Design of Functional Polymeric Systems by the Control of Higher Order Structure

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Background

During the past several decades, much research has been conducted to investigate the polymerization behavior and the structure of formed gratings, with a focus on controlling the grating morphology, phase separation and diffraction efficiency. However, little attention has been paid to the importance of the chemical structure of the component, and definite improvement was not attained duo to unclear phase separation.

Polyhedral oilgomeric silsesquioxanes (POSS) molecules are unique nanometer-sized structures. POSS have a polyhedral core which can be multifunctional and serve as platforms that can be synthetically modified to contain groups for various reactions. The use of POSS as cores for dendrimers is also particularly attractive, because their polyhedral structures produce spherically symmetric dendrimers with smaller generation numbers than conventional cores. However, introduction of substituents to POSS has been mostly achieved by hydrosilation, Heck, and cross-metathesis reactions. Some important aspects of the reaction were not well-established. To further wider aspects of the application on POSS chemistry, it is very important to challenge the new type of reaction. Introduction of novel reactive groups, thus providing the opportunity to design functional materials with well-defined dimensions possessing nanophase behaviour, should be more concerned.

Purpose

In the **Chapter 2**, we focus on siloxane containing compounds for the preparation of holographic gratings. The motivation of using siloxane-containing compounds for the preparation of holographic gratings was driven by the hypothesis that the chemical incompatibility between the hydrocarbon and the siloxane-containing compounds may enhance the LC phase separation. Moreover, the presence of siloxane chain at the LC/polymer interface of the gratings may lower the LC anchoring strength thus lowering the switching voltage. Methacrylate monomer with silyl ether group was used as a component to fabricate a transmission grating of holographic polymer dispersed liquid crystal with high diffraction efficiency and small angular selectivity. Hydrolysis-sensitive silyl ether group played an important role in improving the diffraction efficiency and decreasing the volume shrinkage.

In the **Chapter 3**, our purpose is to develop the synthetic methodology for the silicon-oxygen containing compounds, various functional POSS monomers and to study their performance for further application. Then, in the **Chapter 4**, we will design new functional material containing POSS. For example, self-assembled dendrimers, in particular, mechanically interlocked dendrimers, have attracted much interest as they offered reversible, structural control and relatively large three-dimensional architectures starting from building blocks within the nanometer range. Using the POSS cube as a framework, the dendrimer can be built out in three dimensions leading to a very globular structure. Dendrimer based on POSS containing secondary ammonium ions and crown ether moieties showed potential application in nanomaterials and molecular machines.

Experimental Results and Discussion

In **Chapter 2**, we demonstrated a novel recording system and investigated their effect on the gratings. In TMEMA system shown in **Figure 1**, almost quantitative diffraction efficiency was obtained with 35 wt% TMPTA.

Clear gratings could be formed even with 15 or 10 wt% TMPTA, although the induction time also became longer. Nevertheless, it should be noted that the diffraction efficiency was always higher for TMEMA system with any concentration of TMPTA. Although the multi-functional acrylate TMPTA played a primary role in forming grating, but hydrolysis-sensitive silyl ether component also played an important role.

Atmospheric moisture together with cationic species generated from photo-initiator system can facilitate the hydrolysis of silyl ether groups to afford hydrophilic hydroxyl groups during photo-polymerization, which can efficiently induce phase separation of hydrophobic LC from the polymer matrix.

