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Syntheses and thermostability of N-[4-(N′-8-quinolinyl)aminocarbonyl phenyl]maleimide/styrene copolymer

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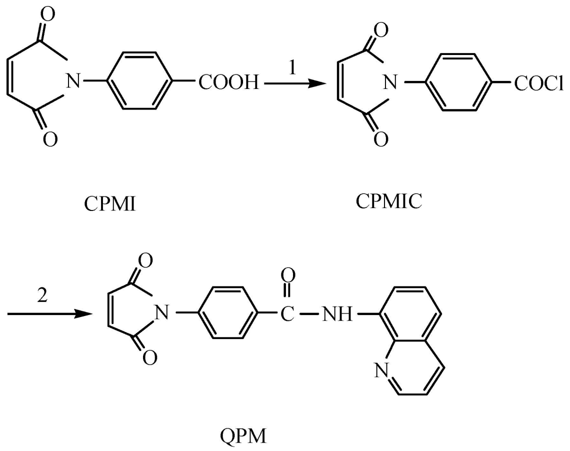
In recent years, there has been considerable interest in the free radical polymerization and copolymerization of N-substituted maleimide (RMI) [1–4]. Poly(RMI) has excellent thermal stability because of a rigid backbone consisting of a five-membered ring structure. Moreover, the copolymers of RMI with various vinyl monomers such as styrene (ST), methacrylates, hydropropyl methacrylate and cyclohexene indicate enhanced heat resistance and mechanical properties [5–9]. The maleimide based polymers have versatile applications in many fields, such as aerospace, medical and microelectronic industry [10, 11]. Among these polymers, Poly[N-(4-carboxyphenyl)maleimide] and Poly[N-(4-hydrophenyl)maleimide] are one of the most attractive classes of polymers. Because of the introduction of phenyl group, the molecular motion of the main chain in the polymers was prevented and glass transition temperatures (T_g) can be raised [12, 13]. Furthermore, the introduction of functional group in the polymers also broadens its practical applications.

Recently, there have been a number of reports on syntheses and polymerization of N-(4-carboxyphenyl)maleimide (CPMI) derivatives [14, 15]. However, the syntheses and polymerization of maleimide derivatives containing aminoquinoline heterocyclic ring structures appears quite limited in the literature.

In this study, a novel monomer N-[4-(N′-8-quinolinyl)aminocarbonylphenyl]maleimide (QPM) was prepared from CPMI and 8-aminoquinoline. The radical copolymerization of QPM with styrene is also reported. The photoelectricity characteristics of 8-aminoquinoline and its derivatives have been reported in the literature [16]. Therefore, poly(RMI) with 8-aminoquinoline groups are worthwhile to be considered as electroluminescent materials. It can be reasonable predicted that polymer containing QPM units may be used for preparing electroluminescent devices.

QPM monomer was synthesized from CPMI and 8-aminoquinoline, as shown in Scheme 1.



Scheme 1

CPMI and N-(4-chlorocarbonylphenyl)maleimide (CPMIC) was prepared according to a previously published procedure [17, 18]. CPMI: yield 90%, m.p.

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242°C. CPMIC: yield 92%, m.p. 168–169°C. Syntheses of QPM: In a three-necked flask equipped with a teflon-stirrer and thermometer and purged with nitrogen gas, a mixed acetone (1.60×10^{-4} m^3) solution of 8-aminoquoline (16 g, 0.11 mol) and triethylamine (11 g, 0.11 mol) was added dropwise to a solution of CPMIC (25 g, 0.11 mol) in acetone (6.00×10^{-4} m^3) and the mixture was stirred at 40–45°C for 4 h. The precipitated product was filtered, dried, and then recrystallized from ethyl acetate to obtain pure QPM, m.p. 244–245°C, yield 36%. Elemental Anal. Calcd. For QPM ($C_{20}H_{13}N_3O_3$, 343.341): C, 69.966; H, 3.816; N, 12.239; O, 13.979. Found: C, 69.979; H, 3.935; N, 12.151; O, 13.935. ^{1}H-NMR spectrum (δ in ppm from TMS in DMSO-d_6): 2.50 (DMSO), 7.25 (2H, CO-CH=CH-CO, imide), 7.61–8.98 (10H, in 8-quinolinyl group and phenyl group), 10.69 (1H, CONH). FTIR spectrum (KBr disk, cm^{-1}): 3368 (NH), 1715 (C=O), 1660 (CONH), 1534 (CONH), 1405 and 1149 (C-N-C), 954 (C=C), 848 (CH in phenyl).

