

Dispersions of carbon black in a non-polar medium stabilized by poly(styrene-*b*-stearyl methacrylate) amphipathic block copolymers

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Well characterized poly(styrene-*b*-stearyl methacrylate) copolymers were synthesized by a living anionic copolymerization process. The polystyrene block of these amphipathic copolymers dissolved in a selective solvent of the poly(stearyl methacrylate) block adsorbs onto carbon black. An experimental isotherm in agreement with the Langmuir equation is observed. Considerations about the area occupied by the copolymers at the carbon black surface in isododecane are in favour of steric stabilization. These copolymers are thus able to stabilize fine and stable carbon black dispersions in isododecane; thus there is a possibility of application in liquid toner electrophotography.

(Keywords: amphipathic block copolymer; poly(styrene-*b*-stearyl methacrylate); carbon black; stabilized dispersions; adsorption)

INTRODUCTION

Stabilizing dispersions of finely divided solids in non-polar media is very important in the preparation of inks and paints. In particular, applications such as the preparation of liquid electrophotographic toners require very fine, stable colloidal pigment dispersions.

In a non-polar medium, steric stabilization of dispersed particles is the main operating mechanism available¹. The most efficient steric stabilizers are found empirically to be amphipathic block or graft copolymers, i.e. macromolecules consisting of a block insoluble in the dispersion medium associated with a soluble one. Adsorbed onto the surface of the particle, the insoluble block is the anchoring block, while the soluble one is referred to as the stabilizing component, and builds up a coalescence barrier responsible for the stability of the colloidal dispersion². Block or graft copolymers are therefore efficient stabilizers as long as the constituent blocks are mutually repulsive and interact selectively with the particle and the dispersion medium, respectively. From that point of view, block copolymers of styrene and stearyl methacrylate (PS-*b*-PSMA) might be of great interest.

Synthesis of this type of copolymer, which relies upon the coupling of telechelic polymers prepared by free-radical polymerization, has been described. It has also been stated that anionic polymerization is not well suited for the preparation of PS-*b*-PSMA, especially in a large-scale process³. This paper aims to report a straightforward anionic method allowing amphipathic PS-*b*-PSMA to be prepared in a controlled way, i.e. with the molecular characteristics required by special applications.

EXPERIMENTAL

Monomers

Styrene and stearyl methacrylate were dried over CaH₂ under a high-purity nitrogen atmosphere and then distilled under reduced pressure. Stearyl methacrylate was kindly supplied by Rohm and Haas Co. Just before polymerization, styrene was distilled under vacuum from a benzene-fluorenyllithium suspension. Stearyl methacrylate was vacuum distilled after addition of a solution of triethylaluminium in hexane. Triethylaluminium reacts preferentially with protonated compounds (water, fatty alcohols and acids) that are highly reactive towards carbanions. The appearance of a greenish yellow colour upon adding triethylaluminium to the methacrylate indicates formation of the triethylaluminium methacrylate complex and is an indicator for the monomer purity⁴.

Initiator

sec-BuLi was purchased as a solution in isopentane. This solvent was removed by vacuum distillation and replaced by dried heptane.

Solvent

Tetrahydrofuran (THF) was refluxed over sodium-benzophenone for several days and distilled from it under a high-purity nitrogen atmosphere.

Polymerization

Polymerizations were carried out in ordinary laboratory glassware. The reaction flask was evacuated on a vacuum line and thoroughly dried by flaming. Solvent and monomer were transferred through stainless-steel capillaries.

In a typical polymerization experiment, 450 ml of dried THF were introduced into a 1000 ml Pyrex flask equipped with a septum-fitted stopcock. A small amount of α -methylstyrene (α -MeSt) (0.5 ml, 3.85×10^{-3} mol) was then added to the solvent and a 0.5 M sec-BuLi solution in heptane was added dropwise until the deep red colour of the α -methylstyryl anion was persistent. At that time, any protic impurities were eliminated, and the required amount of sec-BuLi (1.05×10^{-3} mol) was finally transferred into the reactor.

