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Synthesis of 1,8-Naphthalic Anhydride Derivatives for Use as Fluorescent Brightening Agents for Polymeric Materials

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ABSTRACT

Three fluorescent brightening agents (FBA), imides of 4-methoxy-1,8-naphthalic anhydride, have been synthesized. The compounds contained, in the N-substituent, a triazine ring containing a substituent with a polymerizable centre, this allowing their copolymerization with styrene.

1 INTRODUCTION

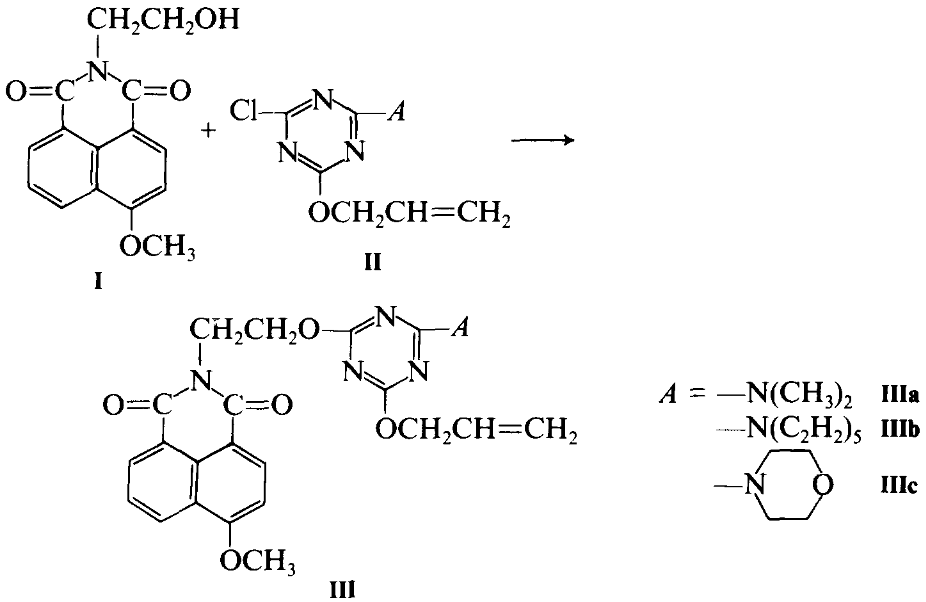
Imides of 1,8-naphthalic anhydride have found application in energy sun collectors,[1] liquid crystals,[2] and as fluorescent dyes and fluorescent brightening agents (FBA) for synthetic polymer materials.[3–6] The presence in such compounds of an unsaturated polymerizable double bond enables them to be used in copolymerization processes with vinyl monomers, forming a covalent bond in the polymer molecule.[6,7]

The synthesis of some triazine-stilbene FBA containing polymerizable moieties in the triazine ring,[8,9] and their application in copolymerization processes with acrylonitrile and styrene, have been investigated,[9,10] and also the application of 4-methoxy-*N*-(2-hydroxyethyl) naphthalimide as an FBA with epoxy resins.[11] We report here data concerning the synthesis and properties of some FBA which are derivatives of 4-methoxy-1,8-naphthalimide, containing a triazine ring substituted by a polymerizable group.

2 RESULTS AND DISCUSSION

2.1 Syntheses

The FBA were prepared by the following route:



Scheme 1

4-Methoxy-*N*-(2-hydroxyethyl)naphthalimide (**I**) was prepared by a previously described method.[11] Introduction of the potentially polymerizable substituent was effected by using the 2-amino-4-allyloxy-6-chloro-1,3,5-triazine derivatives (**II**); these compounds have been used in the synthesis of polymerizable FBA.[12] Acylation of the hydroxy group of **I** by **II** was carried out in benzene in the presence of 50% NaOH and catalytic

TABLE 1
Characterization Data of Compounds **IIIa–c**

FBA	*Yield (%)*	*M.p. (°C)*	*Analysis (%)*					
			C		*N*		*H*	
			Calc.	*Found*	*Calc.*	*Found*	*Calc.*	*Found*
IIIa	93	111–113	61·47	61·38	5·12	5·08	15·59	15·48
IIIb	96	172–173	62·89	62·51	5·66	5·60	14·67	14·46
IIIc	96	153–154	61·10	61·01	5·09	5·00	14·25	14·20

amounts of benzyltriethylammonium chloride (BTEAC) at 50°C for 4 h. The products were isolated after neutralizing, washing with water, and concentration of the organic phase. Characterization data for the compounds thus prepared are given in Tables 1–3. In ethanol, absorption maxima were λ 370 nm; fluorescence emission occurred at λ 450 nm, with Stokes' shift of 80–84 nm.

