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A study on grafting poly(1,4-dioxan-2-one) onto starch via 2,4-tolylene diisocyanate

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Abstract

A new biodegradable copolymer of starch-*graft*-poly(1,4-dioxan-2-one) (starch-*g*-PPDO) was synthesized by solution polymerization in dimethyl sulfoxide using 2,4-tolylene diisocyanate (TDI) as a coupling agent. The length of PPDO graft chains can be controlled easily by using the prepolymers of PPDO with different molecular weights. The copolymers were prepared by two-step reactions. First, the isocyanate–terminated intermediate (PPDO–NCO) was prepared by introducing one NCO group of TDI onto the hydroxyl end-group of PPDO; second, PPDO–NCO was grafted onto corn starch chains by the reaction between the unreacted NCO group and the hydroxyls of starch, and then, starch-*graft*-PPDO was obtained. The chemical structure of PPDO–NCO and graft copolymers was confirmed by using FT-IR and ^{1}H NMR, and the thermal properties of the copolymers were investigated by DSC and TG.

Keywords: Starch; Poly(1,4-dioxan-2-one); Graft copolymer; Synthesis

1. Introduction

Starch as one of the most important biopolymers from agriculture resources, has drawn much attention from the standpoints of ecological and environmental situations. Recently, starch has been widely used for thermoplastic production due to its abundance, low cost and fully biodegradability (Funke, Bergthalle, & Lindhauer, 1998; Wang, Yang, & Wang, 2003).

Starch by itself, however, cannot satisfactorily replace the petroleum-based plastics because of its poor physical properties, including poor long-term stability caused by water absorption, poor mechanical properties, and processability. To solve these problems, various physical or chemical modifications of starch molecule have been studied, such as blending (Peanasky, Long, & Wool, 1991; Schwach & Avérous, 2004), chemical derivation (Woff, Olds, & Hilbert, 1951; Aburto et al., 1999), and graft copolymerization (Bagfey, Fanta, Burr, Doane, & Russel, 1977; Brockway & Seaberg, 1967).

Blends of starch and aliphatic polyesters have been studied due to their good biodegradability and low prices (Kim, Cho, & Park, 2001a,b; Koenig & Huang, 1995). However, because of the poor compatibility of these two components, the use of compatibilizer is necessary to enhance the interfacial adhesion between their phases (Kim, Cho, & Park, 2001a,b; Odusanya, Manan, Ishiaku, & Azemi, 2003). Under this background, lots of studies on the synthesis of starch-*graft*-polyesters have been attempted (Dubois, Krishnan, & Narayan, 1999; Mani, Tang, & Bhattacharya, 1998; Rutot, Duquesne, Ydens, Degée, & Dubois, 2001).

Poly(1,4-dioxan-2-one) (PPDO) is a kind of aliphatic polyester, which has been widely used as biodegradable suture material due to its good tenacity and knotting properties (Yang, Wang, & Wang, 2002). Because of its good physical properties and biocompatibility, PPDO is considered as a candidate not only for medical use but also for universal use such as films, molded products, laminates, foams, nonwovens, and coatings (Nishida, Yamashita, Hattori, & Endo, 2000). Low-cost natural polymers such as starch and cellulose can be blended with PPDO to lower its cost. Previous study (Wang, 2003) has show that there are no compatibility between PPDO and starch. Wang, et al. (2004) had synthesized starch-*graft*-PPDO (SGP) via the grafting reaction between hydroxyl groups of the starch and 1,4-dioxan-2-one (PDO) monomer in the presence of Sn(Oct)$_2$. However, the degree of graft polymerization (DGP) is low (the maximum value is 9.1) because of the poor initiating ability of the starch macromolecule initiator. Previous work (Sakellarious, Estmond, & Miles, 1991) had proved that the graft

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copolymer will have good interfacial activity for the blend when the molecular weight of each block was greater than that of the corresponding homopolymer. It can be expected that the longer the graft PPDO chain is, the better the interfacial activity is.

In this work, we focus on a new way to synthesis starch-*graft*-PPDO by using TDI as coupling agent. The reaction of isocyanates with alcohols and carboxylic acids has been well studied and reviewed earlier (Arnold, Nelson, & Verbanc, 1957). By using the active group of TDI, NCO groups, to react with the hydroxyl groups at the terminal of the PPDO and in the starch molecule, respectively, the PPDO with certain chain lengths are introduced onto the backbone of starch. Starch-*graft*-PPDO was characterized by FT-IR, ^{1}H NMR, TG and DSC.

2. Experimental

2.1. Materials

Corn starch was purchased from the First Chengdu Flour Mill (Chengdu, China), and was dried in a vacuum oven at 80 °C for 24 h under P_2O_5 before used. Dimethyl sulfoxide (DMSO), purchased from The Third Chemical Reagent Factory (Tianjin, China), was dried by refluxing over CaH_2 and purified three times by distillation. 1,4-Dioxan-2-one, PDO, was provided by the Pilot Plant of the Center for Degradable and Flame-Retardant Polymeric Materials (Chengdu, China). 2,4-Tolylene diisocyancate (TDI) was purchased from The First Chemical Reagent Factory (Shanghai, China). Alcohol and 1,2-dichloroethane, which was used for purification of the starch graft copolymers produced, were purchased from Changlian Chemical Reagent Factory and Kelong Chemical Reagent Factory (Chengdu, China), respectively. Phenol and 1,1,2,2-tetrachloroethane were both purchased from Kelong Chemical Reagent Factory (Chengdu, China). These materials were used as received without further purification.

