Polymerization of Benzoguanamine and Pyromellitic Dianhydride under Microwave Radiation and Its Third-Order Optical Nonlinearities

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ABSTRACT: Polycondensation and imidization of benzoguanamine and pyromellitic dianhydride under microwave radation were studied. The effects of the microwave radiation time (power), the composition of the monomer on the imidization, and the polymer yield were discussed. The polycondensates' third-order optical nonlinearities and time responses were measured by a phase conjugate forward, 3-dimensional degenerate, four-wave mixing technique. At the same time they were compared with relevant conventional thermopolymerization. The results showed that the polycondensates had high third-order nonlinear optical coefficients [polyimide (PI) $\chi^{(3)} = 1.181 \times 10^{-13}$ esu] and fast time responses (22 ps). The third-order nonlinear optical coefficients under microwave radiation were higher than that of conventional thermopolymerization (microwave radiation PI $\chi^{(3)} = 1.181 \times 10^{-13}$ esu: thermopolymerization PI $\chi^{(3)} = 0.686 \times 10^{-13}$ esu). The experimental results also showed that the third-order optical nonlinearities were not only affected by the length of the polycondensate chain, but also the polycondensate π-electron density distribution, which was explained and confirmed by computation with the semiempirical Austin method. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 1356–1363, 2001

Key words: microwave; polycondensation; third-order optical nonlinearities; polyimide; imidization

INTRODUCTION

In recent years microwave radiation has been widely studied in the chemical field. In organic chemistry especially, the microwave has received considerable attention because of its excellent properties in organic compound synthesis.[1] However, it has been scarcely used in the reaction of polycondensation until recently. In this work we studied previously unreported polycondensation of benzoguanamine (BGA) and pyromellitic dianhydride (PMDA) in the solution by microwave radiation in a domestic microwave oven. First polyamic acid (PAA) was dehydrated by microwave radiation. At the same time the third-order optical non-
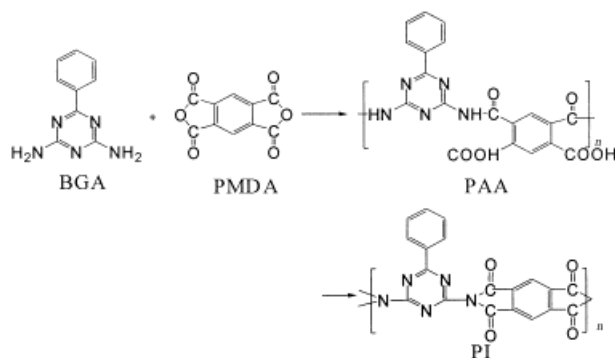
Scheme 1 The polymerization reaction.

linearities of the polycondensate were re-searched. It was shown that the microwave ra-diation procedure affected the optical nonlin-earities of the polymer. As a matter of fact, in this system the polycondensation by microwave radiation may provide a viewpoint for heating and unheating effects to which people pay close attention.

EXPERIMENTAL

Polymerization

The BGA (purity 98–99%, Shanghai Nanda Chemicals Factory) and PMDA (purity $\geqslant$ 98%, Shanghai Jiaohua Factory) were vacuum dried. In the solution polymerization the BGA was dis-solved in DMF under N_2 for about 10 min. After being completely dissolved, the PMDA was added in batches. PAA was precipitated by pouring it
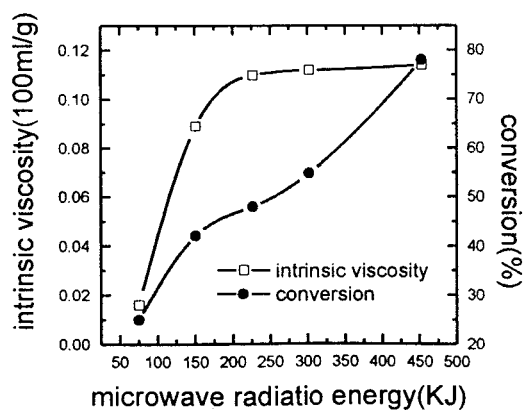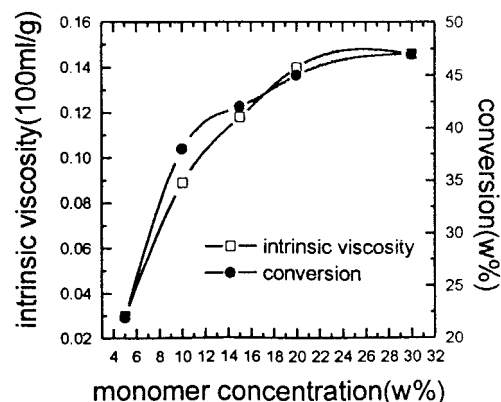

