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Synthesis and Characterization of Poly(dipropargyloxynaphtoates) Containing Polar Azo dyes

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Summary

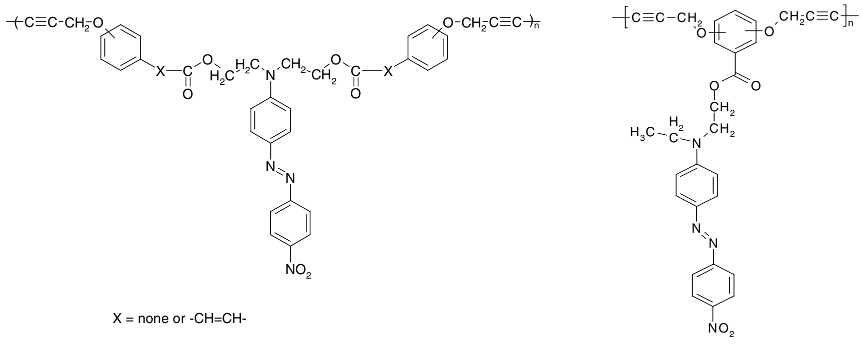
In order to study the relationships between the chemical structures of polymer main chains and second order nonlinear optical properties, novel polymers with hexa-2,4-diynylene-1,6-dioxynaphthoate as a main chain and common azo dyes (*Disperse Red 1* and *13*) in the side chains, were synthesized and characterized. The polymers were soluble in common organic solvents such as chloroform, dimethylformamide, *N*-methylpyrrolidone, etc, and gave films with excellent optical quality by spin coating. Apparent orientation parameters of around 0.25 were observed by the absorption decrease by Corona poling. The steric effect of chlorine atom of the dye on poling was not observed. On heating at 100ºC after poling the order parameters did not return to zero but reached a constant. It is thought that some of the chromophores remain orientated permanently.

Introduction

It has been considered that high glass transition temperature (Tg) was an essential factor for second order nonlinear optical (2-NLO) susceptibility of dye-containing polymers. However, high Tg polymers such as polyamides and polyimides are rigid molecules and their poling is difficult, and therefore their 2-NLO coefficients are low [1,2].

The present authors have shown that the intensity and stability of 2-NLO susceptibility of dye-containing polymers depend most significantly on the type of polymer main chains rather than Tg and hyperpolarizability [3,4]. It is very important for the chromophore orientation that the polymer main chains have stable conformation when poled. If polymer chains are distorted by poling, the orientation efficiency is low and the relaxation of poled chromophores will take place immediately. It seems that the relaxation takes place more easily when the polymer main chains have more freedom of rotation, as observed for the benzoate and cinnamate polymers where *para* benzoate and cinnamate have much higher SHG coefficients and stability than the corresponding *meta* analogues [3,4]. The present authors have also reported the poly(hexa-2,4-diynylene-1,6-dioxy)benzoates containing *Disperse Red 1* [5,6] and *13* [7], and found that the *para* and *ortho* polymers have higher SHG susceptibility than the *meta* polymers. The structures of these polymers are shown in Scheme 1.

It is thought interesting to study the effect of rigidity of main chains on SHG response and stability, the polymers with a naphthoate main chain and polar azo dyes in the side chains, were synthesized and characterized. The SHG response depends on how easily the chromophores are orientated by the Corona poling, and the orientation parameters can be determined from the absorption decrease before and after poling.



