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# Novel photo-cross-linkable polymer bearing spindle-type chromophores for second-order non-linear optical materials

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**Abstract** A new strategy to tackle the orientation-relaxation of the chromophores was developed and used to prepare a film which was consisted of polymethyl methacrylate (PMMA) and photo-cross-linkable polyurethane oligomer (PU). The PU contained spindle-type chromophore and terminated with methacrylolyl groups as cross-linkable group. The chemical reaction process was characterized by infrared spectroscopy and the structure of reaction products were characterized by NMR spectroscopy. The surface morphology of the films was investigated by atomic force microscopy (AFM) images. The electro-optic (EO) coefficient of the prepared film was measured by using Teng-Man technique. The cross-linked films containing 15 wt% of the chromophore units displayed a high EO coefficient up to 41 pm/V. The 5% weight loss temperature was 228 °C for the film after photo-cross-linking. Compared with the uncross-linked films, their thermal and temporal stability were greatly improved.

## Introduction

Second-order non-linear optical (NLO) polymers have potential applications in photonic technologies such as high-speed optical communications, integrated optics, and optical data storage and processing [1–4], because of their large EO coefficients, ultrafast response time, low dielectric constant, small dispersion in the refractive index, structural flexibility, and easy process [5–9].

To achieve a large and stable second-order NLO properties for poled polymers, the temporal and thermal stability must be excellent. However, one of the critical problems in the development of second-order NLO polymers is that the chromophores relax from the non-centrosymmetric arrangement and the NLO character of the polymers decrease quickly with time, especially at elevated temperatures. Most of the current materials suffer from relaxation of the dipole alignments even at room temperature. Therefore, much research effort is needed to overcome this problem before these materials can be used in real devices. One method is synthetic polymer [10–14]. The other method to avoid this instability is to create a network while poling by the cross-linkable polymer. Several approaches have been taken in exploring cross-linkable NLO polymer materials, such as synthesizing thermosetting prepolymers containing NLO chromophore [15, 16]; synthesizing polymers with NLO chromophores in the side-chain and cross-linkable units on the main chain [17, 18]. All these approaches have been shown to be successful in stabilizing the macroscopic second-order optical non-linearities of the resulting polymers. However, the search for polymeric EO materials with sufficient $r_{33}$ values, excellent thermal and temporal stability is still an important challenge. The chromophores generally have to be improved for practical applications such as the orientation-relaxation.

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The structural architecture of the chromophore has greater effect on the temporal stability. The spindle-type chromophore is a two-dimensional chromophore, which requires larger rotational sphere volume than one-dimensional one. Therefore, the orientation-relaxation of this type chromophore molecule is difficult compared to other chromophores, and this is another approach to decrease relaxation of the dipole alignment.

In this article, we report a new family of PU with double-ended photo-cross-linkable groups and containing spindle-type chromophores. The spindle-type chromophore was successful prepared according to our previous method [19]. A preliminary study of the NLO properties of the film is presented. The film was cross-linked by UV-curing. And the cross-linked structure of the film constrained sterical movement of the chromophore segments and restrained the chromophoric orientation relaxing.

## Experimental

### Materials

Tetrahydronfuran (THF) was purified by fractional distillation over sodium with benzophenone as the indicator. When the color of the solution turned deep blue, we collected the middle fraction. 2-Hydroxyethyl methacrylate (HEMA, ACROS) was free from moisture under reduced pressure prior to use. We added hydroquinone as polymerization inhibitor to prevent polymerization of HEMA. 4, 4′-Methylenebis (cyclohexyl isocyanate) was purchased from Aldrich, and purified by distillation under reduced pressure before use. Dibutyltin dilaurate (DBTDL), dichloromethane, methanol, *N*,*N*-dimethylformide (DMF), and acetone were used as received, without further purification.

### Measurements

Nuclear magnetic resonance (NMR) spectra were measured on a Bruker AVANCE NMR spectrometer at a resonance frequency of 500 MHz for $^1$H in $CDCl_3$, and TMS was used as internal standard. IR spectra were taken on an AVATAR 360 FTIR spectrometer. The decomposition temperature of the films was analyzed by using Perkin-Elmer TGA 7 thermogravimetric analyzer (TGA) at a heating rate of 10 °C/min in nitrogen. Thermal degradation temperatures were measured in the range 50–700 °C. Ultraviolet–visible (UV–Vis) absorption spectra were measured on a SHIMADZUUV-3100 spectrophotometer. AFM images were recorded in the tapping mode with a Nanoscope IIIa scanning probe microscope from Digital Instruments under ambient conditions.

