Novel Diacetylene-Containing Polymers for Second Order NLO Applications: Effect of Main Chains and Structure Property Relationships

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Summary: In order to obtain polymers having high second order nonlinear optical (NLO) response, various novel polymers that contain polar dye molecules in side chains and diacetylenic groups in the main chains were synthesized, and their second order NLO properties were studied. Some of these polymers consisting of *para*-benzoate and *para*-cinnamate main chains, showed extremely high NLO coefficients, d_{33} of 200 - 350 pm/V, and the corresponding *meta* polymers showed much inferior NLO coefficients. The polymers having aliphatic main chains had very little NLO response probably because of their low glass transition temperatures and flexibility of main chains. The high SHG responses of these polymers are attributed to their facile orientation of both chromophores and main chains. In the case of *para*-polymers, the main chain orientation of alkoxybenzoate and cinnamate along the chromophore is thought to be a reason for their high NLO coefficients.

Introduction

There are many studies on the polymers, which possess second order nonlinear optical (2-NLO) susceptibility in the last decades, and their majority is concerned with polymers having polar chromophore groups in the side chains.[1-3] Many of them are vinyl polymers such as polymethacrylates containing dye molecules such as Disperse Red 1. However, the monomers having large dye molecules have poor polymerizability, and copolymerization with ordinary monomers is often required, and the concentration of the dye-containing monomers becomes low, and the distribution of the dye monomers in the polymer is not homogeneous due to difference in reactivity of two monomers. In order to obtain polymers with high chromophore concentrations and homogeneous structures it is necessary to obtain polymers consisting of only chromophore-containing monomers. The dye molecules in the polymers are then poled

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for orientation of the chromophores, but the relaxation is inevitable and the NLO effect fades away with time. To avoid the relaxation of poled chromophores, cross-linking is thought to be a solution.[4, 5] However, the introduction of monomer units containing cross-linking groups in copolymerization is not recommendable because it decreases the concentration of chromophore-containing monomers, and the molecular motion between the cross-linked sites cannot be avoided unless very high cross-linking density is attained. Furthermore, irregular cross-linking results in relatively large optical error. Use of high Tg polymers such as polyamides and polyimides has been also studied.[6,7] However, the orientation of chromophores by poling for such high Tg polymers is not easy, and results in poorly orientated polymers having low 2-NLO coefficients.

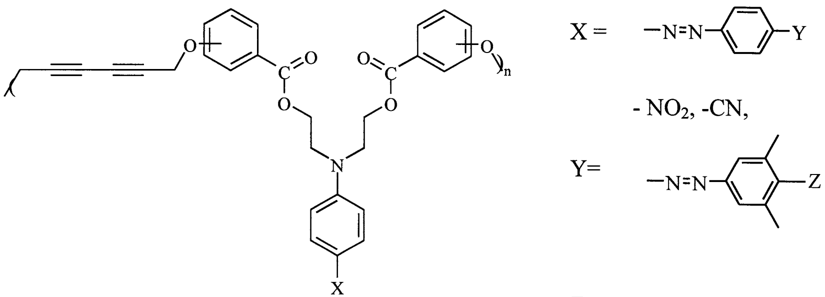
In order to obtain polymers which might satisfy the above requisitions; high chromophore concentration and cross-linking, Dalton and coworkers have reported four different types of polymers containing chromophore of Disperse Red 19 (Aldrich #21,576-7). A polymer consisting of *p*-phenylenediacrylate main chain showed a d_{33} value of 250 pm/V.[8] They attributed the high NLO coefficients to the high chromophore concentration. However, irradiation of their films with a UV light drastically decreased the absorption height due to the trans-cis transformation of the azo dye.

