

Copolymerization of (10-oxo-10-hydro-9-oxa-10 λ^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 λ^5 -phospha-phenanthrene-10-yl)-methyl acrylate (**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 ¹H NMR measurements. The reactivity ratios for free-radical of the monomer (**M**₁) and styrene (**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 **M**₁ is a potential flame retarding monomer for styrenic polymers.

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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 -phospha-phenanthrene-10-yl)-methyl acrylate (DOPO-CH₂O-AA) **M**₁ was synthesized and copolymerized with styrene **M**₂. The thermal degradation of the obtained copolymer **III** including DOPO unit as a pendent group was studied by TGA. And the reactivity ratios for free-radical of **M**₁ and **M**₂ were also investigated.

Compound **II** was prepared according to the method suggested by Shieh and Wang [5]. Melting point is 154 °C.

¹H 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).

M₁ 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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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 CO₂ [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.

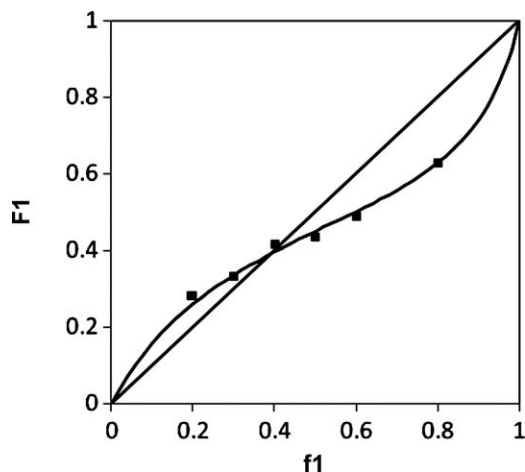


Fig. 1. The copolymer composition curve for DOPO-CH₂O-AA (M_1) and styrene (M_2).

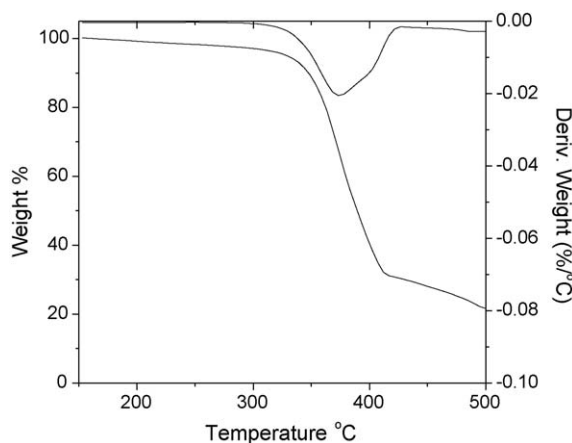


Fig. 2. TGA and DTG curves for the copolymer under air flow. Heating rate is 10 °C/min.

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