

SYNTHESIS OF A NOVEL SELF-ASSEMBLING NLO POLYMERIC FILM*

Shou-fa Han, Dao-rong Dai, Ze Li, Gang Wu and Rong-ben Zhang**
PCLCC***, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

Abstract By covalently binding chromophore NPP, *N*-(4-nitrophenyl)-(L)-prolinol, to a structurally controlled cage-like cross-linking polymer (SCCP), a modified nonlinear optical (NLO) polymeric film prepared by “*in situ*” poling and sol-gel” process successfully overcame the fundamental problem of NPP chromophores subliming out from the cages of the “doped” NLO polymeric film when heated or placed under UV light. Its d_{33} (coefficient of second harmonic generation) is 2.0×10^{-8} esu. measured by IR dichroism. The modified film has a low decay of the SHG signal and preserves 94% of the initial value after 50 days at room temperature. These properties match that of the “doped” film, indicating that the modified film also retains the main advantages of the “doped” film.

Keywords Self-assembling, Orientation, Covalently linked, Sol-gel process

INTRODUCTION

Polymeric materials with second-order NLO properties are of much interest for future applications^[1-3]. For such a material, its important properties include high coefficient of second harmonic generation (SHG) and low decay of its signals^[4]. The size of SHG signal depends on the type of the chromophore used, chromophore number densities and the efficiency of the orientation of chromophores and efforts have been made on those aspects to obtain a high SHG signal^[5-7]. The decay of the SHG signal results from the structural relaxation of the polymer chains and the randomization of chromophores. A variety of methods have been explored to lower the decay of the SHG signal^[8-11]. However, it is of great difficulty to obtain a polymeric film having both properties concurrently.

Enlightened by many new supermolecular structures such as C_{60} molecularly trapped in zeolite^[12], a new method that NPP chromophores were dispersed molecularly to the cages of SCCP each of which can just hold one NPP molecule and so fix the orientation of the chromophore has been explored in our group^[13, 14] to obtain a polymeric film with both a high SHG signal and low decay of the signal. A “doped” NLO polymeric film prepared by this method was uniform and transparent when the molar ratio of chromophore/organosilicon space was 1:1 (50 wt%) without any phase separation. Meanwhile, for doped NLO materials, the chromophore content was usually about 10 wt%^[15]. The high chromophore content gave rise to a high SHG signal ($d_{33} = 3.0 \times 10^{-8}$ esu.). The “doped” film had low decay of its SHG signal and preserved 95% of its initial value

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** Corresponding author: Rong-ben Zhang (张榕本), E-mail: zhangrb@info3.icas.ac.cn

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after 30 days at 65°C. However, when the “doped” NLO film was heated to 140°C or placed under UV light, the NPP molecules sublimed out from cages of the polymer. In this paper, NPP molecules were covalently bound to the SCCP as if they were “doped” to the cages of the polymer and thus, overcame the basic problem of the “doped” polymeric NLO film.

EXPERIMENTAL

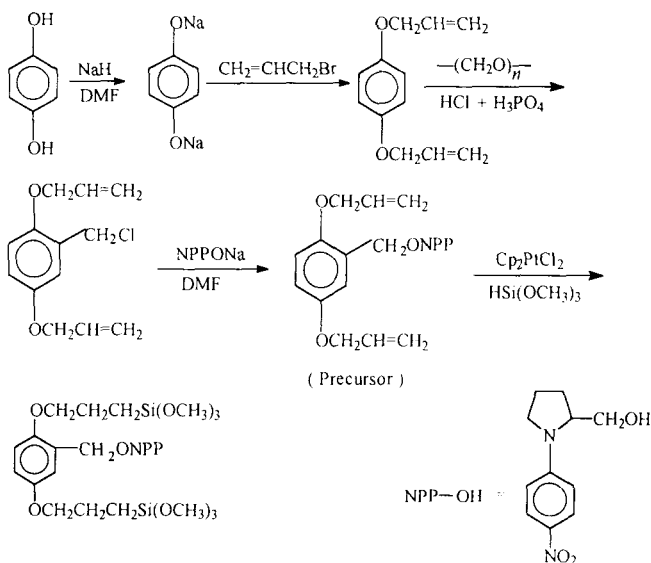
Materials

Hydroquinone (HQ), NaH and paraformaldehyde were commercially available and of analytical grade, N,N-dimethylformamide (DMF) was purified by distillation over Na₂SO₄. Trimethoxysilane was prepared according to Wu^[16] (b.p. 81–82 °C), chromophore NPP was prepared following Zyss^[17]. 1-Methyl-2-pyrrolidinone (MPD) was purchased from Aldrich. Column chromatographic separations were carried out using 100–200 mesh silica gel.

