Partial and saturation swelling in latex particles of polybutadiene, styrene methyl methacrylate copolymers and composite particles

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Partial and saturation swelling experiments in latex particles of styrene methyl methacrylate copolymers, polybutadiene and composite particles containing polybutadiene with styrene and methyl methacrylate grafted were performed with the centrifugation method. Very good agreement is achieved between the experimental results of partial swelling and a simplified theoretical model. The behaviour of monomer partitioning when no monomer droplets are present is independent of polymer type, polymer crosslinking and latex particle diameter. The saturation monomer partitioning experiments also showed good agreement with a simplified thermodynamic theory. The polymer type does not influence the ratio of two monomers (styrene and methyl methacrylate) in the particle and droplet phases. Also, there is no preferential solvation of styrene in polybutadiene. This is an important result for the graft polymerization of styrene and methyl methacrylate. Differences observed in copolymer composition between graft and free copolymers thus cannot be ascribed to monomer partitioning.

(Keywords: swelling; styrene methyl methacrylate copolymers; polybutadiene; graft polymers; latex)

INTRODUCTION

Swelling behaviour of 'seed' latex particles by monomers is of great importance. For example, methyl methacrylate/butadiene/styrene (MBS) and acrylonitrile/butadiene/styrene (ABS) are prepared in two emulsion polymerization steps; in the first step a polybutadiene (PB) seed is prepared (the rubbery core) and in the second step a monomer mixture [e.g. styrene (S)/methyl methacrylate (MMA)] is added and copolymerized (the glassy shell). Some of the latter monomers will graft onto the PB particles. The rest of the monomer will polymerize without chemically bonding onto the PB core, the so-called 'free styrene methyl methacrylate copolymer' (SMMA-f, see Table 1 for abbreviations used). The presence of a PB seed latex in principle may influence the behaviour of partitioning of monomers due to different interactions between monomers and polymers. Different monomer concentrations will then influence the composition of the SMMA copolymer grafted onto PB and the SMMA-f copolymer. Differences in copolymer composition between grafted SMMA (SMMA-g) and SMMA-f copolymers can affect polymer phase separation1. Moreover, the properties of graft polymers depend on the degree of grafting2, particle morphology, the amount and length of the grafts, molecular weight and in the case of copolymers, the copolymer composition and compositional distribution. The influences of process variables on the graft polymerization have been reported by several groups3-4. However, in order to understand the relations between process conditions, polymer characteristics and mechanical properties more fundamental research is necessary. The way monomers partition between several phases has been described by several investigators5-9. The saturation swelling of latex particles has been described by Morton et al.5 and Maxwell et al.6, and the partial swelling where all monomer is solubilized in the aqueous phase and in the latex particles, by Vanzo et al.7, Gardon8 and Maxwell et al.9. some partitioning experiments of S and acrylonitrile (AN) with PB latices and films have been reported by Mathey and Guillot10. They estimated the values for the interaction parameter and the surface tension, and showed by theory that the particle size and crosslinking density of the PB latex influences the monomer concentration in PB particles. Actually the interaction parameter and surface tension are hard to determine experimentally and may also be dependent on the volume fraction of polymer9. Experimentally10, only the S concentration in PB latex particles at saturation was measured. The monomer concentration of the two monomers as a function of different monomer compositions would be of interest because this gives us

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Abbreviations used for different types of polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB</td>
<td>Polybutadiene</td>
</tr>
<tr>
<td>SMMA-i</td>
<td>Styrene methyl methacrylate copolymer formed</td>
</tr>
<tr>
<td></td>
<td>independently, i.e. in the absence of PB seed</td>
</tr>
<tr>
<td>PB-SMMA-g</td>
<td>Composite polymer of PB with grafts of S and MMA</td>
</tr>
<tr>
<td>SMMA-f</td>
<td>Free SMMA copolymer formed during MBS graft</td>
</tr>
<tr>
<td></td>
<td>polymerization</td>
</tr>
<tr>
<td>MBS</td>
<td>Product of grafting process, i.e. PB-SMMA-g</td>
</tr>
<tr>
<td></td>
<td>+SMMA-f</td>
</tr>
<tr>
<td>SMMA-g</td>
<td>SMMA copolymer grafted onto PB</td>
</tr>
</tbody>
</table>

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**Table 2** Seed latex recipes of PB, SMMA-i copolymers and MBS graft polymers (in parts by weight)*

