Polymers from renewable resources: synthesis and characterization of poly(2,5-dihydro-2,5-dimethoxy furan)

Hakan ÇİFTÇİ[2], **Zeki ÖKTEM**[1], **Hasan Nur TESTERECİ**[1,*]

[1]*Department of Chemistry, Faculty of Arts and Sciences, Kırıkkale University,*
TR-71100 Yahşihan, Kırıkkale-TURKEY
e-mail: hntestereci@kku.edu.tr
[2]*Department of Chemistry and Chemical Processing Technologies, Kırıkkale Vocational High School,*
Kırıkkale University, Kırıkkale-TURKEY

The cationic polymerization of cis, trans-2,5-dihydro-2,5-dimethoxy furan (DHMF) was studied in the presence of $HClO_4$, in acetonitrile. Different reaction parameters were investigated such as initiator concentration and temperature with duration. Obtained polymers were soluble in dimethylsulfoxide (DMSO) and dimethylformamide (DMF) and the M_n value was calculated as 2700 g/mol by cryoscopy. The FT-IR and ^{1}H-NMR results indicate that the polymerization proceeds via ring opening. Thermal properties were studied by DSC and TGA.

Key Words: 2,5-Dihydro-2,5-dimethoxyfuran, polyfuran, poly(2,5-dihydro-2,5-dimethoxy furan, cationic polymerization, ring opening

Introduction

Most of the research done concerning polymer science and technology has focused on petroleum-derived monomers. As the reserves of fossil raw materials were considered adequate, the availability of such materials was not called into question. However, it is now predicted that as we continue to rely so heavily on fossil raw materials a drastic depletion of the reserves will occur in the coming years. A lot of new research especially

---

*Corresponding author

on renewable natural products in polymer chemistry can be related directly to concern over supply and the escalating price of petrochemicals.[1−5]

Furan and its derivatives are among the renewable natural products that have attracted study. Researchers are now quite interested in the development of the chemistry of furanic materials, particularly for the preparation of nonpetroleum-derived polymeric materials like polyester, polyamide, and polyurethane.[6,7]

Furan derivatives can be prepared from saccharidic renewable resources. These derivatives are used in a number of chemical processes like dyes, fine chemicals, the synthesis of high value-added compounds for drugs, and the preparation of macromolecular materials possessing very specific mechanical, optical, electronic, photochemical, and ecological properties.[8]

Studies of the chemical and electrochemical polymerization of furan and some of its derivatives have been published in the literature. The chemical polymerization of furan and furan derivatives was overviewed by Gandini.[9] Xue et al.[10] reported on the electrochemical polymerization of furan at low potential (1.2 V) in boron trifluoride-ethyl ether and in the ethyl ether binary solvent system. Önal et al.[11] investigated the electrochemical polymerization of 2,5-di-(2-thienyl)-furan in ethanol solution containing 0.2 M LiClO$_4$ as the supporting electrolyte. Carlini et al.[12] investigated the chemical polymerization of furan in different oxidant and solvent systems. We have previously studied the electrochemical polymerization of 2,5-dihydro-2,5-dimethoxyfuran in our laboratory.[13]

In the present study, we examined the chemical polymerization, initiated by HClO$_4$, of 2,5-dihydro-2,5-dimethoxyfuran in acetonitrile. The characteristics of the resulting polymer were established using various experimental techniques.

Experimental

Chemicals

Cis, trans-2,5-dihydro-2,5-dimethoxy furan(DHMF, Merck) was formed from a mixture of cis and trans isomers. DHMF and HClO$_4$ (Merck) were used as received. The acetonitrile (AN) was purified by drying over CaH$_2$ followed by fractional distillation.

Synthesis of poly(DHMF)

DHMF, HClO$_4$, and acetonitrile were put in a round flask containing a magnetic stirrer and placed in a constant temperature bath. The color of the solution turned from yellow to brownish black at the beginning. After the desired reaction time, the solution was poured into water. The precipitated black solid product was filtered and washed successively with water and acetone and dried under a vacuum. It was soluble in dimethylsulfoxide (DMSO) and dimethylformamide (DMF). The yield was determined gravimetrically.

