

Polymerization of 7,12-Bis(2-hydroxyethyl)benzo[k]-fluoranthate with Aromatic Diacid Chlorides

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ABSTRACT

7,12-Bis(2-hydroxyethyl)benzo[k]fluoranthate (BHBF) was prepared from benzyne intermediate in four steps. Polycondensation of BHBF with isophthaloyl dichloride and terephthaloyl dichloride was performed by solution as well as interfacial techniques. The solution polymerizations were performed in chloroform and in DMAc (*N,N'*-dimethylacetamide)/chloroform system, in the presence of pyridine or triethylamine at room or refluxing temperature. The interfacial polymerizations were performed by DMAc/cyclohexane, an organic/organic system, in the presence of pyridine or triethylamine at room temperature. The above polymerization reactions lead to the formation of novel aromatic polyesters having benzo[k]fluoranthene moieties in the main chain. The resulted polyesters show intense violet fluorescence property and were characterized by IR, ¹H NMR, UV, DSC and the elemental analyses. The fluorescence excitation and emission spectra of the monomer BHBF and one of the polyesters (PS2) were also studied. Some physical properties of these novel polymers are also reported.

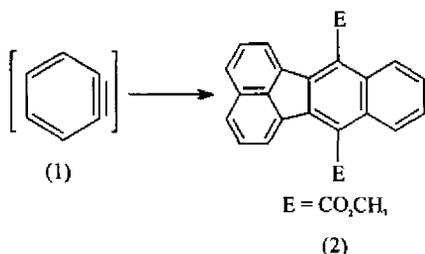
Key Words: polycondensation, solution and interfacial polymerizations, 7,12-bis(2-hydroxyethyl)-benzo[k]fluoranthate, inherent viscosity, photoactive polymers

INTRODUCTION

Aromatic fused hydrocarbons such as benzo[b]fluoranthenes and benzo[k]fluoranthenes are of considerable interest because they are among the most commonly detected polycyclic aromatic hydrocarbons (PAH) in a large variety of combustion in the environment. Some of these compounds have been known as a potent tumour-producing agents in biolo-

gical systems. Synthetic work to supply reference samples for environmental studies is a continuous subject. In addition to HPLC, TLC and GC, methods based on fluorescence and ultra-violet absorption are important methods for detecting of PAH(s) in low concentrations [1].

Recently we reported a convenient one step synthesis of dialkyl benzo[k]fluoranthenes, their chloro-derivatives and tetraethyl bis-benzo[k][k']-



Scheme 1

fluoranthene [2]. These very strongly fluorescent polycyclic aromatic hydrocarbons may be used as a standard reference compound in environmental research. In a previous paper [3] we also reported that compound dimethyl-7,12-benzo[k]fluoranthate (2) can be synthesized from the reactive intermediate benzyne (1) in high yield. This compound was used as a new monomer and its melt polymerization reaction with aliphatic diamines lead to the formation of novel polyamides [4] (Scheme 1).

Polymers with fluorescent properties have been investigated in recent years. These polymers include chromophores in the backbone and polymers having chromophores as a pendant group. They are used as fluorescent labels and photo-harvesters [5-7]. Fluorescent labelling has been used to study specific interactions between macromolecules in polyelectrolytes, water soluble polymers, homopolymers, block copolymers and random copolymers [8-13], water soluble polymers with aromatic chromophores which sensitize the photochemical reactions [14].

Novel polymers containing fluorescent moieties have been reported recently [15,16]. They are soluble in most organic solvents and give films with excellent transparency when casted from solutions. The polymers show intense yellow luminescence in solution and as films. A series of novel polymers containing arylenevinylidene-ethylene groups are also synthesized via the Heck reaction [17]. The resulted polymers are amorphous and soluble in most common organic solvents. Some show strong blue luminescence in the region of 380-480 nm. Another interesting class of photoactive polymers is anthracene contain-

ing polymers. They show intense blue fluorescence and photoconductive properties [18]. Various polymers with vinyl type anthracene-containing have been reported [19].

The purpose of this work was to synthesize the new monomer 7,12-bis(2-hydroxyethyl)benzo[k]fluoranthate, BHBF, (5) and to investigate its polycondensation reactions. Thus, in this paper we are reporting a successful synthesis of novel monomer, BHBF (5) and its polymerization reaction with aromatic diacid chlorides for the formation of the novel aromatic polyesters with photoactive properties.