### Synthesis of NCO-terminated spindle-type chromophore

A 50-mL, three-necked, round-bottom flask containing chromophore (0.45 g, 0.743 mmol) was connected to a reflux condenser and purged with nitrogen for 30 min to remove the atmospheric moisture. 20 mL of dry THF and two equiv (0.39 g, 1.486 mmol) of 4,4′-Methylenebis (cyclohexyl isocyanate), 0.2 mL of Dibutyltin dilaurate (DBTDL) were added, and the reaction mixture was heated to 80 °C and maintained at this temperature for 12 h. The reaction may be considered to reach the completion when the content of the NCO group remained at a constant value for an additional 1 h of heating and the observed IR absorption peak of the NCO group at 2,265 cm$^{-1}$ unchanged comparing with the absorption peak of cyano group on IR spectrum in Fig. 2b. The product was purified by column chromatography on silica gel eluting with dichloromethane to give a red powder (0.723 g, 88%).

### Photo-cross-linkable polyurethane oligomer (PU)

Two equivalent amount of 2-HEMA (0.12 g, 1.04 mmol, according to NCO%) was added into NCO group terminated spindle-type chromophore (0.6 g, 0.52 mmol) through an addition funnel. The reaction mixture was agitated and kept at 80 °C under nitrogen atmosphere. The reaction was completed and stopped when the absorption peak of the NCO group at 2,265 cm$^{-1}$ disappeared in Fig. 2c. The product was purified by column chromatography on silica gel eluting with dichloromethane–methanol (50:1) to give a red powder 0.92 g (80%).

### Preparation of photo-cross-linkable thin films

Photo-cross-linkable PU/PMMA film was prepared by mixing 32 wt% of PU, 1 wt% of photo-initiator (2-hydroxy-2-methylpropionphenone, DARCUR 1173), 67 wt% of PMMA and *N*,*N*-dimethylformide (DMF) as solvent [20]. The solution of PU/PMMA was filtered through syringe with 0.22 μm pore size filter, and dropped on indium-tin-oxide (ITO)-coated glass substrates, which were cleaned by DMF, acetone, distilled water, and THF sequentially in an ultrasonic bath before use. The films were prepared by spin-coating on the ITO substrates at a spin rate of 1,000 rmp for 30 s. Then, the films were baked in air for 1 h to remove the majority of any volatiles. The residual solvent was removed by heating the films in a vacuum oven at 50 °C for 24 h.

### Poling process

Poling conditions were as follows: temperature about 110 °C and applying a high dc voltage 8.0 kV at the tungsten wire across the films for about 1 h at the gap distance 1.0 cm. After that the film was cross linked by UV-curing via a medium-pressure mercury lamp source for 10 min at the gap distance 10 cm with the electric field still applied. Then, the medium-pressure mercury lamp source was removed. Finally, the temperature was lowered to room temperature with the electric field still applied.

## Results and discussion

### Synthesis

The synthetic route of the PU containing spindle-type chromophore is shown in Scheme 1. Spindle-type chromophore is an efficient approach for reducing dipole–dipole interaction in the polymeric system [21, 22], which is composed of alkylamine as the electron donor, and the isophorone derivative as the electron acceptor at both ends and terphenyl-based compound as the $\pi$-conjugate bridge. Based on quantum chemical calculations [23], a polymer containing isophorone derivatives as chromophores shows that the polymer exhibits a large macroscopic non-linear optical coefficient, thermal stability, and good optical transparency. Detailed results of the synthesis and characterization of spindle-type chromophore will be presented in a separate publication [19]. The NCO-terminated spindle-type chromophore was easily obtained from the spindle-type chromophore and 4,4′-Methylenebis (cyclohexyl isocyanate) under the conditions similar to those reported in the literature [24, 25]. The oligomer was formed by the reaction between the hydroxyl and 4,4′-Methylenebis (cyclohexyl isocyanate) in presence of DBTDL as catalyst [26–28]. The reaction process of the compounds was monitored by Fourier transform infrared spectroscopy. The reaction product, photo-cross-linkable oligomer, was finally obtained when the absorbance of the isocyanate groups was consumed completely. In Scheme 1, most of the PU chains contain a chromophore unit, the value of *n* is 0, and few of PU chains contain two or more chromophore units.

