

Nonaqueous poly(methyl methacrylate) dispersions: radical dispersion polymerization in the presence of AB block copolymers of polystyrene and poly(dimethyl siloxane)

John V. Dawkins and Graham Taylor*

Department of Chemistry, Loughborough University of Technology, Loughborough, Leicestershire, LE11 3TU, U.K.

(Received 28 December 1978)

Well defined AB block copolymers of polystyrene (PS) and poly(dimethyl siloxane) (PDMS) have been prepared with PS molecular weights in the range 8 800 to 43 600 and PDMS molecular weights in the range 2 400 to 48 000. Provided the PS and PDMS molecular weights have a ratio within the range 0.5 to 4.0, these block copolymers stabilize particles of poly(methyl methacrylate) in n-alkanes. The particle size over the range 0.1 to 0.5 μm may be varied by performing dispersion polymerizations of methyl methacrylate as a function of monomer content of the seed stage and as a function of the concentration, molecular weight and composition of the block copolymer. From silicon analyses of the poly(methyl methacrylate) particles, values of the surface area stabilized per PDMS chain were established. The results indicate complete surface coverage of the particles.

INTRODUCTION

Polymer particles dispersed in organic media are conveniently prepared by polymerizing in the presence of a preformed block or graft copolymer a monomer dissolved in a diluent which is a precipitant for the polymer. The stabilizing copolymer contains A blocks which are insoluble in the dispersion medium and act as anchors for the B blocks which are swollen by the diluent and which extend away from the particle surface. The thin layer of B blocks around the particle provides a protective layer against flocculation by a mechanism known as steric stabilization¹.

The preparation of nonaqueous dispersions of poly(methyl methacrylate) (PMMA) stabilized by a graft copolymer consisting of a PMMA backbone with short branches of poly(12-hydroxystearic acid) is well documented². The present paper describes the preparation of dispersions of PMMA in aliphatic hydrocarbons, stabilized by well-defined AB block copolymers of polystyrene and poly(dimethyl siloxane), PS-PDMS. This is an interesting system because effective anchoring of the copolymer may be influenced by the degree of compatibility between the A block and the polymer in the particles. Most of the work on the preparation and properties of nonaqueous polymer dispersions has been concerned with copolymer stabilisers having the A block the same as the polymer in the particles^{1,2}. Although block copolymer stabilisers are attractive because well-defined structures may be produced by anionic polymerization, surprisingly little use has been made of AB block copolymers in the preparation of nonaqueous dis-

persions. A near-monodisperse block copolymer would be expected to give a constant layer thickness of B blocks around a particle. Graft copolymers based on poly(12-hydroxystearic acid) are invariably polydisperse. Since our work was completed, Everett and Stageman³ have reported brief details of PMMA particles in hexane, stabilized with a BAB PDMS-PS-PDMS block copolymer. These workers only considered one B block length with a molecular weight of about 7000, whereas we have used AB block copolymers with a PDMS molecular weight in the range 2400 to 48 000. In addition, we have investigated the influence of the concentration, molecular weight, and the anchor/soluble balance (ASB) of the block copolymer on the dispersion polymerization and on the size of the particles produced. The only other preparation of PMMA particles stabilized by a layer of PDMS involved *in situ* covalent grafting⁴.

EXPERIMENTAL

Block copolymers

The synthesis of PS-PDMS block copolymers by anionic polymerization techniques has been described⁵⁻⁹. A series of block copolymers containing short PDMS blocks, molecular weight ≤ 5000 , was prepared according to the procedures described by Saam⁵ using an inert gas blanket technique¹⁰. Such products were shown to contain small amounts of low molecular weight polystyrene impurity. This problem was minimized in the preparation of a second series of block copolymers by polymerizing under conditions of high vacuum, using techniques similar to those of Zilliox, Roovers and Bywater⁸.

* Present address: Department of Physics, Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, UK.

