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ORIGINAL PAPER

Synthesis and characterization of the novel inimer-containing fluorene units and preparation of blue light-emitting polymers

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Abstract The novel inimer-containing fluorene units was successfully synthesized and characterized. Hyperbranched homopolymer and copolymers with methyl methacrylate (MMA) were prepared by the novel inimer via atom transfer radical polymerization where CuBr/1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) were used as catalyst. The copolymerization of inimer and MMA was performed under different ratio of the initial inimer/MMA and the inimer acted as not only the branched point (BP) but also the functional groups which emit blue light. The number-average molecular weight (M_n) and polydispersity index (PDI) of polymers are in the ranges (3.6–18.4) $\times$ 10^3 and (1.3–2.8), respectively. Thermal gravimetric analysis (TGA) results showed all polymers had good thermal stabilities. The number of the inimers acted as branched point in the copolymer backbone is estimated by ^{1}H NMR spectra and UV–Vis absorption spectra.

Keywords Inimer · Blue light-emission polymers · Branched point · Hyperbranched polymer

Introduction

Since the first report of the self-condensation vinyl polymerization (SCVP) by Fréchet et al. [1], this general approach has been applied to various types of living polymerization, i.e., cationic [1], radical [2–4], group transfer [5], and even ring-opening polymerization [6]. The monomers suitable for SCVP are difunctional, possess both a vinyl group and an initiating site and are termed “inimer”. Inimer is designated as AB* where A represents a vinyl group, while B* represents a

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functional group that can be activated and can initiate the polymerization of the double bonds. AB* monomers containing both a polymerizable vinyl group A and an activated halogen atom B* can be homopolymerized using ATRP to yield hyperbranched polymers; the copolymerization of AB* monomers with conventional monomers yields macromolecules with branched structures [7–9]. The development of polymers with well-controlled and/or novel architectures has been the subject of increasing interest among polymer scientists [10]. In particular, dendrimers have been extensively studied as materials with novel physical properties [11, 12]. However, commercialization of dendrimers is prevented by the requirements of multi-step reactions and intermediate purification. Less regular hyperbranched polymers obtained by polycondensation are more easily available, but their preparation was restricted to the polycondensation of AB_n monomers [13–16]. Polymers with a high degree of branching can be easily prepared by the self-condensation vinyl polymerization (SCVP) using AB* monomers [17, 18]. The structure of a macroinimer [19], $A(m)_nB^*$, differs from that of an AB* inimer only by the presence of linear monomer units, (*m*), acting as a spacer between initiator and monomer function. In this article, the *m* not only acted as a spacer but also as light-emitting units.

As it is well known, oligo-, polyfluorene, and their derivatives are considered to be promising blue light-emission materials since they exhibit excellent thermal and chemical properties and high solid-state fluorescence quantum yields [20–27]. Inimers with fluorene or their derivatives should be the promising monomers used to prepare hyperbranched polymer, in which the conjugated units exist inside hyperbranched polymer skeleton and also could be acted as the structural probes when they were copolymerized with vinyl monomers.

In this article, the novel fluorescent inimer with terfluorene was synthesized. The homopolymerization and copolymerization of inimer with methyl methacrylate (MMA) were performed by atom transfer radical polymerization, in which inimer acted as both the initiator and the monomer. The aim of the study is to gain blue light-emitting branched and hyperbranched polymers by inimer with functional units. Furthermore, the incorporation of the inimer into the polymeric backbone was confirmed by ^{1}H NMR spectroscopy, UV–Vis absorption and fluorescence emission spectra and the number of inimers in copolymers was estimated.

Experimental

Materials

(2-Hydroxymethyl-9,9,9′,9′,9″,9″-hexaoctyl-2,2′,2″-terfluorene-7″-yl)-methanol was synthesized according to the literature procedures [28]. CuBr was purified by stirring overnight in acetic acid. After filtration, it was washed with ethanol, ether and then dried. HMTETA was purchased from Aldrich and used without further purification. MMA was vacuum-distilled before use. 2-bromoisobutyryl bromide was purchased from Alfa Aesar and used without further purification. All solvents were purified and dried by standard methods.

