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Third order nonlinear optical susceptibility of films of polydiacetylene-containing polyamides and polyesters

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Summary

The third order nonlinear optical susceptibilities of cast films of diacetylene-containing polyamides, copolyamides and polyesters, were measured using degenerate four-wave mixing with picosecond pulses at 532 nm. The blue films of polyamides which contain aromatic polydiacetylene had $\chi^{(3)}$ values of the order of 10^{-9} - 10^{-10} esu, while the orange films of polyesters having aliphatic polydiacetylenes showed $\chi^{(3)}$ values of the order of 10^{-10} - 10^{-11} esu.

INTRODUCTION

Polydiacetylenes (PDAs) have attracted considerable attention as candidates for materials in nonlinear optical (NLO) applications [1], and the values of their third order NLO susceptibility have been reported in the literature [2]. In order to be applied for optical devices, PDAs should be processable into thin films of satisfactory optical quality. The current interest in PDAs appears to be focused on the processing of diacetylenic materials. One of the methods to obtain PDA-containing films is to synthesize diacetylene (DA) - containing polymers, which are then made into thin films and the DA-groups in the films are cross-polymerized to develop PDA networks. Several such polymers have been synthesized and chracterized [3]. The present authors have studied the synthesis and characterization of a series of high molecular weight DA-containing polyamides and polyesters [4-6], and found that these polymers can give transparent films with excellent mechanical strengths and the DA groups in the polymer films can be cross-polymerized by radiation to develop PDA networks. In this work the third order NLO susceptibility of these films were determined and the results are reported.

EXPERIMENTAL

The polyamides, copolyamides, and polyesters were prepared by the following

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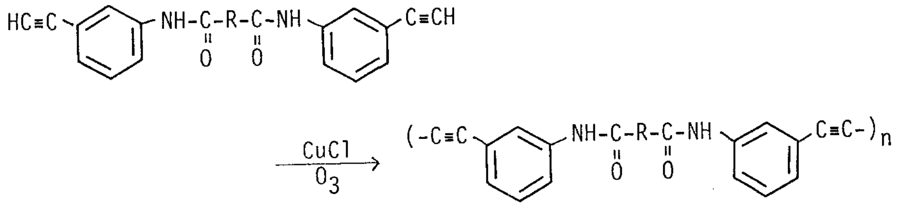
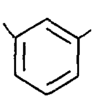
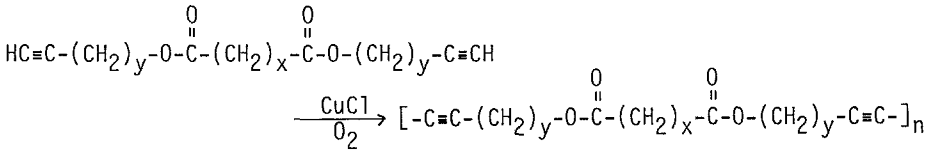
schemes; the details are found in previous reports [4-6].



where R =  : [Poly-1], $-(CH_2)_2-$: [Poly-2], $-(CH_2)_3-$: [Poly-3],
$-(CH_2)_4-$: [Poly-4], $-(CH_2)_8-$: [Poly-5].



$$HC\equiv C-(CH_2)_y-O-\overset{O}{\overset{\|}{C}}-(CH_2)_x-\overset{O}{\overset{\|}{C}}-O-(CH_2)_y-C\equiv CH \xrightarrow[O_2]{CuCl} [-C\equiv C-(CH_2)_y-O-\overset{O}{\overset{\|}{C}}-(CH_2)_x-\overset{O}{\overset{\|}{C}}-O-(CH_2)_y-C\equiv C-]_n$$

where y=1, x=8 : [Poly-6], y=2, x=8 : [Poly-7], y=2, x=2 : [Poly-8],
y=2, x=4 : [Poly-9].

