Diacetylene-Containing Polymers XIV: Poly(octa-3,5-diynylene-1,8-dicarboxyalates) containing some polar azo dyes

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Abstract

A series of novel polymers having polar azo dyes were synthesized and characterized. Although their chromophore contents are very high, their second order nonlinear (2-NLO) response was very poor. The poor 2-NLO responses are thought to be due to poor orientation because of their improper main chain conformations, as well as their low glass transition temperatures. They undergo slow cross-linking on standing at room temperature, and rapidly on heating at temperatures above 150°C, through the diacetylene units of the main chains. Nevertheless, these polymers are interesting materials as azo-polymers because of their very high concentration of azo dyes, which are distributed homogeneously in the polymers. Synthesis and characterization are described, and the most important factor for the 2-NLO polymers is discussed.

Introduction

There have been published a great numbers of studies on azo polymers in the last decades, with expectation of finding organic polymers suitable for the second order nonlinear optical applications (1-3). However, because of their insufficient 2-NLO responses and inevitable relaxation of the poled chromophore, the interest in such materials has faded recently. The use of azo polymers in other fields such as memory materials, using their trans-cis photo-transformation, have attracted much attention, and active research is being made (4-6). The majority of the azo polymers so far studies are those of vinyl polymers, such as polymethacrylates, containing azo dyes in the side chains. In such cases, it is rather difficult to obtain polymers with homogeneous azo dye distribution in the polymers, and the concentration of azo dyes is rather low. In the case of applications for 2-NLO materials, the same can be said, and their 2-NLO coefficients are below 30 pm/V.

Previously the present authors synthesized several new types of polymers; namely poly(hexa-2,4-diynylene-1,6-dioxydibenzoates) and poly(hexa-2,4-diynylene-1,6-dioxydicinna-mates) containing azo dyes, some of them were found to possess

extremely high 2-NLO coefficients of 250 – 350 *pm/V* (7,8). The polymers of *para*-benzoates and *para*-cinnamates had 4 – 5 times higher 2-NLO coefficients that their respective *meta*-polymers. In this report the poor 2-NLO responses of these aliphatic main chain analogues are discussed in order to obtain more real sights on the polymers useful for 2-NLO applications.

Experimental

Pentynoic acid was supplied by GFS Chemicals, and used as received (claimed 98% purity). It was reacted with oxalyl chloride (Aldrich) in dichloromethane to obtain the acid chloride. The dyes were synthesized according to the methods reported in the previous paper (9), and reacted with pentynoyl chloride to obtain the corresponding bisacetylenic monomers, shown below:
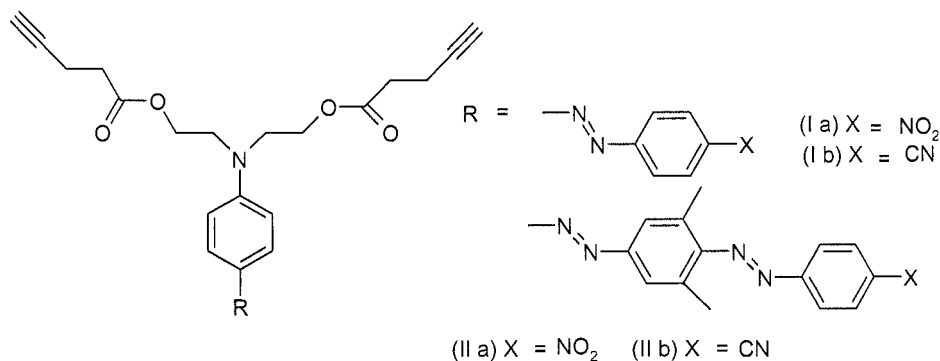
The monomers were purified by repeated recrystallization, and characterized to be absolutely pure from ^{1}H and ^{13}C NMR spectra.

The monomers (2 g) were polymerized at room temperature in n-methylpyrrolidone (NMP) (5 ml) using copper(I) chloride (0.02 g) and N,N,N',N'-tetramethylethylenediamine (TMED)(a few drops) for 8 hours, gently bubbling oxygen into the system with stirring. When the viscosity of the system increased, the content was poured into methanol to precipitate the polymer, which was washed well with methanol and dried in a vacuum desiccator.

