Diacetylene-containing polymers. XV. Synthesis and characterization of poly(dipropargyloxybenzoates) containing Disperse Red 1

CLAUDIA RAMIREZ, MIRIAM F. BERISTAIN and TAKESHI OGAWA *

Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apartado Postal 70-360, Ciudad Universitaria, México DF, 04510, México

Abstract—In order to obtain novel polymers having a very high chromophore density, dipropargyloxy benzoic acids converted to benzoates containing an azo dye, Disperse Red 1, were synthesized and characterized. 2,6-Dipropargyloxy benzoic acid could not be obtained. The bisacetylenic monomers were then polymerized by oxidative coupling reaction. Amorphous polymers with an inherent viscosity of around 0.3 in N-methylpyrrolidone (NMP) were obtained. The polymers were soluble in polar solvents such as dimethylformamide, dimethylacetamide and N-methylpyrrolidone. The solutions in DMF caused precipitation due to the agglomeration of the dye groups on standing for a few days, but the precipitated polymers became soluble again in NMP. The UV irradiation on the spin-coated films at 80 °C cross-linked the films to convert them to thermoset resin films.

Keywords: Diacetylene; azo-polymers; Disperse Red 1; dipropargyloxybenzoic acids.

INTRODUCTION

Although a great number of works on polymeric systems for second-order nonlinear optical (2-NLO) applications has been reported in the last decades [1–4], materials that satisfy the requirements for use in photonic devices have not been found, and it was thought that the photonic technology is yet somewhat far for the future and, therefore, the research activity in the field has faded considerably in recent years. The main problems are: (a) low 2-NLO coefficient and (b) inevitable relaxation of poled chromophores. The majority of the polymeric materials studied in the past have shown low 2-NLO coefficients (d_{33}) of less than 30 pm/V. The only report on high NLO coefficients is that of Dalton and co-workers, in which a polymer showed

---

*To whom correspondence should be addressed. Fax: (52-55) 5616-1201; e-mail: ogawa@servidor.unam.mx

a coefficient of 250 pm/V [5]. The present authors recently synthesized a series of new polymers which contain diacetylenic main chains and polar chromophores in the side chains [6–8] and some of them showed high 2-NLO coefficients (200–350 pm/V), and their films could be totally cross-linked to thermoset resins by the irradiation of UV light at poling temperatures without appreciable *trans–cis* conversion of the azo chromophores [9, 10]. These polymers have main chains consisting hexa-2,4-diynylen-1,6-dioxybenzoates or cinnamate main chains. It was a very interesting discovery that the *para*-benzoate and *para*-cinnamate polymers showed much superior 2-NLO coefficients than the corresponding *meta*-analogues. Atomic force microscopy of the Langmuir–Blodgett membranes of *para*-polymers showed that they had more organized structures than the *meta*-polymers [11]. Their high 2-NLO coefficients are thought to arise from their ordered main chain structures.

Recently, azo-polymers have attracted much interest in their applications in memory materials based on the *trans–cis* photo-isomerization of the azo-group [12]. However, the majority of azo polymers used for the studies are those of vinyl polymers containing azo dyes. Therefore, one of the aims of this work is to provide a series of totally different types of azo polymers for this field.

In this work, as a continuation of the previous studies, a series of novel polymers, poly(dipropargyloxy)benzoates (poly(hexa-2,4-diynylene-1,6-dioxydibenzoates)), which contained Disperse Red 1 dye, were synthesized (Scheme 1) and characterized. The monomer has six isomers (2,3-, 2,4-, 2,5-, 2,6-, 3,4- and 3,5-) and in this work four of these polymers were synthesized and characterized, and some properties and morphology of the four polymers are reported in this article.
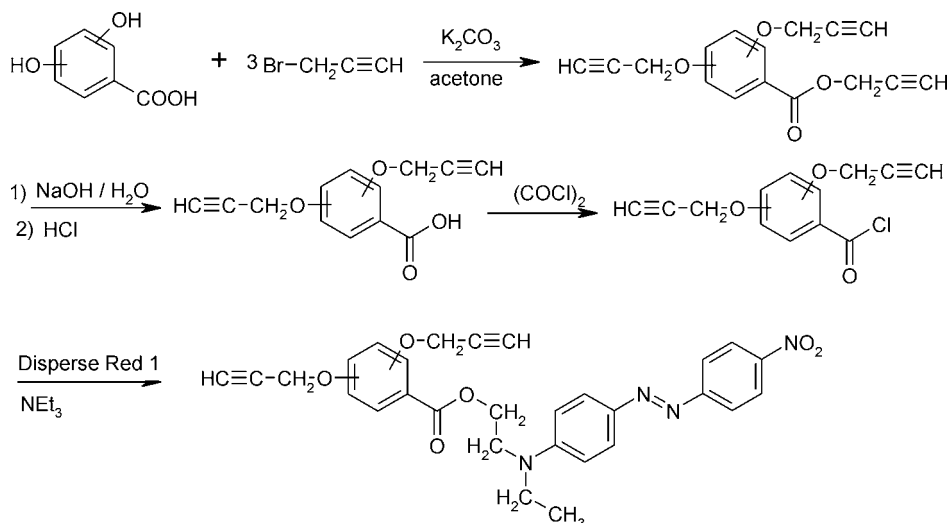
Scheme 1. Synthetic route of dipropargyloxybenzoates containing Disperse Red 1.

EXPERIMENTAL

Synthesis of dipropargyloxybenzoic acids

Propargyl bromide and dihydroxybenzoic acids were supplied by Aldrich, and used as received. The synthetic route is shown in Scheme 1. The reactivity of each dihydroxybenzoic acid with propargyl bromide differed considerably depending the type of the acid. Therefore, typical synthetic procedures for each dipropargyloxybenzoic acid are shown below.

2,4-Dipropargyloxybenzoic acid (Acid-2,4). 10 g Acid-2,4 (0.065 mol) and 22 ml (0.2 mol) propargyl bromide in toluene (80%) were dissolved in 100 ml acetone and 25 ml dimethylformamide (DMF) in a 250-ml round-bottom flask, 32 g potassium carbonate was added and the mixture was stirred at room temperature for 10 days, during which the reaction was monitored by thin layer chromatography and IR spectroscopy. After the reaction the content of flask was poured into water, and the white solid was filtered and dried. The yield was about 90%. IR spectra (KBr, cm^{-1}): 3291, 3225 $\underline{H}$—C≡, 2115 C≡C, 1715 C=O.