Dibenzoate and dicinnamate

Benzoate

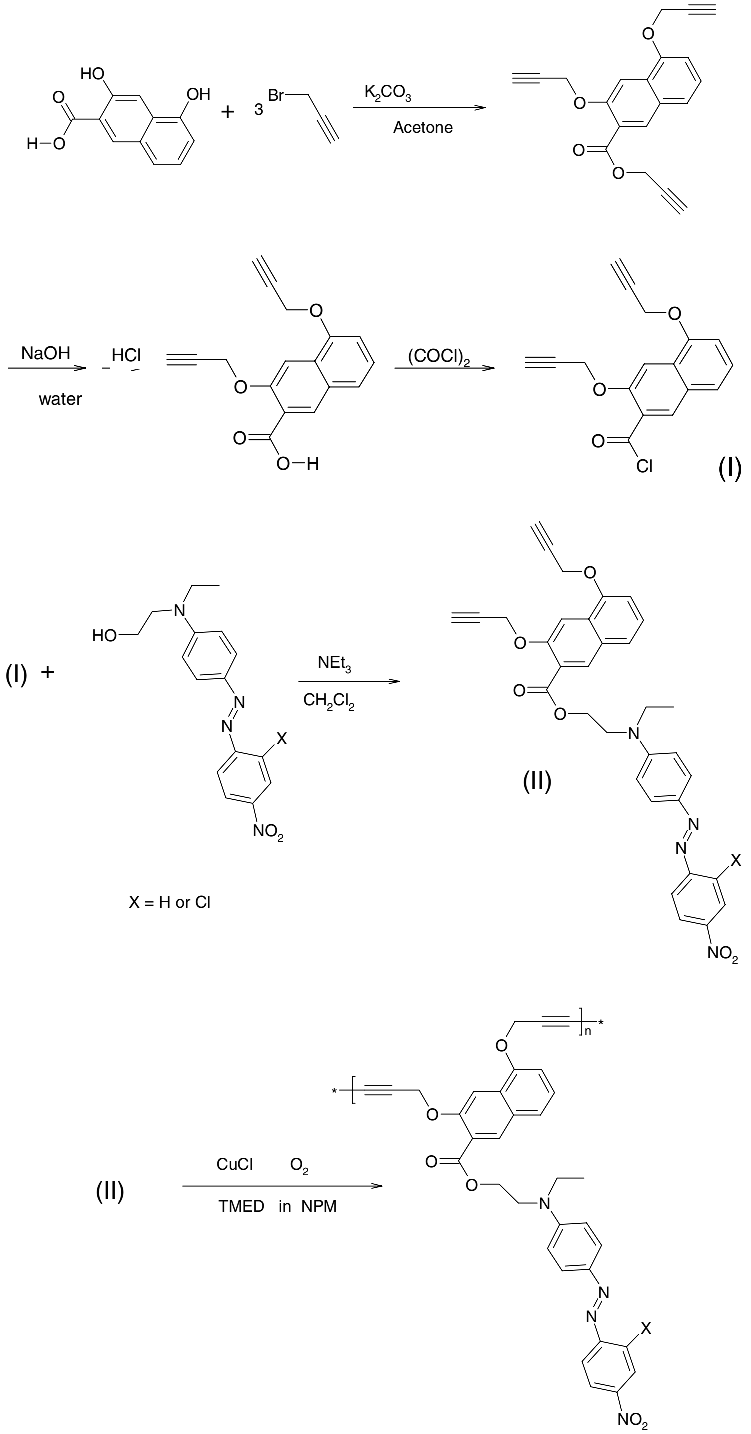
Scheme 1. Structures of poly(hexa-2,4-diynylene-1,6-dioxydibenzoates), poly(hexa2,4-diynylene-1,6-dioxydicinnamates) and poly(hexa2,4-diynylene-1,6-dioxybenzoates) containing polar azo dyes.

Experimental

Synthesis

The synthetic route is shown in Scheme 2. 10 g (0.049 mol) of 3,5-Dihydroxy-2-naphthoic acid (Aldrich), 30 g of potassium carbonate were suspended in 100 ml of acetone, and 17 ml of toluene solution (80%) of propargyl bromide (0.154 mol) (Aldrich) were added. The mixture was heated at 50ºC with stirring for 2 weeks. After filtering off excess potassium carbonate and potassium bromide, the acetone was evaporated, and the solid product was washed with HCl acidified water. The repeated recrystallization from toluene gave yellow crystals with mp. 110ºC with 73% yield. The propargyl ester was suspended in aqueous solution of KOH, and the solution was filtered and acidified with dilute hydrochloric acid. The acid was purified by recrystallization from toluene to obtain a pale yellow powder melting at 149ºC. The acid was then reacted with oxalyl chloride, and the chloride was reacted with dyes in dichloromethane using triethylamine as an acid acceptor.

