

Thermal properties and liquid crystallinity of side-chain azobenzene copolymer containing pendant polyhedral oligomeric silsesquioxanes

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Abstract Vinylated polyhedral oligomeric silsesquioxane (POSS-M) was prepared by the reaction of POSS containing amine groups with acrylic acid. Azobenzene liquid crystalline copolymer (LCP-POSS) was then synthesized with 6.0 mol% POSS-M and 94.0 mol% acrylate monomer containing azobenzene liquid crystalline moiety (Azo-M) by free-radical copolymerization. Homopolymer of Azo-M (LCP) was also synthesized under the same conditions. Their thermal properties and liquid crystallinity were characterized by Thermal gravimetric analysis (TG), differential scanning calorimetry (DSC), Wide-angle X-ray diffraction experiments (XRD) and polarized optical micrographs (POM). The results showed that LCP-POSS has higher thermal stability and glass transition temperature than pure LCP due to the incorporation of the rigid cage-like POSS. Especially, LCP-POSS exhibits enantiotropic smectic and nematic liquid crystalline behaviors, its smectic-nematic transition temperature (T_{SN}) and

nematic-isotropic transition temperature (T_{NI}) are higher than those of pure LCP, which may promote and extend its applications on stimuli-responsive materials and devices.

Keywords Polyhedral oligomeric silsesquioxanes · Liquid crystalline polymers · Azobenzene

Introduction

Polyhedral oligomeric silsesquioxane (POSS) is a unique modifier to high-performance materials due to its hybrid chemical composition with nanosized inorganic silicon and oxygen cage which is surrounded by organic substituents at the corner of silicon atom [1–3]. Since one or more of the substituents can react with organic precursors, while the remaining unreactive groups increase the compatibility of POSS with organic system, POSS molecules have been successfully incorporated into various polymers *via* copolymerization [4], grafting [5, 6], or blending [7, 8]. Subsequently, it leads to the enhancements in thermal, mechanical, and dielectric properties, flame-retardation, and liquid crystal (LC) phase stability of thermoplastic, thermoset and liquid crystalline polymers [9–23]. Especially, LC hybrids based on POSS have attracted considerable interests due to the integrated properties of the organic LC and inorganic silsesquioxane materials. Goodby [17–20] and Laine [21, 22] groups investigated the liquid crystalline behaviors and structures of LC-POSS hybrids by appending mesogenic groups on silsesquioxane cores. Their results confirmed that the incorporation of mesogenic group on POSS cores improved the stability of the liquid crystalline phase, and promoted a tendency to form the LC phase even if the cores were irregularly substituted. Chujo and co-workers [23] synthesized

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LC-POSS hybrids with functionalized silsesquioxanes as pendant groups by the free-radical copolymerization of methacrylate monomers containing phenyl LC moiety and POSS macromonomer with single vinyl group. The resulting hybrids with 10 mol% POSS moieties exhibited monotropic liquid crystallinity behavior during the heating cycle with wider temperature range for LC phase, higher glass-transition temperatures and thermal stability than those of LC homopolymer. The other hybrid polymers with more than 10 mol% POSS moiety show more and more enhanced thermal stability with increasing the content of POSS [23].

Azobenzene side-chain liquid crystalline polymers (LCPs) have attracted increasing attentions due to the photoreversible properties of azo-group and high optical anisotropy in liquid crystalline state [24]. Recently, our group have synthesized multiwalled carbon nanotubes (MWNTs) grafted by azo side-chain liquid crystalline polyurethanes (AzoPU-MWNTs) [25]. The thermal stability of the azo polyurethanes is enhanced by the incorporation of MWNTs. To the best of our knowledge, there is no report on azobenzene liquid crystalline copolymer containing POSS.

In this study, we synthesized an azobenzene side-chain liquid crystalline copolymer containing pendant POSS by a free-radical copolymerization of 6.0 mol% vinylated POSS macromonomer (POSS-M) and acrylate monomer containing azobenzene LC moiety (Azo-M), its thermal properties and liquid crystallinity were investigated. The confinement of the low content of POSS might enhance the thermal and the liquid crystal phase stability to some extent, which may promote and extend its applications on stimuli-responsive materials and devices.

