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Varied Types of Polymers and Dyes in Organic Chemistry

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ABSTRACT

Amongst functional macromolecules, the combination of polymers and dyes is a research field of great potential with regard to high-performance materials. Accordingly, colored polymers have become increasingly important as materials for miscellaneous technical applications in recent years while also being a major part of everyday life. For instance, dye-containing polymers are nowadays widely applied in medicine, painting industries, analytics and gas separation processes. 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.

INTRODUCTION

Natural and synthetic dyes are compounds of great interest since they play an important role in our everyday life. 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.

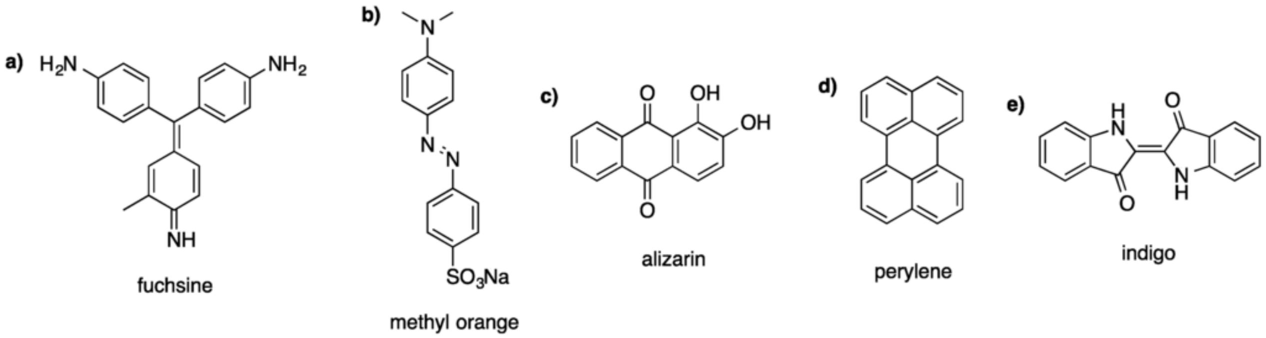

Figure 1: Characteristic representatives of (a) triphenylmethane dyes, (b) azo dyes, (c) anthraquinone dyes, (d) perylene dyes, and (e) indigoid dyes.

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 [1]. 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.

PREPARATION PROCESS

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.[2,3]

Non-Covalent Attachment

Sugar-Based Polymers

A schematic illustration of the non-covalent dye binding to polymeric materials can be found in **Figure 2**.

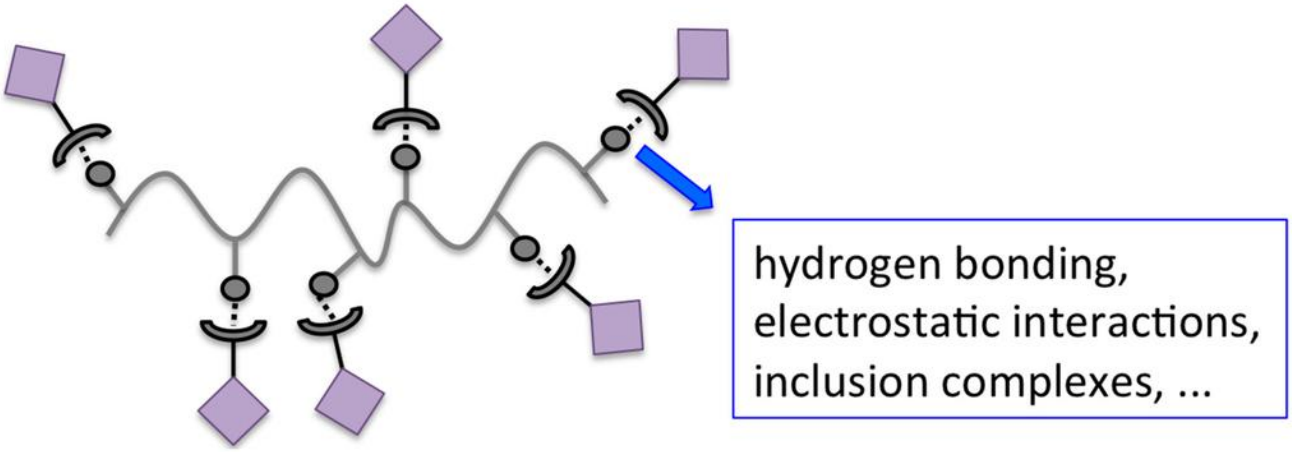

Figure 2: Schematic illustration of non-covalent dye binding to polymers.

