

The first example of a poly(ethylene oxide)–poly(methylphenylsilane) amphiphilic block copolymer: vesicle formation in water

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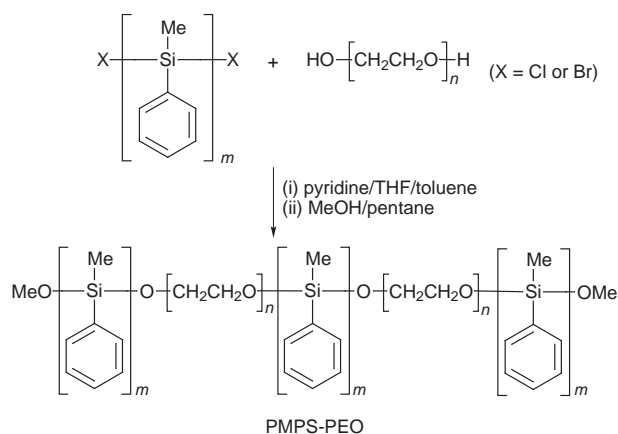
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A new amphiphilic multiblock copolymer of polymethylphenylsilane and poly(ethylene oxide) has been synthesised and demonstrated to form well-defined aggregates in water.

Polysilanes have been the subject of extensive research over the past decade due to their remarkable electronic properties that allow for a number of potential applications as conductive, electroluminescent, non-linear optical and lithographic materials.¹ Many of these properties can be expected to be more fully exploited through the incorporation of polysilanes into copolymer systems² which would allow for greater processability but also allow for the manipulation of the macroscopic order of the materials by supramolecular assembly (*e.g.* by microphase separation or aggregation in aqueous dispersions). The majority of amphiphilic block copolymers, none of which are derived from polysilanes, form spherical micellar structures in aqueous dispersions.³ Recently, further morphologies have been observed in aqueous dispersions such as rodlike, lamellar and vesicular aggregates.⁴ However the formation of vesicles by block copolymers remains rare and is confined to copolymers where the component blocks are monodisperse. We report here the formation of vesicles from the multiblock poly(methylphenylsilane)-co-poly(ethylene oxide) (PMPS-PEO), in which the PMPS blocks have a normal size distribution. We believe that this is the first example of vesicle formation by a multiblock copolymer and the first defined aqueous aggregate formed by a polysilane.

The PMPS-PEO copolymer was synthesised according to Scheme 1 utilising Schlenk techniques under a dry argon atmosphere. A solution of 4.78 g of poly(ethylene oxide) ($M_n = 7000$, 6.8×10^{-4} mol, $M_n/M_w = 1.03$) in toluene was added to a solution of α,ω -dihalopoly(methylphenylsilane)⁵ ($M_n = 4400$, 6.8×10^{-4} mol, $M_n/M_w = 2.00$) in THF and toluene. Subsequently pyridine (3 ml, 3.7×10^{-2} mol) was added and the reaction solution was stirred for 30 min. This solution was then added dropwise to MeOH (300 ml) and pentane (400 ml)



Scheme 1

was slowly added to the resultant mixture. PMPS-PEO was obtained as a yellowish white powder (60% yield, $M_n = 27\,000$, $M_w/M_n = 1.6$) after filtration and vacuum drying for 72 h. The molecular weights quoted are based upon size-exclusion chromatography (SEC) measurements of THF solutions relative to polystyrene standards using a refractive index (RI) detector. The block structure of the copolymer was confirmed by ¹H, ¹³C and ²⁹Si NMR spectroscopy and also by analysis of the molecular weight determinations of the copolymer and its precursors using both UV and RI detectors in the SEC experiment.⁶

Although the molecular weights have been determined relative to polystyrene standards it can be assumed that the hydrodynamic properties of the parent homopolymers and the segments in the copolymer structure are very similar. Thus the M_n value of 27 000 for the copolymer corresponds closely to the structure shown in Scheme 1, [PMPS-PEO]₂-PMPS, with a degree of polymerisation (DP) of 2.5.‡ This is merely the most abundant structure and comprises up to 30% of the overall distribution which ranges from PMPS-PEO to (PMPS-PEO)₁₆.

Direct addition of the copolymer to water (1 mg PMPS-PEO/1 ml H₂O) gave poor quality dispersions with most of the PMPS-PEO remaining as bulk solid. However transmission electron microscopic (TEM) analysis of samples of the aqueous portion of the mixture revealed vesicles [Fig. 1(a)].

