Polymer Bulletin 57, 873–880 (2006)
DOI 10.1007/s00289-006-0668-2

Polymer Bulletin

A rapid synthesis of poly (*p*-dioxanone) by ring-opening polymerization under microwave irradiation

Ying Li, Xiu-Li Wang, Ke-Ke Yang, Yu-Zhong Wang (✉)

Center for Degradable and Flame-Retardant Polymeric Materials, College of Chemistry,
Sichuan University, Chengdu 610064, China
E-mail: yzwang@mail.sc.cninfo.net; Fax: +86-28-85410259

Received: 23 April 2006 / Revised version: 24 July 2006 / Accepted: 31 July 2006

Summary

A rapid synthesis of poly(*p*-dioxanone) (PPDO) was carried out smoothly and effectively from the monomer *p*-dioxanone (PDO) with constant microwave powers of 90, 180, 270, and 360W, respectively, in a microwave oven at a frequency of 2.45GHz. The temperature of the polymerization ranged from 158 to 198 °C. PPDO with a viscosity-average molecular weight (Mv) of 156,000g/mol and yield of 63% was obtained at 270W for 25 min using 1/1000 (mol/mol) $Sn(Oct)_2$ as a catalyst, while it took more than 14h to obtain PPDO with high molecular weight and monomer conversion by conventional heating method when $Sn(Oct)_2$ used as a catalyst. Therefore, it is obvious that the polymerization rate is faster than that of the conventional polymerization method when microwave irradiation is used in polymerization process.

Keywords:

poly(*p*-dioxanone), ring-opening polymerization, microwave irradiation

Introduction

Recently, much attention has been paid on the synthesis of PPDO [1-5], and the properties of PPDO including crystallinity, biodegradability and thermal degradation [6-12]. Among all the catalysts and initiators studied so far, aluminum trialkoxides proved to be highly efficient in initiating the ring-opening polymerization (ROP) of PDO in bulk, yielding high molecular weight PPDO with very short periods of time [13-15]. Dubois et al [16] reported that PPDO with high molar weight could be obtained in a co-rotating twin-screw extruder within a few minutes in the presence of aluminum sec-butoxide. However, when stannous octonate ($Sn(Oct)_2$) is used as a catalyst for ROP of PDO, a relative longer reaction time would be needed in order to obtain PPDO with high molecular weight. Nishida et al. [17] reported that PPDO with Mn of 8.0×10^4 was obtained in 20h at 80ºC. Because $Sn(Oct)_2$ is one of a few catalysts that could be used as a food additive, sanctioned by FDA, it is safe to synthesize PPDO used as biodegradable surgical devices.

So it is a challenge for us to seek excellent methods in order to achieve the synthesis of PPDO under mild conditions and in shorter time in the presence of $Sn(Oct)_2$. The purpose of our work is to synthesize high molecular weight of PPDO in a reduced time when $Sn(Oct)_2$ was used as a catalyst.

Microwave heating, which presents a totally different heating mode from conventional heating, has been proved to be more rapid and efficient. It offers a clean, cheap, convenient and green method of heating. Since Gedye and coworkers [18] reported that the use of microwave heating could accelerate organic reactions, a wide variety of chemical reactions have been performed under microwave irradiation [19]. In the field of polymer chemistry, microwave energy was used for enhancing various kinds of polymerizations including addition polymerization [20,21], condensation polymerization [22,23], graft polymerization [24,25], and ring-opening polymerization (ROP) [26-32]. For monomers containing polar groups that can favor the absorption of microwaves [33], several reports were found in the literature concerning microwave-assisted ROP. Albert et al. [26] compared thermal- and microwave-activated polymerization of caprolactone at 180ºC in the presence of titanium tetrabutylate. Fang et al. [27] studied the ROP of caprolactone and caprolactam under microwave irradiation. Liu et al. synthesized some biodegradable polyesters such as poly(L-2-hydroxy-3-phenylpropanoic acid) [22], poly(lactic acid) [28], and poly(ε-caprolactone) (PCL) [31] by microwave-assisted polymerization. To our best knowledge, however, no reports have been found in the literature concerning microwave-assisted ROP of PDO.

