reaction time was counted from this point. If this experiment involved microwaves, the field was switched on at this point. Time from the beginning of heating to the zero time for the experiment was about 25 min; the same procedure was used for all experiments. By examining the rate of increase of molecular weight for the highest temperature (Fig. 2) and assuming that most polymerization before zero time occurs above 190°C (a time period no longer than 10 mins), the maximum change in molecular weight occuring before zero time is 700 g/mol. The resulting polymer samples were examined by FTIR according to the method of Ward and oth-

Table I Microwave Equipment and Operation

Microwave oven	General Electric, 900 W
Volume of water in field control tube (base case)	195 mL
Field strength (E^2) with microwaves on (base case)	4×10^6 V²/m²

Table II PET Solid-State Experiments in a Fluidized Bed

Particle size	Between #10 and #12 sieves (about 1 mm)
Particle preparation method	As supplied polymer ground to particle size above. Initial molecular weight = 14400
Crystallization steps	See text below
Gas flow rate/superficial velocity	17–17.5 standard liters per minute (about 2.4 m/s)
Purge type and purity	$N_2 > 99.99\%$, $O_2 < 5$ ppm, $H_2O < 3$ ppm
Time from beginning of heating to experiment start (heat-up time)	25 min (because of crystallization)
Time from end of experiment until polymer bed is 60°C (cool-down time)	10 min

ers;[15–17] this procedure generates values for the various end group concentrations as well as the number-average molecular weight.

The conditions of Table III are the base case for the nylon 66 experiments reported in this work; all deviations from these conditions are noted. Where some explanation of table entries is necessary, see the text immediately following the table.

Nylon 66 particles were graciously provided by the DuPont Co. The initial molecular weight was approximately 20,000. Because Gaymans et al.[18] found interesting behavior when starting with lower molecular weight particles, the particles were depolymerized to about 4300 molecular weight prior to the solid-state experiments. This was done in a stainless steel vessel with 45 g of nylon particles and 10 mL of water. The oxygen was removed with a nitrogen purge, the vessel sealed, and the vessel was placed in an oven at 190–200°C. The reaction was allowed to proceed for about 15 h. Following this, the vessel was cooled and the polymer removed.

For each polymerization, the reactor was charged with pellets. The bed of nylon 66 particles was purged with high purity nitrogen for 2 min (flow rate was approximately 3 L/min). The heaters were then turned on and the inlet temperature set point was set at the desired temperature. When the inlet temperature reached 90–100°C, the flow rate was increased to 17 L/min. By this method, the resin bed temperature increased rap-

Table III   Nylon 66 Solid-State Experiments

Particle mass (diameter)	About 15 mg ($\sim$ 3 mm)
Particle preparation method	Depolymerized to 4300 molecular weight (See text below) (DuPont Nylon)
Crystallization steps	None
Gas flow rate/superficial velocity	17–17.5 standard liters per minutes (about 2.4 m/s)
Purge type and purity	$N_2 > 99.99\%$, $O_2 < 5$ ppm, $H_2O < 3$ ppm
Bed weight for each experiment	0.9 g
Heatup procedure	See text below
Time from beginning of heating to experiment start (heat-up time)	10 min
Time from end of experiment until polymer bed is 60°C (cool-down time)	10 min

idly. When the temperature was within 5°C of the reaction temperature, the experiment was considered to have begun, i.e., reaction time was counted from this point. If this experiment involved microwaves, the field was switched on at this point. The time period from the beginning of heating to the zero time for the experiment was about 10 min; the same procedure was used for all experiments. Examination of the reaction rate at the highest temperature (Fig. 6) shows that the heat-up time
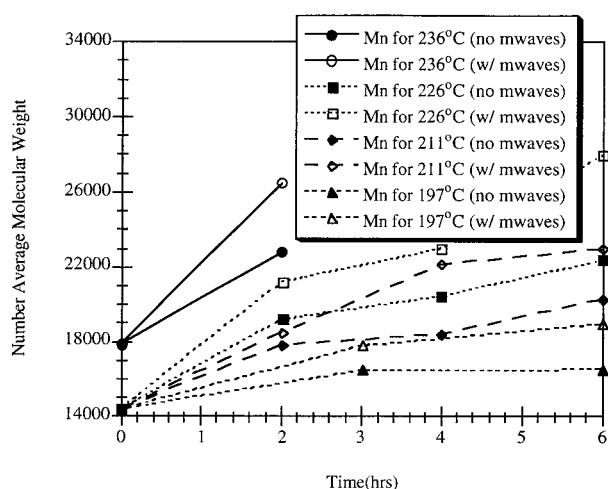

