# Polymerizations in the presence of seeds: 5. Core–shell structure of two-stage emulsion polymers

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Polymeric dispersions with a concentric core–shell structure of the latex particles were obtained by a two-stage emulsion polymerization technique. Conditions for the formation of shells on polymeric seeds are discussed. The process of shell formation was detected by electron microscopy. A small-angle neutron scattering investigation was carried out in order to verify the core–shell structure of the particles.

**(Keywords: emulsion polymerization; core–shell particles; polymer blends; small-angle neutron scattering)**

## INTRODUCTION

Emulsion polymerization is a well known technique for producing dispersions with a well defined structure of the polymer particles. One of these well defined structures is the 'core–shell structure'. There are some advantages of dispersions with polymeric core–shell particles:

(i) It is possible to modify the interfacial properties of polymer particles in the aqueous phase by the addition of only very small amounts of a modifying agent during the last period of the reaction. In this way, the improvement of film properties of such dispersions is uncomplicated and inexpensive.

(ii) Investigations of core–shell structures and of their formation afford a better understanding of emulsion polymerization as a whole, and mainly of the topochemistry of the reaction during the period of particle growth, and of adsorption and absorption phenomena.

(iii) Polymers with core–shell structure are perfect model systems for investigating the material properties of polymer blends and composites because of their regular distribution of one polymer inside a matrix polymer and because of the simple spherical geometry of the system.

The aim of this paper is to show that emulsion polymerization is a useful procedure for obtaining such structures with a very high symmetry. It should be noted that, in principle, some different methods of emulsion polymerization are known which result in core–shell particles:

(i) 'Continuous' core–shell particles can be produced by a batch copolymerization of monomers with different rate constants of copolymerization or by a monomer addition method with a continuous or discontinuous variation of composition of the monomer feed.

(ii) 'Discontinuous' core–shell particles were obtained by a two- or multi-stage process using polymeric seeds.

Variations and combinations of these basic methods are also possible.

The investigations of this paper deal with the two-stage emulsion polymerization process. A set of conditions for the formation of core–shell structures will be discussed and the experimental verification of these structures by small-angle neutron scattering (SANS) will be presented.

## EXPERIMENTAL

The polymerizations were carried out as seeded emulsion polymerizations without any soap in a thermostated half-litre reactor (stirring rate $250\,\mathrm{min}^{-1}$; temperature 343 K). The monomers used (styrene (S), methyl methacrylate (MMA) and vinyl acetate (VAc)) were technical products. They were used after conventional cleaning. Doubly distilled water was added to the reaction vessel and heated with stirring to the reaction temperature. The aqueous solution of initiator ($7 \times 10^{-3}$ $\mathrm{mol\,dm}^{-3}$ $K_2S_2O_8$) was added and, after 10 min, the continuous dosage of monomer I was started. This polymerization was continued to maximum conversion. The latex obtained was the seed latex of the second step.

In this step, the seed latex (polymer I) was also added to the reaction vessel and heated, stirring continuously, to the reaction temperature. Then the aqueous solution of initiator ($7 \times 10^{-3}\,\mathrm{mol\,dm}^{-3}$ $K_2S_2O_8$ referred to the whole mixture and preheated to the reaction temperature) was added, and the continuous dosage of monomer II was started simultaneously under monomer-starved conditions.

The monomer conversion has been determined gravimetrically. The particle size was obtained by conventional light scattering and electron microscopy. The polymers were separated from the dispersion medium by freeze–thaw coagulation or by centrifuging, the samples in both cases then being dried under vacuum. The following polymer I–polymer II combinations were

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studied in order to find an appropriate set of conditions for shell formations: PVAc–PS, PS–PVAc, PS–PMMA, PVAc–PMMA.

Experimental apparatus and calculating procedures of SANS are described in detail elsewhere[1,2]. The intensities were recorded in a scattering vector range of 0.0015–0.02 $Å^{-1}$ for a wavelength $\lambda = 1.085$ Å. Data were corrected for background and desmeared by a modified algorithm of Moore[3]. The SANS investigations were carried out using undeuterated PS and PMMA as the cores and deuterated PMMA as the shell polymer.

