

Synthesis of poly(4-vinylphenol) (PVPh) and polyhedral oligomeric silsesquioxanes-poly(4-vinylphenol) (POSS-PVPh) with low surface energy and their surface properties

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ARTICLE INFO

Article history:

Received 11 June 2011

Received in revised form 6 September 2011

Accepted 8 September 2011

Keywords:

Polymers

Thin films

Chemical synthesis

Surface properties

ABSTRACT

In this paper, we have synthesized poly(4-vinylphenol) (PVPh) and polyhedral oligomeric silsesquioxanes-poly(4-vinylphenol) (POSS-PVPh) with low surface energies and investigated their surface properties. Experimental results reveal that the surface properties of PVPh and POSS-PVPh can be manipulated with the length of PVPh segment and POSS contents, respectively, resulting in the variation of intermolecular hydrogen bonding interactions. In addition, the surface energies of PVPh after thermal treatment of 180 °C for 24 h can be less than 20 mJ m⁻² and those of POSS-PVPh without thermal treatment can be less than 25 mJ m⁻² while those of poly(tetrafluoroethylene) (PTFE) are 22 mJ m⁻².

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1. Introduction

Performances of polymeric materials can be modulated by their surface properties (e.g. wettability, friction, adhesion, etc.). In recent years, hydrophobicity and oleophobicity have attracted tremendous interest due to their miscellaneous applications [1–4]. Both poly(dimethylsiloxane) (PDMS) and poly(tetrafluoroethylene) (PTFE) are two well-known polymeric materials with low surface energies [5–8]. PTFE, with a surface energy of approximately 22 mJ m⁻², may be regarded as the benchmark for polymeric materials with low surface energies and exhibits water repellency [9] as well as other excellent physical properties [10]. Low surface energies of PTFE come from weak intermolecular forces of fluorinated polymer chains because the fluorine atom has small size, high electronegativity, low polarizability, and strong repulsion [11]. However, PTFE and many fluorinated polymers possess some application limitations such as high cost, poor processibility, and the potential to be carcinogenic [12–14]. Therefore, research of an alternative material for PTFE with low cost, easy processibility, and good film-forming characteristics has become an important issue.

Surface properties of polymers highly depend on the hydrogen bonding interactions. Generally, amorphous comblike polymers

with a flexible linear backbone on the side chain exhibit weak intermolecular interaction and low surface energy [15]. In polybenzoxazine system, the intermolecular hydrogen bonds between the hydroxyl groups increase their surface energies [12]. Moreover, Jiang et al. [16] have found that the compact and collapsed conformation of poly(N-isopropylacrylamide) (PNIPAAm), which is induced by intramolecular hydrogen bonds between C=O and N–H groups of main chains, causes a low surface energy and a high contact angle for water at the temperatures above its lower critical solution temperature (LCST). When the temperature is below LCST, however, intermolecular hydrogen bonds between PNIPAAm main chains and water molecules predominate, leading to a higher surface energy and a lower water contact angle. Similarly, Chung and Co-worker [17] have also reported that the amide groups in a fluorinated-main-chain liquid-crystalline polymer system induce strong intermolecular hydrogen bonds, resulting in higher surface energies and higher degrees of hydrophilicity. The nature of pendant chain has a significant effect on the determination of surface energy. Thus, polymeric materials with low surface energies can be obtained by the reduction of intermolecular interactions between the comblike polymers with flexible linear backbones [18].