Measurements

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE600 spectrometer at room temperature in $CDCl_3$. Electronic absorption spectra were obtained on a Shimadzu UV–Visible spectrometer model UV-2500. Fluorescence spectra were recorded on a Shimadzu RF-5301PC. Elemental analyses were performed on a Flash EA 1112 analyzer. TGA (Pyris 1 TGA) measurements were carried out under a nitrogen atmosphere at a heating rate of 10 °C/min to record the thermal gravimetric analysis (TGA). The matrix assisted laser desorption ionization time of flight (MALDI-TOF) MS spectrometric measurements were performed on a Bruker BIFLEXIII mass spectrometer. The gel permeation chromatography (GPC) measurements were performed on a Waters chromatography connected to Waters 410 differential refractometer with THF as an eluent. Calibration was performed with linear polystyrene standards.

Synthesis of inimer with terfluorene unit

1.00 g (0.80 mmol) (2-Hydroxymethyl-9,9,9′,9′,9″,9″-hexaoctyl-2,2′,2″-terfluorene-7″-yl)-methanol and triethylamine (Et_3N, 0.060 mL) were mixed in 20 mL of CH_2Cl_2. This reaction system was cooled to 0 °C before 0.027 mL (0.40 mmol) acrylic acid was added dropwise. Then 1-ethyl-3-(3-dimethyllaminopropyl)carbodiimide hydrochloride (EDC·HCl) (0.077 g, 0.40 mmol) was added. After stirring for 1 h at 0 °C, the mixture was warmed to room temperature (rt) and stirred overnight. After removal of the solvent, the crude product was purified by chromatography on silica gel eluting with ethyl acetate/hexane (1:12, v/v) to give product (**1**) (0.45 g, 87.70%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.80–7.64 (m, 14H), 7.38–7.22 (m, 4H), 6.49–6.46 (d, $J = 18$ Hz, 1H), 6.23–6.19 (m, 1H), 5.86–5.84 (d, $J = 12$ Hz, 1H), 5.30 (s, 2H), 4.78 (s, 2H), 2.11–2.04 (m, 12H), 1.89 (s, 1H), 1.26–1.09 (m, 60H), 0.81–0.73 (m, 30H); ^{13}C NMR (600 MHz, $CDCl_3$): δ 166.15, 151.84, 151.80, 151.69, 151.59, 151.51, 141.09, 140.81, 140.58, 140.56, 140.50, 140.48, 140.10, 140.06, 139.90, 139.82, 134.58, 130.95, 128.54,127.30, 126.21, 126.13, 125.90, 123.08, 121.65, 121.53, 121.51, 120.08, 119.99, 119.94, 119.79, 66.90, 65.85, 55.37, 55.26, 55.25, 40.40, 40.29, 31.82, 31.70, 30.08, 30.05, 30.03, 29.26, 29.23, 23.94, 23.91, 22.63, 14.09; MALDI-TOF-MS, m/z: calcd, 1282.0; found, 1281.1.

