Novel Synthesis of Polyimides of the Third-Order Optical Nonlinearities by Microwave Assistance

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ABSTRACT: The third-order optical nonlinearities and time responses of three new polymeric materials, which were prepared by polymerization of benzoguanamine (BGA) and pyromellitic dianhydride (PMDA), *m,m'*-diaminobenzophenone (*m,m'*-DABP) and PMDA, BGA, and 2,4-tolylenediisocyanate (TDI) under microwave radiation, were measured by a picosecond forward three-dimensional degenerate four-wave mixing technique. The experimental results showed that nonresonant optical nonlinearity [$\chi^{(3)}$] of the three polymers is larger by microwave than by heating and that third-order optical nonlinearities were not only affected by the length of polymer chain, but also by the polymer chain structure. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 87: 1739–1747, 2003

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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 article 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.[1] In the field of synthetic polymer chemistry, microwave energy has been utilized for radical polymerization of vinyl monomers such as 2-hydroxyethyl methacrylate,[2] methyl methacrylate,[3] and styrene[4] and for the curing of polymers such as epoxy resins[5–11] and polyurethanes[12,13] as well as for the imidization of polyamic acids.[14,15] In most cases, the high heat efficiency gave rise to remarkable rate enhancements and a dramatic reduction 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[16,17] and a preliminary study on microwave-assisted rapid synthesis of polyamides from nylon salts have been intensively investigated by Imai et al.[18,19] During the course of our studies, we have already reported on microwave-irradiation solid-state copolymerization in a binary maleic anhydride and dibenzyl maleate system[20] and copolymerization of maleic anhydride and ally thiourea in the solid state.[21] In the polycondensation field, microwave irradiation was widely applied,[22–26] since polyimides are important as photochemical materials in third-order optical nonlinearities. So, we tried to afford useful products by using a method of microwave irradiation. Herein, we report on the polymerization of benzoguanamine (BGA) and pyromellitic dianhydride (PMDA), *m,m'*-diaminobenzophenone (*m,m'*-DABP) and PMDA, and BGA and 2,4-tolylenediisocyanate (TDI) under microwave irradiation. Moreover, third-order optical nonlinearities are discussed.

EXPERIMENTAL

Materials

BGA was purchased from the Shanghai Nanda Chemicals Factory (China) and dried under a vacuum. PMDA was purchased from the Shanghai Jiaohua Factory (China) and dried under a vacuum at 100°C overnight. *m,m'*-DABP was synthesized according to the literature[27] and the purity was 98.5%. TDI-80 was provided by the Suzhou ZhaoQi Factory, (China).

Procedure of polymerization

The polymers were synthesized following the procedures below:
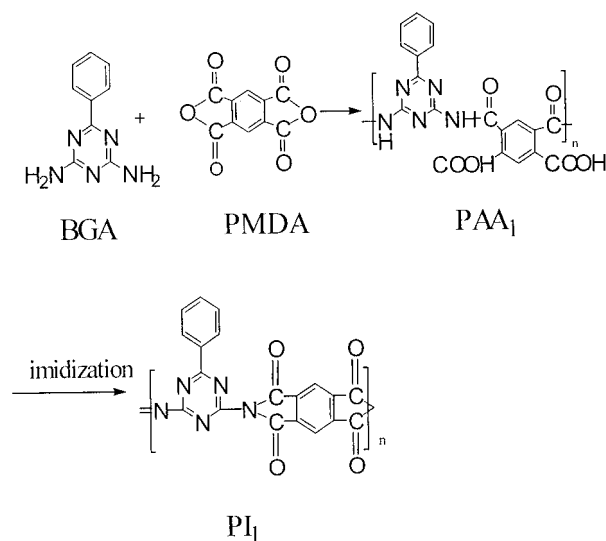
Scheme 1

