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Urethane Ionic Groups Induced Rapid Crystallization of Biodegradable Poly(ethylene succinate)

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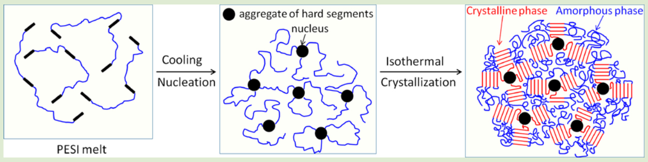
S *Supporting Information*



ABSTRACT: Novel urethane ionic groups were incorporated into biodegradable poly(ethylene succinate) (PES) by chain extension reaction of PES diol (HO−PES−OH) and diethanolamine hydrochloride (DEAH) using hexamethylene diisocyanate (HDI) as a chain extender. The synthesized polymer was a novel segmented poly(ester urethane) ionomer (PESI) in which the soft segments were formed by reaction of HO−PES−OH with HDI and the hard segments that contained ionic groups were derived from reaction of DEAH with HDI. The crystallization rate of PESI was dramatically accelerated when 3 mol % urethane ionic groups were incorporated. However, the crystallization mechanism did not change. The significant acceleration in crystallization rate was attributed to the improved nucleation efficiency by incorporation of the urethane ionic group, because PESI showed significantly enhanced nucleation density but slightly slowed spherurlitic growth rate in comparison with PES which was synthesized by chain extension reaction of HO−PES−OH with HDI. The increased nucleation efficiency was ascribed to the aggregation of hard segments of PESI induced by the ionic interactions.

Succinic acid-based aliphatic polyesters that are synthesized by polycondensation of succinic acid and diols have attracted more and more attention due to their excellent biodegradability, thermal stability, and mechanical properties.[1] In recent years, succinic acid has been successfully produced from biobased resources,[2,3] which would further stimulate the development of those polymers. Poly(butylene succinate) (PBS) and poly(ethylene succinate) (PES) are the most important succinic acid-based polyesters because they have relatively high melting temperatures. Both PBS and PES are semicrystalline polymers of which the processability and physical properties are largely dependent on their crystallization behaviors. Therefore, the crystallization properties including crystal structures, spherulitic morphologies and growth, and crystallization kinetics of both PBS and PES have been widely investigated in recent literature.[4−14] The crystallization rate is a very important parameter for thermal processing of crystalline polymers, especially for those with low glass transition temperature, because their ultimate shapes can only be settled until the crystallization takes place. Comparatively, the crystallization rate of PES is much slower than that of PBS,[12,15] which may be one of the main reasons for the fact that PBS has been commercialized but PES has not, although the latter is much less expensive.

Crystallization rate of PES can be regulated via either blending or copolymerization with other components or compounding with nanoparticles.[15−26] Copolymerization usually reduces the crystallization rate of polymers due to the increased disturbance of molecular chains,[20,25,26] and blending is incapable of accelerating the crystallization rate of PES significantly.[15,18] Compounding with a nanoparticle seems much more efficient in increasing crystallization rate of PES through nucleation.[16,22] In this communication, we report a way of improving crystallization rate of PES by incorporation of novel urethane ionic groups into the molecular chains of PES.

The urethane ionic groups were incorporated into PES by copolymerization of PES diol (HO-PES−OH, with M_n determined by ^{1}H NMR of 5780 g mol^{-1}) and diethanolamine hydrochloride (DEAH) in the presence of hexamethylene diisocyanate (HDI) at 150 °C under nitrogen atmosphere for an hour, as shown in Scheme 1.

The resulting polymer is actually a segmented poly(ester urethane) ionomer (PESI) consisting of soft and hard segments. The soft segments were formed by reaction of PES with HDI and the hard segments were resulted from reaction of DEAH and HDI. Three samples with a molar ratio of PES (based on the molecular weight of its repeating unit) to DEAH of 100:0, 99:1, and 97:3 were synthesized and named PES, PESI1, and PESI3, respectively. The molar ratio of NCO group of HDI to OH group of PES and DEAH for synthesis of all the samples was fixed at 1/1.