0.088 mL (0.72 mmol) 2-bromoisobutyryl bromide was added dropwise to a mixture of product (**1**) 0.46 g (0.36 mmol) and triethylamine 0.049 mL (0.36 mmol) in CH_2Cl_2 (10 mL) at 0 °C. After stirring for 0.5 h at 0 °C,the mixture was warmed to room temperature and stirred overnight. The solution was washed with a large amount of water to remove the salt and the excess of 2-bromoisobutyryl bromide before extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4. After removal of the solvent, the crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (1:20, v/v) to give product (**2**)—inimer. (0.37 g, 71.50%).^{1}H NMR (600 MHz, CDCl3): δ 7.87–7.64 (m, 14H), 7.51–7.38 (m, 4H), 6.49–6.46 (d, $J = 18$ Hz, 1H), 6.23–6.19 (m, 1H), 5.86–5.84 (d, $J = 12$Hz, 1H), 5.32–5.30 (d, $J = 12$ Hz, 4H), 2.11–1.97 (m, 18H), 1.26–1.09 (m, 60H), 0.81–0.73 (m, 30H); ^{13}C NMR (600 MHz, $CDCl_3$): δ 171.47, 166.10, 151.84, 151.80, 151.52, 141.17, 141.08, 140.84, 140.81, 140.49, 140.10, 139.83, 134.62, 134.20, 130.90, 128.56, 127.30, 127.12, 126.23, 126.20, 123.08, 122.81, 121.52, 121.47, 120.09, 120.01, 119.80, 119.75, 68.03 66.88, 55.79, 55.38, 55.27, 40.40, 40.30, 31.93, 31.82,31.70, 30.83, 30.09, 30.05, 30.03, 29.75, 29.29, 29.26, 29.23, 23.93, 23.90, 22.63, 14.10; MALDI-TOF-MS, m/z: Calcd. 1431.0; Found 1431.1

Polymerization of inimer

In a typical run, a glass tube was loaded with CuBr, inimer, MMA (when the reaction is copolymerization) and *o*-dichlobenzene. The glass tube was degassed, the mixture was stirred for 10 min, and then HMTETA was introduced with a syringe. The glass tube was then immersed into an oil bath at 80 °C. After stirring for a period of time, the polymer was precipitated in methanol. The crude polymers were repurified by precipitation from THF into methanol again and dried under vacuum to give polymers. Polymer **P1** was homopolymer of inimer and polymer **P2–P5** were synthesized under different ratio of inimer to MMA.

Polymer **P1**: ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.82–7.63, 7.38–7.33, 5.31, 5.21, 5.12, 4.81, 4.34, 2.10–2.03, 1.59–1.46, 1.29–1.08, 0.82–0.72 (broad); Elemental analyses: Calcd. C 80.50, H 9.29; Found C 77.75, H 8.96.

Polymer **P2**: ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.82–7.64, 7.34–7.26, 6.98, 5.18–5.03, 4.80 4.31, 3.60, 2.27–1.63, 1.43, 1.26–1.11, 0.81–0.72 (broad); Elemental analyses: Calcd. C 72.61, H 8.83; Found C 75.39, H 9.46.

Polymer **P3**: ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.82–7.62, 7.34–7.26, 5.17, 4.80, 4.35, 3.85–3.60, 2.50, 2.04–1.82, 1.63, 1.42, 1.25–1.02, 0.85–0.72 (broad); Elemental analyses: Calcd. C 64.56, H 8.29; Found C 66.87, H 8.68.

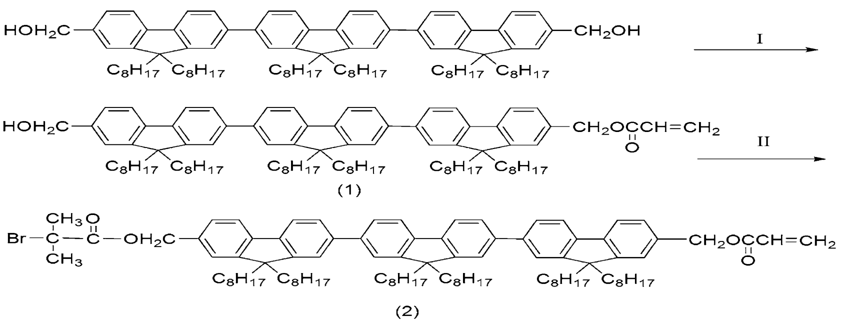
Polymer **P4**: ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.80–7.62, 7.33–7.26, 5.17, 3.60, 2.09–1.81, 1.43, 1.25–1.02, 0.84 (broad); Elemental analyses: Calcd. C 61.37, H 8.09; Found C 62.78, H 8.10.

