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13. ABSTRACT (Maximum 200 words) Several new functionalized chromophores have been prepared and tested in the preparation of optically stable, photopatternable, NLO polymers for second harmonic generation at the diode laser wavelength of 820 nm. In particular, chromophores containing the sulfonamide or sulfonate ester functionalities have been found to be extremely versatile as they allow attachment of a polymerizable group at the electron-poor end of NLO chromophores. The results of model studies confirm that the sulfonamide groups do not have a deleterious effect on NLO properties. Several new monomers containing 4-alkoxy-4'-sulfonamido-stilbene moieties have been prepared. The 4-alkoxy end of the chromophore is designed to allow its incorporation into a linear polymer backbone. The sulfonamido end of the chromophore has a polymerizable double bond that can be photocrosslinked after poling of the chromophores. As it is extremely important to carry out the photopatterning step without affecting the NLO chromophore or introducing any color into the imaged polymer, novel photoinitiators were tested and found to be suitable. The radiation induced photopatterning step can be done without causing isomerization of the stilbene chromophores, or introducing any color into the patterned coating.

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Preparation of Stable Photopatternable Polymeric Materials for Non-linear Optics.

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Abstract.

Several new functionalized chromophores have been prepared and tested in the preparation of optically stable, photopatternable, NLO polymers for second harmonic generation at the diode laser wavelength of 820 nm. In particular, chromophores containing the sulfonamide or sulfonate ester functionalities have been found to be extremely versatile as they allow attachment of a polymerizable group at the electron-poor end of NLO chromophores. The results of model studies confirm that the sulfonamide groups do not have a deleterious effect on NLO properties. Several new monomers containing 4-alkoxy-4'-sulfonamido-stilbene moieties have been prepared. The 4-alkoxy end of the chromophore is designed to allow its incorporation into a linear polymer backbone. The sulfonamido end of the chromophore has a polymerizable double bond that can be photocrosslinked after poling of the chromophores. As it is extremely important to carry out the photopatterning step without affecting the NLO chromophore or introducing any color into the imaged polymer, novel photoinitiators were tested and found to be suitable. The radiation induced photopatterning step can be done without causing isomerization of the stilbene chromophores, or introducing any color into the patterned coating.

Introduction:

Much of the recent intensive activity in the area of polymers for nonlinear optics (NLO) stems from their potential uses in optical signal processing and optical computing. However, before NLO materials can be used in devices, their NLO properties must be stable. One of the most promising techniques for improving the thermal stability of

NLO materials is to incorporate the NLO chromophores into a polymer that can be crosslinked, either thermally¹⁻⁴ or photochemically⁵⁻⁸, after the poling procedure. Photochemical crosslinking allows devices to be created directly through photo-imaging techniques, which is a significant advantage over thermal crosslinking. However, the photochemical crosslinking studied thus far, the 2+2 addition of cinnamoyl moieties, is of limited versatility and is incompatible with the azobenzene and stilbene based chromophores.^{6,7} In addition it has proven extremely difficult to prepare stable NLO materials for frequency doubling of diode lasers at 820nm. This goal is desirable in view of the wide applicability of these frequency-doubled light beams and of the numerous applications that are possible in applications from data storage to high speed communications.

In order to overcome this we have designed polymers that can be crosslinked using a photoinitiated radical process: the polymers have active side-chains consisting of the NLO chromophore with a crosslinkable moiety at its extremity. This design requires the use of a bifunctional monomer with one end designed for the attachment to the polymer and the other end for the attachment of the photocrosslinkable group. We report the synthesis and NLO characterization of a totally new type of chromophore with dual functionality that allows its incorporation into a photocrosslinkable polyurethane.

The system described in this preliminary technical report prepared for the Office of Naval Research, allows the direct patterning of NLO active materials using simple photolithographic techniques. In addition, frequency doubling of diode laser light at 820 nm has been demonstrated in preliminary experiments

Design, synthesis, and evaluation of the new chromophore.

