

Effects of main chains on the second order nonlinear optical susceptibility of poled poly(dipropargyloxybenzoates) containing 2-[4-(2-chloro-4-nitrophenylazo)-*N*-ethyl-phenylamino]ethanol (*Disperse Red 13*)

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ABSTRACT

A series of isomeric polymers containing hexa-2,4-diynylene-1,6-dioxybenzoate group as the main chain and a polar azo dye (*Disperse Red 13*) as in the side chain were synthesized, and their second order nonlinear optical responses were studied. The second order nonlinear coefficients, d_{33} were found to be in the range of 50–90 pm/V. The nonlinear response (d_{33}) with respect to the positions of main chain was found to be in the order; 3,5-(*meta*) > 3,4-(*ortho*) > 2,5-(*para*) > 2,4-(*meta*), but the order of values d_{33}/d_{31} was 3,5-(*meta*) > 2,4-(*meta*) > 2,5-(*para*) > 3,4-(*ortho*). The higher response of the 3,5-polymer may be attributed to the symmetric substitution on the benzene ring, permitting the main chain conformation with less flexibility, as well as a higher Tg.

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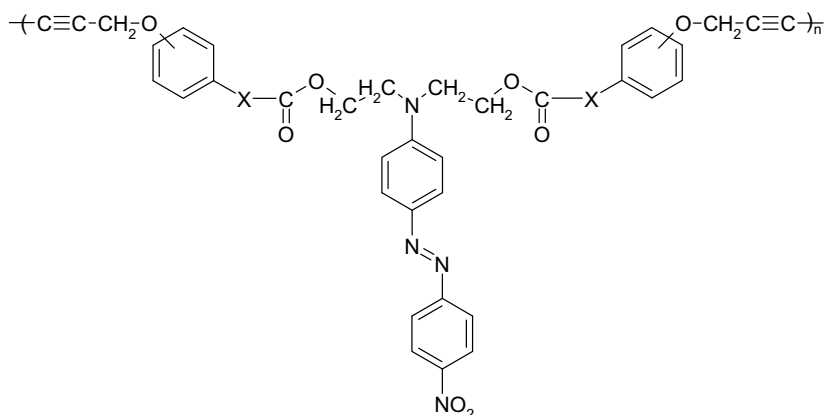
1. Introduction

Organic polymers having nonlinear optical properties were intensively investigated in the past decades [1–4]. In many of these studies high hyperpolarizability of chromophores and high glass transition temperatures (Tg) of polymers, are considered to be important factors. Recently however, the present authors have synthesized a series of new polymers, which showed high and stable second order nonlinear optical responses with relatively low Tg of 100–120 °C. These polymers consist of rather rigid main chains of hexa-2,4-diynylene-1,6-dioxy group connected to benzoate and cinnamate groups, and polar chromophores in the side chains, as shown in Scheme 1 for example [5,6]. The *para*-polymers had 2-NLO coefficients of 250 pm/V while the corresponding *meta*-polymers had those about 50 pm/V and a copolymer showed a value between the two. The importance of these studies is that

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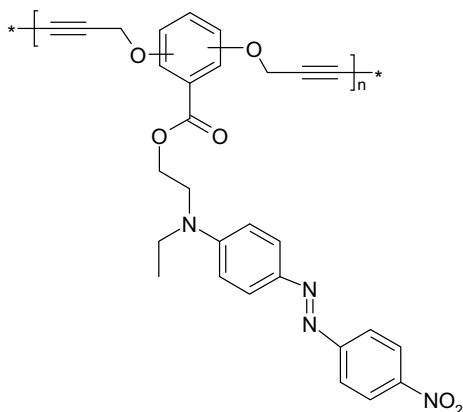
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the second order nonlinear (2-NLO) properties depend most significantly on the main chain conformation, the *para*-polymers showing about five times larger 2-NLO response than the corresponding *meta*-polymers. Emission of green flux was observed with the naked eye during the measurements of the *para*-polymers. They maintain their 2-NLO response even now after a few years since they were poled, although their Tg are only around 100–110 °C. The UV-irradiated cross-linking during poling of these polymers revealed that the *para*-polymers retained the orientation of chromophores than the *meta*-polymers [7]. Thus, it was shown that the polymer main chain conformation is another important factor for 2-NLO susceptibility, in addition to high Tg of polymers and high hyperpolarizability of chromophores. In order to see the effect of main chain conformation on the 2-NLO, the poly(dipropargyloxy)benzoates containing a common azo dye, *Disperse Red 1*, shown in Scheme 2, were previously synthesized [8] and their 2-NLO responses of some of them were briefly studied [9]. These polymers have six geometrical isomers and it was thought interesting to study the effect of polymer main chain conformation on the 2-NLO properties. The results showed that *ortho*- and *para*-polymers were superior in 2-NLO responses to the *meta*-polymers. However, the polymers in Scheme 1 showed much superior 2-NLO



