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Copolymerization of (10-oxo-10-hydro-9-oxa- $10\lambda^5$ -phospha-phenanthrene-10-yl)-methyl acrylate with styrene

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Abstract

A phosphorus-containing monomer (10-oxo-10-hydro-9-oxa- $10\lambda^5$ -phospha-phenanthrene-10-yl)-methyl acrylate ($\mathbf{M_1}$) was copolymerized with styrene to give a potential flame retardant copolymer of high thermal stability. The structures of monomer and copolymer were characterized by FT-IR and 1 H NMR measurements. The reactivity ratios for free-radical of the monomer ($\mathbf{M_1}$) and styrene ($\mathbf{M_2}$) were studied. The calculated results are as follows: $r_1 = 0.225$, $r_2 = 0.503$; $Q_1 = 0.413$, $e_1 = 0.476$; azeotropic point = 0.37. TGA and DTG curves indicated that $\mathbf{M_1}$ is a potential flame retarding monomer for styrenic polymers. © 2009 Yu Bin Zheng. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.

Keywords: Flame retardant; Copolymerization; Phosphorus-containing monomer; Styrene

In the past decade years, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) **I** is considered as an efficient and environment friendly flame retarding unit due to its high phosphorus content and rich aryl group [1]. The derivatives of DOPO are usually used as reactive flame retardant in epoxy resins and polyesters [2,3]. However, as low molecules, DOPO and its derivatives have seldom been applied in polystyrene owing to the migration in polymer [4]. In order to introduce DOPO unit into polystyrene by chemical means, (10-oxo-10-hydro-9-oxa-10 λ^5 -phosphaphenanthrene-10-yl)-methyl acrylate (DOPO-CH₂O-AA) $\mathbf{M_1}$ was synthesized and copolymerized with styrene $\mathbf{M_2}$. The thermal degradation of the obtained copolymer \mathbf{III} including DOPO unit as a pendent group was studied by TGA. And the reactivity ratios for free-radical of $\mathbf{M_1}$ and $\mathbf{M_2}$ were also investigated.

Compound II was prepared according to the method suggested by Shieh and Wang [5]. Melting point is 154 $^{\circ}$ C. 1 H NMR (DMSO-d₆, δ ppm): 4.09, 4.25 (m, 2H, –CH₂–); 5.58 (s, 1H, –OH); 5.86 (m, 3H); 7.29 (m, 2H, benzene ring); 7.45 (t, 1H, benzene ring); 7.61 (m, 1H, benzene ring); 7.80 (t, 1H, benzene ring); 7.95 (m, 1H, benzene ring); 8.19 (d, 1H, benzene ring); 8.25 (m, 1H, benzene ring).

 M_1 was synthesized as follows (Scheme 1).

Compound II 4.92 g (0.02 mol), triethylamine 2.23 g (0.022 mol) and 20 mL CHCl₃ were fed into a round bottom flask equipped with a thermometer, an electromagnetic stirrer, a condenser and an addition funnel. The reaction mixture was cooled to -20 °C with stirring. Acryloyl chloride 2.00 g (0.22 mol) in 5 mL CHCl₃ was added dropwise

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DOPO DOPO-CH₂OH DOPO-CH₂O-AA

I II M₁

a) HCHO O
b)
$$H = H = H$$
b) H_2
C=C-C-CI

Scheme 1. Synthetic route of DOPO-CH₂O-AA.

Scheme 2. Copolymerization of DOPO-CH₂O-AA with styrene.

for 1.5 h at -20 °C. Then the reaction temperature was retained at -10 °C for 1 h and at ambient temperature for further 4 h. The mixture was washed with water and 5% NaOH aqueous solution for several times until the organic phase pH 7. The rude product was obtained when CHCl₃ was gotten rid of. The product was purified by column chromatography on SiO₂ with ethyl acetate as the eluent. The yield is 84%; the melting point is 75 °C.

FT-IR (KBr) (cm⁻¹): 1735 (ν C=O); 1632 (ν C=C); 802 (δ C=C-H); 1236, 1167 (ν COOC); 924 (ν CCO).

