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Poly(alkyl methacrylate-*b*-sulfonated glycidyl methacrylate). A New Amphiphilic Polymeric Surfactant for the Preparation and Stabilization of Polymer Acrylic Latices in Aqueous Medium

L. Leemans, R. Fayt, and Ph. Teyssié*

Laboratory of Macromolecular Chemistry and Organic Catalysis, University of Liège, Sart-Tilman B6, B-4000 Liège, Belgium

N. C. de Jaeger

R & D Laboratory, Agfa-Gevaert, B-2510 Mortsel, Belgium

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ABSTRACT: Poly(alkyl methacrylate-*b*-sulfonated glycidyl methacrylate)s are a class of new amphiphilic block polymeric surfactants that can be used for the preparation and stabilization of very fine and stable polymer acrylic latices in aqueous medium. The strong anionic block polyelectrolyte creates an electrosteric barrier that efficiently prevents particles for flocculation. High critical coagulation concentrations were obtained for these polymeric surfactant-stabilized latices. By substituting the anchoring poly(methyl methacrylate) block by a poly(allyl methacrylate) in the radical emulsion polymerization of latices, the polymeric surfactant becomes covalently linked with the particles, and cross-linking occurs as evidenced by GPC measurements. Photon correlation spectrometry measurements give an estimate of the average adsorbed layer thickness, closely corresponding to the extended chain length of the polyelectrolyte block.

Introduction

Polymer latices, particularly in aqueous medium, represent nowadays a topic of prime importance for both basic science[1] and application research.

Several types of polymer surfactants are being used successfully in the preparation and stabilization of those latices. As a few typical nonlimitative examples, suffice it to cite the following: nonionic amphiphilic block copolymers, such as poly(ethylene oxide-*b*-propylene oxide-*b*-ethylene oxide),[2] and poly(styrene-*b*-vinyl alcohol) used to stabilize polystyrene latices in water;[3] copolymers comprising poly(vinyl alcohol) or poly(acrylic acid), which owe their particular amphiphilic nature to some blockiness[4] of unreacted vinyl acetate or alkyl acrylate units respectively, after hydrolysis; and copolymer containing sequences of quaternized amino groups of, e.g., poly(ionenes), poly(vinylpyridines), and poly(aminoalkyl methacrylates).

Polymer surfactants offer the advantage of important sterical stabilization of dispersions, while most classical low molecular weight (MW) surfactants only operate through electrostatic stabilization. The ideal combination of both mechanisms, which has been called "electrosteric" stabilization by Napper[5] and is beautifully exemplified in nature, should thus be achievable by polymer diblock surfactants comprising one strong polyelectrolyte block.

Many enticing investigations and possible applications ask for such a strong anionic polyelectrolyte block: indeed nonionic poly(ethylene oxide) (PEO) becomes insoluble in water at elevated temperature, while weak polyelectrolyte blocks display pH-dependent ionization, causing variable solvation of polymer coils and consequently changing of steric barrier properties: i.e., poly(meth)acrylic acid and quaternized poly(aminoalkyl methacrylates). In that respect, we want to report here on the properties of polymer latices stabilized with a new family of poly(alkyl methacrylate-*b*-sulfonated glycidyl methacrylate) block polymers (PalkMA-*b*-SPGMA).[6,7] As illustrated hereafter, these block polymers were successfully used as polymer surfactants, as well for the poststabilization of acrylic latices, as for the radical emulsion polymerization of several monomers (e.g., ethyl or butyl acrylate and methyl methacrylate).

Experimental Section

Radical emulsion polymerizations: Latices were prepared batchwise under magnetic stirring, in a Pyrex flask equipped with a reflux condenser. For a typical emulsion polymerization, 20 g of ethyl acrylate in 80 g of water, containing 1 g of PMMA-*b*-SPGMA and 100 mg of $K_2S_2O_8$ was stirred at 150 rpm. After passing a stream of nitrogen through the emulsion, it was heated at 80 °C in a water bath, whereupon the emulsion polymerization quickly started. A bluish white latex had formed after a few minutes, but heating was continued for another 30 min. After filtration a 98% yield was obtained.

