Synthesis and properties of aluminum phthalocyanine side-chain polyimide for third-order nonlinear optics

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Dedicated to Professor Imanishi on the occasion of his retirement

Abstract

A new third-order nonlinear optical polyimide with aluminum phthalocyanine unit as a side-chain (APSPI) has been developed. The poly(hydroxyimide) (PHI) was prepared by the ring-opening polyaddition of 4,4′-(hexafluoroisopropylidene)diphthalic anhydride with 4,4′-diamino-4″-hydroxytriphenylmethane, followed by thermal imidization. The resulting PHI had number- and weight-average molecular weights (M_n, M_w) of 34,000 and 64,000, respectively. The introduction of aluminum phthalocyanine unit (AlPc) to PHI was carried out by the reaction of PHI with chloroaluminum phthalocyanine in the presence of silver triflate. The third-order nonlinear susceptibility $\chi(3)$ of APSPI film with approximately 60 mol% content of AlPc at 1064 nm wavelength was 5.3×10^{-9} esu. This was measured using the closed Z-scan technique. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Third-order nonlinear optical property; Polyimde; Aluminum phthalocyanine

1. Introduction

Third-order nonlinear optical (3rd-NLO) materials are currently of interest to a large number of research groups as they have potential applications such as optical switches, modulations and other nonlinear optical devices. Organic polymeric systems containing conjugated π-electron structure show anomalously large optical nonlinearities and the nonlinear response time is believed to be in femtoseconds because of the delocalized π electrons [1,2].

Polydiacetylenes [3,4], polyacetylenes [5,6], poly(phenylene–vinylene)s [7], and polythiophenes [8,9] as the π-conjugated polymers have been reported to have large third-order nonlinear susceptibility $\chi(3)$ ranging from 10^{-12} to 10^{-9} esu.

Metallophthalocyanines (MPc) are well known organometallic chromophores and two-dimensionally conjugated compounds for third-order NLO properties [10].

Recently, third-order susceptibilities of chloro-gallium and fluoro-aluminum phthalocyanines were determined by third-harmonic generation (THG) at 1064 nm [11]. Wada et al. [12] reported that the $\chi(3)$s of various MPc thin films

obtained by physical vapor deposition techniques were strongly dependent on the central metal and the packing structure.

MPcs, however, are hardly soluble in organic solvents and crystallize easily in matrices. Furthermore, the molecular aggregation of MPcs [13] greatly influences $\chi(3)$. To remedy these problems, modification of MPcs such as the introduction of peripheral substitutions has been carried out [14]. Another approach is to attach MPcs to polymer chains. The last approach has the advantage that a high concentration of nonlinear chromophores can be incorporated into the polymer system without crystallization, phase separation, or the formation of concentration gradients.

On the other hand, several techniques are known for the measurement of the $\chi(3)$ of materials [15,16]. Nonlinear interferometry, degenerate four-wave mixing, nearly degenerate three-wave mixing, ellipse rotation, and beam-distortion measurements are among the techniques reported in the literature [15,16].

The first three methods, interferometry, wave mixing and ellipse rotation are potentially sensitive techniques but require a complex experimental apparatus. Beam-distortion measurements require precise beam scans followed by detailed wave-propagation analysis.

For our experiment, a single-beam technique (Z-scan)

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was used for measuring the sign and magnitude of refractive nonlinearities because of its simplicity as well as high sensitivity [17–21].

This paper reports the synthesis and characterization of a new aluminum phthalocyanine side-chain polyimide (APSPI) as well as its $\chi(3)$, where a closed Z-scan technique was used for measuring $\chi(3)$.

2. Experimental

2.1. Materials

N-Methyl-2-pyrrolidinone (NMP), and N,N-dimethyl-acetamide (DMAc) were stirred over powdered calcium hydride overnight and then distilled under reduced pressure and stored over 4 Å molecular sieves. Tetrahydrofuran (THF) was purified by distillation over sodium chips and benzophenone ketyl. 4,4'-(Hexafluoroisopropylidene)-diphthalic anhydride (6FDA) was recrystallized from acetic anhydride. Chloroaluminum phthalocyanine was purchased from Tokyo Kasei Co. Ltd. Other reagents and solvents were obtained commercially and were used as received.

