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Concentration-induced discoloration properties of poly(alkoxynaphthalene)s synthesized by solid-state oxidative coupling polymerization

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ABSTRACT

Poly(alkoxynaphthalene)s were synthesized by grinding 2-alkoxynaphthalenes with FeCl₃ as the oxidant at room temperature via solid-state oxidative coupling polymerization. Based on the structural characterization and analysis, the condensed structure of 1,4-linked polynaphthalenes is the dominant structure of the polymer, accompanied with the formation of intramolecular coupling. The polymers not only exhibit perfect heat-resistant property, but also show the concentration-induced discoloration property. With the continuously increasing polymer concentrations, the maximum fluorescence bands were observed from the ultraviolet region to 520 nm, eventually red shifting to 620 nm at the polymer concentration above 0.1 mg mL⁻¹. Moreover, the choice of solvent and the extended side-chains can affect the fluorescence spectral changes. In combination with the fluorescence spectral changes of poly(alkoxynaphthalene)s in PMMA films, the concentration-induced discoloration property is mainly dependent on a transition from twisted conformations to planar structures and the formation of polymer aggregates. Moreover, these polymers exhibit obvious enhanced emissions and on/off fluorescent switching which sense THF vapor. It is suggested that poly(alkoxynaphthalene)s are potential materials for fabrication of fluorescence sensors to detect THF efficiently.

1. Introduction

Because of the extended π -electron systems, naphthalene and its derivatives with remarkable inherent properties have been investigated for possible applications as luminescent materials, organic semiconductors, and liquid crystals [1–3]. Compared to the crystallization of small molecular naphthalenes, naphthalene-based polymers have more processing capability and flexible mechanical properties, thereby being attracted more attentions in recent years. Moreover, naphthalenes with various possibilities of connected points in the molecules, are very promising blocks for building novel conjugated polymers [4–6].

Naphthalenes were first applied to synthesize polynaphthalenes with Lewis acid as the catalysis in *o*-dichlorobenzene solution [7,8]. The insoluble powder with low molecular weight opened the prelude to the preparation of polynaphthalenes. Moreover, the naphthalene homopolymers with different linkages of 1,4-, 1,5-, 2,6-, and 2,7- positions were synthesized by Grignard reagents in 1983 [9]. Even though the optical and electronic characterizations of the polymers were hardly carried out because of their poor

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solubility, the pursuit of high-quality fused ring systems and novel conjugated polymers has never stopped. And polynaphthalenes still have been taken up as a subject matter of functional material researches. In addition, the π -conjugated copolymers containing naphthalene unit as a component have been prepared with phenylenevinylene, fluorene, thiophene, carbazole and so on [10,11]. However, the introduction of naphthalene unit generally did not improve the performances of polymers, compared to the corresponding homopolymers.

The study of polynaphthalenes continues. In succession, various polynaphthalenes have been prepared to obtain good optoelectronic and photovoltaic materials by electrochemical synthesis and chemical synthesis [12–14]. For example, by electropolymerization, the blue light-emitting poly(1,10-binaphthol) and blue-green-emitting poly(1,10-binaphthol dimethyl ether) were synthesized and also showed poor solubility, which limited the investigation and application of the polymers [4,15]. Moreover, polynaphthalenes have also been synthesized with different techniques of chemical polymerization including plasma polymerization of naphthalenes, Suzuki coupling, and Bergman cyclization [16–20].

As an easy, economical way to the formation of C-C bond directly, the oxidative coupling reaction has attracted more attention again recently [21]. One advantage of the reaction is the possibility of formation of complex fused aromatic rings due to the numerous reaction activity points of the simple aromatic ring [22]. Moreover, naphthalene is such a suitable monomer with the simplest polycyclic aromatic structure and many activity points. Therein, polynaphthalenes have been prepared by oxidative coupling reaction in solutions [23,24]. After sulfonation, the sulfonated polynaphthalenes were applied in efficient hydrolysis of cellulose into glucose [25]. By solid state oxidative coupling polymerization, we prepared polynaphthalenes with excellent thermal stability and the soluble part was self-assembled to polymeric microspheres with yellow-light emission [26].

