PII: S0032-3861(97)10226-9

Polymer Vol. 39 No. 20, pp. 4977–4981, 1998
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0032-3861/98/$19.00+0.00

Synthesis and characterisation of 1,3-bis(dicyanomethylidene)indane (BDMI)-based nonlinear optical polymers

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(Received 24 September 1997; revised 14 October 1997; accepted 15 October 1997)

New polymers containing nonlinear optical chromophores of electron donor-bridge moieties amino-phenylenethienylidene (APT) coupled with a strong electron acceptor 1,3-bis(dicyanomethylidene)indane (BDMI) were synthesised by coupling the aldehydic APT precursor polymers with acceptor BDMI in acetic anhydride. The aldehydic APT precursor polymers were prepared via traditional condensation or radical polymerisation schemes where the aldehydic group of APT was found intact. Thermal stability of these BDMI-based polymers determined by t.g.a. was up to 500°C depending mainly on the chromophore loading density. The electro-optic coefficient (r_{33}) of 10 pm V^{-1} was obtained in a 30% by weight chromophore loading polymer. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: 1,3-bis(dicyanomethylidene)indane; nonlinear optical polymers; electro-optic materials)

Introduction

Polymeric second-order nonlinear optical (NLO) materials are very promising for applications in photonic devices, such as electro-optic modulators and frequency doublers, due to their large optical nonlinearities, high laser damage thresholds, low dielectric constants, and excellent processibilities[1–3]. To meet the requirements for practical photonic device applications, two important issues must first be addressed from the material point of view. First, the materials must have large, non-resonant second-order optical nonlinearities. Second, the materials must have excellent chemical and thermal stabilities under both device operating as well as fabrication conditions.

NLO chromophores containing amino-phenylenethienylidene (APT) electron donor–bridge systems coupled with strong electron acceptors, such as 1,3-bis(dicyanomethylidene)indane (BDMI) (**1** as shown in *Figure 1*), have recently been demonstrated to exhibit exceptionally large second-order optical nonlinearities as well as excellent chemical and thermal stabilities in composite PMMA films[4–8]. The chromophore doped guest–host system may encounter the problems, however, of chromophore sublimation, solubility, and miscibility difficulty with the host polymer matrix. The covalent incorporation of NLO moieties into the polymer matrix can minimise these shortcomings.

Experimental

Materials. The mono- and di-functionalised APT monomers **2** were prepared as described elsewhere[4]. The comonomer methyl methacrylate (MMA) was purchased from Aldrich and was purified by distillation and stored in a refrigerator under argon. All other comonomers, reagents and solvents were purchased commercially and used without further purification unless noted otherwise.

Preparation of aldehydic polyesters. Dihydroxy-functionalised APT **2** (2.00 mmol) and 2.00 mmol of diacid chloride comonomers (or a combined amount of **2** and neopentyl glycol equals the amount of diacid chloride in the case of co-polymers) were dissolved in 40 ml dry dioxane or THF, then 0.50 ml (6.21 mmol) dry pyridine was added dropwise to the reaction solution. The reaction was then stirred at 50–70°C for at least 12 h. The product suspension was filtered, and the filtrate was diluted with 400 ml methanol. Yellowish aldehydic polyester **3** precipitate was filtered and washed with methanol, then dried in a vacuum oven. The polymer can be further purified by re-dissolving in chloroform and re-precipitating out in methanol. Yields were in the range of 60–90%.

Preparation of aldehydic polymethyl methacrylate. Methyl methacrylate-functionalised **2** (1.00 mmol) (shown in *Figure 2*) was mixed with the desired amount of comonomer methylmethacrylate (MMA) in 4 ml anhydrous DMF. Then a certain amount of initiator, AIBN (the quantity of AIBN is subject to the desired polymer molecular weight) was added. The reaction mixture was sealed at − 78°C in high vacuum in a polymerisation tube. The reaction was stirred and heated at 60–70°C for at least 48 h. The product mixture was poured into 400 ml methanol. Yellowish aldehydic PMMA **3** precipitate was filtered off and washed with methanol. Yields were in the range of 70–90%.

