

Crystallization of POSS in a PEG-Based Multiblock Polyurethane: Toward A Hybrid Hydrogel

Jian Wu¹, Qing Ge¹, Kelly A. Burke¹ and Patrick T. Mather^{2,*}

¹Chemical Engineering Department and Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, CT 06269-3136

²Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106

ABSTRACT

Building upon earlier success in forming materials with crystalline ordering of POSS via the telechelic architecture with POSS end-capping polyethylene glycols, here we report similar ordering in PEG-POSS thermoplastic polyurethane applicable to a novel hybrid hydrogel. Thus, a unique series of hybrid thermoplastic polyurethanes (TPUs) were synthesized using poly(ethylene glycol) (PEG) as soft segment and incorporating an isobutyl-functionalized POSS diol (TMP POSS diol) in the hard segment. The molecular weight of PEG was systematically varied to include 10, 20, and 35 kDa while the mole ratio of PEG to POSS diol (as chain extender) was chosen as 8:1. The diisocyanate employed for TPU polymerization was 4,4'-methylenebis(phenyl-isocyanate) (MDI). Wide-angle X-ray diffraction (WAXD) studies revealed that both the hydrophilic soft segments (PEG) and hydrophobic hard segments (POSS) can form crystalline structures driven by micro-phase separation, itself due to thermodynamic incompatibility. Differential scanning calorimetry (DSC) and rheological studies revealed that thermal history is important in controlling the crystallization of a POSS-rich nanophase. Increasing the cooling rate monotonically decreases the crystallinity of POSS-rich phase and results in a decrease in the ultimate dynamic storage modulus following POSS crystallization and an increase of the loss angle for temperatures above T_m of PEG and below T_m of POSS. We conclude that both composition and thermal history are key factors in determining the internal network built by the POSS nanophase, which will have a significant influence on the properties of the resulting hybrid hydrogels now being studied.

INTRODUCTION

Hydrogels are an important class of polymeric materials with applications ranging from biomedical applications,[1,2] such as delivery systems of bioactive reagents, to tissue engineering,[3] to water absorption applications, among others. Being nontoxic and biocompatible, poly(ethylene glycol) (PEG) is one of the most widely investigated systems.[4-6] PEG-based hydrogels can be obtained either chemically,[4,7] through covalent bonds, or physically through hydrogen bonds, crystallized domains, or hydrophobic interaction. In contrast to chemical hydrogels, physical ones feature the advantages of being reversible, injectable, and processible. Polyhedral oligosilsesquioxane (POSSTM) is a class of hybrid molecule with an inorganic (silicon-oxygen) core and eight variable organic side groups. When covalently incorporated with hydrophilic PEG, hydrophobic POSS macromers can be expected to aggregate and crystallize to form nanoscale crystals due to micro-phase separation. These crystallized species can become the physical cross-links to form a hybrid organic-inorganic network,

resulting in a novel hybrid hydrogel in the water-swollen state. The properties of hydrogels strongly depend on their internal three-dimensional network structure and molecular weight between two closest cross-links (M_c) related to the mesh size (ξ). If the cross-links are crystallized domains, thermal history will have a great influence on them and the formation of the resulting network. During polymer processing, crystallization usually takes place under such non-isothermal conditions, such as for melt-spinning, injection molding, and extrusion. In order to obtain the desired properties, it is thus necessary to evaluate the cooling rate dependence of crystallization and the resulting viscoelastic properties. Recently, our group has successfully synthesized PEG telechelics incorporating polyhedral oligosilsesquioxane (POSS).[9] We are extending this chemical architecture to PEG multi-block polyurethanes incorporating POSS to form a novel hybrid hydrogel. Here, we report the first synthesis of such polymers and the effect of cooling rate on the POSS crystallization, the latter expected to play the role of physical cross-linking in hydrogel form.