2.2. Synthesis of PPDO

The whole controlled synthesis of PPDO with triethylaluminum (AlEt3) initiation was performed as described previously (Yang, 2003). In this way, the PPDO terminated with –OH at one end and –C2H5 at the other end was obtained. In this work, PPDO samples with an intrinsic viscosity of 0.12 and 0.66 dL/g, which were denoted as PPDO1 and PPDO2, respectively, were used to perform the experiments.

2.3. Preparation of PPDO–NCO

PPDO (2.5 g) was placed in a glass reactor and then the reactor was vacuumed and purged with nitrogen gas three times, after that it was placed in an oil bath at 110 °C. After PPDO melted, TDI (18 wt% as PPDO) was slowly added into the reactor by injector with agitation. The reaction was carried out at 110 °C for 0.5 h under nitrogen atmosphere. When the reaction mixture was cooled to room temperature, the light yellow intermediate PPDO–NCO was obtained.

2.4. Synthesis of starch-graft-PPDO (SGP)

Vacuum-dried starch and anhydrous DMSO were added into a reactor at a ratio of 1:20 (w/v), and they were placed in a 60 °C oven until the starch dissolved. Then, the starch solution was slowly added into the reactor containing PPDO–NCO with vigorous stirring at 80 °C. The feed ratio of starch:PPDO:TDI was 1:2.5:0.45 (w/w/w). When the reaction went on for 2 h, the reaction product was precipitated in alcohol and filtered. The unreacted PPDO and PPDO–NCO were removed by Soxhlet extraction with 1,2-dichloroethane until constant weight was reached. The dried pure graft copolymer powder was obtained after further drying under vacuum for 24 h. The yield (Y) and grafting efficiency (GE) were calculated by the flowing equations

$$Y\ (\%) = \frac{W_1 \times 100}{W}$$

$$\mathrm{GE}\ (\%) = \frac{(W_1 - W_2) \times 100}{(W - W_2)}$$

where W is the starting weight of both starch and PPDO, and W_1 and W_2 are the weight of the refined products and starch, respectively.

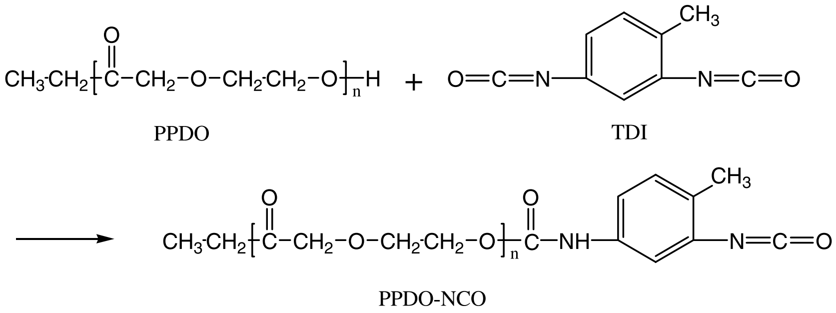
2.5. Characterization

The intrinsic viscosity was measured with Ubbelohde viscosimeter in water bath at 25 °C, using phenol/1,1,2,2-tetrachloroethane (2:3/w:w) as solvent, and the concentration of the solution is 0.1 g/dL. Fourier transform infrared (FT-IR) spectra were measured with an FT-IR spectrometer (Nicolet 170SX), using KBr pellets of the PPDO–NCO and starch graft copolymers. ^{1}H NMR spectra were recorded on a spectrometer (Varian INOVA-400) at 25 °C using DMSO-d_6 as the solvent and tetramethylsilane (TMS) as the internal standard. Thermal stability of the starch graft copolymers was measured with a thermal gravimetric analyzer (Perkin–Elmer TGA7) in a temperature range of 30–500 °C at a heating rate of 10 °C/min. The thermal transition of PPDO and starch graft copolymers were measured by a differential scanning calorimeter (SEIKO EXSTRA6000) under nitrogen flow (10 mL/min), and the heating or cooling scans carried out at a rate of 10 °C/min from -50 to 200 °C after keeping sample at 200 °C for 5 min in order to erase its thermal history.

3. Results and discussion

3.1. Synthesis of starch-g-PPDO copolymers

In general, isocyanates can easily react with compounds containing active protons, such as alcohols, amines, and acids. The intermediate PPDO–NCO produced as shown in Scheme 1, contains a carbamate group and an –N=C=O, indicating that only one of two NCO groups in TDI took part in the addition reaction. Changing the ratios of PPDO to TDI makes it possible to control the side reaction that leads to chain extending as



Scheme 1. Preparation of PPDO–NCO.

shown in Scheme 2. Since chain extending can lead to the increase of the intrinsic viscosity of PPDO, the relationship between the amount of TDI and the variation of the intrinsic viscosity of PPDO should be discussed so as to choose the right ratio of PPDO to TDI, which was shown in Table 1.