Polymer **P5**: ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.78–7.58, 7.30–7.26, 5.17–5.14, 4.78, 4.32, 3.81–3.56, 2.47, 2.24, 2.00–1.77, 1.40, 1.17–0.98, 0.80–0.68 (broad); Elemental analyses: Calcd. C 60.71, H 8.04; Found C 62.32, H 8.35.

Results and discussion

Synthesis and characterization

The synthetic route toward the inimer with terfluorene unit is outlined in Scheme 1. Starting from the (2-hydroxymethyl-9,9,9′,9′,9″,9″-hexaoctyl-2,2′,2″-terfluorene-7″-yl)-methanol which was synthesized via the route published by Xiao et al. [28], desired inimer was obtained via a two-step synthesis. The reaction of excess (2-hydroxymethyl-9,9,9′,9′,9″,9″-hexaoctyl-2,2′,2″-terfluorene-7″-yl)-methanol with acrylic acid using EDC·HCl as catalyst afforded product (**1**) in 87.7% yield. The inimer was accomplished in a yield of 71.5% by the reaction of product (**1**) and



Reagents and conditions: I. CH_2Cl_2, Et_3N, EDC·HCl, rt; II. 2-bromoisobutyryl bromide, CH_2Cl_2, Et_3N, rt.

Scheme 1 Synthesis of inimer

2-bromoisobutyryl bromide in solution of CH_2Cl_2 and triethylamine. The structure of product (**1**) and inimer were confirmed by ^{1}H, ^{13}C NMR spectroscopy and MALDI-TOF-MS. The mass of the major peak matched the expected value of the product (**1**) and inimer.

The self-polymerization of inimer and copolymerizations of inimer and MMA were accomplished by ATRP, where inimer with terfluorene acted as both the initator and the vinyl monomer. Homopolymer **P1** and copolymers **P2**–**P5** were formed by the ATRP polymerization technique in *o*-dichlobenzene at 80 °C using CuBr/HMTETA as catalyst. Desirable outcome did not obtain utilizing dimethylformamide as solvent and CuCl/2,2′-bipy as catalyst although they were traditional catalysts. To achieve copolymers with different degree of branching, the initial inimer/MMA molar ratio ([I]:[M]) was increased from 1:10 to 1:400 (**P2**, 1:10; **P3**, 1:50; **P4**, 1:200; **P5**, 1:400). The reaction conditions and results are listed in Table 1. The structure of homopolymer and copolymers are shown in Fig. 1. All polymers are easily soluble in common organic solvents, such as THF, chloroform,

Table 1 Reaction conditions and results of sample

sample	[I]:[MMA][a]	*o*-dichlobenzene (mL)[b]	Reaction time (h)	Conv. (%)	M_n[c]	M_w[c]	PDI[c]
P1	100% I	0.25	140	54	3600	5900	1.64
P2	1:10	0.25	72	79	7300	20200	2.77
P3	1:50	0.5	72	60	18400	33500	1.82
P4	1:200	0.5	72	22	14700	22900	1.56
P5	1:400	–	46	10	14200	18900	1.33

[a] I stands for inimer; CuBr:HMTETA:inimer = 6:6:1; 80 °C

[b] *o*-dichlobenzene (mL) is the amount according to the inimer when it was 62 mg

[c] Molecular weights and polydispersity index were determined with size exclusion chromatography experiments (THF, room temperature) using polystyrene standards for instrument calibration