The monomers and polymers were characterized by elemental analysis (Desert Analytics, Tucson AZ), and by IR (Nicolet 510p) and NMR (Bruker 400 Avance) spectroscopy. DSC was performed using a TA instrument calorimeter Model 910. UV/Visible spectra were taken using a UNICAM UV 300 spectrometer. X-ray diffractometry was performed using a Siemens D-500 diffractometer with Cu-K$_a$ radiation of 1.540Å. Inherent viscosity was measured at 25°C in DMF. Table 1 shows the characteristics of the four bisacetylenic monomers.

Table 1. Characteristics of the four bisacetylenic monomers

Monomer	Appearance	mp °C		Elemental analysis (%)		
				C	H	N
Ia	Shiny deep red crystals*	87-88	Calcd. for $C_{26}H_{26}N_4O_6$	63.67	5.3	11.42
			Found	63.88	5.39	10.88
Ib	Shiny orange crystals**	86-87	Calcd. For $C_{27}H_{26}N_4O_4$	68.92	5.57	11.90
			Found	69.0	5.54	11.76
IIa	Shiny purple crystals***	77-78	Calcd. for $C_{34}H_{34}N_6O_6$	65.58	5.50	13.49
			Found	65.03	5.12	13.86
IIb	Shiny deep red crystals**	79-80	Calcd. For $C_{35}H_{34}N_6O_4$	69.75	5.68	13.94
			Found	68.68	5.81	13.60

Recrystallized from: *:n-butanol, **:isopropanol, ***:ethanol

Results and Discussion

Figure 1 shows ^{1}H-NMR spectra of **Ia** and its polymer (**P-Ia**), in which the assignments are consistent with the drawn structures. For all of them the chemical shifts of the methylene group in the main chain appear at 2.5 ppm, while the methylene groups in the chromophores appear at 3.7 (N-CH$_2$) and 4.3 (O-CH$_2$) ppm. After polymerization the signal at around 2.0 ppm corresponding to the terminal acetylene proton, disappeared as expected. For the rest the monomers and polymers, the spectra were all in agreement with their respective structures. The ^{13}C NMR spectra of the monomer showed signals of the diacetylenic group at 65(C1) and 76(C2) ppm for $-C(1) \equiv C(2)-C(2) \equiv C(1)-$. The corresponding signals of the polymer were displaced to high field at 70(C1) and 80(C2) ppm for $-C(1) \equiv C(2)-H$. The assignments of all other chemical shifts were in accordance with the structures. Figure 2 shows the ^{1}H-NMR spectra of **IIa** and **P-IIa**, the peaks correspond satisfactorily to the structures.
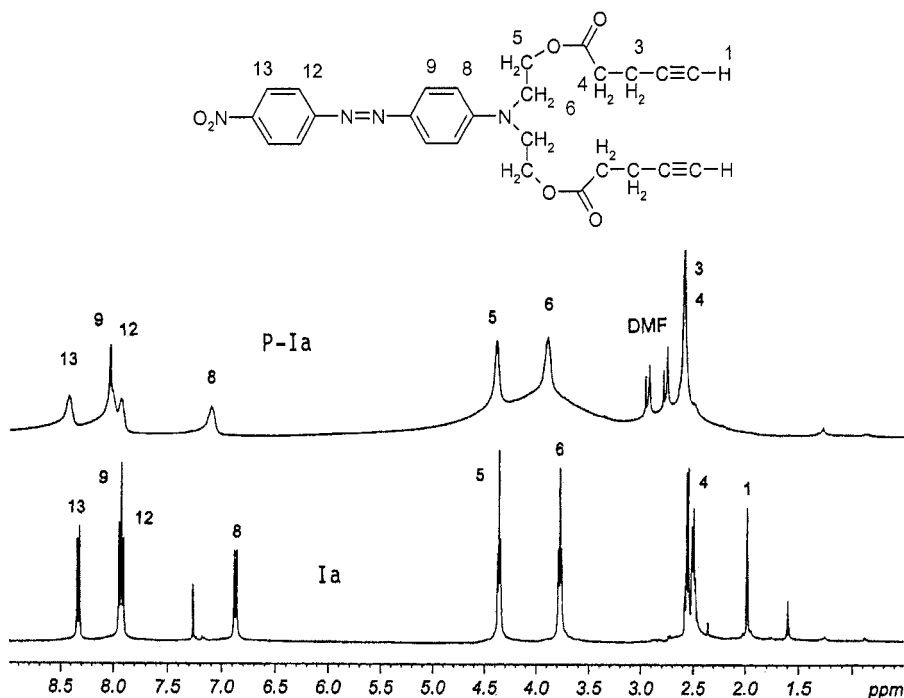
Fig. 1. ^{1}H NMR spectra of **I a** and **P-I a** taken in d-DMF