Diacetylenes are known to polymerize in crystalline state by irradiation or heat to give corresponding crystalline polydiacetylenes. They also undergo polymerization when heated in the amorphous state although the products may not be completely 1,4-polydiacetylenes. Therefore the diacetylene groups are considered to be excellent cross-linking sites. The present authors have reported previously the synthesis of several polymers which contain 2,4-hexadiynylene groups in the main chains and polar chromophores in their side chains,[9,10] and also a few results of the 2-NLO measurements of some of the polymers.[11] In this work, as continuation of the previous work, more polymers which contain diacetylene groups in main chains and polar chromophores in side chains, were synthesized and characterized, and the effects of main chain structures on high 2-NLO coefficients of some of these polymers are discussed in this article.

Experimental

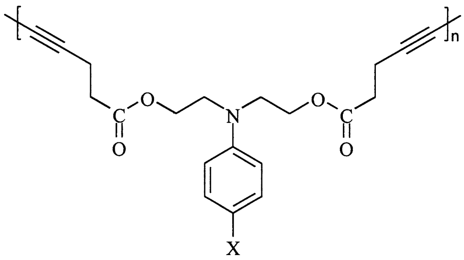
Synthesis

The synthesis of the polymers consisting of the benzoates main chains, were reported in the previous papers.[9, 10] Their structures are shown with Scheme 1.



Scheme 1

The polymers having aliphatic main chains have the following structures (Scheme 2):

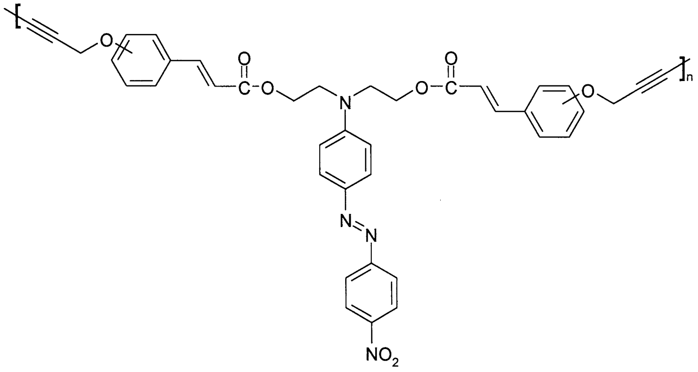


Scheme 2

They were synthesized by the reaction of pentynoyl chloride with the *N,N*-diethanol amino dyes, and the bisacetylenic monomers were polymerized by the oxidative coupling reaction similarly to the cases of the benzoates.

The poly(cinnamates) containing the dye Disperse Red 19 shown with Scheme 3, were synthesized by the reaction of *para-* and *meta*-cinnamic acids or their methylesters with propargyl bromide, followed by the chlorination with thionyl chloride.[12] The propargyloxy cinnamoyl chlorides were then reacted with Disperse Red 19 to obtain the corresponding bisacetylenic monomers, which were polymerized at room temperature in N-methylpyrrolidinone (NMP) for 10 hours by the oxidative coupling reaction using copper (I) chloride and *N,N,N'N'*-tetramethylethylenediamine as catalysts, gently bubbling oxygen into the system. The polymers were precipitated in methanol and purified by reprecipitation from DMF/methanol system. The polymers had inherent viscosity of 0.3-0.7 at 25 °C in NMP.

Films with excellent optical quality were obtained by spin coating from DMF solution at 40 - 50 °C. Langmuir-Blodgett membranes could be prepared from chloroform solutions. The *para*-polymers crystallizes when kept in DMF solution for several hours, and the crystalline polymer is no longer soluble in DMF, but soluble in NMP.