The requirement for the use of a bifunctional chromophore in the preparation of a stable photocrosslinkable NLO-active polymer has led to the investigation of several

Scheme 1

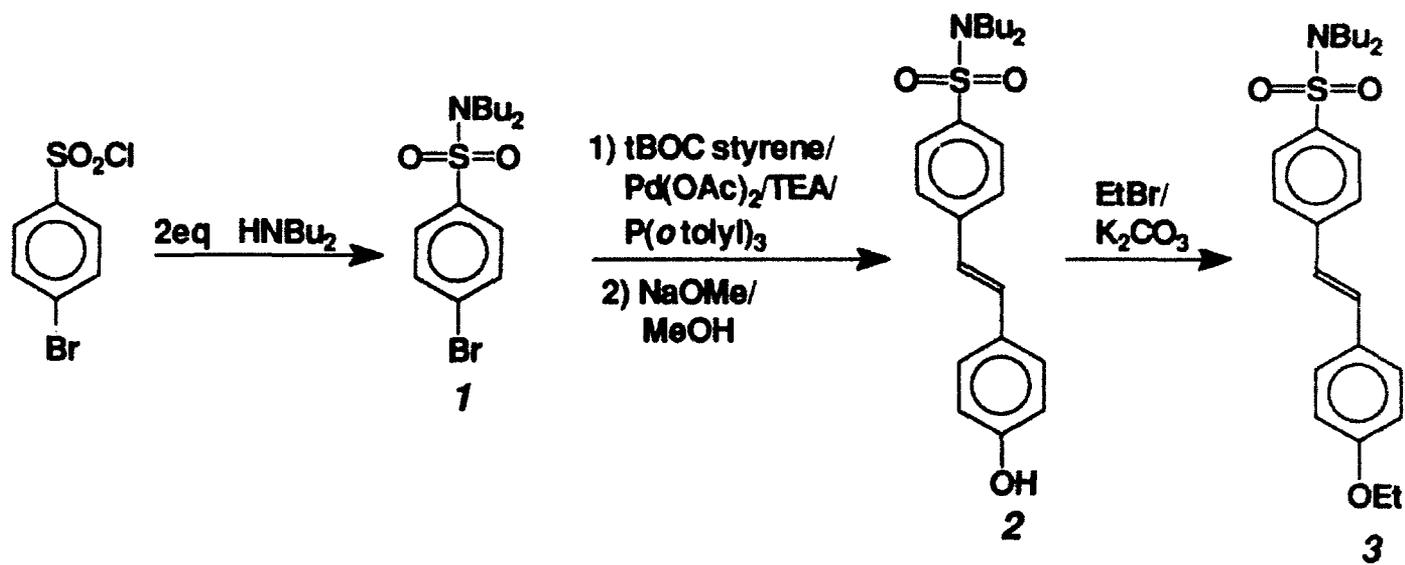
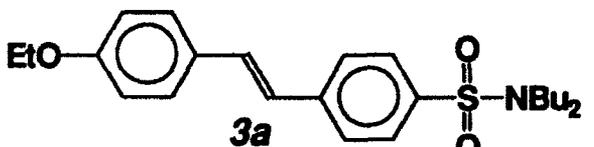
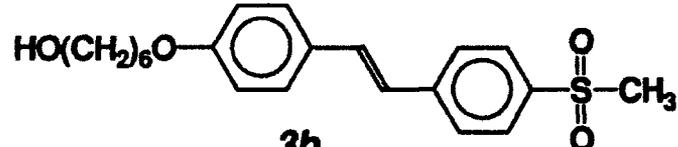


Table 1

Structure	$\mu\beta$	λ_{max} (nm)	λ_{cutoff} (nm)
 <chem>CCOC1=CC=C(C=C1)/C=C/C2=CC=C(S(=O)(=O)N(C)C)C=C2</chem> 3a	100	335	388
 <chem>HO(CH2)6OC1=CC=C(C=C1)/C=C/C2=CC=C(S(=O)(=O)N(C)C)C=C2</chem> 3b	97	336	—

