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# New generation of photosensitive poly(azomethine)esters: Thermal behaviours, photocrosslinking and photoluminescence studies



Wan-Leng Lim, Chuan-Wei Oo<sup>\*</sup>, Yvonne-Shuen-Lann Choo, Shueh-Teng Looi

Department of Organic Chemistry, School of Chemical Sciences, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia

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#### ABSTRACT

Three new series of soluble photosensitive poly(azomethine)esters with even methylene spacers in their backbone and various substituents on their side chain were synthesized. Their molecular structures were elucidated with various spectroscopic methods. The different substituents and length of the methylene spacers were found to influence the thermal stability of the polymers. The  $-OCH_3$  substituted side chain poly(azomethine)esters showed highest thermal stability, followed by -Cl and -H. Meanwhile, poly(-azomethine)esters with longer methylene spacers exhibited lower thermal stability. The photoreactivity of these poly(azomethine)esters revealed that the chalcone moiety dimerized and led to photocrosslinking. The rate of photocrosslinking increased with longer methylene spacers and in the order of  $-H < -Cl < -OCH_3$ . Photoluminescence intensity was found to be enhanced upon UV irradiation. This could be due to the arrangement of the phenyl rings in the position that promoted effective  $\pi-\pi$  stacking interaction and hence led to aggregation of the polymer chains which was confirmed via TEM analysis.

#### 1. Introduction

The last decade has shown a steady increase in the interest towards poly(azomethines) with the recognition of their attractive properties in thermal stability, optical and electrical response, conductivity, syn-anti isomerisation, opto(electronic) and film or fibre forming ability [1]. However, the wholly aromatic rigid polv(azomethine) are neither fusible nor soluble in organic solvents owing to their strong chain-chain interaction. This shortcoming minimizes the feasibility of processing the polymers [1–4]. In order to improve the solubility of the polymers, several chemical modifications can be made. In fact, most of the researchers focus on the semiflexible polymers in which until now enormous semiflexible type of polymers have been reported by introducing flexibility in the polymeric chains [5]. Apart from the approach like incorporation of methylene spacer chain, several literatures have reported the potential of ester groups towards inducing flexibility and also the charge carrier movement along the chain in the polymeric systems [6,7].

The presence of both ester and azomethine units in the polymer backbone resulted in a type of polyazomethine called

\* Corresponding author. E-mail address: oocw@usm.my (C.-W. Oo).

http://dx.doi.org/10.1016/j.polymer.2015.06.041 0032-3861/© 2015 Elsevier Ltd. All rights reserved. poly(azomethine)esters. These polymers are a class of high performance polymers as they present a number of interesting and peculiar properties like excellent thermal, film-forming ability, mechanical and physical properties in various fields such as electronic, electric, photonics as well as in industrial material field [6]. Specifically, poly(azomethine)esters can be used in plastic electronic devices like light-emitting diodes (LED)s, polymeric solar cells, lasers or field effect transistors (FET)s [8]. They can as well as being a very powerful alternative to nanofabrication and to nanomanipulation for the development of nanotechnology as the new perspective in material science [9,10].

Furthermore, the inclusion of photosensitive groups in the polymeric chains have garnered great interest in the development of recent research due to their high process able properties like good solubility, photosensitivity, and thermal stability [11–13]. Photosensitive moieties are well attributed to the  $\pi$  electron density of the photoactive chromophore in the main chains or pendant groups of the polymers, which will be able to crosslink after irradiation with UV light to form highly crosslinked polymers at ambient temperature [14–17].

In fact, photosensitive polymers gain remarkable interests owing to its wide and well-proven technological applications in the field of photoresist, photolithography, printing materials, liquid crystalline [18,19] and energy exchange materials [20]. They can also be employed in various optical applications such as second





polyme

harmonic generation materials in non-linear optics materials [21], as photorefractive polymers [22], holographic recording materials and fluorescent probes for sensing of metal ions, biological macromolecules and microenvironment in micelles [21,23]. Besides, they can be used in manufacturing of industrial products such as integrated circuits, compact discs, cathode ray tubes and printed circuit boards [24].

To the best of our knowledge, incorporating chalcone, a photosensitive group into poly(azomethine)esters is relatively an unexplored area. Hereby, chalcone is introduced into the side chain or branches of the polymer due to poor solubility resulting from the rigid-rod nature of chalcone in the polymers backbone [18]. Chalcone give rise to the additional features of photocrosslinkable ability of the polymers, as it affords high sensitivity to UV radiation besides providing the photoluminescence properties [6,15–17].