The copolymerization of QPM and ST: A solution of QPM (M_1) and ST (M_2) in dimethyl formamide (DMF) was placed in a glass tube which contained a magnetic stirrer, the initiator AIBN was weighed and introduced into the tube, then the tube was degassed and swept with nitrogen 3 times, and finally, the tube was sealed. After polymerization for a given time at 60°C with stirring, the copolymer was precipitated in large amount of tetrahydrofuran (THF). The process of dissolving and reprecipitation was repeated two times to get rid of unreacted monomers. The copolymer was dried under reduced pressure for 3 days.

The FTIR spectra of QPM monomer (a) and QPM/ST copolymer (b) are shown in Fig. 1. For QPM/ST copolymer, absorption band of the C=C within maleimide ring (954 cm^{-1}) and the viny group at 991 and 908 cm^{-1} of ST disappeared completely. The result was further identified by ^{1}H-NMR spectra as shown in Fig. 2. Because of the different solubility for QPM monomer and QPM/ST copolymer, two solvents are used in the determination. Fig. 2a is the ^{1}H-NMR spectrum of QPM monomer (δ in ppm from TMS in DMSO-d_6). Fig. 2b is the ^{1}H-NMR spectrum of QPM/ST copolymer (δ in ppm from TMS in $CDCl_3$). The aromatic protons from both QPM and ST form three broadabsorption at 8.67, 8.02 and 7.39 ppm. Peaks at 3.44 ppm are assigned to the absorption of the -CH- group within maleimide ring and peaks at 1.71–1.54 ppm to the absorption of methylene groups of styrene. Absorption of both monomers is absent in the spectrum. This confirmed that the polymerization reaction happened via the opening of the double bond of both monomers.

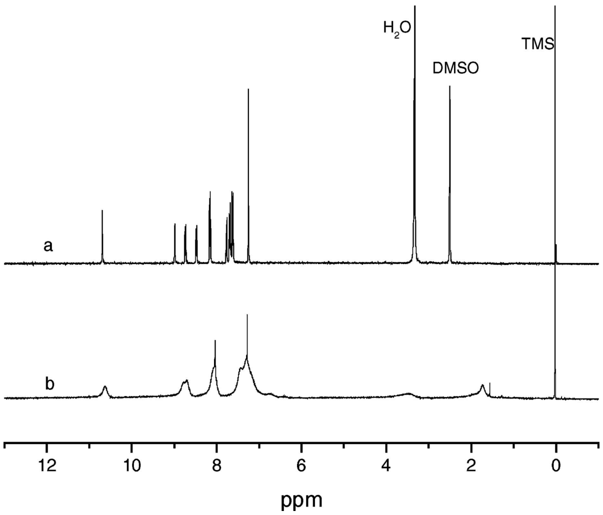

Figure 2 ^{1}H-NMR spectra of (a) QPM monomer and (b) poly(QPM/ST) with 46.8 mol% QPM in the copolymer.

The results of radical copolymerization of QPM (M_1) with ST (M_2) in DMF at 60°C in the presence of AIBN are summarized in Table I.

The copolymerization proceeded in a homogeneous system in DMF. An alternating copolymer was obtained over a wide range of monomer feed ratios (Table I).

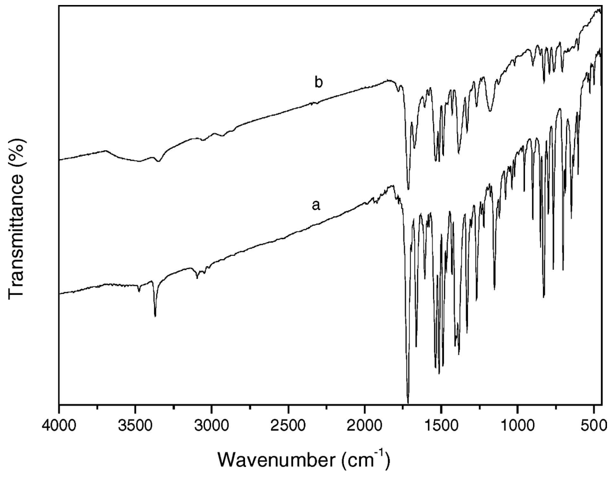

Figure 1 FTIR spectra of (a) QPM monomer and (b) poly(QPM/ST) with 46.8 mol% QPM in the copolymer.

TABLE I Radical copolymerization of QPM (M_1) with ST (M_2) in DMF at 60°C[a]

M_1 in feed (mol%)	Polymer yield (wt%)	M_1 in copolymer (mol%)[b]	$M_n{}^c \times 10^{-4}$	$M_w/M_n{}^c$
10	33.6	25.9	2.7	3.5
20	39.0	35.6	1.8	3.5
30	46.4	43.3	1.1	3.3
40	58.1	46.8	0.7	2.7
50	53.2	47.6	0.6	2.5
60	49.9	49.1	0.5	2.7
70	24.6	49.7	0.5	2.0
80	12.5	51.0	0.3	2.5
90	7.0	56.3	0.2	1.6

[a] [QPM] + [ST] = 500 mol/m^3, [AIBN] = 10 mol/m^3, the reaction time is 4 h.

