

Accelerated Imidization Reactions Using Microwave Radiation

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SYNOPSIS

Microwave radiation has been clearly shown to result in enhancement of the rate of reaction for an imidization reaction. Analysis of the kinetic parameters showed that the apparent activation energy for the reaction was reduced from 105 to 55 kJ/mol, under the conditions of this experiment. The mechanism which has been proposed to explain this enhancement is based on the concept of a nonuniform temperature on a molecular scale, rather than a true reduction in the activation energy. © 1992 John Wiley & Sons, Inc.

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INTRODUCTION

The excellent mechanical properties which are exhibited by a number of modern high performance polymeric materials such as epoxy resins and polyimides, are developed over relatively long thermal processing cycles. The excessive time required for the processing of these materials can become a major limitation in the applications. Attempts to accelerate the reaction rate chemically typically result in increased outgassing, degradation, or different polymer morphologies in which the desirable mechanical properties are no longer retained. Thus, an alternate means of processing in which the process cycle time is reduced while retaining mechanical properties is highly desirable.

The use of microwave radiation for the processing of polymers has received increasing interest due to significant advantages over conventional thermal processing in convection ovens. The mechanism of energy transfer in microwave heating occurs by electric dipolar coupling of the radiation to permanent dipole moments in the polymer, rather than by thermal conductivity as in conventional processing. This has a variety of processing implications, par-

ticularly for parts with thick cross sections, in which very slow temperature ramp rates are conventionally utilized to negate the thermal gradients produced within the material during processing. When microwave radiation is used, however, the absorption of energy is more uniform with depth, following Beer's Law absorption and hence the polymer can be heated significantly faster while maintaining good thermal uniformity. An added advantage is that microwave radiation couples to dielectric materials very efficiently under proper conditions and is thus more cost effective than conventional treatments.

In addition to reducing processing time by allowing faster heating rates, we have found that the rate of conversion of a range of systems is increased when microwave radiation is utilized. This was first observed for epoxy resins in which the microwave conversion-time profile was significantly faster than isothermal conventional treatments.¹ This research has since been extended to a range of functionally terminated poly(ether ketone)s²⁻⁵ and poly(amic acid)s⁶ in which conversion studies using microwave and conventional techniques under isothermal conditions, have been compared. Enhancements of 3-34-fold were observed when microwave processing was used. This acceleration was observed from comparison of small samples cured in the microwave cavity with others from a forced air oven by a combination of DSC, soluble fraction measurements (by

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soxhlet extraction measurements), and FTIR measurements after various processing times. This, combined with long reaction times, removed the uncertainty of contributions from thermal transfer on the conversion-time profiles for these systems. DeLong et al.⁷ also reported reaction rate enhancements for epoxy resins from comparisons of isothermal conversion-time profiles, but the enhancement was smaller than we have typically observed, while Mijovic and Wijaya⁸ claim that the reaction rate was retarded by microwave radiation.

Detailed kinetic analysis of the reactions of these materials to obtain a better understanding of the rate enhancement is very complex due to gelation and vitrification which results in the reaction becoming diffusion controlled at a relatively early stage. To overcome this, the kinetics of a novel imidization technique^{9,10} were studied, in which the reaction was carried out in solution to produce a polyimide which remained soluble over the entire conversion range. In contrast to conventional imidization procedures, in which the kinetics become very complex due to evaporation of the solvent, dissociation of complexes with solvent, vitrification, and ordering processes (for some polyimides) in the solid state, this solution imidization reaction follows first order kinetics over the entire conversion range, thus simplifying the analysis. As a result, this reaction was ideal for examining the extent of reaction