Scheme 2

1. Solution polymerization [synthesis of PAA or polyurethane (PU)]: One of the monomers was dissolved in the solvents (Schemes 1 and 3: tetrahydrofuran; Scheme 2: methanol) and flowing nitrogen for 10 min. After being completely dissolved, another was added in batches. Polymers were produced and precipitated by pouring them into a relevant precipitator (Scheme 1: CHCl$_3$; Scheme 2: H$_2$O; Scheme 3: CH$_3$OH), then washed by methanol and tetrahydrofuran (Schemes 1 and 3: tetrahydrofuran; Scheme 2: methanol).
2. Solid-phase polymerization under microwave radiation [synthesis of polyimide (PI) imidization]:
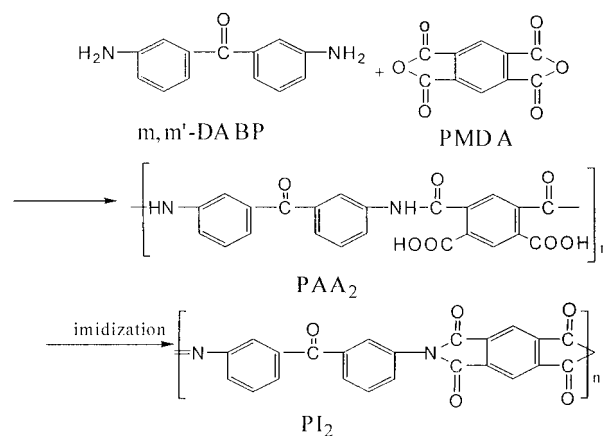
Reactant powders were set into the reactor under N$_2$ and dehydrated under continuous microwave radiation. Temperatures were measured by setting an alcohol thermometer into the polymerization system.
3. Solid-phase thermopolymerization (synthesis of PI imidization): Reactant powders were set into the reactor under N$_2$ and dehydrated at the same temperature as the temperature of solid-phase polymerization under microwave radiation.
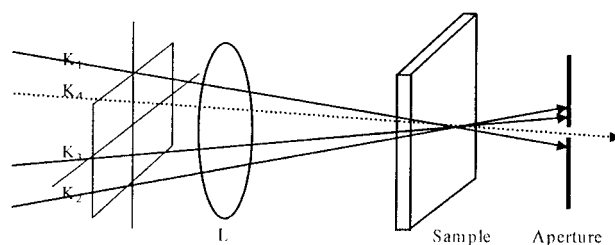
Measurement

The intrinsic viscosity of the polymer was measured by extrapolation in the solvent: DMF at 30 ± 1°C. The imidization degree of PI was measured using the same infrared absorption spectrum as Hasegawa et al.[28] had
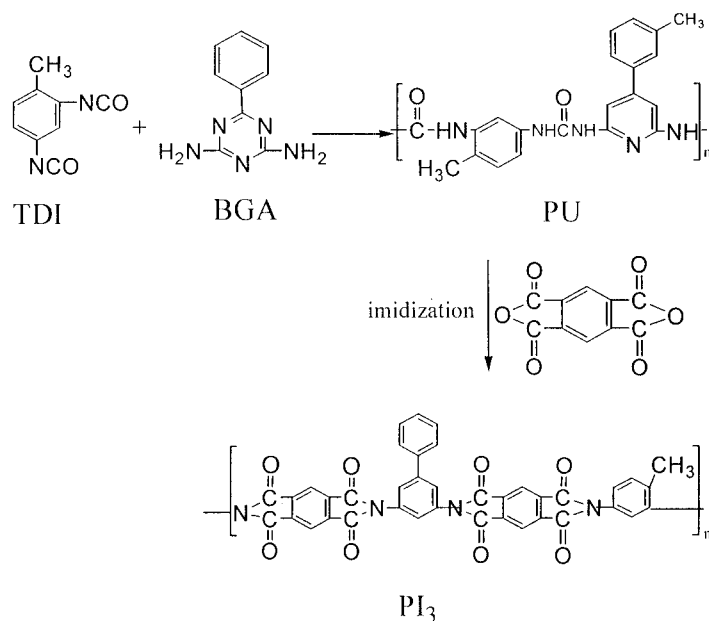
Scheme 3
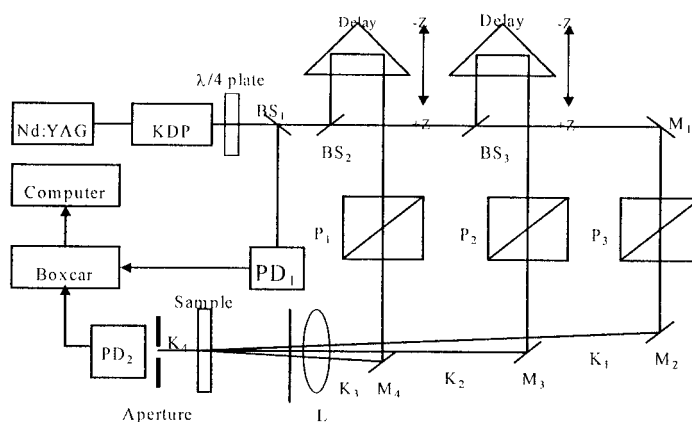
(a) The experimental setup for three dimensional DFWM