Disperse Red 1 and *13* were prepared by the diazo coupling reaction of diazonium salts of 4-nitroaniline and 2-chloro-4-nitroaniline, respectively with 2-(*N*-ethylamino)ethanol (Aldrich), although these dyes are commercially available from Aldrich.



Scheme 2. Synthetic route of poly(3,5-dipropargyloxy-2-benzoates) containing *Disperse Red 1* and *13*.

Their purities were confirmed by ^{1}H NMR and IR spectroscopy. The oxidative coupling polymerization was carried out in *N*-methyl-2-pyrrolidone (NMP). 1.6 g of the monomer was dissolved in 5 ml of NMP and 0.014 g of copper(I) chloride and 3 drops of *N,N,N'N'*-tetramethylethylenediamine (TMED) were added, and the system was stirred for 10 hrs at room temperature. The viscosity increased with time, and the solution was poured into methanol and the polymer was precipitated as a fibrous material. The polymers were purified by reprecipitation process from NMP/methanol system. The inherent viscosities of the polymers in NMP at 25°C were in the range of 0.25-0.30 dl/g.

The poly(3,5-naphthoate) containing *Disperse Red 1* and *Disperse Red 13*, are named hereafter as 3,5-DR1 and 3,5-DR13, respectively. *p*-Nitro-*N,N*-diethanolaniline was also used, but the polymer was not soluble.

Characterization

NMR spectra of the intermediates and products were taken using a Bruker Avance 400 Model using $CDCl_3$ as a solvent. Differential scanning calorimetry (DSC) and thermal mechanical analysis (TMA) were carried out using a calorimeter Universal V3.5B of TA Instrument, and a thermo-mechanical analyzer General V4.1C of DuPont Model 2100, respectively. UV/Visible spectra were taken using a Unicam UV320 spectrophotometer.

Corona Poling

The films were prepared by spin coating of NMP solution on an ITO-coated glass substrate. The films were coated on the ITO side, and then dried at 80°C for 1 hr in vacuum oven to remove residual NMP. The poling was carried out with a needle-point cathode at a distance of 1.4 cm from the surface of film with a voltage of 5-6 kV, at the ambient atmosphere on a temperature-controlled hot plate (Dataplate 5-position digital hot plate) at temperatures just above the Tg of the polymers starting from 60°C with a heating rate of 120°C/h. The order parameter ϕ was calculated from the relationship, $\phi=1-(A2/A1)$ where A1 and A2 are the absorption maxima of film before and after poling, respectively.

Results and Discussion

Fig. 1 shows the ^{1}H NMR spectra of the monomer with *Disperse red 13*. All the peaks correspond to the structure, showing the compound is the correct one. The ^{1}H NMR spectrum of the monomer with *Disperse Red 1* was similar to that of *Disperse red 13*. After the polymerization, the peaks at 3273 cm^{-1} due to the terminal acetylenic bond ($\equiv$C-H) in the FT-IR spectra disappeared indicating that the oxidative coupling polymerization took place.

As can be seen from Fig. 2, DSC did not show the Tg clearly, and they vaguely indicated Tg around 118 and 123°C for 3,5-DR1 and 3,5-DR13, respectively. The TMA which indicates the deformation temperature can be more reliable, and the Tg of 3,5-DR1 and 3,5-DR13 were found to be 134 and 124°C, respectively, as can be seen from Fig. 3. These values are considerable higher than about 80°C of those polymers with benzoate main chains and *Disperse Red 1* in the side chains [5], indicating that the naphthoate main chain is more rigid than that of the benzoate (Scheme 1).