Experimental section

Materials

Aminopropylisobutyl polyhedral oligomeric silsesquioxane (POSS) was obtained from Hybrid Plastics, Inc. Dimethylformamide (DMF) was purified by vacuum distillation before use. High-purity azobis(isobutyronitrile) (AIBN) was recrystallized from 95% ethanol. Spectroscopic grade tetrahydrofuran (THF) and toluene were pre-dried by 4 Å molecular sieves, and distilled from sodium benzophenone ketyl immediately prior to use. *N,N'*-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) were purchased from Chemical Reagent Co., Ltd, Jiangsu, China. Other chemicals were used as received from Sinopharm Group Chemical Reagent Co., Ltd, Shanghai, China.

Measurements

Fourier transform infrared (FTIR) spectra were recorded on a Bruker Equinox 55 spectrometer with a disc of KBr. ^1H nuclear magnetic resonance ($^1\text{H-NMR}$) spectra were carried out on a Bruker AV400 spectrometer using tetramethylsilane (TMS) as an internal standard. Molecular weights were measured by Agilent 1100 gel permeation chromatography (GPC) with PS as the standard and THF as the eluent. Thermal gravimetric analysis (TG) was conducted on a TGA-7 Perkin-Elmer calorimeter under argon flow (20 mL/min) at a rate of 10 K/min. Differential scanning calorimetry (DSC) was carried out in an argon atmosphere with a PE DSC-7 at a rate of 20 K/min. The optical pictures of the samples in solvents were taken with a digital camera (Olympus C-4000 ZOOM). Wide-angle X-ray diffraction experiments (XRD) were carried out on powder with a Philips X' Pert diffractometer with Cu K α radiation 1.541 Å, scanning from 2θ of 2° – 40° with step size 0.02° and time per step 4 s.

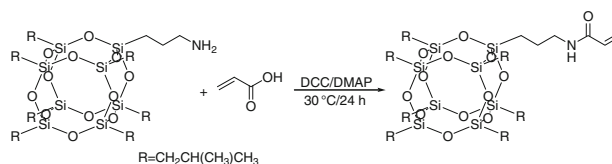
Synthesis of azobenzene LC monomer

The azobenzene LC monomer, 6-(4-methoxy-4'-oxy-azobenzene) hexyl methacrylate (Azo-M), was synthesized according to reference [26]. Yield 21.1%. IR (KBr, cm^{-1}): 3100–3050 (ν C–H, aromatic), 2980–2850 (ν C–H, CH_2 , and CH_3), 1707 (ν C=O), 1640 (ν C=C), 1600–1450 (ν C=C, aromatic), 1450–1380 (δ C–H), 1250–1040 (ν C–O). ^1H NMR (400 MHz, CDCl_3 , δ , ppm): 7.7–7.95 (4H, Ar-H), 6.90–7.0 (4H, Ar-H), 6.1 (2H, $\text{CH}_2=\text{C}-$), 4.2 (2H, $\text{CH}_2-\text{OOC}-$), 4.0 (2H, ArOCH_2), 3.9 (3H, ArOCH_3), 1.2–2.0 (11H, $-\text{CH}_2(\text{CH}_2)_4\text{CH}_2-$, $\text{CH}_3\text{C}(\text{COO})$).

Synthesis of POSS macromonomer (POSS-M)

Polyhedral oligomeric silsesquioxane macromonomer (POSS-M), acrylamino-propyl-heptaisobutyl polyhedral oligomeric silsesquioxane, was synthesized by the condensation reaction of aminopropylisobutyl POSS and acrylic acid as shown in Scheme 1.

In detail, POSS (100 mg, 0.114 mmol) and acrylic acid (10 mL) were dissolved in dried THF, followed by the addition of DCC (24 mg, 0.116 mmol) and DMAP (1 mg, 0.0088 mmol). The reaction mixture was stirred at 303 K



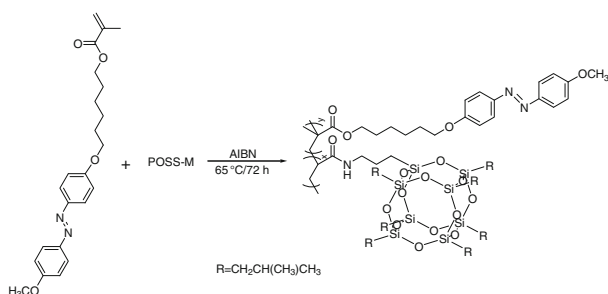
Scheme 1 Synthesis of POSS macromonomer (POSS-M)