Figure 1 shows the DSC cooling scans (Figure 1A) and the second heating scans (Figure 1B) of PES, PESI1, and PESI3 at a scanning rate of 10 °C min^{-1}. For PES, no crystallization could be observed on the cooling scan and it crystallized with a cold crystallization peak temperature (T_{cc}) of 45.5 °C and cold crystallization enthalpy (ΔH_{cc}) of 42.1 J g^{-1} in the subsequent

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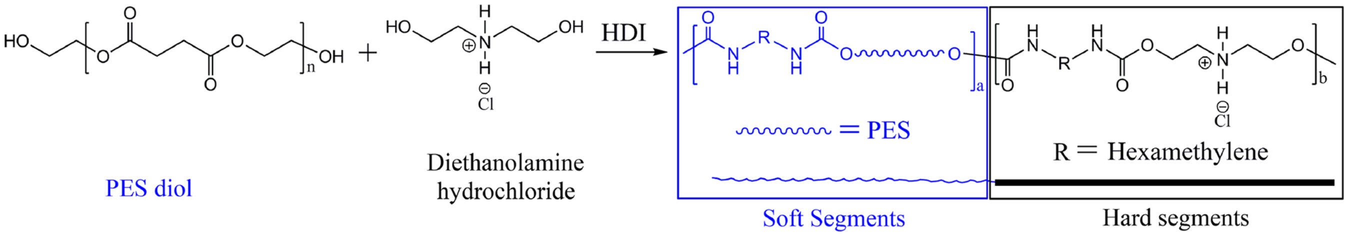
Scheme 1. Process of Incorporation of the Novel Urethane Ionic Group into the Molecular Chain of PES



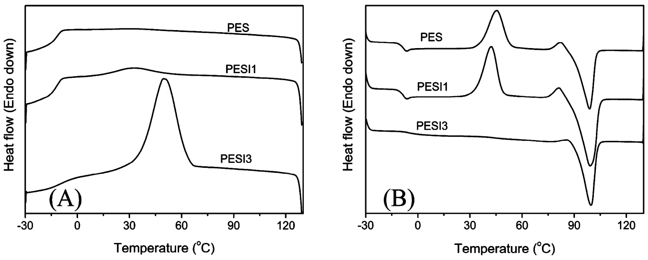


Figure 1. DSC cooling scans (A) and the second heating scans (B) of PES and PESI at a scan rate of 10 °C min^{-1}.

heating process. In the case of PESI1, a small crystallization peak was detected at 32.9 °C with ΔH_c of 6.3 J g^{-1} on the cooling scan, and the crystallization finished in the following heating process with T_{cc} and ΔH_{cc} to be 42.3 °C and 39.2 J g^{-1}, respectively. In regard to PESI3, the crystallization finished during cooling since no cold crystallization peak could be seen on the heating scan. The T_c and ΔH_c of PESI3 were 49.8 °C and 43.6 J g^{-1}, respectively. The results suggest that the crystallizability of PES increased with incorporation and increase in content of urethane ionic group. It is worth noting that the three samples almost showed same glass transition temperature (T_g), melting peak temperature (T_m) and fusion enthalpy (ΔH_m) with the values of around −8 °C, 99 °C, and 45 J g^{-1}, respectively, indicating that the incorporation of urethane ionic groups would hardly influence other thermal properties but only improve the crystallizability of PES.

The isothermal crystallization at 70 °C after quenching from melt was carried out to investigate the effect of urethane ionic group on the isothermal crystallization kinetics of the samples. Figure 2A shows the exothermic curves of the three samples during isothermal crystallization. The exothermic peaks shifted to shorter time with increase in content of urethane ionic group. Figure 2B shows the typical curves of relative crystallinity (X_t) dependence of crystallization time (t) for the three samples. X_t was calculated by integration of the exothermic peak during isothermal process, according to the equation

$$X_t = \frac{Q_t}{Q_\infty} = \frac{X_c(t)}{X_c(t=\infty)} = \frac{\int_0^t \frac{\mathrm{d}H_c(t)}{\mathrm{d}t}\mathrm{d}t}{\int_0^{t=\infty} \frac{\mathrm{d}H_c(t)}{\mathrm{d}t}\mathrm{d}t} \tag{1}$$

where Q_t and Q_∞ are the total releasing heat at crystallization time t and the end of crystallization, respectively, and the term $\mathrm{d}H_c(t)/\mathrm{d}t$ represents the heat flow at crystallization time t. The time needed for PES to finish crystallization was about 65 min and that for PESI1 was reduced to 45 min. PESI3 finished crystallization in less than 10 min which was less than 1/6 of that of PES, suggesting that the crystallization rate of PES was considerably improved when 3 mol % urethane ionic groups were incorporated.

Avrami equation was employed to analyze the isothermal crystallization kinetics of the samples. The equation assumes that the relative crystallinity develops with crystallization time t as

$$1 - X_t = \exp(-kt^n) \tag{2}$$

where X_t is the relative crystallinity at crystallization time t, k is a rate constant depending on nucleation and crystalline growth rate, and n is the Avrami exponent which denotes the nature of the nucleation and growth process.[27] Eq 2 can be rewritten as

$$\log[-\ln(1 - X_t)] = \log k + n \log t \tag{3}$$

A plot of $\log[-\ln(1 - X_t)]$ versus $\log t$ would give a straight line from which both the rate constant and the Avrami exponent can be calculated.

