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Kinetic Study of the Imidization of a Poly(ester amic acid) by FT-Raman Spectroscopy

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ABSTRACT: The kinetics of thermal imidization of a poly(ester amic acid) in solid state was investigated in the temperature range 120−180 °C. FT-Raman spectroscopy was used for the measurement of imidization. Data on changes in intensity were collected on compressed thin specimens that had been isothermally cured. FT-Raman spectral changes as a function of imidization time are adequately modeled by assuming two first-order imidization reactions. Activation energies for the first and second ring closure processes were almost the same, 20.5 and 19.9 kcal/mol, respectively. However, the activation energy increased slightly (24.6 kcal/mol) when the second-order reaction model was adopted for the first reaction. Increase in activation energy was screened by the increase of the pre-exponential factor, implying the absence of significant changes in the reaction rate ratio. A new time dependent model is proposed which is easy to apply and shows good agreement with the experimental data, both quantitatively and qualitatively. The activation energy calculated by the new model was 24.3 kcal/mol. It takes into consideration the evolution of different amic acid stages. The proposed model also correlates the two-step imidization reaction very well.

Introduction

Polyimides are an important class of high-performance polymers used in the electronics industry as interlayer dielectrics in advanced packaging applications and photoresist materials.[1−4] The popularity of the polyimides has been established on the basis of outstanding thermal stability, excellent mechanical properties, and the ability to be fabricated into useful articles. Moreover, the versatility of polyimides has led to their use in a wide variety of applications. Since property requirements in these high-technology areas are stringent and depend on the degree of conversion of poly(amic acid) to polyimide, optimization of processing conditions, especially the cure profile, is very important.[4] Despite the wide spread interest in and innumerable studies of polyimides, their detailed reaction mechanisms are still not completely understood.[5,6] These mechanisms are dramatically affected by reaction conditions. Monitoring of the curing poly(amic acid) has been extensively investigated by many authors,[6,7] using techniques such as Fourier-transform infrared spectroscopy, a thermogravimetric analyzer (TGA), differential scanning calorimetry (DSC), and fluorescence. One recently applied technique is Fourier-transform Raman spectroscopy.[8] This technique is quite useful for obtaining spectral data from highly fluorescent materials, such as polyimides. In addition, it is possible to obtain vibrational spectra of thick and/or opaque samples because of the scattering mode of FT-Raman spectroscopy. Thus curing reactions can be conveniently studied by means of FT-Raman spectroscopy, which affords a unique way to follow the curing of polyimides even in the presence of solvent. So this is a definite advantage over infrared spectroscopy in investigations of imidization kinetics, because such kinetics are strongly dependent on the solvent for chemical imidization.[4−9]

In the classical method of polyimide synthesis, a two-step method is generally employed, i.e., a tetracarboxylic acid dianhydride is added to a solution of diamine in a polar aprotic solvent to generate a poly(amic acid), which is then cyclodehydrated to the corresponding polyimide by extended heating at elevated temperatures or by treatment with chemical dehydrating agents. The most widely used second step in the two-step method of poly(amic acid) synthesis involves heating the poly(amic acid) in the solid state to 250−400 °C. Higher degrees of imidization, i.e., >99%, can be obtained by constant heating at 230−250 °C for 10 min.[9] Similar to the synthesis step, thermal imidization is a complex process that is still under extensive investigation. The use of different methods and procedures to measure imidization has undoubtedly contributed to the general lack of agreement over the degree of imidization even in the solid state, which does not allow unequivocal determination of the order of the reaction. Laius and Tsapovetsky insisted that, although two groups, CONH and COOH, are involved in imidization, this reaction should be treated as first-order, since these groups belong to the same fragment of poly(amic acid), and interaction of the groups with different macromolecules is practically impossible, especially in the solid state, as evidenced by the solubility of numerous polyimides.[5,6]

The most typical feature of the solid-phase thermal cyclization process is a sharp decrease in the rate of reaction at a certain degree of imidization, which depends on the temperature of the experiment.[9] Sometimes the cyclization process is simply represented as involving two steps, fast and slow, with specific rate constants. However this is only a first approximation. In most cases, the rate constant remains invariable only during the initial step of the reaction and then decreases continuously.[5,7,10] The change in the rate constant in the logarithmic scale as a function of degree of imidization can be represented, although arbitrarily, by two straight lines. This implies that there exist kinetically nonequivalent amic acid segments.[5,7] Experimental

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studies of the kinetics of thermal cyclization of poly(amic acid)s have been very numerous. However, a physical model of this process and correlations of theoretical calculations with experiments under any conditions have not yet been thoroughly developed.[6] In the early eighties, Russian researchers proposed two models to account for the kinetically nonequivalent states of amic acid groups.[5] Though their model predictions provided good agreement with experimental data, they relied on an arbitrary density distribution of the amic acid groups over some states in poly(amic acid) and accurate information on the initial rate, which to date has been too obscure to be accurately obtained.

