

# Structural parameters of spherical particles prepared by dispersion polymerization of methyl methacrylate

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Poly(methyl methacrylate) (PMMA) dispersions in decane stabilized by polystyrene-*block*-poly(ethylene-*co*-propylene) copolymer were prepared with various monomer and steric stabilizer concentrations. The number of PMMA macromolecules formed in the dispersion polymerization does not depend on monomer and stabilizer concentrations. The kinetics of polymerization seems to be only slightly affected by the colloidal character of the system. Correlations have been established between the parameters of the whole system, of dispersion particles and of the individual PMMA macromolecules.

**(Keywords: dispersion polymerization; steric stabilization; block copolymers; light scattering; molecular characterization)**

## INTRODUCTION

Advanced applications of polymers often involve macromolecular systems with organized structures. These are closely connected to the design of tailor-made polymers and copolymers of specified molecular architecture, such as block and graft copolymers. For block and graft copolymers selective solvents exist<sup>1,2</sup> which dissolve one type of block while acting as non-solvents for the other type. The colloidal properties of block and graft copolymers play an important role in the process of dispersion polymerization<sup>3,4</sup>. Unlike emulsion or suspension processes, in dispersion polymerization the monomer is completely miscible with the medium; the resulting polymer is insoluble under the same conditions. In contrast to ordinary precipitation polymerization, macroscopic separation of the polymer from the reaction mixture is prevented by the presence of the steric stabilizer. Dispersion polymerization thus defined need not be limited to non-aqueous systems, but can also be performed in water<sup>5</sup>. Nearly uniform spherical particles can be prepared by dispersion polymerization. Attention has centred mainly on the polymerization of methyl methacrylate (MMA) in hydrocarbons<sup>3,4,6-12</sup> and of styrene in mixtures containing alcohols<sup>13-17</sup> but other systems have also been investigated<sup>5,18</sup>.

We decided to prepare and study poly(methyl methacrylate) (PMMA) dispersions stabilized in decane by the polystyrene-*block*-poly(ethylene-*co*-propylene) diblock copolymer [P(S-EP)]. This system has been investigated earlier<sup>19-21</sup> and the methodology of its light scattering characterization has been given in our previous paper<sup>12</sup>. The behaviour of the above diblock copolymer in hydrocarbons has been the subject of several papers<sup>22-27</sup>. The fact that decane is practically isorefractive with MMA ( $n_D^{20} = 1.411$  and 1.414, respectively) may simplify the interpretation of light scattering data; the refractive index of the medium does

not change during polymerization and the potential effect of preferential sorption<sup>28</sup> can be neglected.

In order to analyse the structure and properties of the dispersion particles, the following terminology based on a simple geometric body-shell model is used<sup>12</sup>. We assume that the dispersion particle has a core formed by the polymer (subscript P, PMMA) originating during the dispersion polymerization of a suitable monomer (M, MMA) and by the steric stabilizer [S, P(S-EP)]. Paraffinic blocks of the stabilizer are soluble in the polymerization medium and form the corona (C) (or shell) of the particle. The presence of the shell prevents aggregation of the particles, which would result in a macroscopic precipitation of the polymer. The polystyrene blocks of the stabilizer are insoluble under the same conditions and create the anchor (A). Anchor chains are embedded into or onto the PMMA core. Insoluble components, core and anchor, together form the body (B) of the particle.

In the following discussion, a relationship between the conditions of preparation, the parameters of the dispersion particles and the molecular structure of the resulting polymer is sought.

## EXPERIMENTAL

### *Chemicals*

Methyl methacrylate (Lachema, Czechoslovakia) has been treated with 1 wt% aqueous sodium hydroxide to remove the hydroquinone stabilizer, washed with water, dried over anhydrous magnesium persulphate and distilled on a laboratory column (b.p. 45°C, 13 kPa). The radical initiator, azobisisobutyronitrile (AIBN, BDH, UK), was recrystallized from methanol and dried *in vacuo*.

Decane (pract., 95.2 wt%, Fluka, Switzerland) was used as received. The auxiliary solvents were also used as received.

Polystyrene-*block*-poly(ethylene-*co*-propylene) (Kraton G 1701, Shell, 42 wt% styrene, molar mass  $M_{ws} = 110\,000$ ,  $M_{ws}/M_{ns} \sim 1.1$ ) was used as the steric stabilizer. A stock solution of the diblock copolymer in decane ( $2.5\text{ g cm}^{-3}$ ) was centrifuged for 1 h at  $10\,000\text{ rev min}^{-1}$  on a Beckman L8-55 ultracentrifuge to remove traces of insoluble components. The solution had a bluish opalescence typical for the presence of micelles.

#### Dispersion polymerization

A specified amount of AIBN was dissolved in MMA (it is insoluble in decane). Solutions of initiator, steric stabilizer, pure MMA and decane were mixed in various proportions and  $10\text{ cm}^3$  of each mixture were sealed in glass ampoules in a nitrogen atmosphere. The concentration of AIBN ( $1 \times 10^{-3}\text{ g cm}^{-3}$ ) was kept constant in all experiments. The volume fraction of MMA,  $\phi_M$ , was 0.05, 0.10, 0.15, 0.20 and 0.25 and the steric stabilizer concentration,  $c_s$ , was 0, 0.5, 1.0, 1.5 and  $2.0 \times 10^{-2}\text{ g cm}^{-3}$ . Polymerization was carried out at  $60^\circ\text{C}$  for 70 h without stirring. All initial solutions were visually clear; the first opalescence was observed with the naked eye after 30 min for samples with the highest MMA content. In the absence of steric stabilizer, the resulting PMMA precipitate and the content of the ampoules gradually solidified. In all other cases stable dispersions were formed.

#### Analysis of dispersions

A weighed fraction of each dispersion was precipitated into excess ethanol, and the precipitate was separated and dried. The degree of conversion of polymerization was then calculated from the known amount of material after subtracting the steric stabilizer fraction. The degree of conversion,  $\psi_M$ , was independent of stabilizer concentration but varied with MMA content;  $\psi_M = 0.86, 0.94, 0.98, 0.98$  and  $0.97$  for the volume fraction of MMA in the starting mixture  $\phi_M = 0.05, 0.10, 0.15, 0.20$  and  $0.25$ , respectively.