X = none or -CH=CH-

Scheme 1. Poly[di(propargyloxybenzoates)] and Poly[di(propargyloxycinnamates)] containing *Disperse Red 19*.



Scheme 2. Poly(dipropargyloxy)benzoates containing *Disperse Red 1*.

properties than those in Scheme 2. The latter appeared to be less sensitive to poling, although their T_g are not so different from the formers. The formation of insoluble particles in the solutions of these polymers was observed during storage probably due to the agglomeration of chromophores, and such agglomeration could be a cause of poor response to Corona poling. The coagulated particles dissolved again when the solution was heated, indicating that the coagulation was not due to cross-linking by the diacetylene groups. They have high chromophore contents (60%), which should be favorable for 2-NLO materials. Belardini, et al. [10] have reported that the 2-NLO response increase linearly with increase in the chromophore content. Reyes-Esqueda et al. have reported the effect of chromophore concentration on the 2-NLO response in sol-gel systems, and found the response increased with increase in the chromophore concentration, but when the concentration exceeded about 40% the 2-NLO response started to decrease [11]. Harper, et al. [12] also reported the effect of chromophore contents on optical nonlinearity, and found a similar tendency. In this work therefore, as continuation of the previous studies, four new geometrical isomeric polymers containing a chlorine atom (*Disperse Red 13*), were synthesized (see Scheme 3), in order to study the relationships between the 2-NLO response and the polymer main chain conformation. The steric effect of chlorine atom is thought to decrease the dipole-dipole interaction of chromophores thus making poling more effective.

2. Experimental

2.1. Synthesis

The dipropargyloxybenzoic acids were prepared by the method described in a previous report [8]. *Disperse Red 13* was prepared by the azo coupling of diazonium salt of 4-nitro-3-chloroaniline with 2-(*N*-ethylanilino)ethanol. The yields of the reaction of the dye with the corresponding dipropargyloxybenzoyl chlorides were around 85%. The polymerization was carried out in *N*-methylpyrrolidone (NMP) at 60 °C using copper (I) chloride and *N,N,N',N'*-tetramethylethylene diamine as catalysts. When the viscosity of the system increased, the content was poured into HCl-acidified methanol, and the precipitated polymer was filtered, washed with methanol and dried in vacuum. The polymerization yield was quantitative. The polymers were purified by reprecipitation process from NMP/methanol system.

