

## Poled polymers for frequency doubling of diode lasers

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# Poled polymers for frequency doubling of diode lasers

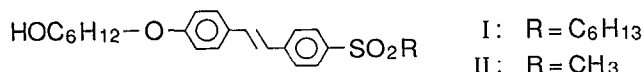
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We report on the design and characterization of methacrylate copolymers with nonlinear optical 4'-alkoxy-4'-alkylsulfone stilbene sidechains, which are transparent down to 410 nm. A fairly stable, polar orientation has been obtained by means of electric field poling, resulting in a reasonably high nonlinearity ( $d_{33} \leq 9$  pm/V).

Aligning polar molecules imbedded in a polymer matrix by means of a high electric field, as demonstrated by Havinga and van Pelt,<sup>1</sup> can introduce a significant polar orientation. This makes these materials suitable for second-order nonlinear optical (NLO) effects, like electro-optical modulation<sup>2,3</sup> and second-harmonic generation (SHG).<sup>3,4</sup> Especially for this last purpose polymeric materials are very promising, as they can easily be applied in optical waveguide geometries, thereby transforming low powers like those emitted by diode lasers into high intensities and consequently giving high conversion efficiencies. However, up to now no poled polymer has been reported that can be used to double the frequency of the emission of the common AlGaAs-GaAs laser diodes ( $\lambda \sim 820$  nm). In this letter we describe polymers that were specifically designed for this purpose and present the optical properties that affect their performance in this specific application.

The major requirements for the NLO moiety are a high first-order hyperpolarizability  $\beta(-2\omega; \omega, \omega)$  and complete transparency at both the fundamental and the second-harmonic wavelength. As a small separation between the charge transfer (CT) band and the second harmonic gives a large resonant enhancement to  $\beta$  (Ref. 3) a narrow CT band is obviously advantageous. After having screened a large number of chromophores for their linear and nonlinear optical properties,<sup>5</sup> we have selected some stilbene compounds containing an alkylsulfone group as electron acceptor and an alkoxy group as electron donor, as favorable candidates. Some relevant properties of these molecules are listed in Table I.



Sidechain copolymers with methacrylate were synthesized, as described elsewhere,<sup>6</sup> with various concentrations of the NLO moiety. The sidechain concentration was limited by the occurrence of semi-crystallinity, giving rise to large scattering losses. This occurred above 25 mass % for compound I and 50 mass % for compound II. Figure 1 shows the solid-state absorption spectrum of such a polymer, with the CT band of the NLO moieties centered around 340 nm. At 800 nm, waveguiding in thin films of

these polymers over many centimeters was observed. The refractive indices  $n$  of these materials were determined using quasi-waveguide techniques<sup>7</sup> at several wavelengths and fitted to a Sellmeier dispersion formula. From this, the coherence length  $L_c = \lambda / (n_{2\omega} - n_\omega)$  can be easily determined. This parameter is essential for phase matching the second-harmonic wave to the fundamental one. At 820 nm we find a coherence length of 5.5  $\mu\text{m}$  for the 25% copolymer (II).

For poling experiments, thin-film samples were prepared by spin coating onto indium-tin oxide (ITO) covered glass substrates and overnight annealing at 370 K under vacuum. The electric field for poling was applied with a corona discharge<sup>8</sup> at a temperature of 370 K, which is about 20 K below the glass transition temperature of these polymers. Typical fields, as determined by a compensation technique<sup>8</sup> were 1.2 MV/cm. Equilibrium  $d_{33}$  is reached in tens of seconds, after which the sample is cooled down to room temperature in 15 min. The nonlinearity shows the expected linear dependence on NLO chromophore concentration (Fig. 2). Only at the highest concentration a (positive) deviation is found, which may be indicative of extra orientation due to some collective behavior of the chromophores. The highest value obtained was 9 pm/V at 820 nm for the 45% copolymer shortly after poling. This is comparable to the nonlinearities found in crystalline materials like LiNbO<sub>3</sub> and KTP. The temporal stability of the nonlinearity, after the poling field was switched off, was fairly good, as shown in Fig. 3, if the sample was stored in a dry environment. The slow loss of nonlinearity is caused by relaxation of the orientation of the NLO groups and can be further suppressed by going to polymer backbones that allow for less local mobility. Storage at ambient conditions caused a rapid drop in  $d_{33}$  after a few days, due to water diffusing into the polymer which acts as a plasticizer.

Fairly high birefringence, due to the chromophore orientation, has been reported for poled polymers.<sup>9,10</sup> From prism coupling refractive index measurements, we found that the as-deposited films showed a larger refractive index for light polarized parallel to the plane of the film. For the

TABLE I. Properties of the NLO chromophore. No significant dependence on the alkyl chain lengths was observed.