Figure 2 The relationships among the monomer con-centration, intrinsic viscosity, and conversion of the polymer.

into $CHCl_3$ and washing with THF. In the solid-phase polymerization under microwave radiation the PAA powders were placed in the reactor un-der N_2, and the PAA was dehydrated under con-tinuous microwave radiation. For solid-phase thermopolymerization the PAA powders were placed into the reactor under N_2, and the PAA was dehydrated at the same temperature as the maximal temperature of the solid-phase polymer-ization under microwave radiation.

Measurement

The intrinsic viscosity of the polymer was mea-sured by extrapolation in the DMF solvent at 30 $\pm$ 1°C.

Figure 1 The relationships among the intrinsic vis-cosity, the conversion of the polymer, and the micro-wave energy.
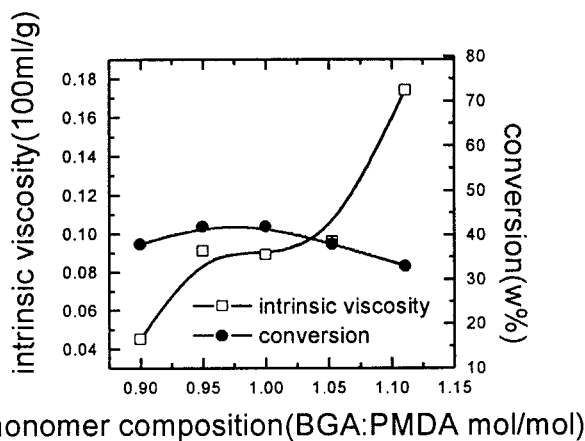

Figure 3 The relationships among the monomer com-position, intrinsic viscosity, and conversion of the poly-mer.
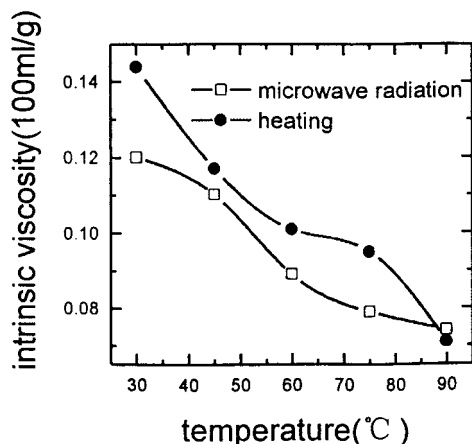
Figure 4 The relationship between the temperature and intrinsic viscosity of the polymer.

The imidization degree of the polyimide (PI) was measured by using the IR absorption spectrum that Hasegawa et al.[2] used. The stretch vibration of the C=O of the PI was expressed as the imidization degree by using the stretch vibration of C=C in the benzene ring as the reference.

The third-order optical nonlinearities of the polymer were measured by the phase conjugate forward, 3-dimensional (3-D) degenerate, four-wave mixing (3-D DFWM) technique (Department of Physics, East China Normal University).