The isolated material was redissolved in toluene and precipitated into cyclohexane. Under these conditions, only PMMA precipitated, while the steric stabilizer remained in solution. Pure PMMA was separated, dried and characterized.

The total concentration of the polymeric material (in  $\text{g cm}^{-3}$ ) was calculated according to the formula  $c = c_s + c_p$ . Here,  $c_p = c_M \psi_M = d_M \phi_M \psi_M$  is the PMMA concentration,  $c_M$  is the monomer concentration and  $d_M$  ( $0.936\text{ g cm}^{-3}$ ) is the density of MMA at  $25^\circ\text{C}$ .

#### Static light scattering (SLS)

The light scattering determination of the mass-average molar mass,  $M_{wD}$ , of dispersion particles, including the potential use of logarithmic Zimm plots for this purpose, has been described previously<sup>12</sup>. The original dispersions were diluted 1000–5000 times with decane to obtain a solution with the highest concentration for SLS measurement; this solution was further diluted. The individual solutions were filtered through a polycarbonate membrane filter of porosity 1 or  $3\text{ }\mu\text{m}$  (Bio-Rad Laboratories, USA). The subsequent SLS measurement was done with a modified Sofica 42.000 apparatus using a 5 mW He–Ne laser as the light source (vertically polarized, 633 nm).

The refractive index increment of the steric stabilizer

in decane,  $0.117\text{ cm}^3\text{ g}^{-1}$  (633 nm,  $25^\circ\text{C}$ ), was determined using a Brice-Phoenix BP-2000-V differential refractometer. The refractive index increment of PMMA, which is insoluble in decane, was estimated from the linear dependence of this quantity on the refractive index of the solvent<sup>29</sup> as  $0.085\text{ cm}^3\text{ g}^{-1}$  (633 nm,  $25^\circ\text{C}$ ). The refractive index increments of the dispersions were calculated by assuming a simple additivity rule.

Static light scattering was also employed for the determination of the mass-average molar mass of PMMA,  $M_{wp}$ , which forms the core of the dispersion particles. These measurements were done in tetrahydrofuran (THF) and evaluated using the refractive index increment  $0.085\text{ cm}^3\text{ g}^{-1}$  (633 nm,  $25^\circ\text{C}$ ).

#### Dynamic light scattering (DLS)

A homodyne photon correlation spectrometer, described elsewhere<sup>30</sup>, was used in DLS measurements (633 nm, scattering angle,  $\theta = 90^\circ$ ,  $25^\circ\text{C}$ ). The photopulse signal was analysed in a laboratory made 96-channel digital correlator operating with three simultaneous sampling times and covering approximately 3.5 decades in delay time,  $\tau$ . The time auto-correlation functions were fitted by the Pearson distribution<sup>31</sup>:

$$z(\tau) = \tau_0^p \tau^{-p-1} \exp(-\tau_0/\tau) / \Gamma(p)$$

where  $\tau_0$  and  $p$  are parameters, and  $\Gamma(p)$  is the gamma function of the parameter  $p$ . The Pearson distribution was chosen for the simplicity of its mathematical treatment. The hydrodynamic radius,  $R_h$ , was calculated from the average collective diffusion coefficient,  $D_0$ , using the Stokes–Einstein equation:

$$R_h = kT / (6\pi\eta D_0)$$

where  $k$  is the Boltzmann constant,  $T$  is temperature and  $\eta$  (0.86 cP) is the viscosity of decane at  $25^\circ\text{C}$ .

The non-uniformity of the particles was described by the mass to number-average molar mass ratio<sup>30</sup>:

$$M_{wD}/M_{nD} = \Gamma(p)\Gamma(p+2/a) / \Gamma^2(p+1/a)$$

For compact spheres,  $a = 1/3$  and  $M_{wD}/M_{nD} = (p+5)(p+4)(p+3) / [(p+2)(p+1)p]$ .

#### Gel permeation chromatography (g.p.c.)

The non-uniformity in mass of PMMA macromolecules, characterized by  $M_{wp}/M_{np}$ , was determined with a Spectra Physics chromatograph (model 8100) using 1,2-dichloroethane as solvent.

## RESULTS AND DISCUSSION

#### Preparation of dispersions

Twenty-four polymerizations were performed with differing initial amounts of monomer and concentrations of the steric stabilizer (Tables 1–3). The concentration of the initiator was kept constant in all cases.

Prior to the evaluation of data and discussion of results, two facts should be clearly established. First, the steric stabilizer is completely incorporated into the dispersion particles; there are no unattached block copolymer molecules or micelles. This was checked by centrifugation of selected dispersions under conditions where only dispersion particles sediment. The clear supernatant liquid did not yield any traces of precipitate when poured into excess ethanol.

**Table 1** Conditions of synthesis and the experimental characteristics of PMMA dispersion stabilized in decane by a diblock copolymer

Code no.	$\varphi_M$	$10^2 c_s$ (g cm <sup>-3</sup> )	$c_p/c_s$	$10^{-6} M_{wD}$ (g mol <sup>-1</sup> ) (SLS)	$M_{wD}/M_{nD}$ (DLS)	$R_h$ (nm) (DLS)
DX1	0.05	0.5	8.06	200	1.47	72
DX2		1.0	4.03	74	1.28	61
DX3		1.5	2.69	59	1.39	59
DX4		2.0	2.02	42	1.57	56
D1	0.10	0.5	17.6	650	2.17	94
D2		1.0	8.80	250	1.93	73
D3		1.5	5.87	110	1.28	65
D4		2.0	4.40	96	1.35	65
D5	0.15	0.5	27.5	4200	1.61	151
D6		1.0	13.8	1400	1.29	121
D7		1.5	9.17	550	1.46	99
D8		2.0	6.88	420	1.88	92
D9	0.20	0.5	36.7	–	–	190
D10		1.0	18.4	–	–	173
D11		1.5	12.2	–	–	180
D12		2.0	9.17	–	–	162
D13	0.25	0.5	45.4	–	–	181
D14		1.0	22.7	–	–	187
D15		1.5	15.1	–	–	191

