Synthesis and Characterization of Organic–Inorganic Hybrid Polymers with a Well-Defined Structure from Diamines and Epoxy-Functionalized Polyhedral Oligomeric Silsesquioxanes

Hongyao Xu, Benhong Yang, Xiaoyan Gao, Cun Li, Shanyi Guang

Department of Chemistry and Chemical Engineering & Key Laboratory of Environment-Friendly Polymer Materials of Anhui Province, Anhui University, Hefei 230039, China

ABSTRACT: A new class of organic-inorganic hybrid polymers with well-defined structure was prepared by reacting diepoxyhexavinyl polyhedral oligomeric silsesquioxanes (DehvPOSS) with diamines of different chain lengths. The structures and properties of these hybrid polymers were well characterized by FTIR, ^{29}Si-NMR, GC-MS, and TGA. A modeling characterization was employed to help identify the structures of organic tethers linked between the POSS cages. The results indicated that at the stoichiometric ratio of DehvPOSS to diamine, well-defined organic–inorganic hybrid polymers with controlled variation of the organic tether architecture can be made, and each organic tether connected four POSS cages. Thermal stability (T_{dec}) increased with an increase in the tether length of the diamine molecules, and the highest T_{dec} was obtained with butanediamine (rather than propanediamine or ethanediamine) as the organic tether. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3730–3735, 2006

Key words: synthesis; polysiloxanes; thermal properties; nanocomposites

INTRODUCTION

Synthetic polymers have played an important role in our daily lives for the last 20 years. However, along with their increasing utilization, their inherent drawbacks have emerged, such as weak mechanical strength and low thermal stability compared to traditional metals or ceramics. Thus, many efforts have been made to solve these problems, generally by adding a second inorganic component to polymeric systems either by physical blending or chemical bonding. The resulting materials are so-called organic–inorganic hybrid polymers that combine the properties of traditional organic polymers (i.e., processability, toughness, cost) with the properties of inorganic compounds (i.e., thermal and oxidative stability). Many organic–inorganic hybrid materials have shown dramatic improvement in macroscopic properties compared with either of their nonhybrid counterparts.[1–8]

Recently, polyhedral oligomeric silsesquioxane (POSS)–based hybrid polymers[9–24] have received much attention because of the unique structure of POSS monomers. With a general formula $[(RSiO_{3/2})_n$, where $n = 8$, 10, etc.], POSS monomers are well-defined cagelike molecules (0.53 nm in diameter) and to the vertexes of the cage are appended eight (when $n = 8$) organic groups (R). These organic groups can be functionalized to yield functional POSS monomers. POSS monomers with single functional group can be used to prepare pendant-type architecture,[9–18] and multifunctional POSS can be used to prepare bead-type or star hybrid polymers.[19–22] In this way, new routes to thermoplastic or thermoset hybrid polymers are developed.[23–24] When using a suitable synthetic method, the molecular structure of hybrid polymer can be precisely controlled. The microstructure and properties of the resulting polymers can be easily tailored at molecular levels. In this article, we report an efficient synthetic route to preparing POSS-containing copolymers with a well-defined structure from diepoxyhexavinyl–POSS precursors and diamines of different chain lengths and our investigation of the relationship between the thermal stability of the hybrids and the lengths of organic tethers (were tether is defined as the chain bound between two POSS cages).

EXPERIMENTAL

Materials

Vinylethoxysilane was purchased from Nanjing Shuguang Co. (Nanjing, China). The *m*-chloroperoxybenzoic acid, used as the oxidizing agent was obtained from Fluka (Buchs, Switzerland). Dichloromethane and anhydrous alcohol were used as media and were purchased from Shanghai Reagent Co. (Shanghai, China). Dichloromethane was dried with P_2O_5 before use. Epoxyethane, ethylenediamine, 1,3-propanediamine, and 1,4-butanediamine were also purchased from Shanghai Reagent Co. and used as received.

