Research Article

Haiyan Pei*, Yingliang Liu*, Dongfang Wang, Jin Wang, Chunjiang Wang, Yanzhao Wu, Wei Pan, Chaohua Su, Meng Song, and Shaokui Cao*

All-optical non-conjugated multi-functionalized photorefractive polymers via ring-opening metathesis polymerization

Abstract: Non-conjugated multi-functionalized all-optical photorefractive (PR) polymers were designed and synthesized via ring-opening metathesis polymerization (ROMP) of two monomers using Grubbs II catalyst as an initiator. The polymers were characterized by infrared (IR) spectrum, gel permeation chromatography (GPC), UV-visible spectrum (UV-Vis), differential scanning calorimetry (DSC), thermogravimetry (TG) and so on. The number-average molar mass (M_n) of the polymers is no less than 8.5×10^4 while their glass transition temperatures of 52ºC and 45ºC are close to the room temperature, which is helpful to the enhancement of PR orientation and the fabrication of PR devices. The polymers have good thermal stability and great solubility in tetrahydrofuran (THF). Without any plasticizer, the transparent optical films can be prepared by solution-casting with THF solution of polymers. Their PR properties at 633 nm were evaluated by two beam coupling (TBC) experiments under zero electric field without prepoling.

It is shown that the single-component polymer has obvious all-optical PR behavior.

1 Introduction

Photorefractive (PR) polymeric materials, including fully functional polymers and polymer composites, have been studied for years owing to their potential applications in phase conjugation, high-density optical data storage, neural network simulations, image processing and so on (1–6). Compared to polymer composites, fully functional PR polymers have more advantages because all the functional bodies with PR effect are covalently bonded on the polymers, which eliminates the problems of phase separation and crystallization, so that the potential devices have better stability and longer warranty period (1,7–10). However, fully functionalized PR polymers are so far reported to be almost having a main-chain conjugated structure being prepared with complicated synthetic processes, which are not beneficial to the potential application (7,8). In the past few years, organic amorphous PR molecular materials have also been developed. Their good PR performance and simple synthesis method can provide theoretical basis for the molecular design of full-functional/multi-functional NCMC polymer (11–14). However, owing to the fact that the synthesis of chromophore functional monomers is not easy, the number of full-functional PR polymers with NCMC structure is relatively limited (9). In other words, due to the large volume of monomers and the side effects of functional groups, the direct polymerization of functional monomers usually presents a low molecular weight polymer, which is not conducive to the film-forming performance (15–19). In order to solve this problem, we focus on ring-opening metathesis polymerization (ROMP). The progress in ROMP of cycloalkene derivatives provides a good way for the

* **Corresponding author: Haiyan Pei,** School of Materials and Chemical Engineering, Zhongyuan University of Technology, Zhengzhou 450002, P. R. China; School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001, P. R. China, e-mail: peihaiyan2008@126.com

* **Corresponding author: Yingliang Liu,** School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001, P. R. China, e-mail: liuylxn@zzu.edu.cn

* **Corresponding author: Shaokui Cao,** School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001, P. R. China, e-mail: caoshaokui@zzu.edu.cn, tel: +86-371-6776-3561

Dongfang Wang, Jin Wang, Chunjiang Wang, Yanzhao Wu: School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001, P. R. China

Wei Pan, Chaohua Su, Meng Song: School of Materials and Chemical Engineering, Zhongyuan University of Technology, Zhengzhou 450002, P. R. China

synthesis of norbornene functional monomers. While, it is rarely used in the preparation of functionalized PR polymers (20–26). In addition, all-optical PR materials have become another important research topic due to the convenient signal-writing without the application of external electrical field (27–29). Therefore, it is an interesting subject to synthesize all-optical multi-functional PR polymers with well-defined structure and high molecular weight by simple ring-opening metathesis polymerization.

In our previous work (26), we have designed norbornene functional monomers with azobenzene chromophores and the polymers were synthesized by ROMP using Grubbs I catalyst. However, due to the high glass transition temperature of the polymer, the plasticizers need to be added to reduce the glass transition temperature when the PR devices were prepared. In addition, the photosensitizer C_{60} was also added, which is not conducive to future application. Therefore, it is our goal to design and synthesize the polymers with glass transition temperature close to room temperature while their PR properties can be displayed without any photosensitizer. In this paper, two norbornene monomers, with/without methine chromophore, were first designed and synthesized via Vilsmeier and Knoevenagel reactions. Then, the fully functional PR polymers with NCMC structure were synthesized by ROMP using Grubbs II catalyst, in which the long alkyl spacer between the functional chromophore and methine group was expected to ensure the low glass temperature and free rotation of PR chromophore. The synthesized polymers were characterized by infrared (IR) spectra, UV-vis spectra, gel permeation chromatography (GPC), differential scanning calorimetry (DSC), thermogravimetry (TG) and so on. As a result, the single-component fully functionalized PR polymers with low T_g and high molecular weight were presented. In the measurement process of TBC carried out at 633 nm, it was found that the polymers were able to take on an all-optical PR performance at room temperature and zero electrical field without any plasticizer, any photosensitizer and prepoling, which provide the convenient precondition for practical PR application.