Polymers reinforced with well-defined inorganic fillers with nano-sizes (i.e. organic/inorganic hybrid nanocomposites) have attracted much attention because of their potential applications. Among these systems, polyhedral oligomeric silsesquioxanes (POSS) compounds, which possess unique cage-like structures and nano-scale dimensions, are of particular interest for utilization

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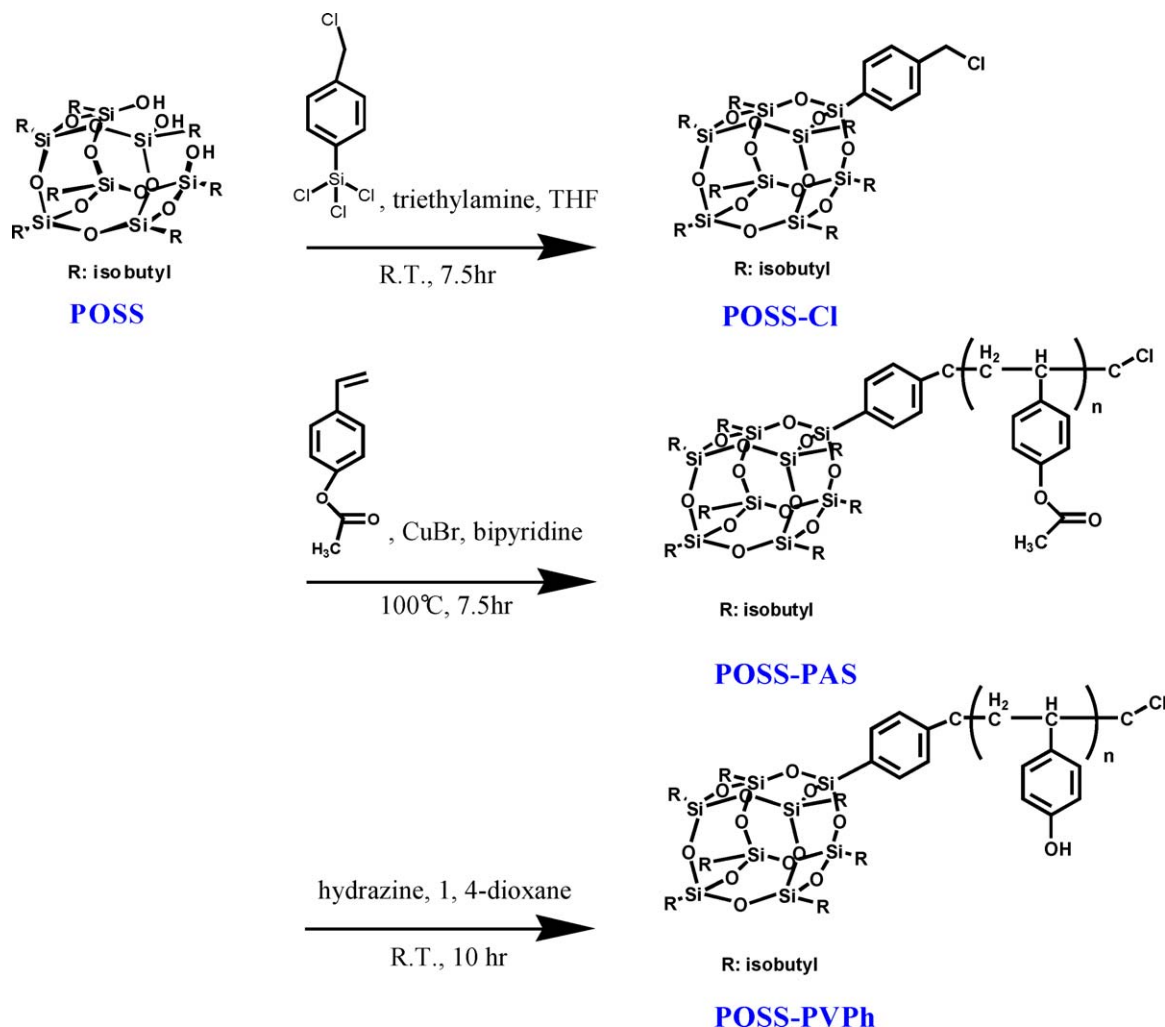


Fig. 1. Procedure for syntheses of POSS-PVPh copolymers.