Scheme 3

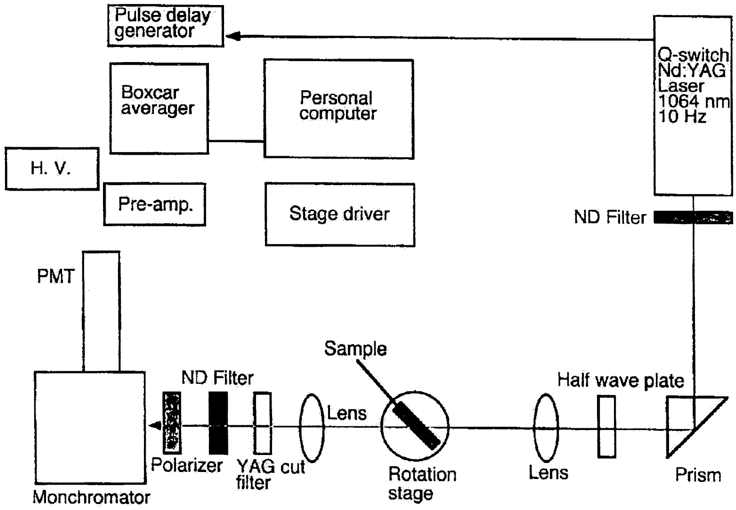


Fig. 1. Schematic diagram of SHG measurement set up.

The polymers were characterized by DSC, NMR, IR. The irradiation of films was carried out using a 400W medium pressure Hg lamp of Ace Glass Co.

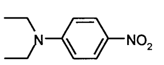
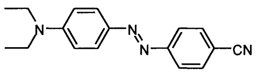
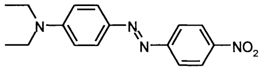
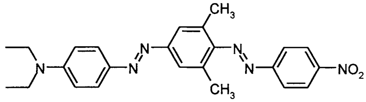
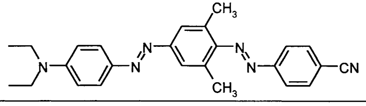
The refractive indexes and film thickness were determined by prism coupling and elipsometry.

The 2-NLO coefficients were measured by the set-up shown in Fig.1. The chromophore density was calculated by the ratio of molecular weight of chromophore over polymer molecular weight.

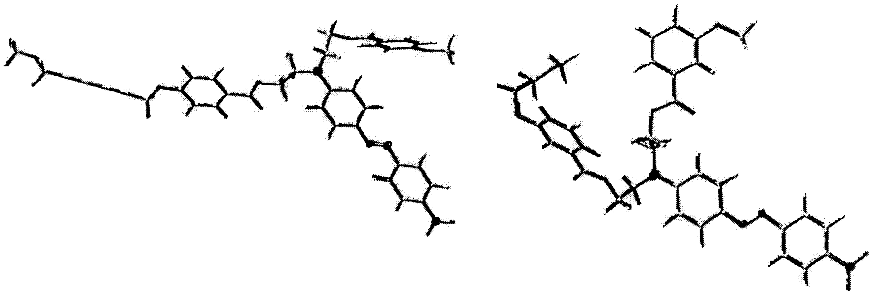
Results and Discussion

The poly(benzoates) and poly(pentynoates) are shown in Table 1. The hyperpolarizability of the chromophores used in this work, are shown in Table 2, and the 2-NLO coefficients are shown in Table 3.

Table 1. Poly(benzoates) and poly(pentynoates) of which NLO properties were determined.

Polymer	Main Chain	Chromophore	Tg (DSC)
1	***p*-benzoate**		100
2	Pentynoate		30
3	***p*-benzoate**		121
4	***m*-benzoate**		50
5	***p*-benzoate**		100
6	***p*-benzoate**		115
7	***p*-benzoate**		120
8	Pentynoate		63