Homogenous dispersions of the copolymer in water could be prepared in two ways. The copolymer was dissolved in THF (100 mg/10 ml THF) and water (3.5 ml) was added dropwise to the stirred solution (the solution became turbid after the addition of *ca.* 1.5 ml water). Subsequently the mixture was subjected to ultrafiltration with continuous concentration and water dilution (3×10 ml water). A homogenous white opaque dispersion resulted (concentration = 1.2 g l⁻¹). TEM analysis of freeze fractured samples of this dispersion showed that the copolymer existed as vesicles with remarkably little micellar material [Fig. 1(b)]. Both convex and concave hemispheres are clearly visible. The diameters of the vesicles ranged from *ca.* 100 nm to *ca.* 180 nm.

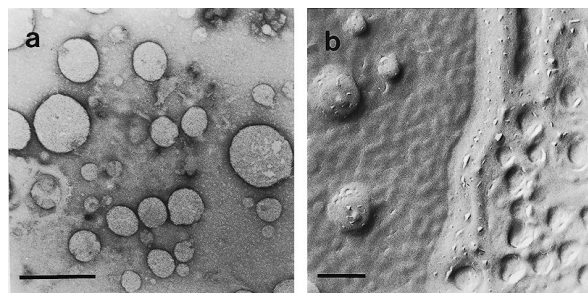


Fig. 1 Transmission electron micrographs of vesicles observed for copolymer dispersions obtained by (a) direct addition to water (negative staining), (b) ultrafiltration/dilution method (freeze-fracture). Bars represent 300 nm.

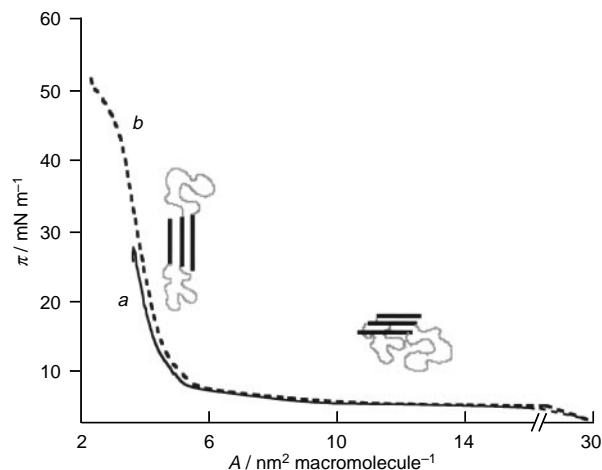


Fig. 2 π - A isotherms of PMPS-PEO at (a) pure water interface and (b) 100 mM NaCl_(aq) interface

Vesicle dispersions could also be prepared by the dialysis procedure reported by Zhang and Eisenberg.⁷ The copolymer dispersion in water-THF was prepared in a similar manner to the aforementioned procedure (3 ml THF, 1 ml water) and placed in a dialysis bag (exclusion limit = 20 000 Da) and dialysed against pure water (500 ml) for 72 h. EM analysis of negatively stained and platinum shadowed samples of the dispersion after this time again showed vesicles to be the predominant aggregate structure.

To confirm that the observed structures were vesicles an encapsulation experiment was performed utilising the water soluble fluorescent dye 5-carboxyfluorescein in the dialysis procedure.⁸ After 72 h the dispersion was eluted (in water) through a Sephadex column (G150, mesh size 40–120 μ). The elution volume of the encapsulated dye (30–110 ml, emission at 519.5 nm) coincided with that of the copolymer (emission 355 nm) indicating that closed vesicles are formed. The elution volume of the free dye was substantially larger (160–190 ml).

To investigate the orientation of the copolymer chains in the vesicle walls surface pressure–area isotherms were recorded for a monolayer of PMS-PEO at the air/water interface.[§] The isotherm revealed a very large lift-off area of ca. 30 nm² molecule⁻¹ which would correspond to the approximate area for three PMPS chains orientated parallel to the water surface. The observed plateau from 30 to 5 nm² molecule⁻¹ (Fig. 2) and the transition to a state characterised by a macromolecular area of 4.7 nm² molecule⁻¹ indicates a pseudo-first-order transition to a phase in which the PMPS chains become orientated perpendicular to the air/water interface. The collapse point is reached at a pressure of ca. 27 mN m⁻¹ where the area per polymer chain is 3.7 nm², which is in remarkably good agreement with the estimated cross-sectional area for three PMPS rods (ca. 3.6 nm² based upon models). When PMPS-PEO was spread upon a subphase containing 0.1 M NaCl the monolayer behaviour was essentially the same, the only substantial exception being the higher collapse pressure. This tends to confirm the above model where the limiting area is defined by the PMPS segments.