The purpose of this paper was to investigate imidization kinetics using FT-Raman spectroscopy and to provide a simple model that could describe the evolutionary progress of poly(amic acid)s in different states. We wanted to use solid poly(amic acid), which removes the complex effect of solvent on imidization.

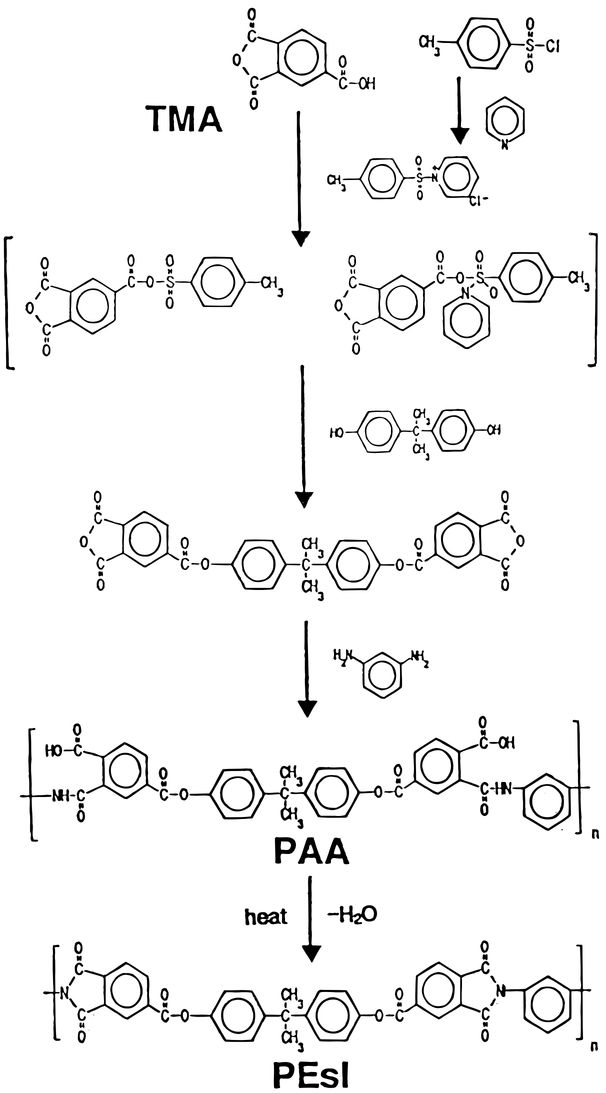
Experimental Section

Materials. The poly(amic acid) was synthesized using a standard synthetic procedure as follows:[11,12] 0.05 mol of trimellytic anhydride and 0.06 mol of *p*-toluenesulfonyl chloride were dissolved in 100 mL of pyridine with stirring at room temperature for 10 min under a nitrogen atmosphere in a three-necked, 500 mL, round-bottomed flask equipped a stirrer and a nitrogen inlet. Then 0.025 mL of bisphenol A was added to the mixture with vigorous stirring. As soon as *p*-toluenesulfonyl chloride was added, an exothermic reaction took place and the solution turned a pale-yellow color. Prior to the addition of bisphenol A, the reaction proceeded in a heterogeneous manner, but when bisphenol A was added, the reaction became homogeneous. Next 0.025 mol of *m*-phenylenediamine was added to the reaction solution, with continuous stirring for 30 min. After a period of time, the mixture was poured into excess methanol (1 L) to remove pyridine, byproducts, and unreacted monomers from the resulting polymer, which was then isolated by filtration. The polymer (poly(amic acid), PAA) was repeatedly washed with methanol and then dried in vacuo for 48 h. The yield was more than 95%. Its chemical structure and synthesis scheme are shown in Scheme 1. The synthesized PAA was ground into a powder to obtain the maximum surface area. To obtain the data from the fully imidized sample, the powder was dried at 70 °C for 1 h and then heated at 265, 275, and 285 °C for 20 min each in a heating oven. Nitrogen was purged in order to remove the evolved water.

Generally, poly(amic acid)s are formed by the reaction of dianhydride with diamine. The formation of polyamic acids from diamines and dianhydride proceeds via nucleophilic substitution on the anhydride carbonyl atom, with the amine acting as a nucleophile.[13] Hence, the reaction rate is strongly dependent on the basicity of the amine, the electrophilicity of the anhydride carbonyl, and the basicity of the solvent. The thermal imidization of poly(amic acid)s involves cyclization through a nucleophilic attack on the acid carbonyl carbon by the free electron pair of the amide nitrogen. Nonconjugated diamines or dianhydrides have spacer groups between aromatic rings that influence the basicity of the amines or the electrophilicity of the anhydride carbonyl mainly by inductive effects, so that their reaction rates are different from those of conjugated systems. The polyamic acid in this study was different from that formed by the reaction of dianhydride with diamine in that the dianhydride group is not conjugated.

