

Synthesis, Characterization and Some Optical Properties of Poly(hexa-2,4-diynylene-1,6-dioxy)dinaphthoates Containing Polar Azo Dye

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Abstract

In order to study the effect of main-chain conformation on the second-order non-linear optical properties, two novel isomeric polymers, consisting of hexa-2,4-diynylene-1,6-dioxynaphthoates main-chains containing a polar azo dye, Disperse Red 19, were synthesized and characterized. The 1,2- and 3,2-polymers had a T_g of 134 and 143°C, respectively. Their spin-coated films were exposed to corona poling, and the orientation behavior was studied. The order parameters of the two polymers were similar, around 0.2. The 3,2-polymer underwent cross-linking during poling. Neither polymer did cross-link when irradiated by UV light during poling, indicating that their chemical structures are not apt to cross-link.

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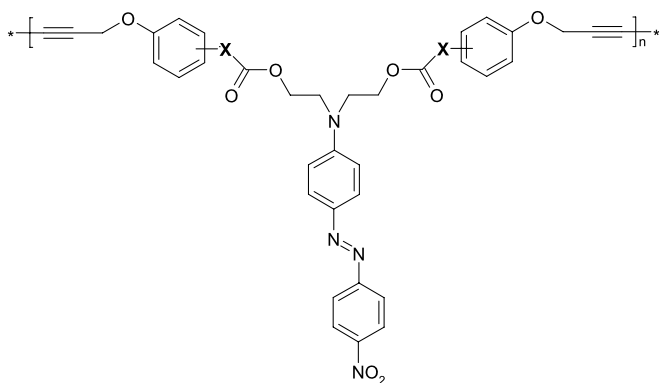
Keywords

Diacetylene-containing polymers, corona poling, poly(propargyloxynaphthoates), photonic polymer

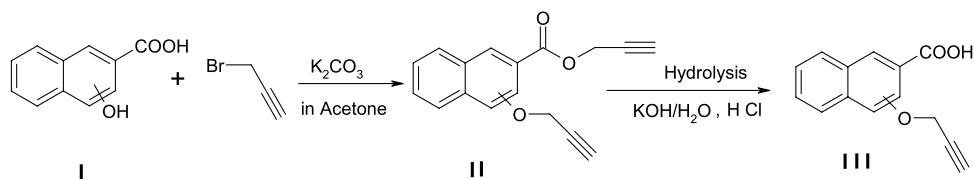
1. Introduction

Organic polymers which have non-linear optical properties have been intensively investigated in the last decades, and many different types of polymers have been synthesized [1–4]. In the case of second-order non-linear optical (2-NLO) polymers, the non-centrosymmetric orientation of chromophores is essential, and high hyperpolarizability of chromophores and high glass-transition temperature (T_g) were thought to be the most important factors, and many novel chromophores have been synthesized. However, even if a chromophore with an extremely high hyperpolarizability was employed, there will be no appreciable 2-NLO effect if they are not properly orientated. High- T_g polymers such as polyimides suffer a drawback in poling, and in general 2-NLO susceptibilities are not high [5, 6]. The present

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Scheme 1. Poly(2,4-hexadiynylene-1,6-dioxydibenzoate)s (X = none) and poly(2,4-hexadiynylene-1,6-dioxydicinnamate)s (X = $-\text{CH}=\text{CH}-$).



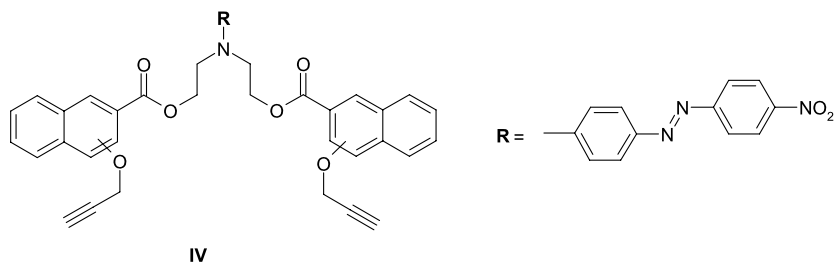
Scheme 2. Synthesis of propargyloxynaphthoates.

authors have studied the effect of polymer main chain on the 2-NLO susceptibility of dye-containing polymers, and found that the main-chain conformation is very important for the orientation of polar dyes linked to the main chains. For example, the *para*-polymers shown in Scheme 1 showed much higher 2-NLO susceptibilities [7, 8] and orientation stability [9] than the corresponding *meta*-polymers. Thus the main-chain conformation has a strong influence on the orientation and its stability of chromophores by corona poling. In this study as a continuation of previous work, two isomeric bispropargyloxynaphthoates were chosen, and their polymers containing an azo chromophore, Disperse Red 19, were synthesized and characterized. Their films were poled by corona discharge and the orientation behavior was studied in order to see the effect of main-chain conformation on the second-order non-linear susceptibility.

