Study on the Imidization Kinetics of Polyether-ester Polyamic Acid in Solid Phase by Microwave Radiation

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SYNOPSIS

The polyether-ester polyamic acid imidization process in a solid state was studied by microwave radiation. The imidization content at different radiation times was calculated quantitatively by FTIR and was confirmed by the results of dynamic mechanical analysis (DMA). The microwave radiation imidization may drop the reaction temperature and cut the reaction time down in comparison with the thermal imidization. It may be expected theoretically that the microwave radiation may generally be suitable for the condensation polymerization reaction and facilitates the reaction, especially at its later stage. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The polyamic acid imidization process is important in polyimide syntheses and practical applications. The process may often be carried out in a solution or solid.[1-4] The imidization is more complex in a solid than that in a solution. Therefore, studying the imidization in a solid state is of great significance.

The imidization process is substantially a dehydration reaction of the intramolecular type (ring-closure) and may be expressed as the following equilibrium:

Snyder et al.[5] approached the thermal imidization kinetic process of aromatic polyamic acid with different architectures via the use of FTIR, and Yu et al.[6] reported a polyether-ester/polyamic acid system with flexible segments. As mentioned above, the imidization reaction is a dehydration process. It is necessary to drive to completion the imidization at higher temperatures and for longer times since the hindrance of rigid bonds renders dehydration more difficult at the later stage of the thermal imidization. Microwave radiation may help to eliminate a trace of small molecules such as water in the condensation polymerization and thus shifts the equilibrium reactions to higher yield. Recently, Lewis et al.[7] and Kishanprosad and Gedam[8] dealt with the imidization process of polyamic acid using microwave radiation and found that the microwave radiation facilitates the imidization reaction in solution. Imai[9] developed a method for facile and rapid synthesis of polyamides and polyimides in the presence of appropriate solvents by microwave-assisted polycondensation.

In this article, the polyamic acid imidization process in a solid state was investigated by microwave radiation. The imidization content at different radiation times was calculated quantitatively by FTIR and was confirmed by the results of DMA tests.

EXPERIMENTAL

Materials

Poly(tetramethylene oxide)glycol di-p-aminobenzoate (APTMO) was a product of the Polaroid Co.; the trade name is POLYMINE-650. The average molecular weight of POLYMINE-650 was deter-

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mined to be 808. Benzenetetracarboxylic acid dia-hydride (PMDA) was a product of the Aldrich Co. The anhydride was distillated in a vacuum before use. Dimethylformamide (DMF) was stored for 2 days over molecular sieves (5 Å) and then was distillated in a vacuum.

Synthesis

The polycondensation reaction was carried out under a dry nitrogen atmosphere. Calculated PMDA was added to a solution of 15 wt % APTMO in DMF and was mixed. The mol ratio of APTMO to PMDA is 1 : 1.015. The mixture was reacted for 5–6 h at room temperature and then stored overnight. So, a viscous solution was obtained. The polymer was precipitated in methanol, filtered, and dried.

Preparation of Samples

The solutions of 10 wt % polyether-ester polyamic acid in DMF were filmed on salt and polytetrafluoroethylene dishes. DMF was devolatilized in a vacuum at room temperature for 48 h and the thickness of films ranged from 5 (salt plate) to 200 μm (thin film).

The salt plates and films of polyether-ester polyamic acid were imidized in a Sanle 450 W microwave oven at a temperature of 60 ± 3°C which was measured by a thermocouple applied to the film surface immediately after intervals of microwave oven turn off and then withdrawn at various time intervals.

Test Methods

Infrared survey spectra were recorded with a Nicolet Co 5DX Fourier transform infrared spectrophotometer. Dynamic mechanical properties were determined by a Rheovibron DDV-II-EA dynamic viscoelastometer. The samples were measured at a frequency of 110 Hz from −100 to 250°C at a heating rate of 2°C/min.

RESULTS AND DISCUSSION

Kinetic Study of the Imidization Reaction

Infrared spectroscopy has been utilized extensively in the kinetics of the thermal imidization of polyamic acids. The absorbance bands of IR at 1780, 1540, 1380, and 720 cm^{-1} are commonly used to monitor

the appearance of imide and the disappearance of amic acid.[5,6,10] The band at 725 cm^{-1} in the polyether-ester polyamic acid is most fit for appraisement of the imidization level. The band at 1780 cm^{-1} is too weak, and those at 1540 and 1380 cm^{-1} overlapped with other bands assigned to aliphatic hydrocarbon species. Absorbance of the 725 cm^{-1} band was measured and compared to an ether C — O — C stretching vibration at the 1115 cm^{-1} reference band to normalize for variations in film thickness.[6] A completely imidized sample was prepared at a cure temperature of 200°C for 3 h. This sample was further heated to 250°C and did not show any increase in the absorbance intensity. Therefore, the imidization was believed to be complete.

