



# Influence of spacer group on the structure and thermal properties of copolymers based on acrylonitrile and methacrylic 1,3-thiazole and 1,2,3-triazole derivatives



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## ARTICLE INFO

### Article history:

Received 23 June 2015

Received in revised form 12 August 2015

Accepted 18 August 2015

Available online 20 August 2015

### Keywords:

Copolymers

Functional monomer

Structure

WAXS

Glass transition temperature

Thermal stability

## ABSTRACT

The influence of spacer group on the binomial relationship between the structure and thermal properties has been studied in different copolymeric families, considering the insertion either mono or bisheterocyclic pendant groups, as well as the ratio between comonomers. In consequence, six different copolymeric systems based on acrylonitrile and methacrylic monomers bearing 1,3-thiazole and 1,2,3-triazole pendant groups, P(AN-co-MTA), have been synthesized with different compositions by free-radical polymerization in anhydrous DMSO solution at 60 °C. These copolymers have been analyzed by size exclusion chromatography (SEC), Elemental Analysis of CHNS, infrared spectroscopy (ATR-FTIR) and wide-angle X-ray diffraction (WAXS). The thermal behavior of copolymers has been also examined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Gordon–Taylor–Wood equation has been used to fit the glass transition temperature variation as a function of acrylonitrile weight molar fraction in the copolymer.

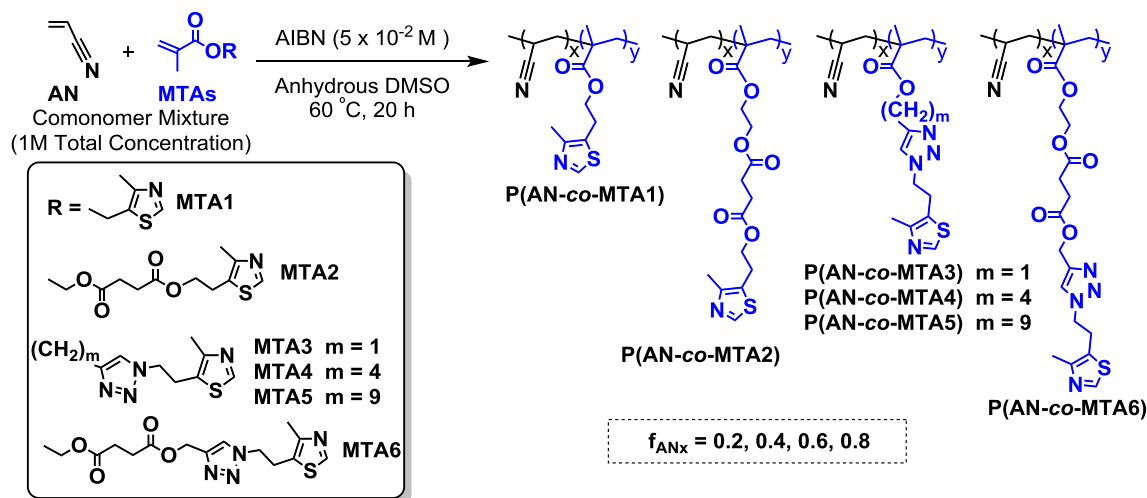
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## 1. Introduction

Polyacrylonitrile (PAN) and copolymers of PAN have been widely used in different applications, mainly in related to fiber technologies. Besides, PAN is used as precursors for producing carbon nanofibers because its high carbon yields [1]. By doping polyacrylonitrile prior to carbonization the physicochemical nature of the polymer under thermal treatment can also be altered [2]. Moreover, the increasing interest in electrospinning process [3] has made of PAN one of polymers more extensively used, especially in the field of carbon nanofibers [4–6] but also in the antimicrobial polymers [1,7–11]. Biaxially oriented PAN films have been described also as good barriers to oxygen since their transmission is much better than that of any other commonly used transparent film, while are also a good moisture barriers [12]. In addition, these present excellent stiffness, high temperature dimensional stability and heat resistance, as well as having good clarity and gloss, and excellent chemical resistance [13,14]. However, PAN has not been commercialized in packaging due to its inability to be melt before that it degrades. Likewise and because of its sufficient chemical stability, PAN is also used in membrane technology for ultra- and microfiltration applications [15–17]. However, these membranes present a serious problem when they are dried, because they became so brittle that could not be bent without breaking. In fact, the moisture entrapped in PAN materials is a plasticizer, although at temperatures above 185 °C dissolves them [18]. In addition, PAN is a semicrystalline polymer with the crystalline melting point at about 300 °C, which also present exhibits thermoreversible gelation in various solvents

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Scheme 1. Synthesis of P(AN<sub>x</sub>-co-MTA<sub>y</sub>) random copolymers.

