

Photo-induced Living Cationic Copolymerization of Isobutyl Vinyl Ether and Vinyl Ether with Carbazolyl Groups*

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Abstract In this work, a fluorescent monomer 2-(9-carbazolyl) ethyl vinyl ether (CEVE) was synthesized in our lab, and its photo-induced living cationic copolymerization behavior with isobutyl vinyl ether (IBVE) was investigated in detail using diphenyliodonium chloride (DPICl)/2,2-dimethoxy-2-phenylacetophenone (DMPA) and zinc bromide (ZnBr_2) initiating system in dichloromethane solution at 5 °C, –5 °C, and –15 °C, respectively. The living nature of this copolymerization system was confirmed by adding fresh comonomer method after the copolymerization almost finished. In addition, the obtained fluorescent copolymer poly(IBVE-co-CEVE) has a low glass transition temperature (T_g), below –10 °C.

Keywords: Photopolymerization; Kinetics (polym.); Copolymerization; Cationic polymerization; Living cationic polymerization.

INTRODUCTION

It is well known that several kinds of monomers such as alkyl vinyl ethers and epoxides cannot be polymerized by a radical mechanism. Thus ionic initiators are usually applied in their polymerizations^[1]. Compared with radical polymerization, oxygen does not inhibit cationic polymerization. However, a dry environment is required because moisture generally terminates the polymerization.

Photo-induced cationic polymerization is generally accomplished with the aid of onium salts. Iodonium^[2] and sulfonium^[3] salts were first described by Crivello. Due to most of the onium salts are responsive to the short-to mid-wavelength UV lights; interests have been directed toward extending the light to near-UV or visible regions. Generally speaking, the following four strategies are often used: (1) introducing additional chromophoric groups to the structure of the onium salt^[4, 5], (2) electron transfer reactions with photoexcited sensitizers^[6], (3) free radical promoted cationic polymerization^[7–10] and (4) electron donor compounds in the excited charge transfer complexes^[11, 12]. Among them, the so-called free radical promoted cationic polymerization (FRPCP) has been widely applied by researchers since it is flexible to extend the wavelength sensitivity to longer wavelength.

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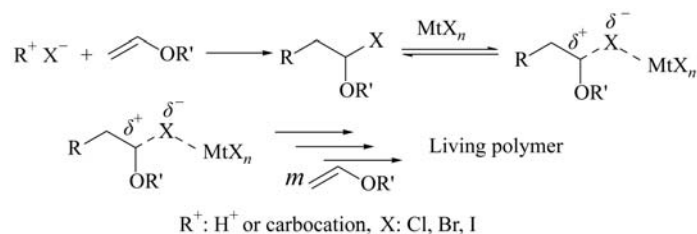
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Recently, much attention has been paid to living cationic polymerization (LCP) since it's an elegant way to obtain polymers with well-defined structures^[13–17]. First living cationic polymerization for isobutyl vinyl ether (IBVE) with the HI/I₂ system was developed by Higashimura *et al.* in 1984^[18]. Subsequently, Kennedy reported the LCP of isobutylene (IB) with the tertiary ester/BCl₃ initiating system in 1986^[19]. Nowadays, tremendous progress has been made in the area of LCP. LCP for vinyl ethers using appropriate combination of Lewis acids in conjunction with added bases has been discussed by several groups. LCP of vinyl ethers with IBVE-HCl adduct/FeCl₃/cyclic ether initiating system was reported by Aoshima and coworkers^[20, 21]. Very fast living polymerization completed in seconds was induced by FeCl₃ in the presence of a cyclic ether with a suitable basicity^[22]. Uncommon cationogens such as simple alcohols functioned as cationogens also gave a good result of living cationic polymerization of VEs^[23]. Polymerization of VEs using acetals, which are regarded as adducts of VE with alcohols, proceeded in similar manners to those using alcohols combined with suitable metal chlorides^[24]. General LCP was accomplished with the aid of Lewis acid; however, a recent case using a combination of a less acidic protonic acid (HCl) and aliphatic ether proceeded a well-defined reaction^[25]. LCP is also utilized to synthesize various polymers with fine architectures, such as block^[26], graft^[27] copolymers and star-shaped polymers^[28]. In addition, LCP of IB coinited by FeCl₃/isopropanol was also achieved by Wu's group^[29]. Scheme 1 shows the general idea of LCP of vinyl ethers^[30]. However, LCP initiated by photochemistry just has few successful examples. The initiating species were formed after the photolysis of the cationic initiators, while the concentration was mainly decided by light intensity. In most LCP including traditional or photochemical cases, unstable carbocations were formed and the key point was the stabilization of the carbocations with suitable nucleophilic counter anion originating from the initiator and the catalyst. Recently, photo-induced LCP of IBVE in the presence of various diphenyliodonium salts and zinc halides was reported by Kwon^[31, 32]. A monomer-HX adduct was formed by the reaction of IBVE with protonic acid generated by photolysis. The terminal carbon-halide (C-X) bond was activated by the coordinating effect of zinc halide. Indirect photo-induced systems using free radical sources as photosensitizers were also applied to extend this methodology^[33]. In another case, a system with substituted vinyl halides in the presence of zinc halide or metallic zinc was successfully used to achieve photo-induced cationic polymerization under longer wavelength, meanwhile, the living nature was also observed^[30, 34].