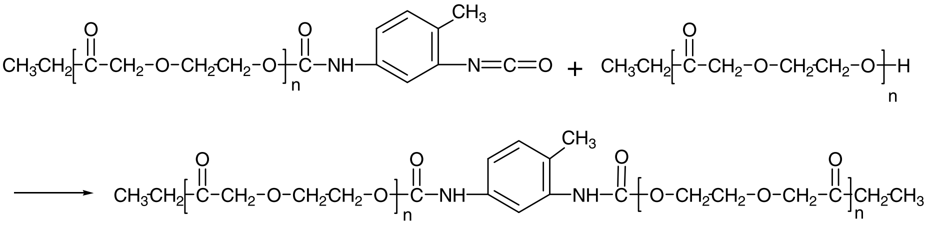
From Table 1 we can see that at the beginning, the intrinsic viscosity of the product increases with the amount of TDI, indicating that the chain extending as the side reaction had probably occurred. When the weight ratio of TDI to PPDO1 reached 0.12, the intrinsic viscosity of PPDO1 reached the maximum (0.30 dL/g). This indicated that the chain extending of the side reaction had probably reacted to its highest extent. Then, with the further increase of TDI amount, the intrinsic viscosity of PPDO1 decreased until reaching a constant value. From this we can infer that, when the weight ratio of TDI to PPDO1 reaches 0.18, the end groups of PPDO1 are likely to be terminated by TDI before the chain extending of the side reaction, hereby the PPDO1–NCO is generated. The ^{1}H NMR spectra have confirmed the above inference. As shown in Fig. 1, the ^{1}H NMR spectra of unreacted PPDO showed a characteristic peak at 3.43 ppm, corresponding to the terminal hydroxyl groups. Due to the incorporation of NCO, the NMR spectra showed several new peaks such as the methyl of TDI at 2.15 ppm, the benzene ring at 7.05 ppm and the newly formed amide NH groups 5.52 ppm, whilst the signal of terminal hydroxyl groups of PPDO completely disappeared, indicating that isocyanation of all the terminals of PPDO was almost completed. Therefore, the ratio of 0.18 of TDI to PPDO1 is just what we expected. In the case of PPDO2–NCO prepared with PPDO2, the condition was similar to those prepared with PPDO1.

Second, the unreacted NCO group in the intermediate can be used in further isocyanation with starch as shown in Scheme 3. The results are shown in Table 2. It can be seen that the yield (*Y*) and grafting efficiency (GE) of SGP change continuously with the ratio of starch:PPDO:TDI. At the beginning, both *Y* and GE increased with the increasing content of starch, because there are more initiating hydroxyls of increased starch for NCO–PPDO to graft onto. Then *Y* and GE reached their climaxes at the optimal starch:PPDO:TDI ratio of 1:2.5:0.45. With the further increase of starch feeding ratio, the hydroxyl of starch was excessive and the graft copolymerizaion had reached saturation, so the increased starch content cannot further promote the graft reaction, and the value of *Y* and GE decreased.

Furthermore, at the same feeding ratio of starch:PPDO:TDI, the values of *Y* and GE of SGP2 are lower than those of SGP1. It is due to the density of end groups in the solution of PPDO2 with larger molecular weights is inevitably smaller than that of PPDO1 with lower molecular weights. On the other hand, the PPDO2 solution had higher viscosity than PPDO1 solution due to the higher molecular weight of PPDO2, causing the poorer mobility of PPDO2 chains.

3.2. Structure characterization

The expected synthesis route and structure of PPDO–NCO and SGP are shown in Schemes 1 and 3. The FT-IR spectra of PPDO, PPDO–NCO and SGP are given in Fig. 2. The FT-IR spectrum of PPDO (Fig. 2(a)) shows a strong hydroxyl peak at 3436 cm^{-1} and a sharp peak at 1733 cm^{-1} for the internal ester groups. By introducing NCO groups onto the PPDO terminal, the FT-IR spectrum of PPDO–NCO (Fig. 2(b)) shows a new sharp peak around 2270 cm^{-1} (marked by arrows) assigned to the NCO groups and at 1540 cm^{-1} for the newly formed amide NH groups, as well as a new peak at 1600 cm^{-1} which is due to the presence of the aromatic group originated from TDI. By grafting PPDO–NCO onto starch, the NCO peak at 2270 cm^{-1} disappears in the FT-IR spectrum of SGP (Fig. 2(c)), which means that the NCO group has been changed into the carbonate group and the absorption of amide NH groups at 1540 cm^{-1} and aromatic



Scheme 2. The side reaction of preparation of PPDO–NCO.