Polyamide films were prepared by casting their N-methylpyrrolidone solutions onto glass slides at room temperature under a reduced pressure. The films were then irradiated with a UV lamp or heated at 180 °C for 10 hrs under nitrogen to from the PDA networks in the films. Those of polyesters were prepared by casting chloroform solutions, and the films were irradiated with an electron beam before or after orientation by an Instron 1135.

The electron beam irradiation was carried out using a Van de Graaf accelerator of 2 MeV (High Voltage Engineering Corporation) with a dose rate of 12 kGy/min. at 1.3 MeV. The film thickness was determined using a Dektak II Sloan surface profilometer. The third order NLO susceptibility was determined using a pico second laser consisting of s mode-locked Quantel Nd:Yag laser that was frequency doubled to 532 nm.

RESULTS AND DISCUSSION

According to the FT-IR spectra of the polyamides [4,5], in the case of thermal cross-polymerization, the absorption bands due to the DA groups disappeared and a new band due to the acetylenic groups of the newly formed en-yne linkages of the

PDA network, appeared at 2200 cm^{-1}. In the case of the UV-irradiated samples, the bands due to the DA groups did not disappear even after prolonged irradiation (3 hrs), because the UV irradiation cannot penetrate into the polymer films. The third order NLO susceptibility, $\chi^{(3)}$ values, of these polyamide films are shown in

Table 1. Composition of copolyamides.

Copolymer.	Monomer ratios. mol%. 1	2	3	4	5
Co-1	50	--	--	--	50
Co-2	--	50	--	--	50
Co-3	--	--	50	--	50
Co-4	--	--	--	50	50
Co-5	--	25	25	25	25

Table 2. Third order nonlinear optical susceptibility, $\chi^{(3)}$, of the polyamides irradiated with UV light.

Polymer	Film morphology.	$\chi^{(3)}$ esu x 10^{10}	max nm
Poly-1(t)	sc	7.2	561, 608
Poly-1(i)	sc	3.8	561, 608
Poly-2(t)	sc	7.2	548, 601
Poly-2(i)	sc	4.1	548, 601
Poly-3(t)	am	0.9	---
Poly-4(t)	sc	8.0	560, 610
Poly-4(i)	sc	4.6	560, 610
Poly-5(t)	sc	6.1	567, 612
Poly-5(i)	sc	3.2	567, 612
Co-1(t)	am	1.3	---
Co-2(t)	sc	10.0	559, 604
Co-2(i)	sc	3.0	559, 604
Co-3(t)	sc	7.0	564, 611
Co-3(i)	sc	2.9	564, 611
Co-4(t)	sc	4.0	564, 607
Co-4(i)	sc	1.4	564, 607
Co-5(t)	am	1.5	---

(t): by heating, (i) by irradiation. am: amorphous, sc: microcrystallites dispersed in the amorphous phase.

Table 3. Third order nonlinear optical susceptibility, $\chi^{(3)}$, of the polyesters.

Polymer	Irradiation dose(Mrad)	$\chi^{(3)}$ esu x 10^{10}
Poly-6	0	0.01
Poly-6	0.2	0.1
Poly-6	0.5	0.16
Poly-6	1.0	0.72
Poly-6	30	0.88
Poly-6	50	0.50
Poly-6	100	0.47
Poly-7	15	0.57
Poly-7	30	0.74
Poly-7	50	1.2
Poly-8	50	3.8
Poly-9	50	7.1

Films were irradiated with electron beam. Irradiated films have λmax around 500 nm and they are semicrystalline.

Table 2. The $\chi^{(3)}$ values of the thermally cross-polymerized polyamides (**Poly-1**, **Poly-2**, **Poly-4**, **Poly-5**, **Co-2**, **Co-3** and **Co-4**) were very similar to each other being about 10^{-9} esu, while those of the polyamides which did not undergo topochemical cross-polymerization (**Poly-3**, **Co-1** and **Co-5**), were smaller, being about 10^{-10} esu. These topochemically inactive polyamides did not give crystalline films by casting, while the other topochemically active polyamides gave films in which microcrystals of about 30-50 Åwere homogeneously dispersed, as observed by transmitting electron microscopy. The lower $\chi^{(3)}$ values of the amorphous films compared with those of the semicrystalline films, are due to their shorter conjugation of PDA chains, as observed in their VIS absorption spectra when no absorption maxima were present. The lower $\chi^{(3)}$ values of the UV-irradiated films are attributed to the incomplete cross-polymerization, as mentioned above.