(b) Configuration for three dimensional DFWM

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

**Figure 1** 3D DFWM setup for measuring third-order optical nonlinearities of the polymer.

used. The stretch vibration of the C=O of PI was expressed as the imidization degree, using the stretch vibration of C=C in benzene ring as the reference.

The third-order optical nonlinearities of the polymer were measured by a picosecond forward three-dimensional degenerate four-wave mixing (3D DFWM) technique (done at the Department of Physics, East China Normal University). The third-order optical nonlinearities of the polymer were measured by a phase conjugate forward 3D DFWM[29,30] as depicted in Figure 1. After passing through a quarter wavelength plate, the pulse laser beam (wavelength, 532 nm; pulse width, 25 ps; repetition rate, 10 Hz; peak irradiance, 10 GW/cm²), from a frequency-doubled picosecond pulse mode-locked Nd:YAG laser, is split into three beams, k_1, k_2, and k_3, with the same energy using reflecting beam splitters,

then temporally and spatially overlapped in the sample with a 205-mm focal-length lens. The angles between the three beams, k_1, k_2, and k_3, are about 1°. In the experiment, the intensity I_4 of the phase conjugate beam k_4 is detected by the PIN photodiode. According to the equation in Figure 1, the third-order nonlinear optical coefficients $\chi^{(3)}$ can be measured by comparing the measured signals for the polymer solution with carbon disulfide as a reference under the same experimental conditions,[31,32] where I is the intensity of signal peak; L, the thickness of the sample; and n, the refractive index; the subscript 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 are for carbon disulfide. The tensor elements of third-order optical nonlinearities for the polymer were calculated.
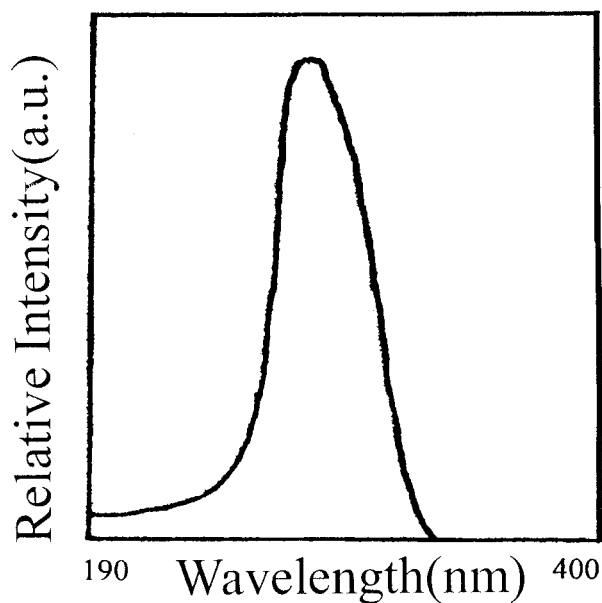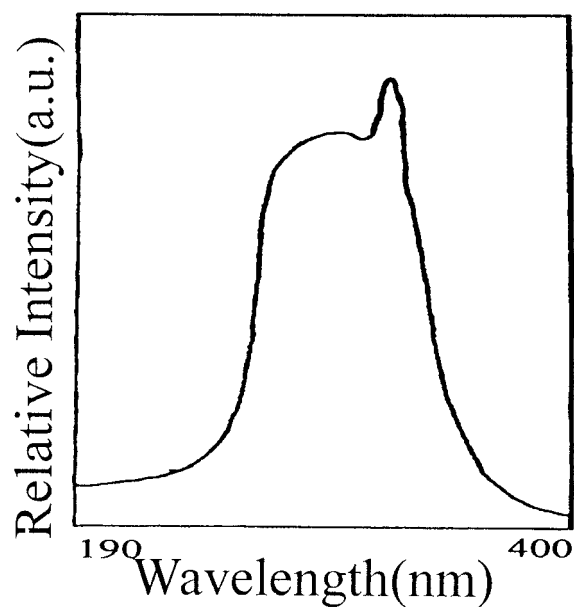
a. PAA
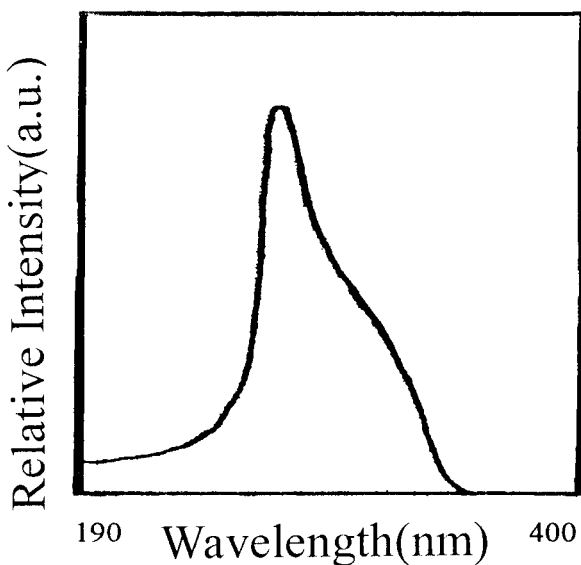
b. PI