2.2. 4,4'-Diamino-4''-hydroxytriphenylmethane

4,4'-Diamino-4''-hydroxy-triphenylmethane (DHTM) was prepared by the reaction of 4-hydroxybenzaldehyde, aniline, and aniline hydrochloride according to a reported procedure [22]. The yield was 63%: mp 200–202 °C (lit [22]. 200–202 °C); ^{1}H NMR (DMSO-d_6) δ: 9.2 (s, OH, 1H), 6.9–6.4 (m, PhH, 12H), 5.1 (s, CH, 1H), 4.9 (s, NH$_2$, 4H) ppm. Anal. Calcd for $C_{19}H_{18}N_2O$: C, 78.60%; H, 6.25%; N, 9.65%. Found: C, 78.62%; H, 6.29%; N, 9.60%.

2.3. Poly(hydroxyimide)

Poly(hydroxyimide) (PHI) was also prepared according to a reported procedure [22], that is, by the polymerization of DHTM with 6FDA, followed by thermal cyclization in refluxing xylene,. The yield was quantitative. The inherent viscosity of the polymer was 0.39 dl/g in NMP at a concentration of 0.50 g/dl at 30 °C: IR (KBr): ν 3430 (O–H) and 1780, 1720 (C=O) cm^{-1}. Anal. Calcd for $(C_{38}H_{20}F_6N_2O_5)_n$: C, 65.34%; H, 2.88%; N, 4.01%. Found: C, 65.30%; H, 2.91%; N, 3.98%.

2.4. Preparation of aluminum phthalocyanine side-chain polyimide

To a stirred solution of chloroaluminum phthalocyanine (0.57 g, 1 mmol) in dry THF (20 ml) was added silver triflate (0.27 g, 1 mmol). The solution was stirred at room temperature for 12 h, and then PHI (0.70 g, 1 mmol) in THF (10 ml) was added. The reaction mixture was refluxed with stirring for 24 h. The solvent was removed in vacuo. The residue was dissolved in NMP and poured into methanol (200 ml). APSPI precipitated was filtered off and dried in

vacuo at 50 °C for 12 h. The yield was 1.04 g (82%). The inherent viscosity of the polymer was 0.41 dl/g in NMP at a concentration of 0.50 g/dl at 30 °C: IR (KBr): ν 3430 (O–H) 1780, 1720 (C=O) and 1170, 1030 cm^{-1} (Al–O–C). Anal. Calcd for $(C_{38}H_{20}F_6N_2O_5)_{1.9}$ $(C_{70}H_{35}F_6N_9O_5Al)_{3.1}$: C, 67.56%; H, 2.98%; N, 8.60%. Found: C, 67.51%; H, 3.00%; N, 8.61%.

2.5. APSPI films

Polymer was dissolved in 20 wt% in DMF at room temperature. Films spin-cast on glass substrate were baked at 80 °C for 10 min. The film thickness was controlled by spin-coat method.

2.6. Measurements

Infrared spectra were recorded on a HORIBA FT-210 spectrometer. UV–visible spectra were obtained on a JASCO V-560 spectrophotometer. ^{1}H NMR spectra were measured on a JEOL EX 270 spectrometer. Thermogravimetric analyses were performed on a Seiko SSC/S200 (TG/DTA 220) thermal analyzer at a heating rate of 10 °C/min. Molecular weights were determined by gel permeation chromatography (GPC) with polystyrene standard using a JASCO HPLC system equipped with a Shodex KD-80M column at 40 °C in DMF containing 10 mmol/l of LiBr. The film thickness was measured using a Dektak 3030 system from Veeco Instruments Inc.

X-ray diffraction (XRD) experiments were carried out on a RAD-rA diffractometer (Rigaku Denki Co. Ltd) equipped with a heating device. Nickel-filtered Cu Kα radiation was employed. Changes in the XRD traces were recorded by a scintillation counter system with a 1.0 mm diameter pin-hole collimator and $1 \times 1°$ receiving slit. Diffractometry was performed in transmission mode. XRD traces were obtained by a step-scanning method: the step width and fixed time were programmed in steps of 0.05° every 4 s. The XRD photographs were taken with a flat Laue camera with a 0.5 mm diameter pin-hole collimator.

