THIRD ORDER NONLINEAR OPTICAL EFFECTS IN CONJUGATED POLYMERS

F. KAJZAR and J. MESSIER
CEA-DTA, DEIN/LPEM, CEN Saclay
91191 Gif-sur-Yvette - Cedex, France
1. INTRODUCTION

The conjugated quasi-one dimensional polymers are characterized by a strong delocalization of π electrons. This highly polarizable electronic cloud responds nonlinearly to the exiting external field. The resultant bulk polarization can be developed into the external field power series and its component along x is given by

\[ P_x(t) = \sum_{y,z,u,...} \left( \chi^{(1)}_{xy} E_y(t) + \chi^{(2)}_{xyz} E_z(t) + \chi^{(3)}_{xyzu} E_u(t) + ... \right) \]  

where \( \chi^{(1)}, \chi^{(2)} \ldots \chi^{(4)} \) are (n+1) rank tensors describing nonlinear optical response of the medium and \( E_y(t), E_z(t) \ldots E_u(t) \) are electric field components in y, z, ... u direction.

Conjugated polymers are principally centrosymmetric and \( \chi^{(2)} = 0 \); thus the first nonlinear term is described by \( \chi^{(3)} \) susceptibility. They are characterized by very large linear (\( \varepsilon > 30 \) at 0.625 μm and at 9K in polydiacetylene, Batchelder (1985)) and nonlinear polarizability (Sauteret et al. (1976)). The principal cubic nonlinear optical phenomena discussed here are listed in Table 1 together with corresponding nonlinear polarizations and susceptibility tensors. The relations given on RHS of Table 1 are true for every non static component of \( \chi^{(3)} \) tensor.

The bulk nonlinear susceptibility \( \chi^{(3)} \) is related to the corresponding microscopic molecular hyperpolarizability \( \gamma_{\alpha\beta\gamma\delta} \) where \( \alpha, \beta, \gamma, \delta \) are molecular directions. The relations between \( \chi^{(3)}_{xyzu} \) and \( \gamma_{\alpha\beta\gamma\delta} \) depends upon the symmetry of the molecular orientation distribution (cf. Flytzanis (1975)). In the particular case when the \( \gamma_{xxxx} \) component is enhanced along the polymer chain direction we have

\[ \chi^{(3)}_{xxxx} = \frac{\nu \cdot N}{\varepsilon_0} \gamma_{xxxx} F \]  

where \( \nu = \frac{1}{5} \) for an isotropic distribution of molecules in three dimensions (three-dimensional disorder)

\[ \nu = \frac{3}{8} \]  

for an isotropic distribution of molecules in a plane (two-dimensional disorder).

\( F \) is the local field factor which for cylindrical molecules is close to unity (cf. Cojan et al. (1977)).

\( N \) is the number of molecules per unit volume and \( \gamma_{xxxx} \) is the second order molecular hyperpolarizability.