FTIR spectra of **Ia** and **P-Ia** (Fig. 3) show the evidence of polymerization, in addition to the NMR spectra, the absorption bands at around 3284 and 2127 cm^{-1} due to the -C≡C-**H** and -C≡C-, respectively, of the monomer, disappearing after the oxidative coupling polymerization. This characteristic was observed for other bisacetylenic monomers indicating that the polymers were obtained. The FTIR spectra of **Ib** and **P-Ib** are the same as those of **Ia** and **P-Ia**, except the latter have the characteristic peak of 2223 cm^{-1} due to the -CN group. The oxidative coupling polymerization is a living polymerization. If monomers are pure, the molecular weights increase with polymerization time, and the polymerization system becomes too viscous to be stirred. If the molecular weights are too high, the solubility decreases and gels are formed. Therefore, the polymerization was stopped before the system became very viscous. The inherent viscosity of the polymers was in the range of 0.2 – 0.5 dl/g.

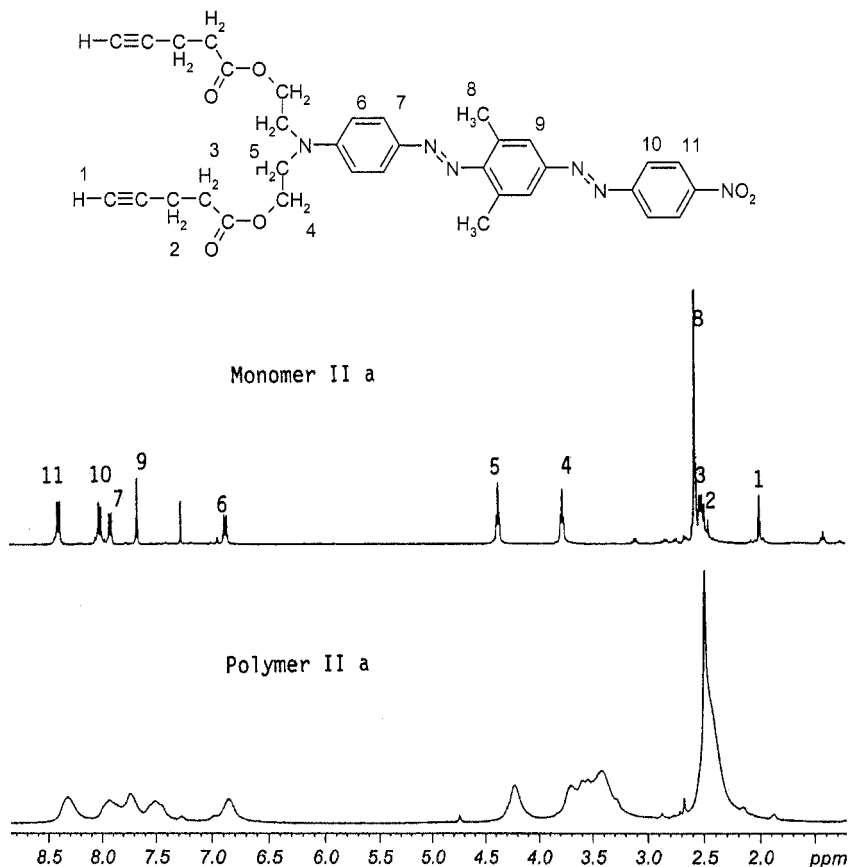**Fig. 2.** ^{1}H NMR Spectra of **II a** and **P-II a** taken in CDCl$_3$ (**II a**) and in DMSO (**P-II a**)