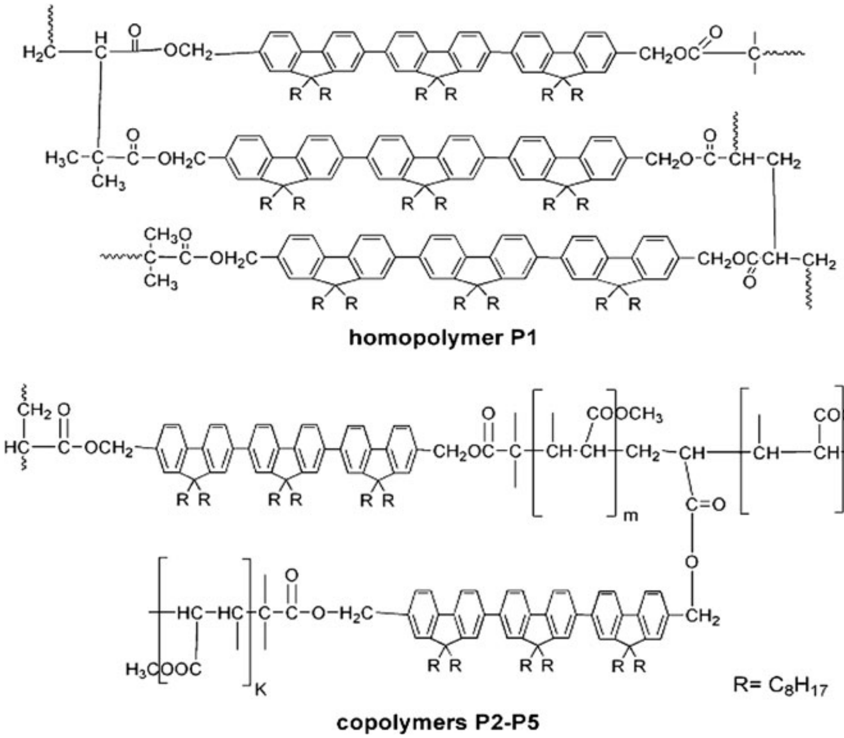


Fig. 1 Structure of homopolymer **P1** and copolymers **P2–P5**

etc. The molecular structure of the polymers was verified by ^{1}H NMR spectroscopy and elemental analysis. The molecular weights of polymers were determined by GPC with THF as the eluent, calibrated against polystyrene standards. As shown in Table 1, the GPC analysis indicated that the number-average molecular weight and polydispersity index (PDI) of polymers are in the ranges $(3.6–18.4) \times 10^3$ and 1.3–2.8, respectively. At the lower concentration of the inimer, the lower concentration of the radicals was generated in the polymerization system, so the conversion decreased (from **P2** to **P5**) as the ratio of inimer to MMA ([I]:[MMA]) decreased.

Figure 2 is the GPC curves of polymers which were synthesized at [I]:[MMA] = 1:600 with other condition unchanged. The GPC curves show that the molecular weight of copolymer was increasing with polymerization time. According to ^{1}H NMR of copolymer with different reaction time, degree of polymerization show increasing trend with time. As we all know, molecular weight of polymer in general radical polymerization increased very quickly in very short period of time. All of the above analysis proved that polymerizations in this article were implemented in accordance with design. The GPC curves were also used to confirm that no trace of the inimer is apparent in the copolymers, which also confirms the incorporation of the initiator into the polymeric chain.

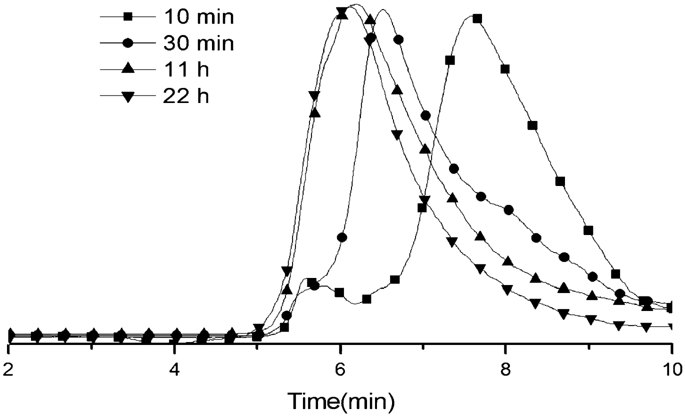


Fig. 2 GPC elution traces of the polymers which were synthesized at [I]:[MMA] = 1:600 with other conditions unchanged

