Cationic Polymerization of 2,3-dihydro-4*H*-pyran Using 12-Tungstophosphoric Acid as a Solid Acid Catalyst

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ABSTRACT: The bulk polymerization of 2,3-dihydro-4*H*-pyran catalyzed by 12-tungstophosphoric acid was investigated. The effects of the time, temperature, and amount of the catalyst on the polymerization reaction were studied. The propagation exclusively involved C=C bonds. Propagation by ring opening was not observed. The total polymerization time and the melting tempera-ture decreased as the proportion of the catalyst and the temperature were increased because of the increase in the number of active centers and the chain-transfer reaction, respectively. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 1431–1435, 2010

Key words: cationic polymerization; catalysts; polyethers

INTRODUCTION

Wide varieties of cyclic organic compounds have been exploited as possible monomers for obtaining polymers of novel structures. Among them, cyclic ethers are of major interest in the field of polymer chemistry because polyethers possess high polarizability and flexibility in their main chain. Thus, they have been the subject of a large number of articles.[1–11] This kind of polymerization is initiated by electrophilic agents such as Brønsted acids [e.g., hydrochloric acid (HCl), sulfuric acid (H_2SO_4), and perchloric acid ($HClO_4$)][12,13] and Lewis acids [e.g., aluminum chloride ($AlCl_3$), boron trifluoride etherate ($BF_3 \cdot OEt_2$), and titanium tetrachloride ($TiCl_4$)].[14,15] However, the protonic acid catalysts used are very noxious, corrosive, and expensive. As for Lewis acids, great amounts are required to achieve acceptable polymer yields. Because of increasing environmental concerns in recent years, a more effective catalytic process has been sought. In this respect, researchers have conducted studies on the development of solid acids so that aggressive and dangerous homogeneous acids can be replaced to overcome the problem of separating the catalysts from the products and from the disposal of solid/liquid waste.

Solid Brønsted acids with superacidic character, such as Keggin-type heteropolyacids, have been used as efficient catalysts for a variety of industrial organic reactions.[16] Because of their unique combination of acid–base and redox properties, they have been used successfully as catalysts in both homogeneous[17,18] and heterogeneous media.[19–25] These compounds catalyze various reactions much more effectively than conventional protonic acids such as H_2SO_4 and nitric acid (HNO_3).[26,27] This article deals with the bulk polymerization of 2,3-dihydro-4*H*-pyran (DHP) with 12-tungstophosphoric acid ($H_3PW_{12}O_{40} \cdot 13H_2O$) as a solid acid catalyst.

EXPERIMENTAL

Catalyst preparation

$H_3PW_{12}O_{40} \cdot 13H_2O$ was prepared according to a now well-known method;[28] that is, 100 g of sodium tungstate dihydrate ($Na_2WO_4 \cdot 2H_2O$) was dissolved in 100 mL of warm distilled water, and then 85% H_3PO_4 (5 mL) and 37.5% HCl (22 mL) were successively added slowly to the solution. The mixture was concentrated to three quarters of its initial volume by heating, and then it was cooled to room temperature. The cooled mixture was extracted with diethyl ether in an HCl medium. The product that formed with ether, which settled at the bottom, was separated from the aqueous phase. The white crystals of $H_3PW_{12}O_{40} \cdot 13H_2O$ were dried at room temperature.

Polymerization procedure

The bulk polymerizations of DHP were carried out in a stirred flask fitted with a condenser. Typically, a fixed amount of the catalyst was added to 10 mL of DHP under stirring at the desired temperature until the viscosity prevented it from occurring. The polymerization was quenched by the addition of a

