Core-Shell Latex Particles Consisting of Polysiloxane-Poly(styrene-methyl methacrylate-acrylic acid): Preparation and Pore Generation

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ABSTRACT: Latexes with a poly(dimethyl siloxane) core and a poly(styrene-methyl methacrylate-acrylic acid) [poly(St-MMA-AA)] shell have been prepared in two steps in order to generate particles that have a core with a very low glass transition temperature. In the first step, poly(dimethyl siloxane) particles were obtained via the ringopening emulsion polymerization of octamethyl tetracyclosiloxane (D_4) . The polymerization was carried out using either an anionic or a cationic catalyst. In the first case, sodium hydroxide was used as catalyst and sodium dodecylbenzene sulfonate as surfactant, while in the second, the alkylbenzene sulfonic acid (ABSA) was used both as catalyst and surfactant. Using a PD_4 latex as seed, a seeded emulsion polymerization of St-MMA-AA was conducted to obtain PD₄-P(St-MMA-AA) core-shell particles. Numerous recipes were attempted and the most successful were those in which the seed was prepared with a cationic catalyst (ABSA) at a relatively low temperature (75°C). The core-shell structure of the particles was identified by transmission electron microscopy, but also via wetting angle, water absorption, and T_{g} measurements. Finally, pores were generated in the core-shell particles via an alkali-acid treatment. Because PD_4 has a very low glass transition temperature, it cannot be easily handled. However, protected by a shell, it could be used as a constituent of composite materials with enhanced impact strength, even at very low temperatures. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2235-2245, 1999

Key words: poly(dimethyl siloxane); styrene copolymer; core–shell latex morphology; emulsion polymerization; porous particles

INTRODUCTION

A common way to prepare new materials is to combine two or more polymers. This can be achieved by grafting, block polymerization, or simple blending. The greater the difference between the combining polymers, the more likely synergistic properties will result from the combination. Polystyrene (PSt) and poly(methyl methacrylate) (PMMA) are among the most popular polymers. Their homo- and copolymers consist of rigid molecular chains and possess high glass transition temperatures (T_g) and high mechanical moduli. In contrast, the organosilicon polymers consist of soft chains, possess very low T_g 's, and have properties, such as polarity, surface energy, temperature performance, and mechanical characteristics, very different from those of PSt and PMMA. Consequently, their combination is of great interest. In fact, studies regarding the combination of vinyl polymers, particularly the various polyacrylates, with the polysiloxanes have been carried out.¹⁻⁹ Nakamura¹ blended an acrylic rubber with poly(heptamethyl monovinyl

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tetracyclosiloxane) using poly(methyldodecyl siloxane) as compatibilizer and obtained a rubber with significantly improved mechanical properties. By changing the compatibilizer or the pending group on siloxane, a number of blends have been prepared.^{2,3} The copolymerization of siloxanes with vinyl monomers, in the presence of a vinyl-containing siloxane, by bulk, solution, or emulsion polymerization, was also carried out.^{4–9}

On the other hand, research on polymer nanoparticles, particularly regarding their applications in biological and pharmaceutical areas, has increased continuously in the last decade.¹⁰⁻¹⁴ The silicon polymers can be employed for biological applications as well as tougheners. However, the silicon polymer particles have a very low T_{σ} and, therefore, cannot be handled easily. The goal of the present work is to prepare core-shell particles with a polysilicon core (PD_4) protected by a shell of P(St-MMA-AA). To make the polysilicon core accessible to the external medium, pores were generated in the shell via an alkali-acid treatment.¹⁵ The core-shell particles thus obtained could be used as a constituent of composite materials with enhanced impact strength even at very low temperatures.