In this article, the heating characteristics of PDO monomer and reaction mixture of PDO with $Sn(Oct)_2$ under microwave oven with various amounts of PDO monomer and microwave power levels are researched. The microwave-assisted ROP of PDO with $Sn(Oct)_2$ as a catalyst is studied, and the effects of microwave power, irradiation time, and catalysts concentration on the polymerization and final product are presented.

Experimental

Materials

p-dioxanone was provided by the Pilot Plant of Center for Degradable and Flame-Retardant Polymeric Materials (Chengdu, China), and it was twice distilled in vacuum immediately before use. The purity of PDO of 99.5% was determined by Gas Chromatography. $Sn(Oct)_2$ (Purity >95%) was purchased from Sigma Chemical and used without any further purification. After dilution with dry toluene, $Sn(Oct)_2$ solution was stored in glass ampules under argon. Toluene, received from Hehong Chemical Reagent Factory (Chengdu, China), was dried by refluxing over Na/benzophnone complex and distilled just before use. The other solvents are all of A. R. grade and used as received.

Microwave equipment

A 2.45-GHz multimode microwave oven (Whirlpool-J220) with a maximum output power of 850W was applied in our study. The output power could be performed at 10 different levels by a power on-off cycle. The temperature of materials was measured by inserting a thermocouple into a self-made ampoule.

Thermal effect of microwave on PDO

A certain amount of PDO was put into an ampoule, which then was vacuum-sealed, and it was irradiated at pointed microwave powers for 25 min. The temperature was recorded every minute.

Microwave-assisted ROP

The typical procedure was given as follows: a mixture of PDO (5mL, PDO monomer was heated to 30ºC, at which it was added with a syringe) with a certain amount of $Sn(Oct)_2$ was put into an ampoule that was sealed under vacuum (20Pa) after three dry-nitrogen/exhaust cycles. The mixture in the vacuum-sealed ampoule was irradiated at pointed microwave powers for a predetermined time. During the polymerization, the temperature was measured every minute and the data were collected. At the end of the reaction, the ampoule was immediately removed from the microwave oven and immersed in ice water. The crude solid product was purified by precipitation from the phenol/1,1,2, 2-tetrachloroethane (2:3, w/w) solution with methanol and dried under vacuum at ambient temperature to a constant weight. The monomer conversion of PDO was determined by weighting the dried PPDO. Reproducibility of polymer recovery method was checked by repetitive experiment, which gave monomer conversion values with a relative error estimated to maximum $\pm 5\%$.

Measurements

As the conventional solvents such as chloroform, tetrahydrofuran, and toluene used in GPC measurements cannot resolve the resulting polymers with higher molecular weights, only the viscosity-average molecular weights of the resulting polymers were measured in phenol/1,1,2,2 –tetrachloroethane (2:3 w/w) solution using an Ubbelohde viscosimeter thermostated at 25ºC. The molecular weights of PPDO can be calculated from the intrinsic viscosity [η] according to Mark-Houwink equation $[\eta] = K\overline{M}_v^{\alpha}$, where α=0.63 and $K=79\times10^{-3}cm^3g^{-1}$[6].

^{1}H-NMR spectra were recorded in $CDCl_3$ on a Varian Germini 400 MHz NMR spectrometer using TMS as internal standard.

Results and discussion

Thermal effect of microwave energy on PDO

The heating characteristics of PDO under microwave irradiation (MI) were investigated at four levels of microwave powers (90, 180, 270, and 360W) using PDO monomers with the amount of 1, 3, 5 and 7mL, respectively. PDO contains a polar carbonyl group that leads to dielectric heating by absorbing microwaves. ROP of PDO was examined at a certain constant temperature that was controlled either by pulsed microwave power [26] or by variable-frequency microwave [27]. However, by the two methods, microwave irradiation is interrupted periodically or microwave frequency is changed successively, and the energy of microwave irradiation is inconstant. Considering that the control system of constant microwave energy is much simpler than that of pulsed microwave power and variable-frequency microwaves, we investigated microwave-assisted ROP of PDO with constant microwave energy. To