Characterization

The ^{1}H-NMR spectra of the polymers were recorded by a Bruker Instrument-NMR Spectrometer (DPX-400) in DMSO. The FT-IR spectra of the polymers were obtained on a Jasco 480 Plus FTIR Spectrometer using KBr

pellets. A Perkin Elmer Diamond DSC Pyris series instrument was used for DSC analysis. Thermogravimetric analysis (TGA) was carried out using a Dupont 910 model Thermogravimetric analyzer with a heating rate of 10 °C/min under nitrogen atmosphere. The cryoscopic method was used for the determination of molecular weight. A Beckmann thermometer was calibrated with sublimated naphthalene in DMSO. Scanning electron microscopy measurements of polymers were made using a JSM 5600 electron microscope.

Results and discussion

The effect of temperature on the rate of polymerization of DHMF was studied at 25, 60, and 80 °C. Plots of percentage conversion versus polymerization time for each temperature are given in Figure 1. The percentage and initial rate of reaction increased with increasing temperature. In particular, the results of increasing the temperature seem not to agree with the trend frequently observed for cationic polymerizations. A similar effect of temperature was observed in other works as well.[14]

The effect of $HClO_4$ concentration on polymer yield is shown in Figure 2. The polymer yield increased with the increase in $HClO_4$ concentration and then remained almost constant. An increase in $HClO_4$ concentration caused the formation of a higher amount of cationic species and caused an increase in polymer yields. Moreover, an increase in the quantity of cationic species caused a greater volume of an unprecipitable oily product. Hence, polymer yields remained constant at high $HClO_4$ concentration.
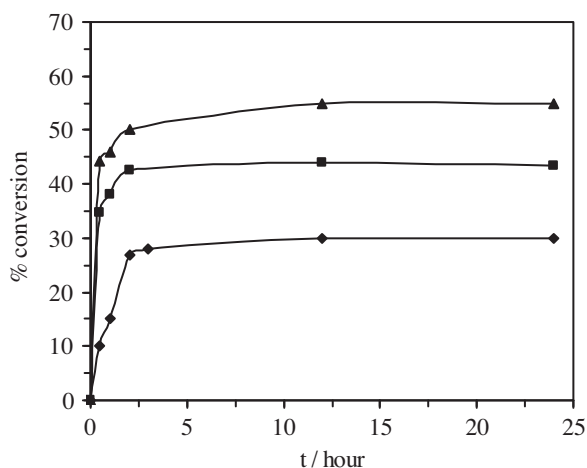
Figure 1. Effect of temperature on the rate of polymerization of DHMF. DHMF = 0.3 mol L^{-1}, $HClO_4$ = 0.02 mol L^{-1}. (▲) 80 °C, (■) 60 °C, (♦) 25 °C.
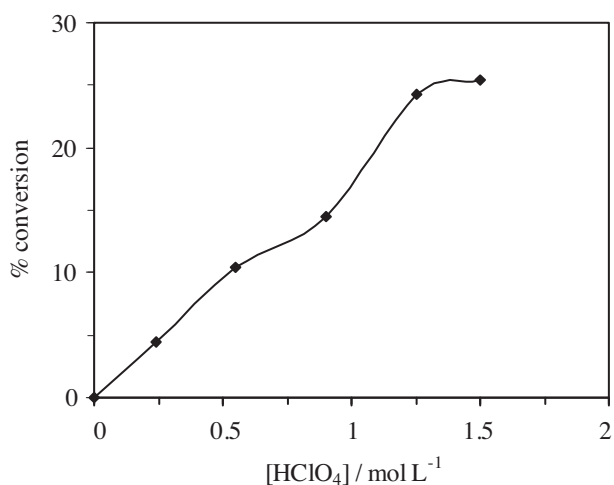
Figure 2. Effect of $HClO_4$ concentration on the rate of polymerization. DHMF = 0.3 mol L^{-1}, t = 12 h, T = 20 °C.

FT-IR Investigation

The infrared spectra of DHMF and polymer are given in Figure 3. Some of the bands in the spectrum of the monomer (Figure 3a) are retained in the spectra of the polymer (Figure 3b). The i.r. absorption spectrum of poly(DHMF) reveals the presence of aliphatic vibrations at about 2930 and 2880 cm^{-1}. The presence of ring