for 24 h. The product was then poured into excess distilled water under vigorous stirring. After filtration, the product was purified with distilled water again to remove excessive acrylic acid. The crude product was purified by column chromatography using dichloromethane as eluent to yield 70.1 mg. The final product was dried in a vacuum oven, giving 60.5 g of white powders. Yield 57.1%. IR (KBr, cm^{-1}): 3300 (ν N–H), 2980–2850 (ν C–H, CH_2 , and CH_3), 1633 (ν C=O), 1577 (ν C=C), 1450–1380 (δ C–H), 1250–1040 (ν C–O), 1109 (ν Si–O–Si). ^1H NMR (400 MHz, CDCl_3 , δ , ppm): 6.2–6.4 (1H, $-\text{NHOCH}=\text{CHH}$ *cis*), 6.0–6.2 (1H, $-\text{NHOCH}=\text{CH}_2$), 5.6–5.7 (1H, $-\text{NHOCH}=\text{CHH}$ *trans*), 5.5–5.6 (1H, $-\text{NHOCH}=\text{CH}_2$), 3.2–3.4 (2H, $-\text{CHO}$ NHCH_2-), 1.8–2.0 (7H, $-\text{CH}_2\text{CH}-$), 1.6–1.7 (2H, $-\text{SiCH}_2\text{CH}_2-$), 0.8–1.0 (42H, $-\text{CH}_2\text{CH}(\text{CH}_3)_2$), 0.5–0.7 (16H, $-\text{SiCH}_2-$).

Synthesis of side-chain liquid crystalline azobenzene copolymer containing pendant POSS (LCP-POSS)

Liquid crystalline azobenzene copolymer containing pendant POSS (LCP-POSS) was synthesized by a conventional free-radical copolymerization of POSS-M and Azo-M, as shown in Scheme 2.

In detail, a mixture of POSS-M (547 mg, 0.59 mmol), Azo-M (3.738 g, 9.44 mmol) and 20 mL dried THF was added in a 150 mL three-neck flask. The mixture was evacuated by nitrogen thrice, and subsequently stirred at 333 K. Then, AIBN (4 mol% based on the monomer) was added to the above mixture as an initiator, and the copolymerization continued for 48 h. The hybrid polymer was precipitated as a yellow solid in an excess of methanol, then purified thrice by re-dissolution in THF, re-precipitation in methanol, and dried under reduced pressure overnight at room temperature, giving 2.05 g of yellow powders. Yield 48.2%. IR (KBr, cm^{-1}): 3300 (ν N–H), 2980–2850 (ν C–H, CH_2 , and CH_3), 1727 (ν C=O), 1600–1450 (ν C=C, aromatic), 1450–1380 (δ C–H), 1250–1040 (ν C–O), 1109 (ν Si–O–Si). ^1H -NMR (400 MHz, CDCl_3 , δ , ppm): 8.0–8.1 ($-\text{NHCO}-$), 7.7–7.95 (Ar–H), 6.90–7.0 (Ar–H), 4.0–4.2 ($-\text{CH}_2\text{COO}-$, ArOCH_2), 3.85–3.95 (ArOCH_3),



Scheme 2 Synthesis of LCP-POSS

2.9–3.0 ($-\text{NHCH}_2-$), 2.6–2.8 ($-\text{CH}_2\text{CONH}-$), 1.0–1.8 ($-\text{CH}_2-$, $-\text{CH}_3$), 0.5–0.7 ($-\text{SiCH}_2-$).

For comparison, homopolymer of Azo-M (LCP) was also synthesized under the same conditions. IR (KBr, cm^{-1}): 3100–3050 (ν C–H, aromatic), 2980–2850 (ν C–H, CH_2 , and CH_3), 1707 (ν C=O), 1600–1450 (ν C=C, aromatic), 1450–1380 (δ C–H), 1250–1040 (ν C–O). ^1H NMR (400 MHz, CDCl_3 , δ , ppm): 7.7–7.95 (4H, Ar–H), 6.90–7.0 (4H, Ar–H), 4.0–4.2 (4H, $-\text{CH}_2\text{OOC}-$, ArOCH_2-), 3.85–3.95 (3H, ArOCH_3), 1.0–1.8 (10H, $-\text{CH}_2-$).

