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The second-order nonlinear optical properties of a series of polyesters containing push-pull azobenzene chromophore in their side chain

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The second harmonic coefficient d_{33} values of a series of polyester nonlinear optical (NLO) polymers, differing in their electron withdrawing substituent, were experimentally measured. The observed order of contribution of the substituents towards d_{33} value was rationalized by a frequency factor dependence. Excellent photostability and the highest d_{33} value among the series have been found for the polyester with 2,4-dinitro substituents in the side chain. A possible influence of intermolecular interaction is also indicated.

1. Introduction

Chromophore attached along the side-chain of a polymer and chromophore (guest)/polymer (host) blend are the two of main and commonly used organic NLO material systems [1]. For photonic applications, side-chain polymers have several advantages over guest/host systems: a much higher chromophore concentration can be incorporated into the polymer system without crystallization and phase separation; the glass transition temperature (T_g) of such system is substantially higher than that of a guest-host system with same concentration of chromophore. For the sake of experimental simplicity examing structure-property relationships, NLO chromophores are usually studied in the guest/host manner. However, for the above mentioned reason, the attached form is more important for practical applications. Since loading density, free volume, state of aggregation and, therefore, the behavior of a chromophore are very different, it is imaginable that conclusions made based upon a guest/host system will not always be applicable to a side-chain attached structure.

On the other hand, one of the advantages of organic materials is that their performance may be optimized by molecular tailoring or molecular designing. Molecular design and, therefore, the research on property-chemical structure relationships are especially important for organic NLO material research. Unfortunately, for macroscopic nonlinearities, as second harmonic coefficient, a structure element, that is a chemical or physical quantity which can be simply related to the observed property, is not available [2]. This is understandable because nonlinearity is a property belonging not only to ground state but also to an excited state; they are related by not only material's intrinsic character, but also by the external probe beam.

In this paper, d_{33} values of a series of polyester polymers with push-pull azobenzene side chains attached were measured, and the relative influence of a series of electron withdrawing groups was obtained. Additionally, a newly derived frequency dependence expression, has been used to obtain theoretical estimates of d_{33} for the materials. They are compared with the experimental values.

2. Experimental

The details of the syntheses has been published elsewhere [3].

2.1. Synthesis of the aniline-containing polyester

2.13 g (8.36 mmol) of *p*-phenylenediacryloyl chloride and 1.54 g (8.44 mmol) of *N*-phenyldiethanolamine were dissolved in 20 ml of dry 1,2-dichloroethane under a nitrogen atmosphere, and stirred at reflux temperature for 4 h. Then, the mixture was poured into ethanol to precipitate the polymer. The product was redissolved and reprecipitated, and dried at 40–50 °C under vacuum for 24 h. 3.02 g (98.1%) of aniline containing polyester was obtained. Softening point: 80 °C.

2.2. Syntheses of PEA1DN

0.2 g (2.90×10^{-3} mol) of sodium nitrite was added in portions into 7 ml of concentrated sulfuric acid

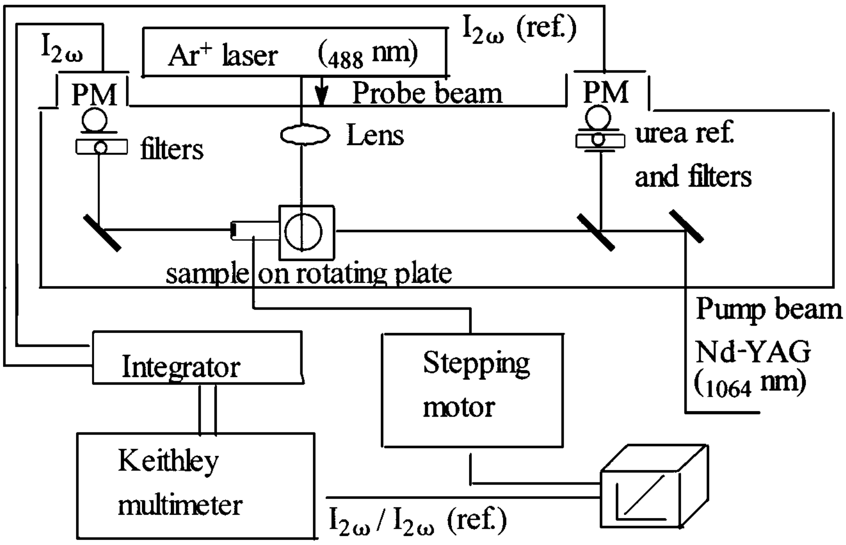

Figure 1 Experimental setup for second harmonic coefficient measurements.