RESULTS AND DISCUSSION

Synthesis of PI

The PI was synthesized by polycondensation of aroma dianhydride and aroma diamine or acyclic
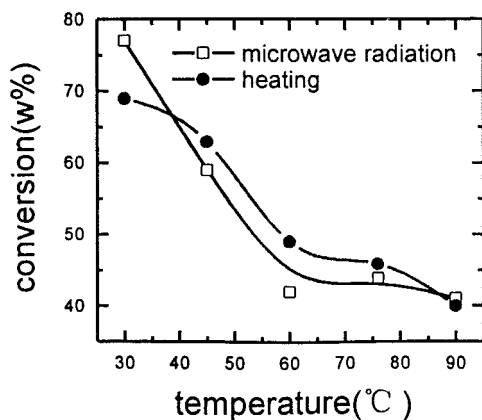

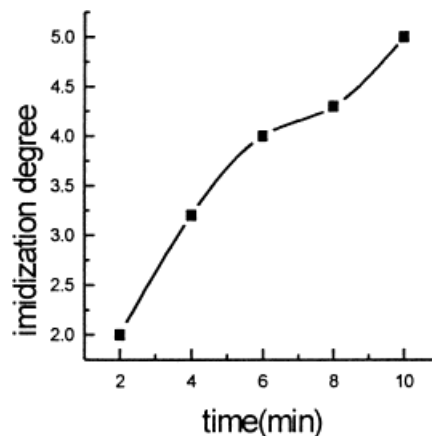**Figure 5** The relationship between the temperature and conversion of the polymer.

Figure 6 The relationship between the microwave radiation time and imidization degree of the polymer.

diamine in two-steps.[3] In this system the PAA was achieved by the polymerization of BGA and PMDA and then the PAA was dehydrated into PI. The procedure of polymerization is shown in Scheme 1.

Solution Polymerization under Microwave Radiation

The PAAs were synthesized by the polycondensation of BGA and PMDA under microwave radiation, and white powders were attained. The factors that affected the polymer follow.

Microwave Radiation Energy

The effect of microwave radiation energy on the intrinsic viscosity and the yield of the polymer are
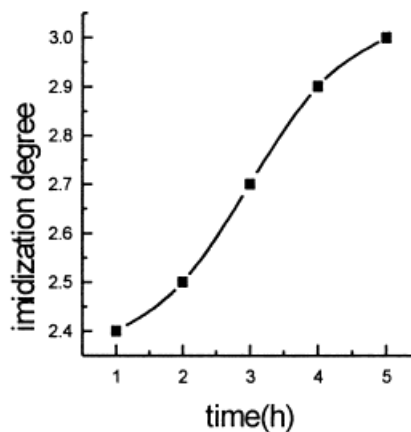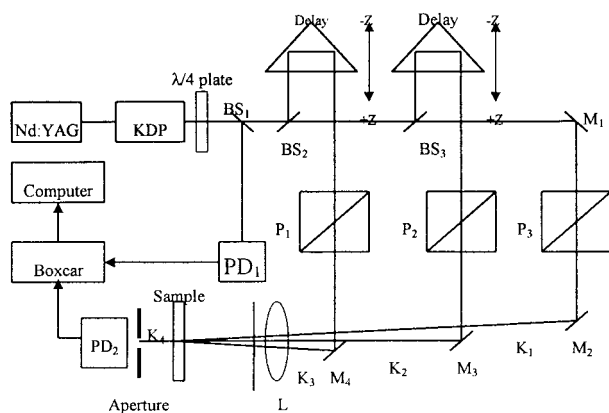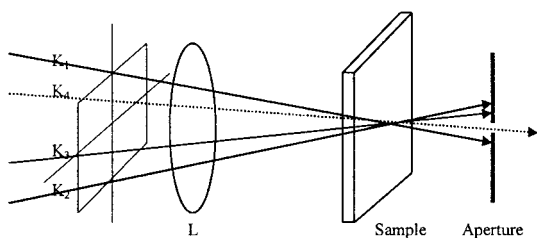

Figure 7 The relationship between the thermopolymerization time and imidization degree of the polymer.

(a) The experimental setup for three dimensional DFWM

(b) Configuration for three dimensional DFWM

Figure 8 The 3-D DFWM setup for measuring the third-order optical nonlinearities of the polymer.

shown in Figure 1. It is apparent from Figure 1 that the intrinsic viscosity and yield increased as the microwave radiation energy increased. This was because the increase of microwave energy increased the low polymer collision probability and therefore increased the polymerization probability and led to increased intrinsic viscosity and yield.