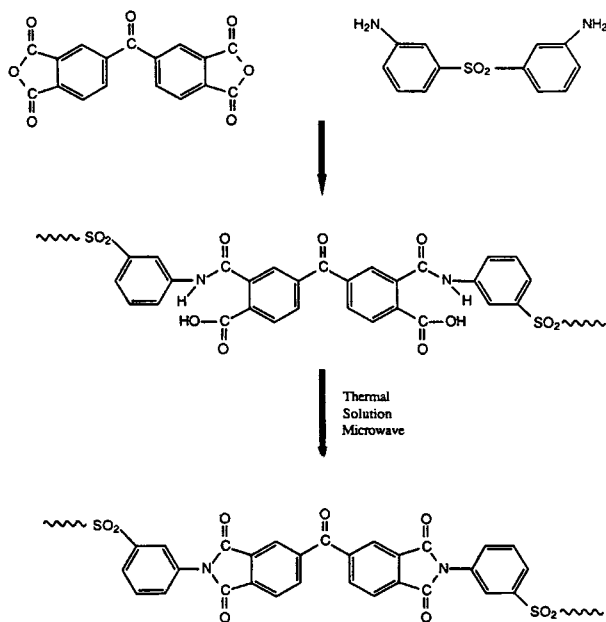


Figure 1. Chemical structures and reaction scheme for BTDA-DDS polyamic acid.

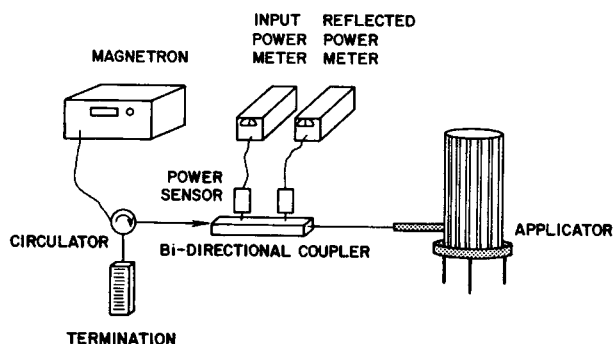


Figure 2. Schematic showing the microwave processing equipment.

rate acceleration during microwave processing and attempting to elucidate the mechanism of this enhancement.

EXPERIMENTAL

The polyamic acid (Fig. 1) precursor was prepared by adding stoichiometric amounts of recrystallized 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and diaminodiphenylsulfone (DDS) to distilled *N*-methylpyrrolidinone (NMP) to a total solids content of 20 wt %. The solution was then stirred for 2 h at room temperature, which has been found to be sufficient to obtain complete reaction to the poly(amic acid), and the solution was stored at 0°C.

The thermal solution imidization was carried out in a 250 mL round bottom flask fitted with a trap, nitrogen inlet, and stirrer. The temperature was monitored using a thermocouple and was controlled to $\pm 1^\circ\text{C}$. Cyclohexylpyrrolidinone (CHP) was added (1 : 4 to NMP) to act as an azeotroping agent to remove the water of imidization and to prevent chain scission occurring during imidization. This ratio of CHP to NMP was found to be effective as an azeotrope solution above 120°C. Small aliquots of the reaction mixture were removed periodically, rapidly cooled, and dropped onto NaCl plates for FTIR analysis to determine conversion. Since the reaction is first order in amic acid, the conversion which occurred during the heating of the reaction vessel (ca. 30 min) does not enter the evaluation, only the rate of change of the reactant and product after a constant temperature has been reached was important.

The microwave equipment used is shown in Figure 2. It consists of a microwave generator producing up to 85 W at 2.45 GHz (Raytheon PGM-10); a

circulator to protect the generator from reflected microwave power, power monitoring equipment, and a 17 cm internal diameter, tunable cavity operating in the TE_{111} mode.¹¹ The temperature was monitored using a Luxtron Model 750 Fluoroptic Temperature Sensor.