Table 1
The intrinsic viscosity (η) of PPDO at varying TDI/PPDO ratios

Reactants	TDI (g)/PPDO (g)	η (dL/g)
PPDO1	0.00	0.12
	0.07	0.24
	0.12	0.30
	0.18	0.14
	0.23	0.14
PPDO2	0.00	0.66
	0.07	1.05
	0.12	1.52
	0.18	0.68
	0.23	0.69

Reaction was carried out at 110 °C for 0.5 h.

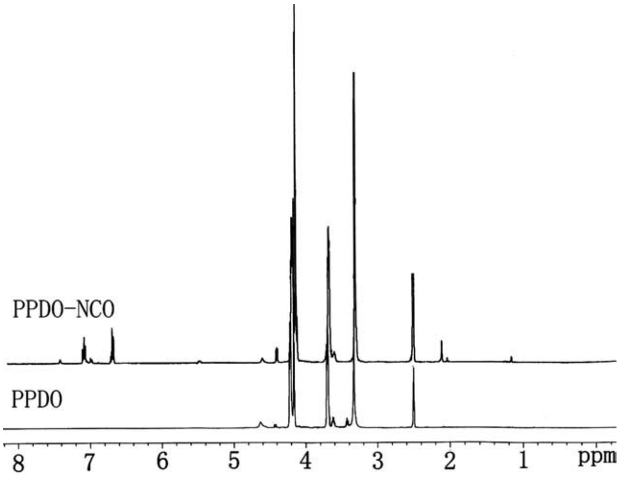


Fig. 1. ^1H NMR spectra of PPDO and NCO–PPDO when the weight ratio of TDI to PPDO1 was 0.18.

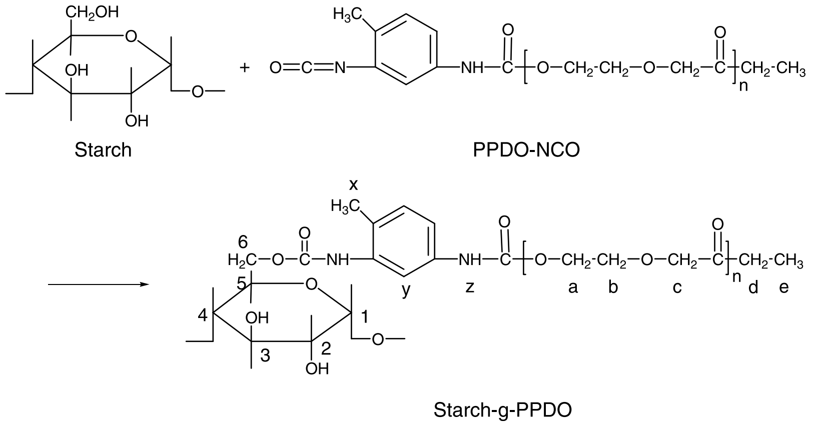
groups at 1600 cm^{-1} are retained. These results suggest that graft copolymer, starch-*graft*-PPDO, are formed via the reactions of the two NCO groups of TDI with hydroxyls of PPDO and starch, respectively.

In order to further confirm the chemistry structure of SGP, we performed the ^1H NMR measurement. The labels of the protons are shown in Scheme 3. Just as shown in Fig. 3, the ^1H NMR spectrum of SGP shows the peaks of both starch and PPDO, indicating the formation of the graft copolymers starch-*graft*-PPDO. The characteristic PPDO protons from side chain are seen in the region from 3.70 to 4.21 ppm (H_a, H_b, H_c), and two small peaks at 4.43 ppm (H_d) and 1.24 ppm (H_e) corresponding to the protons of CH_2 and CH_3 groups of the terminating ethyl group can also be observed. The peak at 5.11 ppm connects to the H_1 from starch, while the majority of peaks from the main chain (starch) are highly overlapped therefore, they cannot be assigned. The ^1H NMR spectrum of SGP also shows resonance at 2.15 ppm for the methyl of TDI, resonance at 7.05 ppm for the benzene ring, and resonance at 5.52 ppm for the newly formed amide NH groups.

3.3. Thermal stability of the starch-g-PPDO copolymer

The TG and DTG curves for the thermal decomposition of starch, PPDO and starch graft copolymers are presented in Figs. 4 and 5, respectively. As shown in Fig. 4(a) and (b), the weight loss of the pure starch starts at 290 °C, and PPDO starts at 219 °C. Although starch was measured in the form of dry powder, it still contained approximately 14% moisture in their molecules, which resulted in the initial weight loss observed in its TG curve. By grafting varied PPDO onto starch, the starch graft copolymers show different thermal stability from pure starch. Just as shown in Fig. 4(c) and (d), SGP1 with shorter side chains that were derived from the raw material PPDO1, starts decomposing at lower temperature (241 °C) and continues decomposing in broader temperature ranges (241–322 °C), while SGP2 with longer side chains that were grafted from PPDO2, has a higher decomposing temperature (304 °C), and its decomposition ends at 440 °C.

From the DTG curves of SGP1 (Fig. 5(c)), it can be observed that the decomposition of SGP1 has two stages. In the first stage, the maximum-decomposing-rate temperature (T_{max1}) appears at 282 °C, corresponding to the decomposition of side chains PPDO1; in the second stage, T_{max2} appears at 322 °C, corresponding to the decomposition of starch. However, this phenomenon cannot be observed from the DTG curves of SGP2 (Fig. 5(d)), on which there is only one



Scheme 3. Preparation of SGP.