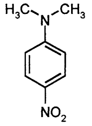
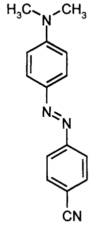
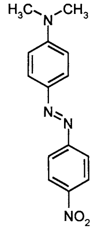
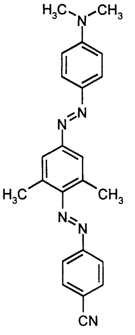
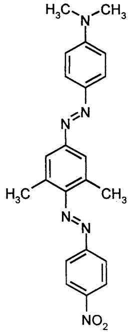
It can be seen clearly that the aliphatic main chain polymers have poor NLO susceptibility compared with those having benzoate main chains, although same chromophores are attached (Polymers 1 and 2). This is probably because the flexible aliphatic main chain polymers have low T_g and the orientation of the chromophore cannot be maintained, and rapid relaxation may be taking place. A significant difference in d_{33} values is observed between the Polymers 3 and 4. The T_g of Polymer 3 (*para*-benzoate) is 121 °C and that of Polymer 4 (*meta*-benzoate) is 50°C, and the relaxation of chromophore will take place more rapidly in the case of Polymer 4. Another possible explanation is that the Polymer 3 contains *para*-alkoxy benzoate group, which will respond to the electric field, and it is also orientated in parallel with the chromophores, and the whole polymer becomes an orientated material. The Fig. 2 shows the lowest energy conformers of model molecules optimized at HF/6-31G level for the *para*- and *meta*-poly(benzoates). It can be seen that the *para*-polymer can be more easily orientated. Imase, et al have reported that strong SHG activities are observed for polar rod-like polyesters, such as poly(4-hydroxybenzoic acid).[13] The fairly large hyperpolarizability of the aromatic polyester is ascribed to the large electronic transition moment. Therefore, in the case of poly(*para*-benzoates), such effect can be taken into account for their high 2-NLO coefficients.



Para Meta

Fig. 2. Lowest energy conformers of model molecules optimized at HF/6-31G level.

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

CHROMOPHORES					
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

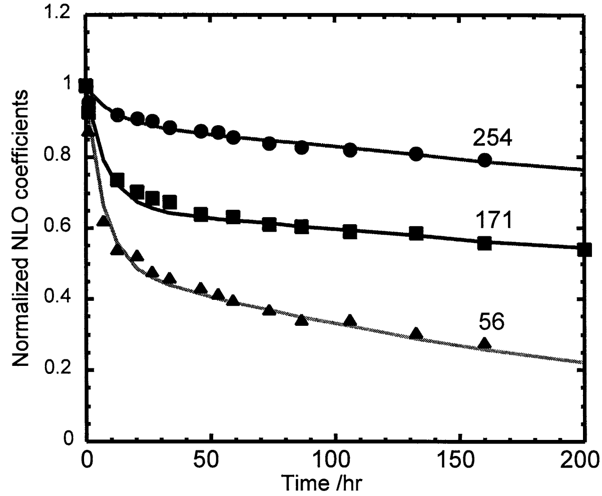
A : Dipole moment/debye. **B**: Hyperpolarizability (ω=0)/10^{-30} esu.
C: Hyperpolarizability (1064 nm)/10^{-30} esu

A tremendous difference is observed between Polymers 6 and 7. The former showed the highest ever 2-NLO coefficient, d_{33}, of 350 pm/V. The both polymers have *para*-benzoate main chain, and the only difference is the electron acceptor groups nitro and cyano. The high value of Polymer 6 is due to the high molecular hyperpolarizability of the chromophore, together with the effect of the *para*-benzoate main chain. In the case of Polymer 7, the low d_{33} value may be attributed to the lower dipole moment and hyperpolarizability of the cyano-chromophore. Further studies are being made to clarify this problem. In the case of Polymer 8, the low T_g of the pentynoate main chain cannot maintain the orientation of the chromophore.

Table 3. NLO coefficients of novel NLO polymers

Sample	λ_{cutoff} (nm)	n	NLO coefficient (pm/V)		d_{33}/d_{31}	S	Chromophore Density %
			d_{31}	d_{33}			
Polymer 1	490	1.6865 (532 nm)	7	18	2.6	-	41.5
Polymer 2	606	1.6594 (532 nm)	-	-	-	-	81.7
Polymer 3	610	1.7382 (633 nm)	21	100	4.8	0.59	50.5
Polymer 4	605	1.7328 (633 nm)	11	39	3.5	0.46	50.5
Polymer 5	635	1.8058 (633 nm)	32	224	7.0	0.61	50.9
Polymer 6	675	1.8837 (780 nm)	118	350	3.0	-	58.5
Polymer 7	650	1.7224 (780 nm)	2	12	6.0	0.54	58.2
Polymer 8	668	1.7391 (780 nm)	0.7	2	2.9	-	89.8