below 10 °C. The system was stirred and heated to 70 °C and then cooled to room temperature. 0.53 g (2.89×10^{-3} mol) of 2,4-dinitroaniline was added with stirring to the reaction mixture and reaction was continued for 40 min. The reaction mixture was then poured with stirring onto 6 g of ice. After filtration, 0.4 g of sodium fluoroborate was added to the filtrate. The precipitate was collected and dried. To an acetone solution of 0.201 g of the above obtained aniline-containing polyester, was added 0.2 g of diazonium salt precipitate. After dissolution, 1 g of anhydrous sodium acetate was added. The mixture was stirring for 10 h at room temperature then poured into water to precipitate the dark red solid, which was washed with water and dried at 40–50 °C under vacuum for 24 h. 0.308 g (100%) of PEA1DC was obtained. IR: 1336, 1707 cm^{-1}; $\lambda_{\max}$ (cyclohexenone): 509 nm; T_g: 153 °C; molecular weight (weight averaged): 15000.

2.3. Syntheses of PEA1N, PEA1DC, PEA1S

The same procedure as for PEA1DN was employed in each case. IR (cm^{-1}): 1336, 1511, 1707 for PEA1N; 2226, 1706 for PEA1DC; 1319, 1705 for PEA1S.

2.4. Preparation of poled polymer films

Films were prepared on glass substrate from cyclohexanone solution. The solutions were first filtered to remove particle impurities, spun at 2000 rpm and finally baked at 100 °C under vacuum to remove solvent. The thin films were heated to 130 °C under an electric field applied by corona discharge method. After 15 min at 130 °C, the films were cooled to room temperature during 1.5 h, and then the electric field removed.

The thickness of the polymer films were measured by a Surface Profilometer (Tencor Alpha Step) at the Department of Physics, Royal Military College of Canada. Molecular weights were obtained on a Waters gel-permeation chromatograph. Thermal analysis were performed using Perkin-Elmer TGA-7 system with a heating rate of 20 °C/min and BJOSW Model 4-1 thermal analyzer with a heating rate of 10 °C/min under a nitrogen atmosphere.

2.5. Second harmonic coefficient (d_{33}) measurements

The fundamental (1.064 μm) of a Q-switched mode-locked picosecond Nd:YAG laser (10 Hz) was used as the probe (or analysis) beam. The experimental setup is shown in Fig. 1.

The poled film was mounted on a rotating plate moved by a stepping motor. After integration, the second harmonic signal ($I_{2\omega}$) was compared with the integrated second harmonic signal generated by a sample of urea power ($I_{2\omega}^{\text{ref}}$). The ratio $\mathrm{I}_{2\omega}/I_{2\omega}^{\text{ref}}$ was calculated by a Keithley multimeter connected to a computer. This ratio measured at 532 nm for p-polarized and s-polarized fundamental was recorded as a function of incidence angle. Absolute values of the second harmonic coefficients were determined by comparison with a x-cut quartz crystal ($d_{11} = 0.5$ pm/V). For both polymer film and quartz crystal, the angular dependence of the second harmonic intensity 12 W was fitted by a theoretical curve according to the classical Maker fringe formula [4, 5].

3. Results and discussion

The chemical structure of the material series is shown in Fig. 2.

The second harmonic (SH) coefficient $(d_{33})_{\text{obs}}$ of the four poled polymer films has been determined experimentally. Correction due to absorption by the chromophore at SH wavelength was considered as follows [6]:

$$d_{33} = (d_{33})_{\text{expt.}} \exp(\alpha L/4)(\alpha L/4)/\sinh(\alpha L/4) \quad (1)$$

The result is shown in Table I.

