ABSTRACT. We introduce a novel class of second order non linear optical (NLO) polymer. Each monomer contains a NLO unit covalently incorporated into the main chain with its dipole moment perpendicular to the main chain. With the aid of a Perot Fabry interferometric technique we measure the two independent components of the second order electro-optical (E/O) susceptibility as well as the two order parameters of the chromophores $<P_1>$ and $<P_3>$. ($P_l$ : Legendre polynomia). The very good stability of the chromophore orientation and the high value of the second order susceptibility show that these polymers are promising candidates for NLO applications.

1. INTRODUCTION

Organic and polymeric materials are promising candidates for integrated electrooptics (E/O) applications. Large non resonant electronic non linearities, low dielectric constant and processability in fibers or films are some of their exciting qualities commonly invoked.

Second order NLO polymeric films consist of hyperpolarisable chromophore units non centrosymmetrically ordered in a polymer matrix. A strong electric field ($10-100 \text{ V/}\mu\text{m}$) is applied to the film in the rubbery state ($T>T_g$) ordering the chromophores in an acentric order. This order is frozen by cooling the sample under its glassy temperature $T_g$.

A very high concentration of chromophores as well as a good orientational stability are now recognized as two important goals. The importance of improving these two characteristics is illustrated by the amount of work done in this area [1].

The guest/host ensembles (azo dye/PMMA or PS) were the first reported quadratic NLO films [2]. In these systems
residual motion of the dye is related to the free volume in the host matrix and cancels the dye polar order over periods of weeks to months [2–3]. Several routes were followed in order to stabilize the dopant orientation. This was accomplished by increasing the chromophore length [4], by inhibiting the conformational mobility of the matrix by physical ageing [4–5] or by cooling the polymer under the secondary transition temperature [5].

A remnant electrical field inside the matrix also stabilizes the chromophore orientation. This remnant field can be induced by space charges injected into the polymer during the corona poling [6,7] or by the use of a ferroelectric host matrix [8]. A similar result can be obtained by building dipole/dipole interactions between the chromophore and the polymer [9]. The use of very rigid, high Tg cross linkable matrix/chromophore systems have also been proposed [10]. However, the stability of these guest/host systems is far from complete.

Recently, covalent attachment of the dopant to the polymeric backbone in a side chain position has been used to increase both the NLO units concentration and the stability [11,12]. However, deorientation is not completely prevented after either contact poling [11] or Corona poling. Nevertheless, like in the guest/host systems, stability is increased by using Corona poling. The electrooptical susceptibilities of these polymers are quite large: $\chi(-\omega, \omega, \omega) - 40-50 \text{ pm V}^{-1}$ after Corona poling under high fields [12]. Further increase of the dopant concentration has been achieved in polyphenyleneoxide (Tg ~ 200°C) functionalized by more than one side chain NLO units per monomer [13]. The $\chi^{(2)}$ decay was about 50% in ten days at room temperature. Covalent attachment of the NLO units within the main chain in a "head to tail" configuration would increase the orientational efficiency of the poling field [14]. Examples of such polymer have been recently synthesized [15]. Finally, very stable $\chi^{(2)}$ values, even at 83°C, have been obtained by M. Eich et al. [16] with a cross linked epoxy with NLO units covalently incorporated into the rigid network.

We present in this paper a novel class of main chain highly functionalized linear polymers. Each monomer contains a chromophore whose donor group is in the main chain and whose dipole moment lies perpendicular to the back bone. The glassy temperature can be varied by adjusting the stiffness of the main chain (see fig. 1)