The flask was cooled to -78°C within a dry ice-acetone mixture. Styrene (St) (4.3 ml, 3.76×10^{-2} mol) was then added and the colour of the solution changed rapidly from deep red to orange. When the styrene feed had completely polymerized, the colour changed again from orange to deep red. At that point, an aliquot of the solution was withdrawn and the PS block analysed by g.p.c.. Stearyl methacrylate (SMA) (13.5 ml, 3.43×10^{-2} mol) was finally added dropwise. Since the monomer droplets immediately froze at -78°C , the flask was raised from the cooling bath. While the solution temperature was rising, the deep red colour suddenly changed to pale yellow, characteristic of the methacrylic anion, and the frozen monomer droplets gradually dissolved in the THF solvent. As polymerization proceeded, the solution became more viscous and opaque. When the temperature reached ca. -10°C , the solution became completely transparent and methanol was added to kill the living polymer. Polymerization thus proceeded gradually from a heterogeneous to a homogeneous system. This technique was preferred to other methods. For instance, SMA dissolved in THF prior to addition into the reactor allowed the polymerization to proceed under homogeneous conditions but led to very viscous solutions at -78°C .

Measurements

G.p.c. measurements were carried out using a Waters 200 instrument in THF at 35°C .

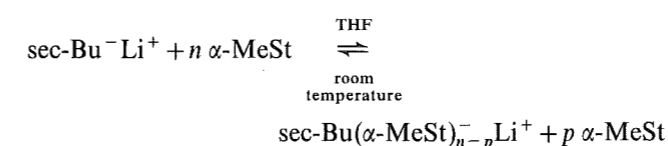
Toner dispersions in isododecane were prepared according to the well known steel-ball milling techniques using carbon black as a pigment and PS-*b*-PSMA copolymers as dispersion stabilizers. The amount of adsorbed block copolymer was determined from dispersions comprising 4 g of carbon black and 100 ml of isododecane. After centrifugation of the dispersion, the supernatant liquid was separated from the carbon black and evaporated to dryness. The equilibrium amounts of adsorbed and dissolved block copolymer were determined by gravimetric analysis.

RESULTS AND DISCUSSION

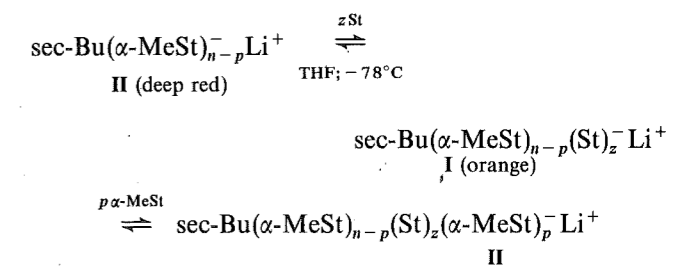
Block copolymerization of styrene and stearyl methacrylate initiated by α -methylstyryl anions

The PS-*b*-PSMA block copolymers were prepared by sequential addition of monomers to the initiator solution. The block copolymerization in THF can be schematically represented by the following reactions and equilibria:

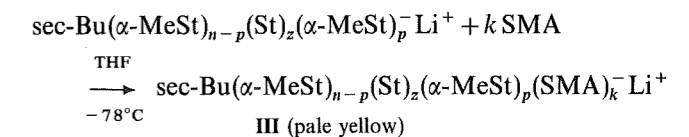
Initiation.



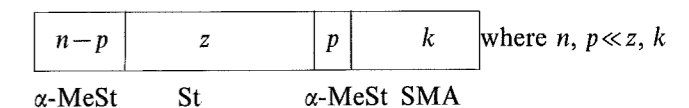
First block.



Second block.



The detailed composition of the α -methylstyryl-initiated block copolymer can thus be represented schematically as follows:



The styrene block was initiated by α -methylstyryl anions to provide α -methylstyryl-capped polystyrene chains⁵. The changes in colour from deep red to orange upon adding styrene to an α -methylstyryl solution and again from orange to deep red after all of the styrene had polymerized are clear evidence for the existence of an α -methylstyryl carbanion at the end of the polystyrene chains. Thus the α -methylstyryl carbanion capped polystyrene chains are then able to initiate the stearyl methacrylate; polystyryl anions on the contrary do not initiate the anionic polymerization of stearyl methacrylate.