Scheme 1 General scheme of living cationic polymerization (LCP)

On the other hand, vinyl polymers with pendant aromatic carbazolyl groups have attracted numerous interests due to their photoconductive properties. The most classical example is certain to be poly(*N*-vinyl carbazole)^[35, 36]. Also, other polymers with pendant carbazolyl groups have been used as organic conductor or photovoltaic devices^[37]. It was also reported that *N*-vinylcarbazole could be used as an additive in visible light initiated cationic polymerization^[38]. In addition, carbazole-containing polymers also played an important role in organic electroluminescent devices and photorefractive materials^[39].

Considering the wide use of carbazole-containing polymers and few reports on their photo-induced LCP, in this work, 2-(9-carbazolyl) ethyl vinyl ether (CEVE) was synthesized in our lab, and its photo-induced living cationic copolymerization behavior with IBVE was investigated. The polymerization was initiated with diphenyliodonium chloride (DPICl) and 2,2-dimethoxy-2-phenylacetophenone (DMPA), and zinc bromide (ZnBr₂) was acted as the catalyst. The fluorescent properties of the as-prepared copolymers in solution and in solid were also studied herein.

EXPERIMENTAL

Materials

Isobutyl vinyl ether (IBVE, 99%, TCI) was washed successively with 10% aqueous sodium hydroxide solution and distilled water, then distilled in the presence of CaH_2 in vacuo. Dichloromethane, sodium sulphate, potassium hydroxide, ethyl methyl ketone were purchased from Shanghai Chemical Reagent Co. Ltd. Dichloromethane was distilled in the presence of CaH_2 with a fractionation column. Carbazole (Aladdin), diphenyliodonium chloride (DPICl, 98%, Alfa Aesar), 2,2-dimethoxy-2-phenylacetophenone (DMPA, 98%, TCI), zinc bromide (ZnBr_2 , anhydrous, J&K), 2-chloroethylvinylether (99%, TCI), tetrabutylammonium hydrogensulfate (TBAHS, Alfa Aesar) were used as received. 2-(9-carbazolyl) ethyl vinyl ether was synthesized according to the literature^[40].

Synthesis of 2-(9-carbazolyl) Ethyl Vinyl Ether (CEVE)

2-(9-Carbazolyl) ethyl vinyl ether was prepared by the reaction of carbazole with an excess of 2-chloroethylvinylether under basic conditions in the presence of a phase transfer catalyst. Carbazole (3.34 g, 20 mmol), 2-chloroethylvinylether (10.1 mL, 100 mmol), sodium sulphate (2.84 g, 20 mmol), potassium hydroxide (6.72 g, 60 mmol) and tetrabutylammonium hydrogensulfate (0.14 g, 0.4 mmol) were stirred in ethyl methyl ketone (20 mL) at 70 °C for 4 h. The crude product was washed by water, then extracted with ethylacetate and recrystallized from ethanol. The final product was white crystal with a yield of 70%.

$^1\text{H-NMR}$ spectrum (400 MHz, $\text{CDCl}_3\text{-d}_1$, δ): 3.9–4.1 (m, 4H, $\text{CH}_2=$, $-\text{OCH}_2-$), 4.4–4.6 (t, 2H, $-\text{CH}_2\text{N}$), 6.35–6.45 (quart, 1H, $-\text{CH}=$), 7.1–7.3 (m, 2H, carbazole), 7.32–7.51 (m, 4H, carbazole), 7.98–8.17 (d, 2H, carbazole).

Elemental analysis for $\text{C}_{16}\text{H}_{15}\text{N}_1\text{O}_1$ (%): calculated C 81.01, H 6.33, N 5.91; found C 81.17, H 6.39, N 5.79.

Photopolymerization

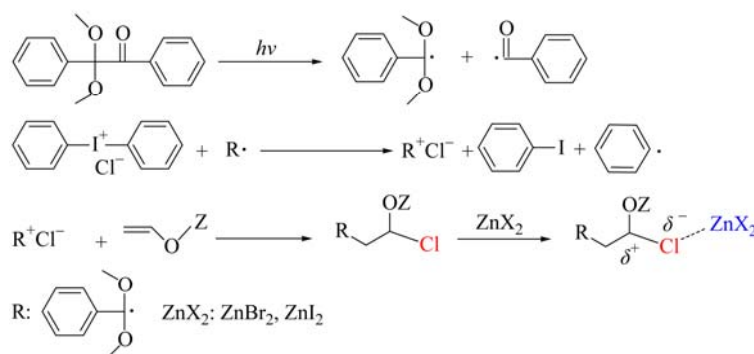
A typical polymerization procedure was carried out in the glove box. All the glassware was dehydrated by heating with a heat gun. IBVE (0.5 mL, $1.92\text{mol}\cdot\text{L}^{-1}$), CEVE ($0.04\text{mol}\cdot\text{L}^{-1}$) solution in CH_2Cl_2 (1.5 mL), initiator (DPICl, $2.5\text{mmol}\cdot\text{L}^{-1}$), photosensitizer (DMPA, $2.5\text{mmol}\cdot\text{L}^{-1}$), and catalyst (ZnBr_2 , $3.0\text{mmol}\cdot\text{L}^{-1}$) were added into the glass tube. Then the tube was sealed and irradiated at 0 °C in a photo reactor with emitting light at 350 nm. The light intensity was $500\text{ }\mu\text{W}\cdot\text{cm}^{-2}$ measured by a radiometer. After 20 min, the mixture was allowed to stand in a cryogenic alcohol bath in dark. After a period of time, the resulting polymer was precipitated by addition of ammoniacal methanol. The polymer was thoroughly washed successively with 10% aqueous sodium thiosulfate solution and distilled water and then dried under reduced pressure at room temperature. Percent conversion was determined by gravimetry.