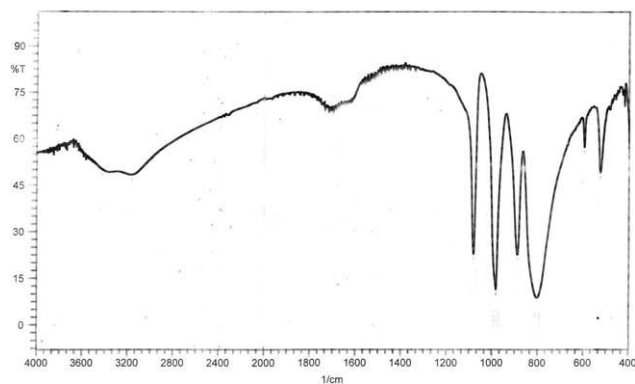**Figure 1** IR spectrum of $H_3PW_{12}O_{40} \cdot 13H_2O$.

saturated, aqueous NaOH solution. The resulting precipitated polymer was filtered off and then dissolved in butanone for the removal of the catalyst, which was insoluble in butanone. The recovered polymer was precipitated into an aqueous ethanol solution, filtered off, dried at 40–50°C *in vacuo*, and weighed. Then, the polymer was purified by dissolution in CH_2Cl_2 and precipitation into ethanol for characterization.

Characterization

The Keggin structure of $H_3PW_{12}O_{40} \cdot 13H_2O$ was checked by infrared (IR) spectroscopy. IR spectra were recorded with a Genesis II FTIR spectrometer (Middleton, WI) (4000–400 cm^{-1}) as KBr pellets. The number of protons was checked by means of thermogravimetric analysis (TGA). TGA was carried out on a PerkinElmer TGA instrument (Milano, Italy) at a heating rate of 5°C/min in flowing N_2.

^{1}H-NMR spectra were recorded on a Bruker Avance 400-MHz spectrophotometer (Wissembourg, France) using 5-mm NMR tubes with deuterated acetone-d_6 as the solvent. A DSC-60 differential scanning calorimeter from Shimadzu (Kyoto, Japan) was used. The specimens weighed about 12 mg each. Each specimen was placed in an aluminum pan. The pan was placed in the differential scanning calorimeter's oven in air at atmospheric pressure. Specimens were heated at a constant heating rate of 5°C/min to 150°C. The specimen was held there for 5 min and then cooled at 5°C/min to room temperature.

RESULTS AND DISCUSSION

Characterization of the catalyst

IR spectra

The spectra of the catalysts are shown in Figure 1. The IR spectra were assigned according to the literature.[29] The main characteristic features of the Keggin structure were observed at 1080–1060 (ν_{as} P—O$_a$), 990–960 (ν_{as} Mo—O$_d$), 900–870 (ν_a Mo—O$_d$—Mo), and 810–760 cm^{-1} (ν_{as} Mo—O$_c$—Mo).

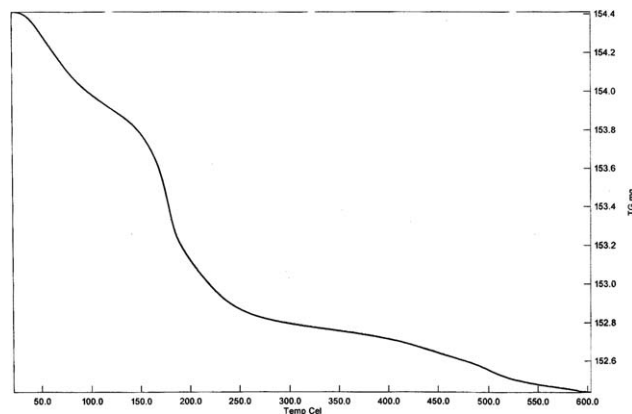**Figure 2** Thermogravimetry (TG) curve of the initial sample of $H_3PW_{12}O_{40} \cdot 13H_2O$ under the ambient conditions (heating rate = 5°C/min).

TGA

Two types of water molecules were observed on the heteropolyacid (Fig. 2): crystallization and constitutional water.[30] The loss of crystallization water (13H$_2$O) occurred before 200°C; a plateau ascribed to the anhydrous acid was observed between 200 and 300°C. Above 300°C, the constitutional water molecules, that is, the protons bounds to the polyanion external oxygens, were lost.