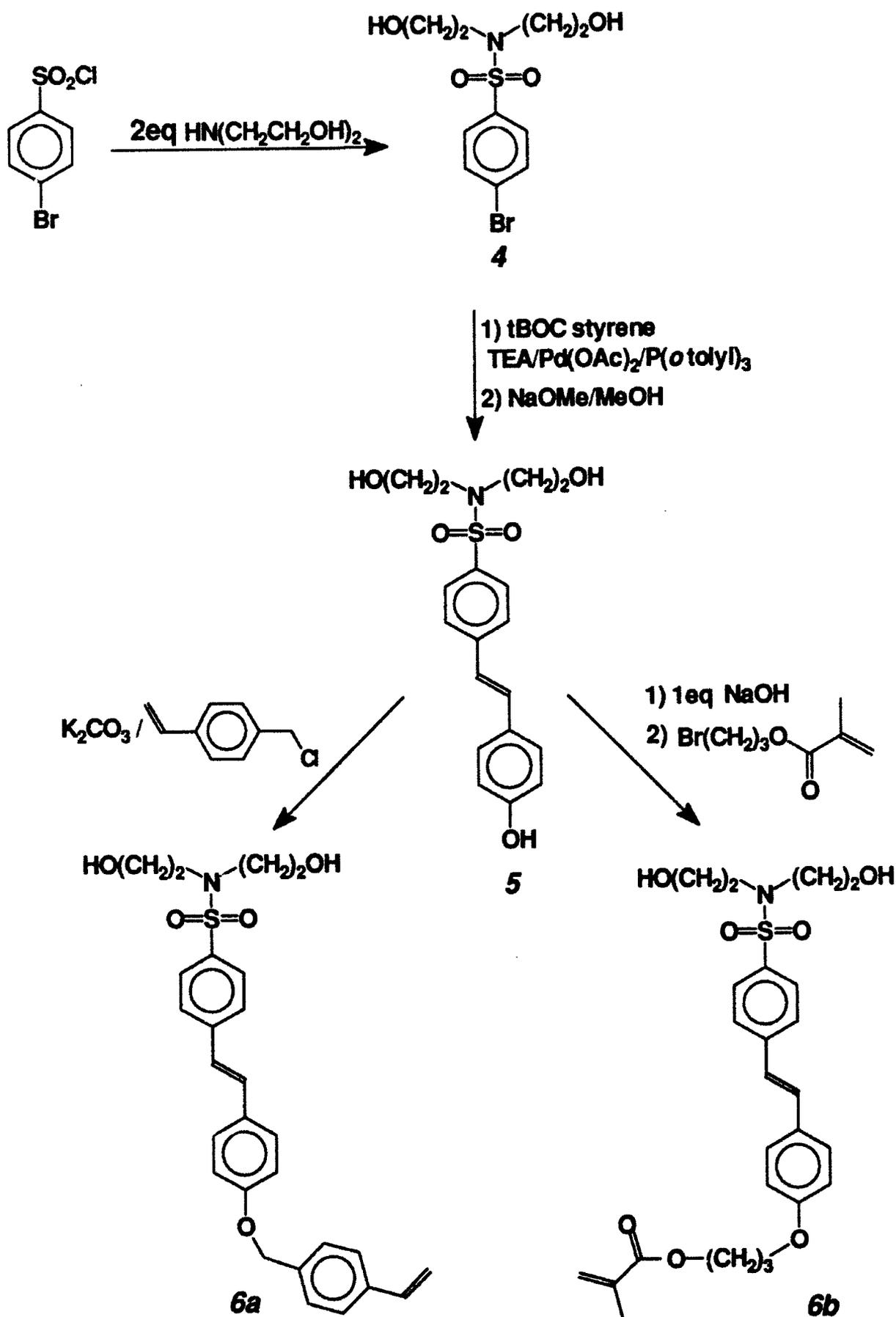
new NLO chromophores. Classical chromophores such as N-substituted 4-amino-4'-nitrostilbenes that show significant NLO activities are not suitable for our purpose since direct polymer attachment is only possible at the electron-rich amino-end and not at the electron-poor nitro end of the chromophore. In contrast, the tetradentate sulfonyl functionality is very attractive for use as the electron-poor component of the NLO chromophore since it provides for the required link to an eventual polymer chain. These considerations, coupled to our target of frequency doubling for an 820nm diode laser, led us to select a chromophore with alkoxy substitution at one end and secondary or tertiary sulfonamide functionality at the other. In order to examine the suitability of this type of chromophore, model compound **3a** was prepared (Scheme 1) and its NLO and UV absorption characteristics were measured. Reaction of 4-bromobenzenesulfonyl chloride with 2 eq. of dibutylamine in chloroform affords the di-*N*-butylsulfonamide **1** in 86% yield. Transformation of **1** into stilbene **2** is achieved in 59 % yield through a Heck reaction with *t*-BOC-styrene⁹ in the presence of 1.5 eq. of triethylamine, 0.01 eq. of palladium(II) acetate, and 0.03 eq. of tri-*o*-tolylphosphine. Finally, alkylation of stilbene **2** with 1.1 eq. of ethyl bromide and 1.5 eq of dry potassium carbonate affords the desired model compounds **3a** in 58% yield.

