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A new method for synthesis of 4-allyloxy-1,8-naphthalimide derivatives for use as fluorescent brighteners

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Abstract

A new method for the synthesis of 4-allyloxy-1,8-naphthalimide derivatives (fluorescent brighteners) using phase transfer catalysis is reported. Four, 4-allyloxy-1,8-naphthalimide fluorescent brighteners were synthesized in good yield and their absorption and fluorescent spectra were determined. The suitability of the monomeric fluorescent brighteners for copolymerization with styrene was also demonstrated. The content of the chemically bound fluorescent brightener in the polymer chain was estimated. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: 1,8-Naphthalimides; Phase transfer catalysis; Polymerizable fluorescent brighteners

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1. Introduction

4-Alkoxy derivatives of 1,8-naphthalimide are well established as fluorescent brightening agents (FBAs) for polymers with an intensive blue fluorescence [1,2]. Their use has also been described in the synthesis of derivatives with photosensitizing or chemiluminescent properties [3,4], and for markers in molecular biology [5].

In previous papers, we reported the synthesis and properties of some 4-allylamino derivatives of 1,8-naphthalimide for use as dyes for polymers [6] and for liquid crystal displays [7]. These derivatives possessed an intense yellow-green fluorescence and were able to co-polymerize with vinyl monomers. The polymers obtained were resistant to wet treatments and to solvents. Because the whitening of the polymers was of importance as well as their coloration, it was deemed of interest to synthesize polymerizable 4-allyloxy-1,8-naphthalimide derivatives for use as FBA's.

N-Methyl-4-allyloxy-1,8-naphthalimide has been synthesized in three steps starting from *N*-methyl-4-chloro-1,8-naphthalimide [3,4]. The method used consists of methoxylation of the chlorine atom with sodium methylate, demethylation of the obtained methoxy group to hydroxyl and, finally, reaction of the latter with allyl bromide. Apart from the long duration of this process (39 h) and the high reaction temperatures used (refluxing in different solvents and water), the yield of the target product is relatively low with respect to the starting material (53%).

Our experience in the synthesis of various organic compounds under phase transfer catalysis (PTC) conditions [8–15] encouraged us to investigate the possibility of obtaining, in a single step, 4-

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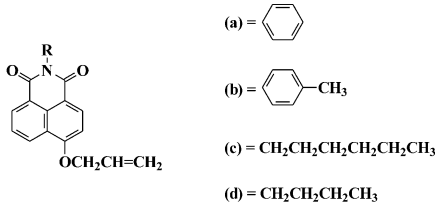
allyloxy-1,8-naphthalimides under such conditions; this is the subject of this paper.

2. Results and discussion

The 4-allyloxy-1,8-naphthalimide derivatives which were synthesized are represented by the general Formula 1, where **R** is:

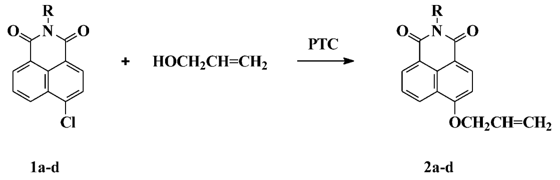


2.1. Synthesis of fluorescent brightening agents

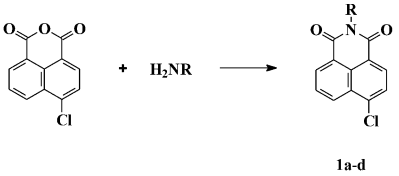
The route employed in the synthesis of 4-allyloxy-1,8-naphthalimides was as follows (Scheme 1).

The starting 4-chloro-1,8-naphthalimides **1a–d** were synthesized (Scheme 2) according to methods previously described [7,16]. The reaction of 4-chloro-1,8-naphthalic anhydride in 1:1 molar ratio with different amines was carried out under reflux in glacial acetic acid (**1a** and **b**) or toluene (**1c** and **d**) for 8 h, giving, respectively, 4-chloro-*N*-substituted-1,8-naphthalimide derivatives **1a–d** in good yields (62–78%).