Table 2
Y And GE of SGP at various weight ratios of starch:PPDO:TDI

Sample	Starch: PPDO:TDI	Results	
	(g:g:g)	*Y* (%)	GE (%)
SGP1	0.5:2.5:0.45	55.8	48.3
	0.75:2.5:0.45	63	53.6
	1:2.5:0.45	72.2	62.7
	1.25:2.5:0.45	70.9	58.6
	1.5:2.5:0.45	52.1	27.7
SGP2	0.5:2.5:0.45	42.2	32.4
	0.75:2.5:0.45	51.7	39.5
	1:2.5:0.45	60.8	47.5
	1.25:2.5:0.45	58.9	41.5
	1.5:2.5:0.4	48.1	21.7

Reaction was carried out in DMSO at 80 °C for 2 h.

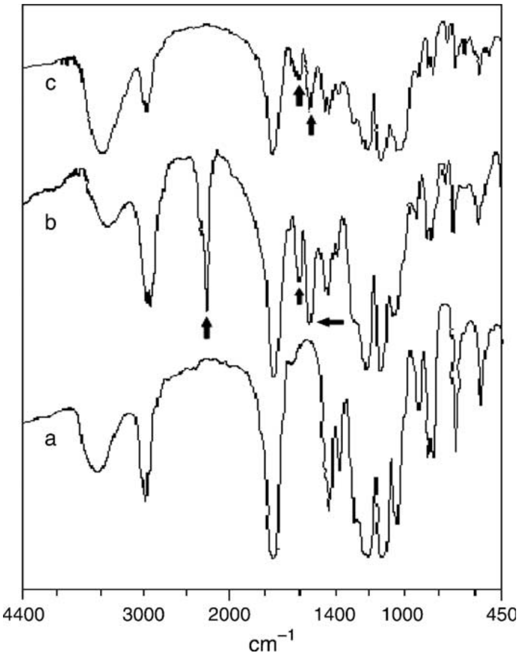


Fig. 2. FT-IR spectra of (a) PPDO, (b) PPDO–NCO, and (c) SGP.

peak. This is due to the fact that SGP1 and SGP2 have different molecular weights of PPDO grafts as side chains, which has an influence on the thermal stability of PPDO. The higher the molecular weight of PPDO grafts, the better the thermal stability of the grafted copolymers. This phenomenon was also reported previously (Yang, Wang, & Wang, 2003). When the intrinsic viscosity of PPDO is 0.66 dL/g, the maximum-decomposing-rate temperature is 299 °C, which is consistent with the temperature range of starch decomposition (290–310 °C), therefore, we cannot observe two peaks on DTG curves. All the detailed data are given in Table 3.

3.4. Thermal transition temperatures of starch-g-PPDO copolymers

The thermal transition temperatures of PPDO and starch-*g*-PPDO copolymers are determined via DSC. The cooling and heating scans are shown in Figs. 6 and 7, respectively. The relevant enthalpies (ΔH_m and ΔH_c), the glass transition (T_g), the crystallization temperature (T_c) and melting temperature (T_m) of them are shown in Table 4.

From the cooling scans of PPDO and SGPs (Fig. 6), we can observe that each of them has a crystallization exothermal peak around 42–45 °C and the crystallization enthalpy (ΔH_c) of SGP2 (-12.8 J/g) is higher than that of SGP1 (-5.6 J/g). From the perspective of crystallization thermodynamics, this result suggests that the crystallization capability of SGP2 is higher than that of SGP1, which can be explained by Choi's theory that the crystallization behaviors of grafted copolymers are related to their molecular structures (Choi, Kim, & Park, 1999). The short graft chains of SGP1 lead to a destruction of regularity of the grafted copolymers, consequently SGP1 has a poorer crystallization capability and a lower crystallization enthalpy as well. In contrast, the longer graft chains of SGP2 have little effect on the regularity of the grafted copolymers, so SGP2 has a stronger crystallization capability and a higher crystallization enthalpy than SGP1 that has shorter graft chains.

In their subsequent heating scans (Fig. 7), both SGP2 and PPDO have one more cold crystallization exothermal peak (T_{c1}),

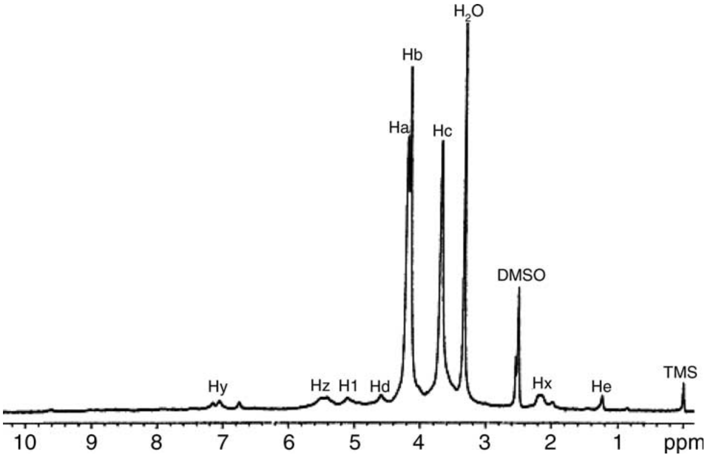


Fig. 3. ^{1}H NMR spectrum of SGP.