The NLO properties of **3** were evaluated through EFISH measurements¹⁰ ($\mu\beta$ value) in chloroform at 1.91 μm . Table 1 lists the $\mu\beta$ values and UV characteristics for compound **3a** as well as previously known¹⁰ reference compound **3b**. The measurements confirm that both sulfonamide **3a** and other somewhat similar compounds prepared for this study have $\mu\beta$ values and UV characteristics that meet our design criteria.

Synthesis of bifunctional monomers and their polymerization.

In view of the ease of access and desirable optical properties of 4-alkoxy-4'-sulfonamido-stilbene moieties, their incorporation into suitable bifunctional monomer

Scheme 2



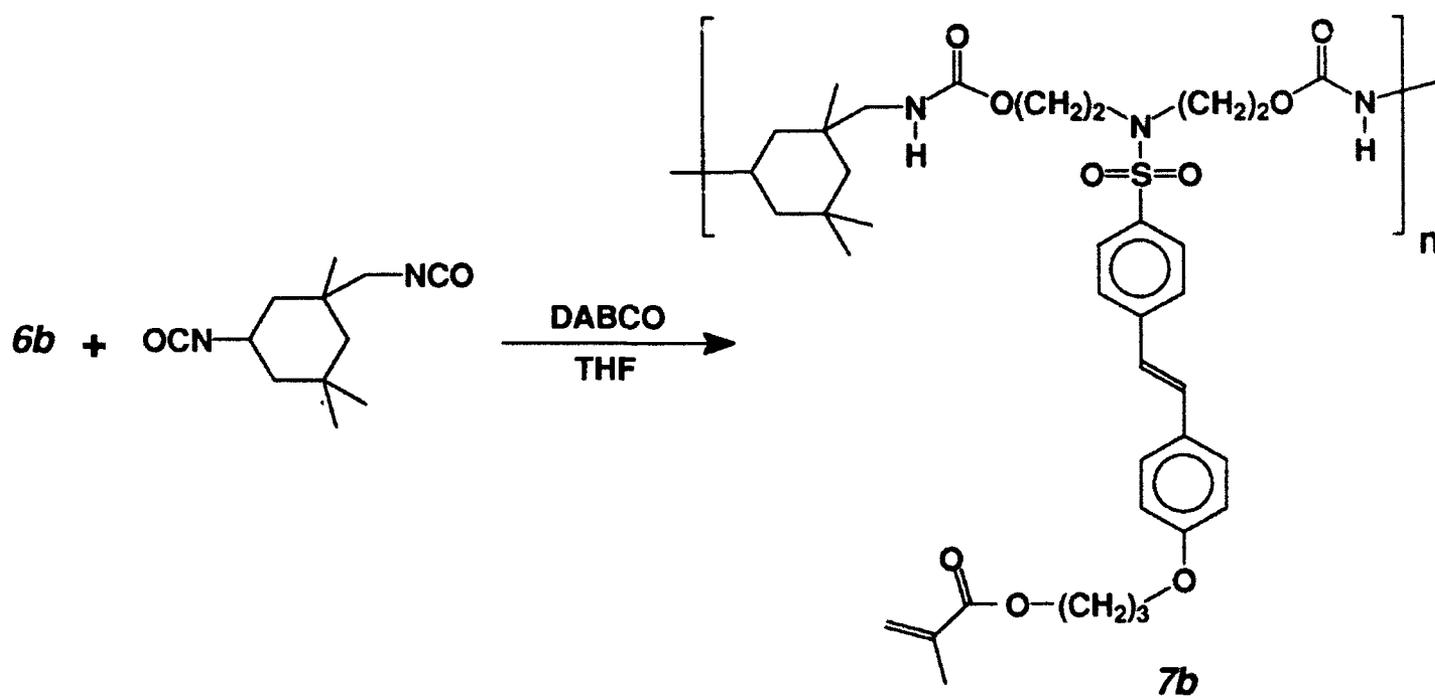
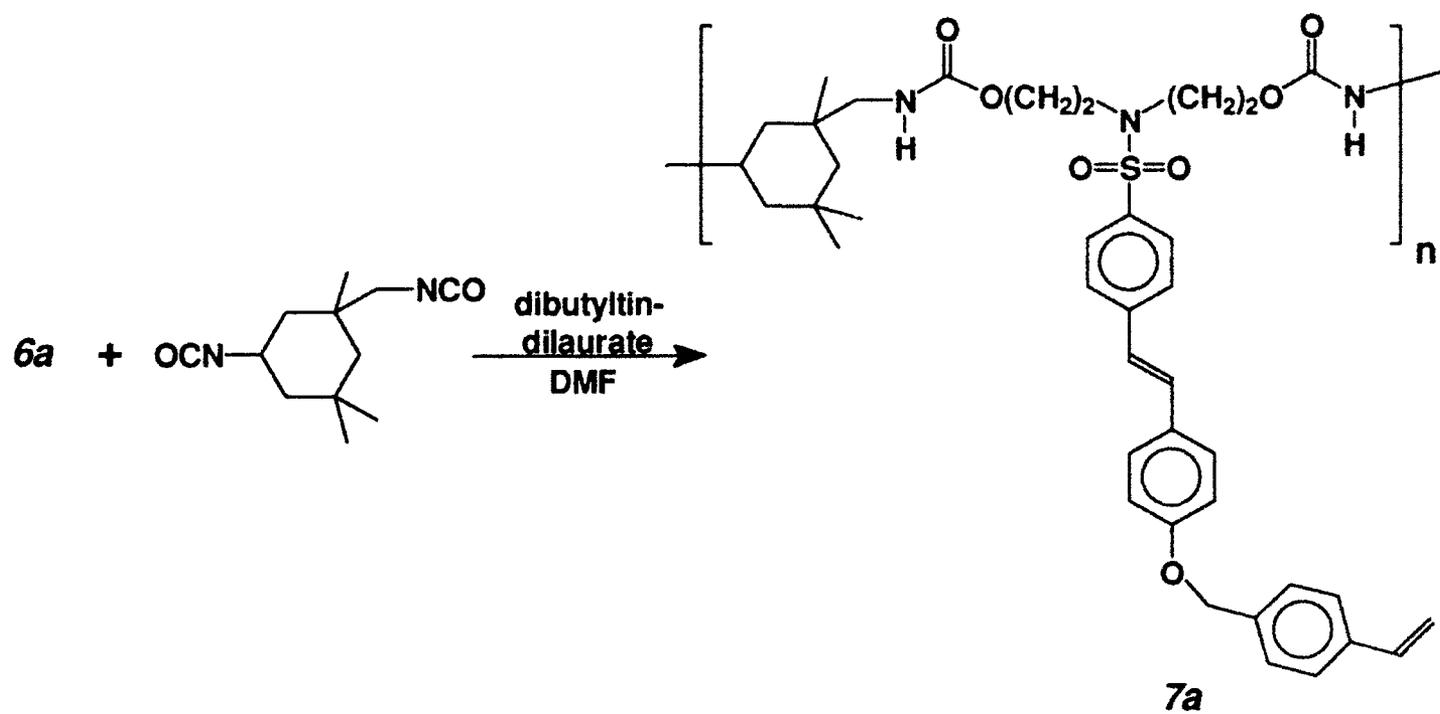
units such as **6a** and **6b** was studied (Scheme 2). These monomers contain a diol functionality that provides for their incorporation into a polymer main-chain through a polycondensation process, as well as a polymerizable double bond for eventual photoinitiated crosslinking. The N,N-diethanolsulfonamide **4** is obtained in 83% yield by reaction of 4-bromobenzenesulfonyl chloride with 2 eq. of diethanolamine in chloroform. A subsequent Heck reaction of **4** with *t*-BOC-styrene followed by removal of the *t*-BOC protecting group affords stilbene **5** in 84% yield. This stilbene is very versatile as it can be converted into either monomer **6a** or monomer **6b** through a simple regioselective alkylation with the appropriate vinyl monomer. Therefore, **6a** is obtained in 70% yield by alkylation with 1.1 eq. of 4-vinylbenzyl chloride in the presence of 1.5 eq. of potassium carbonate. Similarly, **6b** is obtained in 66% yield by reaction of the phenolate derivative of **5** with 3-bromopropyl methacrylate.

