

Synthesis and Characterization of Side-Chain Polyimides for Second-Order Nonlinear Optics via a Post-Azo-Coupling Reaction

YAN-GANG LIU, YU SUI, JIE YIN, JIAN GAO, ZI-KANG ZHU, DE-YIN HUANG, ZONG-GUANG WANG

School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, Shanghai, 200240, China

ABSTRACT: A two-step, generally applicable synthetic approach for nonlinear optical (NLO) side-chain polyimides was developed. This included the preparation of a preimidized, organosoluble polyimide with benzene moiety pendant from main chains, followed by the covalent bonding of the NLO chromophores onto the polyimide backbone via a post-azo-coupling reaction. The degree of functionalization of polyimides was estimated by UV-VIS spectroscopy. The glass transition temperature (T_g) of a polyimide decreased by only 10–20°C after the functionalization, which was much smaller than the decrease in T_g when the chromophores were chemically bonded to the polyimide main chains through an ether linkage using a post-Mitsunobu condensation. The solubility and thermal stability of polyimides were also studied. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 290–295, 2000

Key words: nonlinear optical materials; polyimide; side chain, post-azo coupling

INTRODUCTION

Organic poled polymers offer great promise for the fabrication of integrated optical devices due to their large electrooptic coefficients, low dielectric constants (desirable for high-speed devices), and flexibility in fabrication. Many second-order nonlinear optical (NLO) polymers have been studied, and the thermal stability of the poled state has been one of the major problems requiring improvement for practical device applications.^{1–9} Recent studies on side-chain polyimides for second-order nonlinear optics show some encouraging results. Miller et al.,^{10–15} Yu et al.,^{16–25} Jen et al.,^{26–29} and some other groups^{30–42} have developed new NLO polyimide systems. All these side-chain polyimides exhibit excellent properties, including high temperature alignment stability, good mechanical properties, and low optical loss.

However, most of the side-chain polyimides studied are synthesized via a general condensation reaction between diamines and dianhydrides to afford poly(amic acid) precursor polymers, followed by a high-temperature imidization or a chemical imidization process to produce the projected polyimides. That few chromophores can survive the relatively harsh chemical conditions of the monomer synthesis and the imidization of the polymers severely limits the application of the methodologies. Chen et al.²⁹ reported a facile approach for the synthesis of NLO side-chain aromatic polyimides, which included the preparation of a preimidized, hydroxyl-containing polyimide, followed by the covalent bonding of the NLO chromophores onto the polyimide backbone via a mild post-Mitsunobu condensation to avoid the harsh imidization process. However, the ether linkage formed after the post-Mitsunobu condensation may lower the thermal stability of the NLO side-chain polyimides. The glass transition temperatures (T_g s) of these NLO side-chain polyimides may decrease by up to 130°C after the postfunctionalization.²⁹

Correspondence to: J. Yin.

Contract grant sponsor: Shanghai Novel Materials Research Center.

Journal of Applied Polymer Science, Vol. 76, 290–295 (2000)
© 2000 John Wiley & Sons, Inc.

The azo coupling reaction, a common method used to synthesize azo dyes, was found to be applicable to functionalizing polymer materials. Using an azo coupling reaction to functionalize polymers enables the introduction of the NLO chromophores and the extension of the conjugation length of the chromophores to take place in the same reaction step. One of the first reported polymers used as a precursor to prepare NLO polymers through the azo coupling reaction was a copolymer of methyl methacrylate and methacrylate ester of *N*-ethyl-*N*-(hydroxyethyl)aniline in an acetic acid medium.⁴³ Wang et al.^{44–45} found that the azo coupling reaction between polymer and diazonium salt can be carried out in polar organic solvents (e.g., *N,N*-dimethyl formamide and *N,N*-dimethyl acetamide) with high reaction yield. They prepared a series of novel epoxy-based NLO polymers through a post-azo-coupling reaction. Recently, we found that the azo coupling reaction can be used to postfunctionalize organosoluble polyimides. Two series of organosoluble polyimides with benzene moieties pendant from main chains have been synthesized and fully imidized. The mild azo coupling reaction was then used to introduce the NLO chromophores to the benzene rings at the *para* positions, which possess relatively high electron densities and low steric hindrance. This procedure allows us to synthesize NLO side-chain polyimides with great flexibility in the selection of both the polymer backbones and chromophores. The characterization and properties of polyimides are also reported in this article.