The chromophore possesses a larger rotational radius than one-dimensional chromophores because of their spindle-type structures. Therefore, to provide enough local free volume for polarize orientation, we mixed 67 wt% of PMMA in the PU solution. Figure 1 was the Schematic diagram of the poled and photo-cross-linked PU/PMMA films. The chromophore units were aligned in the poling direction after the film poling and photo-cross-linking.

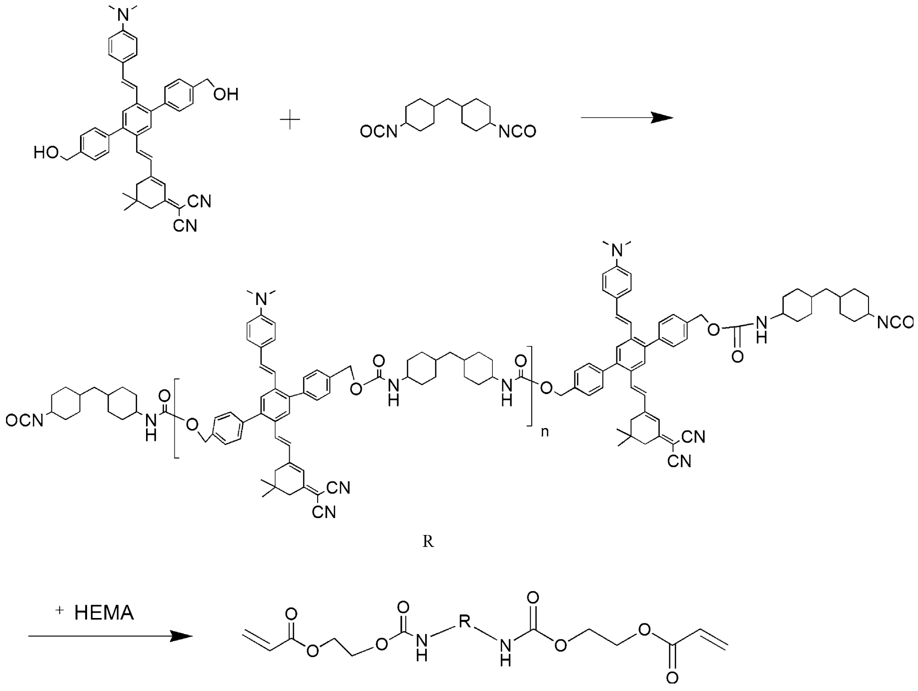
### Characterization

All of the compounds were characterized by spectroscopic methods and gave satisfactory spectral data. $^1$H-NMR and FT-IR spectra data of NCO-terminated spindle-type chromophores and photo-cross-linkable polyurethane oligomer (PU) were listed in Tables 1 and 2, respectively.

### IR spectra

Figure 2 shows the IR spectra of spindle-type chromophores, NCO-terminated spindle-type chromophores,