Figure 2 UV-visible absorption spectrum of the BGA–PMDA polymer.

RESULTS AND DISCUSSION

Mechanism of the third-order optical nonlinearities

In this article, the mechanism of the third-order optical nonlinearities of the polymer were studied by the UV-visible absorption spectrum and the time-response spectrum for the DFWM signal. The UV-visible

absorption spectra of the BGA–PMDA, *m,m'*-DABP–PMDA, and BGA–TDI–PMDA polymers are shown in Figures 2–4, where the absorption bands measured are due to π–π^* transitions of the highly polyconjugated systems, indicative of the distribution range in the p–π-conjugated systems, and the used laser wavelength (532 nm) in the experiment is out of the absorption region.
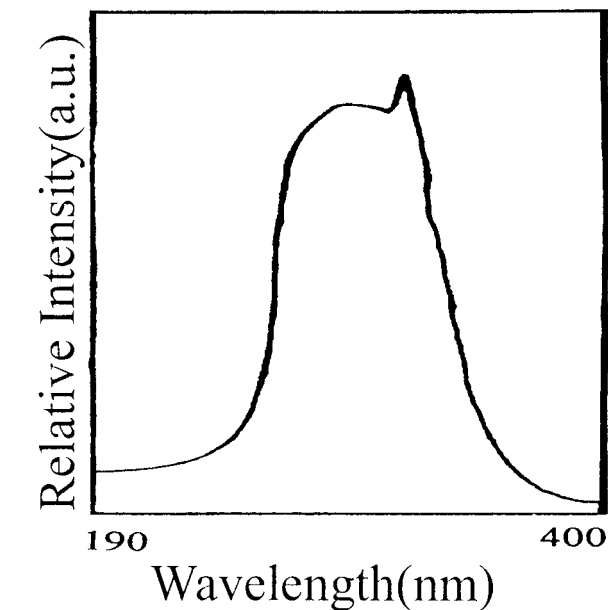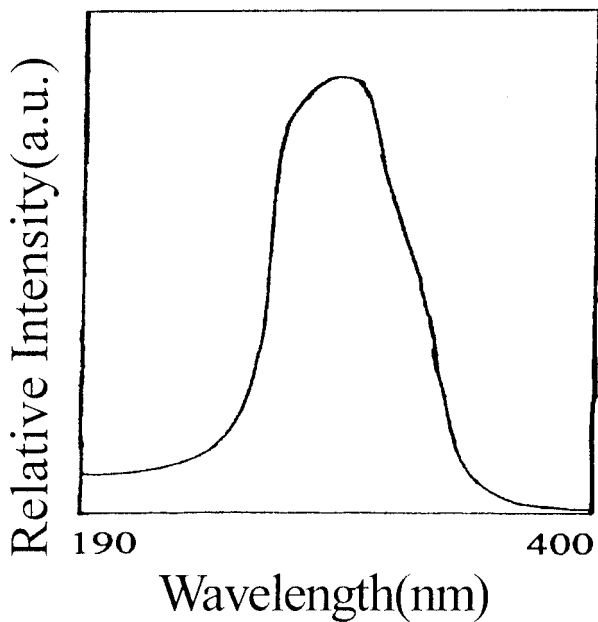