The sample holder in which the microwave imidizations were performed was produced by machining a 1.5 cm diameter hole 1.5 cm deep in a teflon cylinder 3.5 cm in diameter and 3 cm high. The combination of 1 cm thick walls and a small sample volume (with the sample cell $\approx 75\%$ filled) was used with the aim of limiting the temperature gradient from the solution to the air (at ambient temperature) entirely in the walls of the sample holder and thus obtain a uniform temperature distribution throughout the sample container. The sample container was mounted in the geometric center of the cavity by placing it on a 1 cm thick piece of teflon. The power variation across the 1.5 cm diameter region in operating in the TF_{111} mode is less than 2% for an empty, unperturbed cavity. Similarly, the vertical gradient in the electric field is small, thus ensuring that electric field strength, temperature, and hence the kinetics will be spatially uniform over the relatively small sample volume. The spatial uniformity of the temperature over the sample volume was confirmed by placing up to four fiber optic temperature probes in the sample container simultaneously. A loosely fitting cap with two holes (or four holes to check thermal uniformity) for a narrow bore teflon tube for aliquot removal and a Luxtron Model 750 fluoroptic probe was placed on top of the sample container to prevent solvent evaporation but main-

tain atmospheric pressure. The solution was not stirred.

During a typical run, 25 W of microwave power was required to heat the sample to the desired temperature over approximately 80–200 s. A typical temperature-time profile is shown in Figure 3. When the sample reached the desired temperature, the power in the microwave cavity was reduced to approximately 10 W both by decreasing the input power to the cavity and by detuning the microwave cavity (thus reducing the electric field intensity in the sample) to maintain the desired temperature. The temperature could be controlled to within 1°C using this technique. Care was taken to ensure that the mode (and hence the electric field pattern inside the cavity) did not change during the detuning process. After the desired temperature became stable, only minor changes in the electric field strength (microwave power) within the cavity were necessary to maintain the desired temperature.

Small aliquots of the reaction mixture, sufficient for the FTIR studies, were removed and the contents of the teflon removal tube returned to the sample vessel within 5 s. An added benefit to this procedure was that the sample was agitated during the process ensuring thermal uniformity. To ensure that the sampling method had no influence on the results obtained, the reaction was halted after various periods of time and the total reaction mixture analyzed by FTIR. Identical results were obtained. Multiple runs at the same temperature were performed and were found to be highly reproducible, indicating that the experimental technique was reliable and accurate.

The samples were then dried under vacuum at room temperature for 30–60 min to remove the solvent. The IR analysis was performed on a Nicolet MX-1 FT-IR spectrometer at room temperature in the absorbance mode. Since all IR measurements were performed at room temperature, complications due to temperature dependencies of bands, etc., were eliminated. Also, since the polyamic acid used in this study is completely amorphous and the salt plates were all prepared from solution without heating, morphological effects on the IR bands were also minimal. There was no evidence for any side reaction products, e.g., anhydride or isoimide formation, etc.

Resonances at 1778 cm^{-1} (imide carbonyl stretch), 1545 cm^{-1} (amic acid stretch), and 725 cm^{-1} (imide carboxyl bond) were used to determine the extent of imidization. These were referenced to the aromatic carbon-carbon stretch at 1477 cm^{-1} to remove the effect of film thickness on the absorbance

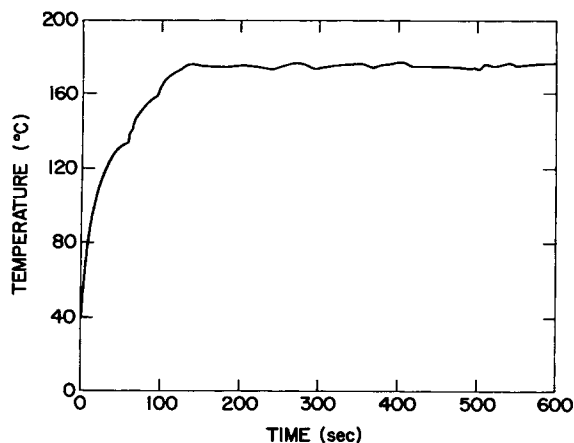


Figure 3. Typical temperature-time profile for microwave curing reactions.

values. These values were corrected for film thickness and then normalized to the absorbance for 0 and 100% imidization (obtained on specimens following 1 h each at 100, 200, and 300°C using conventional processing). The FTIR spectrum was the same for a free standing film cast on glass and a film cast and remaining on NaCl discs during conventional curing procedures.