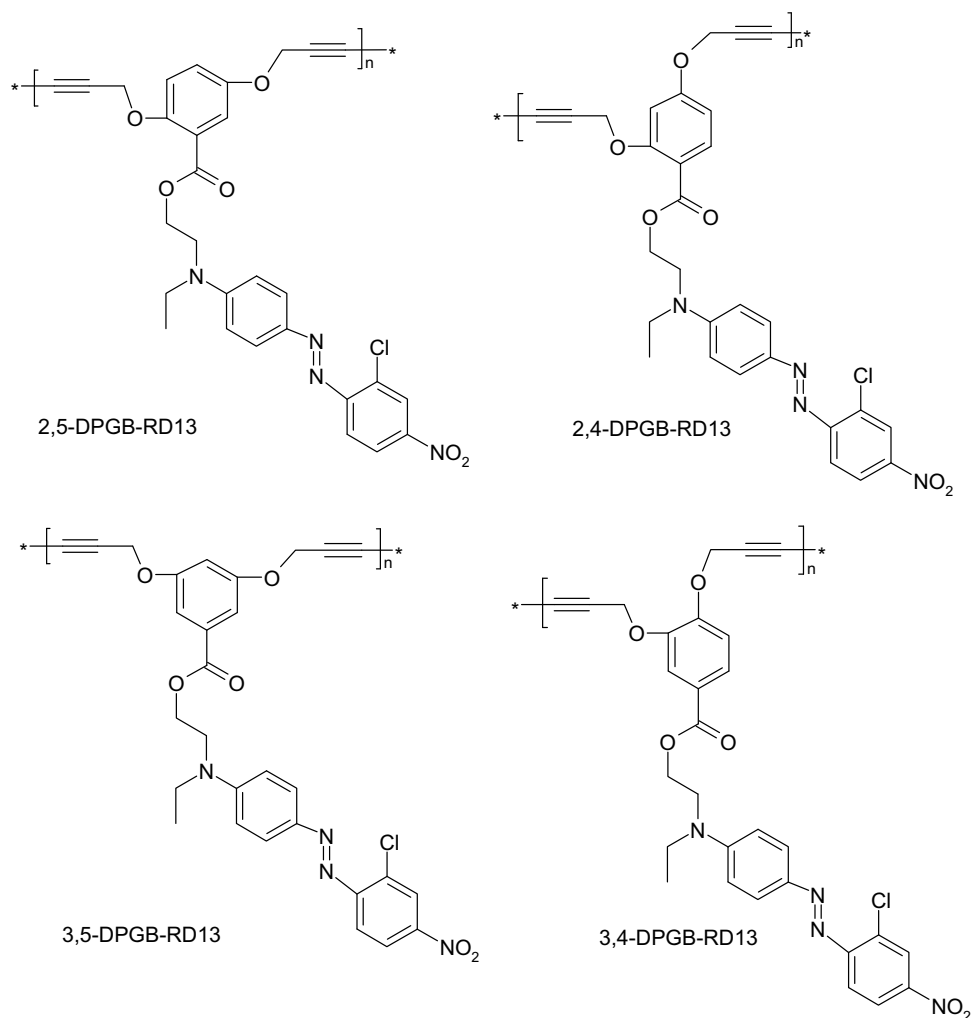
2.2. Characterization

Differential scanning calorimetry (DSC) and thermal mechanical analysis (TMA) were carried out using a DuPont 2100 thermoanalyzer. NMR spectra were taken using a Bruker Avance 400 MHz NMR spectrometer. FT-IR spectra were taken using a Nicolet 510P spectrophotometer. UV/visible spectra were measured for the spin-coated films using a UV-3100PC, UV-VIS-NIR scanning spectrophotometer made by Shimadzu. Molecular weights were determined by light scattering in tetrahydrofuran using a Light Scattering instrument DAWN EOS.

2.3. Film preparation and characterization

Polymer films were prepared by spin-coating with heating at 60 °C and rotation of 3000 rpm for 10 s. One series of films were fabricated for measuring their refractive indices using ellipsometry on fused silica substrates, as well as UV-visible spectra. Additionally, another series of films were prepared on ITO covered glass substrates for in situ SHG measurements. All films were dried in a vacuum oven at 80 °C for 30 min.

Film thickness was measured using a DEKTAK thickness meter. Ellipsometric data were acquired using a spectroscopic ellipsometer (M-150, JASCO), and the refractive indices were obtained by modeling the polymers with two Lorentz oscillators using an analyzing software (MW-305, JASCO).



Scheme 3. The four isomeric poly(hexa-2,4-diynylene-1,6-dioxybenzoates) containing *Disperse Red 13* used for this study.

2.4. Poling in situ SHG measurement

In order to observe electric-field induced alignment, an in situ SHG measurement was performed at a fundamental wavelength of 1064 nm (Q-switched Nd:YAG laser DCR-130, Spectra-Physics). The transmitted second harmonic (SH) beam from the polymer was detected by a photomultiplier and boxcar integrator. AC voltage was applied to ITO-side of substrate to heat the polymer film. The film sample was placed between two tungsten wires in order to perform corona poling, with a distance of 0.5 cm between the

tungsten wire and the film surface, and a discharge of 14 kV was applied, as shown in Fig. 1. A glass substrate with no ITO layer with a window of 0.5×0.5 cm was employed for the laser beam to be transmitted through. Maker Fringe method was also performed to determine SHG coefficients d_{33} and d_{31} , and SH intensity for Y-cut quartz ($d_{11} = 0.3$ pm/V) was measured as reference data. A set-up diagram is shown in Fig. 2. A typical behavior is shown in Fig. 3, showing an example of all other measurements, which behaved similarly.

