

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Epoxy-based Polymer Containing Imidazole-type Azo Chromophores for Integrated Waveguide Applications

Gang Ye^a; Xin Qu^a; Xiaolin Wang^a; Yiming Bai^b; Yaning He^a; Boyu Wu^b; Xiaogong Wang^a

^a Department of Chemical Engineering, Laboratory for Advanced Materials Tsinghua University, Beijing, P. R. China ^b Department of Electronic Engineering, Tsinghua University, Beijing, P. R. China

Online publication date: 12 October 2010

To cite this Article Ye, Gang , Qu, Xin , Wang, Xiaolin , Bai, Yiming , He, Yaning , Wu, Boyu and Wang, Xiaogong(2010) 'Epoxy-based Polymer Containing Imidazole-type Azo Chromophores for Integrated Waveguide Applications', Journal of Macromolecular Science, Part A, 47: 12, 1167 – 1171

To link to this Article: DOI: 10.1080/10601325.2010.518821

URL: <http://dx.doi.org/10.1080/10601325.2010.518821>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Epoxy-based Polymer Containing Imidazole-type Azo Chromophores for Integrated Waveguide Applications

GANG YE¹, XIN QU¹, XIAOLIN WANG¹, YIMING BAI², YANING HE¹, BOYU WU²
and XIAOGONG WANG^{1,*}

¹Department of Chemical Engineering, Laboratory for Advanced Materials Tsinghua University, Beijing, P. R. China

²Department of Electronic Engineering, Tsinghua University, Beijing, P. R. China

In this work, an epoxy-based polymer containing 2-phenylazo-4, 5-dicyanoimidazole chromophores (BP-IZ-DC) was synthesized and characterized by spectroscopic methods. The polymer showed unusual photo-bleachable property and the refractive index of the polymer could be readily modified by irradiation with a laser beam at visible wavelength. The irradiation with a laser beam at 488 nm caused a much more significant change of the refractive index than irradiation with 532 nm laser light. Upon the irradiation with the laser beam (488 nm, 100 mW/cm²) for 1 h, the refractive index decreased from 1.6512 to 1.5802. By using the photo-bleachable azo polymer, channel waveguide was fabricated by light irradiation through a mask and the light-transmission ability of the waveguide was evaluated.

Keywords: Azo polymer, imidazole, photo-bleaching, refractive index, integrated waveguide

1 Introduction

Polymers containing azobenzene and its derivatives (azo polymer for short) have been intensively study in recent years (1–5). When irradiated with light at appropriate wavelengths, azobenzenes can undergo a reversible *trans-cis* isomerization and trigger many photoresponsive variations (6–9). Azo polymers have been prepared by many different methods and studied for those interesting properties (8,9). As one of the feasible preparation methods, azo polymers can be synthesized through post-polymerization azo-coupling reaction (10,11). In the processes, the azo polymers are synthesized by the azo-coupling reactions between precursor polymers containing anilino moieties and diazonium salts in polar organic solvents. This method introduces azo chromophores through an *in situ* formation manner at the final step of the preparation, some possible side-reaction on azo chromophores can be avoided and different types of azo polymers can be prepared by this method (12–16).

Nonlinear optical (NLO) effect is an interesting property of azo polymers, which offers new possibilities for the production of versatile and highly effective optical and electro-optical (EO) devices (17,18). Optical channel waveguide is one of the most common components in EO modulators and integrated optics devices. In a typical waveguide, light is confined in the channel with higher refractive index. Recent years, adjusting refractive index of polymeric films through photo-irradiation has become a recognized technique for waveguide fabrication (19–22). By this technique, the refractive index of the bleached part can be easily tailored by controlling the irradiation condition. The index contrast between the cores and the claddings of the channel waveguides can be adjusted to the desirable values. This technique combined with conventional photolithography or direct UV etching has been applied to different polymer systems, such as acrylic polymers and polyimides (23–25). However, most of the polymer systems reported contain more than one-components and high intensity UV irradiation for a long time is often required (23,24). Moreover, the refractive index change caused by the irradiation is still relatively small. Therefore, developing new one-component polymer system with easily adjustable refractive index is of interest in the channel waveguide preparation and other applications. Although azo polymers have been intensively studied for NLO effect and photophysical properties related to the *trans-cis* isomerization, report concerning the

