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DYES: DEVELOPMENTS AND MEDICINAL USES (A REVIEW)

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ABSTRACT
Since these applications are obviously connected to the dye's nature, which is incorporated into the corresponding polymers, the affinity of certain polymers to dyes is exploited in wastewater work-ups after (textile) dyeing procedures. In this review, we wish to point out the great importance of dye-containing polymers, with a comprehensive scope and a focus on azo, triphenylmethane, indigoid, perylene and anthraquinone dyes. Since a large number of synthetic approaches towards the preparation of such materials can be found in the literature, an elaborated overview of different preparation techniques is given as well.

KEYWORDS: Since these applications azo, triphenylmethane, indigoid, perylene and anthraquinone dyes.

INTRODUCTION

The broad variety of technical and industrial applications, which includes "classical" utilizations like dyeing of textiles and other consumer goods as well as rather new usages such as laser dyes and dyes for organic light emitting diodes (OLEDs), liquid crystal (LC) displays, optical data storage and fluorescent labeling, has produced a great deal of research in this field. The main driving force is the constant demand for improved dyeing efficiency[1,2] or photochemical/photophysical properties[3,4], while also focusing on eco-friendly procedures[5,6], reduced toxicity[7,8] and decreased production costs.[9] A promising approach to fulfilling these requirements is the combination of dyes and polymeric materials, which will be highlighted in this review. The great advantage of such systems is the controllability of many features like solubility, stability, and toxicity through appropriate choice of polymeric material. Widely applied and interesting representatives amongst the large number of dye categories are triphenylmethane, azo, anthraquinone, perylene and indigoid dyes (see Figure 1). Due to the fact that these compounds cover a large spectrum of applications, they are the main focus of this article. Triphenylmethane dyes owe their importance to their cheapness and brilliance of color with typical shades of red, violet, blue and green.[10] The major application of these stains is their use in the textile industry for dyeing nylon, wool, silk, cotton, etc., in the paper and leather industries and in the food and cosmetics industries.[11] Their high dyeing efficiency and the low light fastness are considered the major benefits of these stains. The underlying structures of triphenylmethane dyes are the colorless compounds triphenylmethane and triphenylcarbinol, whose conversion into dyes is achieved through the introduction of amino- or hydroxyl-groups stabilizing the cationic charge that serves as the chromophore. Depending on the resulting substitution pattern, monoamino-, diamino-, triamino- and hydroxyl-triphenylmethane dyes are differentiated.[12] Another important application of some triphenylmethane dyes is their use as indicator dyes due to their pH sensitivity, which is derived from their constitution. Some important examples of this class of dyes are phenolphthalein, fuchsine and fluorescein.

The binding modes leading to the formation of dye-polymer conjugates can be either covalent or non-covalent in nature. While the first approach obviously requires the formation of covalent bonds, non-covalent binding can occur through different kinds of interactions such as ionic and dipole–dipole interactions or through the formation of inclusion complexes.

Due to the large number of polar substituents that enable the formation of dipolar interactions with adequate substrates, sugar-based (macro)molecules are suitable materials for the supramolecular attachment of dyes. Such oligo-/polysaccharides can be obtained from natural products (e.g., starch, cellulose, chitosane) or from chemical linkage of monomeric subunits and are therefore readily accessible. The efficient adsorption of anionic azo dyes bearing sulfonate moieties to starch and β-cyclodextrin polymers was reported.[13] In the underlying studies, the polymers were prepared by cross-linking of β-cyclodextrin and starch, respectively, with hexamethylene diisocyanate. For both types of polymers, the main effects resulting in adsorption of the dyes were found to be hydrogen bonds formed between hydroxyl and amine groups located at polymers and the sulfonate moieties of the azo dyes. Additionally, cyclodextrins are known to form inclusion complexes with several azo dyes and the formation of host guest complexes was therefore expected to contribute to the dye sorption of corresponding cyclodextrin-based polymers. The formation of such supramolecular complexes was verified, but a strong pH dependence was found and the whole effect was found to be inferior to the hydrogen bonding. Furthermore, the efficiency of calix[14]arene-based polymers for azo dye sorption was published.[36] Analogously to the cyclodextrin polymers, p-tert-butylcalix[15]arene-based polymers were prepared via condensation of the monomeric building blocks forming oligomeric structures. Compared to β-cyclodextrin polymers, lower affinity of the simple p-tert-butylcalix[4]arene-based oligomer with anionic azo dyes was determined. A drastic increase in adsorbance was observed when p-tert-butylcalix[16]arene oligomers bearing crown-6 functionalities on the lower rim were utilized. This led to the assumption that the ion pair complexation of sodium ions and the sulfonated azo dyes plays an important role during dye binding.