2.2 Copolymerization of styrene with FBA

The polymerization of styrene in the presence of 0·2 wt% FBA and 0·1 wt% dibenzoylperoxide as initiator of the radical polymerization was investigated. The polymerization was carried out at 80°C for 10 h in an inert atmosphere. Transparent polymers with an intense blue fluorescence were obtained. After 3- to 4-fold precipitation of the polymers out of toluene and ethanol, unreacted FBA was removed. The resulting poly-

TABLE 2
IR and ^{1}H NMR Data of Compounds **IIIa–c**

FBA	*IR (KBr) (cm^{-1})*	*^{1}H NMR (δ, ppm) (CDCl$_3$)*
IIIa	2931 [ν(—CH$_2$—)] 2875 [ν(—CH$_3$)] 1695 [ν(—C=O)] 1645 [ν(=CH$_2$)] 1560 [ν(—C=N)] 1365 [ν(C—O—C)] 772 [δ(CH—Ar)]	1·12–1·26 (s, 3H, O—CH$_3$) 3·09–3·18 (s, 6H, N—CH$_3$) 4·23–4·38 (l, 4H, —CH$_2$—) 4·91–4·98 (d, 2H, =CH$_2$) 5·26–5·36 (m, 2H, —CH$_2$—) 5·94–6·04 (m, 1H, =CH) 8·40–8·70 (m, 5H, ArH)
IIIb	2930 [ν(—CH$_2$—)] 2880 [ν(—CH$_3$)] 1689 [ν(—C=O)] 1645 [ν(=CH$_2$)] 1563 [ν(—C=N)] 1363 [ν(C—O—C)] 770 [δ(CH—Ar)]	1·10–1·20 (s, 3H, O—CH$_3$) 1·36–1·48 (l, 6H, —CH$_2\underline{\mathrm{CH}_3}$) 3·40–3·56 (q, 4H, —$\underline{\mathrm{CH}_2}CH_3$) 4·28–4·40 (l, 4H, —CH$_2$—) 4·88–4·96 (d, 2H, =CH$_2$) 5·24–5·32 (m, 2H, —CH$_2$—) 5·90–6·02 (m, 1H, =CH) 8·36–8·78 (m, 5H, ArH)
IIIc	2932 [ν(—CH$_2$—)] 1693 [ν(—C=O)] 1644 [ν(=CH$_2$)] 1569 [ν(—C=N)] 1368 [ν(C—O—C)] 1273 [ν(CH$_2$—O—CH$_2$)] (morpholine)	1·10–1·26 (s, 3H, O—CH$_3$) 2·06–2·18 (l, 4H, N—CH$_2$—) 2·54–2·68 (l, 4H, —CH$_2$—O—) 4·22–4·40 (l, 4H, —CH$_2$—) 4·90–4·98 (d, 2H, =CH$_2$) 5·20–5·32 (m, 2H, —CH$_2$—) 5·98–6·10 (m, 1H, =CH) 8·30–8·98 (m, 5H, ArH)

TABLE 3
Absorption, Fluorescence and Quantum Yield of Compounds **IIIa–c**

	IIIa	*IIIb*	*IIIc*
Conc. in C_2H_5OH (mol l^{-1})	5×10^{-5}	5×10^{-5}	5×10^{-5}
λ_{abs} (nm)	368	370	370
ε (l mol^{-1} cm^{-1})	12 600	12 800	12 700
λ_{s_1} (nm)	410	410	406
λ_{fl} (nm)	452	450	450
E_{s_1} (kJ mol^{-1})	291·9	291·9	294·8
Stokes' shift (nm)	84	80	80
Quantum yield[a]	0·68	0·64	0·72
τ_{s_1} (s)	$2{\cdot}0 \times 10^{-8}$	$2{\cdot}1 \times 10^{-8}$	$2{\cdot}5 \times 10^{-8}$

[a] Relative to 9,10-diphenylanthracene.

mers retained their intense fluorescence, indicating the presence of a covalent bond between the FBA and the polymeric molecule. It was established, using the standard line method, that more than 90% of the FBA were chemically bonded.

3 EXPERIMENTAL

IR spectra (KBr) were recorded on a Perkin–Elmer 1600 spectrophotometer, UV/Vis spectra (ethanol 5×10^{-5} mol l^{-1}) on a Hewlett Packard 8452A spectrophotometer, and fluorescence spectra on a Perkin–Elmer MPF 44 spectrophotometer.

3.1 General method for FBA synthesis

Compounds **I** (0·01 mol) were dissolved in benzene (50 ml) and 50% aq. NaOH (10 ml) and BTEAC (0·3 g) then added. The solution was vigorously stirred at 50°C for 1 h and a solution of **II** (0·01 M) in benzene (20 ml) added. The mixture was stirred for a further 3 h, and the organic layer separated, neutralized, and washed with water. After removal of solvent, the products were collected and recrystallized from chlorbenzene.

3.2 Copolymerization with styrene

Styrene (10 g), the FBA (0·02 g) and dibenzoylperoxide (0·01 g) were heated in a nitrogen-purged glass ampoule for 10 h at 80°C. The resulting polymers were dissolved in toluene and precipitated with ethanol; this procedure was repeated several times and the polymers were finally dried under vacuum at 40°C.

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