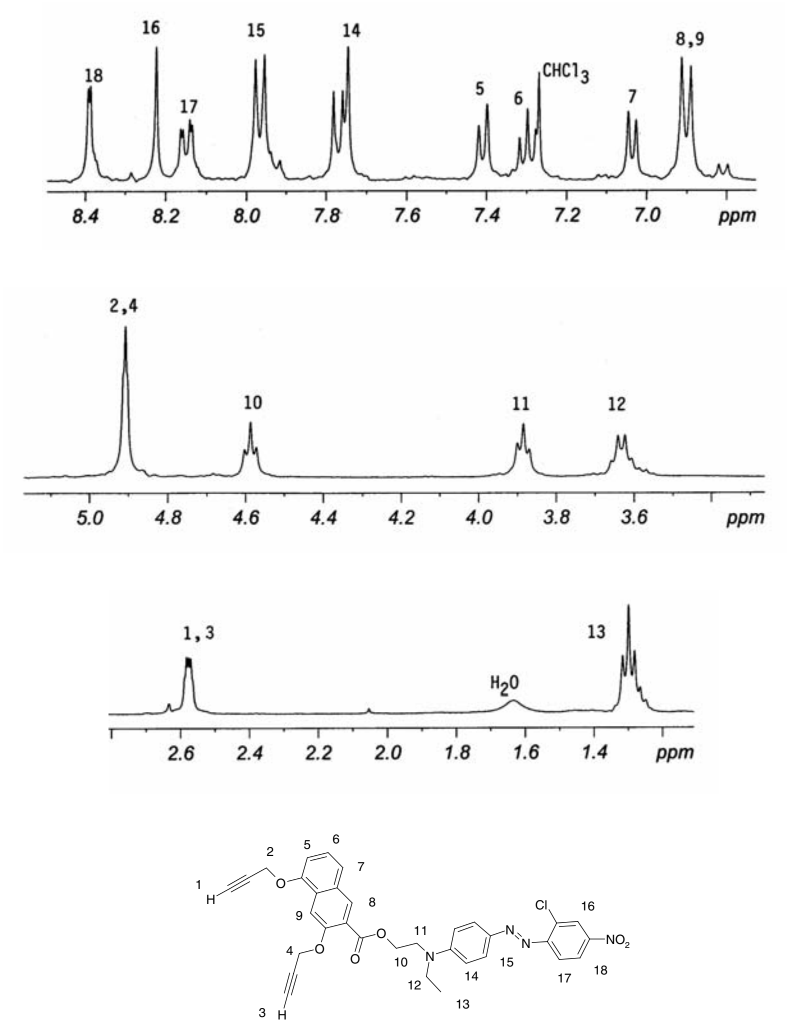


Fig. 1. ^{1}H NMR spectra of dipropargyloxynaphthoate containing *Disperse Red 13*.

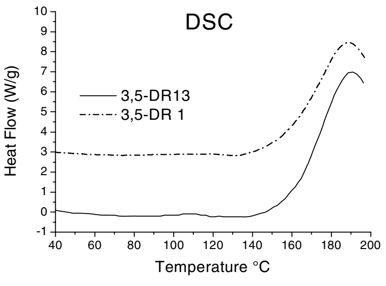


Fig. 2. DSC curves of the two polymers.

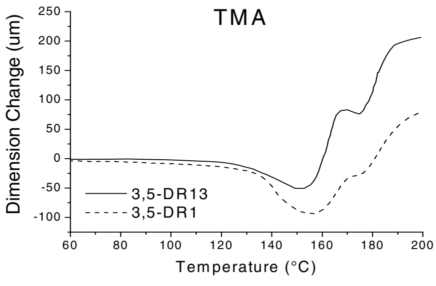


Fig. 3. TMA Curves of the two polymers.

The poling results are shown in Table 1. There was no significant change in the order parameters between the two, indicating that the there is no effect of chlorine atom on the poling. In the case of the benzoate with *Disperse Red 13* (Scheme 1 type) the order parameters were fairly low being 0.12 – 0.14, showing the effect of chlorine atom on the poling [7].

Table 1. Poling results of two polymer films

Polymer	Poling Temp (°C)	Discharge (kV)	Poling time (min)	Order parameter (ϕ)*
3,5-DR13	135	5.5	145	0.23
3,5-DR1	128	6.0	105	0.22

* Average of two sets of experiments.

