

Polycondensation of Sodium Tetrazodiphenyl Naphthionate and Pyromellitic Dianhydride under Microwave Irradiation and the Performance of the Third-Order Nonlinear Optics

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ABSTRACT: Sodium tetrazodiphenyl naphthionate and pyromellitic dianhydride were polycondensed under microwave irradiation and oil-bath heating. The resultant poly(amic acid) was imidized in the solid phase by microwave irradiation and oil-bath heating. The effects of the reaction temperature, the concentration of monomers, the monomer ratio, and the microwave irradiation time on the conversion, intrinsic viscosity, and third-order nonlinear optical (NLO) coefficient of the polymer were investigated. The results

showed that the polycondensates had high third-order NLO coefficients ($\chi^{(3)} = 1.476 \times 10^{-12}$ esu) and very fast time responses (15.79 ps). The $\chi^{(3)}$ values of the polycondensates under microwave irradiation were higher than those of conventional thermopolymerization. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1121–1128, 2003

Key words: polycondensation; NLO; intrinsic viscosity

INTRODUCTION

With the development of microelectronic science, we stepped into the age of information. Since the middle of the 20th century, the developing trend of electronic applications is that the size becomes smaller and smaller and the integrated degree becomes higher and higher. However, in modern society, the continuous development of telecommunications, information processing, and all types of systems makes it difficult for the electronic techniques central to modern technology to keep pace. The investigation of optoelectronic materials with ultrafast responses is the main current of information science.^{1–4} Conjugated polymers as nonlinear optical (NLO) materials have triggered enormous interest in recent years because of their larger susceptibility, fast response, high optical damage threshold, low direct-current dielectric constant, ease of fabrication, and so forth. In this study, we synthesized *p*- π -conjugated polymers with good solubility, good thermal stability, large third-order NLO

coefficients ($\chi^{(3)}$), and fast optical responses. They are quite promising NLO materials.^{5,6}

The study of the use of microwave irradiation in organic chemistry is very active, and it was first applied in organic synthesis by Gedye in the 1980s. With the expansion of the use of microwaves in chemistry, an intersect science, microwave chemistry, came into being. In the field of polymerization, microwaves are mainly exploited for solidifying and crosslinking⁷ and in the bulk polymerization of polar liquid monomers such as styrene and methyl methacrylate.⁸ The study of polycondensation has focused on reducing the reaction time and increasing the polymerization degree for several systems, and it has not been thorough and systematic. In particular, studies on the effects of microwaves on properties and structures are few.^{9–11} In this study, we investigated the polycondensation of sodium tetrazodiphenyl naphthionate (STDN) and pyromellitic dianhydride (PMDA) under microwave irradiation and the polycondensate NLO properties for the first time.

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EXPERIMENTAL

Base materials

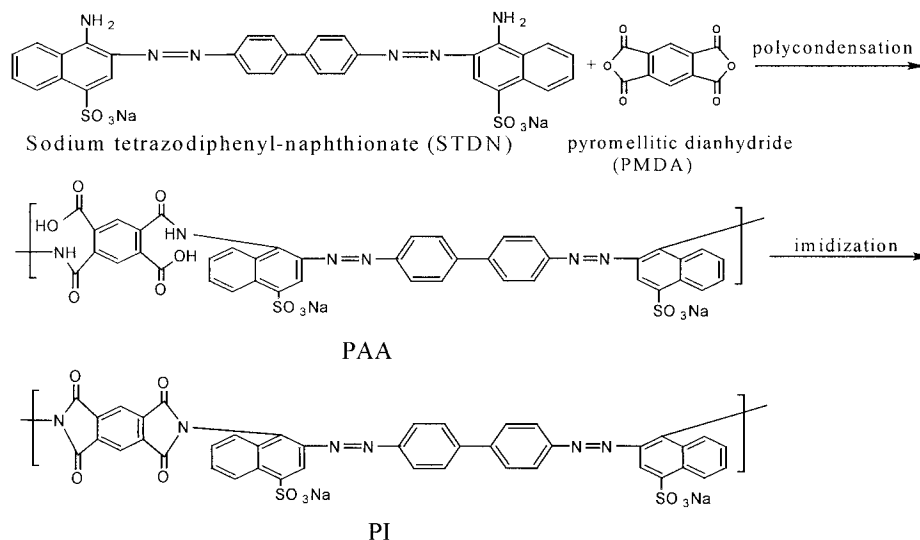
The base materials included STDN (analytically pure; Shanghai Yuanhang Reagent Co.), PMDA (chemically pure and recrystallized with acetic anhydride; Shang-

