

# Third-Order Nonlinear Optical Properties of Polyureas and Polyimide Synthesized by Microwave Irradiation

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**ABSTRACT:** Polymerization of benzoguanamine (BGA) and 2,4-tolylenediisocyanate (TDI), BGA-TDI polycondensation polyurea (PU), and pyromellitic dianhydride (PMDA) in solid phase under microwave radiation was studied. In the system of TDI and BGA, the effect of microwave radiation time, the composition and concentration of monomer, the temperature, and the concentration of catalyst on the third-order optical nonlinearities of polymer were discussed. In the system of PU and PMDA, the effect of imidization degree on third-order optical nonlinearities was also discussed. The results showed that the prepared polymer had high third-order nonlinear optical coefficients (PU:

$\chi^{(3)} = 1.174 \times 10^{-13}$  esu) and fast time responses (24 ps); simultaneously, the third-order optical nonlinearities of polymer were improved greatly by microwave radiation. The results also showed that third-order optical nonlinearities were affected not only by the length of the polycondensate chain but also by the molecular structure, which was explained and confirmed by the computation of the AM1 semiempirical method and UV-visible absorption spectrum. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2611–2617, 2003

**Key words:** microwave; polymerization; third-order optical nonlinearities; polyureas; polyimide

## INTRODUCTION

In recent years, there has been growing interest in applying microwave energy to synthetic organic chemistry and synthetic polymer chemistry as well. Since the appearance of the first study on the use of microwave energy in chemical synthesis, the approach has now developed into a useful technique for a variety of applications in organic synthesis, especially the solventless reactions conducted on solid supports.<sup>1</sup> In the field of synthetic polymer chemistry, microwave energy has been used for the radical polymerization of vinyl monomers such as 2-hydroxy ethyl methacrylate,<sup>2</sup> methyl methacrylate,<sup>3</sup> and styrene,<sup>4</sup> and for the curing of polymers such as epoxy resins<sup>5–11</sup> and polyurethanes,<sup>12,13</sup> as well as for the imidization of polyamic acids.<sup>14,15</sup>

In most cases, the high heat efficiency gave rise to remarkable rate enhancements and dramatic reductions of reaction times. Recently, the rapid synthesis of aromatic polyamides by microwave-assisted direct

polycondensation of aromatic diamines and aromatic dicarboxylic acids with condensing agents,<sup>16,17</sup> and a preliminary study on the microwave-assisted rapid synthesis of polyamides from nylon salts have been intensively investigated by Imai et al.<sup>18,19</sup> During the course of our studies, we have already reported the microwave irradiation solid-state copolymerization in the binary maleic anhydride and dibenzyl maleate system<sup>20</sup> and the copolymerization of maleic anhydride and allyl thiourea in the solid state.<sup>21</sup> In polycondensation, field microwave irradiation has been widely applied.<sup>22–26</sup> Given that polyimides are important as photochemical materials in third-order optical nonlinearities, we have tried to provide useful products by using the method of microwave irradiation.

Herein, we report that the polymerization of benzoguanamine (BGA) and 2,4-tolylenediisocyanate (TDI), BGA-TDI polycondensation polyurea (PU), and pyromellitic dianhydride (PMDA) under microwave irradiation. Moreover, the third-order optical nonlinearities are also discussed.

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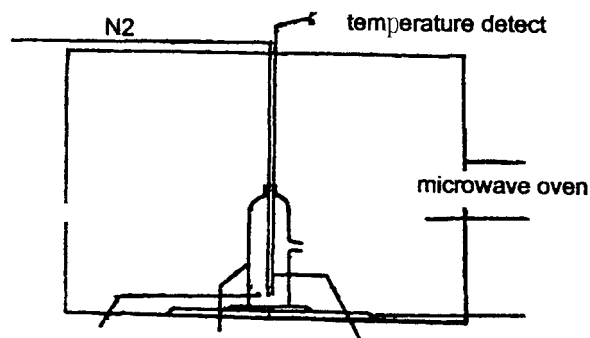
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## EXPERIMENTAL

### Setup

The experimental setup is schematically presented in Scheme 1 and Scheme 2.