For poststabilization purposes, a poly(ethyl acrylate) latex was prepared with similar equipment, using a very low amount (0.1%) of sodium oleyl tauride sulfonate (NaOTS), a classical low molecular weight surfactant, in a radical-initiated ($K_2S_2O_8$) emulsion polymerization in water (80 °C, 30 min): it displayed a mean diameter of 79.1 ± 0.19 nm. To this latex were added (at room temperature) increasing quantities of a solution of PMMA-*b*-SPGMA in water, the systems being kept under stirring overnight for equilibration.

GPC measurements were carried out in THF at 45 °C using a Hewlett Packard 1090 liquid chromatograph equipped with four Polymer Laboratories PL gel columns (10^5, 10^3, 500, and 100 Å) and a Hewlett Packard 1037 refractive index detector. A PS calibration curve allowed estimation of MW's. For cross-linked particles, previous filtration on 0.45-μm mesh eliminated the peak (monitored on a Waters 200 instrument) seen in Figure 6, trace c.

Mean particle diameters were obtained by photon correlation spectroscopy (PCS) at 27 °C. A Malvern apparatus equipped with a 5-mW He–Ne Spectra Physics laser was used. The scattered intensity was measured under a 90° angle.

For determination of the critical coagulation concentration (CCC), a stopped-flow spectrometer and a Tektronix transient recorder were used at room temperature to monitor the difference in optical density (OD) of the lattices after adding KCl electrolyte. The initial slopes of the experimental OD–time plots are directly proportional to the rate of coagulation or inversely proportional to W, the stability ratio, i.e., $d(OD)/dt \sim 1/W$. The CCC is determined as $W = 1$ (i.e., log = 0).[8]

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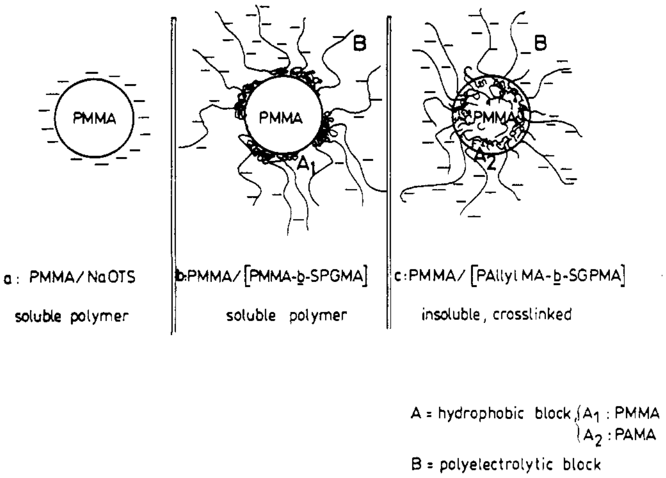
Table I
Characteristic Data for PMMA-*b*-SPGMA Surfactants

	composition,[a] mol %					% S (sulfonation yield)[c]
sample	α-MeSt	MMA	GMA	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[b]	
1	7.9	17.3	74.8	9100	1.08	7.1 (65)
2	8.2	17.5	74.3	6600	1.12	7.5 (72)
3	7.9	17.5	74.6	10500	1.14	7.2 (68)

[a] From inittially added monomer quantities, for a living anionic polymerization with quantitative yield. [b] From GPC, before sulfonation. [c] Elemental S analysis, after sulfonation and purification by dialysis of the block copolymer.

Chart I



Results and Discussion

PalkMA-*b*-SPGMA's were synthesized as previously reported,[6,7] and characteristic data for the three block copolymers used, all of them water-soluble, are reported in Table I.

Characterization of the Electrosteric Barrier in Poststabilized Systems. A block copolymer poststabilized latex can be schematically represented as in Chart Ib, where the hydrophobic PMMA blocks (A_1) are adsorbed at the surface of the latex particle and the well-solvated sulfonated PGMA blocks (B) constitute the electrosterical barrier. Characterization of that barrier was achieved by using photon correlation spectrometry (PCS): for that purpose, poststabilization experiments were carried out by adding an aqueous solution of the polymer surfactant to a classically preformed poly(ethyl acrylate) (PEA) latex having a mean particle diameter of 79.1 ± 0.19 nm (see the Experimental Section).

Successive addition of block copolymer to the latex resulted in a regular increase of the PCS particle size, upon adsorption of the amphiphilic macromolecules at its surface. With PCS one measures the so-called hydrodynamic diameter of the particle. In the case of a monomeric surfactant, this diameter represents the hard particle core plus a small average thickness of adsorbed material. When a sterical barrier is present, the average adsorbed layer thickness is much higher.