EXPERIMENTAL

Materials

Styrene (St), methyl methacrylate (MMA), and acrylic acid (AA) were purchased from Aldrich, and the inhibitors were removed prior to polymerization by passing the monomers through an inhibitor removal prepacked column (Aldrich). The monomer, octamethyl tetracyclosiloxane (D_4 , Aldrich), the coupling agents between the core, and the shell polymers, namely, 2,4,6,8-tetramethyl-2,4,6,8-tetravinyl cyclotetrasiloxane (VD₄, Aldrich) and 3-(trimethoxylsilyl)propyl methacrylate (MATS, 98%, Aldrich), as well as sodium dodecylbenzene sulfonate (SDBS, Aldrich), were used as received. A linear alkylbenzene sulfonic acid (ABSA, assay 98%, Alfa) was employed as catalyst and surfactant in the cationic polymerization of D_4 . ABSA (RC₆H₄SO₃H) is a mixture of alkylbenzene sulfonic acids with 1 wt % R=C₁₀, 40 wt % R=C₁₁, 28 wt % R=C₁₂, and 31 wt % C₁₃ and higher alkyls. A 3N solution of sodium hydroxide (99.99%, Aldrich) was prepared and employed as catalyst in the anionic emulsion polymerization of D₄. The initiators employed in radical polymerizations (ammonium persulfate, APS, 99.99%, Aldrich; or azobis-isobutyronitrile, AIBN, Polysciences Inc.) were used as received. Distilled and deionized water with a conductivity of 0.05 μ S/cm was employed.

Emulsion Polymerization of D₄

The polymerization of D₄ was conducted using a cationic (ABSA) or an anionic (NaOH) catalyst. In the former process, 40 g of water, $12.5 \text{ g of } D_4$, and a selected amount of ABSA and SDBS (the total of the two varied between 1.6-5.0 wt % of the monomer) dissolved in 10 g of water were successively charged to a three-necked, round-bottom flask equipped with a stirrer. The flask was then purged of oxygen by bubbling nitrogen for 30 min at room temperature, with stirring at about 400 rpm. The polymerization started once the flask was introduced into an oil bath of controlled temperature. 1 wt % MATS was added in some experiments. For the anionic polymerization, 50 g of water, 12.5 g of D_4 , and 0.625 g of MATS were introduced into the flask reactor, and then various amounts of SDBS (0.06-0.16 g) were added. After the system was purged of oxygen by bubbling nitrogen, the flask was introduced in an oil bath of a controlled temperature of $80 \pm 1^{\circ}$ C, with stirring at 200 or 400 rpm. Various amounts of a solution of NaOH (3N) were then added to start the polymerization.

Seeded Copolymerization of St-MMA-AA onto PD₄ Latex Particles

In most of the seeded polymerizations, no additional surfactant was added to the system. While the total amount of monomers, St-MMA-AA, was varied in the experiments, their ratios were kept constant (89.6/4.7/5.7 by weight and 87.2/4.8/8.0 by moles). The amount of initiator was 2.5 wt % of the monomers for APS and 1.8 wt % for AIBN. A selected amount of seed latex of PD_4 and water were first charged to the reactor, which was then purged of oxygen by bubbling nitrogen for 30 min. The reactor was then placed in an oil bath (80 \pm 1°C), and the monomer mixture added dropwise at the low rate of about 10 mL/h. In some experiments, a coupling agent between PD_4 and the shell copolymer P(St-MMA-AA), namely, MATS or VD₄, was added and allowed to react for 6 h with the PD_4 particles prior to the seeded polymerization of St-MMA-AA. The amount of coupling agent was 4-5 wt % of PD₄ in the seed

particles. When VD_4 was used, the pH of the media was about 2.0 after adding water and VD_4 to the seed latex. The reaction between the seed particles and VD_4 was carried out at 40°C. When MATS was used, the pH of the media had to be adjusted to about 4.5 by adding a solution of so-dium hydroxide (0.1N) in order to avoid its homopolymerization. Its reaction with PD₄ particles was conducted at room temperature.