¹H NMR (DMSO-d₆, δ ppm): 4.89 (m, 2H, –CH₂–); 5.86 (m, 3H, CH₂=CH–); 7.31 (m, 2H, benzene ring); 7.47 (t, 1H, benzene ring); 7.66 (m, 1H, benzene ring); 7.85 (t, 1H, benzene ring); 8.01 (m, 1H, benzene ring); 8.28 (m, 1H, benzene ring).

The reactivity ratios for free-radical of M_1 and M_2 were studied by the method of slope-intercept using BPO as initiator in DCE at 90 °C (Scheme 2). The copolymer composition (F_1) was characterized by ¹H NMR. ¹H NMR (DMSO-d₆, δ ppm): 0.5–2.1 (H-main chain); 4.0–5.0 (–CH₂O–); 5.8–8.4 (H-benzene ring). Therefore, F_1 could be calculated by the equation below. The data are listed in Table 1

$$\frac{1 - F_1}{F_1} = \frac{d[M_2]}{d[M_1]} = \frac{1/5(\sum_{5.8 \text{ ppm}}^{8.4 \text{ ppm}} H - 4\sum_{4.0 \text{ ppm}}^{5.0 \text{ ppm}} H)}{1/2\sum_{4.0 \text{ ppm}}^{5.0 \text{ ppm}} H}$$

The copolymer composition curve is shown in Fig. 1. The calculated results are $r_1 = 0.225$, $r_2 = 0.503$; $Q_1 = 0.413$, $e_1 = 0.476$; azeotropic point = 0.37.

The copolymerization (Scheme 2) was performed according to the azeotropic point of the copolymer composition. The copolymer was recovered by precipitating the reaction mixture in an excess of methanol. The copolymer was collected by filtration and vacuum dried. The analytic copolymer composition is 0.36. The GPC of the copolymer shows that the *Mn* value is 11781 with polydispersity index 2.06.

The copolymer exhibits 5% weight loss at 340 °C. Then the main stage of decomposition is followed from 340 °C to 410 °C with 64 wt.% mass loss. In addition, there is about 22% residue of this copolymer at 500 °C (Fig. 2). The segments containing DOPO are emitted which produce phosphoric acid formation during the main decomposition stage [6]. The phosphoric acid can increase the char yield by changing the chemical reactions involved in

Table 1 The data of f_1 and F_1 in the copolymerization.

Entry	M ₁ (g)	M ₂ (g)	f_1	Reaction conditions			Conversion %	F_1
				BPO (mol%)	Time (min)	Solvent (mL)		
1	0.6	0.832	0.2	1.5	15	3	8.2	0.282
2	0.9	0.728	0.3	1.5	15	4	6.4	0.333
3	1.2	0.624	0.4	1.5	20	5	6.5	0.415
4	1.5	0.520	0.5	1.5	20	5	6.2	0.435
5	1.8	0.416	0.6	1.5	30	5	4.7	0.488
6	2.4	0.208	0.8	1.5	30	5	3.9	0.628

decomposition in favor of reactions yielding carbon rather than CO or CO_2 [7]. People have proposed that the charring residue on pyrolysis is linearly proportional to oxygen index of halogen-free polymers [8]. Because the char formation will limit the production of combustible gases and decrease the thermal conductivity of the burning materials, which consequently retard the flammability of the materials. The residue of the copolymer reaches to 22% under air flow at 500 °C. It is adequate to exhibit the flame retarding action. Therefore, M_1 is a potential flame retarding monomer for styrenic polymers.

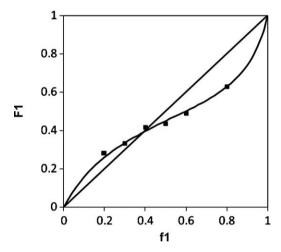


Fig. 1. The copolymer composition curve for DOPO-CH₂O-AA $(\mathbf{M_1})$ and styrene $(\mathbf{M_2})$.

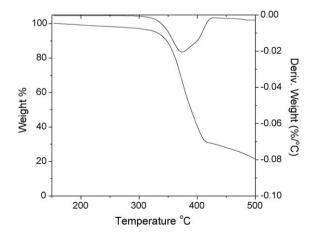


Fig. 2. TGA and DTG curves for the copolymer under air flow. Heating rate is 10 $^{\circ}$ C/min.

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