Sample Preparation. After drying, the poly(amic acid) powder was molded as a thin plate of less than 0.1 mm thickness. The molded polyamic acid was dried in a vacuum oven at 60 °C for 1 h. This plate was placed on a preheated heating stage (Mettler FP81). Then changes in the intensity of special bands were measured using a FT-Raman spectrometer. Since solid poly(amic acid) was used, solvent effect was not a problem. At each predetermined time, the specimen was transferred to a FT-Raman spectrometer to obtain the spectral data. Then it was placed back into the hot stage. The error due to movement was not significant, being less than ±2%. Imidization temperatures below 200 °C were used to prevent the poly(amic acid) from side reactions, such as decomposition.[13]

Scheme 1



FT-Raman Spectrum. The Raman spectra were obtained using a Perkin Elmer System 2000 FT-Raman spectrometer equipped with an Nd:YAG laser (1064 nm). Spectra were obtained in the backscattering mode.

Characteristic Band Determination. Infrared analysis has frequently been used in the kinetic study of thermal imidization of poly(amic acid)s.[9,14] Although IR spectroscopy has been used extensively to monitor the cyclization step, there is little agreement in its sensitivity to the chemical changes taking place. In fact, there is no consensus on which of the various amide or imide bands should be followed. Absorption band characteristics of the imide ring occur at 1770−1800 cm^{-1} because of the symmetric imide carbonyl stretching, at 1370−1380 cm^{-1} from imide carbon nitrogen stretching, and near 720 cm^{-1} because of the imide ring vibration. These bands have been most widely used.[9] The degree of imidization is determined by comparing the intensities of these bands in treated samples to those in a sample that is heated until no changes in the band intensities occur. The majority of IR studies have been carried out on film samples. In order to avoid any effect from variations in film thickness, optical densities are usually normalized against an internal aromatic absorption band. The bands at 1015 and 1000 cm^{-1} appear to be the most satisfactory.[15] The bands at 1780 and 720 cm^{-1}

were found to be insensitive to changes that could be detected by thermal techniques in the later stages.[16] A recent study [8] also found that bands at 1780 and 720 cm^{-1} are affected by anhydride absorption that appears during the thermal cycle. In addition, these bands experience interference between symmetric and antisymmetric carbonyl stretching. It has also been reported that the 1780 cm^{-1} band may deviate from the Beer–Lambert law because of hydrogen bonding in the solvent.[16,17] The imide band near 1380 cm^{-1}, however, does not appear to be affected by any other absorbance. Also, it has been shown that the imide absorbances near 1780 and 720 cm^{-1} in film samples can be affected by anisotropy.[16] The band near 1380 cm^{-1} shows very little effect from anisotropy when it is normalized to the 1500 cm^{-1} aromatic band.[15] The use of different methods and procedures to measure imidization has undoubtedly contributed to the general lack of agreement over the degree of imidization that is attainable. The chemical structure of polyamic acid also affects the imidization process.[12–17]

Since Raman spectra show a strong intensity for the symmetrical stretching of the bonds, this spectroscopic method can eliminate interference from the antisymmetric stretching band. Also, as shown later, poly(amic acid) in this study produced almost negligible (or undetectable) anhydride. We chose the 1780 cm^{-1} band for the imidization characteristic peak. The band at 1740 cm^{-1} was used as an internal standard band. Kinetic data obtained from this band were later compared to those from the band at 1600 cm^{-1} of the aromatic ring vibration. The development of imidization changes the band at 1600 cm^{-1} from a singlet to a doublet. A shoulder band at 1620 cm^{-1} evolves with imidization, and the ratio between these two bands agrees with the imidization amount. Agreement between the kinetic data from this ratio and that from the 1780 cm^{-1} band implies that the anisotropy effect is not significant at least for testing poly(amic acid). We did not use the band around 1380 cm^{-1} because of a high noise level.

Previous Kinetic Models. Many studies of imidization kinetics indicated that in the solid state the reaction rate of thermal imidization slows down as the reaction proceeds.[5–10,12–17] Under isothermal conditions, two stages of cyclization can be distinguished: a fast initial stage and a slow final one. In the first stage the rate constant calculated by the equation for the first-order reaction remains practically unchanged.[5–7] In the second stage it decreases continuously. To account for this reaction rate change, it has been modeled by two first-order reactions. There are two fundamental reasons for the drop in the cyclization rate constant of solid poly(amic acid)s: first, the change in amic acid group reactivity as a result of decreasing molecular mobility when the imide ring content increases and second, the existence of different kinetically nonequivalent states of amic acid groups and the statistical distribution of these groups over these states. In order to simulate the entire imidization process, two models for the solid-state cyclization of poly(amic acid)s were developed.[5] The first is the so-called "cage" model, which is based on the assumption that a spectrum distribution of kinetically nonequivalent states of amic acid groups exists. This model takes two stages into consideration: (1) the diffusion of the amic acid group from the initial state to the present state with a rate constant which depends on the state parameter and (2) the transition of the amic acid group from the present state to the imide state, with the rate constant taking an Arrhenius form. The second model, the so-called variable parameter model, includes a virtual transition state of the amic acid group that virtually changes the kinetics of the reactions to a second-order differential equation. By solving the second-order differential equation numerically, the cyclization kinetics under any temperature and time conditions can be obtained. Though both of these models are able to describe the dependence of kinetics on the imidization degree, it was obtained with the assumption of an arbitrary initial distribution of amic acid group states or by numerical solution. Later, we will propose a simple equation which requires neither an arbitrary state distribution nor a numerical solution.

