Synthesis and Properties of a Novel Polythiophene Derivative with a Side-Chain NLO Chromophore

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A new, solution-processable, thiophene copolymer with a side-chain nonlinear optical (NLO) chromophore, namely, poly(3-octylthiophene-*co*-*N*-(3-thenyl)-4-amino-2-nitrophenol) [POMDT] has been chemically synthesized. The copolymer was further functionalized with a photo-cross-linkable cinnamoyl group and was doped with a photo-cross-linkable NLO dye. The poled, photo-cross-linked, dye-doped copolymer exhibited relatively large second-order NLO effects (d_{33} = 18.6 and 3.3 pm/V at 1.064 and 1.542 μm, respectively). The NLO properties of the photo-cross-linked samples were stable at room temperature for 100 h.

Introduction

Electrically conducting polymers continue to attract great scientific interest, in some measure due to their expanded melt or solution processability. Application of these types of materials in electronics,[1] power equipments,[2] sensors,[3] and nonlinear optics,[4] for example, has been reported. The polyheterocycles, such as polythiophenes and polypyrroles as a class of materials, present special opportunities[5] because of the possibilities of structural modification and ease of formation by either chemical[6] or electrochemical[7] polymerization techniques. Polythiophene is a conjugated conducting polymer with excellent electronic and reasonably good mechanical properties and is stable toward oxygen and moisture at ambient temperatures.[8,9] Unfortunately, the delocalized electronic structures due to π-conjugation make the polymer rigid and intractable. The intractability, in addition to the possible cross-linking at β-position of thiophene during polymerization, makes the polymer insoluble and infusible, causing nonprocessability of this type of materials. The processability of polythiophenes can be improved by introducing a flexible side chain of four or more carbons at the 3-position of thiophene. The long-chain substitution at the 3-position of the thiophene ring reduces both the chain intractability and the β-coupling during polymerization.[10] Thus processability is achieved with no sacrifice in conductivity,[11] but the conductivity decreases with time especially in the presence of oxygen and humidity at high temperatures.[12] The stability of this type of materials is enhanced by thermal annealing,[13] by suitably modifying the structure with the introduction of stable aromatic groups[14] in the side chain, and by copolymerization with 3-methylthiophene.[15]

Modifications in the chemical and physical properties of conjugated polymers such as polythiophenes and polypyrroles are readily achieved by attaching the appropriate functional group in the side chain. The derivitization at the 3-position is easier with the thiophene as compared to pyrrole, where the ring nitrogen must be protected.[16] This makes the thiophene monomer, a suitable material for structural modification,[17] to achieve the desired bulk property in the polymer such as water solubility,[18] optical activity,[19] ionic conductivity[20] or liquid-crystalline properties.[21]

Recently, photovoltage generation was observed in a poled guest–host system of a second-order nonlinear optical (NLO) chromophore in an inert polymer matrix[22] in our laboratory for the first time. The origin of this photo-

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(1) Burroughes, J. H.; Jones, C. A.; Friend, R. H. *Nature* **1988**, *335*, 137.

(2) Schoch, K. F.; Bennet, A. I.; Burghardt, R. R.; Cookson, A. H.; Kennedy, W. N.; Oommen, T. V.; Saunders, H. E.; Smith, J. E.; Voshall, R. E.; Fort, E. M.; Robins, B. *IEEE Trans. Power Delivery* **1992**, *7*, 1681.

(3) Naarmann, H. *Adv. Mater.* **1990**, *2*, 345.

(4) (a) Garnier, F.; Horowitz, G. *Makromol. Chem. Macromol. Symp.* **1987**, *8*, 159. (b) Marder, S. R.; Perry, J. W.; Klavetter, F. L.; Grubbs, R. H. *Chem. Mater.* **1989**, *1*, 171.

(5) (a) Kuo, C. S.; Wakim, F. G.; Sengupta, S. K.; Tripathy, S. K. *J. Appl. Phys.* **1993**, *74*, 2957. (b) Kuo, C. S.; Wakim, F. G.; Sengupta, S. K.; Tripathy, S. K. *Solid State Commun.* **1993**, *87*, 115.

(6) (a) Rapi, S.; Bocchi, V.; Gardini, G. P. *Synth. Met.* **1988**, *24*, 217. (b) Mogammadi, A.; Lundstrom, I.; Salaneck, W. R.; Inganas, O. *Synth. Met.* **1987**, *21*, 169.

(7) (a) Diaz, A. F.; Kanazawa, K. K.; Gardini, G. P. *J. Chem. Soc., Chem. Commun.* **1979**, 635. (b) Krische, B.; Hellberg, J.; Lilja, C. *J. Chem. Soc., Chem. Commun.* **1987**, 1476.

(8) (a) Yamamoto, T.; Sanechika, K.; Yamamoto, A. *J. Polym. Sci., Polym. Lett.* **1980**, *9*, 18. (b) Yoshino, K.; Hayashi, K.; Sugimoto, T. *Jpn. J. Appl. Phys.* **1984**, *23*, L899. (c) Wudl, F.; Kobayashi, M.; Heeger, A. J. *J. Org. Chem.* **1984**, *49*, 338.

(9) For reviews: (a) *Hand Book of Conducting Polymers*; Skotheim, T. J., Ed.; New York, 1986. (b) Roncali, J. *Chem. Rev.* **1992**, *92*, 711. (c) *NLO Properties of Organic and Polymeric materials*; Williams, D. J., Ed.; ACS Symposium Series 233; American Chemical Society: Washington, DC, 1983.