Figure 2C shows the Avrami plots of the samples at crystallization temperature of 70 °C. The n values for the three samples were all around 2.5 and were 2.56, 2.72, and 2.39 for PES, PESI1, and PESI3, respectively, suggesting that the crystallization of all samples may correspond to a three-

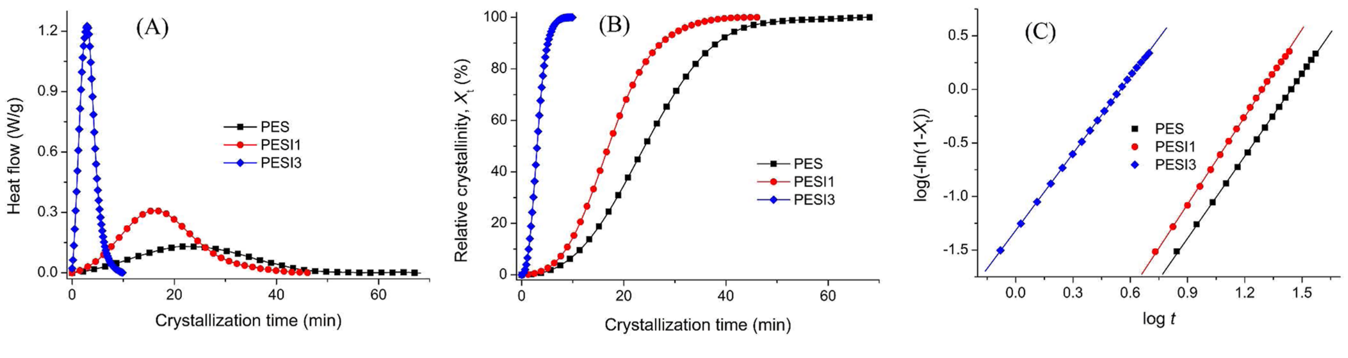


Figure 2. Isothermal crystallization exothermic curves (A), plots of relative crystallinity versus crystallization time (B), and Avrami plots (C) of PES and PESI at crystallization temperature of 70 °C.

dimensional spherulitic growth with heterogeneous nucleation,[28] and that the incorporation of urethane ionic groups did not change the isothermal crystallization mechanism of PES. The rate constant was 2.02×10^{-4} min^{-n} for PES and increased to 2.98×10^{-4} min^{-n} for PESI1. When 3 mol % urethane ionic groups were incorporated, the rate constant was increased by 2 orders of magnitude compared with PES, to be 4.83×10^{-2} min^{-n} for PESI3. Another important parameter, half-time of crystallization ($t_{1/2}$), defined as the time needed to achieve 50% of the final crystallinity, was also employed to describe the isothermal crystallization kinetics. The values of $t_{1/2}$ for crystallization of PES, PESI1, and PESI3 at 70 °C were 24.04, 17.28, and 3.05 min, respectively. The reciprocal values of $t_{1/2}$ (i.e., $1/t_{1/2}$), usually employed to represent the overall crystallization rates of polymers, were 0.0416, 0.0579, and 0.328 min^{-1} for PES, PESI1, and PESI3, suggesting that the overall crystallization rates of the samples increased significantly with incorporation of urethane ionic groups. The results of isothermal crystallization kinetics indicate that the incorporation of urethane ionic groups does not change the crystallization mechanism but increase crystallization rate of PES dramatically.

It is well-known that crystallization is composed of two processes, that is, nucleation and crystal growth. The rates of both processes would significantly affect the overall crystallization kinetics of polymers. We can reasonably suppose that the incorporation of urethane ionic groups does not improve the crystal growth rate of PES because copolymerization usually reduces the polymer chain regularity and would also result in a dilution effect for the crystallization of PES. Both aspects tended to reduce the crystal growth rate. However, the overall crystallization rate was not decreased, but increased considerably. Therefore, the increase in crystallization rate can only be ascribed to the improvement in nucleation efficiency by incorporation of the novel group. To observe the nucleation of the crystallization, the crystalline morphologies of the samples were observed by polarized optical microscope at 70 °C, as shown in Figure 3.

