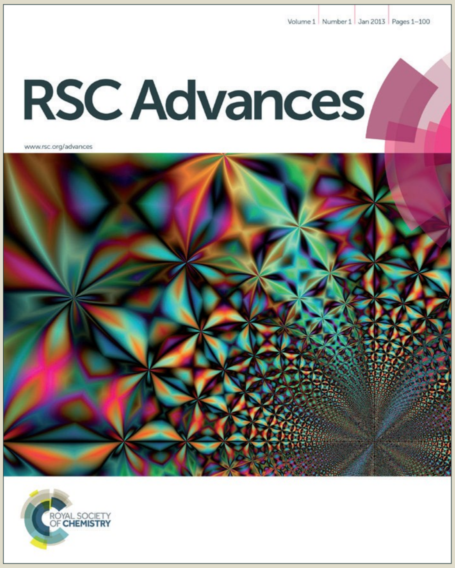
RSC Advances



Modification of PEG-b-PCL Block Copolymer with High Melting Temperature by the Enhancement of POSS Crystal and Ordered Phase Structure

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Abstract:

Alkyne-functionalized polyhedral oligomericsilsesquioxane was successfully prepared by using commercially available propargylic acid as precursor through DCC coupling, and was further used to modify the PEG-b-PCL via click chemistry, resulting in a successful synthesis of POSS grafted PEG-b-PCL block copolymer. The structures of samples were comprehensively confirmed by FTIR, ^{1}H NMR, GPC and Electrospray ionization mass spectrometry (ESI-MS) spectrum. And the thermal properties of the polymers were detected through DSC. The copolymers with grafted POSS showed excellent thermal properties, with an increase of approximate 100 ^{o}C in melting temperature compared with the neat PEG-b-PCL. Furthermore, the side group POSS with high crystallinity ability acted as physical crosslink points and the thermal enhancement agent will effectively induced the ordered phase separation, giving rise to the nano structure with high parallelism and smooth interface.

Key words: POSS, PEG-b-PCL, Phase separation, High melting temperature.

1. Introduction

Biodegradable and biocompatible aliphatic polyester, such as poly (ε-caprolactone) (PCL), poly (lactic acid) (PLA), poly (glycolic acid) (PGA), and their copolymer and blends have received worldwide attention for their potential application in the biomedical materials and environment friendly materials[1]. In particular, micelles formed from block copolymers that contain PEG and PCL segments are widely applied in the design of drug delivery systems because the hydrophilic PEG block is biocompatible and the hydrophobic PCL block is biodegradable[2-4].

There are several methods to synthesize the PCL with lower reaction temperature by using different initiator system or catalyst, such as, zinc bis[bis(trimethylsilyl) amide][4], triethylaluminum[5],calcium catalyst and methane sulfonic acid[6]. However，The traditional approach[7-9] was adopted most widely, with PEG as the macro initiator and stannous as the catalyst giving rise to PEG-b-PCL copolymer. Stannous has the advantage of obtaining a polymer with high yields and high molecular weights[10]. In addition, PEG-b-PCL copolymer can be developed by attaching attractive functional groups, for example, S. Lenoir, et al. [11, 12] and K. Sripha[13] systematically reported the synthesis and modification of PEG-b-PCL by ring opening polymerization (ROP) via α-chloro-ε-caprolactone. They made the Cl element attaching on the PCL side groups, which can achieve some other further side group modification, such as nicotinic acid, p-amino benzoic acid (PABA) [14], phthaloyltryptophan[13], and propargyl benzoate[15], for their use in novel drug delivery systems. However, all the grafted copolymers have melting temperatures lower than 40 °C, which limits the application of the polymer. As far as we know, improvement on the thermal performance of the PEG-b-PCL is rarely reported.

On the other hand, polyhedral oligomeric silsesquioxane (POSS), known as hybrid inorganic-organic monomer, and a well-defined spherosilicate polyhedral molecule with typical composition of $R_8Si_8O_{12}$ or $R^*R_7Si_8O_{12}$, will offer chemical versatility to the polymers [16] and control the crystallinity of the polymer matrix[17, 18]. Several reports have established the modification of PEG-b-PCL via POSS. For example, Chan et al [19] synthesized a series of organic-inorganic hybrid star PCLs using Octakis (3-hydroxypropyl-dimethylsiloxy) octasilsesquioxane (OHPS) as initiator. P. T. Mather et al [20] prepared well-defined POSS-initiated telechelics via ROP and used them to make photo-cured networks. Zheng et al [21] synthesized a novel organic-inorganic amphiphile POSS-capped PCL, which was incorporated into epoxy resin to prepare the organic-inorganic hybrid thermosets.

Overall, POSS-incorporated polymers show an increase in heat[22] and oxidative resistance[16, 23]. In addition, the utilization of chemoselective click chemistry allows for the preparation of well-defined macromolecules with complex compositions and architectures[24]. So in this study, we will prepare alkyne-functionalized POSS through DCC coupling, and use the POSS to modify the PEG-b-PCL by click chemistry, giving rise to poly (ethylene glycol) -b-poly (ε-caprolactone)-(poly (ε-caprolactone)-g-POSS) (PEG-b-PCL-b-(PCL-g-POSS)) block copolymer. Meanwhile, it is expected that the thermal properties, especially melting temperature, will be enhanced remarkably.