## ELECTRON MICROSCOPY

### *Seed latex particle number*

The first technical and scientific information about core–shell latex particles was published in the 1970s[4–8]. Krieger *et al.*[4,5] described the coating of polystyrene particles with vinyltoluene and divinylbenzene. In the case of very high emulsifier concentrations they observed a new particle generation. Williams *et al.*[6–8] created the 'core–shell model' of polystyrene latex particles. This idea was derived from kinetic investigations and electron microscopic observations. The model suggests that the monomer-swollen polymer particle surface is the main reaction locus during the period of particle growth. In spite of some contrary explanations of Williams' results (e.g. ref. 9), the conclusion is accepted that particle growth takes place mainly at the particle surface in homo-emulsion polymerizations (e.g. ref. 10). Hence, it should be possible to produce core–shell particles via a two-stage emulsion polymerization using two or more different monomers if the formation of separate polymer II particles is prevented.

In a previous publication, Schmutzler[11] derived an equation that allows the calculation of the minimal seed latex particle number $N_I$ in order to prevent a new particle generation of polymer II:

$$N_I^2 \geqslant \frac{3k_{11}}{8\pi k_{12}^2 r_0^3 \rho_T} \frac{\mathrm{d}M_{II}}{\mathrm{d}t} \tag{1}$$

where $k_{11}$ and $k_{12}$ are the rate constants of the primary particle aggregation and of the primary particle–polymer particle aggregation, respectively; $r_0$ and $\rho_T$ are the radius and the density of the primary particles, respectively; and $\mathrm{d}M_{II}/\mathrm{d}t$ is the monomer II conversion per unit time. Equation (1) was verified experimentally using polymeric[12] and inorganic[13] seeds. The polymerizations of the present study were carried out with seed latexes having a specific particle number very much higher than the value calculated from equation (1). In the case of a lower specific seed particle number, separate particle formation of polymer II occurs on a very large scale. This is demonstrated in *Figure 1* in the case of PS-seeded emulsion polymerization of PVAc.

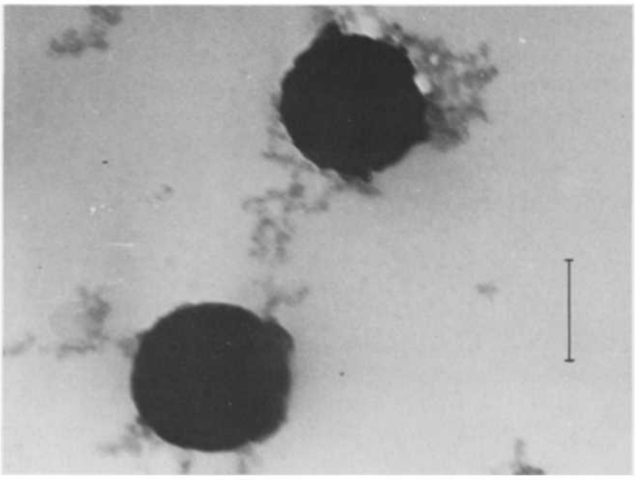

**Figure 1** Electron micrograph of second particle generation in PS-seeded PVAc emulsion polymerization (the bar indicates 250 nm)

### *Method of monomer addition*

Besides the minimal seed particle number, the monomer II addition method influences the formation of structured latexes (e.g. refs. 14–19). These investigations have shown that, in general, equilibrium swelling and semi-batch addition of monomer II produce particles with a more homogeneous or continuously changing radial polymer composition. Monomer II addition under monomer-starved conditions (i.e. feed rate lower than reaction rate of monomer II homo-emulsion polymerization) results in particles consisting of separate polymers or of a radial polymer distribution with a steeper or stepwise change in composition. Therefore, we used monomer addition under starved conditions in order to obtain nearly 'perfect' core–shell systems. Nevertheless, a constant monomer II concentration is maintained by applying this method inside the polymer particles during the period of monomer addition because of the high monomer sorption rate into the particles (8–20 times faster than the corresponding reaction rate[20]). Hence, particle inhomogeneities do not arise from time-dependent monomer concentration variations.

### *Hydrophobicity and compatibility of the polymers*

A further step towards the production of perfect core–shell particles is to use as a core a more hydrophobic polymer than the shell polymer (i.e. the water solubility of monomer I is lower than that of monomer II). This condition is not absolutely necessary in all polymer combinations or reaction runs. In some cases, the formation of polymer I–polymer II core–shell particles may also occur using the opposite relation. Additionally, via this opposite relation, one can obtain inverted core–shell particles (polymer II core and polymer I shell)[21,22] or non-spherical particles[14].

