

Investigation on thermal, rheological, dielectric and spectroscopic properties of a polymer containing pendant spiroacetal moieties



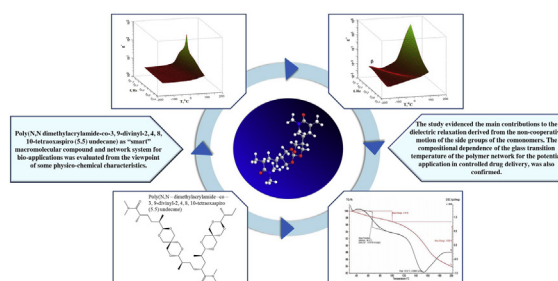
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HIGHLIGHTS

- In depth investigation on poly(*N,N* dimethylacrylamide-co-3, 9-divinyl-2, 4, 8, 10-tetraoxaspiro (5.5) undecane) copolymer.
- The study evaluates the physico-chemical characteristics of the copolymer.
- DSC indicated a single glass transition temperature for the studied copolymer.
- The rheological studies confirmed the non-Newtonian shear-thinning fluid behavior of the copolymer solution.
- The main contribution to dielectric relaxation derived from the non-cooperative motion of the side groups.

GRAPHICAL ABSTRACT



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ABSTRACT

The synthesis of “smart” molecules is in current areas of research as their specific functions can significantly improve the performance in various applications. This study is devoted to the investigation of poly(*N,N* dimethylacrylamide-co-3, 9-divinyl-2, 4, 8, 10-tetraoxaspiro (5.5) undecane) as “smart” macromolecular compound in order to evaluate the physico-chemical characteristics in terms of molecular weight, temperature-sensitive abilities, thermal stability, as well as its rheological, dielectric and spectroscopic properties. Differential scanning calorimetry investigation on the studied copolymer indicated a single glass transition temperature, while the rheological studies (rotational tests) confirmed a non-Newtonian shear-thinning fluid behavior of the copolymer solution. Dielectric properties of the copolymer have been evaluated in order to investigate the relaxation processes. It was found that the main contribution to dielectric relaxation derived from the non-cooperative motion of the side groups. The thermosensitive character was evidenced by the modification of the hydrodynamic radius of the macromolecular chains particles, which were estimated by dynamic light scattering technique. The fluorescence spectroscopy confirmed the structure of the copolymer, the spiroacetal moiety getting an axial conformation which is more stable, has lower energy and is more capable of making specific

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interactions with solvents, phenomena underlined by different shapes of the emission spectra of the copolymer.

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1. Introduction

Development of new and increasingly tailored materials is the key to further advance important applications. In this context, the macromolecular compounds, with their huge potential derived from countless basic structures and the corresponding derivatives, constitute an inexhaustible source [1]. The biodegradable and biocompatible materials with stimuli-responsive characteristics are representing as well a class of interest with paramount importance especially for bio-applications [2]. In this context, the design of “smart” macromolecular systems with stimuli-sensitive abilities is of growing importance. Also, one of the main objectives of polymers research is to study the relationship between the chemical and physical structure and physical properties of polymers which are revealing the acquired abilities [3]. At the same time, the in-depth characterization and comprehensive evaluation of the new compounds contributes not only to understand their properties, capabilities and use in appropriate conditions, but also, to the development of the area of their use and applications. Thus, a proper and deep characterization will highlight the macromolecular compounds specificity in the field they will be used, as well as the effect and influence of different stimuli (temperature, pH, etc.) upon the properties of the compounds, or for example the swelling ability in various conditions in the case of smart gels. One particular monomer that has received much attention last years is *N,N*-dimethylacrylamide (DMA), which can be polymerized into a highly hydrophilic and biocompatible compounds [4]. DMA can be also, copolymerized with hydrophobic monomers, when some properties can be tailored, as for example the glass transition temperature, sorption and desorption kinetics of the synthesized gels in relation with the structure of the new compounds, respectively the concentration of the hydrophobic comonomer. At the same time, hydrophilic/hydrophobic systems are used for controlling the diffusion of both large and small drug molecules, practically to adjust these systems to exhibit zero-order, first-order, or bimodal release. For example literature mention the use of amphiphilic diblock copolymer of DMA with poly(ethylene-*alt* propylene) to form solution state assemblies to be used for bioapplications. Thus, good dissolution profiles for probucol and phenytoin were obtained when spray dried with hydrophilic polymers, poly(*N,N*-dimethylacrylamide-*grad*-methacrylamido glucopyranose) and poly(dimethyl-acrylamide) (PDMA).