Instrumentation analyses

The FTIR spectra were recorded as KBr slices on a Nicolet NEXUS 870 spectrometer. The ^{1}H-NMR spectra were recorded on an AVANCE/DMX-300 MHz Bruker NMR spectrometer using chloroform-*d* as the solvent. Tetramethylsilane (TMS) or chloroform-*d* was used as the internal reference for the ^{1}H-NMR analyses. The solid-state ^{29}Si-NMR spectra were measured on a Bruker DSX-400 spectrometer operating at a resonance frequency of 79.38 MHz. Thermogravimetric analyses (TGA) of the polymers were performed on a Perkin Elmer TGA 7 under nitrogen at a heating rate of 20°C/min. The GC-MS analyses of the organic tethers were carried out using a Varian Saturn 2200 GC/MS analyzer.

Syntheses of monomers and polymers

Octavinyl polyhedral oligomeric silsesquioxane

The octavinyl polyhedral oligomeric silsesquioxane (OvPOSS) was synthesized via hydrolysis and condensation of vinyltriethoxysilane, which was detailed by Baney et al.[25] in 1995. Typically, vinyltriethoxysilane (105 mL, 0.5 mol) was dissolved in 245 mL of anhydrous alcohol with stirring, and then some amount of hydrochloric acid and 30 mL of water were added to adjust the solution to a pH of 3. The system was allowed to react for 10 h at 60°C under N_2. The mixture was cooled to room temperature. The white crystalline powder was filtered, washed with cyclohexane, and recrystallized from tetrahydrofuran/methanol (1:3) to give 7.2 g (yield 18%).

FTIR (cm^{-1}) with KBr powder: 1605, 1414, 1273, 1100. ^{1}H-NMR (ppm): 5.9–6.1 (m, 24H).

Diepoxyhexavinyl polyhedral oligomeric silsesquioxane

Diepoxyhexavinyl polyhedral oligomeric silsesquioxane (DehvPOSS) was synthesized according to a procedure described previously.[26] Octavinyl–POSS [5.0 g

TABLE I
Compositions and Yields of Hybrid Polymers

Polymer	Diamine	Yield (%)
A	Ethylenediamine	85
B	Propanediamine	93
C	Butanediamine	96

(8 mmol)] and *m*-chloroperoxybenzoic acid [0.58 g (2.3 mmol)] were dissolved in 15 mL of anhydrous dichloromethane in a 25-mL flask. The solution was stirred for 7 days at 35°C and then cooled to 0°C. The solid product was filtered, dissolved in toluene, purified with silica gel chromatography, and recrystallized from methanol to give 0.3 g (yield 55%).

FTIR (cm^{-1}): 3066, 2961, 1409, 1275, 1063, 1122, 1233, 878. ^{1}H-NMR (ppm): 2.24–2.26 (m, 2H), 2.77–2.92 (m, 2H), 5.92–6.13 (m, 18H).
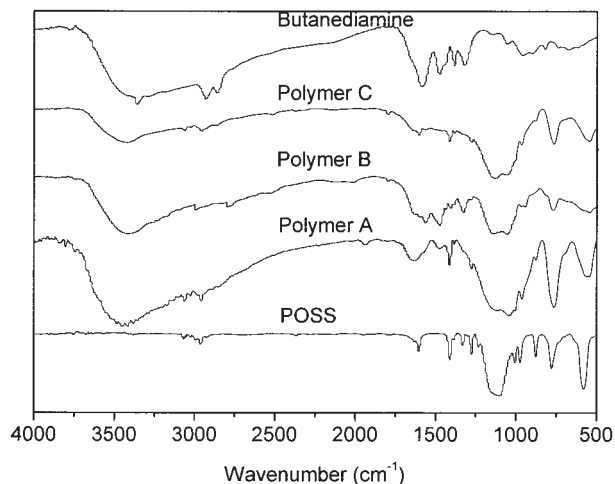
Hybrid polymers

Three diamines (i.e., ethylenediamine, 1,3-propanediamine, and 1,4-butanediamine) were chosen to react with the diepoxyhexavinyl-POSS (DehvPOSS) in stoichiometric ratios to form DehvPOSS/diamine hybrid polymers under nitrogen.