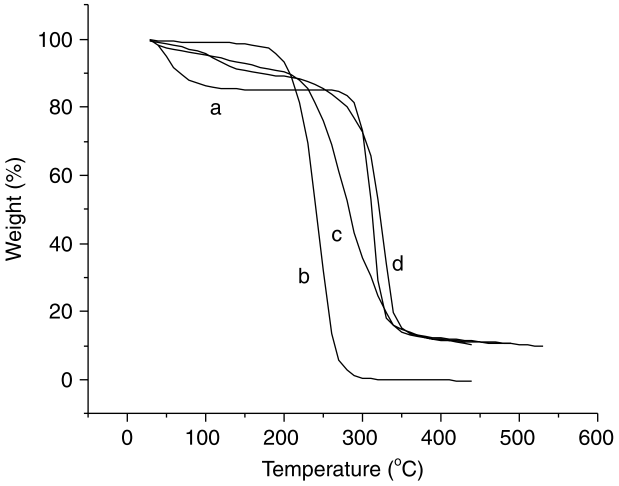


Fig. 4. TG curves of starch (a), PPDO (b), SGP1(c), and SGP2 (d).

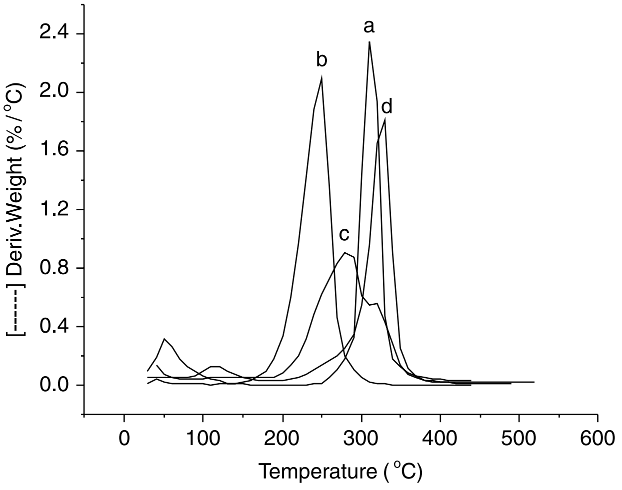


Fig. 5. DTG curves of starch (a), PPDO (b), SGP1(c), and SGP2 (d).

while this phenomenon cannot be found in the heating scan of SGP1. From the perspective of crystallization kinetics, copolymers with strong crystallization capability does not necessarily have fast crystallization rate. Crystallization rate depends on two factors: one is the nucleation rate, and the other is the crystal growth rate. As for SGP copolymers, their crystallization rates mainly depend on the crystal growth rate of PPDO because the nucleation rates of the copolymers with different lengths of PPDO side chains are not quite different due to the same heterogeneous nucleation of starch (Wang, Yang, & Wang, et al., 2004; Wang, Yang, Wang, Wang, & Yang, 2004)). Therefore, the lower the molecular weights of PPDO side chains, the faster the crystallization rate of copolymers due to the better molecular mobility of PPDO chains. In spite of having a stronger crystallizability, SGP2 still crystallizes very slowly due to the higher molecular weights of its side chains, so there is still uncrystallized SGP2 left in the system after the cooling scan. When the temperature rises to the proper crystallization range again, the uncrystallized SGP2 would continue crystallizing, exhibiting one more cold crystallization exothermal peaks in the heating scan. On the contrary, owing to the much lower molecular weight, SGP1 can crystallize fast enough during the cooling scan, so there are not new crystals

Table 3
The data of thermal degradation of starch and graft copolymers

Sample	$T_{20\%}$ (°C)	$T_{50\%}$ (°C)	$T_{\max1}$ (°C)	$T_{\max2}$ (°C)	T_i (°C)	Residue at 440 °C (%)
Starch	292.13	313.27	–	315.25	290.00	10.36
PPDO	221.17	241.40	–	249.07	219.20	0.82
SGP1	245.38	284.58	282.63	322.15	241.19	11.10
SGP2	280.00	323.12	–	325.68	304.37	11.44

$T_{20\%}$ represents the temperature of 20% decomposition conversion. T_i represents the initial decomposition temperature. $T_{\max}$ represents the temperature at which the decomposition rate is maximal.

