

PREPARATION AND SECOND-ORDER OPTICAL NONLINEARITY OF NOVEL PHENOXYSILICON NETWORKS BY SOL-GEL PROCESS*

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Abstract Four phenoxy-silicon networks for nonlinear optical (NLO) applications were designed and prepared by an extended sol-gel process without additional H₂O and catalyst. All poled polymer network films possess high second-order nonlinear optical coefficients (d_{33}) of 10^{-7} ~ 10^{-8} esu. The investigation of NLO temporal stability at room temperature and elevated temperature (120°C) indicated that these films exhibit high d_{33} stability because the orientation of the chromophores are locked in the phenoxy-silicon organic/inorganic networks.

Keywords Phenoxy-silicon networks, Sol-Gel process, Azobenzene chromophore, Stilbene chromophore, Second order optical nonlinearity

INTRODUCTION

Sol-gel technology provides an attractive route for the preparation of chromophore-containing networks^[1-4]. There are many advantages of the sol-gel process to produce hybrid materials with nonlinear optical (NLO) properties, such as good optical quality, high thermal stability, ease of fabrication, etc.. The NLO phenoxy-silicon networks produced by the reaction of trialkoxysilane with aromatic hydroxyl groups exhibit high NLO stability^[5].

In this article, four kinds of NLO phenoxy-silicon were designed and synthesized by an extended sol-gel process through the alcoholysis of trialkoxysilane with the aromatic hydroxyl groups of chromophore-containing glycidyl phenolic resin. After poling and crosslinking of these phenoxy-silicon sol films at 170°C, the second-order NLO coefficient (d_{33}) and the decay of d_{33} as a function of time at room temperature and 120°C were investigated.

EXPERIMENTAL

Materials

4-Nitroaniline (AR, Shanghai Chemicals) was recrystallized before use. 4-Nitrophenylacetic acid, 4-nitro benzaldehyde, 2-methoxy-, 4-hydroxy-benzaldehyde (Aldrich) and poly(phenyl glycidyl ether)-*co*-formaldehyde (Aldrich, Ph100, M_n = 605, 3.8 epoxide groups per molecule) were used as received. Benzyltriphenyl phosphonium chloride (BPC) was prepared as described in Ref. [6]. Phenol (AR, Guangzhou Chemicals) and Epichlorohydrin (AR, Shanghai Chemicals) were distilled under reduced pressure. Dioxane (DOX, AR, Shanghai Chemicals) and Amberlite IRA-400 (Cl) (Heidelberg product) were used as received. γ -Glycidioxypropyl trimethoxysilane (GOTMS, CP) was distilled under reduced pressure.

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Synthesis of Chromophores

4-Nitro-4'-hydroxy-azobenzene (NHA)

NHA was prepared as described in Ref. [7]. FT-IR (KBr, cm^{-1}): 3444 ($-\text{OH}$); 1582, 1461 (benzene ring); 1510, 1342 ($-\text{NO}_2$); 1278 ($=\text{C}-\text{O}$); 857 ($-\text{C}-\text{NO}_2$). Elemental analysis: Calc. for $\text{C}_{12}\text{H}_9\text{N}_3\text{O}_3$ (%): C 59.26, H 3.37, N 17.28; found: C 59.15, H 3.65, N 17.80. ^1H -NMR ($\text{CDCl}_3/\text{DMSO}-d_6$, δ): 9.86–9.96 (s, 1H, OH); 8.24–8.42 (d, 2H, *ortho* to $-\text{NO}_2$); 7.80–8.12 (t, 4H, aromatic, *ortho* to $-\text{N}=\text{N}-$); 6.92–7.10 (d, 2H, aromatic).