EXPERIMENTAL

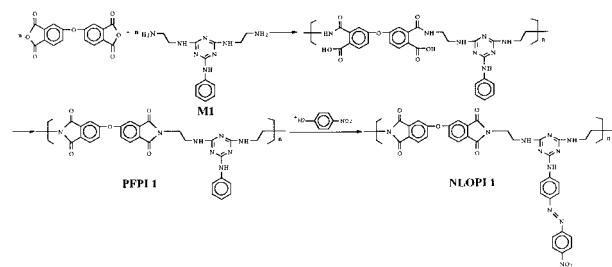
Materials

The laboratory reagent 2,4,6-trichloro-1,3,5-triazine was purchased from the Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan), and purified by the recrystallization in benzene prior to reaction. Trimellitic anhydride acid chloride, another laboratory reagent, was purchased from the Tokyo Chemical Industry Co., Ltd., and used as received. Aniline (analytical reagent grade) was purchased from the Shanghai No. 3 Reagent Company (Shanghai, China) and purified by distillation over calcium hydride. Purchased from the Shanghai Reagent Company (Shanghai, China) were 2-Chloroethanol, ethylene diamine,

p-nitroaniline, and 4,4'-diaminodiphenyl ether (ODA) (all analytical reagent grade); they were used as received. We synthesized 4,4'-diamino-3,3'-dimethyl diphenylmethane (MMDA) in our lab⁴⁶. Diphenylether-3,3',4,4'-tetracarboxylic acid dianhydride (ODPA) (an industrial product) was purchased from Shanghai Research Institute of Synthetic Resins (Shanghai, China) and dried at 190°C for 2 h before use. *N*-methyl-2-pyrrolidone (NMP) (analytical reagent grade) was purchased from the Shanghai Reagent Company and dried over molecular sieves before use. Acetic anhydride (analytical reagent grade) and triethyl amine (analytical reagent grade) were purchased from the Shanghai No. 1 Reagent Company (Shanghai, China) and the Shanghai No. 3 Reagent Company, respectively, and used as received. Common reagents used in organic synthesis such as sodium carbonate and hydrochloric acid were used as received. Common solvents for solubility measurement, such as cyclohexane, toluene, acetone, tetrahydrofuran (THF), chloroform, NMP, *N,N*-dimethyl acetamide (DMAc), *N,N*-dimethyl formamide (DMF), dimethylsulfone (DMSO), and 1,4-butyrolactone were used without purification.

Synthesis of 2,4-di- β -Aminoethylamino-6-phenylamino-1,3,5-triazine (M1)

To a cooled (<5°C) solution of aniline (1.85 g, 0.02 mol) in anhydrous ethanol (30 mL) was added 2,4,6-trichloro-1,3,5-triazine (3.69 g, 0.02 mol). After being neutralized with a 40 wt % sodium carbonate aqueous solution, the solution was stirred for another 6 h. It was then slowly added to a mixture of ethylene diamine (2.40 g, 0.04 mol), water (30 mL), and hydrochloric acid (36%, 3.7 mL, 0.043 mol) under the protection of nitrogen. The mixture was stirred at 40°C for 5 h and then heated to 80°C to remove ethanol by distillation. The mixture was heated to 100°C and refluxed for another 4 h. Upon cooling, the mixture was basified to a pH value of 10. The resulting solid was collected by filtration and washed with water. It was further purified by being dissolved in 100 mL of water while keeping the pH value at 5. The mixture was stirred at 50°C for 30 min under the protection of nitrogen and then filtered. The filtrate was basified to a pH value of 10 and then extracted three times with diethyl ether. Upon the removal of the diethyl ether by distillation, yellow-green crystals were obtained. [IR (KBr): 3481, 3355 (NH₂), 1443 (triazine) cm⁻¹; UV/VIS (ethanol): λ_{\max} (nm) = 267.]



Scheme 1 Synthesis and post-azo-coupling reaction of PFPI 1.