[19]. Accordingly, it is pursued the utilization of different approaches that can disrupt the long range order and can allow the melt processing to occur at lower temperatures, e.g. 100 °C above the glass transition temperature [20].

On the other hand, it is well-known that the incorporation of flexible pendant groups on the main polymer chain is one of the most effective methods to adjust the glass transition temperature ( $T_g$ ) of polymers. Then, copolymerization reaction is one of the most general and straightforward alternatives to modulate the  $T_g$ . Depending on the nature of monomers the variation can be considerable. In this sense, the final mechanical and thermal properties, which depend on the structure-morphology of PAN, are crucial and limiting factors to manufacture it. Consequently, the aim of this work has been the modulation of acrylonitrile characteristics by copolymerization with functional monomers to further use as active systems. Then, six random copolymeric families based on acrylonitrile (AN) and methacrylic monomers with 1,3-thiazole and 1,2,3-triazole pendant groups (MTAs) have been synthesized by conventional radical polymerization. MTA comonomers have been selected to introduce flexibility to PAN and also to give additional antimicrobial functionality in further quaternization reactions. The composition analysis of each series has been performed by Elemental Analysis of CHNS. The incorporation of MTA into the copolymer chain has been followed by Size Exclusion Chromatography (SEC) and by Infrared Spectroscopy using Attenuated Total Reflectance (ATR-FTIR). In addition, the thermal behavior in terms of glass transition and decomposition temperatures has been studied by Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). Finally, taking into account the MTA comonomer structure, the relationship between the structure and the properties of copolymers has been elucidated.

## 2. Experimental

### 2.1. Materials and instrumentation

2,2'-Azobisisobutyronitrile (AIBN, 98%; Acros) was recrystallized twice from methanol (MeOH, 99.9%; Aldrich) prior to use. Acrylonitrile (AN, 99.0%; Aldrich) was distilled prior to use. Anhydrous dimethyl sulfoxide (DMSO, 99.8%) was purchased from Alfa-Aesar and was used as received. Infrared (IR) spectra were recorded on a Perkin Elmer RX-1 instrument with Universal Attenuated Total Reflectance (ATR) Sampling Accessory module and absorptions are given in wavenumbers ( $\text{cm}^{-1}$ ). The number-average molecular weight ( $M_n$ ), weight-average molecular weight ( $M_w$ ) and polydispersity index (PDI) of polymers were measured by Size Exclusion Chromatography (SEC) with a chromatographic system (Waters Division Millipore) equipped with a Waters model 410 refractive-index detector. N,N-dimethylformamide (99.9%; Aldrich) containing 0.1% of LiBr (99.9%, Aldrich), was used as the eluent at a flow rate of 1 mL/min at 50 °C. Styragel packed columns (HR2, HR3, and HR4, Waters Division Millipore) were used. Poly(methyl methacrylate) standards (Polymer Laboratories, Laboratories, Ltd.) ranging from  $2.4 \times 10^6$  to  $9.7 \times 10^2$  g/mol were used to calibrate the columns. Elemental microanalyses were made with a Carlo Erba EA1108 elemental analyzer. Glass transition temperatures ( $T_g$ ) of the copolymers were measured by differential scanning calorimetry (DSC) using a TA Q2000 instrument equipped with an intercooler for low temperatures. The samples were equilibrated at  $-70$  °C and heated to 120 °C, then cooled to  $-70$  °C and again heated to 120 °C in all the runs at 10 °C/min under dry nitrogen (50  $\text{cm}^3/\text{min}$ ). Thermogravimetric analysis (TGA) of copolymers was performed in  $\text{N}_2$  using a TA Instruments, TGA Q500 equipment. The instrument was calibrated both for temperature and weight by standard methods. Non-isothermal experiments were performed in the temperature range 40–800 °C and at heating rate of 10 °C/min. The average sample size was ca. 4–5 mg and the dry nitrogen flow rate was 20  $\text{cm}^3/\text{min}$ . Wide-angle X-ray diffraction (WAXS)

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