Monomer Concentration

Figure 2 exhibits the relationships among monomer concentration, intrinsic viscosity, and conversion of the polymer. The intrinsic viscosity and yield of the polymer increased as the monomer concentration increased. The increase of the monomer concentration increased the reactants' collision probability, increased the polycondensation probability, and led to increased intrinsic viscosity. When too large, the monomer would not be completely dissolved. It is apparent that the increase of monomer concentration can improve polycondensation in the monomer concentration range studied.

Monomer Composition

From Figure 3 it can be learned that the intrinsic viscosity of the polymer increased as the PMDA
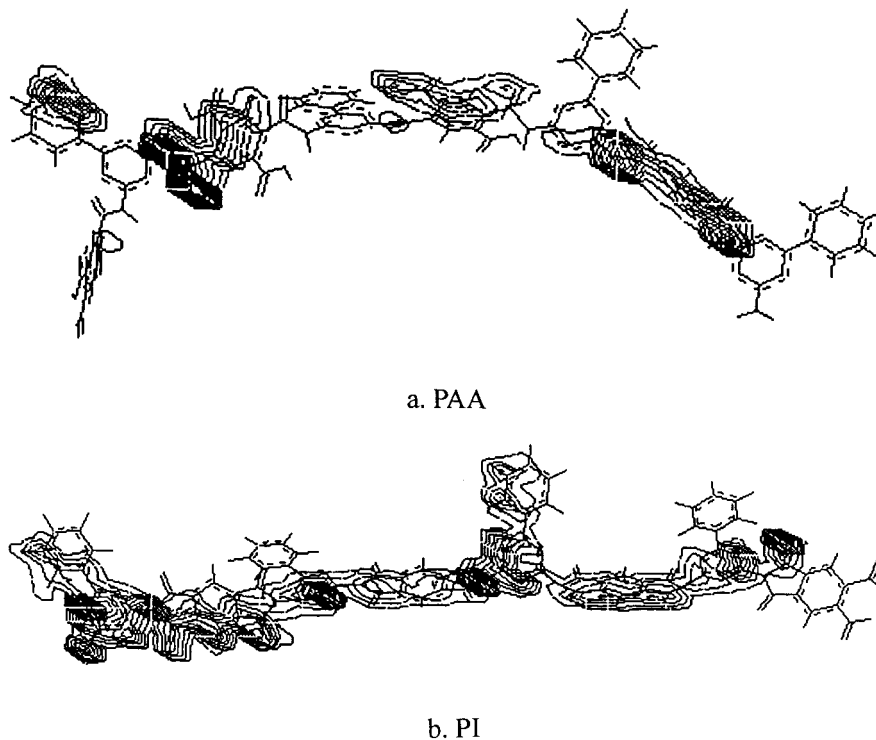

a. PAA

b. PI

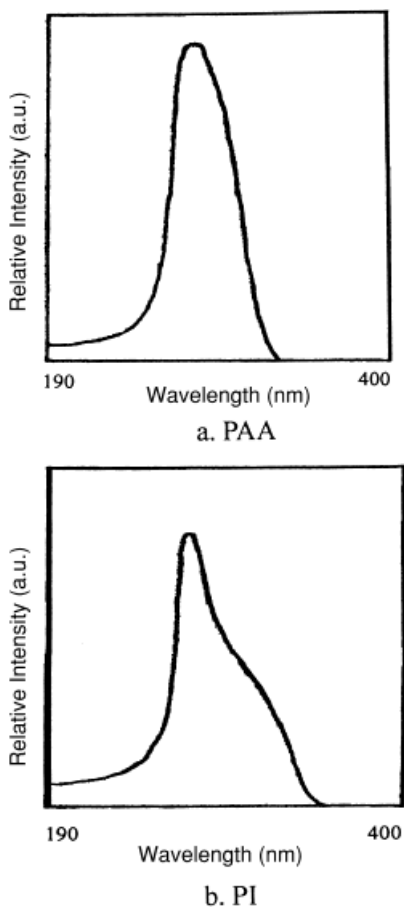**Figure 9** The charge density of the BGA-PMDA polycondensate.