as hybrid materials. POSS compounds exhibit inorganic/organic hybrid architecture since they contain not only an inner inorganic framework composed of $(\text{SiO}_{1.5})_x$ but also organic groups. Because POSS moieties can be readily incorporated into polymer matrices through copolymerization, many types of polymer/POSS nanocomposites have been synthesized [19–28]. In this paper, we have synthesized poly(4-vinylphenol) (PVPh) homopolymers and then introduced POSS into PVPh to prepare POSS-PVPh copolymers, further heightening their thermal stabilities and chemical resistances. Moreover, their surface properties have also been investigated. Experimental results manifest that the surface energies of PVPh homopolymers after thermal treatment increase with the length of PVPh segment and those of POSS-PVPh copolymers decrease with the silicon contents owing to the variation of hydrogen bonds.

2. Experimental details

2.1. Materials and instruments

All the starting materials utilized in this study were purchased from Aldrich Co. and used without further purification. ^1H NMR spectra were recorded on a NMR spectrometer (Varian Unity Inova 500 FT) operated at 500 MHz. Thermal analyses were performed with a differential scanning calorimeter (DuPont DSC-9000) operated at a scan rate of $20^\circ\text{C min}^{-1}$ within a temperature range from 30 to 250°C . The sample was quenched to 20°C from the melt state

for the first scan and then rescanned between 20 and 250°C at $20^\circ\text{C min}^{-1}$. Glass transition temperature (T_g) was obtained at the inflection point of jump heat capacity. Fourier-transform infrared (FTIR) spectroscopic measurements were conducted on a Nicolet Avatar 320 FTIR spectrophotometer and 32 scans were collected with a spectral resolution of 1 cm^{-1} . All the sample preparations for FTIR spectroscopic measurements were under continuous nitrogen flow to ensure minimal sample oxidation or degradation. For the measurements of contact angles, deionized water (H_2O) and diiodomethane (DIM) were chosen as testing liquids because significant amounts of data were available for these liquids. The advancing measurements of contact angle for a polymer sample were determined at 25°C after injection of a liquid drop ($5\ \mu\text{L}$) onto the surface and a goniometer (Krüss GH-100) interfaced to image-capture software was employed to perform the measurement. A two-liquid geometric method was employed to determine the surface energy [29].

2.2. Syntheses of PVPh homopolymers

PVPh homopolymers used in this study was synthesized by living anionic polymerization of 4-*tert*-butoxystyrene followed by selective removal of the *tert*-butoxy protective group through a subsequent hydrolysis reaction. The detailed synthesizing procedures of PVPh homopolymers have been reported previously

Table 1
Physical and surface properties of PVPh homopolymers.

Polymer	Length of PVPh segment ^a	M_w/M_n	T_g (°C)	Before thermal treatment			After thermal treatment		
				Contact angle (°)		γ_s (mJ m ⁻²)	Contact angle (°)		γ_s (mJ m ⁻²)
				H ₂ O	DIM		H ₂ O	DIM	
PVPh ₂₈	28	1.09	138	77	57	34	105	88	14
PVPh ₄₂	42	1.05	178	79	56	33	104	87	15
PVPh ₅₀	50	1.15	183	78	55	34	104	87	15
PVPh ₈₀	80	1.04	184	77	53	35	101	86	16
PVPh ₉₅	95	1.15	188	79	53	35	98	86	16
PVPh ₁₆₀	160	1.06	189	76	53	36	96	84	18
PVPh ₁₆₅	165	1.07	183	77	53	35	94	83	19
PVPh ₂₅₄	254	1.12	184	77	52	36	92	81	20
PVPh ₃₄₆	346	1.15	188	76	54	35	90	79	21
PVPh ₁₂₅₀	1250	1.03	189	75	50	37	77	64	31

^a The repeat unit of PVPh homopolymer is obtained from GPC.

[30,31]. Physical and surface properties of PVPh homopolymers are summarized in Table 1.