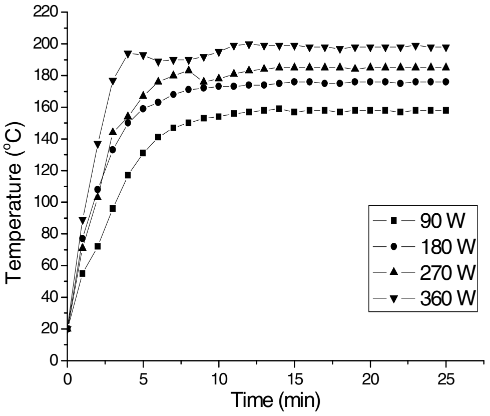


Figure 1 Temperature profile of PDO (5mL) under microwave irradiation

understand the heat effect of constant microwave energy on PDO, we measured the temperature increases of PDO irradiated by microwaves with a frequency of 2.45 GHz. Four levels of microwave powers (90, 180, 270, and 360W) were examined, and the results are shown in Figures 1 and 2.

The temperature of PDO (5mL) rose from 20 to 158ºC when it was irradiated by a microwave power of 90W for 25 min. For the power range of 180, 270, and 360W, the temperatures rose from 20ºC to 176, 185, and 198ºC, respectively. That is to say, the temperature increased by 138ºC for 90W, 156ºC for 180W, 165ºC for 270W, and 178°C for 360W (Fig.1). Therefore, the higher the power level was used the higher the temperature was. A rapid increase in temperature occurred within 5 min. For examples, within 5 min, the temperature rose to 111ºC for 90W, 139 ºC for 180W, 147 ºC for 270W, and 173 ºC for 360W. 5 minutes later the temperature increased slowly and steadily. No increase was measured in the temperature range from 20 to 25min at any of the four power levels, meaning that it is limited to increase the

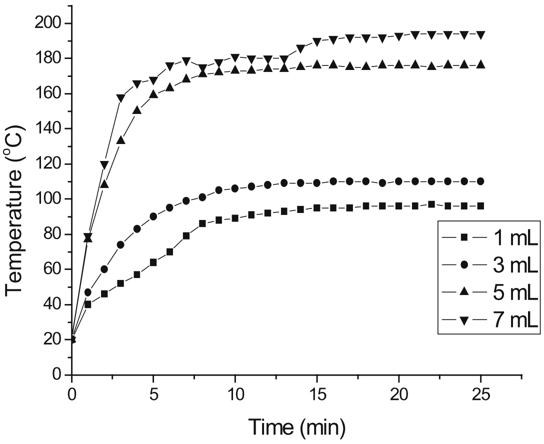


Figure 2 Temperature profile of PDO under microwave (180W) irradiation

temperature by constant microwave power below 450W. On the other hand it was predicted that overheating could be avoided, which is usually thought to destroy a chemistry reaction.

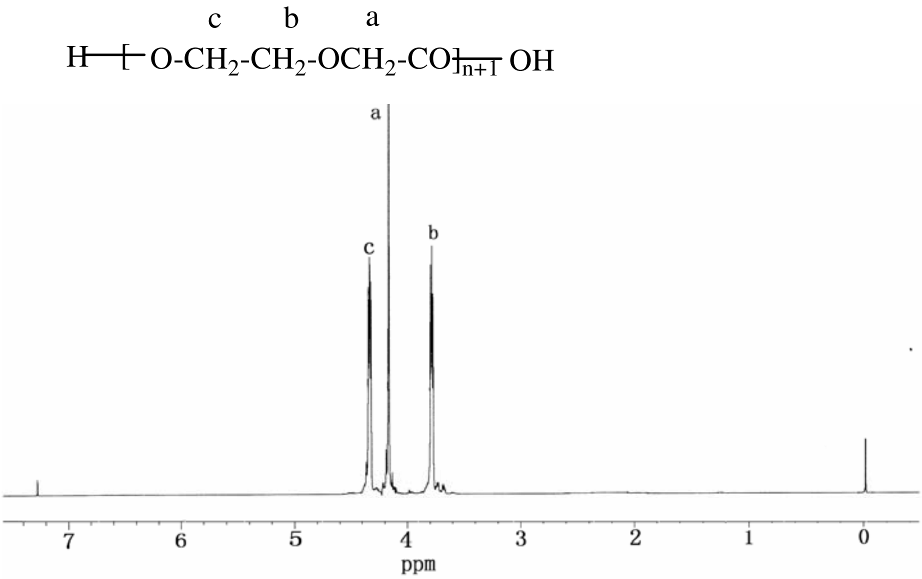
The amount of PDO also had an influence on its heating characteristics. The temperature increased with the increase of the amount of PDO. For an irradiation at 90W for 5 min, the temperature of PDO increased from 64 to 168 ºC when the amount of PDO was increased from 1 to 7mL (Fig.2).