The polymerization of DehvPOSS with diamines was carried out in a 100-mL round-bottomed flask equipped with a magnetic stirring bar under nitrogen. The following procedure is typical of those used (see Table I, polymer A). First, 6.7 g (10 mmol) of DehvPOSS was dissolved in 40 mL of dichloromethane, then, 0.33 mL of ethylenediamine (5 mmol) was added dropwisely to the solution. The reaction mixture was stirred for 72 h at 30°C. White solid polymer was recovered by filtration and redissolved in THF. Then the THF solution was added dropwise to 200 mL of alcohol to precipitate the polymer. The dissolution-precipitation process was repeated three times, and the precipitate finally isolated was dried under vacuum at 40°C to a constant weight (yield 85%).

Model compound syntheses

The polymerization behavior of epoxy/amine mixtures without silsesquioxane cores was investigated using pure epoxyethane and 1,4-butanediamine as the model compounds. Typically, 3 mL of epoxyethane (0.06 mol) was dissolved in 5 mL of dichloroethane; then 3 mL of 1,4-butanediamine (0.03 mol) was dropped slowly into the solution. The mixture was allowed to react for 48 h at 10°C. The product was a viscous liquid and soluble in common solvents. The disappearance of epoxy rings in the mixture during reaction was monitored by ^{1}H-NMR. Typical ^{1}H-NMR signals of epoxide rings occur at 3.14, 2.79, and 2.59

Figure 1 FTIR spectra of hybrid polymers, DehvPOSS, and butanediamine.

ppm. These model compounds were used as the standard in the tether structure studies below.

HF-treated samples for GC-MS analysis

The organic tethers between POSS cages were prepared by dissolving the silica core (POSS) with HF and extracted for GC-MS analyses. Typically, 0.05 g of DehvPOSS/butanediamine hybrid polymers was dissolved in 5 mL of THF in a polytetrafluoroethylene bottle. Then 0.05 mL of 50% HF was dropped into the solution, and the mixture was kept at room temperature for 72 h. Then THF was removed by rotary evaporation. The residual material was mixed with freshly dried ether to extract the organic components. The extracted solution was filtered, and ether in the filtrate solution was removed. A viscous liquid was obtained and dissolved in 1 mL of *N,N*-dimethylformamide for GC-MS analysis.

RESULTS AND DISCUSSION

Polymerization of DehvPOSS and diamine

Generally, the ring-opening addition reaction can readily occur between epoxy rings and amino groups. The POSS-containing hybrid polymers were prepared by the stoichiometric reaction of DehvPOSS and three diamines of different tether lengths (i.e., ethylene diamine, 1,3-propanediamine, and 1,4-butanediamine). The results are shown in Table I.

It can be seen from Table I that the polymer yields were influenced by the chain length of the diamines and increased with an increase in chain length. For example, the yield was 85% using ethylenediamine as the chain molecules, whereas it was 96% with 1,4-

butanediamine, which may be attributed to the effect of steric hindrance.

Structure characterization

Figure 1 shows the FTIR spectra of three hybrid polymers (A, B, and C), as well as pure DehvPOSS monomer.