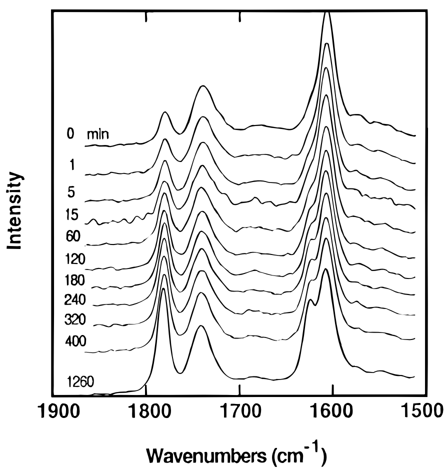


Figure 1. FT-Raman spectra, in the spectral region 1500–1900 cm^{-1} at 120 °C.

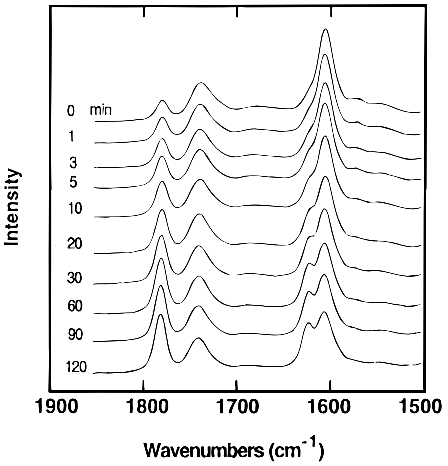


Figure 2. FT-Raman spectra, in the spectral region 1500–1900 cm^{-1} at 140 °C.

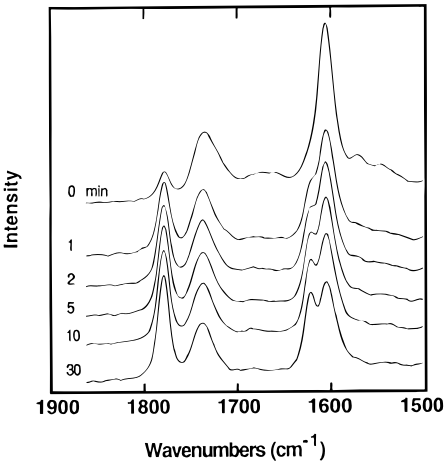


Figure 3. FT-Raman spectra, in the spectral region 1500–1900 cm^{-1} at 160 °C.

Results and Discussion

Figures 1–3 contain the FT-Raman spectra in the frequency region 1500–1900 cm^{-1}, representing the structural changes during imidization in the carbonyl stretching region at 120, 140, and 160 °C, respectively. The high-frequency peak at 1780 cm^{-1} is assigned to the stretching vibration of the carbonyl group. The peak at 1740 cm^{-1} is assigned to ester carbonyl stretching. The peak at 1600 cm^{-1} is from the benzene ring

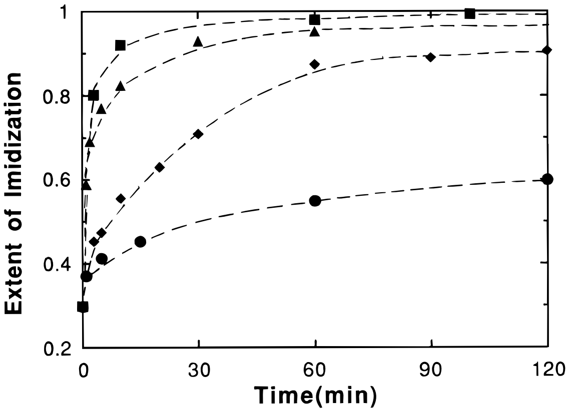


Figure 4. Extent of imidization as a function of time at various temperatures. Dotted lines are guides for the eyes. (●) 120 °C; (◆) 140 °C; (▲) 160 °C; (■) 180 °C.

vibration. The band at 1600 cm^{-1} evolves into two peaks, one at 1600 cm^{-1}, emerging from the original aromatic ring vibration, and the other at 1620 cm^{-1}, which is the imidized aromatic ring vibration. For the polyamic acid, this vibration is the strongest feature in the spectrum, whereas the imide band at 1780 cm^{-1} is more intense in the spectrum of polyimide than the band at 1620 cm^{-1}. The intensity of the ester peak at 1740 cm^{-1} remains constant during the course of the reaction. Thus, the 1740 cm^{-1} band is appropriate for use as the internal standard for obtaining the degree of conversion and comparing reaction rates. The anhydride characteristic band at 1850 cm^{-1} is not observable in all of our spectra. This means that anhydride was not produced significantly or was hardly detectable by FT-Raman spectroscopy. Hence, the band at 1780 cm^{-1} is not affected by interference from the anhydride peak. The reaction proceeds faster with higher temperature, as shown vividly in Figures 1−3.