15 g 2,4-dipropargyloxypropargylbenzoate thus obtained was suspended in 200 ml water containing 3.3 g NaOH and the system was stirred at 60°C for 3 days, by which time the solution became transparent. The solution was acidified with 200 ml water containing 5 ml concentrated HCl, and the precipitate was filtered, washed with water and dried. The yield was about 90%. Recrystallization from toluene gave a colorless crystal melting at 153°. IR spectra (KBr, cm^{-1}): 3285, 3252, 3232 $\underline{H}$—C≡, 2113 C≡C, 1696, 1671 C=O.

3,4-Dipropragyloxybenzoic acid (Acid-3,4). 10 g 3,4-dihydroxybenzoic acid and 22 ml propargyl bromide were dissolved in 100 ml acetone and 15 ml DMF, and 27 g potassium carbonate were added. The mixture was refluxed with stirring for 25 days. The solid was filtered off and evaporating the solvent gave 11.2 g (65%) of a pale brown solid melting at 75–76°C. IR spectra (KBr, cm^{-1}): 3289 $\underline{H}$—C≡, 2124 C≡C, 1696, 1717 C=O. The ester was then hydrolyzed in the same manner as described above. Recrystallization from toluene gave white crystals melting at 179–180°C. IR spectra (KBr, cm^{-1}): 3288, 3265 $\underline{H}$—C≡, 2119 C≡C, 1681 C=O.

2,5-Dipropargyloxybenzoic acid (Acid-2,5). Similar to the above, 10 g 2,5-dihydroxybenzoic acid was dissolved in 150 ml of a mixture of acetone and DMF (2 : 1 by volume), and 27 g potassium carbonate was added. After 20 min, 22 ml propargyl bromide was added. The mixture was stirred for 25 days during which the reaction was monitored by thin-layer chromatography and IR spectroscopy. The reaction system was poured into 1 l water, and the precipitate was filtered, washed with water and dried. A pale brown product (ester) which melts at 80–81°C was obtained with 80% yield (14 g). IR spectra (KBr, cm^{-1}): 3286, 3276, 3236 $\underline{H}$—C≡, 2113 C≡C, 1728 C=O. This was then hydrolyzed to Acid-2,5. IR spectra (KBr, cm^{-1}): 3273, 3243 $\underline{H}$—C≡, 2127, 2117 C≡C, 1071 C=O.

3,5-Dipropargyloxybenzoic acid (Acid-3,5).   Acid-3,5 was obtained by the same method as above, heating the system at 60°C for 15 days, and the ester was obtained with 90% yield (m.p. 96–97°C). IR spectra (KBr, cm^{-1}): 3278, 3266 H—C≡, 2131 C≡C, 1713 C=O. Hydrolysis with potassium hydroxide in a mixture of water and methanol gave Acid-3,5. Recrystallization from toluene gave a white crystalline powder melting at 175–176°C. IR spectra (KBr, cm^{-1}): 3290 H—C≡, 2122 C≡C, 1687 C=O.

2,6-Dipropargyloxybenzoic acid (Acid-2,6).   2,6-Dihydroxybenzoic acid was reacted with 5% excess of propargyl bromide in acetone with potassium carbonate at room temperature for over a month. The carbonate was filtered off and the solvent acetone was evaporated, and the ester 2,6-dipropargyloxypropargylbenzoate, white crystals melting at 88°C, was obtained with 36% yield. However, its hydrolysis with NaOH to obtain the acid was difficult, probably due to the steric effect, and cleavage of the propargyloxy group on the benzene ring took place, giving a phenol when treated with hydrochloric acid.

^{1}H-NMR spectra of these four acids are shown in Fig. 1.

Monomer synthesis

The four acids were converted to the chlorides by the reaction with oxalyl chloride (Aldrich) in dichloromethane. The chlorides were then reacted with 5% excess of Disperse Red 1 (Aldrich) in dichloromethane using triethylamine (dried over calcium hydride) as an acid acceptor. They were purified by recrystallization from ethyl acetate and characterized by IR and NMR spectroscopy.

Polymerization

The oxidative coupling polymerization is a kind of polycondensation eliminating water from acetylenic proton and oxygen, and is a very convenient method to obtain high polymers from bisacetylenic monomers:

$$n\text{HC}≡\text{C}-\text{R}-\text{C}≡\text{CH} + \text{O}_2 \rightarrow -(\text{C}≡\text{C}-\text{R}-\text{C}≡\text{C})_n- + n\text{H}_2\text{O}$$
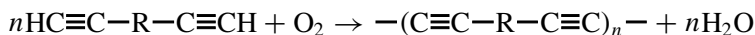
The polymerization was carried out in NMP at room temperature: 2 g monomer was dissolved in 8 ml NMP and 0.1 g copper(I) chloride, and several drops of N,N,N′,N′-tetramethylethylenediamine (TEMED) were added and the solution was stirred for at least several hours during which oxygen was slowly bubbled into the system. The viscosity of the system slowly increased with time. It is important that the polymerization should be stopped before the system becomes very viscous. When the viscosity is very high, the polymers become insoluble in DMF (soluble only in NMP). The adequate inherent viscosity of the polymers for obtaining films by spin coating is around 0.2–0.4 dl/g. The system was poured into 150 ml methanol and the precipitated polymer was filtered, washed well with methanol and dried in vacuum. The yield was almost quantitative. The polymer was purified
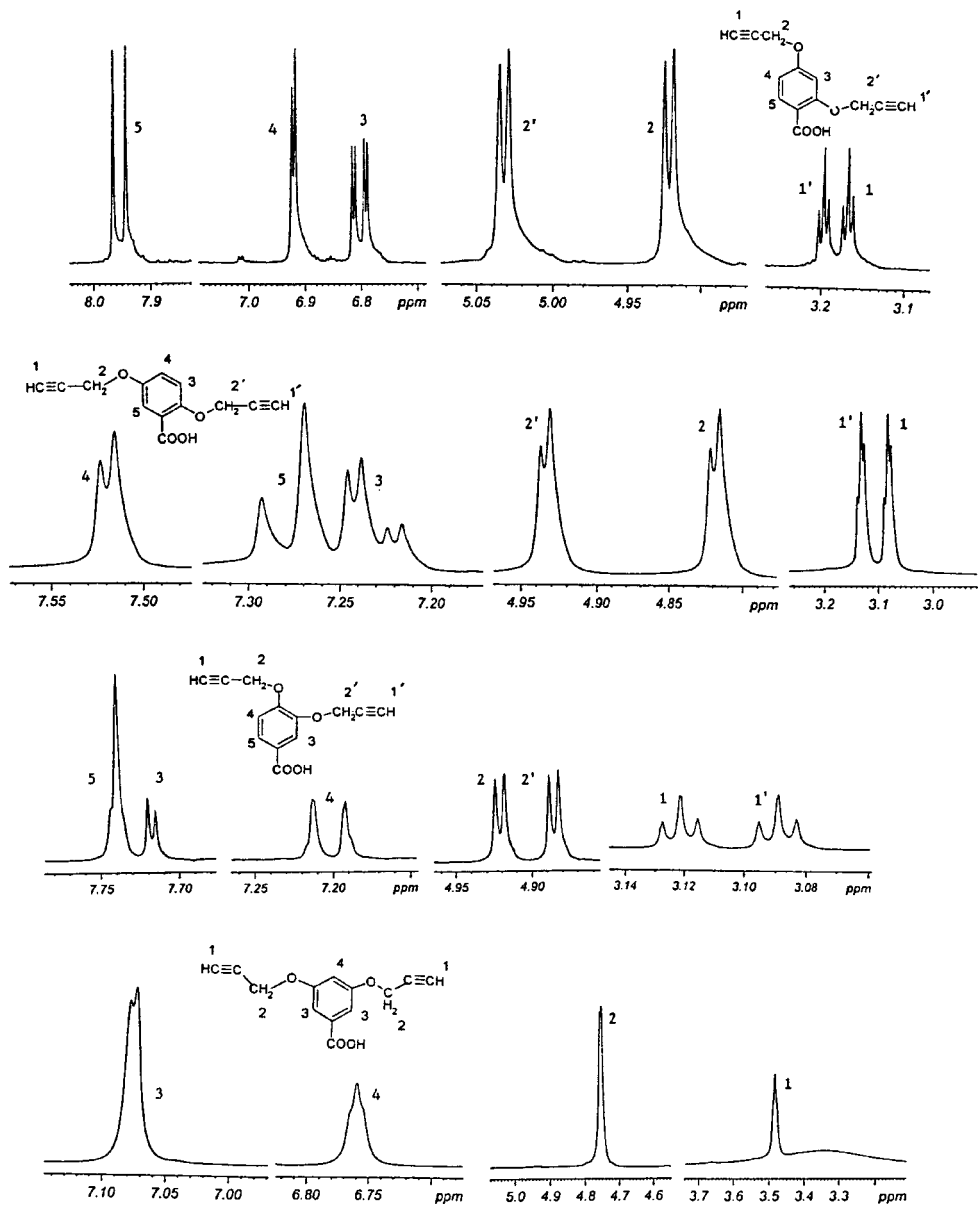
Figure 1. ^{1}H-NMR spectra of dipropargyloxybenzoic acids.

by reprecipitation from DMF or NMP with methanol. The inherent viscosity was determined at 20°C in NMP.

Characterization

^{1}H-NMR spectra of monomers and polymers were obtained using a Bruker 400 MHz NMR spectrometer. FT-IR spectra were obtained using Nicolet 510P spectropho-

tometer. UV-Vis spectra of thin films were obtained with a Unicam UV 300 spec-
trometer. DSC and TGA were performed using calorimeters Model 910 DSC and
951 TGA of DuPont Instruments. TMA (thermomechanical analysis) was carried
out using a calorimeter TMA 2940 of TA Instruments.

RESULTS AND DISCUSSION

Figure 1 shows ^{1}H-NMR spectra of the four dipropargyloxybenzoic acids in
acetone-d. In Fig. 1 each region of peaks was connected to facilitate viewing the
spectra, and the peak heights of the assembled spectra do not correspond to the
numbers of protons. There was no peak due to impurity between the regions shown
in the figure. The peaks exactly correspond to the respective protons. The protons
of the acids appear in the range of 10–12 ppm as broad peaks and are not shown in
the figure. As far as their synthesis is concerned, the above-mentioned method was
found to be most appropriate. If sodium or potassium hydroxide is used instead of
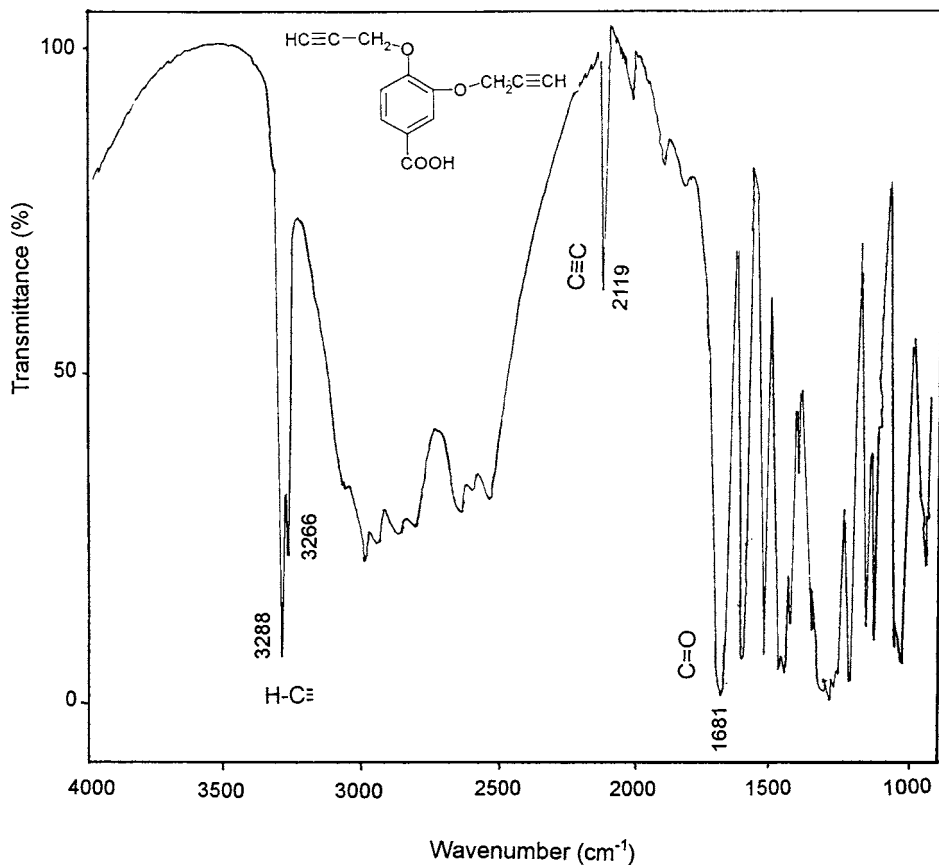