a. PAA
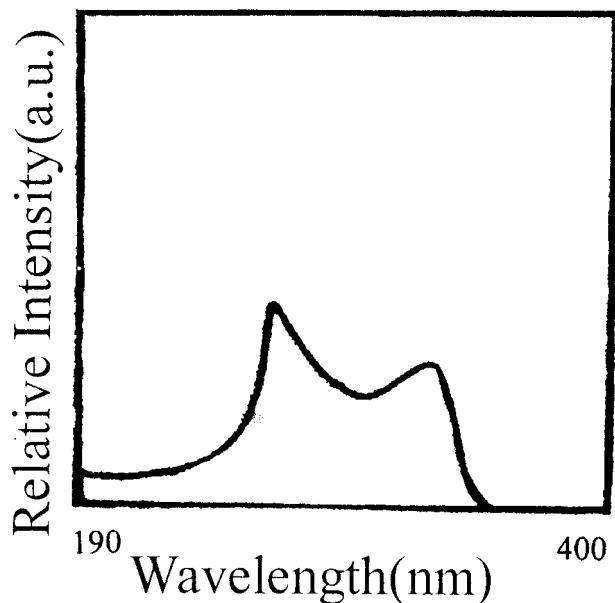
b. PI

Figure 3 UV-visible absorption spectrum of the *m-m'*-DABP–PMDA polymer.

a. PU

b. PI

**Figure 4**   UV-visible absorption spectrum of the BGA–TDI–PMDA polymer.

The three kinds of polymers, with a large quasi-one-dimensional p–π-conjugated structure, contain a high-density of π-electrons that is attributed to third-order nonlinearities. A delay in any one of the three input beams gives almost the same signal envelope. The

time-resolved measured results (solid circle) of 3D DFWM are shown in Figures 5–7.

The envelope of the signal is well fitted by a Gaussian function (solid curve), and the full-width at half-maximum of the fitting envelope is similar to that of 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 that of the experimental time resolution. This means that the time response of the third-order optical nonlinearities is quite fast, and the Kerr effect, which arises from the distortion of the large p–π-conjugate electronic charge distribution of the polymer, is the main reason for generating the DFWM signal.[33]
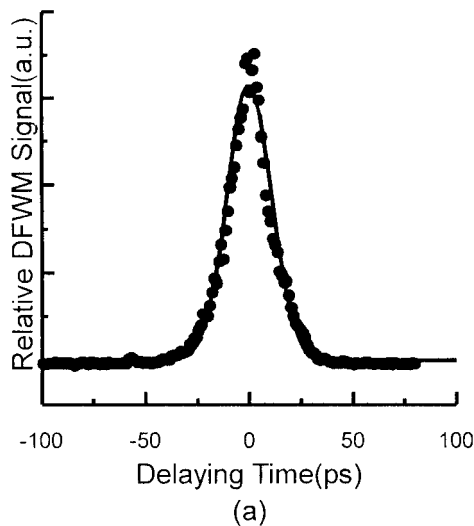
(a)
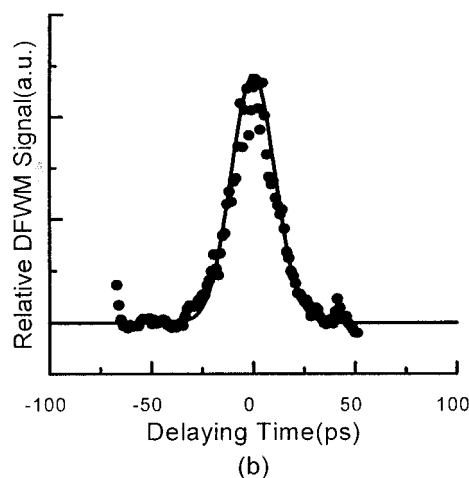
(b)