(10) (a) Sato, M.; Tanaka, S.; Kaeriyama, K. *J. Chem. Soc., Chem. Commun.* **1986**, 873. (b) Jen, K. Y.; Miller, G. G.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1346. (c) Hotta, S. *Synth. Met.* **1987**, *22*, 102. (d) Jen, K. Y.; Oboodi, R.; Elsenbaumer, R. L. *Polym. Mater.: Sci. Eng.* **1985**, *53*, 79. (e) Yoshino, K.; Nakajima, S.; Fujii, M.; Sugimoto, R. *Polym. Commun.* **1987**, *28*, 309.

(11) (a) Hotta, S.; Rughooputh, S. D. D. V.; Heeger, A. J.; Wudl, F. *Macromolecules* **1987**, *20*, 212. (b) Sato, M.; Tanaka, S.; Kaeriyama, K. *Synth. Met.* **1986**, *18*, 229.

(12) (a) Wang, Y.; Rubner, M. F. *Synth. Met.* **1990**, *39*, 153. (b) Gustafsson, G.; Inganas, O.; Nilsson, J. O. *Synth. Met.* **1989**, *28*, C427. (c) Taka, T.; Loponen, M. T.; Laakso, J.; Suuronen, K.; Valkeinen, P.; Osterholm, J. E. *Synth. Met.* **1991**, *41*, 567.

(13) Taka, T.; Punkka, E.; Isotalo, H. *Synth. Met.* **1993**, *55*, 4979.

(14) Pei, Q.; Jarvinen, H.; Osterholm, J. E.; Inganas, O.; Laakso, J. *Macromolecules* **1992**, *25*, 4297.

(15) (a) Pei, Q.; Inganas, O. *Synth. Met.* **1992**, *46*, 353. (b) Billingham, N. C.; Calvert, P. D.; Foot, P. J. S.; Mohammad, F. *Polym. Degrad.* **1987**, *19*, 323.

(16) Roncali, J.; Garreau, R.; Delabouglise, D.; Garnier, F.; Lemaire, M. *Synth. Met.* **1989**, *28*, C341.

(17) Delabouglise, D.; Garnier, F. *Adv. Mater.* **1990**, *2*, 91.

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voltage generation is due to a change in polarization of the medium upon photoexcitation, which is similar to the observed photoinduced polarization in the Langmuir–Blodgett (L–B) films of donor–acceptor molecules.[23] However, due to large internal resistivity of the polymer host, the observed short-circuit current is very small in these types of materials. The photoresponse can be greatly improved by embedding a second-order NLO chromophore in a medium such as a conjugated polymer where facile charge transport is possible. The chromophores must possess a stable poled order in this matrix.

The photorefractive effect in polymers has drawn attention due to the potential applications in image amplification, phase conjugation, 3D optical data storage, etc.[24] For the photorefractive effect to be observed in a material, the presence of photoconductivity, an electrooptic (EO) effect, and small dark conductivity are necessary.[25] Photorefraction was recently observed in a number of dye-doped nonlinear organic polymeric systems[26,27] by several groups. The NLO chromophore itself was found to be responsible for the photoinduced charge generation[26a] in these polymeric systems. Small molecular hole-transport agents such as (diethylamino)benzaldehyde diphenylhydrazone,[27] and 1,1-bis(4-di-*p*-tolylaminophenyl)cyclohexane were added into the matrix by a number of researchers to enhance the charge transport. The response time of a photorefractive material is strongly dependent on the photocarrier generation efficiency in a material. Conjugated polymers such as polythiophenes are excellent photoconductors.[28]

In this work, we seek to design a stable EO polymer with added functionalities for realizing improved photovoltaic and photorefractive effects. For this purpose, the thiophene monomer was functionalized with a NLO chromophore and then was copolymerized with 3-octylthiophene with an objective of producing a processable material, which will also show second-order NLO response. The copolymer was further functionalized with a photocrosslinkable cinnamoyl group. Upon poling, the second-order NLO activity was observed in this NLO copolymer. Furthermore, when this copolymer was doped with a photocross-linkable NLO chromophore, which possesses relatively large molecular hyperpolarizability, poled and photocross-linked, a stable and greatly enhanced second-order optical nonlinearity was measured. The details of the syntheses, structural and thermal characteristics of the copolymer are discussed in this paper. Preliminary results from second-order NLO measurements are also presented.

Experimental Section

(1) Materials. The 3-octylthiophene was obtained from TCI America. All other reagents were obtained from Aldrich Chemical Co. and were used without further purification, except the tosyl chloride. The latter was recrystallized from petroleum ether before its use.

