Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 47 (2006) 3390–3400

polymer

www.elsevier.com/locate/polymer

New β-diketone-containing styrenic monomers and their polymers: Synthesis, keto–enol tautomerism and related fluorescence behavior

Xin Zhang, Zi-Chen Li *, Chun-Feng Lao, De-Chun Zou, Feng-Zhu Lu,
Guang-Qiang Chen, Fu-Sheng Du, Fu-Mian Li

Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, College of Chemistry and Molecular Engineering,
Peking University, Beijing 100871, China

Received 5 October 2005; received in revised form 26 January 2006; accepted 27 February 2006

Abstract

Three new β-diketone-containing styrenic monomers and their polymers were synthesized. The phenol and naphthol groups, and the electron-donating *N*,*N*-dimethylaniline groups were covalently attached to the β-diketone monomers at a designed position. The keto–enol tautomerism was characterized by ^{1}H, ^{13}C NMR and UV–vis absorption spectroscopy. It was found that the β-diketone monomers exist in three forms, i.e. two *cis*-enol forms and one keto form. Their relative contents were determined by NMR spectroscopy. The β-diketone monomers bearing the phenol (**1**) and naphthol (**2**) groups display photoinduced enolization during UV irradiation due to the formation of intramolecular hydrogen bonds between the phenolic or naphtholic hydroxyl groups and the carbonyl groups. For their polymers and copolymers, however, photoinduced ketonization occurred during UV irradiation. The β-diketone monomer bearing *N*,*N*-dimethylaniline group (**3**) is a novel charge transfer fluorophore, which can be potentially employed as a dual-purpose functional monomer.

Keywords: β-Diketone polymers; Keto–enol tautomerism; Photoinduced ketonization

1. Introduction

β-Diketones generally exist in enol and keto forms. One of the most interesting properties is the isomerization between the two forms termed as tautomerism [1,2]. For most β-diketones, the enol form is predominant in solution. The keto–enol tautomerism of β-diketones can be affected by various factors such as substitution groups [3], solvent polarity [4], and environmental stimulation such as pH values and UV light irradiation [5]. The photoinduced ketonization of β-diketones generally occurs after UV irradiation, this process is reversible, the keto form can be converted back into the *cis*-enol form in darkness. Several spectroscopic methods have been employed for the characterization of keto–enol tautomerism such as IR [6], UV–vis [7], Raman [8], ^{1}H and ^{13}C NMR spectroscopy [9]. Recently, Gilli et al. reported the X-ray crystallographic structures of keto–enol tautomers and their H-bonding effects [10,11]. Kenar et al. synthesized long-chain β-diketone compounds and investigated their keto–enol tautomeric equilibrium [12]. However, little attention was paid to β-diketone-containing monomers, polymers and their keto–enol tautomerism [13a].

In recent years, photo-controllable isomerization has attracted considerable interests because of their great potentials as molecular devices and switches [13b–d]. The keto–enol tautomerism induced by UV light irradiation is a photoisomerization process [7]. A further understanding of the H-bonding and macromolecular effect on the keto–enol tautomerism is the main aim of the present work. Here, we described the synthesis of three new β-diketone-containing styrenic monomers, i.e. 1-(2-hydroxy-phenyl)-3-(4-vinylphenyl)-1,3-propanedione (**1**), 1-(2-hydroxynaphthyl)-3-(4-vinylphenyl)-1,3-propanedione (**2**), and 1-(4-(dimethylamino)phenyl)-3-(4-vinylphenyl)-1,3-propanedione (**3**), and their polymers as shown in Chart 1. Compared with general β-diketones, the hydroxyl group and the amine donor were designed at ortho and para position, respectively, in these β-diketone monomers. The keto–enol tautomerism of these monomers and their polymers, as well as the fluorescence behavior of β-diketone monomer **3** were explored.

---

* Corresponding author. Tel.: +86 10 6275 7155; fax: +86 10 6275 1708.
E-mail address: zcli@pku.edu.cn (Z.-C. Li).

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.02.087

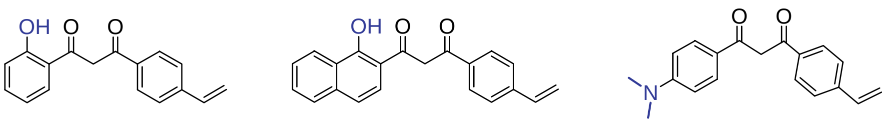


Chart 1.

2. Experimental part

2.1. General methods

All chemicals were purchased from Beijing Chemicals Co. and used without further purification unless otherwise specified. Sodium hydride (51%) was washed with dry petroleum ether to remove the protecting wax before using. Methyl *p*-vinylbenzoate was synthesized from *p*-vinylbenzoic acid and methanol according to the literature [14a]. Methyl methacrylate (MMA) was distilled to remove the inhibitor before using. UV–vis absorption spectra were recorded on a Shimadzu UV-2101 spectrophotometer. The steady-state fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer at room temperature. The slit width of both monochromators was 5.0 nm. All the solvents used were purified to eliminate the interfering impurities for fluorescence measurements. ^{1}H NMR spectra were collected on Bruker 400 MHz NMR spectrometer using *d*-chloroform ($CDCl_3$) as a solvent and tetramethylsilane as an internal standard. Infrared spectra were recorded on a Vector 22 Fourier transform infrared (FT-IR) spectrometer. Mass spectra were obtained using a VG ZAB-HS mass spectrometer in the electron-impact mode. Elementary analysis was performed on a Vario EL elementary analyzer. Melting points were determined using either a Yanaco MP-500 melting point apparatus or a differential scanning calorimeter (Thermal Analysis DSC 2010) at a heating rate of 10 °C/min. Number- and weight-average molecular weights and molecular weight distributions of polymers were measured with a gel permeation chromatography (GPC) system equipped with a Waters 2410 refractive index detector, a Waters 515 HPLC pump, and three Waters Styragel Columns (HT2, HT3 and HT4) with tetrahydrofuran (THF) as an eluent at a flow rate of 1 mL/min at 35 °C. The obtained data were processed against narrow polystyrenes as calibrations using professional software (Millennium 32).

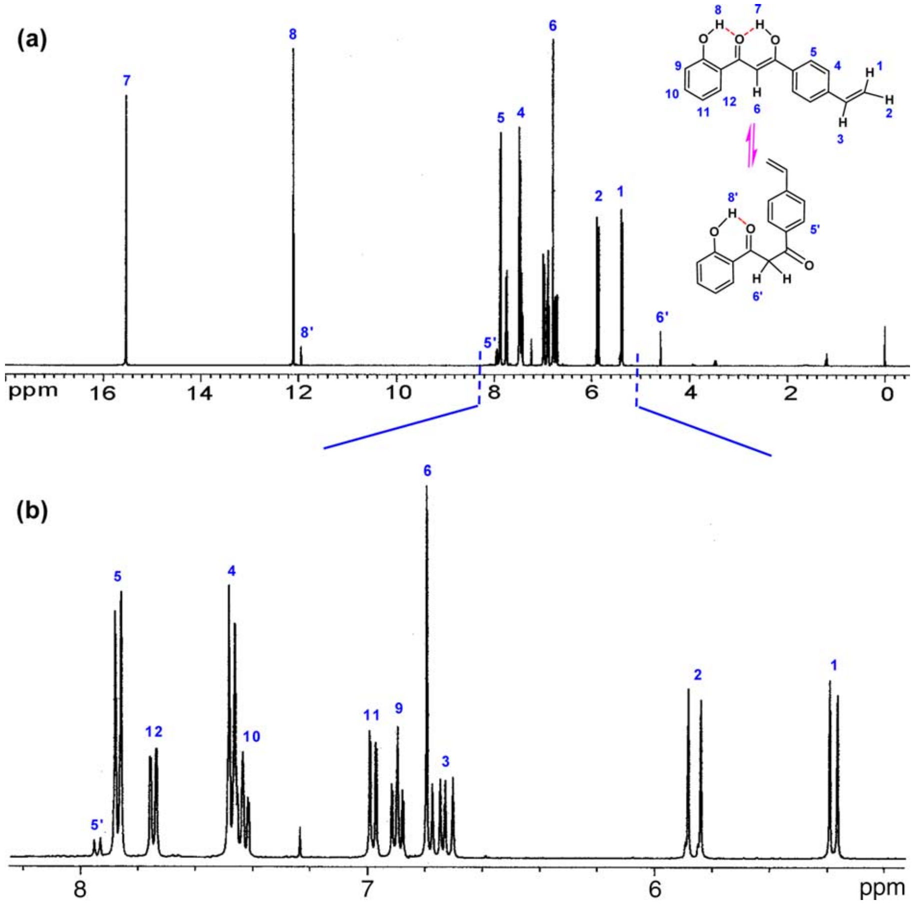
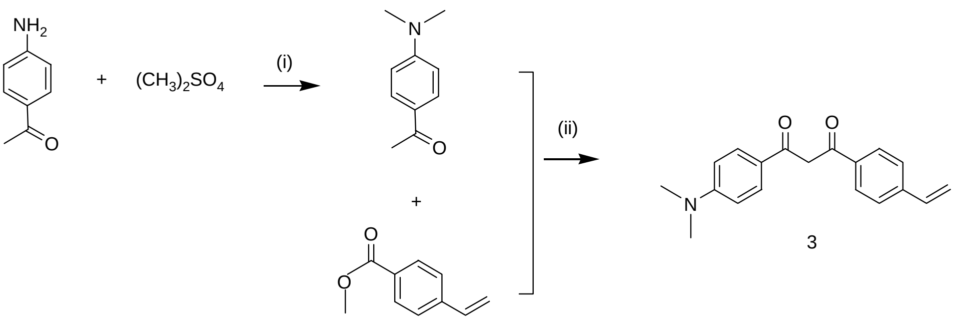