$\varphi_M$  is the volume fraction of MMA in the reaction mixture;  $c_s$  and  $c_p$  are concentrations of the steric stabilizer and of PMMA;  $M_{wD}$  is the mass-average particle mass;  $M_{wD}/M_{nD}$  is the mass to number-average molar mass ratio;  $R_h$  is the hydrodynamic radius of the particles. Initiation by AIBN,  $10^{-3}$  g cm<sup>-3</sup>; 60°C

**Table 2** Calculated characteristics of PMMA dispersions

Code no.	$Q_D$ ( $\mu\text{m}^{-3}$ )	$N_s$	$N_p$	$10^{-15} \sigma_s$ (m <sup>-2</sup> )	$10^{-23} \sigma_v$ (m <sup>-3</sup> )
DX1	200	150	2560	5.62	3.68
DX2	524	115	807	7.47	6.40
DX3	873	103	400	7.56	6.87
DX4	1360	88.7	260	7.84	7.84
D1	93.5	322	4040	5.54	2.45
D2	456	132	1000	4.76	3.04
D3	721	125	539	6.55	5.04
D4	915	131	359	6.89	5.30
D5	32.9	914	15 520	4.66	1.18
D6	81.9	735	4810	6.48	2.05
D7	244	370	1 910	5.53	2.27
D8	425	284	848	5.18	2.35

$Q_D$  is the number of dispersion particles per unit volume of the dispersion system;  $N_s$  and  $N_p$  are the numbers of stabilizer chains per dispersion particle;  $\sigma_s$  and  $\sigma_v$ , respectively, are the numbers of stabilizer chains per unit surface and unit volume of the particle body

Second, the steric stabilizer is not grafted onto PMMA or by PMMA. Both the original steric stabilizer and that recovered from dispersion gave identical g.p.c. traces using refractometric or ultraviolet detection. This would not be the case if even part of the stabilizer was grafted. This result is corroborated by a similar finding made by Dawkins and Taylor<sup>6</sup> who, by using osmometry, observed that the molar masses of the original and recovered steric stabilizer were identical. This means that the nature of the stabilization process is thermodynamic or physical, and it does not involve chemical links between the stabilizer and dispersion polymer. However,

it should be noted that when homopolymers are used as steric stabilizers, e.g. gelatin<sup>5</sup> or hydroxypropyl cellulose<sup>13</sup>, grafting is necessary for an effective stabilizing action.

#### Properties of dispersions and their correlation

Dispersion polymerization and its products can be described on a macroscopic, supermolecular (= particle) and molecular level. Consequently, three basic groups of parameters can be distinguished.

1. Variables related to the whole system. These describe the conditions of polymerization, concentrations of the individual components of the reaction mixture (e.g. the volume fraction of the monomer in the initial mixture,  $\varphi_M$ , the mass concentration of the steric stabilizer,  $c_s$ , and the polymer-to-stabilizer concentration ratio,  $c_p/c_s$ , etc.) (Table 1).

2. Quantities linked to supermolecular structures in the system, i.e. to the dispersion particles. These involve primarily the direct experimental data, e.g. the mass-average molar mass,  $M_{wD}$ , the mass-to-number molar-mass ratio,  $M_{wD}/M_{nD}$ , and the hydrodynamic radius,  $R_h$  (Table 1). Many other characteristics can be calculated (Table 2):

(i) The number of dispersion particles per unit volume of dispersion:

$$Q_D = N_a(c_p + c_s)/M_{nD} \quad (1)$$

where  $N_a$  is the Avogadro constant.

(ii) The number of the stabilizer molecules per dispersion particle:

$$N_s = w_s M_{nD}/M_{nS} \quad (2)$$

**Table 3** Mass-average molar mass,  $M_{wP}$ , mass-to-number-average molar mass ratio,  $M_{wP}/M_{nP}$ , of PMMA (which forms the dispersion particles) and the number of PMMA macromolecules per unit volume of dispersion system,  $Q_P$ 

No.	$10^{-3}M_{wP}$ (g mol $^{-1}$ )	$M_{wP}/M_{nP}$	$10^{-5}Q_P$ ( $\mu\text{m}^{-3}$ )	No.	$10^{-3}M_{wP}$ (g mol $^{-1}$ )	$M_{wP}/M_{nP}$	$10^{-5}Q_P$ ( $\mu\text{m}^{-3}$ )
DX1	170	3.6	5.1	D9	855	3.8	4.9
DX2	205	3.6	4.2	D10	1000	3.9	4.3
DX3	250	3.6	3.5	D11	1030	3.6	3.9
DX4	265	3.9	3.5	D12	1040	4.3	4.6
D1	480	3.4	3.8	D13	1200	4.1	4.7
D2	430	3.7	4.3	D14	1230	4.9	5.4
D3	470	3.5	3.9	D15	1500	4.0	3.7
D4	565	3.5	3.3				
D5	600	3.7	5.1	P1 <sup>a</sup>	130	2.8	5.2
D6	765	3.6	3.9	P2 <sup>a</sup>	310	3.7	6.3
D7	795	4.5	4.7	P3 <sup>a</sup>	450	3.9	7.2
D8	920	4.0	3.6	P4 <sup>a</sup>	740	3.9	5.8
				P5 <sup>a</sup>	990	3.5	4.8

<sup>a</sup>Samples P1, P2, P3, P4 and P5 were prepared in the absence of the steric stabilizer, i.e. by precipitation polymerization, for  $\phi_M = 0.05, 0.10, 0.15, 0.20$  and  $0.25$ , respectively

where  $w_S = c_S/(c_S + c_P)$  is the weight fraction of the stabilizer in a dispersion particle and  $M_{nS}$  is the number-average molar mass of the stabilizer.

