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Synthesis of block copolymers of poly(*p*-dioxanone) block poly(tetrahydrofuran)

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Summary

The triblock copolymers of poly(*p*-dioxanone)-*b*-poly(tetrahydrofuran)-*b*-poly(*p*-dioxanone) were synthesized by ring-opening polymerization of *p*-dioxanone in the presence of dihydroxyl poly(tetrahydrofuran)(PTHF) using stannous octoate ($SnOct_2$) as a catalyst. The effects of feed ratio, reaction time and reaction temperature on the copolymerization were investigated. It was found that the optimal reaction temperature and time were 80 °C and 42 hours, respectively, and the molar ratio of *p*-dioxanone/ $SnOct_2$ (PDO/cat.) had little influence on the inherent viscosity of the copolymers. The triblock copolymers were characterized by various analytical techniques such as ^{1}H-NMR and DSC.

Introduction

Aliphatic polyesters such as polylactide (PLA), polyglycolide (PGA) and poly(ε-caprolactone) (PCL), have been investigated worldwide as biomaterials because of their biocompatibility and biodegradability in recent decades. A series of polyesters and copolyesters have been successfully synthesized [1-6]. In recent years, another aliphatic polyester, poly(*p*-dioxanone)(PPDO) has attracted many researchers' attention. PPDO is a kind of material with excellent biodegradability, bio-absorbability, biocompatibility, and good flexibility, and well known as a good candidate for medical use. It is now considered as a candidate not only for medical uses, but also for universal uses, such as film, moulded products, laminates, foams, nonwoven material and adhesivesand coatings [7-9].

However, PPDO has not become the popular biomaterial because it has some defects such as rigorous synthetic condition, low crystallization rate, low melt viscosity which influenced its processing properties and limited its application seriously. Generally, copolymerization and blending are two effective ways to modifying the properties of the polymer materials and to widening its application. These two approaches [10-13] have already been introduced into PPDO system and some valuable results have been achieved in recent years. Dubois et al [14] and Dong et al [15,16] reported the copolymerization of PPDO with PCL, polytrimethylene carbonate (PTMC) and PEG, respectively. Triblock copolymer of PPDO, PLA and PEG has also been studied [12,13]. Our group investigated the copolymerization and blending of PPDO with starch, poly(vinyl alcohol) (PVA) [17-20]. In this paper, the block copolymers of poly(*p*-dioxanone)-b- poly(tetrahydrofuran) were synthesized by ring-opening polymerization of PDO in the presence of dihydroxyl poly(tetrahydrofuran)(PTHF) using stannous octoate ($SnOct_2$) as a catalyst for the first time.

Experimental section

Materials

PTHF(Mn=2000) was purchased from Shengquan Group Co., Ltd. (Jinan, China) dried under reduced pressure at 25 ºC for 24 hours before use. PDO that was provided by the Pilot Plant of the Center for Degradable and Flame-Retardant Polymeric Materials (Chengdu, China) was dried over CaH_2 for 48 h, distilled under reduced pressure. $SnOct_2$ from Sigma was used after dissolving it in pure and dry toluene.

Copolymerization procedure

PTHF was introduced into a flame-dried glass reactors, then the reactors were evacuated and purged with argon several times prior to addition of PDO and $SnOct_2$ initiator solution with a syringe 30 minutes later. Then the reactors were immersed into a temperature-adjusted silicone oil bath for predetermined intervals. The reactors were rapid cooled down to room temperature and the products were purified by precipitation from the phenol/1,1,2,2–tetrachloroethane (2:3 w/w) solution with methanol and dried under vacuum to a constant weight. Inherent viscosity was measured in phenol/1,1,2,2–tetrachloroethane (2:3 w/w) solution at 25 ºC.

Measurements

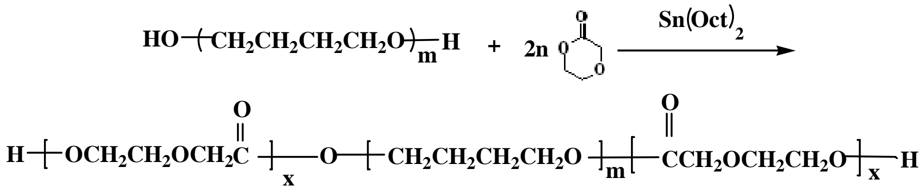
^{1}H nuclear magnetic resonance (^{1}HNMR) spectra were recorded at room temperature with a varian INOVA-400 spectrometer operating at 400 MHz by using DMSO-d_6 as the solvent. Chemical shifts (δ) were given in ppm using tetramethylsilane as an internal reference.