A sharp separation of shell and core polymers can be enhanced if two incompatible polymers or copolymers are used. In this case, some deviations from concentric, spherical particle growth can be observed. The particle growth and the formation of shells around cores can be followed by transmission electron microscopy. In the first period of seeded polymerization, the shell formation is very inhomogeneous if (i) two incompatible polymers are used and (ii) the shell polymer is hydrophobic compared with the core polymer.

On the micrographs (*Figure 2*) one can see small 'islands' of PS on a PVAc core latex particle. These islands grow by continued polymerization according to diameter $\sim c_{PS}^{1/3}$, where $c_{PS}$ is the weight fraction of PS. The number of islands per particle remains nearly constant at 5–7 per particle. These islands touch each other at a shell–core mass ratio of 0.30–0.35, and then they build up closed but non-spherical shells at a ratio of 0.40–0.45. The particles are spherical at a mass ratio equal to or greater than 0.70.

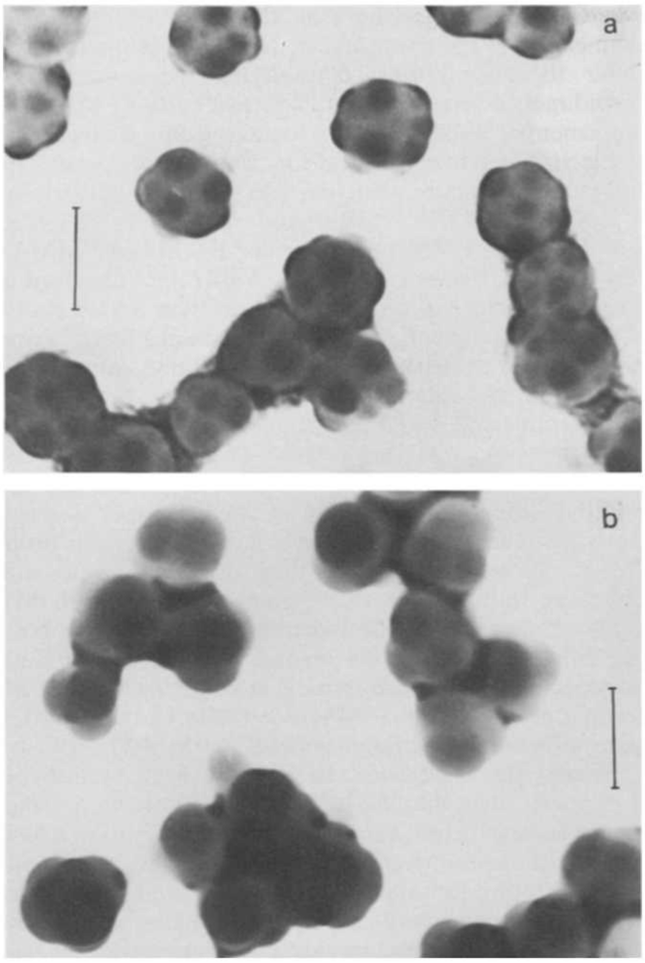

**Figure 2** Electron micrograph of shell formation of PS on a PVAc core latex particle: (a) PVAc/PS = 80/20 by weight; (b) PVAc/PS = 50/50 by weight (the bar indicates 250 nm)

The dimensions and the number of islands on the core depend on the hydrophobicity of core and shell polymers. Hydrophobic core and hydrophilic shell polymers result in a high number of small-sized islands and, therefore, a more continuous and homogeneous shell formation occurs than in the combination shown in *Figure 2*. Similar results have been obtained with the other polymer–polymer systems. In the case of PVAc–PMMA core–shell polymers, the diameters of the PMMA islands are only one-third to one-half as large as the corresponding diameters of the PS islands on PVAc cores at the same shell–core mass ratio. The formation of closed PMMA shells occurs at shell–core mass ratios greater than 0.30. The PS–d-PMMA system exhibits a homogeneous shell formation comparable with the PS–PVAc system discussed above.

