Grafting of styrene and methyl methacrylate concurrently onto polybutadiene in semi-continuous emulsion processes and determination of copolymer microstructure

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Styrene and methyl methacrylate were copolymerized at 323 K in the presence of a polybutadiene seed latex in emulsifier-free semi-continuous and, for comparison, batch processes using cumene hydroperoxide as initiator. Graft polymer characteristics were studied including the intra- and intermolecular microstructure. In contrast to expectation, the free and graft copolymers resulting from the semi-continuous processes under starved conditions appeared to have even broader distributions than the copolymers formed in the batch processes.

(Keywords: grafting; microstructure; polybutadiene)

INTRODUCTION

Two-step emulsion polymers can be produced by various types of polymerization processes, e.g. batch, semi-continuous (semi-batch) or continuous processes. These different types of polymerization processes can have a large effect on polymerization kinetics, microstructure, and thus on polymer properties.

Although many studies are concerned with the qualitative[1–3] and some with the quantitative[4–7] interpretation of the grafting of two monomers onto a rubbery polymer, there is a lack of information on composition drift occurring during the grafting of two monomers on a rubbery polymer seed in emulsion. The combined interpretation of many graft polymer characteristics, as discussed in the accompanying paper[8], is also a neglected aspect in this line of research.

The semi-continuous emulsion copolymerization process is widely used in industry, due to a number of advantages as compared with the conventional emulsion batch processes. These advantages include a convenient control of emulsion polymerization rate in relation to heat removal, and control of particle morphology and chemical composition of the copolymer. In particular, for the high performance polymer latices it can be important to produce copolymers which are homogeneous in chemical composition. High-impact graft polymers are mostly produced by the semi-continuous process, because higher degrees of grafting can be achieved and one might expect smaller distribution according to chemical composition and core–shell morphology[9].

Several monomer addition strategies can be employed, of which the addition of a given monomer mixture at constant rate is most widely used. Two basically different situations can be distinguished with respect to the monomer addition rate: (1) flooded conditions, where the addition rate is higher than the polymerization rate; and (2) starved conditions, where the monomers are added at a rate lower than the maximum attainable polymerization rate. In order to obtain homogeneous copolymers it is necessary to perform the semi-continuous processes under starved conditions, however, this requires long addition times. The latter problem can be overcome by using the optimal monomer addition strategy[10].

The present investigation focuses primarily on differences in homogeneity between the two copolymers formed during graft copolymerization, namely graft copolymer and free copolymer. Therefore, the semi-continuous graft copolymerizations were performed using the strategy of monomer addition under starved conditions. Styrene (S) and methyl methacrylate (MMA) were grafted onto a polybutadiene (PB) seed latex (prepared in emulsifier-free emulsion polymerization), in batch and semi-continuous processes, while varying some crucial parameters.

EXPERIMENTAL

Semi-continuous graft copolymerizations of S and MMA onto PB. The dosage of the monomers in the seeded semi-continuous reactions was performed via an automatic burette (Metrohm, type 665 Multi Dosimat, refillable 10 ml burette). Every 15 min a sample was taken from the reactor for the g.c. and solid weight determination performed to measure the conversion. The reactor was filled with the PB seed, water and part of the initiating system, namely, sodium formaldehyde sulfoxylate (SFS) and iron(II) sulfate ($FeSO_4$). After this the reactor was

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Table 1 Codes for the different MBS polymers used, indicating the deviations from the standard recipe MBSII in Table 1 of reference 8

B1	MBSII: 1 wt% nDM, $F_S=0.25$, $T=323$ K
B2	0 wt% nDM
B3	2 wt% nDM
B4	$F_S=0.5$
SC1	MBSII: 1 wt% nDM, $F_S=0.25$, $T=323$ K
SC2	$F_S=0.5$
SC3	$T=348$ K

B = batch, SC = semi-continuous, F_S = feed fraction of styrene

purged with nitrogen in order to remove the oxygen. The reaction mixture was thermostatically controlled at 323 K. The monomer mixture containing n-dodecyl mercaptan (nDM) and cumene hydroperoxide (CHP) was added dropwise to the PB seed by means of an automatic burette over 6 h. The emulsion was stirred with a six-bladed turbine impeller at 300 rev $\min^{-1}$. The conversion was determined by means of g.c. and dry solid content analysis. The total volume of all samples taken during the entire course of the reaction was always $<4\%$ of the total volume.