Figure 2   Solid-state reaction of PET with microwaves, molecular weights, lines show data trends.

for nylon solid-state polymerization accounts for no more than a 2700 g/mol increase in molecular weight at 226°C and much less at lower temperatures. The number-average molecular weight was analyzed by titration in a solution of about 0.08 g LiCl in 10 mL of CF_3CH_2OH.

RESULTS

PET

Figure 2 shows the effect of microwaves and temperature on solid-state PET polycondensation. Because the reaction is controlled by the diffusion of small molecules, microwave and thermal energy obviously increase the apparent diffusivity. Both the microwave and nonmicrowave data in Figure 2 (as well as the simultaneously determined carboxyl end concentrations of Figs. 4 and 5) were fitted to find Arrhenius expressions for the apparent diffusivity in the solid-state polymerization model of Mallon and Ray.[19] A comparison of the parameters calculated for the data is shown in Table IV. (Because water is evolved in very small quantities relative to ethylene glycol and to keep the number of fitted coefficients at a minimum, the diffusivity of ethylene glycol and water were assumed to be the same.) A quick inspection of the parameters shows that not only does the diffusion coefficient increase but that the activation energy decreases by 4.5 kcal/mol. Data with other catalysts show substantially higher diffusion activation energies[19,20] than found here in the absence of microwaves. This can be attributed to the effect of catalyst on the crystallinity.[21,22]

The data shown in Figures 2, 4, and 5 were generated with the conditions of Tables I and II. Temperatures and durations of the experiments are shown in the figures. The raw data were averaged and error bars were calculated[23] with each error bar representing a range of 1 standard deviation around the central point. The simulations were done with the solid-state model of Mallon and Ray[19] and the parameters of Tables IV, V, and VI.

Figure 4 shows the carboxyl end group data for polymerization with microwaves, and Figure 5 shows the same data for polymerization without microwaves. Superimposed on both figures are the fitted models (diffusion coefficients in Table IV).

Interestingly, the increase in solid-state poly-

Table IV   Effect of Microwaves on Fitted Parameters, PET

Conditions	Diffusion Coeff. at 220°C (Both Ethylene Glycol and Water)	Activation Energy
Polymerization without microwaves	1.19×10^{-6} cm²/s	16,672 cal/mol
Polymerization with microwaves	3.55×10^{-6} cm²/s	12,197 cal/mol

merization rate for the hydroxyl and carboxyl ends with the application of microwaves was not monotonic. One might expect that microwaves would increase diffusion rates for both water and ethylene glycol, affecting the concentrations of end groups equally. However, Table VII shows the percentage decrease in end group concentrations at the end of the experiment when microwaves were used as compared to when they were not. For example, if the final carboxyl concentration with microwaves was 0.10 mol/kg and 0.12 mol/kg without microwaves, then the carboxyl column would show 17% in Table VII. Particularly, Table VII shows that the carboxyl ends decreased far more than hydroxyl ends on a percentage basis.

If microwaves affect the diffusivity of water more, this change would make sense. The experimental microwave frequency was 2.45 GHz, a microwave frequency intended for heating water. If the heating of water is very specific, then microwaves might preferentially increase diffusion rates for water. Then, because the reaction of a carboxyl end with a hydroxyl end produces water while two hydroxyl ends produce ethylene gly-

col, better removal of water will lead to faster reaction of the carboxyl ends. Although this would also reduce the hydroxyl end concentration, the largely unchanged rate of ethylene glycol removal will inhibit further conversion of the hydroxyl ends (and lead to the differences of Table VII).