(iii) The number of polymer (PMMA) macromolecules per dispersion particle:

$$N_P = (1 - w_S)M_{nD}/M_{nP} \quad (3)$$

where  $M_{nP}$  is the number-average molar mass of PMMA.

(iv) Finally, we also considered the ratio of the numbers given by equations (2) and (3):

$$N_P/N_S = (c_P/c_S)(M_{nS}/M_{nP}) \quad (4)$$

The definition of the above quantities does not depend on a specific model of the dispersion particle. If a core-shell model is expected to reflect the physical reality, we can assume that the corona thickness is equivalent to the end-to-end distance of the stabilizer chains. For hydrogenated polyisoprene chains of molar mass  $M_n = 58\,000$  (a value corresponding to the present steric stabilizer in decane) this distance can be estimated as 26 nm. We postulate that the radius of the particle body (consisting of anchor and PMMA chains) is  $R_B = R_h - 26$  nm. Some additional parameters can be then derived.

(v) The number of stabilizer chains per unit surface:

$$\sigma_s = N_S/(4\pi R_B^2) \quad (5)$$

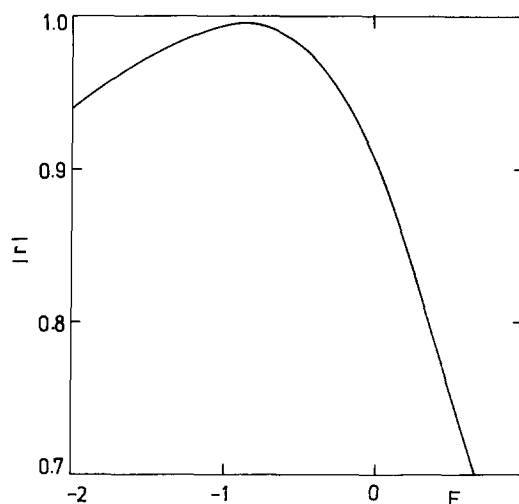
and per unit volume of the particle body:

$$\sigma_v = 3N_S/(4\pi R_B^3) \quad (6)$$

3. Finally, the third group of parameters describes the properties of PMMA macromolecules which form the dispersion particles, namely the mass-average molar mass,  $M_{wP}$ , or the mass-to-number-average ratio,  $M_{wP}/M_{nP}$ . It has been found that there is another quantity of interest, related to the molecular properties, namely, the number of PMMA macromolecules per unit volume of the dispersion system:

$$Q_P = N_a c_P/M_{nP} \quad (7)$$

where  $c_P$  is the PMMA concentration in the system (Table 3).



**Figure 1** Variation of the regression coefficient,  $r$ , with exponent  $E$  in equation (8). Illustration given here corresponds to the correlation of parameters  $Q_D$  and  $N_P$  (cf. also Figure 5d)

It was our aim to find how the properties of the system affect the parameters of the dispersion particles and the molecular structure of the polymer formed, and also to look for a relation between the individual parameters. For this purpose, the following procedure was used.

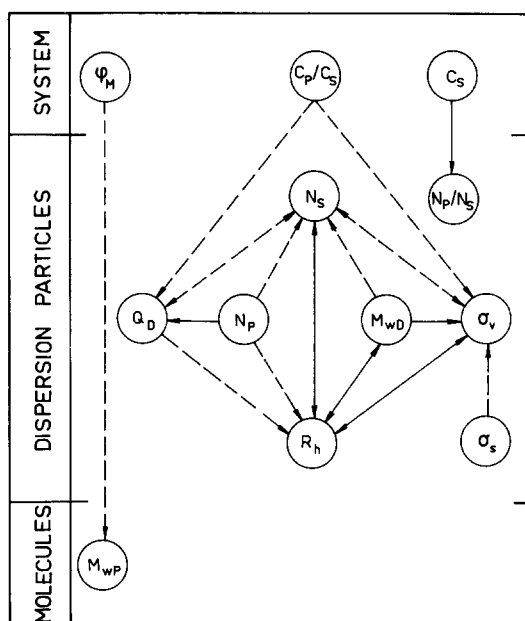
An arbitrary quantity  $y$  was plotted against another quantity  $x$  raised to the power  $E$ , and a straight line was fitted to the points by least-squares analysis:

$$y = A + B(x^E) \quad (8)$$

where  $A$  and  $B$  were the parameters of the line. The correlation coefficient,  $r$ , was calculated for dependence on the exponent  $E$  ( $-10 < E < 10$ ), and the maximum of its absolute value  $|r|_{\max}$  was sought. An example of such dependence is illustrated in Figure 1 for  $y = Q_D$  and  $x = N_P$ . We regarded the correlation as significant if  $|r|_{\max} > 0.97$  (Figure 2); in this case the coefficient  $E$  corresponding to  $|r|_{\max}$  is included in Table 4. For  $0.90 < |r|_{\max} \leq 0.97$ , the correlation was regarded as weaker (Table 4, values of  $E$  in parentheses). If no

maximum was found or  $|r|_{\max} \leq 0.9$ , the correlation was regarded as insignificant and variables  $y$  and  $x$  as independent of each other. It should be noted that if we similarly analyse the inverse dependence of  $x$  on  $y$ , we obtain a different exponent,  $E^*$ . It holds that  $E = 1/E^*$  only if  $A = 0$  in equation (8) (Table 4).