Polymerization of PDO with constant microwave power

In present work, the highest temperatures of PDO (5mL) were 158, 176, 185 and 198ºC under the irradiations of four microwave power levels, by which ROP of PDO would occur. Thus, the four microwave power levels were applied to investigate ROP of PDO.

After PDO was irradiated by microwave for 25min in the presence of $Sn(Oct)_2$, and then the ampoule was immediately immersed in ice water, a solid was produced. The structure of the purified polymer was confirmed to be that of PPDO by ^{1}H-NMR spectrum (Fig.3). The influence of the power level of microwave on the conversion of monomer and the molecular weight of resulting polymers was illustrated in Fig. 4.

The viscosity-average molecular weights (Mv) of PPDO were 95,000, 140,000, 175,000, and 66,000 g/mol at the microwave powers of 90, 180, 270, and 360 W, respectively. Dependence of molecular weights on power levels was found: the molecular weights increased with the increase of the power levels. When the power level was increased to a 360W, however, Mv of PPDO was decreased to 66,000 g/mol. From Fig.1, we know that when the power level is 90, 180, 270 and 360W, the temperature of PDO (5mL) is 158, 176, 185, and 198 ºC, respectively. Therefore, it



$$H\text{–}[\overset{c}{O\text{-}CH_2}\text{-}\overset{b}{CH_2}\text{-}\overset{a}{OCH_2}\text{-}CO]_{n+1}\,OH$$

Figure 3 ^{1}H-NMR spectrum of PPDO

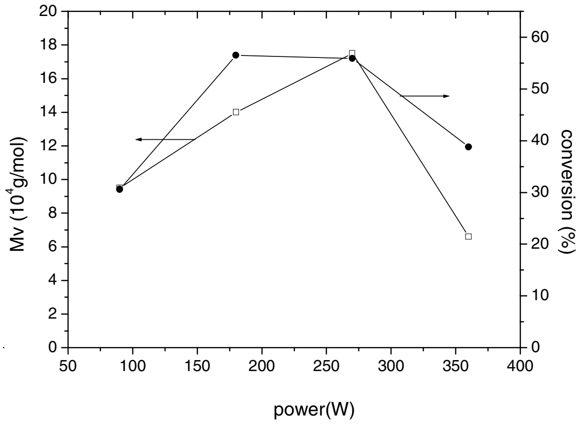


Figure 4 Effect of irradiation power on polymerization [time=25min, M/C(mol/mol)=1000]

was deduced that the ROP of PDO was greatly improved at higher temperatures and made the values of Mv increased and got to the maximum. When the temperature was as higher as 198 °C, the side reaction such as intra-transesterification reactions was obvious and made Mv decreased.

It is well known that the ROP of PDO is thermodynamic equilibrium and the equilibrium conversion decreased with the increasing polymerization temperature [17]. When microwave irradiation was used in the ROP of PDO, the thermodynamic behavior may be different. The value of monomer conversion increased at first and went to the maximum, then the conversion decreased at temperature of 198 °C. So, it still needs the further investigation of the thermodynamic behavior of microwave-assisted ROP of PDO in order to explain this phenomenon.

Without microwave irradiation, ROP took place slowly at 180°C, and it took 1.5h to obtain PPDO with an Mn of 16,000 g/mol using Sn(Oct)$_2$ as catalyst [17]. Obviously, ROP of PDO was greatly accelerated and improved by a constant microwave power.