Some of the results on the 2-NLO property of poly(cinnamates) are shown in Fig. 3. In this case also, the *para*-polymers showed 4 - 5 times greater d_{33} value than the *meta*-polymer. A copolymer of *para*/*meta* 60/40 mole% showed intermediate value. The results agree with those of the benzoates, the *para*-mains chain being the key for the high NLO property. The *para*-polymer maintained its initial coefficient by nearly 80% after 2000 hrs, while the *meta*-polymer lost by 80% after 2000 hrs. The reason why the *para*-polymers possess high 2-NLO properties is not yet clear, but one possible explanation is that the *para*-main chains can orientate by poling in the same direction to the chromophore orientation, as shown in Fig. 4.



● : 100% *para* $d_{33}=0.10*\exp(-t/100) + 0.90*\exp(-t/12000)$

■ : 60% *para* and 40 % *meta* (mole%) $d_{33} = 0.34*\exp(-t/80) + 0.66*\exp(-t/10000)$

▲: 100% *meta.* $d_{33} =0.5*\exp(-t/70) + 0.5*\exp(-t/2400)$

Fig. 3. NLO coefficients as a function of elapsed time after poling for Poly(hexa-2,4-diynylene-1,6-dioxydicinnamates) containing Disperse Red 19 dye. The d_{33} values in the figure are the initial value after poling.

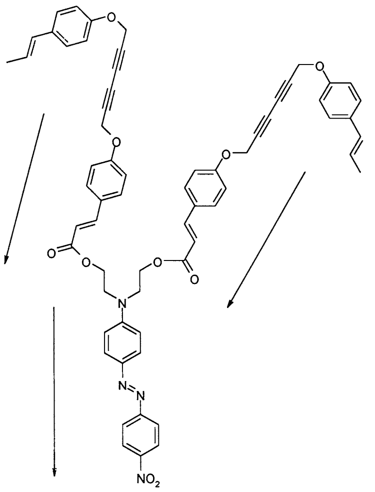


Fig. 4. A schematic picture of poled poly(*para*-cinnamate) indicating orientation of chromophore and main chain component.

Another possibility is that poly(hexa-2,4-diynylene-1,6-dioxydicinnamates) have crystallization tendency. The poly(*para*-cinnamate) having *para*-nitro-N,N-diethanol aniline is highly crystalline and insoluble in organic solvents. Therefore, the rigid structure inhibits relaxation of orientated chromophores.

The discharge dynamic study[14] showed that the *para*-benzoate polymers have a polymer structure very favorable for chromophore orientation by poling, as very little discharge is observed. On the other hand, the *para*-cinnamate polymer showed vigorous discharge below the T_g, and required 4.5 kV or higher voltage for poling the chromophore while the *meta*-cinnamate could be poled with 4 kV. The *para*-cinnamate polymer with Disperse Red 19 crystallizes from its DMF solution. When the solution is left to stand at room temperature for more than 24 hours, its crystalline polymer precipitates, which is soluble only in NMP. Amorphous polymer is recovered by reprecipitation with methanol. Langmuir-Blodgett membranes of the poly(*para*-cinnamate) and poly(*para*-benzoate) are well orientated as observed by the atomic force microscopy of their 2-layer LB membranes.[15] The *para*-benzoate polymer self-assembled on the water surface. It seems that they apparently have a self-assembly character. The d_{33} of the poly(*para*-cinnamate) is somewhat higher than that of poly(*para*-benzoate), 254 and 224 pm/V, respectively. The atomic force microscopy of Langmuir-Blodgett membranes showed that the cinnamate polymer is better orientated than the benzoate analogue. It can be said that the geometrical structures of these 4 polymers (*para*- and *meta*-benzoates and cinnamates) may be quite different, and further studies are being made to clarify the reason for high SHG coefficients.