This work dealt with the synthesis and characterization of new class of soluble photosensitive poly(azomethine)esters, bearing various substituents on the chalcone-based side chain with even methylene spacers on the main chains. The synthesis approach of these polymers mainly focused on the various substituents on the side chain and the spacer length in the backbones which can be easily varied, thereby allowing the possibility to study their influence on the thermal, photocrosslinking and photoluminescence properties of the polymers. The structures of the synthesized polymers were elucidated using various spectroscopic techniques.

#### 2. Experimental

#### 2.1. Materials

Benzaldehyde, 4-chlorobenzaldehyde, 4-methoxybenzaldeh yde, 4-hydroxyacetophenone, 5-hydroxyisophthalic acid, 4-hydro xybenzaldehyde, 1,4-dibromobutane, 1,6-diaminohexane, 1,8diaminooctane, 1,10-diaminodecane and 1,12-diaminododecane were purchased from TCI Chemicals. Potassium hydroxide and potassium carbonate were obtained from Q-Rec Chemicals and solvents (ethanol, acetone, benzene, thionyl chloride and chloroform) were purchased from Merck Chemicals. All the chemicals were used as received without further purification.

#### 2.2. Physical measurements

The IR spectra of the monomers and polymers were recorded using Perkin Elmer 2000-FTIR spectrophotometer in the frequency range of 4000–400 cm<sup>-1</sup> with sample prepared in KBr discs. Brucker Avance 500 MHz ultrashield spectrometer equipped with ultrashield magnets was used to record the <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of the synthesized monomers and polymers. Deuterated chloroform (CDCl<sub>3</sub>) and dimethysulphoxide (DMSO-d<sub>6</sub>) were used as the NMR solvents and TMS as internal standard. Thin layer chromatography (TLC) was performed with TLC sheets coated with silica and spots were visualized under UV light to monitor the progress of the reaction. Perkin Elmer 2400 LS Series CHNS/O analyzer was used to carry out the elemental analysis. Thermal behaviour of the polymers were evaluated via thermogravimetric analyses (TGA) which were performed with Mettler 851e TGA under nitrogen atmosphere with the heating rate of 10 °C/min. Differential scanning calorimetry (DSC) analyses of the polymers were carried out using with Perkin Elmer Pyris 1 Differential Scanning Calorimeter with the heating and cooling rates of 10 °C/min. The average molecular weights of the polymers were determined by using Waters Gel Permeation Chromatography (GPC) equipped with a Waters 1515 Isocratic HPLC Pump and Waters 2414 refractive index (RI) detector. Polystyrene standards (Polymer Laboratories) were used for calibration and THF was used as the eluent. UV absorption spectra were recorded on Shimadzu UV-2600 UV-Vis spectrophotometer while fluorescence measurements were performed using an LS-55 fluorescence spectrophotometer (Perkin Elmer) equipped with a plotter unit and a quartz cell  $(1 \text{ cm} \times 1 \text{ cm})$ . The samples were prepared by dissolving the polymer in chloroform. Photocrosslinking studies were carried out using 6 W highpressure Hg lamp (Vilber Lourmat, 365 nm) by placing the polymer solution in chloroform at a distance of 10 cm from the light source for different time intervals before recording the spectra with UV-Vis spectrophotometer. The morphological studies of the virgin and the photocrosslinked polymers were carried out using Scanning Electron Microscope (SEM) with the model of Leo Supra 50vp. The transmission electron microscopy images (TEM) were recorded on Philips CM12 by placing a drop of sample solution (0.05 mL) onto a copper EM grid. The solubility of the polymers was examined using 0.2–0.3 mg of sample in 5 mL of different solvents at room temperature.

#### 2.3. Synthesis of monomers and polymers

The synthesis steps of all the monomers and polymers were described in Scheme 1. The percentage yields, elemental data and spectral data of the monomers and polymers were illustrated in the Supplementary Material.

#### 3. Results and discussion

## 3.1. Characterizations of PSBH (6–12), PSBL (6–12) and PSBO (6-12)

The structures of the polymers were elucidated via FTIR, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopic techniques. The present of strong band at around 1739 cm<sup>-1</sup> after the polymerization depicted the functional group of C=O ester, which confirmed the success of polymerization [25,26] to form **PSB08** as illustrated in Fig. 1a. The other two homologous series were found to have similar observations. The <sup>1</sup>H NMR spectrum of **PSB08** (Fig. 2.) showed the occurrence of signal broadening, and the complexity of the signals further substantiated that polymerization was successfully carried out [27]. The proton decoupled <sup>13</sup>C NMR spectrum of **PSB08** (Fig. 3.) exhibited the expected peaks for each of the carbon atoms of the polymer in which the chemical shift of C=O ester appeared at 163.90 ppm and the chemical shift of C=O ketone was assigned at 188.76 ppm [24].