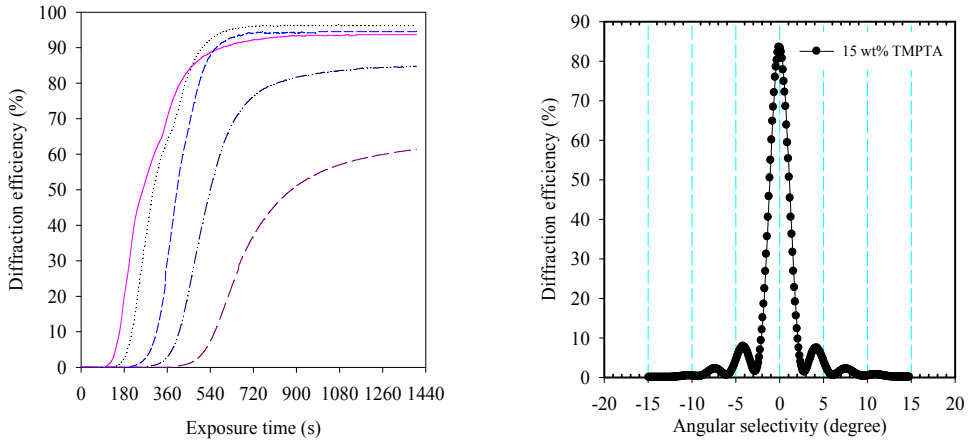
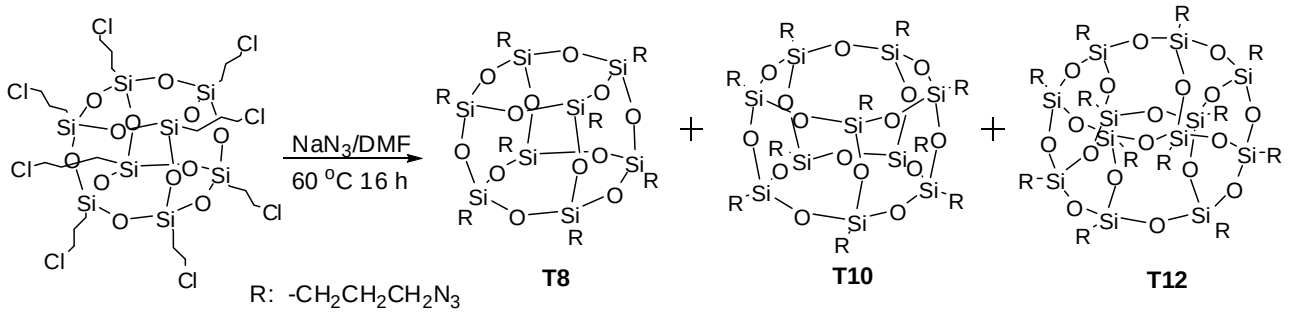


Figure 1. Real-time diffraction efficiency and angular selectivity of gratings

Condition: 85 wt% (TMEMA+TMPTA), 15 wt% NVP, 2 wt% PI, 0.2 wt% PS and 35 wt% LC. (——) 35 wt%, (·····) 25 w t%, (- - - -) 20 wt%, (— · · —) 15 wt%, (— — —) 10 wt%

At the same time, **Figure 1** showed only a little deviation from the theoretical values by Kogelnik's coupled wave theory, which may be attributed to the slight thickness reduction by small volume shrinkage although still existing.

In **Chapter 3**, when we synthesized azido-functional POSS, we noticed extensive rearrangement of the cage under azidation to produce a thermodynamically stable mixture of T_8, T_{10}, and T_{12}. Herein, we first report that sodium azide may play a dual role as a supplier of azide groups and as a nucleophile to induce cage rearrangement (**Scheme 1**).



Scheme 1. Rearrangement of POSS cage

In **Chapter 3**, we have synthesized a novel POSS-based DB24C8 cluster (host) and demonstrated that it could form a stable dendritic complex with POSS-based dibenzylammonium salts (guest). As shown in **Figure 2b**, the ^{1}H NMR spectrum of complex showed a dispersed array of well-defined resonances and a great difference from

those for host (**Figure 2a**) and guest (**Figure 2c**). The partial ^{1}H NMR spectrum of complex revealed that the characteristic benzylic methylene proton (H_a and H_b) signals adjacent to the ammonium ion center observed at 4.42 and 4.01 ppm in the **2**-H·PF_6 were shifted downfield to 4.63 and 4.49 ppm upon complexation. Furthermore, the characteristic peaks for the protons on the crown ether (H_α, H_β and H_γ), which resonated at 4.13, 3.89 and 3.81 ppm in the spectrum of host, were shifted upfield to 4.11, 3.73 and 3.39 ppm in the spectrum of the complex, respectively. These shifts of the NMR signals indicated that complexation was taking place by threading of guest through DB24C8 cavities of host, thus forming the dendritic complex.