An estimate of the average adsorbed layer thickness was obtained by substraction of the initial size value, and Figure 1 clearly illustrates its progressive increase versus the amount of polymer surfactant added. Two different block copolymers were used (samples 1 and 2, Table I), displaying the same composition but different MW's, the higher one building up as expected the thickest adsorption layer. At concentrations higher than 10%, that layer thickness tends to reach asymptotically a constant value of approximately 12 and 8 nm for samples 1 and 2, respectively, probably corresponding to full coverage of the particle with the polymer surfactant, so following probably a Langmuir type of adsorption mechanism.[9] Although, on the basis of the general form of the adsorption isotherm (Figure 1), it appears that the monolayer coverage is reached at rather high block copolymer concentrations. The isotherm is apparently not of the high affinity type following Gibbs isotherm classification. The reason for this phenomenon has probably to do with the fact that the prepared PEA latex is negatively charged and opposes more or less the adsorption of the also negatively charged block copolymer.

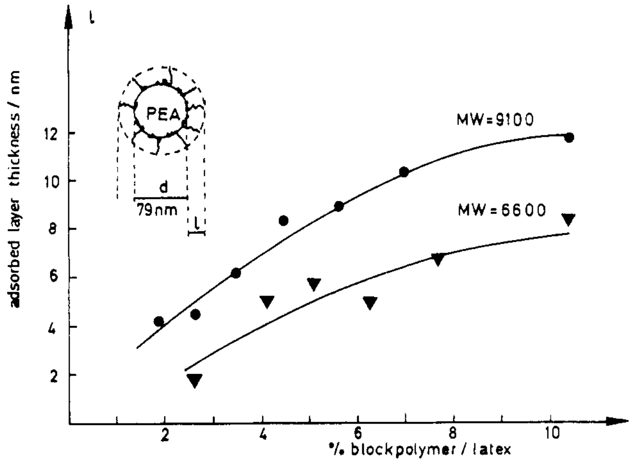


Figure 1. Adsorbed layer thickness of the electrosteric barrier on PEA latex particles versus an added quantity of PMMA-*b*-SPGMA block copolymer.

In a more speculative simple approach, one can now calculate that this adsorbed layer thickness corresponds rather closely to the practically extended chain length of the polyelectrolyte block, i.e., 12.9 and 9.2 Å for samples 1 and 2, respectively, in a monolayer model with a planar zigzag chain conformation. The asymptote concentration also allows an estimation of the mean area occupied by one block copolymer molecule, assuming a 75% adsorption: the cross section at the surface amounts to 900 $Å^2$/molecule in satisfactory agreement with the mean gyration radius of the nonionic block.

Direct evidence for the existence of the sterical barrier is given by transmission electron microscopy (TEM). The diameter of the sterically stabilized particles will be essentially that of the hard core, as there is a complete collapse of the stabilizing moiety in the high-vacuum conditions used.

Figure 2 shows a TEM micrograph of a PMMA-*b*-SPGMA-stabilized PMMA latex. The hydrodynamic diameter as measured by PCS was 92 nm, the average hard-core diameter as measured from the micrograph with the aid of a calibrated polystyrene latex particle (see the center of the micrograph; diameter = 106 nm) was 53 nm. This gives us an adsorbed surface layer thickness of 19 nm. Although fairly high compared to the previously calculated value of 12 nm, we think that the hard-core diameter was underestimated due to electron beam particle melting in the TEM microscope. Nevertheless, it is clear that highly efficient steric barriers can be generated by these adsorbed block copolymers.

Figure 3 shows the electrokinetic properties of the block copolymer PEA latex in comparison with a classical PEA latex prepared with sodium oleyl tauride sulfonate as a function of pH. The ζ potential calculated with the help of the Smoluchowski equation is about the same for the two types of latices and practically independent of pH. This guarantees a stable dispersion over a broad pH range.