N,N-di(2-Hydroxyethyl)aniline

To a mixture of 20 mL ethylene glycol and 10 mL water were added 36.5 mL (0.40 mol) aniline and 10 mL triethyl amine. The mixture was heated to 40°C and then 60 mL (0.89 mol) of 2-chloroethanol was added. The mixture was further heated to 95°C, and 65 mL 30 wt % NaOH aqueous solution was added dropwise over approximately 2 h. The mixture was stirred for another 3 h, and the oil layer was collected and distilled under reduced pressure. White crystals were obtained. [mp 57–58°C; IR (KBr): 3400 (OH), 2900 (CH₂) cm⁻¹].

Preparation of a bis-(Aromatic dicarboxylic acid anhydride) with a Benzene Pendant from Main Chain (M2)

M2 was prepared by a reported method⁴⁷ from trimellitic anhydride acid chloride and *N,N*-di(2-hydroxyethyl)aniline. [mp: 198–199°C.; ¹H-NMR (CDCl₃): δ = 8.38 (s;H²), 8.11 (d;H²), 7.72 (d;H²), 7.16 (m;H²), 6.92 (d;H²), 6.61 (t;H²), 4.51 (m;H⁴), and 3.85 (m;H⁴)].

Preparation of PFPI 1 (Scheme 1)

Diphenylether-3,3',4,4'-tetracarboxylic acid dianhydride (ODPA) (1.08 g, 3.47 mmol) and M1 (1.00 g, 3.47 mmol) were added to 14 mL NMP. After stirring at room temperature for 4 h, the resultant poly(amic acid) (PAA) was imidized with a mixture of acetic anhydride and triethyl amine (diamine–acetic anhydride–triethyl amine = 4:36:9 in mol ratio) at 25°C for 48 h. The resultant polyimide (PFPI 1) was precipitated into a mixture of methanol (100 mL) and water (100 mL). The polyimide was further purified by extraction with methanol for 24 h and then dried at 80°C under vacuum for 2 days.

Preparation of PFPI 2 and PFPI 3 (Scheme 2)

PFPI 2 and PFPI 3 were prepared from M2, 4,4'-diaminodiphenylether (ODA) and 4,4'-diamino-

3,3'-dimethyl diphenyl methane (MMDA), respectively, via a procedure similar to that described above for the synthesis of PFPI 1.

Preparation of NLOPI 1 (Scheme 1)

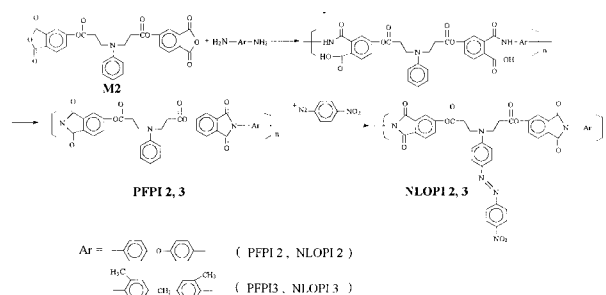
A mixture of *p*-nitroaniline (0.70 g, 5.00 mmol), sodium nitrite (0.375 g, 5.50 mmol), and water (1.4 mL) was added slowly to a solution of hydrochloric acid (36%, 1.5 mL) and ice water (1.5 mL) to maintain the temperature of the reactant at 5–10°C with efficient agitation. The reactant was stirred for 1 additional h and then added to a cooled solution of PFPI 1 (2.5 g) in NMP (20 mL). The mixture was stirred for 1 h and then precipitated into the mixture of methanol (100 mL) and water (100 mL). The orange-yellow solids were obtained and further purified by extraction with methanol for 24 h and then dried at 80°C under vacuum for 2 days.

Preparation of NLOPI 2 and NLOPI 3 (Scheme 2)

NLOPI2 and NLOPI3 were prepared by the reaction between the diazonium salt of *p*-nitroaniline and PFPI 2 or PFPI3, respectively, via a procedure similar to that described above for the synthesis of NLOPI 1.