EXPERIMENTS

Sample Preparations: Hybrid thermoplastic polyurethanes (TPUs) are composed of soft segments, the polyethylene glycols (PEG) and hard segments, 1-[2-Ethyl-2-[(3-dimethylsiloxy)propoxymethyl]-1,3-propanediol]-3,5,7,9,11,13,15-isobutylpentacyclo-[9.5.1^{13,9}.-1^{5,15}.1^{7,13}]-octasiloxane(TMP-Diol/Isobutyl-POSS) and 4,4-Methylenebis(phenyl-isocyanate) (MDI), as shown in Figure 1. We used a one-step method to synthesize the TPUs. Before synthesis, PEG (Fluka) was purified by precipitating THF solution into *n*-hexane several times, and then dried in vacuum oven at room temperature overnight. POSS-diol (95%, Hybrid Plastics) and MDI were used without further purification. In a 100ml three-neck flask, POSS-diol and PEG with prescribed molar ratio were dissolved in toluene (Fisher, ACS Certified), which had been dried over molecular sieve (4Å, Aldrich). Under the protection with the purge of nitrogen, the flask was heated to 50°C and a stoichiometric amount of MDI was added into the 10 wt-% toluene solution. The reaction mixture was further heated up to 90 °C and several drops of Dibutyltin Dilaurate were added through a syringe. The reaction was kept at 90°C for 3 hours under the nitrogen atmosphere and a ‘thickening’ phenomenon could be observed. The product toluene solution was precipitated into an excess of *n*-hexane, filtered, and washed with de-ionized water several times in order to remove unreacted POSS-diol and PEG. The yielded products were then dissolved in toluene and poured into casting dishes, where the solvent evaporated to form the semi-transparent films.

Microstructure Characterization: Wide Angle X-Ray Diffraction (WAXD) was performed to detect the microstructure of TPU films varying POSS content at room temperature on a BRUKER D5005 X-ray diffractometer operated at 40 kV and 40 mA with Cu K $_{\alpha}$ radiation, wavelength (λ)=1.5418Å.

Thermal Analysis: Non-isothermal crystallization processes of POSS incorporated in TPUs were investigated by DSC (TA Instruments DSC2920) equipped with a mechanical intercooler (down to -60 °C) under a continuous nitrogen purge (50 mL/min) by the following procedure. The samples (5~10mg) were heated to 155 °C, held for 5 minutes, and then cooled at different cooling rates to 60 °C. They were finally heated back to 155°C at 10 °C/min to detect the effect of cooling rate on the POSS crystallinity.

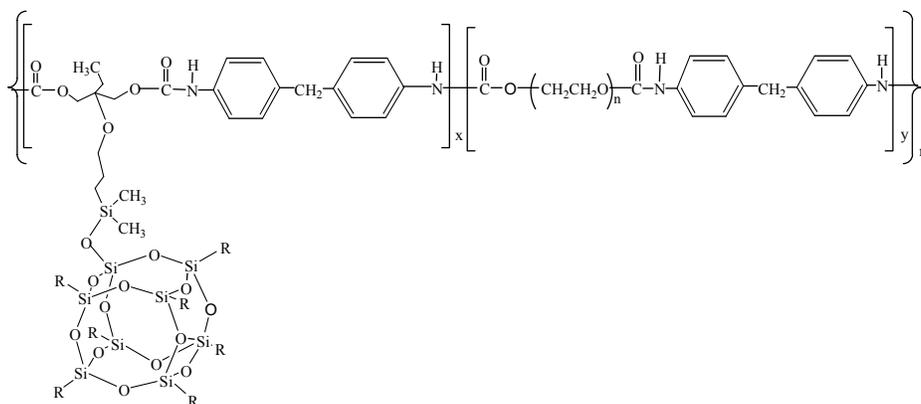


Figure 1. Schematic drawing of chemical structure of PEG-Based hybrid Polyurethane incorporating POSS with isobutyl R-group.

Rheology Measurements: The temperature evolution of TPU's linear viscoelasticity during the cooling was monitored by rheological measurements carried out on ARES rheometer (Advanced Rheometric Expansion System, Rheometric Scientific, Inc.) equipped with auto-adjustment of tool thermal expansion under the protection of nitrogen. The chosen angular frequency and strain amplitude is 1.0 rad/s and 0.1%, respectively. The strain sweep tests were conducted at 75°C to access the effect of cooling rate on the viscoelastic properties of TPU related to POSS crystallization. The strain ranges from 0.01 to 200% under the angular frequency of 1.0 rad/s. The fixture is parallel plates of 10 mm diameter and the samples were ~1.0 mm thick.