EXPERIMENTAL

Materials and Equipment

Reagents were purchased from Fluka, Alderich and Riedel-deHaen AG Chemical Companies. Isophthaloyl dichloride (IPDC) and terephthaloyl dichloride (TPDC) were purified by sublimation under reduced pressure. DMAc (*N,N'*-dimethylacetamide) was dried over BaO, then it was distilled under reduced pressure. Chloroform was dried over CaCl₂, and then it was distilled at normal pressure.

Proton nuclear magnetic resonance (¹H NMR, 90 MHz) spectra were recorded on a Varian EM-390 instrument. Multiplicities of proton resonances are designated as singlet (s), doublet (d), triplet (t), multiplet (m) and broad (br). Tetramethylsilane (TMS) was used as an internal reference.

IR spectra were recorded on Shimadzu 435 IR spectrophotometer. Spectra of solids were carried out using KBr pellets. Vibrational transition frequencies are reported in wavenumber (cm⁻¹). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br). All melting points were taken with a Gallenham melting point apparatus and are uncorrected. Inherent viscosities were measured by standard procedure using a Cannon Fensku routine viscometer. Differential scanning calorimetry (DSC) data were recorded on a DSC-PL-1200 instrument under N₂ atmosphere at a rate of 10 °C/min. Elemental analyses were performed by Research Institute of Petroleum Industry, Tehran.

Table 1. UV-Visible spectra of compound (5) in selected solvents.

Solvent	λ_{\max} (ϵ L. mol ⁻¹ . cm ⁻¹)
Dioxane	294.63 (10016.11), 310.74 (22258.02), 340.94 (5564.50), 355.03 (5565.50), 377.18 (6677.40), 400.00 (7233.85)
CHCl ₃	273.73 (13017.36), 285.85 (16413.18), 300.00 (30297.55), 311.11 (45277.83), 344.43 (7074.49), 359.18 (5376.73), 379.38 (7357.52), 401.91 (7923.58)
CH ₂ Cl ₂	280.54 (14190.84), 296.64 (25042.66), 310.00 (36729.24), 338.92 (6260.66), 355.03 (4730.28), 377.18 (6817.17), 400.00 (7234.55)
Acetone	357.05 (6769.22), 377.18 (6831.97), 397.31 (7287.44)
MeOH	212.08 (17381.83), 236.24 (32665.99), 240.00 (32320.28), 282.55 (14943.64), 296.64 (25717.94), 308.00 (36143.92), 338.92 (5908.32), 355.03 (4517.66), 375.17 (6254.03)
DMF	284.56 (19199.04), 298.66 (2719.64), 314.36 (36531.51), 340.94 (532.91), 357.04 (7199.64), 377.18 (9066.21), 401.34 (9599.52)

UV-Visible spectra were recorded on Shimadzu 240 UV-Visible spectrophotometer. The fluorescence spectra were recorded on Shimadzu RF-5000 spectrofluorophotometer.

Synthesis of Benzo[k]fluoranthene-7,12-dicarboxylic Acid (3)

Into a 250 mL one necked round-bottomed flask were placed 0.50g (1.357×10^{-3} mol) of compound 2, 80 mL of ethanol and 35 mL of 4N NaOH solution. The mixture was refluxed and after 3 h a yellow clear solution was obtained, then it was refluxed for 3 days. The solution was concentrated up to 10–20 mL by simple distillation and then it was diluted with 400 mL of distilled water. The clear yellow solution was acidified with 25 mL of HCl (30.5%). The resulted yellow solid was filtered, dried to give 0.46 g (99.5%) of yellow solid 3, mp>298 °C (dec.). IR (KBr): 3300–2000 (s,br), 1680 (s,br), 1590 (m), 1510 (w), 1480 (w), 1420 (s), 1380 (sh), 1360 (w), 1340

(m), 1305 (s), 1240 (s), 1165 (m), 1140 (w), 1090 (w), 1040 (w), 1000 (w), 910 (m,br), 820 (m), 780 (m,sh), 760 (s), 720 (m), 685 (m), 650 (w) cm⁻¹; ¹H NMR (DMSO-d₆, CDCl₃, TMS): δ 7.55–8.45 (m,10H, aromatic protons), 10.43 (s, very broad, OH) ppm.