If in equation (8)  $A = 0$ , the above method would give the same result as a double-logarithmic plot of  $y$  versus  $x$ ; for  $A \neq 0$  the method used here is more general and never fails to reveal the correlation of the exponential type, given by equation (8), if such correlation exists. On the other hand, an artificial correlation may be sometimes obtained, e.g. if the points are distributed non-uniformly (e.g. if the  $x$ -coordinate of one experimental point greatly differs from the  $x$ -coordinates of the remaining points, then the latter set of points is regarded as nearly 'one point', the line is fitted through 'two points', and a high



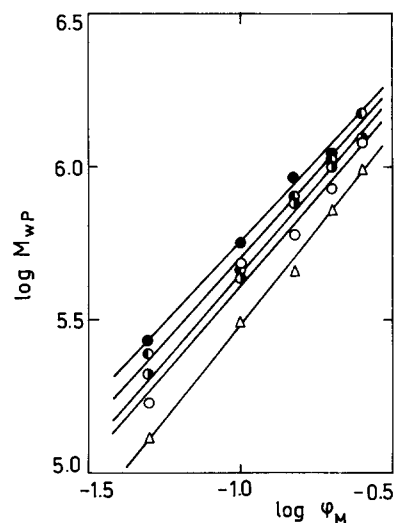
**Figure 2** Scheme of correlations found between the individual quantities. Full lines indicate a pronounced correlation,  $|r|_{\max} > 0.97$ , while broken lines correspond to a weaker correlation,  $0.90 < |r|_{\max} \leq 0.97$

value of the correlation coefficient is found); the results should be therefore assessed critically. In principle, the above procedure may also miss dependences of other than exponential type but it is useful as a rough guide.

#### System of molecular properties

The molecular structure of PMMA prepared by dispersion polymerization was characterized by the mass-average molar mass,  $M_{wP}$ , and the mass to number-average molar mass ratio,  $M_{wP}/M_{nP}$  (Table 3). In the data published on dispersion polymerization, information concerning the molar mass of the resulting polymer is scarce<sup>3,10,15</sup>. A broad molar-mass distribution has been reported by Lu *et al.*<sup>15</sup> and is also found in our case (Table 3).

An analysis of experimental data shows a weak correlation between  $M_{wP}$  and the starting volume fraction of the monomer  $\phi_M$  (Table 4). However, a much better fit is obtained when these dependences are plotted separately for the individual concentrations of the steric stabilizer (Figure 3). The slopes of the double-logarithmic



**Figure 3** Logarithmic plot of the mass-average molar mass of PMMA,  $M_{wP}$ , versus the volume fraction of MMA in the starting polymerization mixture,  $\phi_M$ , for various concentrations of the steric stabilizer,  $c_s = 0$  ( $\Delta$ ), 0.5 ( $\circ$ ), 1.0 ( $\bullet$ ), 1.5 ( $\bullet$ ) and 2.0 ( $\bullet$ )  $\times 10^{-2} \text{ g cm}^{-3}$

**Table 4** Correlation of the quantities. Values of the exponent  $E$  for which the linear dependence  $y = A + B(x^E)$  has the maximum correlation coefficient  $|r| > 0.97$

$x \setminus y$	$M_{wD}$	$R_h$	$N_s$	$N_p$	$N_p/N_s$	$\sigma_s$	$\sigma_v$	$Q_D$	$M_{wP}$
$\phi_M$	—	—	—	—	—	—	—	—	(1.1)
$c_s$	—	—	—	—	-1.0	—	—	—	—
$c_p/c_s$	[2.9]	—	—	[2.4]	—	—	(-0.5)	(-0.6)	—
$M_{wD}$	*	0.27	(0.4)	[1.0]	—	—	-0.57	—	—
$R_h$	4.8	*	1.8	[5.1]	—	—	-4.0	—	—
$N_s$	[5.5]	0.46	*	[6.2]	—	—	(-1.9)	(-0.7)	—
$N_p$	[1.1]	(0.4)	(0.5)	*	—	—	—	-0.86	—
$N_p/N_s$	—	—	—	—	*	—	—	—	—
$\sigma_s$	—	—	—	—	—	*	(5.5)	—	—
$\sigma_v$	[-2.4]	-0.85	(-1.2)	[-2.5]	—	—	*	—	—
$Q_D$	—	(-0.4)	(-0.6)	[-1.3]	—	—	—	*	—
$M_{wP}$	—	—	—	—	—	—	—	—	*

A less pronounced correlation,  $0.90 < |r| \leq 0.97$ , is indicated by parentheses. A marked but biased correlation is denoted by square brackets. If  $|r| \leq 0.90$  for any  $|E| < 10$ , no value of the exponent is given.  $A$  and  $B$  are parameters. For explanation of symbols see Tables 1 and 2. An asterisk denotes that the correlation is meaningless

plots vary from 1.25 (for the unstabilized precipitation polymerization) to 1.03 (for the highest concentration of the stabilizer), i.e. these quantities are nearly proportional. The influence of the steric stabilizer can be regarded as modest. Obviously, the process of polymerization and the steric stabilization of particles are to a great extent independent. This is also supported by the fact that no correlation has been found between the molar mass of PMMA,  $M_{wp}$ , and the variables related to the size and morphology of the dispersion particles.

In the simple low-conversion kinetics of homogeneous radical polymerization one expects molar mass to be proportional to  $M_{np} \sim [M]/[I]^{0.5}$ , where  $[M]$  and  $[I]$  are the molar concentration of monomer and initiator, respectively. Under these conditions, the PMMA concentration in the reaction mixture,  $c_p$ , can be taken as proportional to  $[M]\psi_M$ , where  $\psi_M$  is the degree of conversion. Hence, from equation (7) the number of polymer chains per unit volume  $Q_p \sim \psi/[I]^{0.5}$ . Thus, for polymers prepared by polymerization to low and comparable degrees of conversion,  $Q_p$  depends only on the concentration of the initiator.

Rather surprisingly, in our high-conversion dispersion polymerization carried out at constant overall initiator concentration we find that  $Q_p$  is invariant and depends neither on monomer nor on stabilizer concentration (Table 3). In practice, this means that the number of PMMA macromolecules formed during polymerization is comparable in all investigated cases. This observed experimental evidence helped us to understand some of the correlations discussed below.

No links with other variables have been found for the non-uniformity ratio of PMMA,  $M_{wp}/M_{np}$ . The slight fluctuation in this parameter observed with reaction conditions (Table 3) seems to have a random character.