Thermal analysis was performed with 204 differential scanning calorimeter (NETZSCH, Germany) under an ultrahigh purity nitrogen atmosphere from room temperature to 140 ºC at heating rate of 10 ºC/min.

Results and Discussion

Copolymerization: Triblock copolymers consisting of a PTHF central block and two PPDO lateral blocks were synthesized by ring-opening polymerization of PDO in the presence of PTHF, as shown in Scheme 1.

The copolymers obtained were characterized via ^{1}H NMR. A typical spectrum of copolymer was illustrated in Figure 1. Signals at 1.50 ppm and at 3.47 ppm result from PTHF blocks. The signals corresponding to different methylene protons of PDO units are in the following ranges: 3.71 ppm, 4.17 ppm and 4.33 ppm. The structures of copolymers are shown in Scheme 1. The PDO/THF ratio in the copolymers can be determined from the integration of NMR resonance belonging to PPDO blocks at



Scheme 1 Ring-opening polymerization of PDO in the presence of PTHF using $SnOct_2$ as a catalyst

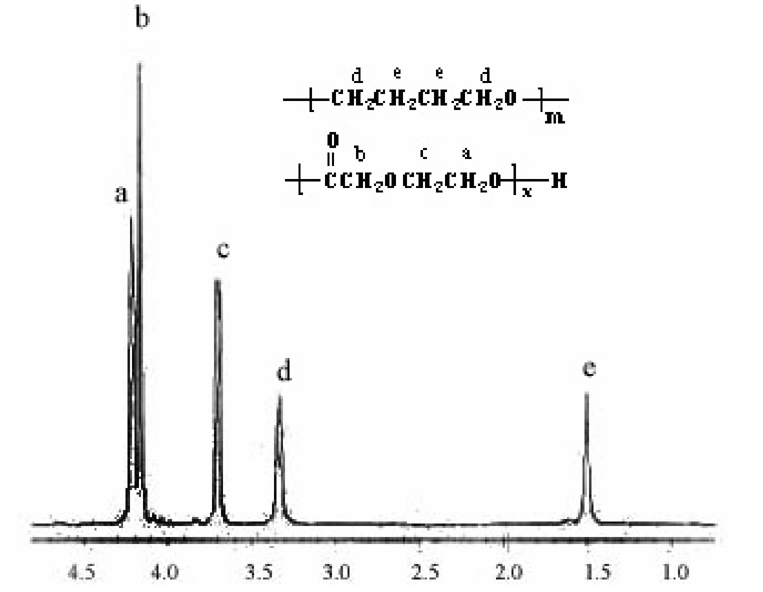


Figure 1. ^{1}H-NMR spectrum of PPDO/PTHF

3.71 ppm and to PTHF blocks at 1.50 ppm. The number average molecular weight, Mn, can be calculated from the PDO/THF ratio in the copolymers because the THF repeat units are constant.

In this case, PTHF with dihydroxyl end acts as macroinitiator, and $SnOct_2$ has been used as catalyst for the ring-opening polymerization of PDO in which the general “coordination-insertion” mechanism [21,22] has been accepted. According to this mechanism, the molecular weight of resulting copolymers only related with the molar ratio of PDO/hydroxyl group (PDO/-OH) but not with the molar ratio of PDO/$SnOct_2$. Figure 2 and Figure 3 illustrated the relationship between the inherent viscosity of products and the molar ratios of PDO/-OH and PDO/$SnOct_2$, respectively. The results matched this mechanism quite well. As shown in Figure 2, the inherent viscosity of copolymers was not changed obviously while the molar ratio of PDO/$SnOct_2$ increased from 200 to 1200. From Figure 3, it could be found that the inherent viscosity increased sharply with the increase of PDO/-OH ratio when the temperature was 80 °C, and the reaction time 48 hours. For example, when PDO/-OH ratio increased from 50 to 1000, the inherent viscosity increased sharply from 0.47 to 1.14 when the PDO/$SnOct_2$ is 2000.

