Emulsifier free grafting of styrene and methyl methacrylate concurrently onto polybutadiene and determination of the copolymer microstructure

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Styrene/methyl methacrylate (75/25) monomer mixtures were copolymerized at 323 K in the presence of a polybutadiene seed latex using either a water soluble (potassium persulfate) or an oil soluble (cumene hydroperoxide) initiator. The polybutadiene seed latex was made via an emulsifier free emulsion polymerization process. The graft copolymerizations were performed over a range of emulsifier concentrations. The emulsifier free polymerization with cumene hydroperoxide shows a very high degree of grafting while neither secondary nucleation nor coagulation was observed. Furthermore, the graft polymers have been extensively studied in terms of intra- and intermolecular microstructure. For this purpose, the breaking of the polymer backbone by means of ozonolysis was necessary. The grafted styrene/methyl methacrylate copolymer is less rich in styrene than the free copolymer. The chemical composition distributions of the graft copolymer were broader than those of the free copolymer.

(Keywords: grafting; microstructure; polybutadiene)

INTRODUCTION

Various important properties of the methyl methacrylate/butadiene/styrene (MBS) polymers are affected by many variables, such as the degree of grafting, particle morphology, and heterogeneity in the inter- and intramolecular microstructure. Differences in microstructure can cause phase separation[1] and reduction of the transparency. The chemical microstructure of the copolymers depends on the reactivity ratios of the monomers, the monomer partitioning behaviour between the various phases in the emulsion system, and the type of process used [batch or (semi-)continuous]. Batch processes are known to give bimodal or very broad chemical composition distributions (CCDs), when there is a strong composition drift[2].

In seeded emulsion polymerization the monomers are distributed between the polymer phase [polybutadiene (PB) or graft polymer], the aqueous phase, and if present the monomer droplets. During emulsion polymerization the local monomer ratio can be quite different from the overall monomer ratio. Any possible differences in monomer concentrations between the reaction domains of graft and free polymer (even when no second crop of particles is formed, since domain formation within the particle may occur), will lead to a different intramolecular microstructure of the free copolymer as compared with that of the graft polymer. The relevant monomer partitioning data were measured and discussed elsewhere[3]. It was found for the composite particles of MBS[3]as well as for other styrene/acrylate systems[4] that the configurational entropy of mixing of two monomers is the dominant thermodynamic factor and that the presence of polymer has no significant effect upon the *ratio* of the two monomers when comparing the polymer and monomer droplet phases. It was quite remarkable that notwithstanding these results of the monomer partitioning experiments, significant differences were found between the microstructure of the graft and free copolymer.

A study was performed to prepare copolymers of styrene (S) and methyl methacrylate (MMA) grafted onto PB. There are some limiting conditions in order to perform this study in a reliable way. First, it is important to avoid coagulation and the formation of new particles. Second, a certain minimum degree of grafting (DG) is required to allow accurate analysis of the grafts. In a series of preliminary experiments the proper conditions to meet these requirements were determined by varying some process parameters, in particular the type of initiator and the emulsifier concentration. The purpose of this study was to investigate the intramolecular microstructure (sequence distribution)[5,6] and intermolecular microstructure (average copolymer composition, CCD[7], molecular weight distribution) of the SMMA copolymer grafted onto PB and of the free SMMA copolymer.

EXPERIMENTAL

The PB seed latex

Materials and preparation. The butadiene (DSM, Hydrocarbons, Geleen, The Netherlands) was purified by

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Table 1 Recipes of the PB seed latex, SMMA-i copolymers and MBS graft polymers (in parts by weight)

	PB	SMMA 25/75	MBSI	MBSII
Water	2800	600	600	762
S	–	30.9	23.180	22.015
MMA	–	89.1	66.82	62.658
B(PB)	1200	–	(30)	(29.75)
SDS	–	2.0	0.875	–
KPS	15.14	0.2	1.427	–
KCB	7.74	–	0.638	–
tDM	12.00	1.2	0.9	0.85
CHP	–	–	–	0.213
SFS	–	–	–	0.213
$FeSO_4$/EDTA	–	–	–	0.005

condensing the vapour from a 27 l storage vessel into a cooled steel recipient. *Table 1* gives the standard recipe for the emulsion polymerization of butadiene. The PB latex was made by means of an emulsifier free emulsion polymerization process[8], which gives a monodisperse latex. The polymerization was performed in a 5 l stainless steel reactor fitted with two 12-bladed turbine impellers. The temperature was 353 K and the impeller speed was 400 rev min^{-1}.

Particle size analysis. The average particle sizes and particle size distributions were determined by means of transmission electron microscopy (TEM, Jeol 2000 FX). The PB samples were first diluted 400 times, after which the double bonds of the PB were stained with osmium tetroxide (OsO_4). Subsequently, the latexes were dried on a 400 mesh grid. Typically 750–1000 particles were counted with a Zeiss TGA-10 particle analyser. The polydispersity is defined as:

$$Pn = \frac{d_w}{d_n} \tag{1}$$

where $d_w = (\Sigma n_i d_i^4)/(\Sigma n_i d_i^3)$ (the weight average diameter), $d_n = (\Sigma n_i d_i)/(\Sigma n_i)$ (the number average diameter) and n_i represents the number of particles with diameter d_i.

The characteristics of the seed latex produced during this research are as follows: $d_n = 209.7$ nm, $d_w = 212.7$ nm, $Pn = d_w/d_n = 1.014$. From these diameters it is obvious that the latex shows a narrow distribution, i.e. the polydispersity is close to one.

Gel content. The determination of the gel content is based on a toluene extraction of the soluble fraction of the PB[9]. The insoluble part is the gel fraction by definition. The isolation of the emulsifier free PB was difficult due to the high degree of stabilization of the latex by the sulfate groups of the initiator. Precipitation only occurs when aluminium nitrate was added in combination with an excess of methanol. The coagulum was washed three times with water and methanol and then dried under nitrogen at 323 K during 5 h. To 1 g of an accurately weighed PB in a stoppered flask, 100 ml of toluene was pipetted, after which the mixture was gently shaken for at least 48 h at room temperature in the dark. The mixture was then filtered over a 100 mesh filter, and 50 ml of the filtrate was evaporated to dryness in a weighed aluminium dish. The gel content was calculated according to $(w_{PB} - 2w_f)/w_{PB}$, where w_{PB} is the weight of the PB sample and w_f is the weight of the dried filtrate. The gel content of the PB latex used in this study was 72%.

Graft copolymerization of S and MMA onto PB seed particles

Materials and preparation of the graft polymers. The batch graft polymerizations were performed in a 1 l stainless steel reactor under nitrogen at 323 K with a 12-bladed turbine impeller and at a stirrer speed of 300 rev min^{-1}.

Before using a PB latex in the graft copolymerizations, the latex was dialysed in a membrane (Medicell International Ltd, London, UK). The water was changed five times every 4 h and this has been found sufficient to remove most inorganic ingredients[10]. After this, the solid content was determined.