Under the experimental conditions of styrene polymerization, i.e. THF at -78°C , stearyl methacrylate crystallizes readily and, accordingly, it is only polymerized on warming up the reactor until dissolution is promoted⁶. Low monomer concentrations ($<5\%$) have to be used in order to prevent as much as possible the solution from becoming highly viscous during polymerization.

Such poorly controlled conditions are usually responsible for a decrease in the monomer conversion and a broadening of the molecular-weight distribution. That the same drawbacks are observed in the anionic polymerization of other acrylic monomers has also been reported by Graham *et al.*⁷. Thus stearyl methacrylate is dissolved in THF before addition to the living poly(α -methylstyryllithium) solution. Nevertheless, at the low temperatures required for polymerization, gelation occurs, which makes the stirring of the reaction difficult.

Figure 1 shows g.p.c. chromatograms for a typical polymerization experiment (L21) in which $\bar{M}_n(\text{PS}) = 10300$ and $\bar{M}_w/\bar{M}_n = 1.15$ while $\bar{M}_n(\text{PS-}b\text{-PSMA}) = 24000$ and $\bar{M}_w/\bar{M}_n = 1.75$ (Table 1). Although the anionic polymerization of stearyl methacrylate results in a broadening of the MW distribution, the monomer conversion is quantitative and the block copolymer is virtually free from homopolymer as supported by selective extraction.

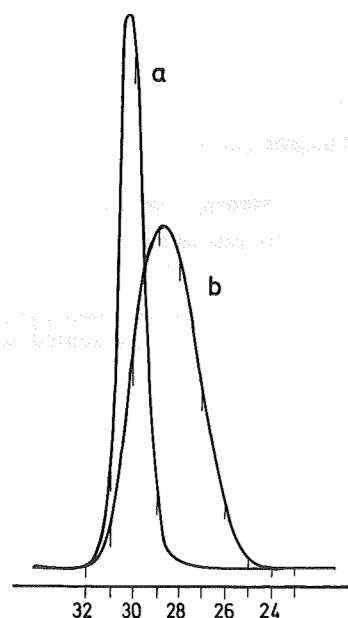
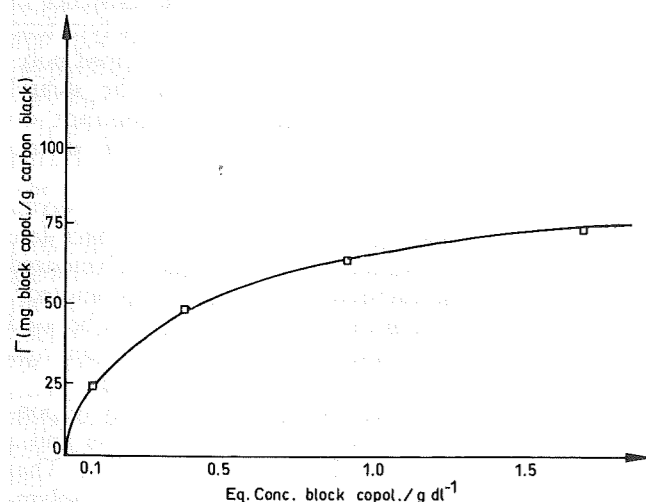
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Table 1 Characteristic data for PS prepolymers and corresponding (PS-*b*-PSMA) block copolymers