Particle Size and Monomer Conversion

The attempts to determine the particle sizes of PD₄ latexes by transmission and scanning electron microscopy (TEM and SEM) have failed because, due to their very low T_g , the particles collapsed and even flowed to form a film on the TEM grid.¹⁶ Even those prepared with 1 wt % MATS (55.8% crosslinked, as tested by Soxhlet extraction with toluene) have been seriously deformed, and no particles could be identified (Fig. 1). The size of the latex particles was determined via light scattering, which provided both the arithmetic average diameter and the deviation from the average. The size and morphology of the latex particles after the seeded polymerization was determined by TEM (Jeol-2010 or Hitachi-H500) and SEM (Hitachi S-4000). An aqueous solution of phosphotungstic acid was used to increase the contrast in the TEM pictures.¹⁷ The conversion of the monomers was determined gravimetrically.

Alkali-Acid Treatment

The seeded latex was diluted to a solid content of about 1 wt %, and 100 g of the diluted latex was introduced into a three-necked, round-bottom flask equipped with a stirrer; 0.1-0.2 g of SDBS was then added to ensure the latex stability upon addition of NaOH and HCl. A selected amount of methyl ethyl ketone (MEK) was first added to the flask with stirring, and this was followed by the alkali and, subsequently, by the acid treatment. In the alkali treatment, a selected pH was first achieved by the addition of a solution of sodium hydroxide (0.1N). The flask, with the mixture in the flask stirred at 100 rpm, was then placed into an oil bath at 90°C, where it was kept for 3 h, after which it was allowed to cool to room temperature. After the pH was changed to a selected lower value by using a solution of hydrochloric acid (1N), the flask was reintroduced into the oil bath at 90°C for another 3 h.



Figure 1 SEM micrograph of PD_4 latex particles prepared with MATS (1 wt % of D_4 monomer) showing that no particles can be identified due to their deformation.

Additional Experiments

For comparison purposes, a latex (denoted hereafter as S_1) of P(St-MMA-AA) with the same composition as that for the second stage of seeded polymerization was prepared in the absence of seed particles. Dry polymers of S_1 and PD_4 , their blends as well as the polymer of the PD₄/P(St-MMA-AA) core-shell latex were obtained by evaporating the water from the latexes at 40°C in a vacuum oven at 29.5 in. Hg for 40 h. The T_g 's of the polymers were determined by using a Du Pont 910 DSC instrument and a temperature scanning from -170 to 230°C at 10°C/min. The contact angles of water droplets on various polymers were determined with an NRL C.A. Goniometer manufactured by Rame-Hart Inc. Disc-shaped polymer tablets of about 0.1 g, which were prepared using a Carver Laboratory Press (model C) with an applied load of 4000 psi at room temperature, were employed in the contact angle experiments. Such tablets were also used for determining the

Runs ^a	SDBS (g)	NaOH [<i>M</i>]	Stirring (rpm)	Reaction Time (h)	Conversion (%)	$D_p^{\mathbf{b}}(\mathbf{nm})$	$rac{10^{-15} N_p{}^{ m c}}{({ m L}^{-1})}$	Latex Stability
A41	0.06	0.51	400	45	62			$\mathbf{F}^{\mathbf{d}}$
A42	0.06	0.26	400	50	48	_	_	\mathbf{F}
A43	0.08	0.26	400	35	51	_	_	\mathbf{F}
A44	0.10	0.26	400	75	60	_	_	\mathbf{F}
A45	0.10	0.30	400	80	66	_	_	\mathbf{F}
A46	0.12	0.26	400	80	70	_	_	\mathbf{F}
A47	0.14	0.26	400	70	90	392 ± 45	5.53	$\mathbf{S}^{\mathbf{d}}$
A48	0.16	0.26	400	70	95.9	143 ± 10	121.87	\mathbf{S}
A21	0.08	0.34	200	50	67.3	351 ± 29	_	\mathbf{F}
A22	0.08	0.26	200	50	50.1	_	_	\mathbf{F}
A23	0.10	0.26	200	90	82.2	260 ± 9	17.26	\mathbf{S}
A24	0.12	0.26	200	120	88.4	268 ± 14	11.54	\mathbf{S}
A25	0.14	0.26	200	90	96.7	192 ± 12	50.22	S
A26	0.16	0.26	200	160	96.0	$180\pm~6$	62.47	\mathbf{S}

Table I D₄ Polymerization with NaOH as Anionic Catalyst

^a H₂O, 50 g; D₄, 12.5 g; MATS, 0.625 g; polymerization at 80°C.

