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Oxazoline-functional polymer particles graft with azo-dye

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ABSTRACT

New cross-linked fluorescent particles, with diameters ranging from 850 to 950 nm, were prepared in two steps. In the first step, cross-linked functional particles (650–750 nm) were prepared by nonaqueous dispersion copolymerization of 2-isopropenyl-2-oxazoline with methyl methacrylate, having different oxazoline contents and cross-linking degrees. The influences of the oxazoline content and of the cross-linking agent upon the morphology, the average diameter, and the size distribution of the particles were highlighted by SEM and DLS techniques. Lower particle diameters, but with broader polydispersity, were obtained by increasing the cross-linker content. A quantitative FTIR spectroscopy method was employed in order to determine the oxazoline content from cross-linked particles with accuracy. The second step consisted in selective grafting a fluorescent azo-dye with carboxyl groups at oxazoline units present on both the surface and inside the particles. The grafting degree was appreciated to range between 54% and 75%. The thermal properties and the morphology of the modified particles were influenced by the azo-dye content. Consequently, after chemical modification the thermal stability of the particles was enhanced by 50 °C, while the surface modification with the azo-dye led to particles with higher diameters. TEM analysis revealed that the dye reacted mostly on and in the irregularities of the particles, while the fluorescence activity of the modified particles was evidenced using steady-state fluorescence spectroscopy.

1. Introduction

Coloured polymer particles, of uniform size, find their use in various applications, including xerography, printing, sensing devices, cell labelling, and medical diagnostic [1–5]. Many of these applications require particles with a narrow size distribution and average diameters ranging from 0.5 to 10 μm. The technique that meets these requirements is dispersion polymerization. Coloured polymer particles are synthesized, either by incorporating dyes by covalent linkage, or by entrapping them in various ways. One approach deals with reactive dyes, fluorescent or not, covalently linked to the polymer backbone by radical copolymerization [6,7]. Another strategy involves the synthesis of cross-linked polymer particles, which are subsequently swollen in an organic solvent containing free dye molecules. After the solvent is evaporated, or the particles are deswollen (by changing the polarity of the medium), the dyes become physically trapped inside the particles [8–10].

Winnik and Ober [11] reported the dispersion polymerization in the presence of polymerizable anthraquinone dyes. They noticed that the final particle sizes changed and the particle size distribution became very broad. Horák et al. [12] studied the dispersion polymerization of styrene and butyl methacrylate in the presence of nonpolymerizable dyes. They reported that the particle size increased with the concentration of the dye and the particle size distribution was significantly broadened. Recently Song et al. [13] managed to obtain coloured monodisperse particles using a two-stage dispersion polymerization.

In all mentioned cases, no other functional monomers, like cross-linking agents were used, due to the fact that these would also interfere with the course of dispersion polymerization and lead to polydisperse particles. Another drawback of dispersion polymerization deals with the low solubility of the dye in the medium, which can provide particles with low dye content. Thus, it is relevant to separate the particle formation stage from the chemical incorporation of the dye. To overcome most of these problems, the grafting of dyes onto particle surface is a valuable alternative method to covalently link chromophores to the particles. Still, using this approach, suitable scaffolds and custom designed dyes have to be synthesized.

One of the most versatile class of monomers are the cyclic imino ethers, also known as 2-oxazolines. The cationic ring-opening

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polymerization of 2-oxazolines is the most intensive studied mechanism. This living polymerization method allows copolymerization of a variety of 2-oxazoline monomers to give a range of tunable polymer properties that enables the obtaining of hard and soft [14] materials. Their potential use as biomaterials [15,16], bio-based surfactants [17] and thermoresponsive materials [18–20], as well as the easy access to defined amphiphilic structures for (hierarchical) self-assembly has opened a new "era" for cyclic imino ethers [21–23]. Oxazoline interest is proved also by the large number of reviews written in the last 10 years [14,24–27].

From the organic chemistry point of view the oxazoline ring can give hydrolysis, oxidation and addition reactions with organic acids, phenols, thiols or anilines [27]. Due to this variety of reactions, 2-oxazolines with dual functionality, which can undergo both radical and cationic polymerization, were early introduced by Kagiya and co-workers [28,29] with his original cyclic imino ether bearing an isopropenyl substituent attached in the 2-position of the oxazoline ring.

Polymers of 2-isopropenyl-2-oxazoline and its copolymers with methyl methacrylate or styrene, obtained through radical mechanism were reported in the literature [30–34]. However the use of oxazoline in radical dispersion polymerization is limited and has not been thoroughly investigated. There is only one paper dealing with the synthesis of oxazoline-functional particles, using 2-(5-methacryloyl-pentyl)-1,3-oxazoline as monomer [35]. As far as our knowledge goes, the use of 2-isopropenyl-2-oxazoline in nonaqueous dispersion polymerization has not been reported in the literature. 2-Isopropenyl-2-oxazoline is a commercial monomer and its synthesis process is not as laborious as 2-(5-methacryloyl-pentyl)-1,3-oxazoline. Addition reactions of poly(2-isopropenyl-2-oxazoline) with carboxylic acids or thiols yielding poly(ester-amide)s and poly(thio-ester-amide)s, respectively, provide effective modification of the substrate, when working at elevated temperatures [27,30,36]. These features underline the usefulness of the 2-isopropenyl-2-oxazoline (co)polymers in the synthesis of various polymeric structures if the modifying agent has a suitable acid group. In a recent paper [37], we described a new strategy for the synthesis of fluorescent polymers starting from oxazoline scaffolds. A proper azobenzene fluorescent dye with designed functions was used, namely 4-(4-hydroxy-phenylazo)benzoic acid.