It is also possible to estimate theoretically the relative magnitude of d_{33} for the material series. Generally,

TABLE I Absorption correction of the second-harmonic coefficients

Sample	$(d_{33})_{\text{obs}}$ (pm/V)	Film thickness (cm × 10^5)	Absorption coefficient α ($\times 10^{-5}$ cm^{-1})	d_{33} (pm/V)	$(d_{33})_{\text{rel.}}$
PEA1N	162	4.53	1.32	510	1.7
PEA1DN	488	0.50	2.63	663	2.2
PEA1DC	126	3.25	1.53	349	1.2
PEA1S	274	3.51	8.75	296	1

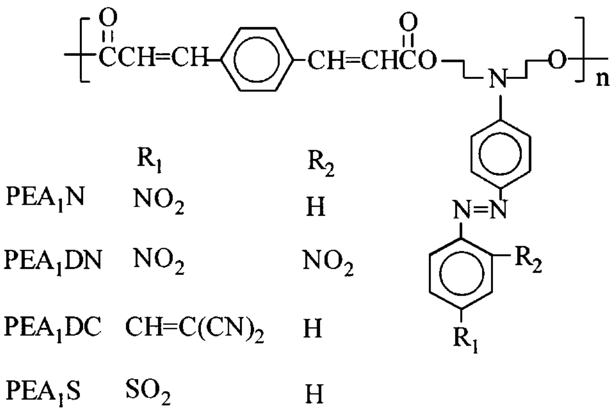

Figure 2 Chemical structures of the polyester polymers.

Expression 2 is used to evaluation of d_{33} [7]:

$$d_{33}(-2\omega;\omega,\omega) = 1/2 N f^{2\omega} f^{\omega} f^{\omega} \beta_{zzz}(-2\omega;\omega,\omega) L_3(p) \quad (2)$$

where the total local field factor, $F_\omega = f^{2\omega} f^{\omega} f^{\omega}$ can be approximated by Onsager's equation, for frequency doubling, typical value are $f^{\omega} \approx f^{2\omega} = 2$, $F_\omega = 8$; $L_3(p)$ is the third order Langevin function which describes the amount the susceptibility is reduced from that of parallel molecular dipoles. $L_3(p)$ is approximately equals to $F_0 \mu E_p / 5kT$. F_0 is the local field factor at zero frequency, μ is molecular dipole moment and E_p is the poling electric field. Meanwhile, starting from two level system model, we have shown that the product of molecular susceptibility and molecular dipole moment $\beta_{zzz}\,\mu$ is linearly proportional to a frequency factor $F(\omega)$, as shown below [7]:

$$\beta_{zzz}\mu = k' F(\omega) \quad (3)$$

$$F(\omega) = \frac{W}{[W^2 - (\hbar\omega)^2][W^2 - (2\hbar\omega)^2]} \quad (4)$$

where W is the energy of the first excited state and $\hbar\omega$, the energy of the photon of the probe beam. At the present experimental condition, temperature T and the poling electric field E_p were fixed, by combining Expressions (4), (3) and (2), Expression (5) could be obtained:

$$d_{33} = k\,NF(\omega) \quad (5)$$

The number density N of nonlinear optical molecules in the poled polymer film can be estimated according to the measured chromophore content n values as shown in Fig. 3.

If the segment weight of the aniline containing part is denoted as M_1 and that of the azobenzene containing part as M_2, then the average segment weight containing one azobenzene chromophore in the polymer chain can be obtained from Equation 6:

$$M = nM_1 + mM_2 \quad (6)$$

Assuming the mass per unit of polymer is equal to one, then the N value for each polymer could be obtained simply from the reciprocal of the M value.