**Scheme 1** The route of preparation optical cross-linkable polyurethane oligomer



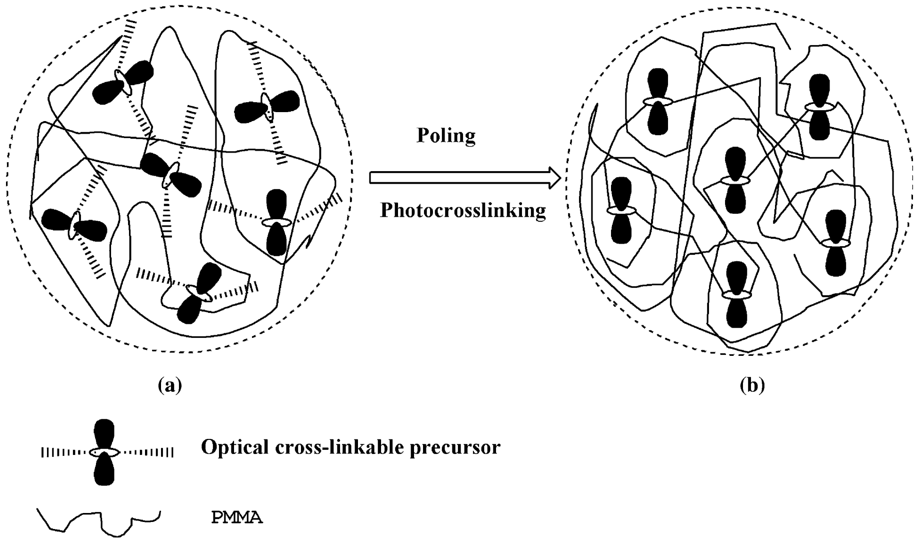


**Fig. 1** Poled and photo-cross-linked PU/PMMA film

**Table 1** H-NMR spectra data of NCO-terminated spindle-type chromophore and photo-cross-linkable polyurethane oligomer (PU)

| δ 500MHz | NCO-terminated (ppm) | PU (ppm) | δ 500MHz | NCO-terminated (ppm) | PU (ppm) |
|---|---|---|---|---|---|
| Ar-Ar-Ar | 7.68 | 7.69 | $CH_2$-$CH_2$ | | 4.31-4.32 |
| Ar-Ar-Ar | 7.66 | 7.65 | $CH_3$-N | 2.96 | 3.15 |
| NH | 7.56 | 7.57 | -$CH_2$- | 2.54 | 2.56 |
| ArH | 7.43-7.46 | 7.42-7.45 | -$CH_2$- | 2.23 | 2.24 |
| N-Ar-CH=CH | 7.28 | 7.28 | $CH_3$-C | 0.90 | 0.89 |
| CH=CH-TDF | 7.09-7.13 | 7.09-7.13 |  | 3.80 | |
| N-Ar-CH=CH | 7.05-7.08 | 7.05-7.08 |  | 3.54 | |
| CH=CH-TDF | 6.91-6.94 | 6.91-6.94 |  | 1.96 | 1.95 |
| CH | 6.77 | 6.78 |  | 1.70 | |
| N-Ar | 6.64-6.66 | 6.64-6.66 |  | 1.55 | |
| $CH_2$=CH- | | 5.59-5.60 |  | 1.44 | 1.25 |
| $CH_2$=CH- | | 5.34-5.35 |  | 1.11 | 1.01 |
| $CH_2$=CH- | | 5.18-5.20 |  | | 3.60 |
| -$CH_2$- | 5.12-5.19 | 5.12-5.14 |  | | 1.72 |
| $CH_2$-$CH_2$ | | 4.37-4.39 | | | |

**Table 2** FT-IR spectra data of NCO-terminated spindle-type chromophore and photo-cross-linkable polyurethane oligomer (PU)

| FTIR | NCO-termnated ($cm^1$) | PU ($cm^1$) |
|---|---|---|
| N–H | 3,341 | 3,362 |
| CHj | 2,923 | 2,927 |
| CHj | 2,852 | 2,850 |
| NCO | 2,265 | |
| CN | 2,220 | 2,219 |
| C=0 | 1,718 | 1,716 |
| C=C | | 1,636 |
| Ar | 1,607 | 1,607 |

photo-cross-linkable polyurethane oligomer, and photo-cross-linked film. There were strong absorption peaks at about 3,379 and 2,220 $cm^{-1}$ in Fig. 2a, which should be ascribed to the signal of hydroxyl and cyano groups, respectively. The strong band around 3,340 $cm^{-1}$ was attributed to the N–H stretching in Fig. 2b. The N–H stretching was broad, which suggested that the urethane linkages underwent hydrogen bonding. However, NCO-terminated spindle-type chromophores exhibited an extra strong absorption peak at 1,718 $cm^{-1}$ which was characteristic of the carbonyl in the urethane, and a new absorption band at 2,265 $cm^{-1}$ due to the NCO group. In Fig. 2c, the absorption of the NCO groups was disappeared completely