Dedicated to the memory of Professor Sukant K. Tripathy

*Address correspondence to: Xiaogong Wang, Department of Chemical Engineering, Laboratory for Advanced Materials, Tsinghua University, Beijing, 100084, P. R. China. E-mail: wxg-dce@mail.tsinghua.edu.cn

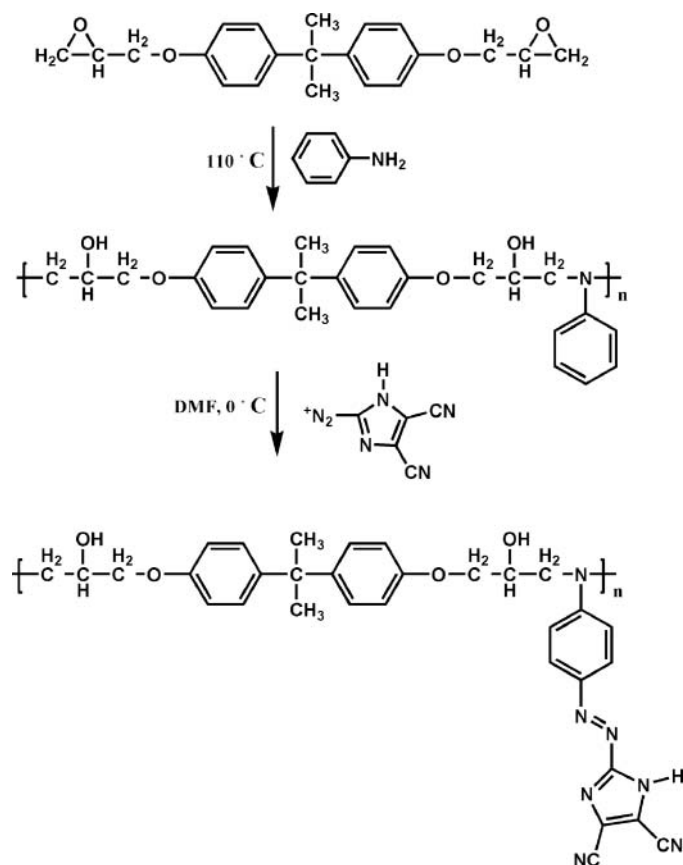
fabrication of azo polymer waveguide through visible light irradiation is still scarce in the literature.

In this work, an epoxy-based polymer containing 2-phenylazo-4, 5-dicyanoimidazole chromophores was prepared. The polymer showed good optical transparency and film-forming ability. The refractive index of the polymer films could be feasibly adjusted by visible light irradiation. The photo-induced refractive index change was studied by irradiation with visible laser light at two different wavelengths (488 nm and 532 nm). By using the azo polymer, channel waveguide was fabricated through light irradiation and its performance was evaluated.

2 Experimental

2.1 Materials

Diglycidyl ether of bisphenol-A ($M_w = 392$) and 2-amino-4,5-imidazoledicarbonitrile were purchased as commercial products from Shell Company and TCI. All other reagents and solvents were obtained from commercial sources and used as received without further purification. The polymer was synthesized according to the schemes shown in Scheme 1. Details of the syntheses and characterization are described in the following sections.



Sch. 1. Synthetic route of azo polymer BP-IZ-DC.

2.2 Characterization

$^1\text{H-NMR}$ spectra were obtained on a JOEL JNM-ECA300 spectrometer (300 MHz for proton). The glass transition temperatures (T_g s) of the polymers were obtained with a TA Instruments DSC 2920 at a heating rate of $10^\circ\text{C}/\text{min}$ under N_2 protection. Molecular weights and molecular weight distributions were determined by using a gel permeation chromatography (GPC) instrument (SHIMADZU, LC-20AD) at room temperature with THF as eluent ($1\text{ mL}\cdot\text{min}^{-1}$). The instrument was equipped with a refractive index (RI) detector (Wyatt Optilab rEX) and fitted with a PLgel $5\ \mu\text{m}$ mixed-D column. The column was calibrated with linear polystyrene standards. The UV-Vis spectra of the samples were recorded by a Perkin-Elmer Lambda Bio-40 spectrophotometer. The refractive indices were measured by prism-coupling method at wavelength of 1315 nm.