The same total amounts were used as in the batch experiment of MBSII (methyl methacrylate/butadiene/styrene) (Table 1 of ref. 8). In *Table 1* the different MBS polymers discussed in this paper are given codes indicating the deviations from the standard recipe.

RESULTS AND DISCUSSION

Results are shown of batch and semi-continuous graft emulsion copolymerization processes to demonstrate the differences in microstructure, degree of grafting (DG), graft efficiency (GE), and number-average molecular weight (M_n) of the SMMA-g (styrene/methyl methacrylate copolymer grafted onto PB) and SMMA-f (free SMMA copolymer formed during MBS graft copolymerization) copolymers in both processes. As already shown in the accompanying paper, the chemical composition distribution (CCD) of a SMMA-g copolymer in batch is very broad[8]. One of the key questions leading to the investigation described in this paper was whether it would be possible with semi-continuous polymerizations to obtain narrower distributions.

Batch emulsion graft copolymerization

Additional batch experiments were performed, in which some process parameters including the n-dodecyl mercaptan (nDM) concentration and the monomer feed ratio were varied.

Effect of the mercaptan concentration. Three experiments were performed with different mercaptan concentrations: 0, 1, 2 wt% per wt monomer. *Figure 1a* shows the effects of the four different mercaptan concentrations on the DG and *Figure 1b* shows the effects on the GE, as a function of conversion. From *Figures 1a* and *b* it can be seen that once mercaptan is added the amount of mercaptan does not further influence the course of the DG and the GE. The latter remains constant over a wide conversion range and steeply increases at a conversion of ~90%. In contrast with the latter experiments, experiment B2, where no mercaptan is used, shows that DG and the GE are increasing continuously with conversion. These results are in agreement with experiments published previously by other groups[7]. The DG is reduced by using a chain transfer agent (CTA), because the radical activity of a grafted chain or polymer backbone is then most likely to transfer to the CTA. Few of the new chains formed by this CTA radical will graft again. *Table 2* shows for the case of MBS experiment B2 (without nDM), the DG, GE, copolymer composition and molecular weight of grafted and of free copolymer, as well as the number of graft sites. The data of experiment B1 (1 wt% nDM) were listed in Table 3 of reference 8. From a comparison of *Table 2*, and Table 3 of reference 8, it becomes clear that from the beginning of the reaction no more graft sites are initiated in the absence of mercaptan. However, the DG and GE are approximately the same in the beginning of the polymerization ($<50\%$ conversion). At the end of the reaction the number of graft sites of MBS B1 (1 wt% nDM) is still less than that of MBS B2 (0 wt% nDM). In experiment B2, there is no transfer to CTA, so more transfer to PB and monomers will take place and as a result more crosslinking will occur at an earlier stage of the reaction than with recipes containing mercaptan.

There are some striking differences in the molecular weight of SMMA-g and SMMA-f between the two experiments labelled B1 (1 wt% nDM) and B2 (0 wt% nDM). The molecular weight of the SMMA-g copolymer and more clearly that of the SMMA-f copolymer is affected by the presence of mercaptan. It is expected that the SMMA-f and the SMMA-g copolymers are formed in different domains, which will have consequences for several important parameters such as the local glass transition temperature (T_g), the mobility of the chains, and the number of radicals in the particle.