Figure 4 shows DSC curves of these polymers, and Table 2 shows the thermal properties of polymers. Considering the flexible nature of the aliphatic main chain, the Tg are fairly high being at around 110°C, except for **P-II b** which showed a Tg at 84.5°C. The T$_g$ of poly(m,m'-hexa-2,4-diynylen-1,6-dioxydibenzoate) containing chromophore **I b** was only 47°C (9). It seems that the main chains having the octa-3,5-diynylene structure are more densely packed each other than the m,m'- hexa-2,4-diynylene-1,6-dioxybenzoate main chains. In the cases of the polymers with two benzene ring chromophores, **P-Ia** and **P-Ib**, the cross-linking takes place in the solid state during the storage for several weeks. On the other hand the polybenzoates do not have this cross-linking nature during the storage. This observation is agreeable with the above, suggesting that the aliphatic main chains are packed more densely each other than the polybenzoates main chains, thus facilitating cross-linking through the diacetylene groups. The polymers with the three benzene ring chrmophores, the cross-linking does not seem to take place on standing, probably the bulky side chains (chromophores) separate the main chains. The DSC curves did not show any endotherm peak corresponding to melting of the material, which indicates that the

polymers are amorphous. X-ray diffraction patterns of the polymers showed that they are completely amorphous. When a diacetylene-containing polymer is crystalline and has a solid structure in which the diacetylene units form crystal packing favorable for topochemical polymerization, the polymer cross-links rapidly by irradiation without heating, developing polydiacetylene networks in the film. If a diacetylene-containing polymer is amorphous or has a crystalline structure not favorable for the topochemical polymerization, this does not happen, but cross-linking occurs between the diacetylene groups when they approach each other. When the polymer is heated and irradiated, any diacetylene-containing polymer undergoes cross-linking through their diacetylene units. All of the polymers cross-linked when irradiated with a medium pressure Hg lamp at 100°C for a half hour, the films becoming insoluble.
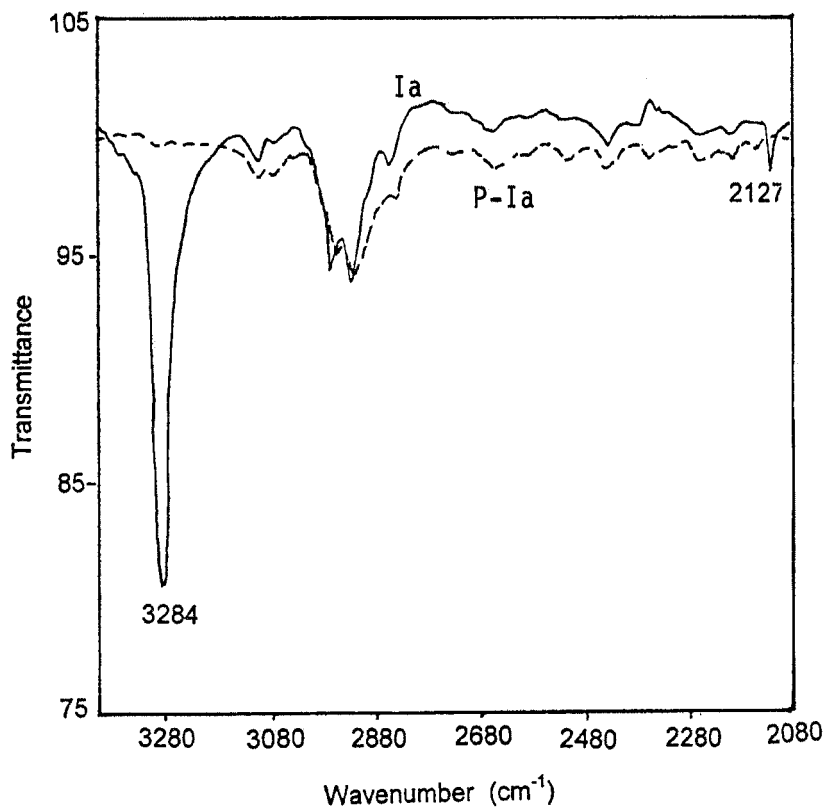