2.3 Azo Polymer Synthesis

BP-AN: BP-AN was obtained from the reaction between diglycidyl ether of bisphenol-A (32.7 g, 0.083 mol) and aniline (7.7 g, 0.083 mol) according to literature (12). GPC: $M_n = 35\ 000$; $M_w = 79\ 000$; MWD = 2.2. The glass transition temperature (T_g) of the polymer was determined to be 87°C . IR (KBr): $3380\ \text{cm}^{-1}$ (O-H, m), $1600\ 1510\ 1463\ \text{cm}^{-1}$ (Benz. ring, s), $1250\ \text{cm}^{-1}$ (C-O, s). $^1\text{H NMR}$ ($\text{DMSO-}d_6$): $\delta = 7.07$ (6H, d), 6.82 (4H, d), 6.72 (2H, d), 6.54 (1H, m), 4.03 (2H, m), 3.87 (4H, s), 3.34–3.75 (4H, m), 1.55 (6H, s).

BP-IZ-DC: BP-AN (1.892 g, 4 mmol) was dissolved in DMF (200 mL) at 0°C . A diazonium salt of 2-amino-4,5-imidazoledicarbonitrile was prepared by adding an aqueous solution of sodium nitrite (0.345 g, 5 mmol in 1 mL of water) into a solution of 2-amino-4,5-imidazoledicarbonitrile (0.586 g, 4.4 mmol) in a homogeneous mixture of 1 mL of sulfuric acid and 15 mL of glacial acetic acid. The mixture was stirred at 0°C for 10 min and then was added dropwise into the BP-AN solution. The solution was stirred at 0°C for 12 h. Then the solution was poured into plenty of water and the precipitate was collected and dried. The product was dissolved in 40 mL THF and precipitated into 400 mL petroleum ether. The final product was vacuum dried at 60°C for 24 h. IR (KBr, cm^{-1}): 3400 (O-H, m), 1600, 1508 (Benz. ring, s), 1230 (C-O, s). $^1\text{H-NMR}$ ($\text{DMSO-}d_6$): $\delta = 7.79$ (CH, 2H, d), 7.12 (CH, 4H, br), 7.03 (CH, 2H, br), 6.86 (CH, 4H, br), 4.17 (CH, 2H, br), 3.95 (CH₂, 4H, br), 3.86 (CH₂, 2H, br), 3.65 (CH₂, 2H, m), 1.57 (CH₃, 6H, s).

2.4 Polymer Film Preparation and Photo-bleaching

The homogeneous solution of BP-IZ-DC in anhydrous *N,N*-dimethylformamide (DMF) (about 10 wt%) was filtered through $0.45\ \mu\text{m}$ membrane and spin-coated onto glass or silica substrates. The film thickness was controlled to be in

the range of 0.5–0.8 μm by adjusting the solution concentration and the spin speed (800–1200 rpm). The spin-coated films were dried at 60°C under vacuum for 48 h and were stored in a desiccator for further measurements. For the photo-bleaching test, the films were vertically irradiated with a laser beam at two different wavelengths (488 nm and 532 nm). The laser beam was from an Ar^+ laser or solid-state diode laser, which was spatially filtered, expanded and collimated. The light intensity of the laser beam was controlled to be 100–120 mW/cm^2 . After exposure to the laser beam for different time periods, the refractive indices of the exposed areas were measured by the prism coupling method.

3 Results and Discussion

3.1 Polymer Synthesis and Characterization

Epoxy-based precursor polymer BP-AN was prepared through polycondensation as shown in Scheme 1. To avoid the reaction between the secondary OH groups formed during the polymerization and the unreacted epoxide groups, the polymerization was carried out at a relatively low temperature (110°C) (12). Number average molecular weight of BP-AN was estimated to be 35000 with polydispersity index of 2.2, obtained by gel permeation chromatography (GPC).