hai Jiaohua Factory), *N,N*-dimethylformamide (DMF; analytically pure and distilled under reduce pressure; Shanghai Chemical Reagent Co., Ltd.), acetic anhydride (analytically pure; Shanghai Chemical Reagent), methanol (analytically pure; Shanghai Zhenxing Chemical 1st Factory); tetrahydrofuran (THF; analytically pure; Suzhou Zhengxing Chemical Factory), and carbon disulfide (CS₂; analytically pure; Shanghai Chemical Reagent).

Synthesis

A two-step method was used for the synthesis of polyimide (PI). First, we synthesized poly(amic acid) (PAA), and then the resultant PAA was imidized. In the first step, PAA was mainly synthesized under microwave irradiation, and for contrast, we also synthesized them by oil-bath heating. STDN and DMF as solvents were added to the three-necked flask, and then the flask was put into the microwave oven. The mixture was stirred for perfect dissolution. Nitrogen

gas was delivered to the solution, and PMDA was added to the solution in batches. The temperature of polymerization was controlled at the expected data by the modulation of the power of the microwave oven. After the reaction was finished, the solution was poured into deionized water, and the precipitate was separated by centrifugation and washed with THF and methanol in turn. In the experiment, when one factor was investigated, the other conditions were fixed; for example, when the influence of the temperature was investigated, the monomer concentration, the monomer ratio, and the microwave irradiation time were 25%, 1:1, and 2 h, respectively. The fixed temperature was 55°C when the parameters except the temperature were studied. The condensate was dried *in vacuo* at 50°C to a constant weight. A purple power of PAA was obtained. In the second step, PAA was imidized by microwave radiation and oil-bath heating for different times. The process of synthesis was as follows:



Measurements

Fourier transform infrared (FTIR) and ultraviolet-visible (UV-vis) spectra

The FTIR spectra of the polymers were measured with a Magna 550 FTIR (Nicolet Corp.); UV-vis spectra were measured with a UV-240 (Shimadzu Corp.).

Intrinsic viscosity

The intrinsic viscosity was determined by a one-point method at $30.0 \pm 0.5^\circ\text{C}$. The inner diameter of the Ubbelohde viscometer was 0.7 mm, and DMF was used as a solvent.

Third-order NLO response

The third-order NLO response of the polymers was detected with a phase-conjugated forward three-dimensional DFWM technique. After passing through a quarter-wavelength plate, the pulse laser beam (wavelength = 532 nm; pulse width = 35 ps; repetition rate = 10 Hz; pulse energy ~ 2.5 mJ) from a frequency-doubled picosecond-pulse mode-locked Nd:YAG laser was split into three beams with the same energy by the use of reflecting beam splitters. Then, it was temporally and spatially overlapped in the sample with a 205 focus length lens (L). The angles between the three beams were about 1° . Figure 1 shows a sketch of the process. In the experiment, the intensity of I_4 was detected with a PIN photodiode (PD2). $\chi^{(3)}$ was ob-

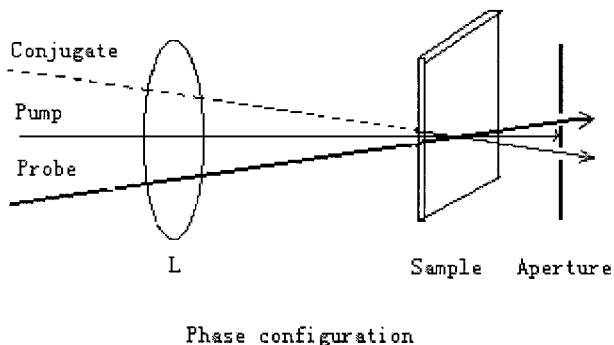


Figure 1 Sketch of the setup for phase configuration.

