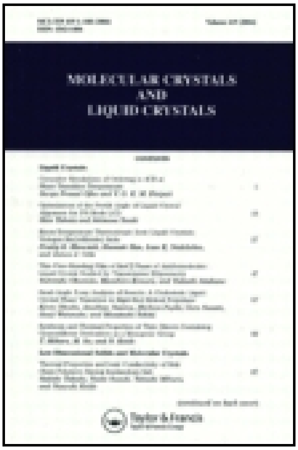

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DEVELOPMENT OF FUNCTIONALIZED POLYETHERIMIDES FOR SECOND-ORDER NONLINEAR OPTICS

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Abstract Two types of NLO active linear polyetherimides (PEI-DANS and PEI-TH/PEI-TCN) derived from Mitsunobu reaction of dimide and hydroxy-functionalized DANS or TCN-type chromophores were prepared. The Tg of the resulting polymers ranged between 144-157 ℃. The poled samples were able to produce PEI-DANS and PEI-TH/PEI-TCN (23.6 % chromophore concentration level) with macroscopic second-order NLO activity, $\chi^{(2)}$, values of 73 pm/V and 56 pm/V, respectively, at 1063 nm. In the latter case, no decay of the second harmonic generation signal was observed up to 125 ℃. Such excellent thermal stability can be attributed to strong chromophore-chromophore and/or chromophore-polymer backbone interactions.

INTRODUCTION

Insufficient temporal and thermal stability of the induced polar ordering of chromphores in nonlinear optical (NLO) polymers at elevated temperatures have been a major hurdle in further development of photonics devices.[1,2] Two main approaches to reduce the randomization have been proposed. One was the use of NLO polymers having thermally or photochemically crosslinkable units.[3,4] The other included high Tg polymer either blended in or having introduced NLO chromophore in the backbone.[5-7] However, with the first approch a significant optical losses caused by the limited uniformity of the crosslinking reaction occurred. Also, in the latter system limited solubility due to the chain rigidity in common organic solvents gave undesirable effects.

To solve these problems, we empolyed polyetherimide (PEI), which showed good solubility and optical transparancy, as the matrix.[8] In this paper, we report the synthesis and characterization of two PEI-based NLO systems with pendant-incorporated chromophores which did not need imidization process. Their second-order NLO propertiy with regard to electric field poling and thermal stability is also presented.

EXPERIMENTAL

4-Bishydroxyethylamino-4'-nitrostilbene (DANS-OH). 19.0 g (64.8 mmol) of N,N-bis(acethyloxyethyl)aminobenzene and 17.7 g (64.8 mmol) of diethyl benzylphosphonate were dissolved in 300 ml of anhydrous tetrahydrofuran (THF) and the solution of potassium t-butoxide (9.0 g, 1.17 eq.) in 100 ml of THF was slowly added to this solution. The mixture was stirred at room temperature for 30 minutes, and then was further reacted at 80 ℃ for 4 h. The reaction mixture was cooled to room temperature and a large amount of cold water was poured into the solution. The precipitated red powder product was collected by filtration, thoroughly dried under reduced pressure, and purified by recrystallization using methanol and hexane solvents. 11.7 g of pure product was obtained by evaporating the solvent (68 % yield).

^{1}H-NMR (DMSO-d_6) δ 8.17 (d, 2H), 7.72 (d, 2H), 7.42 (m, 4H), 7.09 (d, 1H), 6.70 (d, 2H), 4.76 (d, 2H), 3.56-3.45 (m, 6H).

N,N-Bis(2-hydroxyethyl)-4-(2-(thiophene-2-yl)vinyl)aniline (TH-OH). 6.83 g (23.3 mmol) of 2,2'-bis[4-(2,3-dicarboxyphenoxy)phenyl)propane diimide and 5.47 g (23.3 mmol) of diethyl thiophene-2-yl-methylphosphonate were dissolved in 100 ml of anhydrous THF and then the solution of potassium t-butoxide (2.57 g, 1.0 eq.) in 80 ml of THF was slowly added to this solution. The mixture was stirred at room temperature for 24 h. The reaction mixture was cooled to room temperature and extracted with ethyl acetate. The organic layer was concentrated and 50 ml of methanol and 10 ml of the saturated NaOH were added to this mixture. The mixture was refluxed for 24 h and then cooled to room temperature. Excess water was added to this reaction mixture. The precipitated powder product was collected by filtration and thoroughly dried under reduced pressure. 3.82 g of pure product was obtained by evaporating the solvent (57 % yield).

^{1}H-NMR (DMSO-d_6) δ 7.31 (m, 3H), 7.00 (m, 3H), 6.65 (d, 2H), 3.52-3.42 (m, 8H).

