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Surface characterization of poly(methyl methacrylate-co-*n*-butyl acrylate-co-cyclopentylstyryl-polyhedral oligomeric silsesquioxane) by inverse gas chromatography

Qi-Chao Zou[a], Shi-Ling Zhang[a], Qing-qiong Tang[a],
Shi-Min Wang[a], Li-Min Wu[a,b,*]

[a] *Faculty of Chemistry and Material Science, Hubei University, Wuhan 430062, PR China*
[b] *Department of Materials Science, Fudan University, Shanghai 200433, PR China*

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Abstract

The surface properties of poly(methyl methacrylate-co-*n*-butyl acrylate-co-cyclopentylstyryl polyhedral oligomeric silsesquioxane) (poly(MMA-co-BA-co-styryl-POSS)) were studied by means of inverse gas chromatography (IGC) using 10 non-polar and polar solvents as the probes. Thermodynamic parameters of adsorption, e.g., specific retention volume, the dispersive component of the surface free energy, the specific interaction contribution to the free energy of adsorption and the acid/base constants were obtained to investigate the interactions between the surfaces of the copolymers and different solvents. It was found that incorporation of styryl-POSS into polymer resulted in increasing interactions between polymers and solvents, dispersive component of surface free energy of polymer and acidity of the surfaces of the polymers. The more the styryl-POSS were embedded, the stronger the interaction between the polymer surface and solvent, the dispersive component of the surface free energy and the acidity of the polymer surface were.
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Keywords: POSS; Thermodynamic parameter; Polymer; IGC

1. Introduction

In recent years, polyhedral oligomeric silsesquioxane (POSS) molecules, the smallest silica particles, have attracted considerable attention since POSS molecules can be used for hybrid organic–inorganic nanocomposites, space-survivable coatings and synthetic templates for nanostructured material [1,2]. Specifically, POSS moieties can be incorporated into polymer systems via polymerization, grafting, blending, and so forth, resulting in dramatic improvement of polymer properties, including glass transition and degradation temperatures, flammability, mechanical strength, and oxygen permeability [3–6]. For example, Fina et al. [7] studied the mechanism of thermal degradation of several substituted POSS and found that the thermal and thermoxidative behaviours of POSS depended on POSS type of substitution. Kopesky et al. [8] reported the miscibility and viscoelastic properties of acrylic POSS/poly(methyl methacrylate) blends and found that POSS species had a plasticizing effect on poly(methyl methacrylate) by lowering the glass transition temperature and decreasing the melt-state linear viscoelastic moduli.

In this paper, POSS was embedded into polymers via polymerization, 10 different solvents (non-polar, donor or acceptor) as the probes were employed to investigate the interaction between the surfaces of polymers and solvents. The main thermodynamic parameters of adsorption, such as specific retention volume, the dispersive component of the surface free energy, the specific interaction contribution to the free energy of adsorption and the acid/base constants, could be acquired by inverse gas chromatography (IGC) since IGC is relatively rapid and with good accuracy, and can provide valuable thermodynamic informations for physico-chemical characterization of polymers [9–15].

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* Corresponding author. Tel.: +86 21 65643795.
E-mail addresses: lxw@fudan.ac.cn, lmw@fudan.edu.cn (L.-M. Wu).

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2. Experimental

2.1. Materials

Cyclopentylstyryl polyhedral oligomeric silsesquioxane (styryl-POSS) was obtained from Aldrich. Toluene, methyl methacrylate (MMA), *n*-butyl acrylate (BA), AIBN and diatomite support (60–80 mesh) were bought from Shanghai Chemical Reagent Company of China.

Non-polar solvents: *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, and polar solvents: dichloromethane (DCM), trichloromethane (TCM), Ethyl acetate (EtAc), Acetone, tetrahydrofuran (THF) and diethyl ether (DEE) were used as the probes and provided by Shanghai Chemical Reagent Company of China. All these solvents are of analytical grade and used without further purification.