Figure 2. FT-IR spectrum of Acid-3,4.

carbonate, only one phenolic group could be substituted and the systems become colored, probably due to the side reactions such as quinone formation. When the hydroxide was used, there was some loss of propargyl bromide by the nucleophilic substitution to form propargyl alcohol. FT-IR spectrum of the Acid-3,4 is shown in Fig. 2 as an example. The peaks at around 3300 and 2100 cm^{-1} due to $\underline{H}-\underline{C}\equiv$ and $\underline{C}\equiv\underline{C}$, respectively, are the fundamental absorptions for identification.

Figures 3 and 4 show example of IR spectra of bisacetylenic monomers (2,4- and 2,5-) and of their polymerized products. The peaks at around 3282 and 3297 cm^{-1}, and 2115 cm^{-1}, due to the $\underline{H}-\underline{C}\equiv C-$ and $-\underline{C}\equiv\underline{C}-$ of the monomer, respectively, disappeared when polymerized, and the very weak peaks due to the diacetylene, which appear around 2130–2250 cm^{-1}, cannot be seen in the spectra of the polymers, but they were observed only when very concentrated samples were prepared for the spectra. These changes indicate that the oxidative coupling polymerization took place. The ^{1}H-NMR peaks at around 2.5 ppm (in CDCl$_3$) due to
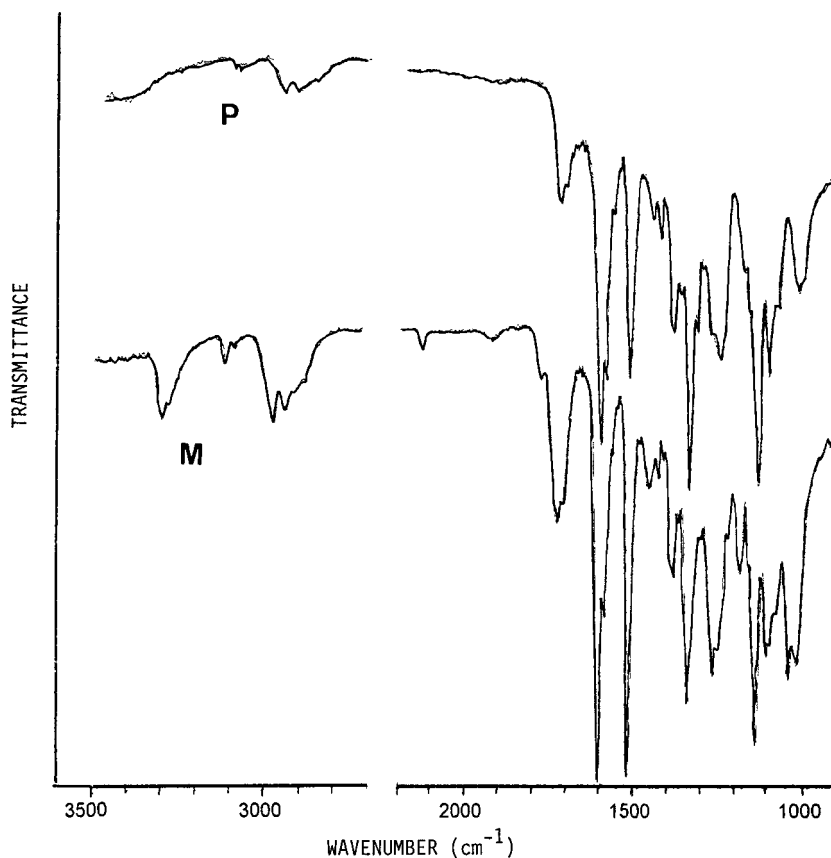

Figure 3. FT-IR spectra of 2,4-dipropargyloxybenzoate containing Disperse Red 1, and its polymer. M, monomer; P, polymer.
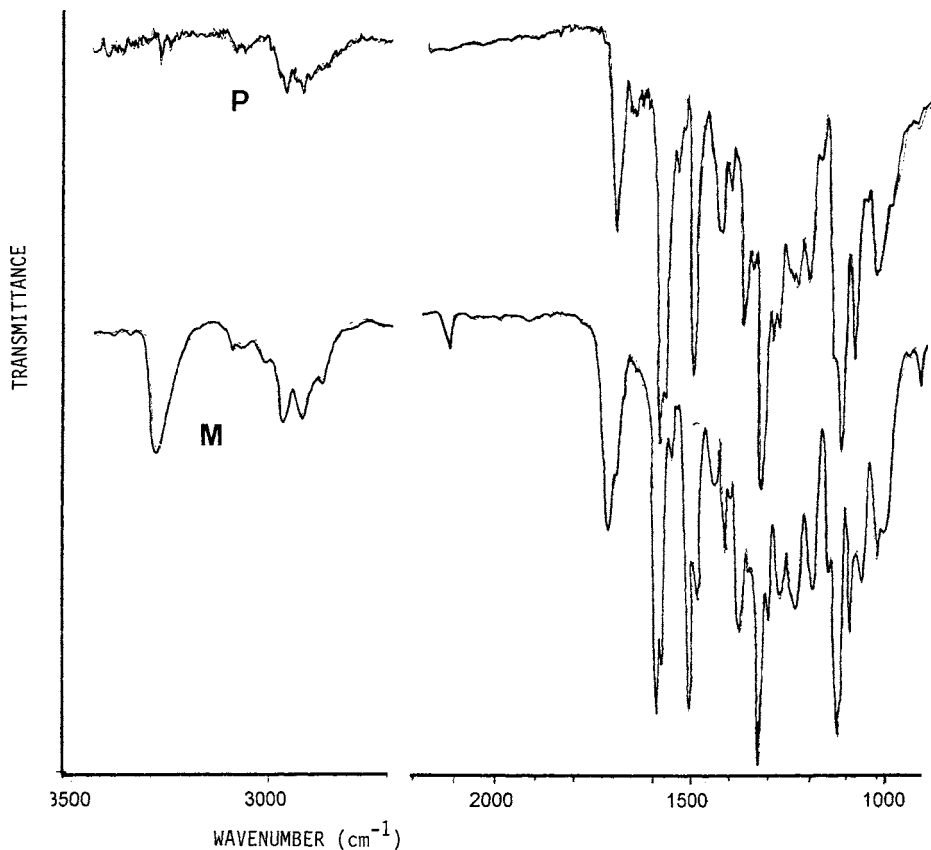
Figure 4. FT-IR spectra of 2,5-dipropargyloxybenzoate containing Disperse Red 1, and its polymer. M, monomer; P, polymer.