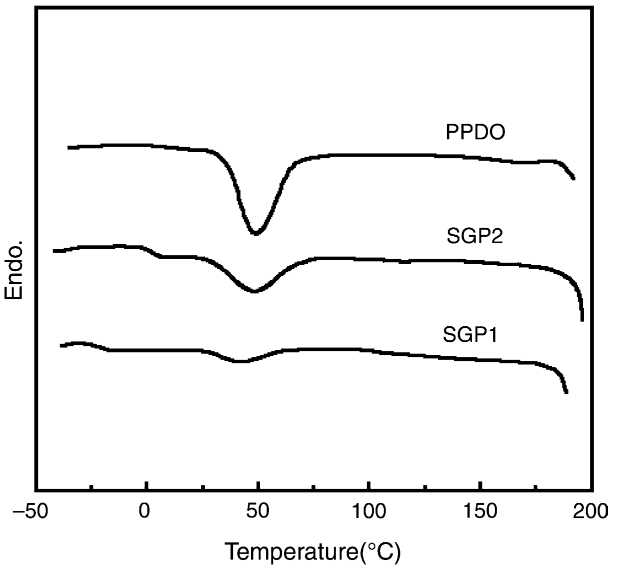


Fig. 6. DSC cooling curves for SGP after erasing thermal history at 200 °C for 5 min, cooling rate: 10 °C/min.

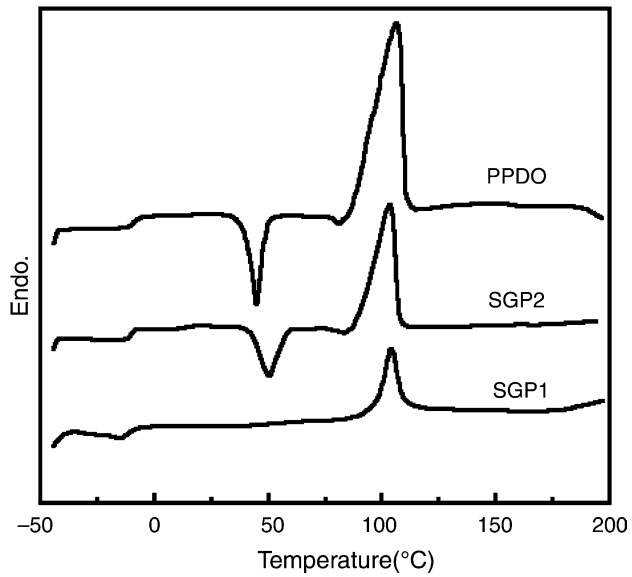


Fig. 7. DSC subsequent heating curves for SGP after the cooling runs shown in Fig. 5, heating rate: 10 °C/min.

Table 4
Relevant data extracted from Figs. 5 and 6

Sample	Cooling			Heating				
	Onset (°C)	T_c (°C)	ΔH_c (J/g)	T_g (°C)	T_{c1} (°C)	ΔH_{c1} (J/g)	T_m (°C)	ΔH_m (J/g)
PPDO[a]	–	43.8	−35.1	−9.0	45.0	−17.4	107.8	58.3
SGP2	57.2	43.6	−12.8	−9.8	50.9	−18.3	104.7	26.9
SGP1	53.7	42.8	−5.6	−12.3	–	–	104.3	11.9

[a] PPDO (Albuerne et al., 2003).

formed in the heating scan, and no more cold crystallization exothermal peak can be observed.

As shown in Fig. 7, a glass transition temperature (T_g) can be observed from each heating scans. Comparing the data shown in Table 4, we can find that the glass transition temperature (T_g) of SGP2 (−9.8 °C) is higher than that of SGP1 (−12.3 °C), which is due to the difference of molecular weights of the grafted PPDO. The higher the molecule weights, the higher the glass transition temperature.

4. Conclusions

By using 2,4-tolylene diisocyanate (TDI) as a coupling agent, PPDOs of different intrinsic viscosity can be easily grafted onto starch to obtain starch-*graft*-PPDO copolymers. The structure of the graft copolymers is confirmed by FT-IR and ^{1}H NMR. From TG and DSC measurement it is found that the thermal properties of SGP1 and SGP2 are different. SGP2, which has longer side chains, exhibits better thermal stability, higher capability of crystallization and higher glass transition temperature than SGP1, which has shorter side chains.

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References

Aburto, J., Alric, I., Thiebaud, S., Borredon, E., Bikiaris, D., Prinos, J., et al. (1999). Synthesis, characterization, and biodegradability of fatty-acid esters of amylose and starch. *Journal of Applied Polymer Science*, *74*, 1440–1451.

Albuerne, J., Marquez, L., Muller, A. J., Raquez, J. M., Degee, P., Dubois, P., et al. (2003). Nucleation and crystallization in double crystalline poly(*p*-dioxanone)-*b*-poly(ε-caprolactone) diblock copolymers. *Macromolecules*, *36*, 1633–1644.

Arnold, R. G., Nelson, J. A., & Verbanc, J. J. (1957). Recent advances in isocyanate chemistry. *Chemical Reviews*, *57*, 47–76.

Bagfey, E. B., Fanta, G. R., Burr, R. C., Doane, W. R., & Russel, C. R. (1977). Graft copolymers of polysaccharides with thermoplastic polymers. A new type of filled plastic. *Polymer Engineering and Science*, *17*, 311–316.