<table>
<thead>
<tr>
<th></th>
<th>PBI</th>
<th>PBII</th>
<th>25/75</th>
<th>52/54/75</th>
<th>MBSI</th>
<th>MBSII</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>2800</td>
<td>691</td>
<td>600</td>
<td>600</td>
<td>600</td>
<td>762</td>
</tr>
<tr>
<td>SDS</td>
<td>-</td>
<td>-</td>
<td>2.0</td>
<td>2.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(S)PPS</td>
<td>-</td>
<td>-</td>
<td>0.875</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SFS</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(S)PCB</td>
<td>15.14</td>
<td>3.74</td>
<td>0.2</td>
<td>0.2</td>
<td>1.427</td>
<td></td>
</tr>
<tr>
<td>tDM</td>
<td>7.74</td>
<td>1.91</td>
<td>-</td>
<td>-</td>
<td>0.638</td>
<td>0.850</td>
</tr>
<tr>
<td>CHP</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.213</td>
<td>0.213</td>
</tr>
<tr>
<td>FeSO4/EDTA</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.005</td>
<td></td>
</tr>
</tbody>
</table>

*SDS, sodium dodecylsulfonate; (S)PPS, sodium- or potassium persulfate; (S)PCB, sodium- or potassium carbonate; tDM, tertiary dodecylmercaptan; CHP, cumene hydroperoxide; SFS, sodium formaldehyde sulfoxylate; FeSO4/EDTA, complex of iron(II)sulfate and ethylenediaminetetraacetic acid

information about the monomer partitioning in copolymerization (it is known that the presence of S in SAN and graft polymer influences the AN concentration in the latex particles11). To understand the swelling behaviour of monomers in PB, it is better to first understand the swelling behaviour of partially water soluble monomers which are good solvents for their own polymer.

In this paper, experimental results of partial and saturation swelling of the monomers S and MMA in SMMA copolymer formed in the absence of PB seed (SMMA-i), in PB and in SMMA-i and PB-SMMA-g (from the MBS graft polymerization) were discussed and compared to predicted results from the semiempirical equations developed recently by Maxwell et al.6, 9. The following parameters were varied in the monomer partitioning experiments: latex particle diameter (of PB), crosslinking density (of PB), polymer type, copolymer composition and degree of grafting (of MBS).

**EXPERIMENTAL**

The PB latices were prepared by emulsifier free emulsion polymerization12 (Table 2), leading to monodisperse seed latices. Butadiene (DSM, Geleen, The Netherlands) was purified by distillation. The polymerizations were performed in a 51 stainless steel reactor fitted with two 12-bladed turbine impellers. A conversion of 95% was reached after 20 h. The larger PB particle diameter sizes were made in a 2.51 stainless steel reactor fitted with a helical ribbon rotator with the first 4 h at 80°C and then 92 h at 60°C (85% conversion). The average particle sizes and particle size distributions were determined by transmission electron microscopy. The details of the PB latices are given in Table 3. Different crosslinking densities are achieved by varying the mercaptan concentrations and by polymerizing to higher final conversions13. High crosslinking densities can also be achieved by heating a PB latex for 8 h at 90°C. The gel content was measured as an indication of the crosslinking density of the PB, and was determined by the solvent extraction method of the soluble fraction of the PB. The insoluble residue is, by definition, the gel fraction. Before using the PB for the monomer partitioning experiments, the latex was dialysed in a membrane tube in order to remove excess surfactant and monomer (Medicell International Ltd, London, UK). The water was changed five times every 4 h for 2 days14, 15. After this, the solid contents were determined by gravimetry.

The SMMA copolymers (SMMA-i) were made in a 11 stainless steel reactor fitted with a 12-bladed turbine impeller, under nitrogen according to a standard recipe given in Table 2. Table 2 also gives the recipe for the graft polymerization of MBS made in the same reactor. These latices were dialysed in the same manner as the PB latices. The monomers used in the monomer partitioning experiments were applied as received without any further purification. The presence of a free radical inhibitor prevents polymerization during the monomer partitioning experiments. The determination of the monomer partitioning was performed with the centrifugation method6, 9. In the partial swelling experiments the latex was mixed with known amounts of MMA and in the saturation experiments with MMA and S. After 2 h of shaking, equilibrium was reached. It is necessary to know the solid content of the latex, the copolymer composition and for the MBS polymer also the degree of grafting. Polymer densities were calculated by the appropriate averaging of the densities of the homopolymers. For the experiments with the MBS polymers the amount of PB-SMMA-g and SMMA-f were calculated from the degree of grafting (measured by n.m.r.)16 and the total weight. The swollen polymer particles phase and aqueous phase (and monomer phase) were separated using an ultracentrifuge (55 000 rev min⁻¹, Centrikon T-2060, 6–15 h) at room temperature. Monomer concentrations in polymer and aqueous phases were determined by gas chromatography. The PB and PB-SMMA-g phases were swollen in toluene with acetone as an internal standard. The SMMA-i and SMMA-f copolymers were dissolved in acetone with toluene as an internal standard. The concentration of MMA in the aqueous phase was determined after adding a standard 2-propanol solution in water to a sample of the aqueous phase. In the monomer phase samples only the monomer ratio was determined.