H−C≡ of the monomers, disappeared when polymerized. The inherent viscosities of these polymers were around 0.2–0.5 dl/g in NMP.

The polymers were soluble in polar solvents such as NMP, DMF and DMA (dimethylacetamide) and poorly soluble in chloroform. However, if the molecular weight is too high ($\eta_{inh} \geqslant$ 0.6 dl/g at 20°C in NMP), they are poorly soluble in DMF. Their DMF solutions were not stable and the polymers precipitated on standing. This is due to the agglomeration of the dye molecules forming cross-linked polymer chains through dipole–dipole interaction. However, the precipitates were soluble in NMP and after reprecipitation in methanol DMF-soluble polymers could be recovered. It seems that a strongly polar solvent such as NMP dissociate the agglomerated dye groups.

The thermal characteristics (DSC) of these polymers are shown in Fig. 5. The large exotherm starting at around 140°C is the thermal polymerization of the diacetylene groups, which leads the polymer to highly cross-linked thermoset resins. The thermal decomposition takes place at above 190°C. The glass transition
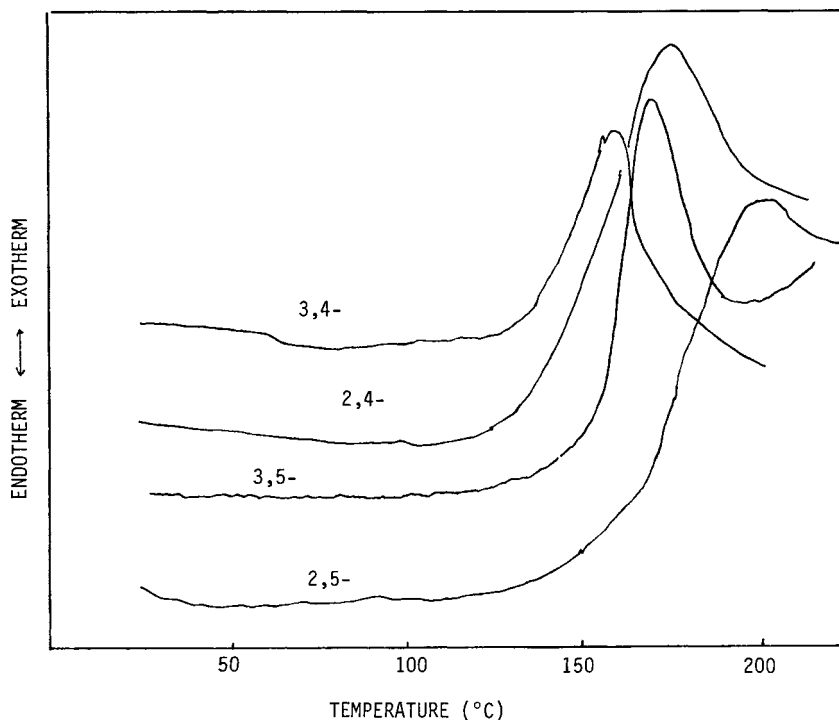
Figure 5. DSC analysis of poly(dipropargyloxybenzoates) containing Disperse Red 1.

temperatures could not be observed clearly in the DSC curves and, therefore, thermal mechanical analysis (TMA) was performed, the results of which are shown in Fig. 6. The temperature at which decrease in dimension starts is considered to be the T_g. The T_g values are fairly low (around $80°C$) and one may say that the low-T_g polymers are useless for 2-NLO applications due to rapid relaxation of poled dye molecules. However, such an argument will apply only to the conventional polymers, such as dye-containing polymethacrylates, and does not apply to the new polymers with completely different main chain conformation, such as poly(benzoates) and poly(cinnamates), which seem to form a stable orientated structure.

The visible absorption spectra are shown in Fig. 7. The absorption in the visible region is that of Disperse Red 1 with an absorption maximum at 478 nm, and this does not change with the type of polymers. Their spin-coated films (about $2-3$ μm) were irradiated by a medium-pressure mercury UV lamp (Ace Glass, 450W), the *trans-cis* transformation of the azo dye takes place and this transformation occurred for all of the four polymers.