In previous studies polymers based on DMA and 3, 9-divinyl-2, 4, 8, 10-tetraoxaspiro (5.5) undecane (U) have been investigated. Their synthesis through radical polymerization procedure, the antioxidant and biocompatible character of the polymer, as well as the carrier ability of the polymeric network, were presented [5–7]. Other properties of these macromolecular compounds such as gel formation capacity, binding properties, amphiphilicity, good oxidative and thermal stability, formers of good films, sensibility to pH and temperature, were also put into evidence. DMA-based hydrogels are known as highly hydrophilic and biocompatible, but copolymerization of DMA with hydrophobic monomers could lead to thermally responsive matrix able to fulfill specific functions [8,9]. In particular, the incorporation of spiroacetal groups into the polymer structure could improve the adhesive properties and ensure intramolecular strategies for coupling of various compounds

[10,11]. Thus, the interest for the copolymers based on these comonomers is thoroughly justified taking into consideration the special properties that they confer.

However, a great attention concerning their physical-chemical characteristics must be devoted and more-in-depth studies are needed in order to fully exploit their potential. In this regard, this study evaluates the physicochemical characteristics of poly(*N,N*-dimethyl- acrylamide-co-3, 9-divinyl-2, 4, 8, 10-tetraoxaspiro (5.5) undecane) (PDMA_U) in terms of temperature-sensitive abilities, thermal stability, rheological, spectroscopic and dielectric properties, as well as the contact angle of the films, for bringing useful information for further specific use of these compounds.

2. Materials and methods

2.1. Materials and polymerization process

The monomers – *N,N*-dimethylacrylamide (DMA) and 3, 9 -divinyl-2, 4, 8, 10-tetraoxaspiro[5.5] undecane – (U) – were supplied by Aldrich Chemical Co. and were used without further purification as well as the solvent (*N,N*-dimethylacetamide, DMAc, from Sigma-Aldrich). Dibenzoyl peroxide (BPO, from Sigma-Aldrich) was dissolved in chloroform and then precipitated with methanol for recrystallization. The water used in all experiments was purified using an Ultra Clear TWF UV System. The synthesis of P(DMA_U) was described previously, in detail [5]. Shortly the copolymer was synthesized by radical polymerization process using BPO as initiator, DMAc as solvent, under nitrogen atmosphere, at 75 °C for 6 h, and at 80 °C for other 2 h as thermal treatment; the reaction was performed in a constant temperature bath, with a stirring rate of 250 rpm. A typical recipe for 100 ml copolymer solution preparation is presented in Table 1. After synthesis the copolymer was precipitated several times with diethyl ether, dried in a vacuum oven and finally freeze-dried by lyophilization for 24 h. Copolymer samples were investigated as nanoparticles, in solution or films.

2.2. Methods

2.2.1. Molecular weight evaluation

The molecular weight and the second virial coefficient (A_2) of the synthesized copolymer were evaluated using a Zetasizer NanoS system that provides a method for measuring the molecular weight of the polymers at only an angle (173°) by using Rayleigh equation (Eq. (1)) – a relationship between the intensity of the scattered light of macromolecules and their weight-average molecular weight (M_w). This examination was made just to confirm the suitability of the copolymer from the view point of the molecular weight for the further performed analysis and investigation [11]. The plot of KC/R_θ versus C was linear with the intercept equivalent to $1/M$ and the slope was equal to the second virial coefficient A_2 . The following relations (Rayleigh equation) were valid:

$$\frac{KC}{R_\theta} = \left(\frac{1}{M} + 2A_2C \right) P(\theta) \quad (1)$$

where

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