tained by a comparison of the measured signals of the samples with those of CS₂ under the same experimental conditions according to the following equation:¹²

$$\chi^3 = \left(\frac{I_4}{I_{4r}} \right)^{1/2} \frac{L_r \left(\frac{n}{n_r} \right)^2}{L \left(\frac{n}{n_r} \right)} \frac{\alpha L \exp(\alpha L/2)}{1 - \exp(-\alpha L)} \chi_r^{(3)} \quad (1)$$

where n is the refractive index, L is the path length in the medium, subscript r denotes the reference CS₂, and α is the absorptivity. $\chi_r^{(3)}$ is 6.8×10^{-13} esu.¹³ The response time of the samples was obtained with eq. (2):

$$Y_{1/2} = 2.354\sigma \quad (2)$$

where σ is the standard deviation, which is obtained by Gaussian fitting of the DFWM signal curve. We measured the third-order NLO response of the polymers in a dilute solution of DMF (0.3 g/L) because of their strong absorption at 532 nm.

RESULTS AND DISCUSSION

FTIR spectra of the polymers

In the FTIR spectrum of PAA, the band at 3414.3 cm^{-1} may be the vibration absorption of N—H, and the band at 1361.8 cm^{-1} may be assigned to the vibration absorption of C—N in —CONH— (Fig. 2). The band at 1045 nm denotes the vibration and C—O in —COOH. In the FTIR spectrum of PI, the bands at $3600\text{--}3240 \text{ cm}^{-1}$ disappear, and the band at 1365.7 cm^{-1} decreases, whereas bands at 1786 and 1710 cm^{-1} appear, being the characteristic absorptions of the imide structure (Fig. 3). This suggests that the structures of PAA and PI from STDN and PMDA are correct.

UV-vis spectra of PAA

A strong absorption band appears at a wavelength of 532 nm in the UV-vis spectrum (Fig. 4). Therefore, the NLO response can resonantly be enhanced near the band. A useful equation of merit that defines the optical switching performance of third-order NLO material is

$$F(\lambda) = \frac{\chi^{(3)}(\lambda)}{\alpha'(\lambda)} \tau \quad (3)$$

where α' denotes the sum of linear and nonlinear absorptivity and τ is the lifetime of the third-order NLO response. The stronger the linear and nonlinear absorptivity is, the larger the probability is of the light-induced thermal effect overwhelming the response and the easier the optical damage is. Additionally, the renounce can limit the response speed.² This

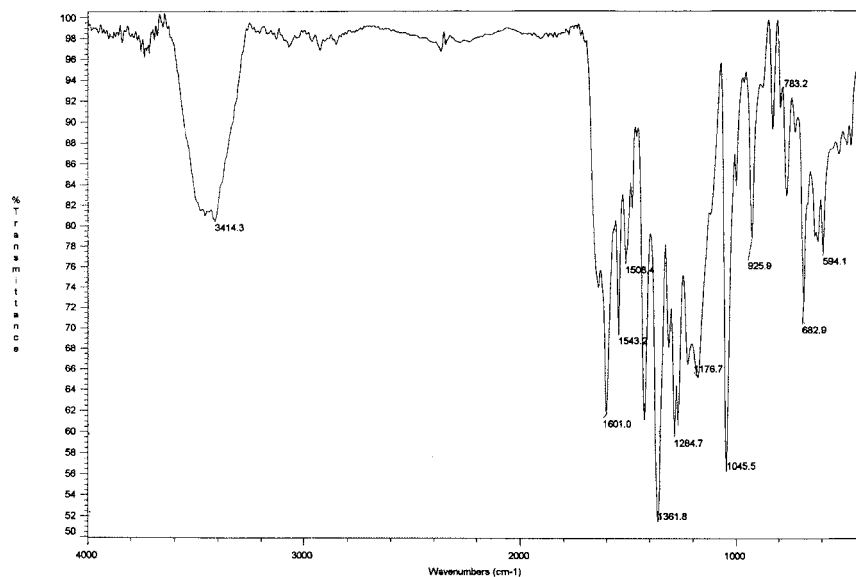


Figure 2 FTIR spectrum of PAA.