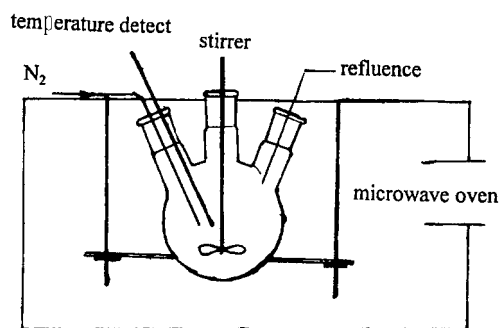


**Scheme 1** Setup of solid-phase polymerization under microwave irradiation.

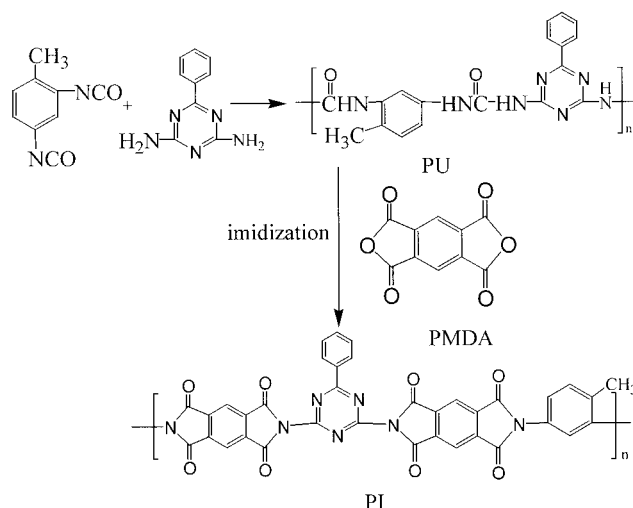
### Procedure of polymerization

The following products were used in this study: TDI-80 (Suzhou Zhao Qi Factory, China); BGA, purity 98–99% (Shanghai Nanda Chemicals Factory, China); and PMDA, purity  $\geq 98\%$  (Shanghai Jiaohua Factory, China), vacuum dried.

1. Solution polymerization (polymerization of BGA and TDI-80): BGA was dissolved in dimethylformamide (DMF) under nitrogen flow in 10 min. After being completely dissolved, TDI and the catalyst triethylenediamine were added. Polycondensation polyureas were precipitated by pouring methanol into the mixture and were then washed by THF.
2. Solid-phase polymerization under microwave radiation [polymerization of BGA–TDI polycondensation PU and imidization of PMDA]: BGA–TDI polycondensation polymer and the PMDA mixture were set into the reactor under  $N_2$ , and reacted under continuous microwave radiation. Temperatures were measured by an alcohol thermometer set into the polymerization system.
3. Solid-phase thermopolymerization [polymerization of BGA–TDI polycondensation PU and imi-



**Scheme 2** Setup of solution polymerization under microwave irradiation. (Note: Reaction temperatures are measured by alcohol thermometer.)



**Scheme 3** The procedure of polymerization.

dization of PMDA]: BGA–TDI polycondensation PU and the PMDA mixture were set into the reactor under  $N_2$ , and reacted at a temperature identical to the maximal temperature of solid-phase polymerization under microwave radiation.

### Measurement

The intrinsic viscosity of the polymer was measured by extrapolation in the solvent DMF at  $30 \pm 1^\circ\text{C}$ .