The elemental analysis result obtained as follows:

C ₂₂ H ₁₂ O ₄	C (%)	H (%)
Calculated	77.64	3.55
Found	77.40	3.60

Synthesis of Benzo[k]fluoranthene-7,12-diacid Chloride (4)

Into a 50 mL one necked round-bottomed flask were placed 0.90g (2.644×10^{-3} mol) of compound 3 and 14 mL of thionyl chloride. The mixture was refluxed and after 10 min a yellow clear solution was obtained, and then it was refluxed for overnight. The thionyl chloride was removed by simple distillation and the resulted solid was recrystallized in hot toluene. The

Table 2. Fluorescence excitation and emission of compound (5) spectra in THF.

Solvent	Concentration (M)	λ_{EX}	$\lambda_{EX} = 314.4$ (nm) λ_{EM}
THF	1.326×10^{-6}	290.0, 302.4, 314.4, 345.2 360.7, 381.2, 402.8	407.2, 432.8 458.5 (sh)

Table 3. Reaction conditions and some physical properties of polyesters resulted from solution polymerization in DMAc/CHCl₃.

Polymer	Acid chloride	Scavenger	Reaction time	Yield (%)	Non-solvent	η_{inh}^a	Dec.point ^b (°C)
PS1	IPDC	TEA ^c	3days/RT	92.4	i-prOH	0.025	158
PS2	TPDC	TEA	3days/RT	97.7	i-prOH	0.085	170
PS3	IPDC	Py ^d	3days/RT	77.4	i-prOH	0.037	153
PS4	TPDC	Py	3days/RT	68.9	i-prOH	0.059	155
PS5	TPDC	Py	3days/RT ^e	77.4	i-prOH	0.035	154
PS6	IPDC	TEA	3days/RT ^e	79.2	i-prOH	0.063	150

(a) Inherent viscosities, measured at a concentration of 0.5 g dL⁻¹; (b) Decomposition points in °C, measured by melting point apparatus; (c) TEA = triethyl amine; (d) Py = pyridine; (e) After 48 h at RT, was refluxed for 24 h. In order to compare the effect of heating on inherent viscosity of PS1 and PS4.

Table 4. Reaction conditions and some physical properties of polyesters resulted from solution polymerization in CHCl₃.

Polymer	Acid chloride	Scavenger	Reaction time	Yield (%)	Non-solvent	η_{inh}^a	Dec.point ^b (°C)
PS7	IPDC	TEA ^c	2days/RT	91.2	i-prOH	0.133	160
PS8	TPDC	TEA	3days/RT	83.6	i-prOH	0.029	165
PS9	IPDC	Py ^d	3days/RT	77.0	i-prOH	0.025	158
PS10	TPDC	Py	3days/RT	92.18	i-prOH	0.119	160

(a) Inherent viscosities, measured at a concentration of 0.5 g dL⁻¹; (b) decomposition points in °C, measured by melting point apparatus; (c) TEA = triethyl amine; (d) Py = pyridine.

Table 5. Reaction conditions and some physical properties of polyesters resulted from interfacial polymerization in MAc/Cyclohexane.

Polymer	Acid chloride	Scavenger	Reaction time	Yield (%)	Non-solvent	η_{inh}^a	Dec.point ^b (°C)
PS11	IPDC	TEA ^c	15 h/RT	93.9	water	0.111	170
PS12	TPDC	TEA	15 h/RT	91.2	water	0.128	170
PS13	IPDC	Py ^d	15 h/RT	72.3	water	0.129	153
PS14	TPDC	Py	15 h/RT	95.1	water	0.079	158

(a) Inherent viscosities, measured at a concentration of 0.5 g dL⁻¹; (b) Decomposition points in °C, measured by melting point apparatus; (c) TEA = triethyl amine; (d) Py = pyridine.

resulted yellow crystals were filtered, dried to give 0.74 g (74.5%) of yellow solid of 3, mp 230–233 °C. IR (KBr): 3050 (w), 1790 (s), 1505 (w), 1480 (w), 1440 (m,sh), 1425 (m), 1310 (w), 1230 (w), 1220 (w), 1140 (m), 1170 (s), 1040 (m), 1010 (w), 960 (w), 880 (w), 860 (m), 840 (m), 820 (w), 790 (s), 770 (s), 760 (m), 720 (m), 680 (m), 640 (m), 560 (w) cm⁻¹.