^b Diameter of particles determined by light scattering.

^c Number of particles per liter of latex.

 $^{\rm d}$ S stands for stable latexes; F implies that the latex flocculated during polymerization or was phase-separated when the stirring was stopped.

water absorption of the polymers: A tablet was immersed in water for 20 h at room temperature, and the water on its surface was wiped off with an absorbent tissue; the water absorption was obtained from the difference of the weights of the tablet before and after immersion. The surface charge density¹⁸ of the latex particles was determined by first diluting 5 mL latex with 145 mL water and then by following the change of the conductivity in the diluted latex with the slow addition of a base (NaOH, 0.1*N*).

RESULTS AND DISCUSSIONS

Preparation of PD₄ Latex by Emulsion Polymerization

The synthesis of polydimethylsiloxane by the ring-opening polymerization of D_3 (hexamethyl tricyclosiloxane), D_4 , or other cyclic siloxane monomers has been described in literature.^{19–24} In general, their solution polymerization yields polymers of low-molecular-weight and broad-mo-

Table II	D ₄ Polymerization	with ABSA as	Cationic (Catalyst
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Runs	ABSA (g)/SDBS (g)	Temperature (°C)	Reaction Time (h)	Conversion (%)	$D_p^{\mathbf{b}}(\mathbf{nm})$	$rac{10^{-15}N_p}{({ m L}^{-1})}$
C1	0.20/0.10	60	30	69	290 ± 14	11.03
C2	0.25/0.10	60	30	84	$270\pm~8$	17.01
C3	0.25/0.10	80	40	88	280 ± 5	15.62
C4	0.63/0.10	80	23	80	290 ± 5	12.78
C5	0.63/0.00	80	23	79	302 ± 6	11.40
$\rm C6^{a}$	0.25/0.00	90	45	78	330 ± 11	8.31
C7	0.25/0.00	90	45	80	390 ± 5	5.21
$C8^{a}$	0.45/0.00	90	29	85	275 ± 3	15.93
C9	0.45/0.00	90	29	84	295 ± 10	12.75
$\mathrm{C10^{a}}$	0.25/0.00	75	60	71	$240\pm~9$	20.60

 $^{\rm a}$ Polymerization with MATS 1 wt % of $\rm D_4$ monomer.

^b Diameter of particles determined by light scattering.

Conversion		$10^{-15} N_{-}$
(%)	$D_p \ ({\rm nm})$	(L^{-1})
43.63	190 ± 11	24.74
51.49	214 ± 14	23.25
52.33	$225\pm~9$	21.02
56.18	252 ± 10	16.01
76.59	$310\pm~8$	10.00
78.18	330 ± 11	8.31

Table IIIParticle Size Evolution in CationicPolymerization (C6)