Nonlinear optical measurements were performed using the Z-scan technique. The third-order nonlinear susceptibility $\chi(3)$ was calculated from the change in the refractive index induced by the fundamental wave (1064 nm: a mode-locked Nd:YAG laser producing 20 ps (full width at half maximum: FWHM) pulses. ZnSe was used as the reference sample.

3. Results and discussion

3.1. Synthesis of aluminum phthalocyanine side-chain polyimide

Recently, a convenient method for connecting aluminum phthalocyanine to phenol via the Al–O bond has been reported [23]. This method involves the formation
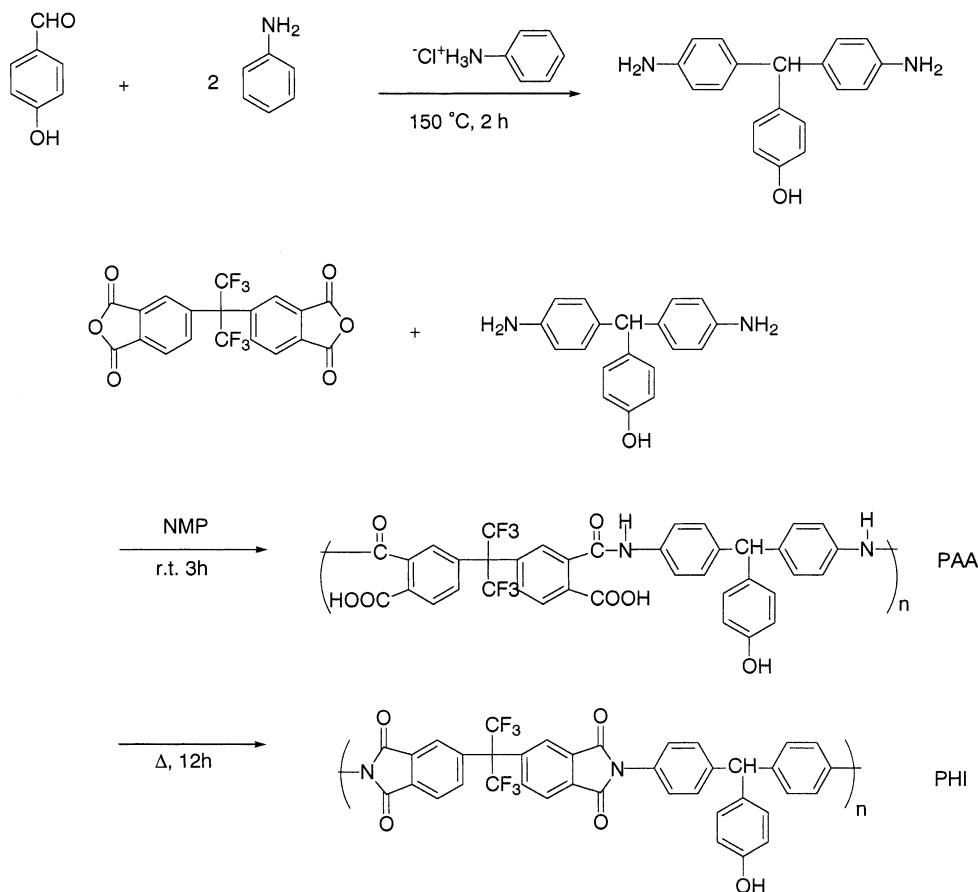
Scheme 1.

of aluminum phthalocyanine triflate from aluminum phthalocyanine and silver triflate, followed by condensation with phenols.

In our previous paper [22], we reported a negative working photosensitive polyimide based on PHI, with 2,6-bis(hydroxymethyl)-4-methylphenol as cross-linker, and diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate as photo-acid generator. We were interested in PHI as the matrix polymer, because PHI has phenol moieties and the distance between the repeating unit of PHI is 22.3 Å which is larger than that of the diameter (13.3 Å) of phthalocyanine (Pc). Thus, the incorporation of Pc to PHI was expected to be easy.