Characterizations

The FTIR spectra of organic intermediates and polyimide thin films were recorded on a Perkin-Elmer Paragon 1000 FTIR spectrophotometer. The thin films were cast from the dilute polyimide solutions on KBr. The ¹H-NMR spectra of the organic intermediates were obtained on a Varian Gemini-300 ¹H-NMR spectrometer. A Perkin-Elmer Lambda 20 UV-VIS spectrophotometer was used to record the UV-VIS spectra of dilute chromophore solutions (10⁻⁴M) in ethanol, using



Scheme 2 Synthesis and post-azo-coupling reaction of PFPI 2 and PFPI 3.

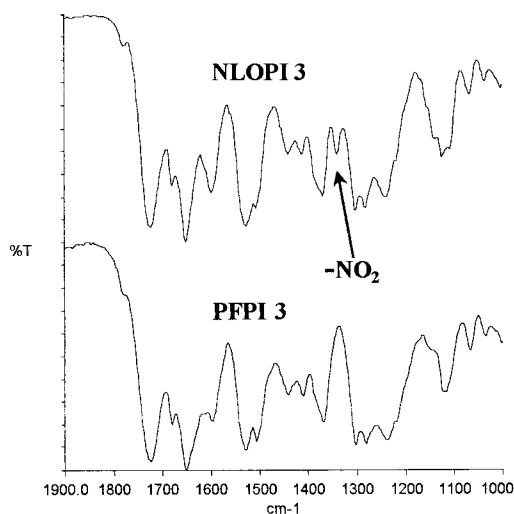


Figure 1 Infrared spectra of PFPI 3 and NLOPI 3.

ethanol as the reference, and polyimide solutions ($10^{-4}M$) in NMP, using NMP as the reference. The solubility of the polyimides was determined by observing the solubility of the solid polyimides in various solvents at room temperature. The glass transition temperatures (T_g) of the polyimides were determined by differential scanning calorimetry (DSC). The DSC curves were recorded on a Perkin-Elmer Pyris I DSC under the protection of N_2 . The scan rate was $20^\circ C/min$. All samples experienced two heating cycles from $25^\circ C$ to $300^\circ C$, and the second one was recorded. The thermal stability of polyimides was characterized by thermogravimetric analysis (TGA). The TGA curves were recorded on a Perkin-Elmer TGA7 under the protection of N_2 . The scan rate was $20^\circ C/min$.

RESULTS AND DISCUSSION

Synthesis and Characterization of NLO Side-Chain Polyimides

Two series of NLO side-chain polyimides were synthesized as shown in Schemes 1 and 2. All the

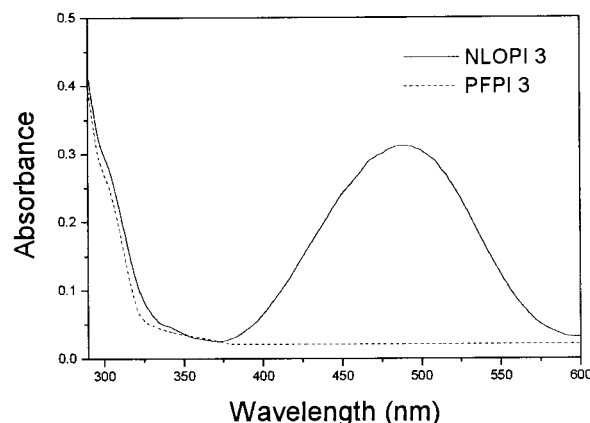


Figure 2 UV-VIS absorption spectra of PFPI 3 and NLOPI 3.

precursor polyimides (PFPI 1, 2, and 3) were synthesized using a traditional two-step synthetic route that includes polycondensation between diamines and dianhydrides to form poly(amic acid) and then chemical imidization to obtain polyimides at room temperature. The precursor polyimides were functionalized to introduce the chromophores at the final stage of the synthetic route. The diazonium salt readily attacks the benzene ring pendent from the backbone at the position with higher electron density. The bulkiness of the attacking group and the resulting steric hindrance limit the electrophilic substitution exclusively at the *para* position. The solvent used was NMP, which is the common solvent for organosoluble polyimides.