**RESULTS AND DISCUSSION**

**Partial swelling of latex particles by one monomer**

The partial swelling of latex particles composed of crosslinked polymer by monomer and solvents can be described by the Vanzo equation in combination with the Flory–Rehner theory9:

\[ \ln(1 - \nu_p) + \nu_p (1 - 1/M_n) + \nu_p^2 \frac{2V_m^2}{V_p^0} (1 + 3R_T/R) \]

where \( \nu_p \) is the volume fraction of polymer in the latex particles, \( M_n \) is the number average degree of polymerization, \( R \) is the gas constant, \( T \) is the temperature, \( \chi \) is

**Table 3** Number average \( D_n \) and weight average \( D_w \) unswellen particle diameters, polydispersity \( P_n \) and gel content of some PB seed latices

<table>
<thead>
<tr>
<th></th>
<th>( D_n ) (nm)</th>
<th>( D_w ) (nm)</th>
<th>( P_n )</th>
<th>Gel content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBIa</td>
<td>209.7</td>
<td>212.7</td>
<td>1.014</td>
<td>72</td>
</tr>
<tr>
<td>PBIb</td>
<td>209.7</td>
<td>212.7</td>
<td>1.014</td>
<td>95</td>
</tr>
<tr>
<td>PBI</td>
<td>305</td>
<td>401</td>
<td>1.313</td>
<td>70</td>
</tr>
</tbody>
</table>
the Flory–Huggins interaction parameter, \( V_m \) is the partial molar volume of the monomer, \( \gamma \) is the particle–water interfacial tension, \( R_o \) is the unswollen radius of the latex particle, \( d_p \) is the density of the polymer, \( M_c \) is the molecular weight between crosslinks, \([M]_{aq}\) is the monomer concentration in the aqueous phase and \([M]_{aq,sat}\) is the monomer concentration in the aqueous phase at saturation. The monomer partitioning behaviour between the aqueous phase and the latex particles can be predicted by this equation. For this it is necessary to know the values of \( \gamma \) and \( \lambda \). Unfortunately, these values are hard to determine and dependent on the volume fraction of polymer. For describing the partitioning, however, it is no longer necessary to know these parameters. Maxwell et al. \(^9\) derived a semiempirical equation where the value of the sum of the residual free energy and the particle–water surface free energy terms in the Vanzo equation are estimated from the saturation swelling volume fraction of polymer\(^8\):

\[
\ln(1-v_p) + v_p(1-1/M_c) + \text{corr.} = \ln([M]_{aq}/[M]_{aq,sat}) \quad (2)
\]

where the correction term is calculated from the Morton equation and saturation swelling data\(^9\):

\[
\text{corr.} = \left[\ln(1-v_{p,sat}) + v_{p,sat}(1-1/M_c)\right] \quad (3)
\]

where \( v_{p,sat} \) is the volume fraction of polymer at saturation in the latex particles. Equation (2) showed very good agreement with experimental results for several styrene methyl acrylate (SMA) copolymers and other polymers\(^9\).

The experimental monomer concentrations of MMA in latex particles of SMMA-i, PB, SMMA-f and PB-SMMA-g during partial swelling are discussed below and compared with the predictions of equation (2).

**Type of polymer.** In Figure 1 the partitioning results are displayed for MMA in two SMMA-i copolymers. The latices differ only in copolymer composition (see Table 2). As has already been shown for the SMA system\(^9\), the copolymer composition has little effect on the partitioning of MA in seed latices. Although the interaction parameter will change with changing copolymer composition, the value of this interaction parameter has a small influence on the monomer partitioning. This also holds for the swelling MMA in PB latex (PBII, Figure 2) and for PB-SMMA-g (Figure 3). From this we can conclude that for varying polymer latices, including those of PB, the free energy associated with the configurational entropy of mixing of monomer and polymer is the dominant term in equation (2). Hence, the changes in partial swelling of different seed latices with one monomer is small.