Applications

Synthetic dyes and especially polymer linked dyes are of growing interest for technical and medical applications due to their versatile properties and increasing environmental consciousness. The advantages over low-molecular compounds seem to be not only the reduced toxicity or the possibility of better recovery and reusability but also improved quality characteristics such as high color fastness in textile dyeing. Therefore, the typical applications of dye-containing polymers are not limited to color impression in paintings or textile dyeing. Moreover, utilization of dye properties in medicine, for analytical purposes or as optical sensors in chemical research, for example, is of great interest. Thereby, the dye does not need to be covalently attached to the polymer, since supramolecular interactions play an important role in dye-polymer chemistry as well. Conversely, the affinity of certain dyes to specific polymers and their non-covalent attachment can also be used for purification processes like waste water extraction. Below, typical applications of dye containing polymers are summarized and discussed in consideration of their properties and linkage to the polymer.

Waste Water Treatment Dyes are valuable materials not only in the textile industry but also in the manufacturing of paper, plastics, cosmetics, medicine and biology. Hence, the environment is also being more and more affected by the steadily increasing frequency of dye pollutants, which induce unwanted color contaminations and sometimes have toxic effects to humans and animals.[11,79] Thus, effective dye extraction from waste water is becoming more important. Plenty of physical, chemical and biological methods such as ozonation, fungal decolorization and degradation, membrane-filtration, activated carbon usage or electrochemical techniques like coagulation have been developed and optimized in recent years.[17-18] Regardless, adsorption and the formation of inclusion complexes still seem to be the most effective and cheapest methods for the purification of effluents. One reason is the high stability of synthetic dyes due to their aromatic structure, which for example impedes degradation. Native adsorbents such as biopolymers, especially, are a good alternative to expensive and, in some cases, unselective purification techniques. For instance, polysaccharide-based materials can be a cheap and effective alternative to commonly used systems.[19-20] They exhibit a high binding capacity and specificity while being non-toxic, stable and renewable. A notable example is represented by calix[21]arenes which have a high removal ability for selected water-soluble azo dyes.[22] Furthermore, biopolymers like starch and chitin are abundant and also modifiable to produce selective and biodegradable compounds like cyclodextrin and chitosan.

Dyes play an important role in medical applications because of both their physicochemical properties and color impression. Since this often involves applications inside the human body, it is quite important to use non-toxic derivatives. To skirt that problem, polymers are a good alternative to low-molecular dyes for in vivo applications like polymer-linked water-soluble rylene dyes for cell Polymers, 7 734 staining. Perylene-dicarboxmonoimide, perylene-tetracarboxdiimide and benzoylterrylen-3,4-dicarboximid were modified with a single poly(ethylene oxide) chain to obtain polymeric rylene dyes which are suitable for staining cellular membranes (Chinese hamster ovarian cell line, bronchial carcinoma cell line and ovarian carcinoma cell line). The special feature of these polymeric materials is their ability to indicate the polarity of their environment due to their high fluorescence in nonpolar solvents and a much lower fluorescence in polar medium caused by aggregation.[23] Another in vivo application of polymer-attached dyes in medicine could be the therapy of rheumatoid arthritis. In this case the dye is instead needed for polymer tracking in the body, as it is used as a fluorescence dye (atto680). Therefore, a copolymer consisting of N-(2-hydroxypropyl)methacrylamide) and N-(3-azidopropyl)methacrylamide is used which allows a postmodification with the fluorescence dye by azide-alkyne click-reaction. Tests with murine models of rheumatoid arthritis proofed that the polymer has a high accumulation in the inflamed joints. The synthesized polymer is hydrophilic and exhibited size-dependent blood circulation. High molecular-weight polymers (54 kDa) had a very good bioavailability and could still be detected 24 hours after injection. Very application-oriented examples of polymers in medicine are artificial iris implants, which are used to treat iris defects by improving vision and reducing glare. Therefore, it is necessary to use polymer-attached dyes which can be polymerized and cross-linked into blanks and afterwards sharpened to the required iris form. Suitable monomers with a broad spectrum of synthesizable colors are methacrylated anthraquinone dyes. They can be synthesized in blue, green and red colors and afterwards copolymerized with 2-hydroxyethylmethacrylate and tetrahydrofurfuryl methacrylate and cross-linked with ethylene glycol dimethacrylate. By mixing different anthraquinone monomers almost every color can be generated.

CONCLUSION

The most important synthetic routes as well as the major applications of dye-containing polymers have been presented. As reviewed in this article, either covalently or supramolecularly polymer-attached dyes find various applications in many fields for up-to-date issues like organic light-emitting diodes, waste water treatment, medical utilizations such as iris implants or in vivo applications, and electrochemistry. Non-covalent connection of the dye to the polymer can be ionic, dipole-dipole driven or caused by inclusion complexes. Sugar-based polymers like oligo-/polysaccharides, such as cross-linked β-cyclodextrin or even calix[4]arene compounds, are quite important for the adsorption of either cationic or anionic azo and anthraquinone dyes in, for example, dye waste water extraction. Covalent attachment can be achieved through polymerization of colored monomers, polycondensation or polymer-analogous attachment either in the main chain or as an end group. According to the number of publications, colored monomers are usually synthesized through (meth)acrylation, as for many azo, anthraquinone and triphenylmethane dyes, whereas polycondensation and polymer-analogous reactions require suitable functional groups in the monomeric or polymeric building blocks.

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