The FTIR spectra of all side-chain polyimides (NLOPI 1, 2, and 3) and their precursor polyimides (PFPI 1, 2, and 3) show clearly the characteristic absorption bands of the imide group at ~ 1780 , $\sim 1720\text{ cm}^{-1}$ (C=O stretching) and $\sim 1375\text{ cm}^{-1}$ (C—N stretching). The post-azo-coupling reaction was also monitored by FTIR spectra. The representative FTIR spectra of PFPI 3 and NLOPI 3 are shown in Figure 1. The clear appear-

Table I Solubility of NLO Side-Chain Polyimides and Their Precursor Polyimides

Polyimide	Cyclohexane	Toluene	Acetone	THF	Chloroform	1,4-butyrolactone	NMP	DMA	DMF	DMSO
PFPI 1	—	—	—	—	—	—	+	+	+	+
PFPI 2	—	—	—	+	—	+	+	+	+	+
PFPI 3	—	—	—	+	—	+	+	+	+	+
NLOPI 1	—	—	—	—	—	—	+	+	+	+
NLOPI 2	—	—	—	+	+-	+	+	+	+	+
NLOPI 3	—	—	+	+	+-	+	+	+	+	+

+, soluble; +-, partially soluble; —, insoluble

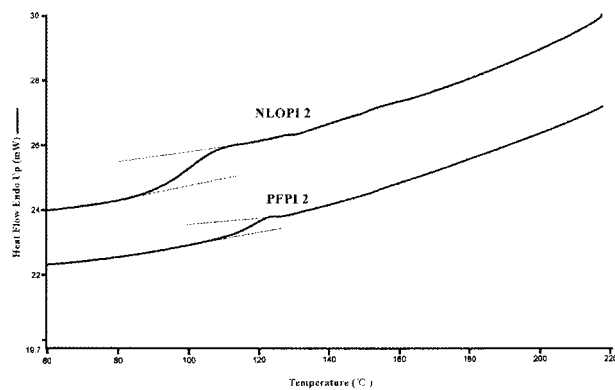


Figure 3 DSC curves of polyimides.

ance of the characteristic absorption band of the nitro group at 1339 cm^{-1} in the spectrum of NLOPI 3 indicates the success of the introduction of NLO chromophores into the backbone of the precursor polyimide.

The representative UV-VIS spectra of PFPI 3 and NLOPI 3 are given in Figure 2. PFPI 3 almost exhibits no absorption in the visible light range. After the post-azo-coupling reaction, one strong absorption band, at about 492 nm, can be observed in NLOPI 3. From the comparison of the peak absorbance of the dilute NLO polyimide solution and the standard curve obtained from the UV-VIS spectra of dilute solutions of the chromophore (DR-19) with various concentration, the degree of functionalization can be estimated. With this method, the degree of functionalization of NLOPI 3 is about 69 mol %, demonstrating that the functionalization with post-azo-coupling reaction is quite efficient, although it cannot be 100%.

Solubility of NLO Side-Chain Polyimides and their Precursor Polyimides

The solubility of the NLO polyimides and the precursor polyimides in various solvents is listed in Table I. It can be observed that all polyimides are soluble in strong polar organic solvents such as NMP, DMAc, DMF, and DMSO. PFPI 2 and 3 and NLOPI 2 and 3 can even be dissolved in THF

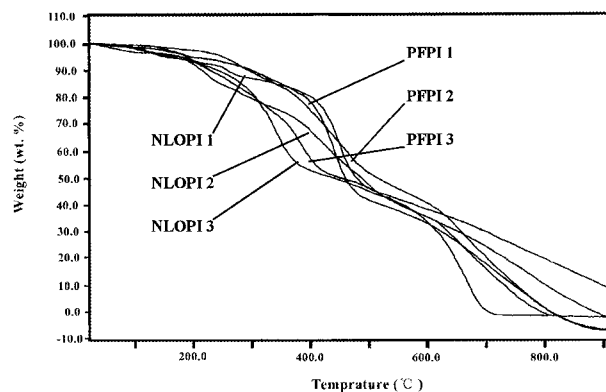


Figure 4 TGA curves of polyimides.

and 1,4-butyrolactone. The good solubility may result from the flexibility of the main chain of these polyimides. After the post-azo-coupling reaction, NLOPI 1, 2, and 3 show better solubility than the corresponding precursor polyimides. NLOPI 3 can even be dissolved in acetone, and both NLOPI 2 and 3 show reasonable solubility in chloroform. The increased solubility of polyimides after the post-azo coupling may be caused by the increased size of the side chain, which leads to the decrease of the intermolecular interactions.