The monomers, S and MMA (both from Merck) were distilled under nitrogen at reduced pressure and subsequently stored at 277 K under nitrogen. The chain transfer agent n-dodecyl mercaptan (nDM, Fluka, for synthesis), the emulsifier sodium dodecylsulfate (SDS, Fluka, purity ~99%) and the buffer sodium hydrogen carbonate ($NaHCO_3$, Merck, p.a.) were used as received without further purification. The water was distilled twice and stored under nitrogen. The initiators used will now be discussed in more detail. The emulsion graft polymerization processes were performed with a water soluble initiator, potassium persulfate ($K_2S_2O_8$, KPS, Fluka, p.a.) or with an oil soluble initiator, cumene hydroperoxide (CHP) in combination with a redox system[11]. The redox initiator system, CHP ($C_9H_{12}O_2$, Fluka, 80% pure), sodium formaldehyde sulfoxylate ($CH_3NaO_3S.2H_2O$, SFS, Fluka), iron(II) sulfate ($FeSO_4$, Fluka) and ethylenediamine tetraacetic acid (EDTA, Fluka) were also used without further purification. The CHP was used as received, a solution was made of SFS and of $FeSO_4$ and EDTA as well, all in oxygen free water at pH = 4. The ratio of the components in the redox system added, CHP/EDTA-Fe^{2+}/SFS, was 1/0.02/1 (w/w/w).

The reactor was filled with the ingredients in the following order; first, the PB seed latex was added to the reactor together with an emulsifier solution (when emulsifier was used). Next, the reaction medium was degassed and purged with nitrogen. After this the monomers were added together with the nDM. The initiator was added after the PB seed latex had been allowed to swell with the monomers for 1 h at reaction temperature. Addition of EDTA-Fe^{2+} and SFS solutions at the beginning of the swelling would lead to premature polymerization (and might yield a conversion of 10–30%). Evidence of this phenomenon had already been found by Anderson and Proctor[12], who stated that the iron/EDTA complex and SFS interact to give a free radical. The standard recipes of the MBS graft polymerizations are given in *Table 1*. MBSI is the graft copolymerization with KPS and an emulsifier concentration at the critical micelle concentration (*CMC*), i.e. 30.4 mg SDS/G PB + *CMC* water (= 2.26 mmol l^{-1}), and MBSII is the graft copolymerization with CHP and without emulsifier.

Separation of graft and free copolymer by solvent extraction. In the graft polymerizations, not all of the monomer added to the PB seed latex will become grafted onto the PB backbone (PB-SMMA-g), but part of it will polymerize without being chemically bonded onto the

PB. This is the so-called free copolymer (SMMA-f). In the literature, several methods are described to separate the free copolymer from the graft polymer. One of the methods is based on the formation of reversible gels[13–15]. Another method which has been used in the present investigation is the solvent extraction method[16]. A good solvent is chosen for the free copolymer, whereafter, in principle, separation can be achieved by ultracentrifugation.

Solvation of MBS took place in acetone. However, at high fractions of styrene in the copolymer, methyl ethyl ketone (MEK) was used instead of acetone. The procedure is as follows: to 1 g of accurately weighed MBS polymer acetone (100 ml) is added, followed by shaking for 70 h at room temperature. The soluble polymer was then separated from the insoluble polymer in an ultracentrifuge (Centrikon T-2060), at 45 000 rev min^{-1} for 45 min. After centrifugation the clear solution was poured into an excess of cold heptane, leading to precipitation of the polymer. The precipitated polymer, SMMA-f, as well as the insoluble residue, was collected and dried in a vacuum oven at 1.3 mPa and 323 K for at least 48 h.

Determination of the DG and the graft efficiency (GE). The DG and GE were calculated from a material balance over the insoluble polymer and the MBS polymer which was added to the acetone solution, according to the following equations:

$$\text{DG} = \frac{\text{amount of SMMA-g}}{\text{amount of PB}} = \frac{w_{\text{res}} - w_{\text{PB}}}{w_{\text{PB}}} \tag{2}$$

$$\text{GE} = \frac{\text{amount of SMMA-g}}{\text{amount of SMMA polymerized}} = \frac{w_{\text{res}} - w_{\text{PB}}}{w_{\text{MBS}} - w_{\text{PB}}} \tag{3}$$

where w_{res} is the weight of insoluble PB-SMMA-g residue resulting from the solvent extraction (g), w_{PB} is the weight of PB in the MBS sample (g), calculated from $w_{\text{PB-a}}[w_{\text{MBS}}/(w_{\text{mon}} + w_{\text{PB-a}})]$, where $w_{\text{PB-a}}$ is the weight of PB added to the reaction (g), w_{mon} is the weight of polymerized monomers (g) and w_{MBS} is the weight of the MBS sample used for the solvent extraction (g).

The data for DG and GE of low conversion samples show larger relative errors (*Figure 1*), because at lower conversions the determinations suffer from lower graft levels. Since the method relies upon the ability to extract free copolymer chains from the grafted rubbery polymer domains, the size of the rubbery polymer granules influences the extraction. The samples at high conversions tended to be almost powdery in the dry state and could be easily dispersed in the acetone extraction solvent. Samples at low conversions were tough and rubbery, preventing the formation of a good dispersion.

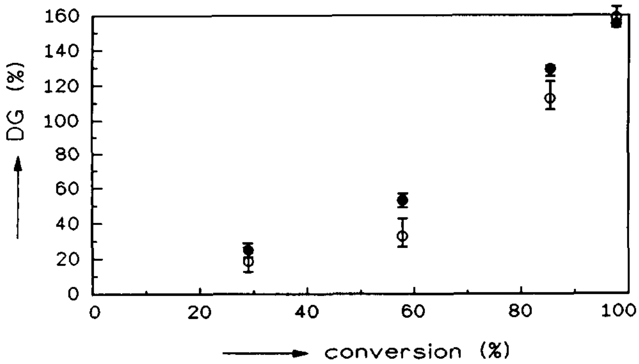


Figure 1 Degree of grafting obtained by solvent extraction (○) and by n.m.r. (●)

Determination of DG, GE and fraction of S (F_s) by means of n.m.r. After the solvent extraction of MBS, the separated polymers (SMMA-f and PB-SMMA-g) were analysed by ^{1}H and ^{13}C n.m.r. The SMMA-f was dissolved in $CDCl_3$ and the PB-SMMA-g was swollen with $CDCl_3$. The ^{1}H n.m.r. spectra were recorded with a 400 MHz (Bruker AM 400) spectrometer at 298 K, using $CDCl_3$ as locking agent. Generally, the spectra were obtained by using a spectral width of 6024 Hz, an acquisition time of 2.7 s, a flip angle of 45°, and a pulse delay of 6 s. Spectra were obtained after accumulating 64 scans, using a sample concentration of 1% (w/v). The ^{13}C n.m.r. spectra were recorded and analysed as described elsewhere[6,17].