The precursor polymer was functionalized to introduce the imidazole-containing azo chromophores through post-polymerization azo-coupling reaction (Sch. 1) (13). The diazonium salts readily attack the benzene rings of the anilino moieties at *para*-positions with higher electron density. The electrophilic substitution exclusively takes place at the *para*-positions also because of the bulkiness of the attacking groups and steric hindrance. For precursor polymer BP-AN, the chemical shifts of aniline moieties, appearing at about 7.10 ppm (overlapped), 6.75 ppm (doublet), and 6.55 ppm (multiplet), are resonances of the protons at *meta*-, *ortho*-, and *para*-positions of the amino groups. After the azo-coupling reaction, the 6.55 ppm resonance corresponding to protons at the *para*-positions of the amino groups disappear. It proves that the substitution has taken place at the *para*-positions with high yield. The analysis data of the polymers are given in the experimental part.

The UV-Vis spectrum of BP-IZ-DC is given in Figure 1, which shows typical spectral feature of pseudo-stilbene type azo chromophores. The strong absorption band appearing in the visible range (λ_{max} at 490 nm) corresponds to the $\pi-\pi^*$ electron transition of the azo chromophores. BP-IZ-DC is an amorphous polymer with the glass transition temperature (T_g) of 173°C determined by differential scanning calorimetry (DSC).

3.2 Photo-induced Refractive Index Change

The influence of light on the refractive index was studied by irradiating BP-IZ-DC films with an Ar^+ laser or a

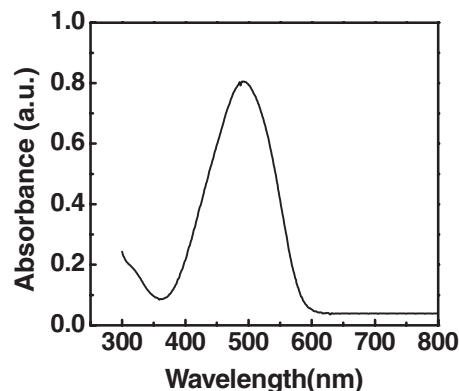


Fig. 1. UV-Vis spectrum of BP-IZ-DC in DMF.

solid-state diode laser. The light irradiation caused significant photo-bleaching effect, which could be observed by the naked eye. Figure 2 gives a photograph of a piece of BP-IZ-DC film, after irradiated with Ar^+ laser beam (488 nm, 100 mW/cm^2) for 30 min. There is an obvious color change in the exposed area (yellowish part) after the irradiation. Figure 3 shows the UV-Vis absorption spectrum of a piece of BP-IZ-DC film on glass substrate before and after exposure to Ar^+ laser light (488 nm, 100 mW/cm^2) for different time. It can be seen that the maximum absorption at around 490 nm decreases significantly and the absorption band is blue-shifted as the exposure time increases. After 60 min irradiation, the intensity of the maximum absorption decreases to about 25% of the original value, and the λ_{max} shifts to 450 nm. The result indicates that the number of the azo chromophores is significantly decreased due to the light irradiation.

To study the effect of the photo-bleaching on the refractive index of the BP-IZ-DC films, the refractive indexes in the exposed areas were measured by the prism coupling method. For comparison, the films were irradiated with a laser beam at two different wavelengths (488 nm and 532 nm), which had the same intensity (100 mW/cm^2). Figure 4 shows the refractive index changes of the BP-IZ-DC films with the exposure time. It can be seen that the refractive indices decrease as the exposure time increases. A larger refractive index decrease is caused by irradiation at 488 nm. After irradiation for 1 h, the

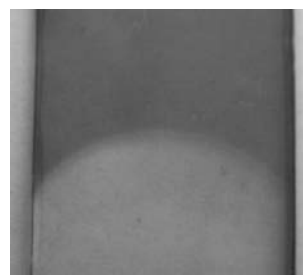


Fig. 2. Photograph of the partially bleached BP-IZ-DC film.