lecular-weight distribution.^{19,24} Regarding the preparation of this polymer via emulsion polymerization, the following contributions should be noted: Hyde and Wehrly²¹ obtained a stable aqueous dispersion of poly(dimethyl siloxane) particles, containing molecules of high molecular weight, using NaOH as catalyst and a cationic surfactant (R₄NCl); Bey et al.^{16,22} succeeded in preparing a PD₄ latex using dodecylbenzene sulfonic acid (DBSA) as both catalyst and surfactant; latexes with particle sizes between 50 and 500 nm were obtained with 1.5-4 g of DBSA (or a combination of DBSA with its sodium salt) for 100 g of siloxane monomer. Recently, de Gunzbourg et al.²⁴ published some preliminary results regarding the polymerization of D_4 in the presence of benzyldimethyl dodecyl ammonium hydroxide as catalyst and surfactant. In the present study, the emulsion polymerization of D_4 was carried out with either an anionic or a cationic catalyst. In the first case, SDBS was employed as surfactant and sodium hydroxide as catalyst. The results are listed in Table I, from which one can see that three main factors (stirring rate, surfactant, and NaOH concentrations) affect the polymerization process. At a stirring rate of 400 rpm and an amount of SDBS less than 0.12 g (A41 to A46), the latexes became unstable at relatively low conversions; the latexes were, however, stable at higher SDBS contents and high conversions were reached. At a stirring rate of 200 rpm, the latexes became stable for SDBS amounts greater than 0.10 g (A23). In the stable latexes, the particle size decreased with increasing surfactant amount at a given stirring rate (compare A47 and A48, A24, A25, and A26). It should be pointed out that, except the latexes A25 and A26, which remained stable on the shelf at room temperature after 3 months, the other latexes, classified as stable immediately after polymerization, flocculated within two months of shelf standing.

The emulsion polymerization of D_4 by cationic catalysis was carried out either with ABSA alone as catalyst and surfactant, or with a combination of ABSA and SDBS. In contrast to the latexes prepared by anionic catalysis, all the latexes prepared by cationic catalysis were stable, even after 5 months. The experiments summarized in Table II indicate that the particle size is significantly reduced by (1) the presence of the coupling agent MATS (compare C6 to C7, and C8 to C9), probably

Table IV Seeded Polymerization of St-MMA-AA with PD_4 Latex Prepared with Anionic and Cationic Catalysts

	Seed Latex			Seeded Polymerization			
Runs ^a	Code	D_p (nm)	$N_p^{\;\;\mathrm{b}}$	M/P ^c	$D_f^{\ d}$ Calcd	$D_f^{\ \mathrm{e}}$ Found	
SP1	A23	260	$1.0 imes 10^{15}$	4	444	mostly < 60 nm	
SP2	A23	260	$2.5 imes10^{15}$	8	522	250, 100	
SP3	A25	192	$2.5 imes10^{15}$	10	414	180, 60	
SP4	A48	143	$3.0~ imes 10^{15}$	8	286	260, 150	
SP5	C6	330	$1.0~ imes 10^{15}$	5	600	475, 225	
$SP6^{f}$	C3	280	$3.0 imes10^{15}$	3.2	450	560, 320	
$\rm SP7^{f}$	C10	240	$0.73 imes10^{15}$	5.5	448	425, 415	

^a Except SP1, for which AIBN was used as the initiator with 0.1 g SDBS added, all the other experiments were carried out using APS as the initiator without further SDBS addition. For SP1 to SP4, the PD₄ seed latexes were prepared by anionic polymerization; for SP5 to SP7, the seed latexes were prepared by cationic polymerization.

^b Number of particles per liter of latex by assuming that no new particles are formed in the second-stage polymerization.

^c Weight ratio of (St-MMA-AA)-PD₄.

^d Calculated particle size (nm) by assuming that no new particle is formed in the second-stage polymerization.

^e Polydispersed particles; only the largest and the smallest particle sizes are given.

 $^{\rm f}$ VD₄ (5% of the PD₄ in the seed) was allowed to react with the seed particles prior to the seeded polymerization of St-MMA-AA.

due to the crosslinking induced by MATS; (2) an increase in the amount of surfactant (ABSA and SDBS; compare C6 to C8, C7 to C9, and C4 to C5). The decrease in particle size with increasing amount of surfactant was also observed in the polymerization of D_4 via the anionic catalysis (see A24, A25, A26, A47, and A48 in Table I).

A general observation was that, along with a constant increase in particle size during polymerization, the particle number has constantly decreased. The data obtained for one of the cationic polymerizations of D_4 (C6 in Table II) are presented in Table III as a representative example. These results indicate that the particle growth during polymerization is, at least partially, accomplished via coagulation.

