N-Phenylated aromatic polyurea: a new non-linear optical material exhibiting large second harmonic generation and u.v. transparency

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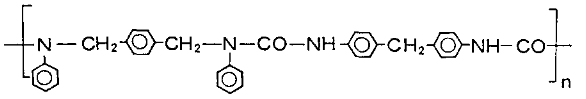
We report for the first time a non-linear optical polymer exhibiting optical transparency down to 307 nm. From the Maker fringe measurements, the non-linear optical d_{33} coefficient of poled aromatic polyurea films was found to be 14 times that of potassium dihydrogen phosphate (KDP) at 1.064 μm fundamental radiation. Aromatic polyurea forms flexible, colourless and transparent films and thermogravimetric analysis showed high thermal stability. The non-linear efficiency and optical transparency make aromatic polyurea a potentially useful material for non-linear optics.

(Keywords: aromatic polyurea; non-linear optics; second harmonic generation; optical transparency; thermal stability)

Introduction

There has been a great deal of interest in the development of organic materials for non-linear optical (NLO) applications. Organic molecules comprising electron acceptor and donor functionalities at opposite ends of a conjugated system, have been considered to be the most suitable materials for second-harmonic generation (SHG)[1–8], if they lack a centre of symmetry. Of particular interest are organic molecules in which electron acceptor and donor functionalities are attached to either benzene, stilbene, azobenzene, benzylidene or tolane derivatives. Donor–acceptor substituted organic molecules can also be used for third-order NLO effects[8] where symmetry requirements are removed. Organic materials are important because of their unlimited architectural flexibility, allowing them to be tailored to optimize optical non-linearities. A wide variety of organic molecular and polymeric materials[4] such as single crystals, Langmuir–Blodgett films, self-assemblies, composites and polar polymers as well as organometallics[5,6] have been investigated for second-order non-linear optics. NLO materials can also be prepared by grafting NLO chromophores to amorphous organic polymer backbones and then poling them under high electric fields to generate non-centrosymmetric structures. Because of the ease of tailoring of organic molecules, this approach is quite convenient for designing and obtaining novel processible NLO materials. Furthermore, ease of fabrication into desired configurations makes NLO chromophore functionalized polymers more interesting since they can be integrated with inorganic semiconductors and other optical interconnectors. In particular, poly(methyl methacrylate) and polystyrene backbones have been mainly utilized for chemically attaching NLO moieties because these amorphous polymers possess high optical quality and material processibility.

In the quest to find potential applications for SHG materials in opto-electronics, organic NLO materials that have large second-order optical non-linearity coupled with high optical transparency are required. Electron donor–acceptor substituted benzene, stilbene, azobenzene, benzylidene or tolane derivatives make it difficult to achieve the desired optical transparency for frequency doublers since the non-linear efficiency transparency trade-off depends on the nature of the incorporated conjugated NLO moieties and polymer matrices. Bearing in mind the efficiency–transparency requirement, we have developed a novel organic polymeric system consisting of urea with no pendant NLO chromophores; instead NLO active urea moieties constitute the main polymer backbone. This main-chain NLO polymer shows large second-order optical non-linearity and simultaneously excellent optical transparency. In this communication, we report the second-order non-linear optical properties of an *N*-phenylated aromatic polyurea having the following chemical structure:



$$\left[\underset{\bigcirc}{\mathrm{N}}-\mathrm{CH_2}-\bigcirc-\mathrm{CH_2}-\underset{\bigcirc}{\mathrm{N}}-\mathrm{CO}-\mathrm{NH}-\bigcirc-\mathrm{CH_2}-\bigcirc-\mathrm{NH}-\mathrm{CO}\right]_n$$

The newly developed aromatic polyurea films show SHG efficiency as large as 14 times that of potassium dihydrogen phosphate (KH_2PO_4) crystals and has an absorption cut-off wavelength at 307 nm. Aromatic polyurea shows thermal stability up to 290°C in air and excellent environmental stability over a long time period.