(2) Synthesis of Monomer. (*a*) *N-(3-Thenyl)-4-amino-2-nitrophenol (MDT).* The 3-thienylmethanol (3-MT) was tosylated using *p*-toluene sulfonyl chloride in the presence of dry pyridine[29] at −20 °C and was precipitated in ice-cold 1 N hydrochloric acid. The precipitated tosylate was dried under vacuum and was then recrystallized from petroleum ether, to produce white needlelike crystals. The *p*-toluenesulfonate (tosyl) derivative of 3-MT (2.68 g, 10 mmol) and triethylamine (1.01 g, 10 mmol) were dissolved in chloroform in a round-bottomed flask. A solution of 4-amino-2-nitrophenol (1.62 g, 10.5 mmol) in chloroform was added slowly to the above mixture, with vigorous stirring. The stirring was continued for 24 h. The contents of the flask were then poured into 200 mL of ice-cold 1 N HCl in a beaker. The organic layer was separated, washed with 3 × 25 mL of cold 1 N HCl and then with 3 × 20 mL of distilled water, dried over anhydrous magnesium sulfate, and filtered. The solvent from the filtered solution was removed by rotary evaporator under vacuum. The residue gave yellow crystals of MDT upon recrystallization from methanol; yield 2.2 g (88%), mp 118 °C. IR (KBr, cm^{-1}) 3200–3600 (s, ν_{O-H}), 3100 (w, aromatic ν_{C-H}), 1540 (w, ν_{N-O}, asymmetric), 1354 (s, ν_{N-O}, symmetric), 850 (ν_{C-N} of NO_2 aromatic carbon). ^{1}H NMR ($CDCl_3$, ppm) δ 2.4 (s, 2H, $-CH_2-$), 5.3 (s, 1H, $-NH-$), 6.9 (d, 1 H, aromatic), 7.1 (m, 2H, aromatic), 7.2 (s, 1H, aromatic), 7.5 (s, 2H, aromatic). UV (λ_{max}, in $CHCl_3$) 350 nm.

(*b*) *Copolymerization.* The 3-octylthiophene and the monomer MDT (in the molar ratio of 2:1) were copolymerized by the chemical dehydrogenation method[30] using anhydrous ferric chloride. A 10 mmol solution of comonomer mixture in chloroform was polymerized using 40 mmol of ferric chloride at room temperature under a nitrogen atmosphere. After being stirred for 48 h, the copolymer (POMDT21) was precipitated in methanol, filtered, washed with acetone–methanol mixture, and then Soxhlet extracted with methanol for 3 days to remove oligomeric and iron impurities. The copolymer was finally washed with aqueous ammonia solution to remove the trace amount of iron impurities. The purified copolymer (yield 90 wt %) was then dried and was extracted with chloroform to separate the soluble copolymer (95%) from high molecular weight insoluble gel (5%). Anal.: C, 66.21; H, 7.19; N, 3.55; S, 15.32; O, 7.14. Calcd for $(C_{12}H_{18}S)_{0.67}(C_{11}H_8N_2SO_3)_{0.33}$: C, 67.29, H, 7.27, N, 3.72, S, 15.30, O, 6.38. IR (KBr, cm^{-1}) 3200–3600 (m, ν_{O-H} and ν_{N-H}), 3100 (w, ν_{C-H}, aromatic), 2922 and 2852 (s, ν_{C-H}), 1542 (w, ν_{N-O}), 1354 (w, ν_{N-O}), 830 (δ_{C-H} out of plane, thiophene ring). ^{1}H NMR ($CDCl_3$, δ in ppm) 0.87 (s, 3 H, $-CH_3$), 1.2–1.5 (broad, 10 H, $-CH_2-$), 1.57 (broad, 2 H, $-CH_2-$), 2.1 and 2.2 (s, 2 H, $-CH_2-NH-$), 2.55–2.85 (s, 2H, $-CH_2-$, for head-to-head, head-to-tail, and mixed coupling), 5.3 (s, 1 H, $-NH-$), 6.95–7.1 (m, 1H, aromatic), 7.2 (s, 1H, aromatic), 7.5 (s, 2H, aromatic). UV (λ_{max}, $CHCl_3$) 430 nm.

(*c*) *Cinnamoylation of POMDT21.* A solution of 0.55 g (3.3 mmol) of cinnamoyl chloride in 10 mL of chloroform was added slowly with stirring, to a mixture of 2.12 g (3.3 mmol of hydroxyl equivalent) of copolymer and 0.27 g (3.5 mmol) of dry pyridine taken in 30 mL of chloroform, at room temperature. The stirring

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(18) Heeger, A. J.; Wudl, F.; Patil, A. O.; Ikenoue, Y. *J. Am. Chem. Soc.* **1987**, *109*, 1858.

(19) Lemaire, M.; Delabouglise, D.; Garreau, R.; Guy, A.; Roncali, J. *J. Chem. Soc., Chem. Commun.* **1988**, 621.

(20) Roncali, J.; Garreau, R.; Delabouglise, D.; Garnier, F.; Lemaire, M. *J. Chem. Soc., Chem. Commun.* **1989**, 679.

(21) Bryce, M. R.; Chissel, A. D.; Gopal, J.; Kathirgamanathan, P.; Parker, D. *Synth. Met.* **1991**, *39*, 397.

(22) Li, L.; Jeng, R. J.; Kamath, M.; Kumar, J.; Tripathy, S. K. In Macromolecular Host–Guest complexes: Optical, Optoelectronic, and Photorefractive Properties and Applications. *MRS Symp. Proc.* **1992**, *161*. 277.

(23) (a) Blinov, L. M.; Dubinin, N. V.; Mikhnev, L. V.; Yudin, S. G. *Thin Solid Films* **1984**, *120*, 161. (b) Blinov, L. M.; Palto, S. P.; Udal'yev, A. A.; Yudin, S. G. *Mol. Eng.* **1991**, *1*, 23.

(24) (a) *Photorefractive Materials and Their Applications*. Gunter, P., Huiguard, J. P., Eds.; Springer-Verlag: Berlin, 1988; Vols. I and II. (b) Feinberg, J.; Heiman, D.; Tanguay, A. R.; Hellwarth, R. W. *Appl. Phys.* **1980**, *51*, 1299.

(25) Scott, J. C.; Pautmeier, L. T.; Moerner, W. E. *Synth. Met.* **1993**, *54*, 9.