UV spectroscopic analysis of the dispersion prepared by ultrafiltration revealed a very weak absorption, due to the σ - σ^* transition, with a maximum at 342 nm (λ_{max} in THF = 339 nm) superimposed upon the scattering background. This is tentatively attributed to chain straightening and an extension of the effective conjugation length.

The freeze fracture electron micrographs, monolayer studies, structural considerations and UV data support a tentative model

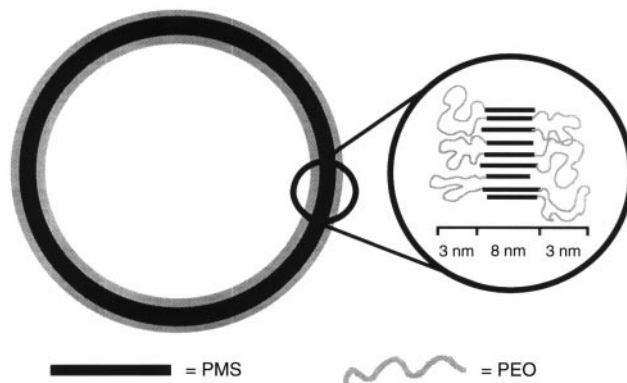


Fig. 3 Proposed model for copolymer organisation in the vesicle walls

of the packing in the vesicle walls as shown in Fig. 3.¶ It is apparent from our results that well-defined and very low polydispersity systems need not necessarily be requirements for the self-assembly of well-defined aggregates. Further work is in progress to study the structures adopted by this remarkable copolymer system.

Notes and References

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‡ A polydispersity of 1.6 (recorded by SEC) corresponds to an extent of reaction, p , of 0.6 in terms of the kinetics of the linear step-reaction polymerisation involved in the block copolymer formation. This in turn specifies a number average degree of polymerisation (DP) of 2.5 in excellent agreement with the expected Flory distribution.⁹

§ Monolayer experiments were carried out at 20.0 ± 0.1 °C using a double barrier R&K trough of dimensions 6×25 cm with a compression speed of $8.8 \text{ cm}^2 \text{ min}^{-1}$. The copolymer was spread from a solution of CHCl_3 .

¶ The lengths of the PMPS segments were calculated from literature data;¹⁰ light-scattering experiments have shown a strong correlation between the molecular weights obtained for polystyrene and PMPS in THF solutions by SEC.¹¹ The lengths of the PEO chains were based upon the molecular weight characteristics supplied by Aldrich; the width of the PEO coronae were calculated assuming repeated folding of the chain parallel to the orientation of the PMPS chains and the value given is therefore the minimum width expected.

- R. D. Miller and J. Michl, *Chem. Rev.*, 1989, **89**, 1359; *Inorganic Polymers*, ed. J. E. Mark, H. R. Allcock and R. West, Prentice-Hall, New Jersey, 1992, ch. 5, p. 186.
- K. Sakamoto, K. Obata, H. Hirata, M. Nakajima and H. Sakurai, *J. Am. Chem. Soc.*, 1989, **111**, 7641; S. Demoustier-Champagne, A.-F. de Mahieu, J. Devaux, R. Fayt and P. J. Teyssie, *J. Polym. Sci., Polym. Chem.*, 1993, **31**, 2009; E. Fossum, K. Matyjaszewski, S. S. Sheiko and M. Möller, *Macromolecules*, 1997, **30**, 1765.
- C. Price, in *Developments in block copolymers*, ed. I. Goodman, Applied Science Publishers, London, 1982, vol. 1, p. 39; J. Selb and Y. Gallot, in *Developments in block copolymers*, ed. I. Goodman, Applied Science Publishers, London, 1985, vol. 2, p. 327; Z. Tuzar and P. Kratochvil, in *Surface and Colloid Science*, ed. E. Matijevic, Plenum Press, New York, 1993, vol. 15, p. 1.
- L. Zhang and A. Eisenberg, *Science*, 1995, **268**, 1728.
- R. C. Hiorns, R. G. Jones and F. Schue, unpublished results.
- R. G. Jones and S. J. Holder, *Macromol. Chem. Phys.*, 1997, **198**, 3571.
- L. Zhang and A. Eisenberg, *J. Am. Chem. Soc.*, 1996, **118**, 3168.
- J. M. Fendler, *Membrane Mimetic Chemistry*, Wiley, New York, 1982.
- P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York, 1953, ch. 8.
- W. J. Welch, J. R. Damewood, Jr. and R. C. West, 1989, **22**, 2947.
- C. Strazielle, A.-F. de Mahieu, D. Daoust and J. Devaux, *Polymer*, 1992, **33**, 4171.

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