The elemental analysis result obtained as follows:

C _n H _m O ₂ Cl ₁	C (%)	H (%)
Calculated	70.05	2.67
Found	71.40	2.80

Synthesis of 7,12-Bis-(2-hydroxyethyl)benzo[k]-fluoranthate (5)

Into a 100 mL two necked round-bottomed flask were placed 0.50g (1.33 × 10⁻³ mol) of compound 4, 5 mL

Table 6. UV-Visible spectra of polymer PS2 in selected solvents.

Solvent	λ_{\max} (ϵ L. mol ⁻¹ . cm ⁻¹)
Dioxane	280.54 (25662.36), 296.64 (41701.34), 310.74 (57902.28), 340.94(10264.95), 357.04 (8019.49), 377.188 (10906.51), 401.34 (11548.06).
CHCl ₃	284.17 (25798.70), 300.3 (38098.08), 312.31 (52197.37), 342.46 (86.99.58), 356.94 (6599.67), 378.64 (8999.55), 401.75 (9599.52)
CH ₂ Cl ₂ ^a	298.66 (31013), 312.75 (47997.6), 340.94 (8122.67), 357.04 (7915.03), 377.18 (8856.46), 400.00 (9599.52)
Acetone ^b	357.5 (5808.59), 377.18 (289.37), 400.00 (9599.52)
MeOH ^c	212.8 (18461.68), 236.24 (30000.23), 282.55 (14767.96), 296.69 (18461.68), 308.72 (22611.06), 340.94 (9230.84), 357.04 (8526.62), 377.188 (8999.55), 397.31 (9230.4).
DMF	284.56 (19199.04), 298.66 (2719.64), 314.36 (36531.51), 340.94 (532.91), 357.04 (7199.84), 377.18 (9066.21), 401.34 (9599.52)

(a) Saturated solution, the concentration was calculated from the ratio of absorbance of the solution at $\lambda_{\max} = 400$ nm over ϵ of the chloroform solution at the same wavelength; (b) Saturated solution, the concentration was calculated from the ratio of absorbance of the solution at $\lambda_{\max} = 400$ nm over ϵ of the chloroform solution at the same wavelength; (c) Saturated solution, the concentration was calculated from the ratio of absorbance of the solution at $\lambda_{\max} = 377$ nm over ϵ of the chloroform solution at the same wavelength.

of ethylene glycol and 0.22 mL of pyridine. The mixture was heated to 140 °C for 30 min, and then it

was heated at 65 °C for overnight. The yellow solution was cooled and precipitated in 200 mL of water. The resulted yellow solid was filtered, dried to give 0.52 g (91.5%) of yellow solid of 3, mp>170 °C (dec.). IR (KBr): 3600–3100 (s,br), 3050 (w), 2900 (m), 1710 (s,br), 1620 (w,sh), 1510 (m), 1480 (w), 1430 (s), 1380 (s), 1345 (m), 1300 (s), 1220 (s,br), 1130 (s), 1070 (s), 1020 (s), 960 (m,br), 890 (m,br), 820 (m), 765 (s), 690 (w), 670 (w), 550 (w) cm⁻¹. ¹H NMR (DMSO-d₆, TMS): δ 3.95 (t,4H), 4.35 (s,br,2H), 4.80 (t,4H), 7.45–8.25 (m,10H) ppm.

The elemental analysis result obtained as follows:

C _x H _y O _z	C (%)	H (%)
Calculated	72.89	4.71
Found	72.40	4.60

Polymer Synthesis

Solution Polymerization

The monomer 5 was dissolved in minimum amount of DMAc, and isophthaloyl dichloride (IPDC) or terephthaloyl dichloride (TPDC) was dissolved in minimum amount of chloroform. Then triethylamine or pyridine was added. The mixture was stirred at room temperature or refluxed. The mixture was precipitated in isopropanol. The yield of the resulted polyesters are 68.9–97.7%.

The solution polymerization was repeated and chloroform was used as the only solvent. The yield of the resulted polyesters are 77.0–92.2%.