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.[4,5]

The efficient adsorption of anionic azo dyes bearing sulfonate moieties to starch and β-cyclodextrin polymers was reported . 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[4]arene-based polymers for azo dye sorption was published .Analogously to the cyclodextrin polymers, *p*-*tert*-butylcalix[4]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[4]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. Employing alkylamine derivatives of calix[4]arene polymers proved to be a promising approach as well .Reaction with *p*-dibromo-xylene results in the formation of copolymers showing a strong affinity to anionic azo dyes. In this case, hydrogen bonds and electrostatic interactions formed between the amino residues and the hydroxyl groups of the azo dyes and the calix[4]arene units interactions are the most important effects leading to the dye adsorption.[6,7]

Moreover, β-cyclodextrin polymers exhibited efficient adsorption of cationic dyes . The polymers were prepared by cross-linking of β-cyclodextrin with epichlorhydrin in the presence of carboxymethyl cellulose.

DISCUSSION

As another example of polymerizable triphenylmethane dyes, a radically polymerizable phenolphthalein derivative was obtained through reaction of phenolphthalein with *N*-(hydroxymethyl)acrylamide. The latter compound possesses a relatively high reactivity towards nucleophilic attacks, which enables condensation with electron-rich aromatic substances under Friedel-Crafts-like conditions. The versatility of the reaction products, namely a monofunctional monomer as well as a bifunctional cross-linker, was demonstrated in several publications.

Furthermore, the preparation of different radically polymerizable anthraquinone derivatives of blue, red, and green color was introduced (see **Figure 3**) .Mixing of these fundamental dyes enables a broad color spectrum to be covered. The different dye derivatives were prepared starting from 5,8-dichloro-1,4-dihydroxyanthraquinone, 1,4-dichloroanthraquinone and 1-chloroanthraquinone, respectively. As a first step, the compounds were reacted with a hydroxy-functionalized amine in a nucleophilic aromatic substitution reaction. The free aliphatic hydroxy groups were then methacrylated by treatment with methacryloyl chloride or methacrylic anhydride, respectively. The bifunctional cross-linkers and the monofunctional monomer obtained were polymerized with different methacrylate-based comonomers and the resulting polymers were found to be stable against UV radiation.[8,9]

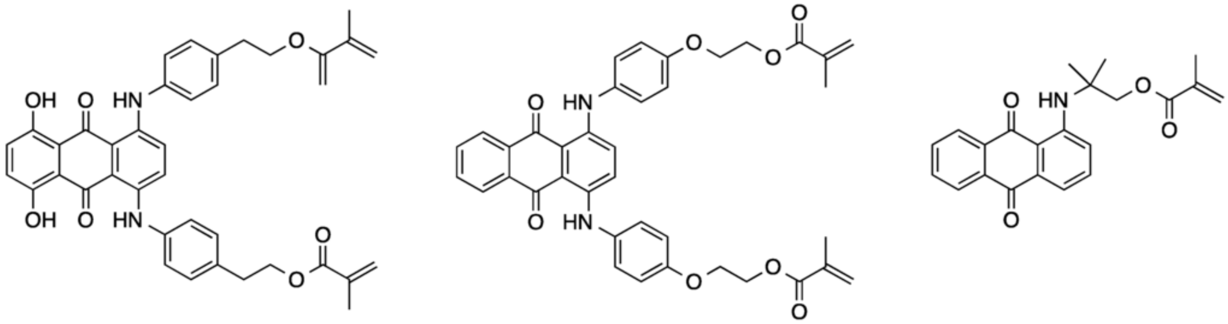

Figure 3: Chemical structures of several polymerizable anthraquinone derivatives.

Several further examples of polymerizable dye derivatives belonging to different classes of dyes were described. For instance, the covalent emplacement of laser dyes into polymeric materials offers a variety of advantages such as improved handling and increased lasing efficiency.

CONCLUSIONS

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.[10,11]

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