The three samples showed compact spherulites with clear Maltese cross. There were only two big spherulites in the viewing field for PES after crystallization finished, and the diameter of the spherulite was about 200−300 um. For PESI1, the spherulite diameter was reduced to 100−200 um and the number of spherulite was about 7 in the same viewing field. In the case of PESI3, a large number of spherulites with diameter of around 20−50 um were observed. The spherulitic growth rate (G) was measured by the increase of diameter with time. The results were obtained from the slopes of the plots of crystal diameter versus crystallization time, as shown in Figure 3D. The G values of PES, PESI1, and PESI3 for crystallization at 70 °C were 0.166, 0.164, and 0.147 $\mu\text{m s}^{-1}$, respectively, which indicates that incorporation of the urethane ionic group could reduce the crystal growth rate of PES. The results suggest that the nucleation efficiency of the samples was significantly improved by incorporation of the urethane ionic groups, which confirmed our assumption that the increase in overall crystallization rates of the samples was attributed to the improved nucleation efficiency not to the crystal growth rate.

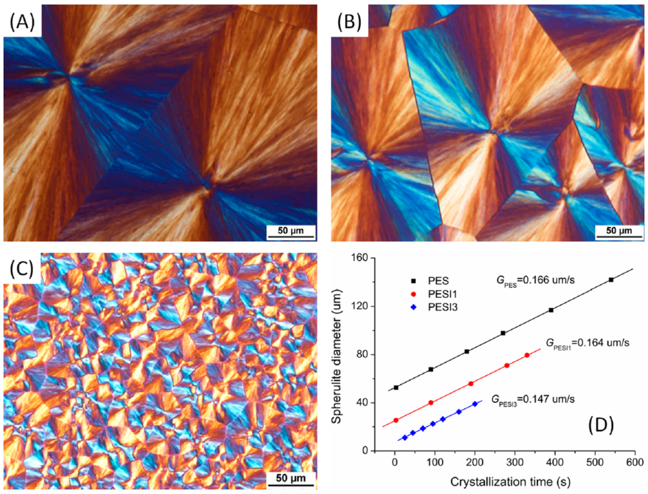


Figure 3. Crystalline morphologies of PES (A), PESI1 (B), and PESI3 (C) formed at crystallization temperature of 70 °C and spherulitic growth rate calculation of PES and PESI (D).

Such a significant improvement in nucleation and crystallization rate was not observed for other poly(ester urethane)s (PEU), which were also composed of similar soft segments and hard urethane segments and were synthesized by chain extension reaction of similar aliphatic polyester diol with diisocyanate and conventional small molecular diol, such as ethylene glycol and butanediol.[29,30] The different crystallization behaviors could be reasonably ascribed to the difference in their chemical structures, especially in their hard segments. The hard segments of the PESI contain urethane groups and ionic groups while those of conventional PEUs do not have ionic groups. The main interaction in hard segments of PEU is hydrogen bonding stemming from urethane groups. But the hard segments of the present PESI contain not only hydrogen bonding but also ionic interaction caused by the ionic groups. Ionic interaction is usually much stronger than hydrogen bonding. Thus, the ionic interaction plus hydrogen bonding should be strong enough to drive hard segments to aggregate and then to form nucleation sites for crystallization of PESI. The possible process for crystallization of PESI is schematically shown in Figure 4.

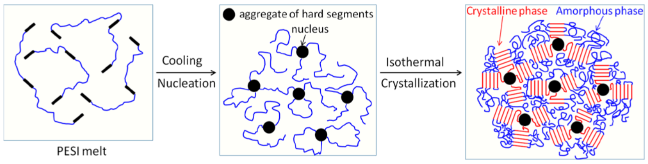


Figure 4. Schematic representation for crystallization of PESI.

In the first step, nucleation occurred by aggregation of ionic group containing urethane hard segments when the melt of PESI was cooled to crystallization temperature; in the second step, the obtained crystal nucleus initiated crystal growth until crystallization completed. Because the nucleation was caused by the aggregation of hard segments, thus, the concentration or content of hard segments played an important role in nucleation efficiency (especially number of nuclei). The nucleation sites should increase with the content of hard segments of PESIs when they were crystallizing at same temperature, which was demonstrated by POM observation in the above.

In summary, we developed a novel way to improve crystallization rate of biodegradable PES by incorporation of novel urethane ionic groups into the molecular chain of PES.

The crystallization rate of PES was significantly accelerated when 3 mol % urethane ionic groups were incorporated. The acceleration was mainly ascribed to the improvement in nucleation efficiency, which was possibly resulted from the aggregation of hard segments predominantly driven by ionic interaction. With such a significant improvement in crystallization rates, the processability of the biodegradable PES would be improved significantly, and it is able to find more application.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed information about the synthesis and chemical structure of PESI. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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