Nylon

In the previous section, microwave energy was shown to enhance solid-state polycondensation of PET—particularly enhancing the conversion rate of carboxyl end groups. Because the concentration of carboxyl ends is controlled by the water concentration at equilibrium, differential enhancement of water diffusivity over that of ethylene glycol could explain the difference. Because nylon consists entirely of water labile ends and linkages, solid-state polyamidation of nylon could show an even larger effect from microwaves. This idea is countered by the high equilibrium constant of nylon. Because nylon will tolerate a higher concentration of water, removal of water is less important than with PET. In other words, the inter-

Table V   Parameters for PET Simulation

Parameter	Value	Source
Kinetics and equilibria	Table VI	Ravindranath et al.[24]
Crystallizing rate	$3.6517 \times 10^{-14} \exp(23186/RT)$	Mallon and Ray[19]
Maximum crystallinity	$0.390 + 0.0025 (T-470)$	Mallon and Ray[19]
Diffusivity (water and ethylene, glycol, cm²/s)	Table IV	Data fit
Mass transfer	Volatile species conc. = 0 at surface	Assumption
Radial colloc. points number	4	Adequate from preliminary simul.
Temperature	Varies (see plots)	—
Initial carboxyl fraction of total endgroups	0.156	Measurement
Energy balance	Isothermal	This work
Ratio of cryst. density/ amorph. density	1.139	—
Amorphous density	1.33	—
Particle shape	Sphere	Assumption
Particle radius (cm)	0.10	Measurement
Initial crystallinity	0.30	Assumption

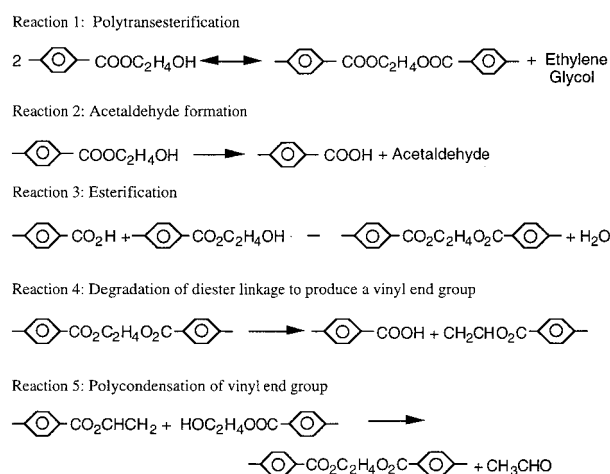**Table VI   Converted PET Kinetic Constants of Ravindranath et al.[24]**

Reaction (see Fig. 3)	Polycondensation	Acetaldehyde Formation	Esterification	Diester Group Degradation	Polycondensation of Vinyl End Group
Activation energy kcal/mol	18.5	29.8	17.6	37.8	18.5
Frequency factor kg/mol/h[a]	9.91×10^7	5.0×10^9	1.52×10^8	2.2×10^{11}	9.91×10^7
Equilibrium constant	0.5	—	1.25	—	—

[a] Reactions 2 and 4 are unimolecular and have units of h^{-1}.

play of the importance of water and equilibrium constant will determine the relative behavior of nylon compared to PET.

Figure 6 shows the enhancement in solid-state polymerization rates with microwaves compared to simulation (Mallon and Ray[19] with parameters in Tables VIII and IX). The experiments were done according to the parameters of Tables I and III. First, like PET, microwaves definitely increase the molecular weight produced. In all cases, there was a definite enhancement in the number average molecular weight by using microwaves.

The simulations in Figure 6 were calculated by fitting the data to the model of Mallon and Ray[19] using an Arrhenius expression for the diffusivity. Table IX shows that, just like for PET, the activation energy decreases by about 5 kcal/mol when the system is exposed to microwaves.