For the PB-SMMA-g, a new set of equations had to be derived to determine the DG, GE and fraction of S in the SMMA-g copolymer grafted onto PB (F_s-g). In *Figure 2* a typical ^{1}H n.m.r. spectrum of a grafted polymer (PB-SMMA-g) is shown. From the different signal areas we can calculate the amount of styrene per proton ('S'), the amount of butadiene per proton ('PB') and the amount of MMA per proton ('MMA') using the following equations:

$$\text{'S'} = \frac{A_{\delta=7.5-6.5}}{5} \tag{4}$$

$$\text{'PB'} = \frac{A_{\delta=5.4} - 1/2A_{\delta=4.9}}{2} + \frac{A_{\delta=4.9}}{2} \tag{5}$$

$$\text{'MMA'} = \frac{A_{\delta=3.7-0.2} - 3/5A_{\delta=7.5-6.5} - 3/2A_{\delta=4.9} - 2(A_{\delta=5.4} - 1/2A_{\delta=4.9})}{8} \tag{6}$$

where $A_{\delta=7.5-6.5}$ is the total signal area of the aromatic protons of S, $A_{\delta=5.4}$ is the signal area of the olefinic protons of the *cis* and *trans* units and one methine proton of the olefinic protons of the vinyl sequence, $A_{\delta=4.9}$ is the signal area of the olefin CH_2 of the vinyl 1,2-sequence, and $A_{\delta=3.7-0.2}$ is the signal area of all aliphatic protons of S, MMA and PB.

With these formulae we can easily calculate F_s-g by using equations (4) and (6):

$$F_{\text{S-g}} = \text{'S'}/(\text{'S'} + \text{'MMA'}) \tag{7}$$

The DG (in mol%) can be calculated using the following definition:

$$\text{DG} = \frac{\text{amount of SMMA-g}}{\text{amount of PB}} = \frac{\text{'S'} + \text{'MMA'}}{\text{'PB'}} \tag{8}$$

If equations (4)–(6) are multiplied by the molecular weight of S (104.15 g mol^{-1}), butadiene (54.09 g mol^{-1}) and MMA (100.12 g mol^{-1}), respectively, the DG and GE (by weight) are obtained.

$$\text{GE} = \frac{\text{amount of SMMA-g}}{\text{amount of SMMA polymerized}} = \frac{\text{DG(wt)}w_{\text{PB-a}}}{w_{\text{mon}}} \tag{9}$$

where DG is measured by n.m.r. The DG and GE can be compared with the solvent extraction data. This is shown for one experiment (MBSII without nDM) in *Figure 1*. It appears that the agreement between the two independent methods is satisfactory. The n.m.r. results are believed to provide the more reliable values.

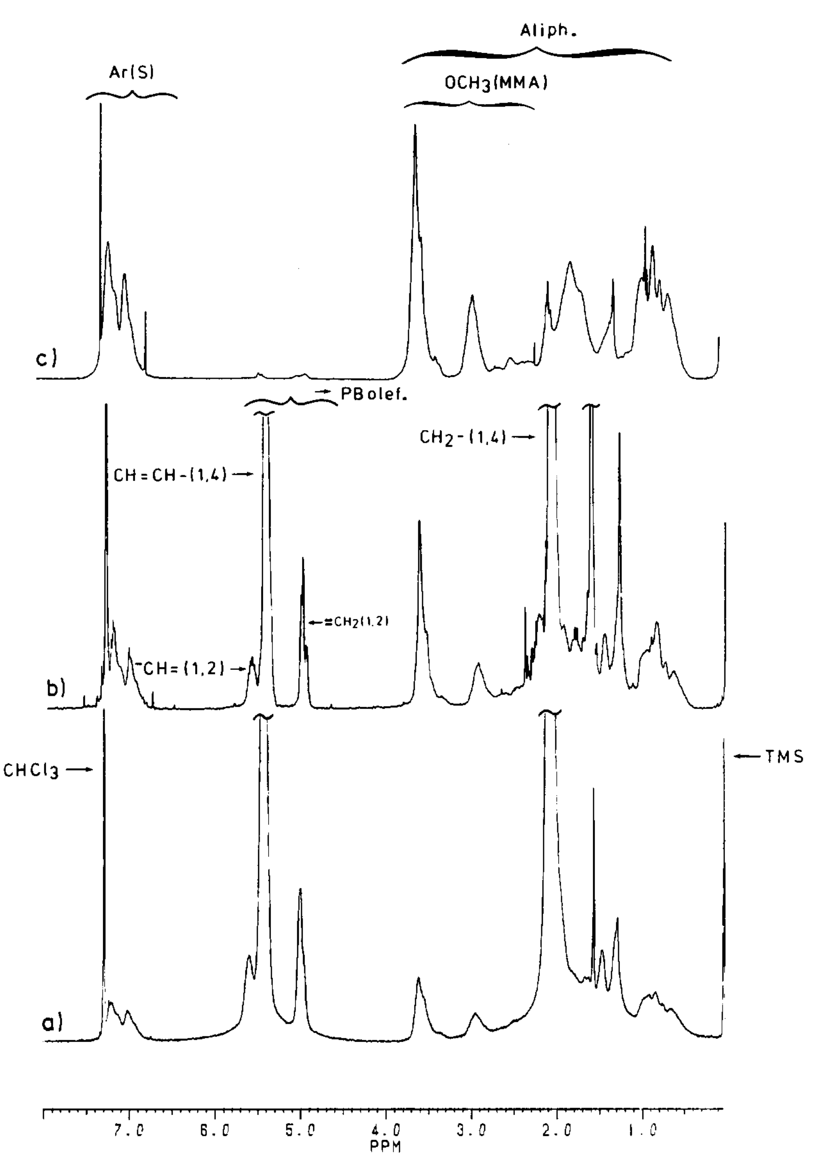


Figure 2 400 MHz ^1H n.m.r. spectra in $CDCl_3$ at 298 K of (a) PB-SMMA-g polymer from MBSII at 78% conversion, (b) PPB-SMMA-g polymer from MBSII at 95% conversion and (c) free SMMA copolymer from MBSII at 95% conversion. Ar(S) represents the resonance of the aromatic protons of the styrene unit, PBolef. represents the olefinic protons of the PB unit and Aliph. represents all the aliphatic protons of the styrene, MMA and PB units

Breaking the polymer backbone by ozonolysis. In order to determine the molecular weight distribution and the CCD of the copolymers grafted onto PB, these grafted chains have to be isolated. This can be done by breaking the polymer backbone through oxidation of the residual double bonds of the PB. A number of methods have been developed to achieve this purpose; Kranz *et al.*[18] made an overview and compared several methods based on the use of OsO_4 and $KMnO_4$. Barnard[19] showed that the use of ozone gives good results when applied to graft polymers. Ozone reacts with the double bond of PB to form an ozonide. This ozonide then can be reduced or oxidized. In this study the PB backbone has been broken by the ozone method.

Ozone was generated by passing oxygen gas through an ozone generator (OREC) at room temperature. Each graft phase sample (0.5–3.5 g) was dispersed and homogenized in methylene chloride (250 ml). Before the ozone was purged through the solution, butyl sulfide (5 ml, Aldrich) was added and the solution mixture was cooled with dry ice and acetone to a temperature of ~196K. This temperature was maintained during the whole ozonolysis. A flow of ~2% of 2.5 $l\ min^{-1}$ ozone was passed through the solution for 40 min. After ~30 min, the solution mixture turned blue, indicating that almost no more ozone would be absorbed by the sample and the butyl sulfide.