Synthesis of PEI-DANS. Mixture of DANS-OH (0.5 g, 1.52 mmol), diimide DI (0.788 g) and triphenylphosphine (0.837 g, 2.1 eq.) was dissolved in 20 ml of anhydrous THF. To this solution was added 0.582 g of the diethyl azodicarboxylate. The mixture was stirred at room temperature for 24 h. Excess methanol was poured into this reaction mixture for the isolation of polymer. The precipitated red polymer was collected and purified by soxhlet extraction using methanol solvent for 2 days. 1.1 g of polyetherimide was obtained (88 % yield).

^{1}H-NMR ($CDCl_3$) δ 8.13 (d, 2H), 7.70 (m, 2H), 7.50 (d, 2H), 7.29-7.13 (m, 8H), 7.05-6.74 (m, 10H), 3.84 (br, 4H), 3.64 (br, 4H), 1.72 (m, 6H).

Synthesis of PEI-TH. This polymer was prepared in a similar manner to PEI-DANS (85 % yield).

^{1}H-NMR ($CDCl_3$) δ 7.70-7.66 (m, 2H), 7.30-7.13 (m, 10H), 7.06-6.63 (m, 12H), 3.75 (br, 4H), 3.57 (br, 4H), 1.62 (br, s, 6H).

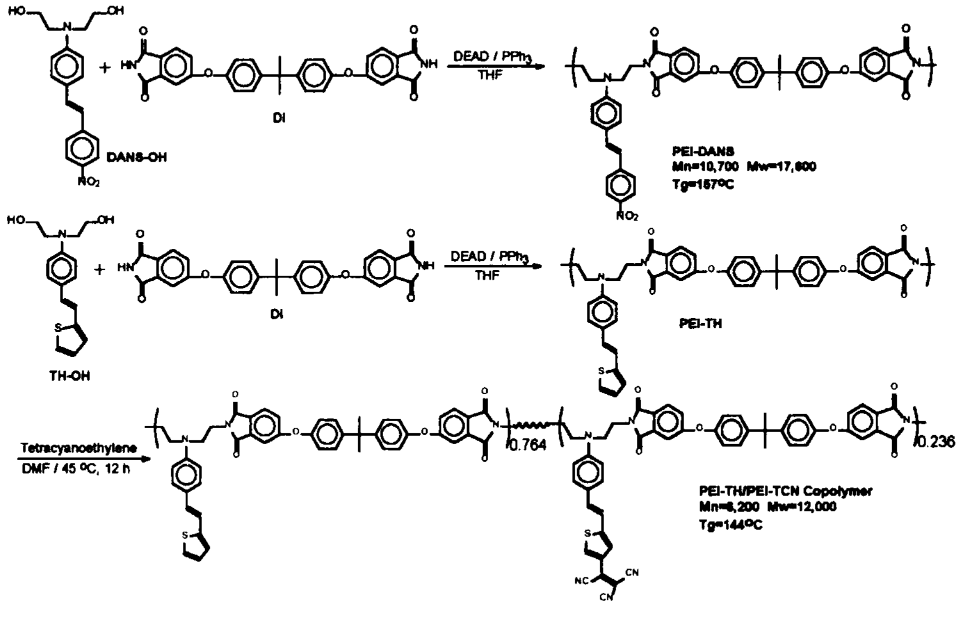
Synthesis of PEI-TH/PEI-TCN. 0.80 g of PEI-TH and 0.16 g of tetracyanoethylene were dissolved in dimetylformamide (DMF). The mixture was stirred at 45 ℃ for 12 h. Excess methanol was poured into this reaction mixture for the isolation of polymer. The precipitated blue polymer was collected and 0.68 g of polyetherimide was obtained.

^{1}H-NMR ($CDCl_3$) δ 7.63-7.59 (m, 2H), 7.24-7.09 (m, 11H), 6.88-6.63 (m, 9H), 3.75 (br, 4H), 3.57 (br,4H), 1.62 (br, s, 6H)

RESULTS AND DISCUSSION

The synthetic procedures for PEI-based polymers are shown in Scheme 1. The diol monomers, 4-bishydroxyethylamino-4'-nitrostilbene (DANS-OH) and N,N-bis(2-hydroxyethyl)-4-[2-(thiophene-2-yl)vinyl]aniline (TH-OH) were synthesized by Horner-Emmons reaction using dialkylaminobenzaldehyde with diethyl-4-nitrobenzyl phosphate or diethylthiophenylmethylphosphate, respectively. The polymerization reactions between the diimide (DI) and diols were performed by the Mitsunobu rection using diethyl azodicarboxylate (DEAD) and triphenylphosphine in anhydrous THF. The soxhlet extractions using methanol were executed to purify PEI-DANS and PEI-TH polymers. The PEI-TH was further reacted with tetracyanoethylene in DMF and gave a blue-colored PEI-TH/PEI-TCN copolymer, which has partly substituted tricyanovinyl group.