Fig. 1. ^{1}H NMR spectrum of **1** (a) and local expansion (b) in $CDCl_3$.



Scheme 1. Representative synthetic route toward **3**. Reagents and conditions: (i) $NaHCO_3$, 18–22 °C for 1.5 h, 60–65 °C for 0.5 h; (ii) NaH, ethyl ether/diethylene glycol dimethyl ether (5/1: v/v), rt.

2.2. Synthesis of monomers

*2.2.1. 1-(2-Hydroxyphenyl)-3-(4-vinylphenyl)-1,3-propanedione (**1**)*

Methyl *p*-vinylbenzoate (2.4 g, 15 mmol) and sodium hydride (51%, 2.0 g, 40 mmol) were added into dry ethyl ether (50 mL) and dry diethylene glycol dimethyl ether (10 mL) with stirring at room temperature under nitrogen atmosphere. 2-Hydroxyacetophenone (1.2 mL, 10 mmol) and dry ethyl ether (10 mL) were added dropwise into the above solution. The reaction solution was stirred at room temperature under nitrogen atmosphere for 18 h. The reaction mixture was then poured into 10% sulfuric acid aqueous solution (50 mL). The organic ether phase was separated, and the aqueous phase was extracted twice with ethyl acetate (50 mL). The combined organic phases were washed sequentially with saturated $NaHCO_3$ (sodium hydrogen carbonate) aqueous solution (100 mL), distilled water (100 mL), and saturated NaCl (sodium chloride) aqueous solution (100 mL), then dried over sodium sulfate. The above solution was concentrated in a vacuum to give a yellow crude product, which was recrystallized twice from ethyl ether. Yellow crystals (1.12 g) were obtained. Yield: 43%. Mp: 123–124 °C. ^1H NMR ($CDCl_3$, TMS, ppm) (Fig. 1): δ 4.59 (s, 0.12H, $H_{6'}$), 5.37–5.39 (d, 1H, $J=5.4$ Hz, H_1 and H_2), 5.84–5.89 (d, 1H, $J=17.6$ Hz, H_3), 6.71–6.83 (dd, 1H, $J_1=17.6$ Hz, $J_2=5.4$ Hz), 6.80 (s, 0.88H, H_6), 6.88–7.88 (m, 8H, Ar-H), 11.94 (s, 0.06H, $H_{8'}$), 12.10 (s, 0.94H, H_8), 15.53 (s, 1H). ^{13}C NMR ($CDCl_3$, TMS, ppm) (Fig. S-3): δ 92.05, 116.4, 118.7, 119.0, 126.5, 127.1, 128.4, 129.2, 132.6, 135.7, 135.9, 137.1, 141.5, 162.4, 176.9, 195.4. IR (KBr pellet, cm^{-1}) (Fig. S-5): 3044 ($\nu_{as,\ H2C=}$), 1608 ($\nu_{C=O}$) 1552, 1486, 1409, 1333, 1297, 1181, 1121, 1084, 1032, 988.3, 908 (γ_{CH}, $-CH=CH_2$), 851.9 (γ_{CH}, $R_1R_2=CHR_3$), 802.7, 725.2, 654.4. MS (*m/e*): 51, 65, 77 (base), 103, 131, 266 (M^+). UV (cyclohexane) λ_{max} (ε) 375 nm ($3.9\times10^4\ M^{-1}\ cm^{-1}$). Anal. Calcd for $C_{17}H_{14}O_3$ (%): C, 76.68; H, 5.30. Found: C, 76.49; H, 5.44.

*2.2.2. 1-(2-Hydroxynaphthyl)-3-(4-vinylphenyl)-1,3-propanedione (**2**)*

Compound **2** was synthesized in a similar procedure as **1** except for the starting materials and the solvent dimethylsulfoxide. Yield: 33% (1.04 g). Mp: 121–122 °C. ^1H NMR ($CDCl_3$, TMS, ppm) (Fig. S-1): δ 4.69 (s, 0.19H, $H_{6'}$), 5.40–5.43 (d, 1H, $J=10.9$ Hz, H_2), 5.88–5.93 (d, 1H, $J=17.6$ Hz, H_1), 6.71–6.85 (dd, 1H, $J_1=17.6$ Hz, $J_2=10.9$, H_3), 6.90 (s, 0.81H, H_6), 7.31–8.50 (m, 10H, ArH), 13.71 (s, 0.14H, $H_{8'}$), 13.77 (s, 0.86H, H_8), 15.56 (s, 1H, H_7). ^{13}C NMR ($CDCl_3$, TMS, ppm): δ 92.42, 112.3, 116.4, 117.3, 118.5, 123.2, 124.3, 124.6, 125.6, 126.5, 127.1, 127.3, 129.2, 129.8, 130.5, 132.9, 136.0, 137.1, 141.5, 162.4, 176.3, 195.1. IR (KBr pellet, cm^{-1}) (Fig. S-5): 3054 ($\nu_{as,\ H2C=}$), 1595 ($\nu_{C=O}$), 1504, 1467, 1429, 1385, 1326, 1260, 1233, 1151, 1121, 1076, 987.1, 914.4 (γ_{CH}, $-CH=CH_2$), 848.1 (γ_{CH}, $R_1R_2=CHR_3$), 786.6, 735.9, 708.7, 651.1, 609.3. MS (*m/e*): 39, 51, 77 (base), 103, 121, 115, 131, 170, 316 (M^+). UV (cyclohexane) λ_{max} (ε) 362 and 362 nm ($3.9\times10^4\ M^{-1}\ cm^{-1}$) and 408 nm ($3.7\times10^4\ M^{-1}\ cm^{-1}$). Anal. Calcd for $C_{21}H_{16}O_3$ (%): C, 79.73; H, 5.10. Found: C, 79.56; H, 5.28.