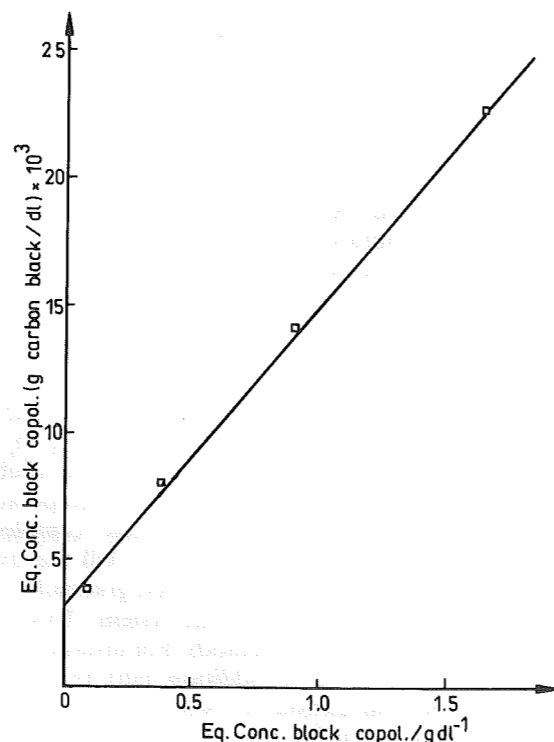
Sample	\bar{M}_n (PS)	\bar{M}_w/\bar{M}_n (PS)	\bar{M}_n (PS- <i>b</i> -PSMA)	\bar{M}_w/\bar{M}_n (PS- <i>b</i> -PSMA)
L21	10300	1.15	24000	1.75
L45	7900	1.15	26000	1.80
L56	3300	1.20	13000	1.80

**Figure 1** G.p.c. curves for (a) PS first block (initiating sequence) and (b) PS-*b*-PSMA block copolymer (L21)**Figure 2** Adsorbed quantity of PS-*b*-PSMA block copolymer L45 per gram of carbon black versus equilibrium concentration of block copolymer**Adsorption of PS-*b*-PSMA block copolymer at carbon black in isododecane**

The Langmuir adsorption equation may be written as:

$$\Gamma = \frac{\Gamma_{\max} k C_A}{1 + k C_A}$$

where Γ is the adsorbed quantity of product A at the surface, Γ_{\max} is the maximum value of Γ for a surface completely covered by the product A, C_A is the equilibrium concentration of A in solution and k is a measure of the

**Figure 3** Langmuir isotherm of L45 (PS-*b*-PSMA) block copolymer on carbon black (cf. Figure 2)

adsorption affinity. Strictly speaking, Langmuir's theory is only valid for the adsorption of a monomolecular gas, with formation of a monolayer at the surface. However, many systems involving adsorption of polymers on solid surfaces show experimental isotherms as pictured in Figure 2, where Γ (milligrams of polymer adsorbed per gram of carbon black) is a function of the equilibrium polymer concentration⁸. The observation of a plateau corresponds to the saturation of the surface by the adsorbed polymer. The above expression of the Langmuir equation can be rewritten as follows:

$$\frac{C_A}{\Gamma} = \frac{C_A}{\Gamma_{\max}} + \frac{1}{k\Gamma_{\max}}$$

and Γ can be calculated from the C_A/Γ versus C_A plot (Figure 3). Let us consider PS-*b*-PSMA block copolymer with a number-average molecular weight (\bar{M}_n) of 26000, a molecular-weight distribution $\bar{M}_w/\bar{M}_n=1.8$ and comprising a PS block with a \bar{M}_n of 7900. The maximum quantity of block copolymer adsorbed at complete surface coverage amounts to 86.9 mg block copolymer per gram of pigment. The specific surface for this carbon black amounts to 30 m² g⁻¹, and the area occupied by one macromolecule at the surface can thus be estimated at 16 nm²; i.e. the adsorbed chain would have a 'diameter' of about 4.5 nm. The root-mean-square end-to-end distance of random coils may be approximated by their 'diameter'

with $\langle r^2 \rangle^{1/2}/nm \sim 0.06M^{1/2}$ (M = molecular weight)². Using this approximation, $\langle r^2 \rangle^{1/2}$ for the aforementioned block copolymer amounts to 10 nm; the diameter for the PS block is thus ~ 5.3 nm, i.e. close to the previously calculated value of 4.5 nm.