IR(KBr): 3400 (m,br), 3050 (w), 2900 (m), 1720 (s,br), 1640 (m), 1610 (m), 1500 (w), 1485 (w), 1430 (s), 1400 (s), 1380 (m,sh) 1345 (m,sh), 1260 (s,br), 1240 (s,br), 1150 (s), 1110 (s,br), 1090 (s), 1040 (s,br), 1015 (s,br), 870 (m), 820 (m), 770 (s), 725 (s), 750 (w), 690 (w), 600 (w), 550 (w), cm⁻¹; ¹H NMR (CDCl₃, TMS): δ 4.35–5.25 (m, two triplets which are overlapped, 8H), 7.20–8.55(m,14H) ppm. The elemental analysis result for PS7 obtained as follows:

C _x H _y O _z	C (%)	H (%)
Calculated	73.11	3.97
Found	71.60	4.20

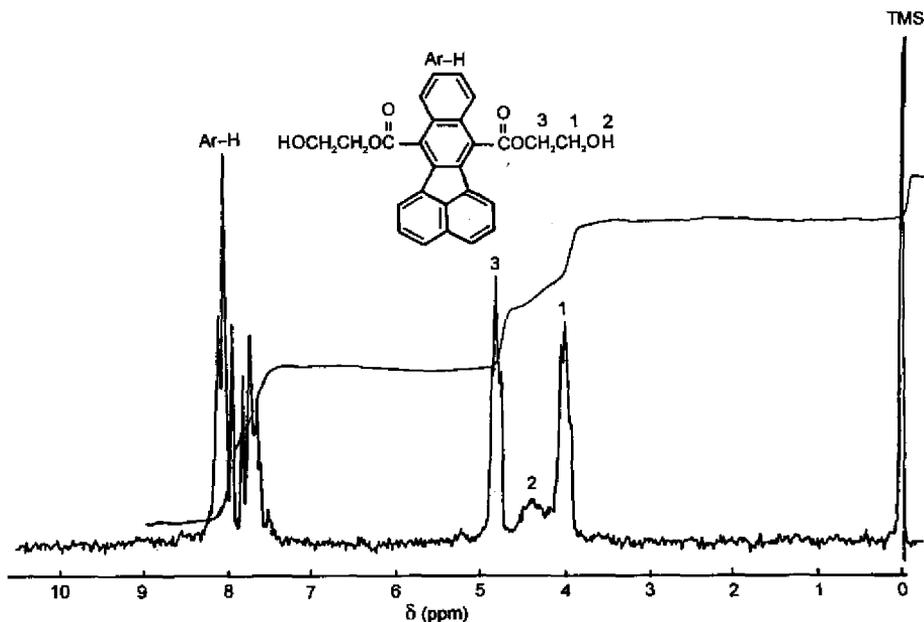


Figure 1. ^1H NMR (90 MHz) spectrum of monomer (5) in DMSO-d_6 at RT.

The elemental analysis result for PS10 obtained as follows:

$\text{C}_x\text{H}_y\text{O}_z$	C (%)	H (%)
Calculated	73.11	3.97
Found	71.70	4.70

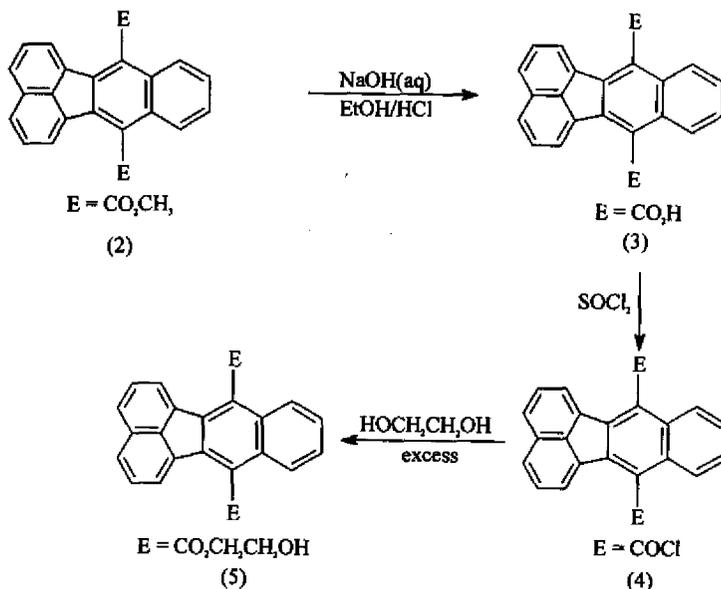
Interfacial Polymerization

Two different solutions were prepared as follows: (1) 0.1083g (2.53×10^{-4} mol) of monomer 5 was dissolved in 0.5 mL of DMAc, (2) the same number of moles, as above, of monomer IPDC or TPDC was dissolved in 1.0 mL of cyclohexane. Then these solutions were mixed, and triethylamine was added. The mixture was stirred at room temperature for overnight, and it was precipitated in water. The yield of the resulted polyesters PS11 and PS12 are 91.2–93.9%.