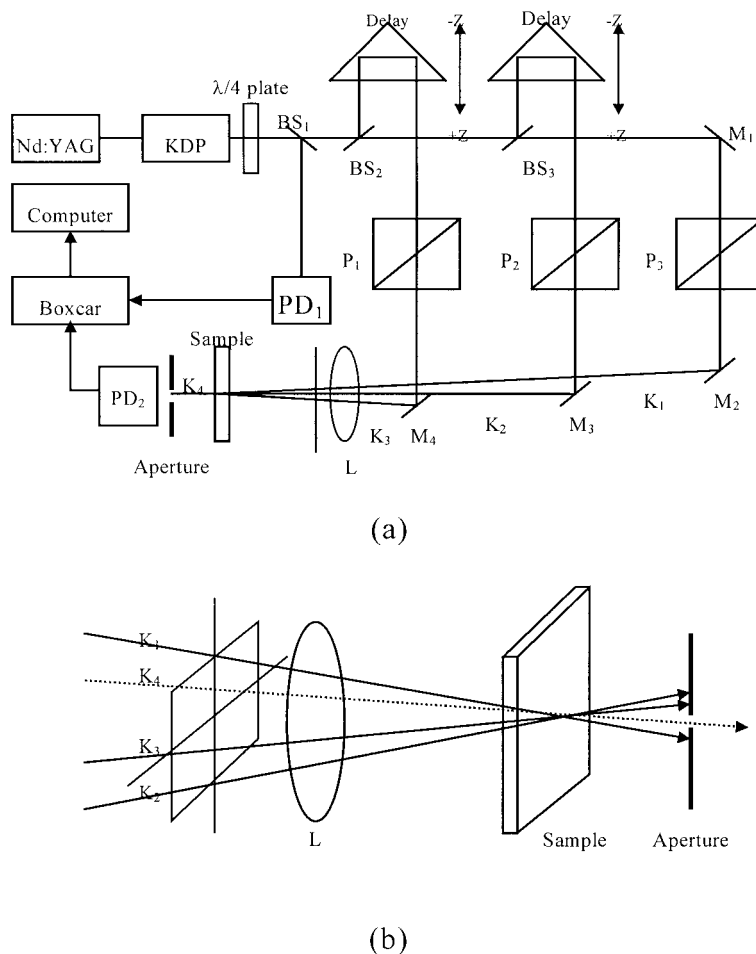
The degree of imidization of PI was measured by using the same infrared absorption spectrum used by Hasegawa.<sup>2</sup> The stretch vibration of  $\text{C}=\text{O}$  of polyimide was expressed as the degree of imidization by using the stretch vibration of  $\text{C}=\text{C}$  in the benzene ring as reference.

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

## RESULTS AND DISCUSSION

### Synthesis of polymer

This polymer was synthesized in two steps: (1) polycondensation of TDI and BGA to produce PU polymer; (2) imidization of PU polymer and PMDA to produce PI polymer. In this polymerization, microwave irradiation and regular heating methods were used. The polymerization procedure is shown in Scheme 3.



**Figure 1** The three-dimensional DFWM setup for measuring the third-order optical nonlinearities of the polymer: (a) experimental setup; (b) configuration.

**Third-order optical nonlinearities of BGA-TDI-PMDA polymer**

Setup for measuring the third-order optical nonlinearities of polymer

The third-order optical nonlinearities of the BGA-TDI-PMDA polycondensate were measured by the phase-conjugated forward 3-D DFWM technique,<sup>27,28</sup> as depicted in Figure 1. After passing through a quarter-wavelength plate, the pulse laser beam (wavelength 532 nm, pulse-width 15 ps, repetition rate 10 Hz, peak irradiance 10 GW/cm<sup>2</sup>), from a frequency-doubled picosecond pulse mode-locked Nd : YAG laser, was split into three beams, *k*<sub>1</sub>, *k*<sub>2</sub>, and *k*<sub>3</sub>, with the same energy by use of reflecting-beam splitters, which temporally and spatially overlapped in the sample with a 205-mm focal-length lens. The angles between the three beams *k*<sub>1</sub>, *k*<sub>2</sub>, and *k*<sub>3</sub> were about 1°. In the experiment, the intensity *I*<sub>4</sub> of the phase-conjugated beam *k*<sub>4</sub> was detected by PIN photodiode.

According to the following formula, the third-order nonlinear optical coefficients  $\chi^{(3)}$  can be measured by

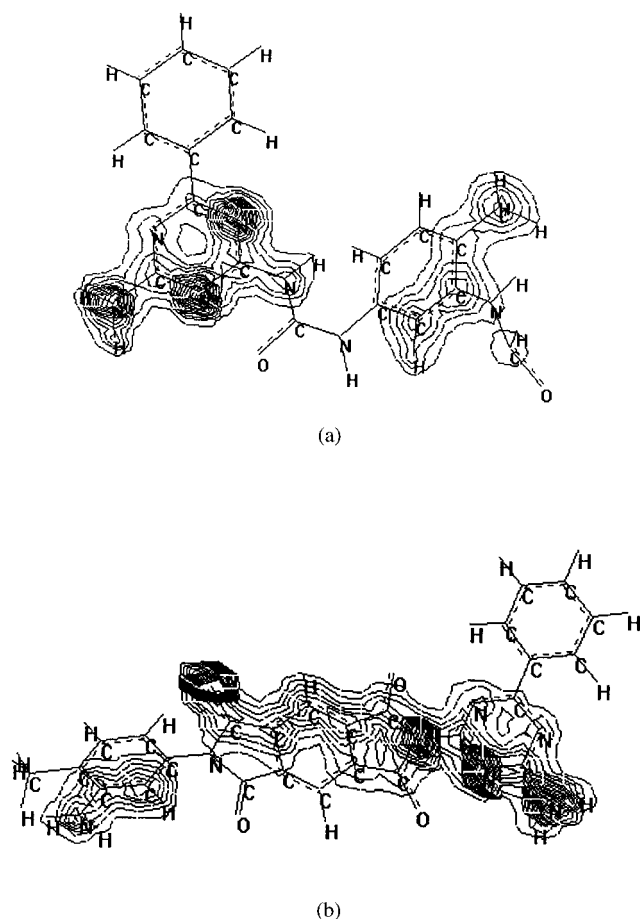
comparing the measured signals for solution with that for carbon disulfide as a reference under the same experimental conditions<sup>29</sup>:

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

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

**Mechanism of the third-order optical nonlinearities**

In this study, the mechanism of the third-order optical nonlinearities of polymer were confirmed by the AM1 (= Austin mode one) semiempirical method, UV-vis-



**Figure 2** Charge densities calculated by use of the AM1 semiempirical method: (a) PU; (b) PI.

ible absorption spectrum, and the time-response spectrum for the DFWM signal.

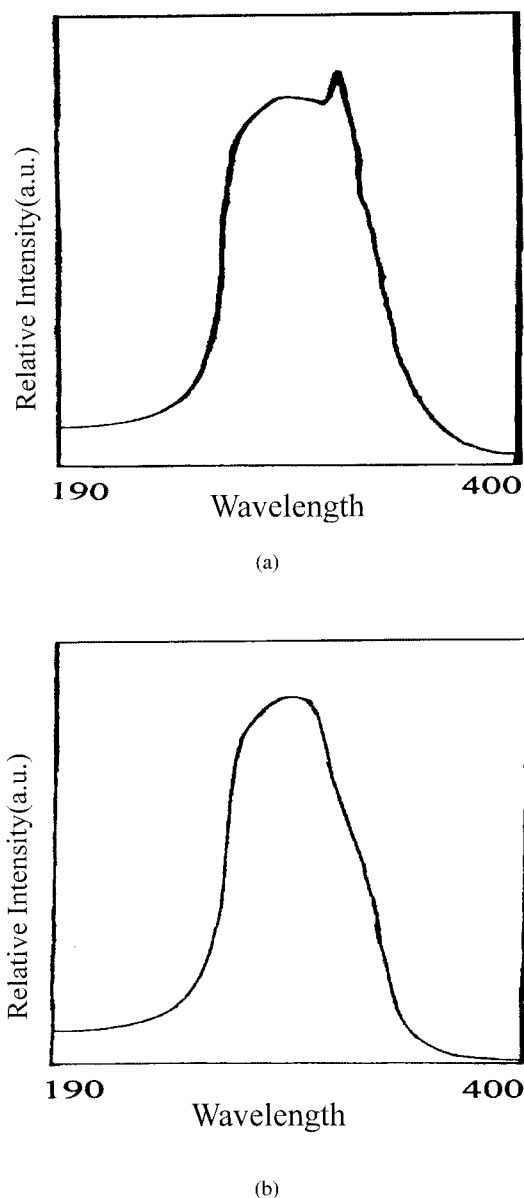
1. *The charge density.* To study the  $p$ - $\pi$ -conjugated structure of BGA-TDI PU and PU-PMDA polyimide, the charge densities were calculated by the computation of the AM1 semiempirical method. The results are shown in Figure 2.

The result showed that the PU and PI polymers constituted the  $p$ - $\pi$ -conjugated systems.