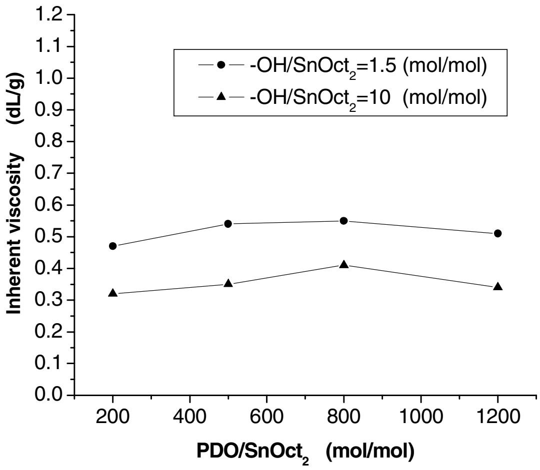


Figure 2. Effect of PDO/ $SnOct_2$ on inherent viscosity

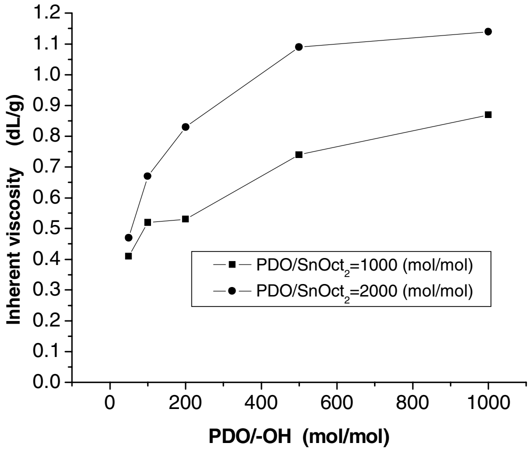


Figure 3. Effect of PDO/-OH on inherent viscosity

Besides the feed ratio of monomer to catalyst, the reaction temperature and reaction time also act important roles during the copolymerization. Keeping the ratios of PDO/cat and PDO/-OH unchanged, a series of copolymerization reactions have been carried out by changing the reaction temperature from 60 ºC to 100 ºC and the reaction time from 24 hours to 72 hours. The results are shown in figure 4. From Figure 4, we can see that the inherent viscosity increases firstly with the increase of reaction temperature and reaction time, but then gradually decreases when the reaction temperature and time further increase. In the case of copolymerization at 80 ºC, when the reaction time is 24 hours, the inherent viscosity is 0.62; when reaction time increases to 36 hours, the inherent viscosity increases to 0.74. However, with the further increase of reaction time to 72 hours, the inherent viscosity decreases to 0.59. In the case of copolymerization for 48 hours, when the reaction temperature is 60 ºC, the inherent viscosity is 0.59, when reaction temperature rise to 80 ºC the inherent

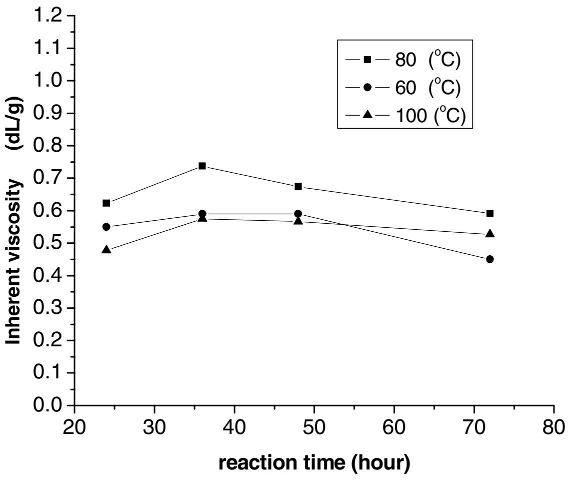


Figure 4. Effect of reaction time and temperature on inherent viscosity

viscosity increases to 0.67. However, with the further increase of reaction temperature to 100 ºC, the inherent viscosity decreases to 0.56. The possible reason is that at first, the increases of reaction time and reaction temperature are both good for the propagation of chains. On the contrary, with the further increase of reaction time and reaction temperature, the degradation and chain cleavage occur, and these side reactions cause chain transfer, which causes the molecular weight and the inherent viscosity of the copolymers to decrease. So it is not easy to obtain the copolymers with high inherent viscosity at high temperature. The optimal reaction time can be found to fall into the range from 38 hours to 42 hours, and a temperature of around 80 ºC is the optimum for the copolymerization.

