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Short communication

Synthesis and properties of conjugated copolymers with 2-pyran-4-ylidene malononitrile

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Abstract

A conjugated polymers were prepared by an condensation polymerization of *N*-ethyl-3,6-diformylcarbazole, *N*-(2-ethylhexyl)-3,6-diformylphenothiazine, 4,4′-diformyl-triphenylamine and (2,6-dimethyl-4*H*-pyran-4-ylidene)malononitrile. The structure of the copolymers were characterized by elemental analysis, ^{1}H NMR, UV–Vis and FT-IR spectra. Fluorescence spectra showed that the copolymers are red light emitting materials.

Keywords: DCM; Emitting polymer; Triphenylamine; Carbazole; Phenothiazine

A large number of light emitting polymers have been introduced during the last 10 years [1]. Conjugated polymers have been incorporated as active materials into several kinds of electric device, such as diodes, transistors [2] and light-emitting diodes [3].

Cyano-containing poly(2,5-dialkoxy-1,4-phenylenevinylene) [4–6] and poly(3-alkylthiophene) derivatives [7] are well-known red-emitting polymeric materials.

Eastman kodak's DCM dyes are well-known as low molecular weight red-emitting material, which can be synthesized by a relatively simple procedure [8].

Recently, Kim and Lee reported on the synthesis of poly(*p*-phenylenevinylene) derivative with 2-pyran-4-ylidene malononitrile in the main chain and its electroluminescence property [9].

In this work, we report the synthesis of conjugated polymers which have both phenothiazine, carbazole, triphenylamine moiety and 2-pyran-4-ylidene malononitrile units linkage in the main chain and the spectral properties of the resulting polymers.

(2,6-Dimethyl-4*H*-pyran-4-ylidene)malononitrile was synthesized from 2,6-dimethyl-4-pyrone as a monomer by the method of Woods [10].

Dialdehydes **2**, **3** and **4** could be obtained via the Vilsmeier reaction employing the DMF/POCl$_3$ from triphenylamine, *N*-(2-ethylhexyl)phenothiazine, *N*-ethylcarbazole, respectively [11]. Conjugated polymers **5–7** were prepared according to the method in the reference [12]. 4,4′-Diformyltriphenylamine was refluxed with (2,6-dimethyl-4*H*-pyran-4-ylidene)malononitrile **1** in the presence of piperidine in *n*-propanol at boiling point (about 100 °C) for 24 h. After refluxing the solution was cooled, precipitated solid was filtered and washed with *n*-propanol and dried at 50 °C overnight. Yield 90%. The product obtained was dissolved in chloroform and precipitated with ethyl acetate, filtered and dried at 50 °C. Other polymers were prepared with same method (Scheme 1) [13].

In Table 1, the results of the polymerization are summarized. The molecular weights of the resulting

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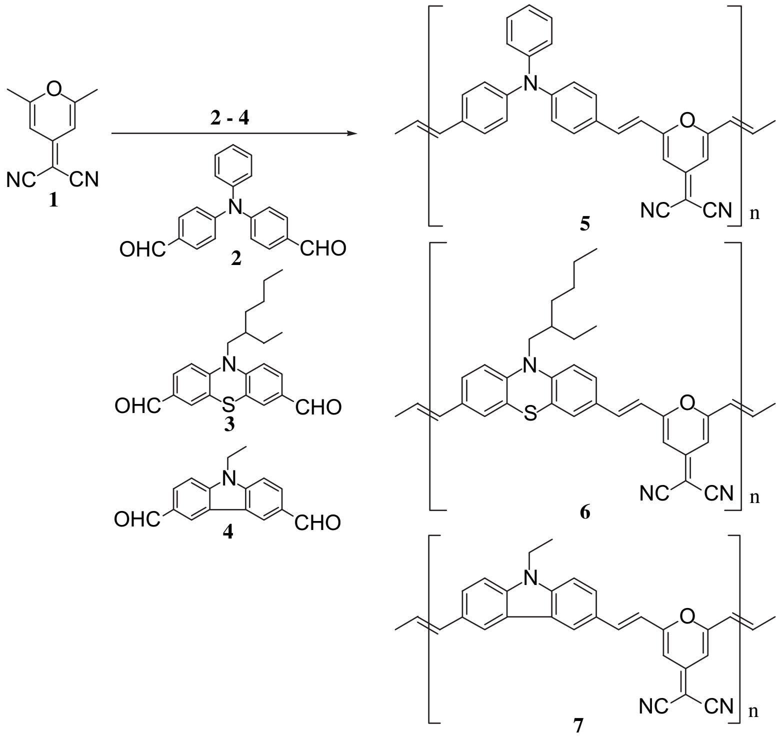

Scheme 1.

polymers were estimated by gel-permiation chromatography (GPC) to be in the range 2.34×10^3–5.71×10^3 and polydispersity of the resulting polymers were in the range of 1.18–1.53.

Thermal stabilities of the polymers were evaluated by means of thermo-gravimetric (TG) and differential thermo-analysis (DTA) in the temperature range of 20–500 °C with temperature-raising rate of 5 °C (Fig. 1). It was observed that the polymers are much stable at the temperature below 375 °C. Weight loses observed from TG curves of the polymers are smaller than 1% in the temperature range from 20 to 350 °C. The TG curves indicated that the polymer **7** begins to decomposite at 375 °C, for the polymer **5** and **6** the decomposition temperatures are higher than 400 °C. After the samples of the polymers were heated up at 200 °C for 60 min, photoluminescence spectra of the heated polymers in chloroform solution were measured again. Fluorescence intensities of the heated samples do not change much comparing with that of unheated samples. That shows the polymers have perfect thermostabilities (Fig. 1).