#### System and dispersion properties

The only pronounced correlation between experimental properties of the whole system and parameters of the dispersion particles was the dependence of the ratio  $N_p/N_s$  on the reciprocal stabilizer concentration,  $N_p/N_s \sim c_s^{-1}$ . This is the expected result. Since  $M_{ns}$  in equation (4) is constant and the ratio  $c_p/M_{np} = Q_p/N_a$  has been found to be invariant (Table 3), the relation  $N_p/N_s \sim c_s^{-1}$  (Table 4) follows.

Dawkins and Taylor<sup>6</sup> found that the particle radius is dependent on the concentration of the polystyrene-*block*-poly(dimethylsiloxane) steric stabilizer as  $R \sim c_s^{-0.77}$ . In our case, we did not observe any overall correlation of these two quantities. However, for the individual monomer concentrations  $\phi_M$  the logarithmic plots of hydrodynamic radii  $R_h$  versus  $c_s$  can be approximated by straight lines with slopes  $-0.18$ ,  $-0.28$  and  $-0.37$  for  $\phi_M = 0.05$ ,  $0.10$  and  $0.15$ , respectively (Figure 4). For higher monomer contents this partial correlation deteriorates.

#### Properties of dispersion particles

One of the most obvious relationships is that between the dimension of the particles, e.g. the hydrodynamic radius  $R_h$ , and the mass of the particles, e.g. molar mass  $M_{wD}$ . The scaling  $R_h \sim M_{wD}^{1/3}$  would be expected for compact homogeneous spheres. For dispersion particles, where  $R_h$  is strongly affected by the shell while mass is

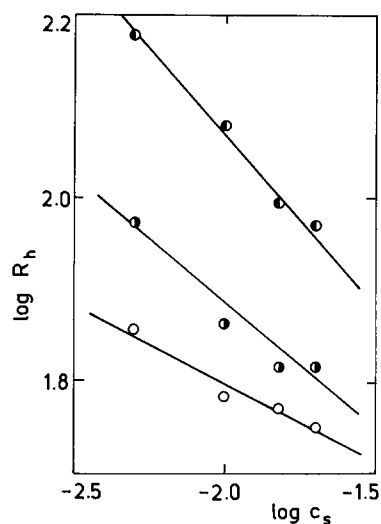


Figure 4 Logarithmic plot of the hydrodynamic radius,  $R_h$ , versus the concentration of the steric stabilizer,  $c_s$ , for various volume fractions of MMA in the starting mixture,  $\phi_M = 0.05$  (○),  $0.10$  (◐) and  $0.15$  (●)

controlled mainly by the body of the particle,  $R_h \sim M_{wD}^{0.27}$  is found (Table 4, Figure 5a).

The hydrodynamic radius  $R_h$  can be linked to other parameters, e.g. to the number of stabilizer chains per particle,  $R_h \sim N_s^{0.46}$  (Table 4, Figure 5b) or per unit volume of the particle body,  $R_h \sim \sigma_v^{-0.85}$  (Table 4, Figure 5c).

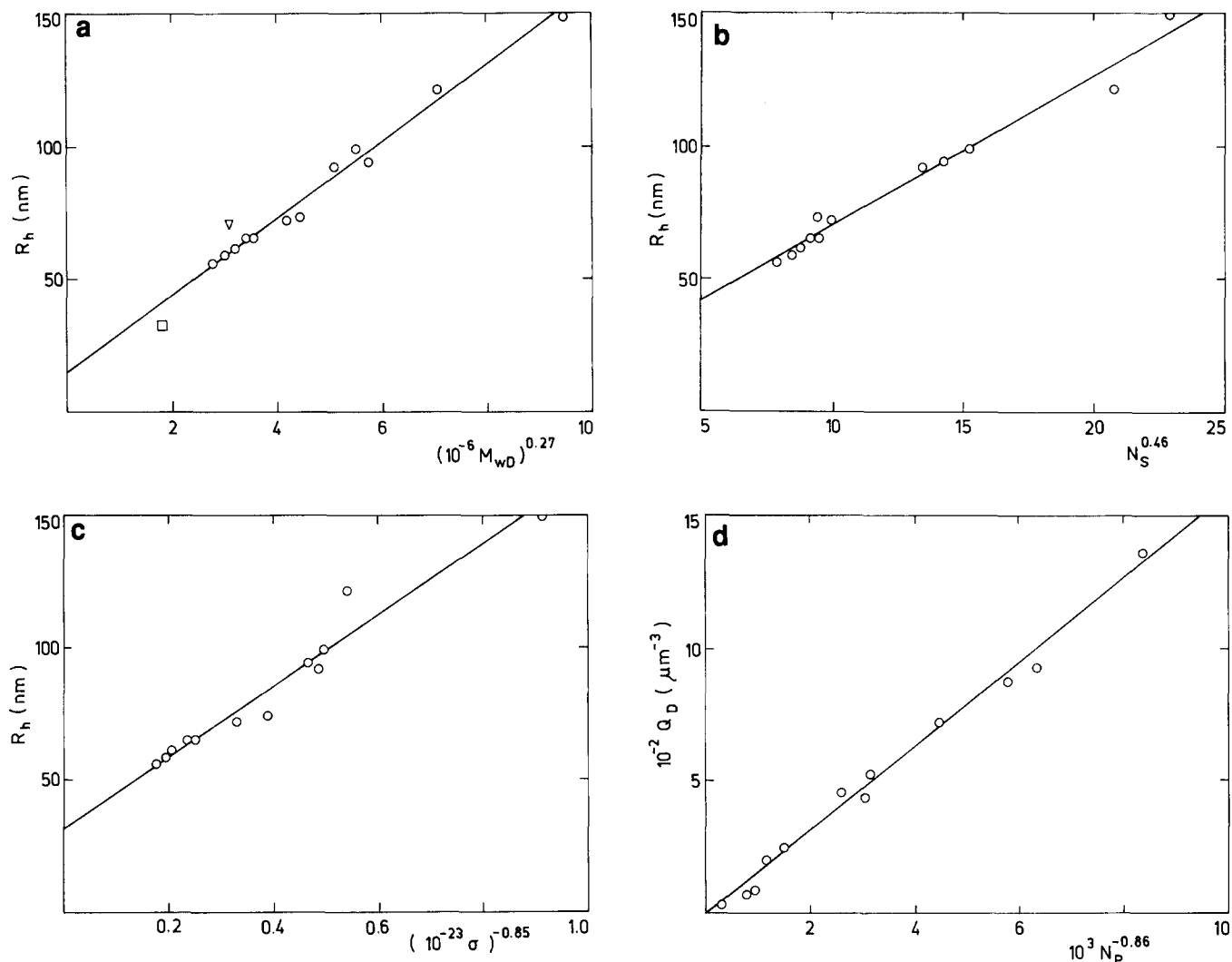
A very good correlation is found between the number of dispersion particles per unit volume,  $Q_D$ , and the number of PMMA macromolecules per dispersion particle,  $N_p$  (Table 4). The nearly inverse proportionality,  $Q_D \sim N_p^{-0.86}$  (Figure 5d), is not unexpected. A given number of PMMA chains can be distributed between many small particles (i.e.  $Q_D$  high and  $N_p$  low) or between few large particles (i.e.  $Q_D$  low and  $N_p$  high). The number of PMMA chains per unit volume,  $Q_p$ , is practically invariant (Table 3). From equations (1), (3) and (7) we have  $Q_D = Q_p/N_p$ , and the observed dependence comes as a logical, though not trivial, consequence.