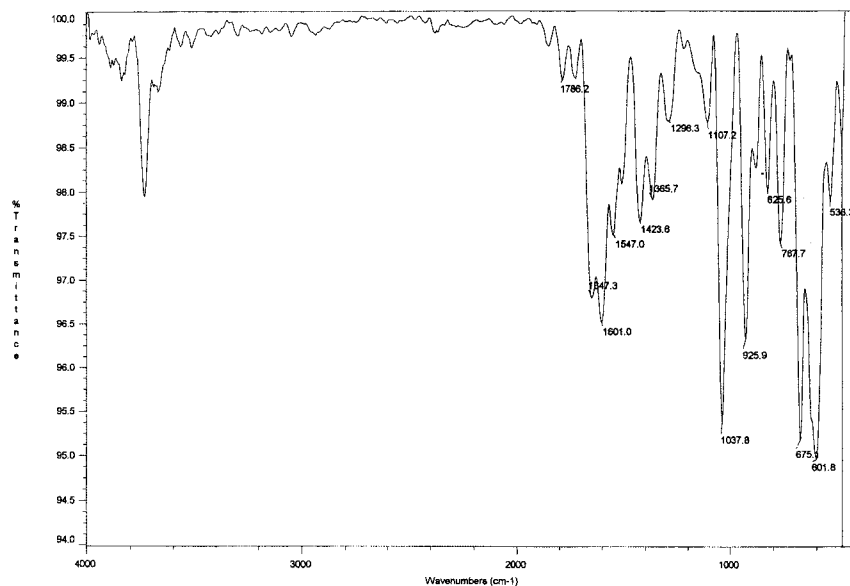


Figure 3 FTIR spectrum of PI.

formula shows that the switching performance of the material is related to the absorptivity. Therefore, the resonant contribution to $\chi^{(3)}$ is not expected.

Imidization degree of PAA

PAA was imidized under microwave irradiation and oil-bath heating. We measured the imidization degree by an FTIR spectrum method according to ref. 14. The stretch and contract vibration absorption peak of the carbon-carbon double bond was selected as the inner criterion. By a comparison with carbonyl, the resultant ratio denotes the imidization degree.¹⁴ Table I gives the data for the imidization degrees obtained with the

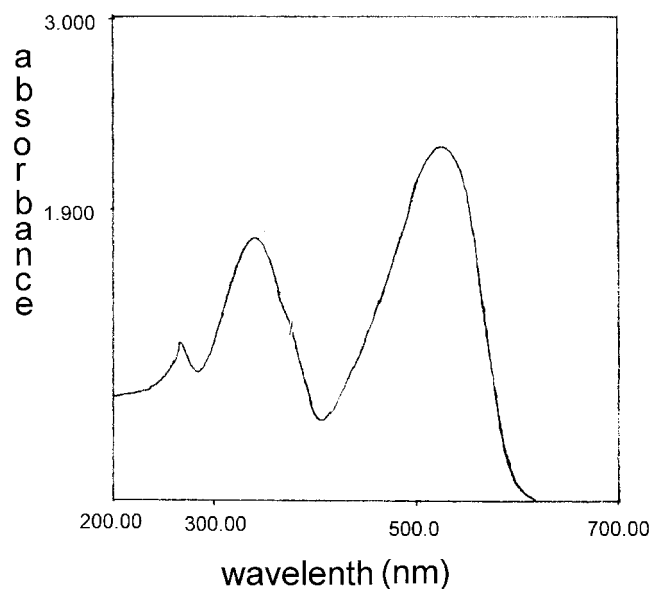


Figure 4 UV-vis spectrum of PAA.

two approaches. A large imidization degree was obtained under microwave irradiation because of the fast heating rate. After irradiation for 9 min, the imidization degree decreased radically. This might be related to the decomposition of molecular chains induced by the microwave irradiation. In oil-bath-heating imidization, the oil temperature was controlled at 190°C. The imidization degree was only 56.08% after 5 h of heating. Therefore, we have concluded that the use of microwave irradiation for imidization is an energy-saving and effective approach as long as the power and irradiation time can be well controlled.

