Nanoscale reinforcement of polyhedral oligomeric silsesquioxane (POSS) in polyurethane elastomer

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Abstract: A unique class of polyurethane (PU) elastomer containing inorganic molecules (polyhedral oligomeric silsesquioxane, POSS) as molecular reinforcement in the hard segment was investigated by means of wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) techniques. WAXD results indicate that POSS molecules form nanoscale crystals showing distinct reflection peaks. The formation of POSS crystals is probably prompted by the microphase separation between solid-like hard segments and rubbery soft segments in PU. The microphase separation of hard and soft segments was observed by SAXS, which shows a long period of 111 Å for 34 wt% POSS-PU and 162 Å for 21 wt% POSS-PU, and hard segment domains with sizes of about 34 Å for both of them. WAXD results from a series of POSS compounds with a corner substituted by a functional group of varying length were compared with POSS-PU, which also confirms the presence of nanoscale POSS crystals in the polymer matrix.
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INTRODUCTION

Segmented polyurethane (PU) based elastomers have versatile mechanical and thermophysical properties due to the formation of microphase separation from the thermodynamic incompatibility (immiscibility) of solid-like hard segments and rubbery soft segment sequences.[1–3] The hard segments usually involve interchain interactions by means of van der Waals' forces and hydrogen bonding, which determine the strength of the hard segment and thus macroscopic properties. In this study, we have investigated a unique class of PU containing polyhedral oligomeric silsesquioxane (POSS) cages pendent to the polymer chain. The purpose of this POSS incorporation is to molecularly reinforce the hard segment and improve mechanical and physical properties of PU.

The POSS molecule contains a polyhedral silicon–oxygen nanostructured skeleton with intermittent siloxane chains (general formula $(SiO_{3/2})_n$),[4–9] which

was first reported in 1946.[10] Recently, these molecules have been successfully incorporated in different polymers by scientists from the Air Force Research Laboratory (AFRL).[11–15] These hybrid polymers show improved properties such as higher T_g, increased oxygen permeability, reduced flammability and enhanced mechanical strength. In this study, the chosen POSS molecule has $n = 8$ (cage-like), with the corner group as cyclohexyl (molecular weight greater than $1000 \, g \, mol^{-1}$). This molecule is considered large (approximately 15 Å in molecular axis, with an inner Si–Si diameter of 5.4 Å) as compared to the regular size of PU hard domains (25 Å).[16] Our goal in this study is to understand the nature of POSS molecules within segregated hard segment domains.

EXPERIMENTAL

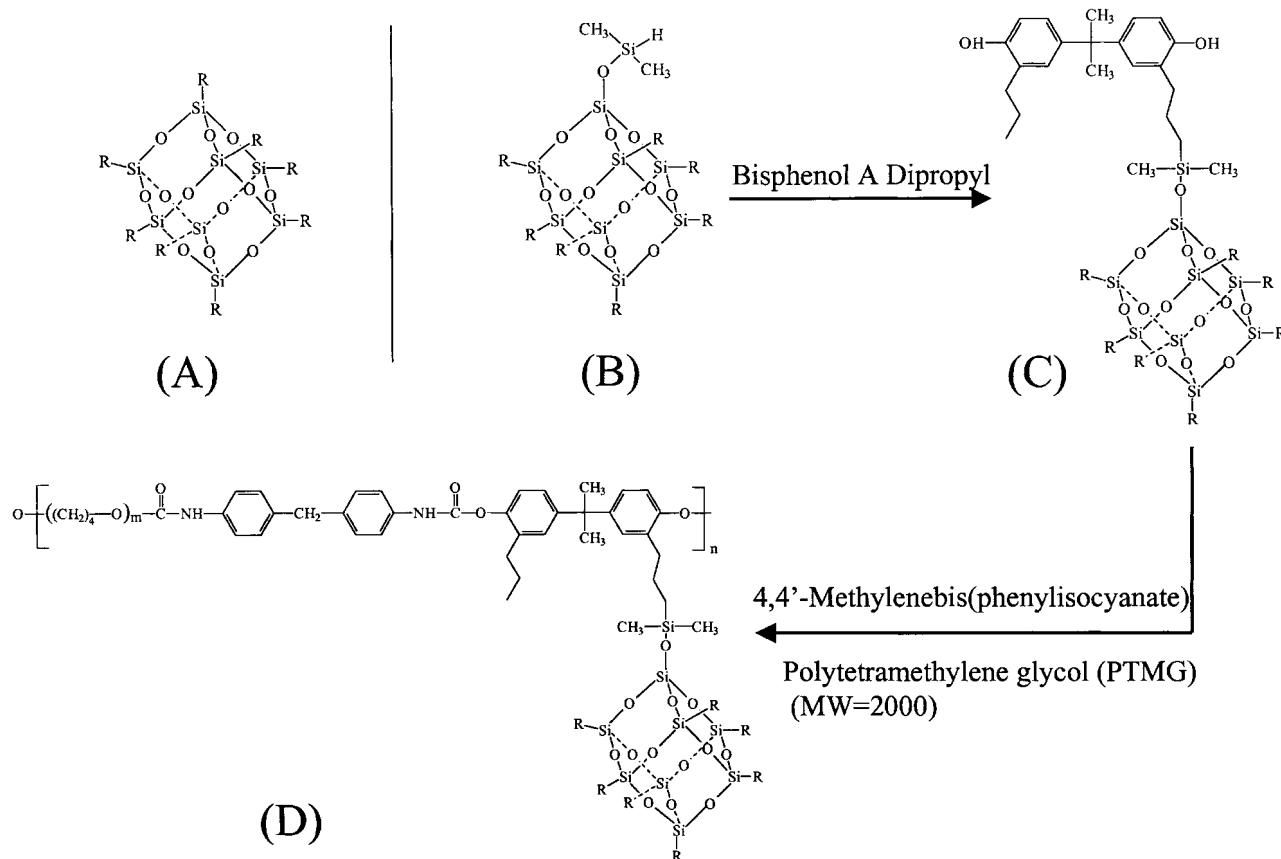The chosen POSS molecule $(SiO_{3/2}R)_8$ contains