Preparation of PD₄–P(St-MMA-AA) Core–Shell Latex Particles

Among the PD₄ latexes prepared by anionic catalysis, A23, A25, and A48 of Table I were selected for seeded polymerization of St-MMA-AA because of their stability and small particle sizes; and among those prepared by cationic catalysis, C3, C6, and C10 of Table II were selected as seeds because of the low surfactant amounts employed during their preparation, thus reducing the probability of generation of new particles involving only P(St-MMA-AA).

The oil-soluble AIBN was first used as initiator in the seeded polymerization. When no additional SDBS was added to the system, none of the polymerizations was successful due to a complete or partial flocculation of the seed and newly formed P(St-MMA-AA) particles. When additional (0.1 g) SDBS was added, the flocculation could be avoided, and a large number of tiny particles (<60 nm) of P(St-MMA-AA) was produced (SP1 in Table IV). It is clear that the monomers have not polymerized on the surface of the seed particles but in the monomer droplets produced by stirring. The particles flocculated in the absence of surfactant but remained as a stable dispersion when additional surfactant was introduced.

Further, the water-soluble initiator APS was employed. Experiments were first carried out with PD_4 latexes prepared by anionic catalysis. As a general observation, stable latexes, with limited flocculation during polymerization, were obtained. In the run SP2 (where 0.1 g of SDBS was employed in the seed latex preparation), the latex was partially flocculated (about 20%); in SP3 (where 0.14 g of SDBS was employed in the seed



Figure 2 TEM micrographs of latex particles after the seeded polymerization of St-MMA-AA with seed latex of PD₄ prepared by anionic polymerization and APS as initiator. (A) Seeded polymerization based on PD₄ seed particles of 192 nm, showing that numerous new particles were formed. (B) Seeded polymerization based on PD₄ seed particles of 143 nm showing that core-shell particles were generated along with new particles.

latex preparation), less than 10% flocculated; and little flocculation was found in SP4 (0.16 g SDBS used in the seed latex preparation).

The latexes were subjected to TEM observation, and the results are presented in Table IV. This table indicates that new particles were generated, particularly when the seed particles were large (SP2 and SP3 in Table IV), and no coreshell particles were detected [Figure 2(A) consti-



Figure 3 TEM micrographs of latex particles after seeded polymerization of St-MMA-AA using a PD₄ seed latex prepared by cationic polymerization and APS as initiator: (A) seed particle size, $D_p = 330$ nm (SP5 in Table IV); (B) seed particle size, $D_p = 280$ nm (SP6 in Table IV), with VD₄ coupling before the seeded polymerization; (C) seed particle size, $D_p = 240$ nm (SP7 in Table IV), with VD₄ coupling before the seeded polymerization.

tutes a micrograph of SP3]. The seeded latex (SP4), prepared under the same conditions but with smaller seed particles ($D_p = 143$ nm), however, contains core-shell particles [Fig. 2(B)]. The core size (~ 150 nm) in some of the particles is in agreement with that of the seed particles (A48) of 143 nm. Table IV indicates that SP4 also contains numerous small particles formed during the seeded polymerization.

The subsequent experiments were carried out using seed latexes prepared by cationic catalysis. The results are also presented in Table IV. The



Figure 4 TEM micrograph of P(St-MMA-AA) latex (S_1) (St/MMA/AA: 87.2/4.8/8.0 by moles).

TEM micrographs of SP5, SP6, and SP7 of Table IV are given in Figure 3(A)–(C), which clearly shows that particles with core–shell morphology are present. In Figure 3(A), the sizes of the cores are very different, with the largest being around 450 nm, and the smallest being around 200 nm, while the average size of the seed particles used was 330 nm (SP5 in Table IV). This could be attributed to the particle size dispersity in the seed latex itself. However, the relatively small size dispersity of the seed particles (Table II) suggests that the large dispersity of the core–shell particles is caused by coalescence during the second stage of polymerization for the larger sizes

and by a possible contraction of the flexible PD_4 particles for the smaller ones. When the seed particle size decreased from 330 to 280 nm (SP6 in Table IV), the core–shell morphology could be identified in all the particles, but again the core size varied between 200 and 300 nm, a range smaller than that observed for SP5. The different behaviors of SP5 and SP6 are due most likely to the employment of the coupling agent, VD_4 , before the seeded polymerization. When a seed latex with a smaller particle size of 240 nm and the coupling agent VD_4 were employed, the core–shell particles became of more uniform size [SP7 and Fig. 3(C)].