2.3. Syntheses of POSS-PVPh copolymers

With corner-capping reaction, as shown in Fig. 1, POSS-Cl was firstly prepared by reacting trichloro[4-(chloromethyl)phenyl]silane (1.00 mL) with POSS (4.05 g) in the presence of triethylamine (2.20 mL) and dry THF (30 mL) at room temperature for 7.5 h under argon. After filtration to remove the HNET₃-Cl byproduct and precipitation with acetonitrile, POSS-Cl was obtained (yield: 95%). Then POSS-PAS was prepared with POSS-Cl (0.33 g) and 4-acetoxystyrene (3.00 g) in the presence of CuBr (0.15 g) and bipyridine (0.55 g) by the atom transfer radical polymerization at 100 °C for 7.5 h (yield: 76%). Finally, POSS-PVPh was synthesized by the hydrolysis of POSS-PAS (1.27 g) in the presence of hydrazine (3.00 mL) and 1,4-dioxane (27.00 mL) under nitrogen at room temperature for 10 h. The product was eventually concentrated by evaporation of toluene, washed with deionized water, and dried in a vacuum oven at room temperature for 2 days (yield: 93%).

The POSS-PVPh copolymers were characterized by FTIR (Fig. 2), ¹H NMR (Fig. 3) and gel permeation chromatography (GPC). Physical and surface properties of POSS-PVPh copolymers are summarized in Table 2.

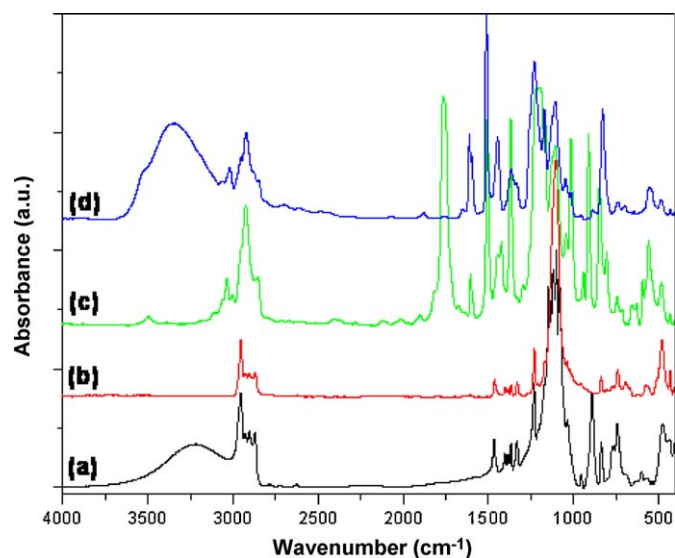


Fig. 2. FTIR spectra of (a) POSS, (b) POSS-Cl, (c) POSS-PAS, and (d) POSS-PVPh.

2.3.1. FTIR and ¹H NMR analyses of POSS

FTIR (KBr): 3350 cm⁻¹ (hydrogen bonded OH), 3000–2850 cm⁻¹ (Si-CH₂ rocking), 2957 cm⁻¹ (CH₂ stretching), 1200–1000 cm⁻¹ (Si-O-Si asymmetric stretching), 500–450 cm⁻¹ (Si-O-Si bending).

¹H NMR (500 MHz): δ = 0.91 ppm (6H, SiCH₂CH(CH₃)₂), δ = 0.55 ppm (2H, SiCH₂CH(CH₃)₂).

2.3.2. FTIR and ¹H NMR analyses of POSS-Cl

FTIR (KBr): 3000–2850 cm⁻¹ (Si-CH₂ rocking), 2957 cm⁻¹ (CH₂ stretching), 1200–1000 cm⁻¹ (Si-O-Si asymmetric stretching), 500–450 cm⁻¹ (Si-O-Si bending).

¹H NMR (500 MHz): δ = 0.91 ppm (6H, SiCH₂CH(CH₃)₂), δ = 8.0–7.0 ppm (4H, aromatic CH), δ = 0.55 ppm (2H, SiCH₂CH(CH₃)₂).