The ozonides were then reduced by adding a solution of sodium borohydride (0.5 g, $NaBH_4$, Aldrich) dissolved in methylene chloride (100 ml) and methanol (100 ml)[20,21]. The mixture was stirred for at least 1 h at room temperature. The borohydride reaction was quenched by adding a 15% aqueous hydrochloric acid (100 g) solution. The solvent was substantially removed in a rotavaporator until the polymer precipitated. Then the remaining solution was decanted and the polymer was redissolved in methylene chloride, rotavaporated until dryness and loosened from the sides of the flask by adding methanol (150 g). The liquid and polymer were poured into a fritted filter and washed twice with additional methanol. Finally, the copolymers were dried in an air-circulating oven at 5 kPa and 323 K for at least 24 h. The SMMA copolymer

Table 2 Comparison of the average molecular weight (measured by s.e.c.) of a PB-SMMA-g sample after one and two exposures to ozone

		Ultraviolet			Refractive index		
No. of times ozonolysed	Analysis	M_n (kg mol^{-1})	M_w (kg mol^{-1})	M_w/M_n	M_n (kg mol^{-1})	M_w (kg mol^{-1})	M_w/M_n
Single	1	33.8	180	5.32	36.6	159	4.33
	2	33.4	138	4.12	34.7	137	3.96
Double	1	29.4	158	5.37	31.7	185	5.82
	2	28.0	109	3.9	29.9	87.6	2.93

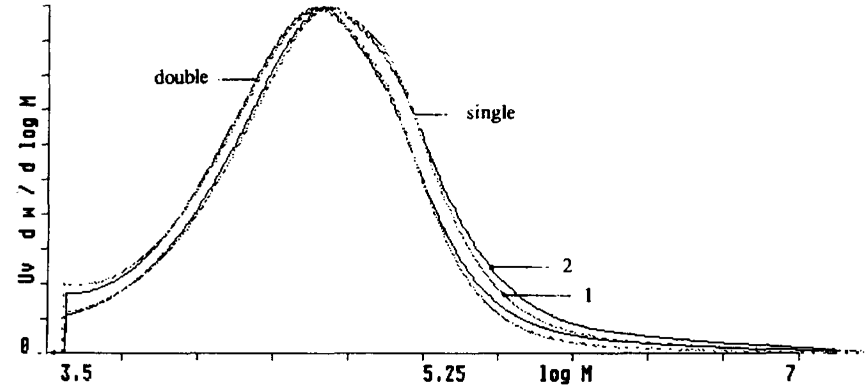


Figure 3 Molecular weight distributions of one PB-SMMA-g sample after single ozonolysis (measured twice) and double ozonolysis (measured twice)

is somewhat attacked by ozone, as is shown in *Table 2* and *Figure 3* where the number- and weight-average molecular weights (M_n and M_w, respectively) of one sample with single and double exposures to ozone were measured twice. *Figure 3* shows that the molecular weight distributions of the SMMA-g copolymer after two exposures are somewhat shifted to lower molecular weights, which is also reflected in the average values of M_n and M_w (*Table 2*).

Determination of the CCD. High performance liquid chromatography (h.p.l.c.) with u.v. detection or with a moving wire flame ionization detector (f.i.d.) has been found to be a useful method for determining the CCD of styrene/acrylate copolymers[7]. U.v. detection causes problems at low fractions of S in the copolymer. By contrast, the moving wire f.i.d. (a carbon-sensitive detector) can detect even acrylate homopolymers.

Solvent gradients were created with a system controller (model 720) and two h.p.l.c. pumps (model 510, Millipore-Waters Corp., Milford, MA, USA). A Waters Intelligent Sample Processor (Wisp, model 710) was used to inject 10–200 μl of the samples (0.2 wt% copolymer solution in tetrahydrofuran, THF). The measurements of SMMA and SMA copolymers were performed on a silica column at ambient temperature.

In the case of SMMA copolymers an elution gradient according to equation (10) was applied as shown in *Table 3*.

$$\%\text{A} = \%\text{A start} + (\%\text{A end} - \%\text{A start})\left(\frac{t - t_0}{t_1 - t_0}\right)^2 \quad (10)$$

where A is heptane, t is the time elapsed after injection, t_0 is the time elapsed from the beginning of the segment and t_1 is the time elapsed from the end of the segment. Under these conditions the separation was probably dominated by the so-called precipitation mechanism[22], and the retention time then will be independent of molecular weight[23]. Low conversion solution SMMA copolymers were used to calibrate the h.p.l.c. measurements.

Table 3 Elution gradient used in the h.p.l.c. measurements, determining the chemical composition distribution of the SMMA copolymers

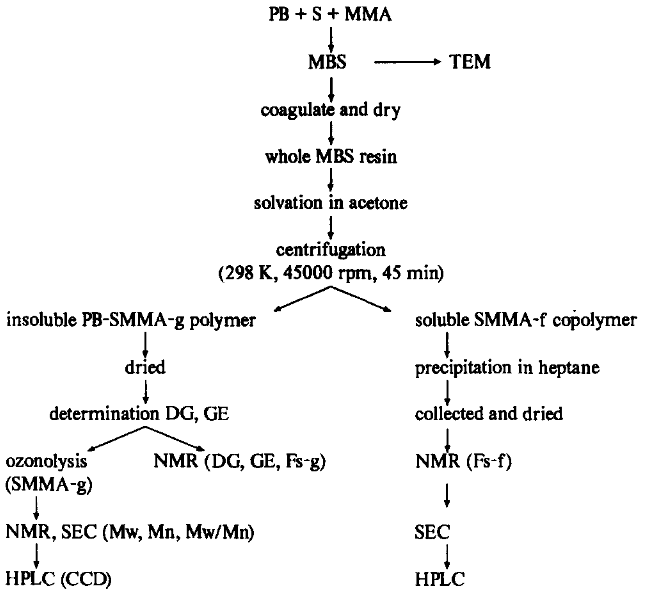
Time (min)	Flow (ml min^{-1})	A[a] (%)	B[b] (%)
0	1.0	80	20
7	1.0	35	65

[a] A = heptane

[b] B = 90 vol% dichloromethane + 10 vol% methanol

Determination of molecular weight. Size exclusion chromatography (s.e.c.) of SMMA copolymers (also of the isolated SMMA-g after ozonolysis) was performed on a chromatographic system (Waters Associates) equipped with a differential refractometer (Waters 410, 313 K) and a u.v. detector (Waters 440, 254 nm, 295 K). A series of two columns (Shodex KF-80 M) thermostatically controlled at 313 K was used. The s.e.c. columns were calibrated using 12 polystyrene (PS) samples (Polymer Laboratories), with narrow molecular weight distributions. The PS standards could be used here, since it was shown that the individual calibration curves for PS and PMMA in THF are in extremely close proximity[24]. The THF flow rate was set at 1.0 ml min^{-1}. All emulsion copolymers were dissolved in THF and after 24 h the samples were filtered over a 0.2 μm filter, and 100 μl of this sample [0.05 (%w/v)] was injected.

Determination of the morphology. The latexes were diluted 400 times with distilled water to a concentration of 0.05 wt%. To this solution 1 ml of a 2% aqueous



Scheme 1

OsO_4 solution was added, and allowed to stain the PB in the grafted polymer for 1 h. The stained latex was placed on a 400 mesh grid and dried. The morphology was examined by TEM (Jeol 2000 FX).