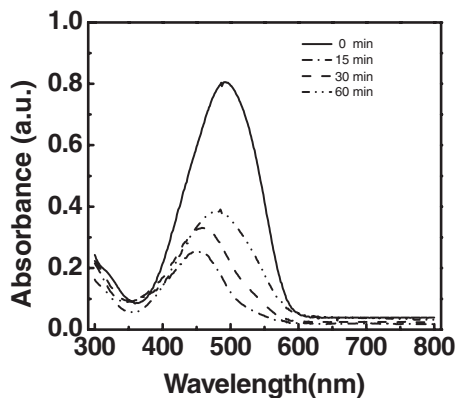


Fig. 3. UV-vis absorption spectra of a BP-IZ-DC film before and after exposed to Ar^+ laser beam (488 nm, $100 \text{ mW}/\text{cm}^2$) for 15 min, 30 min, and 60 min.

refractive index of the BP-IZ-DC film changes from 1.6512 to 1.5802. When irradiated with the light at the wavelength of 532 nm for 1 h, the refractive index only changes from 1.6512 to 1.6075. The results indicate that the refractive index change is related with the electron excitation of the azo chromophores. The 488 nm light is close to the absorption band of the $\pi - \pi^*$ transition ($\lambda_{\text{max}} = 490 \text{ nm}$) of the azo chromophores, which can more efficiently cause the excitation of the π electrons in the conjugated system.

3.3 Photo-fabrication of Channel Waveguide

Channel waveguide was fabricated by a procedure illustrated in Figure 5. First, BP-AN and isocyanate crosslinking agent M20S were dissolved in DMF to obtain a homogeneous solution. The bottom cladding layer was obtained by spin-coated the solution on the Si substrate and curing properly. After that, BP-IZ-DC as the core layer was spin-coated on the cladding layer and vacuum-dried. The thickness of the core layer was controlled to be $1 \mu\text{m}$. A beam from Ar^+ laser (488 nm) was used as the light source,

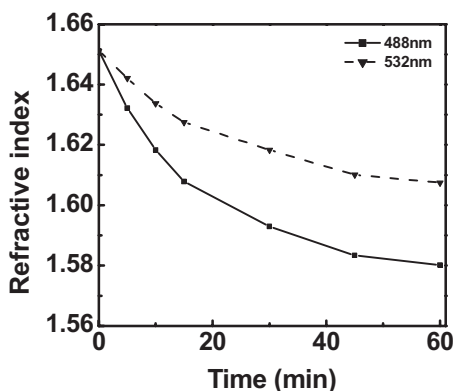


Fig. 4. Refractive index variation of BP-IZ-DC films upon irradiation with the lasers at two different wavelengths.

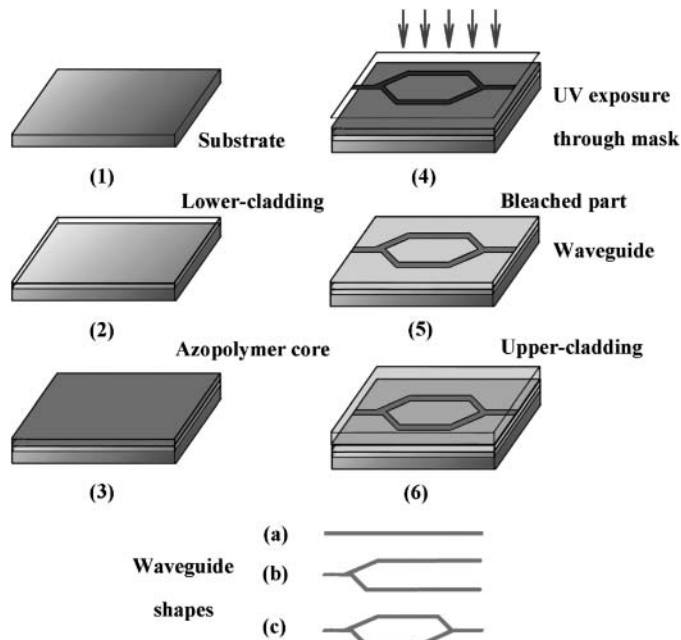


Fig. 5. Schematic of the fabrication of waveguide through a photo-bleaching approach.