The $\chi^{(3)}$ values of polyesters irradiated with an electron beam are shown in Table 3. The unirradiated **Poly-6** film did not show NLO response, and therefore it is obvious that the NLO susceptibility of these films originated from the PDA network formed by the irradiation. It increased with an increase in the irradiation dose but saturated at 30-50 Mrads which corresponds to the completion of the cross-polymerization as observed by FT-IR spectra (Fig. 1). The $\chi^{(3)}$values of the other polyester films were higher than those of **Poly-6**, because they are more crystalline

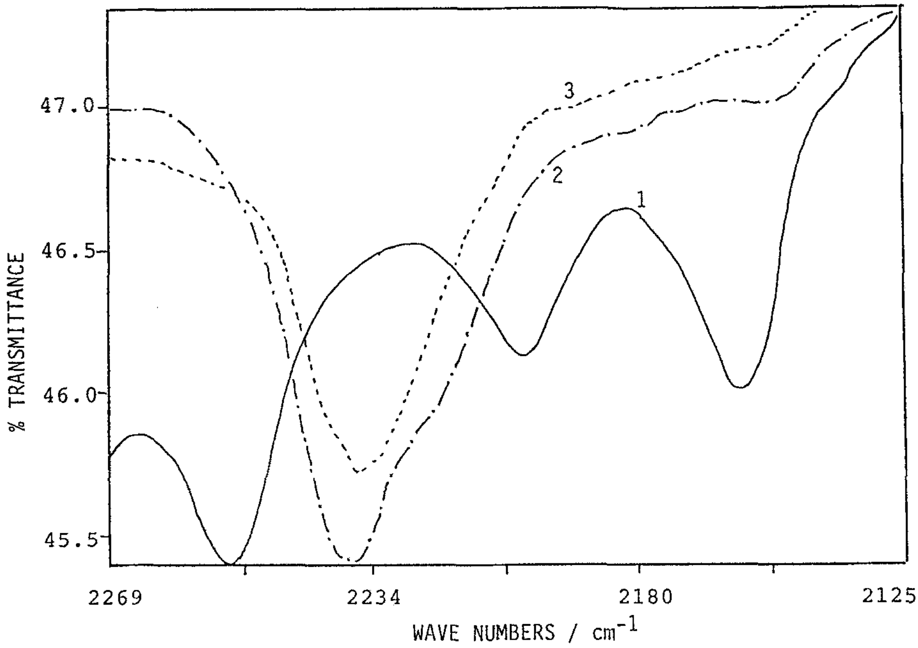


Fig. 1. FT-IR Spectra of the diacetylenic groups of Poly-6 before and after irradiation with electron beam.
1 : Before irradiation, 2 : Irradiated with dose of 30 Mrads, and 3 : Irradiated with 50 Mrads.

(degree of crystallinity: 25 and 43 % for **Poly-6** and Poly-7, respectively). In general, the $\chi^{(3)}$ of polyesters are about one order less than dose of the polyamides, because they lack the contribution of phenyl rings, the former having absorption maxima at around 600 nm and the latter at about 500 nm. These polyesters can be oriented by stretching to a few hundred percent. It was found for **Poly-7** that the $\chi^{(3)}$ values do not change appreciably by orientation of the film. This is because the PDA chains formed in the stretched films are not orientated in one direction, although the polymer main chains are oriented in one direction. The electron beam-induced cross-polymerization of DA groups in the orientated polymer films can take place in random directions, and therefore the PDAs in polymers cannot be orientated like other conjugated polymers whose $\chi^{(3)}$ values increase by orientation [7,8].

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