In this study, we first compared the spectroscopic data with the first-order kinetics for two different reactions: the poly(amic acid) imidization to produce poly(amide imide) and the reaction of poly(amide imide) to polyimide. Thermal imidization was followed by a change in intensity of the 1780 cm^{-1} band in the spectrum, using the ester band at 1740 cm^{-1} as the internal standard. The conversion was calculated from eq 1

$$\alpha_t = \frac{(I_{1780}/I_{1740})_t}{(I_{1780}/I_{1740})_\infty} \quad (1)$$

where $(I_{1780}/I_{1740})_t$ represents the ratio of the height of the peak at 1780 cm^{-1} to that of the peak at 1740 cm^{-1} at time t. $(I_{1780}/I_{1740})_\infty$ is the ratio after complete imidization. We used the ratio from polyimide which has undergone high-temperature cyclization. The extent of imidization at various temperatures is shown in Figure 4. The imidization rate increases rapidly with temperature and is characterized by an initial rapid cyclization, which changes into a slower cyclization process. The data do not allow unequivocal determination of the order of the reaction. Data on the appearance of imide were subsequently fitted into the first-order rate expression:

$$\ln\left(\frac{1}{1-\alpha}\right) = kt + \text{constant} \quad (2)$$

A plot of $-\ln(1 - \alpha)$ as a function of time at various temperatures is given in Figure 5. Though arbitrary

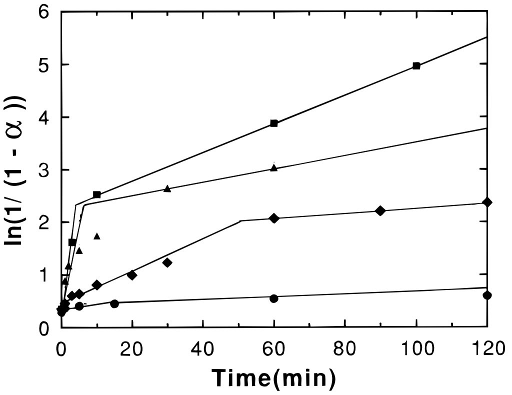


Figure 5. Two first-order step kinetics plots of ln(1/(1 − α)) as functions of time at various temperatures: (●)120 °C; (◆) 140 °C; (▲) 160 °C; (■) 180 °C.

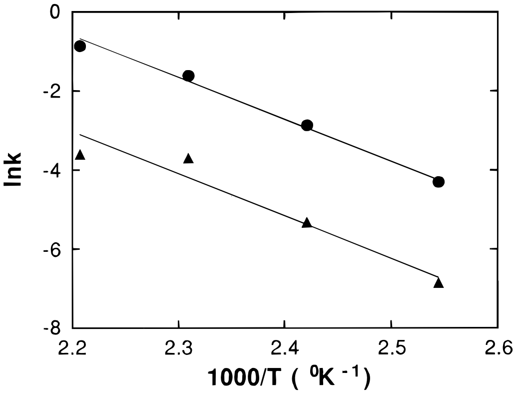


Figure 6. Arrhenius plot of ln k_1 (●) and ln k_2 (▲) versus $1/T$.

fittings were applied, it shows that the two-step process correlates well with the imidization process. Using the Arrhenius relationship, activation energy can be obtained from the plot of ln k versus $1/T$ (Figure 6). The activation energy for the first process was 20.5 kcal/mol, while the analogous energy for the second imide ring closure was about 19.9 kcal/mol. The difference was not significant. This is because of the independence of the two imide ring closures due to the nonconjugated structure of poly(amic acid). The pre-exponential factors were also similar to each other (3.8 × 10^9/min for the fast reaction and 1.2 × 10^9/min for the slow reaction), which again indicates that the two-step reactions proceed independently from each other.[14] This is clearly different from the reaction rate constant and pre-exponent values observed for the conjugated structure of polyimides. These small pre-exponential factor values, compared with the theoretical value of the order of 10^{14}/min, imply a large negative entropy of activation for the reaction.[19] The activation energy values are similar to those reported by Kreuz et al.[17] and Lauver.[19] The ratio of the slow and fast rate constants is about 0.1, indicating a much faster rate for the first process. A wide range of pre-exponential factors has also been reported for imidization, depending on the chemical structures and the state of the samples.[5−10]