$\lambda_{\text{max}}$ (nm)	$\mu$ (D)	$\beta$ ( $10^{-30}$ esu)		
		1907 nm	1064 nm	820 nm
335	6.5	10	24	45

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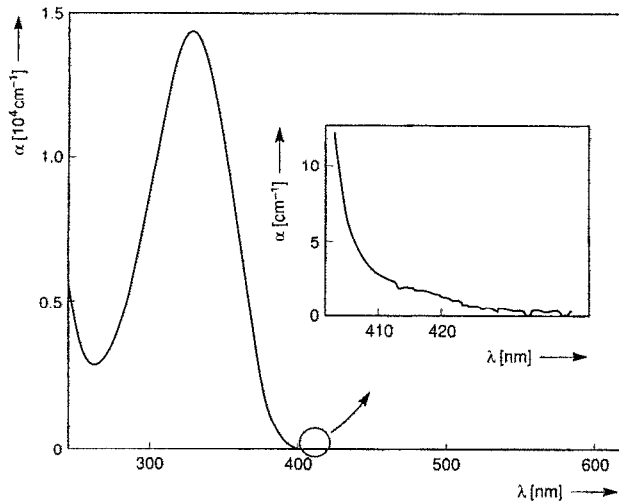


FIG. 1. Absorbance vs wavelength of a thin film of the 25% copolymer (II).

25% polymer (II) this amounted to  $n_{\perp} - n_{\parallel} \sim -2.10^{-3}$ , probably due to flow induced alignment of the sidechains. On annealing at 370 K for 24 h, this difference strongly decreased. Electric field poling introduced the expected positive birefringence, albeit too small for phase-matching purposes [for 25% (II)  $n_{\perp} - n_{\parallel} + 1.10^{-3}$  at 413 nm, whereas  $n_{410\text{ nm}} - n_{820\text{ nm}} = 5.10^{-2}$ ].

Phase matching may be obtained by periodic spatial modulation of the nonlinearity.<sup>11</sup> This has been achieved in polymers by periodically modulating the poling field.<sup>12</sup> As such a setup is difficult to realize on a micrometer length scale, we have chosen a different approach. With UV light that falls within the CT absorption band, the NLO moieties in the polymer can be easily bleached, as is witnessed by the strong decrease of their CT absorption band after irradiation (Fig. 4). This results in a strong loss of nonlinearity of the polymer, which is largely irreversible. Al-

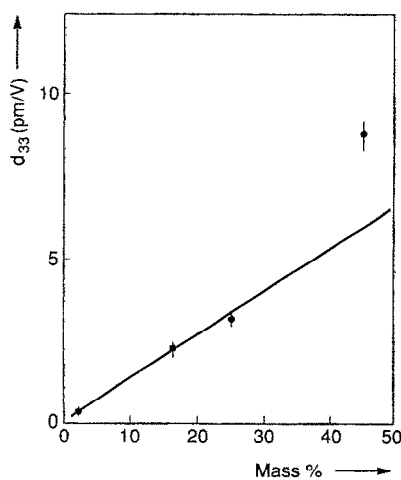


FIG. 2. Second-order susceptibility vs NLO chromophore concentration at 820 nm fundamental wavelength, shortly after poling at 1.2 MV/cm. Lowest concentration was a solution, others were copolymers. A linear dependence is indicated.

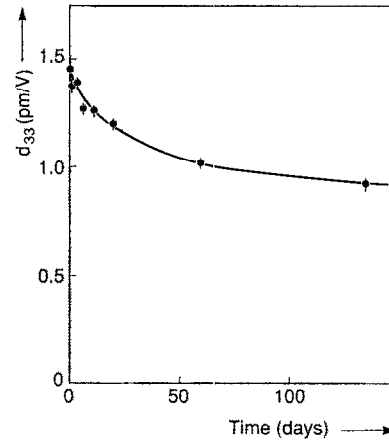


FIG. 3. Second-order susceptibility vs time at 1064 nm fundamental wavelength of the 25% copolymer (II) after poling at 1.2 MV/cm, when stored in a dry environment. The curve is only meant to guide the eye.

though the exact mechanism for the bleaching has not yet been established, a likely route is *trans* to *cis* isomerization, followed by ring closure, resulting in a molecule with a much smaller hyperpolarizability. Using gratingwise photobleaching, we have accomplished the desired spatial modulation and we have observed quasi-phase matching. Further work on this method is in progress. As we have also succeeded in defining channel waveguides in these polymers by photobleaching, an entirely "photographic" definition of a frequency doubling device seems feasible.

In conclusion, we have described the design and characterization of methylmethacrylate copolymers with 4-alkoxy-4'-alkylsulfone stilbene sidechains as nonlinear optical moieties, which are suited for frequency doubling of 820 nm diode lasers.

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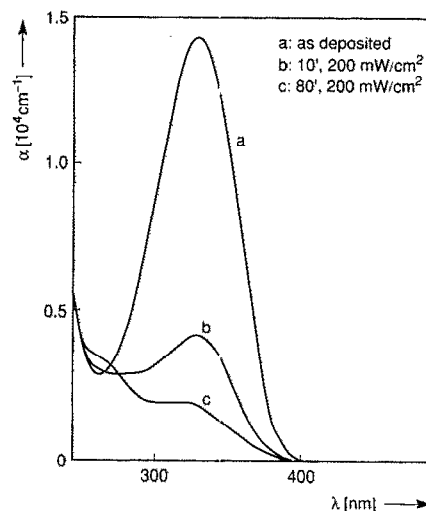


FIG. 4. Absorbance vs wavelength of the 25% copolymer (II) before (curve a) and after UV irradiation that causes bleaching of the NLO chromophore; curve b was measured after 10 min of irradiation with 200 mW/cm<sup>2</sup> at  $\lambda = 365$  nm, curve c after 80 min of irradiation.

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