According to the reported procedure [22], the synthesis of poly(amic-acid) (PAA) was carried out by the ring opening polyaddition of 6FDA and DHTM in NMP. Then, the resulting PAA was converted to PHI by refluxing in xylene for 90 min, followed by thermal treatment at 180 °C for 16 h. (Scheme 1.)

The polymer was confirmed to be PHI by infrared spectroscopy and elemental analysis. The IR spectrum of PHI showed characteristic absorptions of imide carbonyls at 1780 and 1720 cm^{-1}, and the phenolic hydroxyl absorption was observed at around 3430 cm^{-1}. Elemental analysis also supported the formation of the expected polymer.

The PHI obtained was a reddish powder product. It is soluble in polar aprotic solvents at room temperature, and soluble in 2-methoxyethanol, THF, bis(2-methoxyethyl) ether, and 1-methoxy-2-acetoxypropane at room temperature. A transparent film was cast from the PHI solution in these solvents.

The molecular weight of the PHI with the inherent viscosity of 0.39 dl/g was determined by GPC. The GPC trace was unimodal with a polydispersity of 1.9. The chromatogram indicated that the relative M_n and M_w are 34,000 and 64,000, respectively.

3.2. Preparation of aluminum phthalocyanine side-chain polyimide

The introduction of aluminum phthalocyanine to PHI backbone was carried out in THF by the reaction of PHI with aluminum phthalocyanine triflate, which was obtained from chloroaluminum phthalocyanine and silver triflate (Scheme 2.). The resulting APSPI was purified by re-precipitation from the NMP solution into methanol. This re-precipitation was repeated three times to remove the unreacted AlPcs.

The amount of AlPcs attached to the polymer backbone was determined by visible spectroscopy and elemental
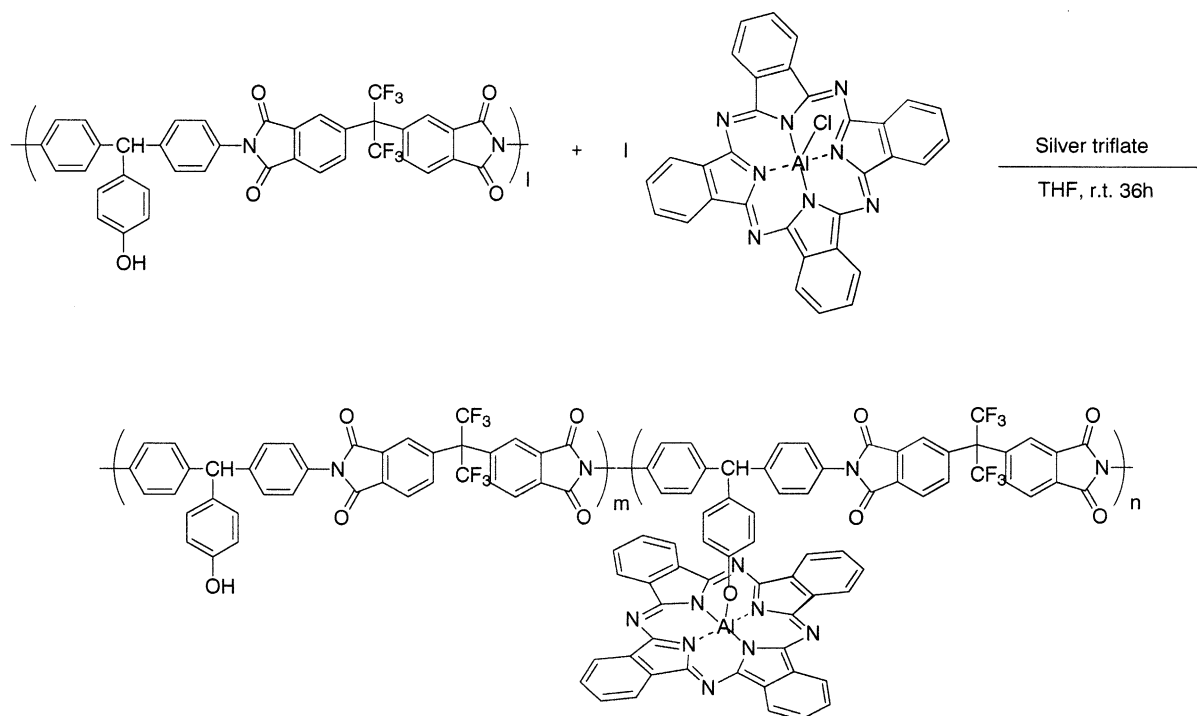
Scheme 2.