To ensure that this core-shell morphology is not an artifact caused by a possible phase separation in P(St-MMA-AA) itself, a latex of P(St-MMA-AA), with the same monomer composition as in the seeded polymerization, was prepared under similar experimental conditions, in the absence of a PD_4 seed latex. The TEM micrograph in Figure 4 shows that no core-shell morphology was generated.

Properties of the Core-Shell Latex and its Polymer

The experimental results summarized in Tables V and VI were carried out to provide supplementary information regarding the core-shell morphology of the PD₄-P(St-MMA-AA) particles. The T_g determinations (Table V) revealed that the core-shell polymer, as well as the polymer blends of PD₄ with S₁, exhibit the following two T_g s: one around -106°C, representing that of PD₄, and another at 103°C, representing that of P(St-MMA-AA) copolymer. This provides evidence that polysiloxane is indeed present in the core-shell particles. The contact angles of water droplets and the water absorption of the polymers, listed in Table V, provide additional support for the

Samples	S_1	SP7	PD_4/S_1 (15/85 wt)	$\begin{array}{c} \mathrm{PD}_4\!/\!\mathrm{S}_1 \\ (50\!/\!50 \ \mathrm{wt}) \end{array}$	$\begin{array}{c} \mathrm{PD}_4\!/\!\mathrm{S}_1 \\ (75\!/\!25 \ \mathrm{wt}) \end{array}$	PD_4
Glass transition temperature $(T_{\sigma}/^{\circ}C)$	103	-106 & 103	-105 & 103	-104 & 105	-105 & 103	-115
Contact angles (water-polymer)	$46 \pm 5^{\circ}$	$60 \pm 4^{\circ}$	$70 \pm 2^{\circ}$	$92 \pm 3^{\circ}$	$90 \pm 2^{\circ}$	$110 \pm 7^{\circ}$
Water adsorption (water-polymer wt %)	26.70	18.61 ± 0.09	15.14 ± 0.05	15.05 ± 0.08	7.77 ± 0.10	0.78 ± 0.03

Table V Physical Properties of PD₄, P(St-MMA-AA) (S₁), Their Core-Shell Polymer, and Blends

Samples	\mathbf{S}_1	SP7	PD_4/S_1^{a} (15/85 wt)	PD_4
D_{n} (nm)	450	420	_	250
Spec surface $(10^5 \text{ cm}^2/\text{g})$	1.26	1.37	1.44	2.45
OH ⁻ -polymer (mmol/g)	0.53 ± 0.02	0.29 ± 0.02	0.45 ± 0.02	0
$\frac{10^{-15} \text{ COO}^-}{(\text{cm}^{-2})}$	2.55 ± 0.10	1.30 ± 0.09	1.90 ± 0.08	0

Table VI Surface Charges on Latex Particles of PD₄, P(St-MMA-AA) (S₁), and of the Core-Shell Polymer

^a Calculated based on the composition using the data obtained for S_1 and PD_4 latexes.

presence of a core-shell morphology in the PD₄-P(St-MMA-AA) latex particles. The table shows that PD_4 is characterized by a very large contact angle and a low water absorption, and S_1 is characterized by a small contact angle and a high water absorption due to its higher hydrophilicity. The blend samples display values between those of PD₄ and S₁ polymers. By comparing the coreshell polymer SP7 with any other polymers of Table V, one can see that its contact angle and water absorption are the closest to those of S_1 . This indicates that P(St-MMA-AA) constitutes the shell of the core-shell particles in the SP7 sample. Finally, the surface charge density due to the carboxyl groups was determined for the latexes SP7, S_1 , and PD_4 (Table VI). As expected, PD₄ did not display any detectable carboxyl groups. A value of 1.30×10^{15} COO⁻/cm², comparable to that of the S_1 latex particles, was obtained for the core-shell particles of SP7.