Characterization

The FT-IR determination was performed on an IFS 113V-FTIR. The ¹H-NMR measurement was carried out on an Unity 200 analyser of Varian Co. UV-vis spectra were recorded on a Hitachi-340 analyser and the MS investigation was carried out on a ZHP-5A (FAB) instrument.

Procedure



Scheme 1 Synthetic route for the monomer

Synthesis of *p*-Diallyloxybenzene (DAB)

22 g (0.2 mol) HQ in 50 mL DMF was placed in a 500 mL three-necked round-bottom flask flushed with dry argon. 250 mL DMF and 24 g NaH were added and stirred at 150°C for 0.5 h. The reaction mixture was stirred additionally for 2 h before it was cooled to 60°C and 150 mL allyl bromide was added. Then the mixture was further stirred for 3 h at 90°C. Subsequently, it was filtered to obtain a solution. DMF was removed and the residue was extracted with 400 mL CH₂Cl₂. The CH₂Cl₂ solution was washed with 500 mL 1.0 mol/L NaOH and HCl solutions, respectively. Then CH₂Cl₂ was removed from the solution and the residue was distilled under reduced pressure to obtain crude DAB (125–130°C/5 mmHg), which was then recrystallized from hexane to get 35 g (in 95% yield) white flaky crystal, m.p. 33°C.

The elemental analysis gave: calcd (%): C 75.76, H 7.42, O 16.81; found (%): C 75.68, H 7.46, O 16.70.

$^1\text{H-NMR}$ (CDCl_3 , δ) 4.5 (*d*, 4H, $=\text{CH}_2$), 5.2~5.4 (broad, 4H, OCH_2), 5.9~6.2 (broad, 2H, $=\text{CH}$), 6.8~6.9 (*s*, 4H, phenyl)

Synthesis of 2-Chloromethyl DAB

A mixture of 5.0 g (0.03 mol) DAB in 20 mL *n*-hexane, 1.0 g paraformaldehyde, 30 mL concentrated hydrochloric acid and 10 mL H_3PO_4 in a 150 mL round-bottom flask equipped with a reflux condenser was stirred for 24 h at 40°C . The organic layer was distilled to remove hexane and the residue was purified by column chromatography to obtain 3.0 g (in 50% yield) 2-chloromethyl-DAB which is a transparent liquid at room temperature.

MS: $M = 238$. $^1\text{H-NMR}$ (CDCl_3 , δ) 4.5 (broad, 4H, OCH_2), 4.65 (*s*, 2H, CH_2Cl) 5.2~5.5 (broad, 4H, $=\text{CH}_2$), 5.9~6.1 (broad, 2H, $=\text{CH}$), 6.7~6.8 (*d*, 2H, 5,6-H in phenyl), 6.9 (*s*, 1H, 3-H in phenyl)

Synthesis of the Precursor

0.7 g 2-chloromethyl-DAB in 10 mL DMF was added to a three-necked round-bottomed flask previously flushed with dry argon in which 1.0 g NPP in 20 mL DMF was stirred with 0.6 g NaH for 0.5 h at about 20°C . The mixture was stirred for another 0.5 h and poured into 100 mL H_2O to get a yellow solid. The solid was crystallized from ethanol to obtain 0.8 g yellow crystal in 60% yield, m.p. $93.0\sim93.5^\circ\text{C}$.

MS: $M = 424$. $^1\text{H-NMR}$ (CDCl_3 , δ) 2.0~2.2 (broad, 6H, H in pyrrolidine in NPP) 3.2~3.7 (broad, 2H, H in OCH_2 in NPP), 4.0 (*s*, 1H, N-CH-R in NPP), 4.4 (*t*, 4H, $=\text{CH}_2$), 4.5~4.6 (*s*, 2H, CH_2O in NPP), 5.2~5.4 (broad, 4H, OCH_2 in DAB), 5.9~6.2 (broad, 2H, $-\text{CH}=\text{}$ in DAB), 6.75 (*d*, 2H), 6.95 (*s*, 1H; phenyl in DAB), 6.6 (*s*, 2H), 8.0~8.2 (*d*, 2H, phenyl in NPP).

The elemental analysis gave: Calcd (%): C 67.91, H 6.65, O 18.84, N 6.60; found (%): C 67.87, H 6.72, O 18.80, N 6.63.

Synthesis of the Monomer

0.7 g crystal of the precursor, 0.7 mL $\text{HSi}(\text{OCH}_3)_3$ and 0.3 mL (1 mg/mL) solution of CP_2PtCl_2 in THF were added into a 25 mL three-necked round-bottom flask previously flushed with dry argon and stirred for 40 h at 60°C . Then the unreacted $\text{HSi}(\text{OCH}_3)_3$ was removed by distillation and 5 mL of 1-methyl-2-pyrrolidinone (MPD) was added, thus, a monomer solution formed.