Figure 10 The UV–visible absorption spectra of the BGA-PMDA polycondensate.

content of the mixture decreased. However, the yields of the polycondensation fluctuated only a little as the PMDA content of the mixture decreased. It may be that PMDA has lower activity, which would decrease the collision probability.

Comparison of Solution Polymerization by Microwave Radiation or Heating

Effect of the Intrinsic Viscosity and Conversion of Polymer

The effect of the microwave radiation and heating on the polymer intrinsic viscosity and conversion is shown in Figures 4 and 5. The conversion of the polymer results were the same as the intrinsic viscosity. This was because the increase of the reaction temperature resulted in the increase of the reversible reaction velocity. Thus, the intrinsic viscosity and conversion of the polymer decreased.

Effect of Microwave Radiation and Heating on Imidization Degree

From Figures 6 and 7 it is obvious that the imidization degree of the polymer increased as the microwave radiation time and heating time increased. However, the imidization of thermopolymerization was much slower than microwave polymerization, and the imidization degree of thermopolymerization was lower than microwave polymerization. The results showed that microwave radiation not only had fast heating velocity and complete imidization but also saved time and resources. This proved that microwave radiation solid-phase polymerization is much better than thermopolymerization.
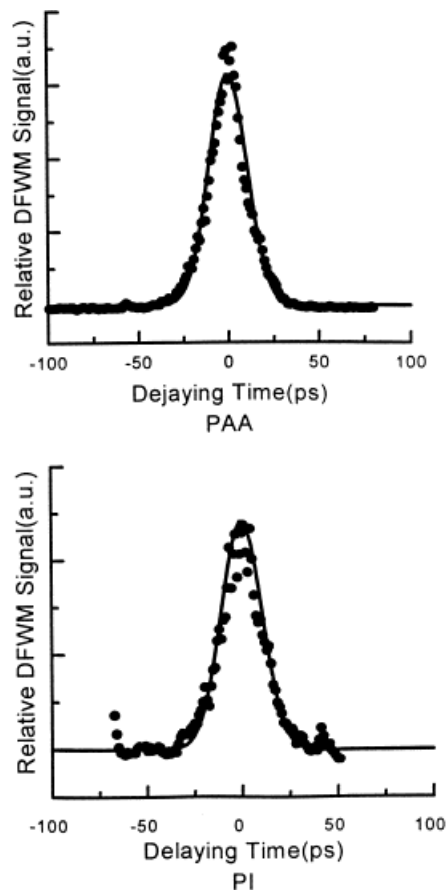

Figure 11 The DFWM time response spectra for the BGA-PMDA polycondensate.

Table I   Time Response for DFWM Signal of BGA-PMDA Polycondensate

Sample	Response Time (ps)
BGA-PMDA PAA	25
BGA-PMDA PI	25

Third-Order Optical Nonlinearities of BGA-PMDA Polymer

Setup for Measuring Third-Order Optical Nonlinearities of Polymer

The third-order optical nonlinearities of the BGA-PMDA polycondensate were measured by the 3-D DFWM technique[4,5] as depicted in Figure 8. After passing through a quarter wavelength plate, the pulse laser beam (532-nm wavelength, 15-ps pulse width, 10-Hz repetition rate, 10 GW/cm^2 peak irradiance) from a frequency-doubled picosecond pulse mode-locked Nd : yag laser was split into three beams (k_1, k_2 and k_3) with the same energy by using reflecting beam splitters and then temporally and spatially overlapping in the sample with a 205-mm focal-length lens. The angles between the k_1, k_2, and k_3 were about 1°. In the experiment the intensity (I_4) of the phase conjugate beam (k_4) was detected by a PIN photodiode. According to the following formula, the third-order nonlinear optical coefficients ($\chi^{(3)}$) can be measured by comparing the measured signals for the solution with that for carbon disulfide as a reference under the same experimental conditions[6]:

$$\chi^{(3)} = \left(\frac{I_{\text{sample}}}{I_{\text{reference}}}\right)^{1/2} \frac{L_{\text{reference}}}{L_{\text{sample}}} \left(\frac{n_{\text{sample}}}{n_{\text{reference}}}\right) \chi^{(3)}_{\text{reference}}$$

where I is the intensity of the signal peak, L is the thickness of the sample, n is the refractive index, r refers to carbon disulfide, and the tensor elements $\chi^{(3)}_{xxxx} = 6.8 \times 10^{-13}$ esu and $\chi^{(3)}_{yxxy} = 7.6 \times 10^{-14}$ esu for carbon disulfide. The tensor elements of the third-order optical nonlinearities for the BGA-PMDA polycondensate were calculated.