2.Experimentals

2.1. Materials

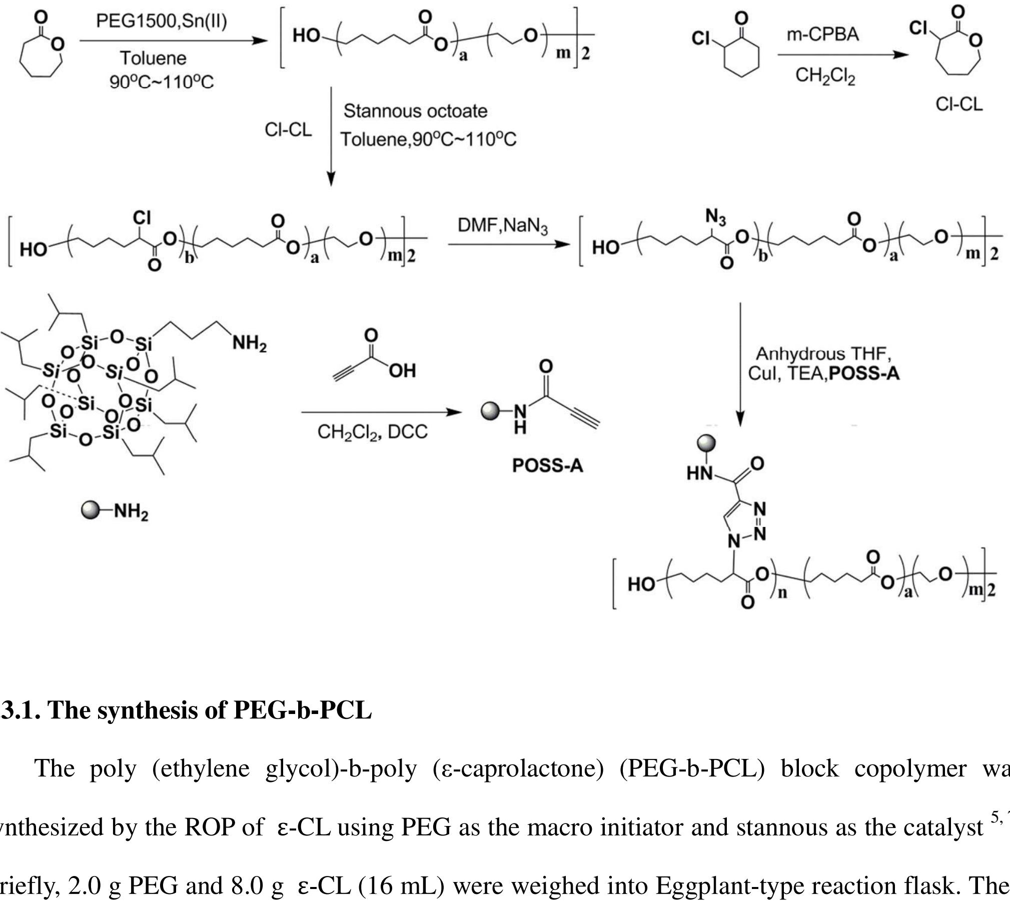
ε-caprolactone (ε-CL, Alfa Aesar) was purified by toluene azeotropic distillation (50 g/100 mL) via the Dean-Stark apparatus for 2 days. PEG1500 (Mn=1730 g/mol, Alfa Aesar) was dried in vacuum oven for 48h at 95 °C. Tetrahydrofuran (THF),Dichloromethane (DCM) and toluene were purified by distillation over CaH_2. Tin (II) 2-ethylhexanoate, 96% (Alfa Aesar), 3-Chloroperoxybenzoic acid (75%) (Alfa Aesar), Propiolic acid, 98+% (Alfa Aesar), Aminopropyllsobutyl POSS (Hybrid Plastics), 2-Chlorocyclohexanone, 97% (Alfa Aesar), Cuprous Iodide (CuI), 99% (Alfa Aesar), and N，N’-Dicyclohexylcarbodiimide，99%(Alfa Aesar)were used as received. Other solvents were obtained from Beijing Chemical works, such as Triethanolamine (TEA) and Sodium azide.

2.2. Characterization

^1H NMR spectra were recorded in $CDCl_3$ at 400MHz in the AV400(BRUKER) at 25 °C with deuterium solvents and TMS as an internal reference. Electro spray ionization mass spectrometry (ESI-MS) was detected with UPLC-Q-Tof-MS (WATERS) using CH_3OH as solvent. Fourier transform infrared (FTIR) spectra were recorded with Bruker Tensor-27 Fourier transform infrared spectrometer by using the KBr disk method. Gel permeation chromatography (GPC) was performed on the system (Water 1515, Isocratic HPLC Pump and Water 2414 Refractive index Detector) to obtain the molecular weight and molecular weight polydispersity index (PDI) of all kinds of polymers at room temperature. THF was used as mobile phase with a flow rate of 1.0 mL/min with column temperature at 35 °C, and monodisperse polystyrene standard samples were used for calibration. And the number average molecular weight (Mn) of PEG measured by GPC was 1708 g/mol. Differential scanning calorimetry(DSC) was performed using a DSC-200PC (NETZSCH).The X-ray diffraction (XRD) data of the triblock copolymers were recorded with BRUKER D8 ADVANCE diffract meter using Cu Kα radiation from 5° to 60° at room temperature. Thermal gravimetric analysis (TGA) was carried out with a TG209 (NETZSCH) at 10 K/min. Transmission electron microscopy (TEM) was performed with a Tecnai $G^2$20 (FEI) microscope.