Polymerization

To investigate the activity of the catalyst, we carried out the bulk polymerization of DHP with changes to the polymerization time, catalyst proportion, and polymerization temperature. The obtained polymers were characterized with IR, ^{1}H-NMR, differential scanning calorimetry, and viscosity measurements.

IR spectra

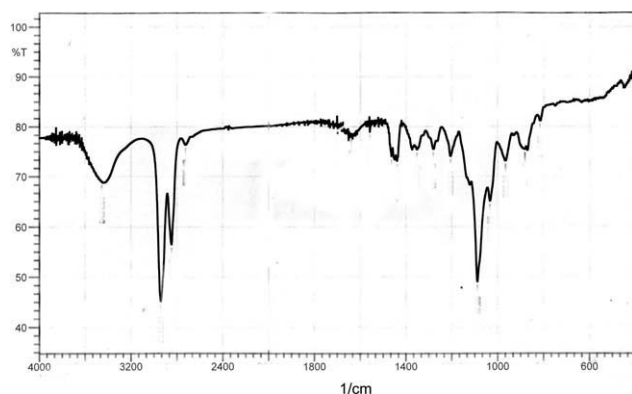The IR spectrum is depicted in Figure 3. These results show that the bands at 1224.16 and 1647.21 cm^{-1},

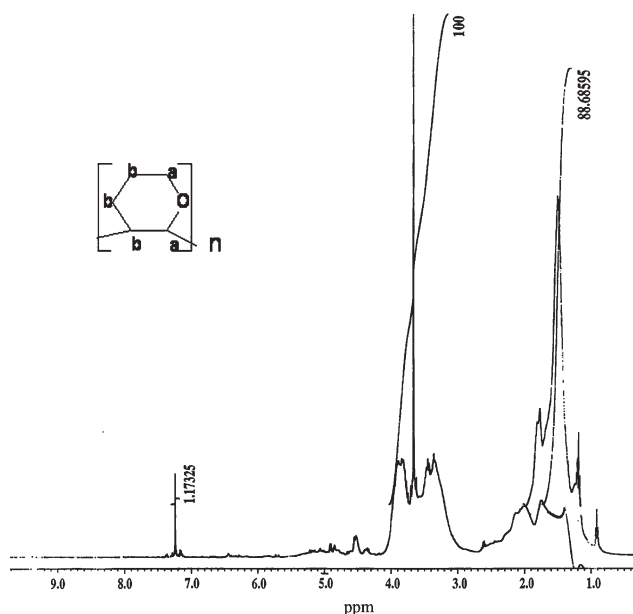**Figure 3** IR spectrum of poly(DHP) over $H_3PW_{12}O_{40} \cdot 13H_2O$.

Figure 4 ^{1}H-NMR spectrum of poly(DHP) in CD_3OCD_3.

which were assigned to the double bond C=C, and the band at 1087.85 cm^{-1}, which was assigned to the C—H bond, were absent in the polymer. The presence of the band at 1087.85 cm^{-1}, which was assigned to the ether bond C—O—C, indicates that ring opening did not occur.

The ^{1}H-NMR spectrum (Fig. 4) shows a wide band between 1.0 and 2.0 ppm corresponding to CH$_2$ (b) and a wide band between 3.0 and 4.0 corresponding to the CH$_2$ (a) neighbor of the oxygen atom, and this indicates the formation of poly(2,3-dihydro-4*H*-pyran) [poly(DHP)]. It is worth noting that the double bond and the signal corresponding to the proton of the aldehyde were not observed in the spectrum (Table I). This implies that the polymerization occurred by propagation via the double bonds and not via ring opening (Scheme 1).

Kinetic procedure

The effect of the polymerization time on the conversion is shown in Figure 5. The conversion was directly proportional to the reaction time. The time to achieve total polymerization (135 min) indicates that this catalyst is effective for the cationic polymerization of unsaturated cyclic ethers.