Preparation of BDMI polymers. Aldehydic polymers **3** (1.0 mmol) were mixed with 1.5 mmol of BDMI acceptor in 10–20 ml acetic anhydride, then the suspension was heated at 60–70°C overnight. After cooling to room temperature, the dark precipitate was filtered, and washed with methanol, giving the final BDMI polymers **4** in 80–100%

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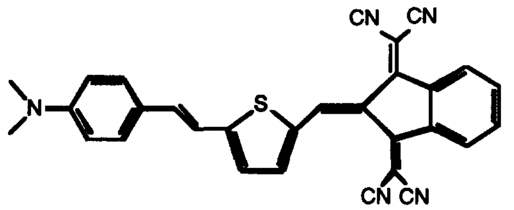

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APT-BDMI

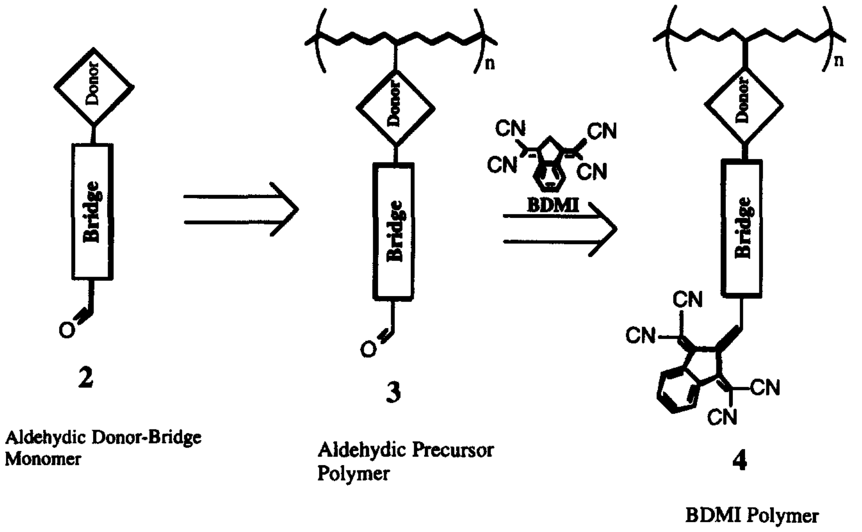

Figure 1 Structure of APT-BDMI and general synthetic scheme of BDMI polymers

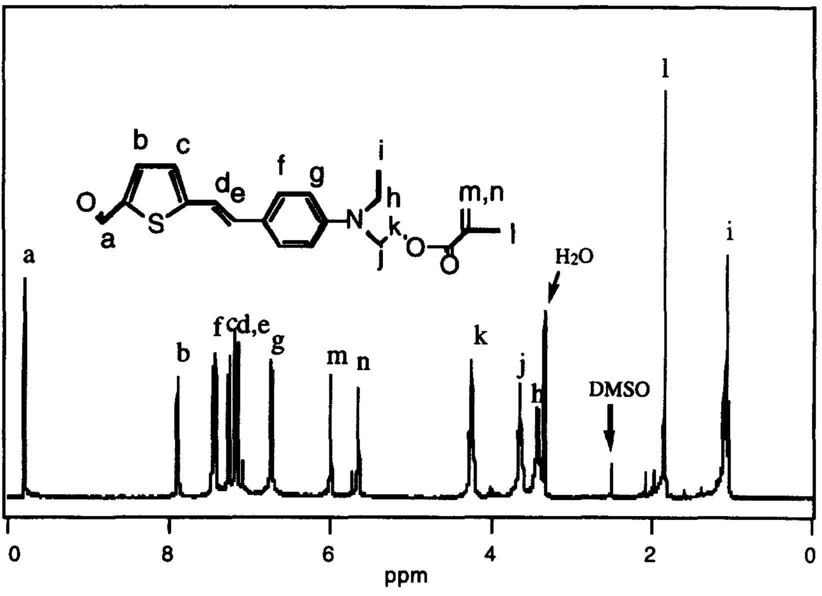

Figure 2 ^{1}H n.m.r. spectrum of aldehydic MMA-APT donor–bridge monomer

yield. The polymer can be further purified by re-dissolving in chloroform and precipitating out again with methanol.