With respect to the chromophore density, Dalton[8] attributed the high d_{33} values, 108, 250, 19, and 223 pm/V) of their 4 polymers to the high chromophore density (48, 68, 47, and 52%, respectively). However, high chromophore density alone cannot explain high NLO coefficients. In the case of this work also the chromophore densities are high, being around 50%, but d_{33} values depend more on the type of main chains polymers. The type of chromophore is important as can be seen in the comparison among Polymers 1, 3, 5, 6 and 7. It is obvious that when the main chains are the same each other, the greater the hyperpolarizability of chromophores, the greater the 2-NLO effect.

These polymers can be cross-linked thermally through the diacetylene groups in the main chains. However, as can be seen in Fig. 5, the temperature at which the thermal cross-linking takes place is much higher than T_g, and therefore, the orientation cannot be maintained due to vigorous thermal motion. Therefore, simultaneous thermal cross-linking and poling cannot be performed. Dalton and coworkers[8] have irradiated their films with UV light and cross-linked their polymers. In their work, the absorption peak due to the Disperse Red 19 at 468 nm drastically decreased it intensity due to the trans to cis transformation of the azo group by the irradiation. In the case of this work, the trans-to-cis transformation was not appreciable when irradiated with a UV lamp at 100-120°C (poling temperature), as reported in the previous papers for poly(benzoate)[10] and for poly(cinnamate).[12] This is probably due to the thermal cis-to-trans transformation which compete the photochemical trans-to-cis transformation.

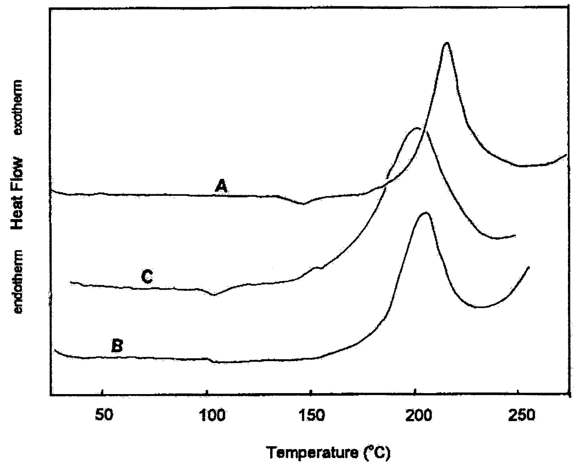


Fig. 5. DSC Curves of Polymer 6 (**A**), Polymer 5 (**B**), and poly(*m*-cinnamate) (**C**) .

After the irradiation the films were completely cross-linked, and converted to thermoset resin films which are totally insoluble in DMF, and did not swell nor pealed off from the substrate when immersed in DMF. The irradiation at room temperature showed consistent decrease in absorbance with irradiation time. This observation suggests that the simultaneous poling and cross-linking can be done satisfactorily.

Conclusion

It was shown that the main chain structure is very important for designing the SHG polymers. It seems that the poly(*para*-cinnamates) and poly(*para*-benzoates) are so far the best candidates for obtaining polymers with high 2-NLO coefficients. The aliphatic main chain polymers such as polypentynoates may not give high NLO coefficients even if they have proper T_g of around 100-120 °C, although their chromophore density is very high. The nitro group was found much better acceptor group than cyano group, as expected from the difference in their hyperpolarizability and dipole moment.

The NLO stability of these polymers is being studied, and the results will be reported in future. It looks that little relaxation takes place for *para*-benzoates and *para*-cinnamates even without cross-linking.

Considering from extremely fine optical quality of the films, very high NLO coefficients, and the NLO durability of these polymers, the *para*-polymers can be satisfactorily used for constructing various photonic devices.

Acknowledgement

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