Thermal Properties of NLO Side-Chain Polyimides and their Precursor Polyimides

The representative DSC curves of PFPI 2 and NLOPI 2 are shown in Figure 3, and the T_g s of NLO side-chain polyimides and their precursor polyimides are listed in Table II. It can be observed that after the post-azo-coupling reaction, the T_g s of the side-chain polyimides decrease slightly ($<20^\circ\text{C}$). The bulky side chain preventing the tight packing between polymer main chains may cause this decrease in T_g . The introduction of NLO chromophores by this post-azo-coupling reaction leads to a much smaller decrease in T_g than the commonly used post-functionalization with the post-Mitsunobu condensation. The T_g s of PFPI 2 and 3 and NLOPI 2 and 3 are rather low

Table II Glass Transition Temperature (T_g) of the Side-Chain Polyimides

Sample	PFPI 1	PFPI 2	PFPI 3	NLOPI 1	NLOPI 2	NLOPI 3
T_g ($^\circ\text{C}$) ^a	247	118	152	230	100	140

^a Measured with DSC under the protection of N_2 with a scan rate of $20^\circ\text{C}/\text{min}$.

because of the higher flexibility of the backbones of these polyesterimides.

The TGA curves of PFPI 1-3 and NLOPI 1-3 are shown in Figure 4. It can be observed that side-chain NLO polyimides exhibit lower thermal stability after the post-azo-coupling reaction. PFPI 1 and NLOPI 1 show quite high thermal stability because of the relatively high backbone rigidity. When the ester linkages are introduced to the backbones, as in the cases of PFPI 2, PFPI 3, NLOPI 2 and NLOPI 3, the thermal stability is largely decreased.