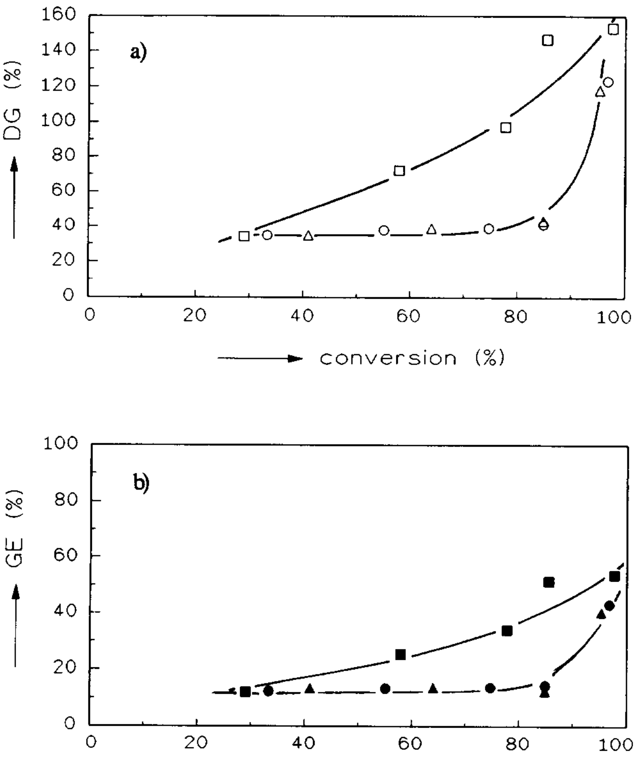

Figure 1 (a) DG and (b) GE as a function of conversions of MBS B1 (1 wt% nDM, circles), B2 (0 wt% nDM, squares), B3 (2 wt% nDM, triangles)

Table 2 Characteristics of MBS experiment B2 (without nDM) as a function of conversion

X^a (%)	DG (wt%)	GE (wt%)	F_S-g (mol%)	M_n-g (kg mol^{-1})	M_w-g (kg mol^{-1})	P(g)^b	N^c ($\times 10^{-4}$)	F_S-f (mol%)	M_n-f (kg mol^{-1})	M_w-f (kg mol^{-1})	P(f)^b
29.0	34.2	11.9	26	28.4	47.8	1.68	6.50	32	60.2	226	3.75
57.9	72.2	25.2	25	46.7	82.3	1.76	8.33	–	–	–	–
77.8	97.2	33.9	22	54.9	120	2.19	9.55	29	128	675	5.28
85.5	146.8	51.3	25	–	–	–	–	28	–	–	–
97.7	153.3	53.6	23	45.6	126	2.76	18.1	26	137	584	4.26

[a] X = conversion
[b] P(g) and P(f) = the polydispersity = M_w/M_n of SMMA-g and SMMA-f, respectively
[c] N = mol chains grafted/mol butadiene units

Table 3 Characteristics of MBS experiment B4 (F_S = 0.5) as a function of conversion

X (%)	DG (wt%)	GE (wt%)	F_S-g (mol%)	M_n-g (kg mol^{-1})	M_w-g (kg mol^{-1})	P(g)	N ($\times 10^{-4}$)	F_S-f (mol%)	M_n-f (kg mol^{-1})	M_w-f (kg mol^{-1})	P(f)
95.7	54.8	19.8	43	39.1	84.5	2.16	7.61	52	62.2	143.7	2.31

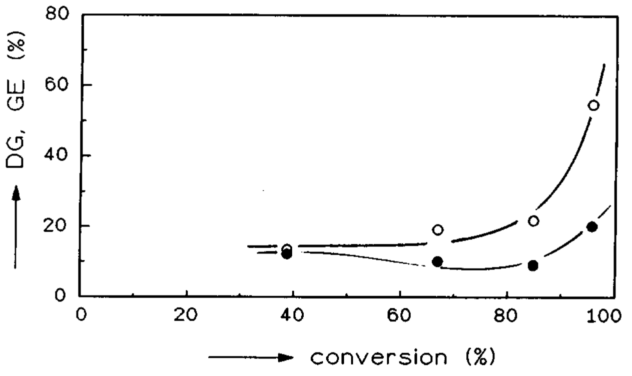

Figure 2 DG (○) and GE (●) as a function of conversion of MBS B4 (F_S = 0.5)

Influence of monomer feed ratio. On the grounds of the observations in the batch reactions, one would expect less composition drift in SMMA-g as the feed of the monomers contains more S. This makes it interesting to change the monomer feed ratio.

