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Polyurethanes containing boron chromophores as sidechains for nonlinear optics

Catherine Branger^{a,1}, Minh Lequan^a, Rose Marie Lequan^a, Maryanne Large^b, François Kajzar^b

^a Laboratoire de Chimie et d'Electrochimie des Matériaux Moléculaires, CNRS, URA 429, ESPCI, 10 rue Vauquelin, 75231 Paris Cedex 05, France

^b LETI Technologies Avancées, DEIN / SPE / GCO CEA Saclay, 91191 Gif-sur-Yvette Cedex, France

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Abstract

An azo-dye containing dimesityl boron as the electron acceptor group is synthesized and incorporated as side chains in polyurethane matrices. These new polymers have been poled under an external electrical field by the corona technique. They exhibit high nonlinear response and a remarkable temporal stability. It appears that the poling time is a crucial parameter not only in terms of obtaining a good second harmonic response but also in the temporal stability. © 1997 Elsevier Science B.V.

1. Introduction

The development of photonics over the last decade has created a need for materials having high nonlinear activity. Much research in this field has focused on the use of organic materials, and, in particular, on functionalized polymers [1,2]. The reasons for this interest in polymers centre on issues of integrability with semi-conductor technology, low manufacturing costs, and the wide variety of organic molecules which can be incorporated into the materials.

The materials generally used for quadratic nonlincar optics have in common a large intramolecular charge transfer system. They are composed of a donor acceptor pair separated by a conjugated chain. Classical electron acceptor groups include nitro, cyano and sulfone substituents. In this work we consider a chromophore in which the attracting group is a Lewis acid: boron. Previous studies have demonstrated the efficiency of boron azo-dye as a nonlinear optical material [3]. In this work we investigate the properties of polyurethane containing a boron azo-dye attached to the polymer as pendant chains.

The main challenge in the development of such materials for nonlinear optics is to achieve efficient materials for which the optical properties are preserved over long periods of time and at high temperatures. NLO active chromophores grafted as side chains onto a polymer backbone can significantly increase the temporal stability of polymers compared to doped systems. Grafted systems are preferable to doped systems as they allow a high density of chromophores to be incorporated without difficulties associated with phase separation, or a lowering of the

¹ Present address: Ecole Normale Supérieure de Cachan, PPSM-CNRS URA 1908, 61 Av. du Président Wilson, 94235 Cachan Cedex, France.

glass transition temperature, as is the case in doped systems. A wide variety of polymer matrices have been used in the preparation of such materials, but the active chromophores remain principally DR1 or DR19 azo-dyes for which the acceptor is the nitro group. Drawbacks of nitro derivatives include their thermal instability, large absorption at the second harmonic of the Nd–YAG laser, and their relatively fast decay when poled under an external static field.

We have recently investigated a 'push-pull' azodye containing the dimesityl boron as the acceptor group and N-dimethyl amino as electron donor. Electron delocalization is achieved through an unsaturated azo-benzene chain (BNA) [3]. It is demonstrated that the replacement of the nitro moiety by the dimesityl boron one, changes principally the physical properties of the chromophore, while keeping a high value of the quadratic hyperpolarizability in solution. The BNA molecule is larger than DR1 and has a weaker dipole moment. These two properties are thought to be the determining factors in slowing the decay of oriented polymers. With this in mind, we have incorporated the BNA molecule as side chains on a polyurethane backbone.

2. Synthesis and film preparation

In order to attach the model molecule to the polymer matrix the N-dimethyl amino group of BNA is replaced by the N-dihydroxy ethyl group. The synthesis of the new molecule is shown in Scheme 1.

Polycondensation of 3 (MB-DiOH) with diisocyanates leads to polyurethanes. In this work we have chosen to use the diisophorone (IDI) and the 2,4-tolylene diisocyanate (TDI). The corresponding polyurethanes, named MB-IDI and MB-TDI respectively, are illustrated in Scheme 2. They are stable in air and in the presence of water, and do not photodegrade.

The glass transition temperatures (T_g) of these materials are high: 146°C for MB-IDI and 159°C for MB-TDI. Thermogravimetry measurements confirm their thermal stability over a range of temperatures from ambient to more than 200°C (250°C for MB-IDI and 210°C for MB-TDI with weight loss beginning at 175°C). Both can therefore be heated to T_g without risk of decomposition.



Scheme 1. (i) Pyridinium salt of para-toluene sulfonic acid (PPTS) in dichloromethane. (ii) (a) Butyl lithium (BuLi)/hexane/THF -50° C; (b) (PPTS), EtOH, 60°C.