The above reactions were repeated and pyridine was used as a scavenger and the yield of the polymers (PS13, PS14) were 72.3 and 95.1%.

RESULTS AND DISCUSSION

Benzyne (1) as a reactive intermediate from anthranilic acid was trapped with 2-oxo-1,3-bis(methoxycarbonyl)-2-H-cyclopenta-acenaphthylene via [4+2] Diels-Alder cycloaddition reaction. The resulted adduct 7,12-dimethylbenzo[k]fluoranthate (2) was obtained in quantitative yield (Scheme 1). This diester was hydrolyzed with NaOH(aq) in ethanol solution and the diacid (3) was obtained in high yield. The IR spectrum of compound 3 showed peaks between $3300\text{--}2000\text{ cm}^{-1}$ for O–H stretching and 1680 cm^{-1} for the carbonyl group. The ^1H NMR of compound 3 showed a very broad peak for the acidic OH proton at 10.4 ppm and a multiplet peak for the aromatic protons. The reaction of this diacid (3) with thionyl chloride was performed under refluxing temperature in a neat condition. The resulted diacid chloride (4) was obtained as a pure crystalline compound from toluene. The IR spectrum of the compound 4



Scheme II

showed a strong peak at 1790 cm^{-1} which is a characteristic peak for the acid chloride carbonyl group. Diacid chloride (4) was reacted with excess ethylene glycol and 7,12-bis (2-hydroxyethyl)benzo-[k]fluoranthate (BHF) (5) was obtained in high yield (Scheme II). The $^1\text{H NMR}$ (Figure 1) of compound 5 showed two triplets for the CH_2 protons, a broad peak for the OH proton and a multiplet peak for the aromatic protons.

The UV-Visible spectra data for the compound 5 in various solvents are summarized in Table 1. In each case, the spectrum qualitatively resembled that of the parent hydrocarbon benzo[k]fluoranthene [20, 21]. All of the λ_{max} for the compound 5 are given and could be used for the environmental research. Introduction of the carbonyl groups would not exert any bathochromic influence on the absorption bond.

The fluorescence excitation and emission spectra data for the compound 5 in THF are summarized in Table 2. In order to obtain the emission spectra, the known concentration of compound 5 was excited at 314.4 nm.

Polymerization Reactions

The polycondensation reaction of monomer 5 with IPDC or TPDC was performed by solution polymerization reaction in DMAc/ chloroform as well

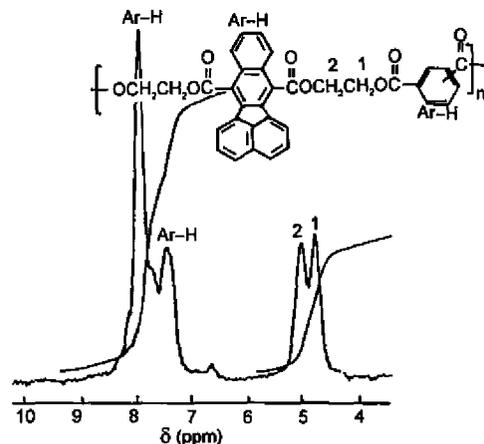
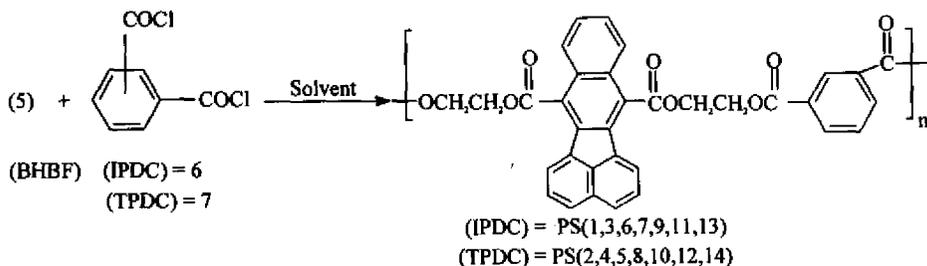


Figure 2. $^1\text{H NMR}$ (90 MHz) spectrum of polyester PS12 in CDCl_3 at RT.