Experiment B1 is performed with a monomer molar feed ratio of 25% S and 75% MMA. In bulk copolymerizations of SMMA the azeotrope lies at a molar ratio of 52.5/47.5. Experiment B4 is performed under azeotropic conditions, therefore the composition drift should be far less. In *Figure 2* the DG and GE of MBS B4 (F_S = 0.525) are given, and appear to be comparable with those found in MBS B1 (F_S = 0.25). Other characteristics of MBS B4 are given in *Table 3*. It cannot be concluded that there is azeotropic behaviour in these seeded emulsion polymerizations, because the SMMA-g and SMMA-f show different behaviour in copolymer composition. However, the conclusions drawn by Aerdts *et al.*[11], that the monomer feed ratios inside the particles are always equal to those in the monomer droplets lead to the conclusion that rather than different monomer ratios, locally different kinetic mechanisms, reactivities or conditions must be operative.

Semi-continuous emulsion graft copolymerizations under starved conditions

Stability of the semi-continuous process. The semi-continuous processes were performed by adding a monomer/initiator mixture of constant composition, while maintaining starved conditions. The transmission electron micrograph of experiment SC1 (standard) in *Figure 3c* shows a uniform core–shell morphology. However, there are some stabilization problems when the conversion reaches 68%. Addition of 0.5 mmol l^{-1} emulsifier sodium dodecyl sulfate (SDS) could avoid the formation of coagulum. The cause of this coagulum formation can be two-fold. First, the surface area is growing so rapidly that too few sulfate groups are present to stabilize the particle. Second, the sulfate groups which stabilize the PB particles may become shielded because the migration of these groups to the surface of the latter particle is hindered by diffusion (far below the T_g, ~350 K). The T_g of a polymer is somewhat lowered by the presence of monomer. The experiment carried out at 348 K (SC2) supports the second hypothesis, because under the same conditions as in experiment SC1 (323 K), except for the higher temperature, no coagulum is formed. This means that with the same growth of surface area (*Figure 3d*) and the same number of sulfate groups, this number of sulfate groups is enough to stabilize the particle, so the second explanation given above is the most likely. At 348 K and at a weight fraction of 0.9 of polymer in the particle, the migration of the sulfate groups to the surface area is apparently fast enough. This shows at the same time that most of the sulfate group containing chains are not completely immobilized onto the PB network.

Influence of temperature and feed composition. In *Figures 4a* and *b* the dependencies of DG and GE on conversion are shown for the semi-continuous experiments SC1, SC2 and SC3. A steady increase of the DG is observed over the entire conversion range. As compared with the batch processes the semi-continuous processes lead to much higher values of DG and GE. This must be caused by the low monomer concentration, maintained over the entire conversion range. The probability of chain transfer of monomeric and polymeric radials to the PB backbone then will increase, so initiating more graft sites, which in turn leads to higher GE values. In *Table 4* the number of graft sites is listed for experiment SC1 (under standard conditions) as a function of conversion. The final product has about four times more graft chains than

