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Synthesis and crystallization kinetics of silsesquioxane-based hybrid star poly(ε-caprolactone)

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Abstract

A series of silsesquioxane-based hybrid star poly(ε-caprolactone) with different arm length (SHPCL-4, SHPCL-10, SHPCL-40) were synthesized from ring-opening polymerisation of ε-caprolactone as a monomer initiated by silsesquioxane-based hybrid polyol (SBOH). Two linear poly(ε-caprolactone)s, LPCL-25 and LPCL-35, were also prepared for comparison. The sequence of LPCL-25 < LPCL-35 < SHPCL-4 < SHPCL-10 < SHPCL-40 for total molecular weights (M_n) and the sequence of SHPCL-4 < SHPCL-10 < LPCL-25 < LPCL-35 < SHPCL-40 for average molecular weight per arm (M_{arm}^{NMR}) were determined by ^{1}H NMR and GPC measurements. The ^{1}H NMR data also suggested that SHPCLs possess a spheric architecture with 29.2 arms in average. The crystallization kinetics study by non-isothermal DSC showed that the starting temperature of crystallization (T_s), the ending temperature (T_e) and the peak temperature of exothermic curve (T_p) are in the order as: SHPCL-4 < SHPCL-10 < LPCL-25 < SHPCL-40 ≈ LPCL-35, while the crystallinity (X_c) follows the order of SHPCL-4 < SHPCL-10 < SHPCL-40 < LPCL-25 < LPCL-35. The corrected overall crystallization rate constant (K_c) calculated from Avrami equation were found to be in the order as: SHPCL-4 < SHPCL-10 < LPCL-35 < LPCL-25 ≈ SHPCL-40, which was further evidenced by the real time morphological observation with polarized light microscopy (POM). It is also found by the POM measurements that the inorganic core and star architecture greatly retards the nucleation of SHPCLs with short arms, while it helps the nucleation of SHPCL with longer arms.

Keywords: Star polymer; Crystallization; DSC

1. Introduction

Poly(ε-caprolactone) (PCL) is a crystalline polymer with a glass transition temperature of about −60 °C. Linear PCL (LPCL) usually has a melting temperature of 59–64 °C, depending on its molecular weight. PCL is one of the most extensively studied and most widely used aliphatic polyesters, mainly due to its miscibility with different commercial polymers (SAN, ABS, PVC, nitrocellulose), ability to disperse pigments, low-temperature adhesiveness, and biocompatibility and biodegradability [1]. PCL is attracting interest especially in drug delivery systems and scaffolds for tissue engineering [2–5]. However, the mechanical brittleness at physiologic temperature and in vitro or in vivo inhomogeneous degradation behaviours due to the high crystallinity limit its further applications. A great number of research have been done to reduce the crystallinity of PCL, such as through copolymerization of ε-caprolactone and other cyclic monomers [6–9], block extension with ester or urethane bonds [10,11], and introduction of branched structures [12–14], etc.

Highly branched polymers, such as star-shaped polymers, dendrimers, and hyperbranched polymers, have shown unique properties compared with their linear counterparts due to their higher segment density within the distance of gyration radius [15,16]. They usually possess smaller hydrodynamic radius, and lower melting and solution viscosity. The branched architecture also has great influence on the packaging of molecular chains [17]. Ascribing to their unique structures, some star-shaped, dendritic and hyperbranched PCLs have been synthesized and used as precursors for powder coatings [13,14], hydrogels [18] and templates for preparing nanoparticles [19]. The crystallization kinetics of PCL in semi-crystalline polymer blends has been extensively studied in recent years [20], and found that the crystallization process has great influence on the final mechanical properties of blends [21–23]. There are a few papers concerning the crystallization of PCL with star-shaped, dendritic or hyperbranched

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architectures [13,24,25]. However, all of them dealt with pure organic systems up to now.

Organic/inorganic hybrid materials have achieved great success in the last decades due to the synergetic effect of organic and inorganic components in nanoscales [26–28]. Organic/inorganic PCL hybrid materials have been prepared through sol–gel method or by intercalation of layered silicate by several groups [29–32]. Their mechanical properties and the crystallinity of PCL in inorganic silica network were studied. However, PCL/silica hybrids with well defined architecture and multi-functional groups for further modification are more desired. Recently, Chang et al. prepared organic/inorganic hybrid star PCL based on nanostructured polyhedral oligomeric silsesquioxanes, and studied their inclusion complexes with cyclodextrin [33].