Experimental

The *N*-phenylated aromatic polyurea was synthesized by reacting an equimolar mixture of α,α'-dianilino-*p*-xylene with 4,4′-diphenylmethane diisocyanate using the method described by Oishi *et al.*[9]. In our procedure, the polymerization reaction was carried out in *sym*-tetra-

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chloroethane solvent under nitrogen atmosphere at 80°C over a 12 h period. The polymer was purified and dried under vacuum at 60°C. The polymer was characterized by employing various spectroscopic techniques. The ^{1}H n.m.r. spectrum was recorded in chloroform solution at room temperature on a JEOL n.m.r. spectrometer (model JNM-GSX400 FT-NMR), at 400 MHz. Optical absorption spectra of spin-coated thin films and chloroform solution were recorded using a Hitachi spectrophotometer (model 330). Thermal stability of polyurea was recorded by a Shinku-Riko differential thermogravimetric analyser (ULVAC model TGD 7000) using nitrogen as the purge gas at a heating rate of 10°C min^{-1}.

Transparent polyurea thin films on conducting glass slides were prepared by spin coating at 80°C. The thickness of polyurea films used in the SHG measurements was 0.2 μm. The corona poling of thin films was done at 130°C (above T_g) using an electric field of 6–8 kV for 60 min. The samples were then cooled down to room temperature under the influence of the same electric field. No dielectric breakdown of thin films was noticed. This thermoelectret technique assists in molecular alignment since dipoles can easily rotate in the glassy state under high electric field[10], therefore it introduces a non-centrosymmetry. The SHG experiments were performed as described elsewhere[11]. A Q-switched Nd: YAG laser operating at 1.064 μm fundamental wavelength was used. The pulse width was 10 ns and the repetition rate was 10 Hz. The second-order NLO susceptibility was measured by the Maker fringe method by scanning the incident angle.

Results and discussion

The ^{1}H n.m.r. spectrum recorded in chloroform solution at room temperature confirmed the chemical structural formula of the *N*-phenylated aromatic polyurea. The thermal stability of polyurea was investigated by thermogravimetric analysis (t.g.a.) at a heating rate of 10°C min^{-1} and the polymer was thermally stable up to 290°C in air. Aromatic polyurea has a glass transition temperature (T_g) around 123°C. The *N*-phenylated aromatic polyurea is highly soluble in a variety of organic solvents and can be cast into flexible, colourless and transparent stiff films. *Figure 1* shows the optical absorption spectra of aromatic polyurea thin films coated on glass slides as well as polymer solution in chloroform. Both spin-coated film and solution spectra show an absorption maximum at 253 nm and the cut-off wavelength was 307 nm. Mostly organic molecular and polymeric NLO materials[1–6] have cut-off wavelength over ~500 nm. The cut-off wavelength of aromatic polyurea is about 200 nm shorter than those of other organic NLO materials. With this unique optical transparency, polyurea films can be used as a frequency doubler for applications in semiconductor and u.v. lasers. Aromatic polyurea is the first example of an organic NLO polymer that can be used at such low fundamental wavelengths.

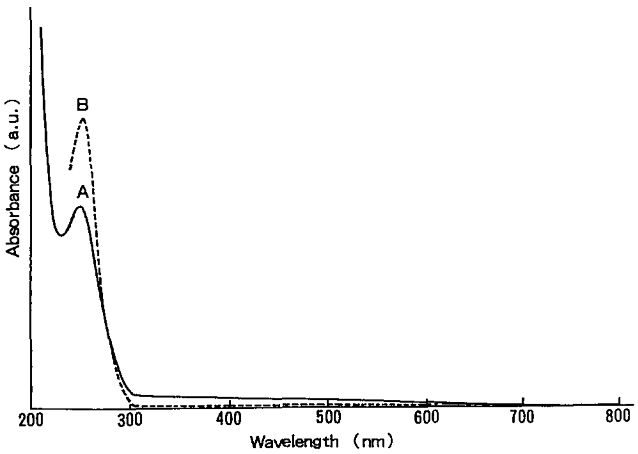

Figure 1 Optical absorption spectra of aromatic polyurea thin film spin-coated on a glass substrate (A) and in chloroform solution (B)