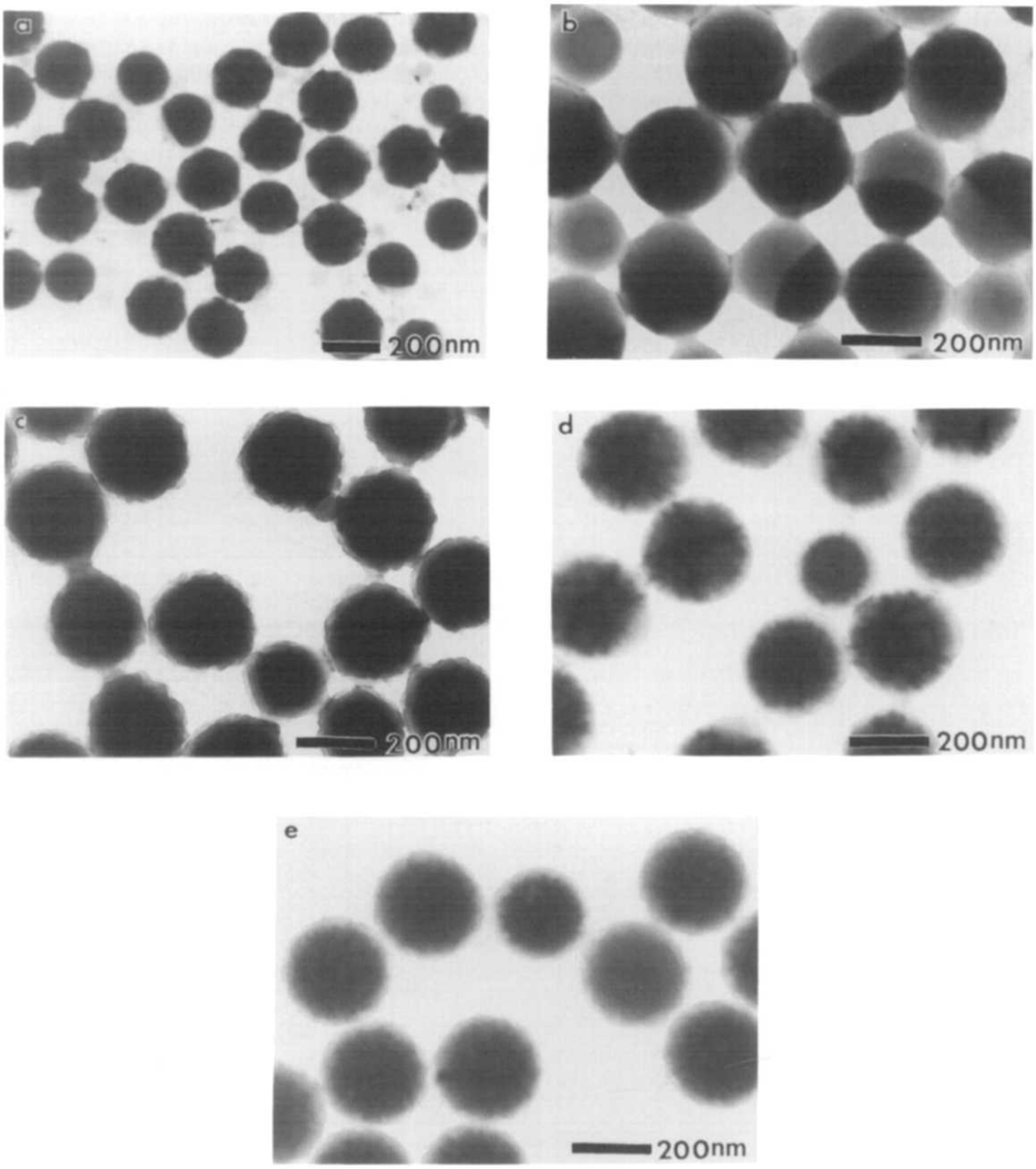

Figure 3 Transmission electron micrographs of MBS graft polymers: (a) MBS B1 (standard), $X=33\%$; (b) MBS B4 ($F_S=0.5$), $X=95\%$; (c) MBS SC1 (standard), $X=80\%$; (d) MBS SC2 ($F_S=0.5$), $X=90\%$; (e) MBS SC3 (348 K), $X=96\%$