2.3. Synthesis route

Scheme 1. Strategy for the Chemical Modification and Grafting "POSS" of PEG-b-PCL by Click Chemistry



2.3.1. The synthesis of PEG-b-PCL

The poly (ethylene glycol)-b-poly (ε-caprolactone) (PEG-b-PCL) block copolymer was synthesized by the ROP of ε-CL using PEG as the macro initiator and stannous as the catalyst [5, 7]. Briefly, 2.0 g PEG and 8.0 g ε-CL (16 mL) were weighed into Eggplant-type reaction flask. Then 0.2~1wt % of Stannous was dropped into the mixture and degased by connecting a vacuum pump for 30 min. The flask was immersed in an oil bath at 90 ^{o}C~110 ^{o}C with magnetic stirring for 24 h. The product was precipitated into ether or methanol (400 mL). After filtration and drying at vacuum oven at 40 ^{o}C for 24 h, a white crystal was obtained. And it was purified as follow: dissolved the solids by $CHCl_3$ (15 mL), put into 20 equiv. of n-hexane, after drying at 50 ^{o}C for 24 h, 9.1 g white solid were obtained (91% yield). The polymer showed good solubility in many organic solvents, such as THF, Acetone, N, N-Dimethylformamide (DMF), Ethyl acetate, and Chloroform. The only difference comparing bulk polymerization with solution method is the reaction temperature can be 90 ^{o}C~140 ^{o}C without solvent. FTIR (cm^{-1}, KBr window): 3438.93 (-OH), 2946.07-2867.24 ($-CH_2-CH_2-$), 1726.17 (C=O), 1189.11 (C-O-C). ^{1}H NMR in $CDCl_3$ (ppm):δ4.245 (t, ***J***=4.85Hz, $-OCH_2C\mathbf{H}_2O(C=O)-$), δ4.081 (t, ***J***=6.70Hz, $-CH_2C\mathbf{H}_2O(C=O)-$), δ3.665 (s, $-OC\mathbf{H}_2C\mathbf{H}_2-$), δ2.327 (t, ***J***=7.52Hz, $-O(C=O)-C\mathbf{H}_2CH_2-$), δ1.711-1.628 (m, $-O(C=O)-CH_2C\mathbf{H}_2-$), 1.441-1.365(m, $-CH_2C\mathbf{H}_2CH_2-$).

2.3.2. Baeyer-Villiger Oxidation of α-Chlorocyclohexanone

The monomer was synthesized using the similar procedure as discussed earlier[11, 12, 25]. 3-Chloroperoxybenzoic acid (18.01 g, 75%) with 100 mL DCM was mixed with 9.14 g **α**-Chlorocyclohexanone directly. Stirring was continued for additional 96 h at room temperature. The reaction flask was cooled to below 0 ^{o}C for 3 h. After filtration, the solution was washed with an aqueous solution of $NaHCO_3/NaHSO_3$ and with water for 3 times to remove all the inorganic salts. After drying over $MgSO_4$, the organic layer was purified by column chromatography on silica gel (200 mules) with the mobile phase Hexane: EtOAc=3:1(TLC R_F~0.3). Evaporation of the solvent at 35 ^{o}C, 8.10 g of α-chloro-ε-caprolactone (Cl-ε-CL) with 79.1% yield was obtained. FTIR (KBr window) (cm^{-1}): 2942.97, 2867.88($-CH_2-$), 1750.67(C=O), 1157.50(-CO-O), 571.74(C-Cl). ^{1}H NMR in $CDCl_3$(ppm): δ4.727-4.761 (m, $-CH_2-ClC\mathbf{H}-(C=O)-$), δ4.439-4.471 (m, $-ClCH-(C=O)-O-C\mathbf{H}_2-$),δ4.172 (s, $-ClCH-(C=O)-O-C\mathbf{H}_2-$),δ1.739-1.765 (m, $-CH_2C\mathbf{H}_2CH_2-$), δ1.910-1.992 (m, $-C\mathbf{H}_2CH_2-O-$),δ2.045-2.070 (m, $-C\mathbf{H}_2-ClCH-(C=O)-$).ES$^+$-MS (CH_3OH): Calculated 148.5, found 148.9 $(M+H)^+$.

2.3.3. The synthesis of PEG-b-PCL-b-(PCL-g-Cl)

The PEG-b-PCL-b-(PCL-g-Cl) triblock copolymer was synthesized by the ROP of Cl-ε-CL using PEG-b-PCL (2200 g/mol, PDI=1.12) diols as the macro initiator and stannous as catalyst. PEG-b-PCL (3.63 g) and Cl-ε-CL (1.80 g) were weighed into Eggplant-type reaction flask. Then 4 drops of stannous and 10 mL toluene were added into the mixture. The mixture was degased by the same method as previous step. The flask was immersed in an oil bath at 90 °C with magnetic stirring for 48 h. The product was precipitated into n-hexane (200 mL). After filtration and drying at vacuum oven at 35 °C for 48 h, 4.68 g soil yellow oil was obtained with 86.2% yield. FTIR (cm^{-1}, KBr window): 3439.97 (-OH), 2945.34-2866.84 ($-CH_2-CH_2-$), 1725.98(C=O), 1192.04 (C-O-C). ^1H NMR in $CDCl_3$ (ppm): δ4.282-4.238 (m, -ClC**H**-), δ4.226-4.145 (m, -CHCl-(C=O)-OC**H**$_2$-),δ4.065 (t,***J***=6.67Hz,-CH$_2$-(C=O)-OC**H**$_2$-), δ3.57 (s, -OC**H**$_2$C**H**$_2$O-), δ2.22 (t, ***J***=7.54, -CH$_2$C**H**$_2$(C=O)-O-).

