Dyes and Pigments 115 (2015) 50–57

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Synthesis of amphiphilic spiropyran-based random copolymer by atom transfer radical polymerization for Co^{2+} recognition

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ARTICLE INFO

Article history:
Received 24 September 2014
Received in revised form
28 November 2014
Accepted 10 December 2014
Available online 19 December 2014

Keywords:
Amphiphilic copolymer
Stimuli-responsive polymer
Atom transfer radical polymerization (ATRP)
Spiropyran
Cobalt ion recognition
Complexation

ABSTRACT

An amphiphilic spiropyran-based random copolymer containing methacrylic acid unit has been prepared and investigated with obvious negative solvatochromism in five different solvents. It was found that the polarity of comonomer influenced the photochromic behavior of spiropyran. The synthesized copolymer exhibited a good reversible behavior in aqueous solution: the addition of strong acid promoted the isomerization from spiropyran (SP) to merocyanine (MC), and the inverse process was achieved by the introduction of strong base. Much more importance, the effect of comonomer was utilized for the selective Co^{2+} recognition. The locations of the maximum absorption peak stay almost as same as MC when it is complexed with Cu^{2+}, Mn^{2+} and Hg^{2+}. The location, however, moves from 551 nm to 526 nm upon complexation with Co^{2+}. The obvious color change of the solution from purple to claret-red after complexation with Co^{2+} was observed. This interesting phenomenon is practically convenient for the visual recognition of Co^{2+}.

1. Introduction

Cobalt, one of the essential elements to human health, produces physiological effects in the form of vitamin B2. Cobalt is also an indispensable element to microorganism for metabolism [1–3]. However, excess cobalt may lead to many serious health problems, such as low blood pressure, paralysis, diarrhea etc. The World Health Organization has set the maximum allowable level of cobalt in daily intake at 350 μg. Meanwhile, cobalt contamination and its potential toxic effects on human beings continue to be challenging problems throughout the world due to the widespread utilization of Co^{2+} in industrial manufacture. Therefore, it is desirable to synthesis selective probes for Co^{2+} recognition.

Various scientific and accurate methods, such as atomic absorption spectrometry [4], inductively coupled plasma mass spectroscopy (ICPMS) [5], and inductively coupled plasma atomic emission spectrometry (ICP-AES) [6], have been developed for the detection of Co^{2+}. However, these methods are usually time-consuming, complicated, and expensive. Photochromism, on the contrary, has proved to be a convenient method for metal ions detection, due to its high sensitivity and efficiency [7,8]. Photochromism involves the reversible interconversion of a chemical species between two isomers induced by light which results in a change in UV–VIS spectra. Families of photochromic compounds commonly used in polymeric system include azobenzenes, spiropyrans, spirooxazines, diarylethenes and fulgides [9–11]. Among these compounds, spiropyrans have been extensively studied due to their quick response to external stimuli. Spiropyrans consist of two orthogonal aromatic rings which are connected by a carbon atom of sp^3 hybridization [12–14]. Upon the irradiation of ultraviolet light, the colorless, nonpolar and hydrophobic spiropyran (SP) undergoes the cleavage of C–O bond, forming the colorful, polar and hydrophilic merocyanine (MC) [15–17]. The merocyanine can complex with metal cations via the phenolate oxygen atom as shown in Scheme 1 [18–20]. Increasing attentions have been focused on the design of photochromic probes for divalent metal ions, such as Hg^{2+} [21], Cu^{2+} [22], Ni^{2+} [23], and Co^{2+} [24]. Locklin synthesized spiropyran-based random copolymer by atom transfer radical polymerization (ATRP), and the resulting