The complete experimental procedure is summarized in *Scheme 1*.

RESULTS AND DISCUSSION

Grafting of S and MMA onto PB

Normally in emulsion polymerization a water soluble initiator like KPS is used. In emulsion graft polymerizations, however, oil soluble initiators are more widely used because these tend to give higher GE values. Nevertheless, it is found in the literature that oil soluble initiators of different water solubility do not show much variety in their GE values[11]. In this research, batch processes of grafting S and MMA onto PB were studied using both types of initiators, KPS or CHP, over a range of emulsifier concentrations and conversions.

Emulsifier concentration and type of initiator

The seeded batch graft polymerizations were performed in the so-called stage III of emulsion polymerization. This means that there is no separate monomer phase present. The swelling behaviour of S and MMA in PB is described elsewhere[3]. At a comonomer feed composition of 25% S, there will be no separate monomer phase at a monomer to polymer molar ratio of 77/23. The PB seed latex was prepared by means of the emulsifier free polymerization process, so the latex particles are stabilized by sulfate groups (from the initiator) chemically bonded to the surface[9].

In *Table 1* the standard polymerization recipes are given for both types of initiators. Before the seeded reactions were performed, the apparent *CMC* in the presence of the PB seed latex was measured by means of conductometric titration. Note, however, the possible decrease of the *CMC* caused by addition of monomer to the system was not taken into account[25]. From these titration experiments for MBSI, an amount of 30.4 mg SDS g^{-1} PB is found taking into account that the *CMC* of water in the presence of KPS and NCB is 2.26 mmol l^{-1}. The same experiments were done for MBSII in the presence of the initiator system $CHP/FeSO_4/SFS$. With a *CMC* of 3.78 mmol l^{-1} of the water phase, a value of 31.5 mg SDS g^{-1} PB was determined.

Figures 4a and *b* show the DG and GE at 100% conversion (measured by n.m.r.) as a function of the emulsifier concentration for the polymerizations with KPS (MBSI) and CHP (MBSII), respectively.

On the left-hand side of *Figure 4a* below the *CMC* (7.5 mmol l^{-1}) a decrease in DG and GE is seen. As a result of the decrease of emulsifier concentration coagulation occurs, probably due to a lack of electrostatic repulsion. If coagulation takes place at decreasing emulsifier concentrations, the total surface area will decrease and the DG will also decrease. Furthermore it should be noted that there are no data available for an emulsifier free polymerization with KPS as the initiator. The grafting of S and MMA onto PB seeds, emulsifier free with KPS as initiator, gives latexes with a very high viscosity, resulting in a relatively creamy dispersion of small aggregates rendering the grafting behaviour incomparable with that of the other experiments. On the right-hand side of *Figure 4a* it can also be seen that above the *CMC* (7.5 mmol l^{-1}) the DG decreases, due to the occurrence of secondary nucleation. Above the *CMC* more free micelles exist in the water phase: these can be initiated to form a new crop of particles, so there will be less monomer left for grafting. *Figure 5a* shows the morphology of MBSI at the *CMC*, where the maximum DG was reached.

In *Figure 4b* the DG and GE as a function of the emulsifier concentration are shown, where grafting took place with the $CHP/FeSO_4/SFS$ redox system. In these polymerizations a different behaviour is observed: at the *CMC* the DG is very low due to the occurrence of

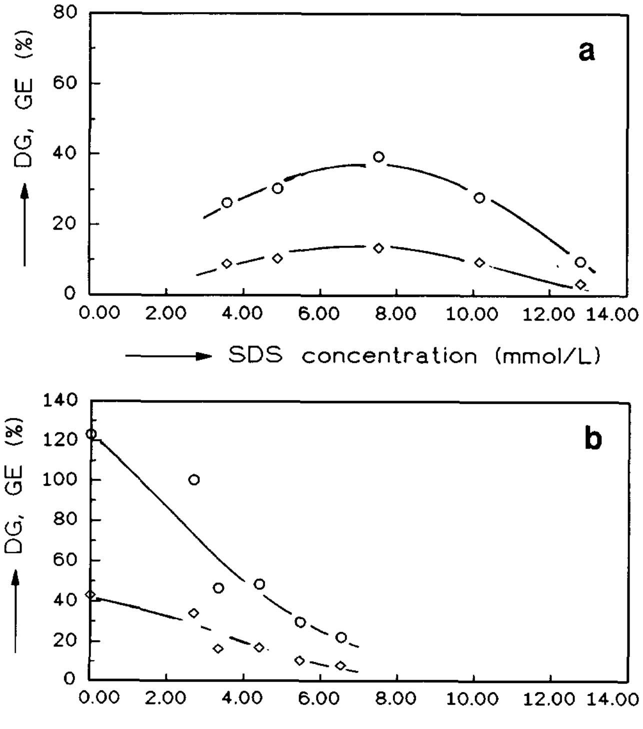


Figure 4 Degree of grafting (○) and grafting efficiency (◇), as a function of the emulsifier concentration: (a) KPS as initiator (MBSI); (b) $CHP/FeSO_4/SFS$ as initiator (MBSII)

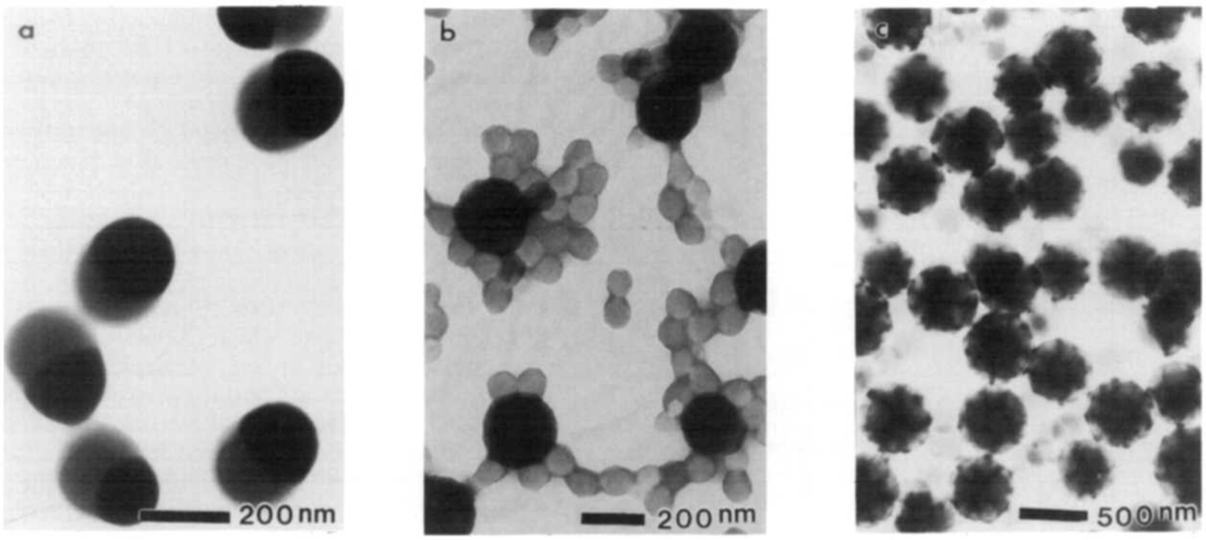


Figure 5 Transmission electron micrographs of MBS graft polymer (100% conversion), prepared with different initiators and emulsifier concentrations: (a) MBSI (KPS) at the *CMC*; (b) MBSII (CHP) at the *CMC*; (c) MBSII (CHP) without emulsifier

secondary nucleation (*Figure 5b*). Therefore no experiments were performed above the *CMC*. Below the *CMC* the DG is strongly increased and neither coagulation nor secondary nucleation of any importance takes place (*Figure 5c*). In the latter case the latex remains stable. This can be understood realizing that the PB latex particles are stabilized by chemically bonded sulfate groups. The sulfate groups can migrate to the surface in the seeded polymerization step provided that the diffusion of the chains with a sulfate end group is fast enough, which implies that these chains are not crosslinked. Taking into account the particle morphology (occlusion and a very thin shell) it is assumed that during this batch reaction the chemically bonded sulfate groups do not become shielded, thus maintaining latex stability.

