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Synthesis and thermal characterization of xylan-*graft*-polyacrylonitrile

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ABSTRACT

In this study emulsion polymerization of acrylonitrile using xylan from agricultural waste material (corn cob) and cerium ammonium nitrate was investigated in terms of catalyst acid. Stock ceric solutions were prepared using either nitric or perchloric acid as catalyst. Optimum conditions were determined using different parameters such as reaction time, temperature, and component concentrations. Nitric acid catalyzed reactions resulted in maximum conversion ratio (96%) at 50 °C, 1 h where ceric ion, acrylonitrile, xylan, and catalyst concentrations were 21.7 mmol l^{-1}, 0.5 mol l^{-1}, 0.2% (w/v), and 0.1 mol l^{-1}, respectively. However, 83% conversion was obtained with perchloric acid catalysis at 27 °C, 1 h where concentrations were 5.4 mmol l^{-1}, 0.8 mol l^{-1}, 0.5% (w/v), and 0.2 mol l^{-1}, respectively. Copolymer synthesis using perchloric acid was realized at milder conditions than using nitric acid. Thermal analyses of obtained polymers were conducted to characterize copolymers. Results showed that calculated activation energy, maximum degradation temperature, and heat of thermal decomposition changed relying mainly on molecular weight.

1. Introduction

Xylan, which is a naturally occurring polysaccharide, is composed of neutral sugars (mainly xylose and arabinose) and small portions of uronic acid (glucuronic acid and 4-*O*-methyl derivative). It can be extracted from wastes of annual crops (e.g. corn cobs and wheat straw) under oxidizing alkaline conditions (Doner & Hicks, 1997; Ebringerová, Hromádková, Alföldi, & Hribalová, 1998; Sun, Tomkinson, Geng, & Wang, 2000; Xiao, Sun, & Sun, 2001). More than 25% corn cobs' dry weight consist of xylan, and this occurrence makes the corn cobs one of the the main resources. Xylan can find application in fields including thickener (Doner & Hicks, 1997), additive to plastics (due to increasing their stretch, breaking resistance, and makes them more susceptible to biodegradation) (Gáspár, Juhász, Szengyel, & Réczey, 2005). Ceric ions are versatile reagents which are used for oxidations of many organic functional groups (Nagarajan & Srinivasan, 1998; Pottenger & Johnson, 1970) and they can be used as redox initiators in aqueous solutions for copolymerization of vinyl monomers such as acrylonitrile and acrylamide (Atici, Akar, Ayar, & Mecit, 1999; Lutfor, Sidik, Haron, Rahman, & Ahmad, 2003; Mino & Kaizerman, 1958). Properties of the products are involved with the type of the reducing agent, temperature, catalyst type and concentration (Czappa, 1974). Radicals are produced from reducing agents (i.e. alcohol, polyol, ketone, aldehyde, amine, carboxylic acid, hydroxy acid, or amino acid) in several steps. Offered mechanisms show that a complex forms between reducing agent and Ce^{4+}, then this complex decomposes giving a free radical and Ce^{3+} in acidic medium. Formed radicals attack vinyl monomers to start a polymerization, if there are any, in reaction medium. Polysaccharides can also be employed as reducing agent for graft copolymerization (Galioğlu, Soydan, Akar, & Saraç, 1994; Khullar, 2008; Mishra, Clark, Vij, & Daswal, 2008; Pourjavadi & Zohuriaan-Mehr, 2002b); however, ceric ions can also lead to oxidation (Pottenger & Johnson, 1970). Equilibrium between oxidation and polymerization can be controlled via reaction conditions. Studies about polymerizations involved with xylan and ceric ion were mainly on the effect of component concentrations, oxygen presence, etc. (Mishra et al., 2008; Pourjavadi & Zohuriaan-Mehr, 2002a, 2002b); none of them was about the role of catalyst type on polymerization conditions.

This work mainly focuses on the effect of acid catalyst and thermal characterization of polyacrylonitrile copolymers. Effect of acid catalysts on redox polymerization was studied; initiator and reducing agent were ceric ammonium nitrate and xylan. Nitric acid (HNO_3) and perchloric acid ($HClO_4$) were used as catalysts in initiator solution. Optimum conditions for obtaining xylan-*graft*-polyacrylonitrile copolymers (X–PAN) were searched for maximum conversion. Obtained copolymers were characterized using viscometric, spectral, and thermal methods. Thermal characterizations of obtained copolymers were also done in terms of activation energy of decomposition and heat of decomposition.

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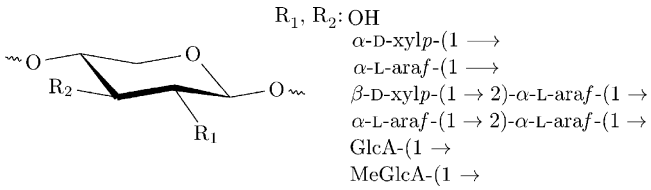


Scheme 1. Simplified representation of xylan.

