



## Controlled cationic polymerization of furfuryl alcohol



Halil Ünver, Zeki Öktem\*

Department of Chemistry, Faculty of Arts and Sciences, Kırıkkale University, 71450 Yahşihan, Kırıkkale, Turkey

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### ABSTRACT

CuCl/N,N,N',N'',N'''-pentamethyldiethylenetriamine catalyst system was used successfully in the controlled cationic polymerization of furfuryl alcohol initiated with benzyl bromide in acetonitrile. Polymerizations were carried out at 110 °C open to air. The effect of reaction time, amount of initiator and solvent on the rate of polymerization was studied. The linear kinetic plot of  $\ln([M]_0/[M])$  versus polymerization time, linear dependence of the molecular weight on the monomer conversion and low polydispersity of the polymers (1.07–1.50) showed the characteristics of the controlled polymerization. Soluble polymers with  $M_n$  up to 6.6 kg/mol were obtained. The structural analysis of the polymer was carried out by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, FTIR and UV–VIS spectroscopies. Formation of carbonyl groups and  $-\text{CH}_2-\text{O}-\text{CH}_2-$  bridges on poly(furfuryl alcohol) chains were observed. Thermal properties of the polymer were studied by DSC and TGA analyses.

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### 1. Introduction

Petroleum derived monomers are used extensively in many researches and developments related to polymer science and technology. Due to the environmental and economical concerns development of eco-friendly materials hence, the exploitation of renewable resources takes attention of the researchers. Furfural and 5-hydroxymethylfurfural, which are suitable starting materials for the preparation of several monomers, can be obtained economically from the hydrolysis of agricultural or forestry wastes containing pentoses in sufficient amounts [1–4]. Furan and its derivatives undergo cationic polymerization by both Lewis and Brønsted acids to produce low molecular weight branched products [2–6]. The reaction of furan and its derivatives with strong nucleophiles produces a mixture of low molecular weight products due to the ring opening and uncontrolled addition reactions. Therefore, only few monomers could be polymerized anionically in

special conditions [2–4]. Also, simple furans without an external polymerizable functional group are incapable of radical homopolymerizing and they are not good comonomers for radical copolymerization. Due to the resonance stabilization of the formed furyl radicals, either coupling or hydrogen abstraction reactions take place rather than propagation. Even though, radical polymerization and copolymerization of some furanic monomers with highly electron donating comonomers have been reported [2–4,7,8].

Furfural can be reduced into furfuryl alcohol (FA) by simple reduction processes. FA has been polymerized by several organic, mineral and Lewis acids [9–14]. The acid catalyzed polymerization of FA inevitably leads to a black, crosslinked product. Many studies have been carried out in order to clarify the mechanism of coloration and crosslinking. It was concluded that hydrogen atoms of the methylene bridges between two furan rings play essential role in favoring the side reactions related to color formation and crosslinking of chains [1–3,10–12]. Poly(furfuryl alcohol) (PFA) as a crosslinked thermosetting polymer, has found applications in metal-casting cores and molds, graphitic electrodes from carbonaceous products, coating for corrosion resistance, wood adhesives and binders, polymer

\* Corresponding author. Tel.: +90 318 3572840x4081; fax: +90 318 3572461.

E-mail address: [zoktem@kku.edu.tr](mailto:zoktem@kku.edu.tr) (Z. Öktem).

concretes, materials possessing low flammability and low smoke release and synthesis of nanoporous carbons, and polymer nanocomposites [3,13–17].

Controlled/living polymerization is characterized by the absence of significant chain transfer or irreversible chain termination reactions and it provides control over the molecular weight and architecture of the polymer produced [18]. HI/I<sub>2</sub> is the first system used for the controlled cationic polymerization of vinyl ethers [19]. Since then, many systems have been developed for the controlled cationic polymerization of several cationically polymerizable monomers [20–23]. To the best of our knowledge, controlled cationic polymerization of FA has not yet been reported. In this paper, we describe the controlled cationic polymerization of FA with CuCl/PMDETA as the catalyst and benzyl bromide as the initiator in acetonitrile at 110 °C. The effect of initiator concentration and polymerization time on the polymerization of FA, kinetic analysis of the controlled polymerization and characterization of PFA are reported.

## 2. Experimental

### 2.1. Materials

Furfuryl alcohol (FA) (98%), N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA) (98%), copper(I) chloride (98%), benzyl bromide (BzBr) (98%) and analytical grade benzoyl peroxide (BPO) were purchased from Merck. Dicumyl peroxide (DCP) (97%) was the product of Fluka and acetonitrile (AN) (99.9%) of Sigma. All of the reagents and solvents were used as received.