Scheme 1



The UV/visible absorption spectra of the PEI derivatives are shown in Figure 1. The absorption maxima of PEI-DANS, PEI-TH and PEI-TH/PEI-TCN are at 441, 365 and 365/669 nm, respectively. Two peaks in the copolymer are due to the intrinsic absorption of TH and substituted TCN. All polymers were soluble in DMF, cyclohexanone, THF, etc. and can be processed into optical quality films by spin coating. The resulting Tg ranged between 144 ~ 157 ℃. The macroscopic second-order susceptibility $\chi^{(2)}$ of the polymer films was determined by measuring their SHG signal. After optimizing the poling conditions, we were able to produce PEI-DANS film with an $\chi^{(2)}$ value of 73 pm/V at 1063 nm. The SHG signal intensity of PEI-DANS slowly decreased with increasing temperature, as presented in Figure 2. The rate of decrease of SHG signal became significant over 125 ℃. Furthermore, when the temperature reached 150 ℃, which is in the T_g range, a fast signal decay sets on, causing SHG signal to

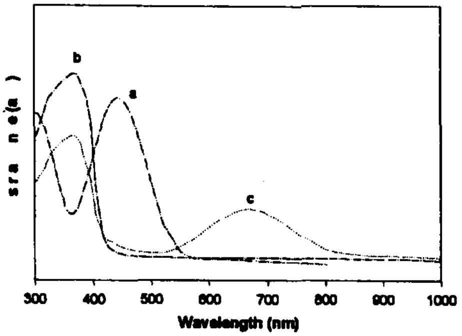


FIGURE 1 UV/vis spectra of (a) PEI-DANS, (b) PEI-TH and (c) PEI-TH/PEI-TCN coplymer

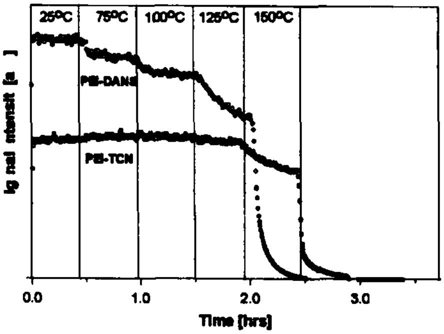


FIGURE 2 Thermal stability of SHG signal of poled polyetherimides

disappear within 30min. Decay process of PEI-DANS shows similar to those of other side chain NLO polymer reported. The PEI-TH/PEI-TCN sample with a relatively low chromophore concentration level (23.6%) was measured to have an $\chi^{(2)}$ value of 56 pm/V at same wavelength and its NLO activity showed an excellent temporal and thermal stability. No decay in the value of the SHG signal was observed up to 125 ℃. The enhanced temporal stability pattern of the SHG signal in this polymer is quite similar with that of crosslinked type NLO polymers. This excellent thermal and temporal stability can be attributed to the strong chromophore-chromophore and/or chromophore-polymer backbone interactions from electron-rich nonbonding electron of thiophene and tricyanovinyl group having high electron attracting power.

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REFERENCES

1. K.-S. Lee, M. Samoc, and P. N. Prasad, in Comprehensive Polymer Science, edited by S. L. Aggarwal, and S. Russo, (Pergamon Press, Oxford, 1992), Chap. 16, pp. 407-447.
2. D. M. Burland, R. D. Miller, and C. A. Walsh, Chem. Rev., 94, 31 (1994).
3. M. Eich, B. Reck, D. Y. Yoon, G. Willson, and G. C. Bjorklund, J. Appl. Phys., 66, 3241 (1989).
4. B, J, Mandal, J. Kumar, J. C. Huang, and S. K. Tripathy, Makromol. Chem. Rapid Commun., 12, 63(1991).
5. L. P. Yu, W. Chan, and Z. Bao, Macromolecules, 25, 5609(1992).
6. M. Stahelin, C. Walsh, D. Burland, R. Miller, R. Twieg, and W. Volksen, J. Appl. Phys., 73, 8471(1993).
7. K.-J. Moon, H.-K. Shim, K.-S. Lee, J. Zieba, and P. N. Prasad, Macromolecules, 29, 861 (1996).
8. K.-S. Lee, K.-Y. Choi, J. C. Won, B. K. Park, and I.-T. Lee, US Patent 5,212,277, May 18, 1993.