Though there is no general consensus on why the rate of cyclization decreases, the following explanation of the imidization process has been proposed:[5,9] (1) There are two nonequivalent kinetic states. One state is activated for cyclization, while the other is not. The active groups rapidly cyclize during the first stage of imidization. The remaining ‘inactive groups’ are cyclized in the second stage. (2) The imidization process is enhanced by the presence of solvent. (3) The decrease in the rate of cyclization is due to the decrease in molecular mobility in the glassy state. Since solid film is imidized in this study, we reject the second explanation as not appropriate for our case. For solid imidization, the evidence for the first explanation can be traced from the preexponential factor and the activation energy. In our case, the activation energies for the fast and slow steps are almost the same. Thus the major factor differentiating the rates lies in the orientation or probability factor and not in the energy of activation. Different entropic states of polyamic acid exist, indicating that some poly(amic acid)s have a favorable conformation for the imide ring closure. In the early stage, the molecule has more freedom because the low glass transition temperature provides a better orientation of the amide group for the reaction. There is considerable evidence that the transition from the first stage to the slow stage is, to a large extent, due to a decrease in molecular mobility in the polymer backbone.[5] Thus when a poly(amic acid) is heated its T_g increases as its imide content increases. When the T_g reaches the temperature of the sample, the polymer is transformed from a rubbery to a glassy state, and segmental motion ceases. As a result, it is very difficult for the amic acid groups to attain suitable conformations for cyclization. Imidization proceeds in the glassy state, but at a much slower rate. The T_g of the poly(ester imide) used in this study was 222 °C.[11] In the beginning, molecular mobility was high and transitions between kinetically nonequivalent states took place easily. As the polymer passed from the rubbery to the glassy state, the transitions became more and more difficult and began to limit the process rate. The rate constant decreased dramatically and became dependent upon conversion. At this point, there was a distribution between the amic acid conformations that were kinetically favored and unfavored for cyclization. This distribution determined the further kinetics of the process.[5,7] On the basis of UV spectroscopy, Pyun et al.[7] proposed a catalytic effect of poly(amic acid) in solid films. The catalytic effect was dominant and overshadowed the electronic effect, thus leading to a very large value of the reaction rate. In order to take into account the decrease in the concentration of the catalytic amic acid group, Pyun et al. used kinetic equations of different orders, i.e., second order for the first step and first order for the second step. A rising glass transition temperature would reduce the mobility of the catalytic group, which could decrease the changes in the catalytic group so that it was in a favorable conformation. The kinetic equation for the second-order reaction was

$$\frac{\alpha}{1-\alpha} = kt + \text{constant} \tag{3}$$

Here, the activation energy and the pre-exponential factor for the second-order catalytic reaction are 24.6 kcal/mol and 1.09×10^{12}. The reaction rate is reduced by half. Though the catalytic effect shows a faster first reaction, its effect is not so dramatic as to change the order of the reaction rate ratio. This is different from Pyun et al.'s result. In our case, the activation energies of the first and second steps were almost the same for the first-order reaction, and the first was greater than the latter for the second-order reactions, while it was smaller than the latter in Pyun et al.'s experiment; and hence, the reaction rate ratio was very small. The principal difference in the rate expressions describing the two stages was a large negative entropy factor for the slower reaction.

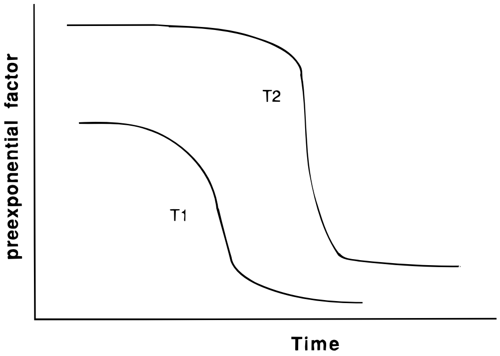


Figure 7. Schematic dependence of the pre-exponential factor on reaction time at different temperatures $T_1 < T_2$.

In the imidization process, it is generally accepted that the glass transition serves to change the rate-determining stages.[5,16,19,20] In the softened state, chain segment mobility is unrestrained, and the transitions between kinetically nonequivalent states are very rapid. The rate-determining stage is that of the chemical conversion of the amic acid group to imide rings. The rate of the process is high. Its parameters depend only slightly on the degree of conversion and are close to those for the reaction in solution. When the polymer is solidified, the transitions between kinetically nonequivalent states are hindered, and they begin to limit the process rate. Now the chemical reactivity is no longer of significant value. The rate of amic acid group transition from the unfavorable to favorable states becomes the main factor. The effective rate of the chemical reaction starts to be controlled by the distribution of amic acid group states.[5] From the physical reasoning, the pre-exponential factor is a decreasing function of time, initially a constant or very weakly dependent on the cyclization degree and later showing an exponential decaying function form with the cyclization degree (or time), as shown in Figure 7. We assume all the amic acid group states are combined into two: the favorable (activated) state and the unfavorable (inactive) state. If both the amide and acid groups in polyamic acid are in proper conformation for cyclization, then it will produce polyimide, but if not, they may return to the inactive state. Hence, part of the activated state will be deactivated, and by the same token, part of the deactivated state can be transformed into the active state. The state function can be expressed as $\exp(-at)$, where a is a rate constant. Then the deactivated state density will be of the order of $\exp(-2at)$ because the conversion requires deactivation of both the acid and amide groups at the same time with distribution densities of $\exp(-at)$, respectively. Considering that part of the excited state reverts to the previous conformation and then moves again to re-excitation, the reacting state density can be expressed as