### 2.2. Polymerization

The catalyst was prepared by mixing 19.8 mg (0.20 mmol) CuCl with 0.042 ml (0.20 mmol) of PMDETA in 2.0–10.0 mL of acetonitrile. The mixture was stirred for 30 min at room temperature and then filtered. The undissolved CuCl was dried under vacuum. The amount of dissolved CuCl was calculated from the weighed amount of undissolved CuCl. Polymerization solution was prepared by adding FA (2.0 mL, 22.7 mmol) and benzyl bromide (0.015–0.027 mL, 0.08–0.20 mmol) into the homogenous acetonitrile solution of CuCl/PMDETA. Polymerization was carried out at 110 °C under a reflux condenser. Obtained polymer was precipitated in plenty of water and dried under vacuum. Conversion was calculated from the amount of the obtained polymer. Preparation of the catalyst and polymerizations were all carried out open to air.

### 2.3. Characterization

FTIR spectroscopic characterization of the samples was carried out on a Jasco, FTIR-480 Plus FTIR spectrometer using films prepared on KBr pellets. <sup>1</sup>H and <sup>13</sup>C NMR spectra of the polymer were recorded in DMSO using a Bruker Spectrospin Avance DPX-400 spectrometer. DSC and TGA measurements were carried out on TA Q2000 and Q500 instruments under nitrogen atmosphere with a heating

rate of 5 and 10 °C/min, respectively. A Shimadzu 1800 UV–VIS spectrometer was used for the UV–VIS absorption spectrum of the polymer.

Number average molecular weight ( $M_n$ ) of the polymer samples in benzene was determined by cryoscopy. A vacuum jacketed system, equipped with a Beckmann thermometer was used. Cryoscopic constant was determined by using purified naphthalene. Reproducible freezing point was obtained by melting and freezing the solution for several times.  $M_n$  was calculated from the obtained linear  $\Delta T/c$  vs.  $c$  curve. Relative molecular weight and polydispersity of the polymers were measured on an Agilent 1100 Series GPC equipped with a refractive index detector. 0.01 M LiBr/DMF with toluene as flow marker, was used as eluent at 50 °C with a flow rate of 0.7 mL/min. Conventional calibration was applied with linear poly(methyl methacrylate) standards between 2500 and 270,000 g/mol.

## 3. Results and discussion

### 3.1. Optimization of polymerization conditions

Polymerization of furfuryl alcohol (FA) was carried out in acetonitrile (AN) at 110 °C using benzyl bromide (BzBr) as the initiator and CuCl/PMDETA as the catalyst. The system did not produce any polymeric product when the polymerization was carried out in benzene and xylene, and when the polymerization temperature was kept below 110 °C. A polymeric product was obtained from the polymerization carried out in AN at 110 °C, which also indicated the sufficient solubility of the catalyst in AN. Several solvent/monomer ratios ( $1:2 \leq \text{AN/FA} \leq 5:1$ , V/V) were used with 2 mL (23.0 mmol) FA, 0.042 mL (0.20 mmol) PMDETA and 0.024 mL (0.20 mmol) BzBr. The amount of dissolved CuCl increased with the increase in the volume of AN, and with the ratio  $\text{AN/FA} \geq 5:2$ , V/V, CuCl (19.8 mg, 0.20 mmol) dissolved completely. On the other hand, conversion to polymer decreased with the increase in the amount of dissolved CuCl (Fig. 1). High conversions, ca. 97–98%, were obtained with the solutions having ratios  $\text{AN/FA} \leq 1:1$ ,

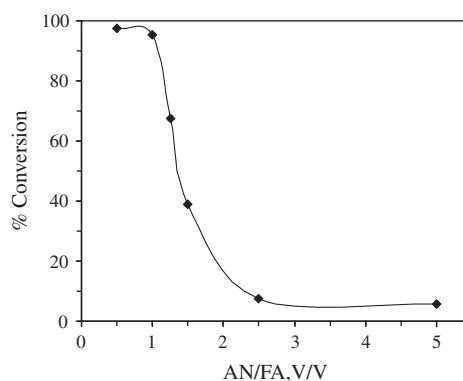


Fig. 1. Variation of % conversion with solvent/monomer ratio.  $V_{\text{FA}} = 2$  mL (23.0 mmol),  $V_{\text{PMDETA}} = 0.042$  mL (0.20 mmol),  $V_{\text{BzBr}} = 0.024$  mL (0.20 mmol),  $W_{\text{CuCl}} = 19.8$  mg (0.20 mmol).  $T = 110$  °C,  $t = 120$  min.

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