(26) (a) Li, L.; Lee, J. Y.; Kumar, J.; Tripathy, S. K. *Appl. Phys. B* **1991**, *53*, 279. (b) Moerner, W. E.; Walsh, C.; Scott, J. C.; Ducharme, S.; Burland, D. M.; Bjorklund, G. C.; Twieg, R. J. In Non Linear Optical Properties of Organic Materials. *SPIE* **1991**, *1560*, 278. (c) Tamura, K.; Padias, A. B.; Hall, H. K.; Peyghambarian, N. *Appl. Phys. Lett.* **1992**, *60*, 1803.

(27) Schildkraut, J. S. *Appl. Phys. Lett.* **1991**, *58*, 340.

(28) (a) Binh, N. T.; Gailberger, M.; Bassler, H. *Synth. Met.* **1992**, *47*, 77. (b) Binh, N. T.; Minh, L. Q.; Bassler, H. *Synth. Met.* **1993**, *58*, 39.

(29) *Reagents for Organic Synthesis*; Fieser, M., Fieser, L. F., Eds.; Wiley-Interscience: New York, 1972; Vol. 1.

(30) Sugimoto, R.; Takeda, S.; Gu, H. B.; Yoshino, K. *Chem. Express* **1986**, *1*, 635. (b) Niemi, V. M.; Knuuttila, P.; Osterholm, J. E.; Korvola, J. *Polymer* **1992**, *33*, 1559.

was continued overnight. The solution was concentrated to 20 mL using a rotary evaporator under reduced pressure and was poured into 250 mL of methanol to precipitate the copolymer. The precipitated copolymer was then washed with acetone and dried overnight under vacuum; yield 2.4 g (60% cinnamoylation). IR (KBr, in cm^{-1}) 1729 (m, $\nu_{C=O}$).

(3) Preparation of Samples. The cinnamoylated copolymer was dissolved in chlorobenzene/toluene (3/1 w/w ratio) mixture, filtered through 0.2-μm Gelman filters and spin coated on indium-tin oxide (ITO) coated glass slides for second harmonic generation (SHG) measurements. The spin-coated specimens were dried overnight under vacuum at 70 °C. The films were then poled to align the chromophores using the corona discharge method.[31] The aligned chromophores were arrested by [2+2]photo-cross-linking of the cinnamoyl groups,[32] by exposing the specimen to UV light (254 nm) for 5 min. The polymer becomes insoluble after photo-cross-linking. To enhance the second-order NLO chromophore concentration and the cross-linking density, the copolymer was dissolved with a photo-cross-linkable second-order NLO chromophore, viz., 3-cinnamoyloxy-4-[4-((diethylamino)-2-cinnamoyloxy)phenylazo]nitrobenzene (CNNB-R) in 3:1 (w/w) chlorobenzene/toluene solvent mixture. The aforementioned procedure was repeated to obtain poled, cross-linked films on ITO-coated glass slides. The second-order NLO properties of the poled specimens were measured by the SHG technique using a Q-switched Nd:YAG laser (at 1.064 μm) and its Raman-shifted line (at 1.542 μm). The SHG method was also used for investigating the temporal stability of the poled order in the chromophore-conjugated conducting polymer system over a period of time.

(4) Characterization. The ^{1}H NMR spectral data were obtained from Bruker WP-270 NMR spectrometer. The IR spectra were recorded on a Perkin-Elmer 1760X FTIR spectrometer. The ultraviolet–visible (UV–vis) spectra were recorded using a Perkin-Elmer Lambda-9 UV–vis–NIR spectrophotometer. The spectrophotometer was equipped with a variable-temperature apparatus to allow the measurements of the spectra at different temperatures.

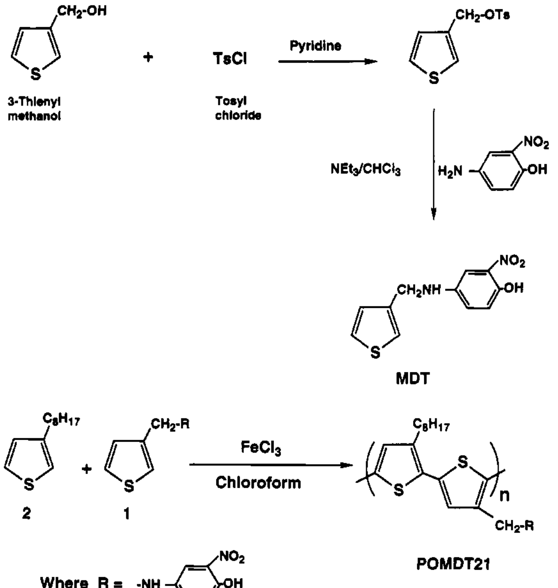
The number- and weight-average molecular weights were determined using a gel permeation chromatography setup (GPC-Waters Model 510 pump, Model 410 refractive index detector, and Model 730 module with 500–10^5 Å Ultrastyragel columns in series), relative to polystyrene standards. The column was injected with 100 μL of the copolymer solution in chloroform (1 mg/mL) and was eluted with chloroform.

A differential scanning calorimeter (DSC 2910, TA Instruments) was used at a heating rate of 10 °C/min to record the thermograms of the copolymer. The thermal degradation temperatures (T_d) of the polymers were determined using a thermogravimetric analyzer (TGA 2950, TA Instruments, Inc.) at a heating rate of 20 °C/min.