analysis. Fig. 1 shows the absorption spectrum (Q band) of APSPI and those of PHIs containing various mol% of AlPcs in NMP. By comparing these absorptions, it was estimated that approximately 60 mol% of the hydroxy groups reacted with AlPcs and the other 40 mol% remained intact. Furthermore, the content of the side-chain AlPcs was estimated to be 61 mol% from elemental analysis.

3.3. Characterization of APSPI

The polymer was confirmed to be the corresponding APSPI by infrared, UV–visible spectroscopies and elemen-

tal analysis. The IR spectrum of APSPI showed characteristic imide group bands at 1780 and 1750 cm^{-1}, and the Al–O bands at 1170 and 1030 cm^{-1}. Elemental analysis also agreed with the theoretical formula weight.

The APSPI obtained was a blue powder product. It is soluble in polar aprotic solvents and THF at room temperature. A transparent film was cast from the solution of the APSPI in these solvents. The UV–visible spectrum of the APSPI thin film (1 μm) exhibited characteristic absorptions at 300–400 (the Soret band) and 600–700 nm (Q band) due to the AlPc.

The thermal behavior of APSPI was studied by thermogravimetry (TG). A typical trace of APSPI is shown in Fig. 2. A rapid weight loss was observed at around
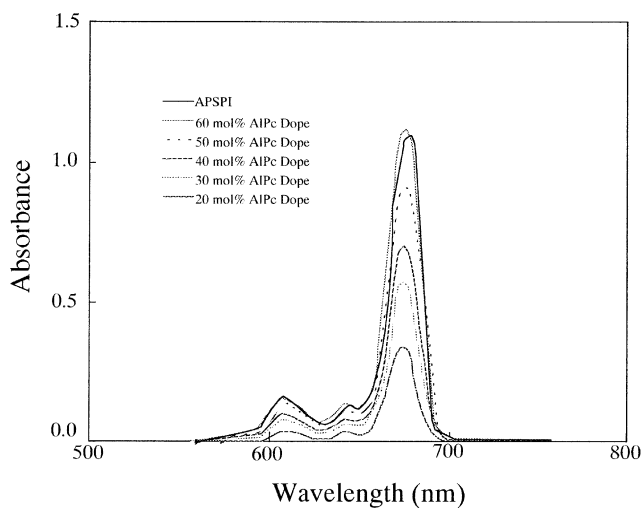

Fig. 1. Visible spectra (Q band) of APSPI and PHIs containing various mol% of aluminum phthalocyanine in NMP.
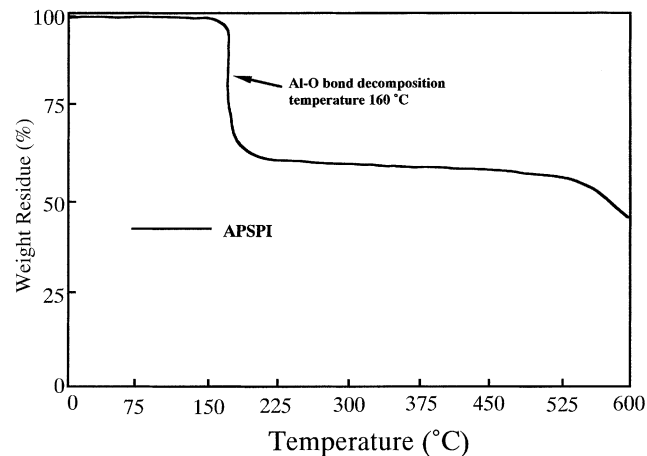