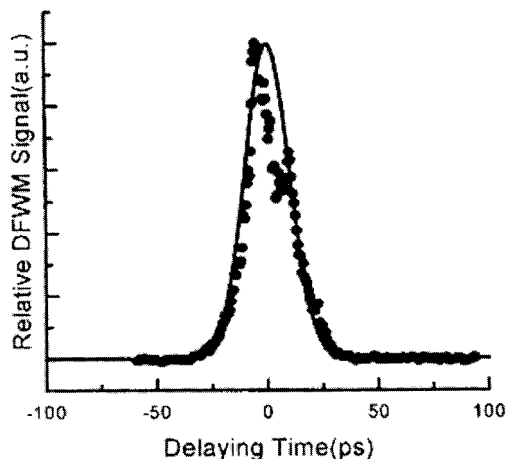
2. *The UV-visible absorption spectrum.* The UV-visible absorption spectra of two polymers are shown in Figure 3, where the absorption bands in the region of 240–355 nm of PU and 246–357 nm of PI are attributed to the  $\pi$ - $\pi^*$  transitions of the highly polyconjugated systems, indicative of the distribution range in the  $p$ - $\pi$ -conjugated systems, and the laser wavelength (532 nm) used in the experiment was out of the absorption region.

3. *The time-response spectrum for the DFWM signal.* BGA-TDI-PMDA polymer, with a large quasi one-dimensional  $p$ - $\pi$ -conjugated structure, contains a high density of  $\pi$ -electrons that are attributed to third-order nonlinearities. A delay for any one of the three input

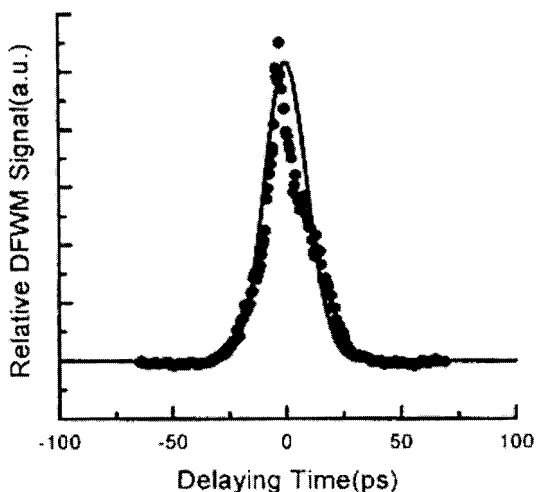
beams gives almost the same signal envelope. The time-resolved measurement results of 3-D DFWM are shown in Figure 4. The envelope of the signal is fitted extremely well by a Gaussian function, and the half-width of the fitting envelope (about 25 ps) is similar to the autocorrelated pulse duration. The signal profile shows the symmetry about the maximum signal (the zero time delay), which indicates that the response time (in Table I) of the third-order optical nonlinearity is shorter than the experimental time resolution ( $<25$  ps). It means that the time response of the third-order optical nonlinearity is quite fast, and the Kerr effect, which arises from the distortion of the large  $p$ - $\pi$ -conjugated electronic charge distribution of the polymer, is the main reason for generating DFWM.<sup>27</sup>



**Figure 3** UV-visible absorption spectra of BGA-TDI PU and PU-PMDA PI: (a) PU; (b) PI.



(a)



(b)

Figure 4 DFWM time-response spectra for BGA-TDI-PMDA polymer: (a) PU; (b) PI.

**The effect factors of the third-order optical nonlinearities of polymer**

Effect of the conjugated chain length

The relationship between the third-order optical nonlinearities and the intrinsic viscosity of polymer is shown in Figure 5 (varying the microwave radiation energy) and Figure 6 (varying the monomer composition). It can be learned that the third-order nonlinear

**TABLE I**  
Time Response for the DFWM Signal of the BGA-TDI-PMDA Polymer

Sample	Response time (ps)
BGA-TDI PU	24
BGA-TDI-PMDA PI	22

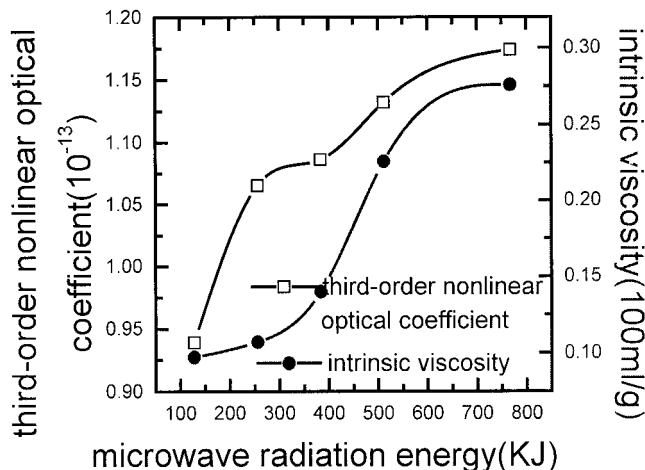


Figure 5 Relationship among third-order nonlinear optical coefficient of PU, microwave energy, and intrinsic viscosity.