Fig. 3. FT-IR spectra of **Ia** and **P-Ia**

Table 2. Thermal properties of polymers from DSC and TGA

POLYMER	T_g (°C)	T_{cs} (°C)	T_{cm} (°C)	T_5 (°C)
P-Ia	103.5	130	-	279
P-Ib	110	140	186	265
P-IIa	113	150	207	226
P-IIb	84.5	140	151	270

T_g: Glass transition temperature. T_{cs}: Temperature at which cross-linking start. T_{cm}: Temperature of exothermal peak. T_5: Temperature at which polymers had lost 5% of their original weight.
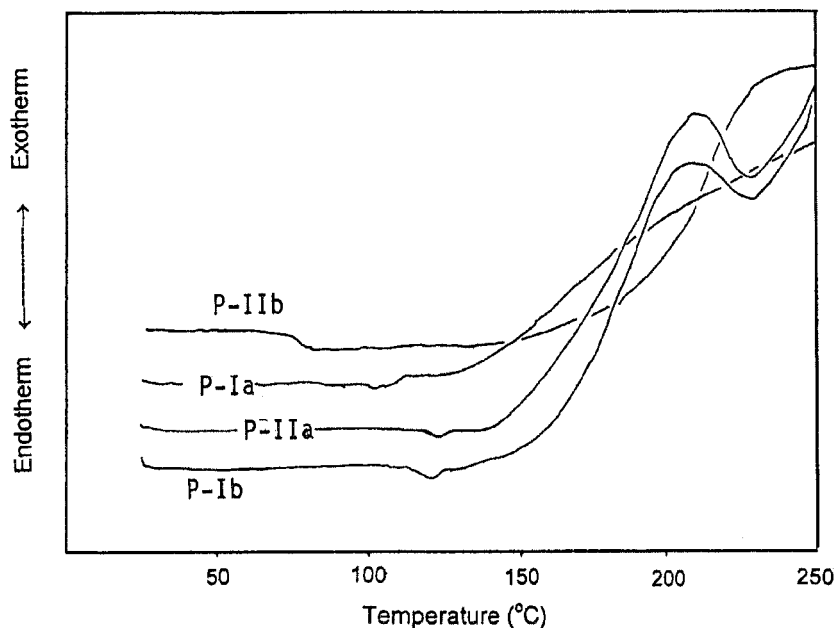

Fig. 4. DSC of the 4 polymers. Heating rate= 10°C/min. under N_2

Fig. 5 and Table 3 shows data of UV/Vis spectra of the poly(pentynoates) taken for spin coated films (about 2μm) on a quartz substrate. It can be seen that there are differences in the absorption maxima between the polymers with the nitro group and with the cyano group, the first ones possessing an absorption maximum at longer wave length than the latter. The polymers **P-II a** and **P-II b** which contain three benzene ring chromophores have absorption maximal at longer wavelength and a very wide cut-off absorption window than the **P-I a** and **P-I b** with the two benzene ring chromophores, due to the extended conjugation of the three ring chromophores. The hyperpolarizabilities of these four chromophores were reported previously (7), and it is obvious that nitro group is more suitable than cyano group for 2-NLO chromophores.

Table 3. Wavelengths of the spectra of the four polymers and hyperpolarizability of chromophores

POLYMER	λ_{st} [a] (nm)	λ_{max} [b] (nm)	λ_{cutoff} [c] (nm)	$\beta*$
P-Ia	360	454	620	8.32
P-Ib	350	440	588	22.8
P-IIa	398	482	706	14.4
P-IIb	388	466	672	41.0

[a]: Wavelength at maximal absorption starts   [b]: Maximal absorption   [c]: Cutoff of absorption window.   *Hyperpolarizability ($\omega=0$) 10^{-30} esu calculated by MOPAC-PM3 for the dimethylamino derivatives.