Characterizations

The number-average molecular weight ($M_{n,\text{GPC}}$) and molecular weight distribution (M_w/M_n) of the resulting polymers were determined using a Waters 1515 gel permeation chromatograph (GPC) equipped with a refractive index detector (Waters 2414), using HR1 (pore size: 10 nm, 100–5000 Da), HR2 (pore size: 50 nm, 500–20000 Da), and HR4 (pore size 1000 nm, 50–100000 Da) columns ($7.8 \times 300\text{ mm}$, $5\text{ }\mu\text{m}$ beads size) with a molecular weight range of 100–100000 Da, calibrated with polystyrene standard samples. Tetrahydrofuran (THF) was used as the eluent at a flow rate of $1.0\text{ mL}\cdot\text{min}^{-1}$ and 39.3 °C. GPC samples were injected using a Waters 717 plus autosampler. The $^1\text{H-NMR}$ spectra were recorded on an Inova 400 MHz nuclear magnetic resonance (NMR) instrument using CDCl_3 as the solvent and tetramethylsilane (TMS) as the internal standard at ambient temperature. Fluorescence spectra in solution were measured on a HORIBA fluoromax-4 spectrofluorometer in dichloromethane and the excitation and emission slit width was 5 nm. Steady state fluorescence emission spectra of the spin-coated films were observed on a fluorescence spectrophotometer (FLS920, Edinburgh Photonics) with an angle of incidence 45° to the surface normal of the films and $\lambda_{\text{ex}} = 293\text{ nm}$. Differential scanning calorimetry (DSC) measurements were carried out using a Perkin Elmer Diamond DSC, a 5–10 mg sample of each polymer was packed tightly in an aluminium DSC pan.

RESULTS AND DISCUSSION

DMPA has long been used as a useful radical source in photo-induced cationic polymerization^[41], the so-called FRPCP is an elegant procedure since most radical sources can absorb light in mid- to long-wavelength. Generally speaking, photo-induced LCPs were just reported by several groups. In the present system, the electron donor ketyl radicals were formed, which can be easily oxidized by the onium salt. The key point of the living nature lies on the formation of monomer-X adducts. Due to the presence of zinc halide, the carbon-halide can be activated by coordinating effect^[42]. The general process is shown in Scheme 2^[32].



Scheme 2 General scheme of the mechanism of photo-induced living cationic polymerization

Living Cationic Copolymerization of IBVE and CEVE at Different Temperatures

Photopolymerization can be conducted at a relatively low temperature. In order to investigate effect of temperature on the copolymerization of IBVE and CEVE, the polymerizations were first carried out in the dark at various temperatures after irradiated 20 min at 0 °C. The results are shown in Table 1. It can be seen that the monomer conversion can reach up to 85.4% within 30 min at 5 °C but M_w/M_n is broad (2.01) (entry 1 in Table 1), indicating uncontrollable cationic polymerization. Once the temperature decreases, the polymerization rate decreases accordingly but the controllability is improved significantly (entries 2–4 in Table 1). For example, a monomer conversion of 56.3% can be obtained in 180 min with an M_w/M_n value of 1.27 at –15 °C. It is attributable to that the chain transfer process can be suppressed largely at lower temperatures. Therefore, a suitable temperature is needed for a successful LCP process. In this case, –15 °C may be acceptable for the copolymerization of IBVE and CEVE.

Table 1. Effect of temperature on the copolymerization of CEVE and IBVE in the presence of zinc bromide

Entry	Temperature (°C)	Time ^a (min)	Conv. (%)	$M_{n,GPC}$ ^b (g/mol)	M_w/M_n ^b
1	5	30	85.4	38400	2.01
2	–5	180	80.0	58300	1.66
3	–15	180	56.3	53000	1.27
4	–30	180	33.3	34400	1.37

Polymerization conditions: $V_{IBVE} = 0.5$ mL, $[IBVE]_0 = 1.92$ mol·L^{–1}; $[CEVE]_0 = 0.04$ mol·L^{–1}; $[DPICl]_0 = [DMPA]_0 = 2.5$ mmol·L^{–1}; $[ZnBr_2]_0 = 3$ mmol·L^{–1}; solvent: CH₂Cl₂; Irradiation time = 20 min.