The strong increase of the DG and GE lowering the emulsifier concentration can be explained by the enhanced presence of initiator at the surface. Some parts of the redox initiator systems are in the aqueous phase and others in the oil phase, therefore it is expected that the initiator will be most active at the surface.

Emulsifier free grafting with CHP as initiator

Further discussion in this paper concerns the emulsifier free batch graft polymerization with CHP/$FeSO_4$/SFS as the redox initiator system. It has been shown in the Experimental section that the average copolymer composition can be determined simultaneously with the DG and GE, directly from the ^1H n.m.r. spectrum of PB-SMMA-g. For the determination of the chemical composition distribution and the M_n and M_w of SMMA-g, breaking of the PB backbone is necessary.

Degree of grafting and grafting efficiency

In *Figure 6a* the DG and GE are shown as a function of conversion. There are several striking points in this figure.

1. According to the literature, at the very beginning (<10% conversion) of the polymerization the GE is assumed to be high (almost 100%) as a result of the highly probable penetration of free radicals into the PB seed particles[26–29].

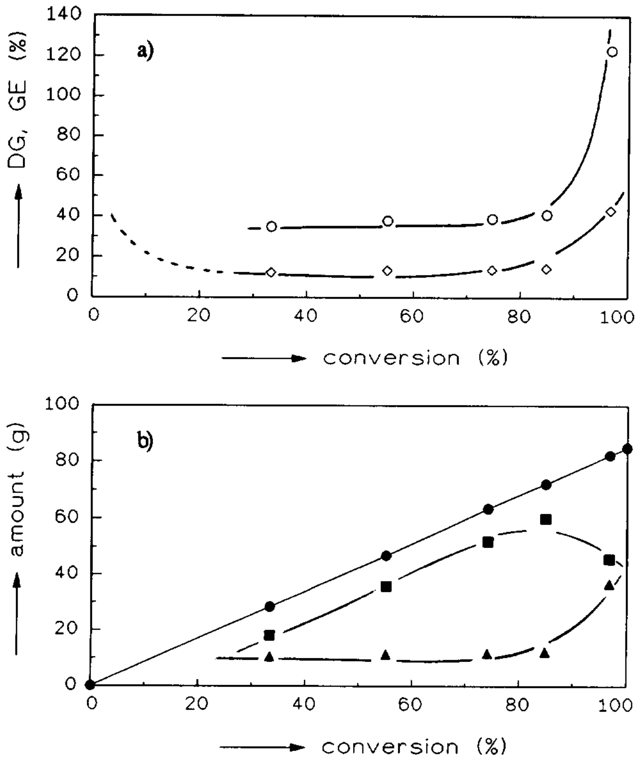


Figure 6 (a) Degree of grafting (○) and grafting efficiency (◇), as a function of conversion with CHP/$FeSO_4$/SFS as initiator and emulsifier free. (b) Variation of the amount of SMMA-g (▲) and SMMA-f (■) as a function of conversion. The closed circles are the total amount of S and MMA polymerized

2. As the polymerization proceeds, the GE decreases and then remains constant[26] (between 10% and 85% conversion).
3. Then, at high conversions (>85%), a sudden increase in the DG and GE takes place, which is not observed in other studies of grafting S onto PB[26–29]. The sudden increase of the GE can be explained by the decrease in the monomer concentration at higher conversion. There, at low monomer concentration, the probability for chain transfer to PB will increase, so more graft sites (*N*) are initiated (*Table 4*), leading to an increased

Table 4 Characteristics of MBSII as 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})	$P(f)^b$
33.3	34.9	12.2	21	49.8	101	2.03	3.79	32	60.8	181	2.98
55.1	37.9	13.2	24	63.8	115	1.81	3.21	28	69.8	162	2.32
74.7	39.0	13.6	32	61.4	107	1.75	3.44	27	–	–	–
84.9	41.1	14.3	24	–	–	–	–	27	–	–	–
96.8	123.2	43.1	21	50.6	116	2.3	13.1	24	64.9	148	2.28

[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

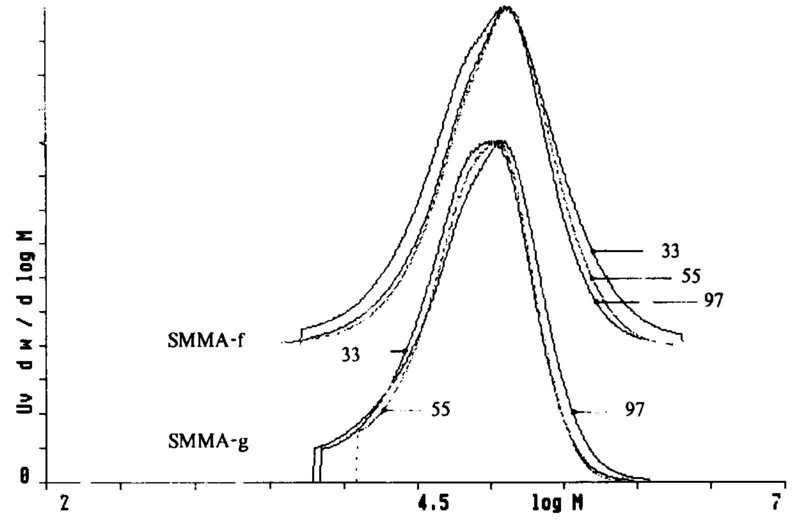


Figure 7 Molecular weight distributions of SMMA-g and SMMA-f copolymer of MBSII as a function of conversion (percentage conversion is shown in the figure)

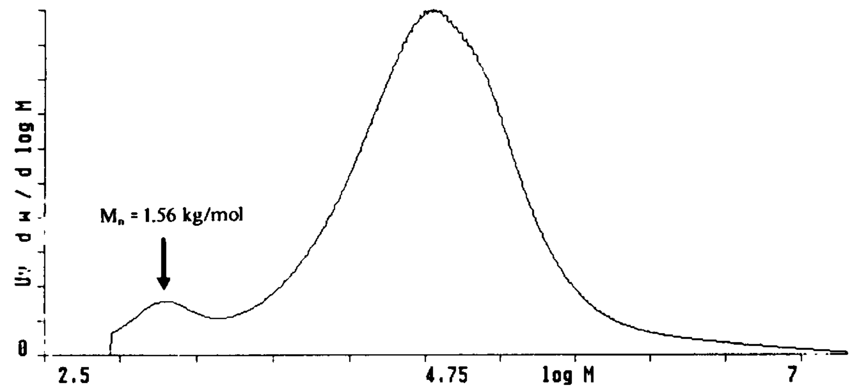


Figure 8 Molecular weight distribution of a SMMA-g copolymer of MBSII at 97% conversion

GE. Transfer reactions are certainly dependent on the type of monomer, i.e. the chemical structure and the mobility of the monomer, as shown in the literature[26–29] discussing the different behaviours of the DG as a function of conversion.

