

# Structural Modification of Expandable Polystyrene. II. Copolymerization with Silicone Acrylate

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**ABSTRACT:** Conventional expandable polystyrene (EPS) was modified by the preparation of copolymers containing 0.10%, 0.25%, and 0.50% silicone acrylate. Copolymeric expandable polystyrene (CEPS) samples were characterized with various techniques. <sup>1</sup>H-NMR spectroscopy was used for the determination of composition, and gel permeation chromatography was used for the determination of molecular weight and molecular weight distribution. Differential scanning calorimetry showed that the glass-transition tem-

peratures of the CEPS samples increased with an increasing silicone acrylate content. The surface properties of the copolymers were investigated by contact angle measurement and SEM imaging. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 128–132, 2006

**Key words:** polystyrene; modification; silicones; synthesis; structure-property relations

## INTRODUCTION

Controlling the surface structure of polymers can be accomplished in many industrial applications. Polymer surface properties are related material functionality, such as adhesion, friction, fracture, and antistatic properties.<sup>1,2</sup> Surface modification of copolymers containing siloxane has been studied previously.<sup>3,4</sup> Silicone improves chain flexibility; oxidative, thermal, and UV stability; gas permeability; and biocompatibility. Surface modification of polystyrene latex particles also can be achieved by the ATRP technique.<sup>5</sup> In the present study, graft polymerization was performed on the surfaces of modified crosslinked polystyrene (PS) particles. The effects of silicone chain length on surface modification also was investigated.<sup>6–8</sup> Enrichment of polydimethylsiloxane (PDMS) surfaces in the blends also depended on length.

In the first article of this series we reported copolymerization with  $\alpha$ -methylstyrene for an increasing glass-transition temperature ( $T_g$ ).<sup>9</sup> The aim of the present study was to improve the surface properties of styrene with silicone acrylate prepolymer. Expandable polystyrene (EPS) can be produced by a suspension polymerization process.<sup>9,10</sup> For structural modification purposes, silicone acrylate was added to the suspension polymerization system at the beginning of the

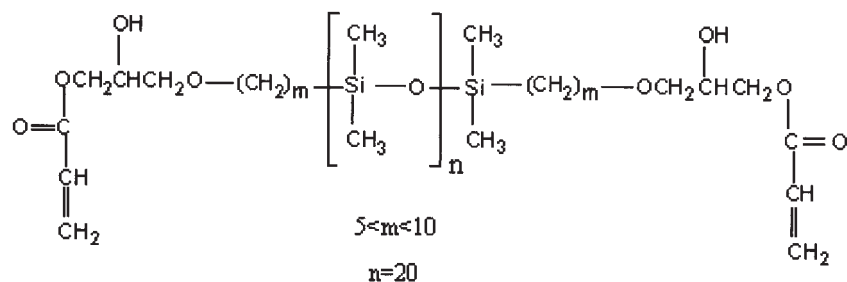
reaction. At the end of the reaction a homogeneous cellular structure in closed cells formed copolymeric EPS. Copolymer structure was characterized using spectroscopic methods; thermal and surface properties also were examined.

## EXPERIMENTAL

### Materials

Polymerization-grade (99.9%) styrene monomer with the inhibitor tert-butylcatechol (10 ppm) was provided by Petkim Petrochemical Co. (Kocaeli, Turkey). Polyvinyl alcohol (PVA) was purchased from Kuraray (Osaka, Japan), tricalcium phosphate and calcium stearate were obtained from Chemische Fabrik Budenheim (Mainz, Germany), calcium chloride (77%) was supplied by Kemira Kemi (Helsingborg, Sweden), *n*-pentane was purchased from Riedel de Haën A.G. (Seelze, Germany), and linear alkyl benzene sodium sulfonate (LABSS) was supplied by Cognis (Kocaeli, Turkey). Initiator dibenzoyl peroxide (DBPO; 75%) was obtained from Peroxide Chemie GmbH (Munich, Germany), and initiators tertiary butyl perbenzoate (TBP) and dicumyl peroxide were supplied by Interchim (Worgl, Austria).  $\alpha$ - $\omega$  Dihydroxy polydimethylsiloxane (PDMS; Tegomer V-Si 2250,  $M_n$  = 2038  $\pm$  70 g/mol), a kind of silicone acrylate prepolymer, was obtained from Goldschmidt A.G. (Düsseldorf, Germany). PDMS is a liquid at room temperature with a density of 1  $\pm$  0.02 g/cm<sup>3</sup> at 25°C. The structural formula of V-Si 2250 is

