# THIRD-ORDER NONLINEAR OPTICAL PROPERTY AND EXCITED-STATE ENHANCEMENT OF POLY(2,5-DIALKOXYPHENYLENE)

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## ABSTRACT

The third-order nonlinear optical(NLO) property of a soluble, π–backbone conjugated polymer: poly(2,5-dialkozyphenylene) ( abbreviation called PPP) is studied. The near resonance third-order hyperpolarizability $\gamma_{xxxx}$ is $8.2\times10^{-30}$esu, and the corresponding macroscopic third-order susceptibility $\chi^{(3)}(-\omega;\omega,\omega,-\omega)$ and nonlinear refractive index $n_2$ are estimated to be $6.3\times10^{-10}$esu and $1.4\times10^{-8}$ esu, respectively. Furthermore, the nonlinear optical excited-state enhancement has been observed in PPP by two-wave coupling method. The enhancement is more than one order in our experiments. The time response of the enhancement has been studied and a three-level model was used to explain time phenomena.

## INTRODUCTION

Organic polymers with π-electron delocalization are currently of wide interest as nonlinear optical materials with potential applications as optical switches, modulators and other nonlinear optical devices[1]. Recently, the study is focused on finding conjugated polymers with large nonlinear optical effects, fast responses and also good solubility, processibility and high durability[2]. Polydiacetylenes, polyacetylene and polythiophene have been reported to have large third-order electric susceptibilities $\chi^{(3)}$ ranging from $10^{-12}$ to $10^{-9}$esu, and the response time has been found to be order of several picoseconds or faster. In addition, it has been observed from theories and experiments that the hyperpolarizability γ and third-order nonlinear optical coefficients $\chi^{(3)}$ increase with the extent of π-electron delocalization of the molecule[3][4]. This fact has guided the current approaches to the molecular design and optimization of polymers with large $\chi^{(3)}$ values.

In recent, the enhancement of nonlinear optical susceptibilities from optically pumped electronic excited states of conjugated linear chains has been studied both theoretically[3] and experimentally[4]. The enhancement is valuable to approach the practical application of polymeric nonlinear optical materials.

The polyphenylene oligomer family is a new class of promising nonlinear optical materials[5]. Molecular orbital calculations suggest that polyphenylenes should have higher $\chi^{(3)}$ responses than do the polythiophenes, possibly because of the relative ease with which charge can slosh along the symmetric polyphenyl structure. Furthermore, the polyphenylenes have low linear absorption in the visible and infrared region, which can improve figure of merit at the region.

In this letter, the third-order NLO property and its large excited-state enhancement of a polyphenylene oligomer, poly(2,5-dialkozyphenylene) referred to as PPP has been reported. PPP, which molecular structure shown in Fig.1, remains the large $\pi$ backbone and shows easier to polymerized because of two butoxy have been added to benzene. Moreover, it improves charge transport extent and processibility, also solubility and durability of materiel.

## EXPERIMENTS

The absorption spectrum of PPP/dioxane solution is shown in Fig.2, $\lambda_{max}$=380nm, and 532nm is just out of absorption region. The molecular weight $M_n$=60,000 and $M_w$=300,000 are calculated from data of viscosity measurements.

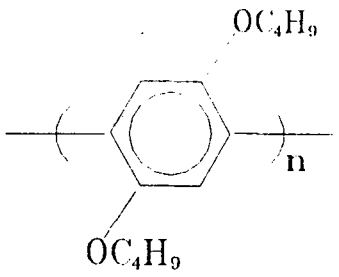


**Fig.1** structure of PPP

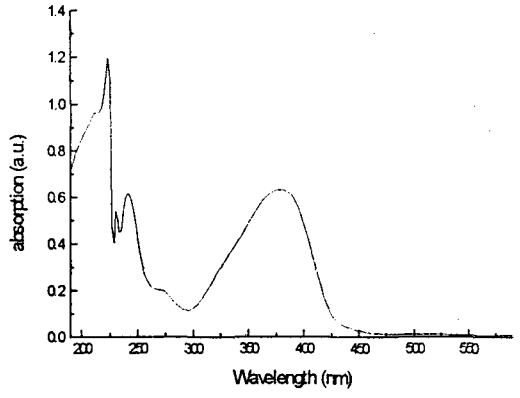


**Fig.2** absorption spectrum of PPP

The third-order nonlinear optical coefficient of PPP is measured by phase conjugate retroreflection degenerate four beams mixing(DFWM) method in dioxane solutions. The laser is a mode-locked $Nd^{3+}$YAG system, the 1064nm output is doubled frequency by a KD*P crystal. The 532nm output (pulse repetition rate is 10Hz, with 35ps FWHM and 0.5mJ average energy) is split into three beams with same energy which are temporally and spatially overlapped in the sample. The angle between pump and probe beam is 3° degree. In the experiment, the measured quantity is the phase conjugate reflectance.

Assuming the small reflectivity, low linear & non-saturate absorption and quasi-static approximation, and with $CS_2$ as the reference, we calculated the third-order nonlinear optical coefficient.

The excited-state enhancement of nonlinear optical effect is studied by two-wave coupling(TWC), which is a kind of phase mismatch degenerate four-wave mixing method. The wavelength of exciting optical pulses is 355nm, within the strong absorption region of PPP. The wavelength of coupling wave is 532nm.