4-Nitro-4'-hydroxystilbene (NHS)

NHS was prepared as described in Ref. [8]. FT-IR (KBr, cm^{-1}): 3410 ($-\text{OH}$); 1630 ($-\text{C}=\text{C}-$); 1510, 1335 ($-\text{NO}_2$). Elemental analysis: Calc. for $\text{C}_{14}\text{H}_{11}\text{NO}_3$: C 69.70, H 4.60, N 5.81; found: C 68.97, H 4.53, N 5.55. ^1H -NMR ($\text{CDCl}_3/\text{DMSO}-d_6$, δ): 9.2 (s, 1H, OH); 8.14–8.24 (d, 2H, *ortho* to $-\text{NO}_2$); 7.55–7.65 (d, 1H, $\text{CH}=\text{CH}$ *trans*); 7.37–7.47 (4H, *ortho* to $-\text{C}=\text{C}-$); 7.0–7.2 (d, 1H, $\text{CH}=\text{CH}$, *cis*); 6.8–6.9 (d, 2H, aromatic)

4-Nitro-2'-methoxyl-4'-hydroxystilbene (MNHS)

MNHS was prepared by the procedure as NHS. FT-IR (KBr, cm^{-1}): 3493 ($-\text{OH}$); 1630 ($-\text{C}=\text{C}-$); 1496, 1328 ($-\text{NO}_2$); 1257 ($-\text{O}-\text{CH}_3$). Elemental analysis: Calc. for $\text{C}_{15}\text{H}_{13}\text{NO}_4$: C 66.41, H 4.83, N 5.16; found: C 66.64, H 4.73, N 5.16. ^1H -NMR (CDCl_3 , δ): 8.20–8.22 (2H, *ortho* to $-\text{NO}_2$); 7.59–7.61 (2H, nitro-phenyl, *ortho* to $-\text{C}=\text{C}-$); 7.18–7.22 (1H, $\text{CH}=\text{CH}$, *ortho* to nitrophenyl); 7.00 (1H, $\text{CH}=\text{CH}$); 7.07–7.09 (2H, *ortho* to $-\text{C}=\text{C}-$); 3.975 (3H, $-\text{OCH}_3$); 6.93–6.94 (1H, *ortho* to $-\text{OH}$); 5.777 (1H, $-\text{OH}$)

Synthesis of Chromophore-Containing Phenolic Resin (CPR)

Preparation of phenolic resin

Phenolic resin ($M_n = 498$) was synthesized according to Ref. [9].

Synthesis of glycidyl phenolic resin (GPR)

Epichlorohydrin (0.26 mol) and KI (3.25 g) were dissolved in 65 mL acetone and stirred for 24 h at room temperature, then a calculated amount of the phenolic resin and K_2CO_3 were added. The mixture was filtered after being stirred and refluxed for 12 h. The filtrate was passed through an Amberlite resin column. The GPR was obtained after removing the solvent and unreacted epichlorohydrin from the solution. Yield $\approx 60\%$.

On changing the ratio of epichlorohydrin and phenolic resin and the reacting time, two kinds of phenolic resin were prepared. One was denoted Ph25 with a M_n of 565 and an epoxide number of 0.214; the other was denoted Ph50 with a M_n of 636 and an epoxide number of 0.371.

Synthesis of chromophore-containing phenolic resin (CPR)

Four kinds of CPRs were synthesized according to Scheme 1(A). The elemental analysis data and chromophore content are summarized in Table 1.

CPR and chromophore (molar ratio of epoxy group/OH=1:1.05) together with BPC (1 wt%) as catalyst were dissolved in dry DOX. The solution was stirred at 70°C for 0.5 h and then refluxed for another 3–4 h. After the reaction, the solution was cooled to room temperature. The product was isolated by precipitation, filtration and washed with distilled water and dried under vacuum to yield a red powder CPR.