Dawkins and Shakir<sup>19</sup> prepared PMMA dispersions using an almost identical steric stabilizer as in our study, but in *n*-heptane. The surface coverage of dry particles by the steric stabilizer was estimated from ultraviolet spectrometry. By combining this quantity with dimensions obtained by electron microscopy, they found that the surface area per stabilizer chain is 40.6–47.3 nm<sup>2</sup> for particles with radii 66–144 nm, i.e. fairly constant<sup>6,19</sup>.

Also in our case the surface fraction of the swollen particle body per stabilizer chain,  $1/\sigma_s$ , is only slightly dependent on the particle radius and varies between 128 nm<sup>2</sup> and 217 nm<sup>2</sup> (i.e.  $\sigma_s = 4.6 \times 10^{15}$ – $7.8 \times 10^{15}$  chains m<sup>-2</sup>, Table 2). As PMMA particles are considerably swollen (20–60 vol% of the medium<sup>12</sup>), the surface area stabilized by one chain is larger compared with the dry particles.

#### Block copolymer micelles

Dispersion particles stabilized by block copolymers in selective solvents can be viewed as block copolymer micelles 'stuffed' with the polymer formed during the polymerization. Obviously, the behaviour of block copolymer micelles and of dispersion particles stabilized by these copolymers must have many features in



**Figure 5** Selected dependences  $y = A + B(x^E)$  plotted for the exponent  $E$  which yields the maximum absolute value of the correlation coefficient,  $|r|_{\max}$  (cf. Table 4). Quantities  $y$  and  $x$  are: (a)  $R_h$  and  $M_{wD}$ ; (b)  $R_h$  and  $N_S$ ; (c)  $R_h$  and  $\sigma_v$ ; (d)  $Q_D$  and  $N_p$ . In (a) the symbols  $\nabla$  and  $\square$  correspond to the original and heated block copolymer micelles, respectively

common. However, our attempt to characterize the micelles of P(S-EP) in decane failed to give an unambiguous answer.

The diblock copolymer is easily soluble in decane at room temperature. In the concentration range  $c < 4 \times 10^{-4} \text{ g cm}^{-3}$ , the molar mass of micelles,  $M_w = 65.7 \times 10^6 \text{ g mol}^{-1}$ , is obtained from SLS. Dynamic light scattering yields the hydrodynamic radius  $R_h = 71 \text{ nm}$ . The solutions are stable and their properties do not change for months. If these solutions are exposed to temperatures exceeding  $\sim 55^\circ\text{C}$  and then cooled down to room temperature, much smaller and stable particles are observed,  $M_w = 8.7 \times 10^6 \text{ g mol}^{-1}$  and  $R_h = 32 \text{ nm}$ . A similar phenomenon has already been reported by Price *et al.*<sup>25,32</sup>.

Classical spherical diblock micelles are believed to be nearly ideally uniform in size<sup>1</sup>. Our preliminary DLS experiments indicate a broad particle size distribution, which gets broader as the polymer concentration increases ( $M_w/M_n = 2.2$  for  $c = 5 \times 10^{-4} \text{ g cm}^{-3}$  and  $M_w/M_n > 5$  for  $c > 7.5 \times 10^{-3} \text{ g cm}^{-3}$ ). The extent of non-uniformity remains comparable even after the solutions have been heated and cooled again.

In SLS, moderately concentrated solutions ( $5 \times 10^{-3} - 2 \times 10^{-2} \text{ g cm}^{-3}$ ) show dissymmetry of scattered light,

$Z = I_{45}/I_{135}$ , lower than unity. Such behaviour is found in systems of strongly interacting and/or ordered macromolecules, e.g. with strong polyelectrolytes<sup>33</sup>. In the non-polar systems under investigation such results were rather unexpected, but had been reported in several cases<sup>22,23,25</sup> for P(S-EP) in alkanes. This behaviour becomes less pronounced, but is still present, after the heating of solutions to  $100^\circ\text{C}$  and cooling. Internal ordering of the micellar system seems to be an inevitable conclusion<sup>21</sup>, although its presence in highly diluted solutions is puzzling.

These experimental observations are far from being fully understood and require further investigation. Consequently, the desired link between the characteristics of block copolymer micelles and properties of dispersion particles could not be established.

#### Unresolved problems

It is somewhat surprising to find that the PS blocks act so well as anchors in the stabilization of PMMA dispersions. Since PS and PMMA are virtually immiscible, one would intuitively expect the PS block to associate into block copolymer micelles and PMMA simply to precipitate. In our opinion this means that polymerization proceeds inside the swollen micelles, and

PS chains get trapped, at least partly, inside the particle core.