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### Analysis and tests

The syntheses were carried out in a Buchi Glassuster 5-L metal reaction vessel equipped with an adjustable mechanical stirrer, a thermostat (Haake N3), a temperature indicator and a controller, vacuum and nitrogen lines, and a pentane inlet line. Gas chromatography (GC) measurement was performed on a Chrompack CP 901 model instrument with a setup consisting of CD-WAX packed columns and a column flow of 2 mL/min. The analyses were carried out between 50°C and 210°C. A Normandie Labo Cannon Fenske SR.200 (E 346) viscometer was used to measure the viscosity of the samples. <sup>1</sup>H-NMR spectra of all the samples were obtained on a Bruker AC (200 MHz). CDCl<sub>3</sub> solvent was used without TMS in the measurements because of the siloxane content of the copolymeric samples. Gel permeation chromatography (GPC) measurement was performed with a setup consisting of a Waters pump (model 600E) and three ultrastyrogel columns with porosities of 10<sup>4</sup>, 500, and 100 Å. The detection was achieved with a Waters differential refractometer (model 410). All the samples were characterized by GPC analyses. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1 mL/min. Molecular weight was calculated with respect to polystyrene standards. The thermal characteristics of samples were measured with a Shimadzu TA-501 instrument (model DSC-5). Scanning electron microscopy (SEM) was performed on a JEOL JXA-840 model electron microscope. The samples were prepared by precise cutting of the beads and subsequent application of a gold coating of approximately 200 Å. The average particle size ( $D_{50}$ ) and particle size distribution ( $D_{50}/D_{84}$ ) were calculated through sieve analysis,<sup>9</sup> which was done with an EML model shaker and seven test sieves (Retsch) with a mesh size between 300 and 1400 μm. The static contact angles of the homo- and copolymer films were measured with a Kernco (El Paso, TX) contact angle meter (model G-111) at room temperature, using deionized and triple-distilled water. The homo- and copolymer films were prepared by casting from 1% (w/v) chloroform solutions. The water droplet volume was 20 μL.

### Syntheses of EPS and copolymeric expandable polystyrene (CEPS)

#### Synthesis of EPS

The synthesis details of EPS were outlined in our previous report.<sup>9</sup>

#### Synthesis of CEPS

A previously reported experimental procedure was applied to the copolymerization of styrene with silicone acrylate.<sup>10,11</sup> Silicone acrylate along with styrene monomer was fed to the reactor at the beginning of polymerization. The synthesis conditions of the styrene homopolymerization and silicone acrylate/styrene copolymerization are given in Table I.

### Characterization

Residual monomer content after low- and high-temperature cycles was determined by GC, which also was used to determine the pentane content of the samples after the pentane impregnation and expansion stages. The solution viscosity of the polymers was determined according to the ASTM D-445 standard. A solution (8%) of expandable polystyrene beads in toluene was prepared. Sample viscosity was estimated in cSt units with a Cannon-Fenske viscometer. Sieve analysis was conducted according to the ASTM D-1921 test method.