RESULTS AND DISCUSSIONS

The novel hybrid thermoplastic polyurethanes composed of POSS with isobutyl R-group and PEG segments are detailed in Table 1. WAXD patterns of TPUs shown in Figure 2 reveal that there are three significant diffraction peaks. Compared with WAXD patterns of pure PEG and TMP POSS-diol, the two diffraction peaks at d -spacing of 4.6Å ($2\theta=19.2^\circ$) and 3.8Å ($2\theta=23.4^\circ$) are attributed to 120 and 132 reflection peaks of PEG, respectively. The peak at d -spacing of 10.7Å ($2\theta=8.2^\circ$) is attributed to 101 reflection peak of POSS-crystals, although it is a little bit smaller than the reflection peak of TMP POSS-diol at d -spacing of 11.1Å ($2\theta=7.9^\circ$). Obviously, the hydrophilic segment of PEG and hydrophobic POSS can form crystalline microstructures driven by micro-phase separation due to thermodynamic incompatibility.

The effect of cooling rates on POSS crystallinity is shown in Figure 3. Figure 3(a) shows the DSC cooling trace curves of one typical TPU sample with POSS:PEG =8:1 (molar ratio) and PEG = 10 kDa. The corresponding heating trace curves reflect the effect of cooling rate on the POSS crystallinity, shown in Figure 3(b). Figure 3(c) summarizes the melting enthalpy of POSS crystalline phase with varying POSS content under different cooling rates. We see that the melting enthalpy of POSS monotonically decreases with an increase of cooling rate and has an increasing function of POSS content.

During the cooling process, POSS aggregates and crystallizes to form POSS-rich phase and the sample changes from liquid-like to solid-like. This transition can be seen as gelation, with rheological measurements offering an effective way to detect this transition. Figure 4 reports the evolution of the storage modulus, G' , of three samples with varying PEG block length. For the sample with PEG=10 kDa, all of the G' traces feature a significant increase under different

cooling rates. As to samples with PEG=20 kDa and PEG=35 kDa, it is interesting to find that there are two transitions. One at higher temperature, possibly due to micro-phase separation, and another at lower temperature attributed to POSS crystallization. The reason why we do not observe these two kinds of transition in the sample with PEG = 10 kDa may be that these two transitions overlap. In order to confirm this hypothesis, future work will include *in-situ* wide-angle X-ray diffraction and small angle X-ray scattering under the same thermal procedure. The final value of G' has a decreasing function of cooling rate in all three samples.

In order to evaluate the effect of cooling rate on the physical cross-linking density due to POSS nano-crystalline species, we measured the linear viscoelastic properties above T_m of PEG and below T_m of POSS. Figure 5 (a) and (b) show this data 75°C under angular frequency of 1.0 rad/s after the cooling procedure. The modulus reflects the physical cross-linking density and the resulting molecular weight between two cross-links due to POSS-crystal species. According to rubber elasticity theory,[10] the relationship between the modulus (G) and the molecular weight (M_s) between cross-links can be expressed as follows:

$$G = \frac{\rho RT}{M_s} \quad (1)$$

where ρ is the density of network, R is gas constant and T is the absolute temperature. The strong cooling rate dependence of shear modulus implies that the physical cross-linking density and the segment length between two closest cross-linking points can be effectively tuned by thermal history. Furthermore, it is interesting for us to find that cooling can induce the transition from solid to liquid over the complete thermal cycle in the sample of PEG=35 kDa. As expected, the modulus is also the function of POSS content. Higher POSS contents leading to higher moduli.