Brockway, C. E., & Seaberg, P. A. (1967). Grafting of polyacrylonitrile to granular corn starch. *Journal of Polymer Science Part A: Polymer Chemistry*, *5*, 1313–1326.

Choi, E. J., Kim, C. H., & Park, J. K. (1999). Structure–property relationship in PCL/starch blend compatibilized with starch-*graft*-PCL copolymer. *Journal of Polymer Science Part B: Polymer Physics*, *37*, 2430–2438.

Dubois, P., Krishnan, M., & Narayan, R. (1999). Aliphatic polyester-grafted starch-like polysaccharides by ring-opening polymerization. *Polymer*, *40*, 3091–3100.

Funke, U., Bergthalle, W., & Lindhauer, M. G. (1998). Processing and characterization of biodegradable products based on starch. *Polymer Degradation and Stability*, *59*, 293–296.

Kim, C. H., Cho, K. Y., & Park, J. K. (2001a). Reactive blends of gelatinized starch and polycaprolactone-*graft*-glycidyl methacrylate. *Journal of Polymer Science*, *81*, 1507–1516.

Kim, C. H., Cho, K. Y., & Park, J. K. (2001b). Reactive blends of gelatinized starch and polycaprolactone-*graft*-glycidyl methacrylate. *Journal of Polymer Science*, *81*, 1507–1516.

Koenig, M. F., & Huang, S. (1995). Biodegradable blends and composites of polycaprolactone and starch derivatives. *Polymer*, *36*, 1877–1882.

Mani, R., Tang, J., & Bhattacharya, M. (1998). Synthesis and characterization of starch-graft-polycaprolactone as compatibilizer for starch/polycaprolactone blends. *Macromolecular Rapid Communications*, *19*, 283–286.

Nishida, H., Yamashita, M., Hattori, N., & Endo, T. (2000). Thermal decomposition of poly(1,4-dioxan-2-one). *Polymer Degradation and Stability*, *70*, 485–496.

Odusanya, O. S., Manan, D. M. A., Ishiaku, U. S., & Azemi, B. M. (2003). Effect of starch predrying on the mechanical properties of starch/poly(-caprolactone) composites. *Journal of Applied Polymer Science* , 877–884.

Peanasky, J. S., Long, J. M., & Wool, R. P. (1991). Percolation effects in degradable polyethylene–starch blends. *Journal of Polymer Science Part B: Polymer Physics*, *29*, 565–579.

Rutot, D., Duquesne, E., Ydens, I., Degée, P., & Dubois, P. (2001). Aliphatic polyester-based biodegradable materials: New amphiphilic graft copolymers. *Polymer Degradation and Stability* , 561–566.

Sakellarious, P., Estmond, G. C., & Miles, I. S. (1991). Interfacial activity of polycarbonate/PMMA graft copolymers in polycarbonate/PMMA blends: Effect of copolymer concentration. *Polymer*, *32*, 2351–2362.

Schwach, E., & Avérous, L. (2004). Starch-based biodegradable blends: Morphology and interface properties. *Polymer International*, *53*, 2115–2124.

Wang, X. L. (2003). *Biodegradable poly(1,4-dioxan-2-one)/starch blends: Preparation, structures and properties*. Doctoral dissertation of Sichuan University, p. 88.

Wang, X. L., Yang, K. K., & Wang, Y. Z. (2003). Properties of starch blends with biodegradable polymers. *Journal of Macromolecular Science Part C: Polymer Reviews*, *43*, 385–409.

Wang, X. L., Yang, K. K., & Wang, Y. Z. (2004). Crystallization and morphology of starch-*graft*-poly(1,4-dioxan-2-one) copolymers. *Polymer*, *45*, 7961–7968.

Wang, X. L., Yang, K. K., Wang, Y. Z., Wang, D. Y., & Yang, Z. (2004). Crystallization and morphology of a novel biodegradable polymer system: Poly(1,4-dioxan-2-one)/starch blends. *Acta Materialia*, *52*, 4899–4905.

Wang, X. L., Yang, K. K., Wang, Y. Z., Zhou, Z. X., Jin, Y. D., & Wu, B. (2004). Synthesis and nuclear magnetic resonance analysis of starch-*graft*-poly(1,4-dioxan-2-one) copolymers. *Journal of Polymer Science Part A: Polymer Chemistry*, *42*, 3417–3422.

Woff, I. A., Olds, D. W., & Hilbert, D. E. (1951). Triesters of corn starch, amylose, and amylopectin. *Industry Engineer Chemistry*, 43, 911–914.

Yang, K. K. (2003). *Synthesis of poly(p-dioxanone) and its properties*. Doctoral dissertation of Sichuan University, p. 31.

Yang, K. K., Wang, X. L., & Wang, Y. Z. (2002). Poly (*p*-dioxanone) and its copolymers. *Journal of Macromolecular Science Part C: Polymer Reviews*, *42*, 373–398.

Yang, K. K., Wang, X. L., & Wang, Y. Z. (2003). Kinetics of thermal degradation and thermal oxidative degradation of poly(*p*-dioxanone). *European Polymer Journal*, *39*, 1567–1574.