2.3.4. The synthesis of PEG-b-PCL-b-(PCL-g-N_3)

PEG-b-PCL-b-(PCL-g-Cl) (Mn=2970 g/mol) 4.68 g were dissolved into 20 mL DMF, sodium azide (0.6 g) was added into the system. After reaction for 24 h at 20 °C, the salt was removed by centrifugation (9000 rpm at 25 °C for 10 min), and the liquid was added into 200 mL n-hexane. After drying at room temperature for 48 h, 4.38 g brown oil was obtained with 89.2% yield. FTIR (cm^{-1}, KBr window): 3440.86 (-OH), 2946.06-2867.13 ($-CH_2-CH_2-$), 2108.01 ($-N_3$), 1726.20 (C=O), 1191.22 (C-O-C). ^1H NMR in $CDCl_3$ (ppm): δ4.21 (t, ***J***=6.62Hz, -(C=O)-OC**H**$_2$CH$_2$CH$_2$CH$_2$CH$_2$-), δ4.08(t, ***J***=6.67Hz, -(C=O) OC**H**$_2$CH$_2$CH$_2$CH$_2$CHN$_3$-), δ3.85 (q, ***J***=5.09Hz, -N$_3$C**H**-), δ3.669 (s, -OC**H**$_2$C**H**$_2$O-), δ2.326 (t, ***J***=7.50Hz, -CH$_2$C**H**$_2$(C=O)-O-).

2.3.5. The synthesis of alkyne-functional POSS

Propynoic acid (0.2 mL, 3.25 mmol) was added at 0 °C to a stirred solution of DCC (0.8 g, 3.9 mmol, 1.2 eq.) in 25 mL of dichloromethane. After 30 min, aminopropyllsobutyl POSS dissolved in 5 mL dichloromethane was added drop wise and the resulting mixture stirred for 1 h at 0 °C. And the mixture was allowed to rise to 20 °C and stirred for an additional 10 h. The completion of the reaction was monitored via TLC, after which the mixture was filtered, and the filtrate was concentrated to afford a crude product. The product was purified via column chromatography using as the gradient n-hexane/ Ethyl acetate (3:1 TLC R_F~0.45). A yellow solid was isolated. The solid was dissolved in hexane, suspended in CH_3CN and after filtration, drying and recrystallization, 5.6 g (65%) light yellow powder was obtained. FTIR (cm^{-1}, KBr window):3295.58, 2114.28 (-C≡H), 2956.65-2872.25 (-CH_2CH_2-), 1729.49, 1635.62, 1539.76 (-CONH-), 1465.66 (C-NH), 1103.48 (Si-O-Si).^{1}H NMR in $CDCl_3$ (ppm): δ5.898 (s, -CON**H**-), δ3.33 (q, ***J***=6.76Hz, -C**H**$_2$NHCO-), δ2.784 (s, -C≡**H**), δ1.929-1.822 (m, -CH_2C**H** $(CH_3)_2$), δ1.697-1.621 (m, -CH_2C**H**$_2$$CH_2$NH-), δ0.992-0.972 (q, -C**H**$_3$), 0.644-0.617 (q, -C**H**$_2$$CH(CH_3)_2$). MS in CH_3OH: Found, 926.3165 [M+H]$^+$, 948.2988 [M+Na]$^+$, 964.2729 [M+K]$^+$.

2.3.6. The synthesis of PEG-b-PCL-b-(PCL-g-POSS) by Click Chemistry

PEG-b-PCL-b-(PCL-g-N_3) (0.90 g) was transferred into an anhydrous THF (10 mL) containing glass reactor. 0.5 g alkyne-functional POSS, 0.1 equiv. of CuI, and 0.1 equiv. of TEA were then added to the mixture. The solution was stirred at 40 °C for 20 h under N_2 atmosphere. The salt was removed by centrifugation (9000 rpm at 25 °C for 10 min). The polyester can dissolve in the hexane, and after precipitation and drying in vacuum at 40 °C for 48 h, the 0.6 g solid was obtained. FTIR (cm^{-1}, KBr window):3417.63(-OH), 2957.38, 2874.89(-CH_2-), 1743.67(C=O), 1662.68(Triazole ring), 1576.97(-(C=O)-NH-), 1465.35(C-N), 1103.10, 481.46 (Si-O-Si).^{1}H NMR in $CDCl_3$（ppm):δ8.433-8.304(s，-N**H**)，δ5.421(s，N-C**H**-)，δ3.666(s，-OC**H**$_2$C**H**$_2$O-)，δ3.475-3.461(m)，δ1.909-1.943(m)，δ0.983-0.966, δ0.639-0.612(POSS).

3. Results and discussion

3.1. Synthesis and characterization of the PEG-b-PCL

The PEG-b-PCL here is the PCL diols with two hydroxyl end groups synthesized via ROP of ε-caprolactone with PEG1500. It is found that the reaction of the ROP can take place in a wide temperature range from 90 °C to 140 °C by bulk polymerization. We can obtain the PEG-b-PCL, white crystals, with high yield (>90%) and low PDI (Table 1).The mechanism of the reaction is that of coordination polymerization[9]. The optimum reaction condition in our study is with amount of stannous of 0.5~1wt% at 120 °C. Moreover, the solvents for precipitation consist of n-hexane, cyclohexane, methanol, anhydrous ethyl ether, and all of which provide a good crystallization condition for the products. Fig. 1(a) shows a typical ^{1}H NMR spectrum of PEG-b-PCL block copolymer in $CDCl_3$. The peak f at 4.30 ppm belongs to methylene protons of the PCL-CO-OC$\underline{\mathbf{H}}_2$-CH_2-O-PEG segment, which indicates the successful synthesis of the

PCL-b-PEG.