2 Experimental

2.1 Materials

Grubbs II catalyst, 5-norbornene-2-formyl chloride, 6-chlorohexanol and 9-bromo-1-nonanol, respectively, were purchased, respectively, from Sigma-Aldrich, Puyang Huicheng Chemical Co. Ltd, Shanghai Bangcheng Chemical Co. Ltd

and Beijing Isomersyn Technology Co. Ltd. Other analytical or chemical purity chemicals were also obtained from Chinese reagent companies and used directly. Before using, tetrahydrofuran (THF) needs to be dried with sodium using benzophenone as indicator, and dichloromethane (CH_2Cl_2) should be purified by calcium hydride distillation under N_2.

2.2 Characterization

The melting point was measured by an X-5A melting point tester. The ^{1}H-NMR spectra were recorded by Bruker DRX-400 NMR spectrometer with $CDCl_3$ as solvent. IR spectra were determined on a Nicolet-460 FTIR spectrometer. Elemental analysis was performed on the EA 1110 CHNS-O instrument. The GPC measurement calibrated using polystyrene standards was measured with THF as eluent at 40°C by a Waters M515 instrument. Shimadzu 3010 UV-visible spectrometer was used to determine the UV-vis spectra with THF as solvent. Under a nitrogen atmosphere, the DSC measurement was performed on a TA-100 DSC with a heating rate of 10°C/min. TG analysis was carried on a Netzsch-209 TGA system with a heating rate of 10°C/min.

2.3 Synthesis

The synthetic route of monomers and polymers is shown in Scheme 1. Compounds **1** and **6** were prepared according to our previously reported synthetic procedures (15,26).

2.3.1 Preparation of compound 2 (30)

Compound **1** (9 g) and acetic anhydride (70 mL) were added to a single-necked flask. The solution was heated to reflux for 1 h under stirring. After cooling, the solution was poured into a large amount of ice water and extracted with chloroform. After that, the resulting solution was dried overnight with anhydrous magnesium sulfate. The filtrate was filtered by suction. The solvent was removed by rotary evaporator to obtain light yellow solid with a yield of 90%. ^{1}H-NMR ($CDCl_3$, TMS, δ): 8.0 (d, J = 7.6 Hz, 2H), 7.4 (m, 2H), 7.3 (d, J = 8.4 Hz, 2H), 7.2 (m, 2H), 4.3 (t, 2H, J = 7.2 Hz, NCH_2), 4.0 (t, J = 6.4 Hz, 2H, OCH_2), 2.0 (d, 3H, J = 4.4 Hz, $COCH_3$), 1.8–1.9 (t, J = 7.6 Hz, 2H), 1.5–1.6 (t, J = 7.2 Hz, 2H), 1.3–1.4 (m, 4H).
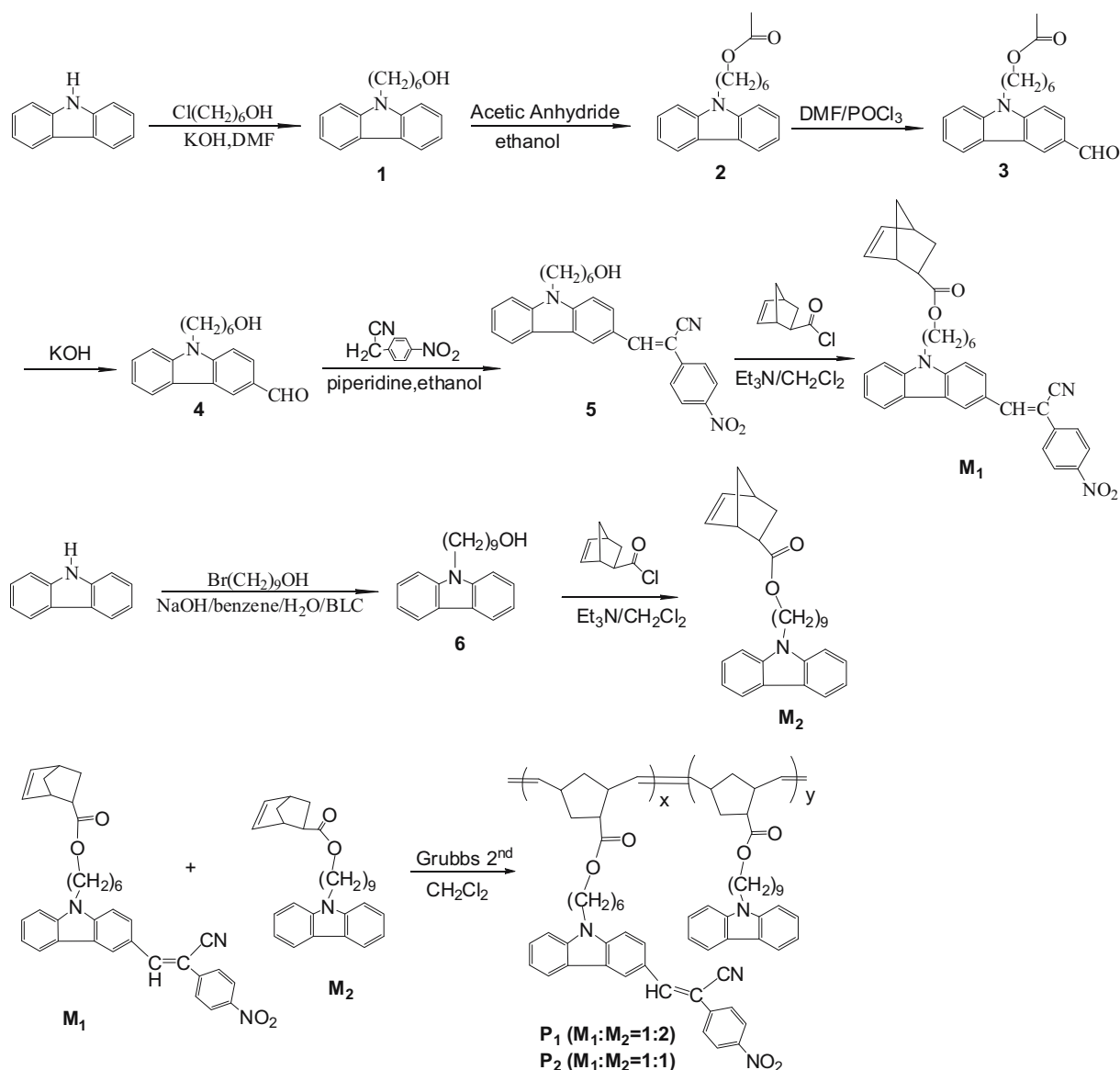
Scheme 1: Synthetic route of PR polymers.