The molecular weights of the resulting polymers were determined via gel permeation chromatography (GPC). The number average and weight average molecular weights of the **PSBO** were found to be in the range of 2051–4196 and 3502 to 5946, respectively with the polydispersity indexes of 1.42–1.84. **PSBL** were found to have number average and weight average molecular weights in the range 2136–4236 and 3388 to 5425, respectively with the polydispersity indexes of 1.28–1.70. **PSBH** have number average and weight average molecular weights in the range of 2997–5217 and 4061 to 6994, respectively with the polydispersity indexes around 1.34 to 1.43.

All of the synthesized polymers were found to be insoluble in alcoholic solvents and some non polar solvents like benzene, nhexane and toluene but they were soluble in various organic solvents like chloroform, tetrahydrofuran, dimethylformamide, dimethylsulfoxide and dichloromethane. The polymers were soluble in most of the organic solvents may be due to the induction of the flexibility via the spacer chain in the polymer backbone in addition to the inclusion of bent shaped dicarboxylic acid monomers which then make them more processable and feasible for various potential applications.



Scheme 1. Synthesis routes towards formation of monomers 1a-1d, monomer 6 and their respective polymers, PSBH, PSBL and PSBO.

#### 3.2. Thermal properties of PSBH, PSBL, PSBO

The thermal properties of the polymers, **PSBH**, **PSBL** and **PSBO** were evaluated using thermogravimetric analysis under nitrogen atmosphere with the heating rate of 10 °C/min from 30 °C to 900 °C



Fig. 1. FT-IR spectra of photocrosslinkable **PSBO8** (a) before and (b) after 5 min of UV irradiation.

as in Fig. 4a, b and c for PSBH, PSBL and PSBO, respectively. All polymers showed reasonably good thermal stability. The degradation of these polymers occurred in two steps manner. The first step may be due to the decomposition of the flexible chain which was much easily decomposed than the rigid regions [28,29]. The first decomposition for all the polymers can be observed at temperatures between 200 °C and 300 °C while the polymers showed a rapid weight loss at temperature above 450 °C. The decomposition temperatures of 5% ( $T_{5\%}$ ), 50% ( $T_{50\%}$ ) weight loss and the percentage char yield at 900 °C were found to be relatively higher for -Cl and -OCH<sub>3</sub> substituted side chain polymers (**PSBL** and **PSBO**) compared to unsubstituted polymers (**PSBH**), and was depicted to be increased with the decrease of the methylene spacer lengths (R' = 6, 8, 10, 12). This may be ascribed to the change in the dipolemoment introduced by the substituents  $(X = OCH_3, Cl and H)$  [30]. The size of the substituent increase from  $-H < -Cl < -OCH_3$ . The bigger the size of the substituent, the greater the polarizability as the valence electron will be much further apart from the nucleus, hence leading to the increase in dipole moment and Van der Waals forces between the molecules giving higher thermal stability. Longer spacer length may give more flexibility to the polymers which then induced the dilution of the main core and hence



Fig. 2. <sup>1</sup>H NMR spectra of polyester, PSB08 before UV irradiation and CPSB08 after 5 min of UV irradiation.



Fig. 3. <sup>13</sup>C NMR spectrum of PSBO8.

lowered their thermal stabilities [31,32]. The glass transition temperature,  $T_g$  of the synthesized polymers were tabulated in Table 1. It was depicted that polymers with methoxy substituent, **PSBO** have higher  $T_g$  with the range of 97–47 °C as compared to chloro substituted polymers, **PSBL** and unsubstituted polymers, **PSBH** with the range of 70–40 °C and 67–42 °C, respectively. However, as the length of spacer chain increased, the  $T_g$  decreased for all the polymers. These observations clearly indicated the influence of various substituents of the side chain as well as spacer lengths on the thermal behaviour of the polymers.

#### 3.3. Photocrosslinking studies of PSBH, PSBL and PSBO

The photocrosslinking studies of the polymers were carried out upon irradiation with 365 nm light, and the changes in the UV absorbance were monitored by UV–Vis spectrophotometer. The peculiar property of these types of polymers is their ability to



Fig. 4. TGA thermograms of polymers, (a) PSBH, (b) PSBL and (c) PSBO.