TABLE I
Chemical Shifts of the Polymer Protons

Proton type	a	b
δ (ppm)	3.4	1.2
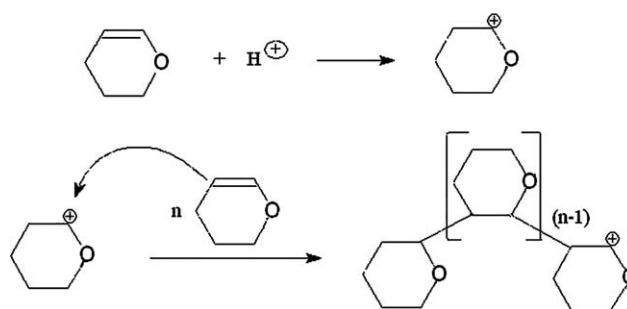
Scheme 1 Mechanism of the polymerization.

Effect of the amount of $H_3PW_{12}O_{40}\cdot13H_2O$ on the polymerization

The effect of the amount of the catalyst on the time for achieving total polymerization was studied. Table II and Figure 6 show that the polymerization rate increased (the total polymerization time decreased) with an increase in the concentration of the catalyst, whereas the melting temperature decreased. The decrease in the melting temperature when the catalyst amount increased can be explained by the fact that many chains were activated simultaneously, so one chain did not have enough time to grow. A possible explanation is that propagation took place through a high concentration of active centers. The polymerization rate increased with the amount of $H_3PW_{12}O_{40}\cdot13H_2O$, and the effect of $H_3PW_{12}O_{40}\cdot13H_2O$ as a cationic catalyst of DHP was clearly shown. This phenomenon was probably the result of the number of initiating active centers responsible for inducing polymerization; this number was prorated to the amount of the catalyst used in the reaction. Similar results were obtained by
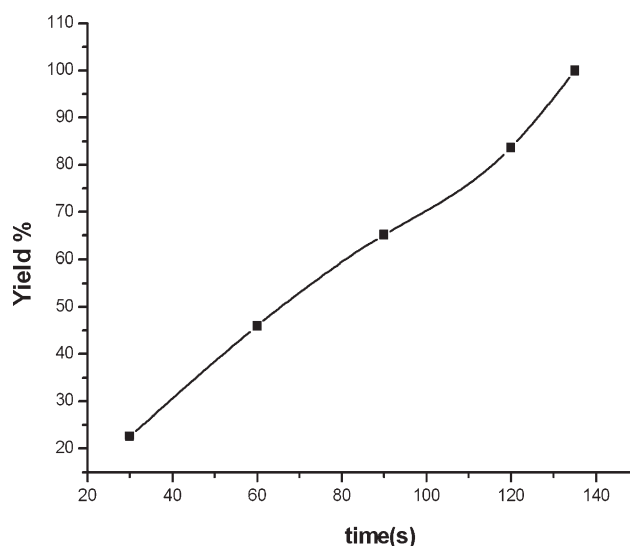

Figure 5 Effect of the reaction time on the conversion over $H_3PW_{12}O_{40}\cdot13H_2O$ (catalyst mass = 0.025 g).

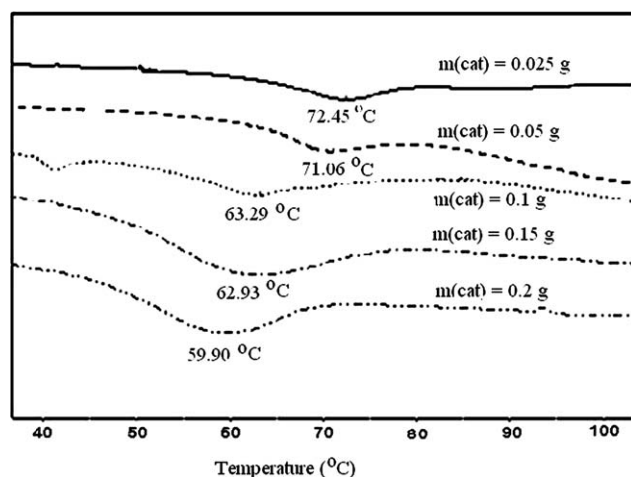| Catalyst weight (g)	0.025	0.050	0.100	0.150	0.200
Time (min)	135	78	55	42	31