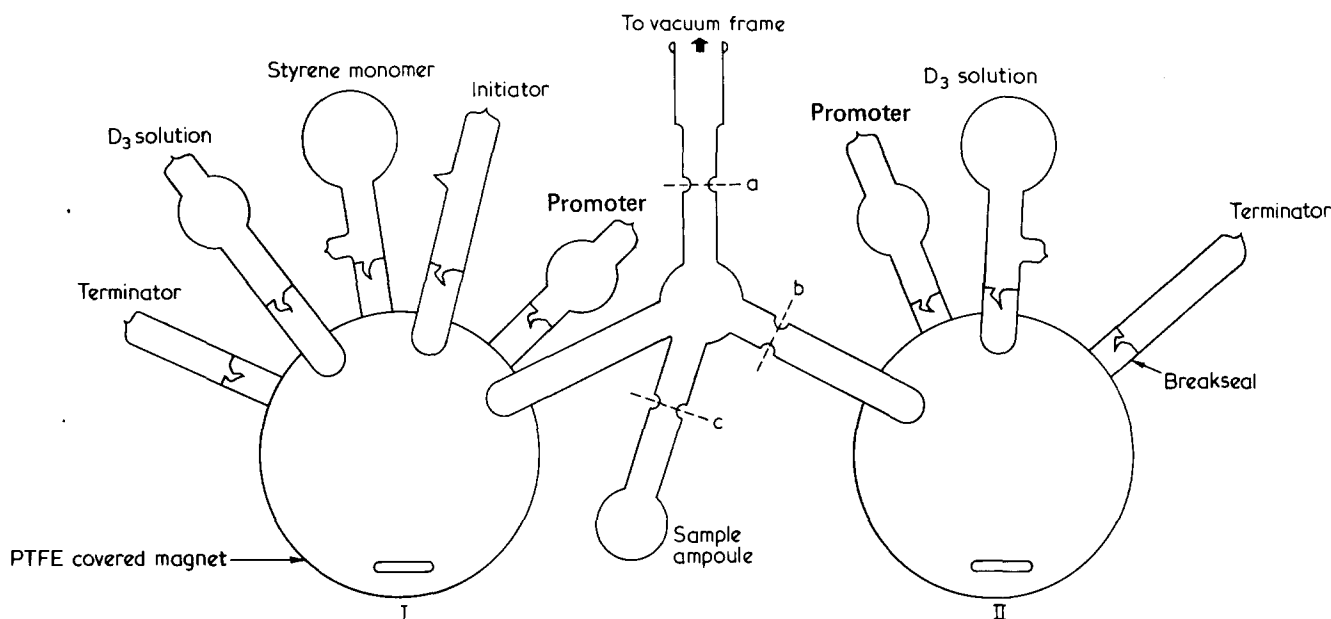


Figure 1 Reactor for block copolymer synthesis under high vacuum

Solvents and monomers were dried and purified following general methods described by Fetters¹¹. Styrene (BDH) was destabilized using aqueous KOH, dried over a slurry of freshly ground calcium hydride and extensively purified by flash distillation over successive sodium mirrors, until no further degradation of the mirror was detectable. Hexamethylcyclotrisiloxane D₃ (supplied by Dow Corning, Barry) was obtained as a double-distilled white solid (boiling point 407 K) and was dried in toluene solution under vacuum over a slurry of freshly-ground calcium hydride. The entire solution was distilled into a preflamed glass ampoule equipped with a breakseal. *n*-Butyl lithium (Pfizer), supplied as a solution in *n*-hexane (1.66M), was standardized using a modified Gilman double titration method¹² and used without further purification. Diglyme (Fisons), used as a promoter, was distilled from sodium wire onto sodium and naphthalene, and distilled from the resulting dark-green complex directly into calibrated glass ampoules. A few drops of well-degassed methanol or chlorotrimethylsilane, sealed into an ampoule, served as terminator.