 Table 1

 The molecular weights, thermal decomposition values and DSC data of polymers

 PSBH, PSBL and PSBO.

Polymer	Mw	DSC T <sub>g</sub> (°C)	TGA		
			T <sub>5%</sub> (°C)	T <sub>50%</sub> (°C)	Char yield (%)
PSBH6	6994	67	232	448	28
PSBH8	4281	50	218	446	23
PSBH10	4384	42	210	445	21
PSBH12	4061	44	193	445	15
PSBL6	5424	70	273	462	32
PSBL8	4517	68	273	450	29
PSBL10	4266	52	251	449	27
PSBL12	3388	40	216	449	24
PSBO6	5946	97	391	465	35
PSBO8	5412	96	382	462	33
PSBO10	3502	88	280	450	28
PSBO12	4821	47	227	460	31

undergo rapid photocrosslinking without the addition of any photoinitiators. A representative absorption spectrum under UV irradiation of polymer **PSBO8** was shown in Fig. 5. The absorption band around 315–325 nm with small shouldering was corresponded to  $\pi$ – $\pi$ \* transition of the olefinic double bond in the chromophore. During the subsequent irradiation, decrease in absorption maxima was observed. This behaviour may be due to the dimerization of the olefinic double bonds of the polymeric chain which involved  $2\pi$ + $2\pi$  cycloaddition in forming a cyclobutane ring. This ring formation partly destroyed the conjugation of the  $\pi$ -electron system thus gave a decrease in the absorption maxima of  $\pi$ – $\pi$ \* transition, with a concomitant in the absorbance at a shorter wavelength which was due to the single bond formation from the cyclobutane ring [28,29].

Furthermore, the time taken to achieve maximum photocrosslinking as well as the rate of photocrosslinking were depended on the nature of the substituents of the side chain, which varies in term of their electron withdrawing/donating nature and thus altered the resonance effect. Among the polymers, the present of methoxy group as the substituent on the side chain showed highest rate of photocrosslinking, and took shortest time to achieve maximum photocrosslinking compared to the chloro and unsubstituted polymers at the same duration of UV irradiation (10 s) as depicted in Fig. 6. The presence of electron donating group strengthen the electron density of the -CH=CH- of the olefin group through an extended conjugation therefore increase the crosslinking efficiency of **PSBO** [33,34]. Meanwhile, the time taken



Besides that, the increase in methylene spacer length on the backbone will shorten the time to achieve maximum photocrosslinking. The longer the methylene carbon chains, the faster the photocrosslinking for all the three series of polymers bearing different substituents on the side chain. Increasing the length of this spacer group will give more flexibility to the backbone, hence created more photocrosslinking possibility among the side chains.

FT-IR analysis was conducted on the polymers to obtain a better idea on the photocrosslinked system of the polymers. As similar spectra were obtained for all polymers thus comparative FT-IR spectra of **PSB08** were used in the discussion as depicted in Fig. 1a and b. After 5 min of UV irradiation, the intensity of the absorption band of the olefinic double bond (-C=C-) at 1601 cm<sup>-1</sup> was found to be decreased and the absorption band of C=O at 1648 cm<sup>-1</sup> was shifted to higher frequency at 1654 cm<sup>-1</sup>. These changes suggested the formation of cyclobutane ring attributed to the opening of the unsaturated bond of the olefinic functional group from the fully conjugated -C=C-(CO)- into unconjugated -CH-CH-(CO)- group [33].

**PSBO8** prior to and after UV irradiation was subjected to <sup>1</sup>H NMR analysis (Fig. 2). Monomer 6c was synthesized and used as the model compound to assign the polymers signals (Fig. 7.). The photocrosslinked PSBO8 and 6c were designated as CPSBO8 and C6c, respectively. After UV irradiation the proton peaks of 6c were shifted to upfield. H6 (7.11 ppm) from 6c was shifted to 6.85 ppm (H6') in C6c and H1 (7.03 ppm) from 6c was shifted to H1' in C6c at 6.65 ppm. Similarly, this was in agreement with the shifting of signals for H1 (7.01 ppm) to H1' (6.51 ppm) and H6 (6.95 ppm) to H4' (6.76 ppm) when **PSBO8** crosslinked to form **CPSBO8**. However, the rest of the proton signals for CPSBO8 were observed to be around the same as that of PSBO8 except at reduced intensity. This could be due to the low percentage of photocrosslinking. Therefore the originals proton signals were still present even after photocrosslinking. Signal broadening caused the proton signals barely to be identified due to overlapping. Other than that, the two weak signals at 4.06 ppm (H4') and 4.43 ppm (H3') in C6c were attributed to the proton signals of cyclobutane ring formed from the photocrosslinked reaction. However, these weak proton signals were not



Fig. 5. UV-Vis Spectra of **PSB08** in chloroform upon 365 nm UV irradiation at various time intervals.