3. Results and discussion

^1H NMR spectra of 3,4-monomer and its polymer are shown in Figs. 4 and 5, respectively as an example. The terminal acetylenic protons (1 and 8 in Fig. 4) disappeared when polymerized, and the broadening of polymer spectrum indicates that polymerization is taking place. Other isomers showed the similar spectra. As can be seen in the IR spectra of the 3,5-monomers and polymers shown in Fig. 6, the peak due to the terminal acetylenic C–H of the monomer (3279 cm^{-1}) disappeared and a characteristic peak due to $-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-$ appeared at 2054 and 1899 cm^{-1} appeared when polymerized.

All of the polymers were soluble in DMF and NMP, their solutions were stable, and no coagulation was observed after storage. This is an important difference as compared to the polymers containing *Disperse Red 1*, where the solutions were not stable, as they

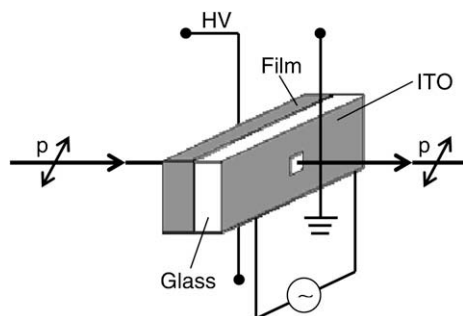


Fig. 1. Schematic representative of in situ SHG measurement and sample preparation.

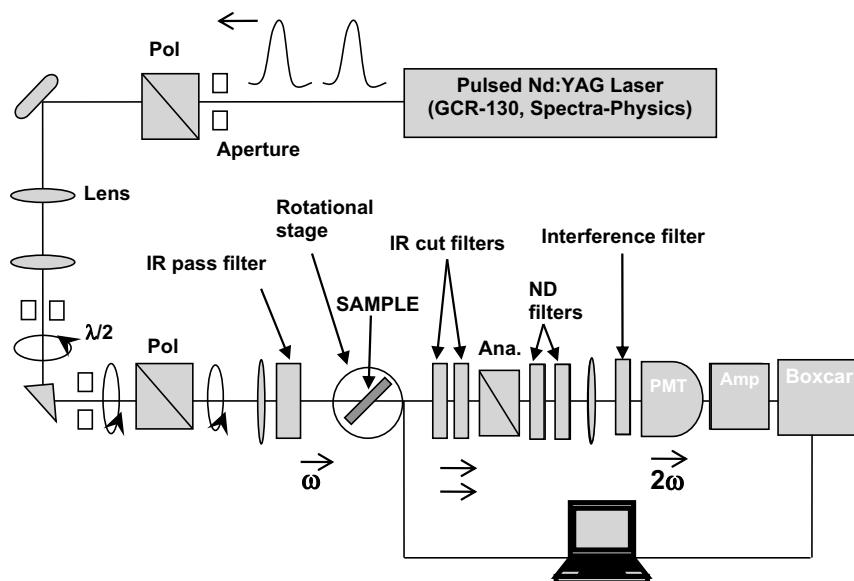


Fig. 2. Experimental set up for SHG measurement.

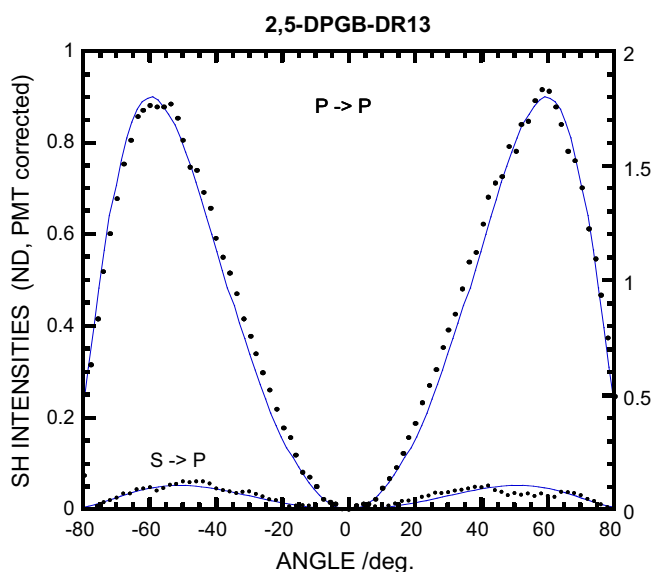


Fig. 3. Typical behavior of Maker Fringe measurement. (Example 2,5-polymer).

precipitated due to the dipole-dipole interaction when left standing for a few days [8]. It appears that the chlorine atom on this dye decreases the dipole-dipole interaction between chromophores. Physical characterization data are shown in Table 1. The T_g was determined by DSC and thermo mechanical analysis (TMA). The higher T_g of 3,5-polymer can be attributed to its symmetric substitution, (1,3,5-) of benzene ring. The others have more irregular substitutions, and this could cause a difference in the T_g . The molecular weights of the polymers obtained differ depending on the monomer structure. The cyclization is inevitable in the oxidative coupling polymerization, and those monomers that have structures favorable to cyclization always give low molecular weight polymers even when polymerized under the same conditions.