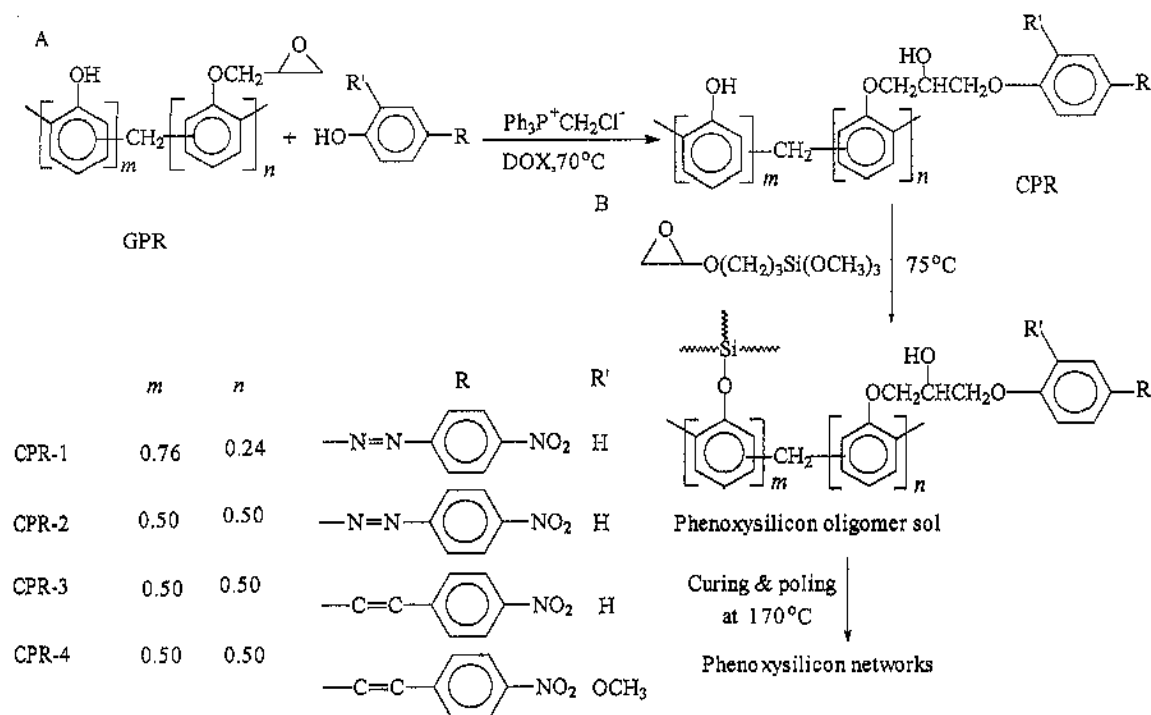
The Sol-Gel Process

The respective CPR sols were prepared by the alcoholysis of GOTMS with different CPRs at 70°C in DOX without additional H_2O and catalyst according to Scheme 1(B).

Instrumentation

^1H -NMR spectra were obtained on a JEOL FX 90Q NMR spectrometer, IR spectra were recorded on a Nicolet 205 FTIR spectrometer, and ultraviolet-visible spectra were taken on a Shimadzu 240 spectrophotometer. Elemental analysis was performed with a Perkin-Elmer 240 elemental analyzer. Number-average molecular weights of GPRs were measured with a VPO instrument (Karl Kolb GmbH Co. KG No.11.00), using diphenyl

ketone as the standard and butanone as the solvent. T_g was obtained from a differential scanning calorimeter (DSC) using a Perkin-Elmer DSC-7c at a heating rate of 10 K/min under nitrogen. The thermal degradation was determined by a TA instrument TGA with a heating rate of 10 K/min.



Scheme 1

Table 1. Elemental analysis data and chromophore contents

CPR	C (wt%)		H (wt%)		N (wt%)		Chromo. cont. (wt%)		Degree of substitution (%)
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	
1	71.5	73.1	5.13	5.30	5.67	5.12	40.5	36.6	90.3
2	68.1	70.1	6.26	6.42	8.22	7.73	58.7	55.2	94.0
3	73.1	74.9	5.30	5.39	2.75	2.51	58.4	53.3	91.3
4	71.2	73.2	5.38	5.42	2.60	2.39	61.0	56.1	92.0

The calc. values were calculated on the assumption that all the epoxy groups of GPRs were substituted by chromophores. In the same way, the calc. chromo. cont. and the degree of substitution were obtained.