Scheme III

as only chloroform solution. When triethylamine was used in DMAc/chloroform solution for both IPDC and TPDC the yield of the resulted polyesters, PS1 and PS2, are greater than 93%, but the inherent viscosity for TPDC (PS2) is about 0.085 dL/g and for the IPDC (PS1) is rather low and is about 0.025 dL/g (Scheme III). In case of IPDC with TEA, when the reaction mixture was heated for one day, the inherent viscosity of the resulted polymer (PS6) was increased about three folds.

The polymerization reaction for the formation of polymer (PS2) was repeated and the reaction mixture was stirred for one day and the resulted polymer was obtained in lower yield (79.3%) and lower inherent viscosity (0.056 dL/g). Solution polymerization in DMAc/cyclohexane in the presence of pyridine gave polymers also with lower yield and inherent viscosities (PS3–PS5).

Solution polymerization in chloroform in the

presence of the TEA gave low inherent viscosity for TPDC (PS8) and high inherent viscosity for IPDC (PS7), i.e., 0.134 dL/g. But in the presence of pyridine higher viscosity was obtained for the TPDC (PS10). The polymerization reaction for the formation of polymer (PS10) was repeated and the reaction mixture was stirred for one day and the resulted polymer was obtained in lower yield (73.5%) and lower inherent viscosity (0.036 dL/g).

When polymerization reactions were performed by interfacial technique, in both cases IPDC and TPDC in presence of TEA, higher viscosities were obtained which are in a range of 0.111–0.130 dL/g. Reaction conditions and physical properties of polyesters PS1 and PS14 resulted from various techniques are summarized in Tables 3–5.

The IR spectra of the resulted polymers showed a strong peak at 1720 cm^{-1} for the ester carbonyl group, a peak at 1610 cm^{-1} for the carbon-carbon

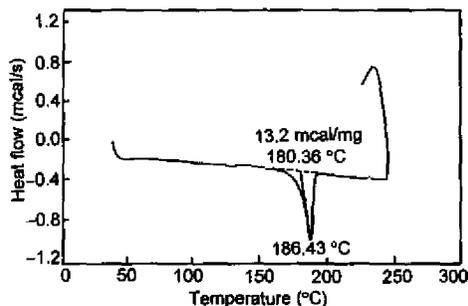


Figure 3. DSC curve of the monomer (5).

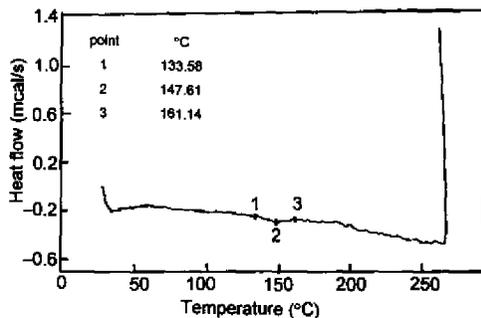


Figure 4. DSC curve of the polymer (PS7).

Table 7. Fluorescence excitation and emission spectra of polymer PS2 in selected solvents.

Solvent	Concentration (M)	λ_{ex} (nm)	λ_{em} (nm)
CHCl ₃	3.22×10^{-5}	260.7, 290.5, 304.7, 316.4, 344.1, 351.2, 381.6, 403.6	408, 433.6, 459.52 (sh)
dioxane	2.24×10^{-7}	284.1, 302.4, 314.4, 345.2, 360.9, 381.0, 403.2	413.0, 438.1, 464.3 (sh)
THF ^a	2.74×10^{-6}	315.0, 381.2, 403.2	413.2, 438.0

(a) The last three highest wavelengths are reported, (its spectra pattern is similar to dioxane solution).

double bonds and a broad peak at 1240 cm^{-1} for the C–O group. The ¹H NMR spectrum of the resulted polyesters (Figure 2) showed peaks for the aromatic protons and peaks for the CH₂ protons.

All of these polymers have yellow colour and are soluble in solvents such as chloroform, dioxane, DMSO, and DMF and are insoluble in solvents such as methanol, isopropanol and non-polar solvents. Their solution in solvents such as DMF or chloroform show intense violet fluorescence.