2. Experimental

2.1. Synthesis

The reagents used were supplied by Aldrich unless otherwise mentioned. 3-Hydroxy-2-naphthoic acid and 1-hydroxy-2-naphthoic acid were reacted with propargyl bromide in acetone by the following manner. The synthetic route is shown in Scheme 2.



Scheme 3. Monomers (bispropargyloxydinaphthoates).

Of each acid, 10.0 g (53.19 mmol) was dissolved in 100 ml acetone, and 9.45 g (69.14 mmol) of potassium carbonate and 10.58 ml (106.38 mmol) of propargyl bromide in 80% toluene solution were added. The reaction mixture was stirred for 3 weeks at room temperature. The solid was filtered off and washed with acetone. The mother liquor was then evaporated with a rotary evaporator, and the remaining solid was washed with water until the pH reached 7. The pale brown solid was then recrystallized from toluene. **(II)** 3-Propargyloxy-2-propargylnaphthoate; mp 86°C, yield 83%. 1-Propargyloxy-2-propargylnaphthoate; mp. 77°C, yield. 80%. The esters were hydrolyzed with KOH solution stirring for 72 h until clear solutions were obtained, which were then filtered and dilute hydrochloric acid was added to precipitate the acids. A pale yellow solid was obtained. **(III)** 3-Propargyloxy-2-naphthoic acid: mp 133°C, yield 65%; 1-propargyloxy-2-naphthoic acid; mp 128°C, yield 68%. Compounds **(III)** were then converted to the corresponding chlorides by the reaction with oxalyl chloride, and then reacted with Disperse Red 19 in dichloromethane at 40°C, stirring with a magnetic stirrer for a week using triethylamine as an acid acceptor. Disperse Red 19 was prepared by the coupling of diazonium salt of *p*-nitroaniline with *N*-phenyldiethanolamine. After evaporation of the solvent, the product was separated from ethylacetate/water system. The products (Scheme 3) were then recrystallized from toluene and the bisacetylenic monomers **(IV)** were obtained. 3,2-Monomer: mp 115°C, yield 59%; 1,2-monomer: mp 110°C, yield 69%.

The oxidative coupling polymerization was performed as follows: 1 g of each monomer was dissolved in 5 ml NMP and 0.067 g CuCl and 3 drops of *N,N,N',N'*-tetramethylethylene diamine were added, and the system was stirred at room temperature for 4 days under slow bubbling of oxygen gas. The polymerization was monitored by the viscosity increase. The system was poured into acetone, and the fibrous precipitated was washed with acidified methanol, and with water and dried in vacuum. The polymers (Scheme 4) were purified by re-precipitation from their NMP solution by methanol.

2.2. Characterization

NMR spectra were recorded using a Bruker Avance 400. Differential scanning calorimetry (DSC) was performed using a Universal V3.5B calorimeter (TA In-

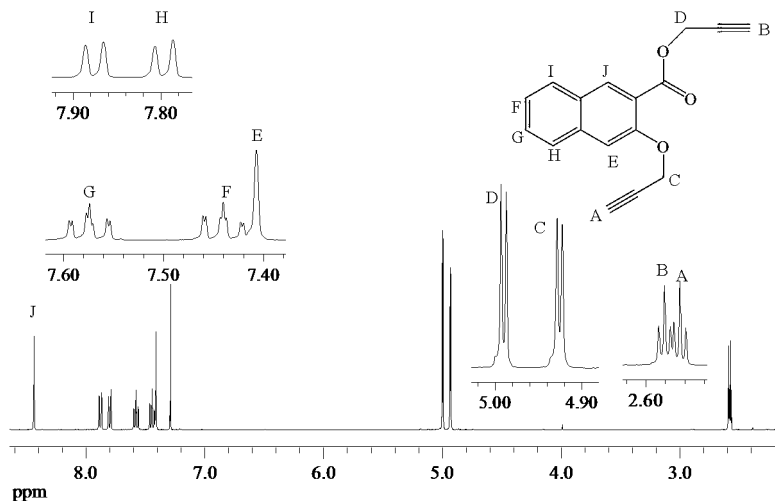


Figure 1. $^1\text{H-NMR}$ spectra of 3-propargyloxy-2-propargylnaphthoate in CDCl_3 .