The UV/visible spectrum of 2,5-polymer film is shown in Fig. 7. The other three polymers gave similar spectra. The λ_{max} of these polymer films is shown in Table 2 and did not vary appreciably

among the isomers, being in the range of 510–518 nm. Therefore, the effect of main chain conformation on the electronic structure of chromophore is minimum. The films are completely amorphous and have homogeneous chemical structures, and therefore the scattering is considered to be negligible. The absorption spectra of 2,4-polymer are shown as an example in Fig. 8. It can be seen that the absorption decreased after poling due to the orientation of chromophore groups. When the electric charge was removed, the absorption increased due to the disorientation of chromophores. The rest of the polymers also showed the same tendency. However, the absorption did not return to the initial value, suggesting that poling damaged the surface of the films. This seems to be unavoidable during high voltage poling of organic polymer films, and especially in this work, as severe conditions of poling in situ cause the surface damage. It is worth mentioning that when absorption returns to the relaxation stage (C-stage) 2-NLO response could not be observed probably because the chromophores were almost completely disorientated. Similar effects on the fact described above have also been observed for some other dye-containing polymers [13,14].

Table 2 shows the order parameters, which were calculated from the difference in absorption between (B) and (C) shown in Fig. 8, excluding the damage effect caused by poling. The values between (A) and (B) are also shown for comparison. By any means the order parameters are not high (0.10–0.18), suggesting that these polymers with high chromophore contents are difficult to be poled. However, the coefficients d_{33} are higher than those of polymers of the same series with *Disperse Red 1* [9], where the highest d_{33} value was 54 pm/V with order parameter of 0.13. This indicates that the chlorine atom on the dye decreases the dipole-dipole interaction so that the polymer chain can move more freely during the poling process. However, they were much lower compared with those of poly(dibenzoates) containing *Disperse Red 19* ($d_{33} = 224$ pm/V, order parameter of 0.3) [5,6]. This difference may arise from the chemical structure of the polymers, although further studies are required to understand the relationships between poling ease and chemical structure.

The difference in the 2-NLO coefficients (d_{33}) among these four isomers is appreciable. The order was found to be 3,5-(*meta*) > 3,4-(*ortho*) > 2,5-(*para*) > 2,4-(*meta*), but for the ratio d_{33}/d_{31} the order was: 3,5-(*meta*) > 2,4-(*meta*) > 2,5-(*para*) > 3,4(*ortho*). The orienta-

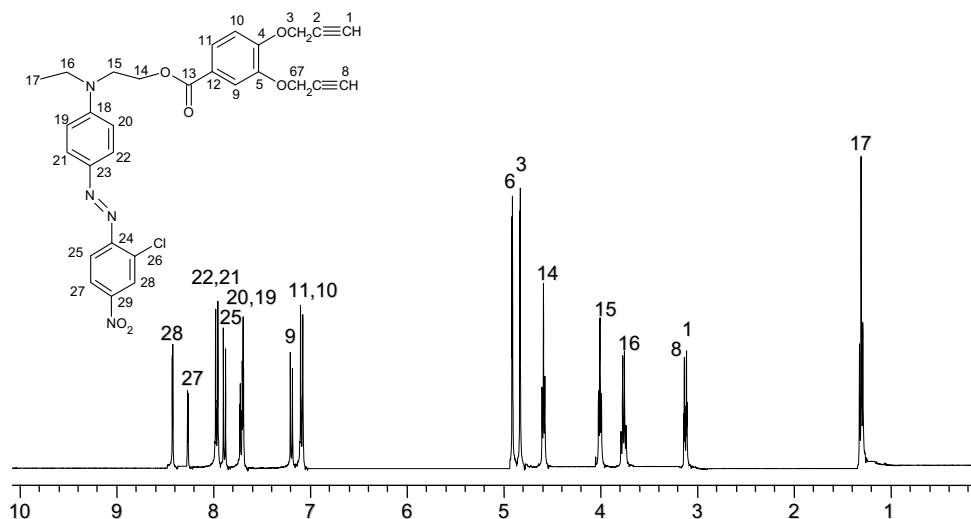


Fig. 4. NMR (^1H) spectra of 3,4-DPGB-DR13 monomer.