Reaction 1: Polytransesterification

Reaction 2: Acetaldehyde formation

Reaction 3: Esterification

Reaction 4: Degradation of diester linkage to produce a vinyl end group

Reaction 5: Polycondensation of vinyl end group

Figure 3 Reaction mechanisms for PET (simplified from Ravindranath et al.[24]).

DISCUSSION

Modeling of Thermal Increase

In Figures 2 and 6, microwaves clearly enhanced the rate of polymerization. The observation can be argued to represent just a temperature effect if the microwaves significantly heat the polymer above the purge gas temperature. In this section, the amount of microwave heating to be expected in a nylon pellet will be calculated. The expected associated increase in molecular weight is small compared to the experimentally observed one, which makes the explanation attributing the higher polymerization rates to microwave heating (i.e., thermal effects) inconsistent with the data.

The particles for purposes of modeling can be considered as spheres. The characteristic equilibration time can be calculated for a particle in a fluidized bed. The time varies, depending on the assumptions, but for the system studied, making reasonable assumptions leads to characteristic
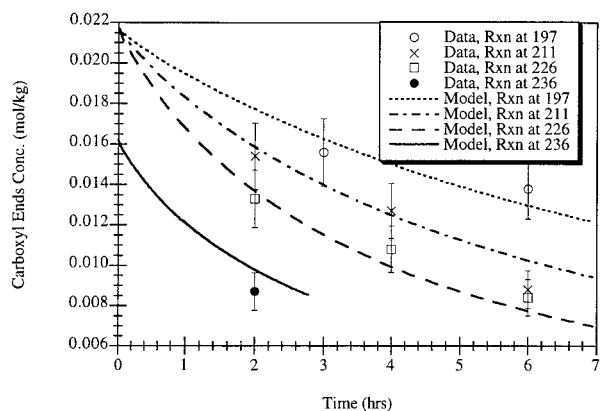
Figure 4 Solid-state reaction of PET with microwaves, carboxyl end concentrations.
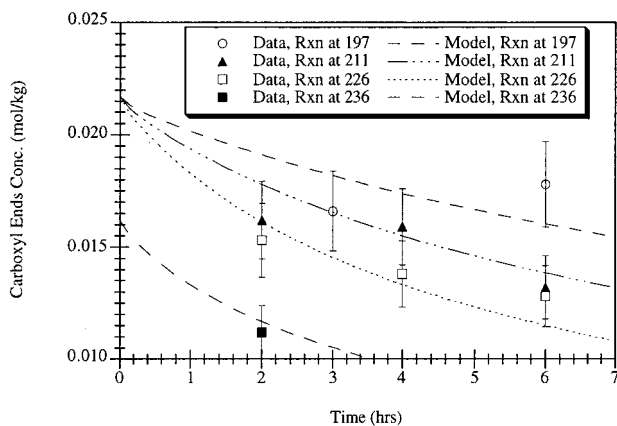
Figure 5 Solid-state reaction of PET without microwaves, carboxyl end concentrations.

Figure 6 Microwave effect and model for nylon 66 solid-state reaction.

times of less than a minute for thermal equilibration, compared to reaction times on the order of hours. Hence, making a steady-state assumption for the thermal equation will be reasonable.

Particles in a fluidized bed can exhibit two different resistances to heat transfer, depending on the values of the physical constants. For energy to be removed, it must first be conducted from the interior to the boundary of the particle. At the boundary, a heat transfer resistance can exist as well. In other words, a particle can be isothermal and still not be the temperature of the fluidizing gas. The situation is depicted in Figure 7.

Equation 1 shows the energy balance for the interior of a particle. The steady-state assumption has been made (above). The parameter P_{abs} represents the volumetric (microwave) heating that heat conduction will remove.

$$0 = k \frac{1}{r^2} \frac{d}{dr}\left(r^2 \frac{dT}{dr}\right) + P_{abs} \qquad (1)$$

By using eq. (2), P_{abs} can be calculated. The electric field strength was calculated to be about 2000 V/m based on water heating experiments. The value for the dielectric loss coefficient at 200°C was estimated to be 0.24 from nylon 12 data of Chen et al.[26]

$$P_{abs} = 2\pi f E^2 \varepsilon_0 \varepsilon_r'' \qquad (2)$$

Equation (1) can be integrated twice to yield the steady-state thermal rise in the particle.