The reactants were all contained in evacuated glass ampoules equipped with breakseals. These ampoules were sealed onto an all-glass reactor (Figure 1) which was then extensively flamed and evacuated. The design of the reactor was such that two products of equal A-block length but differing B-block lengths could be prepared simultaneously by splitting a 'living' solution of polystyryllithium and adding differing amount of D₃ to each portion. The required volume of solvent (toluene) was distilled directly into the reactor, which was then sealed off from the vacuum line at 'a'. Bulb I was surrounded by a cold water bath and initiator added by breaking the appropriate breakseal with the magnetic stirrer bar. The initiator ampoule was rinsed with condensing solvent, and styrene monomer was then added dropwise to the stirred solution. The characteristic deep-orange colour of polystyryl anions developed virtually immediately and upon completion of the styrene addition, polymerization proceeded at room temperature. The exothermic reaction was again checked with a cold water bath. After one hour the bath could be removed and the polymerizing solution was left for a period of 3–5 h to ensure almost complete monomer conversion.

The 'living' polystyryllithium solution was then equally divided between bulbs I and II by tilting the reactor, and a sample (10 cm³) introduced into the sample ampoule for subsequent characterization of the A block. The solutions in each section of the reactor were then frozen and the reactor separated at 'b' and 'c'. The PS-homopolymer sample was immediately terminated by opening the ampoule under methanol. Each half of the reactor was then treated separately. A solution of D₃ and promoter were added to the stirred solution of polystyryllithium at room temperature, and polymerization continued for times up to 50 h depending on the PDMS molecular weight required. The 'living' system was terminated by introducing either methanol or chlorotrimethylsilane. The resulting block copolymer was precipitated and washed with excess methanol and distilled water.

Block copolymer characterization

Samples of the polystyrene A block and the block copolymer were characterized by gel permeation chromatography (g.p.c.). A Waters Associates ALC/GPC 501 instrument was used with four commercially available Styragel columns of nominal porosity 10³ Å, 10⁴ Å, 10⁵ Å and 10⁶ Å (Waters designation). The instrument was operated at room temperature using tetrahydrofuran as eluent, and was calibrated using a series of polystyrene standards (Waters Associates). The polydispersity, the ratio of the weight and number average molecular weights \bar{M}_w/\bar{M}_n , was generally less than 1.25 for the block copolymers.

The number average molecular weight of both homopolymers and block copolymers was determined by high speed membrane osmometry. A Hewlett-Packard 502 instrument was used at room temperature, using degassed toluene as solvent. The osmotic pressure of a series of polymer solutions at concentrations 4–10 g dm⁻³ was measured for each sample.

Block copolymer samples were analysed for silicon content using a Technicon Auto Analyser¹³. From the g.p.c. estimate of the molecular weight of the polystyrene block and a silicon analysis, the number average molecular weight of the PDMS block could be calculated. The sum of the PS