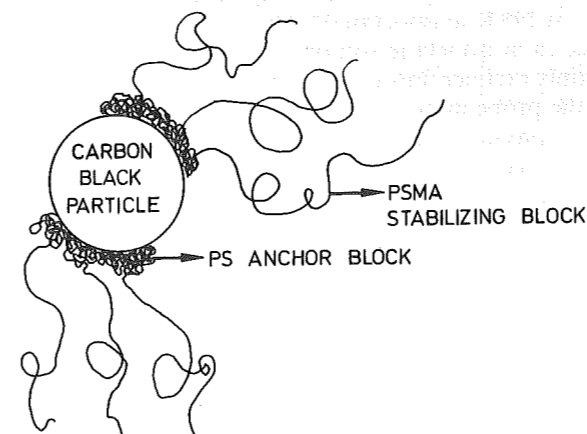
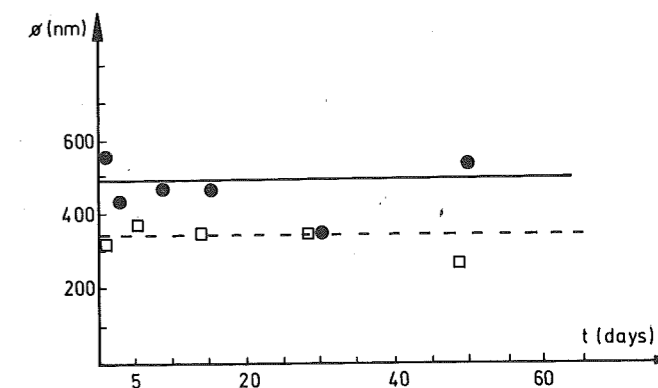
Despite crude approximations, results are consistent with a model of steric stabilization in which a collapsed PS block is physically adsorbed onto the carbon black surface from which a well solvated PSMA chain protrudes into the selective aliphatic solvent. Figure 4 shows the schematic representation of a carbon black particle stabilized by an amphipathic PS-*b*-PSMA block copolymer.

Stability of the particle dimensions of carbon black dispersions in isododecane stabilized by PS-*b*-PSMA block copolymer

Dispersions of carbon black particles in isododecane are efficiently stabilized by block copolymers of styrene and stearyl methacrylate. Particle diameters are indeed constant over a period of nearly two months. Figure 5 illustrates that behaviour for dispersions stabilized by the block copolymer L56 (PS-*b*-PSMA) of $\bar{M}_n=13000$ and $\bar{M}_w/\bar{M}_n=1.8$ and comprising a PS block of $\bar{M}_n=3300$ ($\bar{M}_w/\bar{M}_n=1.2$). Fluctuations in diameter might be due to uncertainties in the particle size measurements.

The L45 block copolymer, the PS block of which is twice as long as that of L56, has quite a similar efficiency.

These experimental observations support the very strong adsorption of the PS block onto the carbon black surface as well as the efficient coalescence barrier formed by the PSMA blocks. Similar observations were made for the stabilization of polymethacrylate particles by AB block copolymers of polystyrene and polydimethylsiloxane; indeed no variation in the strong anchoring efficiency was apparent for PS anchor blocks having varying molecular weight⁹. Both PS-*b*-PSMA block copolymers L56 and L45 behave similarly when the stability of carbon black dispersions in isododecane is considered; the lower MW copolymer L56, however, seems to stabilize smaller carbon black particles (302 nm) than the higher MW copolymer L45 (carbon black particle diameter 480 nm). All these features of course favour a very strong adsorption of the PS sequence at the surface and an efficient steric stabilization by the PSMA block, but the MW and composition of the copolymer are certainly key parameters for optimizing that situation.

**Figure 4** Schematic representation of a carbon black particle stabilized by an amphipathic PS-*b*-PSMA block copolymer**Figure 5** Particle diameters versus time for a carbon black dispersion in isododecane stabilized with PS-*b*-PSMA block copolymers L45 (—●—) and L56 (---□---)**CONCLUSIONS**

The synthesis of polystyrene-*block*-poly(stearyl methacrylate) by anionic polymerization proved to be a very interesting method for the preparation of well characterized amphipathic block copolymers. Dissolved in a selective solvent these block copolymers of PSMA adsorb strongly onto the carbon black surface. They display an experimental isotherm in agreement with the Langmuir predictions. Considerations about the area occupied by the macromolecules at the pigment surface are in favour of a model of steric stabilization wherein the insoluble PS block is adsorbed onto the carbon black and the soluble PSMA block protrudes into the isododecane medium, forming a steric barrier.

Solutions of these block copolymers in isododecane can be used for the stabilization of carbon black dispersions, which are very fine and remain stable over very long periods of time; thus there is a possible application in liquid toner electrophotography.

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