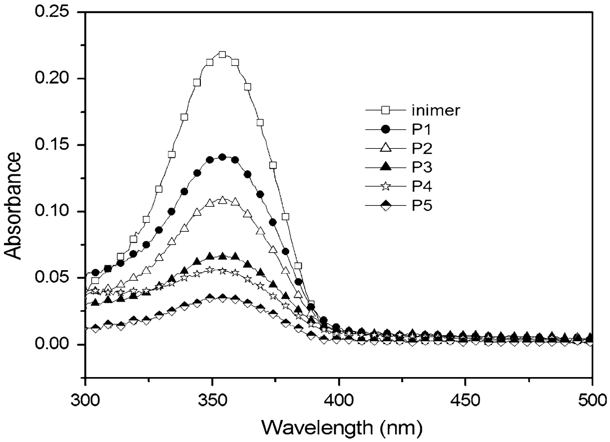


Fig. 3 UV–Vis absorption spectra at room temperature of polymers and inimer in THF solutions (polymers: 4.88×10^{-3} g L^{-1}; inimer: 4.14×10^{-3} g L^{-1})

Optical properties

The inimer and polymers **P1–P5** were investigated with absorption and emission spectroscopy in dilute THF solution. The inimer and polymers have similar absorption spectra in THF solution as shown in Fig. 3. It is noted the polymers in the experimental condition exhibited a maximum absorption peak at around 354 nm attributed to terfluorene segments, which was almost same as that of the inimer. The absorption peak of P1–P5 is decreases due to the fact that the percentage of the terfluorene part in the polymeric chain decreases as well.

Figure 4 illustrates the fluorescence emission spectra of inimer and the polymers in dilute THF solutions. All the samples exhibited emission spectra with two main

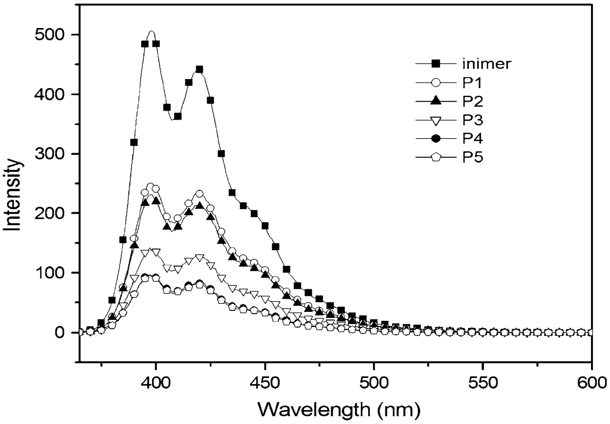


Fig. 4 Fluorescence emission spectra at room temperature of polymers and inimer in THF solutions (polymers: 4.88 × 10^{-3} g L^{-1}; inimer: 4.14 × 10^{-3} g L^{-1})

peaks located at about 397 and 419 nm, which showed the emitting peaks located in the blue light range. The similar emission spectra also suggested that similar radiational species—inimer with terfluorene derivatives were involved in their photoluminescence processes. The fact also shows that the flexible chains do not affect the luminescent properties of the chromophore [29, 30]. From the above, the incorporation of the inimer in the polymer backbone was also confirmed.

Inimer and the polymers show similar UV–Vis and photoluminescent properties in dilute solution indicating their similar effective conjugation length [31].

Solid films of inimer and polymers on quartz plates used for UV–Vis and fluorescence were prepared by spin-coating from a 1%THF solution at 1,500 rpm. All polymers formed homogeneous films. The UV–Vis and photoluminescence spectra of inimer and polymers in film are shown in Figs. 5 and 6. The absorption maxima of the inimer and polymers in thin films were almost identical with those in solution, which indicates that there was nearly no change in conformation of the inimer and polymers from the solution to the solid state. However, the fluorescence emission spectra of inimer and polymers showed slightly difference when changing from solution to films. Compared with the corresponding to those in solution emission spectra, the peaks at about 397 nm of inimer and polymers in solid state were weaken and vanished.