As can be seen from Figure 1, a sharp, strong, and symmetric Si—O—Si stretching peak at approximately 1120 cm^{-1}, which is typical of silsesquioxane cages,[27] was in the spectra of all the hybrids. The consistent presence of this peak suggests that the cage structures survived in the hybrid polymers. Several functional groups were easily observed in the spectra. However, epoxy ring asymmetric stretching and symmetric bending at approximately 1230 and 880 cm^{-1}, respectively, were relatively clear in pure POSS monomer but disappeared or weakened in all the polymer samples, and new, strong absorption bands at 3200–3500 and 1040 cm^{-1}, attributed to O—H and C—N stretching absorptions, respectively, appeared in the spectra of the polymers, confirming that the epoxy rings in the POSS monomers have been opened and combined with the amino groups in diamines to yield new hybrid polymer. Simultaneously, no N—H stretching band appeared at approximately 3360 cm^{-1}, suggesting that all the amino groups (—NH$_2$) had been consumed, meaning each amino group connected two epoxy groups (see Scheme 1). Therefore, the resulting polymers were well crosslinked net-
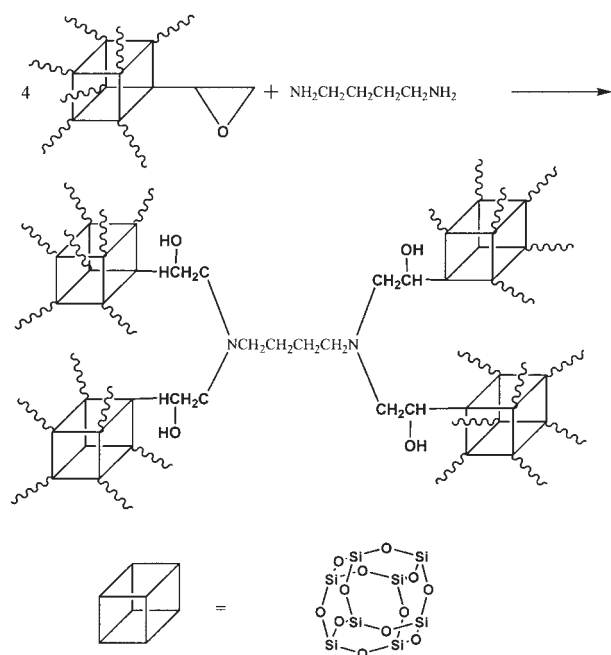
Scheme 1 Polymerization of DehvPOSS with 1,4-butanediamine.
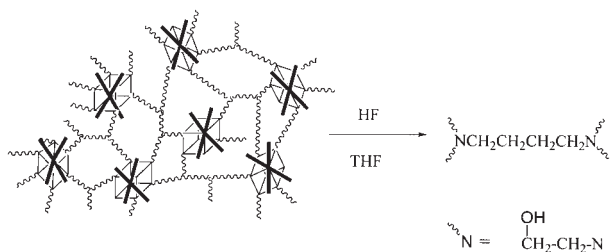
Scheme 2 Preparation of real tethers by digestion of POSS with HF.

works, as expected. This provided further support for the insolubility of all the tested solvents.

Model polymerization investigations

Because of the crosslinking, it would be impossible to study the real polymerization behavior or to characterize the network using conventional techniques such as ^{1}H-NMR or GPC, which need solutions of samples. In addition, direct characterization of the crosslinked structure would produce more complicated data because of the complexity of the crosslinked network. Likewise, preliminary solid-state NMR studies failed to generate definite results.

Therefore, aiming to probe the formation of hybrid polymers, a model polymerization study was undertaken. Typically, epoxyethane and butanediamine were allowed to react stoichiometrically in the same conditions for the syntheses of hybrid polymers. Because the organic product is soluble in dimethylformamide solvent and readily vaporized before decomposition, GC-MS analysis was employed to study the components and structures of the product. Simultaneously, we used HF to digest the POSS cages in the hybrid polymer C (see Scheme 2). The resulting organic compounds were soluble in common solvents. Thus, the overall network structures could be clearly characterized by analysis of the organic compounds and structures with GC-MS.

Figure 2(a,b) shows the GC results of a model compound and an HF-digested hybrid polymer. A single peak was observed in the GC chromatograms of both the model compound and the HF-digested hybrid polymer, suggesting that all epoxy rings reacted with the amino groups in the butanediamine molecules and, thus, that the butanediamine was completely tetrafunctional. This is consistent with the results of the FTIR spectra. Simultaneously, it also provided us with an easy method to the investigation of the tether structure between the POSS cubes in the hybrid polymers, which is discussed below.