For obtaining organic/inorganic hybrid materials with best synergetic effect, further study about the influence of inorganic components on organic polymeric chains at nanoscale dimensions is needed. In this work, a series of well defined organic/inorganic hybrid star PCL were prepared through ring-opening polymerisation (ROP) of CL initiated by silsesquioxane-based nanoparticles with a high density of hydroxyl groups on the surface (58 hydroxyl groups per nanoparticle).The synthesized multifunctional star hybrid PCL containing inorganic silsesquioxane core possess potential as starting materials for the applications in tissue engineering and drug delivery systems. It is expected that the inorganic core and star architecture may disrupt the orientation of PCL chains and lead to PCL having high molecular weight PCL with low crystallinity. The crystallization kinetics of such prepared organic/inorganic hybrid star PCL was studied to illustrate the influence of inorganic core and star architecture on PCL arms.

2. Experimental section

2.1. Materials

3-Aminopropyltriethoxysilane and glycidol were purchased from Sigma–Aldrich and used as received. ε-Caprolactone supplied by Sigma–Aldrich was distilled over calcium hydride under reduced pressure, and then kept with 4 Å molecular sieve in a desiccator. The stannous octoate ($Sn(Oct)_2$) and ethylene glycol were supplied by Shanghai First Reagent Co. (China), and distilled under reduced pressure before use. Tetrahydrofuran (THF) and methanol were used as received with analytical grade.

2.2. Synthesis

2.2.1. Silsesquioxane-based polyol (SBOH)

The starting silsesquioxane-based polyol (SBOH) was prepared according to the procedure developed by Mori et al. [34,35]. 287.82 g (1.558 mol) the adduct of 3-aminopropyltriethoxysilane and glycidol according to the ratio of 1:2 was dissolved in 1400 ml methanol, then 42.06 g aqueous HF solution (3.225%) was introduced. After stirring for 4 h at ambient temperature, the reactant was distilled under vacuum to remove water, ethanol and methanol, and then dried at 40 °C in vacuum for 72 h, resulting in a glassy solid at room temperature, named SBOH.

2.2.2. Silsesquioxane-based star hybrid poly(ε-caprolactone) (SHPCL)

The obtained SBOH was used as an initiator for ROP of CL monomer (Scheme 1). The different molar ratios of CL to SBOH (Table 1) were employed to prepare star polymers with different molecular arm length and thus different molecular weights. The following is a representative procedure: 5.260 g SBOH (81.515 mmol –OH) was melted in a flame-dried 50 ml round-bottom bottle at 130 °C in nitrogen atmosphere, and then degassed under reduced pressure for 4 h. 35.952 g CL (314.982 mmol) was introduced into the melted SBOH at 150 °C to form a homogenous and transparent solution. After the solution was cooled down to room temperature, a catalytic amount of $Sn(Oct)_2$ (0.255 g, 0.630 mmol) was injected. The reactant solution was stirred at 140 °C for 20 h under nitrogen atmosphere. The resultant product was dissolved in a large amount of THF and precipitated from cold methanol in order to remove un-reacted CL and the catalyst. This procedure was repeated for three times. The final yields were about 80–95% for different CL/OH ratios. The obtained pale yellow or white powders were kept at 40 °C in vacuum oven for 4 days before measurements.

Table 1
Molecular weights and melting points of SHPCLs and LPCLs

Sample	[CL]/[OH][a]	$M_n^{theo\,b}$	$M_{arm}^{NMR\,c}$	$M_n^{NMR\,c}$	$M_n^{GPC\,d}$	PI.[d]	T_m (°C)[e]
SHPCL-4	4.0	30,368	1301	41,749	26,016	1.60	47.0
SHPCL-10	10.0	70,290	3139	95,419	44,464	2.28	52.8
SHPCL-40	40.0	269,840	10,318	305,046	106,765	3.13	57.7
LPCL-25	25.0	5769	6694	6694	10,746	1.22	52.7
LPCL-35	35.0	8052	9650	9650	17,341	1.35	55.5

[a] The molar ratio of ε-caprolactone to hydroxyl group.

[b] Theoretical total molecular weight per molecule (M_n^{theo}).

[c] Average molecular weight of each arm (M_{arm}^{NMR}) and total molecular weight per molecule (M_n^{NMR}), calculated from NMR measurements.

[d] Number-average molecular weight (M_n^{GPC}) and polydispersity index (PI.) measured by GPC.

[e] Measured from the peak temperature of endothermal curves in DSC heating at 10 °C/min.