Results and discussion

Molecular weight and composition of LCP-POSS

Molecular weights of LCP and LCP-POSS were measured by GPC. Table 1 summarizes the molecular weight and composition of LCP-POSS hybrid polymer. Apparently, when the feed molar ratio of POSS-M and Azo-M is 1:16, LCP-POSS has a slightly higher molecular weight than LCP, i.e., 13,580 and 11,670, respectively. The results may be related to their lower reactivity derived from the bulkiness of the POSS macromonomer [23] and a radical deactivation by the azobenzene sidegroup, respectively [27]. Similar phenomena have been observed in the copolymers with different feed ratio of POSS-M and LC monomer, 6-[4-(4'-cyanophenyl) phenoxy] hexyl methacrylate [23]. Based on ^1H -NMR spectrum of LCP-POSS (Fig. 1b), molar ratio (x/y) of POSS and LC units in LCP-POSS can be calculated by the peak integration areas of the methylene protons connected with amide (k (2H, $-\text{COONHCH}_2-$) 4.0–4.2 ppm) and phenyl protons (a (4H, Ar–H) 7.7–7.95 ppm and b (4H, Ar–H) 6.90–7.0 ppm).

Thermal stability of LCP-POSS polymer

Figure 2 shows TG and DTG curves of LCP and LCP-POSS. Similar to the previous report [28], decomposition of LCP shows three regimes, corresponding to the cleavage of N=N bonds in azobenzene side chains of LCP at 533–643 K, the breakdown of ester bonds combined with

Table 1 Molecular weight, composition, and TG results of LCP-POSS

Run	Feed ratio ^a	M_n^b	M_w^c	T_{10}/K	T_{max}/K
LCP	–	3,696	11,670	600	636
LCP-POSS	1:16	3,780	13,580	621	646