Tether structure studies by GC-MS

From the above investigation, we realized that because the product in the above model polymerization

possessed an ideal structure, its GC chromatogram could be used as a standard to identify the peaks in the GC chromatograms of the real tethers.

Both the model samples and the HF-digested real samples were extracted with dimethylformamide, and analyzed by GC-MS. Figure 2 compares the chromatograms of the model and real samples. A single peak at 1.7 min observed in both samples implied that the structures of the organic tethers in the hybrid polymers were same as those in the model chains. That is, the organic tethers were probably four-armed molecules. Otherwise, if the amino groups were not completely reacted with the epoxy rings in the POSS monomers, the HF-digested polymer sample would be a mixture, possibly with tethers of four arms, three arms, two arms, one arm, or even no arms, and consequently, more peaks would appear on the GC chromatograms. Because only one peak was observed, we inferred that the organic tethers between the POSS cubes held four-armed structures. This inference was supported by the data from the MS spectra.

Figure 3 shows the MS spectra of both the model and real samples. Two spectra were very similar because most fragment ion peaks held the similar positions (m/z) in the spectra. This suggests that the model chain and real tether had a similar structure. The molecular ion peak was at 264 (m/z). Its poor intensity resulted from the relatively long tether with four branches, which was rather low in stability. The high intensity of the characteristic ion peak at 31 revealed that an α splitting of the hydroxyl occurred, and thus an ion of $HO^+ = CH_2$ had been generated. The appearance of M-18 ($m/z = 246$) and M-36 ($m/z = 228$) ion peaks accounted for the dehydration of the molecular ions because each had four hydroxyls at the ends. Scheme 3 shows a possible fragmentation pathway for
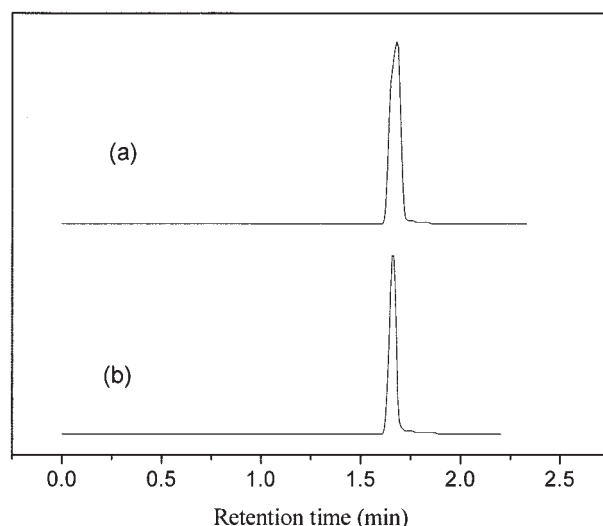
Figure 2 GC chromatograms of both (a) model compound and (b) HF-digested polymer.
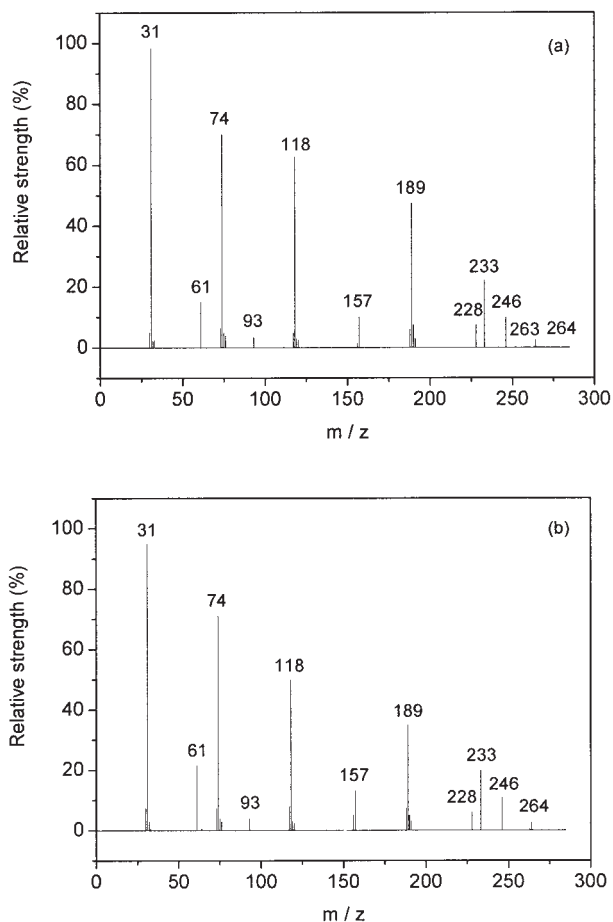
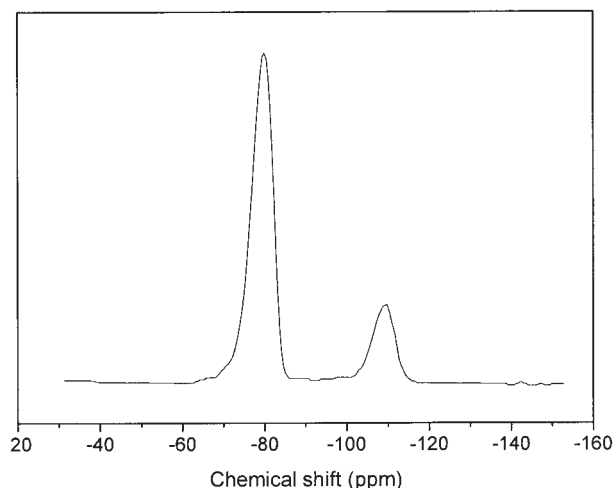Figure 3   MS spectra of (a) model and (b) real tethers.