The polymers contain very high chromophore contents of 57% (MW of dye/MW of monomer unit). Therefore, coagulation of polymers in solution takes place due to the dipolar interaction on standing. Thus, it is recommended that films should be prepared as soon as the solution is prepared.
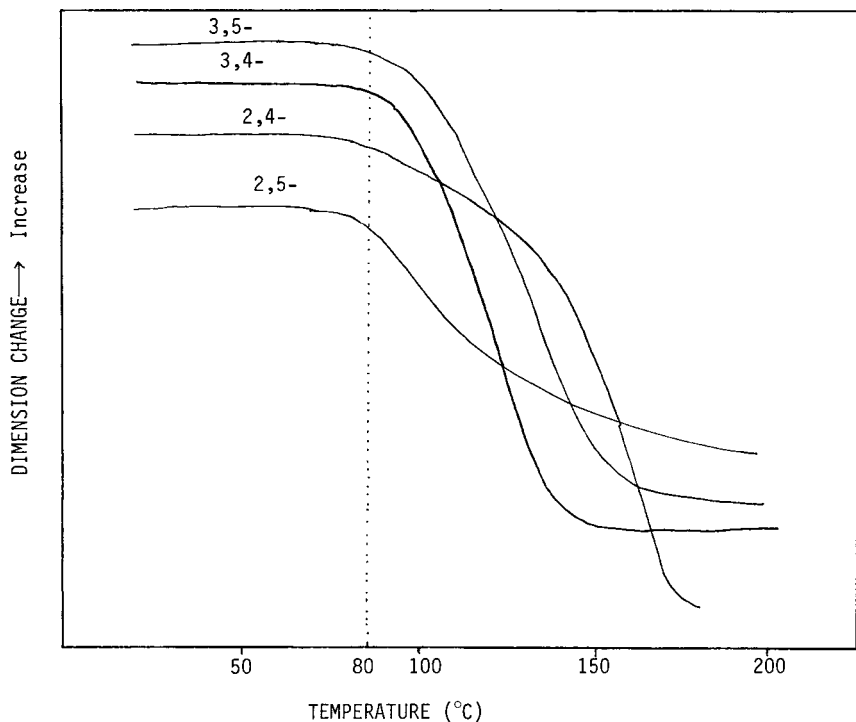
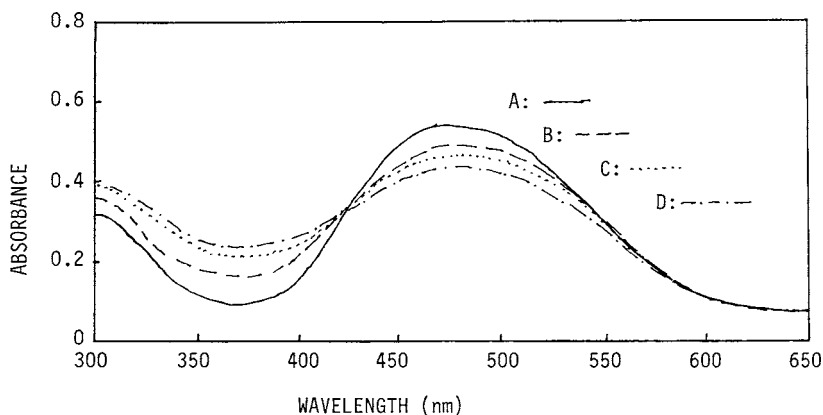**Figure 6.** TMA of poly(dipropargyloxybenzoates) containing Disperse Red 1.

Figure 7. Visible absorption spectra of poly(3,5-dipropargyloxy benzoate) containing Disperse Red 1. (A) Before irradiation, (B) 20 min irradiation, (C) 40 min irradiation, (D) 60 min irradiation.