Fig. 6. Rate of photocrosslinking of PSBH, PSBL and PSBO upon 365 nm UV irradiation.



Fig. 7. <sup>1</sup>H NMR spectra of monomer before (6c) and after UV irradiation (C6c).

seen in **CPSBO8** which may be due to the overlapping of these proton signals with the  $-NCH_2$  and  $-OCH_2$  proton signals.

The fluorescence spectra of all the polymers were recorded in chloroform solvent with irradiation under UV lamp at 365 nm at various time intervals under the excitation of 345 nm. They showed similar trend in the increment of the photoluminescence intensity when the polymers were exposed to longer irradiation time. PSBO8 (Fig. 8.) was used as the representative compound for discussion. The formation of cyclobutane rings brought the polymeric chains closer together inducing higher degree of molecular packing after photocrosslinking. These rings formation would then increased the rigidity of the photocrosslinked network, thus restricted molecular rotation to an extent resulting in a more effective  $\pi - \pi$  stacking interaction among the phenyl rings that attributed to the enhancement of the photoluminescence intensity. This could be evidenced by the transformation of weak greenish blue fluorescence into highly intense cloudy blue emission after UV irradiation in chloroform solvent (Fig. 9.). The cloudy solution observed after the UV irradiation suggested the aggregation of the polymer chains. This was further confirmed using transmission electron microscopy (TEM) analysis. As shown in Fig. 10a, the virgin PSBO8 was



Fig. 8. The changes of emission maxima of **PSBO8** in chloroform upon UV irradiation at various time intervals.

presented as filaments while the photocrosslinked **CPSB08** (Fig. 10b.) showed that the filaments coalesced and aggregated.

Additionally, the polymers were further examined for the effects of substituents on the side chain and methylene spacer lengths towards their relative photoluminescence intensity (Fig. 11.). The  $-OCH_3$  substituted polymers have higher relative photoluminescence intensity than -Cl and unsubstituted polymers. Similarly, as the spacer length increased, the relative photoluminescence intensity was found to be increased. This could be corresponded to the higher rate of photocrosslinking for the polymers with longer methylene spacer and  $-OCH_3$  substituted side chain. When the spacer length increased, the flexibility of the polymeric chain increased, which allowed more side chains to



Fig. 9. Images for PSBO8 in chloroform with the absent (a) and present (b) of UV source.



Fig. 10. TEM images of (a) virgin PSBO8; (b) CPSBO8 after 5 min of exposure to UV light.



Fig. 11. Relative photoluminescence intensities with respect to different spacer lengths and substituents on the side chain after maximum photocrosslinking.

interact and crosslink among each others. This further enhanced the  $\pi$ - $\pi$  stacking and induced greater electron clouds interaction, which then led to the enhancement of the photoluminescent intensity.

#### 4. Conclusion

Photosensitive poly(azomethine)esters bearing various substituents on the chalcone-based side chain with even methylene spacers on the main chains were successfully synthesized via polycondensation method. It was observed that these polymers were found to have good solubility in organic solvents. The molecular structures of the monomers and polymers were characterized by FT-IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectral analysis. The thermal stability of the polymers decreased with the increasing of spacer length, while decreased in the order of -OCH<sub>3</sub>, -Cl and unsubstituted polymers (-H). While the UV studies revealed that the polymers underwent photocrosslinking upon UV irradiation, with the formation of cyclobutane rings that crosslinked the polymeric chains. The photocrosslinking ability was further substantiated with FT-IR and <sup>1</sup>H NMR analyses. The rate of photocrosslinking showed that longer spacer lengths and -OCH<sub>3</sub> substituted polymers gave higher rate of photocrosslinking comparatively. After UV irradiation, the photoluminescence intensities of the polymers were enhanced, illustrating that effective  $\pi-\pi$  stacking interaction among the phenyl rings may occur due to aggregation of the polymeric chains. The formation of aggregates was confirmed with TEM analysis. Besides, the relative photoluminescence intensity was found to be increased with the increasing rate of photocrosslinking. These new class of polymers could be potentially exploited as photoluminescent materials in chemosensors as well as opto-electronic applications which are worth to be explored.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2015.06.041.

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