Figure 4 ^{29}Si-NMR spectrum of hybrid polymer C.

the tether molecules in MS analysis, from which almost every peak in the MS spectra could find its corresponding fragment ion to tally with.

Polymer structure studies by solid-state ^{29}Si-NMR

Because the hybrid polymers synthesized in our work had a crosslinking structure, they were hardly soluble in almost all the solvents. Therefore, a solid-state ^{29}Si-NMR technique was employed to characterize the structure of the hybrid polymers.

Figure 4 shows the ^{29}Si-NMR spectrum of the hybrid polymer from DehvPOSS and butanediamine (polymer C). The two main peaks observed, at −79.9
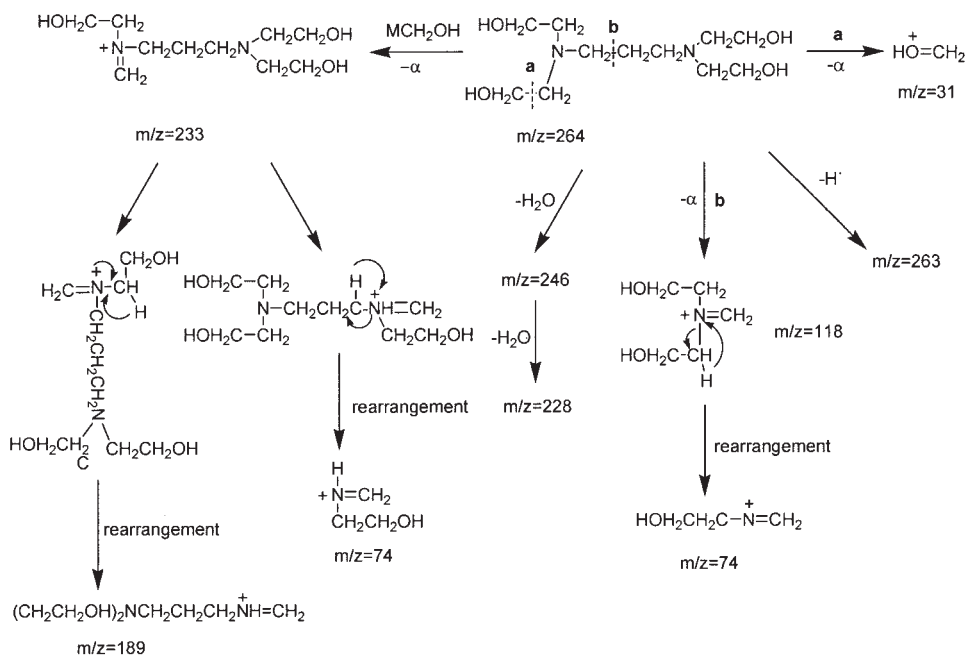
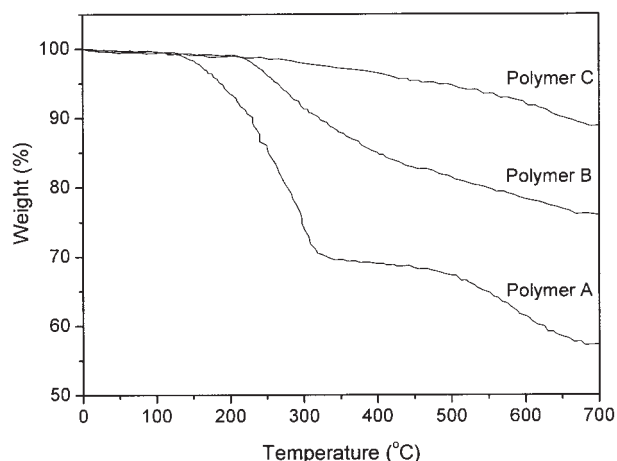Scheme 3   Fragmentation pathway for the tether molecules in MS analysis.

Figure 5 TGA tests of hybrid polymers.

CONCLUSIONS

An efficient synthetic route for preparing well-defined POSS-containing network hybrid polymers has been described as direct polymerization of double epoxy-functionalized POSS with diamine molecules. The hybrid polymers were characterized with FTIR, ^{29}Si-NMR, the model method, and GC-MS, and their thermal properties were studied by TGA. The results show that novel well-defined hybrid polymers can be prepared by tailoring the nanoarchitecture, and the thermal stability of hybrid polymers is strongly related to the length of the diamine tethers between POSS cubes, increasing with an increase in the length of the organic tethers between bulky POSS cages. The higher molecular tension results in decreased thermal stability, and hindrance of inorganic POSS cages effectively increases the thermal stability of POSS-containing hybrid polymers.