IR spectrum (cm^{-1}): 2943 CH_3 , 2842 $-(\text{CH}_2)_3-$, 1089 $\text{Si}-\text{O}-\text{C}$ and 1230 $\text{R}-\text{O}-\text{C}$.

Preparation of the NLO Film by "In-situ Poling and Sol-Gel Process"

4 drops of the monomer solution (0.5 mol/L) were dropped onto the clean surface of a glass plate or a NaCl plate ($1.5\text{ cm} \times 1.2\text{ cm}$). Then the film was placed in a corona discharge poling system under the following conditions: $E = 5000\text{ V/cm}$, $T = 60^\circ\text{C}$, $t = 0.5\text{ h}$; $T = 100^\circ\text{C}$, $t = 22\text{ h}$. Then the film was cooled to room temperature with E unchanged.

Characterization of the Modified NLO Polymer Film

The IR dichroism modified NLO film was measured according to Ye^[18]. The d_{33} was 2.0×10^{-8} esu.

The investigation of the decay of the film was measured by UV spectroscopy. The absorption spectrum of a unpoled film was first measured so as to compare with that of the same film measured regularly over a period of 50 days after poling. Each time before the measurement of NLO polymer film, the UV detector was first rectified using an unoriented film to remove the variations of the detector under different conditions (the result is shown in Fig. 1).

RESULTS AND DISCUSSION

Synthesis of DAB

In the preparation of DAB, when tetrahydrofuran (THF) was used as the solvent and Na was

replaced with NaH, the yield was only 30%. During the reaction, disodium hydroquinone and NaBr formed was insoluble in THF, therefore, the reaction mixture became too viscous to be stirred and disodium hydroquinone was covered by NaBr, so the reaction was impeded.

Improved synthesis of DAB was explored. We substituted THF for DMF to make more disodium hydroquinone dissolve in the solvent, so the problem mentioned above was overcome. The temperature of the reaction mixture was cooled to 60 °C to add allylbromide so that the temperature of the reaction mixture was below the boiling temperature of allyl bromide. Through the two approaches above, the product was obtained in 95% yield.

Chloromethylation of DAB

In order to get 2-chloromethyl-DAB in high yield, we have tried various reaction conditions, i.e. catalysts: SnCl₄, ZnCl₂, HCl and so on; solvents: CH₂ClCH₂Cl, CS₂, CH₂Cl₂, C₆H₁₄, CH₃COOH and mixed solvents; chloromethylation reagents: CH₃OCH₂Cl and ClCH₂O(CH₂)₄OCH₂Cl and under different temperatures from -20 °C to 60 °C. However, the yield was very low.

It was very difficult to chloromethylate DAB, because the substituting groups of DAB are electron donors which greatly activate the molecule in electrophilic reactions to produce analogous oligomer or polymer as the product of phenol formaldehyde resin. Finally, in the presence of conc. hydrochloric acid, H₃PO₄ and -(CH₂O)_n-, DAB in n-hexane (CH₂O/DAB = 1.2:1 in molar ratio) was chloromethylated at 50 °C to obtain 2-chloromethyl-DAB. The product (in 50% yield) was purified by column chromatography.

Synthesis of the Precursor

The precursor, a new compound, was prepared via the Williamson reaction. The yield was only 10% when the precursor was synthesized by the following procedure: NaH was added to the solution of NPP in DMF and stirred at 50 °C until no NPP can be detected by TLC. Then 2-chloromethyl-DAB was added into the reaction mixture and stirred. However, when the amount of DMF was doubled to render more NPPONa to be dissolved and the temperature of the reaction system was kept at room temperature, the yield increased to 60%. The reasons are that the by-product of the reaction, which is a red polymer, can be greatly reduced at room temperature and NaH can react with NPP effectively at room temperature.

Synthesis of the Monomer via Hydrosilylation

In the hydrosilylation of the precursor, the catalyst chosen for this reaction is Cp₂PtCl₂. The catalyst is stable under the reaction conditions of this reaction system and is very efficient. An excess amount of trimethoxysilane was added to increase the yield. When the reaction was finished, unreacted trimethoxysilane was removed by distillation. The IR spectrum of the target product shows that there were no absorption peaks of Si-H (2240 cm⁻¹) and C=C (1640 cm⁻¹), indicating that 2-chloromethyl-DAB was hydrosilylated completely and no trimethylsilane was left.