The target 4-allyloxy-1,8-naphthalimide derivatives **2a–d** were obtained by nucleophilic substitution of the chlorine atom at position 4 in compounds **1a–d** with an allyloxy group by reaction with allyl alcohol under PTC conditions.



Scheme 1.



Scheme 2.

The implementation of the reactions under PTC conditions avoided the above mentioned shortcomings of the known method [3, 4]. All reactions were carried out in a liquid/liquid two-phase system at room temperature and the desired products **2a–d** were obtained in high yield.

2.1.1. Selection of the favourable phase transfer catalysis conditions

The correct choice of the two-phase system was very important for the synthesis. The choice was determined by the solubility of both the reactants and the final products in organic solvents. As their solubility in water-immiscible organic solvents was sufficient, reaction was carried out in a liquid/liquid two-phase system. The good solubility of the reaction products in the organic phase was of technological importance, as it provided the opportunity for their isolation in high yield. The starting 4-chloro-1,8-naphthalimides **1a** and **b** displayed good solubility in 1,2-dichloromethane, while 4-chloro-1,8-naphthalimides **1c** and **d** had better solubility in toluene. Consequently, 1,2-dichloromethane was used as the organic phase in the synthesis of 4-allyloxy-1,8-naphthalimides **2a** and **b** and toluene was used in the synthesis of 4-allyloxy-1,8-naphthalimides **2c** and **d**.

It was experimentally established that optimum results were obtained in a toluene (1,2-dichloromethane)/50% aq. sodium hydroxide two-phase system with the use of tetrabutylammonium bromide (TBAB) as phase transfer catalyst. A small excess (0.1 mol) addition of allyl alcohol to the 4-chloro-1,8-naphthalimides **1a–d** and 5 mol% of TBAB to the allyl alcohol allowed the desired products **2a–d** to be obtained in high yield after 10 h at room temperature. This can be explained with reference to the higher reactivity of the unsolved alcoholate anion in a non-polar organic medium [17].

The synthesis was monitored by TLC on silica gel and the target products **2a–d** were characterized and identified by their melting points, TLC R_f values, elemental analyses, UV/vis, fluorescence, FT–IR and ^{1}H-NMR spectra.

The yields of 4-allyloxy-1,8-naphthalimides **2a–d** obtained under PTC conditions as well as their melting points and TLC R_f values are shown in Table 1.

2.2. Spectrophotometric investigations

The absorption and fluorescence spectra of the synthesized FBA's **2a–d** were recorded in toluene and the data are presented in Table 2. The long-wavelength band of the absorption spectrum in the UV region is due to $\pi \rightarrow \pi^*$ electron transfer in $S_O \rightarrow S_1$ transition. In toluene solution, the FBAs **2a** and **b** were colourless and had intense fluorescence, with an absorption maxima in the near UV-region (λ_A = 358–364 nm). Fluorescence emission was observed in the region 350–500 nm with well-pronounced maxima, λ_F, at 438–444 nm. The substituents **R** at the nitrogen atom had a negligible effect upon λ_A and λ_F values.

2.3. Polymerization with styrene

The co-polymerization of the synthesized FBAs **2a–d** with styrene was carried out at 80 °C in the presence of 0.1 wt.% of dibenzoylperoxide (DBP) as initiator and 0.1 wt.% of the corresponding FBA. The transparent (with blue fluorescence) polymers thus obtained were purified by several-fold precipitation from toluene with methanol. The intense fluorescence was retained in the polymers, thus indicating a covalent bond between FBA's and the polymer. The UV/vis absorption spectra for the precipitated polymers showed the same λ_{max} as the parent FBA. It was established spectrophotometrically, using a standard calibration curve method, that more than 85% of the initial amount of the FBA's in the monomeric mixture had been incorporated into the polymer molecule, which was enough to provide good whiteness.