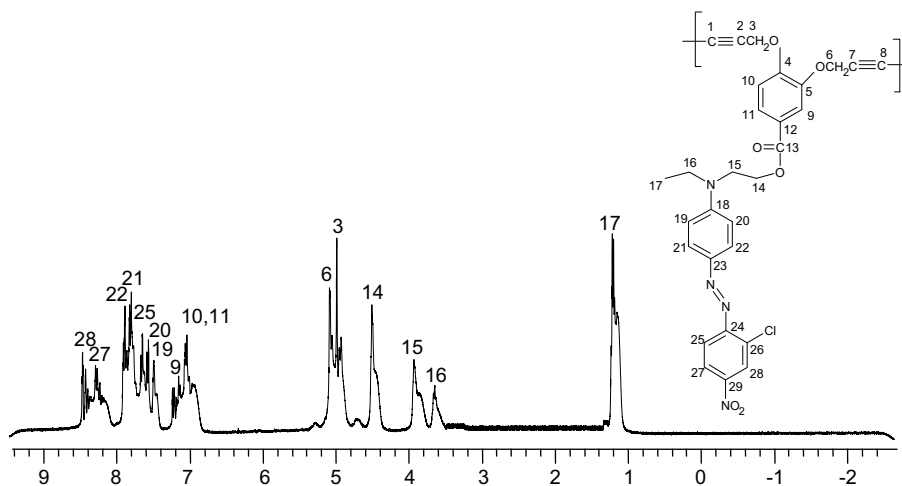


Fig. 5. NMR (^1H) spectra of 3,4-DPGB-DR13 polymer.

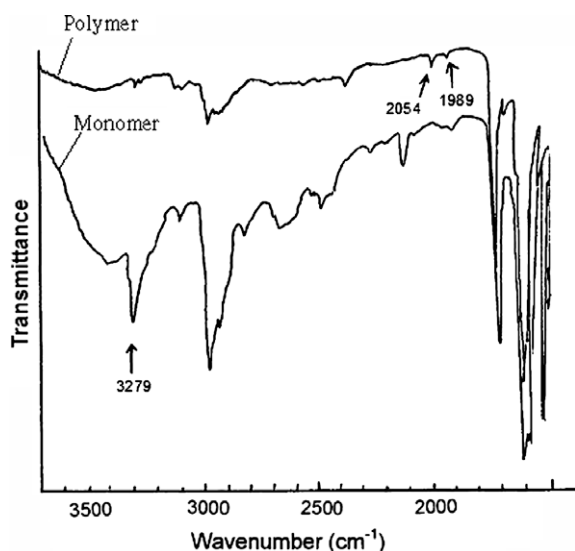


Fig. 6. FT-IR spectra of 3,4-DPGB-DR13.

Table 1
Polymers properties (thin films on fused silica).

Polymer	T _g (°C)		Mw	Mw/Mn
	DSC	TMA		
2,4-DPGB-RD13	88	87	8261	1.15
2,5-DPGB-RD13	87	94	13,970	1.27
3,4-DPGB-RD13	94	82	12,360	1.32
3,5-DPGB-RD13	123	124	19,430	1.23

tion dynamics of the four polymers is shown in Fig. 9. It can be observed that 2,4- and 3,5- isomers tend to orientate slowly and the intensity of second harmonic generation (SHG) increased also slowly. When heating was stopped, a partial relaxation occurred, and the SHG signals decreased gradually until reaching constant values. On the other hand, for the 2,5- and 3,4-polymers the SHG intensity increased rapidly and reached a greater value than that of 2,4- and 3,5-polymers. In contrast, when heating was stopped, the SH signals also decreased rapidly to constant values which were lower than the former isomers. Although differences are not very noticeable, these observations suggest that the later two