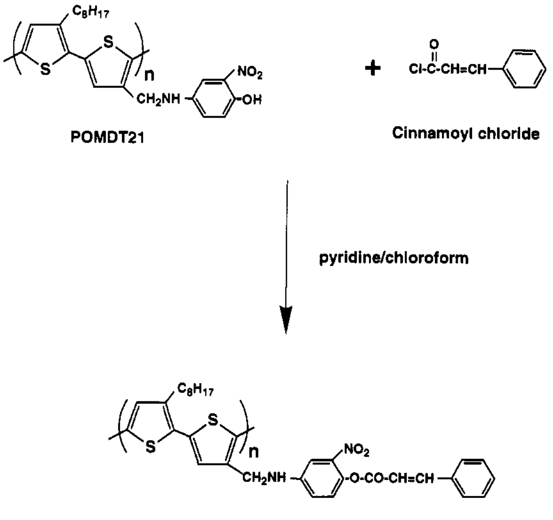
Results and Discussion

The NLO dye attached monomer *N*-(3-thenyl)-4-amino-2-nitrophenol (MDT) and the copolymer POMDT21 were synthesized as shown in Scheme 1. The thiophene derivative MDT can be homopolymerized, but the resultant polymer is insoluble in common organic solvents and is soluble only in concentrated hydrochloric acid. The polymer precipitates when the yellowish polymer solution in concentrated HCl is diluted with water. The monomer MDT was copolymerized with 3-octylthiophene to improve the processability of the resultant conjugated polymer. Among various compositions tried, the copolymer with the composition 2:1 (3-octylthiophene: MDT) was found to be highly soluble in solvents such as THF, chlorinated solvents, dioxane, toluene, etc., forming a reddish brown solution which upon dilution becomes yellow. The copolymer is insoluble in acetone, methanol, and acetonitrile and any of these solvents can be used to precipitate the copolymer. The copolymer was further cinnamoylated as shown in Scheme 2. The cinnamoylated copolymer is soluble in common organic solvents in the absence of photodimerization. As expected the cinnamoylated copolymer becomes insoluble, upon photo-cross-linking at 254 nm.

Scheme 1. Syntheses of Monomer MDT and Copolymer POMDT21



Scheme 2. Cinnamoylation of POMDT21



The GPC results are tabulated in Table 1 and are compared with poly(3-octylthiophene) prepared under similar conditions. A 30 mol % MDT dye functionalized monomer insertion in the copolymer is inferred from the elemental analysis data.

The IR spectrum was recorded by casting a film on a KBr plate. The presence of the imino and hydroxyl groups were confirmed from the band of stretching frequencies from 3200 to 3600 cm^{-1}. The presence of nitro group[33] in the copolymer was confirmed from the peaks at 1542 and 1354 cm^{-1}. The peak at 830 cm^{-1} is due to the bending vibration of the backbone proton, which is characteristic

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[31] Mandal, B. K.; Chen, Y. M.; Jeng, R. J.; Takahashi, T.; Huang, J. C.; Kumar, J.; Tripathy, S. K. *Eur. Polym. J.* **1991**, *27*, 735. This paper explains in detail the experimental setup used for corona poling.

[32] Mandal, B. K.; Kumar, J.; Huang, J. C.; Tripathy, S. K. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 63.

Table 1. Gel Permeation Chromatographic Results of POMDT21 and Poly(3-octylthiophene)

	POMDT21	poly-(3-octylthiophene)
1. monomer:ferric chloride ratio	1:4	1:4
2. reaction time (h)	12	12
3. M_n (g/mol)	20 000	40 000
4. M_w (g/mol)	81 000	87 000
5. PDI[a]	4.05	2.18

[a] The polydispersity index (PDI) for the poly(3-octylthiophene) is low compared to the literature values. This might be due to the Soxhlet extraction with acetone, used in the sample purification step, which dissolves most of the oligomers.

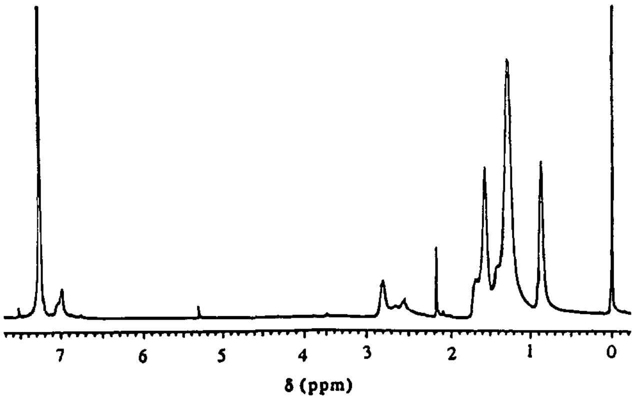

Figure 1. ^{1}H NMR spectrum of POMDT21.

of 2,3,5-trisubstituted thiophene ring,[34] indicating the existence of a linear polymer chain. A peak at 1729 cm^{-1} appeared upon cinnamoylation of POMDT21, which shows the presence of the dye in the copolymer.

The ^{1}H NMR (Figure 1) signals at δ = 2.85 and 2.65 ppm correspond to the α-CH$_2$– group of the 3-octylthiophene unit for the head-to-tail and head-to-head coupling, respectively.[35] The intensities of these two peaks suggests the presence of about 15% of head-to-head coupling of the 3-octylthiophene units in the copolymer. Up to 30% of head-to-head coupling is reported in the synthesis of poly(3-alkylthiophene) using ferric chloride oxidation method. These results are consistent with the 2:1 ratio of alkylthiophene and MDT in the copolymer. Similarly, the peaks at δ = 2.1 and 2.2 ppm correspond to the α-CH$_2$– group of the MDT unit for the head-to-head and head-to-tail coupling, respectively. The intensities of these two peaks indicate a very low amount of head-to-head coupling among MDT units. This is expected due to the steric crowding of the aromatic units. Further few MDT diads are expected in a random copolymer with the given composition. The peak at δ = 2.55, which is not found in the poly(3-octylthiophene) is suggested to be due to the α-CH$_2$– units of the mixed coupling between the 3-octylthiophene unit and a MDT unit. This fairly high intensity peak shows the random nature of the copolymerization. The peak between 6.9 and 7.1 is not well resolved and has multiplet splitting, which is due to the β-proton of the thiophene ring for various regioisomeric units in the polymer chain.