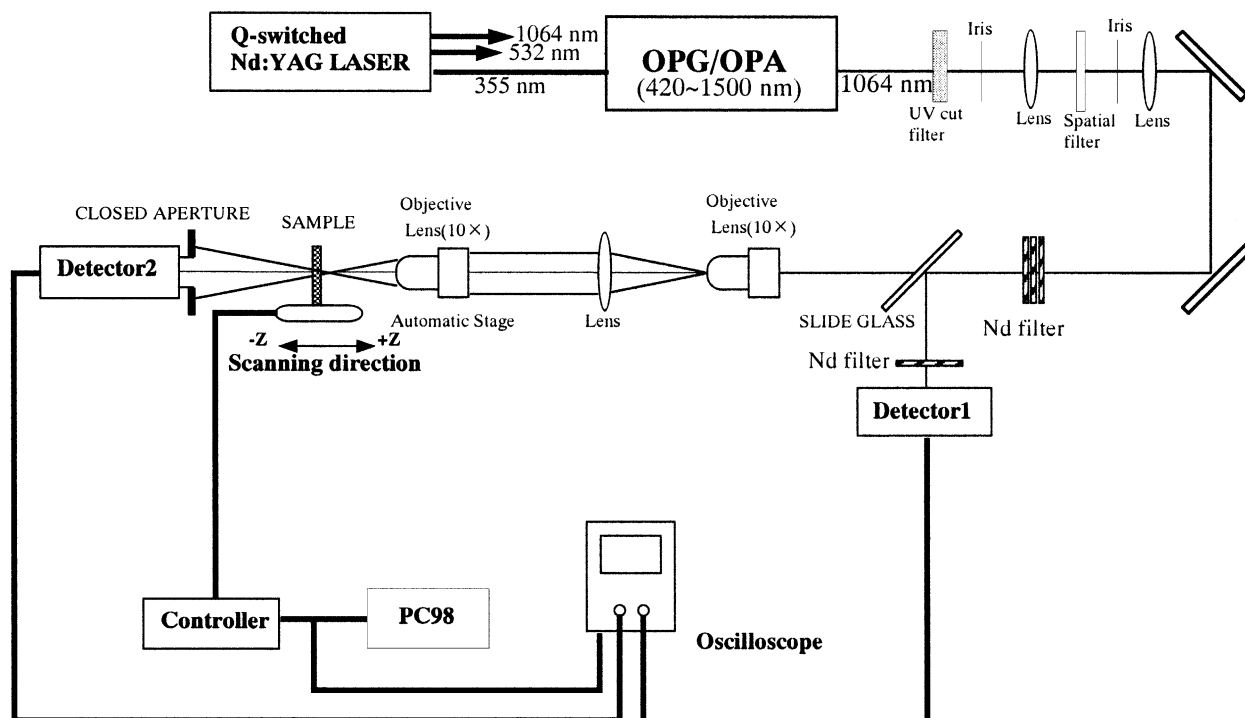Fig. 2. The TG trace of APSPI film under nitrogen.

Fig. 3. Schematic diagram of the experimental setup for measuring nonlinearities refractive using Z-scan technique.

160 °C. The weight loss which was 31% is in good agreement with the expected weight loss for the elimination of the AlPc unit.

The XRD pattern of AlPc represented clear refractions at $2\theta = 8, 11, 26$ and $29°$. On the other hand, the APSPI showed an amorphous profile as which was expected.

3.4. Nonlinear optical properties

The light source employed was a optical parametric generator pumped by the third harmonic of a mode-locked Nd:YAG laser, producing 20 ps (FWHM) pulse tunable from 420 to 1500 nm range, with a pulse repetition rate of 10 Hz. The real third-order nonlinear susceptibilities $\chi(3)$ without resonance enhancement were measured by the closed Z-scan technique at 1064 nm. The closed Z-scan experimental set up is shown in Fig. 3. The low repetition rate was used to avoid thermal effects due to the sample. For the Z-scan experiments a 16 mm focal-length was used, and the intensity at the focal spot was determined by calibration with ZnSe single crystal, whose nonlinear parameters were known [24]. The far-field on-axis transmittance of laser from a nonlinear medium was recorded as a function of Z, the distance from the focusing laser beam waist. In this technique, the sample is scanned along the wave-propagation-axis in the focal region of the focusing gaussian beam. The transmittance changes of the sample on the automatic stage were measured with a detector placed behind an aperture in the far field, and recorded under the control of a microcomputer (NEC PC-9801).