*2.2.3. 1-(4-(Dimethylamino) phenyl)-3-(4-vinylphenyl)-1,3-propanedione (**3**)*

Compound **3** was synthesized from 4-(dimethylamino)acetophenone in a similar method as **1** except for the starting materials. The synthetic route toward **3** was shown in Scheme 1. The precursor, 4-(dimethylamino)acetophenone, was synthesized according to the literature [14b] in 67% yield (10.5 g) with the melting point of 102–104 °C (lit. [14c] 105.5 °C). Compound **3** was then recrystallized twice from cyclohexane to yield yellow flake crystals. Mp: 110.0–110.5 °C. ^1H NMR ($CDCl_3$, TMS, ppm) (Fig. S-2): δ 3.06 (s, 6H, H_{10}), 4.51 (s, 0.16H, $H_{6'}$), 5.35–5.37 (d, 1H, $J=10.9$ Hz, H_2), 5.84–5.87 (d, 1H, $J=17.7$ Hz, H_1), 6.75 (s, 0.84H, H_6), 6.69–6.72 (d, 2H, Ar-H), 6.70 (m, 1H, H_3), 7.48–7.50 (d, 2H, Ar-H), 7.90–7.93 (m, 4H, Ar-H), 17.21 (s, 1H, H_7). IR (KBr pellet, cm^{-1}) (Fig. S-5): 3475, 3414 (ν_{as}, ν_s NH_2), 2985 ($\nu_{as,\ H2C=}$), 1605 ($\nu_{C=O}$), 1570, 1525, 1491, 1372, 1299, 1231, 1189, 1056, 916 (γ_{CH}, $-CH=CH_2$), 852 (γ_{CH}, $R_1R_2=CHR_3$), 824.0, 788.2, 712.0, 631.1. MS: 77 (base), 103, 121, 148, 161, 293 (M^+). UV (cyclohexane) λ_{max} (ε) 390 nm ($6.1\times10^4\ M^{-1}\ cm^{-1}$). Anal. Calcd for $C_{19}H_{19}NO_2$ (293.36) (%): C, 77.79; H, 6.53; N, 4.77. Found C, 77.63; H, 6.58; N 5.11.

*2.3. Polymerization of **1**, **2** and **3***

Compound **1** (0.53 g), 2,2′-azo-bis-isobutyronitrile (AIBN, 0.01 g) and freshly distilled tetrahydrofuran (THF) (5 mL) were added into a glass tube ($10\times10\times150\ mm^3$), which was

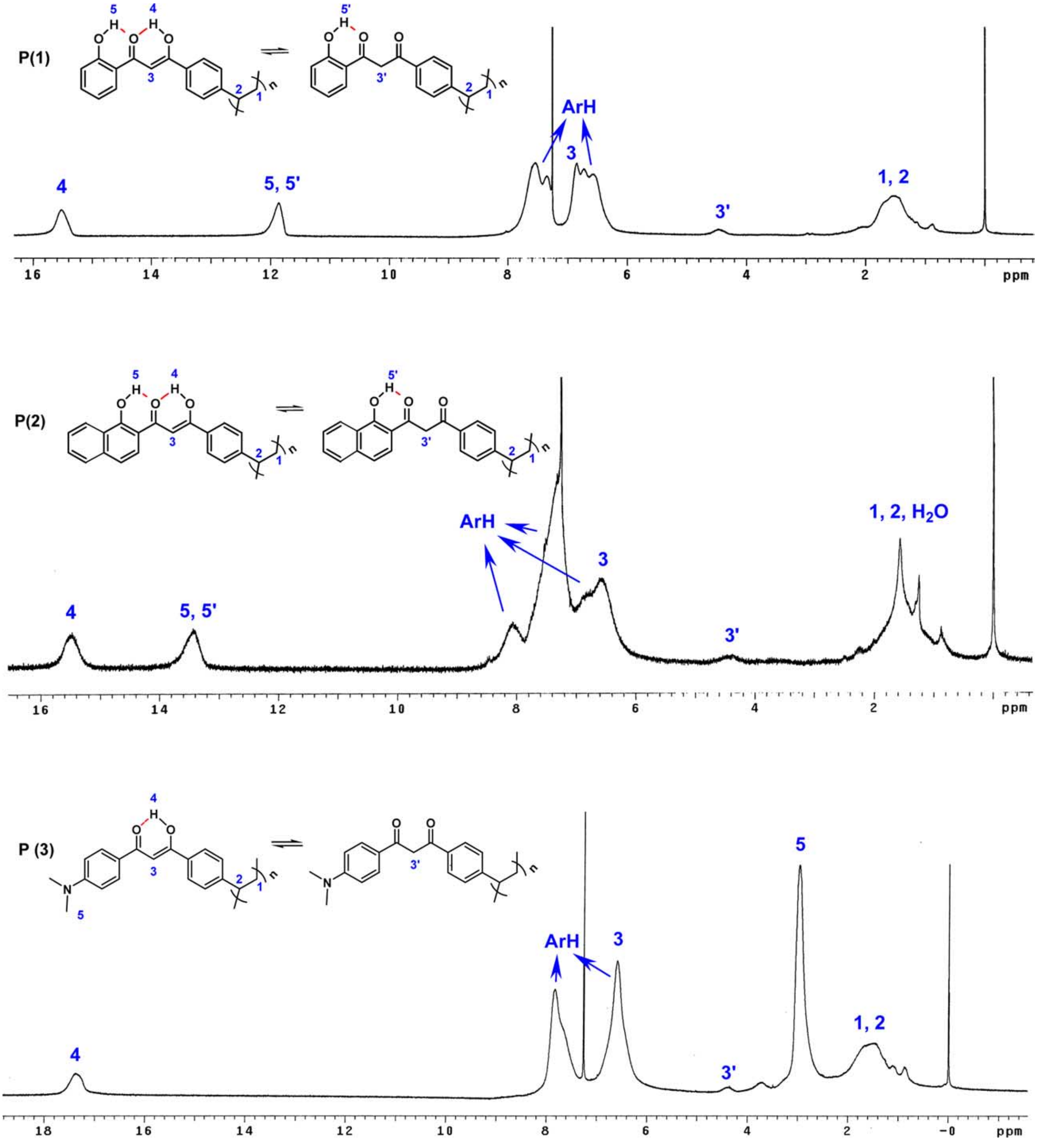


Fig. 2. ^{1}H NMR spectra of P (**1**), P (**2**) and P (**3**) in CDCl$_3$.

purged with nitrogen for 10 min, and sealed in a vacuum, then heated at 60 °C in an oil bath for 24 h. The reaction mixture was poured into methanol (50 mL). The precipitation was collected by suction filtration. The crude products were dissolved in THF (10 mL). The insoluble residue was removed by suction filtration. The THF solution was poured into methanol (50 mL). The yellow precipitation was collected, then dried in a vacuum at 60 °C. Yellow polymer (P (**1**), 0.40 g) was obtained. Yield: 75%, $M_n = 4.24\times10^3$. M_w/M_n (polydispersity, PD) = 1.7. ^{1}H NMR (CDCl$_3$, TMS, ppm) (Fig. 2): δ 1.54 (br, 3H, H_1 and H_2), 4.23, 6.85 (s and s, 1H, H_3 and $H_{3'}$), 6.58, 6.73 (d, 4H, Ar-H), 7.61, 7.39 (d, 4H, ArH), 15.52 (s, 1H, H_5 and $H_{5'}$), 15.52 (s, 1H, H_4). Compounds **2** and **3** were polymerized in the same procedure. Polymer of **2** (P (**2**)): Yield: 81%, $M_n = 5.79\times10^3$, M_w/M_n (polydispersity, PD) = 1.9. ^{1}H NMR (CDCl$_3$, TMS, ppm) (Fig. 2): δ 1.57 (br, 3H, H_1 and H_2), 4.38, 6.57 (s and s, 1H, H_3 and $H_{3'}$), 7.93, 7.33, 6.91 (m, 10H, ArH), 13.44 (s, 1H, H_5 and $H_{5'}$), 15.48 (s, 1H, H_4). Polymer of **3** (P (**3**)): Yield: 78%, $M_n = 5.40\times10^3$, M_w/M_n (polydispersity, PD) = 1.5. ^{1}H NMR (CDCl$_3$, TMS, ppm) (Fig. 2): δ 1.43 (br, 3H, H_1 and H_2), 2.98 (s, 6H, H_5), 4.35, 6.59 (br, H_3 and $H_{3'}$), 7.83, 6.59 (br, 8H, ArH), 17.39 (s, 1H, H_4).