vibrations at about 1630 cm^{-1} and 1450 cm^{-1} with respect to –C=C, and the peak at 1217 cm^{-1} corresponding to the (-C-O-C-) vibration, provide an indication of the methoxy group of the polymer. The presence of –OH and –C=O bands at about 3450 cm^{-1} and 1750 cm^{-1}, respectively, reveals ring opening with the consequent generation of a non-conjugated structure.[14,15]
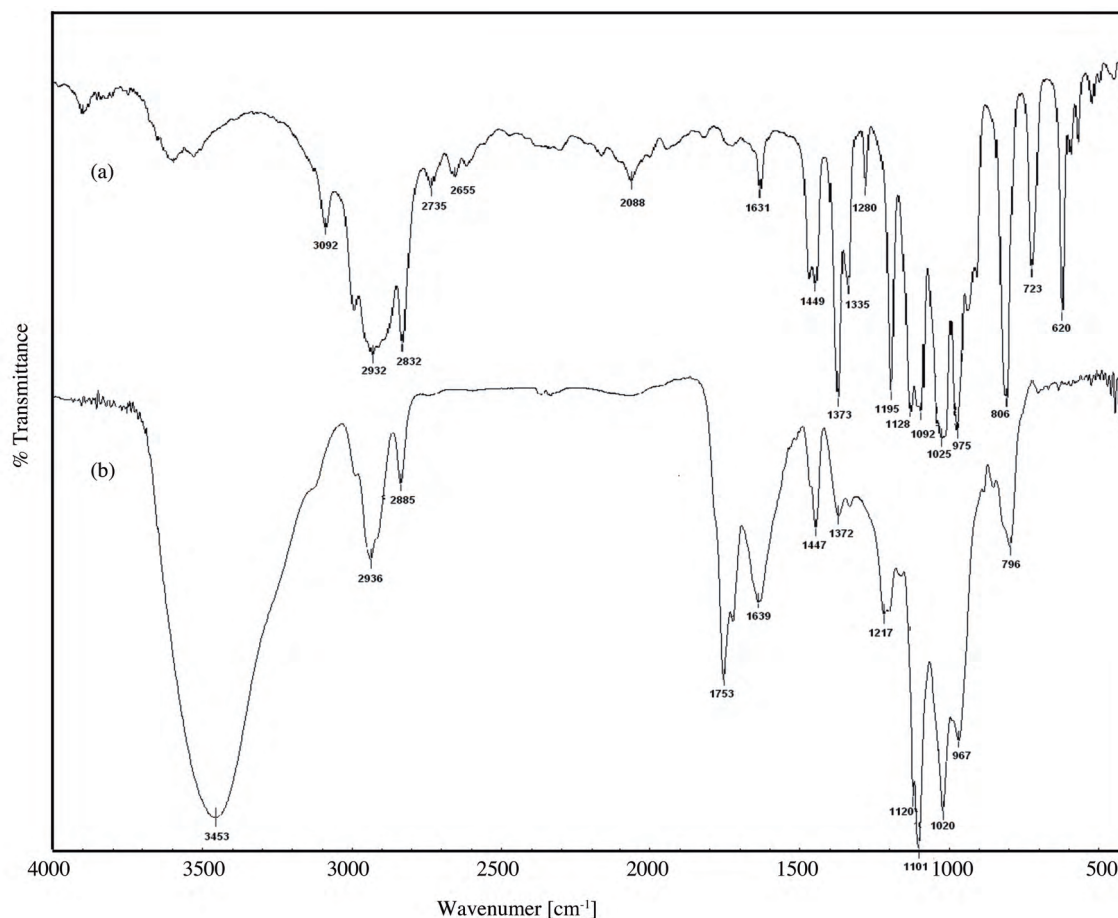
Figure 3. FT-IR spectra of DHMF (a) and poly(DHMF) (b) (DHMF = 0.3 mol L^{-1}, HClO$_4$ = 0.02 mol L^{-1}, t = 5 h, T = 80 °C).