The 2-NLO property of these polymers is being investigated, and the results will be reported in the future. A preliminary result on a 3,4-polymer containing an azo dye with a cyano group instead of the nitro group of Disperse Red 1 showed that the polymer had a 2-NLO coefficient of 70 pm/V, and much higher values
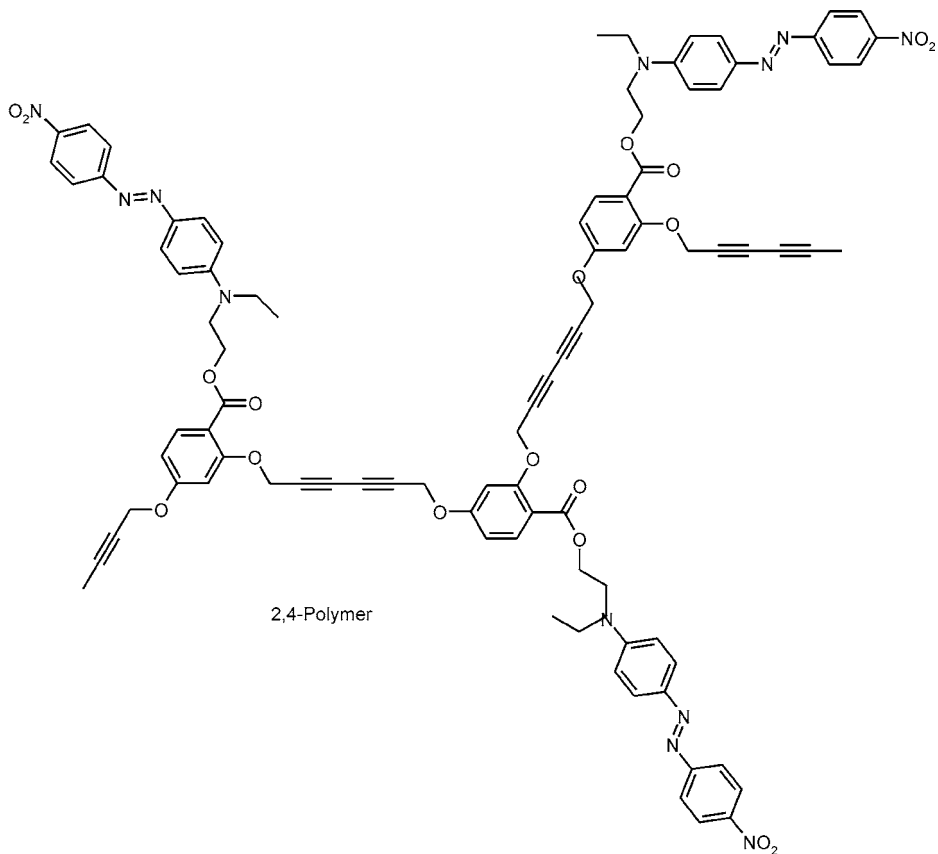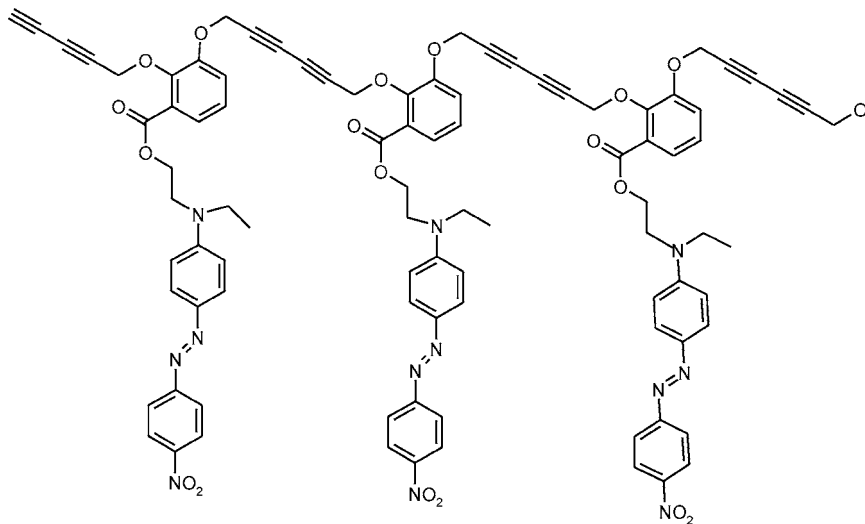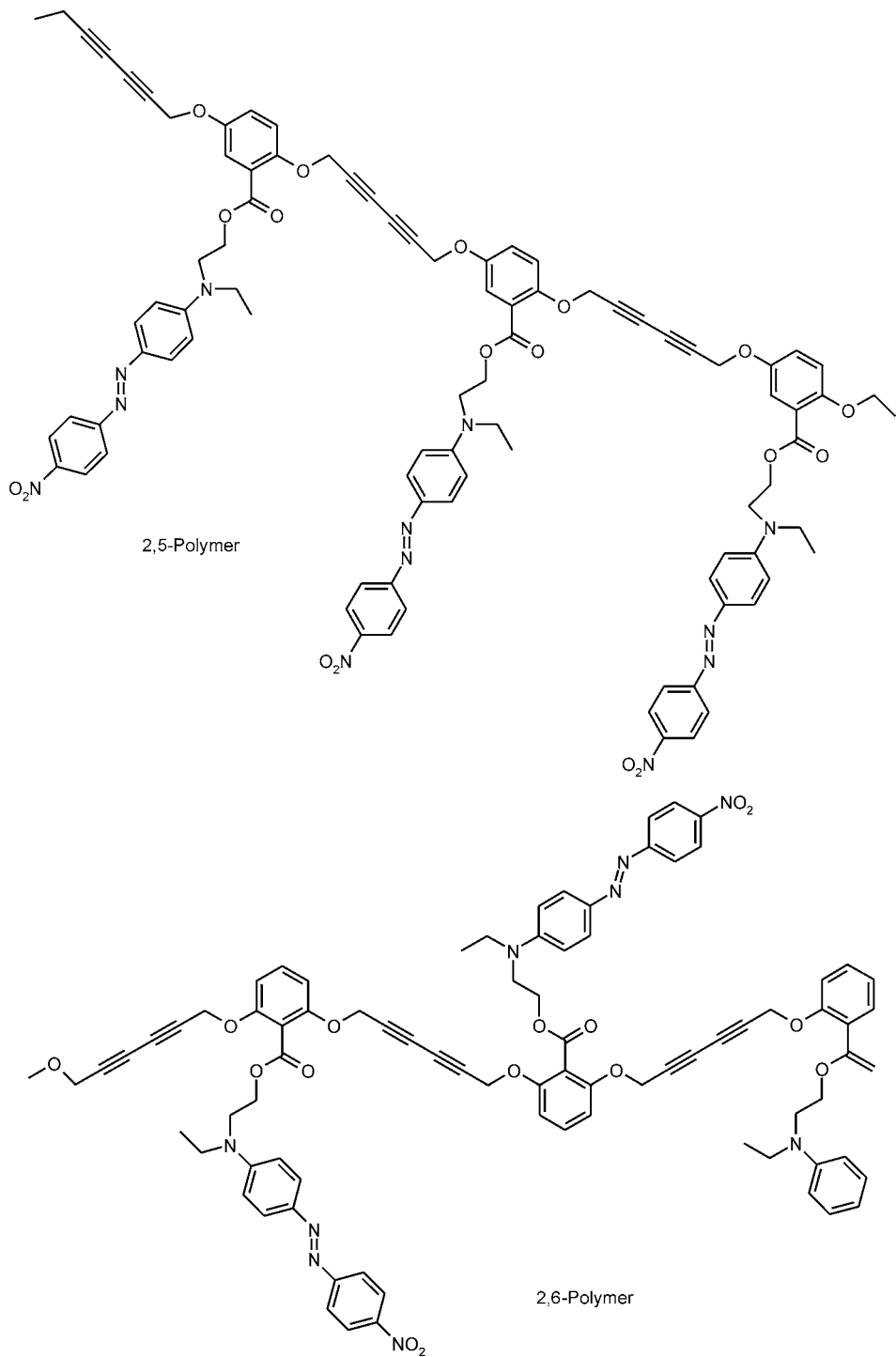
Figure 8. Possible two dimensional structures of the 6 isomeric poly(dipropargyloxy benzoates) containing Disperse Red 1.