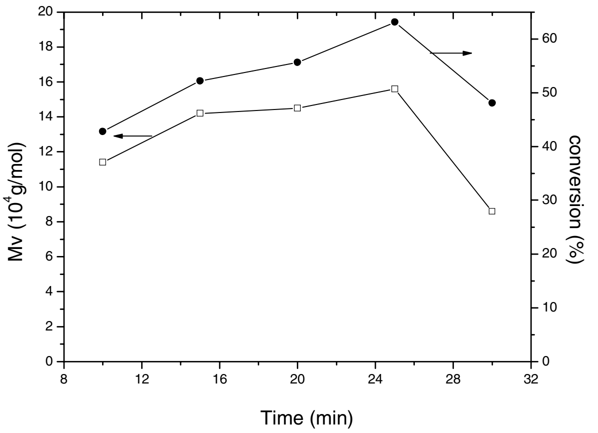


Figure 5 Effect of irradiation time on polymerization [power=270W, M/C(mol/mol)=1000]

The influence of irradiation time on ROP can also not be neglected. As indicated in Figure 5, catalyzed by $Sn(Oct)_2$ and irradiated at 270W for only 10min, the polymerization took place rapidly, resulting in PPDO with Mv of 111,000g/mol. When the polymerization lasted for 25 min, the Mv increased to 156,000 g/mol. When the reaction time further increased, however, the Mv of PPDO was lowed. At this time the occurrence of intra-transesterification reactions was predominant, leading to the formation of cyclic PPDO oligomers, and to some extent, PDO monomer. This was also demonstrated by Libiszowski [5]. Therefore, it was deduced that within 30 min, there were maybe two kinds of chemical reactions: the ROP of PDO and the intra-transesterification of resulted PPDO macromolecules. The dominative reaction was ROP in the presence of the monomers, but intra-transesterification became obvious after most of the monomers were consumed.

The influence of catalyst concentration on ROP was investigated at 270W. In the case of $Sn(Oct)_2$ as a catalyst, the molar ratio of monomer to catalyst was selected as 1000, 2000, 3000, 4000, and 5000, and the reaction mixtures were irradiated for 25 min. An increase in Mv of PPDO was observed with the ratio of $Sn(Oct)_2$ decreased from 1/1000 to 1/5000, and the highest Mv value was 193,000 g/mol at the molar ratio of $Sn(Oct)_2$/PDO of 1/4000. However, a lower concentration of $Sn(Oct)_2$ (1/5000) led to a lower Mv (143,000 g/mol) [Fig.6].

It could be found that the conversion of PDO was not high in this work as the polymerization temperature was around 180ºC. Nishida *et al* [17] reported that bulk polymerization of PDO could proceed homogeneously in the range of 100-180ºC, but the equilibrium conversions were almost the same at each temperature even though the polymerization rates using different catalysts were distinctly different. The equilibrium conversions decreased in a similar manner with increasing polymerization temperature. These results indicate that whichever initiator/catalyst is used for the polymerization of PDO, the conversion of polymerization converges to a thermodynamic equilibrium. When the temperature was 180ºC, the conversion of PDO was 50.5%. Although the conversion value is not high, the microwave assisted ROP still is a competitive method due to its cleanness, low cost, fast and convenient process. Furthermore, we are investigating the methods for enhancing the monomer conversion, which will be reported in the next paper.

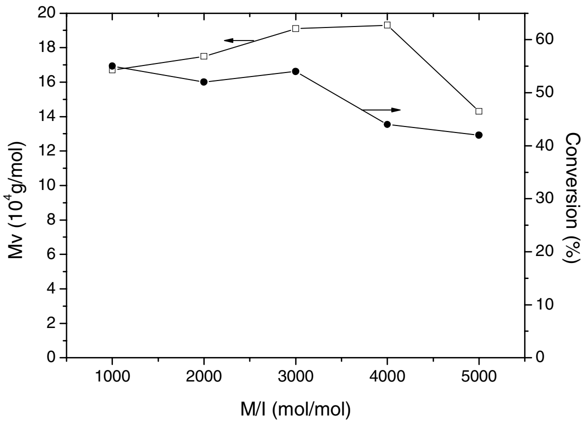


Figure 6 Influence of catalyst concentration on polymerization (power: 270 W, time: 25 min)

Conclusions

PDO can be heated when it is irradiated with constant microwave power. Its temperature increases rapidly within 5 min, but it changes slightly 5 min later. The ROP of PDO catalyzed by $Sn(Oct)_2$ proceeds smoothly with constant microwave power. Poly(*p*-dioxanone) with Mv value of 156,000g/mol and yield of 63% was obtained when ROP of PDO was carried out with a microwave forward energy of 270W for 25 min. Compared with the thermal methods, the microwave assisted polymerization of PDO was greatly accelerated and improved even though the conversion of PPDO synthesized was not high. A further study for improving the microwave-assisted synthesis of PPDO is underway.