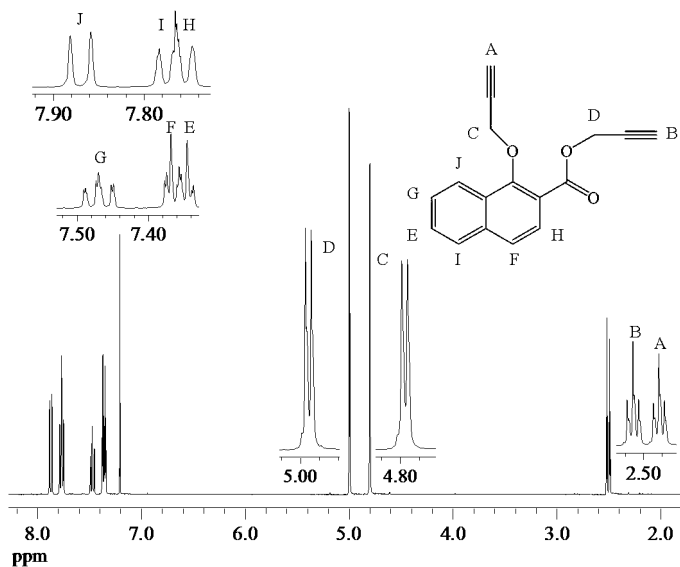


Figure 2. $^1\text{H-NMR}$ spectra of 1-propargyloxy-2-propargylnaphthoate in CDCl_3 .

(2.3 ppm) disappeared. In the FT-IR spectra also, the characteristic absorption peaks of the terminal acetylene, $-\text{C}\equiv\text{C}-\text{H}$, at 3285 cm^{-1} of the monomers disappeared when polymerized. The molecular weights of these polymers were found to be in the range of 1×10^4 . They were not very high, but sufficient to prepare films by spin coating. If the polymerization was allowed to continue the molecular weight increased and the solubility decreased.

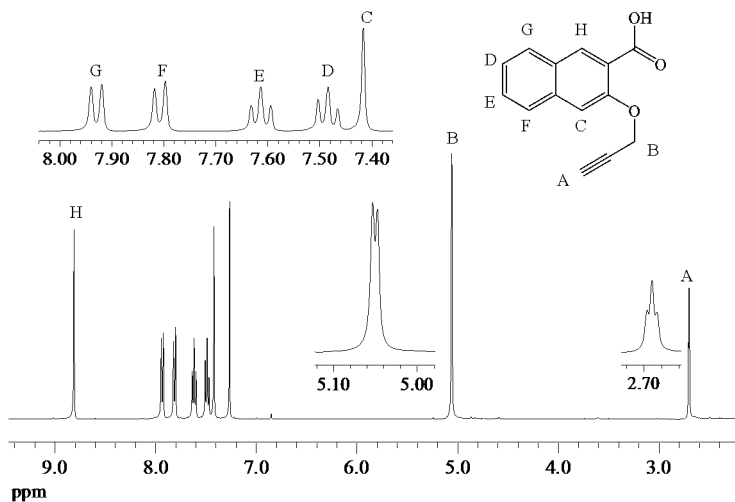


Figure 3. $^1\text{H-NMR}$ spectra of 3-propargyloxy-2-naphthoic acid in CDCl_3 .

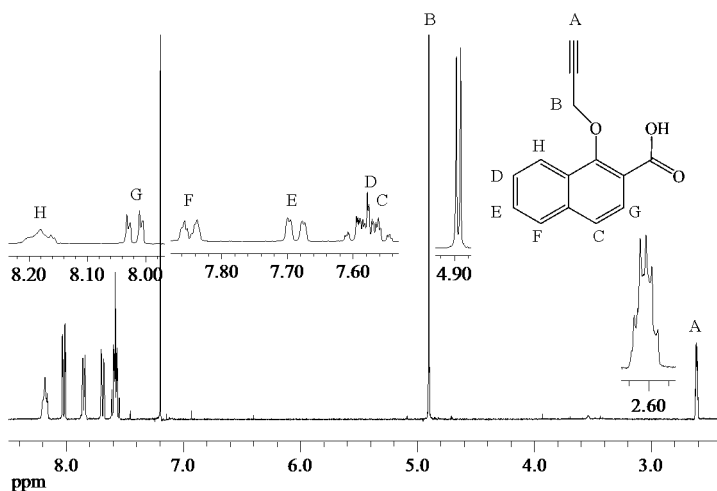


Figure 4. $^1\text{H-NMR}$ spectra of 1-propargyloxy-2-naphthoic acid in CDCl_3 .