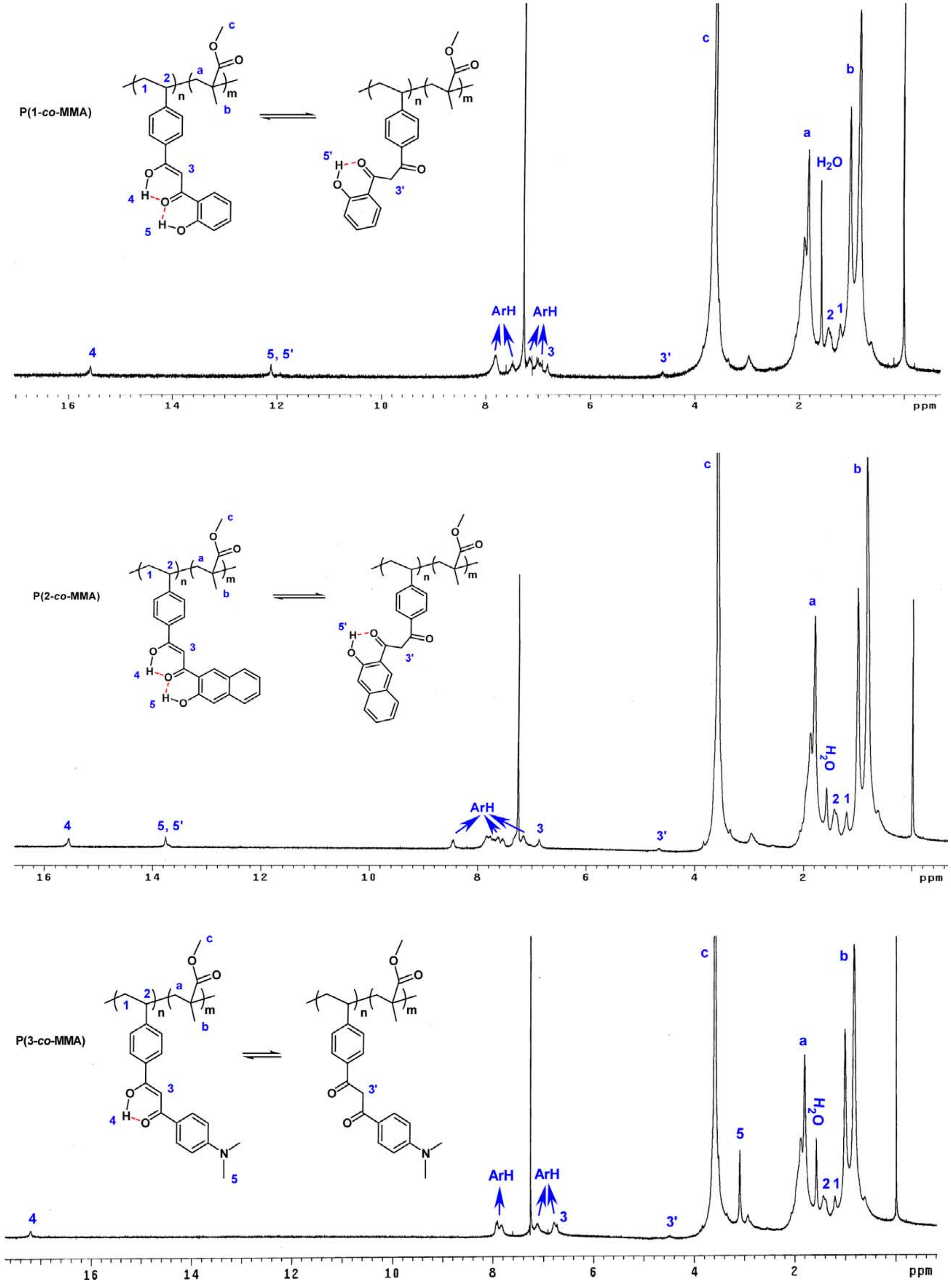


Fig. 3. ^{1}H- NMR spectra of P (**1**-*co*-MMA), P (**2**-*co*-MMA) and P (**3**-*co*-MMA) in $CDCl_3$.

*2.4. Copolymerization of **1** (or **2**, **3**) with methyl methacrylate (MMA)*

Compound **1** (or **2**, **3**) (0.10 g), MMA (1.0 mL), AIBN (0.01 g) and freshly distilled tetrahydrofuran (10 mL) were added into a glass tube (10×10×150 mm^3). The copolymers P (**1**-*co*-MMA), P (**2**-*co*-MMA) and P (**3**-*co*-MMA) were obtained in the same procedure as P (**1**). The contents of β-diketone monomers **1**, **2** and **3** in the copolymers were 10.3 wt% (molar percent: 3.73%), 9.2 wt% (molar percent: 3.11%), 11.5 wt% (molar percent: 4.24%), respectively, determined by ^{1}H NMR and UV–vis absorption spectroscopy according to previous methods [15a,b].

2.5. Photoinduced keto–enol tautomerism

The acetonitrile solution of the monomers or polymers was added into a quartz cell (10×10×45 mm^3) and irradiated by a 300 W high-pressure mercury lamp with the center to center distance of 10 cm. UV–vis spectra were recorded at irradiation intervals.

3. Results and discussion

3.1. Spectroscopic characterization of the keto and enol tautomers

β-Diketone monomers **1**, **2** and **3** were synthesized by Claisen condensation of methyl *p*-vinylbenzoate and acetophenone derivatives in the presence of sodium hydride. A representative synthetic route to β-diketone monomer **3** was shown in Scheme 1.

Fig. 1 shows the ^{1}H NMR spectrum of β-diketone monomer **1** in deuterated chloroform (CDCl$_3$) at room temperature. The enol and keto forms of **1** are distinguishable from the ^{1}H NMR spectrum. The peak at δ 4.59 ppm was assigned to the methylene protons (–CO–CH_2–CO–) of the keto tautomer. The single peak at 6.80 ppm was assigned to the vinyl proton (–(–OH)C=C*H*–) of the enol tautomer. The peaks at δ 7.86, 7.89 ppm (doublet) and δ 7.91, 7.93 ppm (doublet) were assigned to the aromatic protons H$_5$ and H$_{5'}$ (Fig. 1(b)). Three single peaks were observed at δ 11.9, 12.1, 15.5 ppm corresponding to the phenolic protons (O*H*) of the keto and the enol tautomers, and the hydroxyl proton (O*H*) of the enol tautomer, respectively. Compared with general hydroxyl protons, the NMR peaks of the hydroxyl protons of the β-diketones became sharp and moved downfield, suggesting the formation of a strong hydrogen bond. These indicate that **1** exists in keto and enol forms in CDCl$_3$. The ^{1}H NMR spectra of **2** and **3** were also measured and shown in Figs. S-1 and S-2 (Supporting Information), respectively, together with the assignment of each proton. These spectra were similar to that of **1**, confirming the existence of keto and enol forms in solution.

Monomers **1**–**3** were free radical polymerized to give the homopolymer P (**1**), P (**2**) and P (**3**) and copolymer P (**1**-*co*-MMA), P (**2**-*co*-MMA) and P (**3**-*co*-MMA). Due to the inhibiting effect of the hydroxyl groups in free radical polymerization [15c,d] and the large side groups attached to the styrene, the molecular weights of the polymers were not so high. Their ^{1}H NMR spectra were shown in Figs. 2 and 3. Keto–enol tautomerism also existed in these polymers and copolymers.