After expansion of the beads, all the samples were characterized qualitatively by FTIR. The film samples (20 μm) were prepared by the molding method. <sup>1</sup>H-NMR analysis of standard EPS and silicone acrylate/styrene copolymeric samples was performed. GPC

TABLE I  
Synthesis Conditions of EPS

Sample	Amount of monomer (%)	
	Styrene	V-Si 2250
EPS.01	100	0.00
EPS.02	100	0.10
EPS.03	100	0.25
EPS.04	100	0.50

**TABLE II**  
Experimental Results after *n*-Pentane Impregnation Stage

Sample	Conversion (%)	Residual monomer content (%)	After pentane impregnation			After expansion density (g/cm <sup>3</sup> )
			$D_{50}$ (μm)	$D_{84}/D_{50}$ (μm)	Pentane (%)	
EPS.01	99.41	0.59	960	2.06	5.92	10.98
EPS.02	99.18	0.82	1150	2.26	4.98	18.06
EPS.03	99.46	0.80	1200	2.12	5.60	17.50
EPS.04	99.21	0.79	1300	2.07	5.73	17.16

analysis of the samples was performed in order to determine molecular weight. The  $T_g$  values were determined from the second derivation of the differential scanning calorimeter (DSC) curves in the related temperature zones in the thermograms so that a precise estimation could be made from the observation of very small changes in  $T_g$ . SEM micrographs were taken of sample cross sections (both inner and outer surfaces). Contact angle measurement of water droplets on the homo- and copolymer films was performed at room temperature.

## RESULTS AND DISCUSSION

It was important to determine the residual monomer content because the inhibition effect of additives was checked. At the end of the reaction the residual monomer content was measured by GC. The residual styrene contents of CEPS and EPS samples are given in Table II. Residual styrene content did not increase if there was an increase in the amount of silicone acrylate used. This means that the presence of silicone acrylate did not retard the reaction rate.

EPS and expandable poly(silicone acrylate-*co*-styrene) samples were prepared in adequate yields (Table II). According to the sieve analyses results, silicone acrylate played a role in average particle size and average particle size distribution. When EPS and CEPS particles were compared, CEPS particles were larger because of the V-Si 2250 group in the polymer chain. Particle size increased relative to V-Si 2250 content of the poly(silicone acrylate-*co*-styrene) samples. But the particle size distribution of CEPS samples

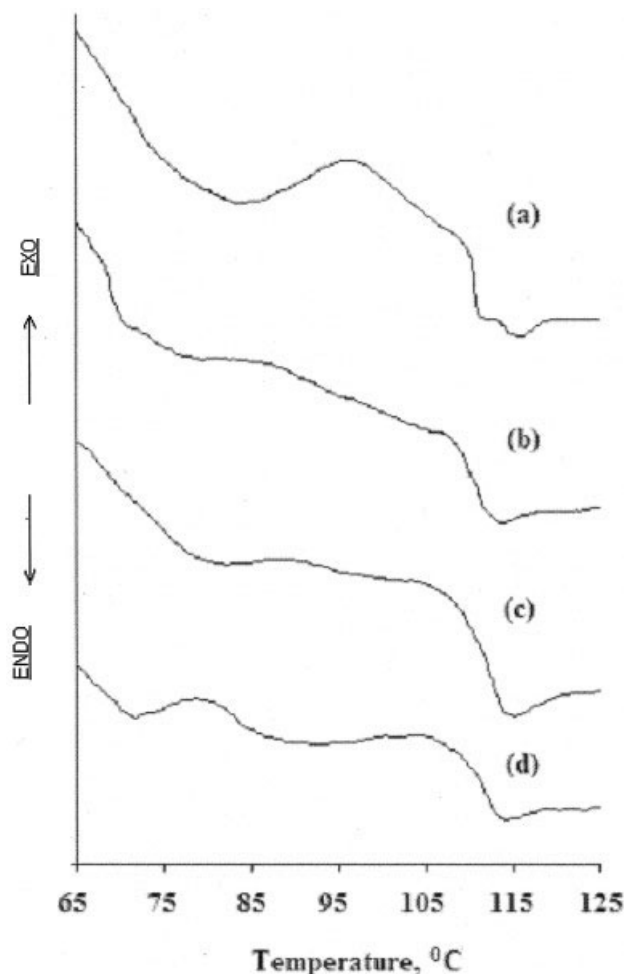
showed the reverse effect. The size distribution of CEPS particles was broader at the lowest V-Si 2250 level. The higher was the V-Si 2250 content, the narrower was the particle size distribution, too. This narrower distribution can be explained by the enhancement of the surface properties of the CEPS particles because of the V-Si 2250 group in the macromolecular structure.