^a Molar ratio of POSS-M to Azo-M monomers used in synthesis

^b Number-average molecular weight by GPC

^c Weight-average molecular weight by GPC

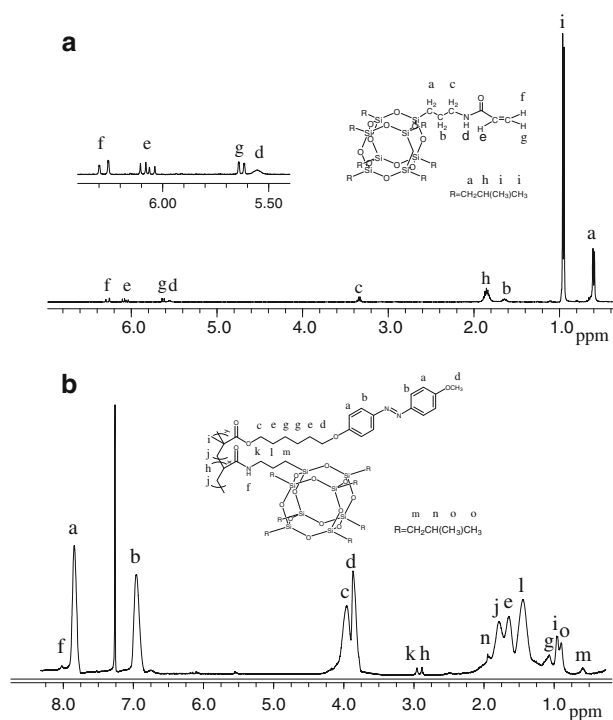


Fig. 1 ^1H NMR spectra of POSS-M and LCP-POSS

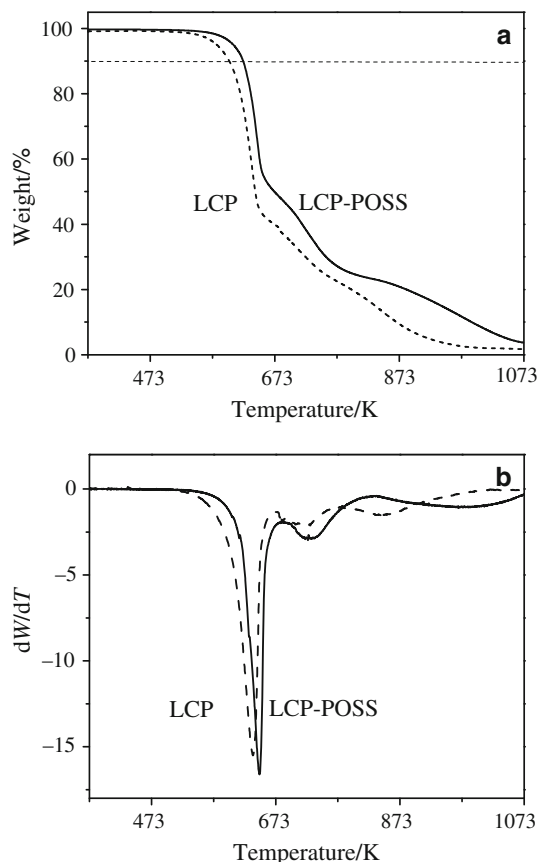


Fig. 2 TG (a) and DTG (b) curves of LCP and LCP-POSS

aliphatic flexible spacers in side chains at 643–763 K, and the degradation of main chains of LCP at 763–1,053 K. Interestingly, LCP-POSS exhibits higher thermal stability than LCP even the molar content of POSS is only 6.0%. The 10% mass-loss temperature (T_{10}) of LCP-POSS increases to 621 K from 600 K of LCP, and the maximum mass-loss temperature (T_{max}) of LCP-POSS also increases to 646 K from 636 K of LCP. In other word, LCP-POSS were more thermally robust with the incorporation of the inorganic POSS nanoparticles.

LC behavior of LCP-POSS polymer

Figure 3 shows the polarized optical micrographs (POM) of LCP and LCP-POSS at different temperatures. Similar to other azobenzene side-chain liquid crystalline copolymers with the flexible spacers $(\text{CH}_2)_n$ ($n > 4$) [29, 30], LCP exhibits a nematic phase with a schlieren texture at 363 K (Fig. 3a) and a smectic phase with a broken-fan texture at 338 K (Fig. 3b). The incorporation of the rigid cage-like POSS does not change the liquid crystalline structure of LCP-POSS, only decreases the size of its liquid crystal domains in nematic (Fig. 3c) and smectic (Fig. 3d) phases due to the confinement of POSS on the formation of liquid crystal phases. From XRD patterns of POSS, LCP, and LCP-POSS shown in Fig. 4, sharp diffraction peaks appear at $2\theta = 8.2, 11.0$ and 19.4° , corresponding to d -spacings of 10.7, 8.0, and 4.6 Å for POSS, indicative of a structure with high crystallinity. The peak corresponding to a d -spacing of 10.7 Å is attributed to the size of POSS molecule, while the other two peaks are attributed to the rhombohedral crystal structure of POSS molecules [31]. However, only a broad peak at $2\theta = 20^\circ$ appears for LCP, indicative of an amorphous structure of LCP at room

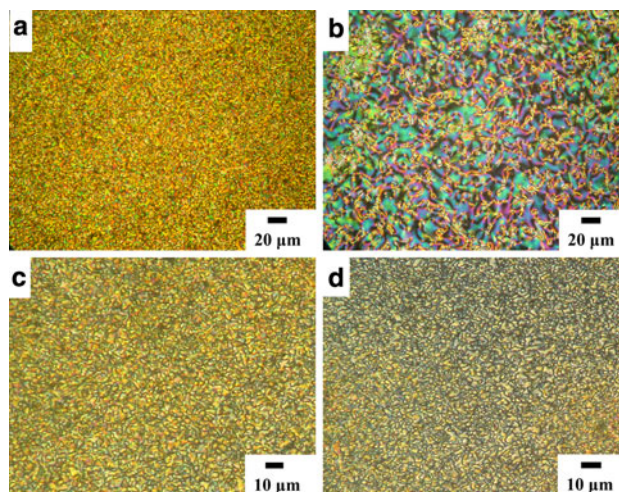


Fig. 3 Polarized optical micrographs of LCP at 363 K (a) and 338 K (b), LCP-POSS at 363 K (c), and 338 K (d)