2.3.2 Preparation of compound 3 (30)

The flask containing compound **2** (4.0 g, 0.014 mol) was placed in an ice water bath and then DMF (20 mL) was added to dissolve it. After stirring for 10 min, POCl₃ (2.4 mL) was slowly added to the solution. The solution was stirred at 100°C for 3 h and then cooled to room temperature. The resulting yellow solution was poured into ice water and neutralized with diluted KOH solution to pH = 6–8. Then, the obtained solution was extracted with chloroform and dried by anhydrous magnesium sulfate. After removing the solvent, the residue was purified by silica gel column chromatography with chloroform as eluent, and the yellow solid was obtained in 53% yield. ^{1}H-NMR (CDCl₃, TMS, δ):

10.0 (s, 1H, aldehyde proton), 8.6 (s, 1H), 8.1 (d, J = 7.6 Hz, 1H), 8.0 (m, 1H), 7.5 (m, 1H), 7.4 (d, J = 8.4 Hz, 2H), 7.3 (m, 1H), 4.3 (t, J = 7.2 Hz, 2H, NCH₂), 4.0 (t, J = 6.8 Hz, 2H, OCH₂), 2.0 (d, J = 4.4 Hz, 3H, COCH₃), 1.9 (t, J = 7.2 Hz, 2H), 1.5–1.6 (t, J = 6.8 Hz, 2H), 1.2–1.4 (t, J = 7.2 Hz, 4H).

2.3.3 Preparation of compound 4 (30)

Ethanol (100 mL) was added to compound **3** (4.0 g, 4 mmol), stirred for 10 min and then KOH (4.0 g, 70 mmol) was added. Then, the obtained solution was cooled after heating to reflux for 3 h. Half of the solvent was removed before the mixture was poured into the water to obtain the sediment.

The sediment was filtered and fully cleaned with water. After drying under vacuum, the yellow solid was obtained by recrystallization with ethanol, and the yield was 30%. ^{1}H-NMR (CDCl$_3$, TMS, δ): 10.0 (s, 1H, aldehyde proton), 8.6 (s, 1H), 8.1 (d, $J = 7.6$ Hz, 1H), 8.0 (m, 1H), 7.5 (d, $J = 8.0$ Hz, 1H), 7.4 (m, 2H), 7.3 (m, 1H), 4.3 (t, $J = 7.2$ Hz, 2H, NCH$_2$), 3.6 (t, $J = 6.4$ Hz, 2H, OCH$_2$), 1.8–1.3 (m, 8H).

2.4 Preparation of compound 5 (30)

Compound **4** (2 g, 6.4 mmol) and 4-nitrophenylacetic acid (1.2 g, 7.44 mmol) were dissolved with anhydrous ethanol. Then, piperidine (1.2 mL) was added to the solution under stirring drop by drop. The mixed solution was heated to reflux for 2 h and then cooled. The residue was poured into the ethanol to obtain the sediment. The sediment was filtered and recrystallized with anhydrous ethanol. Then, the orange solid was obtained and the yield was 58%. ^{1}H-NMR (CDCl$_3$, TMS, δ): 7.3–8.3 (m, 12H), 4.4 (t, $J = 7.6$ Hz, 2H, OCH$_2$), 3.4 (t, $J = 6.8$ Hz, 2H, NCH$_2$), 1.3–1.8 (m, 8H).