RESULTS AND DISCUSSION

The plot for first-order kinetics of \ln absorbance versus time was linear for the full conversion range and was coincident for all three absorption bands, as can be seen in Figure 4. This indicates that the imide groups form at the same rate as the disappearance of the amic acid groups, confirming that side reactions are minimal, under the conditions used. The rate constants, determined from the slopes of such a plot, are shown in Table I along with the rate constants for conventional thermal processing. Comparison of the two rate constants at ca. 160°C indicates a 34-fold enhancement in the reaction rate constant, while at ca. 170°C, the enhancement was 20-fold. Since the imidization reaction is pseudo-unimolecular, polymer concentration and solution viscosity effects can be ignored. Importantly, this was confirmed by reactions at 12 and 8 wt % solids. This also confirms that solution viscosity dependence on the reaction temperature can be ignored.

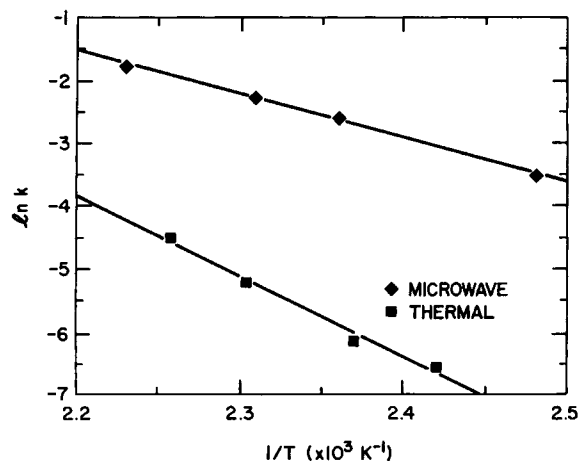


Figure 4. First-order kinetic plot showing formation of 725 cm^{-1} and 1778 cm^{-1} imide bands and disappearance of 1545 cm^{-1} amic acid band for $T_{\text{observed}} = 130^\circ\text{C}$ using microwave radiation.

Table I. Rate Constants for Solution Imidization

Temperature ($^\circ\text{C}$)	k_{thermal} (min^{-1})	$k_{\text{microwave}}$ (min^{-1})
130		0.030
140	0.0014	
149	0.0022	
150		0.076
160		0.103
161	0.0055	
170	0.011	
175		0.169

The Arrhenius plot in Figure 5 clearly demonstrates the differences between the microwave solution imidization processes and those obtained from conventional treatments. The activation energy determined from this treatment was 105 ± 14 kJ/mol for the thermal imidization and 57 ± 5 kJ/mol for microwave imidization (at the 96% confidence level). The values of \ln (pre-exponential factors) were 24 ± 4 and 13 ± 1 for thermal and microwave treatments, respectively.

The physical phenomenon which provides the

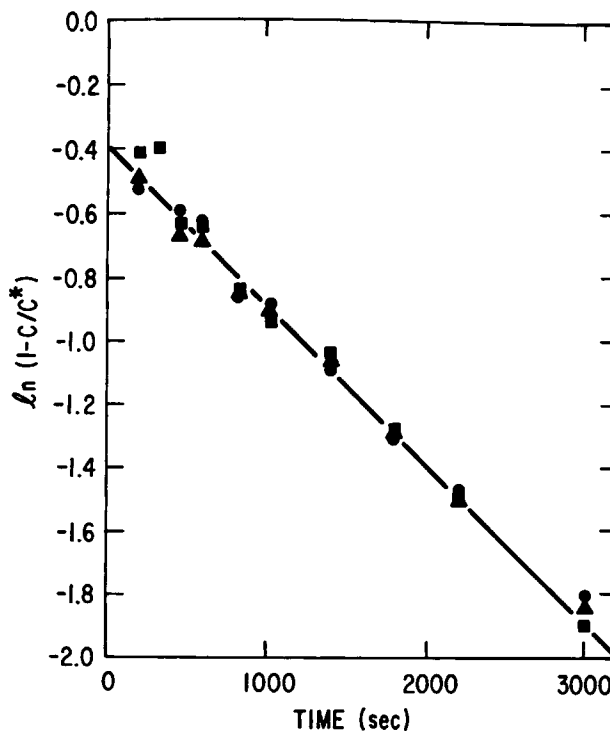


Figure 5. Arrhenius plot for microwave and thermally induced solution imidization reactions.