$$a_0 e^{-at}(1 - e^{-2at}(1 - e^{-2at}(1 - e^{-2at}(...)))) = a_0 e^{-at}(1 - e^{-2at} + e^{-4at} - e^{-6at} + ...)$$

$$= a_0 \frac{e^{-at}}{1 + e^{-2at}} = \frac{a_0}{2} \frac{2}{e^{at} + e^{-at}} = \frac{a_0}{2} \operatorname{sech}(-at) \tag{4}$$

where a_0 is the initial distribution factor for reaction. Then the pre-exponential factor can be expressed as the following nonlinear function form:

$$f(t) = b\ \mathrm{sech}(-at) \qquad (5)$$

where a and b are constants. The $\mathrm{sech}(-at)$ function has a constant value initially and weakly depends on time; later it becomes an exponentially decreasing function of time. This function's nonlinear form can simulate the variation in the amic acid group state with time, represented by the sum of exponents, and each of them is used with its own weight.[21] Then the kinetic equation can be written as

$$-\frac{\mathrm{d}x}{\mathrm{d}t} = b\ \mathrm{sech}(-at)x \qquad (6)$$

where b is a constant. Integration gives

$$-\ln(1-\alpha) = -\frac{2b}{a}\tan^{-1} e^{-at} + \text{constant} \qquad (7)$$

The correlation with experimental data is shown in Figure 8. The good agreement shows the validity of this model, which describes the entire imidization process with just two parameters. After fitting this equation with the experimental data, we obtain the activation energy from a, 24.3 kcal/mol (Figure 9). Though it is close to that from the catalytic two-step imidization process, the current model does not correlate well with the second-order kinetic data. This is again ascribable to the difference in imidization processes between Pyun et al.'s and our poly(amic acid)s. The pre-exponential factor of this model is 1.11×10^{11}/min, which is higher than that of two-step models. The constant b/a rises with temperature, but very slowly compared to a, which means the reaction rate for the activation state rises with temperature more rapidly than the imidization reaction rate. Hence the activated state increases and the degree of imidization at the kinetic stop also increases, in accordance with the experiment and other models.[5] Though the current model is based on physical reasoning, this model has general features required for a correct description of the process, in the course of which the rate-determining stage changes.[21] In the initial stage, it can describe slow reaction rate variation (limited by the chemical conversion of poly(amic acid) into the imide rings), and in the later stages, it shows a rapidly decreasing reaction rate (limited by the diffusion rate of the amic acid group from the inactive to the activated state), shown in Figure 8. This model is similar to the variable parameter model in that there is only one inactive site, but the probability of amic acid group transition to the active state varies with the degree of imidization.[5] This model can also predict the effect of activation by rapid temperature increase.[21]

In this study, we used the 1740 cm^{-1} ester band as the internal standard. Degree of reaction was obtained from the data on the two-peak ratio, i.e., the 1780 cm^{-1} imide band to the 1740 cm^{-1} internal standard band. We can check the validity of this standardization. The Raman spectra in Figures 1−3 show the evolution of another band at 1620 cm^{-1}. As already mentioned, this band shows the aromatic ring (C=C bond) vibration from the imidized benzene ring. Hence the ratio of the band at 1620 cm^{-1} to that at 1600 cm^{-1} after deconvolution should match the imidization rate data. This is illustrated in Figure 10. The agreement is very good, indicating that the band at 1780 cm^{-1} can be used for imidization kinetics, at least for the poly(ester amic acid) used in this study. This also verifies that our data were not affected by anisotropy as suggested by Pryde,[16] who claimed that the average orientation of the imide group changed during the course of the cure; or, at least, we believe that anisotropy had no significant effect on the Raman spectrum.

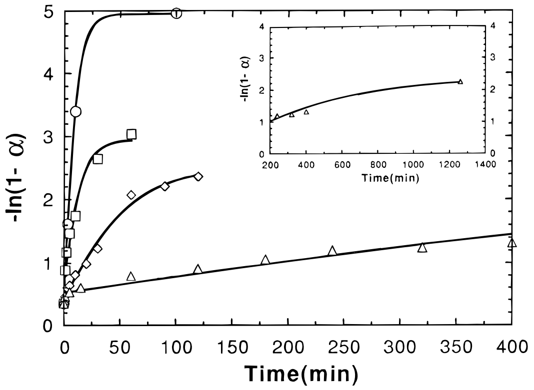


Figure 8. Kinetic plots of ln(1/(1 − α)) as functions of time at different temperatures: (△) 120 °C; (◇) 140 °C; (□) 160 °C; (○) 180 °C. Lines represent the new model calculations. Inset is ln(1/(1 − α)) after a long time at 120 °C.

