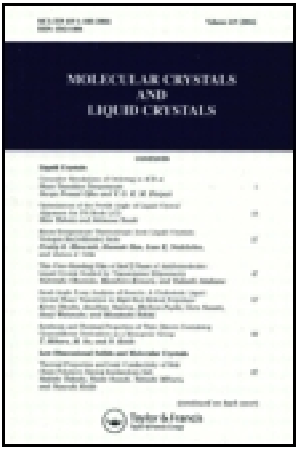

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Nonlinear Optical Epoxy Polymers with Polar Tolan Chromophores

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Abstract

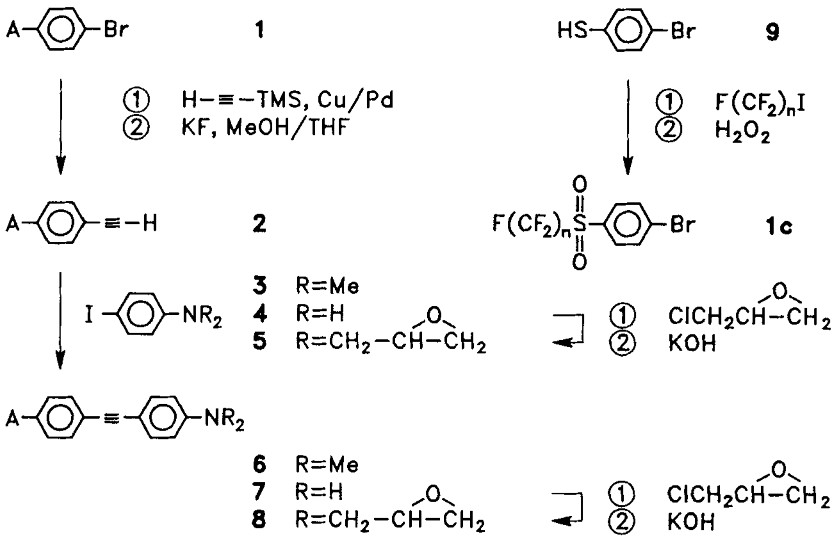
A variety of optically nonlinear tolan chromophores and epoxy based polymers containing them have been prepared and studied. The molecular hyperpolarizabilities of the dye chromophores have been measured by the EFISH technique while the polymers containing them have been examined by calorimetry, X-ray diffraction, dielectric spectroscopy as well as the appropriate linear and nonlinear optical techniques. Novel liquid crystalline behavior has been encountered in some of these monomers and polymers.

INTRODUCTION

Poled polymers appear to be particularly well suited for implementation in waveguide integrated optoelectronic devices. Yet, practical realization of this application still requires significant enhancement in understanding of many basic issues in both the physics and materials science areas. Since the first demonstration of creation of bulk polar order leading to second order optical nonlinearity in polymer thin films by electric field poling[1] numerous chromophore and polymer combinations have been examined.[2,3] These combinations may be classified by the following criteria: type of chromophore, covalent bonding relationship between chromophore and polymer, secondary noncovalent interactions (liquid crystallinity, hydrogen bonding, etc.) and molecular weight and bonding changes during processing. A simple summary of this complex endeavor is as follows: identify a processible, nonlossy polymeric media with large and permanent bulk optical nonlinearity.

RESULTS

Much of our preliminary study of NLO polymers has involved either linear main chain or thermally crosslinking epoxy systems.[4] This class of polymers was a chemically convenient starting point and the linear



A=**a**, NO_2; **b**, SO_2CH_3; **c**, $SO_2(CF_2)_nF$ (n=1,2,6,12)

Figure 1a. Synthesis scheme for tolan monomers

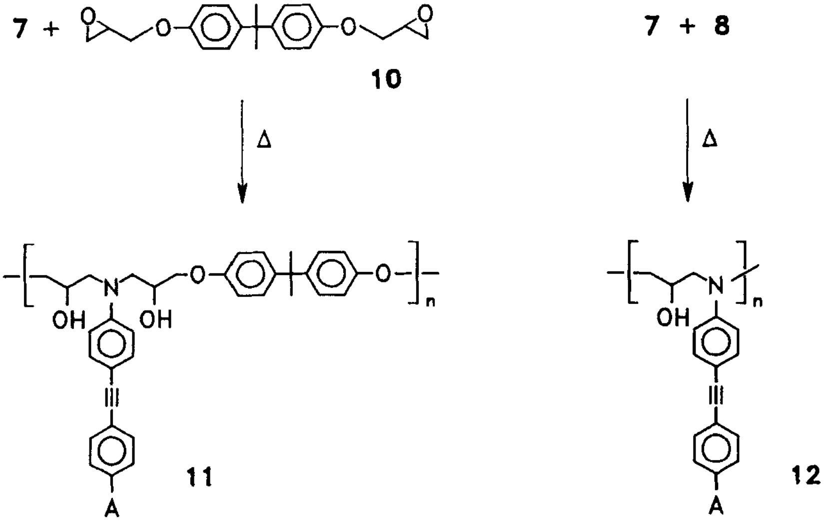


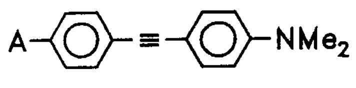
Figure 1b. Synthesis scheme for tolan polymers

systems have proved to be of some practical value and additionally can be further modified to provide novel photochemically crosslinked systems.[5] Here we will focus only on a subset of epoxy polymers which contain the polar tolan chromophore appended as side groups to a linear (noncrosslinked) main chain.