2,5-Polymer

2,6-Polymer

Figure 8. (Continued).
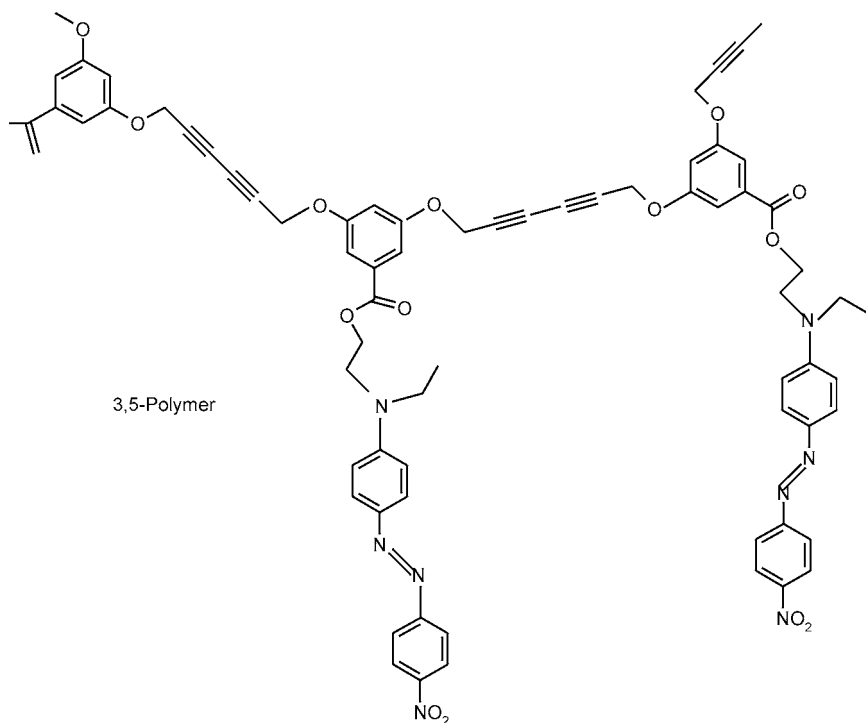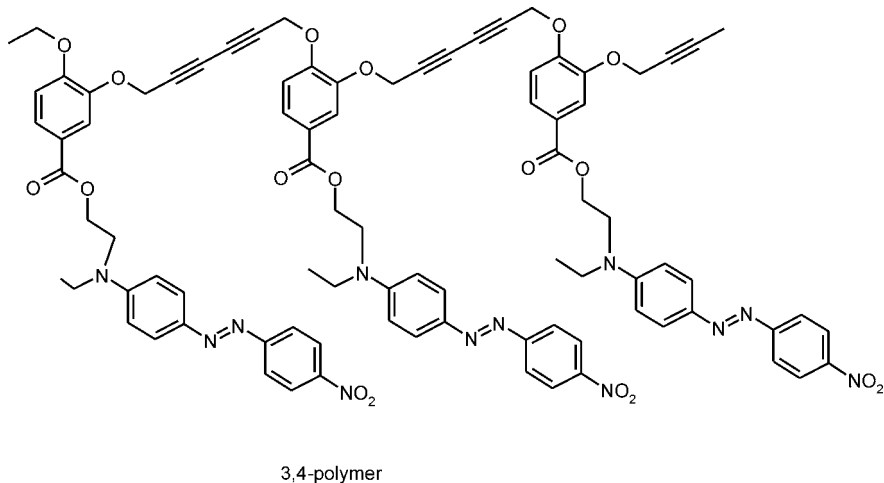
3,4-polymer

3,5-Polymer

Figure 8. (Continued).

are expected for these polymers because the dyes with nitro group have higher hyperpolarizability than those with cyano groups.

The possible two-dimensional structures that these polymers could form are shown in Fig. 8. Some of them might present a self-assembly nature, as in the case of poly(p,p'-hexa-2,4-diynylene-1,6-dioxy-dibenzoate), containing Disperse

Red 19, which exhibits a self-assembly characteristic when its Langmuir–Blodgett film is prepared [11]. It is expected that there will be a large difference in the NLO property among the isomers of poly(dipropargyloxybenzoates) containing Disperse Red 1. When their films are poled, the chromophores orientate perpendicularly to the film and, therefore, such two-dimensional pictures may not give a precise prediction on the NLO property. However, some of these polymers such as 2,3-, 2,5- and 3,4-polymers are expected to have stable conformation and consequently high 2-NLO coefficients. In the cases of poly(benzoates) and poly(cinnamates) containing Disperse Red 19, the *para*-polymers showed much higher NLO coefficients than the corresponding *meta*-polymers [9, 10]. In the case of poly(dipropargyloxy-benzoates) it is expected that the polymers having main chains at *ortho*- (2,3- and 3,4-polymers) and *para*- (2,5-polymers) positions of benzoates, will have higher NLO coefficients than those at *meta*-position (2,4-, 2,6- and 3,5-polymers) as well.

CONCLUSIONS

Four different novel polymers, poly(dipropargyloxybenzoates) containing Disperse Red 1 were synthesized and characterized. These polymers had a relatively low T_g (around $80°C$) and the thermal reaction of the diacetylene groups commences at around $140°C$, which leads the polymers to intractable resins. The polymers were soluble in DMF, DMA and NMP, and gave transparent films with excellent optical quality by spin coating at $50–100°C$. However, the polymers in DMF solution precipitate on standing due to agglomeration of the polar dyes, but the precipitated polymers are soluble in NMP. Irradiation with a UV lamp caused the *trans–cis* transformation of azo group. It is expected that there will be substantial differences in NLO property among these isomers.

REFERENCES

1. J. Messier, F. Kajzar, P. Prasad and D. Ulrich (Eds), *Nonlinear Optical Effects in Organic Polymers*. Kluwer, Dordrecht (1989).
2. G. A. Lindsay and K. D. Singer (Eds), *Polymers for Second-Order Nonlinear Optics,* ACS Symposium Series 601. ACS, Washington, DC (1995).
3. S. Miyata and H. Sasabe (Eds), *Poles Polymers and Their Applications to SHG and ED Devices, Advances in NLO, Volume 4*. Gordon & Breach, Amsterdam (1997).
4. N. S. Nalwa and S. Miyata (Eds), *Nonlinear Optics of Organic Molecules and Polymers*. CRC Press, Boca Raton, FL (1997).

5. M. Chen, L. Yu, L. R. Dalton, Y. Shi and W. H. Steier, *Macromolecules* **24**, 5421 (1991).
6. S. Hernandez and T. Ogawa, *Polym. Bull.* **47**, 127 (2001).
7. S. Hernandez, M. F. Beristain and T. Ogawa, *Designed Monomers Polymers* **5**, 125 (2002).
8. H. Miura and T. Ogawa, *Polym. Bull.* **49**, 103 (2002).
9. S. Hernandez, T. Ogawa, T. Watanabe and S. Miyata, *Mol. Cryst. Liq. Cryst.* **374**, 503 (2002).
10. S. Hernandez, H. Miura, M. F. Beristain, T. Ogawa, T. Watanabe and S. Miyata, *Macromol. Symp.* **192**, 123 (2003).
11. M. P. Carreon-Castro, J. Ramirez, M. Rivera and T. Ogawa, submitted (2003).
12. A. Natansohn and P. Rochon, *Chem. Rev.* **102**, 4139 (2002).