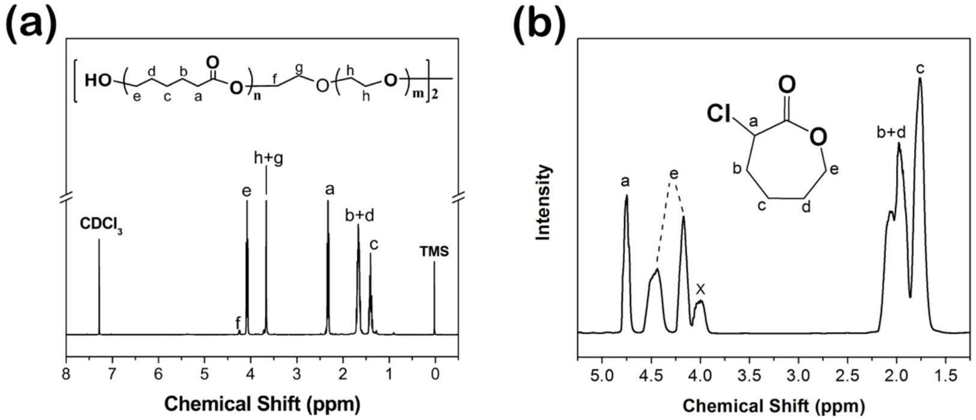


Fig. 1 ^{1}H NMR of (a) PEG-b-PCL, (b) α-chloro-ε-caprolactone.

3.2. Synthesis and characterization of α–chloro-ε-caprolactone

α-chloro-ε-caprolactone, which is a light yellow liquid at room temperature and freezes to white crystal in refrigerator, will degenerate quickly even under a low temperature (~0 °C) in 10 days. The ^{1}H NMR spectra is showed in Fig. 1(b), in which the characteristic peaks a, b, c, d and e of product and peak x, which is attributed to residual eluent, are marked. And the amount of eluent does no influence on the polymerization. Importantly, the reaction temperature should be lower than 30 °C. Otherwise, a light yellow oil that is insoluble in DCM will be produced, which would lead to a lower yield. α-chloro-ε-caprolactone was dried by azeotropic distillation of toluene just before polymerization.

3.3. Synthesis and characterization of alkyne-functional POSS

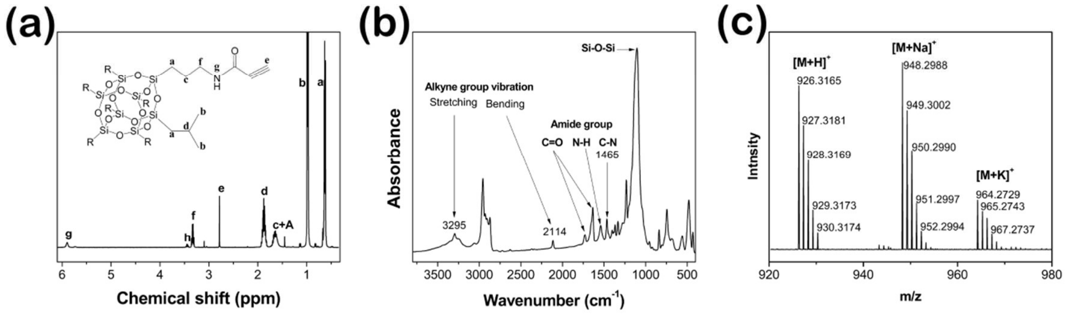


Fig. 2 (a) ^{1}H NMR spectra, (b) FTIR and (c) ESI-MS of alkyne-functional POSS.

Alkyne-functional POSS is synthesized by amide formation between propiolic acid and aminopropyllsobutyl POSS through DCC Coupling [26, 27]. The ^{1}H NMR spectrum of alkyne-functional POSS is shown in Fig. 2(a). The signals at 2.85 ppm and 5.90 ppm are respectively assigned to the alkyne and -CONH- groups. In addition, the FTIR spectrum also confirms the successful reaction by means of the peaks at 3295 cm^{-1} and 2114 cm^{-1}, which ascribe to the stretching vibration and bending vibration of the alkyne group respectively. As can be seen from Fig. 2(b), the frequency at 1103 cm^{-1} is characteristic of the absorption of Si-O-Si. Based on the ^{1}H NMR, FTIR and ESI-MS (Fig. 2(c)), alkyne-functional POSS is successfully prepared. Moreover, it dissolves in both nonpolar solvents, e.g. n-hexane, and polar solvents, DMF.

3.4. Characterization of PEG-b-PCL-b-(PCL-g-Cl) and PEG-b-PCL-b-(PCL-g-N$_3$)

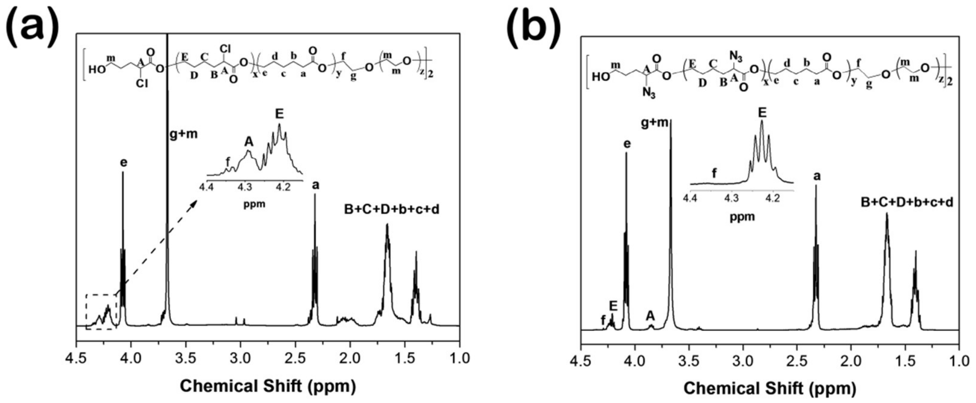


Fig. 3 ^{1}H NMR of (a) PEG-b-PCL-b-(PCL-g-Cl), (b) PEG-b-PCL-b-(PCL-g-N$_3$)

The spectra resolutions are displayed in Fig. 3 (a) for PEG-b-PCL-b-(PCL-g-Cl) and Fig. 3(b) for PEG-b-PCL-b-(PCL-g-N$_3$). ^{1}H NMR confirms that all the pendent Cl transforms into N$_3$. Namely, the resonance peak at 4.30 ppm for C**H**Cl protons (Fig. 3(a), peak A) disappears in favor of a new signal at 3.85 ppm, typical of the C**H**N$_3$ protons (Fig. 3(b), peak A).