Influence of the reaction temperature on the conversion and intrinsic viscosity

Figures 5 and 6 show the relationship between the reaction temperature and the conversion as well as the intrinsic viscosity of the PAAs. At a lower temperature stage, the conversion and intrinsic viscosity increased with the temperature. After 70°C was passed, they decreased gradually. The PAAs synthesized under microwave irradiation and oil-bath heating showed the same trend. This reason for this may be that it was hard to surpass the energy barrier of the reaction

TABLE I
Imidization Degree under Microwave Irradiation and Oil-Bath Heating

Oil-bath heating					
Heating time (h)	1	2	3	4	5
Imidization degree (%)	11.70	36.76	55.15	55.37	56.08
Microwave irradiation					
Irradiation time (min)	6	8	9	10	11
Imidization degree (%)	53.92	56.37	83.58	32.50	22.25

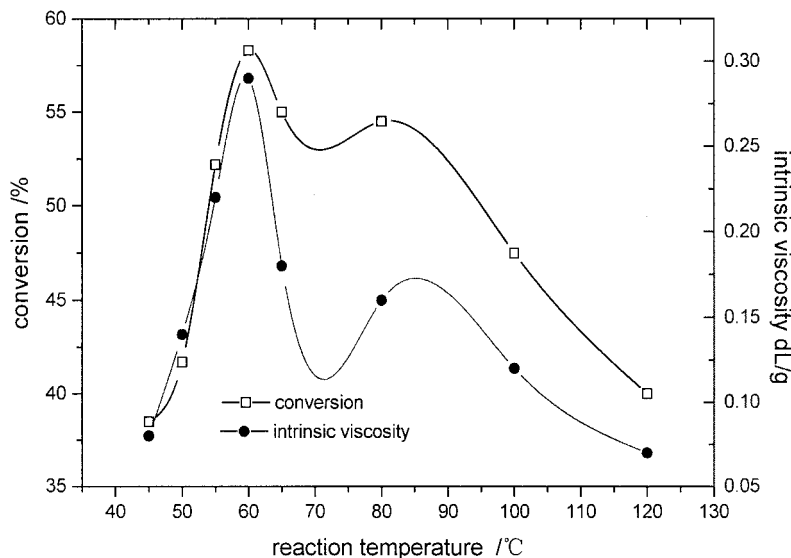


Figure 5 Effect of the reaction temperature on the conversion and intrinsic viscosity under heat polycondensation (monomer concentration = 25%; STDN/PMDA = 1:1; heating time = 2 h).

when the temperature was too low; however, the reverse reaction was obvious when the temperature was too high. Therefore, at low and high temperatures, the conversion and intrinsic viscosity were relatively low. The best temperature was 55–70°C. In comparison with oil-bath-heating polymerization, microwave irradiation could increase the conversion and intrinsic viscosity of PAAs to a certain degree.

Influence of the monomer concentration on the conversion and intrinsic viscosity

Figure 7 show that the concentration of the monomers had an obvious influence on the conversion and intrinsic viscosity. The probability of molecular collision

was so small when the concentration of the monomers was low that it resulted in decreasing conversion and intrinsic viscosity. However, when the concentration was too high ($\geq 30\%$), turbidity appeared during the process of the reaction that made it difficult for the polymerization to continue. The accepted concentration range was 25–30%.

Influence of the monomer ratio on the conversion and intrinsic viscosity

With variations in the monomer ratio, the conversion and intrinsic viscosity were maximum, as expected (Fig. 8). In polycondensation, the reaction degree could quickly reach its largest value, and the oligomer