2.4.1 Preparation of M1 (31)

Compound **5** (9 g, 20 mmol) was dissolved in purified dry dichloromethane (30 mL). At room temperature, triethylamine (2.4 g, 24 mmol) was added with stirring. Then, 5-norbornene-2-formyl chloride (6.6 g, 20 mmol) was added slowly and reacted at room temperature for 4 h. The solvent was removed and the crude product was purified by silica gel column chromatography with CH$_2$Cl$_2$ as eluent. The yellow solid compound **M1** with the yield of 99% was finally obtained by recrystallization from *n*-hexane. M_p = 133.4–134.5°C. ^{1}H-NMR (CDCl$_3$, TMS, δ): 8.7 (s, 1H), 8.1–8.4 (m, 2H), 8.1–8.2 (d, $J = 7.6$ Hz, 2H), 7.8–7.9 (d, $J = 6.4$ Hz, 3H), 7.2–7.6 (m, 4H), 6.0–6.2 (m, 2H, –CH=), 4.3–4.4 (t, $J = 6.8$ Hz, 2H, NCH$_2$), 4.0 (m, 2H). 2.2–3.0 (m, 3H, CH), 1.0–2.0 (m, 12H, CH$_2$). ^{13}C-NMR (δ, CDCl$_3$): 25.8, 26.9, 28.5, 29.2, 30.3, 41.6, 42.5, 43.4, 45.7, 46.6, 49.7, 64.3, 99.0, 104.6, 109.2, 109.4, 118.4, 120.2, 120.8, 123.4, 124.0, 126.0, 127.7, 135.7, 137.8, 138.1, 140.9, 141.4, 146.5, 147.1, 176.4. Elemental analysis, calcd: C, 75.11; H, 5.94; N, 7.51. Found: C, 74.85; H, 6.02; N, 7.42.

2.4.2 Preparation of M2 (31)

Compound **M2** was prepared by a similar procedure to M$_1$ and obtained as a buff viscous matter in the yield of 70%. ^{1}H-NMR (CDCl$_3$, TMS, δ): 8.1 (d, $J = 7.6$ Hz, 1H), 7.2–7.5 (m, 7H), 6.2 (m, 2H), 4.3 (t, 2H, $J = 7.2$ Hz), 4.0 (m, 2H), 2.9–3.2 (m, 3H), 1.2–2.2 (m, 10H). ^{13}C-NMR (δ, CDCl$_3$): 32.4, 34.5, 68.8, 71.1, 73.3, 76.8, 79.0, 83.6, 86.4, 88.8, 90.5, 100.5, 131.7, 132.1, 132.4, 144.6, 144.8, 159.5, 162.8, 163.4, 165.8, 183.2. Elemental analysis, calcd: C, 81.08; H, 8.21; N, 3.26. Found: C, 79.61; H, 7.905; N, 3.077.

2.4.3 Polymer synthesis (31)

Polymers **P1** and **P2** were synthesized according to the same procedure as follows: the air in the two polymerization reaction tubes was removed by vacuum pump, and the air in the tube was replaced by argon. After repeated operation for three times, the monomer (total molar amount: 1 mmol) was dissolved in dried dichloromethane under the protection of nitrogen. Then, the dichloromethane solution (2 mL) of Grubbs II catalyst (2 μmol) was injected into the mixture by a microinjector after the reaction was performed at room temperature for 12 h. The target polymer was obtained by precipitation with methanol, filtration and vacuum drying.

- Polymer **P1**: elemental analysis, found: C, 77.80; H, 7.02; N, 5.01.
- Polymer **P2**: elemental analysis, found: C, 77.10; H, 6.77; N, 5.28.

2.5 PR device fabrication and TBC measurement

The PR device fabrication and TBC measurement were similar to our previous work (26). However, compared with the previous work, there is an obvious difference. In this work, the samples for PR measurement were fabricated by single-component polymers without any plasticizer and photosensitizer.

3 Results and discussion

3.1 Synthesis of monomers and polymers

The synthetic route of monomers and polymers is shown in Scheme 1. The synthesis of compounds **1** and **6** is carried out according to the previously reported procedures (15,26). In the preparation process of monomers, many more efforts