Films were prepared by spin coating a polymer solution at a concentration approximately 35 g/l in chloroform on clean glass slides. The solutions were successively filtered through 5 μ m and 0.5 μ m Millipore filters before casting. The thickness of the dried films was measured with an alpha-step profilometer to an estimated accuracy of about 10 nm. The number N of chromophores by unit volume was calculated by using the UV-VIS absorption and assuming that the oscillator strength f remains constant for the film and for the solution (Table 1).

$$\left\{\left(1/Nt\right)A\Delta\nu_{1/2}\right\}_{\text{film}}=\left\{\varepsilon_{\max}\Delta\nu_{1/2}\right\}_{\text{sol}}=K,$$

where t stands for thickness, A the absorbance of the film and $\Delta v_{1/2}$ the half bandwidth of the absorption band, and K is a constant.



Table 1 Determination of the number N of active chromophores in the polymers

Polymers	t (μm)	Absorbance	λ_{max} (nm)	$\frac{\Delta \nu_{1/2}}{(\mathrm{cm}^{-1})}$	$\frac{N}{(\text{mol}\text{cm}^{-3} \times 10^{20})}$
MB-IDI	0.35	1.007	430	5886	7.4
MB-TDI	0.20	1.000	430	5649	12.3

Films were poled using the corona poling method introduced by Comizzoli [4] with the needle electrode set at a distance of approximately 2 cm from the sample. A more detailed description of the poling apparatus is given by Gadret et al. [5]. Films were poled at their glass transition temperature T_{o} under an external static field of 6.3 kV. The order parameter ϕ was determined using UV-VIS spectroscopy, by comparing the absorption spectra before and after polarization. The order parameter is then given by

$$\phi = 1 - \left(A_{\rm pol} / A_{\rm iso} \right),$$

where A_{pol} and A_{iso} denote the absorbance of the poled and isotropic films at normal incidence with the polarization parallel to the substrate plane and perpendicular to the poling plane.

Second harmonic measurements were performed in the transmission configuration, with the optical pathlength of the sample being varied by rotation. The resulting fringes of harmonic intensity were fitted using the equations given in Swalen and Kajzar [6].

A polarizer was used to fix the polarization state of the input beam and measurements were made in both the S-P and P-P configurations. These values were then calibrated against a quartz reference to give absolute values for the quadratic susceptibilities d_{31} and d_{33} . A calibration value of $d_{11} = 0.5 \text{ pm/V}$ was used for quartz [7]. Calculation of d_{31} and d_{33} was done by using the values of d_{eff} obtained for S–P and P–P configurations, respectively.

The quadratic susceptibilities d_{33} and d_{31} were measured as a function of poling time. It was also possible, by mounting the heating platform and corona poling apparatus within the second harmonic generation experiment, to make in situ SHG measurements of the poling and depoling dynamics.

3. Results and discussion

When the dc voltage is applied to the sample at the glass transition temperature the second harmonic signal increases rapidly for the first ten seconds (Fig. 1), after which the intensity grows weaker. If the poling is stopped after a few minutes, the order parameter ϕ is small and the polymer exhibits a fast relaxation of the oriented chromophores. The magnitude of SHG signal is dependent on the poling time, as shown in Table 2. The order parameter for MB-IDI has not reached saturation at the poling times used (30 min), or MB-TDI (1.5 h). Computer simulation indicates that a saturation of about 26% could be obtained for poling times of 3 h.

When polymer MB-TDI was poled at 160°C for 15 min it displayed an order parameter comparable to that of MB-IDI (12.4%). However when the poling time was extended to 85 min the order parameter increased to 22.6%, corresponding to a value of d_{33} of 70 pm/V.

The dynamic relaxation was also investigated. At ambient temperature the intensity signal $I_{2\omega}$ of both samples remained stable after a period of 2.5 months. At higher temperatures the decay obeys a bi-exponential law

$$\frac{d_{33}^{(t)}}{d_{33}^{(t=0)}} = a \,\mathrm{e}^{-t/\tau_1} + b \,\mathrm{e}^{-t/\tau_2} \,.$$

1.2

The MB-IDI sample was completely depolarized at its glass transition temperature T_{g} and repolarized for 30 min. The temperature was then lowered to the studied temperature (in the range 40-120°C) and the electric field turned off (t = 0) (Fig. 2). Two relax-

Square root of second harmonic signal (arbitrary units) 1 0.8 0.6 experimental values 0.4 ,26-1,0831exp(-0,311t) ,016exp(-0,0029t) 0.2 0 0 20 40 60 80 Time (s)

Fig. 1. Dynamic polarisation of MB-IDI at 146°C.