The tolan monomer synthesis, outlined in Fig. 1a, is straightforward and relies on the flexibility and compatibility of the acetylene coupling reaction with a wide range of functional groups. The donor end of the tolan is an iodoaniline derivative **3**-**5** while the acceptor end is a derivative of bromobenzene bearing different electron withdrawing groups (**1a**, NO_2; **1b**, SO_2CH_3; **1c**, $SO_2(CF_2)_nF$ with $n = 2,6,12$). The free aniline amino group can be converted to a bisepoxy form at either the iodoaniline **4** → **5** stage or preferentially at the tolan **7** → **8** stage. In the case of the fluorinated sulfones the immediate bromobenzene precursors **1c** are not commercially available and must be prepared by SET alkylation of the sulfide **9** and oxidized. The different lengths $n = 2,6,12$ of fluorocarbon tail were prepared to see if there is any influence on the ultimate polymer properties, particularly on the stability of the poled order. The 4-amino-4′-perfluorododecylsulfone tolan monomer **7c** (n = 12) is itself liquid crystalline K 190 S_A 199 I which is surprising in that mesogens with either free amines and/or sufones are quite uncommon.

The nonlinear properties of representative tolan chromophores have been examined by EFISH on model compounds as found in Table 1.[6] The measurements are made in dioxane with a 1.06 μm fundamental. The dimethylamino donor as found in **6** is comparable to the dialkylamine donor in the polymerized epoxy form **11** or **12**. The different acceptors influence the ground state dipole moment, absorption maxima, hyperpolarizability (β_0 obtained by the two-level model) in an unexceptional way.

TABLE 1. Properties of Model Tolan NLO Chromophores



#	A	μ_g (D)	λ_m (nm)	β ($x10^{-30}esu$)	β_0 ($x10^{-30}esu$)
6a	SO_2CH_3	7.5	358	40	19
6b	SO_2CF_3	8.4	388	86	35
6c	NO_2	7.1	402	102	38

The preparation of some of the polymers studied are found in Fig. 1b and some of the physical properties are collected in Table 2. Most materials are of the "copolymer" variety **11** prepared simply by melt condensation polymerization at 150°C of a 1:1 mixture of the appropriate aminotolan **7** and Bis-A-diglycidyl ether **10** partners. In a few cases the more highly concentrated "homopolymer" analog **12** has also been prepared which requires prior synthesis of the tolan bisepoxide **8** . The glass transitions determined on samples directly from the melt condensation are remarkably independent of the identity of the sulfone substituent. However, there may be some influence on these values by the differences and dispersivity of molecular weight particularly due to the influence of low molecular weight plasticizers. The absorption properties determined on thin films are quite interesting. The methylsulfone **11b** has a charge transfer λ_m = 366 nm and the perfluoroethylsulfone **11c** (n=2) has the anticipated lower energy transition at λ_m = 386 nm. This difference of 20 nm is comparable to that of 30 nm found for the two related monomers **6a** and **6b** in dioxane solution (Table 1). Remarkably, the charge transfer band λ_m for the thin film samples of longer perfluoralkylsulfones shifts to higher energy and becomes more broad. This may be due to some change in anisotropy of the film or a "solvent" effect in which the charge transfer band is responding to the increasingly less polar environment resulting from increases in the fluorocarbon content. In addition, the perfluorododecyl sulfone copolymer **11c** (n=12) also shows mesogenic behavior above its glass transition *g* 126 S_A 182 *I*.

TABLE 2. Properties of Tolan Chromophore Bis-A Copolymers

	11b	**11c**(n=2)	**11c**(n=6)	**11c**(n=12)
rex'n time (hr)	22 hr	17 hr	16 hr	4 hr
M_W (GPC)	27,600	31,900	66,300	18,900
M_N (GPC)	14,400	15,000	20,600	13,500
T_g (°C)	128	127	128	126
λ_m (nm)	366	386	372	361

One motivation to examine these sulfones is due to their enhanced transparency relative to the nitro substituted polymers. This is most dramatic when one compares the nitro- **11a**, methylsulfone- **11b** and pentafluoroethylsulfone- **11c** substituted polymers (Fig. 2). The λ_{max} for the sulfones is not only at higher energy but also the cutoff is much sharper than that of the nitro compound. Studies on electric field poling and nonlinear measurements on both the copolymer and homopolymers have been done and some detailed results on the nitrotolan **11a** are described elsewhere.[7] A related and more recent example is the methylsulfonyltolan analog **11b** which has been corona poled as in Fig. 3 to give a maximum nonlinear coefficient of d_{33} = 15 pm/V.