and −109.3 ppm, suggest that there were two environmentally different silicons in the polymers representing silicon atoms connected to vinyl groups and organic tethers, respectively. According to Laine's work,[26] the monomer DehvPOSS showed two ^{29}Si-NMR signals, at −79.8 (Si-vinyl) and −77.5 (Si-epoxy) ppm. However, the signal at −77.5 ppm (Si-epoxy) disappeared when DehvPOSS copolymerized with acetylstyrene, and meanwhile, a new signal at −109 ppm appeared in the ^{29}Si-NMR spectra of the polymers, which may attributed to the polymerization. This result was consistent with the analysis of GC-MS, further supporting our hypothesis that each amino group connected two epoxy groups.

Thermogravimetric analysis of hybrid polymers

Figure 5 shows the thermal stability (under N_2) of the three hybrid polymers. Compared with the thermal stabilities of the hybrid polymers, the temperature at 5% mass loss was defined as T_{dec}.

Of the three hybrid polymers, polymer A had the lowest thermal stability and began to decompose at 136.5°C, and its T_{dec} was 180°C. Polymer B began to decompose at 225.0°C, and its T_{dec} was 255°C. However, polymer C was rather stable at 282.5°C, and its T_{dec} was about 460.0°C, showing that the thermal stability of the DehvPOSS/diamine hybrid polymers increased with an increase in the length of the organic tethers.