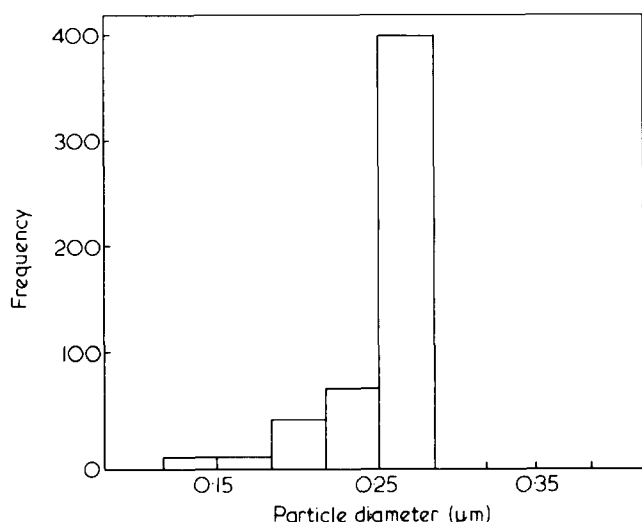
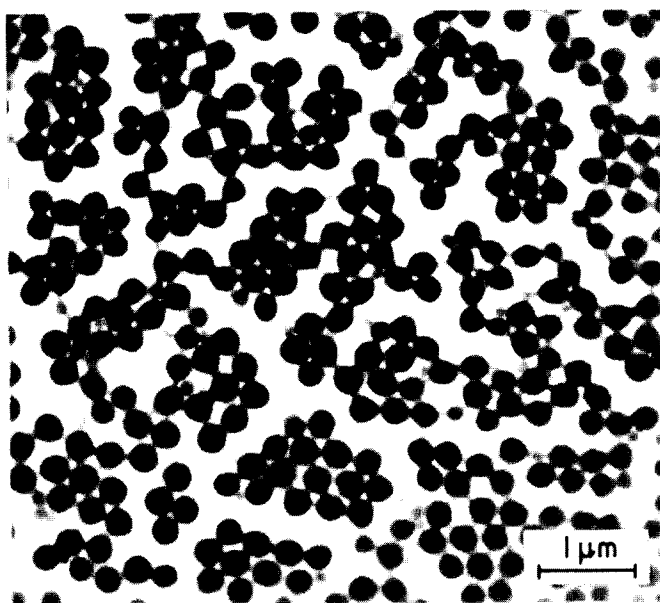


Figure 2 Transmission electron micrograph and particle size distribution of a typical poly(methyl methacrylate) dispersion

and PDMS molecular weights was in good agreement with the value of \bar{M}_n for the block copolymer determined experimentally by osmometry.

Dispersion polymerization

Nonaqueous dispersions of PMMA were prepared using radical polymerization techniques similar to those described by Barrett². Monomer, destabilized using aqueous KOH, initiator (e.g. azobisisobutyronitrile) and PS-PDMS stabilizer were dissolved in the selected dispersion medium (e.g. n-hexane) and heated with stirring to the polymerization temperature (50–70°C). Particle formation occurred soon after the commencement of initiation. A 'seeding' technique was frequently used to overcome problems arising from the decreasing solvency of the dispersion medium during the course of a one-stage dispersion polymerization. This changing solvency is a consequence of the solubility of PMMA in its own monomer. The seeding technique involved initially polymerizing a small proportion of the monomer (e.g. 10%) along with an equivalent concentration of stabilizer and initiator. Typically, the seed stage lasted 1–2 h. The rest of the monomer, stabilizer and initiator was then added incrementally over a period of up to 5 h, giving a total poly-

merization time of about 8 h. The effects of varying the stabilizer type and concentration, and the proportion of monomer in the seed-stage were investigated.

In order to remove unconverted monomer, unadsorbed stabilizer and initiator residues from the dispersions prepared above, the dispersions were subjected to several redispersion cycles. The dispersion was centrifuged at 10 000 r.p.m. for 15 min and the supernatant above the precipitated polymer particles was replaced by fresh dispersion medium. The particles were redispersed by vigorous shaking or ultrasonic vibration, and the redispersion cycle repeated. Analysis of the supernatant by infrared spectroscopy showed that three such redispersion cycles are usually sufficient to reduce to negligible proportions the excess stabilizer content. Redispersions also provided a way of exchanging the dispersion medium for a different one, and products prepared in n-hexane have been redispersed in n-heptane, n-decane, n-dodecane, cyclohexane and Freon 113 (1,1,2-trichloro-1,2,2-trifluoroethane) in this way.

Particle characterization

Transmission electron microscopy (t.e.m.) was used to determine particle size, shape and size distribution. Samples were prepared by placing one drop of the diluted dispersion (~0.1% w/v polymer content) directly onto a carbon-coated copper grid and evaporating to dryness. Samples were examined at magnifications of 2–100 × 10³ times using an AEI EM6 instrument calibrated with a replica of a 2160 lines mm⁻¹ grating. Particle size and size distribution were calculated from direct measurement of individual particles on the enlarged micrographs. At least 150 particle diameters were measured, and histograms were constructed to show the particle size distribution. During the preparation of dispersion samples for t.e.m. examination, the swollen surface layer of PDMS collapses onto the surface of the particle when the dispersion medium is removed. The dimensions of this collapsed layer are negligible compared with the particle core diameter. Hence, the measured diameter was taken as that of the core.