$$\Delta T = \frac{P_{abs}}{6k} R^2 \qquad (3)$$

Table VII Comparison of Endgroup Concentrations after Solid State Polymerization with Microwaves Versus the Same Experiment Without Microwaves

Solid State Reaction Temperature	Difference in Carboxyl Ends	Difference in Hydroxyl Ends
197°C	23%	11%
211°C	33%	9%
226°C	21%	18%
236°C	21%	12%

Table VIII Simulation Parameters for Figure 6

Mass transfer	Diffusion parameters specified in Table IX
	Diffusion is calculated for free water (not total water)
	Free water is calculated by method of Mallon and Ray[25]
	Conc. of water = 0 at surface
Initial water content in polymer	1 mol/kg
Crystallinity (from Mallon and Ray[19])	0.78 for 182 and 202°C polymerizations
	0.77 for 226°C polymerization
Particle size	0.16 cm

Table IX   Effect of Microwaves on Fitted Parameters, Nylon 66

Conditions	Diffusion Coeff. at 202°C	Activation Energy
Polymerization without microwaves	1.09×10^{-6} cm²/s	21,435 cal/mol
Polymerization with microwaves	2.22×10^{-6} cm²/s	16,520 cal/mol

Taking 0.43 W/m/K for k (from the Polymer Handbook[27]) and the particle radius (R) of 0.15 cm, ΔT (intraparticle heat transfer) is found to be 0.1°C.

The ΔT for the particle boundary layer can be calculated in a similar fashion. Wakao et al.[28] developed a relation for the Nusselt number in packed beds as a function of the Prandtl and Reynolds numbers [eq. (4)]. This relation was used to estimate heat transfer in a fluidized bed because eq. (4) gives values intermediate between two correlations for fluidized beds.

$$Nu = 2 + 1.1 Pr^{1/3} Re^{0.6} \qquad (4)$$

Substituting the process values in eq. (4) gives a heat transfer coefficient of 365 W/m²/K. Because the time constants are small compared to the process time, steady state will again be assumed and the energy balance for the boundary layer can be written.

$$0 = hA\Delta T - P_{abs}V \qquad (5)$$

Solving for ΔT gives 0.15°C.

Combining the two temperature increases, this analysis shows that the maximum expected temperature rise in a 3-mm nylon particle is 0.25°C. Such a deviation is on the order of the control accuracy of the process. Furthermore, such a temperature rise applied to the whole particle (using the model in Mallon and Ray[19]) would increase

Figure 7   Modes of particle heat transfer for a particle undergoing internal heating.

the molecular weight by 200 after 6 h at 202°C. Such an increase would be almost unnoticeable, given the measurement error. In fact, a much larger increase in the number-average molecular weight is observed when microwaves are used— about 5000 (Fig. 6). For this reason, increased temperature does not seem to explain the observed increases in reaction rate.

This conclusion is contrary to the results of Breitschaft et al.,[29] who found considerable heating with applied radiation. However, the above analysis depended on small particles with high heat transfer areas accompanied by a fast stream of gas to carry off any heat. Breitschaft et al. do not report particle size, gas flow rate, field frequency, or field strength. Appropriate variation of these factors could easily change the above conclusion, which remains correct for the studied conditions.

Experimental Evaluation of Thermal Increase

In the above section, a theoretical study showed that the increases in reaction rate with microwave energy could be not attributed to dielectric heating of the polymer; experiments lead to the same conclusion.

