



Novel Diacetylene- and Chromophore-Containing Polymers and their Second Order Nonlinear Optical Properties.

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Several new polymers, which contain diacetylene groups in the main chains and polar chromophores in the side chains were synthesized and characterized. The polymers gave films with excellent optical quality by spin coating or casting due to their amorphous nature. The SHG measurements showed that the main chains have very important role to determine the second order nonlinear properties. For example the polymers having *para* benzoate chains had much higher SHG values than *meta* benzoate chains and pentynoic chains. Some of these polymers demonstrated very high SHG values, and this is probably because their extremely high order parameters, which is around 0.5 - 0.6.

Keywords: diacetylenic groups, polar dyes, second order nonlinear optics, high orientation parameter.

INTRODUCTION

There are a great number of papers reporting polymeric materials which contain highly polar dye molecules, prepared with the objective of obtaining organic materials for applications in the second

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order nonlinear optics (NLO) [1]. Many of these materials consist of vinyl polymer main chains such as poly(methylmethacrylate), to which dyes such as Disperse Red 1 are linked. Such polymers are then made to thin films and are subjected to orientate their polar dye molecules in such a manner that there is no centrosymmetry. This is achieved by poling the polymer films at temperatures above their glass transition temperatures. The NLO properties of such polymers have been intensively investigated [2,3].

The orientation of dye molecules by poling should depend on the nature of main chains, although this has been little discussed so far. The main chains such as polymethacrylates are not so flexible because of the tetra-substituted carbon atoms, and therefore the polymer orientation by poling probably causes torsion in the polymer chains, and this helps the cancellation of the orientation of dye molecules. In order to avoid the relaxation of poled dye molecules, high glass transition polymers such as polyamides and polyimides have been reported [4,5]. However, such polymers are even more difficult to be orientated, and the poor orientation efficiency seems to be the main reason why polymeric materials with satisfactorily high SGH have not obtained. Therefore, it is most important to find polymers, which facilitate the orientation of dyes (chromophores) by poling.

The present authors have synthesized various polymers which contained diacetylene groups in their main chains[6]. The polyesters and polyethers containing diacetylene groups are flexible polymers, and the diacetylene groups are readily cross-polymerized in the polymer films, giving totally insoluble thermoset resins. The cross-linking of dye-containing polymers is an important tool to avoid the relaxation of orientated chromophores, and one of the aims of this study was to obtain polymers whose chromophores are permanently orientated by cross-linking.

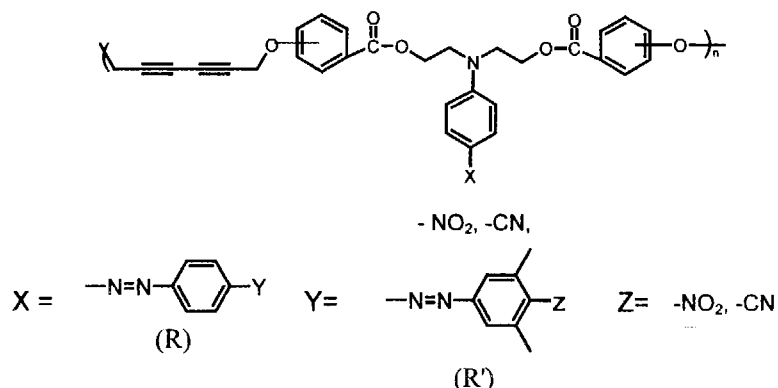
In this paper some preliminary results of the SHG obtained for several novel polymers containing diacetylene groups in the main chains and chromophores in the side chains.

EXPERIMENTAL

The detailed synthesis and characterization of benzoate monomers and polymers are reported in the literature[7,8]. The general structures of the polymers are shown in Scheme 1. The poly-pentynoates were synthesized from pentynoylchloride and diols the polymer structures are shown in Scheme 2.

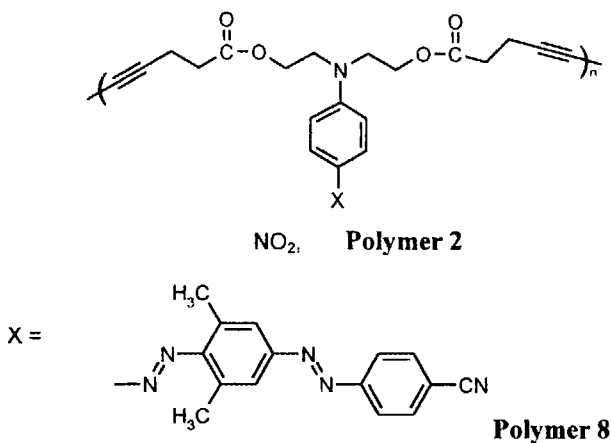
The polymers were made into thin films by spin coating from their chloroform or dimethylformamide solutions on glass substrates. The films were poled by corona discharge at a distance of 5 cm between the electrode and film at temperatures 5 - 8 °C above the respective T_g .