[b] Determined by elemental analysis.

[c] By GPC, using DMF (1.667×10^{-8} m^3/ s) as the eluent.

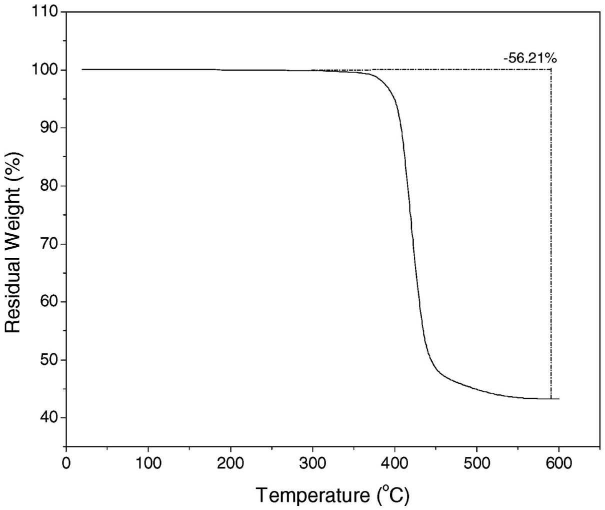

Figure 3 TGA curve of poly(QPM/ST) with 46.8 mol% QPM in the copolymer.

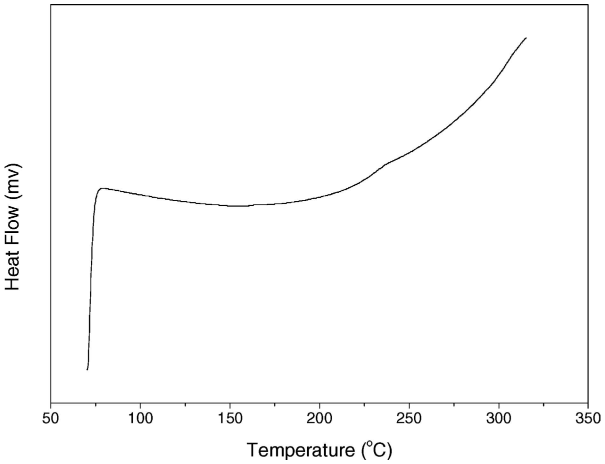

Figure 4 DSC curves of poly(QPM/ST) with 46.8 mol% QPM in the copolymer.

The thermal stability of the copolymer of QPM/ST was investigated by thermogravimetric analysis (TGA). TGA was carried out in a stream of nitrogen at a heating rate of 10 °C/min. The TGA curve of QPM/ST was shown in Fig. 3. It can be seen that the onset decomposition temperature for the comopolymer was 380°C, which indicated that the copolymer had excellent thermal stability.

The T_g of poly(QPM/ST) was determined by DSC. It can be seen in Fig. 4 that the T_g of the copolymer was 229°C. The high T_g value of poly(QPM/ST) can be explained that the bulkiness of N-substituents group in QPM prevents molecular motion of the main chain and the glass transition temperature can be raised. Moreover, the copolymerization was also confirmed by DSC curve as only one glass transition appeared in the thermogram.

The fluorescence characteristics of poly(QPM/ST) was also investigated. It can be seen that poly(QPM/ST) exhibits stronger fluorescence (Fig. 5), which will make it useful as emitting layer in electroluminescent devices, the excitation wavelength is 328 nm. Further investigation will be carried out on the potential utilities of QPM copolymers in photoelectricity materials field.

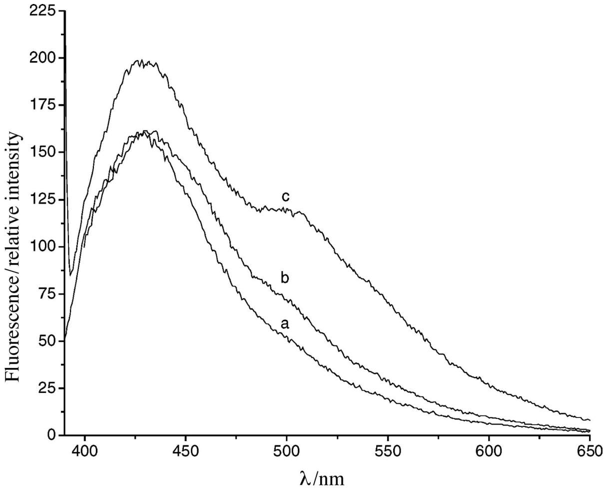

Figure 5 The fluorescence characteristics of poly(QPM/ST) with 46.8 mol% QPM in the copolymer at different concentration. (a) 2.25×10^2 g/m^3; (b) 6.25×10^2 g/m^3; (c) 1.150×10^3 g/m^3.

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