The APSPI film is first placed in the front of the focus ($-z$ in Fig. 3). As the sample stage is moved toward the focus, the increase in irradiation leads to a self-lensing effect that tends to collimate the beam. Thus this effect increases the aperture transmittance (corresponding to the maximum transmittance). As the scan along z-axis is continued, the APSPI film passes the focal plane to the positive z direction, the self-defocusing increases the beam divergence at the aperture, and thus decrease the transmittance (corresponding to the minimum transmittance).

In the Z-scan measurement, the $\chi(3)$ was calculated from the observed transmittance changes ΔT_{p-v}, which is the difference between the normalized peak (the maximum) and valley (the minimum) transmittance: $T_p - T_v$ [24]. Especially, the closed Z-scan measurement was high sensitivity to detect on ΔT_{p-v}. Therefore, the aperture size was very important to determined the nonlinear refractive index n_2 is estimated from phase shift. According to the report of Z-scan measurement [24], n_2 and $\chi(3)$ were calculated from ΔT_{p-v}.

Fig. 4 shows the normalized transmittance of the Z-scan profiles using 3 μm of the APSPI film with the 60% closed aperture at 1064 nm. The values of n_2 and the $\chi(3)$ were determined from ΔT_{p-v}. The value for the APSPI film was $\Delta T_{p-v} = 0.54$ at $I = 0.41$ MW/cm^2 corresponding to $\chi(3) = 4.2 \times 10^{-9}$ esu.

Materials showing optical Kerr effects act as objective lens that focuses beam diffusion [25]. The optical Kerr efficiency is directly proportional to the film thickness of the APSPI film, which in turn is proportional to the molar
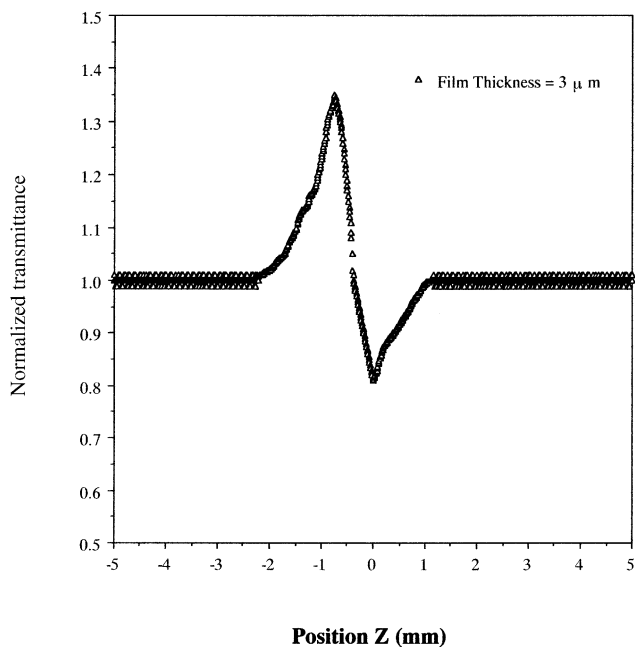
Fig. 4. Normalized transmittance of the Z-scan measurement using sample. The peak power was 0.41 MW/cm^2 for sample.

Fig. 5. Relationship between APSPI film thickness and third order susceptibility $\chi(3)$.

concentration of AlPcs in the APSPI film. To investigate the relationship between film thickness and third order nonlinearity, $\chi(3)$ was measured by controlling film thickness from 0.7 to 5 μm at constant beam intensity. In the Z-scan measurement, the diffraction length of the beam depth (z_0) is expressed by

$$Z_0 = \frac{\pi\omega_0^2}{\lambda}$$

where ω_0 is beam waist radius and λ is the laser wavelength. The sample thickness (L) should be very small, that is, $L \ll Z_0$, so changes in the beam diameter within the sample due to either diffraction or nonlinear refraction can be neglected. In our case, a less than 5 μm film was used. A 0.7 μm thick sample showed no transmittance change, because the sample thickness is much less than the wavelength of the focused beam, and the laser light does not propagate in the medium. The ΔT_{p-v} should be observed over 1 μm film thickness. The increase of transmittance changes was observed from 1 μm up to 5 μm film thickness, and the value of $\chi(3)$ reached to the value of 5.3×10^{-9} esu. These results are shown in Fig. 5. The linearity between the film thickness and values $\chi(3)$ was confirmed.