Table 1
Yields, melting points and TLC R_f values of the 4-allyloxy-1,8-naphthalimides **2a–d**

FBA	Yield (%)	M.p. (°C)	R_f
2a	76	234–236	0.58
2b	72	228–230	0.57
2c	88	63–65	0.65
2d	83	82–84	0.64

Table 2
Absorption and fluorescence characteristics of the 4-allyloxy-1,8-naphthalimides **2a–d**

FBA	λ_A (nm)	log ε	λ_F (nm)	Φ[a]
2a	358	4.06	438	0.43
2b	360	4.02	440	0.47
2c	362	4.08	442	0.48
2d	364	4.12	444	0.51

[a] Relative to quantum yield of quinine bisulphate [18].

3. Experimental

3.1. Materials

Commercial grade 4-chloro-1,8-naphthalic anhydride (Aldrich) as well as aniline, 4-methylaniline, *n*-hexylamine, *n*-butylamine, allyl alcohol and tetrabutylammonium bromide (Fluka products), were used without purification. Commercial styrene (Nephtochim, Bulgaria) was used after distillation under reduced pressure in a nitrogen (99.9%) atmosphere and dried over sodium sulfate. Dibenzoyl peroxide (DBP, Fluka), recrystallized from chloroform, was used as initiator of the free radical copolymerization. The solvents used were pure or of spectrophotometric grade.

The 4-chloro-1,8-naphthalimides **1a–d** were obtained according to described methods [7,16].

3.2. Analysis

IR spectra were recorded on a Perkin-Elmer 1600 FT–IR spectrometer at 4 cm^{-1} resolution using KBr pellets. ^{1}H-NMR spectra were recorded on a Jeol JNM-PS spectrometer, operating at 100 MHz in $CDCl_3$ and using TMS as internal standard (chemical shifts are given as δ in ppm). UV/vis spectra were recorded on a Hewlett Packard 8452A UV/Vis spectrophotometer with 2 nm resolution, at room temperature in toluene. Fluorescence spectra were taken on a Perkin-Elmer MPF 44. The fluorescence quantum yields (Φ) were measured relative to quinine bisulphate as standard

(Φo = 0.55) by using published procedures [18]. Elemental analyses were obtained using a Perkin-Elmer 240 automatic analyzer. The reaction course and purity of the final products were followed by TLC on silica gel (Fluka $F_{60}254$ 20×20; 0.2 mm), using as eluant *n*-heptane/acetone = 1:1. The melting points were determined by means of a Kofler melting point microscope.

3.3. Synthesis of 4-allyloxy-1,8-naphthalimides **2a–d**

The 4-allyloxy-1,8-naphthalimides **2a–d** were synthesized by using the following general procedure:

A solution of 4-chloro-1,8-naphthalimide **1a–d** (0.1 mol) in 200 ml of water-immiscible organic solvent (1,2-dichloromethane, toluene) was added dropwise to a mixture of 6.4 g of allyl alcohol (7.5 ml, 0.11 mol), 1.8 g of TBAB (5 mol% to the allyl alcohol) and 10 ml of 50% aq. sodium hydroxide for 30 min at room temperature under vigorous stirring. The resulting mixture was stirred for 10 h under the same conditions, then diluted in 100 ml of water before separation of the organic layer. The latter was washed with water, dried over anhydrous sodium sulfate and evaporated under reduced pressure to give colourless crystals of pure **2a–d** after recrystallization in *n*-hexane.