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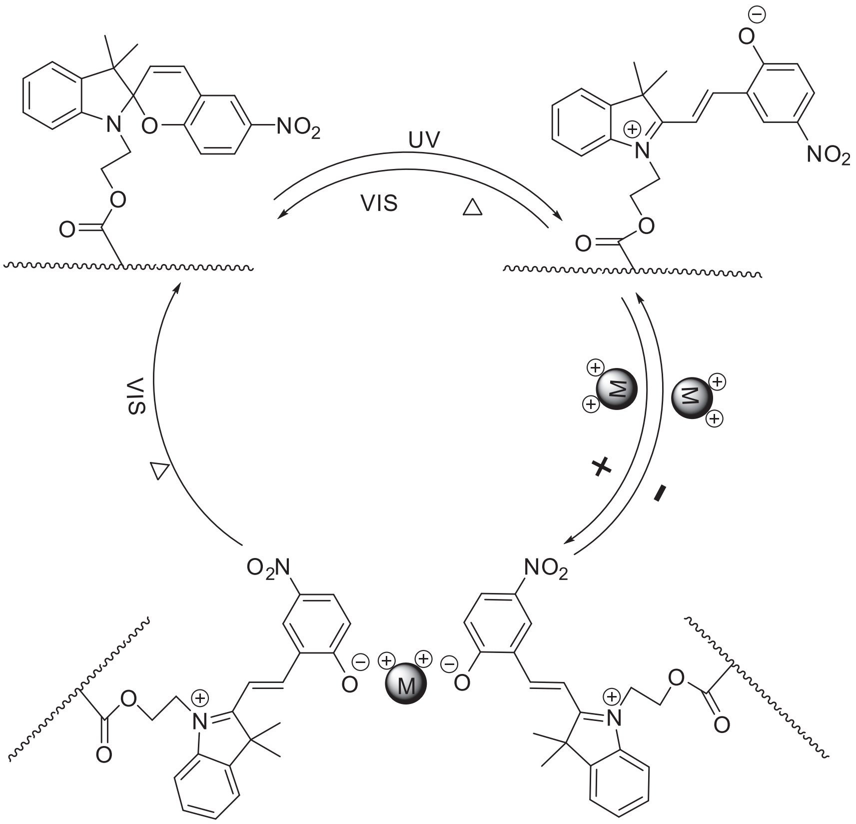
http://dx.doi.org/10.1016/j.dyepig.2014.12.008



Scheme 1. Switching equilibrium among SP, MC and the MC-metal complex.

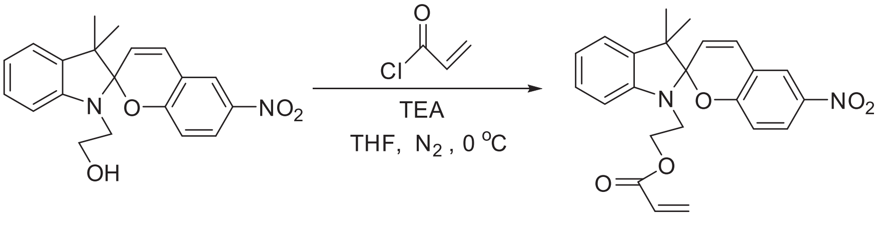
spiropyran-containing random copolymer P($MMA_{0.9}$-co-$SPMA_{0.1}$) could identify multiple metal ions simultaneously. This report provided a convenient synthetic route, and greatly broadened the application domain of spiropyran-based copolymer in ions detection [25]. Nevertheless, the copolymer exhibited light-responsive behaviors only in organic solvents. It is difficult to be employed for the selective recognition of Co^{2+} because of the cross-sensitivity toward other metal ions. In this regard, there is still a great demand for the development of effective and convenient probes for the recognition of Co^{2+} with high selectivity. Vamvakaki synthesized two kinds of spiropyran-based random copolymers with different comonomers and compared the photochromism in different solvents. The "negative" solvatochromism of the photochromic species of the PDMAEMA-co-PSP copolymer was visually observed upon the increasing polarity of the solvents, however, this phenomenon was not found in PMMA-co-PSP. It was attributed to the nonpolar character of MMA comonomer which could not stabilize the open MC form [26]. The polarity of comonomer has an effect on the photochromism of spiropyran, therefore, the stabilization of specific chromophore isomers by tuning the polarity of the comonomer is very promising for the development of materials with high specificity in terms of optical properties. These excellent investigations provide a direction to prepare a convenient and efficient probe for the detection of Co^{2+} with high selectivity.

In the present work, we use tert-butyl methacrylate (tBMA) as the precursor monomer to copolymerize with [1'-(2-acryloxyethyl)-3′,3'-dimethyl-6-nitrospiro-(2H-1-benzopyran-2,2'-indoline), SPMA)], and the amphiphilic spiropyran-based random copolymer P(SPMA-co-MAA) is obtained by the hydrolysis of the resulting intermediate product P(SPMA-co-tBMA) in acidic solution. The photochromic behavior and application in metal ions recognition of the copolymer are investigated in details.

2. Experimental

2.1. Materials

The monomer tert-butyl methacrylate (tBMA, 99%, Aladdin) was passed through a column of basic alumina to remove inhibitors before use. Ethyl 2-bromoisobutyrate (EBiB, 98%, TCI) as the initiator



(SP-OH)

(SPMA)

Scheme 2. The synthesis of photo-responsive monomer.