DSC curve of the compound (5) is shown in Figure 3. This monomer showed an endotherm peak with a maxima of $186.43 \text{ }^\circ\text{C}$. DSC curves of polymers PS7 and PS10 are shown in Figures 4 and 5. PS7 showed endotherm peak with maxima around $148 \text{ }^\circ\text{C}$ and PS10 showed endotherm peak with maxima around $146 \text{ }^\circ\text{C}$.

The UV-Visible spectral data for the polymer PS2 in various solvents are summarized in Table 6.

The fluorescence excitation and emission spectral data for the polyester PS2 in various solvents are summarized in Table 7.

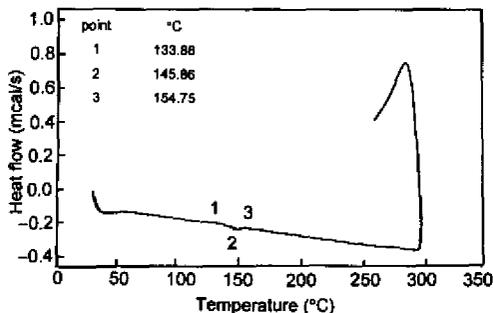


Figure 5. DSC curve of the polymer (PS10).

In order to obtain the emission spectra, the known concentration of polymer PS2 was excited at 316.4, 314.4 and 315 nm in chloroform, dioxane and THF, respectively.

CONCLUSION

The monomer 7,12-bis(2-hydroxyethyl)benzo[k]fluoranthate (BHBF) (5) can be readily synthesized from benzyne reactive intermediate in high yield. This compound is used as a new monomer and its polycondensation reactions with aromatic diacid chloride give novel aromatic polyesters. The best condition in order to obtain a relatively high inherent viscosity will result from interfacial polymerization of organic/organic phases. These novel polymers show strong violet fluorescence photoactivity and can be used as fluorescent labelling materials. On the other hand, all small compounds (3–5) synthesized in this project are novel and show strong violet fluorescence. Such compounds can be used as standard references in environmental research.

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REFERENCES

1. Wiersum U.E., *Janssen Chimica Acta.*, **10**, 3, 1992.
2. Mallakpour S.E. and Nasr-Isfahani H., *Org. Prep. Pro. Int.*, **28**, 691, 1996.
3. Mallakpour S.E., *Iran. J. Polym. Sci. and Technol.*, **2**, 90, 1993.
4. Mallakpour S.E. and Hajihaidari D., *Iran. J. Polym. Sci. and Technol.*, **4**, 2, 1995.
5. Weber S.E., *Chem. Rev.*, **90**, 1469, 1990.
6. Fox M., Jones W., and Watkins D. *Chem. Ing. News*, **71**, 38, 1993.
7. Winnik M., *Acc. Chem. Res.*, **18**, 83, 1985.
8. Dajamel J., Yekta A., Hu Y., and Winnik M. *Macromolecules*, **25**, 7024, 1992.
9. Herkstroeter W., Matric P., Hartman S., Willims J., and Farid S., *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 2473, 1983.
10. Chu D. and Thomas J., *Macromolecules*, **17**, 2142, 1984.
11. Arora K. and Turro N., *J. Polym. Sci., Chem. Ed.*, **25**, 259, 1987.
12. Stramel T., Nguyen C., Webber S., and Rodgers M., *J. Phys. Chem.*, **92**, 2934, 1988.
13. Coa T., Munk P., Ramireddy C., Tuzar Z., and Webber S., *Macromolecules*, **23**, 4411, 1990.
14. Nowakowska M., Foule V., and Guillet J., *J. Am. Chem. Soc.*, **115**, 5975, 1993.
15. Fomine S., Pineda A., Ogawa T., Perez R., and Sotelo, M., *Polym. J.*, **27**, 712, 1995.
16. Tlencopatchev M., Fomine S., Miranda E., Fomina L., and Ogawa T., *Polym. J.*, **27**, 1173, 1995.
17. Fomine S., Fomina L., Quiroz H., Mendez J.M., and Ogawa T., *Polym. J.*, **27**, 1085, 1995.
18. Wachman and Frank C., *Polymer*, **29**, 1191, 1988.
19. Simenesci C. and Grigoras M., *Acad. Repub. Soc. Rom. Met. Sect.*, **7**, 51, 1984.
20. Friedel R.A., *Appl. Spectroscopy*, **11**, 13, 1957.
21. Pierce R.C. and Katz M., *Anal. Chem.*, **47**, 1743, 1975.