^{1}H-NMR Investigation

The ^{1}H-NMR spectra of monomer and the polymer in CDCl$_3$ and d-DMSO solution are shown in Figures 4 and 5, respectively. In the ^{1}H-NMR spectrum of the monomer (Figure 4), the peaks are assigned as follows: -OCH$_3$ at 3.24 ppm, cis H2-H5 at 5.52 ppm, and the H3-H4 protons at 5.93 ppm. As the integration of the signals at 5.52 ppm to 5.75 ppm shows, the mixture is 54:46 cis to trans isomer. The signals in the polymer spectrum at 1.09 and 1.23 ppm correspond to –CH$_2$ and 4.33 and 5.07 ppm correspond to –CH protons. The signal at 3.2 ppm is –OCH$_3$ and the small signal at around 10 ppm is due to the aldehyde group in the polymer chain. The signal in the polymer spectrum at 2.5 ppm shows the solvent d-DMSO. Although some small peaks indicate that some side reactions took place, all the major peaks were assigned.
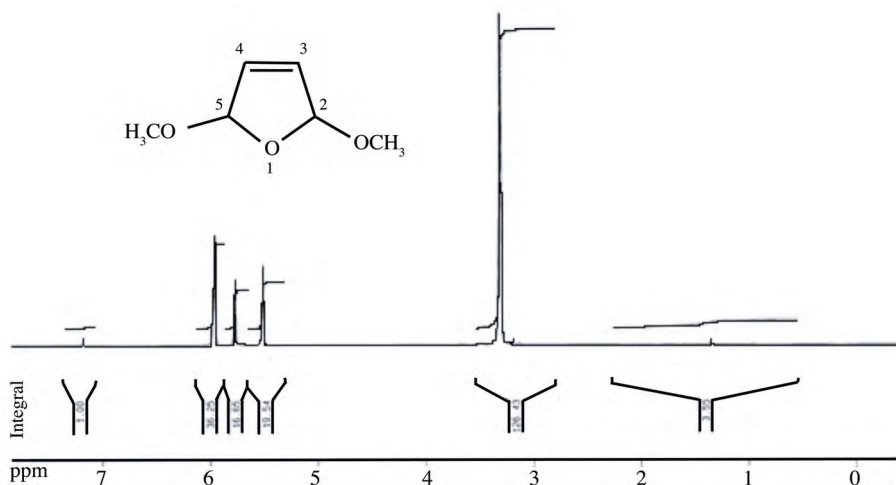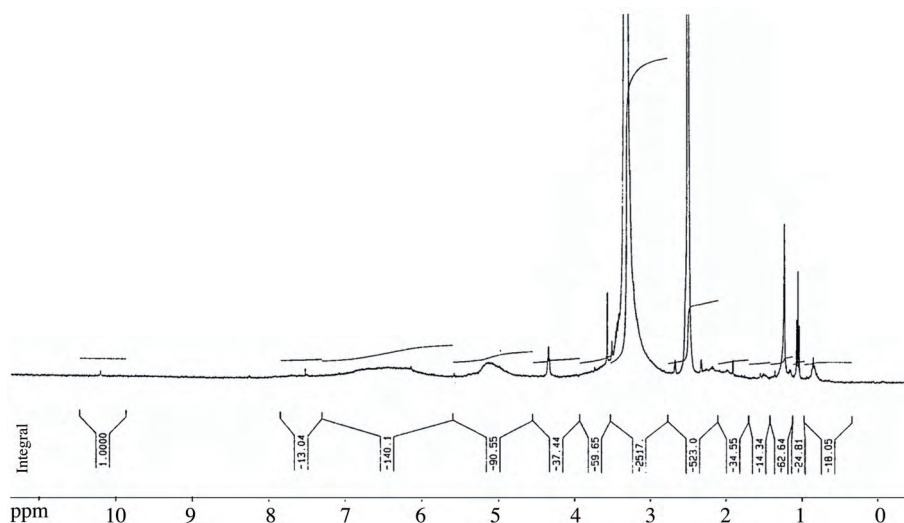
Figure 4. ^{1}H-NMR spectrum of DHMF.

Figure 5. ^{1}H-NMR spectrum of poly(DHMF) (DHMF = 0.3 mol L^{-1}, HClO$_4$ = 0.02 mol L^{-1}, t = 5 h, T = 80 °C).

The FT-IR and ^{1}H-NMR results indicate that the polymerization proceeds via ring opening. The polymerization mechanism of DHMF is suggested in Figure 6.

The decomposition temperatures obtained from TGA thermograms of poly(DHMF) are shown in Figure 7. Poly(DHMF) shows a 2-step weight loss. The first weight loss of 4% below 100 °C probably occurs due to the loss of residue solvent, monomers, and low molecular weight oligomers. The second degradation between 200 and 600 °C shows the decomposition of poly(DHMF).