2. Experimental

2.1. Materials and methods

Corn cobs were collected locally from Adapazarı, Turkey, and xylan was extracted from these corn cobs via alkaline peroxide treatment using procedure described elsewhere (Ünlü, Günister, & Atıcı, 2009). Acrylonitrile monomer, ceric ammonium nitrate (CAN), nitric acid (65%, 1.40 g ml^{-1}), and perchloric acid (70%, 1.67 g ml^{-1}) were Merck brand, and were used as received.

FTIR spectra were recorded on Thermo Nicolet 380 in 4000–400 cm^{-1} region, using KBr pellets with 1% (w/w) sample concentration.

Molecular weight measurements of X–PAN copolymers were done using capillary viscometry. Relative viscosity of the samples was measured using Ubbelohde Typ I viscometer, and sequential dilutions were performed for different concentrations. Intrinsic viscosity values were calculated via Solomon–Ciuță equation for each point (Pamies, Cifre, del Carmen López Martínez, & de la Torre, 2008; Solomon & Ciuță, 1962), where $[\eta]$, η_{sp}, η_{rel}, and C were intrinsic viscosity (dl g^{-1}), specific viscosity, relative viscosity, and concentration (g dl^{-1}).

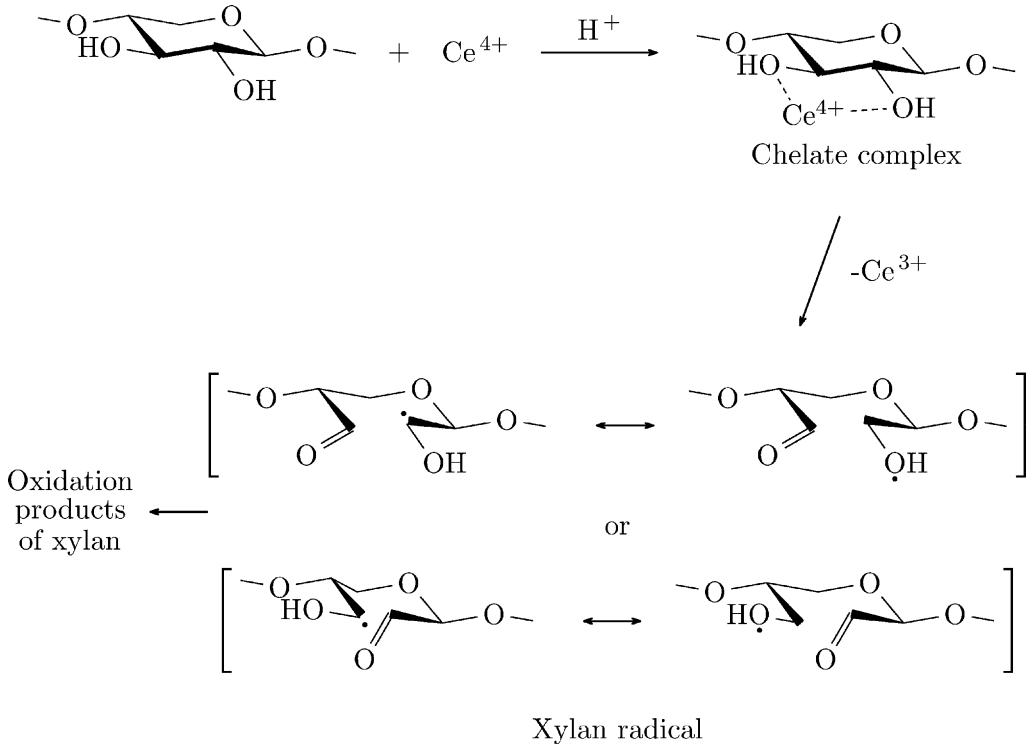
$$[\eta] = \frac{\sqrt{2 \cdot (\eta_{sp} - \ln \eta_{rel})}}{C}$$

Molecular weight (M_V) determination of obtained copolymers was done using intrinsic viscosity and Mark–Houwink equation for polyacrylonitrile ($[\eta] = 3.35 \times 10^{-4} M_V^{0.72}$) in DMF at 30 °C (Shibukawa, Sone, Uchida, & Iwahori, 1968).

Differential scanning calorimetry (DSC) measurements were performed under N_2 atmosphere on TA Instruments Q10 model DSC. Samples were first heated to 130 °C to evaporate adsorbed water, then cooled to −50 °C and reheated to 400 °C; heating (cooling) rate was 10 °C min^{-1}. Heat of decomposition was calculated using area under curve from plot of heatflow (W g^{-1}) versus time (s). Thermogravimetric analyses (TGA) were done with TA Instruments Q50 heating samples from ambient temperature to 700 °C with a rate of 10 °C min^{-1}. Activation energy of decomposition was calculated using TGA data following Broido's method (Broido, 1969). Calculations were carried out using Python 2.7 with NumPy and SciPy modules.

2.2. Polymerization of acrylonitrile

Xylan was dissolved in water and solution was stirred at reaction temperature for 30 min. Then acrylonitrile was added to the solution and stirred for an additional 15 min. Polymerization was initiated with dropwise addition of stock ceric solution in 10 min. After 1-h polymerization, reaction was stopped by pouring the mixture into 500 ml water. Obtained copolymer was washed first with



Scheme 2. Reaction mechanism of oxidation of carbohydrates with ceric ion.