3.5. Characterization of PEG-b-PCL-b-(PCL-g-POSS)

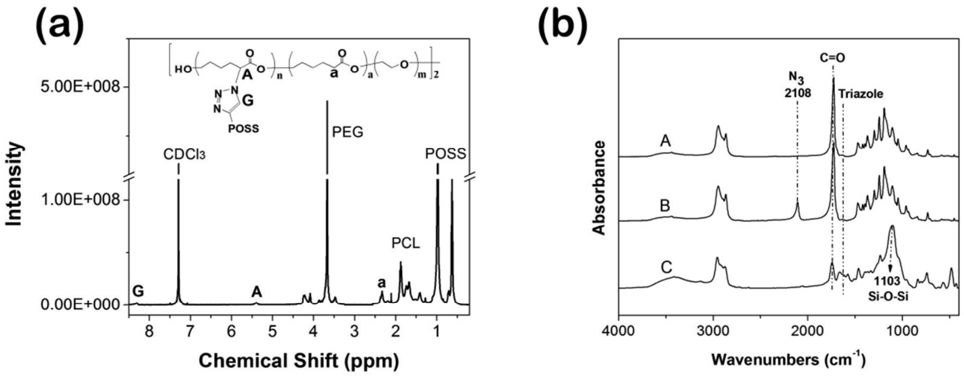


Fig. 4 (a) ^{1}H NMR of PEG-b-PCL-b-(PCL-g-POSS) , (b) FTIR spectra of A, PEG-b-PCL-b-(PCL-g-Cl), B, PEG-b-PCL-b-(PCL-g-N_3), and C, PEG-b-PCL-b-(PCL-g-POSS).

The alkyne-functional POSS is attached to the backbone through click chemistry using CuI and TEA as catalysts at 35 ^{o}C for less than 20 h, because the hydrolysis of PCL in the alkaline environment [14]. In Fig. 4(a), the emergence of characteristic peaks at 8.30 ppm (peak G), which is attributed to the methyne triazole ring and 5.30 ppm (peak A) corresponding to the peak of methyne proton of caproyl unit adjacent to triazole ring both confirm the successful POSS-grafting via click reaction. On the other hand, Fig. 4(b) illustrates the FTIR spectrum of the grafted copolymers, which shows characteristic absorption of the azide at 2108 cm^{-1}. Based on the FTIR, the click reaction is completed after 20 h with the complete disappearance of azide peak at 2108 cm^{-1}, while the triazole peak [14] at 1630 cm^{-1} is observed. All confirms the successful grafting of target-moieties. Asymmetric and symmetric stretching vibrations of C-H bonds are at 2975 cm^{-1} and 2919 cm^{-1}. And some other peaks are marked in Fig. 4(b).

3.6. The properties of PEG-b-PCL-b-(PCL-g-POSS)

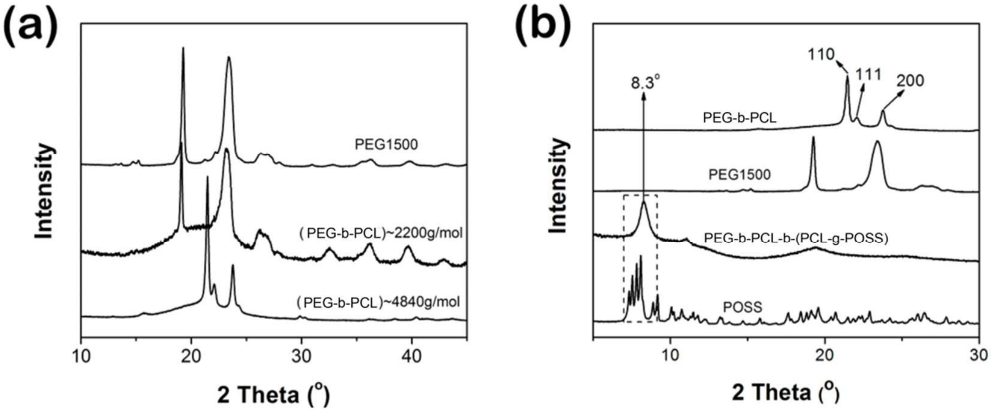


Fig. 5 (a) XRD of PEG-b-PCL with different Mn, (b) XRD of PEG-b-PCL with M_n 11000g/mol, PEG1500, PEG-b-PCL-b-(PCL-g-POSS) and Alkyne-functional POSS.

XRD of the selected copolymers are shown in Fig. 5. As shown in Fig. 5(a), PEG1500 displays good crystallinity. However, there is no PEG peak in the copolymer when M_n of PEG-b-PCL is 4840 g/mol, indicating that the PEG segments in the copolymer is amorphous with the PCL molecule weight increasing. Moreover, in Fig. 5(b), the PEG-b-PCL shows very sharp crystalline reflections at $2\theta = 21.4°$ (4.15 Å) and 23.6° (3.76 Å), corresponding to the (110) and (200) lattice planes of an orthorhombic unit cell of PCL[19], respectively. According to Fig. 5(b), PEG-b-PCL (M_n 11000 g/mol), PEG and POSS have good crystallinity. But the grafting of POSS leads to the nearly both amorphous structure of the PEG and PCL segments. However, the POSS also can form good crystallinity even after grafting on the copolymer, which can be affirmed by the appearance of peak at $2\theta=8.3^{o}$ (10.4 Å) in the Fig. 5 (b).