The DSC measurement of poly(DHMF) was carried out in the temperature range from 25 to 300 °C at a heating rate of 10 °C/min. Two endothermic transitions were observed at 117 °C and 209 °C in the first run. The transition at 117 °C disappeared during the repetitive measurements, while the transition at 209 °C was not affected. The first transition coincides with the vaporization of AN and water and evaporation of low

molecular weight volatiles. The second transition is assigned to the glass transition temperature, Tg, of the polymer (Figure 8).[16]
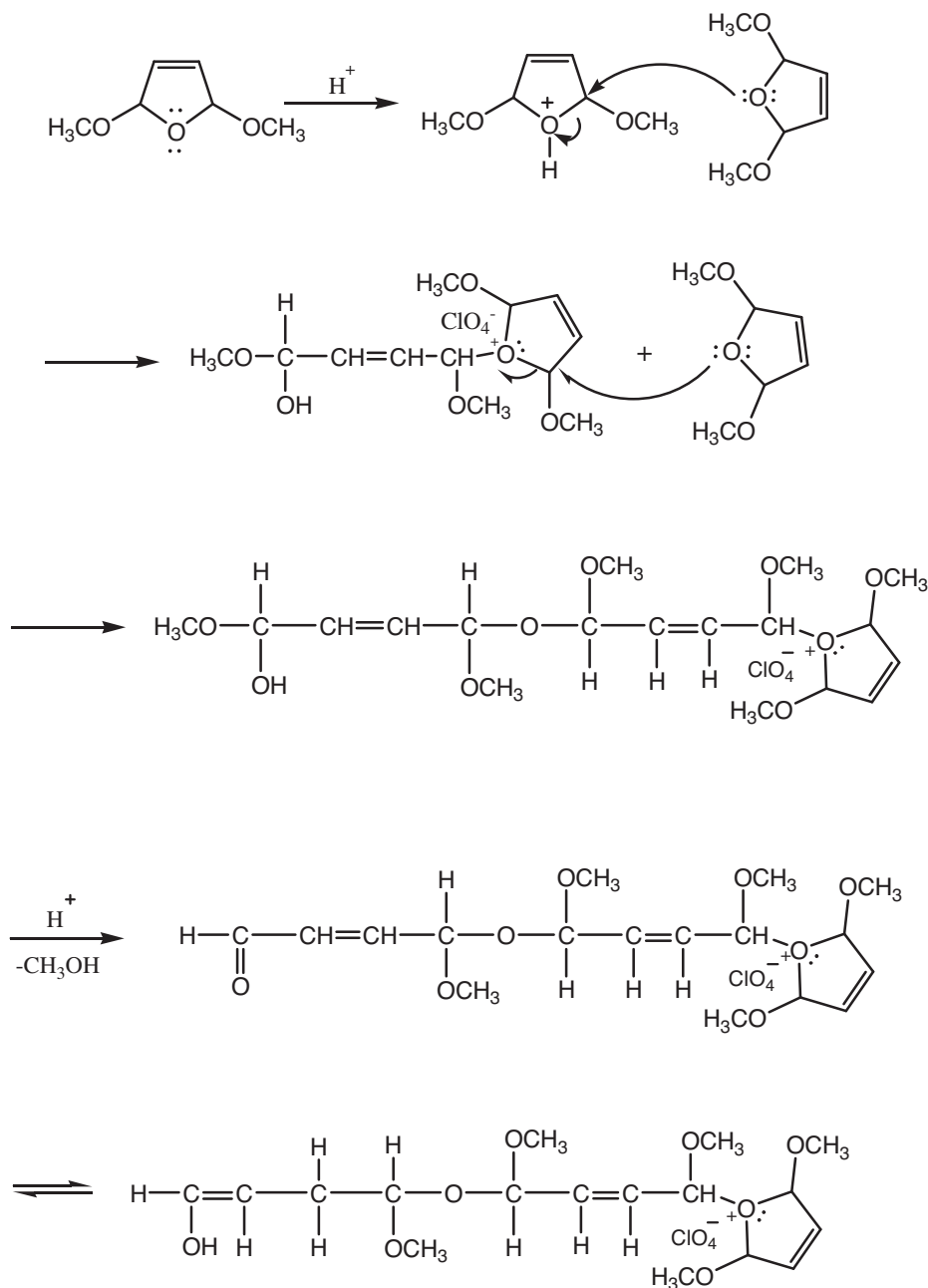

Figure 6. Suggested mechanism for polymerization of DHMF.