Figure 6b shows a decrease in the absolute amount of free copolymer with conversion instead of remaining constant as would be expected. Crosslinking reactions probably take place between SMMA-f and either PB or PB-SMMA-g. Above 85% conversion, S is almost depleted. The aqueous phase is acting as a buffer for MMA, so the monomer concentration in the particle is very low. At high weight fraction of polymer in the particle the intraparticle viscosity increases, which in turn increases the number of radicals in the particle because termination is diffusion controlled. The SMMA-f chains then may be reinitiated by the increasing of transfer by PB radicals or by SMMA-g radicals, and become grafted chains.

The average molecular weight (M_w, M_n) and molecular weight distributions

The molecular weights are given in *Table 4* and the molecular weight distributions in *Figures 7* and *8*. In *Table 4* it is seen that the SMMA-g copolymer has a lower molecular weight than SMMA-f in spite of the possible crosslinking reactions in the latter case. Differences in molecular weight are not only caused by the parts of the chain destroyed by ozonolysis, but may be also due to chain transfer processes. The number-average chain length, M_n, will be equal to the rate of chain propagation divided by the total rate of termination plus chain transfer. The propagation rate of the polymer chains is assumed to be almost equal for SMMA-f and SMMA-g. So, the different processes of transfer and termination leading to SMMA-g or to SMMA-f should explain the different molecular weights. From the molecular weight data as a function of conversion listed in *Table 4*, the molecular weight distributions in *Figure 7*, and the absolute amount of graft and free copolymer as a function of conversion (*Figure 6b*), it can be concluded that cross-termination between a free polymeric radical and either PB-SMMA-g or a PB radical, cannot be neglected. In *Figure 7* it is shown that with increasing conversion an increase in the relative amount of chains with a higher molecular weight occurs, resulting in a somewhat bimodal molecular weight distribution.

It should be noted that in all molecular weight distributions of SMMA-g (*Figure 8*) a second peak exists of $M_n = \sim 1500$ g mol^{-1}, i.e. ~15 monomeric units. The appearance of these small chains is believed to arise from either the attack of ozone or from a chain transfer or cross-termination of a growing polymeric chain coming from the aqueous phase to PB or with a PB radical.

The average copolymer composition, CCDs and sequence distributions

Another ambiguity arises from *Table 4*. There is a small difference in copolymer composition (measured by n.m.r.) between SMMA-g and SMMA-f which cannot easily be explained. This difference in F_S between the SMMA-g and SMMA-f copolymer is confirmed by an independent h.p.l.c. experiment. In *Figure 9* two CCDs of SMMA-g as a function of the conversion and the CCD of SMMA-f (MBSII, at 97% conversion) are displayed. The average fraction of S at 97% conversion in SMMA-g is 19% and in SMMA-f is 29%. This is comparable with the n.m.r. results of 18 and 28%, respectively (*Table 5*). The CCD of SMMA-g is broader and has more composition drift towards MMA-rich copolymers than the CCD of SMMA-f, as is clearly shown in *Figure 9*. The CCD is broad but the copolymers formed over this wide composition range would not phase separate or demix. Nevertheless some haze may occur due to the wide range of refractive indices as a result of the very broad CCDs. In principle, MBS copolymers can be transparent because the refractive indices of styrene ($n^D = 1.595$) and MMA ($n^D = 1.492$) may, dependent on copolymer composition, match that of butadiene ($n^D = 1.5155$).

It should be noted that the broadening of the CCD may have been slightly increased by the selective adsorption of the hydroxy end groups of the SMMA-g chains onto the silica column. These hydroxy groups are formed in the ozonolysis procedure when the ozonides are reduced. This is not assumed to be a significant effect at molecular weights higher than 20 kg mol^{-1}, which is supported by the fact that the F_S determined by n.m.r. perfectly agrees with that measured by h.p.l.c.

The CCDs of SMMA-g and SMMA-f can be compared with the CCD of a conventional SMMA copolymer prepared in batch emulsion. In *Figure 10* the CCDs of two SMMA copolymers (25/75 mol/mol) are shown prepared at a monomer/water ratio of 0.2 and 0.05, respectively (SMMA, *Table 1*). The CCDs of SMMA-g and SMMA-f in *Figure 9* clearly show differences with those in *Figure 10*. The differences in composition drift

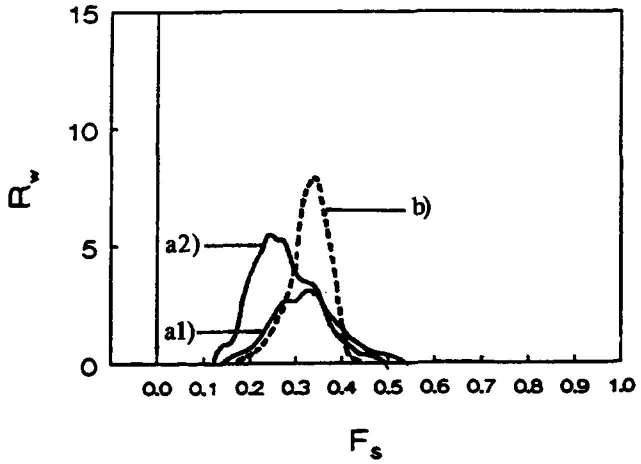


Figure 9 Chemical composition distributions of MBSII determined by means of h.p.l.c. of (a) SMMA-g at two different conversions [(a1) 33%, (a2) 97% conversion] and (b) SMMA-f at 97% conversion

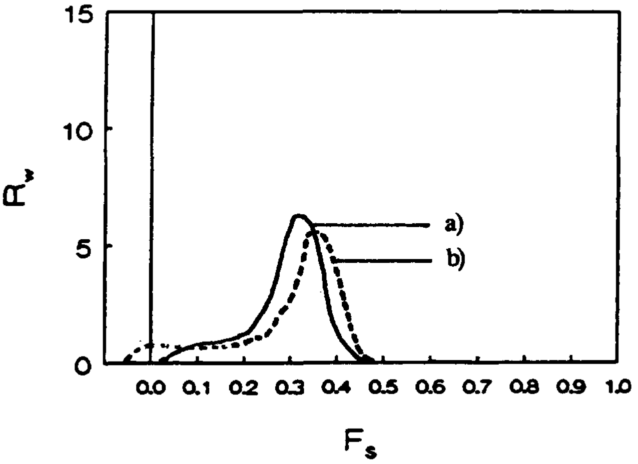


Figure 10 Chemical composition distributions determined by means of h.p.l.c. of (a) SMMA with monomer/water = 0.2 and (b) SMMA with monomer/water = 0.05