2.3.3. FTIR and ¹H NMR analyses of POSS-PAS

FTIR (KBr): 3000–2850 cm⁻¹ (Si-CH₂ rocking), 2957 cm⁻¹ (CH₂ stretching), 1765 cm⁻¹ (C=O stretching), 1603 cm⁻¹ (in-plane aromatic C-C stretching), 1200–1000 cm⁻¹ (Si-O-Si asymmetric stretching), 500–450 cm⁻¹ (Si-O-Si bending).

¹H NMR (500 MHz): δ = 7.0–6.0 ppm (4H, aromatic CH), δ = 2.41 ppm (3H, OCOCH₃), δ = 0.91 ppm (6H, SiCH₂CH(CH₃)₂), δ = 0.55 ppm (2H, SiCH₂CH(CH₃)₂).

2.3.4. FTIR and ¹H NMR analyses of POSS-PVPh

FTIR (KBr): 3525 cm⁻¹ (free OH), 3350 cm⁻¹ (hydrogen bonded OH), 3000–2850 cm⁻¹ (Si-CH₂ rocking), 2957 cm⁻¹ (CH₂

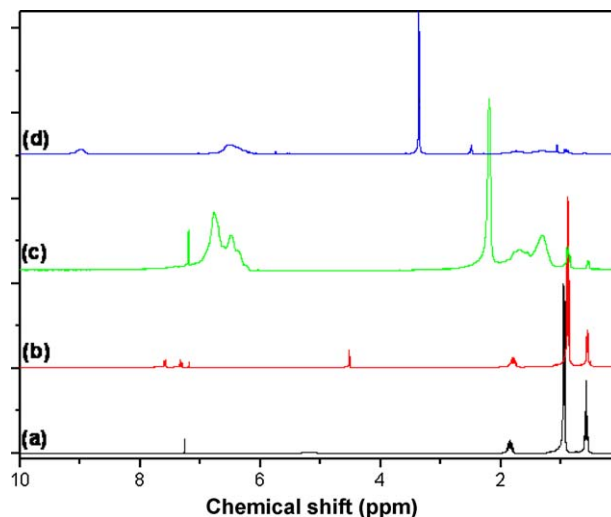


Fig. 3. ¹H NMR spectra of (a) POSS, (b) POSS-Cl, (c) POSS-PAS, and (d) POSS-PVPh.

Table 2
Physical and surface properties of POSS-PVPh copolymers.

Copolymer	Length of PVPh segment ^a	M_w/M_n	T_g (°C)	Contact angle (°)		γ_s (mJ m ⁻²)	Silicon content (mol %)
				H ₂ O	DIM		
POSS-PVPh ₉	9	1.19	210	113	71	23	14.54
POSS-PVPh ₃₅	35	1.41	209	110	69	24	11.05
POSS-PVPh ₁₂₀	120	1.38	205	109	69	24	8.79
POSS-PVPh ₂₆₄	264	1.33	203	108	68	25	7.92

^a The repeat unit of PVPh segment of POSS-PVPh is obtained from ¹H NMR.

stretching), 1765 cm⁻¹ (C=O stretching), 1603 cm⁻¹ (in-plane aromatic C–C stretching), 1200–1000 cm⁻¹ (Si–O–Si asymmetric stretching), 500–450 cm⁻¹ (Si–O–Si bending).

¹H NMR (500 MHz): δ = 7.37 ppm (H, –OH), δ = 7.0–6.0 ppm (4H, aromatic CH), δ = 2.41 ppm (3H, OCOCH₃), δ = 0.91 ppm (6H, SiCH₂CH(CH₃)₂), δ = 0.55 ppm (2H, SiCH₂CH(CH₃)₂).