Obviously, the oligomers and macroradicals generated in the aqueous phase will be adsorbed at the seed particle surface (or into a seed particle surface layer) in the case of a sufficiently high seed particle number. These discrete loci of adsorption are preferred to absorb further monomer II and/or to adsorb further oligomers or macroradicals compared with the bare seed surface. As a result, these discrete loci of adsorption became discrete loci of polymerization. The higher the hydrophilicity of the shell polymer, the smaller the tendency of adsorption of oligomers or macroradicals, and the smaller the tendency of absorption of monomer II. This effect results in a decrease of the degree of preference of these loci in the adsorption or absorption processes compared with the bare surface. Hence, the probability of formation of new islands at the core particle surfaces increases and the inhomogeneity of particle growth decreases. In the case of compatible polymers or in the 'extreme' case of homo-seeded emulsion polymerization, spherical particle growth without inhomogeneities is always to be expected and is in fact also observed (see e.g. PMMA–d-PMMA).

### *Conditions of shell formation*

Applying the procedure of seeded emulsion polymerization discussed above one can summarize the general conditions for shell formation as follows:

(i) the use of water-soluble initiator;

(ii) monomer addition under monomer-starved conditions;

(iii) sufficiently high seed particle number;

(iv) hydrophobicity of the core in comparison with the water solubility of the second monomer; and

(v) incompatibility of core and shell polymers.

It should be noted here that the conditions discussed above are only one way of obtaining core–shell structures. However, they are applicable for all polymer–polymer combinations used in this study. In this connection, the influence of the glass transition temperature of the polymers on shell formation has not yet been examined in depth.

## SMALL-ANGLE NEUTRON SCATTERING

The core–shell particles used in the SANS experiments (PS–d-PMMA and PMMA-d-PMMA) are of a distinct concentric spherical geometry. The polymer II fraction is so high that inhomogeneities of shell formation of the PS–d-PMMA system at the beginning of seed polymerization can be neglected. Analysing the results from electron microscopy, there is no conclusive evidence that the formation of islands takes place only at the particle surfaces (i.e. without any polymer II buried in the core). Ultra-thin cross-sections of the samples gave no better insight into the particle structure by transmission electron microscopy.

However, the structure of such particles can be obtained by scattering investigations. X-ray scattering is difficult to interpret because of the small differences in the electron densities of the polymers and the large difference between the polymers and the surrounding water. Therefore, small-angle neutron scattering was used in order to detect the core–shell structure. When using this technique, it is necessary to guarantee a sufficiently large contrast between core and shell. This contrast was made using completely deuterated monomers in the second stage, while undeuterated monomers were used in the first stage to produce the cores. The total scattering length $b$ per unit volume is then given by:

$$b = b(\text{core}) + b(\text{shell}) + b(\text{dispersion medium}) \quad (2)$$

The core scattering was matched by using a mixture of $H_2O$ and $D_2O$. Then, the scattering intensities observed arise only from hollow-sphere scattering. By taking into account some geometric considerations and using procedures for desmearing the experimental scattering curve and for correcting other instrumental effects, one may obtain core radius and shell thickness