which was spatially filtered, expanded and collimated and had an intensity of $100 \text{ mW}/\text{cm}^2$. The film was irradiated with the light through a chromium mask with the waveguide pattern. During the process, the mask was tightly attached on the core layer surface to avoid possible diffraction. After writing the channel waveguide, UV-curable agent NOA73 as top cladding layer was spin-coated on the core layer. The top cladding layer was cured under irradiation of a high-pressure Hg lamp ($54 \text{ mW}/\text{cm}^2$) and post-baked by conventional method. The waveguide was then cut to a required size and connected with the optical fibers.

Figure 6 shows the microscopic images of the waveguide and the coupling optical fiber. The photo-bleaching

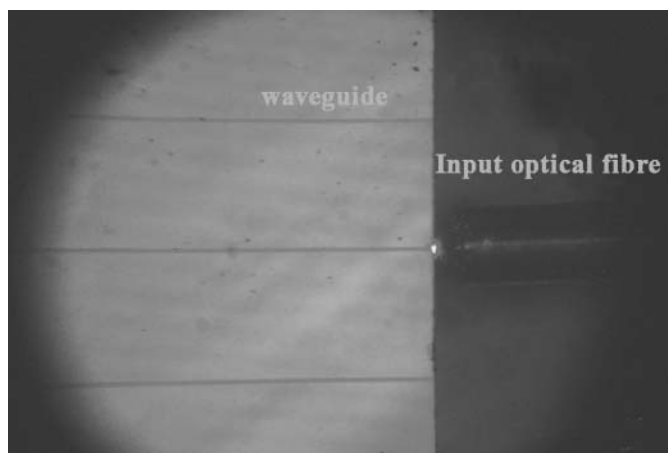


Fig. 6. Microscopic images of waveguide and connected optical fiber.

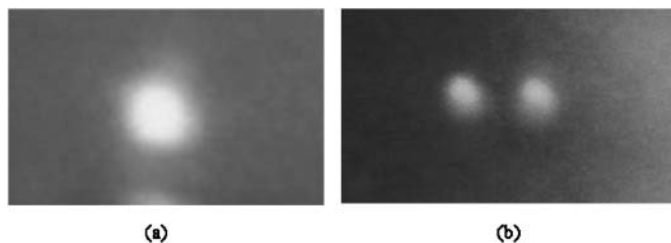


Fig. 7. Photographed light spots output from (a) the single waveguide, (b) the Y-branched waveguide.

at the exposed area can be clearly seen. Optical waveguide transmission measurement was performed by using commercial single-mode optical fibers and infrared light with wavelength of $1.341\ \mu\text{m}$. The light spots output from the single waveguide and the Y-branched waveguide were photographed (Fig. 7). The optical loss was calculated by comparing the intensity of the input and output light. The total loss including the propagation loss and the coupling loss for the 2.2 cm long waveguide was 36.7 dB. The coupling loss between the fiber and waveguide at each end was previously measured to be 4.0 dB. The propagation loss was estimated to be 13.05 dB/cm.

The above results indicate that the channel waveguide can be prepared by the light irradiation process. Although the waveguide preparation is simple, the optical loss is obviously too high for many applications. As there is huge room for improvements from materials to fabrication, we believe that this interesting property of BP-IZ-DC, possibly also for some other azo polymers, can be further explored to meet the requirement for real applications.

4 Conclusions

In this work, an epoxy-based azo polymer (BP-IZ-DC) was synthesized by post-polymerization azo-coupling reaction. The polymer showed unusual photo-bleaching effect and the refractive index of the polymer films could be readily modified by irradiation with a visible laser beam. The irradiation with 488 nm light induced a more significant decrease in the refractive index than irradiation with 532 nm light. After irradiation with the laser beam (488 nm, $100\ \text{mW}/\text{cm}^2$) for 1 h, the refractive index of the BP-IZ-DC film decreased from 1.6512 to 1.5802. The channel waveguide of BP-IZ-DC was successfully prepared by laser irradiation method but the optical loss of the waveguide was high.