have been paid to the synthesis of compound **4** owing to the existence of two reaction sites, in which the terminal hydroxyl group can react with 5-norbornene-2-formyl chloride yielding norbornene monomer for ROMP and the reaction of aldehyde group in the 3-position of carbazole ring will yield C=C by Knoevenagel condensation reaction with the compounds bearing active hydrogen, by which electron acceptor substituent is introduced into carbazole ring by Knoevenagel condensation reaction with aldehyde group in the 3-position. Therefore, the multi-functional monomer **M1** is prepared by the reaction of 5-norbornene-2-formyl chloride with compound **5**, which is achieved by the reaction of compound **4** with 4-nitrophenylacetic acid. The successful achievement of **M1** is proven by ^{1}H-NMR, ^{13}C-NMR, IR spectra and elemental analysis. Its chemical structure is in accordance with Scheme 1. Polymers **P1** and **P2** are synthesized by the ROMP copolymerization of the monomers **M1** and **M2** utilizing Grubbs II catalyst on the basis of the adjusted course in the references (25,26). The ratio of monomer to initiator ([M]/[I]) is set to be 500:1. After 12 h of reaction at room temperature, the polymerization was terminated with an excess of ethyl vinyl ether. After the reaction is carried out for 12 h at room temperature, the polymerization is terminated with excess ethyl vinyl ether. Polymers **P1** and **P2** are obtained through precipitation from methanol in the high yield of ~95%. As listed in Table 1, two polymers have a higher M_n of 1.5×10^5 and 8.5×10^4 than our previous work using Grubbs I catalyst, which is less than 2.3×10^4. Their molecular weight distribution index is 1.44 and 2.13, respectively. All the GPC data are listed in Table 1. The broad proton signals of ^{1}H-NMR in Figure 1 are the typical characteristics of the polymers.

The solubility is an important requirement for organic PR composites, because the samples for PR measurement were generally fabricated by a simple solution-casting. Herein, at room temperature, the solubility of the polymer was tested in a common solvent such as THF, CH$_3$Cl and CH$_2$Cl$_2$ using a 10 mg/mL polymer solutions, as listed in Table 2. The results showed that two polymers have an excellent solubility in common solvents, indicating that the optical films for PR measurement can be made by solution-casting.

3.2 Thermal stability

The thermal stability of polymers P_1 and P_2 was investigated under nitrogen atmosphere at a heating rate of 10°C/min. The TG and differential thermogravimetric (DTG) curves are shown in Figure 2. The TG curves of the polymers began to

Table 1: GPC data of the norbornene polymers*

Polymer	M_n ($\times 10^4$)	M_w ($\times 10^4$)	Polydispersity
P$_1$	15.4	22.2	1.44
P$_2$	8.5	18.1	2.13

*Calibrated with polystyrene standard.

incline at the beginning of temperature rise, that is to say, the chromophore containing nitrile group on the polymers was slowly removed. As we all know, the molecules with large polarity are more likely to be activated and decomposed by external energy than those with small polarity. Evidently, Polymers **P$_1$** and **P$_2$** have two weight-loss processes derived from the decomposition of different groups. All the TG and DTG data are listed in Table 3.

The glass transition temperature (T_g) is a very important parameter for the study of the polymers with nonlinear optical effects (32). The DSC curves of two polymers are illustrated in Figure 3 and T_g of the polymers are listed in Table 3. Before the test, the samples were heated to 200°C at a heating rate of 10°C/min, then cooled to –30°C rapidly, so that both the polymer samples had the same thermal history. It can be seen from the DSC curve that both polymers have no melting and recrystallization peaks, but only a single glass transition, indicating that the synthesized polymers are amorphous polymers. The amorphous structure of PR polymers is favorable to the formation of a uniform and transparent film, which normally leads to low optical loss in transmission and a consequent enhancement of their photorefraction (18). The T_g of **P2** is 52°C, which is higher than 45°C of **P1** due to the increase in volume and polarity of rigid side chain through the introduction of methine group. Their T_g values are lower compared with our previous work, in which the polymers have a higher T_g value from 75°C to 153°C (26). The low T_g value facilitates PR measurement and device fabrication at room temperature and the PR devices are able to be fabricated without the help of any plasticizer.

3.3 UV-vis absorption

The UV-vis spectra of the monomers and polymers are shown in Figure 4. All the monomers and polymers except for M2 have a similar absorption in the visible region from 350 to 500 nm, which is assigned to the charge transfer from carbazole to methine chromophore. It is obvious that the absorption maximum of the polymers is almost located at the same position as **M1**. Additionally, the relationship
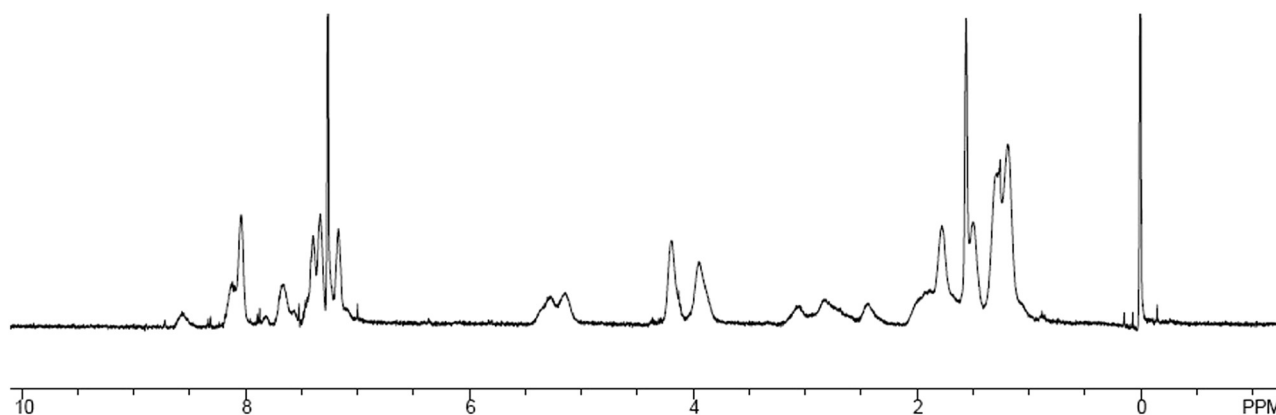
Figure 1: ^{1}H-NMR spectrum of polymer **P1**.