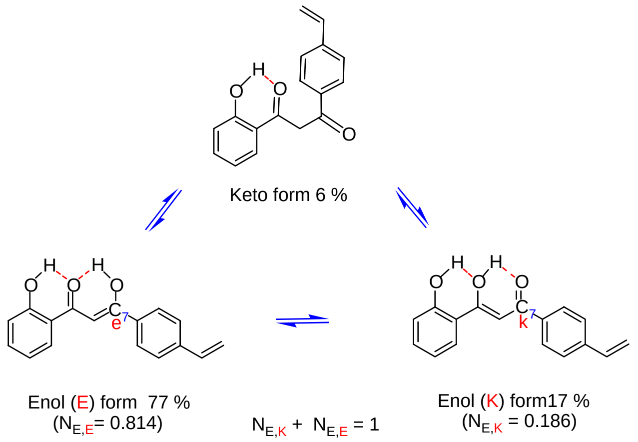
Table 1
Contents of the enol (K), enol (E) and keto forms of **1**, **2** and **3** in CDCl$_3$

β-Diketone monomers	δ_{C7}	Enol (K)	Enol (E)	Keto	Others
1	176.9	0.17	0.77	0.06	<0.01
2	176.3	0.14	0.73	0.13	<0.01
3	185.1	0.44	0.48	0.08	<0.01

According to the assignments of the ^{1}H NMR peaks, the relative contents of enol and keto tautomers of the three monomers were calculated from the integral ratios of NMR peaks of the enolic vinyl and ketonic methylene protons as summarized in Table 1. It can be seen that the enol forms of **1**, **2** and **3** are predominant in CDCl$_3$. The keto content (13%) of **2** is about twice as large as that of **1** (6%). The larger keto content of **2** can be explained as follows. (1) The keto form of **2** is more stable than that of **1** due to the larger conjugation formed by additional H-bonding interaction between naphthol and carbonyl group. (2) The molecular modeling and the energy minimum conformation of the enol form of **2** were calculated by a semiempirical (AM1) method using a GAUSSIAN 98 program. For the enol form of **2**, the carbonyl conjugation leads to a larger rigid structure. However, the rigid structure has a torsion plane, which leads to a large curvature tension (Scheme S-1 in Supporting information). Therefore, the enol form of **2** is not very stable.

Further analysis indicates that the enol tautomer should exist in two *cis*-enol forms, i.e. enol (K) and enol (E) forms as shown in Scheme 2. Only one single peak was observed for the hydroxyl proton (H$_7$: δ 15.5 ppm) of enol tautomer in the ^{1}H NMR spectrum as shown in Fig. 1, implying that the two *cis*-enol forms can not be differentiated by ^{1}H NMR spectroscopy.

The ^{13}C NMR spectrum of β-diketone monomer **1** was measured in CDCl$_3$ and provided in Supporting Information (Fig. S-3). The two *cis*-enol forms are also undistinguishable



Scheme 2. Chemical structures of the enol (K), enol (E) and keto forms of **1**.

by ^{13}C NMR spectroscopy. However, the ^{13}C NMR chemical shift (δ value) of the carbon C_7 (shown in Scheme 2) was strongly correlated to the relative contents of the two *cis*-enol forms according to Mansri et al. [16]. The relative contents of the two *cis*-enol forms were thus calculated using the empirical Eq. (1) proposed by Mansri et al. [16]

$$\delta_{C7} = \delta_{E,E}N_{E,E} + \delta_{E,K}N_{E,K} = 171.7N_{E,E} + 199.7N_{E,K}$$
$$N_{E,E} + N_{E,K} = 1 \qquad (1)$$

$N_{E,E}$ and $N_{E,K}$ are the fractional contributions from the enol (E) form (C_7 in the enol form) and the enol (K) form (C_7 in the keto form) to the whole *cis*-enol tautomer, respectively, as shown in Scheme 2. $\delta_{E,E}$ (171.7 ppm) and $\delta_{E,K}$ (199.7 ppm) are the chemical shifts of the carbon in the enol and keto forms, respectively [16,17].

The calculated contents of two *cis*-enol forms of **1**, **2** and **3** were also listed in Table 1. For **3**, the enol (E) contents (0.48) are close to the enol (K) contents (0.44), which agrees with the enol (E) contents of general β-diketones reported (0.4–0.5) [17e]. For **1** and **2**, the enol (E) contents (0.77 and 0.73) are much higher than **3** (0.48). This interesting result can be reasonably explained from the difference in the chemical structures between **1** (or **2**) and **3**. The higher enol (E) contents can be attributed to the additional formation of intramolecular hydrogen bonds between the phenolic (or naphtholic) groups and the carbonyl groups as shown in Scheme 2.

3.2. Photoinduced keto–enol tautomerism

Fig. 4 shows the UV–vis absorption spectra of β-diketone monomers **1**, **2**, and their polymers in acetonitrile. The absorption bands at the long wavelength of 320–430 nm were attributed to the enol structures [18], where π electrons were delocalized in the whole conjugated molecule according to Gilli et al. [11]. The absorption band at the short wavelength of 230–270 nm was attributed to the keto structures [18]. The absorption spectra of the copolymers P (**1**-*co*-MMA) and P (**2**-*co*-MMA) are close to those of the monomers **1** and **2**. The absorption peaks and intensities of the homopolymers P (**1**) and P (**2**) are slightly broader and lower than those of their monomers and copolymers at the same chromophore concentration as shown in Fig. 4. In homopolymers, the chromophores were very close and crowded with each other, which favored the chromophoric interaction at excited state, even at ground state, and led to various de-active pathways such as energy transfer and migration. excimer formation et al. [19a–c]. Therefore, slightly broader absorption peaks and lower intensities were observed for homopolymers.

The tautomeric equilibrium of the β-diketones is well known to be affected by UV light irradiation [7,18]. Generally, the keto tautomer content increases, while the enol tautomer content decreases after UV irradiation. This process is called as photoinduced ketonization or photoketonization [7].

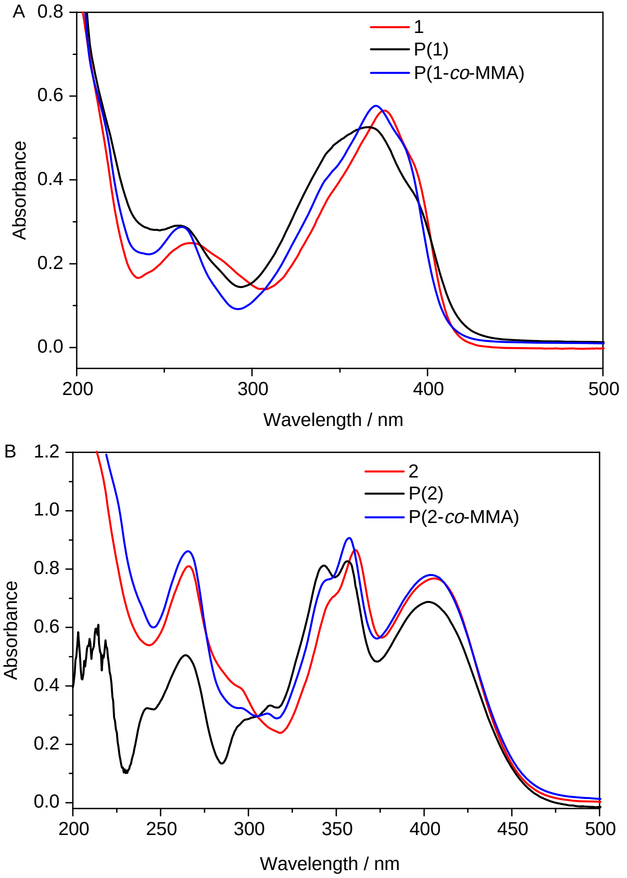


Fig. 4. (A) UV–vis absorption spectra of **1**, P (**1**) and P (**1**-*co*-MMA) in acetonitrile; (B) UV–vis absorption spectra of **2**, P (**2**) and P (**2**-*co*-MMA) in acetonitrile. [chromophore] = 2.0×10^{-5} M.

As expected, the absorption intensity of **3** and its homopolymer P (**3**) at the short wavelength of 230–270 nm increases, and the absorption intensity at the long wavelength of 350–430 nm decreases in acetonitrile during UV irradiation as shown in Figs. 5(C) and 6, implying that the keto tautomer increases and the photoinduced ketonization occurs. This phenomenon is consistent with that of widely reported β-diketones [18]. However, for β-diketone monomers **1** and **2**, the absorption intensities at the long wavelength of 320–430 nm were interestingly found to increase, and the absorption intensity at the short wavelength of 230–270 nm decreases during UV irradiation, and an isosbestic point was observed at 307 nm for **2** as shown in Fig. 5(A) and (B), and Supporting information (Fig. S-6), implying that the enol tautomers of **1** and **2** increase, and the keto tautomers decrease in acetonitrile during UV irradiation.