Attaching flexible side-chains to the repeat units has proven to be a concept of general value to achieve solubility of these polymers in common solvents. The presence of flexible side-chains increases the configuration entropy of the polymers in the transition from the solid to the solution state, in which, various polymer conformations can be formed due to the strong influence of solvents on the rigid backbones and flexible side-chains [27]. It is of interest to investigate the effects of the polymer concentrations on the polymer conformations and aggregations, thus on the fluorescence properties. We focus again the structure of polynaphthalenes, because they have the chemical structures with the rigid planar π -conjugated unit and much torsion between the units [28], which result in not only the short-wavelength emission due to the extensity of the π -conjugation localizing in the naphthalene unit, but also the red shift of the luminescence if the π -interaction between polynaphthalene chains exists.

Rapid sensing or detecting of pollutional organic molecules plays a significant role in life sciences, environmental science and medicinal science [29–31]. Because of facilitated detection and manipulation and high sensitivity, the fluorometric methods have gained much attention. Conjugated polymers have been studied and present potential applications in the area of chemical sensor [31]. So, it is very significant to develop special luminescent conjugated materials as chemical sensors.

In this paper, we chose 2-alkoxynaphthalene as the monomer to prepare the novel polynaphthalenes from solid-state oxidative coupling polymerization, which can be soluble in common organic solvents to investigate the optical properties. The structure and polymerization process were also discussed in our experiment. The solvents and the polymer concentrations were tested to find the controlling factors in the fluorescent emission of polymers. The fluorescence spectra of cast films formed from the polymer in PMMA were measured as a function of polymer concentration, a technique which further allows us to apply the polymer matrix isolation effect [32]. This research gives a useful guide to the relationship between the polymer conformations and the optical properties. The polymers are also investigated to be used as the reusable fluorescent probe for various organic molecules, and show a high selective fluorescence switching behavior in THF vapor.

2. Experimental

2.1. Materials

2-Naphthol, bromoalkane (bromoethane, bromobutane, bromohexane, bromooctane), potassium hydroxide, dimethyl sulfoxide (DMSO), anhydrous FeCl_3 , toluene (Tol), dichloromethane (CH_2Cl_2), Tetrahydrofuran (THF), trichloromethane (CHCl_3), Hexane (Hex), methanol (MeOH), and ethanol (EtOH) were all A. R. and purchased from Sinopharm Chemical Reagent Co., Ltd (China, Shanghai) and used without further purification. Poly(methyl methacrylate) (PMMA) with a number-average molecular weight (M_n) of 100×10^3 was purchased from Aldrich and used as-received.

2-Alkoxynaphthalenes were synthesized from 2-naphthol and bromoalkane via an etherification procedure, as shown in Scheme 1. The synthetic procedure is illustrated by 2-octyloxynaphthalene as an example: Bromooctane (10.4 mL, 60 mmol) was added dropwise to a stirred DMSO solution of 2-naphthol (7.2 g, 50 mmol) and KOH (5.6 g, 100 mmol) at 95 °C. After stirred for 12 h, the solution was poured into ice-water mixture. The solid product was collected and recrystallized from EtOH, and obtained 10.5 g of white crystals with the yield of 90.0%. FT-IR (KBr, cm^{-1}): 3060 (C–H, Ar), 2990, 2825 (C–H), 1620, 1475 (C–C, Ar), 1255, 1040 (C–O–C), 825, 725 (C–H, Ar). ^1H NMR (400 MHz, CDCl_3) δ 7.89–7.74 (m, 1H), 7.50 (s, 1H), 7.39 (s, 1H), 7.26–7.16 (m, 1H), 4.12 (t, $J = 6.6$ Hz, 1H), 1.99–1.84 (m, 1H), 1.64–1.51 (m, 1H), 1.49–1.29 (m, 3H), 0.98 (dd, $J = 6.9, 5.8$ Hz, 1H).

2.2. General polymerization

The poly(alkoxynaphthalene)s (PANs) were polymerized by solid-state oxidative coupling reaction of 2-alkoxynaphthalene in the presence of FeCl_3 at room temperature. The synthetic route is shown in Scheme 1 and the synthetic procedure of poly(2-octyloxynaphthalene) (PON) is an example and described below.

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