The irradiance-dependence for the transmittance changes ΔT_{p-v} was investigated using the 3 μm thick APSPI film at the beam irradiance $I < 5$ MW/cm^2. This dependence is shown in Fig. 6, where the measured transmittance changes of ΔT_{p-v} varies linearly with the irradiance power. The linearity of transmittance changes indicates clearly optical Kerr effects.
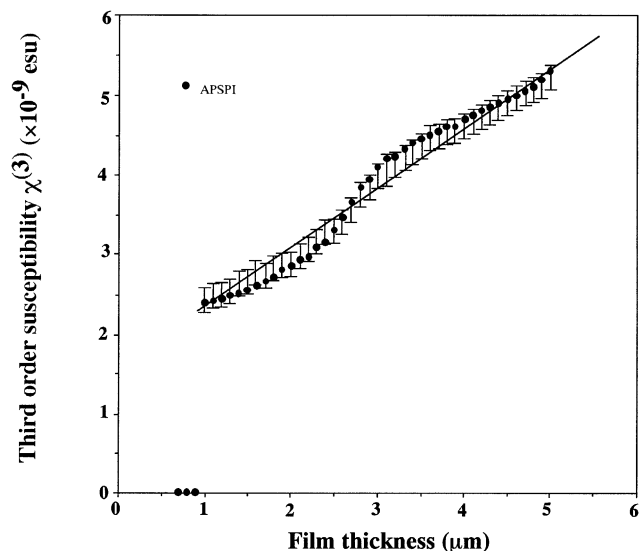
4. Conclusions

A new side-chain third-order nonlinear optical polyimide was successfully prepared by the reaction of poly(hydroxyimide) with aluminum phthalocyanine in the presence of silver triflate. The amount of the side-chain AlPcs in the polymer was determined by visible spectroscopy and supported by elemental analysis 60 mol%. The $\chi(3)$ of APSPI film (5 μm) at the wavelength of 1064 nm was 5.3×10^{-9} esu, evaluated by closed Z-scan technique.

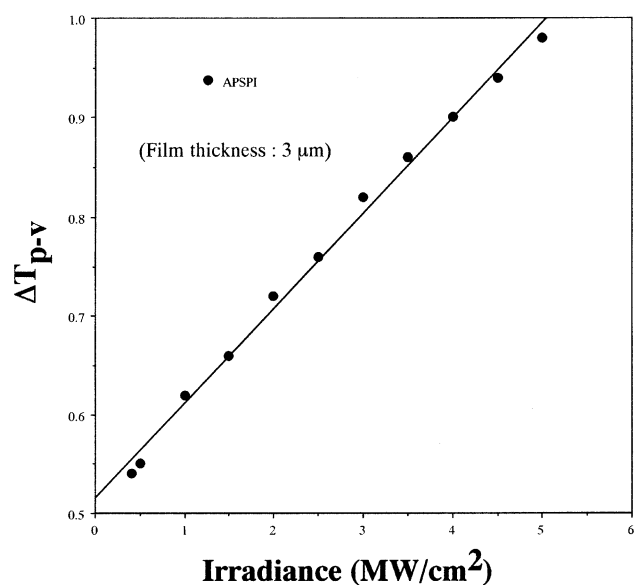This $\chi(3)$ value is very large compared to the largest

Fig. 6. The change of ΔT_{p-v} versus the peak irradiance from the Z-scan measurements using 3.0 μm APSPI film.

reported $\chi(3)$ value (8.1×10^{-11} esu) of vanadyl phthalocyanine thin film at 1907 nm wavelength [26].

Our approach for incorporating organometallic chromophores and two-dimensionally conjugated compounds into a polymer system without crystallization and phase separation will be helpful in developing a high 3 rd-NLO polymer.

Acknowledgements

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