The photoinduced enolization process can thus be attributed to the additional intramolecular hydrogen bonds between the phenolic (or naphtholic) groups and the carbonyl groups in these β-diketones. After the keto tautomer was irradiated by UV light, the hydrogen bond was destroyed. The carbonyl groups became relatively free due to the rotation of carbon–carbon σ-bonds, which leads to the increasing coplanar probability for the free carbonyl group and another carbonyl group. The process favors the formation of enolic six-member rings through a new and more stable intramolecular H-bonding formation. The schematic illustration for the photoinduced enolization of **2** was shown in Scheme 3. It should be noted that

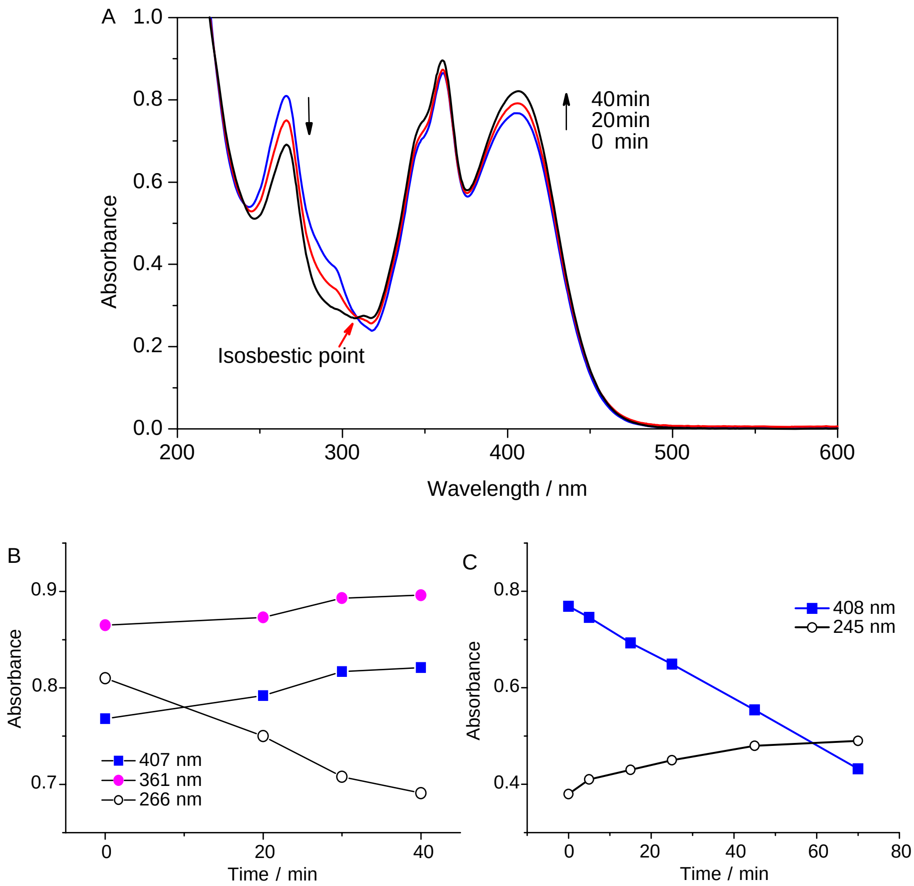


Fig. 5. (A): UV–vis absorption spectra of **2** in acetonitrile during UV irradiation; (B): absorbance changes of **2** at 266, 361, 407 nm in acetonitrile during UV irradiation; (C): absorbance changes of **3** at 245 and 408 nm in acetonitrile during UV irradiation. Concentration: 2.0×10^{-5} M. Irradiation power at 365 nm: 1.1 mW/cm^2.

all the absorption peaks decrease after long-time UV irradiation, which may be due to the photolysis of β-diketones [19d].

Interestingly, the homopolymers P (**1**) and P (**2**), and copolymers P (**1**-*co*-MMA) and P (**2**-*co*-MMA) display opposite phenomena in solution upon UV irradiation. The absorption intensity at the short wavelength of 230–270 nm increases and the absorption intensity at the long wavelength of 320–430 nm decreases during UV irradiation (Fig. 7). The results indicate that the photoinduced ketonization occurred, which was also confirmed by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of copolymer P (2-co-MMA) was measured after UV irradiation for 40 min (Fig. S-4 in Supporting information). The NMR peak at 6.87 ppm assigned to the enolic vinyl proton (H_3) was found to decrease, while the peak at 4.69 ppm assigned to the ketonic methylene protons ($H_{3'}$) was found to increase during UV irradiation. The photoinduced ketonization of the polymer is interestingly opposite to the photoinduced enolization of their monomers. This may be due to the macromolecular effect. The enolic tautomers require that the H-bonding directed six-member rings of enolic hydroxyl and carbonyl groups lie in one plane in the *cis*-enol form according to Delchev [20]. In the polymers and copolymers, the six-member rings of the enolic tautomers are sterically hindered and less favorable due to the side groups and polymer chains as illustrated in Scheme 4. Therefore, the photoinduced ketonization favorably occurred in the polymers and copolymers as compared with the photoinduced enolization of their monomers **1** and **2** during UV irradiation.

To explore the enol/keto forms of polymers, the molecular modeling and the energy minimum conformations of the enol

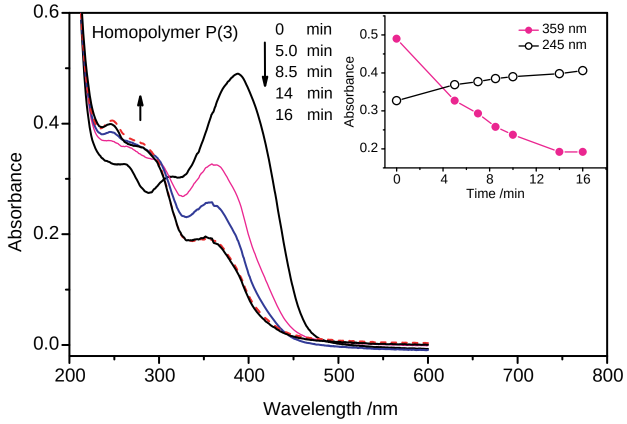
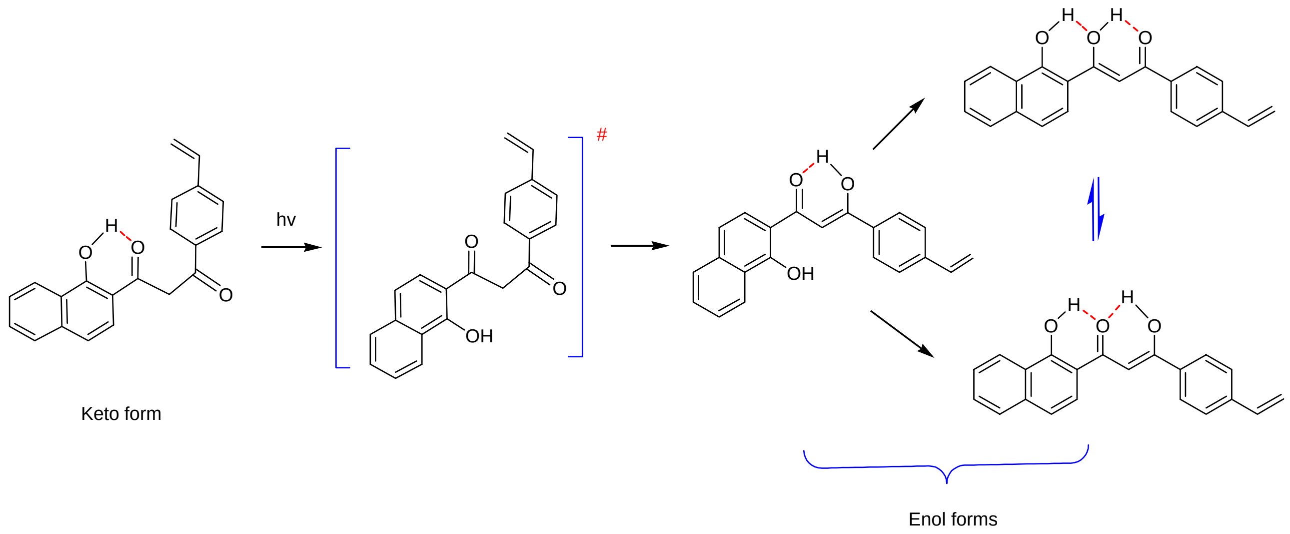


Fig. 6. UV–vis absorption spectra of P (**3**) in acetonitrile during UV irradiation. Irradiation power at 365 nm: 1.1 mW/cm^2. Inset: absorbance changes at 245 and 359 nm. [chromophore] $=2.0\times10^{-5}$ M.