**Particle size and crosslinking.** The PB latices are prepared by batch emulsion polymerization processes. Depending on the conversion, temperature and mercaptan concentration, the crosslinking density will vary\(^13\). In order to show the effect of particle size and crosslinking density on the partial swelling of latex particles with MMA, experiments were performed with different PB latices (Table 3). The gel content is used as an indication of the crosslinking density. PBII has a particle diameter of 209.7 nm, and PBII and PBIIb have gel contents of 72 and 95%, respectively. PBII has a particle diameter of 305 nm and a gel content of 70%. Experimental results of the swelling of different PBs with MMA are shown in Figure 2. Both the particle size and the crosslinking density do not significantly affect the monomer partitioning, which is in agreement with the results of Maxwell et al.\(^9\), who showed that the free energy due to the configurational entropy of mixing of monomer and polymer is the dominant factor.

Higher crosslinking densities occur when a PB seed is used for a graft polymerization, resulting from 6 h of polymerization at 50°C and from grafting. Partial swelling experiments were performed with two types of MBS (Table 4), only differing in the degree of grafting (defined as the ratio of SMMA-g over PB in PB-SMMA-g). Again, no difference is found in partitioning between the PB-SMMA-g and the MMA-f formed during graft polymerization (Figure 3). From Figures 1–3,
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Table 4 Characteristics of two MBS latices measured by n.m.r.  
| Degree of | $F_i$ in | $F_i$ in |
| grating   | SMMA-g  | SMMA-f  |
| MBSSI     | 0.41     | 0.18     | 0.26     |
| MBSSII    | 0.85     | 0.19     | 0.28     |

$F_i$, fraction of styrene in the copolymer

Figure 4 Experimentally determined MMA concentrations in the water phase as a function of the MMA concentration in the particle phase (concentrations normalized to saturation) in SMMA-i (25/75) and in PBIa (©).

it appears that during partial swelling (stage III in emulsion polymerization) the relationship between the monomer concentration in the water phase and the monomer concentration in the particle phase $(1 - v_p)$ is convex. Thus the monomer concentration in the water phase is closer to saturation than in the particle phase. This relation does not change if the monomer concentration in the water phase is plotted on a non-logarithmic scale (Figure 4). This means that in stage III of emulsion polymerization with high water soluble monomers, a significant amount resides in the water phase, which reduces the monomer concentration and the rate of polymerization in the latex particles.

Saturation swelling of latex particles by two monomers

At equilibrium the partial molar free energy of each monomer will be equal in each of the three phases, i.e. the polymer particle, the monomer droplet and the water phase. This leads to the following equation for monomer $i$:

$$v_i = \ln (1 - m_{ij}) v_{pj} + v_p + x_{ij} v_{pj}^2 + x_{ip} v_p^2 + v_p (x_{ij} + x_{ip} m_{ij}) + (2 V_{mi} v_{p}^{1/3})/R R_0 T$$

where $v_p$ and $v_{pj}$ are the volume fractions of monomers $i$ and $j$ in the latex particles, respectively, $x_{ij}$ is the interaction parameter between monomers $i$ and $j$, and $x_{ip}$ and $x_{ip}$ are the interaction parameters between each of the monomers $i$ and $j$, respectively, and the polymer. The term $m_{ij}$ is the ratio of the molar volumes of monomers $i$ and $j$, $v_{pj}$ represents the volume fraction of monomer $i$ in the droplets, and $v_{pj}$ the volume fraction of monomer $j$ in the droplets, and $[M_i]_{aq}$ and $[M_j]_{aq,sat}$ are the monomer $i$ concentrations in the water phase and in the water phase at saturation, respectively.

A similar equation applies for monomer $j$.

One important assumption made in equation (4) is that a polymer seed does not change the relationship between the water and monomer phases; water soluble monomers show a proportional relationship between the water phase and the monomer phase, obeying Henry’s Law. From Figure 5 it can now be derived that the same assumption of Henry’s law can be made in the presence of PB seed latex particles: the concentrations of monomer in the particle phase and droplets are still proportional.

Equation (4) and a similar equation for monomer $j$ can be used to predict the monomer partitioning for latex systems containing two monomers. However, the values for the interaction parameters and the interfacial tension are hard to determine and are dependent on the volume fraction of polymer in the latex particles as well as on the monomer ratio. Hence, the monomer partitioning is very hard to predict.

Simplifications to the theory of swelling of latex particles with two monomers recently made by Maxwell et al. are that the volume fractions of monomers are equal or similar, the interaction parameter of mixing of two monomers is rather small, and the interaction parameters for each monomer with the same polymer are equal ($x_{ij} = x_{ij}$). These assumptions lead to the following result:

$$f_{pi} = f_{di}$$  (5a)
$$f_{pj} = f_{dj}$$  (5b)

where the monomer volume fraction of monomers $i$ and $j$ in the droplets is given by $f_{di}$ and $f_{dj}$ in the particle phases. Polymerization with high water soluble monomers, a significant amount resides in the water phase, which reduces the monomer concentration and the rate of polymerization in the latex particles.