Figure 7 shows the DSC and thermo-mechanical analysis (TMA) results. It was rather difficult to observe the T_g by DSC. The TMA indicated the approximate T_g in the range 134–144°C for the both polymers, higher than those of their analogues of benzoate and cinnamate polymers, which are around 100–110°C [7, 8]. This is due to the bulky naphthalene ring. The T_g values were also higher than those of poly(dipropargyloxynaphthoates) containing polar azo dyes, which were around 120°C [10]. The huge exothermic peaks that start at around 140°C are due to the reaction of diacetylene groups in the main chains, which are always observed for diacetylene-containing polymers forming highly cross-linked structures. The starting temperature varies depending on the type of polymers.

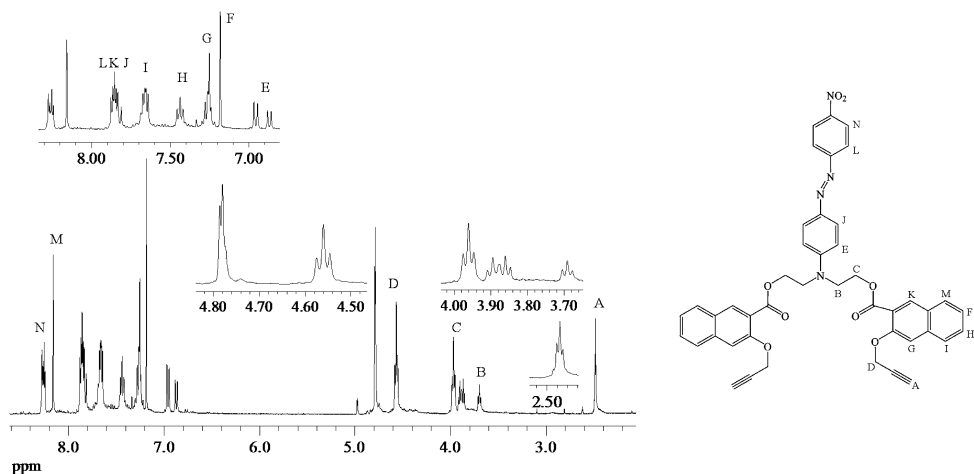


Figure 5. $^1\text{H-NMR}$ spectra of 3,2-monomer in CDCl_3 .

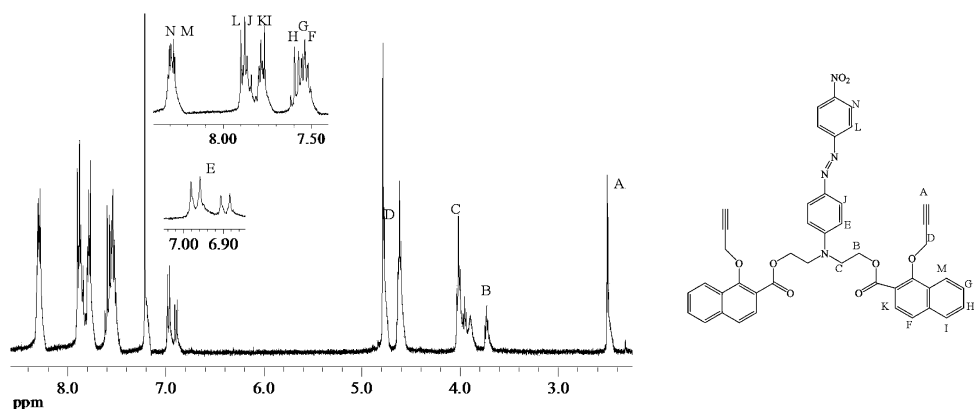


Figure 6. $^1\text{H-NMR}$ spectra of 1,2-monomer in CDCl_3 .