^a Polymerization was carried out in the dark; ^b Measured by GPC based on polystyrene standards

Copolymerization Kinetics at Different Temperatures

As discussed above, temperature has great effect on the living nature of the copolymerization of CEVE and IBVE. In order to further investigate the detailed polymerization behavior, the copolymerization kinetics was studied at 5 °C, –5 °C and –15 °C, respectively. Figure 1 shows time-conversion curve, kinetic plot of $\ln([M]_0/[M])$ via time and dependence of $M_{n,GPC}$ and M_w/M_n of the resulting polymer on monomer conversion at 5 °C. It is noted that during the polymerization, the polymerization system was transparent and heterogeneous before UV irradiation; while after irradiation, the whole system turned to opaque, which indicated that the

photoinitiator was almost photochemically decomposed. Meanwhile, a C—X adduct was generated, which was responsible for the cationic propagation as shown in Scheme 2. Figure 1(a) shows that the conversion of the monomer can reach 95% within 40 min. However, the number-averaged molecular weight doesn't increase with the monomer conversion and the M_w/M_n values remain broad (more than 2.0), which shows an uncontrollable process in this case as indicated from entry 1 in Table 1. These results further confirm that C—Cl terminal is not stable enough to suppress chain breaking process if the polymerization temperature is above 0 °C.

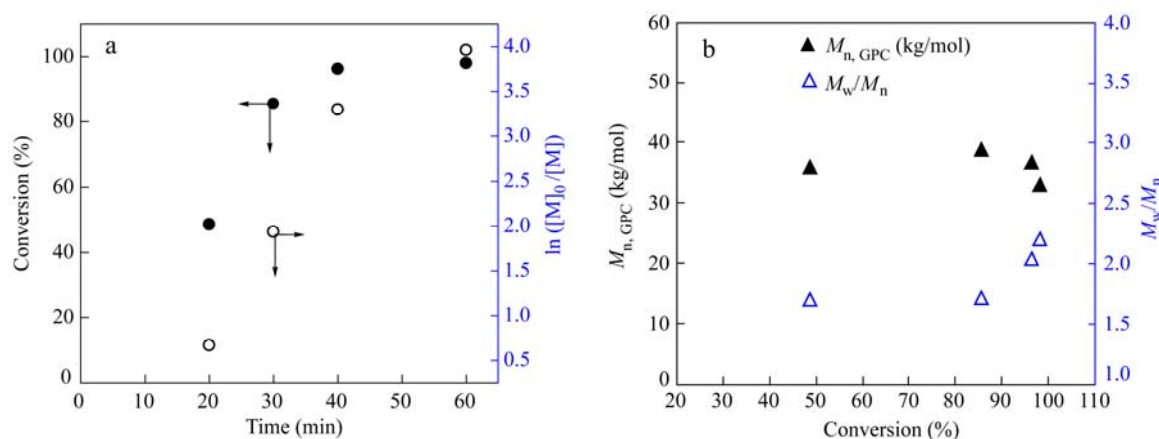


Fig. 1 Conversion and $\ln([M]_0/[M])$ as a function of time (a) and dependence of M_n and M_w/M_n on monomer conversion (b) for the copolymerization of CEVE and IBVE with DPICl/DMPA in dichloromethane in the presence of zinc bromide at 5 °C in the dark

Polymerization condition: $V_{IBVE} = 0.5$ mL, $[IBVE]_0 = 1.92$ mol·L⁻¹, $[CEVE]_0 = 0.04$ mol·L⁻¹, $[DPICl]_0 = [DMPA]_0 = 5$ mmol·L⁻¹, $[ZnBr_2]_0 = 6$ mmol·L⁻¹.

When the polymerization temperature decreases to -5 °C, its kinetics is shown in Fig. 2. It can be seen from Fig. 2(a) that the monomer conversion increases with polymerization time, and molecular weight increases with monomer conversion linearly while keeping relative narrow M_w/M_n values ($M_w/M_n = 1.38$ – 1.75), which indicates that the process has living nature somewhat.

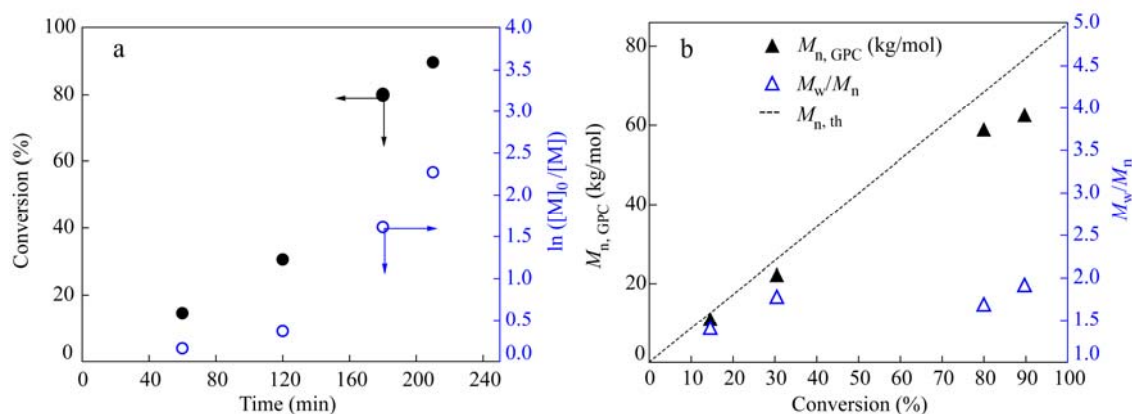


Fig. 2 Conversion and $\ln([M]_0/[M])$ as a function of time (a) and dependence of M_n and M_w/M_n on monomer conversion (b) for the copolymerization of CEVE and IBVE with DPICl/DMPA in dichloromethane in the presence of zinc bromide at -5 °C in the dark