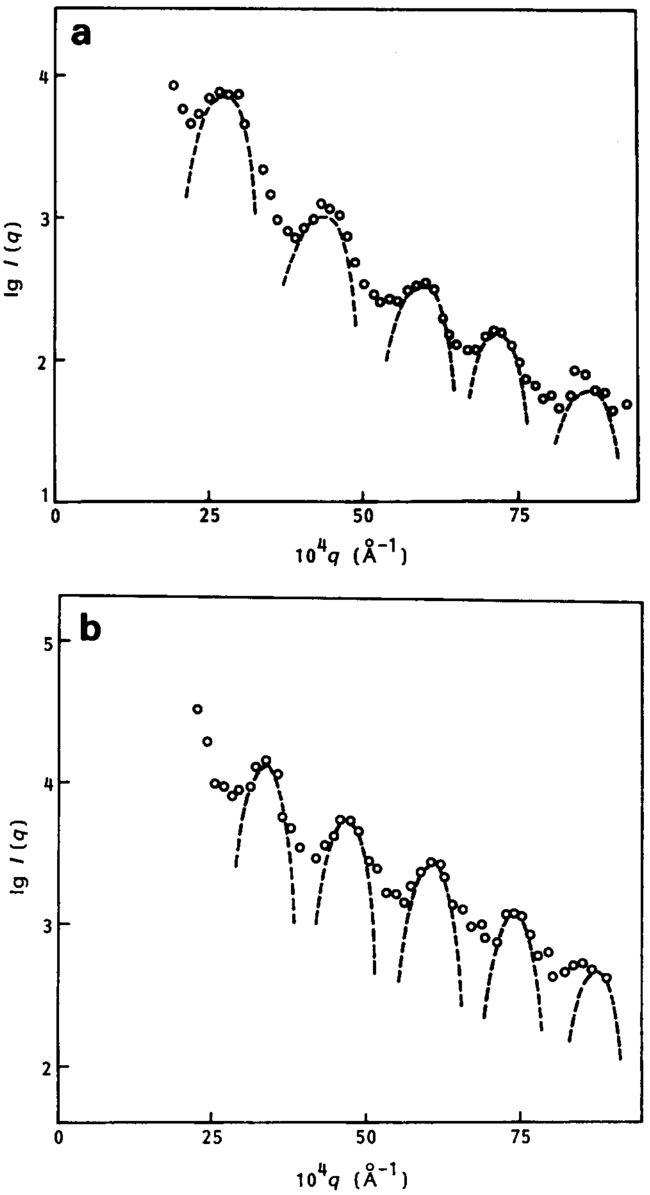

**Figure 3** Neutron scattering intensity as a function of wavevector (desmeared and corrected values). (a) Monodisperse polystyrene latex: (○) experimental; (---) calculated for sphere of radius 215 nm. (b) Core–shell latex (PS core, d-PMMA shell): (○) experimental; (---) calculated for hollow sphere of 40 nm shell thickness

**Table 1** Parameters of particles

| | Core radius (nm) | | Shell thickness (nm) | |
|---|---|---|---|---|
| | Light scattering | SANS | Chemical composition | SANS |
| PS–core | 219 | 215 | – | – |
| PS–d-PMMA | (219) | (215) | 50 | 40 |
| PMMA–core | 51 | 50 | – | – |
| PMMA–d-PMMA | (51) | (50) | 11 | 17 |

from the scattering intensity profile[1,2] (see *Figure 3* and *Table 1*):

$$S_{\text{shell}}(q)=\left(\frac{A}{(qr)^3(\Delta^3-1)}[\sin(q\Delta r)-\sin(qr)+(qr)\cos(qr)-(q\Delta r)\cos(q\Delta r)]\right)^2 \quad (3)$$

where $d=r(\Delta-1)$ is the shell thickness, $r$ is the core diameter, $q$ is the scattering vector and $\Delta$ is the ratio of outer to inner radius. Considering the accuracy of turbidimetric determination of particle radii (±8%), the agreement of SANS with light scattering data is excellent.

Electron microscopy confirms the monodispersity of both core and core–shell particle latex (polydispersity $\bar{r}_w/\bar{r}_n=1.006$, 1.010, 1.019 and 1.021 of PS–core, PS–PMMA, PMMA–core and PMMA–d-PMMA, respectively). Fisher *et al.*[23] and Wai *et al.*[24] observed a stronger increase in polydispersity in their SANS study of seeded polymerization using smaller-sized core particles and a higher monomer II addition rate.

The numerical fit of experimental data was made using the parameters listed in *Table 1*. The very small polydispersity was neglected. The shell thickness calculated from the neutron scattering profile corresponds to the volume fraction of shell polymer derived from the reaction recipe. The differences between both values are very small but they deviate in opposite directions in both core–shell systems investigated in this study. Possibly, this effect permits the conclusion that the diffusion layer of the second stage monomer and polymer inside the core particle is larger in the case of compatible polymers (PMMA–d-PMMA) than in the case of incompatible polymers (PS–d-PMMA).

Hence, the discussion of the previous section is supported by the SANS results. Following the aforementioned conditions distinct shell formation takes place on given seed particles via the emulsion polymerization technique. This indicates that the surface layer of monomer-swollen polymer particles is the main reaction locus during emulsion polymerization using water-soluble initiators.

The thermodynamic characterization of two-stage emulsion polymers will be presented in a subsequent publication. In that paper, the existence of an interfacial layer between core and shell polymer as indicated by the SANS results will be discussed in detail.

## SUMMARY

The two-stage emulsion polymerization technique is a useful procedure for obtaining a concentric core–shell structure of polymer particles. The experimental conditions of shell formation are: (i): sufficiently high seed particle number; (ii) use of water-soluble initiator; (iii) monomer addition under monomer-starved conditions; (iv) hydrophobicity of the core in comparison with the water solubility of the second monomer; and (v) incompatibility of core and shell polymers. The core–shell structure of the polymer particles produced by this procedure can be conclusively detected by small-angle neutron scattering.

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