The expansion densities of the samples were compared. The densities of the CEPS samples were notice-

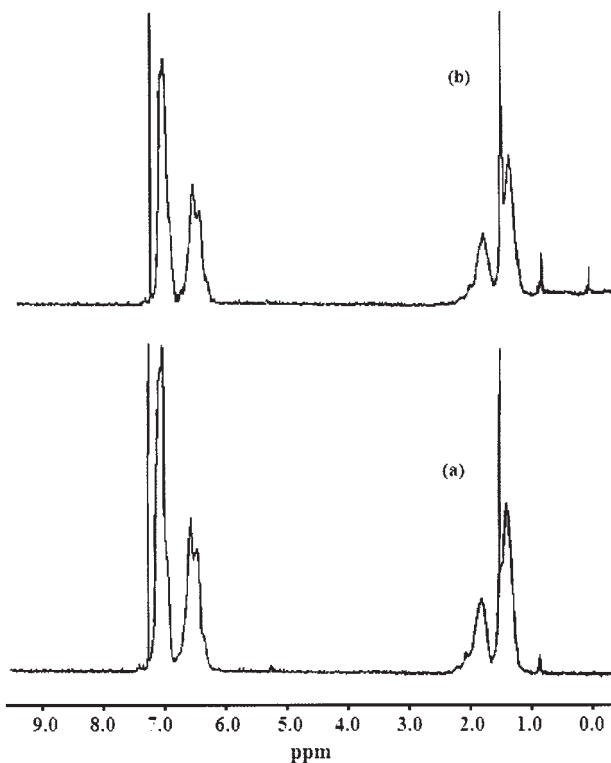
**TABLE III**  
Characterization of EPS Samples

Sample	$M_n$	$M_w$	Polydispersity ( $M_w/M_n$ )	Kinematic Viscosity (cSt)	$T_g$ (°C)
EPS.01	91,000	152,000	1.67	8.65	110.5
EPS.02	100,000	157,000	1.57	8.57	112.0
EPS.03	116,000	200,000	1.72	10.97	112.0
EPS.04	115,000	243,000	2.11	11.17	112.1

$M_n$ , number-average molecular weight;  $M_w$ , weight-average molecular weight.



**Figure 1** DSC thermograms of (a) sample EPS.01, (b) sample EPS.02, (c) sample EPS.03, and (d) sample EPS.04.



**Figure 2**  $^1\text{H-NMR}$  spectra of (a) sample EPS.01 and (b) sample EPS.04

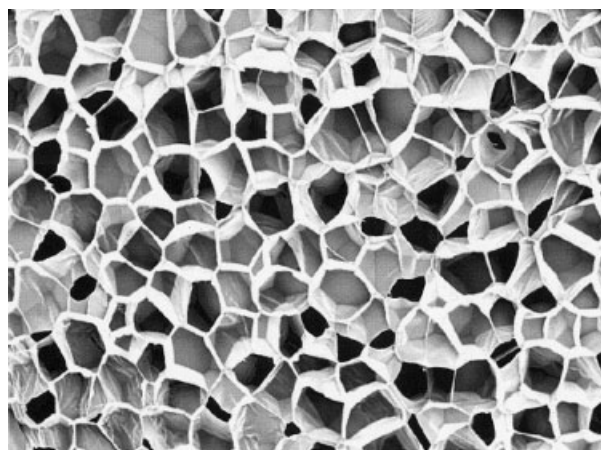
ably higher than those of the standard EPS because of improvement in surface properties such as adhesion, gloss, and antistatic properties related to the functionality of the silane group in the polymer chain. A similar effect was observed in the copolymers containing siloxane.<sup>3,4</sup>

