



Design, synthesis and photoisomerization behavior of novel azobenzene-based dyes containing different alkyl chains and isolation groups



Ihor M. Tkachenko, Yaroslav L. Kobzar, Olha G. Purikova, Alexander L. Tolstov, Oleg V. Shekera, Valery V. Shevchenko*

Institute of Macromolecular Chemistry of the National Academy of Sciences of Ukraine, 48 Kharkivske shosse, Kiev 02160, Ukraine

ARTICLE INFO

Article history:

Received 3 September 2016
Revised 17 October 2016
Accepted 26 October 2016
Available online 27 October 2016

Keywords:

Azo dyes
Photoisomerization
Isolation group
Chromophore-chromophore aggregation

ABSTRACT

A series of reactive azo dyes based on 4-phenylazophenol, containing hexenyloxy-, allyloxy-ethoxy-propoxy- and tetramethyl-disiloxanyl-propoxy substituents were synthesized. Additionally, allyl-functionalized azo-based chromophores with changeable isolation groups (hydroxymethylene-, trimethyl-siloxymethylene- and pentafluorophenoxymethylene-) as well as with an additional azobenzene unit were successfully obtained. The photoisomerization behaviors of the synthesized azo dyes were investigated in solution as well as in films. Importantly, the occurrence of photoisomerization (at least near the surface after UV treatment) was confirmed in the crystalline dye films. The resulting compounds can be employed for the synthesis of a wide variety of azo-based materials which may be suitable for optical and electrooptical applications.

© 2016 Elsevier Ltd. All rights reserved.

Introduction

Organic dyes containing an azobenzene fragment are extensively used as tunable and light-responsive chromophores due to reversible *cis-trans* photoisomerization [1–10]. This isomerization is reversible by photochemical and thermal pathways. However, the low thermal stability of azobenzene dyes and high ability to aggregate in the solid phase have limited their applications in devices [11–14]. One approach to solve these problems is to incorporate the organic azo chromophores into a polymer backbone (generally, polymers with azo units in the side chains) as well as the polyhedral oligomeric silsesquioxane (POSS) core [13–20]. Additionally, such azo-containing systems are able to form uniform and ultrathin films. It is known that organic films which are smooth and homogeneous over large areas possess advanced optical and optoelectronic properties [21]. Many potential applications have been proposed for azo-containing polymers or star-shaped molecules with the POSS core and azobenzene dye arms, such as optical data storage, liquid crystal displays, molecular switches, nonlinear optical devices, surface relief gratings, and as a stable active medium to induce reversible plasmonic modulations of embedded metal nanostructures. Therefore, the development of

new azo-containing dyes bearing reactive substituents is of significant importance.

Literature reports have clearly demonstrated that the flexible spacer chain length of azobenzene dyes plays an important role in regulation of the optical and liquid crystalline properties of materials based on such dyes [17,20,22–26]. Thus, it is crucial to control the distance between the azobenzene unit and the terminal reactive group, that is, to regulate the spacer chain length of dyes. At the same time the influence of the chemical nature of flexible alkyl chains on the photoisomerization behavior of azo-containing materials has been poorly studied. On the other hand, incorporation of bulky groups into the azo chromophore with constant spacer lengths between the azo dyes and medium (polymer, POSS) represents another effective way to regulate the photooptical properties of azo-containing materials. More importantly, these chemical bulky groups can suppress crystallization of azo-containing materials (crystallinity leads to poor quality film surfaces) as well as serve as so-called suitable isolation groups which are introduced to decrease the intermolecular dipole-dipole interaction of chromophore fragments [27–29].

Thus, the current work represents an approach to the design of reactive azobenzene dyes possessing flexible alkyl chains of different chemical natures and lengths as well as azo dyes containing allyl tails and isolation groups of different sizes. Additionally, the photoisomerization behaviors of the synthesized dyes were thoroughly investigated in solution as well as in films.

* Corresponding author.

E-mail address: valshevchenko@yandex.ru (V.V. Shevchenko).