The conversion of each sample was calculated according to Beer's law. The FTIR spectra of polyether-ester polyamic acid are exhibited in Figure 1 under various imidization conditions. The imide content was plotted against different microwave radiation times for 60°C in Figure 2. First-order kinetic plots of the imidization reaction are shown in Figure 3. The kinetics curves were not fully linear. A linear region occurred below about 55%.

The first-order reaction rate constant, K was calculated to be 1.12×10^{-4} s^{-1}. The rate constant of the thermal imidization reaction, K, is 6.05×10^{-5} s^{-1} at a temperature of 115°C, from which the authors considered that the imidization can proceed
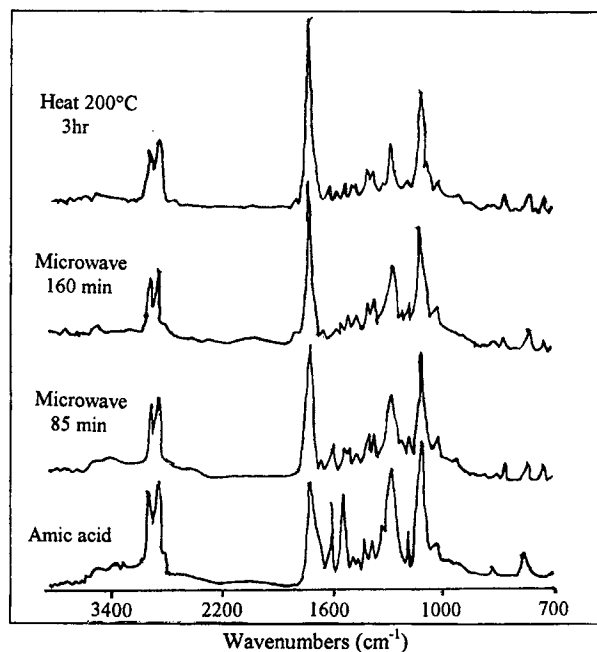
Figure 1 FTIR spectra of polyether-ester polyamic acid under various imidization conditions.
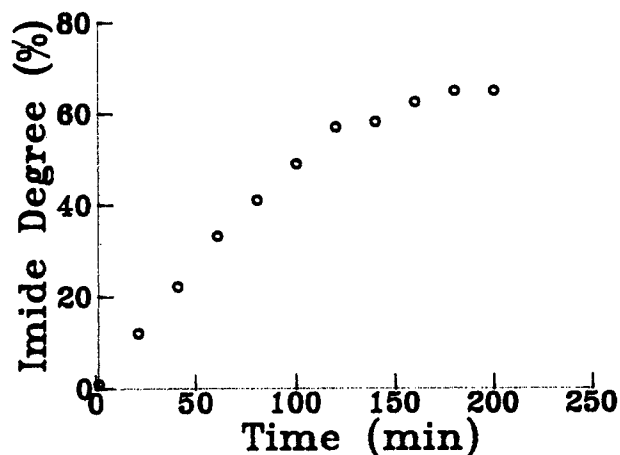
Figure 2 Plot of imide content vs. times of different microwave radiation at 60°C.

Figure 3 First-order kinetic plot of the imidization reaction for microwave radiation at 60°C.

in the solid state by microwave radiation or by heating because the introduction of polyether soft segments into the polyamic acid backbone increases its mobility, which makes the amic acid groups more reactive. Apparently, the microwave radiation imidization may reduce the reaction temperature and shorten the reaction time required for a given level of reactions. For example, 68.3% amic acids were converted to imide at 115°C in 12 h in the solid-phase thermal imidization, while 65.0% identical acids at 60°C were in 3 h in the solid-phase microwave radiation.

A comparison between these two experiments implies that microwave radiation is particularly effective in the imidization reaction. The imidization reaction is an equilibrium reaction of the intramolecular ring-closure type. Water molecules preferentially absorb the microwave radiation and, hence, are readily evaporated. As a result, the reaction proceeds to higher yields. There exists a question worthy of notice with amic acids filmed from DMF solvent: DMF may be fully removed from the films in a vacuum. At room temperature, however, it is difficult to remove them completely. So, it is not excluded that remnant DMF plays a role to some degree in the assistance of the imidization reaction.