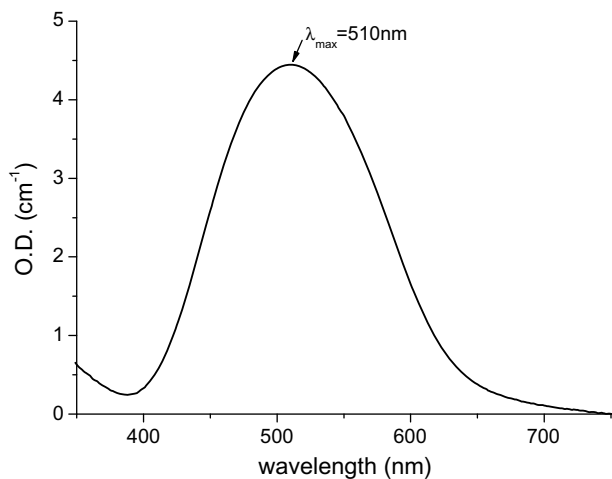


Fig. 7. UV-vis spectra of 2,5-DPGB-RD13 polymer film on fused silica.

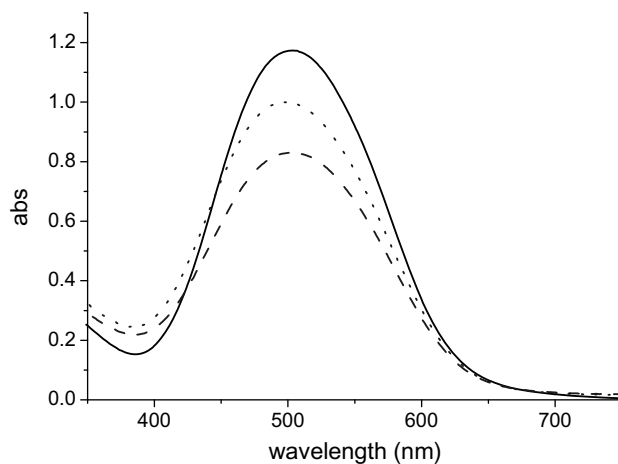


Fig. 8. UV-vis spectra of 2,4-DPGB-RD13 polymer film on ITO substrate. Before poling (A), — orientation stage (B) and relaxation at 108 °C (C).