Table 4 Characteristics of MBS SC1 (standard) as a function of conversion

X (%)	DG (wt%)	GE (wt%)	F_S-g (mol%)	M_n-g (kg mol^{-1})	M_w-g (kg mol^{-1})	P(g)	N ($\times 10^{-4}$)	F_S-f (mol%)	M_n-f (kg mol^{-1})	M_w-f (kg mol^{-1})	P(f)
22.9	32.1	47.6	22	–	–	–	–	25	21.9	75.3	3.44
40.6	–	–	–	18.5	39.9	2.16	–	25	16.2	71.2	4.41
45.3	70.7	50.4	20	19.5	48.5	2.49	20.7	24	30.0	83.8	2.80
49.9	123.6	79.0	22	–	–	–	–	23	25.3	92.1	3.64
60.0	–	–	–	20.0	50.0	2.47	–	–	20.7	113	5.43
80.2	180.1	67.1	22	19.9	57.5	2.88	48.9	21	–	–	–

the batch products (Table 3 in ref. 8), however, due to the low monomer concentration in the particle, the average molecular weight is low. As a result, the core–shell structure shown in *Figure 3c–e* should have a morphology of long-term stability. The average copolymer composition of SMMA-g and SMMA-f listed in *Table 4* do not show significant differences. In *Figure 5* two CCDs of SMMA-g (SC1, standard) at two different conversions are shown. The distributions are very broad, and a composition drift is observed towards more MMA-rich copolymers in SMMA-g.

In *Figure 6* the CCDs are shown of MBS SC2 ($F_S=0.5$). The same effects in composition drift are observed as in MBS SC1 ($F_S=0.25$). In *Tables 5* and *6* the characteristics are listed of MBS SC2 ($F_S=0.5$) and SC3 (348 K), respectively. When comparing the three experiments in *Figure 4b* it can be seen that the GE of SC2 ($F_S=0.5$) is the highest (GE = 90%) but the number of graft sites is lower and the chains have higher average molecular weights.

The higher GE values at higher temperatures (GE = 70%) can be explained by the very low actual monomer concentrations in the latex particles. Also, the higher temperatures will give an increase in penetration of free radicals from the aqueous phase. This should promote a large number of graft sites at the expense of shorter chains.

The present results, indicating a constant or even an increasing GE (when a shell is already formed), do not completely fit in with the conclusions reported by Merkel *et al.*[12] for MMA grafting on PB in emulsion. These authors inferred that as soon as a certain shell thickness of the second stage polymer is reached the grafting reaction becomes less probable due to the reduced availability of PB. In *Figures 3c–e* (thick shells) and *Table 6* (DG and N) it is seen that the thick shell has no