Characterisations. Conventional ^{1}H and ^{13}C n.m.r. spectra were taken using a Bruker-250 *FT*-n.m.r. spectrometer operating at 250 MHz. Elemental analyses were performed by Atlantic Microlab, Inc. Mass spectra data were obtained from the UCR Mass Spectrometry Facility. *FT*-i.r. spectra were obtained using a Perkin-Elmer 1760 FTIR spectrophotometer. UV–VIS spectra were measured on a Perkin-Elmer Lamda-4C spectrophotometer operating in the range of 190–900 nm. Polymer molecular weights (M_w) were measured by size exclusion chromatography (SEC) using tetrahydrofuran (THF) as the mobile phase and polystyrene as the reference standard. Melting points and glass transition temperatures (T_g) were determined by a Perkin-Elmer DSC-7 system. Thermal decomposition temperatures (T_d) were measured by a Perkin-Elmer TGA-7 system.

Film preparation and NLO characterisation. BDMI polymer thin films were prepared by dissolving the polymer directly in dioxane or chloroform, filtering through a 0.2-μm filter, then spin casting onto ITO-coated glass slides. The films were dried in a vacuum oven at 50°C for at least 24 h. Thicknesses of the films selected for NLO characterisations were between 1.5 and 3 μm. In situ and static stage corona discharge poling set-ups[9] were used to pole the NLO films. Electro-optic coefficients r_{33} (pm V^{-1}) were measured at a wavelength of 1.064 μm using the attenuated total reflectance (ATR) technique [10].

Results and discussion

This study demonstrated that a general method of incorporating APT-BDMI push–pull NLO chromophores into polymer matrices was to polymerise the functionalised aldehydic donor–bridge monomers **2** first by employing various polymerisation schemes to yield the corresponding aldehydic polymers **3**, which were condensed with the BDMI acceptor to give the final product BDMI polymers **4** (*Figure 1*). Such a strategy of building the NLO polymers by reaction of acceptor species directly with a polymeric substrate is particularly attractive to those electron acceptors which are sensitive to either chromophore monomer functionalisation or polymerisation reaction conditions, such as the BDMI acceptor. Jen and co-workers reported[11] synthesising a polyimide first then coupling the tricyanovinyl acceptors to the polyimide donor–bridge moiety. This was necessary because the tricyanovinyl acceptor was found to be sensitive to the harsh polyimide reaction conditions. The difference in our situation, though, was that the aldehyde moiety was found intact throughout the monomer functionalisation and various polymerisation schemes (e.g. base-catalysed polyester condensations, or AIBN-catalysed radical PMMA reactions) without degradation or side reaction. For example, in the case of radical PMMA reaction, ^{1}H n.m.r. spectra showed that the olefin *m* and *n* protons of the aldehydic MMA–APT monomer (*Figure 2*) at 6.00 and 5.66 ppm disappeared, while the aldehyde protons at 9.80 ppm (as well as all other protons of the monomer and comonomers) remained, although expectedly broadened due to the polymer formation (*Figure 3*). After the BDMI acceptor coupling reactions, the aldehyde proton peak of the aldehydic PMMA at 9.8 ppm disappeared and was accompanied by the appearance of acceptor proton peaks at 8.2–8.8 ppm (*Figure 4*). The stoichiometric structures of the polymers were also confirmed by elemental analysis. UV–VIS absorbance spectra of the aldehydic and final BDMI polymers showed a significant red shift of the chromophore charge transfer absorption maxima (420 nm for aldehydic APT precursor polymers **3**, to 680 nm for APT-BDMI polymers **4**) upon attachment of the acceptor. This red shift in wavelength is basically the same as that of the corresponding chromophore (430 nm for APT **2**, to 690 nm for APT–BDMI **1**).