3.3.1. 4-Allyloxy-N-phenyl-1,8-naphthalimide **2a**

FTIR (KBr) 1698 (ν^{as} C=O), 1662 (ν^{s} C=O) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 100 MHz) δ: 8.62–8.08 (*m*, 3H, ArH), 7.63–6.78 (*m*, 7H, ArH), 6.06 (*m*, 1H, CH=), 5.42 (*m*, 2H, =CH_2), 4.78 (*m*, 2H, OCH_2). Anal. calcd. for $C_{21}H_{15}NO_3$ (329): C 76.60%, H 4.56%, N 4.25%. Found: C 75.92%, H 4.65%, N 4.33%.

3.3.2. 4-Allyloxy-N-(4-methylphenyl)-1,8-naphthalimide **2b**

FTIR (KBr) 1694 (ν^{as} C=O), 1658 (ν^{s} C=O) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 100 MHz) δ: 8.62–7.86 (*m*, 3H, ArH), 7.56–6.51 (*m*, 6H, ArH), 5.92 (*m*, 1H, CH=), 5.28 (*m*, 2H, =CH_2), 4.64 (*m*, 2H, OCH_2), 2.24 (*s*, 3H, $ArCH_3$). Anal. calcd. for $C_{22}H_{17}NO_3$ (343): C 76.97%, H 4.96%, N 4.08%. Found: C 77.55%, H 5.03%, N 4.14%.

3.3.3. 4-Allyloxy-N-(n-hexyl)-1,8-naphthalimide **2c**

FTIR (KBr) 1688 (ν^{as} C=O), 1650 (ν^{s} C=O) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 100 MHz) δ: 8.52–7.98 (*m*, 3H, ArH), 7.58–6.72 (*m*, 2H, ArH), 5.84 (*m*, 1H, CH=), 5.24 (*m*, 2H, =CH_2), 4.52 (*m*, 2H, OCH_2), 3.22 (*t*, 2H, NCH_2), 1.48 (*m*, 8H, 4×CH_2), 0.96 (*t*, 3H, CH_3). Anal. calcd. for $C_{21}H_{23}NO_3$ (337): C 74.78%, H 6.82%, N 4.15%. Found: C 74.02%, H 6.73%, N 4.22%.

3.3.4. 4-Allyloxy-N-(n-butyl)-1,8-naphthalimide **2d**

FTIR (KBr) 1682 (ν^{as} C=O), 1648 (ν^{s} C=O) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 100 MHz) δ: 8.56–7.94 (*m*, 3H, ArH), 7.60–6.68 (*m*, 2H, ArH), 5.82 (*m*, 1H, CH=), 5.20 (*m*, 2H, =CH_2), 4.56 (*m*, 2H, OCH_2), 3.26 (*t*, 2H, NCH_2), 1.54 (*m*, 4H, 2×CH_2), 0.98 (*t*, 3H, CH_3). Anal. calcd. for $C_{19}H_{19}NO_3$ (309): C 73.79%, H 6.15%, N 4.53%. Found: C 74.46%, H 6.22%, N 4.45%.

3.4. Polymerization with styrene

In an ampoule flushed with dry nitrogen, 10 g of purified styrene, 0.01 g of the appropriate compound **2a–d** and 0.01 g of DBP were mixed. The ampoule was sealed and heated at 80 °C in a thermostat for 8 h. The resultant transparent polymers with an intense blue fluorescence were dissolved in toluene and reprecipitated several times with methanol until the filtrates were free of fluorescence under UV light. The precipitated copolymers were repeatedly washed with methanol, recovered by filtration and dried at 35 °C in vacuum to constant weight.

4. Conclusions

A novel method for the synthesis of 4-allyloxy-1,8-naphthalimide derivatives was developed. Four novel polymerizable fluorescent brighteners were synthesized in good yield by nucleophilic substitution of the chlorine atom in the 4-chloro-1,8-naphthalimide with allyloxy group under phase transfer catalysis conditions at room temperature. All products were colourless and displayed intense blue fluorescence in organic solvents. The results achieved show that the synthesized monomeric 1,8-naphthalimide derivatives are suitable for preparing polystyrene with intensive blue fluorescence emission.

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