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Figure 1. Schematic diagram of the synthesis route for POSS–polyurethane: (A) octacyclohexyl-POSS, with R = cyclohexyl; (B) hydrido-POSS; (C) BPA-POSS; (D) POSS-PU.

R = cyclohexyl (octacyclohexyl-POSS). We have also investigated its derivative with one corner group substituted by: (1) hydridomethylsiloxy group (hydrido-POSS), and (2) 3-(allybisphenol-A) propyldimethylsiloxy group (BPA-POSS). The BPA-POSS compound is a diol, which was used in the PU synthesis as the chain extender.[16] The POSS-PU contains soft segments of polytetramethylene glycol (PTMG) ($M_w = 2000$), and hard segments of 4,4′-methylenebis(phenylisocyanate) (MDI) and BPA-POSS. Two weight fractions of POSS were prepared for the POSS-PU: 34% and 21%. A typical synthetic scheme is shown in Fig 1.

Simultaneous wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) measurements were carried out at the Advanced Polymers beamline, X27C, National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). The wavelength used was 1.307 Å, and the beam was about 0.4 mm in diameter at the sample position. Two Fuji imaging plates were used to detect both WAXD (having an opening allowing the passage of the SAXS signals) and SAXS images. The chosen sample-to-detector distance for WAXD was 140 mm and for SAXS was 1190 mm. The WAXD profiles were calibrated by the silicon standard, while SAXS profiles were calibrated using silver behnate.
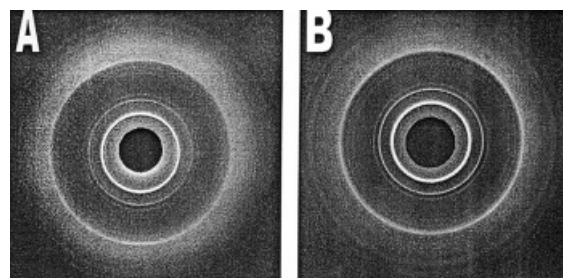

Figure 2. Two-dimensional WAXD pattern of polyurethane with (A) 21 wt% POSS and (B) 34 wt% POSS. The exposure time of each pattern was 1 min.

RESULTS AND DISCUSSION

Two-dimensional WAXD patterns of 34 wt% POSS-PU and 21 wt% POSS-PU are shown in Fig 2. Unlike typical PU, these POSS modified PUs show distinct crystal reflection peaks, resulting from the POSS crystals. The strongest peak can be indexed as the 101 reflection ($2\theta = 6.52$, at $\lambda = 1.307$ Å) of the POSS crystals.

Circularly averaged one-dimensional WAXD profiles of octacyclohexyl-POSS, its two derivatives (hydrido-POSS and BPA-POSS) and POSS-PU are shown in Fig 3. A systematic decrease in the number of reflections (at high angles) is seen from the POSS monomers to the modified PUs. However, the posi-
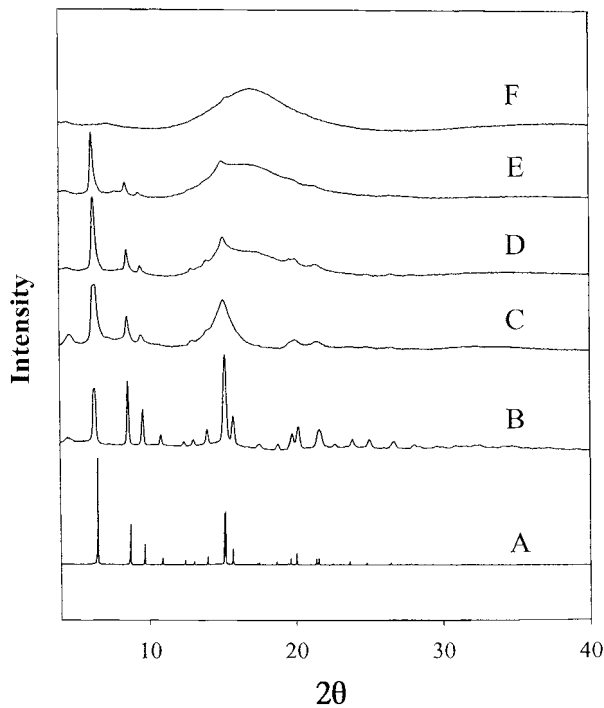
Figure 3. X-ray powder diffration profiles from POSS monomers and POSS-PU: (A) octacyclohexyl-POSS; (B) hydrido-POSS; (C) BPA-POSS; (D) 34wt% POSS-PU; (E) 21wt% POSS-PU and (F) PU.