Scheme 3. Schematic representation for the photoinduced enolization of **2**.

and keto forms of P (**2**-*co*-MMA) chain segment were calculated by a semiempirical (AM1) method using a GAUSSIAN 98 program. The energy minimum conformation of the enol form displays a planar six-member ring structure through H-bonding formation, which forms a large conjugated and rigid structure. In contrast, the energy minimum conformation of the keto form displays an unplanar state between two carbonyl groups, and the whole molecule losts a rigid and conjugated structure (Scheme S-2 in Supporting information).

3.3. Steady-state fluorescence spectroscopy

β-Diketone monomer **3** displays a strong fluorescence emission with large Stokes' shifts (∼120 nm) in polar solvents as shown in Fig. 8. Dual fluorescence was observed in nonpolar cyclohexane. The fluorescence spectrum in cyclohexane was fitted into two fluorescence peaks. According to Rettig [21], the relative narrow fluorescence peak at 429 nm is attributed to a locally excited (LE) state, and the broad structureless

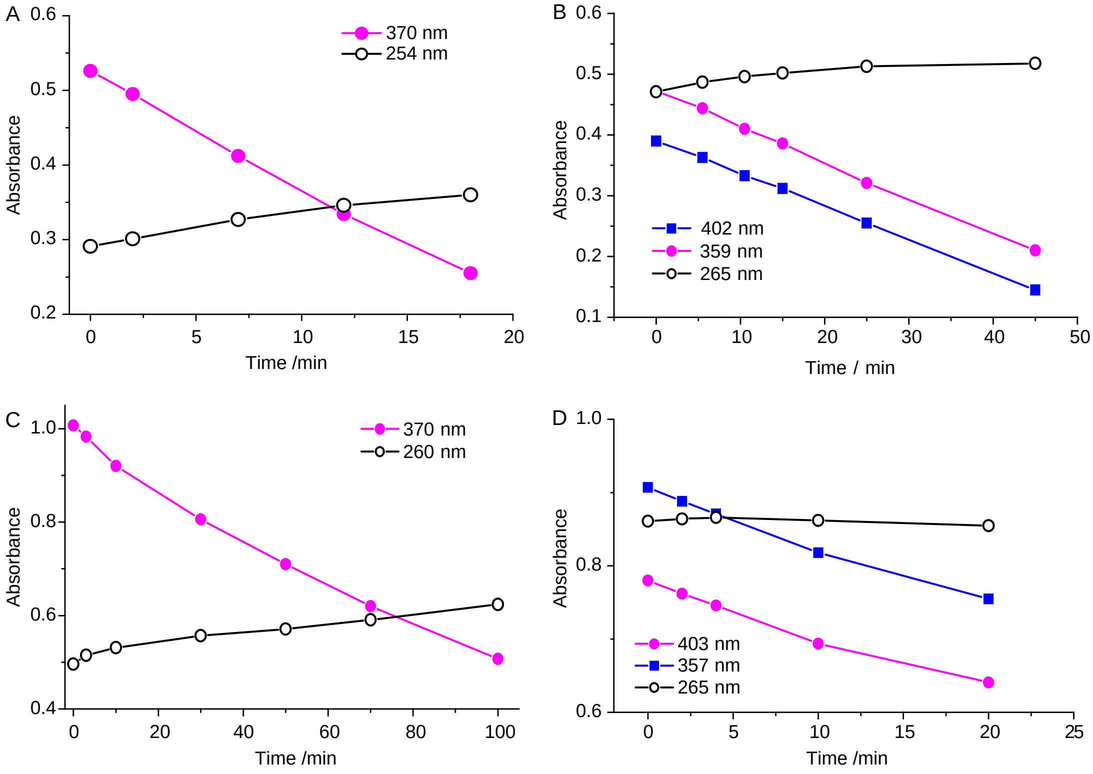
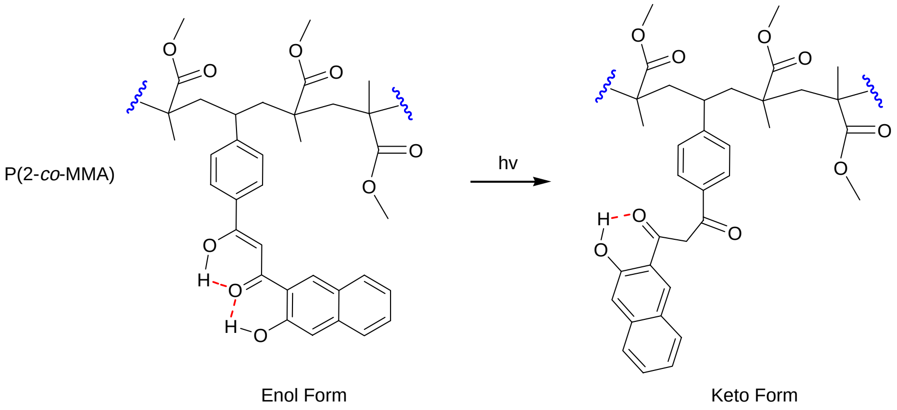


Fig. 7. Absorbance changes of P (**1**) at 254 and 370 nm (A), P (**2**) at 265, 359 and 402 nm (B), P (**1**-*co*-MMA) at 260 and 370 nm (C), P (**2**-*co*-MMA) at 265, 357 and 403 nm (D) during UV irradiation in acetonitrile. [chromophore] $=2.0\times10^{-5}$ M. Irradiation power at 365 nm: 1.1 mW/cm^2.



Scheme 4. Photoinduced ketonization of P (**2**-*co*-MMA).

fluorescence peak at 448 nm is attributed to a charge transfer (CT) excited state. In polar solvents, the emission of locally excited state disappears, a strong bathochromic effect was observed. The broad structureless emission displays large and sensitive red shifts with increasing the solvent polarity, indicating typical CT emission properties as shown in Fig. 8.

To gain a quantitative analysis for the CT characteristics of β-diketone monomer **3**, Lippert–Mataga equation [22] was used as follows:

$$\Delta\nu = \nu_{\mathrm{ab}} - \nu_{\mathrm{em}} = \frac{2}{hc}\frac{(\mu_{\mathrm{E}}-\mu_{\mathrm{G}})^2}{a^3}\Delta f + \text{constant}$$

Δf is the solvent parameter termed as orientation polarizability $\Delta f = [(\varepsilon - 1/2\varepsilon + 1) - (n^2 - 1/2n^2 + 1)]$. ν_{ab} and ν_{em} are the wavenumbers (cm^{-1}) of the absorption and emission, respectively. μ_{G} and μ_{E} are the dipole moments of ground state and excited state, respectively. ε and n are the dielectric constant and the refractive index of solvents, respectively. $(2/hc)\times((\mu_E-\mu_G)^2/a^3)$ was determined from the plot slope (1.90×10^4) of the Stokes' shifts ($\Delta\nu$) against Δf in various solvents as shown in the inset of Fig. 8. On the basis of the average cavity radius ($a = 5.9$ Å) of **3** calculated from a semiempirical (AM1) method using a GAUSSIAN 98 program, the change ($\Delta\mu = \mu_{\mathrm{E}} - \mu_{\mathrm{G}}$) in dipole moments between the first excited singlet state and the ground state was obtained to be 19.7 D for **3**. This value falls in the range of typical CT fluorophores (18.0–35.0 D) with the same cavity radius according to Lakowicz [23]. One Debye unit (1.0 D) is 1×10^{-18} esu. 19.7 D is comparable to the dipole moment resulted from a charge separation of one unit charge (4.8×10^{-10} esu) by 4.10 Å. The value (4.10 Å) is close to the cavity radius ($a = 5.9$ Å) of **3**, suggesting that almost complete photoinduced charge transfer (CT) occurs in **3** at the excited state. Therefore, β-diketone monomer **3** is a novel CT fluorophore, which is very sensitive to environmental polarity, and can be potentially employed as a novel fluorescence label or probe. The environmental sensitivity of fluorescence behavior was also observed for its polymer P (**3**), where **3** served not only as a monomer, but also as an intrinsic CT fluorophore.