Figure 5   DFWM time-response spectra for the BGA–PMDA polymer: (a) PAA; (b) PI.
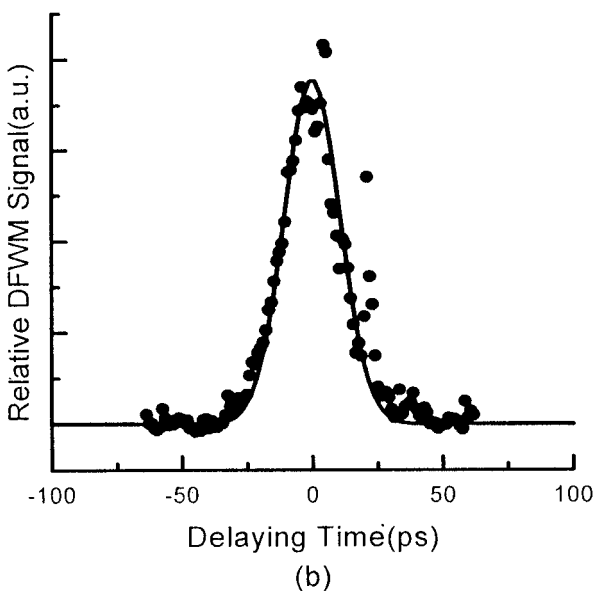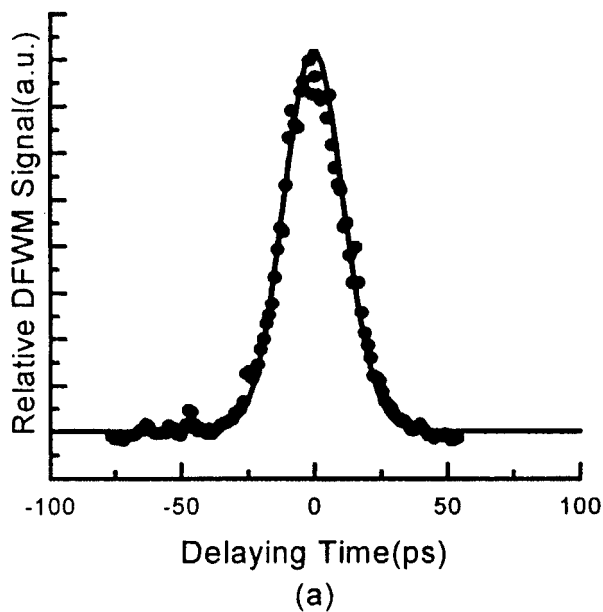
Figure 6 DFWM time-response spectra for the *m-m'*-DABP–PMDA polymer: (a) PAA; (b) PI.

Figure 7 DFWM time-response spectra for the BGA–TDI–PMDA polymer: (a) PU; (b) PI.

Effect factors of the third-order optical nonlinearities of polymers

In this article, we tried a useful new method—microwave irradiation—for synthesizing optical nonlinear materials. A comparison of the third-order optical nonlinerities by microwave irradiation and the heating method is shown in Figures 8 and 9. In Figure 10, we find that the $\chi^{(3)}$ synthesized by microwave irradiation is larger than that by heating. It may be that the distribution of the molecular weight of the polymer synthesized under microwave irradiation is not only narrow, but also that the molecular structure is relatively regular.

To study the relationship between the third-order optical nonlinearities and the intrinsic viscosity, the results of the polymer prepared at various times under

TABLE I
Time Response for the DFWM Signal of the Polymer

Sample	Response time (ps)
BGA–PMDA PAA	25
BGA–PMDA PI	25
m,m'-DABP–PMDA PAA	27
m,m'-DABP–PMDA PI	25
BGA–TDI PU	24
BGA–TDI–PMDA PI	22

Figure 8 Relationship between the third-order nonlinear optical coefficient of the BGA–PMDA polymer and the reaction temperature.