Polymerization condition: $V_{IBVE} = 0.5$ mL, $[IBVE]_0 = 1.92$ mol·L⁻¹, $[CEVE]_0 = 0.04$ mol·L⁻¹, $[DPICl]_0 = [DMPA]_0 = 2.5$ mmol·L⁻¹, $[ZnBr_2]_0 = 3$ mmol·L⁻¹. Theoretical molecular weight $M_{n, th} = ([IBVE]_0/[DPICl]_0) \times \text{conversion} \times M_{IBVE} + ([CEVE]_0/[DPICl]_0) \times \text{conversion} \times M_{CEVE}$.

However, when the temperature becomes $-15\text{ }^{\circ}\text{C}$, the polymerization shows better controllability as shown in Fig. 3. From Fig. 3(b), it can be seen that the molecular weights of the obtained copolymer poly(IBVE-*co*-CEVE) increased linearly with monomer conversions while keeping narrow M_w/M_n values. When the conversions are less than 70%, M_w/M_n values of the resultant poly(IBVE-*co*-CEVE) can maintain less than 1.5. All these results at various temperatures indicate that temperature plays an important role in the propagation step actually. Compared with classical base-assisting LCP, the obtained M_w/M_n values are relatively high. This is due to that indirect systems involve several reaction sequences such as photo-induced radical generation, oxidation and adduct formation although at longer wavelengths. Therefore, growing polymer chains with some differences in chain lengths are formed in our cases.

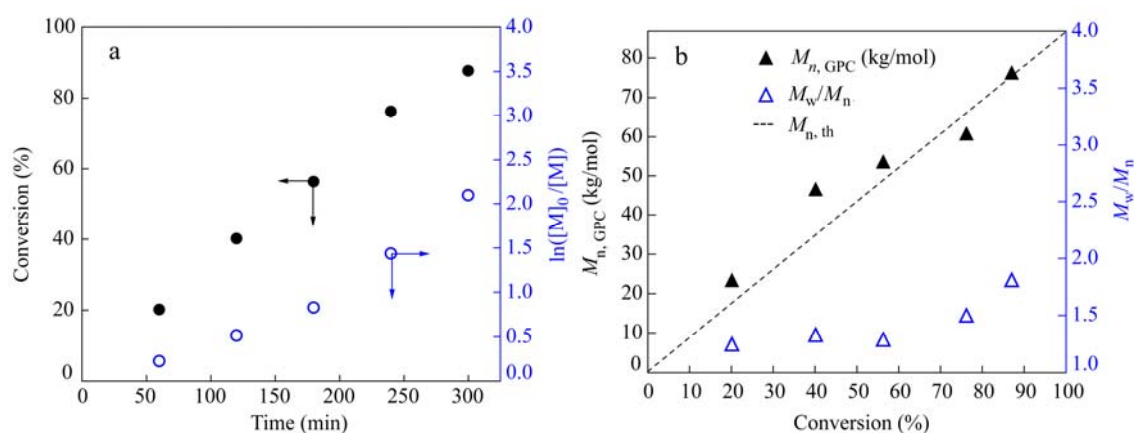


Fig. 3 Conversion and $\ln([M]_0/[M])$ as a function of time (a) and dependence of M_n and M_w/M_n on monomer conversion (b) for the copolymerization of CEVE and IBVE with DPICl/DMPA in dichloromethane in the presence of zinc bromide at $-15\text{ }^{\circ}\text{C}$ in the dark
Polymerization condition: $V_{IBVE} = 0.5\text{ mL}$, $[IBVE]_0 = 1.92\text{ mol}\cdot\text{L}^{-1}$; $[CEVE]_0 = 0.04\text{ mol}\cdot\text{L}^{-1}$, $[DPICl]_0 = [DMPA]_0 = 2.5\text{ mmol}\cdot\text{L}^{-1}$, $[ZnBr_2]_0 = 3\text{ mmol}\cdot\text{L}^{-1}$. Theoretical molecular weight $M_{n, th} = ([IBVE]_0/[DPICl]_0) \times \text{conversion} \times M_{IBVE} + ([CEVE]_0/[DPICl]_0) \times \text{conversion} \times M_{CEVE}$.