Figure 4. SAXS patterns of (A) 34wt% POSS-PU and (B) 21wt% POSS-PU. (By using the correlation function analysis, the long period was determined as 111Å for 34wt% POSS-PU and 162Å for 21wt% POSS-PU.)

tions of the major reflections appear to remain constant. We have determined the crystal structure of octacyclohexyl-POSS by the powder diffraction method (results to be published elsewhere), which is rhombohedral with $a = 11.57\,\text{Å}$, $\alpha = 95.5°$ (or $a = 17.12\,\text{Å}$, $c = 18.03\,\text{Å}$ in an equivalent hexagonal cell). This structure is consistent with the one published before by Barry *et al* in 1955.[17] The diffraction pattern of hydrido-POSS appears to be identical to that of octacyclohexyl-POSS, which suggests that the substitution of a corner group does not affect the molecular packing in the POSS crystal. We attribute this behaviour to the rapid rotation of the corner group to the silicon–oxygen skeleton, which will also be discussed elsewhere.

In Fig 3, the pure PU with no POSS shows a broad amorphous hump. As the POSS content increases to 21wt%, the WAXD pattern exhibits four distinct reflection peaks at d-spacings equal to 11.5, 8.6, 7.6 and 4.96Å These peaks are fingerprints of POSS crystals. As the POSS content increases to 34wt%, these characteristic POSS peaks become more apparent and some weaker peaks (d-spacings = 5.76, 5.41, 3.80 and 3.50Å) also appear. The chain extender BPA-POSS exhibits a pattern very similar to that of 34wt% POSS-PU. This suggests that the microstructure of the crystals of BPA-POSS may dominate the POSS crystal formation in POSS-PU. As all the prominent peak positions in POSS monomers and polymers are identical, we conclude that the POSS crystals have the same structure under different chemical environments, perhaps differing from each other only in their size and perfection. In POSS-PU,
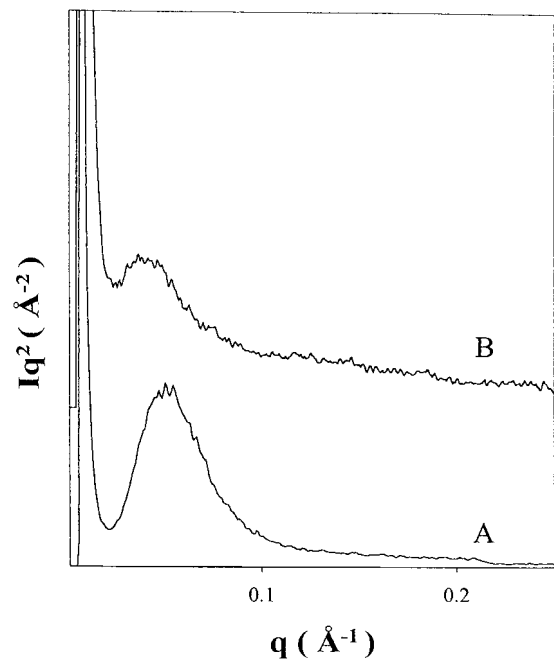
we further believe that the POSS molecules form crystals in the hard domains.

Evidence of microphase formation is seen in Fig 4, where SAXS profiles of 34wt% POSS-PU and 21wt% POSS-PU are shown. A scattering maximum is seen in each profile, which results from the interference of the hard segment domains. The average distance between the adjacent domains is about 111Å for 34wt% POSS-PU and 162Å for 21wt% POSS-PU, and the average hard segment domain size is about 34Å from both samples (using the correlation function method of the SAXS data).[18] This suggests that the nanoscale POSS crystal in the hard domain can be as small as the size of a 10 POSS chemical unit crystal.

CONCLUSIONS

We have studied the structure of a unique PU system having inorganic POSS molecules in their hard segments as nanoscale reinforcing agents. Simultaneous WAXD and SAXS techniques were applied to reveal the crystal structural and morphological changes from POSS monomers with different corner substituted groups to POSS containing PU. The POSS molecules appear to form nanoscacle crystals in the hard segment domains of PU. We believe the POSS molecules also enhance the microphase separation between the hard and soft segments. The structure of the POSS crystals in PU appears to be the same as that of POSS monomers (rhombohedral unit cell with $a = 11.57\,\text{Å}$, $\alpha = 95.5°$). Evidence for microphase separation between the hard and soft segments was seen by SAXS, with the average distance

between the hard segment domains being about 111 Å for 34 wt% POSS-PU and 162 Å for 21 wt% POSS-PU, and the average size of the hard segment domain being about 34 Å.

ACKNOWLEDGEMENTS

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