Film Preparation

Films were prepared by spin-coating the DOX solutions of CPR sols onto transparent glass, quartz and silicon substrates, respectively. The films were air-dried in a desiccator for 2 days, then vacuum-dried at 50 °C for 2 h. The typical thickness of the films was about 3 μm. The respective films prepared from CPR 1, 2, 3, 4 were denoted Ph25AS, Ph50AS, Ph50SS, Ph50MSS respectively.

Poling and NLO Measurement

The poling was performed in a corona poling field under 8 kV voltage. The films were poled and crosslinked at 170 °C for 1 h, then cooled immediately to 30 °C to freeze the alignment of chromophores. The SHG measurement set-up was shown in our previous paper^[10]. Calculation of the d_{33} value was described in Ref. [11]. The temporal stability of the films was studied by the decay of d_{33} as a function of time at room temperature and 120 °C.

RESULTS AND DISCUSSION

Formation of Phenoxysilicon Polymer Networks

Trialkoxysilane can react with aromatic hydroxyl group to form a phenoxysilicon compound possessing excellent thermal stability^[12]. Thus, novel phenoxysilicon networks were synthesized by alcoholysis of GOTMS with the aromatic hydroxyl group of CPR (at molar ratio $\text{OCH}_3/\text{OH} = 1$) in DOX at 75°C without additional H_2O and catalyst.

In order to obtain uniform and good rheological sol, this extended sol-gel process has to be controlled carefully. Miscellaneous factors such as the amount of solvent DOX (conc. of precursor solution), the reaction temperature and time of alcoholysis, molar ratio of aromatic OH and OCH_3 play an important role in this process.

This extended sol-gel process involves the alcoholysis and condensation of silicon alkoxide, which was monitored by FTIR at different time intervals. Figures 2 and 3 are the FTIR spectra of Ph50SS before and after poling. Compared with the FTIR spectrum of GOTMS (Fig. 1), Fig. 2 shows the formation of Si—O—Ph (1257 and 960 cm^{-1}) and the obvious decreases of Si—OCH₃ stretching (1170 cm^{-1}) and unsymmetrical bending (1445 cm^{-1}) peaks in the sol stage. However, after poling, as shown in Fig. 3, the Si—O—Ph peaks (1257 and 960 cm^{-1}) become sharper and the Si—O—CH₃ peaks at 1445 and 1770 cm^{-1} almost disappear. The aromatic OH absorption at 3440 cm^{-1} also decreases dramatically, it indicates that the sol-gel system was further crosslinked at 170°C.

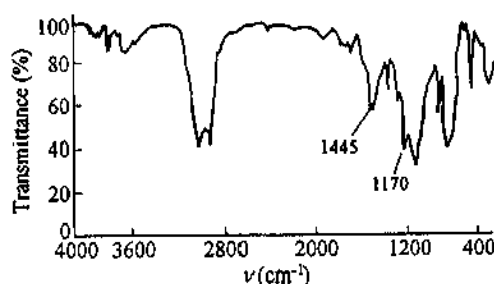


Fig. 1 IR spectrum for GOTMS

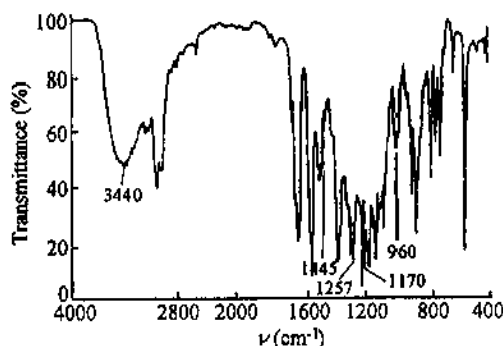


Fig. 2 IR spectrum for Ph50SS (pristine)