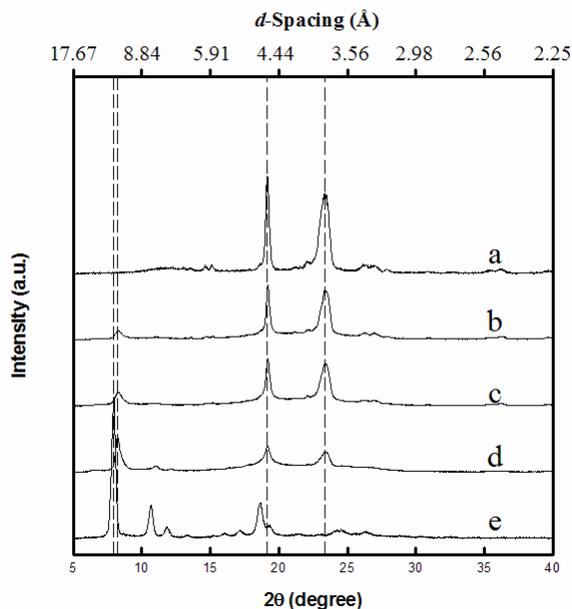


Figure 2. WAXD patterns of TPUs from PEG and TMP POSS-diol macromers indicated in Table 1: (a) PEG, (b) TPU, PEG=35k, (c) TPU, PEG=20k, (d) TPU, PEG=10k, (e) TMP POSS-diol. The x-ray wavelength (λ) is 1.5418Å.

Table 1 POSS-PEO hybrid thermoplastic polyurethanes.

M_w of PEG (g/mol)	POSS:PEG ^a	M_w (g/mol) ^b	M_w/M_n
10k	8:1	49,200	1.30
20k	8:1	55,300	1.87
35k	8:1	45,600	1.76

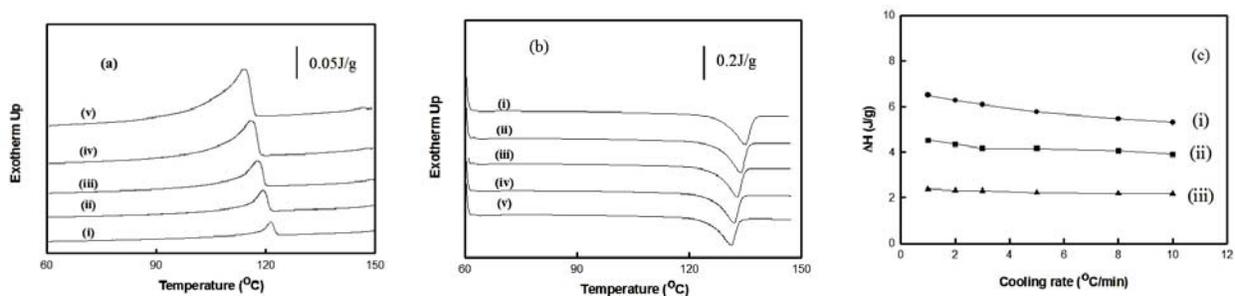
^aFeed molar ratio of TMP POSS-diol to PEG^bMolecular weight data was obtained from GPC (in THF)

Figure 3. The effect of cooling rate on the POSS crystallization in TPUs. (a) DSC trace curves of TPUs with molar ratio of POSS to PEG (8:1) and PEG=10k under different cooling rate: (i) 1.0 (ii) 2.0, (iii) 3.0, (iv) 5.0 and (v) 10.0 °C/min. (b) The following DSC heating trace curves after cooling experiments with heating rate of 10°C/min. The marks stand for the cooling rate shown in (a). (c) Summarize effect of cooling rate on the melting enthalpy of POSS crystals in TPUs with the same molar ratio of POSS to PEG (8:1) and different PEG block length: (i) 10k (ii) 20k and (iii) 35k.