The surface coverage of PDMS on the particles was conveniently estimated from silicon analyses. Samples of the dispersions were washed by redispersion cycles to remove excess stabilizer. The dispersion medium was then evaporated under vacuum and the dried particles subjected to silicon analysis¹³.

RESULTS AND DISCUSSION

Polymerization kinetics

The conversion, when followed gravimetrically and plotted versus time, showed a sigmoidal curve characteristic of the dispersion polymerization of methyl methacrylate. The acceleration in the rate of polymerization is attributed to the occurrence of a 'gel' effect². The molecular weight of PMMA thus prepared was typically in the range 10⁴–10⁵, as estimated by g.p.c. PMMA of lower molecular weight was successfully prepared by polymerizing in the presence of a suitable chain transfer agent (e.g. carbon tetrabromide).

Particle formation

Stable dispersions of PMMA particles in n-alkanes were prepared in the presence of AB block copolymers having \bar{M}_n (PS block) in the range 8800–43 600, \bar{M}_n (PDMS block) in the range 2400–48 000 and ASB values, calculated from the molecular weights of the A and B blocks, in the range 0.5 to 4.0. The PMMA particles were shown by t.e.m. to be spheres of a narrow particle size distribution, (see Figure 2).

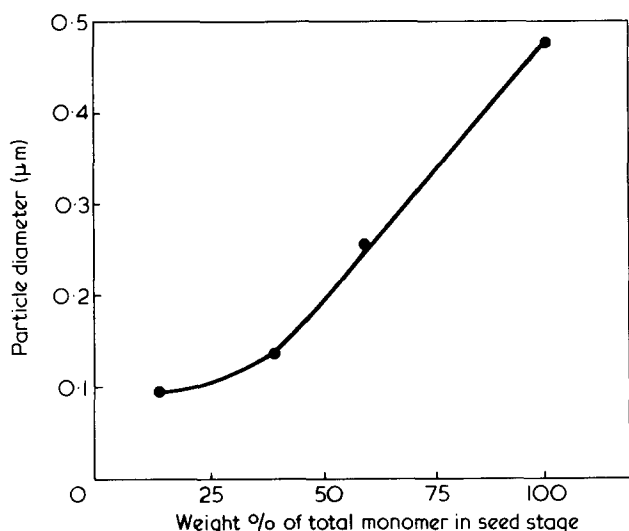


Figure 3 Dependence of particle diameter on monomer content in the seed stage in seeded dispersion polymerizations of methyl methacrylate

Even one-stage polymerization yielded regular particles. In seeded polymerizations, the proportion of monomer present in the seed stage, and hence the initial solvency of the dispersion medium, had a marked effect on the average particle size. Figure 3 shows the variation of particle size of dispersions prepared with an increasing proportion of monomer in the seed stage. When less than about 30% of the total monomer was polymerized in the seed stage, the lower limit of particle size (0.1 µm for this system) was reached. As the monomer content of the seed stage increased, the overall solvency of the dispersion medium increased. Thus, larger particles were produced, until in the limit with all the monomer in the seed stage (i.e. a one-stage polymerization) particles of 0.48 µm were produced.

Figure 4 shows the variation of average particle size of dispersions prepared in the presence of differing concentration of stabilizer. As the stabilizer concentration increased, smaller particles were produced, as predicted by the theories of particle formation². The data in Figure 4 plotted on logarithmic axes gave a straight line, which obeyed the relationship

$$D \propto c^{-0.77}$$

in which D is the particle diameter and c is the concentration of stabilizer in solution. A similar relationship for dispersions of PMMA stabilized by graft copolymers has been reported by Barrett² who found that the exponent was in the range -0.5 to -0.6.