The step-growth polymerization of monomers **6a** and **6b** with isophorone diisocyanate in a polycondensation process is outlined in Scheme 3. The styrene monomer **6a** was polymerized in DMF with isophorone diisocyanate in the presence of a catalytic amount of dibutyltin dilaurate. After purification by repeated precipitation into diethyl ether, polymer **7a** was obtained in 90% yield ($M_n = 4,500$; $M_w = 5,000$; $T_g = 122^\circ\text{C}$). In contrast, the polycondensation of monomer **6b** with isophorone diisocyanate could not be achieved using dibutyltin dilaurate as a catalyst due to the occurrence of a troublesome transesterification side reaction of the methacrylate moiety. Therefore, diazabicyclo[2.2.2]-octane was used to catalyze the polymerization of monomer **6b** with isophorone diisocyanate. After purification by successive precipitations into ether, then into hexanes, polymer **7b** was obtained with $M_n = 3,300$, $M_w = 6,300$, and a glass transition temperature of 85°C .

Photoinitiated crosslinking of polymers **7a and **7b**.**

Since each of the two polymers **7a** and **7b** contain two different types of reactive

Scheme 3



polymerizable vinyl groups, it is important to select polymerization conditions that only involve the styrenic or methacrylic double bonds while leaving the stilbene moieties untouched. Any photoactivated *trans* to *cis* isomerization of the stilbene chromophores would adversely affect the NLO efficiency of these materials. Since isomerization of stilbenes is known to proceed either via direct or sensitized irradiation, the photoinitiator used to crosslink the polymer must be photoactive outside of the absorption region of the chromophore and also it must not sensitize isomerization of the chromophore. Study of a variety of commercial and experimental photoinitiators showed that titanocene **8** meets these requirements. It polymerizes methacrylate moieties efficiently in the absence of oxygen, exhibits strong absorption beyond 500 nm, bleaches upon photoreaction, and is stable up to 250°C.¹¹ The photoreaction of titanocene **8** with polymer **7b** in the solid-state was monitored by infrared spectroscopy (Figure 1). The C=C stretching frequency of the methacrylate group at 1636 cm⁻¹ decreases upon exposure to visible light at 436nm, while the C=C stretching frequency of the stilbene moiety at 1590 cm⁻¹ remains unchanged. Additionally, a shift from 1717 cm⁻¹ to 1721 cm⁻¹ in the carbonyl absorption corresponding to a loss of conjugation can be observed. A similar study of the photocrosslinking of polymer **7a** is in progress.

Conclusion.

These studies confirm the validity of the concepts used in the design of photo-patternable polymers **7a** and **7b**. These polymers are proving useful in the direct patterning of NLO devices using simple photolithographic techniques. Our work on the actual patterning of these polymers and the measurement of their NLO properties is continuing. Additional studies with other polymerizable and photocrosslinkable monomers also containing sulfonamide or sulfonyl ester groups with other NLO chromophores will be reported in the near future.