The molecular weights of the samples were measured by GPC, and the results are given in Table III. There were distinguishable differences between the molecular weights and the distributions. Molecular weight and heterogeneity index increased when the amount of silicone acrylate used increased. The kinematic viscosity values shown in Table III indicated results similar to those of GPC. Chains of very different lengths were formed during suspension polymerization. So the presence of a V-Si 2250 group caused an increase in the molecular weight of styrene-based droplets where polymerization occurred, and the silicone group joined the polymer chain as a comonomer.

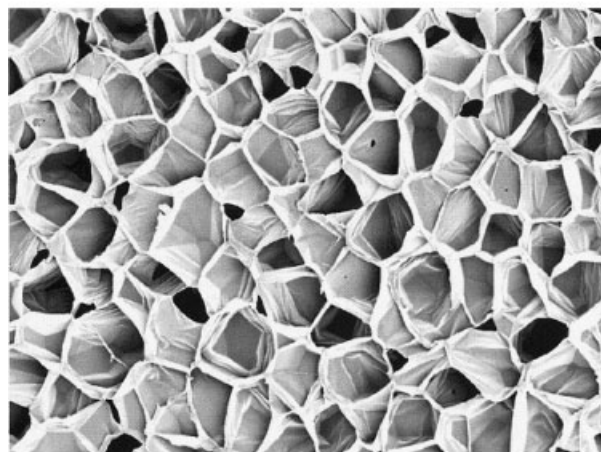
DSC thermograms of the samples are shown in Figure 1(a–d). The  $T_g$  of the standard homopolymer (sample EPS.01) was  $110.5^\circ\text{C}$ , and the  $T_g$  values of samples containing 0.10%, 0.25%, and 0.50% silicone acrylate (samples EPS.02, EPS.03, and EPS.04) were  $112.0^\circ\text{C}$ ,  $112.0^\circ\text{C}$ , and  $112.1^\circ\text{C}$ , respectively (Table III). The  $T_g$  was about  $112^\circ\text{C}$  and did not change with the amount of silicone acrylate added to the reaction. These values were higher than the  $T_g$  of standard

expanded homopolymer, which showed a small percentage of crosslinking.

Standard and modified EPS samples were characterized by  $^1\text{H-NMR}$  spectroscopy.  $^1\text{H-NMR}$  spectra of samples EPS.01 and EPS.04 are presented in Figure 2(a,b), respectively, which show two main peaks, at 6.25–6.83 ppm for protons closer to the main chain of polystyrene and at 6.83–7.20 ppm for protons farther from the main chain of polystyrene. These were the characteristic peaks of polystyrene. Sample EPS.01 [Fig. 2(a)] showed a peak at 1.25 ppm because of the  $\text{CH}_3$  group in the polymer. Because there was no proton splitting in this single peak, there must have been a neighboring proton in the  $\text{CH}_3$  group. This indicated that homopolystyrene contained styrene homologue impurities such as  $\alpha$ -methylstyrene. The percentage of impurities from the styrene monomer was calculated from the areas under curves of the peak at 1.25 ppm to the peak coming from phenyl protons between 6.26 and 7.20 ppm. The results showed 99%



(a)