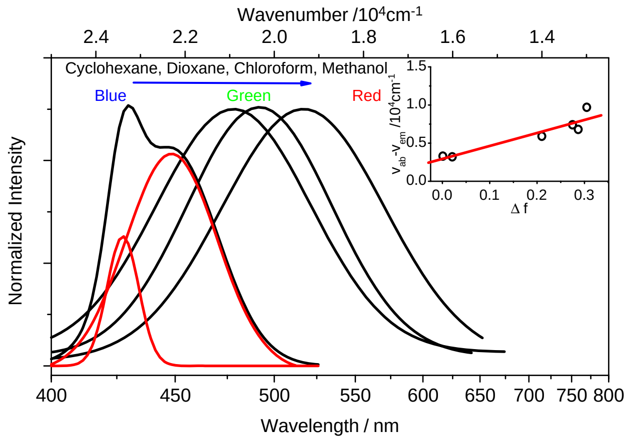


Fig. 8. Fluorescence spectra of **3** in cyclohexane, dioxane, chloroform and methanol. The fluorescence spectrum in nonpolar cyclohexane was fitted into two peaks at 429 and 448 nm. $\lambda_{\mathrm{ex}} = 390$ nm. Inset: Lippert–Mataga plot for **3**. $\Delta f = (\varepsilon - 1)/(2\varepsilon + 1) - (n^2 - 1)/(2n^2 + 1)$.

4. Conclusion

β-Diketone monomers bearing the phenol and naphthol groups (**1** and **2**), and the electron-donating *N*,*N*-dimethylaniline groups (**3**), and their polymers and copolymers were synthesized. These β-diketone monomers were found to exist in one keto form, and two *cis*-enol forms, i.e. enol (K) and enol (E) forms. Their relative contents determined by NMR spectroscopy are 6–13% keto form, and 14–44% enol (K) and 48–77% enol (E) forms. The enol (E) contents of **1** and **2** were much higher than those of **3** due to the additional intramolecular H-bonding interaction. The photoinduced enolization occurred in the β-diketone monomers **1** and **2** during UV irradiation. On the contrary, the photoinduced ketonization occurred in their polymers and copolymers during UV irradiation. β-Diketone monomer **3** was found to be a novel charge transfer fluorophore, which displays a great potential as a dual-purpose functional monomer.

Acknowledgements

Financial support from the National Natural Science Foundation of China (No. 50003001) is gratefully acknowledged. Authors thank Mr Kai-Bo Li, Dr Liu-He Wei, Mrs. Ning Xu, Mr. Song Lin for kind help.

Supplementary data

Supplementary data associated with this article can be found at doi:10.1016/j.polymer.2006.02.087.

References

[1] (a) Temprado M, Roux MV, Umnahanant P, Zhao H, Chickos JS. J Phys Chem B 2005;109:12590.
  (b) Dziembowska T, Rozwadowski Z. Curr Org Chem 2001;5:289.
[2] Markov P. Chem Soc Rev 1984;13:69.
[3] (a) Jaafari A, Ouzeau V, Ely M, Rodriguez F, Chane-ching K, Yassar A, Aaron JJ. Synth Met 2004;147:183.
  (b) Godsi O, Turner B, Suwinska K, Peskin U, Eichen Y. J Am Chem Soc 2004;126:13519.
[4] Tumambac GE, Francis CJ, Wolf C. Chirality 2005;17:171.
[5] Iglesias E. J Org Chem 2003;68:2680.
[6] Matanovic I, Doslic N. J Phys Chem A 2005;109:4185.
[7] Du FS, Zhang X, Chen GQ, Li ZC, Li FM, Pan H, Gao QY. J Chem Chin Univ-Chin 2003;24:374.
[8] Tsaryuk V, Zolin V, Legendziewiez J, Szostak R, Sokolnicki J. Spectroc Acta Part A-Mol Biomol Spectr 2005;61:185.
[9] Bolvig S, Hansen PE. Curr Org Chem 2000;4:19.
[10] Gilli P, Bertolasi V, Pretto L, Ferretti V, Gilli G. J Am Chem Soc 2004;126:3845.
[11] Gilli P, Bertolasi V, Ferretti V, Gilli G. J Am Chem Soc 2000;122:10405.
[12] Kenar JA. J Am Oil Chem Soc 2003;80:1027.
[13] (a) Masuda S, Sertova N, Petkov I. J Polym Sci, Polym Chem 1997;35:3683.
  (b) Yagai S, Karatsu T, Kitamura A. Chem Eur J 2005;11:4054.
  (c) Shibaev V, Bobrovsky A, Boiko N. J Photochem Photobiol A, Chem 2003;155:3.
  (d) Zhang X, Li ZC, Li KB, Du FS, Li FM. J Am Chem Soc 2004;126:12200.
[14] (a) Haba O, Yokota K, Kakuchi T. Chirality 1995;7:193.
  (b) Smith C. J Org Chem 1964;29:488.
  (c) Weast RC. Handbook of chemistry and physics. 48th ed. Cleveland OH: Chemical Rubber Co.; 1967.
[15] (a) Zhang X, Jin YH, Diao HX, Du FS, Li ZC, Li FM. Macromolecules 2003;36:3115–27.
  (b) Zhang X, Du FS, Li ZC, Li FM. Macromol Rapid Commun 2001;22:983.
  (c) Cativiela C, Serrano JL, Zurbano MM. J Org Chem 1995;60:3074.
  (d) Masuda S, Sertova N, Petkov I. J Polym Sci, Polym Chem 1997;35:3683.
[16] (a) Mansri A, Casals PF, Oulmidi A, Guemra K, Reyx D. Eur Polym J 1996;32:269.
  (b) Mansri A, Casals PF, Oulmidi A, Guemra K, Reyx D. Eur Polym J 1996;32:277.
[17] (a) Imagawa H, Kurisaki T, Nishizawa M. Org Lett 2004;6:3679.
  (b) Ramon DJ, Yus M. J Org Chem 1991;56:3825.
  (c) Hasegawa E, Ishiyama K, Horaguchi T, Shimizu T. J Org Chem 1991;56:1631.
  (d) Trofimov BA, Sobenina L, Mikhaleva AI, Ushakov IA, Vakul'skaya TI, Stepanova ZV. Synthesis 2003;8:1272.
  (e) Pocker Y, Spyridis GT. J Am Chem Soc 2002;124:10373.
[18] Huang FX, Wu YQ, Gu DH, Gan FX. Spectrosc Spectr Anal 2005;25:141.
[19] (a) Siegoczynski RM, Ejchart W. Macromol Symp 2004;212:575–80.
  (b) Shoji O, Higashi Y, Hishinuma S, Sato M, Annaka M, Yoshikuni M, et al. Macromolecules 2002;35:2116–21.
  (c) Munson CA, Kane MA, Baker GA, Pandey S, Perez SA, Bright FV. Macromolecules 2001;34:4624–9.
  (d) Wetz F, Routaboul C, Lavabre D, Garrigues JC, Rico-Lattes I, Pernet I. Photochem Photobiol 2004;80:316.
[20] Delchev VB. J Struct Chem 2003;44:574.
[21] Grabowski ZR, Rotkiewicz K, Rettig W. Chem Rev 2003;103:3899.
[22] (a) Mataga N, Kaifu Y, Koizumi M. Bull Chem Soc Jpn 1956;29:465.
  (b) Von Lippert E. Z Electrochem 1957;61:962.
[23] Lakowicz JR. Principles of fluorescence spectroscopy. 2nd ed. New York: Plenum Press; 1999 p. 192.