The SHG measurements were carried out at room temperature using a Q-switched Nd:YAG laser (1064 nm, 8 n, 10Hz).



Polymer 1 : $X = \text{---NO}_2$. **Polymer 3** : *para*-benzoate $X=R, Y = \text{---CN}$
Polymer 4 : *para* benzoate $X=R, Y = \text{---NO}_2$, **Polymer 5** : *meta* benzoate $X=R, Y = \text{---CN}$, **Polymer 6** : *para* benzoate $X = R, Y = R', Z = \text{---NO}_2$, **Polymer 7** : *para* benzoate $X = R, Y = R', Z = \text{---CN}$.

Scheme 1. The benzoate polymers studied in this work.

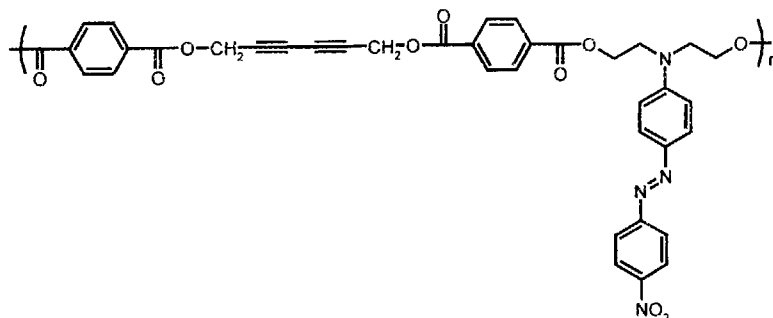


Scheme 2. Polymers from pentynoate.

UV irradiation of films was carried out using a medium pressure mercury lamp of 450 W supplied by Ace Glass Co.

RESULTS AND DISCUSSION.

The polymers obtained in this work had inherent viscosity of the range of 0.5 - 0.8 dl/g, which are thought to correspond to medium molecular weights. The polymerization of this work is oxidative coupling reaction, and very high molecular weight polymers can be obtained. However, extremely high molecular weights polymers tend to lose their solubility and therefore the polymerization were stopped when the systems became viscous. The direct polycondensation reactions between acid chlorides and diols are not adequate to obtain good polymers, and they result in low molecular oligomers which give fragile films. Dalton and his coworker [9] have reported previously a few polymers containing a diacetylene group and a chromophore as shown below:



They employed the method of direct polycondensation of *p*-phthalic dichloride with hexa-2,4-diyne-1,6-diol and *p*-*N,N*-diethanolamino-*p*'-nitroazobenzene. They reported a d_{33} value of 119 pm/V for the above polymer. The polymers had inherent viscosity of 0.2-0.3.

Table 1 shows the DSC results of glass transition temperatures, T_g and the temperatures at which starts the cross-polymerization of the diacetylene groups, T_p for the polymers synthesized in this work. It can be seen that the polymers can be cross-linked thermally at temperatures around 150-160 °C, while the pentynoates have higher cross-linking temperatures than the benzoates in spite of their lower T_g . Low T_g polymers are not suitable for orientation of chromophores because of relaxation can readily take place. As shown in the results of SHG mea-

surements, the polymers from pentynoates had no or very little NLO effect.

Table 1. Thermal behaviors of polymers.

Polymer	T_g	T_{cs}	T_{cm}
1	100	150	220
2	30	130	142
3	121	150	189
4	106	160	204
5	50	162	180
6	115	152	181
7	120	150	180
8	63	155	181

T_g : Glass transition temperature. T_{cs} : Temperature at which cross-linking stated. T_{cm} : Temperature of exotherm peak.

Table 2 shows dipole moment and molecular hyperpolarizability of the chromophores calculated by MOPAC-PM3. The nitro group is clearly superior to cyano group.

Table 2. Dipole moment and molecular hyperpolarizability of the chromophores calculated by MOPAC-PM3.

CHROMOPHORE					
	1	2	3	4	5
A	7.01	5.65	8.11	4.88	7.75
B	8.32	22.8	26.9	14.4	41.10
C	27.0	87.0	98.3	77.2	184

A : Dipole moment/debye. **B**: Hyperpolarizability ($w=0$)/ 10^{-30} esu.