Figure 5 shows the DSC scan curves of one sample, which contains 93 mol% of PDO. The cooling scan of the sample exhibits a crystallization exothermal peak around

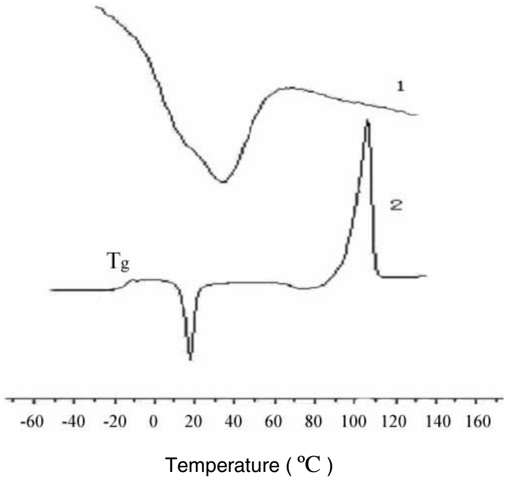


Figure 5. DSC curve of PPDO/PTHF: 1 cooling curve; 2 heating curve

35 ºC, and the heating scan of the sample exhibits another crystallization exothermal peak around 18 ºC. This sample exhibited a glass transition at –16 ºC. There is no significant difference between the glass transition temperatures (T_g) and melting temperatures (T_m) of this sample and neat PPDO [7].

Conclusions

When PTHF was used as a macroinitiator and stannous octoate as catalyst, ABA type triblock copolymers (PDO-b-THF-b-PDO) could be synthesized in bulk by ring-opening polymerization of PDO with PTHF. The optimal reaction conditions are as follows: temperature 80 ºC, reaction time 38-42 hours, and the molar ratio of monomer to catalyst has no significant influence on the inherent viscosity of the copolymers. The crystallization behaviors of copolymers with high content of PPDO have almost no variation with PPDO.

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References

[1] Li S. (1999) J Biomed Mater Res 48:342
[2] Kikkzwa Y,Abe H, Iwata T,Inoue Y, Doi Y(2001) Biomacromolecules 2:940
[3] Christine A, Jeannie H,Yu YS,Dusica M. (2000) J Controlled Release 63:275
[4] Kweon HY, Yoo MK. (2003) Biomaterials 24:801
[5] Yu ZJ, Liu LJ (2004) Eur Polym J 40 (9):2213
[6] Rajeev AJ,(2000) Biomaterials 21;2475
[7] Yang KK, Wang XL, Wang YZ.(2002) J Macromol Sci Polym Rev 42:373
[8] Lipinsky ES, Sindair RG, Browning JD. US 5767222 1993
[9] Forschner TC. WO 9721753 1997
[10] Zheng L, Wang YZ, Yang KK. (2005) Eur Polym J 41:1243
[11] Wang XL,Yang KK, Wang YZ. (2004)Acta Mater 52:4899
[12] Narayan B, Kim HY. Eur Polym J (2003) ;39:1365-1375
[13] Narayan B, Kim HY. Polym Degrad Stab (2002) ;78 :423-433
[14] Raquez, J.-M.; Degee, Ph.; Narayan, R; Dubois, Ph. (2000) *Macromol. Rapid Commun.* 21: 1063
[15] Wang H, Dong,J H, Qiu QY, Gu ZW (1998) J Polym Sci: Part A: Polym Chem. *36*: 1301
[16] Wang H, Dong JH, Qiu KY (1997) *Acta Polym Sin 6*: 319-323
[17] Wang XL, Yang KK, Wang YZ, (2004) *Acta Mater* 52(16): 4899
[18] Wang XL, Yang KK, Wang YZ, (2004) *J Polym Sci, Part A Polym Chem* 42:3417
[19] Zhou ZX, Wang XL, Wang YZ , (2006) *Polym Intl* 55:383
[20] Chen SC, Zhou ZX, Wang YZ, Wang XL , Yang KK, (2006) *Polymer* 47:32
[21] Shen YQ, Shen ZQ, Zhang YF, (1996) *Polym Bull* 37:21
[22] Dubois PH, Jerome R, Teyssie PH, (1989) *Polym Bull* 22:475