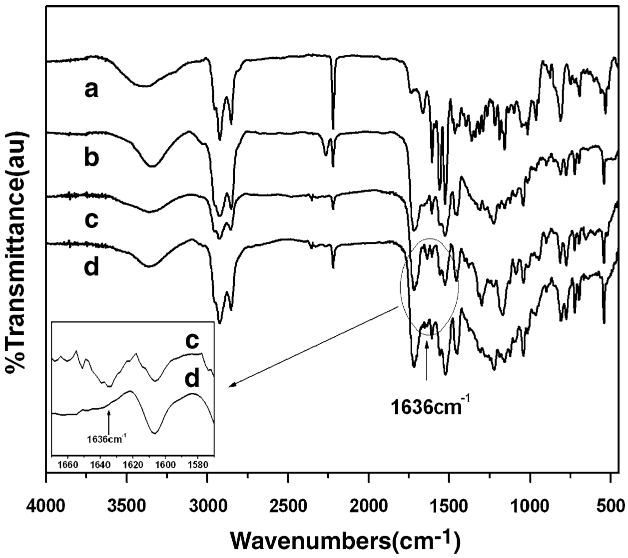


**Fig. 2** FT-IR spectra of spindle-type chromophore (**a**), NCO-terminated spindle-type chromophore (**b**), photo-cross-linkable polyurethane oligomer (**c**), and photo-cross-linked film (**d**)

and there was an absorption peak of the vinyl groups at about 1,636 cm$^{-1}$. In Fig. 2d, the absorption peak of the vinyl groups was disappeared completely after 10 min UV irradiation, which implied that cross-linked network structure formed in the films.

## UV–Vis spectra

Figure 3 shows the UV–Vis absorption spectra of PU/PMMA film containing spindle-type chromophores. To evaluate the non-centrosymmetric alignment of the chromophore units in the films, the absorption spectra of the films before and after poling were compared. Poling causes a decrease of the absorption intensity and a larger wavelength shift of the absorption maximum. The reduction of maximum absorbance was ascribed to the orientation of the spindle-type chromophore unit dipoles aligning along the direction of the electric field by electric poling. The maximum absorption peak moved from 377 to 350 nm, which increased the optical transparency in the visible region. Therefore, the optical film possessed good optical transparency. The spectral blue shift has been reported for other cross-linked main chain polymers [29, 30], which is in contrast to the red shift observed in most side-chain polymers [31]. The optical quality of the films after poling and curing remains excellent.

The order parameter ($\Phi = 1 - A_1/A_0$, $A_0$ and $A_1$ are the absorbance of the PU/PMMA films before and after poling) was used to characterize the poling efficiency. Under the conditions of 8 kV poling voltage applied to the tungsten wire at 110 °C for 1 h, the order parameter value of PU/PMMA film was estimated to be 0.19. The temporal stability tests showed that the photo-cross-linked PU/PMMA film had a very good temporal stability, and the order parameters could retain 98% at room temperature after 40 days.

It was found that the photo-cross-linked PU/PMMA film was insoluble in common organic solvents such as acetone, dichloromethane, chloroform, THF, and DMF. The TGA thermograms of the before and after photo-cross-linking films were shown in Fig. 4, and the 5% weight loss temperatures were 212 and 228 °C for the film before and after photo-cross-linking, respectively. The films formed a cross-linked network structure by UV-curing process. As a comparison, the $T_d$ of the cross-linked film increased about 16 °C. The cross-linked film possessed better temperature