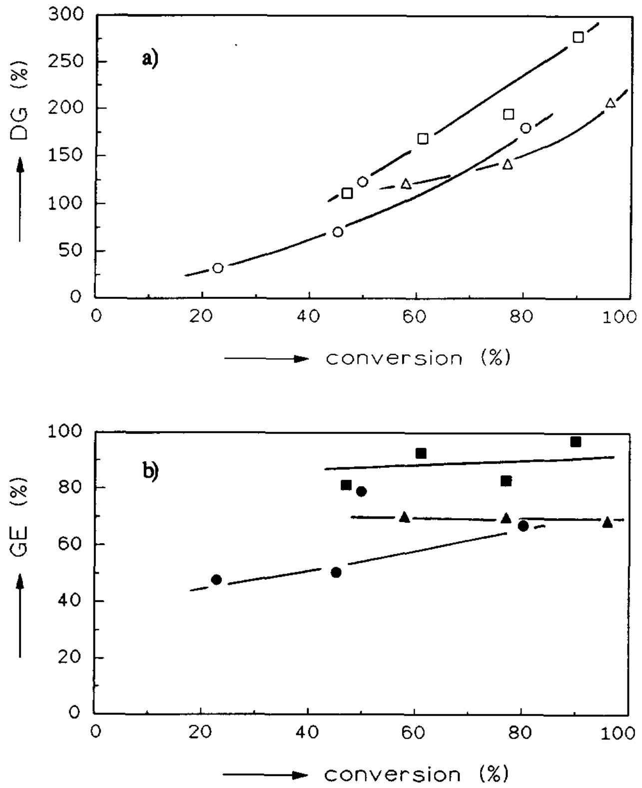

Figure 4 (a) DG and (b) GE as a function of conversion of MBS SC1 (standard, circles), SC3 (348 K, triangles) and SC2 ($F_S=0.5$, squares)

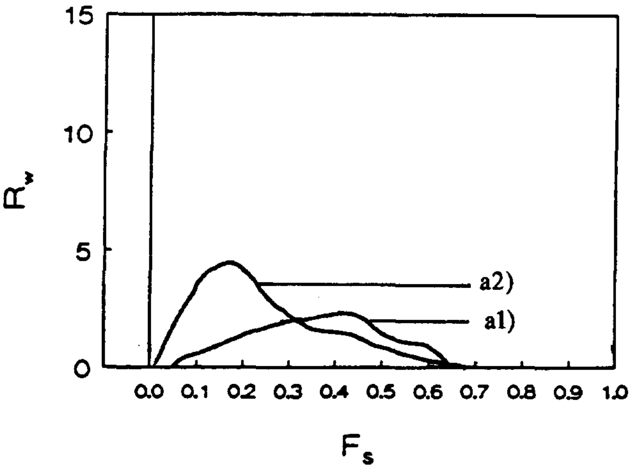

Figure 5 Chemical composition distributions of SMMA-g copolymer of MBS SC1 (standard) at: (a1) 40.6% conversion; (a2) 80% conversion

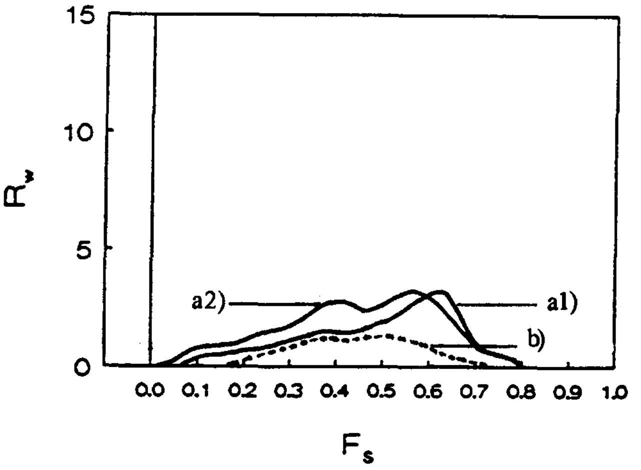

Figure 6 Chemical composition distributions of MBS SC2 ($F_S=0.5$): (a1) SMMA-g at 47% conversion; (a2) SMMA-g at 90% conversion; (b) SMMA-f at 90% conversion

Table 5 Characteristics of MBS SC2 ($F_S=0.5$) as a function of conversion

X (%)	DG (wt%)	GE (wt%)	F_S-g (mol%)	M_n-g (kg mol^{-1})	M_w-g (kg mol^{-1})	P(g)	N ($\times 10^{-4}$)	F_s-f (mol%)	M_n-f (kg mol^{-1})	M_w-f (kg mol^{-1})	P(f)
47	111.5	81.2	38	46.2	122	2.64	13.1	–	46.7	164	3.51
61	169.2	92.8	35	44.2	117	2.65	20.7	42	–	–	–
77	194.8	82.9	42	46.9	123	2.63	22.3	45	–	–	–
90	278.3	97.2	46	33.7	167	4.96	44.5	44	51.3	196	3.82