2.4. Preparation of PVPh and POSS-PVPh thin films

PVPh or POSS-PVPh (5 wt.%) was dissolved in the THF solution. Then the polymeric solution was stirred for 6–8 h and cast onto a wafer. After solvent evaporation at 60 °C for 1 day and vacuum drying at room temperature for 2 days, PVPh or POSS-PVPh thin films were obtained. Both PVPh and POSS-PVPh thin films were transparent. Thermal treatment was carried out by placing the prepared polymer films in a vacuum oven at 180 °C for 24 h and then quenching to ambient temperature.

3. Results and discussion

3.1. Surface properties of PVPh homopolymers

As shown in Table 1, the surface properties of PVPh homopolymers before and after thermal treatment have been investigated. In order to avoid polymer degradation, we chose 180 °C as the thermal treatment temperature as this is far lower than the thermal decomposition temperature (350 °C). Furthermore, a high temperature above T_g tends to partially disrupt the formation of hydrogen bond. Before thermal treatment, as shown in Table 1, the surface properties of PVPh homopolymers are independent of the length of PVPh segment. After thermal treatment of 180 °C for 24 h, however, the surface properties of PVPh homopolymers dramatically depend on the length of PVPh segment due to the variations of hydrogen bonds. The experimental results indicated that the contact angles of PVPh homopolymers after thermal treatment decreased (i.e., the surface energy increased) with increasing PVPh segment length due to increased hydrogen bonding interactions. The thermal treatment

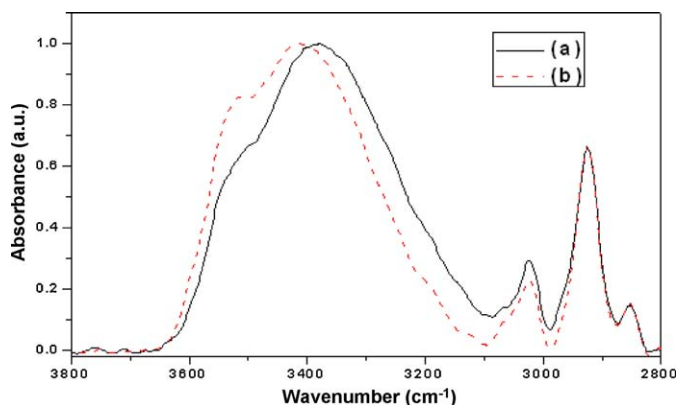


Fig. 4. FTIR spectra of PVPh₈₀ (a) before thermal treatment; (b) after thermal treatment of 180 °C for 24 h.

causes the decrease of hydrogen bonds for PVPh homopolymers because the peaks at wavenumber ~3500 and 3380 cm⁻¹ (i.e. free hydroxyl groups) in the FTIR spectra blue-shift to be respectively 3525 and 3420 cm⁻¹ after thermal treatment as shown in Fig. 4. Since the thermal treatment effectively reduces the intermolecular hydrogen bonding interactions of PVPh homopolymers, the surface energies for all of the samples with thermal treatment are lower than those without thermal treatment. Furthermore, the surface energies after thermal treatment increase with the length of PVPh segments as shown in Fig. 5 owing to the raise of hydrogen bonds while those before thermal treatment are independent of the length of PVPh segments. With thermal treatment, lab-made PVPh homopolymers are potential alternative materials for PTFE because all their surface energies are lower than 22 mJ m⁻² except PVPh₁₂₅₀.

3.2. Surface properties of POSS-PVPh thin films

Although PVPh homopolymers are good materials with low surface energies, their thermal stabilities as well as chemical resistance are dissatisfactory and thermal treatment is necessary for the promotion of surface properties. In addition, thermoplastic PVPh homopolymers are conformation sensitive and unstable as compared with thermosetting polybenzoxazine in a previous study by Chang's group [12]. Therefore, we have tried to introduce POSS into PVPh homopolymers (Fig. 1), generating POSS-PVPh copolymers. As manifested in Table 2, incorporation of POSS into the PVPh raises T_g (>200 °C) and all lab-made POSS-PVPh copolymers exhibit low surface energies (≤ 25 mJ m⁻²) without thermal treatment. Moreover, the contact angles of POSS-PVPh copolymers increased (i.e., surface energy decreased) with silicon content (Fig. 6) due to decreased hydrogen bonding interactions. Preliminary experimental results reveal that the surface energies of POSS-PVPh copolymers can