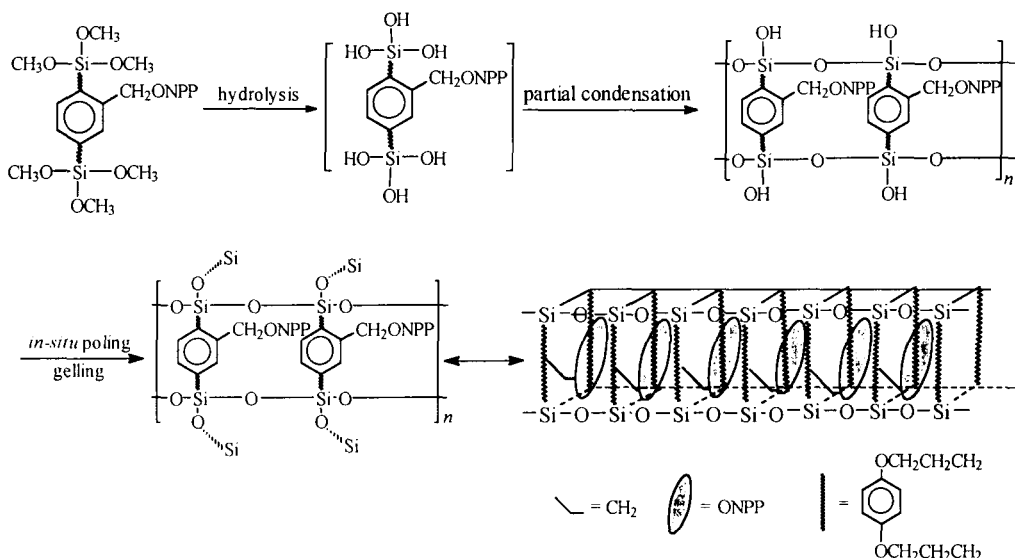
Preparation of the Modified NLO Polymeric Film

In the "sol-gel" process, evaporation of the solvent, orientation of the NPP molecules and crosslinking of the polymer take place *insitu* concurrently. In order to make a desirable transparent polymeric film without bubbles, MPD (b.p. 202 °C) was chosen as the solvent and its evaporation rate must be controlled. Using other solvents, such as THF, the evaporation rate was too fast to be controlled. In our experiments, the monomer solution was purified by column-chromatography to remove tiny crosslinked particles formed during the hydrosilylation process. The system was heated from 20 °C to 90 °C within 30 min. Then, the film was placed in an electric field and poled for 22 h and then cooled to the room temperature with E unchanged. A modified NLO film was obtained.

Stability of the Modified NLO Polymer Film

NPP chromophores may sublime out from the cages of the “doped” NLO film. When the “doped” polymer film was placed under UV light, its yellow appearance gradually faded and finally became colorless. When the “doped” film was heated at 140°C, NPP molecules aggregated beneath the bottom of the watch-glass that covered the “doped” film.

To prevent NPP chromophores from escaping from a NLO film and keep other advantages of the “doped” film, a monomer was synthesized by covalently binding NPP⁺ to the precursor. Once the novel modified NLO polymer film was constructed from the monomers, NPP⁺ seemed to be nailed to the wall of the cage of the polymer (Scheme 2). The modified NLO film was stable under 140°C or under UV light. This means that, by “nailing” NPP to the wall of the cage with a chemical bond, NPP molecules cannot escape from the cage under high temperature or under UV light. It indicates that the modified film has improved thermal stability, and the main defect of the “doped” NLO polymer has been successfully overcome.



Scheme 2 Formation of the modified NLO film

Properties of the Modified NLO Polymer Film

The d_{33} of the modified NLO polymeric film was 2.0×10^{-8} esu., which was almost unchanged with the elapse of time (Fig. 1). This value is equal to the corresponding coefficient of LiNbO_3 , thus, the modified NLO polymer has its potential applicability.

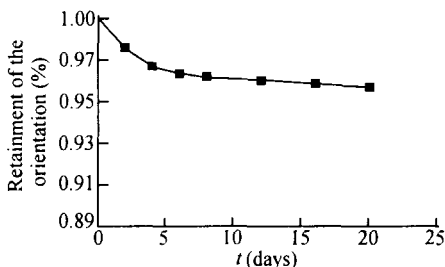


Fig. 1 Stability of the modified NLO film in time

The relation between the retainment of the orientation of chromophores and the time after poling was shown in Fig. 1. The SHG signal preserved 94% of its initial value after 50 days at ambient conditions, indicating that the decay of the SHG signal was very slow.

CONCLUSION

In conclusion, the modified NLO polymeric film has a better thermal stability than the “doped” NLO polymeric film. Other properties of the modified NLO polymeric film are comparable to that of the “doped” NLO polymeric film, and this means that the modified film maintains all the advantages of the “doped” film.

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