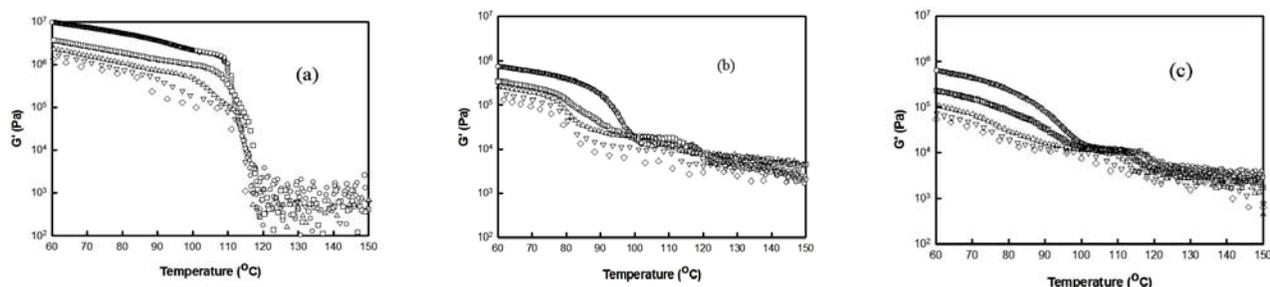


Figure 4. Shear storage modulus, G' , trace curves of TPUs during the cooling process with different cooling rate: (○) 1.0; (□) 2.5; (◇) 5.0; (△) 10.0 (▽) 20.0 °C/min. TPUs have the same molar ratio of POSS to PEG (8:1) varying PEG block length: (a)10k; (b) 20k and (c) 35k.

CONCLUSION

We have successfully synthesized the novel organic-inorganic hybrid polyurethane incorporating PEG and POSS. POSS crystals region plays the physical cross-linking role in the system, reflected in the rubbery plateau between the melting points of PEG and POSS. The modulus

decreases with the increase of POSS content. Besides, thermal history is another key factor to tune the network based on the POSS nano-crystals. Above PEG melting point and below POSS crystal one, rubbery plateau modulus has a decreasing function of cooling rate. Faster cooling rate depresses the POSS crystallization and results in the lower physical cross-linking density contributed by POSS nano-crystal species. Undoubtedly, the control of thermal history is an effective way to tune and optimize the internal network structure of our hybrid TPUs formed by POSS nano-crystal region. Based on the chemical composition and architecture, our novel polyurethane nano-composites can be a new class of hybrid hydrogel candidates. The effect of POSS crystallization under different thermal conditions on properties of this novel hybrid hydrogels will be studied in the future work.

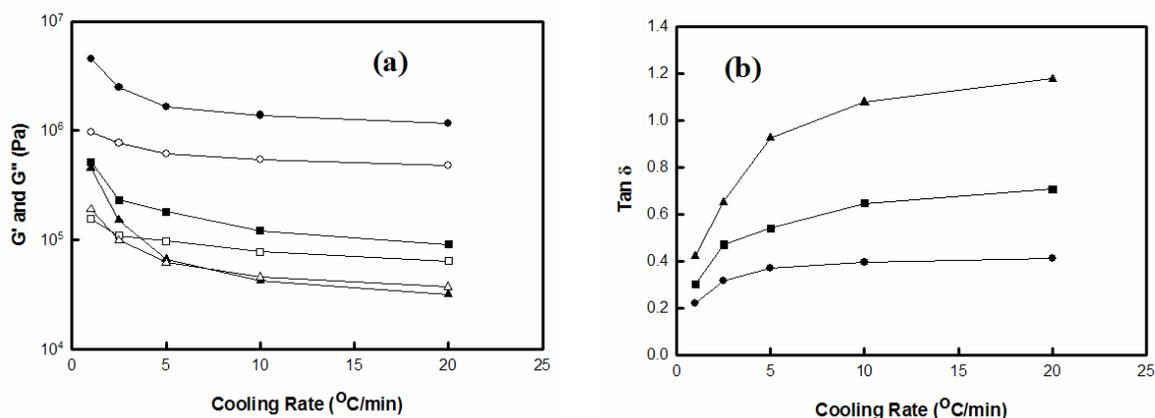


Figure 5. The effect of cooling rate on the linear viscoelastic properties of TPUs. (a) G' (shear storage modulus, solid symbols) and G'' (shear loss modulus, open symbols); (b) $\tan\delta$. The values were obtained from the linear window of the strain sweep tests with angular frequency of 1.0 rad/s at 75°C. TPUs feature the same molar ratio of POSS to PEG (8:1) and varying PEG block length. The symbols of circle, square and up-triangle represent 10, 20, and 35 kDa PEG molecular weights, respectively.

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