¹H-NMR Analysis and Living Nature Confirmation

Figure 4 shows the ¹H-NMR spectrum of the copolymer in CDCl₃. Chemical shifts at $\delta = 7.10\text{--}8.20$ (a, 8H) were assigned to the aromatic protons in the carbazolyl groups. The signals at $\delta = 4.00\text{--}4.60$ (b, 2H; c, 2H) can be assigned to the protons of methylene arising from PCEVE. The signals at $\delta = 0.80\text{--}1.00$ (d, 6H) were from the methyl protons of PIBVE. Signals at $\delta = 2.90\text{--}3.70$ (f, 2H; h, 2H) were from the methylene of poly(IBVE-*co*-CEVE) repeat unit. Signals at $\delta = 1.30\text{--}2.00$ (e, 1H; g, 1H) correspond to the $-\text{CH}-$ group in the repeat unit of the copolymer. The spectrum indicates the copolymerization of IBVE and CEVE was successful.

Furthermore, copolymer composition was also determined by ¹H-NMR. The molar ratio of PCEVE units was calculated by the integrals of aromatic protons (2H, integral value = $I_{8,10} = 1.00$) and methyl protons of PIBVE (6H, integral value = $I_{1,00} = 104.02$) according to the equation 1, and the compositions of the copolymers (shown in Fig. 3) are listed in Table 2.

$$R = (I_{8,10}/2)/[(I_{1,00}/6) + (I_{8,10}/2)] \quad (1)$$

Table 2. Molar ratios of PCEVE units in the copolymers shown in Fig. 3

Entry	$M_{n, GPC}$ (g/mol) ^a	R ^b
1	22800	0.0147/1
2	46000	0.0168/1
3	53000	0.0219/1
4	60300	0.0281/1
5	75700	0.0198/1

^a Measured by GPC based on polystyrene standards; ^b Molar ratio of PCEVE to PIBVE

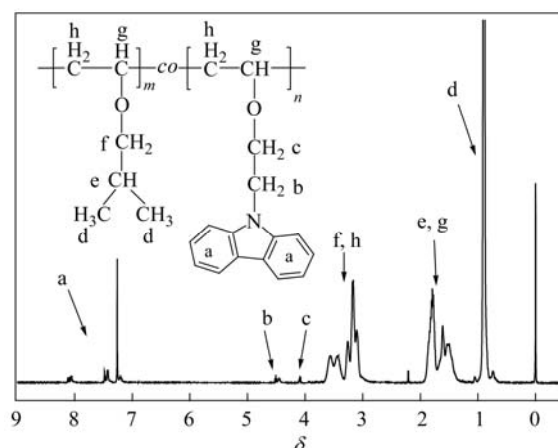


Fig. 4 ^1H -NMR spectrum of the copolymer ($M_{n,\text{GPC}} = 60300 \text{ g}\cdot\text{mol}^{-1}$, $M_w/M_n = 1.48$) in CDCl_3

The living nature of this polymerization system was further demonstrated by the method of adding fresh comonomer. In our case, fresh monomers with original fed portions were added to the polymerization system where the monomer conversion of the original batch reached up to around 90%. As it indicates in Fig. 5, both the yield of copolymer and $M_{n,\text{GPC}}$ increase linearly, which strongly suggest that the chain end of the copolymer remains active in the later stage of the polymerization.

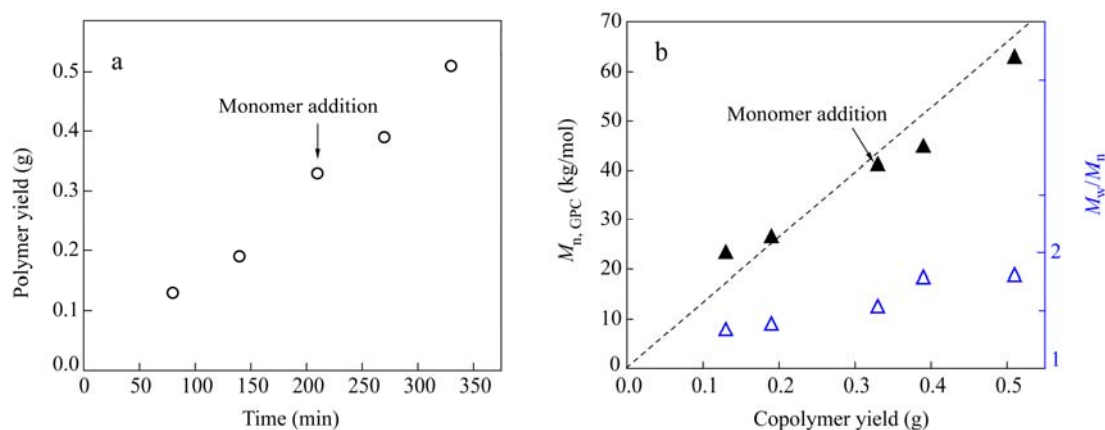


Fig. 5 An evidence of the living nature confirmed by subsequent monomer addition method. Fresh monomers were added to the system when the conversion of original feed reached up to around 90%. Polymerization conditions: $V_{\text{IBVE}} = 0.5 \text{ mL}$, $[\text{IBVE}]_0 = 1.92 \text{ mol}\cdot\text{L}^{-1}$; $[\text{CEVE}]_0 = 0.04 \text{ mol}\cdot\text{L}^{-1}$; $[\text{DPICl}]_0 = [\text{DMPA}]_0 = 5 \text{ mmol}\cdot\text{L}^{-1}$; $[\text{ZnBr}_2]_0 = 6 \text{ mmol}\cdot\text{L}^{-1}$; temperature $= -15^\circ\text{C}$. Photoirradiation was carried out at 0°C for 20 min before the polymerization.