The chromophore density is said to be an important factor for high 2-NLO coefficients (10). It is calculated as a ratio of molecular weight of chromophore to that of the monomer unit. The chromophore density with chromophore **P-I a** is 67.2 %, and that with **P-II a** is 74.2%. The chromophore densities of the poly(*para*-benzoates) containing the same chromophores, **I a** and **II a**, to the above, are 50.9 and 58.5 %, respectively, and they showed 2-NLO coefficients of 224 and 350 *pm/V* respectively (7). Therefore, the **P-II** with the three-ring chromophore was expected to possess high SHG signal than the others. However, its SHG coefficient observed was not as high as expected. For example, **P-II a** showed a 2-NLO coefficient (d_{33}) of only 2 *pm/V*, compared with 350 *pm/V* of poly(*para*-benzoate) containing **IIa** dye, indicating that the aliphatic main chains are less responsive to poling. The poly(*para*-benzoate) containing a *para*-nitro-N,N-dihydroxyethylaniline (11) showed a coefficient, d_{33} of 18 pm/V, while the same dye with poly(pentynoate) showed no 2-NLO signal. These results clearly show that the type of main chains determine the orientation of chromophores. Even chromophores have high hyperpolarizability, 2-NLO coefficients cannot be high if suitable polymer main chains are selected.
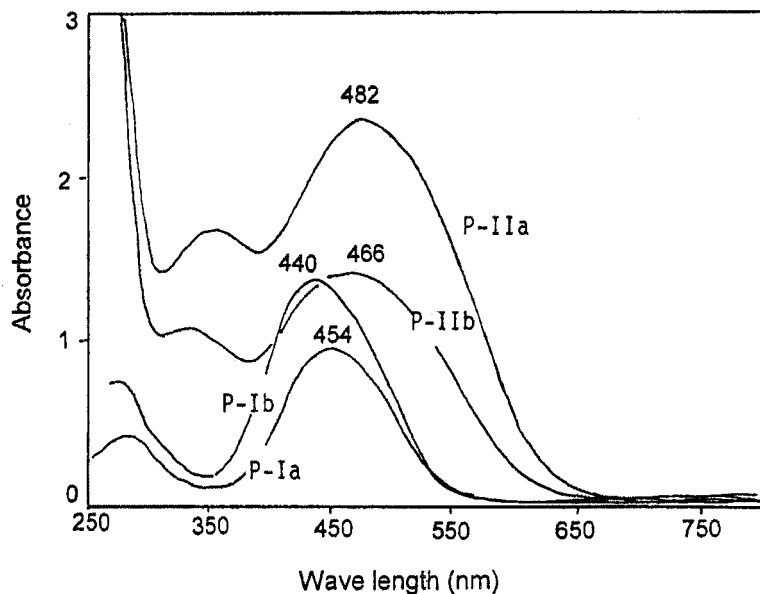
Fig. 5. Visible absorption spectra of the four polymers at room temperature (Spin coated films. approx. 2 μm)

Conclusion

Novel polymers consisting of octa-3,5-diynylenedicarboxylate as main chains and of various azo dyes as side chains, were synthesized and characterized. The polymers were amorphous and had T_g at around 100°C. Those having the two benzene-ring chromophores cross-linked during storage. The 2-NLO properties of these polymers appeared to be very poor, because they do not possess suitable conformation for orientation of chromophores, and therefore do not respond properly to poling, and probably the poled chromophores rapidly return to the random state. This is clear evidence that the main chain conformation is very important for 2-NLO polymers. The poly(para-benzoate) (9) and poly(para-cinnamate) (12) having the same chromophore (DR-1), showed 2-NLO coefficients of 250 pm/V, and furthermore, their relaxation at room temperature is negligible over a few years (13). It is said by many that the chromophore contents, T_g, and high hyper-polarizability of chromophores, are most important for high and durable 2-NLO polymers. However, this work showed that the type of main chain is an extremely important factor for 2-NLO polymers, which has been neglected in the past studies.

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