The objective of this work is the synthesis of cross-linked coloured polymer particles with fluorescent properties. Consequently, we proposed a synthetic strategy which involves two steps. In the first step we synthesized highly cross-linked poly(methyl methacrylate–2-isopropenyl-2-oxazoline) particles by conventional nonaqueous dispersion polymerization. In the second stage we used the effective reaction of oxazoline with carboxylic acids to graft the fluorescent azobenzene dye onto the particles.

2. Experimental

2.1. Materials

1,4-Butanediol dimethacrylate (BDDMA, Merck, 99%), diethylene glycol dimethyl ether (DIGLYM, Aldrich, 99.5%), tetrahydrofuran (THF, Merck, 99%) and *n*-heptane (Merck) were used as such. 2-Isopropenyl-2-oxazoline (IPRO, Aldrich, 99%) and methyl methacrylate (MMA, Merck, 99%) were purified by low pressure distillation. 2,2′-Azobis(2-methylpropionitrile) (AIBN, Aldrich) was recrystallized from ethanol prior to use.

The stabilizer, Sol-TH-2312, supplied by ENI Polimeri Europa, is a polystyrene-*b*-poly(ethene-alt-propene)-*b*-polystyrene with a polystyrene content of 28% and the number-average molecular weight of 78,000 Da. The azo-dye used, C_0, 4-(4-hydroxy-3,5-dimethylphenylazo)benzoic acid was in-house synthesized as earlier reported [37], with a purity better than 99% checked by LC–MS.

2.2. Physico-chemical characterization

2.2.1. General measurements

Fourier transform infrared analysis: FTIR spectroscopy was performed on Bruker Vertex 70 spectrometer fitted with a Harrick MVP2 diamond ATR device at room temperature.

Nuclear magnetic spectroscopy: ^{1}H NMR spectra were recorded on a Varian Unity Inova 400 spectrometer in $CDCl_3$, at 30 °C.

Elemental analysis: The elemental analysis was carried out on a Costech ECS 4010 CHNS analyzer.

Thermogravimetric analysis: The thermal analysis (simultaneous TGA–DSC, MS hyphenated) was performed on a NETZSCH STA 449C Jupiter system, coupled to an Aeolos II MS detector. TGA–DSC scans were typically carried out, for all the samples, from ambient temperature up to 700 °C at a heating rate of 5 °C/min under helium gas flow.

Dynamic light scattering analysis: Particle diameters and size distributions were measured on a Malvern Instruments, Zetasizer Nanoparticle analyzer Nano ZS, model ZEN3600 apparatus equipped with a He–Ne laser operating at 633 nm. The DLS measurements were made on diluted dispersions in THF.

Scanning electron microscopy: Particle morphologies were observed with a scanning electron microscope QUANTA INSPECT F at 30 kV accelerating voltage. The samples were prepared by dispersing small amounts of polymer powder on a conductive adhesive foil.

Transmission electron microscopy: The samples were prepared by spraying diluted dispersions onto carbon-coated copper grids and were analyzed with a TECNAI F30 G^2 high resolution transmission electron microscope operated at an accelerating voltage of 300 kV.

Fluorescence spectroscopy: Steady-state fluorescence measurements were carried out on an Edinburgh Instruments FLSP920P spectrofluorimeter. Excitation was set at 380 nm monitoring the emission from 400 to 550 nm.

2.2.2. Theory section

Quantitative infrared spectroscopy can provide certain advantages over other analytical techniques. This approach may be used for the analysis of one component of a mixture, especially when the compounds in the mixture are chemically alike or have very similar physical properties (for example, structural isomers).

The absorbance *A* of a vibration in infrared spectroscopy is given by equation:

$$A = \varepsilon c l \tag{1}$$

From the Lambert–Beer law, Eq. (1), where ε is the molar absorptivity, l the sample thickness and c the concentration, one can see that in the same spectrum, the ratio of the absorbance of the signals does not depend on the film thickness:

$$\frac{A_1}{A_2} = \frac{\varepsilon_1 c_1 l_1}{\varepsilon_2 c_2 l_2} = \frac{\varepsilon_1 c_1}{\varepsilon_2 c_2} \tag{2}$$

In a copolymer system, the sum of molar ratios is equal to one:

$$x_1 + x_2 = 1 \tag{3}$$

Therefore, the ratio of the absorbances is,

$$\frac{A_1}{A_2} = \frac{\varepsilon_1 x_1}{\varepsilon_2 x_2} = \frac{\varepsilon_1}{\varepsilon_2}\left(\frac{x_1}{1 - x_1}\right) = k\left(\frac{x_1}{1 - x_1}\right) \tag{4}$$

where k is a constant given by the molar absorptivities,

$$k = \frac{\varepsilon_1}{\varepsilon_2} \tag{5}$$