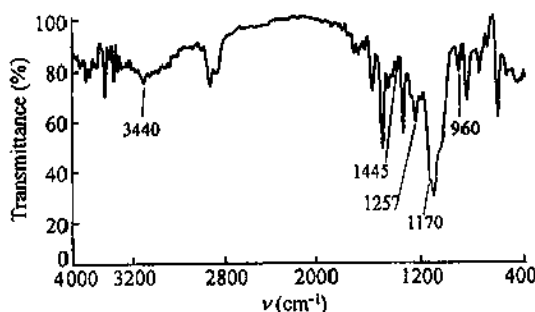


Fig. 3 IR spectrum for Ph50SS (cured)

SHG Measurement and SHG Decay at Various Temperatures

The SHG measurements of four films are shown in Table 2.

Figures 4–6 are the SHG decay curves of the four films under various temperatures. The d_{33} stability of the four films is quite good. At room temperature, as shown in Figs. 4 and 5, the major decay of d_{33} occurred during the first three days, then in the following one month, the d_{33} values kept almost unchanged. Furthermore, their d_{33} values remained over 77% after 3 h at 120°C (Fig. 6).

Table2. SHG results of phenoxysilicon networks

Sample	$E_f^{2\omega}$ (mJ)	$\chi^{(2)}$ (esu)	d_{33} (esu)
Ph25AS	1.324×10^{-10}	3.7×10^{-8}	1.85×10^{-8}
Ph50AS	4.987×10^{-10}	7.18×10^{-8}	3.59×10^{-8}
Ph50SS	9.539×10^{-9}	3.14×10^{-7}	1.57×10^{-7}
Ph50MSS	4.572×10^{-10}	6.87×10^{-8}	3.44×10^{-8}

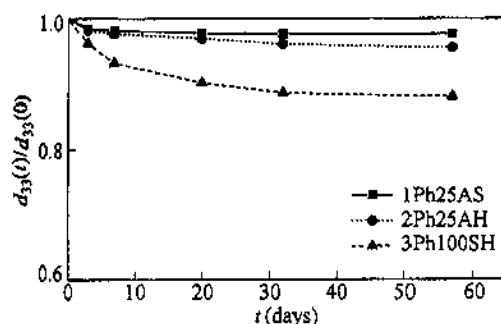


Fig. 4 SHG decay of Ph25AS, Ph25AH and Ph100 SH at room temperature

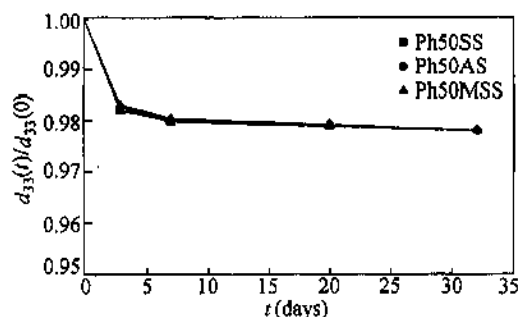


Fig. 5 SHG decay of Ph50AS, Ph50SS and Ph50MSS at room temperature

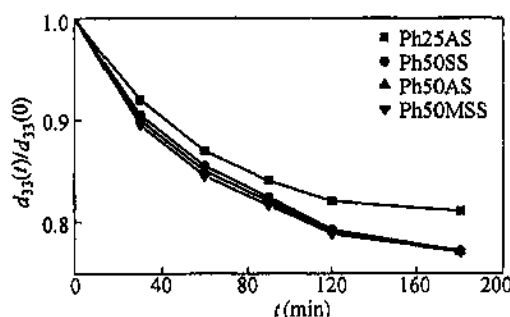


Fig. 6 SHG decay of Ph25AS, Ph50SS, Ph50AS and Ph50MSS at 120°C

To permit comparison with the traditional sol-gel process, two contrast experiments were conducted. Ph100, one kind of GPR purchased from Aldrich with all its aromatic OH substituted by epoxy groups, was used to synthesize Ph100NHA like other CPRs. Then an organic/inorganic hybrid network named Ph100SH was obtained by mixing Ph100NHS, GOTMS and water together to undertake a conventional sol-gel process at pH = 3 and room temperature. Another organic/inorganic hybrid network named Ph25AH was synthesized via the same process using CPR1.