The poled polymers belong to point group ∞ mm. Among five non-zero tensor components, three components are independent[12]. The non-zero *d* coefficients for a poled polymer film are $d_{31} = d_{21}, d_{33}$ and $d_{15} = d_{24}$. For a corona poled film which is *p*-polarized, the d_{eff} is written as:

$$d_{\text{eff}} = 2d_{15}\cos\theta_1\sin\theta_1\cos\theta_2 + \sin\theta_2(d_{31}\cos^2\theta_1 + d_{33}\sin^2\theta_1) \qquad (1)$$

From Kleinman symmetry[13], $d_{15} = d_{31}$ and for a poled polymer film $d_{31} = 1/3d_{33}$ (ref. 14). The typical Maker fringe curve for a corona poled polyurea film as a function of incident laser beam angle was recorded. A quartz plate was used as the reference ($d_{11} = 1.19 \times 10^{-9}$ esu)[15]. The non-linear d_{33} coefficient was determined by comparison to d_{11} of quartz and the SHG measurements for a corona-poled thin film showed d_{33} coefficient to be 13×10^{-9} esu which is 11 times the d_{11} of quartz. The d_{31} coefficient was estimated to be 4×10^{-9} esu. Eckardt *et al.*[16] reported absolute and relative NLO coefficients of KDP, $d_{36} = 0.38$ pm V^{-1}, barium metaborate (BaB_2O_4) $d_{22} = 2.2$ pm V^{-1} and potassium titanyl phosphate (KTP), $d_{\text{eff}} = 3.2$ pm V^{-1} by phase-matched SHG at 1.064 μm*. From experimental parameters, the NLO d_{33} coefficient from SHG measurements of aromatic polyurea was estimated as follows:

$$d_{33} = 14.5 \times d_{36}\text{KDP}(d_{36} = 0.907 \times 10^{-9}\,\text{esu})$$

It can be seen that second-order optical non-linearities of polyurea films are large, exceeding the SHG coefficients of classical inorganic single crystals such as LiB_2O_5, β-BaB_2O_4, KDP and $NH_4H_2PO_4$. On the other hand, SHG efficiency is also larger or comparable to NLO chromophore grafted organic polymers[4] and 4 times larger than urea (non-linear coefficient = 1.4 pm V^{-1})[17].

The observation of a large second-order optical non-linearity in aromatic polyurea is surprising. The *N*-phenylated polyurea structure has two active groups arranged in the polymer backbone so that the longitudinal dipoles cancel leaving a resolved transverse component. Furthermore, the polyurea backbone has a bulky segment that also dilutes the NLO contribution. A possible explanation for the large optical non-linearity may be the role of the interchain hydrogen bonding that contributes in aligning of dipoles under the influence of the electric fields generated by the corona poling. As a result, the overall NLO contribution arising from the polyurea backbone is large. It is also important to mention that polyurea belongs to a different class of materials called 'piezoelectric polymers' which are inherently active to NLO responses[10,18]. Examples of piezoelectric polymers are poly(vinylidene fluoride) and

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* 1 pm V^{-1} = 2.387×10^{-9} esu

its copolymers with trifluoroethylene and tetrafluoroethylene, odd nylons, and copolymers of vinylidene cyanide[10].

No decay in d_{33} was measured for several hours. Since aromatic polyurea has no pendant NLO chromophores and is a polymer with main-chain chromophores, the relaxation process, if any, is assumed to be very slow. Furthermore, hydrogen bonding may also play a significant role in retaining optical non-linearity of polyurea systems. The aromatic polyurea forms mechanically stiff thin films which have a tensile strength equal to that of nylon 66 and polystyrene[19]. Aromatic polyureas are easy to process and show good environmental stability. Therefore, the present study shows aromatic polyurea to be a high performance NLO material. The polyurea backbone also offers many possibilities of chemical modifications to tailor high performance NLO materials with desired optical transparency and large optical non-linearity[20] and further investigations are now in progress.

Conclusions

We have demonstrated a new NLO material composed of urea polymer backbone, which exhibits a large second-order optical non-linearity comparable to classical inorganic and organic NLO materials. This main-chain NLO polymer of urea is the first example of an NLO polymeric material that shows optical transparency down to 307 nm in the u.v. region of the spectrum. The extremely low cut-off wavelength allows non-resonance enhanced frequency doubling of fundamental wavelengths as low as 615 nm, making aromatic polyurea a potentially useful material for semiconductor and u.v. lasers.

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