## RESULTS AND DISCUSSION .

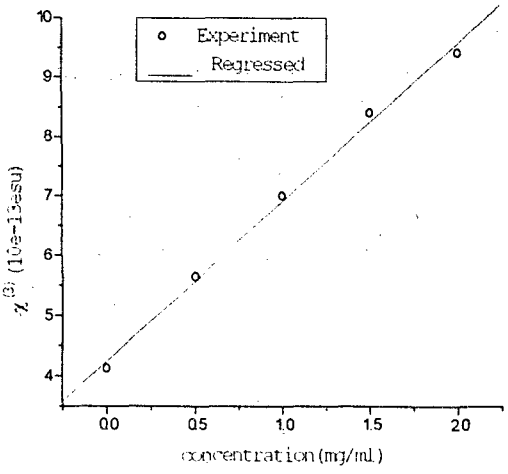


**Fig.3** dependence of $\chi^{(3)}$ coefficient and concentration of PPP solution

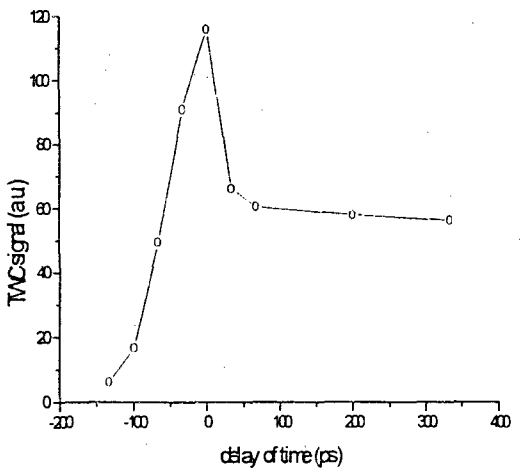


**Fig.4** time responses of NLO excited-state enhancement

Fig.3 shows the dependence of $\chi^{(3)}$ on the concentration of the polymer. From parameters of the regression, the $\gamma_{xxxx}$ of PPP is $8.2\times10^{-30}$ esu. The estimated corresponding value of $\chi^{(3)}$ $(-\omega;\omega,\omega,-\omega)$ is $6.3\times10^{-10}$esu, by using an estimated density of PPP, 1.2g/cm$^3$ and an index of refractive of 1.66 from Lorentz & Lorenz Equation. We have also measured the phase conjugate signals that result from $\gamma_{xyyx}$, the measured value is $3.0\times10^{-30}$esu. The corresponding value of $\chi^{(3)}_{xyyx}$ is $2.3\times10^{-10}$esu. The ratio of $\gamma_{xyyx}$ /$\gamma_{xxxx}$ is 2.7 indicates a nonabsorptive origin for our observed $\chi^{(3)}$ and the Kerr effect is the main reason of DFWM. The time-resolved measurements show that the phase conjugate signal is much faster than 35ps, the pulse limit.

From calculation, the nonlinear refractive index of PPP, $n_2=1.4\times10^{-8}$esu, which is larger than most of the organic and inorganic materials. The absorption $\alpha$ of neat PPP at 532nm is estimated experimentally less than 60cm$^{-1}$, so the figure of merit $\chi^{(3)}/\alpha$ is about $10^{-11}$esu, accords with the demands of optical signal processing application.

The dynamic responses of TWC excited-state optical enhancement show two time constant processes, see Fig.4. When probe pulse prior to exciting pulse, no exciting and no TWC enhancement observed. With exciting pulse delay becomes small and overlaps probe pulse, the TWC signal enhances gradually. When time delay is about zero, the enhancement is the biggest. Then TWC enhancement weakens sharply, the time of process can not be measured because it is short than our experimental laser pulse width, 50ps. When exciting pulse preceding further, an order of nanosecond process of TWC enhancement presents. From picture, we can find the TWC signal enhance near 20 times.

The time responses of TWC enhancement in PPP will be understood with the three-level model which has one ground state $S_0$ and two excited states $S_1$, $S_2$. The position of $S_2$ is higher than that of $S_1$. When PPP is excited from $S_0$ to $S_2$, which is very fast, the TWC enhancement begins to show. The fast process of enhancement decreasement is contributed to the fast nonradiative decay from $S_2$ to $S_1$. Here we suppose the TWC excited-state enhancement is larger on $S_2$ state than on $S_1$ state. This nonradiative transition is a phonon process and usually very fast. The transition from $S_1$ to $S_0$ is a radiative, nanosecond, process, which is the reason of slow process in PPP excited-state dynamic enhancement.

In conclusion, we studied the near resonance third-order optical nonlinearity of a soluble, $\pi$ backbone conjugate polymer, PPP with picosecond response. We have shown that PPP as we expected have good nonlinear optical property. At near resonance region of 532nm, the third-order hyperpolarizability $\gamma_{xxxx}$ is measured $8.2\times10^{-30}$esu, and the $\chi^{(3)}(-\omega,\omega,\omega,-\omega)$ and nonlinear refractive index $n_2$ are estimated to be $6.3\times10^{-10}$esu and $1.4\times10^{-8}$ esu. As low absorption, the figure of merit reaches about $10^{-11}$esu at 532nm and should be larger at the off-resonance region. A large excited-state enhancement of nonlinear optical effect is observed and its dynamic responses are studied and explained by three-level model.

**Reference**


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