REFERENCES

- Service, R. *Science* 1995, 267, 1918.
- Eaton, D. *Science* 1991, 253, 281.
- Singer, K. *Polym Prepr* 1994, 35(2), 86.
- Burland, D.; Miller, R.; Walsh, C. *Chem Rev* 1994, 94, 31.
- Bloembergen, N. *Int J Nonlinear Opt Phys* 1994, 3(4), 439.
- Marks, T.; Ratner, M. *Angew Chem Int Ed Engl* 1995, 34, 155.
- Marder, S.; Perry, J. *Science* 1994, 263, 1706.
- Ghebremichael, F.; Kuzyk, M.; Lackritz, H. *Prog Polym Sci* 1997, 22, 1147.
- Bosshard, C.; Sutter, K.; Pretre, P.; Hulliger, J.; Florsheimer, M.; Kaatz, P.; Gunter, P. *Organic Nonlinear Optical Materials—Advances in Nonlinear Optics Series*; Gordon & Breach: Langhorne, PA, 1995; Vol. 1.
- Miller, R.; Burland, D.; Daeson, D.; Hedrick, J.; Lee, V.; Moylan, C.; Twieg, R.; Volksen, W.; Walsh, C. *Polym Prepr* 1994, 35(2), 122.
- Moylan, C.; Twieg, R.; Lee, V.; Miller, R.; Volksen, W.; Thackara, J.; Walsh, C. *Proc SPIE* 1994, 2285, 17.
- Verbiest, T.; Burland, D.; Jurich, M.; Lee, V.; Miller, R.; Volksen, W. *Science* 1995, 268, 1604.
- Miller, R.; Burland, D.; Jurich, M.; Lee, V.; Moylan, C.; Thackara, J.; Twieg, R.; Verbiest, T.; Volksen, W. *Macromolecules* 1995, 28, 4970.
- Miller, R.; Lee, V.; Volksen, W.; Sekkat, Z.; Knoesen, A.; Pretre, P.; Knoll, W.; Wood, J.; Aust, E. *Polym Prepr* 1998, 39(2), 312.
- Sekkat, Z.; Knoesen, A.; Lee, V.; Miller, R.; Wood, J.; Knoll, W. *ACS Symp Ser* 1998, 695, 295.
- Peng, Z.; Yu, L. *Macromolecules* 1994, 27, 2638.
- Yang, S.; Peng, Z.; Yu, L. *Macromolecules* 1994, 27, 5858.
- Yu, D.; Yu, L. *Polym Prepr* 1994, 35(2), 132.
- Yu, D.; Yu, L. *Macromolecules* 1994, 27, 6718.
- Yu, D.; Gharavi, A.; Yu, L. *Appl Phys Lett* 1995, 66, 1050.
- Yu, D.; Gharavi, A.; Yu, L. *Polym Prepr* 1995, 36(2), 39.
- Yu, D.; Gharavi, A.; Yu, L. *Macromolecules* 1995, 28, 784.
- Yu, D.; Gharavi, A.; Yu, L. *Macromolecules* 1996, 29, 6139.
- Yu, D.; Gharavi, A.; Yu, L. *Polym Prepr* 1996, 37(2), 374.
- Saadeh, H.; Gharavi, A.; Yu, D.; Yu, L. *Macromolecules* 1997, 30, 5403.
- Jen, A.; Drost, K.; Cai, Y.; Rao, V.; Dalton, L. *J Chem Soc, Chem Commun* 1994, 8, 965.
- Jen, A.; Drost, K.; Rao, V.; Cai, Y.; Liu, Y.; Minini, R.; Kenney, J.; Binkley, E.; Marder, S.; Dalton, L.; Xu, C. *Polym Prepr* 1994, 35(2), 130.
- Chen, T.; Jen, A.; Cai, Y. *J Am Chem Soc* 1995, 117, 7295.
- Chen, T.; Jen, A.; Cai, Y. *Macromolecules* 1996, 29, 535.
- Lin, J.; Hubbard, M.; Marks, T. *Chem Mater* 1992, 4, 1148.
- Sotoyama, W.; Tatsuura, S.; Yoshimura, T. *Appl Phys Lett* 1994, 64, 2197.
- Wang, J.; Marks, T. *Polym Prepr* 1995, 36(2), 308.
- Bu, X.; Lai, G.; Ahmed, M.; Rutherford, J.; Mintz, E. *Polym Prepr* 1997, 37(2), 254.
- Peesapati, V.; Rao, U.; Pethrick, R. *Polym Int* 1997, 43, 8.
- Lee, K.; Moon, K.; Woo, H.; Shim, H. *Adv Mater* 1997, 9, 978.
- Lee, H.; Lee, M.; Han, S.; Kim, H.; Ahn, J.; Lee, E. M.; Won, Y. *J Polym Sci, Part A: Polym Chem* 1998, 36, 301.
- Lee, K.; Moon, K.; Shim, H. *Mol Cryst Liq Cryst Sci & Technol* 1997, 294 241.
- Tsutsumi, N.; Morishima, M.; Sakai, W. *Macromolecules* 1998, 31, 7764.
- Jung, C.; Jikei, M.; Kakimoto, M. *J Photopolym Sci Technol* 1998, 11, 211.
- Sakai, Y.; Haba, O.; Kato, S.; Ueda, M.; Fukuda, T.; Matsuda, H. *J Photopolym Sci Technol* 1998, 11, 217.
- Woo, H.; Lee, K.; Shi, H. *Polym Prepr* 1998, 39(2), 1097.
- Si, J.; Mitsuyu, T.; Ye, P.; Li, Z.; Shen, Y.; Hirao, K. *Opt Commun* 1998, 147, 313.
- Schilling, M.; Katz, H.; Cox, D. *J Org Chem* 1988, 53, 5538.
- Wang, X.; Kumar, J.; Tripathy, S. *Macromolecules* 1997, 30, 219.
- Wang, X.; Chen, J.; Marturunkakul, S.; Li, L.; Kumar, J.; Tripathy, S. *Chem Mater* 1997, 9, 45.
- Lu, Q.; Yin, J.; Xu, H.; Zhang, J.; Sun, L.; Zhu, Z.; Wang, Z. *J Appl Polym Sci* 1999, 72, 1299.
- Jen, A.; Rao, V.; Drost, K.; Cai, Y.; Mininni, R.; Kenney, J.; Binkley, E.; Dalton, L. *Proc SPIE* 1994, 2285, 49.