Dispersion polymerizations of MMA were usually performed in the presence of about 5% stabilizer in solution. It should be noted that despite this relatively high concentration, only up to 20% of the stabilizer was actually incorporated into the PMMA particles. Higher concentrations of stabilizer than those used in equivalent dispersion polymerizations of styrene were required¹⁰. With a stabilizer concentration of 2%, a dispersion polymerization of MMA produced coarse particles with a wide particle size range (0.3–1.0 µm).

The use of stabilizers containing higher molecular weight PDMS blocks led to smaller particles. This was because the larger PDMS chains were capable of stabilizing a larger surface area of the particle surface. Figure 5 shows the effect on particle size of varying the molecular weight of the

PDMS block of the stabilizer. The dispersions considered were all prepared in the presence of similar concentrations of PDMS.

We were not able to produce dispersions of PMMA in the presence of stabilizers with ASB values greater than 4.4. Such stabilizers irreversibly micellise in the dispersion medium². Whilst stabilizers with ASB > 4.4 have been used successfully as a seed in dispersion polymerizations of styrene¹⁰, they did not yield stable particles in MMA polymerizations. When PMMA radicals grow to the threshold molecular weight for precipitation, they are probably prevented from entering into the PS core of a micelle because of the incompatibility of PS and PMMA. Consequently, PMMA particles are nucleated in the dispersion medium.

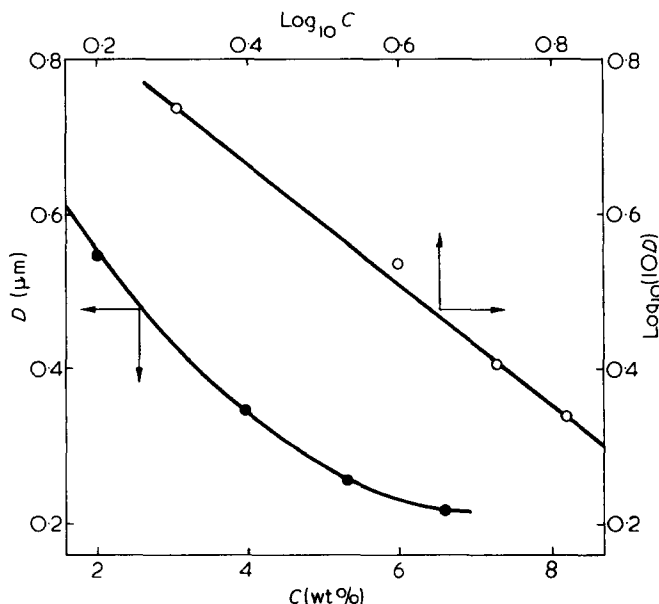


Figure 4 Dependence of particle diameter on the concentration of block copolymer in dispersion polymerizations of methyl methacrylate

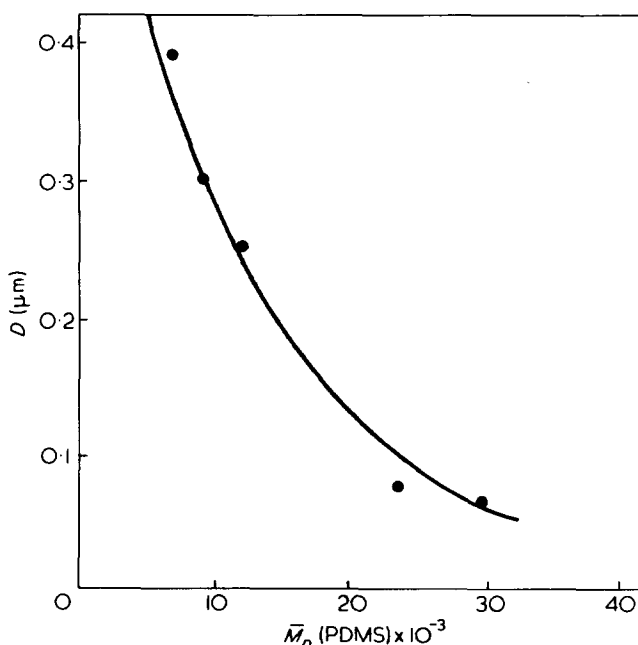


Figure 5 Dependence of particle diameter on the molecular weight of the PDMS block in the block copolymer, at constant PDMS concentration, in dispersion polymerizations of methyl methacrylate