Examining Figure 2 shows that the enhancement of solid-state reaction rate due to microwaves is about equivalent to an increased reaction temperature of between 10 and 15°C. Because the higher temperature experiments were conducted close to the melting point, microwaves should cause otherwise solid polymer to melt if the microwaves caused a substantial change in temperature. Experimentally, as the reaction temperature was increased, small clumps of particles in the final material became more common; however, microwaves being on or off had no effect on the clumps. More specifically, Figure 8 shows a DSC trace from a polymerization for 2 h at 236°C without microwaves (conditions of Figs. 2 and 5). Even a small increase in particle temperature would put the material in the middle of a melting transition. This data point further confirms the hypoth-
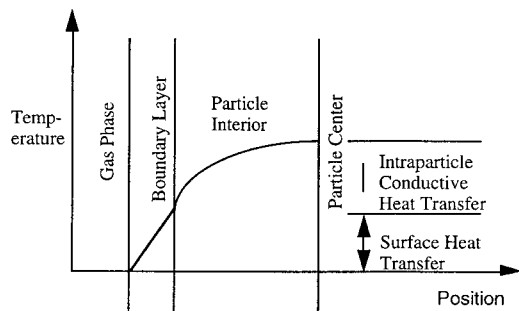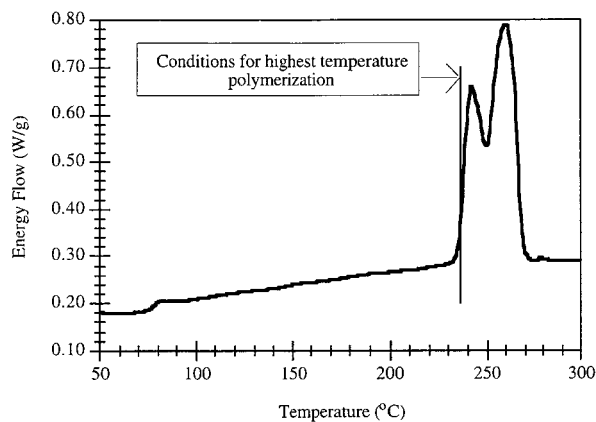
Figure 8 DSC trace of PET reacted at 236°C for 2 h without microwaves.

Figure 10 Final molecular weight after nylon 66 solid-state polycondensation as a function of microwave field strength.

esis of substantially isothermal conditions when the system is exposed to microwaves.

From eq. (2), the dielectric energy absorbed by a given material is known to vary linearly with the field strength (E^2). Furthermore, because eq. (3) shows the rise in temperature to be linear with the volumetric heating rate, the temperature should rise linearly with the field strength (E^2). Because Figure 2 shows that the temperature has a large effect on polymerization rates (as well as the microwaves), the molecular weight produced should increase dramatically with field strength if there are appreciable heating effects.

A series of solid-state polymerizations was carried out for PET according to the conditions of Tables I and II but varying the field strength (Fig. 9). The final molecular weights at three different temperatures are plotted vs. the microwave field strength and show that, within experimental er-
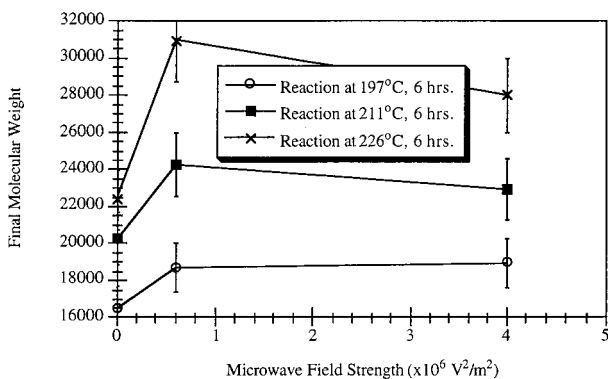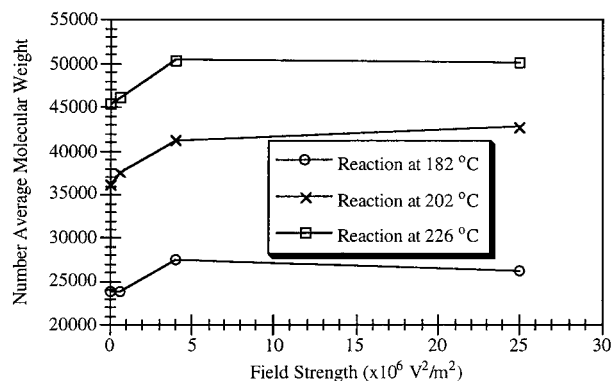
ror, the polymerization is unaffected by microwaves after the initial increase (for 1-mm particles, see Table II). This is consistent with the above theoretical analysis; microwave energy does not substantially heat the polymer.