Mechanism of Third-Order Optical Nonlinearities

In this study the mechanism of the third-order optical nonlinearities of the polycondensate were found with the semiempirical Austin method 1
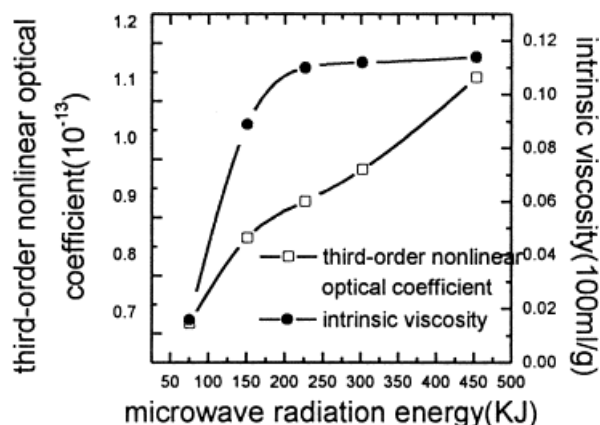

Figure 12   The relationships among the third-order nonlinear optical coefficient of PAA, the radiation energy, and the intrinsic viscosity.

(AM1), the UV–visible absorption spectrum, and the time response spectrum for the DFWM signal.

Charge Density. In order to study the p-π-conjugated structure of the BGA-PMDA polycondensate, the charge densities were calculated by computation with the semiempirical AM1. The results are shown in Figure 9.

The results showed that the polycondensate was the p-π-conjugated system.

UV–Visible Absorption Spectrum. The UV–visible absorption spectra of the BGA-PMDA polycondensate are shown in Figure 10. The absorption bands in the 253–320 nm region of PAA and 255–334 nm of PI were due to π–π* transitions of the highly polyconjugated systems, which we indicative of the distribution range in the p-π-conjugated systems. The laser wavelength (532 nm) used in the experiment was out of the absorption region.

Time Response Spectrum for DFWM Signal. The BGA-PMDA polycondensate with a large quasi-

Table II   Calculated Energy Gap (E_g) for Conjugated Lengths of Polymer by AM1 Semiempirical Method

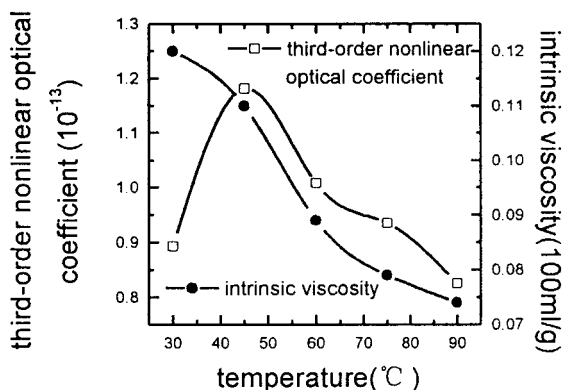| Sample | E_g (eV) | | | |
	$n = 1$	$n = 2$	$n = 3$	$n = 4$
BGA-PMDA PAA	7.403	7.139	6.835	6.811
BGA-PMDA PI	7.157	7.132	7.100	7.040

Figure 13 The relationships among the third-order nonlinear optical coefficient of PI, the temperature, and the intrinsic viscosity (two steps: solution polymerization by microwave, and solid polymerization by microwave).