Table 2: Polymer solubility at room temperature*

Polymer	THF	CH$_3$Cl	CH$_2$Cl$_2$
P$_1$	+	+	+
P$_2$	+	+	+

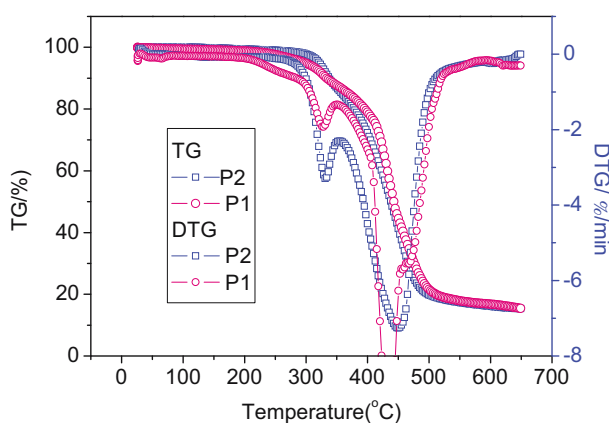*Tested with a solution concentration of 10 mg/mL; solubility: +, soluble; −, insoluble; ±, partially soluble.

Figure 2: TG and DTG curves of polymers **P1** and **P2**.

Table 3: Thermal analytic data of the polymers

Polymer	T_g (°C)	T_{onset} (°C)	T_d (°C)	T_p (°C)
P$_1$	45	253	302	328, 437
P$_2$	52	296	325	330, 450

between the absorbance and the solution concentration at the absorption maximum is measured using the THF solutions of **P1** and **P2** with different concentrations, as plotted in Figure 5. Obviously, the polymer solutions at different concentrations have the same absorption maxima.
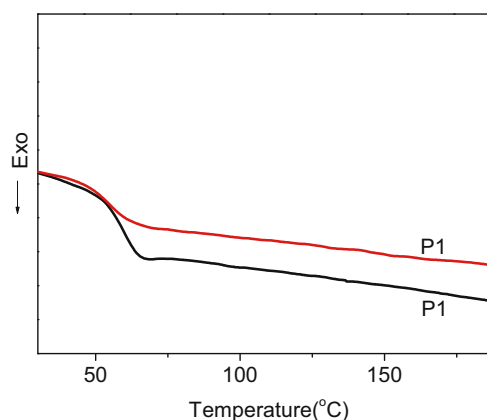
Figure 3: DSC curves of polymers **P1** and **P2**.

This point shows that no another intermolecular interaction is produced with the increase in solution concentration. And that, with the change in concentration, there was no significant blue shift or red shift in the position of maximum absorption. The molar absorption coefficient at the absorption maximum is calculated by the formula: $\varepsilon = A/bc$. Here, A is the absorbance value; b is the cuvette thickness; c is the solution concentration of repeating units. The results suggest that the molar absorption coefficients of **P1** and **P2** are 1.47×10^4 L/mol cm and 1.99×10^5 L/mol cm, respectively.

3.4 All-optical PR property

The PR effect can only be confirmed by holographic optical technology. Two wave coupling (TBC) experiment is the most commonly used holographic optical technology to evaluate the PR properties of the materials (1). The all-optical PR effect is measured by TBC experiments at zero electric field using
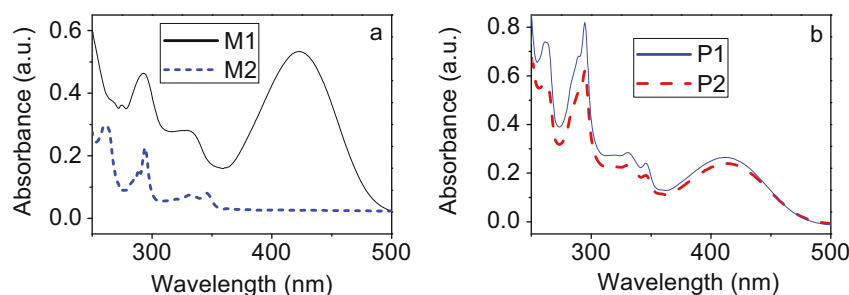
Figure 4: UV-vis absorption spectra of monomers (a) and polymers (b) in THF.
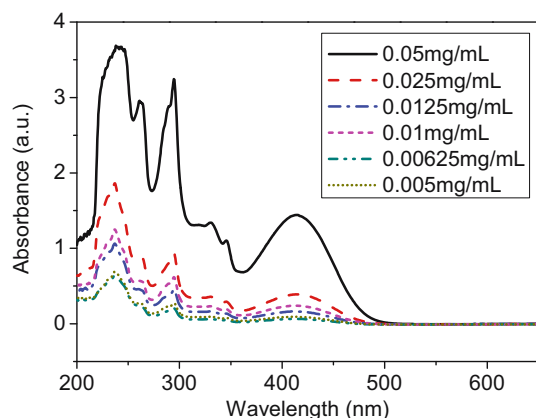