This is supported by the finding of Dawkins and Taylor<sup>6</sup> and also by our observation that many dispersions remain stable even when a large excess of cyclohexane is added (and also at elevated temperatures). Under these conditions both the corona and anchor chains are soluble and the stabilizing effect should vanish. Since we know that the steric stabilizer is not chemically grafted to or by PMMA, it has to be trapped within the core or at least in its surface layer. In our opinion, a strong adsorption of PS onto PMMA, which is an alternative explanation, does not seem to be likely.

## CONCLUSIONS

Well-defined PMMA dispersions can be prepared in a non-aqueous medium by using P(S-EP) as steric stabilizer. The kinetics of polymerization and the process of steric stabilization are independent to a great extent. The number of PMMA macromolecules formed during the dispersion polymerization was found to be practically unaffected by the monomer and steric stabilizer concentrations.

On the particle level, the number of stabilizer chains per unit surface of the particle body varies only weakly with reaction conditions and thus seems to control the size of the particles.

A rather complex behaviour of the steric stabilizer in decane did not allow us to establish an unambiguous link between the properties of block copolymer micelles and of dispersion particles.

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## REFERENCES

- 1 Tuzar, Z. and Kratochvíl, P. *Adv. Polym. Interface Sci.* 1976, **6**, 201
- 2 Tuzar, Z. and Kratochvíl, P. *Surf. Colloid Sci.* in press
- 3 Barrett, K. E. J. and Thomas, H. R. *J. Polym. Sci. A1* 1969, **7**, 2621
- 4 Barrett, K. E. J. (Ed.) 'Dispersion Polymerization in Organic Media', J. Wiley & Sons, London, 1975
- 5 Stejskal, J., Straková, D. and Kratochvíl, P. *J. Appl. Polym. Sci.* 1988, **36**, 215
- 6 Dawkins, J. V. and Taylor, G. *Polymer* 1979, **20**, 599
- 7 Dawkins, J. V. and Taylor, G. *Colloid Polym. Sci.* 1980, **258**, 79
- 8 Golubev, S. V., Tikhonova, Z. A. and Semchikov, Yu. D. *Vysokomol. Soed.* 1984, **A26**, 594
- 9 Antl, L., Goodwin, J. W., Hill, R. D., Ottewill, R. H., Owens, S. M. and Papworth, S. *Colloid Surf.* 1986, **17**, 67
- 10 Winnik, M. A., Lukas, R., Chen, W. F., Furlong, P. and Croucher, M. D. *Makromol. Chem., Macromol. Symp.* 1987, **10/11**, 483
- 11 Golubev, S. V., Mamaeva, A. V. and Tikhonova, Z. A. *Vysokomol. Soed.* 1988, **A30**, 1848
- 12 Stejskal, J., Kratochvíl, P., Koubík, P., Tuzar, Z., Urban, J., Helmstedt, M. and Jenkins, A. D. *Polymer* 1990, **31**, 1816
- 13 Ober, K. C., Lok, K. P. and Hair, M. L. *J. Polym. Sci., Polym. Lett. Edn* 1985, **23**, 103
- 14 Tseng, C. M., Lu, Y. Y., El-Aasser, M. S. and Vanderhoff, J. W. *J. Polym. Sci., Polym. Chem. Edn* 1986, **24**, 2995
- 15 Lu, Y. Y., El-Aasser, M. S. and Vanderhoff, J. W. *J. Polym. Sci., Polym. Phys. Edn* 1988, **26**, 1187
- 16 Okubo, M., Ikegami, K. and Yamamoto, Y. *Colloid Polym. Sci.* 1989, **267**, 193
- 17 Winnik, F. M. and Paine, A. J. *Langmuir* 1989, **5**, 903
- 18 Bromley, C. W. A. *Colloid Surf.* 1986, **17**, 1
- 19 Dawkins, J. V. and Shakir, S. A. *Colloid Polym. Sci.* 1987, **265**, 329
- 20 Higgins, J. S., Blake, S., Tomlins, P. E., Ross-Murphy, S. B., Staples, E., Penfold, J. and Dawkins, J. V. *Polymer* 1988, **29**, 1968
- 21 Higgins, J. S., Tomlins, P. E., Dawkins, J. V., Maghami, G. G. and Shakir, S. A. *Polym. Commun.* 1988, **29**, 122
- 22 Mandema, W., Zeldenrust, H. and Emeis, C. A. *Makromol. Chem.* 1979, **180**, 1521
- 23 Price, C., Hudd, A. L. and Wright, B. *Polymer* 1982, **23**, 170
- 24 Candau, F., Heatley, F., Price, C. and Stubbersfield, R. B. *Eur. Polym. J.* 1984, **20**, 685
- 25 Price, C. *Pure Appl. Chem.* 1983, **55**, 1563
- 26 Price, C., Kendall, K. D., Stubbersfield, R. B. and Wright, B. *Polym. Commun.* 1983, **24**, 200
- 27 Schouten, M., Dorrpaal, J., Stassen, W. J. M., Vlak, W. A. H. M. and Mortensen, K. *Polymer* 1989, **30**, 2038
- 28 Kratochvíl, P., Straková, D., Stejskal, J. and Tuzar, Z. *Macromolecules* 1983, **16**, 1136
- 29 Ochiai, H., Kamata, K. and Murakami, I. *Polym. Commun.* 1984, **25**, 158
- 30 Koňák, Č., Štěpánek, P. and Sedláček, B. *Czech. J. Phys.* 1984, **A34**, 497
- 31 Jakeš, J. *Collect. Czech. Chem. Commun.* in press
- 32 Price, C., Chan, E. K. M., Hudd, A. L. and Stubbersfield, R. B. *Polym. Commun.* 1986, **27**, 196
- 33 Stejskal, J., Beneš, M. J., Kratochvíl, P. and Peška, J. *J. Polym. Sci., Polym. Phys. Edn.* 1974, **12**, 1941