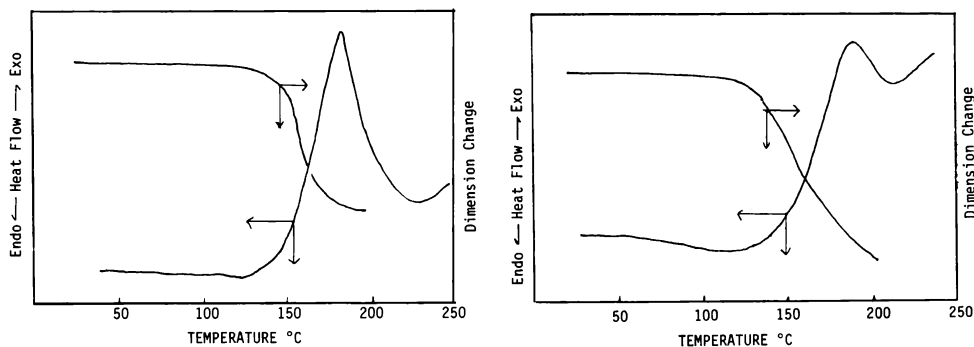


Figure 7. DSC and TMA thermograms of 3,2-polymer (left) and 1,2-polymer (right).

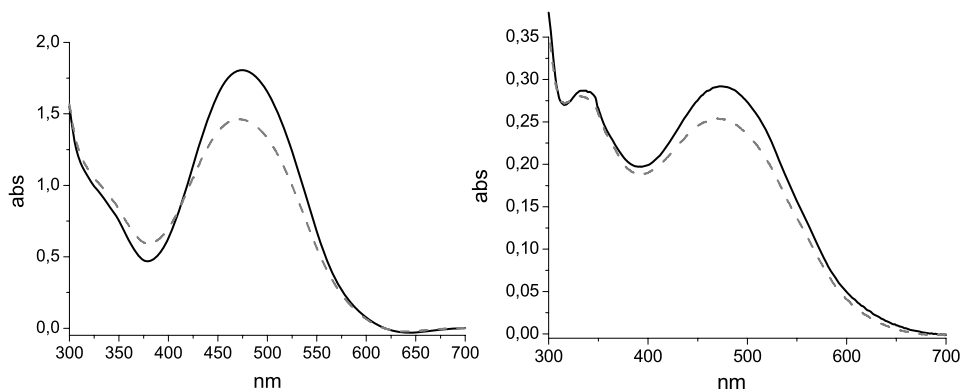


Figure 8. The poling effect of 3,2-polymer (left) and 1,2-polymer (right). (—) Before poling, (---) after poling.

Table 1.

Poling conditions and relaxation of orientation

Polymer	Poling temperature (°C)	Heating rate (°C/h)	Discharge (kV)	Poling time (min)	Order parameter (ϕ)	
					After poling	After 30 days*
3P2NA	135	100	9–9.5	90	0.19	0.17
1P1P2N	130	120	9–9.5	160	0.17	0.17

* At room temperature.

Figure 8 shows the visible absorption spectra of the films before and after poling. The poling conditions are shown in Table 1. The decrease in absorption peak height is considered to be due to the orientation of the chromophore, although surface burning by the corona discharge (poling) could be involved in a small extent. When the poled films were left to stand at room temperature for 30 days, the order parameters did not decrease appreciable as shown in Table 1. The poled films were left at 80°C for 3 h but the order parameters did not decrease drastically and maintained 80–90% orientation. However, when heated at 100°C for 13 h, the orientation of chromophores was almost lost the order parameters becoming 0.12 (3,2-polymer) and 0.07 (1,2-polymer). In order to see if UV irradiation might cause the cross-linking through the diacetylene groups, the films were irradiated with UV light at the poling temperatures for 30 min. However, no cross-linking took place under the irradiation conditions. It seems that the bulky naphthalene rings inhibit the cross-linking. The observed initial orientation factors of around 0.2 of these polymers are smaller than those of the benzoates and cinnamates analogues [7, 8]. This might be also due to the bulky naphthalene rings. The rigid polymers are usually less susceptible to poling and, therefore, the 2-NLO susceptibilities of aromatic polyamides [5] and polyimides [6] are poor. The 3,2-polymer became insoluble during poling

for 90 min, while the 1,2-polymer remained soluble. It is obvious that the former cross-linked, maintaining its orientation.

4. Conclusion

Novel polymers consisting of naphthalene, polar dye and diacetylene groups were synthesized, and their orientation by corona poling was studied. The order parameters were found to be around 0.2, which is a common value for many polymers with second order non-linear optical property. The 3,2-polymer cross-links during poling and maintained its orientation better than the 1,2-polymer.

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