Figure 5: UV-vis absorption spectra of polymer **P2** in THF at different concentrations.

the pure polymer film without prepoling and any plasticizer. The temperature is a very important parameter in the measurement of PR effect, because it will affect the whole process of PR effect, including the generation, transport, capture of charge and the orientation of chromophore in the electric field (1,32). Generally speaking, when the operating temperature is near T_g, the PR dynamic performance is controlled by the chromophore orientation rate (1), so the best operating temperature should be near T_g. If the PR test is

carried out at room temperature, the material design should consider making its T_g close to room temperature (32) in order to obtain higher PR properties. In other words, the chromophore reorientation would be facilitated when T_g is close to the experimental temperature, which is the room temperature in our experiments, resulting in the more excellent orientation enhancement effect. Because the T_g value (45°C) of **P2** is closer to room temperature than **P1** (52°C) as shown in Table 3, Polymer **P2** takes on a higher coupling coefficient Γ of 26 than 10 cm^{-1} of Polymer **P1**. Notably, the photoassisted *trans–cis–trans* isomerization of methine group results in the vibration of TBC signal, as shown in Figure 6. Finally, the PR NCMC polymers, which bear an evident all-optical PR property without prepoling and any plasticizer, are achieved. This kind of single-component PR device will make the practical PR application more easy, safe and convenient.

4 Conclusions

Non-conjugated multi-functionalized all-optical PR polymers are presented by ROMP using Grubbs II catalyst as an initiator. The polymers have a higher number-average molecular weight (M_n) than 8.5×10^4 and the T_g of 52°C and 45°C close to the room temperature, which is advantageous to the PR orientation enhancement. The good thermal stability and excellent solubility in THF allow us to fabricate the optically transparent films through solution-casting without any plasticizer. The evident all-optical PR performance at 633 nm is achieved at zero electrical field from the single-component polymers, affording more easy, safe and convenient PR practical application.
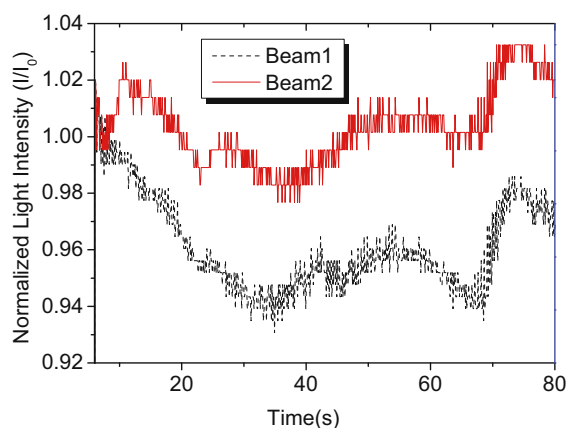
Figure 6: TBC signal of pure polymer **P2** at zero electric field.

References

(1) Ostroverkhova O, Moerner WE. Organic photorefractives: mechanisms, materials, and applications. Chem Rev. 2004;104(7):3267–314.

(2) Day D, Gu M, Smallridge A. Rewritable 3D bit optical data storage in a PMMA-based photorefractive polymer. Adv Mater. 2001;13(12–13):1005–7.

(3) Tay S, Blanche PA, Voorakaranam R, Voorakaranam P, Tunc AV, Lin W, et al. An updatable holographic three-dimensional display. Nature. 2008;451:694–8.

(4) Xu SG, Fang C, Wu YZ, Wu WB, Guo Q, Zeng J, et al. Photorefractive hyper-structured molecular glasses constructed by calix[4]resorcinarene core and carbazole-based methine nonlinear optical chromophore. Dyes Pigm. 2017;142:8–16.

(5) Marder SR, Kippelen B, Jen AKY, Peyghambarian N. Design and synthesis of chromophores and polymers for electro-optic and photorefractive applications. Nature. 1997;388:845–51.

(6) Talarico M, Golemme A. Optical control of orientational bistability in photorefractive liquid crystals. Nat Mater. 2006;5:185–8.

(7) You W, Cao SK, Hou ZJ, Yu LP. Fully Functionalized Photorefractive Polymer with Infrared Sensitivity Based on Novel Chromophores. Macromolecules. 2003;36(19):7014–9.

(8) Zong WS, Wang S, Li J, Wang JT, Li MM, Liu YL, et al. An all-optical photorefractive miktoarm star polymer synthesized via a combination of RAFT polymerization and click reaction. React Funct Polym. 2019;143:104321–9.