Branched point

The double bonds in inimer could be initiated by the radicals to participate polymerization, and so the branched points inside backbone of the copolymer should be formed attributed to double bond and initiating site. The inimer acts as branched point in copolymers. ^{1}H NMR spectra, the UV–Vis absorption spectra could give a clue to estimate the branched points, and as well as the method to detect the microenvironment of inimer.

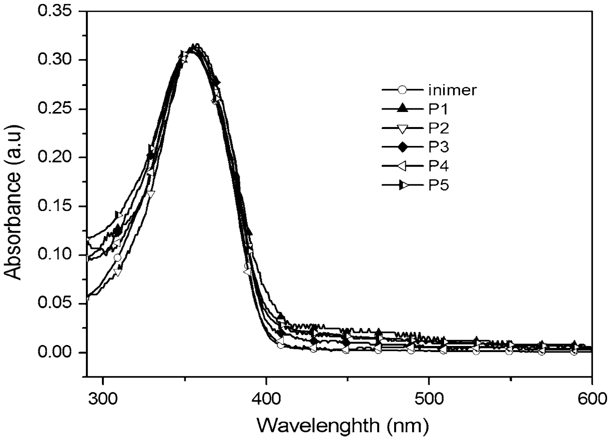


Fig. 5 UV–Vis absorption spectra of polymers and inimer in film

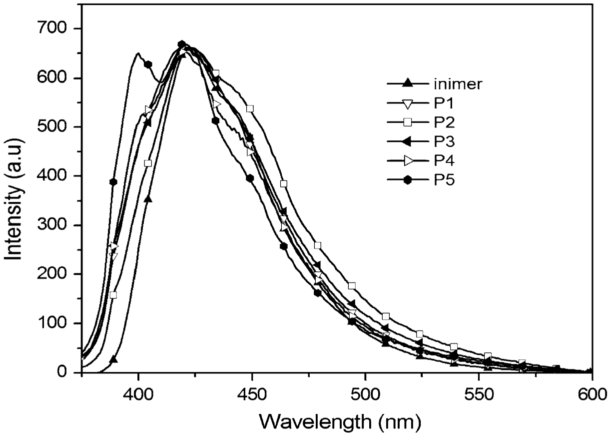


Fig. 6 Fluorescence emission spectra of polymers and inimer in film

In Fig. 7, the ^{1}H NMR spectra of the inimer (A) and the copolymer (B) (for example polymer **P4**) are presented. Most of the characteristic signals of the inimer, that is signals in the aromatic region in the range of $\delta = 7.3–7.9$ ppm are clearly shown in the spectrum of the copolymer, indicating the successful integration of the inimer structures into copolymers. The compositions ratio of inimer to MMA per copolymer can be estimated from the integration of the aromatic region –H in inimer at 7.3–7.9 ppm to that of –OCH_3 in MMA units at 3.6 ppm. The number of the inimer in copolymers can be calculated according to M_n and the results were summarized in Table 2.

The number of the inimer incorporated into the copolymer can also be estimated based on the UV–Vis absorption spectra. Molar absorption coefficient of inimer $\varepsilon = 7.513 \times 10^4$ L/mol cm was obtained from absorbance of inimer, then the number

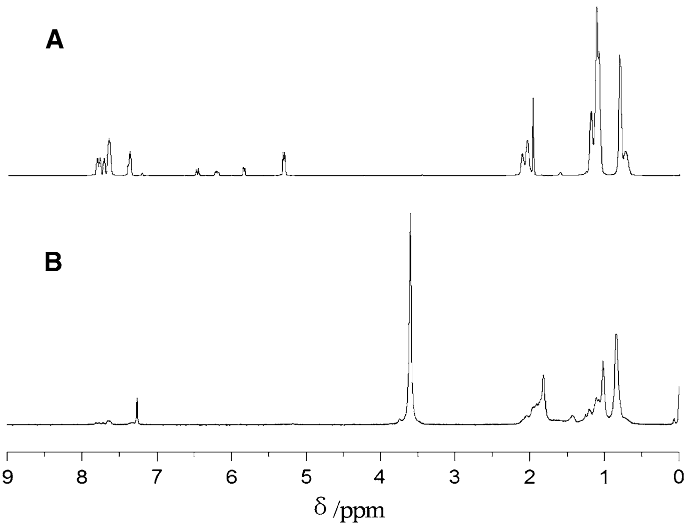


Fig. 7 ^{1}H NMR spectra of inimer (**a**) and copolymer **P4** (**b**) in $CDCl_3$ at room temperature