1-D p-π-conjugated structure contained a high density of π electrons that were attributed to third-order nonlinearities. A delay for any one of the three input beams gave almost the same signal envelope. The time-resolved measurement results of the 3-D DFWM are shown in Figure 11. The envelope of the signal was fitted very well by a Gaussian function, and the half-width of the fitting envelope (about 12 ps) was similar to the autocorrelated pulse duration. The signal profile showed the symmetry about the maximum signal (the zero time delay), which indicated that the response time (Table I) of the third-order optical nonlinearity was shorter than the experimental time resolution (<12 ps). It also meant that the
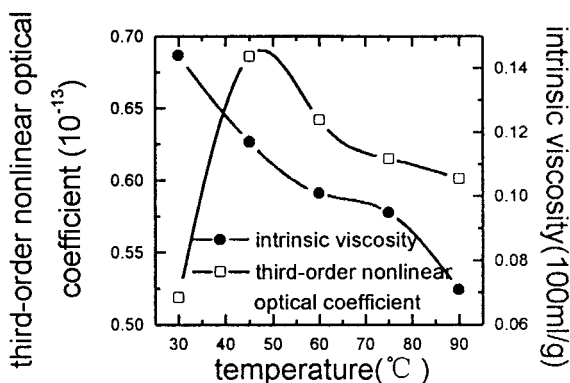

Figure 15 The relationship between the third-order nonlinear optical coefficient of PI and the temperature.

time response of the third-order optical nonlinearity was quite fast and the Kerr effect, which arose from the distortion of the large p-π-conjugate electronic charge distribution of the BGA-PMDA polycondensate, was the main reason for generating the DFWM.

Effect Factors of Third-Order Optical Nonlinearities of Polymer

Effect of Conjugated Chain Length

The relationship between the third-order optical nonlinearities and the intrinsic viscosity of the polymer are shown in Figure 12 (varying the microwave radiation energy). It is clear that the third-order nonlinear optical coefficient $\chi^{(3)}$ in-

Figure 14 The relationships among the third-order nonlinear optical coefficient of PI, the temperature, and the intrinsic viscosity (two steps: solution thermopolymerization and solid polymerization by microwave).
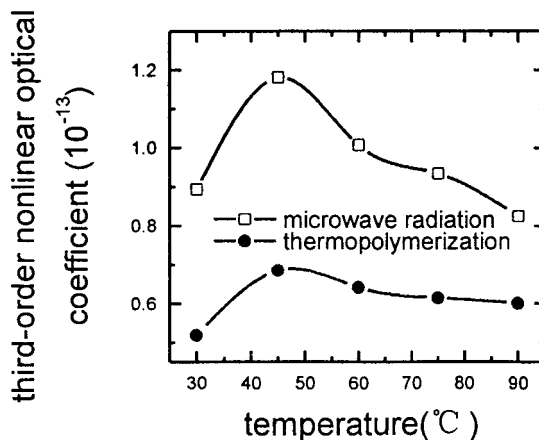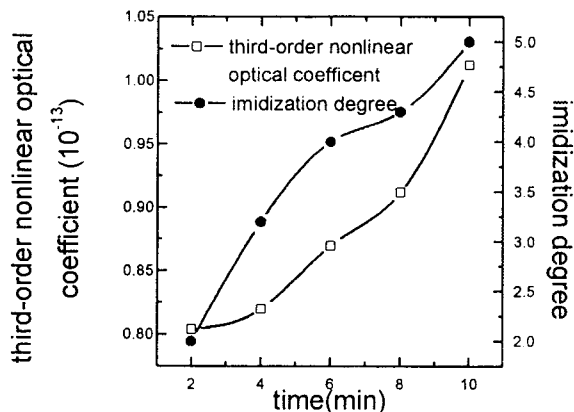

Figure 16 The relationships among the third-order nonlinear optical coefficient of PI, the heating time, and imidization degree for PI made in the solid phase by microwave.

creased as the intrinsic viscosity of polymer (the conjugated length L) increased in the experimental range. Because the nonlinear polarization was relative to the molecular energy level of excitation, especially the inverse proportion to the energy gap between the lowest unoccupied and highest occupied molecular orbitals.[4,7]

The energy gap (E_g) values for the various conjugated lengths of the polymer were calculated by AM1 (see Table II). The E_g decreased as the conjugated length of the polymer chain increased, and the variation also decreased as the conjugated length of the polymer chain increased. This was because the increase of the conjugated degree resulted in the decrease of the E_g. As a result, the conjugated electrons generated the transition quickly and the distortion of the conjugated electrons was easy. The results showed that the third-order optical nonlinearities of the conjugated polymer increased as the length of the p-π-conjugated structure increased, and there was less and less variation.