Table 1 Effect of particle core diameter on the area of PMMA particle surface stabilized by a PDMS chain ($\bar{M}_n = 11\,200$)

Dispersion	$D(\mu\text{m})$	$A(\text{nm}^2)$
D76	0.096	11.7
D84	0.13	12.6
D91	0.22	11.1
D44	0.25	12.0
D55	0.48	13.0

The stabilizer is not free to diffuse from the irreversibly associated micelles to these incipient nuclei, and so flocculation quickly occurs.

Surface coverage

Analysis of the silicon content of samples of the dried particles was combined with an estimate of the particle size from t.e.m. to give information about the surface coverage of the PDMS chains. The area A occupied, or stabilized, by a given PDMS chain was found to be constant over the range of particle sizes considered, see Table 1. This implies that 'total' surface coverage may be assumed for such dispersions. Values of A have also been determined for AB block copolymers of PS-PDMS stabilizing polystyrene particles¹⁰. These results suggest that the area stabilized by a given PDMS chain is similar on both PMMA and PS particle surfaces. From these results A is independent of the molecular weight of the PS anchor block, so it is suggested that the PS anchor block does not extend significantly into the dispersion medium and the PDMS chains may be thought of as being terminally anchored at the particle surface. It was also observed that the area which one chain is capable of stabilizing increases with increasing molecular weight of the PDMS chain.

Dispersion stability

The PMMA dispersions were shown to be sterically stabilized by changing the solvency of the dispersion medium. Addition of a non-solvent (e.g. ethanol) for PDMS to the dispersion medium eventually caused gross flocculation of the particles. It was shown that the system lost stability when the dispersion medium was close to theta-conditions for PDMS¹⁰.

The results have shown that copolymers with polystyrene anchor blocks are suitable for stabilizing PMMA particles. The long-term stability of these dispersions after removal of excess stabilizer suggests there is little desorption of the stabilizer. The observation that dispersions retained stability after some seventeen redispersion cycles, and also when subjected to ultrasonic vibration, again points to a strong anchoring mechanism for the stabilizer. No variation in anchoring efficiency was apparent for polystyrene anchor blocks having molecular weights in the range 8800 to 44 000.

Because two different polymers are often not compatible on mixing¹⁴, the anchoring mechanism and the conformation of the polystyrene blocks for PMMA particles may be influenced by a tendency to minimise contacts between PS and PMMA. The efficiency of the anchoring mechanism was demonstrated by redispersing the PMMA particles in cyclohexane. Such dispersions, when held at 333 K for 60 h, showed only slight flocculation, implied from a slightly increased rate of sedimentation. Cyclohexane at 307 K is a well known θ -solvent for PS¹⁴. If the stabilizer were not

firmly anchored to the particles, heating such a dispersion to 333 K would lead to gross flocculation, owing to the desorption and dissolution of the PS anchor blocks. The slight flocculation observed possibly suggests limited desorption, which is reversible upon cooling the dispersion to 298 K, and may be related to the conformation of the polystyrene blocks. The PS anchor blocks should have a random coil conformation when embedded within a PS particle. For PMMA particles two other possible anchor conformations may arise. First, a PS block may collapse into a tightly coiled ball which is trapped within the matrix of a PMMA particle during particle growth. Alternatively, a PS block is adsorbed onto the particle surface in trains, with an occasional train being trapped just beneath the surface of the PMMA particle. This second model may explain the observation in the cyclohexane experiment. Initial results on the direct determination of the conformation of the anchor blocks by small-angle neutron scattering experiments¹⁵ do suggest differences between PS and PMMA particles.