Table 2 [I]:[MMA] and the number of branched point in copolymers calculated by ^{1}H NMR spectra and UV–Vis absorption spectra

Sample	[I]:[MMA] (reaction)	[I]:[MMA]$_{(NMR)}$[a]	[I]:[MMA]$_{(UV-Vis)}$[b]	BP$_{(NMR)}$[c]	BP$_{(UV-Vis)}$[d]
P2	1:10	1:8.7	1:18.9	3.2	2.2
P3	1:50	1:43.5	1:39.8	3.2	3.4
P4	1:200	1:81.1	1:63.0	1.5	1.9
P5	1:400	1:101.6	1:87.0	1.2	1.4

[a] [I]:[MMA]$_{(NMR)}$ was calculated by ^{1}H NMR spectra

[b] [I]:[MMA]$_{(UV-Vis)}$ was calculated by UV–Vis absorption spectra

[c] BP$_{(NMR)}$ was the number of branched point in copolymers calculated by ^{1}H NMR spectra

[d] BP$_{(UV-Vis)}$ was the number of branched point in copolymers calculated by UV–Vis absorption spectra

of the inimer in copolymers was calculated based on UV–Vis absorption spectra of copolymers using lambert–beer law and the ratio of inimer to MMA in the copolymers were also estimated according to M_n. The results were summarized in Table 2.

Thermal properties

The thermal properties of a series of polymers were investigated by TGA shown in Fig. 8. Polymers **P1–P5** exhibited good thermal stability with onset degradation temperatures (T_d) above 250 °C under nitrogen. TGA measurement of **P2–P5** revealed a two-step degradation process with the first level at 250–500 °C and further mass stability until 600 °C. TGA experiments showed major weight loss in the range of 250–500 °C and the weight loss of **P2–P5** were 72, 83, 87, 91%, respectively. The results shown that weight loss in the first stage was expected

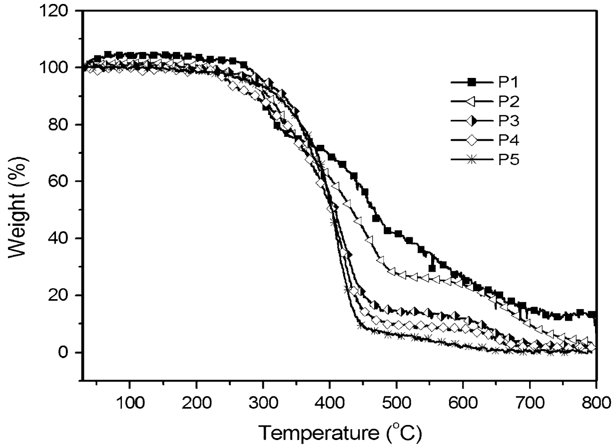


Fig. 8 TGA traces of polymers **P1**–**P5** under a nitrogen atmosphere

increased gradually as the fraction of inimer, as well as the proportion of the aromatic ring in the copolymers decreased from **P2** to **P5**.

Conclusions

In summary, photoluminescent, substituted terfluorene derivative was synthesized. This oligomer with double bond and an initiating site was used as inimer. Homopolymer of inimer and copolymers of inimer and MMA have been synthesized by utilizing atom transfer radical polymerization. These polymers were soluble in common organic solvents and exhibited good thermal stability. These polymers have the ability to emit blue light when excited in the near-UV region in solution. This provided a way to obtain functional and light-emitting branched polymer and hyperbranched polymer.

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