As seen in Table I, there is a dramatic increase in the calculated d_{33} values in the sequence of substituents: sulfone → nitro → dicyanovinyl → 2,4-dinitro. Katz and coworkers have correlated very nicely the molecular second order susceptibility β_0 with Hammitt constant σ_R^- for nitro- and dicyanovinyl substituted aniline compounds. However, Hammett constant frequently do not provide acceptable relationships between chemical structure and NLO properties due to the fact that excited states are also involved [8]. The frequency factor, $F(\omega)$, as shown in Expression (4), depends on a combination of material's excited state and ground state, and

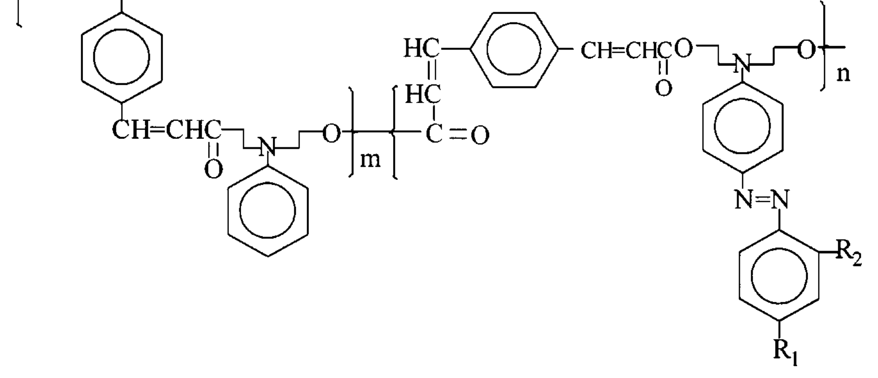

Figure 3 Calculation of the number density of the segment which contains one chromophore.

TABLE II Theoretical estimates of relative d_{33} values and related data

Sample	chromo. cont. %[a]	λ_{max} (nm)	F(ω) ($\times10^{-34}$ esu)	N ($\times10^{-3}$ M/ml)	d_{33} (Rel.)
PEA1N	84	472	7.50	2.05	1.7
PEA1DN	100	506	21.80	1.80	4.4
PEA1DC	98	504	20.30	1.86	4.3
PEA1S	43	440	4.01	2.20	1

[a] Chromophore content (%), see [3].

the external acting laser beam. The result, computed by Equation 5, is listed in Table II. The increase in d_{33} on moving from PEA1S → PEA1N → PEA1DC → PEA1DN is rationalized by the frequency dependence relationship.

It is also worthwhile to mention that the experimental observed d_{33} values of PEA1DN and PEA1DC are not as high as were predicted by the frequency dependence expression. The depression may be due to intermolecular interactions. Actually, the chromophore content, as shown in Table II for these materials, is quite high. Dalton indicated recently [9] that such intermolecular interactions reduce acentric order parameter and, therefore, second harmonic properties significantly with increasing of chromophore concentration. Moreover, such effect will also become pronounced if the molecular volume or dipole moment is large, just as in the cases of PEA1DN and PEA1DC.

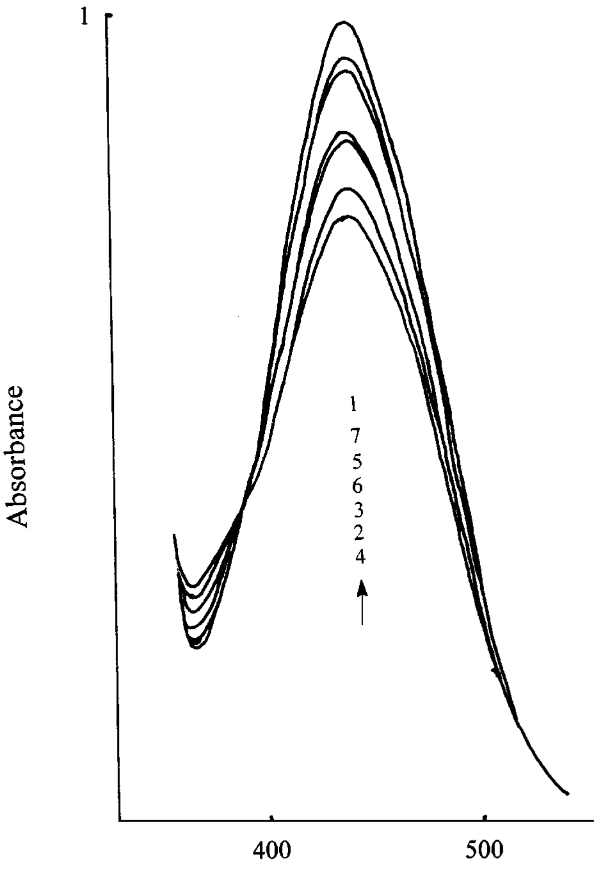

Figure 4 UV/vis spectra of PEA1S in THF after different irradiation periods. Spectra 1–6 were obtained after 0, 4, 8, 18, 54, and 114 min of irradiation, respectively. Spectrum 7 was recorded after 114 min irradiation and 2 days in the dark.