Table 6 Characteristics of MBS SC3 ($T=348$ K) as a function of the conversion

X (%)	DG (wt%)	GE (wt%)	F_S-g (mol%)	M_n-g (kg mol^{-1})	M_w-g (kg mol^{-1})	P(g)	N ($\times 10^{-4}$)	F_s-f (mol%)	M_n-f (kg mol^{-1})	M_w-f (kg mol^{-1})	P(f)
45	–	–	–	20.6	53.3	2.60	–	21	–	–	–
58	122.3	70.3	21	20.0	54.8	2.74	33.0	–	12.2	32.4	2.65
77	142.7	70.0	19	19.0	54.0	2.85	40.6	23	–	–	–
96	207.8	68.8	20	19.1	55.2	2.89	59.1	34	19.8	63.4	3.20

influence on the GE, which remains constant up to very high conversions.

Comparison of the morphology of the batch and semi-continuous graft copolymers

It is evident that the semi-continuous operations yield more graft sites but at the same time lead to lower average molecular weights. Also, the mechanism of grafting causes an enhanced composition drift. The radicals entering the particles from the aqueous phase are highly liable to graft. Therefore, the semi-continuous experiments do not lead to the expected homogeneous graft copolymers. Another important difference between the batch and semi-continuous polymers is the particle morphology. Particle morphology is not only important in the interpretation of kinetic results, but also strongly determines the mechanical properties of the products. *Figure 3* shows transmission electron micrographs of the products of some batch and semi-continuous experiments.

Control of particle morphology in emulsion graft (co)polymerization processes is important for optimizing the properties of a latex system and those of the resulting polymer products in a given application. A large number of factors can affect the morphology of composite latex particles. Some of these are inherent to the choice of the monomers and others arise from the way in which the synthesis was conducted. The final morphology in polymer microparticles involves the movement of at least two molecular species under the influence of driving forces towards the creation of new interfaces (a change of the free energy), leading to rearrangement through phase separation. This means that the interfacial tensions play an important role, and these can be affected by temperature, type, amount and mode of monomer addition, and depend on the initiator, the emulsifier, and the presence of CTAs. Many of these factors affecting the structure of the multistage composite particles are still poorly understood.

The morphology of composite latex particles of acrylonitrile/butadiene/styrene is known to show combinations of different morphologies within the same particle, such as occlusions, core–shell, hemispheres or raspberry-like structures.

Figure 3 shows the various morphologies of the present MBS graft polymers resulting from different processes and process conditions. Figure 5c of reference 8, MBS B1(standard), shows a lot of occlusions and a very thin shell. Shifting the polarity of the systems by changing the feed ratio to more S, leads to a large increase in hemispheric structure (*Figure 3b*).

The products of the semi-continuous process SC1 shown in *Figure 3c*, give a very distinct core–shell structure. It seems that occlusions also exist. On increasing the fraction of S in the monomer feed and at higher reaction temperatures, the semi-continuous MBS morphologies show only small differences. A tendency towards hemispheric structures can be observed (see *Figures 3d* and *e*, respectively).

Occlusions are expected to arise from free polymer formation under flooded conditions. As a consequence, these occlusions will not be formed at the end of the batch polymerization[9], but already at the beginning of the reaction, as can be observed very clearly in *Figure 3a* for experiment B1(standard) at 33% conversion (cf. Figure 5c of ref. 8).

CONCLUSIONS

The semi-continuous experiments give much higher GE values and also larger DG values than the batch processes when grafting S and MMA onto PB. Other important differences are observed in the particle morphology, the number of graft sites, the average molecular weight and the microstructure of the copolymers. The CCD of the semi-continuous graft copolymer is even broader than that of the batch graft copolymer. It can be concluded that the desired properties will strongly depend on how the process is performed. In this case, comparison of the mechanical properties of the different MBS polymers is extremely difficult due to the change in more than one polymer characteristic at the same time. Furthermore, the results presented here show that the present information, clearly exceeding the information available (i.e. DG and GE), provides far more insight into the relevant process (characteristics).

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