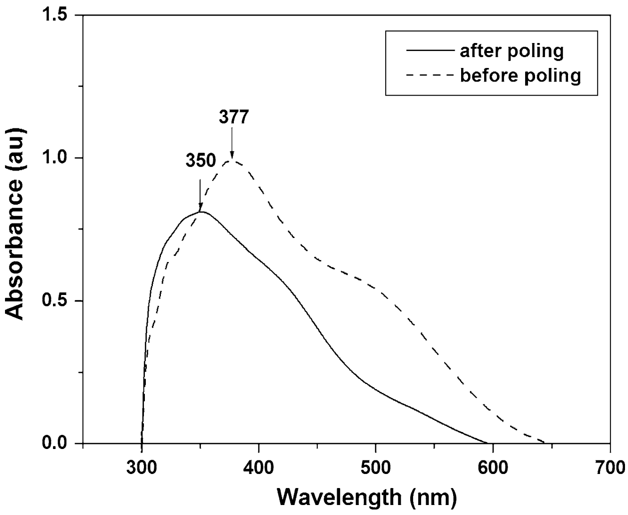


**Fig. 3** Absorption spectra of the film before and after electric poling and photo-cross-linking

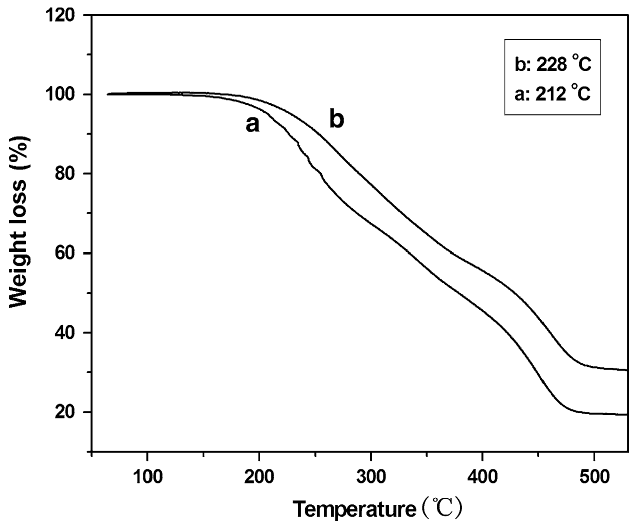


**Fig. 4** TGA thermograms of PU/PMMA film before (**a**) and after (**b**) photo-cross-linking measured in nitrogen at a heating rate of 10 °C/min

stability than uncross-linked film on heating from 50 to 600 °C as shown in Fig. 4. This result indicated that the cross-linked network structure of the film can be benefited its stability against heating.

The AFM images were represented here as three-dimensional figure and the *Z* scale was magnified in order to enhance the surface morphology. Figure 5 displays the surface topography of the spin-coated films before and after poling and photo-cross-linking by AFM scan. Figure 5a shows an AFM scan, typical for the spin-coated film before poling. It is found that the surface of the film is extremely flat. The revealed root mean square (rms) surface roughnesses value of the AFM images film before poling is only 0.713 nm in 2.5 × 2.5 μm$^2$ scan areas. However, this excellent quality film was dramatically changed after poling, resulting in numerous hills and valleys in the surface structure in Fig. 5b). The chromophore units were aligned along the poling direction [32–35], and the roughness of the surface topography of the film is up to 1.197 nm after poling.

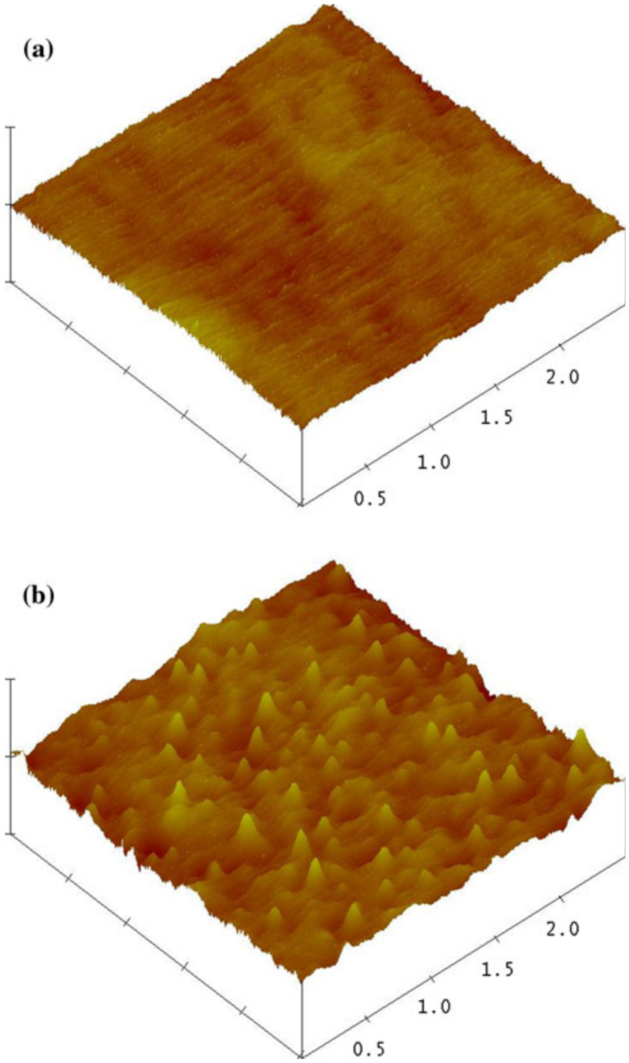


**Fig. 5** The AFM image of the spin-coated surface of the PU/PMMA films before (**a**) and after (**b**) poling (2.5 μm × 2.5 μm)