(9) Zong WS, Wang LX, Guo Q, Li J, Wu WB, Liu YL, et al. A calix[4] resorcinarene-based hyper-structured molecule bearing disperse red 1 as the chromophore with enhanced photorefractive performance under non-electric field. Dyes Pigm. 2019;160:579–86.

(10) Chen YW, He YK, Wang F, Chen HY, Gong QH. Synthesis and characterization of bi-functional photorefractive polymers. Polymer. 2001;42:1101–7.

(11) Shi J, Huang MM, Xin YR, Chen ZJ, Gong QH, Xu SG, et al. Synthesis and characterization of a series of carbazole-based monolithic photorefractive molecules. Mater Lett. 2005;59:2199–203.

(12) Zhang L, Shi J, Jiang ZW, Huang MM, Chen ZJ, Gong QH, et al. Photorefractive performance of hyperstructured cyclotriphosphazene molecular glasses containing carbazole moieties. Adv Funct Mater. 2008;18:362–8.

(13) Zhang L, Xu SG, Yang Z, Cao SK. Photorefractive effect in triphenylamine-based monolithic molecular glasses with low T_g. Mater Chem Phys. 2011;126:804–10.

(14) Shi J, Jiang ZW, Cao SK. Synthesis of carbazole-based photorefractive polymers via post-azo-coupling reaction. React Funct Polym. 2004;59:87–91.

(15) Zhang L, Huang MM, Jiang ZW, Yang Z, Chen ZJ, Gong QH, et al. A carbazole-based photorefractive polyphosphazene prepared via post-azo-coupling reaction. React Funct Polym. 2006;66:1404–10.

(16) Shi J, Jiang ZW, Cao SK. A postfunctionalization strategy to develop carbazole-based photorefractive polymers with low T_g. React Funct Polym. 2005;62:223–230.

(17) Shi J, Huang MM, Chen ZJ, Gong QH, Cao SK. Carbazole-based azo group-containing single component polymer exhibiting photorefractive performance. J Mater Sci. 2004;39:3783–5.

(18) Zhang L, Shi J, Huang MM, Jiang ZW, Yang Z, Chen ZJ, et al. Photorefractive properties of polyphosphazenes containing carbazole-based multifunctional chromophores. Polymer. 2008;49:2107–14.

(19) Hawker CJ, Wooley KL. The convergence of synthetic organic and polymer chemistries. Science. 2005;309:1200–5.

(20) Nuyken O, Pask S. Ring-opening polymerization—an introductory review. Polymers. 2013;5:361–403.

(21) Biswas S, Belfield K, Das R, Ghosh S, Hebard A. Superparamagnetic nanocomposites templated with pyrazole-containing diblock copolymers. Polymers. 2012;4:1211–25.

(22) Suriboot J, Bazzi H, Bergbreiter D. Supported catalysts useful in ring-closing metathesis, cross metathesis, and ring-opening metathesis polymerization. Polymers. 2016;8:1401–23.

(23) Cui J, Yang JX, Li YG, Li YS. Synthesis of high performance cyclic olefin polymers (COPs) with ester group via ring-opening metathesis polymerization. Polymers. 2015;7:1389–409.

(24) Liaw DJ, Wang KL, Lee KR, Lai JY. Ring-opening metathesis polymerization of new norbornene-based monomers containing various chromophores. J Polym Sci Part A: Polym Chem. 2006;45:3022–31.

(25) Grubbs RH. Olefin-metathesis catalysts for the preparation of molecules and materials (Nobel Lecture 2005). Adv Synth Catal. 2007;349:34–40.

(26) Pei HY, Li W, Liu YL, Wang DF, Wang J, Shi J, et al. Ring-opening metathesis polymerization of norbornene derivatives for multifunctionalized all-optical photorefractive polymers with a non-conjugated main chain. Polymer. 2012;53:138–44.

(27) Andrzej M, Jaroslaw M, Piotr P, Marcin Z. Photorefractive-like all-optical switching in nematic-photoconducting polymer liquid crystal cell. Mol Cryst Liq Cryst. 2008;489:119–34.

(28) Lee WK, Chan TS. Photorefractive hologram writing with high modulation depth in photovoltaic media under different boundary conditions. Opt Commun. 2008;281:5884–8.

(29) Liu YL, Pei HY, Zhang L, Shi J, Cao SK. Advances in organic all-optical photorefractive materials. Macromol Symp. 2012;317–318:227–39.

(30) Kim DW, Moon H, Park SY, Hong S. Synthesis of photoconducting nonlinear optical side-chain polymers containing carbazole derivatives. React Funct Polym. 1999;42:73–86.

(31) Liaw DJ, Wang KL, Lee KR, Lai JY. Ring-opening metathesis polymerization of new norbornene-based monomers containing various chromophores. J Polym Sci. 2007;45:3022–31.

(32) Ribierre JC, Cheval G, Huber F, et al. Direct comparison of mechanical and electro-optic responses of a low T_g photorefractive doped polymer. J Appl Phys. 2002;91:1710–2.