Effect of Microwave Radiation and Heating on Solution Polymerization

It is obvious in Figures 13–15 that the third-order nonlinear optical coefficients $\chi^{(3)}$ of PI, which were synthesized by microwave radiation or heating, increased as the intrinsic viscosity increased, but the $\chi^{(3)}$ appeared to downtrend when the intrinsic viscosity continued to go up. The $\chi^{(3)}$ of PI synthesized by microwave radiation was larger than by heating.
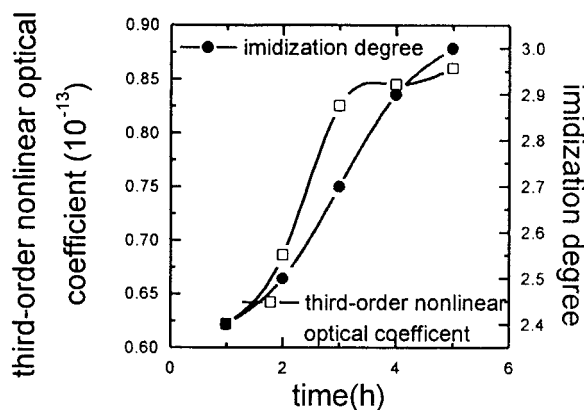

Figure 17 The relationships among the third-order nonlinear optical coefficient of PI, the heating time, and imidization degree for PI made in the solid phase by heating.
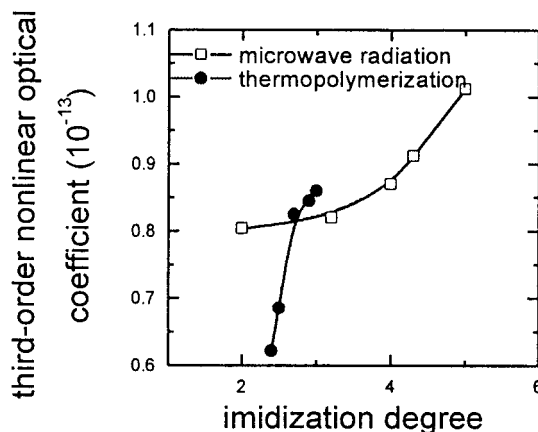

Figure 18 A comparison of the third-order nonlinear optical coefficient of PI synthesized in the solid phase by microwave radiation or heating.

It may be that the distribution of the molecular weight of the polymer synthesized by microwave radiation was not only narrow, but the molecular structure was also relatively regular.

Effect of Microwave Radiation and Heating on Solid-Phase Polymerization

Figures 16–18 show that the $\chi^{(3)}$ of PI, which was synthesized in the solid phase by microwave radiation or by heating, increased as the imidization degree increased. The $\chi^{(3)}$ of PI, which was synthesized in the solid phase by heating, was smaller than by microwave radiation. We showed that microwave radiation could improve the third-order optical nonlinearities of the polymer and took on the unheating effect.

REFERENCES

1. Zhang, I.; Ding, J.; Gu, H. Synth Chem 1996, 4, 23.
2. Hasegawa, M.; Arai, H.; Mita, I.; Yokota, R. Polym J 1990, 22, 875.
3. Tianbai, H.; Hanjie, H. Advancement of Overseas Polymer Science; Chim. Indu. Press: 1997; p 19.
4. Maloney, C.; Byrne, H.; Dennis, W. M.; Blau, W. Chem Phys 1988, 121, 21.
5. Yang, L. N.; Dorsinville, R.; Wang, Q. Z.; Zou, W. K.; Ho, P. P.; Yang, N. L.; Alfano, R. R. J Opt Soc Am B 1989, 6, 753.
6. Boyd, R. W. Nonlinear Optics; Academic: San Diego, CA, 1992; p 159.
7. Cojan, C.; Agrawal, G. P.; Flytzanis, C. Phys Rev B 1978, 17, 776.