The polymer was found to be completely soluble in DMSO. Therefore, the M_n of the polymer could be determined by cryoscopy technique with DMSO as the solvent.[17] The moisture absorption of DMSO was prevented by using a specially designed and constructed closed system. The cryoscopic constant, $Kf = M\Delta T/c$, was determined from the slope of the plot of $M\Delta T$ vs. c by using purified naphthalene as a standard, where M

is the molecular weight of naphthalene, ΔT is the freezing point depression, and c is the solute concentration per 100 g of the solvent. Kf is found to be equal to t54.18° Cg/mol. M_n of the polymer. $M_n = Kf/(\Delta T/c)c = 0$, is calculated from the intercept of the ΔT vs. c plotted as 2700 g/mol (Figure 9).
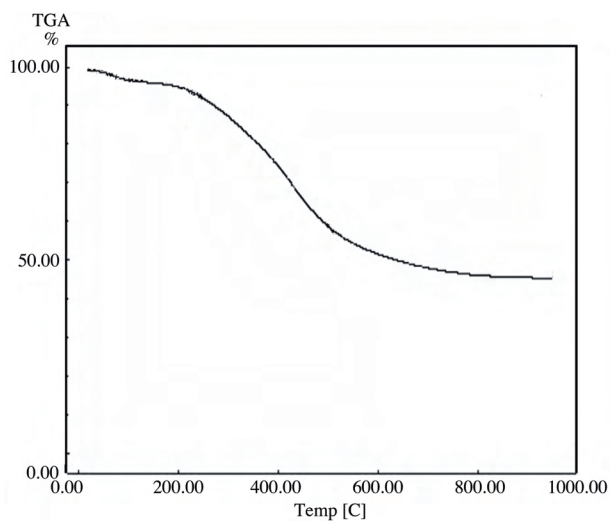
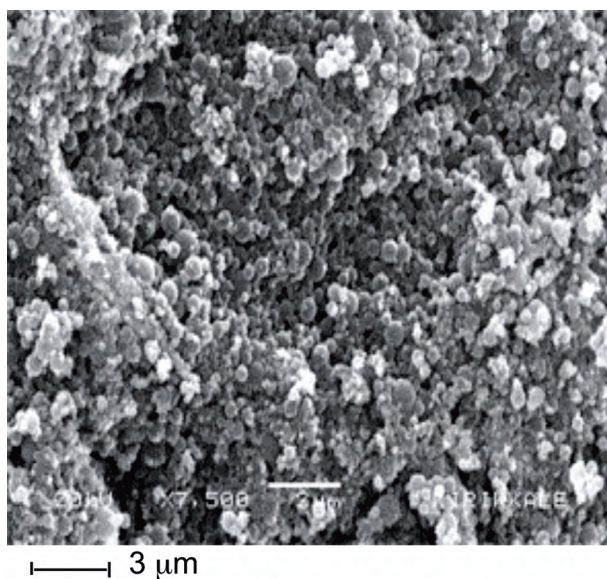**Figure 7.** TGA thermogram of poly(DHMF) (DHMF = 0.3 mol L^{-1}, HClO$_4$ = 0.02 mol L^{-1}, t = 5 h, T = 80 °C).
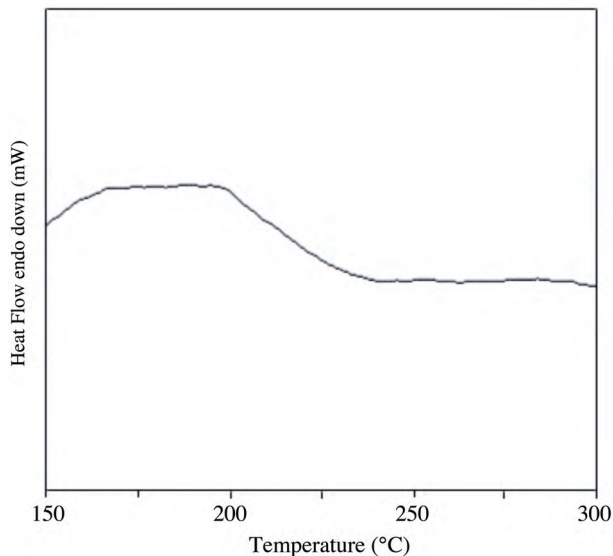
Figure 8. DSC curve of poly(DHMF) (DHMF = 0.3 mol L^{-1}, HClO$_4$ = 0.02 mol L^{-1}, t = 5 h, T = 80 °C).
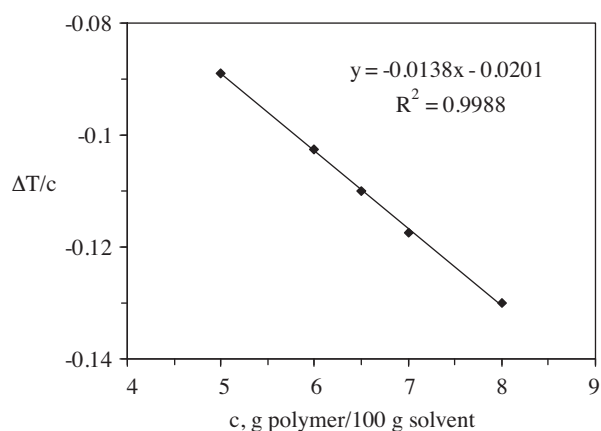
Figure 9. Freezing point depression-concentration curve of poly(DHMF).