The Dynamic Mechanical Properties

A variation of mechanical properties of polyamic acids (as measured by DMA) was observed at different times for microwave radiation. Figures 4 and 5 show, respectively, the tan δ vs. temperature curve at different times for the radiation and the storage modulus vs. temperature curve. As observed from
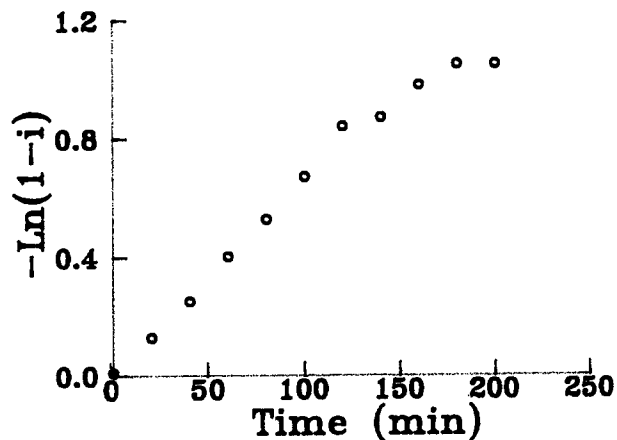
these figures, when the radiation time is zero, this sample appears to be a sample that has not undergone imidization. Its dynamic viscoelastic spectra display the behavior of a typical linear polymer. With an increase in radiation times, the degree of imidization increased and, therefore, the lower transition temperatures shifted to still lower-temperature regions, whereas higher transition temperatures shifted to still higher temperature regions. As a consequence, the storage modulus vs. temper-
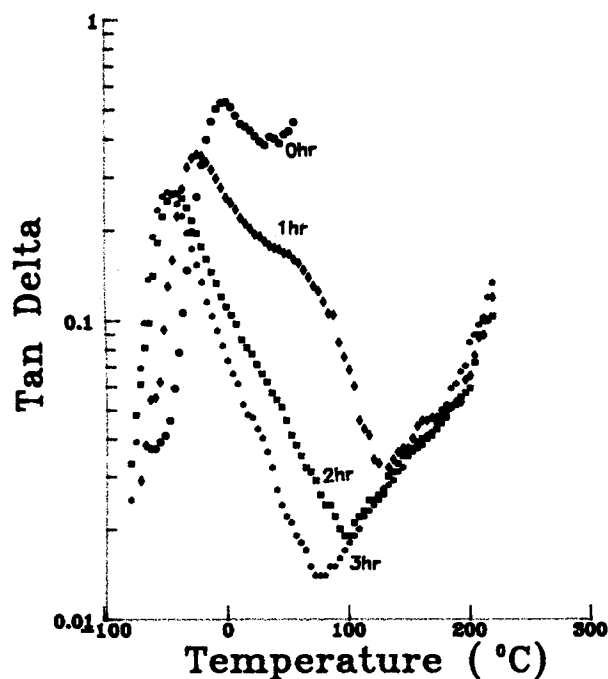

Figure 4 The tan δ vs. temperature curve at different times for the radiation.
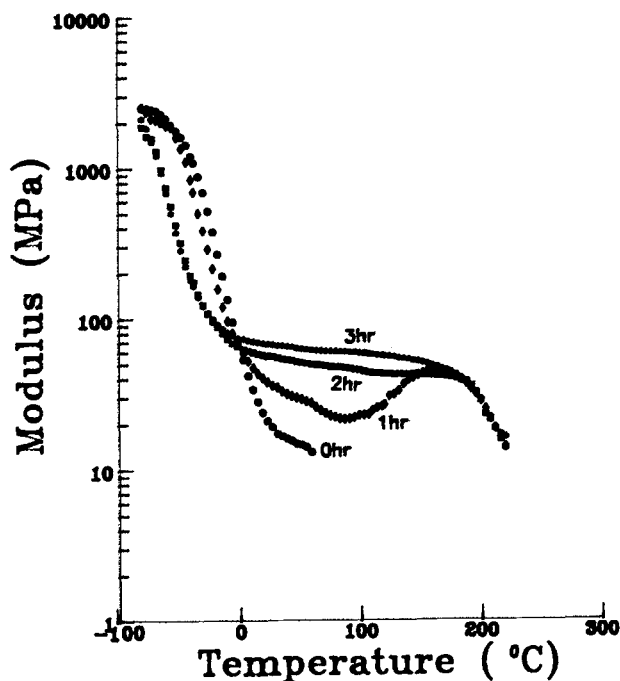
Figure 5 The storage modulus vs. temperature curve at different times for the radiation.

CONCLUSION

1. The microwave radiation imidization may lower the reaction temperature and cut down the reaction time.
2. It may be expected theoretically that microwave radiation may generally be suitable for the condensation polymerization reaction and facilitates the reaction especially at its later stage.

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ature curve shows a rubbery plateau. This indicates that the phase separation of the samples gradually increases with increasing degree of imidization. The modulus vs. temperature curves exhibits a peak around 150°C for the sample radiated for 1 h. The reason is that the thermal imidization reaction continues to proceed at about 150°C for the examined sample with a lower content of imidization. Results from the DMA are in accordance with ones from the IR.