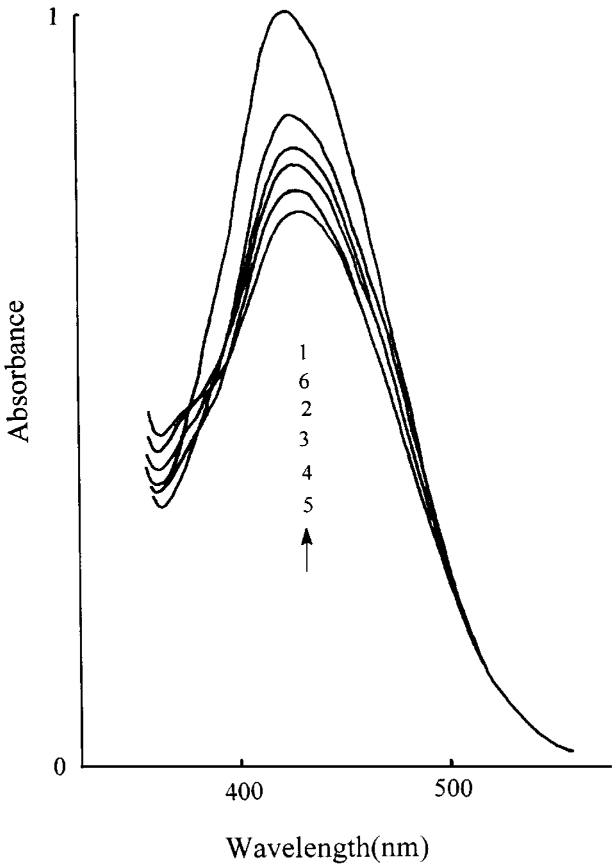

Figure 5 UV/vis spectra of PEA1DC in THF after different irradiation periods. Spectra 1–5 were obtained after 0, 4, 8, 18, 54 min of irradiation, respectively. Spectrum 6 was recorded after 114 min irradiation and 2 days in the dark.

The photostability of the polymers was also examined in THF solution under irradiation by the output of a 500 W high pressure mercury lamp, filtered by an aqueous solution of $CuSO_4$. Figs 4 and 5 are two typical sets of UV/vis spectra recorded during the process.

PEA1N and PEA1DN behave similarly to PEA1S, but PEA1DC behaved quite different.

There are clear differences between the spectra of PEA1S and PEA1DC. An isosbestic point and thermal reversibility were found on the spectra of PEA1S (Fig. 4) while the reversion of the photoproducts were less for PEA1DC (Fig. 5).

Similar experiments to test photostability were also conducted on films of the polymers. Basically, the same tends as in the solution were also observed.

Usually the absorption bands of trans- and cis-push-pull azobenzenes overlap but with much smaller extinction coefficient for the cis- form. The rate of isomerization from cis to trans is much faster in substituted push-pull azobenzenes than unsubstituted symmetrical homologue [10]. The mechanism responsible for the curves recorded in Fig. 4 can be ascribed to cis-trans isomerizations, and the rather slow thermal reversal process can be understood as the result of the influence of the polymer environment. The photoreaction of dicyanovinyl substituted PEA1DC is not only cis-trans photoisomerization, but some non-reversible reaction, also. The mechanism of this photoreaction will be investigated in future work.

In summary, the d_{33} values of the four polymers have been measured. The frequency factor dependence of d_{33} values has been deviated and a good correlation with experimental data has been demonstrated. Analyses indicate that the measured d_{33} values of PEA1DN and PEA1DC might be doubled if there were no intermolecular interaction involved. From the point of view of molecular design, the NLO chromophore in PEA1DN, that is the 2,4-dinitro substituted pattern is rather promising for providing much higher d_{33} values than those of mono nitro substituents, as well as much better photostability than the dicyanovinyl group.

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