The absorption changes with poling are shown in Fig. 4. The order parameters in the Table 1 are smaller than those of the *para*-benzoate and *para*-cinnamate (Scheme 1) which showed the order parameters of around 0.45 [8]. Therefore the 2-NLO coefficients of these polymers will be lower than 200-250 *pm/V* (1064nm) of the *para*-polymers of dibenzoate and of dicinnamate (Scheme 1) [3], and may be the similar to those of the benzoates [6].

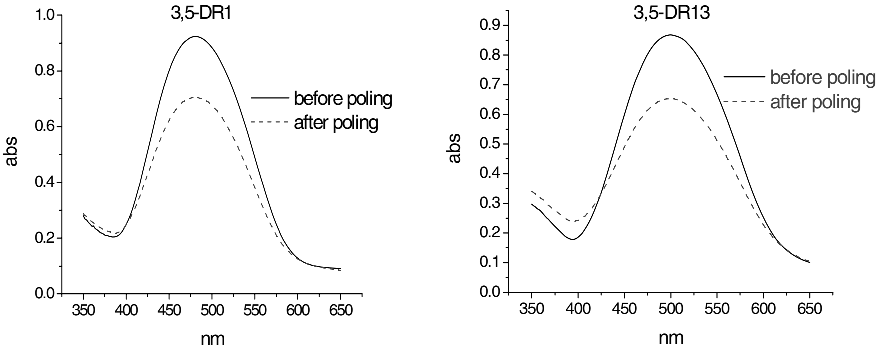
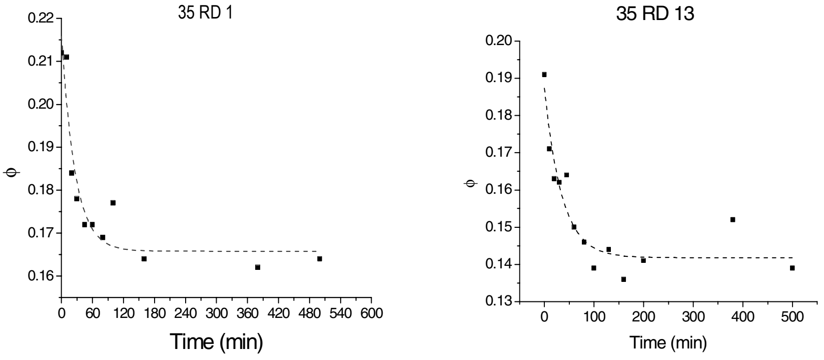


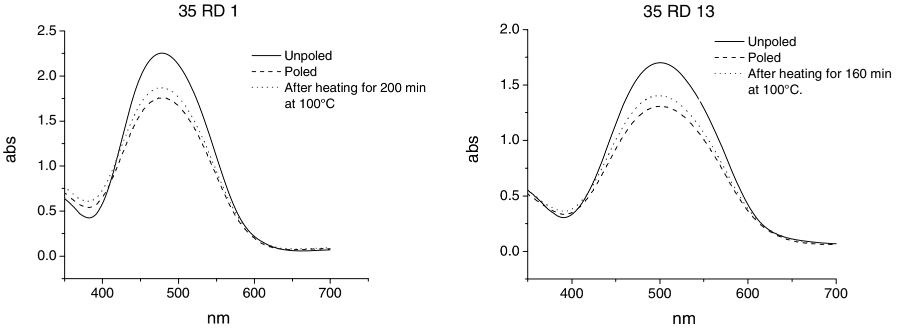
Fig. 4. Decrease in the absorption maxima with poling under the conditions shown in Table 1.