The difference between a latex prepared with NaOTS and one prepared with PMMA-*b*-SPGMA block polymer

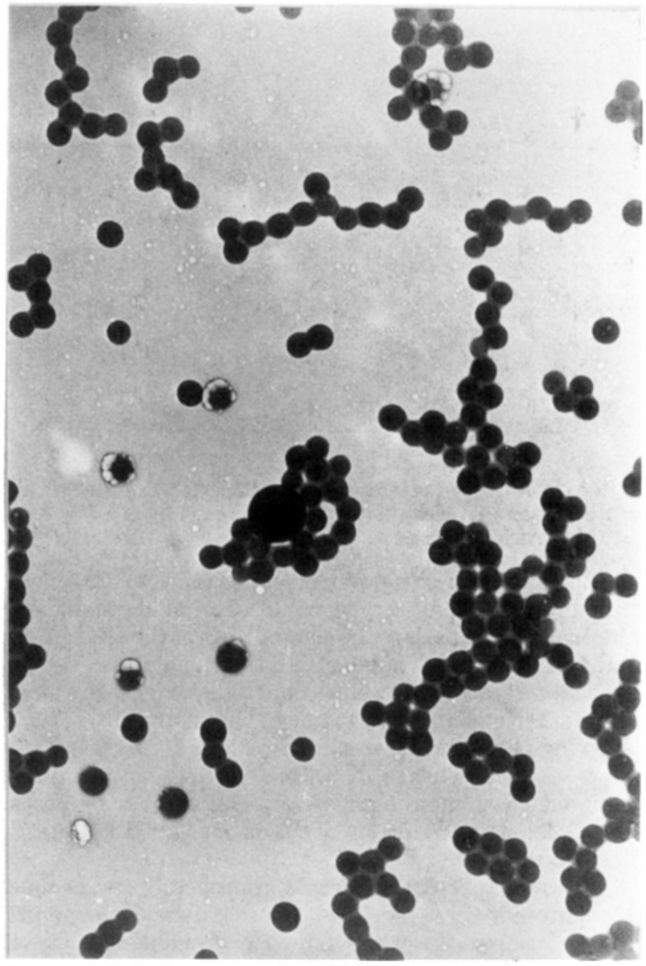


Figure 2. TEM micrograph of PMMA latex particles prepared with PMMA-*b*-SPGMA (center of micrograph is a 106-nm calibration PS latex particle).

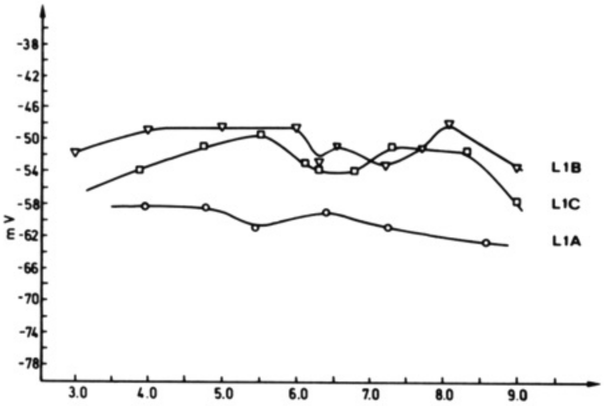


Figure 3. ζ potential of PEA latex as a function of pH. L1A: PEA latex with NaOTS. L1B: PEA latex with PMMA-*b*-SPGMA ($\bar{M}_n$ = 10 500). L1C: PEA latex with (PMMA-*b*-SPGMA) ($\bar{M}_n$ = 27 000).

lies in the fact that the electrostatic repulsion starts to act on an approaching particle much further away from the solid particle surface in the case of a block polyelectrolyte stabilized PEA (Chart I). As a result of this, the attraction energy, which is high in a close approach situation, is completely shielded and out of operation.

The aforementioned data finally indicate that the so-formed electrosteric barrier should be highly efficient in preventing these particles from flocculation. This was indeed demonstrated by measurement of the critical coagulation concentration (CCC) by stopped flow spectrometry. For a PEA latex stabilized with a PMMA-*b*-SPGMA surfactant, a CCC of 1.2 M was determined (see the Experimental Section), in sharp contrast to the CCC values of many colloidal systems stabilized with classical low MW surfactants and having CCC's lower than 0.15 M.[10] Figure 4 shows the dependence of the stability ratio *W* (see the Experimental Section) as a function of added KCl. The onset of the horizontal part of the curve, where the system shifts from a slow to a fast flocculation mechanism, is the CCC representative for the stability of the latex toward flocculation.