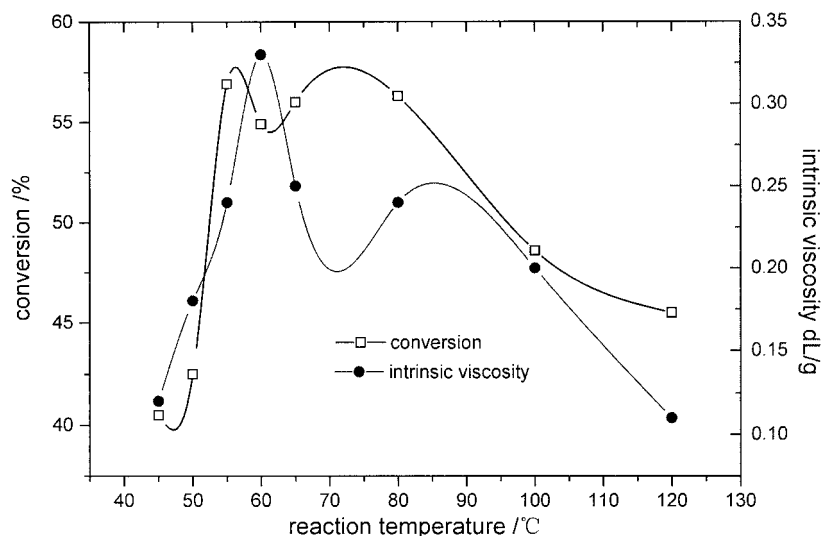


Figure 6 Effect of the reaction temperature on the conversion and intrinsic viscosity under microwave irradiation (monomer concentration = 25%; STDN/PMDA = 1:1; microwave irradiation time = 2 h).

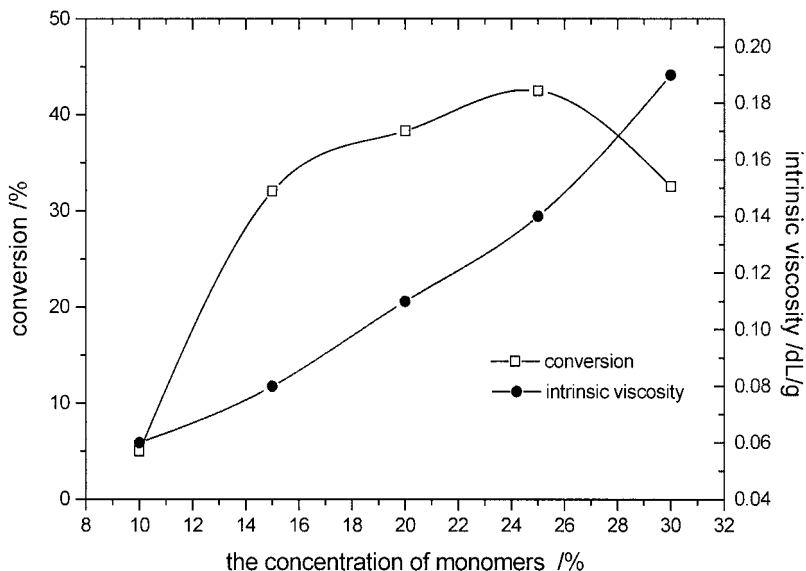


Figure 7 Effect of the monomer concentration on the conversion and intrinsic viscosity (reaction temperature = 55°C; STDN/PMDA = 1:1; heating time = 2 h).

was obtained. Most of the oligomer had the same terminal groups if one of the monomers was excessive. Under such conditions, the molecule chains could not continue increasing. However, the oligomer could not be precipitated completely, and it was easy to loss during washing, so the conversion was also low when one of the monomers was excessive.

Influence of the irradiation time on the conversion and intrinsic viscosity

Figure 9 shows that the conversion and intrinsic viscosity continued increasing with the lengthening of

the irradiation time. We controlled the power of the microwave oven at definitive data in the experiment, so the presented energy was proportional to the irradiation time. The influence of the molecular chain on the reaction activity of the groups could be neglected when the polymerization degree was not too large. This approximation was the base for the dynamical study on step-growth polymerization.¹⁵ Therefore, the macromolecules condensed continuously as long as energy was given. This explained the reason for the increasing conversion and intrinsic viscosity with the lengthening of the irradiation time.