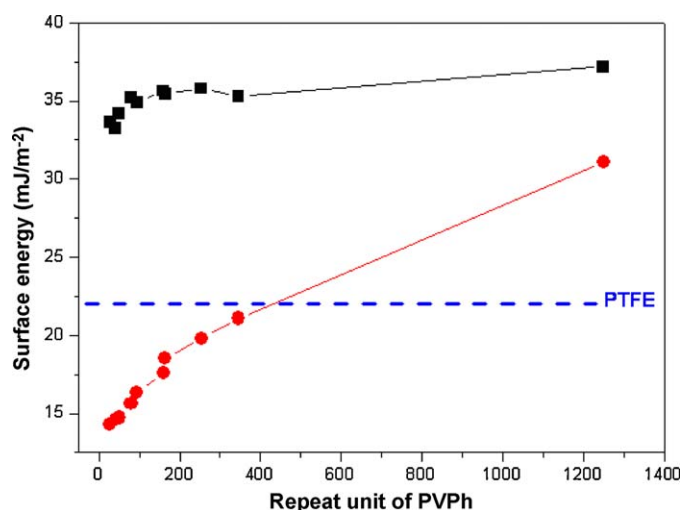


Fig. 5. Dependence of surface energies of PVPh homopolymers on repeat units of PVPh (■) before thermal treatment; (●) after thermal treatment of 180 °C for 24 h.

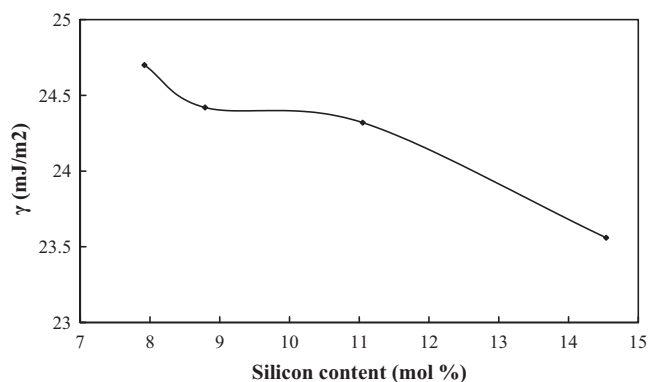


Fig. 6. Dependence of surface energies of POSS-PVPh copolymers on silicon contents.

be modulated with POSS contents and they are good polymeric materials with low surface energies because of their high thermal stabilities, easy processibility, and chemical resistance. Although PVPh homopolymers and POSS-PVPh copolymers are prepared from different methods and exhibit different polydispersities, no dependence of polydispersities on their surface properties can be observed in the present study. Further research for the impact of POSS macromolecules on morphology, the phase segregation, ²⁹Si NMR spectra, more IR spectra of POSS and PVPh systems, thermogravimetric analysis (TGA) data of PVPh homopolymers as well as PVPh-POSS copolymers, and the surface properties of POSS-PVPh copolymers with thermal treatment will be executed in the near future.

4. Conclusions

PVPh homopolymers and POSS-PVPh copolymers with low surface energies have been successfully synthesized and their surface properties highly depend on the intermolecular hydrogen bonds. In case of PVPh homopolymers, the surface energies of PVPh homopolymers with the thermal treatment of 180 °C for 24 h have drastically been heightened owing to the decrease of intermolecular hydrogen bonding interactions. In case of POSS-PVPh copolymers, however, the surface energies of POSS-PVPh copolymers increase with POSS contents since the intermolecular hydrogen bonding interactions reduce.

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