acceleration of the reaction rates is unclear. Microwave radiation is not sufficiently energetic to cause either ionization or electronically excited state chemistry to occur, so the overall reaction stoichiometry is the same as that for the thermal reaction. The large differences observed in the kinetic parameters might be due to intermediate products being formed (which is discounted by the coincidence of the formation and disappearance rates for the products and reactants) or from the way in which the microwave radiation interacts with the reactants, the solvent, or the complexes between the solvent and reactants.

The presence of solvent in the system (which will couple to the microwave radiation) does not appear to play a primary role in the acceleration mechanism since reaction rate increases have also been observed for epoxy resins,^{1,7} and functionally terminated thermoplastics²⁻⁵ in which no solvent was present.

NMP is known to complex strongly with certain amic acids, notably PMDA-ODA poly(amic acid)s. Brekner and Feger^{12,13} have shown that these complexes start to dissociate at approximately 80°C in PMDA-ODA poly(amic acid)s, depending on the heating rate employed, and are completely dissociated at 130°C, regardless of the heating rate. The complex in BTDA-DDS is weaker than that in PMDA-ODA and is therefore expected to completely disappear at a correspondingly lower temperature.¹⁴ The temperatures utilized in this work are higher than this dissociation temperature and hence such a species is not expected to play a role in the kinetics. If there was an initial contribution to the kinetics (due to the rapid heating rate employed) the plot in Figure 3 would be curved. If a residual concentration of these species occurred at the lower temperatures and had a significant effect on the reaction rate, the Arrhenius plot would be curved, which is not the case, as can be seen in Figure 5.

The above arguments would suggest that the acceleration is not due to the environment around the reactants and, therefore, must be due directly to the interaction of the microwave energy with the reactants, although the presence of solvent, etc. may have a secondary effect on the kinetic parameters. It is unlikely that the activated complex, formed by the collision of the acid moiety and amide group will be directly affected by the microwave radiation since the lifetime of such an interaction is thought to be of the order of one vibration at $< 10^{-12}$ s, much shorter than the period of the microwave radiation (10^{-10} s).

An assumption which is inherent in the Arrhenius analysis is that the temperature of the reacting system is uniform and equal to the observed temperature on both the macroscopic and molecular scales. This is certainly the case for conventional thermal reactions, and on a macroscopic scale is the case for the microwave curing reaction. However, since the forced oscillation of the dipole moments is the predominant mechanism for absorption coupling of microwave radiation to dielectric materials, and such strong dipoles were the reactive functional groups, we propose that the energy of the dipole moments, on a local scale, was higher than for nonpolar bonds or groups in the molecule. This higher, localized energy would be observed as an enhanced statistical temperature at the dipole. An apparent reduction in the activation energy would result, since the overall energy of the reactants was greater than that predicted from the observed temperature and the degrees of freedom of the system. It is expected that the relative temperature in the region of the energy receiving dipole reached a steady state for continuous microwave radiation, with the statistical temperature of bonds adjacent to the dipole decreasing rapidly as energy was conducted away from the absorption site through rotations, vibrations, and collisions. The flux of energy away from the dipole, the incident power, and the dielectric loss of the samples (which is a macroscopic value for the contributions of, principally, the dipole moments in nonconducting polymers) governed the steady state temperature of the reactive dipole.