Effect of Feed Ratio on Copolymerization of IBVE and CEVE

The effect of monomer feed ratio on copolymerization was also investigated in this work. The polymerization results are presented in Table 3. It can be seen that polymerization rate decreases with the increase of the amount of CEVE in the composition, which indicates the reactivity of monomer IBVE is higher than that of CEVE. At the same time, the molecular weight distribution of the copolymer becomes broader with the increase of the amount of CEVE.

Table 3. Copolymerization with different monomer feed ratios at $-15\text{ }^{\circ}\text{C}$

Entry	[CEVE] ₀ (mol/L)	Time ^a (min)	Conv. (%)	$M_{n,\text{GPC}}^b$ (g/mol)	M_w/M_n^b
1	0	120	24.8	20900	1.32
2	0.04	180	56.3	53000	1.27
3	0.096	300	89.1	75300	1.42
4	0.192	300	60.1	52100	1.49
5	0.384	300	30.0	25200	1.80

Polymerization conditions: $V_{\text{IBVE}} = 0.5\text{ mL}$, $[\text{IBVE}]_0 = 1.92\text{ mol}\cdot\text{L}^{-1}$; $[\text{DPICl}]_0 = [\text{DMPA}]_0 = 2.5\text{ mmol}\cdot\text{L}^{-1}$; $[\text{ZnBr}_2]_0 = 3\text{ mmol}\cdot\text{L}^{-1}$; Solvent: CH_2Cl_2 ; Irradiation time = 20 min; temperature = $-15\text{ }^{\circ}\text{C}$

^a Polymerization was carried out in the dark; ^b Measured by GPC based on polystyrene standards

Fluorescent Behavior of the Copolymer in Solution and in Solid Film

Fluorescence of the copolymer in solution has a so-called “concentration self-quenching effect”^[43]. Dichloromethane is a good solvent for the copolymer at ambient temperature. Figure 6(a) shows the effect of copolymer concentration on the fluorescence emission. Peaks found at 350 nm and 365 nm are presented regardless of the concentration of the chromospheres. Highest fluorescent intensity was found when the concentration was $2.5 \times 10^{-5}\text{ mol}\cdot\text{L}^{-1}$. The structured fluorescence characteristic of carbazolyl group appears at 350 nm, and excimer emission around 430 nm has no appreciable intensity, indicating that the carbazole chromophores were isolated from each other in dilute copolymer solutions. Theory teaches that flexible chain molecules resist strongly mutual interpenetration. It is confirmed that copolymer coils tend to be isolated in dilute solutions^[44]. In addition, copolymers poly(IBVE-co-CEVE) with different molecular weights were dissolved in dichloromethane, respectively, to analyze the fluorescent properties. Investigation of the effect of chain length to the fluorescence intensity was also carried out here (Fig. 6b). The results indicate that when the concentration of CEVE structure units keeps the same, chain length has little effect on the fluorescent intensity of the copolymer in dilute solutions.

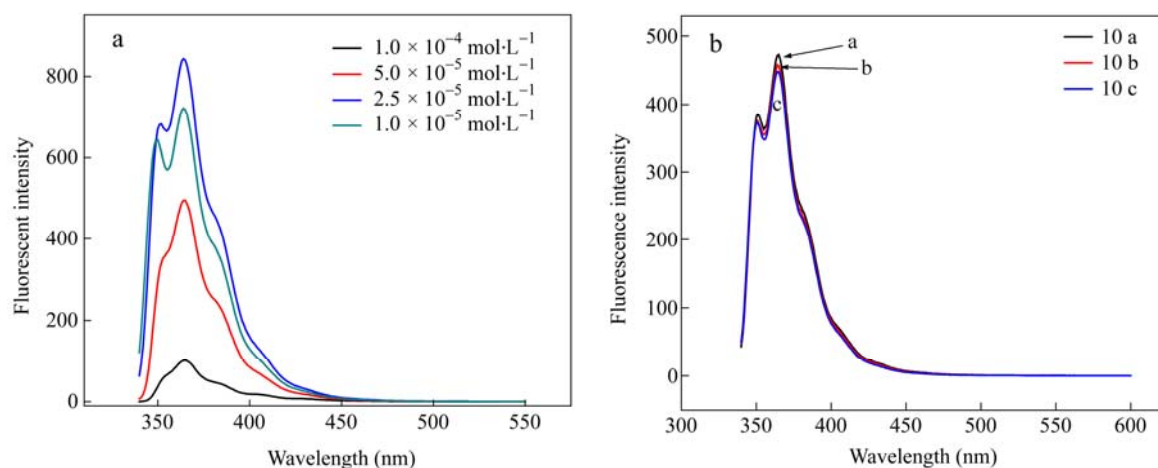


Fig. 6 Effect of copolymer concentration on fluorescence emission in dichloromethane solution (a), $\lambda_{\text{ex}} = 320\text{ nm}$, ($M_n = 53000\text{ g}\cdot\text{mol}^{-1}$, $M_w/M_n = 1.27$); effect of molecular weight of copolymer on fluorescence emission in dichloromethane solution (b), $\lambda_{\text{ex}} = 320\text{ nm}$, copolymer 10a: $M_n = 24000\text{ g}\cdot\text{mol}^{-1}$, $M_w/M_n = 1.37$; copolymer 10b: $M_n = 45000\text{ g}\cdot\text{mol}^{-1}$, $M_w/M_n = 1.67$; copolymer 10c: $M_n = 60300\text{ g}\cdot\text{mol}^{-1}$, $M_w/M_n = 1.48$; Concentration of CEVE structure units: $2 \times 10^{-4}\text{ mol}\cdot\text{L}^{-1}$ (Calculated by $^1\text{H-NMR}$).