Acknowledgements. This work was supported financially by the National Science Fund for Distinguished Young Scholars (50525309) and the Key Project of International Cooperation of China (2004DFA04700)

References

[1] Kricheldorf HR, Damrau DO, (1998) Macromol Chem Phys 199:1089
[2] Wang H, Dong J H, Qiu QY, (1997)Acta Polym Sinca 6:319
[3] Forschner TC. WO 9721753 1997
[4] Bhattarai N, Kim HY, Lee DR, Park SJ, (2003) Polym Int 52:6
[5] Libiszowski J, Kowalski A, Szymanski R, Duda A, Raquez J M, Degee P, Dubois P, (2004) Macromolecules 37:52
[6] Sabino MA, Feijoo JL, Mer AL, (2000) Macromol Chem Phys 201 2687
[7] Nishida H, Konno M, Ikeda A, Tokiwa Y, (2000) Polym Degrad Stab 68: 205
[8] Nishida H, Konno M, Tokiwa Y, (2000) Polym Degrad Stab 68:271
[9] Yang K K, Wang X L, Wang Y Z, Wu B, Jin Y D, Yang B, (2003) Eur Polym J 39:1567
[10] Wang X L, Yang K K, Wang Y Z, Wu B, Liu L, Yang B, (2003) Polym Degrad Stab, 81:215
[11] Andjelic S, Fitz B D, (2000) J Polym. Sci, Part B: Polym Phys 38:2436
[12] Nishida H, Yamashita M, Endo T, (2002) Polym Degrad Stab 78:129
[13] Raquez J M, Degee P, Narayan R, Dubois P, (2001) Macromolecules 34: 8419
[14] Raquez J M, Degee P, Narayan R, Dubois P, (2000) Macromol Rapid Commun 21: 1063
[15] Raquez J M, Degee P, Narayan R, Dubois P, (2004) Polym Degrad Stab 86:159
[16] Raquez J M, Balakrishnan S, Degee P, Narayan R, Dubois P,(2005) Polym Eng Sci 45:622
[17] Nishida H, Yamoshita M, Endo T, Tokiwa Y, (2000) Macromolecules 33:6982
[18] Gedye R, Smith F, Westaway K, Ali H, (1986) Tetrahedron Lett 27:279
[19] Wiesbrock F, Hoogenboom R, Schubet US, (2004) Macromol Rapid Commun 25:1739
[20] Correa R, Gonzalez G, Dougar V, (1998) Polymer 39:1471
[21] Porto AF, Sadicoff BL, Amorim MCV, Mattos MCS, (2002) Polym Test 21:145
[22] Keki S, Bodnar I, Borda J, Deak G, Zsuga M, (2001) Macromol Rapid Commun 22:1063
[23] Velmathi S, Nagahata R, Sugiyama J, Takeuchi K, (2005) Macromol Rapid Commun 26:1163
[24] Xu WL, Bao JJ, Zhang JC, Shi MW, (1998) J Appl Polym Sci 70:2343
[25] Liu L, Li Y, Fang Yue-e, Chen L X, (2005) Carbohydr Polym 60:351
[26] Albert P, Wasth H, Muelhalpt R, Janda R, (1996) Makromol Chem Phys 197:1633
[27] Fang X M, Hutcheon R., Scola DA, (1998) Polym Mater Sci Eng Proc ACS Boston Meeting
[28] Fang X M, Hutcheon R., Scola DA, (2000) J Polym Sci Part A: Polym Chem 38:1379
[29] Liu L J, Zhang C, Liao LQ, Zhuo RX, (2001) Chin Chem Lett 12:663
[30] Barbier-Baudry D, Brachais CH, Cretu A, Loupy A, Stuerga D, (2002) Macromol Rapid Commun 23:200
[31] Liao L Q, Liu L J, Zhang C, He F, Zhuo R X., (2002) J Polym Sci Part A: Polym Chem 40:1749
[32] Yu Z J, Liu L J, (2004) Eur Polym J 40:2213
[33] Mingos D M P, (1999) Chem Soc Rev 20:1