optical coefficient  $\chi^{(3)}$  increases as the intrinsic viscosity of the polymer (the conjugated length  $L$ ) increases in this experimental range. It is known that when the wavelength of the Strong-Resonance field is the region of materials' absorption, the nonlinear Kerr effect of resonant strengthening will be produced. On this condition, the molecules are approximately regarded as two energy-level systems.<sup>32</sup> The nonlinear polarization is relative to the molecular energy level of excitation, inversely proportional to the energy gap between the lowest unoccupied molecular orbital and the highest occupied molecular orbital.<sup>28,31</sup>

The energy gap ( $E_g$ ) values for the various degree of polymerization conjugated lengths of polymer (PU) were calculated by the AM1 semiempirical method (see Table II). The  $E_g$  decreased as the conjugated length of the polymer chain increased. It may be that the increase of the conjugated degree led to a decrease

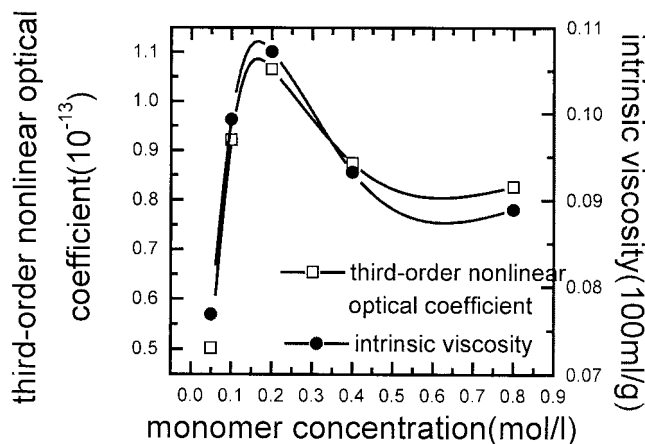


Figure 6 Relationship among third-order nonlinear optical coefficient of PU, monomer concentration, and intrinsic viscosity.

**TABLE II**  
Calculated Energy Gap  $E_g$  for Various Conjugated Lengths of Polymer by AM1 Semiempirical Method

Sample	$E_g$ (eV)		
	$n = 1$	$n = 2$	$n = 3$
BGA-TDI PU	6.692	6.316	6.215

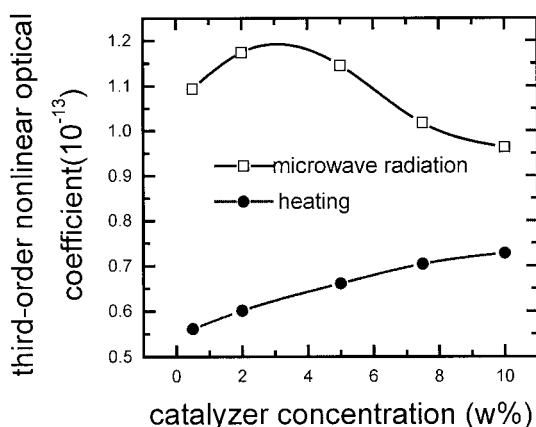
in the  $E_g$  value. As a result, the conjugated electrons quickly generated the transition and the distortion of conjugated electrons could easily have occurred. The results show that the third-order optical nonlinearities of conjugated polymer increase as the length of the  $p$ - $\pi$ -conjugated structure increases.

Effect of microwave radiation and heating on solution polymerization (polycondensation of TDI and BGA)