The poling behavior of the homopolymer materials **12** is especially interesting in that higher nonlinearities and stabilities are anticipated due to the high density of large aspect ratio chromophores. In the case of the nitrotolan homopolymer **12a** turbidity due to liquid crystallinity prevents the analysis of the nonlinear properties of the poled films. A related system in which some crosslinking has been introduced nonetheless possessed a large birefringence which remained near constant even for days at 100°C indicating a high degree of stability.[8] The analogous methylsulfonyltolan **12b** is not liquid crystalline but now the glass transition temperature ($\simeq$180°C) is so high that some difficulty in attaining effective poling were encountered. Nonetheless, a $d_{33} \simeq$ 30 pm/V has been obtained for this material.

CONCLUSIONS

The tolan based chromophore combined with linear epoxy polymer backbone provides an interesting set of NLO polymers. The polymer morphology and NLO behavior is strongly dependent on both the exact type of acceptor group and the constitution (homopolymer or copolymer), of the main chain.

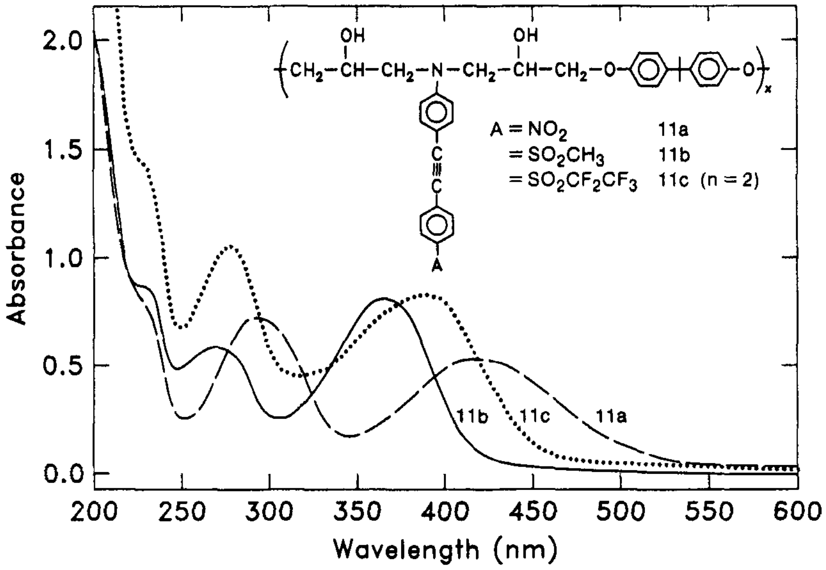


FIGURE 2. Thin film absorption spectra comparing sulfone and nitro substituted epoxy polymers.

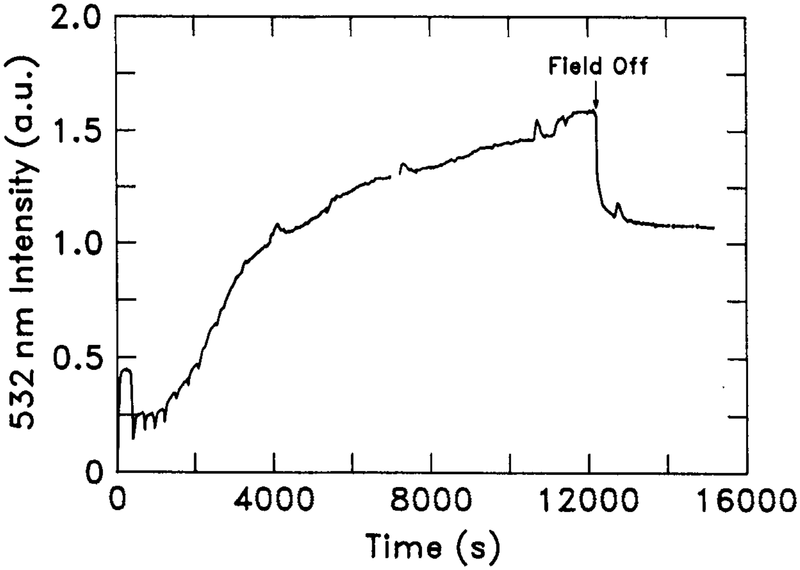


FIGURE 3. *In situ* corona poling of the polymer **11b**; temperature ramp to 130° at 11000 sec then cooled to ambient and field off at 12000 sec accompanied by an intensity decay due to surface charge effects.

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