Figure 10 shows the same effect occurs for solid-state polycondensation of nylon 66 as for PET. A series of solid-state polymerizations was carried out according to the conditions of Table III but varying the field strength (Fig. 10). As the field strength is increased, the molecular weight increases initially, but then stops. Such an observation is inconsistent with appreciable microwave heating of the polymer because Figure 6 clearly shows that not only do microwaves enhance polycondensation rates, but that raising the temperature has an even larger effect. This leads to the same conclusion as for PET; the increase in polymerization rates with microwaves is not consistent with thermal heating.

Effect of Microwaves on Diffusant

So far, temperature has been shown not to be the primary cause of the enhanced reaction rates in solid-state polymerizations with microwaves. For this reason, an alternative theory is needed. In a manner similar to that of Gibson et al.,[8] one can theorize that local directed heating of the diffusant is occurring. Heating of the diffusant and not the polymer matrix is plausible because microwaves excite rotational states of small molecules (not polymer chains). The heated diffusant would then more easily overcome the activation energy barriers leading to the reduction in apparent diffusion activation energy. The heating of the condensate could only continue to the point where

Figure 9 Final molecular weight after PET solid-state polycondensation as a function of microwave field strength.

significant energy would be otherwise transferred to the polymer matrix. Additional microwave energy would then no longer increase the diffusion rate and would allow the expression of the plateaus in Figures 9 and 10.

Very High-Field Strength Melting

During the experiments, at very high-field strengths and close to the melting transition, the microwave energy can cause the polymer to melt (both nylon and PET). Superficially, this data would indicate significant dielectric heating of the polymer, and hence, rebut the arguments advanced earlier regarding the isothermal nature. However, further examination of the data leads to contrary conclusions.

When nylon 66 was reacted at 226°C at field strengths of 0.6 and 4.0 ($\times 10^6$ V^2/m^2) (with other parameters than those of Table III), no melting was observed. The same reaction attempted with 25×10^6 V^2/m^2, yielded runaway melting. At the end of the reaction, there was just one large chunk of discolored nylon in the reactor. Because the polymer initially has a large amount of water to be vaporized, one might suppose that this high water content material was being heated preferentially. An experiment was done to test this by first polymerizing for 1.5 h without microwaves to dry the polymer and then introducing the high-strength field. The product of this experiment was the same as a polymerization carried out at 4.0 $\times 10^6$ V^2/m^2—a free-flowing particulate with the same molecular weight. Similar effects were seen for PET. In other words, runaway melting can be avoided with more thorough drying.

This pair of experiments, though initially appearing negative, confirms some of the ideas underlying the microwave enhancement arguments. First, microwaves appear to selectively excite (and heat) the condensate in the polymer. Runaway melting was only seen at high-water contents. Second, selective excitement of the water confirms the picture of microwave energy helping to desorb water and thus allow faster diffusion rates.

SUMMARY

This work has shown that microwaves definitely enhance solid-state polycondensation. That the enhancement is not due to heating of the polymer was seen from a number of points of view. First, the enhancement was shown to be greater than could be explained by a theoretical analysis. Second, the reaction rate of different end groups in PET did not increase evenly with the application of microwaves. Microwaves heating the polymer would cause more even increases. Third, for both PET and nylon 66, the increase in molecular weight eventually plateaus with increasing field strength. This, too, is not consistent with a thermal contribution. Instead, the microwaves seem to selectively excite the diffusant. Particularly, in both cases studied, the activation energy for the fitted diffusion constant was less for the microwave-treated polymers over those without microwaves.

Overall, microwaves enhance diffusion rates in PET and nylon independently of temperature. This increase in diffusion rate then leads to increases in reaction rate for diffusion limited polymerizations like PET and nylon.

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