Many previous studies have shown that thermal energy generated from pulsed lasers is dissipated extremely rapidly, before a reaction occurred. These experiments were performed on gaseous compounds at relatively low pressures, quite different from the present work. The collision frequency is orders of magnitude lower for these systems than in a highly viscous liquid, thus allowing greater time for energy randomization and migration from the site of absorption. Hence, the possibility of enhanced localized energy regions is greater in the condensed phase than in the gas phase.

To estimate the magnitude of the energy difference between the average temperature measured by the fluorescent probe and the reaction "temperature," which is necessary to produce the difference in the reaction rates observed, we assume that the differences in the kinetic parameters with microwave processing is entirely due to the higher temperature at the reaction site. Then, the temperature of the microwave reaction becomes $T + \Delta T$, where T is

the observed temperature and ΔT is the increased energy at the reaction site, in terms of temperature. When the reaction rate constants at a selected, observed temperature, T , are ratioed and $T + \Delta T$ is substituted for the observed temperature in the microwave case, eq. (1) is obtained:

$$\frac{k_{\text{microwave}}}{k_{\text{thermal}}} = \frac{\left(A \exp\left(\frac{-E_a}{R(T_{\text{observed}} + \Delta T)}\right) \right)}{\left(A \exp\left(\frac{-E_a}{RT_{\text{observed}}}\right) \right)} \quad (1)$$

Upon rearrangement to obtain ΔT , equation 2 results:

$$\Delta T = \frac{\left[T_{\text{observed}}^2 R \ln\left(\frac{k_{\text{microwave}}}{k_{\text{thermal}}}\right) \right]}{\left[E_a - RT_{\text{observed}} \ln\left(\frac{k_{\text{microwave}}}{k_{\text{thermal}}}\right) \right]} \quad (2)$$

When values of k (determined from interpolation from Fig. 5) are substituted into eq. (2), ΔT is determined to be 54°C for an observed temperature of 150°C and 50°C for an observed temperature of 160°C.

It should be pointed out that while we have obtained a value for ΔT of about 50°C for this system, it is anticipated that this value will vary for other systems, depending on the chemical structure, physical state, energy transfer mechanisms, etc.

Although a steady-state temperature is proposed for the continuous microwave treatment used in this work, pulsed microwave radiation would be expected to produce different effects, based on the model described in this article. The temperature may reach a steady state (depending on energy transfer mechanisms) during a typical 1 μs pulse, but after the pulse is completed, the energy will thermalize and the excess dipole energy (ΔT) will decrease and approach the observed temperature. It can also be predicted that the dependence of the heating rate and kinetics on pulse frequency may be independent of each other since heating rate will depend on heat transfer through and from the dipole and the other on retaining the excess temperature to allow enhanced or different reactions. This would provide an explanation for the different chemical structures which were obtained at different pulse frequencies by Thullier et al.¹⁵ On-off temperature control is analogous to using very long pulses and it is expected that the reaction kinetics will behave closer to that

obtained for conventional thermal processing, perhaps explaining the smaller acceleration in the reaction rate observed by DeLong et al.⁷

CONCLUSIONS

We have demonstrated that microwave radiation acts to enhance the kinetics of an ideal, pseudo-first order solution imidization reaction over that obtained for more conventional treatments by 20 to 34 times, depending on the measured temperature of the reaction. This confirms earlier observations for systems in which accurate kinetic analysis was difficult to obtain and interpret. The results presented here, combined with previous data for a range of other systems, suggests that this acceleration may be a general phenomenon for systems where dipole moments react, but the magnitude of the acceleration will vary.

The apparent activation energy for this solution imidization reaction, determined from an Arrhenius analysis, was reduced from 105 to 55 kJ/mol when microwave radiation was utilized rather than conventional thermal processing.

A model for the mechanism of the reaction rate enhancement and reduction in the apparent activation energy in which a non-uniform temperature profile on a molecular scale has been proposed. The theory predicts a temperature enhancement of about 50°C in the vicinity of the dipole moment which couples to the radiation. This model can be used to satisfactorily explain a range of phenomena reported in the literature and observed in our laboratory relating to microwave processing.

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