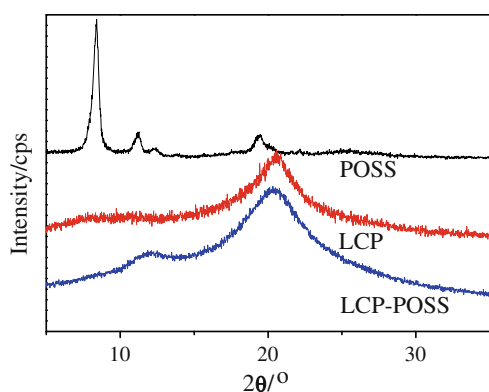


Fig. 4 X-ray diffraction curves of POSS, LCP, and LCP-POSS

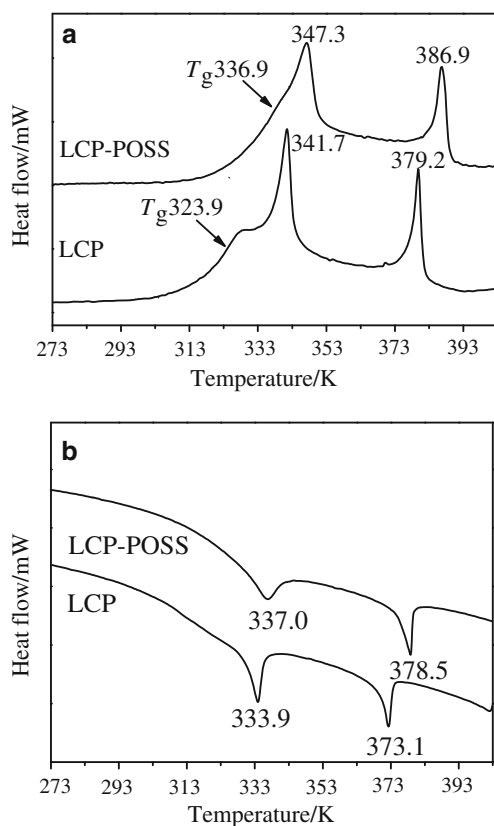


Fig. 5 DSC heating and cooling curves of LCP and LCP-POSS at a rate of 20 K/min

temperature. For LCP-POSS, the weak broad peak at $2\theta = 11.8^\circ$, concerning POSS crystallinity may show the presence of small or disordered regions of POSS crystals [32]. The peak at $2\theta = 20^\circ$ suggests that LCP-POSS is still amorphous as LCP at room temperature. The heating and cooling DSC curves of LCP and LCP-POSS are shown in Fig. 5. Based on the POM and XRD results, the LCP exhibits a glass-transition temperature (T_g) at 323.9 K, smectic–nematic transition temperature (T_{SN}) at 341.7 K, nematic–isotropic transition temperature (T_{NI}) at 379.2 K

during heating. The glass-transition temperature was obtained from the inflection point. For LCP-POSS, the incorporation of 6.0 mol% POSS units into LCP increases T_g , T_{SN} and T_{NI} to 336.9, 347.3, and 386.9 K (increment of 5.6–13.0 K), respectively. Although all the increments of the thermal transition temperature are not much, LCP-POSS hybrid polymer exhibits an enantiotropic liquid crystalline behavior as LCP.

However, LC-POSS copolymer of 10 mol% POSS macromonomer with single vinyl group and methacrylate monomers containing biphenyl LC moiety only exhibits monotropic liquid crystallinity during the heating cycle [23]. These suggest that the incorporation of POSS units (i.e., 6.0 mol%) into LCP does not destroy the liquid crystalline order of LCP-POSS, and increases T_g and the liquid crystalline phase transition temperature (T_i). In this case, the rigid POSS units physically restrict the motion of polymer segments, and the dipole–dipole interaction between POSS siloxane and the polar carbonyl of Azom moiety also plays a positive role on the enhancements of T_g . The effect of POSS on T_g of the polymer has been investigated in detail [33]. The phenomenon that the incorporation of POSS to LC system exhibited higher T_i has been observed in LC-POSS system as well. Goodby et al. synthesized two organic–inorganic hybrid materials containing a central POSS core by reacting octavinylsilsequioxane with a three or four aromatic rings liquid crystal [17]. Compared with the LC, the LC-POSS with four aromatic rings showed that a rise of isotropization temperature and smectic C phase temperature by 22 K (from 397.0 to 419.0 K and 53 K (from 333.2 to 386.2 K), respectively. The three aromatic rings LC-POSS exhibited 11.4 K higher isotropization temperature (from 312.3 to 323.7 K). And, an underlying smectic phase was observed from both LC-POSS materials. They attributed this promotion of the stability of the mesomorphic state to the incorporation of a suitably functionalized inorganic core. In addition, in this case, the slightly higher molecular weight of LCP-POSS might benefit the increase of T_i , which has been described elsewhere [34].

Conclusions

Due to the confinement of the rigid cage-like POSS, LCP-POSS exhibits higher glass-transition temperature and thermal stability than LCP homopolymer. Especially, LCP-POSS exhibits enantiotropic smectic and nematic liquid crystalline behaviors, its smectic–nematic transition temperature (T_{SN}) and nematic–isotropic transition temperature (T_{NI}) are higher than those of pure LCP. A further study about the effect of POSS content in LCP-POSS copolymer on liquid crystallinity and thermal stability is in progress.

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