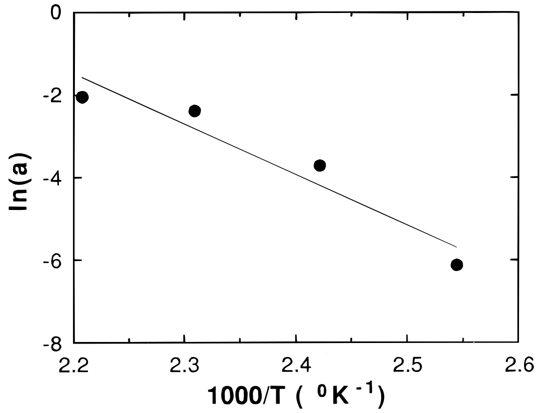


Figure 9. Arrhenius plot of the new model rate constant.

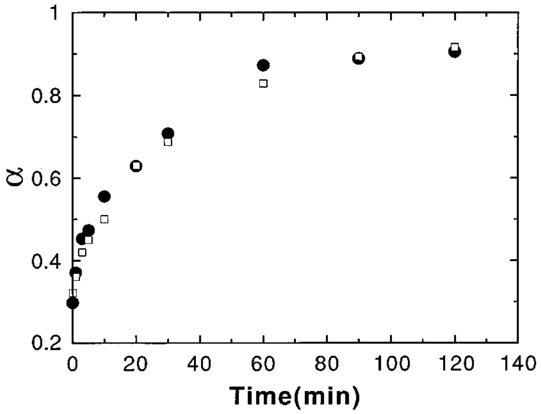


Figure 10. Extent of imidization at 140 °C obtained from (a) the imide band at 1780 cm^{-1} using the internal standard band at 1740 cm^{-1} (●) and (b) the relative band ratio at 1620 cm^{-1} versus that at 1600 cm^{-1} (□) (evolution of the benzene ring vibration with imidization).

Conclusion

We studied the kinetics of a poly(amic acid) when it is converted to polyimides by heat treatment at low temperatures. FT-Raman spectroscopy was used to obtain the reaction rate data. The FT-Raman spectrum has some advantages over IR, which has quite often been used for imidization kinetics. The band at 1780 cm^{-1} was used to extract kinetics information on the imidization reaction rate, which was compared to the internal standard peak at 1740 cm^{-1}. The validity of this standardization was confirmed by comparison of the standard peak ratio with that for the aromatic ring vibration bands of poly(amic acid) and the imidized one at 1620 cm^{-1} and 1600 cm^{-1}, respectively.

Cyclization is very slow for poly(amic acid) below 180 °C, which provides good experimental conditions for imidization kinetics. The imidization process is characterized by an initial rapid cyclization, which changes into a slow one in the late stages. This trend is attributed to the increase in the glass transition temperature and hence the reduced entropy of poly(amic acid) with imidization, as noted from the pre-exponential factor.[14] Activation energies for the first process and the second ring closure were almost equal (20.5 and 19.9 kcal/mol), and the reaction rate depended more significantly on the pre-exponential factor, which was the entropic effect.[17] Though the imidization process can be simulated by two fast and slow first-order reaction rates, the data did not allow an unequivocal determination of the order of reaction. The activation energy from the second-order kinetic equation was 24.6 kcal/mol, and the pre-exponential factor was 1.09×10^{12}. The second-order kinetic equation, taking into consideration the catalytic action by the amic acid group, showed a faster first reaction but did not show remarkable change.

In order to account for the peculiar feature of imidization kinetics, i.e., its very strong dependence on the physical state of the polymer, a simple nonlinear model equation was proposed on the basis of the assumption of kinetic nonequivalence of the amic acid groups. The model favorably describes the conformation development of the amic acid group with imidization. The activation energy obtained from the new model (24.3 kcal/mol) is close to that of the second-order model, but the current model does not correlate well with the second-order kinetics data in our case. Comparison of the pre-exponential factor reveals that the major factor differentiating the rates in this study lies in the orientation (conformation) probability factor and not in the energy of activation. This means that collisions between carbonyl and carboxyamide groups in the early stage are more effective in producing imide structures than those in later stages. In the later stages, poly(amic acid) conformations that are unfavored for cyclization are converted into kinetically-favored ones, but conversion probability decreases with the process because of the lower mobility of the amic acid group with imidization. The current model describes this behavior very well with just two parameters. Also, the current model describes the imidization process in the presence of solvent and that after reactivation, which is presented elsewhere.[21] The model will be useful for analyzing the imidization process without arbitrary fitting of the process with two first-order kinetic models.

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