The low thermal stability of polymers A and B may have resulted from the higher molecular tension as a result of the short organic tethers between the bulky POSS cages. The molecular tension decreased with an increase in organic tether length, which resulted in increased thermal stability. The good thermal stability of polymer C may have been a result of the double contribution of low molecular tension and hindrance of the bulky inorganic POSS cages with high thermal stability.

References

1. Loy, D. A. Hybrid Org-Inorg Mater 2001, 26, 364.
2. Kojima, Y.; Usuki, A.; Kawasumi, M. J Mater Res 1993, 8, 1185.
3. Sanchez, C.; Lebeau, B. MRS Bull 2000, 26, 377.
4. Pyun, J.; Matyjaszewski, K. Chem Mater 2001, 13, 3436.
5. Matejka, L.; Dukh, O. Macromol Symp 2001, 171, 181.
6. Scott, B. J.; Wirnsberger, G.; Stucky, G. D. Chem Mater 2001, 13, 3140.
7. Rajeshwar, K.; de Tacconi, N. R.; Chenthamarakshan, C. R. Chem Mater 2001, 13, 2765.
8. Gomez-Romero, P. Adv Mater 2001, 13, 163.
9. Haddad, T. S.; Lichtenhan J. D. Macromolecules 1996, 29, 7302.
10. Mater, P. T.; Jeon, H. G.; Romo-Uribe, A.; Haddad, T. S.; Lichtenhan, J. D. Macromolecules 1999, 32, 1194.
11. Romo-Uribe, A.; Mater, P. T.; Haddad, T. S.; Lichtenhan, J. D. J Polym Sci, Part B: Polym Phys 1998, 36, 1857.
12. Zheng, L.; Farris, R. J.; Coughlin, E. B. Macromolecules 2001, 34, 8034.
13. Tschucida, A.; Bolln, C.; Sernetz, F.; Frey, H.; Mulhaupt, R. Macromolecules 1997, 30, 2818.
14. Xu, H. Y.; Kuo, S. W.; Huang, C. F.; Chang, F. C. J Appl Polym Sci 2004, 91, 2208.
15. Xu, H. Y.; Kuo, S. W.; Lee, J. S.; Chang, F. C. Macromolecules 2002, 35, 8788.
16. Xu, H. Y.; Kuo, S. W.; Huang, C. F.; Chang, F. C. J Appl Polym Sci 2002, 9, 239.
17. Xu, H. Y.; Kuo, S. W.; Chang, F. C. Polym Bull 2002, 48, 469.
18. Xu, H. Y.; Kuo, S. W.; Lee, J. S.; Chang, F. C. Polymer 2002, 43, 5117.
19. Zhang, C.; Babonneau, F.; Bonhomme, C.; Laine, R. M.; Soles, C. L.; Hristov, H. A.; Yee, A. F. J Am Chem Soc 1998, 120, 8380.
20. Choi, J.; Harcup J.; Yee, A. F. Zhu, Q. Laine, R. M. J Am Chem Soc 2001, 123, 11420.
21. Constable, S. G.; Lesser, J. A.; Coughlin, E. B. Macromolecules 2004, 37, 1276.
22. Chen, W. C.; Lee, L. H.; Chena, B. F.; Yen, C. T. J Mater Chem 2002, 12, 3644.
23. Zhang, C.; Laine, R. M. J Am Chem Soc 2000, 122, 6979.
24. Laine, R. M.; Choi, J.; Lee, I. Adv Mater 2001, 13, 800.
25. Baney, R. H.; Itoh, M.; Sakakibara, A. Chem Rev 1995, 95, 1409.
26. Zhang, C.; Laine, R. M. J Organomet Chem 1996, 521,199.
27. Wallace, W. E.; Guttman, C. M.; Antonucci, J. M. Polymer 2000, 41, 2219