Figure 10. Scanning electron microscopy (SEM) obtained at 20.00 kV with a 7500× zoom of poly(DHMF) (DHMF = 0.3 mol L^{-1}, HClO$_4$ = 0.02 mol L^{-1}, t = 5 h, T = 80 °C).

The scanning electron micrograph picture of poly(DHMF) is given in Figure 10. The poly(DHMF) demonstrates a granular, morphological structure and almost a homogeneous particle size distribution in nano-scale. A porous structure of polyfuran films was also found by Talu et al.[18]

Conclusion

DHMF can be polymerized using acetonitrile-$HClO_4$ as a solvent-initiator couple. The polymer yield increased with increasing temperature and $HClO_4$ concentration. A soluble polymer was characterized using FT-IR, ^{1}H-NMR, DSC, TGA/DTA, and SEM measurements. FT-IR and ^{1}H-NMR techniques show that polymerization proceeds at the furan ring opening. The number of average molecular weight, M_n, was found to be about 2700 g/mol.

Acknowledgment

References

1. Gandini, A.; Belgacem, M. N. *Prog. Polym. Sci.* **1997**, *22*, 1203-1379.

2. Pillai, C. K. S.; Rohatgi, P. K.; Gopalkumar, K. *J. Sci. Ind. Res.* **1981**, *40*, 154-165.

3. Manjula, S.; Sudha, J. D.; Bera, S. C.; Pillai, C. K. S. *J. Appl. Polym. Sci.* **1985**, *30*, 1767-1771.

4. Ray, S. S.; Kundu, A. K.; Maiti, S. *J. Appl. Polym. Sci.* **1988**, *36*, 1283-1293.

5. Sperling, L. H.; Manson, J. A.; Linne, M. A. *J. Polym. Mater.* **1984**, *1*, 54-67.

6. Gandini, A.; Belgacem, M. N. *Actualité Chim.* **2002**, 56-61.

7. Sillion, B. *High. Perform. Polym.* **1999**, *11*, 417-436.

8. Moreau, C.; Belgacem, M. N.; Gandini, A. *Topics in Catalysis* **2004**, *27*, 11-30.

9. Gandini, A. *Adv. Polym. Sci.* **1977**, *25*, 47-96.

10. Wan, X.; Yan, F.; Jin, S.; Liu, X.; Xue, G. *Chem. Mater.* **1999**, *11*, 2400-2407.

11. İçli, M.; Cihaner, A.; Önal, A. M. *Electrochim. Acta* **2007**, *52*, 8039-8043.

12. Benvenuti, F.; Galetti, A. M. R.; Carlini, C.; Sbrana, G. Polym. **1997**, *38*, 4973-4982.

13. Çiftçi, H.; Testereci, H. N. *Polym. Bull.* **2004**, *52*, 33-40.

14. Elibol, H.; Hacıoğlu, B.; Akbulut, U.; Toppare, L. *J. Macromol. Sci-Pure Appl. Chem.* **1994**, *A31*, 593-611.

15. Şen, S.; Bardakçı, B.; Yavuz A. G.; Gök A U *Eur. Polym. J.* **2008**, *44* 2708-2717

16. Gök, A.; Sarı, B.; Talu, M. *Synth. Met.* **2004**, *142*, 41-48.

17. Newitt, E. J.; Kokle, V. J. *Polym. Sci Part A-2* **1966**, *4*, 705-714.

18. Kabasakaloğlu, M.; Talu, M.; Yıldırım, F.; Sarı, B. *Appl. Surf. Sci.* **2003**, *218*, 85-97.