Figure 6 Effect of the catalyst mass [m(cat)] on the melting temperature of poly(DHP).

Yahiaoui et al. [31] and Njopwouo et al. [32] in the polymerization of cyclohexene oxide by maghnite–H^+ and styrene by montmorillonite–H^+ (Brønsted solid acid catalysts), respectively.

Effect of the temperature on polymerization

The effect of the polymerization temperature on the time for achieving total polymerization is depicted in Table III. The polymerization rate increased with decreases in the polymerization temperature, whereas the melting temperature (Fig. 7) decreased. The latter decreased from 74.59 to 59.49°C when the temperature increased from 20 to 50°C. This result is in agreement with the results reported in the literature.[33–36] The decrease in the melting temperature when the reaction temperature increased can be explained by the fact that increasing the temperature caused an increase in the rate of the chain-transfer reaction of the growing polymer cation (intermolecular and intramolecular).[37,38]

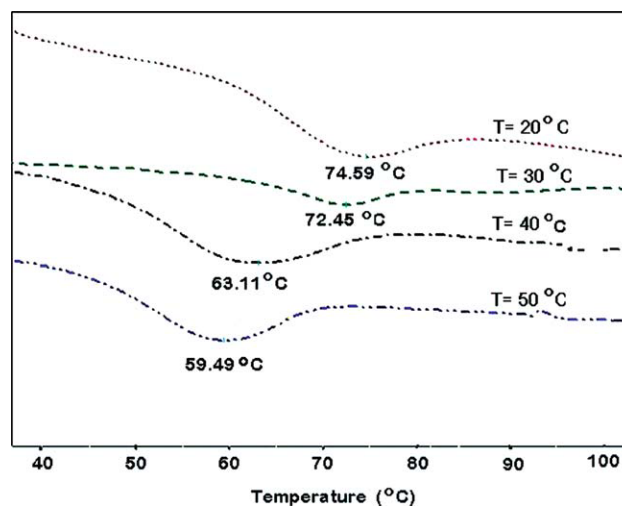| Temperature (°C)	20	30	40	50
Time (min)	210	135	65	32

Figure 7 Effect of the reaction temperature on the melting temperature of poly(DHP). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

CONCLUSIONS

This work shows that $H_3PW_{12}O_{40} \cdot 13H_2O$ is an effective solid acid catalyst for the cationic polymerization of unsaturated cyclic ethers. The polymerization proceeds under mild conditions by a very simple procedure, and the catalyst is recovered by simple filtration.

The propagation process of the polymerization with this superacid exclusively involves the reaction of carbon–carbon double bonds. Polymerization involving ring opening was not observed.

The catalyst activity depends on the catalyst proportion and the reaction temperature. Increases in the catalyst proportion and reaction temperature increase the rate of polymerization but decrease the melting point.