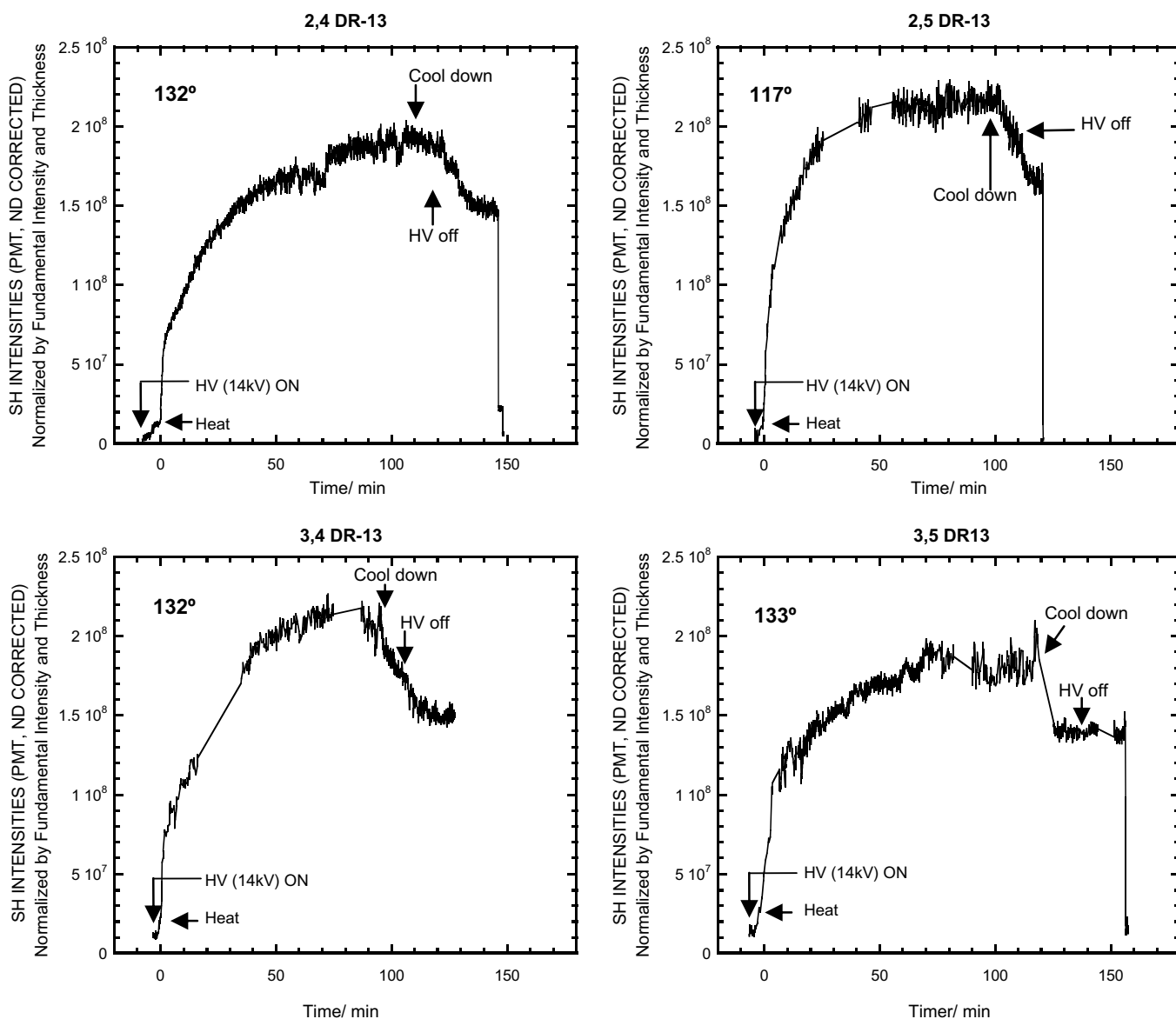


Fig. 9. Poling dynamics measured by in situ SHG measurement. High voltage (HV) of 14 kV was applied to tungsten wires before time zero, the sample was heated to a temperature close to T_g for each polymer at $t = 0$, and cooled around 100 min, The HV was turned off around 20 min after cool down.

Table 2
Poling in situ condition and 2-NLO responds of polymer thin films on ITO-glass substrate.

Polymer	Poling temperature (°C)	n		λ_{\max} (nm)	Abs 532 nm	Thickness (Å)	Order parameter		d_{33} (pm/V)	d_{31} (pm/V)	d_{33}/d_{31}
		532 nm	1064 nm				(A)–(B)	(C)–(B)			
2,4-DPGB-RD13	132	1.709	1.723	518	0.7663	2423	0.292	0.169	54.10	18.82	2.87
2,5-DPGB-RD13	117	1.776	1.809	510	0.9052	2737	0.276	0.142	62.29	25.62	2.43
3,4-DPGB-RD13	132	1.884	1.847	513	0.5532	1600	0.405	0.180	74.50	31.59	2.36
3,5-DPGB-RD13	133	1.826	1.821	513	0.4900	1472	0.295	0.104	87.18	27.29	3.16

have more flexible main chains, and the former are more rigid. The T_g of the 3,5-polymer was found to be higher than the others, and this could be a reason of its higher susceptibility.

4. Conclusion

It was shown that the polymer main chain conformation significantly influenced the 2-NLO response. The 2-NLO coefficients d_{33} of a series of four isomeric polymers containing *Disperse Red 13* were found to be in the range of 50–90 pm/V, which are higher than those of the same main chains with *Disperse Red 1* (11–54 pm/V) [9], the both being determined under the same conditions. These values are considerably lower than those of the *para*-dibenzoates [5] and *para*-dicinnamate [6] series, where 2-NLO coefficients were found to be over 150 pm/V. The order parameters were found to be less than 2, and this can be a cause of low 2-NLO responses. The 3,5-(*meta*) polymer showed the highest response, probably because of the stable main chain conformation, with symmetrical substitution on the benzene ring. The 3,5-polymer exhibiting the highest 2-NLO response, had the lowest order parameter. This suggests that the 3,5-polymer has a structure with some degree of orientation before the poling process. The orientation parameters determined from visible absorption spectra cannot always be considered to be a reliable information, because there is possibility that some polymers originally have a certain degree of orientation depending their polymer main chain conformation. The 2-NLO coefficients depend most significantly on how efficiently the chromophores are orientated and how stable is the orientation. Although there exists sufficient physical information on the orientation of chromophores by poling, there are still questions to be answered on the relationships between poling efficiency, orientation stability, chemical structures and main chain conformation of polymers. Further studies are needed to clarify these relationships, especially the effects of physical and chemical polymer structures in order to obtain materials which satisfy the requirements to be used for practical devices.

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