Figure 4 illustrates the d_{33} decay curves of Ph25AS, Ph25AH and Ph100SH at room temperature. It indicates that Ph25AS has the best and Ph100SH has the worst d_{33} stability. These results may be attributed to the formation of phenoxysilicon networks after crosslinking. During the sol-gel process, Ph25AS might form part of the phenoxysilicon networks because the original GPR Ph25 still carried aromatic OH groups. In contrast, such a structure did not form in the case of Ph100SH because the aromatic OH groups of Ph100 were totally substituted by epoxy groups. According to the observations shown in Fig. 6, the d_{33} stability of Ph25AS at 120°C is comparatively high. This means the less the epoxy substitution of the original GPR, the more phenoxysilicon networks are finally formed. Thus the randomization of aligned chromophores is prevented in these organic/inorganic networks even at elevated temperature.

On the other hand, almost no difference of d_{33} stability has been found both at room temperature (Fig. 5) and 120°C (Fig. 6) between the various chromophore-containing phenolic resins derived from the same original GPR.

CONCLUSIONS

Four novel phenoxysilicon polymer networks were synthesized by an extended sol-gel process without additional H_2O and catalyst. These four poled polymer films exhibit fairly high d_{33} values and good d_{33} stability. Their d_{33} values remained over 97% of their original values for at least one month at room temperature, and remained over 77% of their original values after three hours at 120°C. These results indicated that the formation of phenoxysilicon networks could improve the NLO stability significantly.

REFERENCES

- 1 Kim, J., Plawsky, J.L., Lapesuta, R. and Korenowski, G.M., *Chem. Mater.*, 1992, 4: 249
- 2 Lindsay, G.A., *Trends Polym. Sci.*, 1997, 5(3): 91
- 3 Jeng, R.J., Chen, Y.M., Jain, A.K., Kumar, J. and Tripathy, S.K., *Chem. Mater.*, 1992, 4: 972
- 4 Novak, B.M. and Davies, C., *Macromolecules*, 1991, 24: 5481
- 5 Jeng, R.J., Chen, Y.M., Jain, A.K., Chen, J.L., Kumar, J. and Tripathy, S.K., *Macromolecules*, 1993, 26: 2530
- 6 Sherwood, D.W., Calvin, M., *J. Am. Chem. Soc.*, 1942, 64: 1350
- 7 Wang, B.R. "Organic Synthesis Reaction (2)", Academic Press, Beijing, 1985, p.771
- 8 Cullinare, N.M., *J. Chem. Soc.*, 1923, 123: 2053
- 9 Sorenson, W. and Campbell, T.W. "Preparative Methods of Polymer Chemistry", Interscience Publisher, Inc., New York, 1961, p.295-296
- 10 Liang, Z.X., Yan, X.Z., Chen, Y.L., Cai, Z.G., Yang, P.Q. and Xu, Z.L., *React. Funct. Polym.*, 1997, 32: 75
- 11 Kajikawa, K., Nagamori, H., Takezoe, H., Fukuda, A., Ukishima, S., Takahashi, Y., Ijima, M. and Fukada, E., *E. Jpn. J. Appl. Phys.*, 1991, 30 (10): 737
- 12 Claud, C., Gartz, B., Okamoto, Y. and Tripathy, S., *Mater. Lett.*, 1992, 14: 336