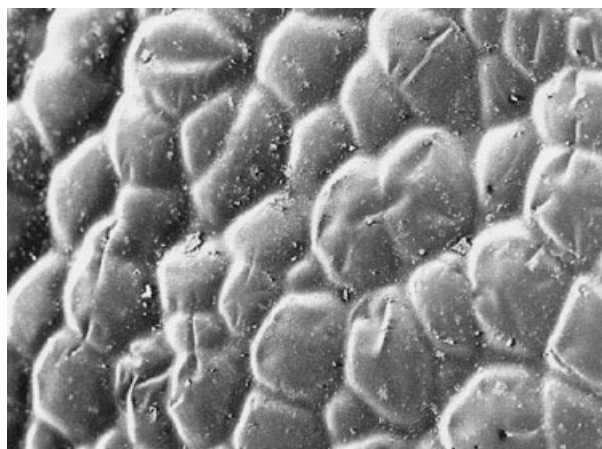


(b)

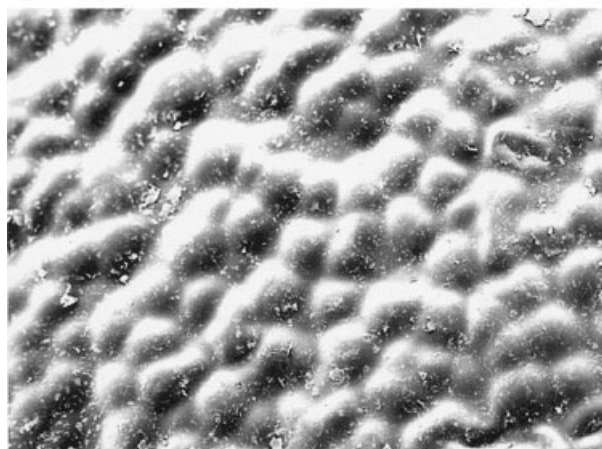
**Figure 3** Scanning electron micrographs (SEM) of the inner parts of (a) sample EPS.01 (magnification  $\times 150$ ) and (b) sample EPS.04 (magnification  $\times 150$ ).

pure homopolystyrene. The peak at 0.069 ppm showed the incorporation of siloxane into the polystyrene backbone, although the peak was small because the amount of V-Si 2250 used was so small.

SEM micrographs of the samples are shown in Figures 3 and 4. Cross-sectional views of the samples EPS.01 and EPS.04 are shown in Figure 3(a,b), respectively, showing that the cell structures of the styrene homo- and copolymers were similar. In addition, the homogeneity of cell size also was nearly the same, although the cell size of sample EPS.04 was bigger than that of sample EPS.01. The outer surface of EPS appeared rough [Fig. 4(a)]. However, the outer surface of CEPS [Fig. 4(b)] appeared smooth and glossy because of the existence of siloxane in the copolymer structure. This shows that PDMS chains resided in the side chain of the molecule and accumulated on the polymer surface. These results were consistent with those reported in the literature.<sup>4,6,12–14</sup>



(a)



(b)

**Figure 4** Scanning electron micrographs (SEM) of outer surfaces of (a) sample EPS.01 (magnification  $\times 200$ ) and (b) sample EPS.04 (magnification  $\times 200$ ).

**TABLE IV**  
Contact Angles of EPS Samples

Sample	Styrene (%)	V-Si 2250 (%)	Contact Angle, $\theta$ ( $^{\circ}$ ) Cast films (air side)
EPS.1	100	0.00	78
EPS.2	100	0.10	96
EPS.3	100	0.25	96
EPS.4	100	0.50	100

The SEM results were proven by contact angle measurements. Contact angle measurement results, given in Table IV, were reproducible at  $\pm 1^{\circ}$ . The contact angles of copolymeric films exceeded 17%–28% with respect to homopolystyrene because of siloxane accumulation on the surface.

## CONCLUSIONS

From these results, the following conclusions can be drawn: (1) three expandable poly(silicone acrylate-co-styrene) (CEPS) samples were prepared by suspension polymerization; (2) thermal modification was achieved in this way; (3) outer surface smoothness and gloss were attained by copolymerization with silicone acrylate only up to 0.5%; and (4) surface properties of the CEPS samples also were improved because of the silane group in the polymer structure.

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