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At equilibrium the partial molar free energy of each monomer will be equal in each of the three phases, i.e. the polymer particle, the monomer droplet and the water phase. This leads to the following equation for monomer $i$:

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where $v_p$ and $v_{pj}$ are the volume fractions of monomers $i$ and $j$ in the latex particles, respectively, $x_{ij}$ is the interaction parameter between monomers $i$ and $j$, and $x_{ip}$ and $x_{ip}$ are the interaction parameters between each of the monomers $i$ and $j$, respectively, and the polymer. The term $m_{ij}$ is the ratio of the molar volumes of monomers $i$ and $j$, $v_{pj}$ represents the volume fraction of monomer $i$ in the droplets, and $v_{pj}$ the volume fraction of monomer $j$ in the droplets, and $[M_i]_{aq}$ and $[M_j]_{aq,sat}$ are the monomer $i$ concentrations in the water phase and in the water phase at saturation, respectively.

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$$f_{pi} = f_{di}$$  (5a)
$$f_{pj} = f_{dj}$$  (5b)

Figure 5 Experimentally determined MMA concentrations in the drop phase as a function of the fraction MMA in the droplet phase with S as comonomer in the presence of a PB latex.
cannot be ascribed to monomer partitioning effects. In the droplet phase. In the SMMA-i and SMMA-f copolymer phases. The monomer concentrations in SMMA copolymers are determined. Again, no differences were observed in the MMA fraction in PB, SMMA-i and SMMA-f copolymer phases. The monomer concentrations in SMMA copolymers are given by equation (6) for the experimental results and the theoretically predicted monomer concentrations according to equation (6), for any ratio of monomers in the droplets. CONCLUSIONS MMA monomer concentrations in the latex particle, monomer droplet and water phases were measured with the centrifugation method. Experiments showed that the partitioning of MMA is independent of the type of polymer/SMMA copolymers of different composition and PB. Moreover, the partitioning of MMA in PB is independent of particle size, polymer crosslinking density and MMA monomer concentrations in the PB and PB-SMMA-g particle phases are plotted against the fraction of MMA in the droplet phase. The absolute value of the degree of swelling depends upon polymer and monomer type (an effect of different interaction parameters and interfacial tensions). The monomer concentrations in SMMA copolymers and in the free copolymer formed during the grafting process are the same (see Figure 7a). Obviously (Figure 7b) the MMA concentration in the PB-SMMA-g polymer is higher than in PB, and the S concentration is also increased, but not to the same extent. However, it should be emphasized that the higher concentrations in the particle phases do not change the ratio between the two monomers, but only could have an effect on the polymerization rates in the latex particles. The lines in Figures 7a and b are the predictions of equation (6); only the concentrations of the two monomers, when exclusively swelling a particular latex, are required. In these calculations very good agreement is achieved between the experimental results and the theoretically predicted monomer concentrations according to equation (6), for any ratio of monomers in the droplets.
and the presence of SMMA-g. These experiments also show that the partitioning of monomer between the aqueous and latex particle phases, when there is no separate monomer phase present, can be predicted using the semiempirical equation of Maxwell et al.\(^9\), which only requires the values of the saturation concentration of the monomer in the particle and aqueous phases. This result can be understood\(^9\) when realizing that the contribution of the configurational entropy of mixing of monomer and polymer dominates the free energy of monomer partitioning, and that both the interfacial free energy and residual free energy terms do not significantly influence the degree of swelling.

Experiments were also carried out at saturation swelling of different polymers by two monomers. The results of these experiments show that the mixing of the two monomers, \(S\) and MMA, is independent of the polymer type and that again the ratio of monomers in droplet and particle phases is equal. The saturation partitioning of monomers between latex particles and droplet phases could be predicted by the simplified equations of Maxwell\(^6\). This equation only requires the individual saturation concentrations of the two separate monomers in the latex particles. These results were based on the finding that the entropy of mixing of two monomers is the dominant contribution to the thermodynamic equilibrium reached\(^6\). Hence, the monomer ratio becomes independent of the type of polymer phase considered. Only the absolute value of the degree of swelling depends upon the monomer and type of polymer.

This is an important result with respect to the graft polymerization of \(S\) and MMA onto PB. In all the systems considered, namely SMMA-\(i\), PB, PB-SMMA-\(g\), SMMA-\(f\) and monomer droplets, the ratio of the two monomers is equal.

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