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Current trends in redox polymers for energy and medicine

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ABSTRACT

Polymers with redox properties are electroactive macromolecules containing localized sites or groups that can be oxidized (loss of electrons) and reduced (gain of electrons). This review highlights trends in the chemistry, characterization and application of polymers with redox properties. In the first part, we overview the synthetic advances in the design of innovative redox polymers. Special attention is given to state-of-art techniques for the characterization of redox polymers and their important properties are also explained. The last part is devoted to the redox polymers applied in energy and medicine. First, the main redox polymers investigated in energy technologies such as batteries, supercapacitors, solar cells, biofuel cells or thermoelectric cells are reviewed. Second, the emerging applications of redox polymers in medicine technologies such as drug delivery, biosensors, actuators or smart surfaces are explained in detail.

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1. Introduction

Polymers with redox properties are electroactive macromolecules containing localized sites or groups that can be oxidized (loss of electrons) and reduced (gain of electrons). Redox polymers are defined by IUPAC as polymers containing groups that can be reversibly reduced or oxidized. Redox reactions can take place in a polymer side-chain, as in the case of a polymer carrying ferrocene functional group. However, the redox process may also take place in the polymer main-chain, as in the case of conjugated electrically conducting polymers, such as polyaniline [1].

A redox process may be associated with changes in the properties of the polymeric material. Thus, depending on their oxidation state (oxidized or reduced) the polymer usually presents different chemical, electronic, optical or mechanical properties. Due to the reversibility and easy external control of the redox process, these polymers are interesting targets for different applications and for the design of a number of electrochemical devices such as batteries, electrochromic devices, optoelectronic devices, biosensors or biofuel cells. Furthermore, these polymers are finding new applications in medicine, for example, on the development of new types of actuators and drug delivery vehicles. Redox polymers are also very attractive materials for electrochromics and electroluminescence devices or organic solar cells due to their optoelectronic properties [2–4]. However, these developments in optoelectronic polymers are not included on this review. Usually polymers applied in optoelectronic devices are not known as redox polymers but by other names, such as electroluminescent or electrochromic polymers.

Thus, this review article highlights the trends in the chemistry, characterization and application of polymers with redox properties. The first part, presents the synthetic advances in the design of innovative redox polymers and the state-of-art techniques to characterize redox polymers. The second part is devoted to redox polymers applications in energy and medicine. The main polymer families used in each application and their role in energy devices such as batteries, supercapacitors, solar cells, biofuel cells or thermoelectric cells or medicine technologies such as drug delivery, biosensors, actuators or smart surfaces are explained in detail. The goal of this review is to present the most recent developments of redox polymers including the most recent literature to give a better understanding of each particular redox polymer or application.

2. Synthesis of new redox polymers

Redox polymers emerged in the early 1980s as a new type of electroactive polymers. Initial chemical structures were based in ferrocene containing polymers or conducting polymer backbones such as polyacetylene. Currently, redox polymers constitute a wide variety of chemical structures, including different conjugated polymer backbones and/or electroactive organic or inorganic/organometallic moieties. Redox polymers have been historically classified using three criteria: (i) the redox center in the polymer backbone or as a pendant group, (ii) the nature of polymer backbone, conjugated/semi-conducting or non-conjugated and (iii) the redox center being organic or inorganic. Because of the large variety of redox polymers that have been developed, these classifications always included exceptions and hybrid forms.

In this review, we classify the redox polymers using a simplistic view on the chemical nature of the redox center. First, we focus on polymers having fully organic redox centers (formed by C, H, N, O, P and S), followed by a description of recent polymers with organometallic or with alternative atoms in the redox moiety. Next, we present examples of the most recent advances of both redox polymer families.

2.1. Redox polymers with electroactive organic redox couples

Redox polymers, including organic chemical groups such as nitroxyl, verdazyl, phenoxyl, carbazol, quinones, viologens, or hydrazyl have been actively pursued by the scientific community in the last years. Concerning the nitroxyl group, Nishide and coworkers were pioneers on developing polymers containing stable nitroxide radicals such as 2,2,6,6-tetramethyl-1-piperidinyloxy, free radical (TEMPO) moieties [5,6]. A variety of redox polymers with nitroxide pendant groups have been synthesized that are good candidates for organic batteries and supercapacitors due to their fast electron transfer kinetics (Fig. 1, **polymer 1**) [7]. New block copolymers containing nitroxide radicals and charge-compensating ions, have been reported that have organic resistive memory properties (**polymer 2**) [8]. Other block copolymers containing nitroxide stable radical such as TEMPO as pendant group in one of their blocks were developed by Gohy and co-workers for the formation of organic cathodes [9]. Aydin et al. went further ahead and synthesized a TEMPO-thiophene functional polymer. This polymer showed a combined effect between the redox