microwave radiation are shown in Figure 11. It can be observed that the third-order nonlinear optical coefficients $\chi^{(3)}$ are proportional to the intrinsic viscosity (the length of the conjugated chain L) for the same type of polymer in this experimental range. The third-order optical nonlinearities of the m,m'-DABP–PMDA polymer PAA are the largest, and those of the BGA–PMDA polymer PU are larger than those of the BGA–TDI polymer PAA. The experimental re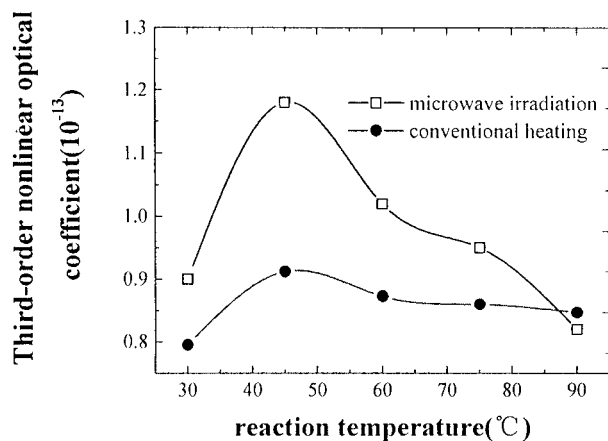sults show that the third-order optical nonlinearities are affected not only by the conjugated length of the polymer chain, but also by the polymer chain structure.

It is obvious that the third-order optical nonlinear coefficients of the m,m'-DABP–PMDA polymer PAA, the BGA–TDI polymer PU, and the BGA–PMDA polymer PAA decrease orderly (see the data in Table II). The molecules of BGA–PMDA PAA have the unsaturated heterocycle including nitrogen atoms and link up the benzene that takes on the weak property of the
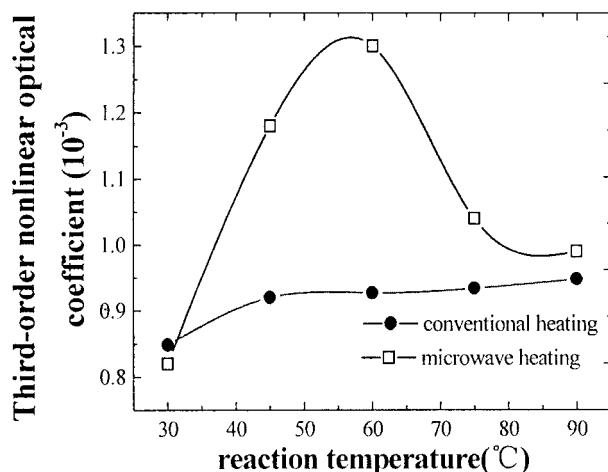

Figure 10 Comparison of microwave irradiation and conventional heating on the optical coefficient of BGA–TDI–PMDA.

absorbing electron. The molecules of BGA–TDI PU are similar to those of BGA–PMDA PAA, but methyl takes on the weak property of the excluding electron in benzene. The absorbing-electron groups decrease the charge density of the p–π conjugated structure, while the excluding-electron groups have the contrary effect. The deference of the molecule structure may result in the variation of the third-order optical nonlinearities of the polymer in the three systems. Now, we explain the effects of the polymer structure on the third-order optical nonlinearities by the UV-visible absorption spectrum, the fluorescence spectrum, and the energy gap. The results are as follows:

The absorption and fluorescence spectra of the solid-phase polymer were measured by a Japan Shimadzu RF-540 spectrometer, and the wavelength of the excitation ray was 200 nm. The peaks of the absorption and fluorescence spectra move gradually to

Figure 9 Comparison of microwave irradiation and conventional heating on the optical coefficient of m-m'-DABP–PMDA.
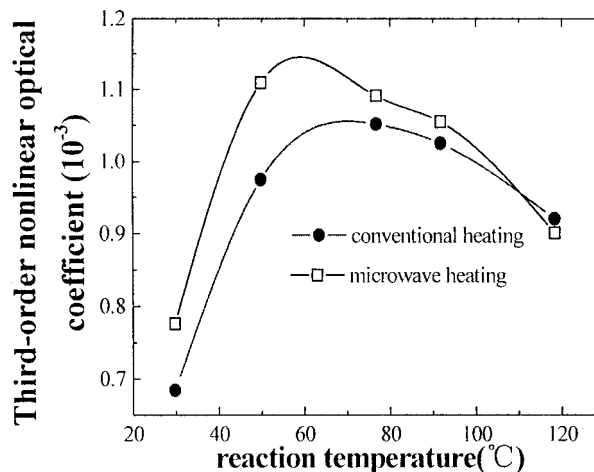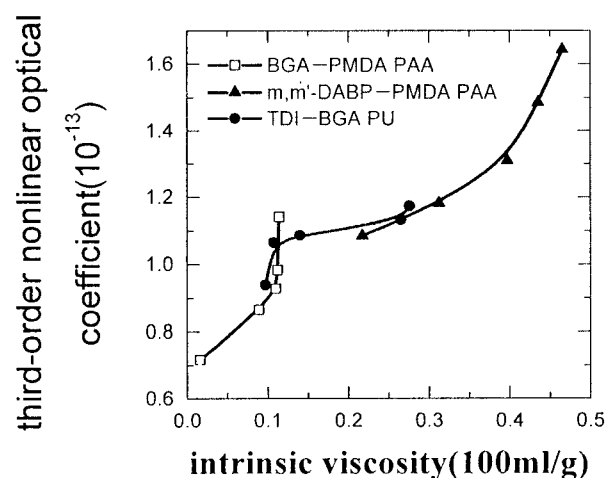