The phase morphology is further detected by TEM. The copolymer thin films were prepared by dropping the polymer solution with 1 mg/mL, and THF as solvent, on the Copper grid. The samples are annealed at 25 ^{o}C, that is, much higher than the glass transition temperature of the system, under vacuum for 24 h to induce phase separation. As can be seen from Fig. 6(a), the dark phase is assigned to PCL domains because the PEG1500 in the copolymer (PEG-b-PCL with Mn 4840 g/mol) is amorphous, leading to PEG with lower density than PCL phase, which is with both amorphous and crystal regions (Fig. 6(c)). In addition, as we know, POSS is grafted onto the PCL segments and POSS crystals, which are shown in upper-right corner of Fig. 6(b)), accounts for PCL segments being with higher density than that of PEG segments, so the dark phase here is also assigned to PCL domains. As illustrated in Fig. 6(d), POSS molecules on PCL chains perform strong interaction and form nano crystals (diameter ~2 nm according to the HRTEM) which act as physical cross-linking points. This assumption is supported from the POSS crystalline reflections from XRD (Fig. 5(b)). Furthermore, the phase structure of PEG-b-PCL-b-(PCL-g-POSS) (Fig. 6(b) and Fig. 6(d)) shows higher parallelism and smoother interface than that of PEG-b-PCL (Fig. 6(a) and Fig. 6(c)), indicating the interaction of POSS molecules induced effectively self-assembly of block copolymer and formed ordered nano phase separation. Because in one side high hydrophobicity of POSS increased the phase separation tendency between PCL and PEG, thus performed smoother interface; in another side, as showed in Fig. 6(d), POSS were chemical grafting onto the polymer, strong crystallization ability of POSS would induce intermolecular interactions, thereby inducing the formation of the nano structure with high parallelism and smooth interface.

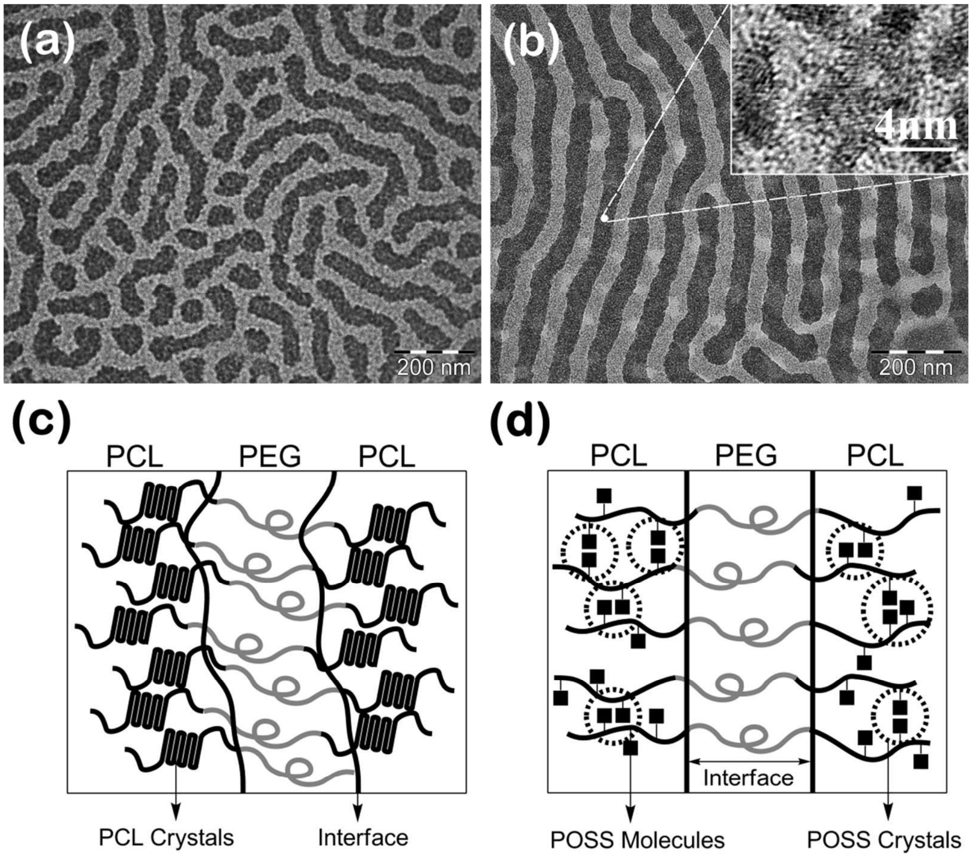


Fig. 6 (a) TEM of PEG-b-PCL with Mn=4840 g/mol; (b) TEM of PEG-b-PCL-b-(PCL-g-POSS); the upper-right corner of (b) is HRTEM of

PEG-b-PCL-b-(PCL-g-POSS); and schematic illustration of (c) PEG-b-PCL, (d) PEG-b-PCL-b-(PCL-g-POSS) forming nanodomains.