It might be argued that the strong anchoring of PS-PDMS to PMMA particles could arise during dispersion polymerization from a grafting reaction between the poly(methyl methacrylate) radicals and the block copolymer. Literature values for chain transfer constants for the reaction between PMMA radicals and PS and between PMMA radicals and PDMS are very small^{16,17}. In order to eliminate the explanation of covalent grafting of block copolymer to the particles, we have isolated block copolymer from a washed and dried sample of a PMMA dispersed phase ($\bar{M}_n = 15\,800$). Acetonitrile was used as solvent in a Soxhlet extraction for 70 h, removing PMMA homopolymer and leaving the block copolymer. This residue was washed, dried, and analysed by g.p.c. The results of the original ($\bar{M}_n = 22\,600$) and extracted block copolymer were comparable. No increase in the molecular weight of the block copolymer was apparent, suggesting that block copolymer had not been grafted onto the particles.

CONCLUSIONS

These results demonstrate that AB block copolymers of PS-PDMS are effective stabilizers for poly(methyl methacrylate) particles dispersed in n-alkanes. The particle size in dispersion polymerization may be controlled by the concentration of monomer in the seed stage, by block copolymer concentration, and by the molecular weight and composition of the AB block copolymer. Silicon analyses on the dispersed PMMA phase indicate complete coverage of the particles by the PDMS blocks, and reasonable estimates have been obtained for the surface area stabilized per PDMS chain.

ACKNOWLEDGEMENTS

The authors wish to thank Dr D. P. Jones for his interest in this work, Dow Corning for providing the D₃ monomer and for silicon analyses, Mr M. Hayles for the electron micrographs, and the Science Research Council for a C. A. S. E. award.

REFERENCES

- 1 Vincent, B. *Adv. Coll. Interface Sci.* 1974, 4, 193
- 2 Barrett, K. E. J. *Dispersion Polymerization in Organic Media*, Wiley, New York, (1975)

Nonaqueous poly(methyl methacrylate dispersions: John V. Dawkins and Graham Taylor

- 3 Everett, D. H. and Stageman, J. F. *Coll. Polym. Sci.* 1977, **255**, 293; Paper presented at *Faraday General Discussion*, **65**, Lunteren, The Netherlands, April (1978)
- 4 Saam, J. C. and Tsai, C. H. *J. Appl. Polym. Sci.* 1974, **18**, 2279
- 5 Saam, J. C., Gordon, D. J. and Lindsey, S. *Macromolecules* 1970, **3**, 1
- 6 Davies, W. G. and Jones, D. P. *IEC Prod. Res. Dev.* 1971, **10**, 168
- 7 Saam, J. C. and Fearon, F. W. G. *IEC Prod. Res. Dev.* 1971, **10**, 10
- 8 Zilliox, J. G., Roovers, J. E. L. and Bywater, S. *Macromolecules* 1975, **8**, 573
- 9 Marsiat, A. and Gallot, Y. *Makromol. Chem.* 1975, **176**, 1641
- 10 Taylor, G. *Ph.D Thesis*, Loughborough University of Technology, (1977)
- 11 Fetters, L. J. *J. Res. NBS. A* 1966, **70**, 421
- 12 Gilman, H. and Haubein, A. H. *J. Am. Chem. Soc.* 1944, **66**, 1515
- 13 Analyses performed by Dow Corning Ltd., Barry, Glamorgan, UK
- 14 Flory, P. J. *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, N. Y. (1953)
- 15 Higgins, J. S. Imperial College, unpublished results
- 16 Brandrup, J. and Immergut, E. H. *Polymer Handbook*, Wiley, New York, (1976)
- 17 Saam, J. C. and Gordon, D. J. *J. Polym. Sci. (A-1)* 1970, **8**, 2509