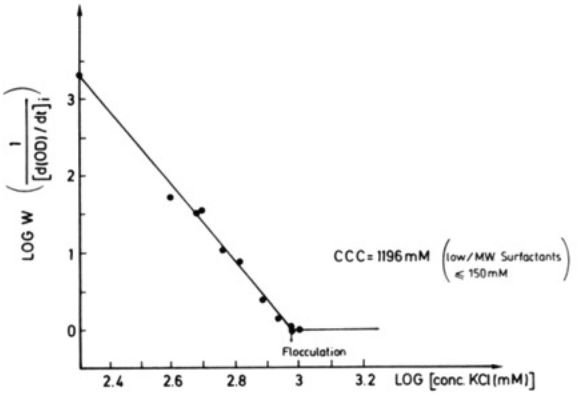


Figure 4. Plot of the logarithm of the stability ratio *W* versus added concentration of KCl electrolyte (CCC = 1.2 M for log *W* = 0).

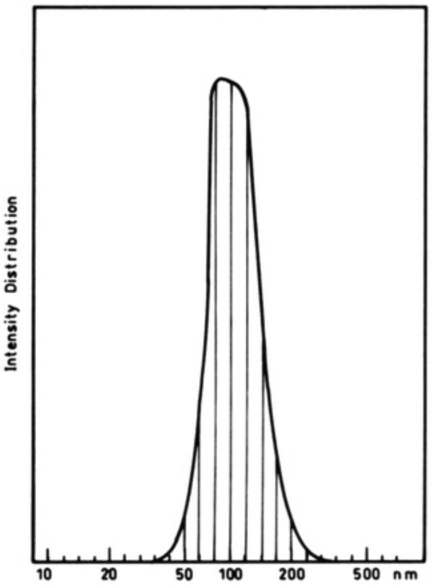


Figure 5. Particle size distribution of a PMMA latex measured by photon correlation spectroscopy (polymerization conditions: see the Experimental Section).

Radical "Emulsion" Polymerization with PMMA-*b*-SPGMA as a Polymeric Surfactant. Latices were prepared according to the Experimental Part, using a PMMA-*b*-SPGMA copolymer (sample 1). A reasonably narrow particle size diameter is obtained with a *Z*-average mean of 99.0 nm and a standard deviation of 31.1 nm, based on a log normal fit of the data. A typical particle size distribution is shown in Figure 5.

Another important size feature is the content of microscopic coagulum as defined in ref 10. This coagulum cannot be measured by using a PCS technique, due to the fact that PCS requires a very high dilution, so that the small quantity of the upper micron particles (between 10^{-2} and 10^{-5} vol %) disappears. Monitoring this small quantity can be only achieved with a so-called Coulter threshold technique.[10] Table II shows a comparison of a classically prepared PEA latex and the block polymer prepared latex

Table II
Evolution of the Number of Upper Micron Particles on Mixing of PEA Latices Prepared with NaOTS (Sample 1) and PMMA-*b*-SPGMA (Samples 2–5) with Gelatin

sample	$C_{\text{block polymer}}$/ %	$n > 5$ μm/mL	$n > 5$ μm/mL in gelatin	increase factor
1. PEA latex	0	2.2×10^4	5.2×10^4	2.41
2. PEA latex + B_1[a]	2.5	3.4×10^4	3.8×10^4	1.11
3. PEA latex + B_1	5.0	9.0×10^4	9.8×10^4	1.08
4. PEA latex + B_2[b]	2.5	4.3×10^4	1.0×10^5	2.40
5. PEA latex + B_2	5.0	6.1×10^4	9.5×10^4	1.56

[a] $\bar{M}_n$(PMMA-*b*-SPGMA) (before sulfonation) = 10 500. [b] $\bar{M}_n$(PMMA-*b*-SPGMA) (before sulfonation) = 27 000.