Acknowledgement

The financial support from MOST under 863-Projects 2007AA03Z409 is gratefully acknowledged.

References

- Xie, S., Natansohn, A. and Rochon, P. (1993) *Chem. Mater.*, 5(4), 403–411.
- Natansohn, A. and Rochon, P. (1999) *Adv. Mater.*, 11(16), 1387–1391.
- Dalton, L. R. (2000) *Opt. Eng.*, 39(3), 589–595.
- Rochon, P., Batalla, E. and Natansohn, A. (1995) *Appl. Phys. Lett.*, 66(2), 136–138.
- Kim, D. Y., Tripathy, S. K., Li, L. and Kumar, J. (1995) *Appl. Phys. Lett.*, 66(10), 1166–1168.
- Kumar, G. S. and Neckers, D. C. (1989) *Chem. Rev.*, 89(8), 1915–1925.
- Cojocariu, C. and Rochon, P. (2004) *Pure Appl. Chem.*, 76(7–8), 1479–1497.
- Natansohn, A. and Rochon, P. (2002) *Chem. Rev.*, 102(11), 4139–4175.
- Delaire, J.A. and Nakatani, K. (2000) *Chem. Rev.*, 100(5), 1817–1845.
- Wang, X.G., Chen, J.I., Marturunkakul, S., Li, L., Kumar, J. and Tripathy, S.K. (1997) *Chem. Mater.*, 9(1), 45–50.
- Wang, X.G., Kumar, J., Tripathy, S.K., Li, L., Chen, J.I. and Marturunkakul, S. (1997) *Macromolecules*, 30(2), 219–225.
- Wang, X. G., Yang, K., Kumar, J., Tripathy, S. K., Chittibabu, K. G., Li, L. and Lindsay, G. (1998) *Macromolecules*, 31(13), 4126–4134.
- He, Y.N., Wang, X.G. and Zhou, Q.X. (2002) *Polymer*, 43(26), 7325–7333.
- Che, P.C., He, Y.N. and Wang, X.G. (2005) *Macromolecules*, 38(21), 8657–8663.
- Wang, D., Ye, G., Zhu, Y. and Wang, X. (2009) *Macromolecules*, 42(7), 2651–2657.
- Wang, D.R., Ye, G. and Wang, X.G. (2007) *Macromol. Rapid. Comm.*, 28(23), 2237–2243.
- Hattori, T., Shibata, T., Onodera, S. and Kaino, T. (2000) *J. Appl. Phys.*, 87(7), 3240–3244.
- Ivanov, M., Todorov, T., Nikolova, L., Tomova, N. and Dragostinova, V. (1995) *Appl. Phys. Lett.*, 66(17), 2174–2176.
- Rochford, K.B., Zanoni, R., Gong, Q. and Stegeman, G.I. (1989) *Appl. Phys. Lett.*, 55(12), 1161–1163.
- Diemeer, M., Suyten, F., Trommel, E.S., McDonach, A., Copeland, J.M., Jenneskens, L.W. and Horsthuis, W. (1990) *Electron. Lett.*, 26(6), 379–380.
- Aramaki, S., Assanto, G. and Stegeman, G.I. (1990) *Electron. Lett.*, 26(16), 1300–1301.
- Beeson, K.W., Horn, K.A., McFarland, M. and Yardley, J.T. (1991) *Appl. Phys. Lett.*, 58(18), 1955–1957.
- Koo, J.S., Smith, P., Williams, R.B., Grossel, M.C. and Whitcombe, M.J. (2002) *Chem. Mater.*, 14(12), 5030–5036.
- Koo, J.S., Smith, P., Williams, R.B., Riziotis, C. and Grossel, M.C. (2003) *Opt. Mater.*, 23(3–4), 583–592.
- Sarkisov, S., Teague, Z., Venkateswarlu, P., Abdeldayem, H., Frazier, D. and Adamovsky, G. (1997) *J. Appl. Phys.*, 81(6), 2889–2891.