References

1. Dale, J. Tetrahedron 1993, 49, 8707.
2. Warwel, S.; Wiege, B.; Fehling, E.; Kunz, M. Eur Polym J 2000, 36, 2655.
3. He, J.; Ni, P.; Liu, C. J Polym Sci Part A: Polym Chem 2008, 46, 3029.
4. Allgaier, J.; Willbold, S.; Chang, T. Macromolecules 2007, 40, 518.
5. Dimitrov, P.; Rangelov, S.; Dworak, A.; Tsvetanov, C. B. Macromolecules 2004, 37, 1000.
6. Paddock, R. L.; Nguyen, S. T. Macromolecules 2005, 38, 6251.
7. Xiao, Y. L.; Wang, Z.; Ding, K. L. Macromolecules 2006, 39, 128.
8. Penezek, S.; Kubissa, P.; Matyjaszewski, K. Adv Polym Sci 1985, 1, 68.
9. Heitz, W.; Kress, H. J. Makromol Chem Rapid Commun 1981, 2, 427.
10. Muller, H.; Hucher, H.; Hoffman, H. U.S. Pat. 4,243,799 (1988).
11. Shibayama, M.; Takahashi, H.; Nomura, S.; Imai, M. Polymer 1998, 39, 3759.
12. Masamoto, J. Prog Polym Sci 1993, 18, 1.
13. Wern, W.; Jaacks, V. J Polym Sci 1960, 48, 399.
14. Rodriguez-Baeza, M. Polym Bull 1991, 26, 521.

15. Yagci, Y.; Reetz, I. Prog Polym Sci 1998, 23, 1485.
16. Okuhara, T. Chem Rev 2002, 102, 3641.
17. Ishii, Y.; Yamawaki, K.; Ura, T.; Yamada, H.; Yoshida, T.; Ogawa, M. J Org Chem 1988, 53, 3587.
18. Weinstock, I. A.; Barbuzzi, E. M. G.; Wemple, J. J.; Cowan, M. W.; Reiner, R. S.; Sonnen, D. M.; Heintz, R. A.; Bond, J. S.; Hill, C. L. Nature 2001, 414, 191.
19. Shanmugam, S.; Viswanathan, B.; Varadarajan, T. K. J Mol Catal A 2004, 223, 143.
20. Sharma, P.; Vyas, S.; Patel, A. J Mol Catal A 2004, 21, 281.
21. Yang, L.; Qi, Y.; Yuan, X.; Shen, J.; Kim, J. J Mol Catal A 2005, 229, 199.
22. Das, J.; Parida, K. M. J Mol Catal A 2007, 264, 248.
23. Parida, K. M.; Mallick, S. J Mol Catal A 2007, 275, 77.
24. Kozhvnikov, I. V. Chem Rev 1998, 98, 171.
25. Misono, M.; Ono, I.; Koyano, G.; Aoshima, A. Pure Appl Chem 2000, 72, 1305.
26. Chen, X.; Xu, Z.; Okuhara, T. Appl Catal A 1999, 180, 261.
27. Blasco, T.; Corma, A.; Martinez, A.; Martinez-Escolano, P. J Catal 1998, 177, 306.
28. Rocchiccioli-Deltcheff, C.; Fournier, M.; Franck, R.; Thouvenot, R. Inorg Chem 1983, 22, 207.
29. Rocchiccioli-Deltcheff, C.; Fournier, M. J Chem Soc Faraday Trans 1991, 87, 3919.
30. Fournier, M.; Feumi-Jantou, C.; Rabia, C.; Herve, G.; Launay, S. J Mater Chem 1992, 9, 971.
31. Yahiaoui, A.; Belbachir, M.; Soutif, J. C.; Fontaine, L. Mater Lett 2005, 59, 759.
32. Njopwouo, D.; Roques, G.; Wandji, R. Clay Miner 1987, 22, 45.
33. Yahiaoui, A.; Belbachir, M.; Hachemaoui, A. Int J Mol Sci 2003, 10, 548.
34. Wang, L. Y.; Wu, Q. Eur Polym J 2007, 4, 3970.
35. Bielawskia, C. W.; Grubbs, R. H. Prog Polym Sci 2007, 32, 1.
36. Al Obaidia, F.; Yea, Z.; Zhua, S. Polymer 2004, 45, 6823.
37. Goethal, A. Pure Appl Chem 1976, 48, 335.
38. Vijayakrishna, K.; Sundararajan, K. G. Polymer 2006, 47, 3363.