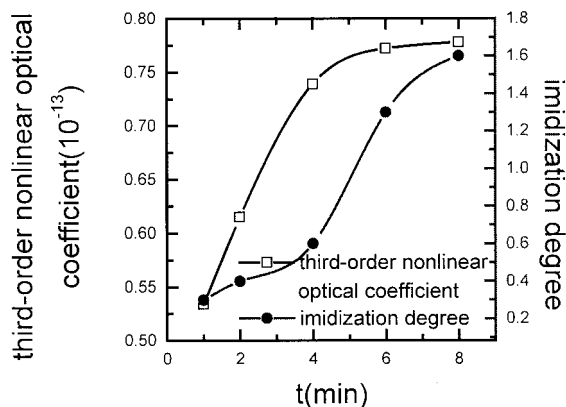
It may be learned from Figure 7 that the third-order nonlinear optical coefficient  $\chi^{(3)}$  of PU, synthesized by microwave radiation, increases as the catalyst concentration increases, after which it decrease as the catalyst concentration continues to increase. However, the  $\chi^{(3)}$  of PU, synthesized by thermopolymerization, increases as the catalyst concentration increases. The  $\chi^{(3)}$  value of PU, synthesized by microwave radiation, is much greater than that synthesized by heating. It showed that microwave radiation could improve the third-order optical nonlinearities of polymer, and acquired the nonheating effect, which may have had a particularly efficient action.

Effect of microwave radiation and heating on solid-phase polymerization (imidization of PU and PMDA)

From Figures 8 and 9, it may be seen that  $\chi^{(3)}$  increased with an increase in the degree of imidization. It may be that the degree of molecular orientation increased concomitantly with the degree of imidization, which



**Figure 7** Comparison of third-order nonlinear optical coefficient of PU synthesized in solution by microwave radiation or by heating.

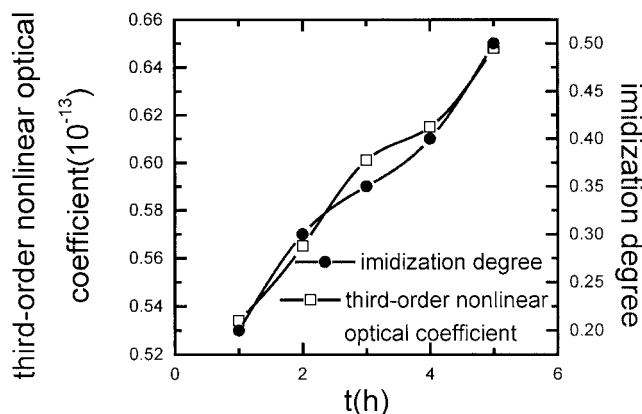


**Figure 8** Relationship among third-order nonlinear optical coefficient of PI synthesized in the solid phase under microwave, the time, and degree of imidization.

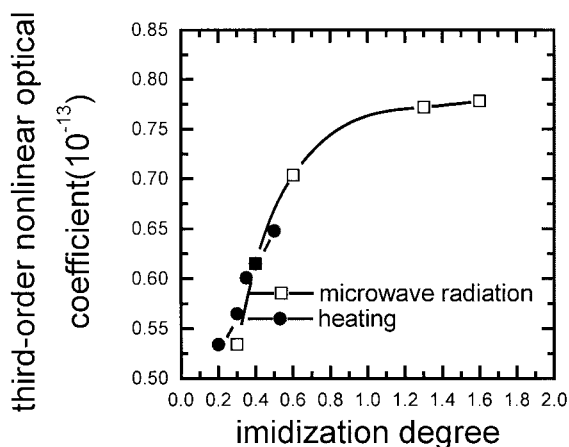
caused  $\chi^{(3)}$  to increase. A comparison of Figures 8 and 9 shows that the degree of imidization (1) under microwave irradiation reached a maximum value in 8 min and (2) by heating reached a maximum value in 5 h, respectively. Thus, microwave irradiation can greatly decrease the reaction time. From Figure 10, it is obvious that the degree of imidization and  $\chi^{(3)}$  under microwave irradiation are higher than that by heating; further, it shows that microwave radiation can improve the degree of imidization and the third-order optical nonlinearities of polymer, and acquired the nonheating effect, which may have had a particularly efficient action.

## CONCLUSIONS

We observed a significantly fast time response of third-order optical nonlinearity from a  $p$ - $\pi$ -conjugated polymer. The value of  $\chi^{(3)}$  is relatively high [in general,  $\chi^{(3)}$  may be  $10^{-11}$ - $10^{-14}$ ], which is quite satisfactory. The merit was that microwave irradiation



**Figure 9** Relationship among third-order nonlinear optical coefficient of PI synthesized in the solid phase by heating, the time, and degree of imidization.



**Figure 10** Comparison of third-order nonlinear optical coefficient of PI synthesized in the solid phase by microwave radiation or by heating.

was a new method by which to synthesize polymers that can decrease the polymerization time and improve polymer properties.

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