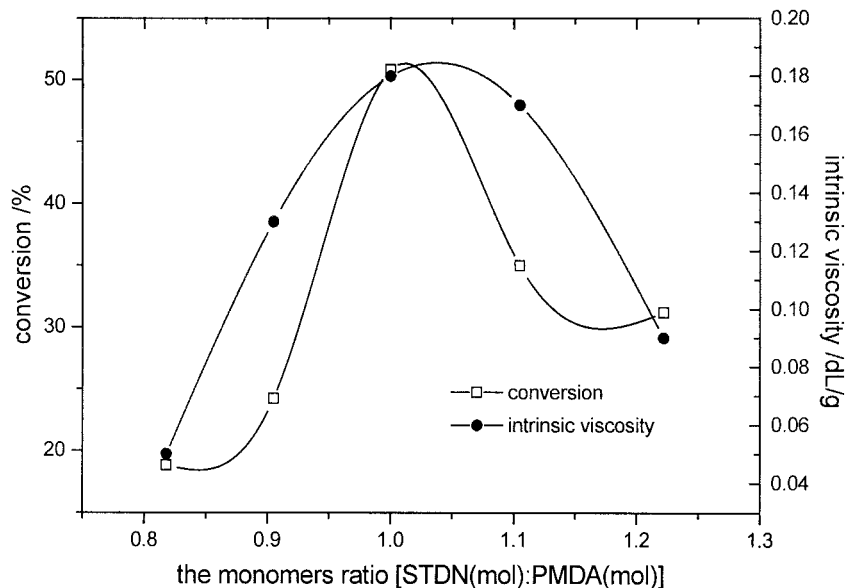


Figure 8 Effect of the monomer ratio on the conversion and intrinsic viscosity (reaction temperature = 55°C; monomer concentration = 25%; heating time = 2 h).

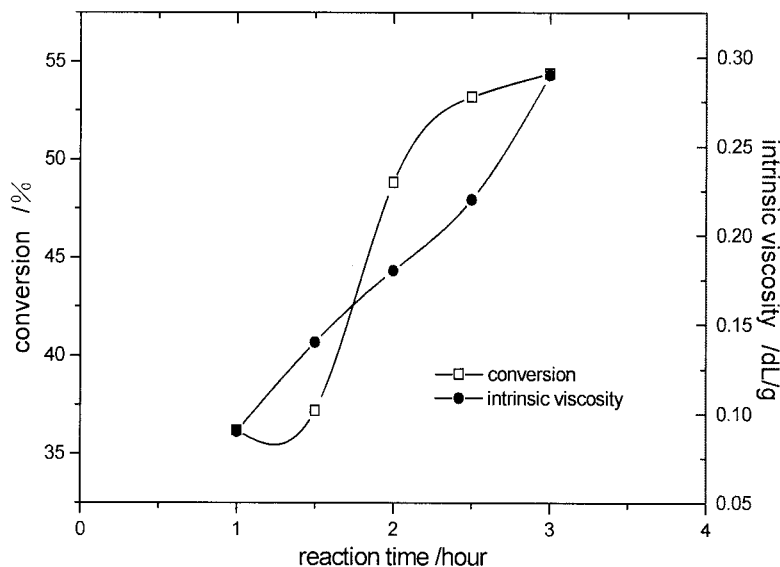


Figure 9 Influence of the irradiation time on the conversion and intrinsic viscosity (reaction temperature = 55°C; monomer concentration = 25%; STDN/PMDA = 1:1).

Third-order NLO properties of PAAs and PIs

The NLO process is composed of two components. First, the NLO response can be induced in a medium by the input of intense light (often a laser), and then the medium counter acts on the light. The latter process is nonlinear, and it obeys Maxwell's equations.¹⁶ The DFWM technique can be used to detect the NLO properties of materials by the measurement of the intensity of phase-conjugated light produced by the NLO response of the medium. Figure 10 shows the relationship between the delay time and the DFWM signal intensity. In this study, we synthesized PAAs under different conditions, and some of the PAAs

were selected for imidization. PAA and PI had large values of $\chi^{(3)}$ and very fast responses because of the delocalization of the electron cloud over the whole chain. The $\chi^{(3)}$ values of PAAs synthesized under different conditions are presented in Table I. The changing trends of $\chi^{(3)}$ were consistent with those of the intrinsic viscosity. As we know, the NLO response is induced by electron transitions between different energy levels. Therefore, the lower the energy gaps are between energy levels, the easier the electron transition is. The energy gaps depend strongly on the conjugated chain length. The intrinsic viscosity (η) is related to the chain length by the equation $\eta = KM^\alpha$.