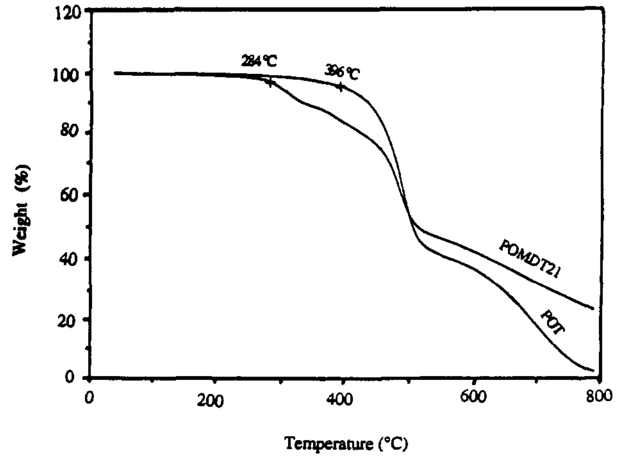

Figure 2. TGA diagrams of POMDT21 and poly(3-octylthiophene) at a heating rate of 20 °C/min.

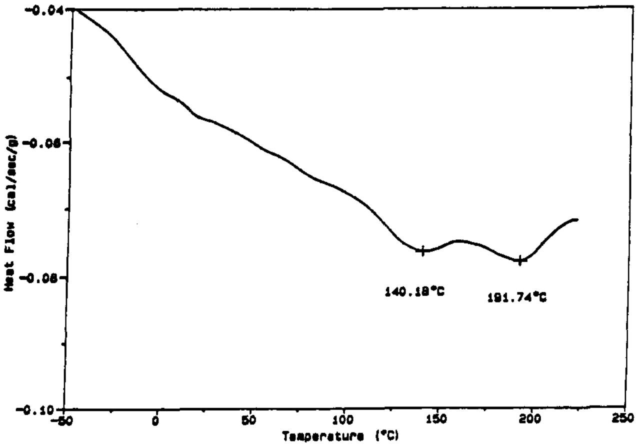

Figure 3. DSC thermogram of POMDT21 at a heating rate of 10 °C/min.

Thermal Characterization. The TGA studies at a heating rate of 20 °C/min (Figure 2) of the copolymer POMDT 21 showed that this copolymer is stable up to about 285 °C under nitrogen atmosphere, while the poly(3-octylthiophene) prepared under similar conditions is stable up to 395 °C [the literature value[36] agrees with this onset temperature for poly(3-octylthiophene)]. The introduction of a dye molecule in poly(3-alkylthiophene) reduces the thermal stability of the polymer by about 110 °C, which is mainly due to the onset of thermal degradation of nitro group at higher temperatures. A number of other nitro group containing dye-functionalized polymers are also reported[37] to start degrading at around 280 °C. The copolymer also yielded a higher char at temperatures above 600 °C compared to poly(3-octylthiophene), which is due to the high C/H ratio of the aromatic unit of the dye.

The DSC thermogram of the copolymer at a heating rate of 10 °C/min has been shown in Figure 3. While the poly(3-octylthiophene) shows a weak single melting endotherm[38] in the temperature range 130–150 °C, the new copolymer shows two melting endotherms at 140 and 192 °C, respectively, in addition to a weak glass transition at −10 °C. This result shows the possible presence of two different crystalline phases in the copolymer.

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(33) *Spectrophotometric Identification of Organic Compounds*, 4th ed.; Silverstein, R. M., Bassler, G. C., Morrill, T. C., Eds.; John Wiley and Sons: New York, 1981.

(34) Zagorska, M.; Krische, B. *Polymer* **1990**, *31*, 1379.

(35) (a) Leclerc, M.; Diaz, F. M.; Wegner, G. *Makromol. Chem.* **1989**, *90*, 3105. (b) Sato, M.; Shimizu, T.; Yamauchi, A. *Synth. Met.* **1991**, *41*, 551. (c) Maior, R. M. S.; Hinkelmann, K.; Eckert, H.; Wudl, F. *Macromolecules* **1990**, *23*, 1268.

(36) (a) Gustafsson, G.; Inganas, O.; Nilsson, J. O.; Liedberg, B. *Synth. Met.* **1988**, *26*, 297. (b) Chen, S. A.; Ni, J. M. *Polym. Bull.* **1991**, *26*, 673.

(37) Jeng, R. J.; Chen, Y. M.; Chen, J. I.; Kumar, J.; Tripathy, S. K. *Macromolecules* **1993**, *26*, 2530.

(38) Chen, S.; Ni, J. *Macromolecules* **1992**, *25*, 6081.