Pore Generation in the Silicon-Containing Core-Shell Particles

Pores have been generated in these particles by an alkali–acid treatment¹⁷ (Table VII), and some typical TEM micrographs are presented in Figure 5.

As noted in a previous article regarding the coreshell latex particles of P(St-MMA)-P(St-MMA-AA),²⁵ a larger volume increase of the particles was obtained for lower pH values during the acid treatment. This observation is confirmed in the present case as well, the volume increase being 31% at a pH of 1.2–1.5 [Fig. 5(A)] and only 15% at a pH of 2.0– 2.2 [Fig. 5(B)]. In the alkali treatment step, at pH 12.0, the volume expansion was larger than that obtained at pH 12.2. Figure 6 presents micrographs of the particles just after the alkali treatment at pH 12.0 [Fig. 6(A)] and pH 12.2 [Fig. 6(B)].

A further examination of the latex particles of Figure 5(A) shows that the following two types of porous latex particles are present: particles with a darker core, similar to those present before the alkali-acid treatment, as well as particles in which the cores disappeared after the alkali-acid treatment. The diffusion of the PD₄ polymer chains away from the particle center during the treatment constitutes a possible explanation.

CONCLUSIONS

Core–shell latexes with a poly(dimethyl siloxane) $[PD_{4}]$ core and a poly(styrene-methyl methacry-

Pores

Yes Yes Yes

Yes

$\Delta \mu = 0$							
pH in Alkali–Acid Treatment	D_p (nm) after Alkali Treatment	D_p (nm) after Acid Treatment (D_f)	$D_f/D_p^{\rm a}$	$\Delta V^{ m b} \ (\%)$			
		100	1				
12.0/1.5	475	460	1.095	31.3			
12.0/1.2	475	460	1.095	31.3			
12.2/2.2	440	440	1.048	15.1			
12.2/2.0	440	440	1.048	15.1			

Table VII Alkali-Acid Treatment of the Core-Shell Particles of PD./P(St-MMA-AA)

^a Particle size ratios after (D_f) and before $(D_p = 420 \text{ nm})$ the alkali-acid treatment.

^b Particle volume increase after alkali-acid treatment.



Figure 5 PD_4 -P(St-MMA-AA) core-shell latex particles after the alkali-acid treatment for the pH's: (A) 12.0/1.2; (B) 12.2/2.0.

late-acrylic acid) [P(St-MMA-AA)] shell have been prepared via the seeded emulsion polymerization of St-MMA-AA upon PD_4 seeds. The seeds have been obtained via the ring-opening emulsion polymerization of octamethyl tetracyclosiloxane by using an anionic or a cationic catalyst. The most successful procedure was based on a cationic catalyst (alkylbenzene sulfonic acid). The most uniformly seeded particles have been achieved when the seed particles have been sufficiently small and a coupling agent, 2,4,6,8-tetramethyl-2,4,6,8-tetravinyl cyclotetrasiloxane (VD₄), between the seed and shell was used. The seeded particles were subjected successively to alkali and acid treatments to generate pores in the shell in order to make the core accessible to the external medium.



Figure 6 PD_4 -P(St-MMA-AA) core-shell latex particles after the alkali treatment for the pHs: (A) 12.0; (B) 12.2.

The silicon polymers are interesting for the following two reasons: (1) they are biocompatible, and (2) they have low glass transition temperatures. Because they have very low T_g 's, they cannot be handled easily. However, as the cores of core-shell latexes, they could be useful as constituents of composite materials with enhanced impact strength, even at very low temperatures.

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