In order to see thermal relaxation behaviors, the poled films were subjected to heating at 100ºC for 500 min, monitoring the changes in absorption spectra. The results are shown in Figs. 5 and 6. Both polymers rapidly decreased their orientation but after 100 minutes further decrease was not observed and the orientation apparently remained constant. This might be due to the change in chemical composition during the poling. FTIR-ATR (attenuated total reflection) spectra of poled film surfaces were taken but there were no appreciable changes in the spectra before and after poling. Change in the chemical compositions of the films, were analyzed by the Rutherford Backscattering Spectroscopy (RBS) using a Van der Graff accelerator with H^+ 700 kV beam and a scattering angle of 145°. This technique allows the determination of the C:N, C:O and C:Cl ratio through the scattering of energetic particles with energies that depend on the atomic weight and position of the elements. However, no significant changes in elemental composition were observed, indicating that there was no chemical reaction during poling. When positive charges accumulate on the film surface, the surface area increases due to the repulsion among the positive charges, and at the temperature of Tg a surface pattern with numerous micro-spots is formed [9, 10] and the film thickness will change. In order to see if thermal decomposition might take place at the poling temperatures, thermogravimetric analysis (TGA) was performed and the results are shown in Fig. 7. Both polymers do not show any sign of decomposition, a very slight weight loss can be seen at temperatures above 150ºC. The color of the films did not change by heating at the poling temperatures. The thermal reactions of diacetylene groups start to take place above 140ºC (Figs. 2 and 3). Therefore, thermal decomposition during poling is unlikely.



(a) (b)

Fig. 5. Changes in the apparent order parameters with heating at 100ºC for 3,5-RD1 (a) and 3,5-RD13.



(a) (b)

Fig. 6. Decrease in absorption on heating of poled polymer films: (a) 3,5-RD1 and (b) 3,5-RD13.

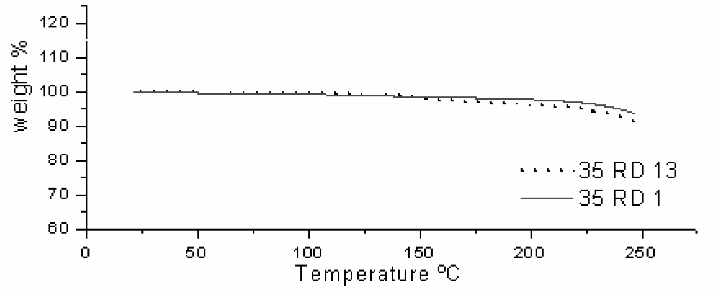


Fig. 7. Thermogravimetric analysis of the two polymers. Under N_2.

However, considering from these possible effects, the simple calculation of order parameters from absorption spectra is in general not completely reliable. The decay of order parameters with time are shown in Fig. 5. The relatively large remaining order parameters after 100 minutes (Fig. 6) could be due to some chemical changes caused during poling, or it is possible that the orientation is very stable and the chromophores in the polymers are remain orientated. The poled polymers from *para*-dibenzoate and *para*-dicinnamate were much more stable than the corresponding *meta*-polymers [8]. The order parameters of *meta*-polymers returned to nearly zero on heating, indicating that there was no change in chemical composition during poling, while the *para*-polymers maintained their minimum order parameters at around 0.13 (benzoate) and 0.19 (cinnamate). It is thought that in some polymers having main chain conformation without distortion when poled, parts of the chromophores remain orientated permanently, as in the cases of the *para* polymers [8]. In the case of the polynaphthoates, probably they behave similarly to the above, and because of their rigid structure orientation can be maintained. The another possible reason for this remaining orientation is partial cross-linking during poling, because the poling temperature is not very far from the thermal reaction of the diacetylenic groups in the main chains. In order to see if cross-linking occurred, the poled and unpoled polymer films were dissolved in NMP. The unpoled films were soluble although they were left to stand for four months at room temperature, indicating they do not cross-link. The 3,5-RD1 film poled at 128°C was still soluble, but the 3,5-RD13 poled at 135°C was partially insoluble showing the film was cross-linked. The higher temperature of poling (135°C) can be the reason of cross-linking. However, 3,5-RD1 also showed remaining orientation although it is not cross-linked. Therefore, this remaining orientation cannot be solely attributed to the possible cross-linking.

It is concluded that the poly(dipropargyloxynaphthoates) can have order parameter of around 0.20. These values are much lower than those of the polydibenzoates and cinnamates. But the steric effect of chlorine on the chromophore orientation was not observed.

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