The emission spectrum of the copolymer film by spin-coating was investigated as shown in Fig. 7. Morphologically stable films were prepared by various rotating speeds. Compared with the fluorescence emission spectrum in solid, emission spectrum in solution has a slightly red-shift of 3 nm which can be clearly identified. This minor shift may have arisen from the difference in microenvironment. In addition, it is intriguing

to find two new emission peaks at 400 nm and 425 nm. This can be attributed to the excimer emission. In the solid state, intermolecular excimer was formed^[45].

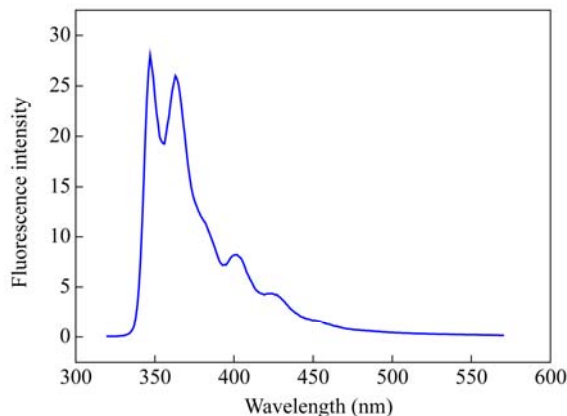


Fig. 7 Fluorescence emission of spin-coated film, $\lambda_{\text{ex}} = 293 \text{ nm}$

T_g of the Copolymers

Thermal properties of copolymers with different compositions were studied by DSC under a nitrogen atmosphere. The samples were annealed at 150 °C prior to running DSC to erase thermal history, and then the samples were cooled to −50 °C and heated to 150 °C. DSC traces recorded during the second heating cycle of the copolymer samples are presented in Fig. 8. T_g of the homopolymer PIBVE was −20 °C according to the literature^[46]. It can be seen that all the T_g values of copolymers are below −10 °C, and that the T_g (−14.4 °C) of the copolymer 11a (obtained from LCP of IBVE and CEVE with a molar ratio of $[\text{IBVE}]_0/[\text{CEVE}]_0 = 24/1$) is slightly lower than that (−10.8 °C) of the copolymer 11b (obtained from LCP of IBVE and CEVE with a molar ratio of $[\text{IBVE}]_0/[\text{CEVE}]_0 = 10/1$). This is attributable to the existence of more carbazolyl units in the copolymer 11b due to more feed molar ratio of CEVE added in this case.

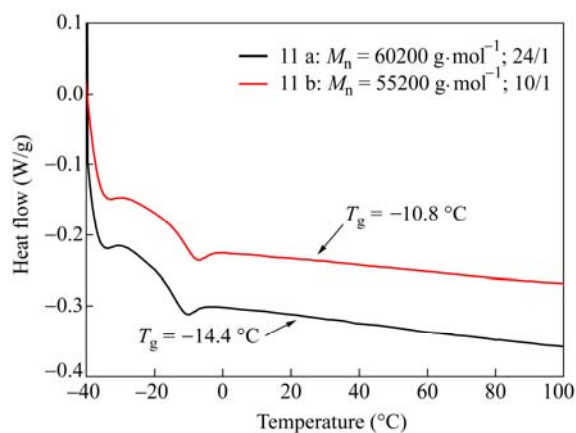


Fig. 8 DSC curves of copolymers 11a and 11b under a heating rate 10 K/min and N_2 atmosphere
Copolymer 11a: $M_{n,\text{GPC}} = 60200 \text{ g}\cdot\text{mol}^{-1}$, monomer feed ratio: $[\text{IBVE}]_0/[\text{CEVE}]_0 = 24/1$; Copolymer 11b: $M_{n,\text{GPC}} = 55200 \text{ g}\cdot\text{mol}^{-1}$, monomer feed ratio: $[\text{IBVE}]_0/[\text{CEVE}]_0 = 10/1$.

CONCLUSIONS

Photo-induced living cationic copolymerization of IBVE and CEVE was successfully carried out using DPICl/DMPA/ ZnBr_2 initiating system in CH_2Cl_2 . A linear dependence of number-average molecular weight of

the resulting copolymer on monomer conversion suggests the living nature of this system. Its living nature was further confirmed by using the fresh monomer addition method. DSC results reveal that the resultant fluorescent copolymers have a glass transition temperature below $-10\text{ }^{\circ}\text{C}$, which indicate that poly(IBVE-*co*-CEVE) may have potential application in functional coatings.

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