C: Hyperpolarizability (1064 nm)/ 10^{-30} esu

Table 3 shows physical properties and NLO coefficient of the polymers. Polymers 4 and 6 had very high NLO coefficients compared with the others. They have nitro group as an acceptor group. The cyano group was found less effective, especially the difference between Polymer 6 and Polymer 7 was incredibly large. This may be due to the difference in the hyperpolarizability as shown in Table 2, but there may be another unknown factor for such a large difference. There was also a large difference between the *meta* and *para* benzoate main chains. The d values were much less with *meta* benzoate chains, and this may be due to the low T_g of the *meta* benzoate chain. It can be seen that the pentynoate polymer chains have low T_g and NLO coefficients were almost negligible. It is most interesting to observe that the nature of polymer main chains influence tremendously the NLO effects even though same chromophores are attached to polymers.

Table 3. Physical properties and NLO coefficients of novel NLO polymers

Sample	T_g (°C)	T_c (°C)	λ_{cutoff} (nm)	n	NLO coefficient (pm/V)		d_{32}/d_{31}
					d_{31}	d_{32}	
Polymer 1	100	220	490	1.6865 (532 nm)	7	18	2.6
Polymer 2	30	142	606	1.6594 (532 nm)	-	-	-
Polymer 3	121	166	610	1.7382 (633 nm)	21	100	4.8
Polymer 4	100	204	635	1.8058 (633 nm)	32	224	7.0
Polymer 5	50	180	605	1.7328 (633 nm)	11	39	3.5
Polymer 6	115	181	675	1.8837 (780 nm)	118	350	3.0
Polymer 7	120	117	650	1.7224 (780 nm)	2	12	6.0
Polymer 8	63	177	668	1.7391 (780 nm)	0.7	2	2.9

T_c : cross-linking temperature λ : cutoff: cutoff wavelength n: refractive index

Table 4 shows relationships between NLO coefficients, order parameter and chromophore density. It can be seen that the order parameters of these polymers are very high compared with those reported for most polymers so far investigated. Their values are equivalent to those of liquid crystals. The reason for this is being investigated and will be reported in future.

Table 4. NLO coefficients, order parameter and chromophore density.

Polymer	T _g (°C)	NLO coefficient (pm/V)		d_{33}/d_{31}	S	Chromophore density %
		D_{31}	D_{33}			
1	100	7	18	2.6	-	41.5
2	30	-	-	-	-	81.7
3	121	21	100	4.8	0.59	50.5
4	100	32	224	7.0	0.61	50.9
5	50	11	39	3.5	0.46	50.5
6	115	118	350	3.0	-	58.5
7	120	2	12	6.0	0.54	58.2
8	63	0.7	2	2.9	-	89.8

S: order parameter.

Order parameter is estimated from d_{33}/d_{31} value.

The chromophore density was calculated by dividing the molecular weight of chromophore diol by the molecular weight of the polymer unit. These polymers have high chromophore densities, but it can be seen clearly that this is not the most important factor for high NLO values, as can be seen in the cases of Polymers 2 and 8.

The durability of NLO properties of these polymers are being investigated, and will be reported in future. No decrease has so far been observed for a few months at room temperature. It is expected that the polymers which can easily be poled, have no distortion of polymer chains, and therefore the relaxation of orientated chromophores may be slow.

It is of interest to cross-link these polymers through the diacetylenic groups. When the polymers are heated at above 150 -160°C the cross-linking takes place. Diacetylenes are heat and light sensitive, independently of the solid state morphology. If the diacetylene groups are located in such manner that topochemical polymerization can take place, polydiacetylene net works are developed. If they are in the amorphous state like the case of the polymers of this work, only cross-linking takes place.

The temperatures at which the cross-linking starts are rather too high for maintaining the NLO properties. It seems that thermally induced molecular motion overcomes the orientation force by poling, thus NLO response disappears during poling at temperatures of cross-linking. Therefore, photo-cross-linking was attempted, and it was successfully carried out by irradiating the films with a mercury lamp at the temperature of poling. For example, by irradiation at 120°C for 30 minutes the films became totally insoluble in the solvents in which the polymers were readily soluble, and even they did not swell nor peeled off from the glass substrate. This results suggests us that cross-linking can be carried out simultaneously with poling.