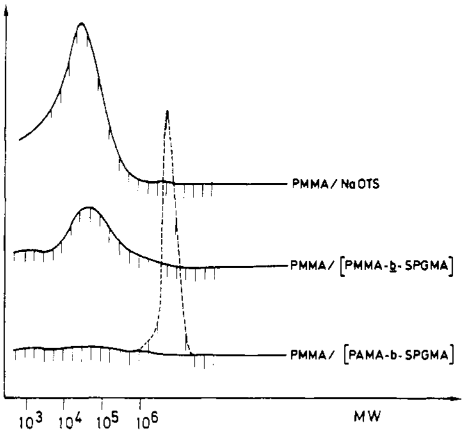


Figure 6. GPC chromatograms of PMMA latices prepared (a) with NaOTS, (b) with PMMA-*b*-SPGMA, (c) with PAMA-*b*-SPGMA, (- - -) without filtration prior to elution, and (—) after filtration on 0.45-μm mesh.

with respect to the number of upper micron particles present. Typically this quantity determines the filtration properties of the latices[10] and affects its coating properties.

In addition, the same table shows the increase of the amount of microscopic coagulum when the latices are mixed with a high molecular weight polyelectrolyte such as gelatin. The increase is typically due to the bridging flocculation. The block polymer–PEA latex apparently shows a better protection against this phenomenon than a latex prepared with a classical low molecular weight emulsifier (NaOTs) for block polyelectrolyte stabilizing chains of not too high molecular weight.

While PMMA-*b*-SPGMA stabilizes latex particles by adsorption of the hydrophobic part of the polymer at their surfaces, a molecular modification of the polymeric surfactant can lead to another still more interesting anchoring mechanism. Poly(allyl methacrylate-*b*-sulfonated glycidyl methacrylate) (PAMA-*b*-SPGM) proved indeed to be also a very efficient polymeric surfactant for the radical emulsion polymerization. Acrylic latices with a mean particle diameter (*Z*-average) of about 150 nm were readily prepared in nearly quantitative yield. Moreover, as polymerization proceeds, this surfactant will be covalently linked to the particles and will thus lead to their cross-linking by the allyl moiety. This was supported by GPC chromatograms of latices to which THF was added to dissolve the soluble polymer. Three different latices were prepared: (a) with NaOTS, (b) with PMMA-*b*-SPGMA, and (c) with PAMA-*b*-SPGMA. Latices a and b give GPC chromatograms (Figure 6a,b) showing the existence of a soluble polymer with a broad molecular weight distribution, roughly going from 10^3 to 10^6 with a peak MW of about 2×10^5. In contrast, the GPC chromatogram of latex c (Figure 6c) displays an entirely different elution pattern: it hardly shows soluble polymer in the 10^3–10^6 range, but one important peak appears at the exclusion limit of the GPC; when no filtration was done, this peak is suppressed when finer mesh (0.45-μm) preliminary filtration is applied. That should be due to cross-linked latex particles having a very large hydrodynamic volume as compared to soluble polymer coils and thus passing through the columns without separation (see the Experimental Section). It is thus plausible that preparation of latices in the presence of PAMA-*b*-SPGMA leads to the expected cross-linking with the polymeric surfactant covalently anchored on these particles.

That situation promotes striking properties, as illustrated by the fact that small particles with a relatively narrow size distribution can equally be prepared this way, the stability of which against coagulation is amazingly high since these latices can be diluted with, e.g., 1 M Al $(NO_3)_3$ solutions, withoug noticeable macroscopic precipitation. Chart Ic illustrates this latter situation, as compared to the other possible stabilization mode and morphologies (low-MW surfactant (a) and adsorbed block copolymer (b)).

Conclusions

The use of an amphilic block polymer containing one strong polyelectrolyte moiety as a polymer surfactant in the radical emulsion polymerization of different monomers allows for the preparation of very fine and stable latices. By substitution of the adsorbing PMMA block for a PAMA block, the emulsifier becomes covalently linked with the particles and cross-linking occurs as evidenced by GPC experiments. On the other hand, it was shown that the adsorption of the block polymer at a latex particle surface leads to an increase in that particle diameter, creating an electrosteric barrier and possible applications for the polymeric surfactant as a poststabilizer of preformed latices. High CCC values for all these polymeric surfactant stabilized latices are indicative of their remarkable resistance against flocculation. These results are to be related to previous studies[11] illustrating the high efficiency of a poly(styrene-*b*-stearyl methacrylate) diblock copolymer in stabilizing upon adsorption of carbon black particle (ca. 300 nm) dispersions in isodecane. Such approaches obviously pave the way for a powerful control of surface properties, morphologies, and dynamic behavior of particle dispersions in liquids, either organics or water.

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Registry No. $H_2C{=}CHCO_2Et$ (homopolymer), 9003-32-1.