Figure 11 Relationship between the third-order nonlinear optical coefficient of the polymer and the intrinsic viscosity.

TABLE II
Data of the Third-order Nonlinear Optical
Coefficient for PAA

Sample	Time of microwave radiation (h)				
	1	2	3	4	6
	$\chi^{(3)}$ ($\times 10^{-13}$)				
m,m'-DABP–PMDA PAA	1.084	1.181	1.309	1.485	1.642
BGA–TDI PU	0.939	1.065	1.086	1.132	1.174
BGA–PMDA PAA	0.717	0.865	0.928	0.983	1.141

TABLE IV
Calculated Energy Gap (E_g) for the Various Conjugated
Lengths of the Polymer by the 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
m,m'-DABP–PMDA PAA	6.152	5.711	5.675	5.587
BGA–TDI PU	6.692	6.316	6.215	

the position of the long wavelength (see Table III). This is because the energy gap of the π–π^* transition of the *m,m'*-DABP–PMDA, BGA–TDI, and BGA–PMDA polymers increase (see Table IV), and their third-order optical nonlinearities increase gradually.

The nonlinear polarization is relative to the molecular energy level of excitation, especially the inverse proportion to the energy gap between the LUMO and the HOMO.[29,32] The energy gap E_g values for the various conjugated lengths of the polymers were calculated by the AMI semiempirical method (see Table IV). The E_g decreases as the conjugated length of the polymer chain increases. The variation also decreases as the conjugated length of the polymer chain increases. This is because an increase of the conjugated degree results in a decrease of the E_g. As a result, the conjugated electrons generate a transition quickly and distortion of the conjugated electrons can come into being easily. The results showed that the third-order optical nonlinearities of a conjugated polymer increased as the length of the p–π-conjugated structure increased.

From the E_g values of the *m,m'*-DABP–PMDA, BGA–TDI–PMDA, and BGA–PMDA polymers, it can be learned that the E_g values increase in that order. It was proved that the π–π^* transition energy of three kinds of polymers increased successively. This is because the absorbing-electron group decreased the charge density of the p–π conjugated structure, while the excluding-electron groups had the contrary effect. So, the third-order optical nonlinearities of the *m,m'*-DABP–PMDA, BGA–TDI–PMDA, and BGA–PMDA polymers decreased gradually.

TABLE III
Data of the Absorption and Fluorescence Spectra
for the Polymer

Sample	Absorption peak (nm)	Fluorescence peak (nm)
BGA–PMDA PAA	280	467
BGA–PMDA PI	272	467
m,m'-DABP–PMDA PAA	298, 322	471
m,m'-DABP–PMDA PI	267, 331	468, 517
BGA–TDI PU	296, 317	467, 490, 510
BGA–TDI–PMDA PI	295	467, 490, 510

CONCLUSIONS

The *m,m'*-DABP–PMDA, BGA–TDI–PMDA, and BGA–PMDA polymers prepared under microwave irradiation have large third-order optical nonlinearities and time responses, as expected. In the nonresonance region of 532 nm, the measured third-order nonlinear optical coefficients $\chi^{(3)}$ of *m,m'*-DABP–PMDA PAA, BGA–TDI–PMDA PU, and BGA–PMDA PAA are 1.6 $\times 10^{-13}$, 1.2 $\times 10^{-13}$, and 1.1 $\times 10^{-13}$ esu, respectively. The third-order optical nonlinearities are proportional to the conjugated chain length of the polymer in the experimental range. The results show that the absorbing-electron groups of the polymer structure are advantageous in improving the third-order optical nonlinearities of the polymer.

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