Table 2 Determination of the order parameter ϕ and the quadratic susceptibilities d_{31} and d_{33} [8]

Samples	Polarization time (min)	Order parameter, ϕ (%)	d ₃₁ (pm/V)	d ₃₃ (pm/V)
MB-IDI	5	7.2	_	_
	10	9.7	_	_
	15	11.1	2.2	19.0
	30	-	3.35	38.2
MB-TDI	15	12.4	_	-
	35	16.3	2.7	36.3
	85	22.6	4.7	70.0

ation regimes can be observed: an initial rapid process followed by a slower one. Fits of the data at 120°C yield time constants of $\tau_1 = 2$ s and $\tau_2 = 667$ s. Investigations were carried out for several temperatures and the corresponding values of τ_2 are given in Table 3. The results confirm the temporal stability of the material at 40°C. The initial rapid decay is presumed to be related to the dispersion of surface



Fig. 2. Relaxation of (a) MB-TDI at 100° C and (b) MB-IDI at 120° C.

Table 3	
Calculated values of the time constant τ_{*}	for MB-IDI

-	
τ_2 (s)	
50000	
11111	
5000	
2500	
1111	
667	

charges from the sample and the longer process to the reorientation of the chromophores.

The same experiment was carried out for MB-TDI. After polarization for 85 min, it is notable that the sample was extremely difficult to depolarize even at the glass transition temperature 159°C. The sample was therefore submitted to depolarization at 100°C. The resulting relaxation curve is characterized by very large time constants: $\tau_1 = 15$ s and $\tau_2 = 10^5$ s (28 h). The sample, in other words, retains 88% of its nonlinear properties after 20 min and 50% after 19 h at 100°C.

The role of the poling temperature for the polymer MB-IDI is shown in Fig. 3. The maximum intensity was obtained at 100°C ca. 46°C lower than the glass transition temperature T_g ; by contrast, no change in the intensity was observed when poling was carried out at higher temperature, the curve $I_{max}(2\omega)$ vs. T (temperature) exhibits a plateau from 100°C up to 180°C.

It is clear from the results that the poling time plays a crucial role, both in obtaining a high value of d_{33} and in the long-term temporal stability of poled



Fig. 3. SHG signal versus temperature of poling of MB-IDI.

samples. This poling-time-dependent temporal stability may be interpreted in part as the consequence of a slow diffusion of positive and negative charges (holes and/or electrons) near the surface into the bulk. Some of these charges will be neutralised by impurities, the others by charge traps, among them probably the oriented dipoles themselves (Fig. 4). These 'charge pairs' help to maintain the stability of the oriented dipoles, avoiding mutual repulsion which would lead to a disorganisation back toward an isotropic medium. Short poling times stabilize only a small fraction of the dipoles, allowing the majority of dipoles to relax rapidly after the cancellation of the electrical field. Repeated the poling process would result in a successive increase in the number of stabilized dipoles at each run, until an equilibrium was reached. After each subsequent run, the number of dipoles requiring stabilization diminishes, so that the time necessary to reach this equilibrium decreases. This hypothesis may partly explain the 'memory effect' described in the reapplied poling experiments [9-13]. Lavi and Berkovic have also confirmed the role of charge injection in electrically poled samples.

This interpretation of the relationship between poling time, charge diffusion and orientational stability is currently the subject of further study. Other authors (e.g. Refs. [14] and [15]) have also noted a relationship between poling time and temporal stability. Flipse et al. [15] considered the stability of samples through cycles of polarisation and repolarisation, and found the 'older' samples to have enhanced stability. They interpreted this, not in terms of charge diffusion, but in terms of the annealing, giving rise to a re-arrangement of free volume. That is, the enhancement of stability is the result of



Fig. 4. (a) Polarization and diffusion of charges (holes and/or clectrons) (b) stabilizations of chromophores by 'charge pairs' (c) natural tendency of dipoles to pair.

molecular motions which can occur, leading to an optimisation of free volume. Another effect which should be considered in this context is the complete removal of solvent from the sample. Solvent remaining in the film may act as a plasticizer, increasing the rate of both polarisation and relaxation. For this reason, extended or repeated heating may increase stability purely by removing the remaining solvent. Pre-annealing to remove the solvent completely before polarisation is therefore an important step to be considered in this context.

4. Conclusion

We have synthesized new polyurethanes having azo-dyes with a dimesityl boron group as an electron acceptor. These materials have high glass transition temperature (T_g) and high quadratic susceptibilities. They are also chemically and thermally stable, as would be required for potential optical applications. Poling may be carried out far below T_g and the poling time is an important parameter in both the optimization of the nonlinear optical response and the temporal stabilization of the polymers. A tentative interpretation based on the low diffusion of charges into the bulk matrix is given. The optical properties of these materials can therefore be considered somewhat better than their DR1 analogue.

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