## Calculation for the EO coefficient of the photo-cross-linked film

The EO coefficient of the prepared film was measured by Teng-Man technique following the conventional way [36]. The a.c. voltage (20 Vrms at 1 kHz) was applied to each sample film to observe the modulated signal ($I_m$). The EO coefficient $r_{33}$ of the poled and photo-cross-linked film was calculated based on the following Eq. 1 as reported in literature [37].

$$r_{33} = \frac{3\lambda I_{\mathrm{m}}}{4_{\mathrm{II}} V_{\mathrm{m}} I_{\mathrm{c}} n^2} \frac{\left(n^2 - \sin^2\theta\right)^{3/2}}{\left(n^2 - 2\sin^2\theta\right)} \frac{1}{\sin^2\theta} \qquad (1)$$

where $\lambda$ is the optical wavelength and $n$ is the refractive index at 1,300 nm. $I_{\mathrm{m}}$ is the amplitude of the modulation and $V_{\mathrm{m}}$ is the alternating current (a.c.) voltage applied to the sample. $\theta$ is the incident angle. $I_{\mathrm{c}}$ is the intensity of incident light where phase retardation is 90° between transverse electric (TE) and transverse magnetic (TM) mode. By calibrating the $r_{33}$ data versus the GaAs data, the EO coefficient of the prepared film was calculated up to 41 pm/V.

The thermal dynamic stabilities of the NLO property are very important for the practical use of NLO materials. The thermal dynamic stabilities of the unphoto-cross-linked film and photo-cross-linked film were investigated by depoling experiments [38], in which the real time decays of their EO coefficient $r_{33}(t)/r_{33}(t_0)$ were monitored as poled films were heated from 10 to 130 °C in air at a rate of 10 °C/min. Figure 6 illustrates the thermal dynamic

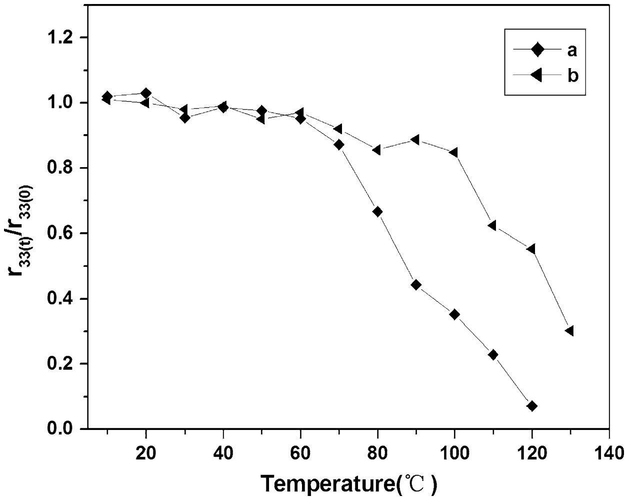


**Fig. 6** Decay of the EO coefficient for the unphoto-cross-linking film (**a**) and photo-cross-linked film (**b**)

stabilities of the EO coefficient for the unphoto-cross-linked film (a) and photo-cross-linked film (b). The results indicated that the effective relaxation temperature become higher when the film was cross linked. The cross-linked structure of the film constrained sterical movement of the chromophore units and restrained the chromophoric orientation relaxing. Therefore, the photo-cross-linked film exhibited the best thermal stability with the onset temperature for decay at about 100 °C. The thermal stability of the cross-linked film was better than the other reported photo-cross-linked film in the literature [39].

## Conclusions

In this article, we have successfully synthesized novel photo-cross-linked NLO materials (PU/PMMA) containing spindle-type chromophores. The second-order optical property of the prepared film was measured by Teng-Man technique. The content of chromophore units in the film is 15 wt%. The EO coefficient of the film was calculated up to 41 pm/V. The results showed that the films had the same second-order optical non-linear properties before and after cross-linking, but the thermal and temporal stabilities of the film were improved by photo-cross-linking. The onset temperature of the photo-cross-linked film for decay was about 30 °C higher than the uncross-linked film. The photo-cross-linked films are good candidate for the optical communication applications.

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