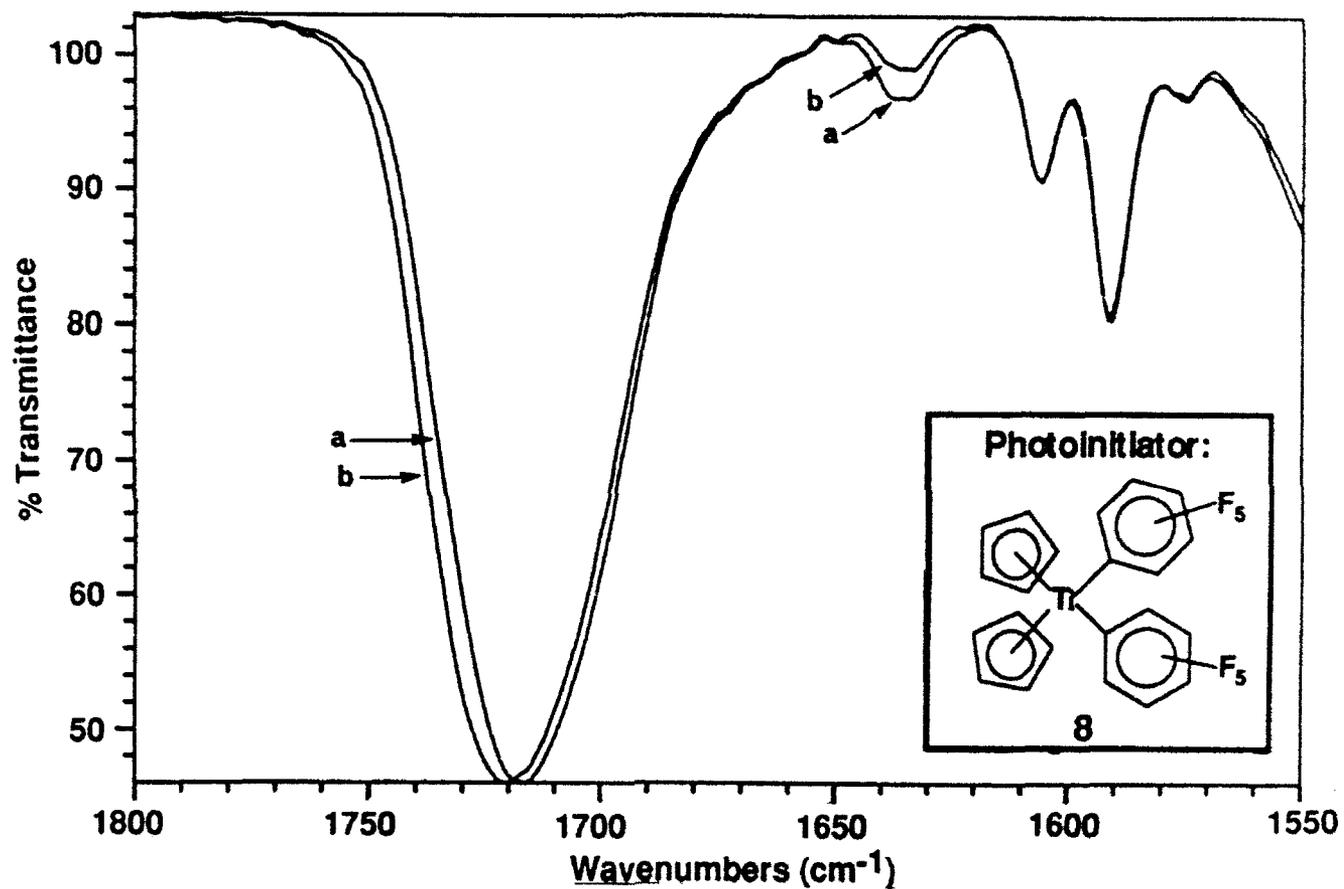


Figure 1. IR spectrum of double bond region for polymer 7a before (a) and after (b) irradiation in the presence of titanocene 8

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