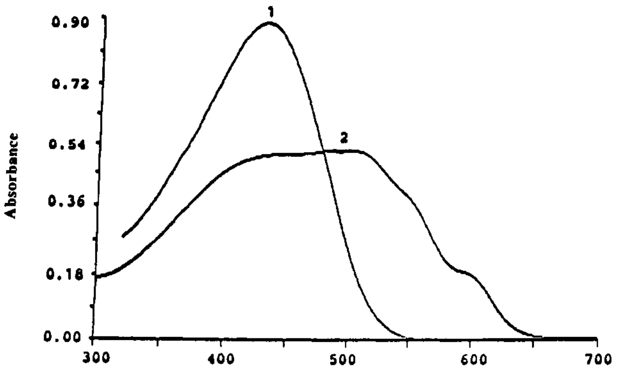


Figure 4. UV–vis spectra of POMDT21: (1) in chloroform (0.0233 mg/mL); (2) of spin-coated film.

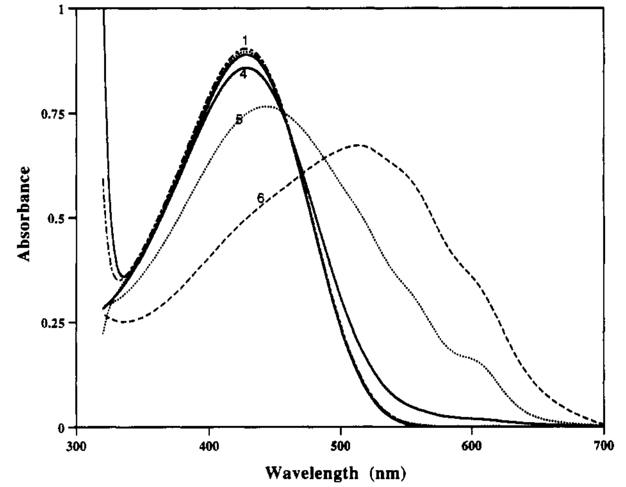


Figure 5. Optical absorption spectra of POMDT21 by mixing a solution of polymer in chloroform with methanol at different ratios of chloroform/methanol (v/v): (1) 10/0; (2) 9/1; (3) 8/2; (4) 7/3; (5) 5/5; (6) 1/9. All the measurements were done at 22 °C.

Solvato- and Thermochromic Studies. The UV-visible spectra of the copolymer in chloroform and in solid state are presented in Figure 4. The copolymer showed an absorption maximum at $\lambda_{\max} = 430$ nm in chloroform with a tail extending up to 550 nm indicating the presence of extended conjugation and multiple conjugation lengths along the main chain of the polymer. The polymer showed a $\lambda_{\max}$ of 500 nm with two shoulders at 604 and 552 nm similar to poly(3-alkylthiophenes) in the solid state. The copolymer shows solvatochromic (chloroform is a good solvent for the POMDT21, there is a red shift of about 90 nm upon addition of a nonsolvent such as methanol, acetone, and acetonitrile, etc., to the dilute polymer solution) and thermochromic effects as shown in Figures 5 and 6 respectively. The results are similar to that obtained for poly(3-alkylthiophenes),[39] which can be explained on the basis of a high molar concentration of the 3-octylthiophene units present in the copolymer. The thermochromic behavior is reversible at least up to 150 °C. This phenomenon is irreversible when the material is heated beyond 200 °C.

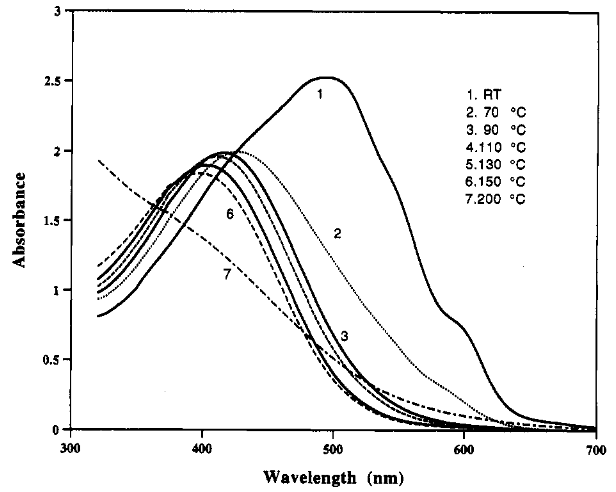
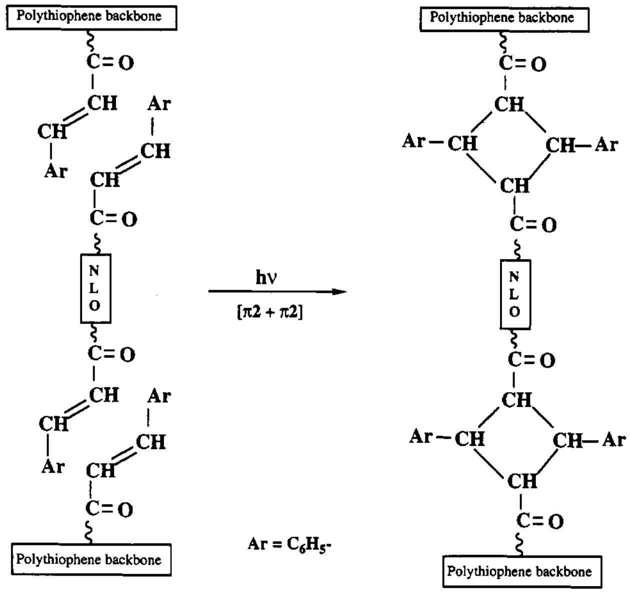


Figure 6. Optical absorption spectra as a function of temperature of a thin film of POMDT21 cast on ITO glass slide.