Visible and emission spectra of polymers **5**–**7** in solution and their solvents effects are summarized in Table 2. Polymer **5**, **6** and **7** absorbed at 490, 476 and

Table 1
Polymerization results of polymers **5**–**7**

Polymer	Yield (%)	M_n[a]	M_w/M_n[a]	Analysis (%)		
				Found/Calc.		
				C	H	N
5	90	5712	1.53	81.13 82.36	4.91 4.38	9.53 9.60
6	87	3350	1.42	75.77 76.31	6.36 5.80	8.61 8.34
7	92	2343	1.18	79.47 80.60	4.92 4.42	9.98 10.85

[a] M_n and M_w/M_n of the polymers were determined by GPC using polystyrene standards.

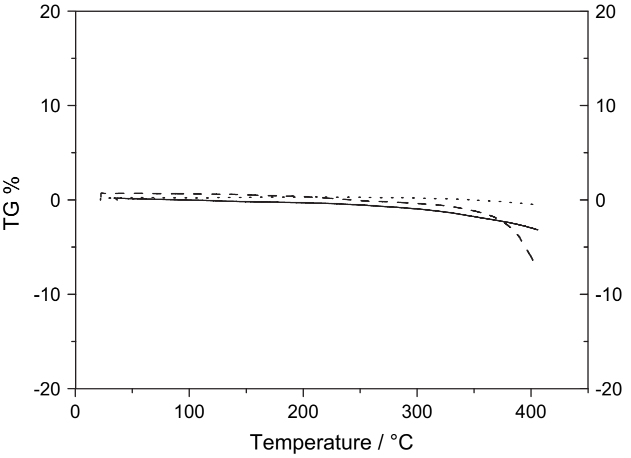

Fig. 1. Thermal analysis for the polymer dyes **5** (line), **6** (dash) and **7** (dots).

Table 2
Visible and fluorescence spectra of polymers **5–7**

Polymer	λ_{max} (nm)		F_{max} (nm)[a] (SS)[b]	
	$CHCl_3$	CH_2ClCH_2Cl	$CHCl_3$	CH_2ClCH_2Cl
5	490	488	599(109)	657(169)
6	476	488	648(172)	666(178)
7	452	463	560(108)	613(150)

[a] Fluorescence maximum excited at λ_{max} value.

[b] Stock's shift.

452 nm in chloroform and polymers absorbed at similar wavelength region in dichloroethane.

Fluorescence maximum (F_{max}) of polymers in chloroform and dichloroethane were quite different and their Stock's shift (SS) were determined. Polymers showed red fluorescence with quite large SS values of 108–178 nm.

Acknowledgements

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[11] All analytical data agree with the proposed structure for compounds **2–4**.
2: Yield 46%. Elemental analysis: found, C 79.74, H 5.12, N 4.47; calculated for $C_{20}H_{15}NO_2$, C 79.72, H 5.02, N 4.65. IR (KBr), cm^{-1}: 1693, 1590, 1509, 1295, 1169, 1509, 823, 761. ^1H NMR ($CDCl_3$, δ): 7.16–7.20 (m, 6H), 7.27 (m, 2H), 7.40 (m, 1H), 7.76–7.79 (m, 4H), 9.89 (s, 2H). MS 301(M^+, 100%).
3: Yield 69%. Elemental analysis: found, C 71.15, H 6.98, N 3.15; calculated for $C_{22}H_{25}NO_2S$, C 71.90, H 6.86, N 3.81. IR (KBr), cm^{-1}: 3053, 2965, 2926, 1687, 1601, 1585, 1463, 1337, 1290, 1264, 1198, 823, 689. ^1H NMR ($CDCl_3$, δ): 0.76–0.83 (m, 6H), 1.18–1.36 (m, 8H), 1.85 (m, 1H), 3.79 (d, 2H), 6.93 (d, 2H), 7.57 (d, 2H), 7.62 (q, 2H), 9.78 (s, 2H). MS 367(M^+, 81%).
4: Elemental analysis: found, C 75.89, H 5.30, N 5.60; calculated for $C_{16}H_{13}NO_2$, C 76.48, H 5.21, N 5.57. IR (KBr), cm^{-1}: 3053, 2971, 1687, 1627, 1595, 1570, 1488, 1385, 134, 1240, 1205, 1123, 830, 802, 710. ^1H NMR ($CDCl_3$, δ): 1.51 (t, 3H), 4.45 (q, 2H), 7.55 (d, 2H), 8.08 (q, 2H), 8.64 (d, 2H), 10.12 (s, 2H). MS 251 (M^+, 88%).

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[13] ^1H NMR data agree with the proposed structure of polymers **5–7**.
5: Yield: 90%, ^1H NMR ($CDCl_3$, δ): 6.67(m, 2H), 7.16(m, 4H), 7.35–7.49(m, 7H), 7.74(d, 6H).
6: Yield: 87%, ^1H NMR ($CDCl_3$, δ): 0.89(m, 6H), 1.23–1.28(m, 6H), 1.39–1.45(m, 2H), 1.57–1.93(m, 1H), 3.81(m, 2H), 6.52(m, 2H), 6.98(m, 4H), 7.35(m, 4H), 7.65(m, 2H).
7: Yield: 92%, ^1H NMR ($CDCl_3$, δ): 1.59(m, 3H), 4.37(m, 2H), 6.49–6.61(m, 2H), 7.29–7.42(m, 4H), 7.58–7.64(m, 4H), 7.96–8.20(m, 2H).