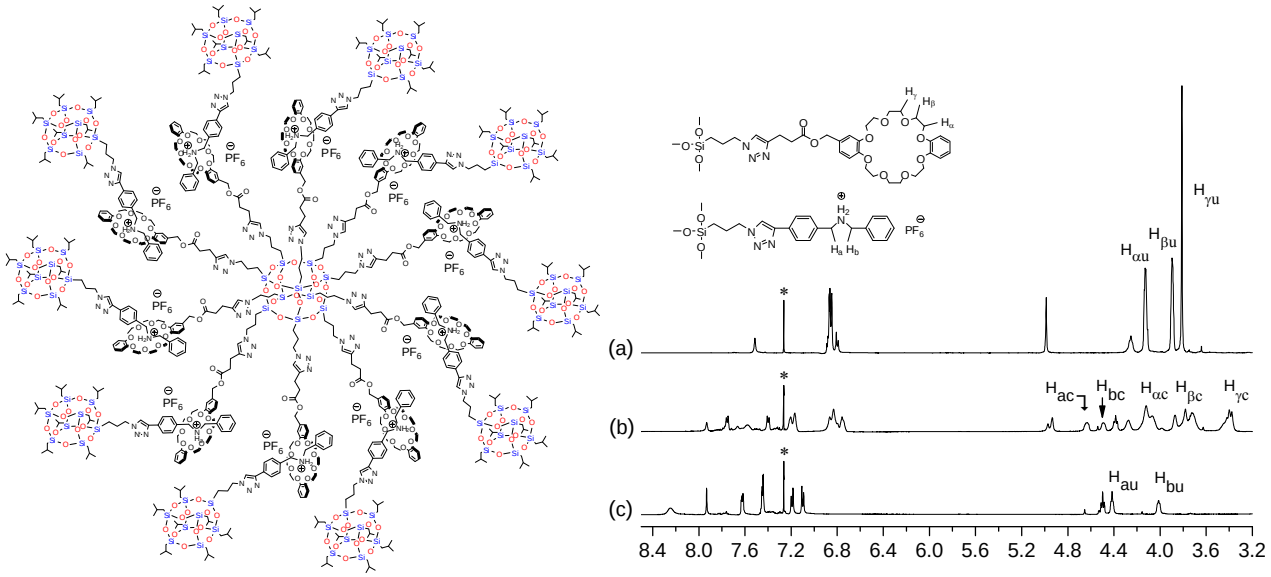


Figure 2. Structure of dendrimer and partial ^{1}H NMR spectra of (a) free host, (b) host and 10 equiv of guest, (c) free guest ([host]$_0$ = 3.9 mM, u = uncomplexed, c = complexed, and ∗ = solvent residue).

One of the reasons for assemblying mechanically interlocked compounds is to construct molecular machines on the nanoscale level, wherein their operation can be controlled through external input, such as acid and base. As shown in **Figure 3**, it indicates that the switching process is pH-controlled and completely reversible.

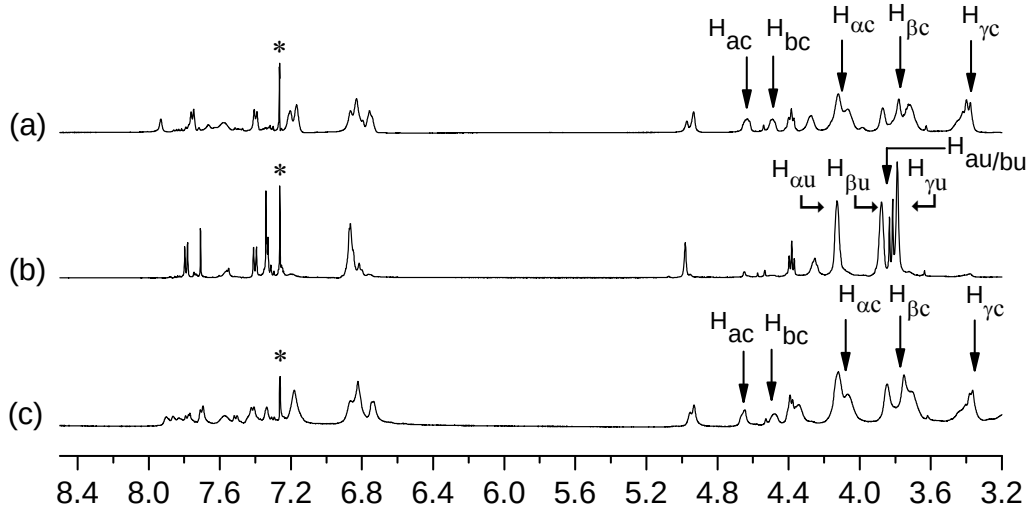


Figure 3. Partial ^{1}H NMR spectra of (a) complex of host and 10 equiv of guest (b) TEA base-treated, and (c) TFA acid-treated ([host]$_0$ = 3.9 mM, u = uncomplexed, c = complexed, and ∗ = solvent residue).

Content of the Dissertation

Publications

1. Xin Wang, Yeonghee Cho, and Yusuke Kawakami. "Improvement of the performance of transmission holographic grating by hydrolysis-induced change of the property of polymer matrix", *Polymer Journal* **2008**, 40(7), 601-606.
2. Vuthichai Ervithayasuporn, Xin Wang and Yusuke Kawakami. "Synthesis and characterization of highly pure azido-functionalized polyhedral oligomeric silsesquioxanes (POSS)", *Chem. Commun.* **2009**, 5130-5132.
3. Xin Wang, Vuthichai Ervithayasuporn, Yanhong Zhang and Yusuke Kawakami. "Reversible self-assembly of dendrimer based on polyhedral oligomeric silsesquioxanes (POSS)", in preparation.