Scheme 3. Photo-Cross-Linking Reaction between Cinnamoyl Moieties Present in POMDT21 and CNNB-R Dye



Second Harmonic Generation Measurements. The second-order NLO coefficient d_{33} of the poled and photo-cross-linked polymer film was measured using the SHG technique. The photo-cross-linking was done to stabilize the poled order. The general schematic of the photo-cross-linking process is shown in Scheme 3. The experimental arrangement for the SHG measurement is reported elsewhere.[40] The d_{33} coefficient of the polymer sample was measured with a Y-cut quartz crystal[41] as a reference ($d_{11} = 0.5$ pm/V).

The poled and photo-cross-linked cinnamoylated POMDT21 film showed a small SH signal, due to very low concentration and molecular hyperpolarizability of the NLO dye used in the copolymer. The copolymer was also doped with 17 wt % of CNNB-R, whose structure is shown in Figure 7. The optical quality of the prepared films were good, without any dopant aggregation.[42] The poled, and photo-cross-linked, CNNB-R dye-doped, cinnamoyl-

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[39] (a) Hotta, S.; Rughooputh, S. D. D. V.; Heeger, A. J.; Wudl, F. *Macromolecules* **1987**, *20*, 212. (b) Rughooputh, S. D. D. V.; Hotta, S.; Heeger, A. J.; Wudl, F. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 1071. (c) Inganas, O.; Salaneck, W. R.; Osterholm, J. E.; Laakso, J. *Synth. Met.* **1988**, *22*, 395. (d) Inganas, O.; Gustafsson, G.; Salaneck, W. R.; Osterholm, J. E.; Laakso, J. *Synth. Met.* **1989**, *28*, C377.

[40] Mandal, B. K.; Chen, Y. M.; Jeng, R. J.; Takahashi, T.; Huang, J. C.; Kumar, J.; Tripathy, S. K. *Eur. Polm. J.* **1991**, *27*, 735.

[41] Palik, E. D. *Handbook of Optical Constants*; Academic Press: Orlando, 1985; pp 719–731.

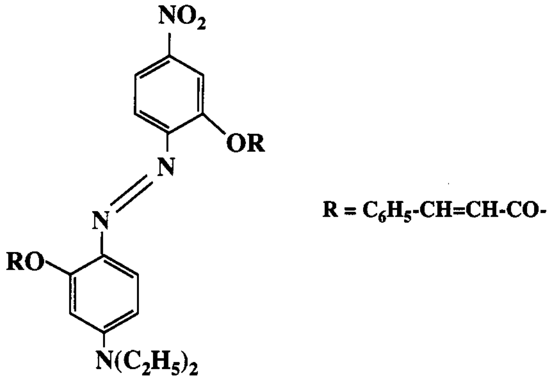

Figure 7. Chemical structure of photo-cross-linkable CNNB-R dye.

ated POMDT21 exhibited a large SH signal (the d_{33} values of the poled, and photo-cross-linked, CNNB-R-doped conducting polymer film were determined to be 18.6 pm/V at 1.064 μm and 3.3 pm/V at 1.542 μm). The temporal behavior of the second order NLO properties of the poled polymer films with and without photo-cross-linking was investigated by monitoring the decay of SH intensity at 532 nm as a function of time after poling. Figure 8 shows the relaxation behavior of SH intensity of the dye-doped polymer films at room temperature. It is clear that the poled, and photo-cross-linked polymer sample exhibits significantly enhanced stability of the SH intensity compared to the un-cross-linked sample. This is expected due to the frozen in alignment of the chromophores by the photo-cross-linking process as reported earlier.[32]

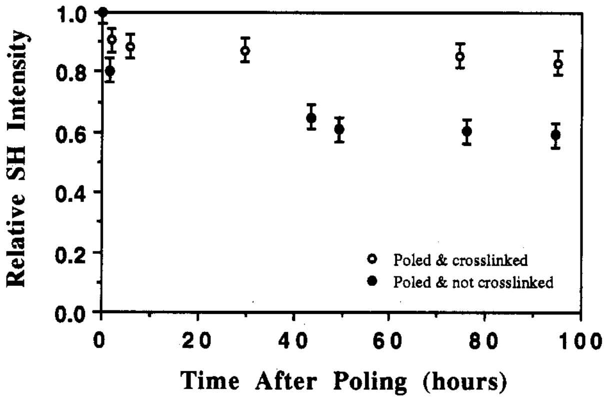

Figure 8. Temporal behavior of the second harmonic intensity of the CNNB-R-doped POMDT21 at room temperature.

Conclusions

We have synthesized the novel, solution-processable, photo-cross-linkable, polythiophene derivative POMDT21, with a second-order NLO chromophore as a side chain. ^{1}H NMR studies, FTIR spectral data, and the thermogravimetric analysis clearly demonstrated the incorporation of NLO species in the conducting copolymer. The DSC thermogram showed two melting endotherms, which were attributed to the coexistence of two differently ordered structure in the bulk amorphous state. The copolymer showed low second-order NLO activity. Large second-order optical nonlinearity was obtained by doping the cinnamoylated POMDT21 with a photo-cross-linkable NLO chromophore. The poled, photo-cross-linked, and dye-doped copolymer exhibited good temporal stability at room temperature. We are presently investigating the photoconductive, photovoltaic, and photorefractive properties of the POMDT21 and dye-doped POMDT21 systems. Results from these studies will be reported in a subsequent communication.

Acknowledgment. Financial support from the ONR is gratefully acknowledged.

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[42] Mandal, B. K.; Chen, Y. M.; Lee, J. Y.; Kumar, J.; Tripathy, S. K. *Appl. Phys. Lett.* **1991**, *58*, 2459.