The molecular weight (M_w) of the BDMI-based polyesters determined by size-exclusion chromatography (SEC) are typically in the range of 4000–20 000 for a typical 1-day reaction at 50–60°C with a base such as pyridine as catalyst. The BDMI-based polymethyl methacrylates synthesised usually have molecular weights from 20 000 up to 200 000, depending on the reaction controls, such as the amount of initiator AIBN used, reaction time and temperature. The problem associated with too low a molecular weight (such as in the case when the molecular weight is smaller than 2000) is the poor optical quality thin films when spin coating. However if the molecular weight is too high (such as in the case when the molecular weight is over 50 000), the final BDMI polymer has poor solubility in common organic solvent. We have found that polyesters with a molecular weight of about 4000 have very good solubility in common organic solvents and also produce high optical quality thin films when spin cast.

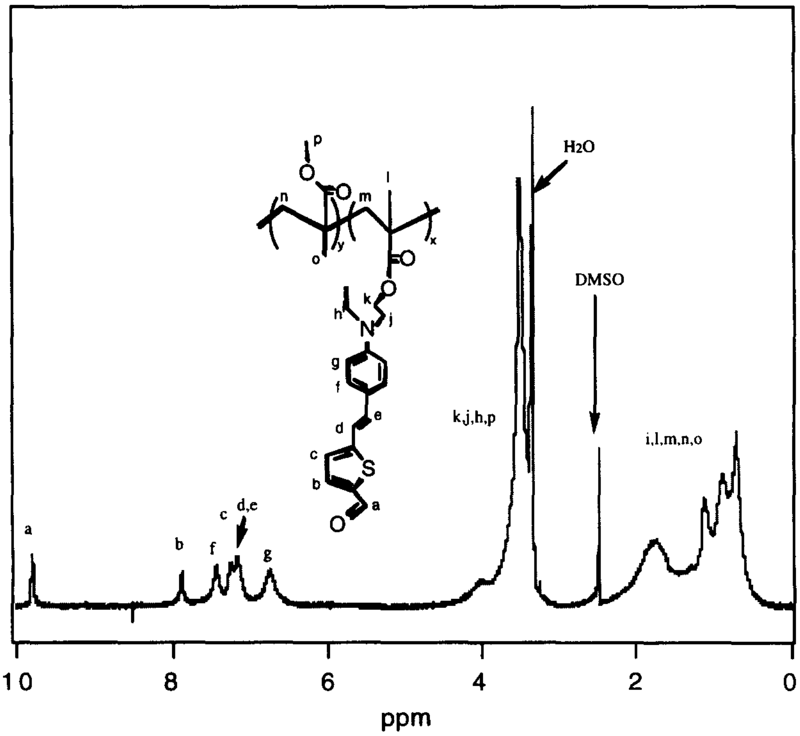

Figure 3 ^{1}H n.m.r. spectrum of aldehydic PMMA

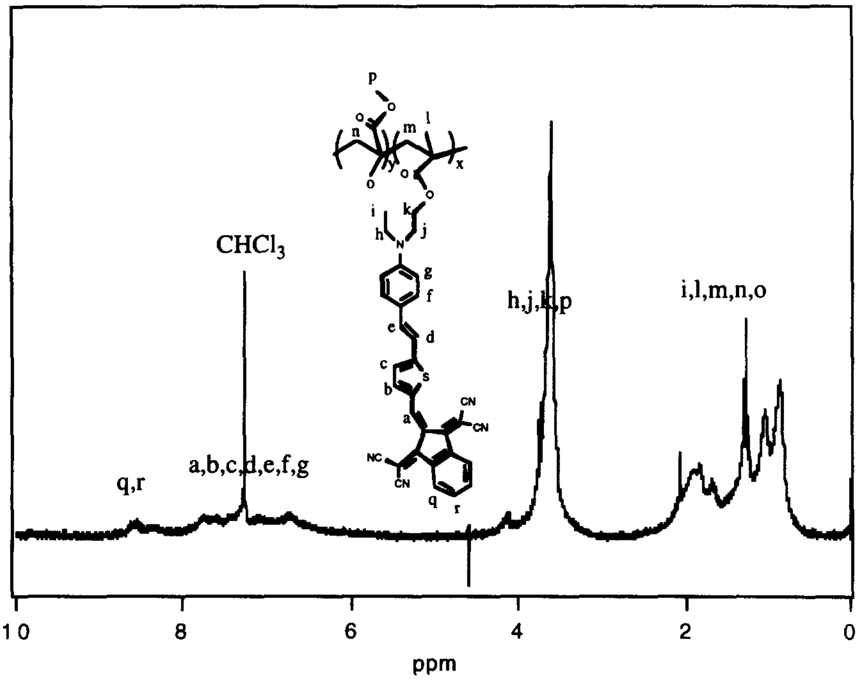

Figure 4 ^{1}H n.m.r. spectrum of BDMI PMMA

Thermal analyses of these BDMI polymers demonstrate glass transition temperatures (T_g) in the range of 90–150°C; the decomposition temperatures (T_d, measured under inert gas atmosphere) range from 280 to over 500°C. We have observed that, in general, the lower the APT-BDMI chromophore loading in the polymer, the higher the T_g and T_d. Since the chromophore itself decomposes at 280°C, it is therefore anticipated that the interaction between polymer backbone moieties and the chromophores helps improve the thermal stability of the chromophores.

For the BDMI polyesters synthesised, the diacid chloride comonomers we used include oxalyl chloride, terephthaloyl chloride (polymer **5** in *Figure 1*), bisphenol A bis(chloroformate), or a combination of the two comonomers, terephthaloyl chloride and neopentyl glycol. The introduction of the dihydroxy comonomer, neopentyl glycol, is to better control and tailor the APT-BDMI chromophore loading density in the polymer matrix. We have found that, when the chromophore loading density in polymer matrix is too high, such as in the case when the comonomers are oxalyl chloride (correspond to an APT-BDMI loading density of about 90% by weight), terephthaloyl chloride (70% by weight), or bisphenol A bis(chloroformate) (50% by weight), the BDMI polymers thus formed could not be poled at all with our current 9-kV corona poling set up. No NLO signal and no absorbance change before and after poling indicated the absence of chromophore alignment. For the 30% by weight loaded BDMI co-polyester, we measured an electro-optic coefficient