2.2. Synthesis of copolymers

Styryl-POSS (0.111–0.554 mmol), MMA (0.06 mol), BA (0.04 mol), AIBN (0.061 g), and toluene (12 ml) were poured into a 25 ml round-bottomed flask under a N_2 atmosphere. The mixture was heated to 85 °C and stirred at that temperature for 10 h at a slow stream of N_2 to obtain poly(MMA-co-BA-co-POSS) (BMSP) solution. The copolymer solution was slowly poured through a small bore funnel into well-stirred methanol to obtain fibrous polymers, which were then added into methanol/toluene mixture and stirred for 1 h, followed by filtering through a glass funnel to remove residual unreacted POSS. The copolymers were dried for a week at 40 °C under vacuum.

The samples MBSP with 1 wt.%, 3 wt.% and 5 wt.% styryl-POSS were designated as MBSP-1, MBSP-3 and MBSP-5, respectively, where the percentages of styryl-POSS indicated the initial styryl-POSS contents in formulations, the sample of poly(MMA-co-BA) was abbreviated as MB.

2.3. DSC analyses

The thermal transitions for the copolymers were determined by differential scanning calorimetry (DSC) with a TA Q10 instrument used under a nitrogen atmosphere at a scan rate of 20 °C/min.

2.4. IGC analyses

The support for the preparation of the chromatographic columns, diatomite, was coated with MBSP copolymer solution in TCM according to the soaking method of Al-Saigh and Munk [9], then dried at room temperature to constant weight in a vacuum oven to obtain 10 wt.% polymer coated based on the weight of support. The coated support was packed into 2000 mm × 4.0 mm stainless steel columns (Shimadzu, Japan) and conditioned at 100 °C under nitrogen for 24 h prior to use.

IGC analyses were performed on a GC-16A gas chromatograph (Shimadzu, Japan) equipped with a flame ionization detector and HW-2000 chromatography workstation (Nanjing Qianpu Company, China). Dried nitrogen was used as a carrier gas with a flow rate of 30 ml/min. Methane gas was used as a non-interacting marker to correct for dead volume in the column. A small quantity of solvent was injected manually with a 0.5 μl Hamilton syringe.

3. Results and discussion

3.1. Specific retention volume

As mentioned in the introduction, IGC measurement is widely employed to determine some thermodynamic parameters of adsorption, such as enthalpy, free energy and entropy of adsorption, dispersive components of the surface free energies, and acid/base constants since this method is relatively fast and accurate compared to other techniques. Generally, IGC experiments are performed below glass transition temperature (T_g) of polymer if only the surface properties of polymers are considered. This is mainly because probe molecules could probably diffuse into the polymer bulk if measurement is carried out above T_g. However, more and more researchers used this method for surface characterizations of polymers above their T_g at high carrier gas flow rates if the dwell times of probe molecules at the polymer surface were too short to permit diffusion into the bulk [16,17]. Although in this paper, the T_g of the polymers determined by DSC and shown in Table 1, were in the range of around 295–303 K, we still used IGC to characterize the surface properties of POSS-based hybrid polymers in the range of 307–327 K at carrier gas flow rate of 30 ml/min compared to the traditional carrier gas flow rate range of 5–20 ml/min.

The solvent–adsorption property of the copolymer was investigated at infinite dilution condition in order to eliminate the interactions between the probe molecules adsorbed at the surface of the copolymer. The thermodynamic functions of the adsorption of organic compounds onto the support may be calculated from the specific retention volume of the solvent, V_g^0 (ml/g), as follows [18]:

$$V_g^0 = \frac{273.15(t_p - t_m)Fj}{T_r w} \frac{P_0 - P_w}{P_w} \tag{1}$$

where t_p, t_m are the retention times of probe and marker, respectively; F is the gas carrier flow rate measured at the end of the column at room temperature (T_r); w the mass of the polymer; and j the James–Martin gas compressibility correction factor, and used to correct for the gas carrier compressibility.

Table 1
Characteristics of copolymer

Polymer	Abbreviation	POSS content (wt.%)[a]	T_g (K)
Poly(MMA-co-BA)	MB	0	303.3
Poly(MMA-co-BA-co-styryl-POSS)	MBSP-1	1	298.8
Poly(MMA-co-BA-co-styryl-POSS)	MBSP-3	3	294.6
Poly(MMA-co-BA-co-styryl-POSS)	MBSP-5	5	301.2

[a] Initial styryl-POSS contents.

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