Results and discussions

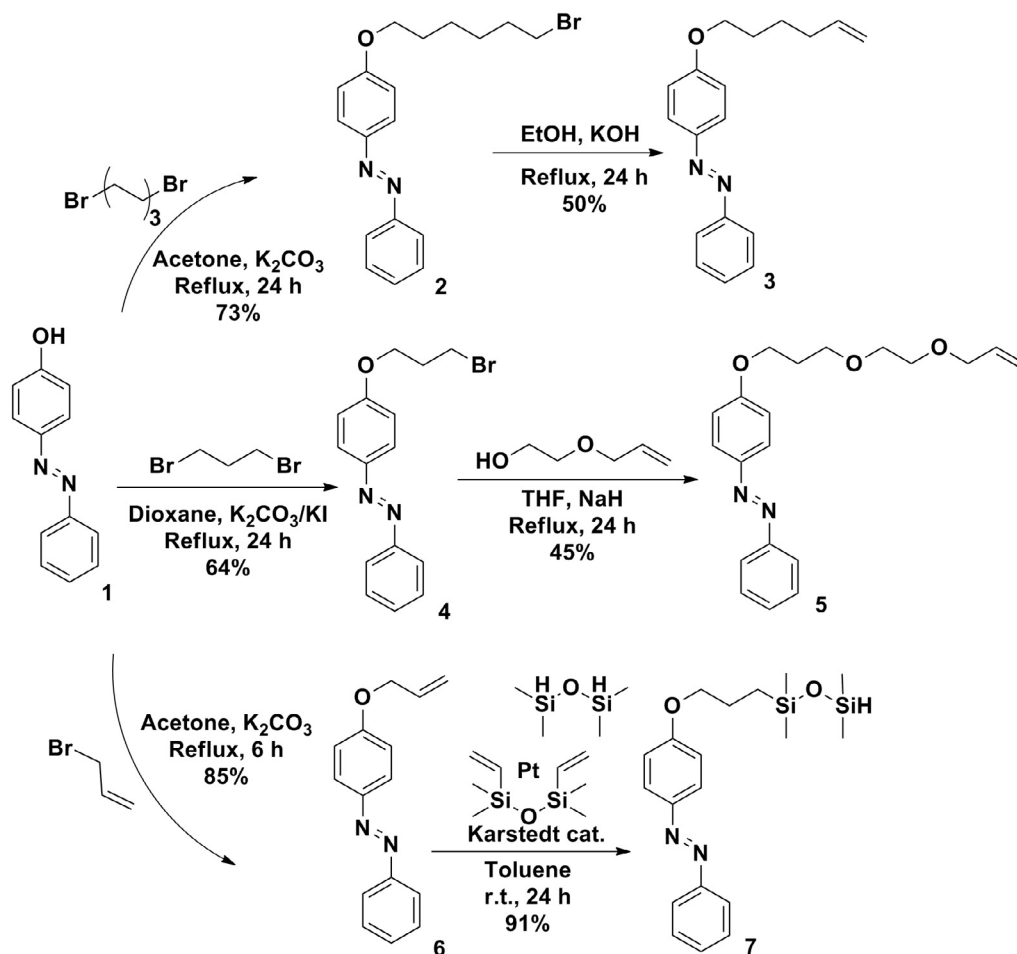
For the synthesis of dyes **3**, **5** and **7** containing flexible and reactive hexenyloxy-, allyloxy-ethoxy-propoxy-, and tetramethyl-disiloxanyl-propoxy fragments, respectively, commercially available 4-phenylazophenol (**1**) was chosen as the initial precursor (Scheme 1). The obtained dye **2**, synthesized according to a literature method [22], was readily transformed into the corresponding hexenyloxy-substituted dye **3** by dehydrohalogenation using the KOH-ethanol system. It should be noted that the synthesis of azo dye **3** has previously been reported from dye **1** and the prohibitively expensive 6-bromo-1-hexene [30]. However, our approach to the synthesis of dye **2** provides an easy and inexpensive synthetic method. Dye **5** with the allyloxy-ethoxy-propoxy substituent was prepared *via* etherification of compound **1** with excess 1,3-dibromopropane [31], and subsequent reaction of dye **4** with 2-allyloxyethanol in the presence of NaH.

Several recent studies demonstrated that inserting a flexible disiloxane segment into the lateral alkyl chain of azo dyes can improve their photo-responsive properties [32,33]. Therefore, 1,1,3,3-tetramethyldisiloxane was used for the synthesis of dye **7** containing the tetramethyl-disiloxanyl-propoxy substituent, and consequently, the terminal hydride functional group. Thus, dye **6** was synthesized from the reaction of dye **1** with allyl bromide [19] and subsequently converted into the azo chromophore **7** *via* a hydrosilylation reaction. A 8-fold excess of 1,1,3,3-tetramethyldisiloxane was used to ensure formation of the mono-substitution product.

Hence, the synthesized dyes **3**, **5** and **7** consist of the following structural units: azobenzene fragments, flexible spacers of different lengths and a terminal reactive vinyl group (**3** and **5**) or Si-H group (**7**).

The introduction of isolation groups to the chromophore moieties should be an efficient approach to minimize azobenzene aggregation and the crystallinity of materials based on such dyes. Thus, we chose 5-[2-phenyldiazen-1-yl]-2-(prop-2-en-1-yloxy)benzaldehyde (**8**) [34], carrying the reactive aldehyde group at the *ortho*-position to the allyloxy-fragment of the aromatic ring, as a scaffold for the attachment of a variety of isolation groups, including an additional azobenzene unit (Scheme 2).

The synthesis of azo dye **9** containing a hydroxymethylene group on the aromatic ring was accomplished by reduction of the aldehyde group of dye **8** with NaBH₄. The obtained dye **9**, due to the presence of the vinyl group, can be potentially used for hydrosilylation reactions with Si-H containing compounds. In that context, protection of the hydroxyl groups of dye **9** is essential because they can easily react with Si-H bonds (*O*-silylation). [35,36] Thus, we obtained the trimethylsilyl-protected dye **10** (Scheme 2), and hence, OH-functionalized materials can be easily prepared where necessary. Notably, dye **10** was easily hydrolyzed by atmospheric moisture. As a result, the photoisomerization behavior of dye **10** was not studied. Although dye **10** is easily hydrolyzed, it may provide a useful starting material for subsequent reactions, and due to the presence of the hydroxyl group, it is capable of further functionalization.



Scheme 1. Synthetic pathways for the synthesis of dyes **3**, **5** and **7**.

Download English Version:

<https://daneshyari.com/en/article/5258253>

Download Persian Version:

<https://daneshyari.com/article/5258253>

[Daneshyari.com](https://daneshyari.com)