r_{33} of 10 pm V^{-1}, while for a 10% APT-BDMI weight loaded co-polyester, an r_{33} of 8 pm V^{-1} was obtained. The causes of the poling difficulty, especially at higher chromophore loadings, may be due to both the steric hindrance of the bulky BDMI acceptors tangled in polymer chains, and the strong electrostatic chromophore dipolar interaction (also known as London Forces). Such a strong dipolar interaction tends to counter-align the chromophore dipoles to each other to form centric-aligned dipole pairs[4,7,12], thus negating their nonlinear contribution. From this point of view, it is expected that the lower the chromophore loading density, the longer the average distance between chromophores, and the better the poling efficiency. On the other hand, the bulk optical nonlinearity of the material is proportional to the NLO chromophore loading density. Therefore, the best optical nonlinearity of the BDMI polymer would be for a chromophore loading density that compromises these two competing factors. In our case, the 30% APT-BDMI weight loading seems to provide the best results. From the measured material macroscopic nonlinearity, the molecular microscopic nonlinearity, and the chromophore loading density, we estimated the poling efficiency is about 6%[4]. This means, we still have much room to improve the bulk optical nonlinearity, for instance, via molecular modifications, to reduce the inter-molecular dipole interactions or to reduce the steric hindrance in poling.

Conclusions

The amino-phenylenethienylidene–1,3-bis(dicyanomethylidene)indane (APT-BDMI)-based push–pull second-order nonlinear optical chromophores have been covalently incorporated into various types of polymer matrices via an aldehydic precursor polymer route. This synthetic scheme has been proven to work because the aldehyde group was found intact during both donor–bridge monomer functionalisation and the polymerisation reactions we have surveyed so far. This synthetic method may also be applicable for other strong electron acceptors which are sensitive to either chromophore monomer functionalisation or polymerisation reaction conditions. The poling difficulty of these BDMI polymers may be due to the steric hindrance of the bulky acceptor tangled in polymer chains, as well as by the 'centric alignment' mechanism due to strong electrostatic dipolar interactions. Future work includes molecular modifications to minimise these side effects and develop polymer lattice-hardening protocols to lock in the poling-induced noncentrosymmetry.

Acknowledgements

This research was supported by the National Science

Foundation (DMR-9528021) and the Air Force Office of Scientific Research (F49620-94-1-0201).

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