Dalton and coworkers have reported that the *trans*-to-*cis* isomer-

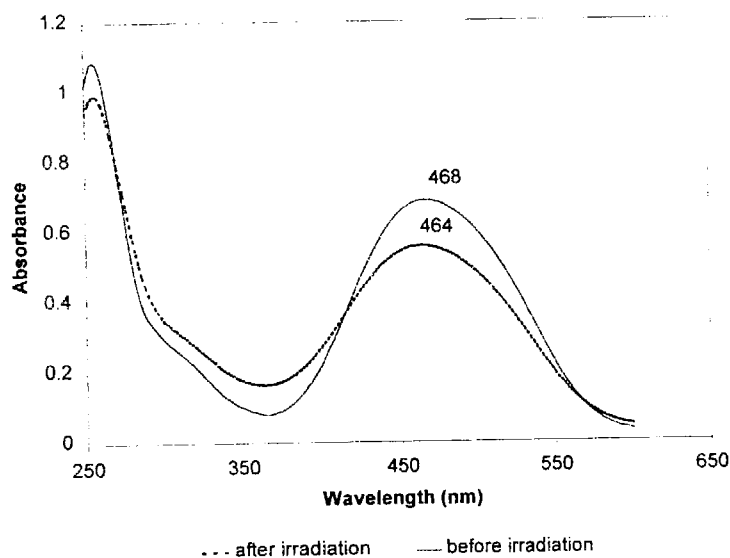


FIGURE 1. Visible Absorption Spectra of Polymer 4 before and after Irradiation with UV light at 120°C for 30 minutes

zation of the azo chromophore takes place significantly thus decreasing the NLO effects. Figs. 1 and show the absorption spectra of Polymers 4 and 7. In both cases some decrease in absorption is observed, but not so significantly as in the case of the Dalton's polymer [8]. The trans-to-cis transformation depends on conditions such as the light wavelength and temperature. The optimum conditions to cross-link with minimum trans-to-cis transformation should be sought in future.

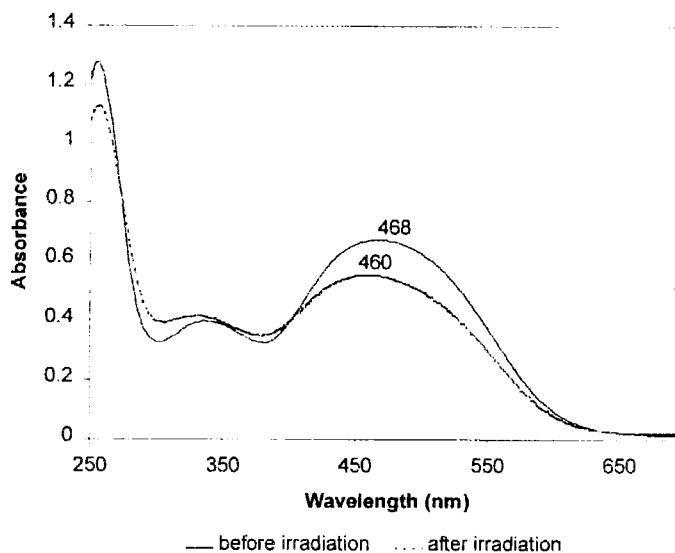


FIGURE 2. Absorption spectra of Polymer 7 before and after Irradiation with UV light at 120°C for 30 minutes.

CONCLUSION

The nature of main chains is one of the most important factors influencing SHG properties. Polymer 4 and 6 having nitro group as an electron acceptor had very high NLO coefficients, and the polymers with nitrile group were inferior to those with nitro group. The polymers 2 and 8 having an aliphatic main chain were totally useless as NLO polymer probably because of their low glass transition temperature. In the cases of the benzoate main chain polymers, order parameters were

found to be extremely high, and this can be the main reason for such high NLO coefficients. It is not known at this moment why these benzoate main chain polymers have such a high order parameter.

Further studies on the details of NLO properties will be reported in near future.

REFERENCES

- [1] J. Messier, F. Kajzar, P. Prasad, D. Ulrich, edits, *Nonlinear Optical Effects in Organic Polymers*, Kluwer Academic Publications, Dordrecht (1989)
- [2] M.G.Kanatizdis and Y.Park, *Chem. Mater.*, **2**, 99 (1990)
- [3] A. Amano and T. Kaino, *J.Appl.Phys.*, **68**, 6024 (1990)
- [4] R. D. Miller, D. M.Burland, M. Jurich, V. Y. Lee, P. M. Lundquist, C. R. Moylan, R. J. Twieg, J. I.T hackara, T. Verbiest, Z. Sekkat, J. Wood, E. F. Aust, and W. Knoll, in *Photonic and Optoelectronic Polymers*, pp100-122, ACS Symp. Ser. 672, American Chemical Society, Washington, DC(1995)
- [5] D. Y. Wenjie, L. A. Gharavi, and L. Yu, , in *Photonic and Optoelectro-nic Polymers*, pp123-132, ACS Symp. Ser.672, AmericanChemical Society, Washington, DC(1995)
- [6] T. Ogawa, *Prog. Poly.Sci.*, **20**, 948(1995).
- [7] S. Hernández, M. F. Beristain, T. Ogawa, *Designed Monomers and Polymers*, in press.
- [8] S. Hernández and T. Ogawa, *Polym. Bull.*, submitted for publication.
- [9] M. Chen, L. Yu, L.R. Dalton, Y. Shi, and W. H. Steier, *Macromolecules*, **24**, 5421 (1991).