It can be suspected that POSS regulatory nano-crystalline phase will affect the properties of the copolymer. Herein, the thermal properties are detected by DSC. A typical DSC spectrum is shown in Fig. 7, which demonstrates that both PEG-b-PCL-b-(PCL-g-Cl) and PEG-b-PCL-b-(PCL-g-N_3) have the lower melting temperatures than PEG-b-PCL which are no more than 60 ^{o}C from Fig. 7(a). The covalently side-capping PCL with -Cl or -N_3 macromers disrupted the crystallization of PCL, resulting in lower melting temperatures. The appearance of cold crystallization indicates that the modified polymers possess lower crystallization degrees at room temperature but with moderate crystallization ability. Namely, it still can form crystals under a certain thermal field due to the flexibility of the PCL molecular chain. In addition, there is no significant glass transition in sample A compared with that in sample B and C. It is mostly attributed to the high crystallinity, which would restrict the movement of chain segment below the melting point in sample A. Some other data are listed in Table 1.

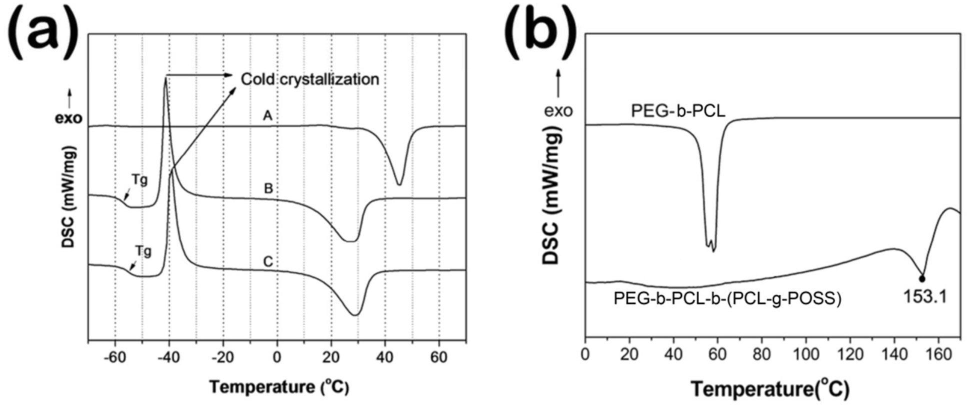


Fig. 7 (a) DSC spectrum of copolymers, A, PEG-b-PCL (Mn~4800 g/mol), B, PEG-b-PCL-b-(PCL-g-Cl) (Mn~5800 g/mol), C, PEG-b-PCL-b-(PCL-g-N_3);(b) DSC of the PEG-b-PCL-b-(PCL-g-POSS) with Mn~4200 g/mol compare to the neat PEG-b-PCL (Mn~4800 g/mol).

Table 1. DSC, GPC of PCL-b-PEG and the grafted copolymers.

Sample	$M_{n,NMR}$[a] (g/mol)	Mn[b] (g/mol)	PDI[b]	Tg[c] (mid.)/ °C	Tm[c]/ °C	ΔHc[c] (J/g)	ΔHm[c] (J/g)
PEG	-	1730	1.08	NF	52.1	NF	-181.7
PEG-b-PCL-1	-	4840	1.18	-57.9	43.7	NF	-45.46
PEG-b-PCL-2	2160	2200	1.12	-59.6	45.2	NF	-117.8
PEG-b-PCL-b-(PCL-g-Cl)-1	10870	5800	1.20	-56.6	31.9	46.57	-40.33
PEG-b-PCL-b-(PCL-g-Cl)-2	2770	2970	1.08	-57.1	27.6	57.53	-67.62
PEG-b-PCL-b-(PCL-g-N_3)-1	10990	5790	1.24	-53.9	32.6	33.47	-30.55
PEG-b-PCL-b-(PCL-g-N_3)-2	2790	2950	1.31	-55.1	28.8	44.34	-54.8
PEG-b-PCL-b-(PCL-g-POSS)	6470	4250	1.38	NF	153.1	NF	-

[a] Determined by ^{1}H NMR spectroscopy. [b] Obtained from GPC. [c] Obtained from DSC.

As we know, the influence of molecular weight on T_g can be approximately described by the Flory Equation:

$$T_g = T_{g,\infty} - \frac{K}{M}$$

where $T_{g,\infty}$ is the value of Tg for very high molecular weight, and K is a constant. Namely, within a certain range, T_g increases when the molecular weight increases. Herein, for example, T_g of PEG-b-PCL with Mn~4840 g/mol is slightly higher than that of PEG-b-PCL with Mn~2200 g/mol, as shown in Table 1. T_g of the block copolymer increases from below -59.6 °C for PEG-b-PCL (2200 g/mol) to -55.1 °C for PEG-b-PCL-b-(PCL-g-N_3) (2950g/mol), and the melting temperature decreases from 43.7 °C for PEG-b-PCL to 32.6 °C for PEG-b-PCL-b-(PCL-g-N_3). Because the chemical regularity of the copolymer chain is destructed by incorporated -N_3, leading to reduction in crystallinity. However, what is paradoxical is the melting temperature is improved significantly (with increasing about 100 °C) after the introduction of POSS. As we known, PEG and PCL blocks are amorphous based on XRD, thus, the melting temperature at 153.1 °C (Fig. 7(b)) is attributed to the POSS nano crystals which are grafted on the PCL chains. Herein, POSS nano crystals act as physical crosslink points and the thermal enhancement agent.

4. Conclusion

Alkyne-functional POSS was successfully synthesized using acid and aminopropyllsobutyl POSS through the DCC coupling. The grafting POSS along PEG-b-PCL with an increase of approximate 100 °C in melting temperature were successfully achieved via Click Chemistry. In addition, the presence of POSS will promote phase regularity at nanoscale, which accounts for the formation of further excellent orderliness phase structure. Simultaneously, POSS crystals as physical crosslink points and the thermal enhancement agent support the melting properties of the copolymer.

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