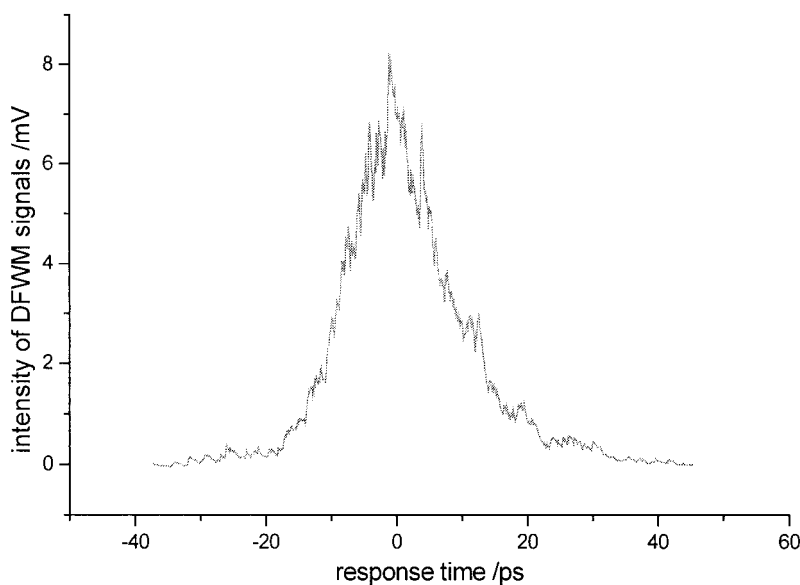


Figure 10 NLO behavior of PI.

TABLE II
 $\chi^{(3)}$ ($\times 10^{-13}$ esu) of PAAs Synthesized under Different Conditions

	1	2	3	4	5	6	7	8
Temperature								
Oil-bath heating	5.684	5.47	6.148	7.898	8.944	7.96	6.546	5.24
Microwave irradiation	7.344	8.161	8.432	8.681	9.354	8.16	7.362	5.462
Concentration of monomers	7.078	8.383	8.543	8.677	8.638	—	—	—
Monomer ratio (STDN/PMDA)	7.075	8.242	8.693	7.789	5.911	—	—	—
Microwave irradiation time	6.504	7.932	8.651	9.172	10.577	—	—	—

The numbers 1–8 denote the experiment order:

- (1) For the temperature, the numbers 1–8 denote 45, 50, 55, 60, 65, 80, 100, and 120°C, respectively;
- (2) For the concentration of monomers, the numbers 1–5 denote 10–30% increased by 5%;
- (3) for the monomer ratio, the numbers 1–5 denote the ratio of STDN to PMDA and was 1.222, 1.105, 1.000, 0.905, and 0.812, respectively; and
- (4) for the microwave irradiation time, the numbers 1–5 denote 1–3 h, increased by one half of an hour.

Theory calculation results for other conjugated systems have shown the same law. Therefore, theory results show that the saturation behavior will appear when the conjugated chain reaches a definitive length.² We can observe in Table II that $\chi^{(3)}$ continued increasing with the lengthening of the irradiation time, so the PAAs did not reach their saturation length. Compared with the data of $\chi^{(3)}$ of PAAs, those of PIs had increments in a certain degree (e.g., $\chi^{(3)}$ of one of the samples increased from 8.681×10^{-13} to 1.476×10^{-12} esu after imidization for 9 min). This might be interpreted as the better orientation and increased rigidity of the molecules after imidization.

CONCLUSIONS

Using microwave irradiation for the condensation of STDN and PMDA contributed to increasing the polymerization degree and reducing the imidization time. The imidization time was reduced from hours to minutes, and the imidization degree was obviously increased. The PAAs and PI synthesized had large $\chi^{(3)}$ values and ultrafast responses. The largest NLO coefficient was 1.476×10^{-12} , and the shortest response time was 15.79 ps.

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