Table 5 Experimental values (%) of the cumulative average chemical composition of triad sequences (measured by ^{13}C n.m.r.) of SMMA-g and SMMA-f high conversion batch graft polymerization prepared at (monomer/water)$_0$ = 0.11 (g/g) and (S/MMA)$_0$ = 0.33 (mol/mol) ratios (MBSII)

	X	F_s	MMM	MMS	SMS	SSS	SSM	MSM
SMMA-g	33.3	21	0.45	0.40	0.15	0.05	0.34	0.61
	96.8	18	0.5	0.38	0.12	0.03	0.32	0.65
SMMA-f	33.3	32	0.35	0.48	0.17	0.08	0.36	0.56
	96.8	28	0.41	0.45	0.14	0.07	0.33	0.60

between SMMA-g and SMMA-f cannot be explained unambiguously. From Aerdts *et al.*[3] it becomes obvious that the main factor determining the partitioning of the two monomers is the configurational entropy of mixing. So monomer partitioning behaviour cannot provide an explanation for the above discrepancy. It is expected that chain transfer or cross-termination processes involving a growing polymeric chain coming from the aqueous phase and PB play an important role.

The sequence distributions of the MMA-centred and S-centred triads of SMMA-g and SMMA-f measured by ^{13}C n.m.r.[6,17] fail to provide additional information. The sequence distributions of SMMA-g and SMMA-f at two different conversions are listed in *Table 5*. The differences between these copolymers are small, and the peak assignment of the C1 and the α-CH_3 carbons is too complex to obtain significant results in this case. Therefore, in the next section, the sequence distributions of the SMA-g and SMA-f copolymers, which are easier to obtain, will be compared, where similar differences between F_S-g and F_S-f are observed.

Grafting S and MA onto PB

In an attempt to obtain more insight into the behaviour of grafted systems, the composition drift was also studied in the batch emulsion graft copolymerization of S and MA onto PB seed particles. The composition drift occurring during the copolymerization of S and MA in batch emulsion processes is very large. This is caused by a large difference in reactivity ratios, namely $r_{MA} = 0.19 \pm 0.05$ and $r_S = 0.73 \pm 0.05$, and by the large difference in water solubility between the monomers, i.e. $[S]_{max} = 3$ mmol l^{-1} and $[MA]_{max} = 600$ mmol l^{-1} at 323 K. Larger effects in composition drift will enhance the compositional and microstructural phenomena already observed in the graft copolymerization of S and MMA. The methyl acrylate/butadiene/styrene (MABS) graft polymers were polymerized according to the recipe of MBSII (*Table 1*), where MMA is replaced by MA and the monomer ratio is kept at 25 mol% S and 75 mol% MA.

In *Figure 11* the DG and the GE are displayed. When compared with *Figure 6a*, in the present case the DG and GE do not remain constant over the entire conversion range till 85% conversion, but increase already from 60% conversion. *Figure 11b* shows that simultaneously the absolute amount of SMA-f copolymer is decreasing dramatically. It has been shown before[30] that at a monomer/water ratio of 0.11, S is almost depleted at 60% conversion, leaving a substantial amount of MA in the water and polymer phases. This means that from this point on the monomer concentration in the latex particles is decreasing, and the freely formed SMA copolymers become chemically bonded by grafting. From *Table 6* it is obvious that with increasing conversion the fraction of S in SMA-g is decreasing more rapidly than the fraction of S in SMA-f. Normally, in the batch emulsion copolymerizations of S and MA, the average fraction of S will change from 50 to 25 mol% S at a molar feed ratio S/MA of 25/75[30]. *Figure 12* shows the expanded n.m.r. spectra of the methoxy region of SMA-g and SMA-f at two different conversions. The assignment of the methoxy protons as a function of compositional and configurational sequences is given in the literature[30]. Peak x is mainly determined by the triad MMM sequence (three MA monomer units next to each other). It is clearly shown that there is stronger composition drift towards MA-rich copolymers in the SMA-g (strong increase of peak x) as compared with the SMA-f copolymer. It should be noted that the SMA-g copolymers obtained (after

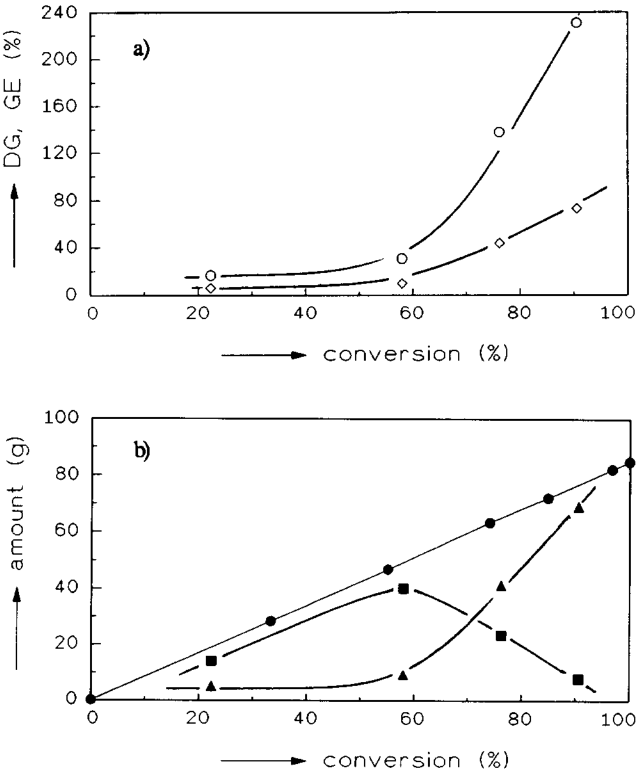


Figure 11 (a) Degree of grafting (○) and grafting efficiency (◇), as a function of the conversion with $CHP/FeSO_4/SFS$ as initiator and emulsifier free. (b) Variation of the amount of SMA-g (▲) and SMA-f (■) as a function of conversion. The closed circles are the total amount of S and MA polymerized

Table 6 Experimental values (%) of the cumulative average chemical composition and triad sequences (MA-centred by ^{1}H n.m.r. and S-centred by ^{13}C n.m.r.) of SMA high conversion batch graft polymerizations all prepared at $(monomer/water)_0 = 0.11$ (g/g) and at $(S/MA)_0 = 0.33$ (mol/mol) ratios. The coisotacticity parameter $\sigma = 0.9$

	X	F_s	MMM	MMS	SMS	SSS	SSM	MSM
SMA-g	22.3	48.5	8.1	40.9	51.0	–	–	–
	57.9	40.1	30.5	48.8	20.7	–	–	–
	76.29	20.9	55.3	37.6	7.1	1.8	20.6	77.6
	94.9	7.0	84.4	15.6	0.0	0.0	21.9	78.1
SMA-f	22.3	53.4	12.3	46.0	41.7	–	–	–
	57.9	47.1	20.6	48.0	31.4	–	–	–
	76.2	43.0	19.5	49.6	30.9	3.8	22.1	74.1
	94.9	40.2	20.1	48.5	31.4	–	–	–

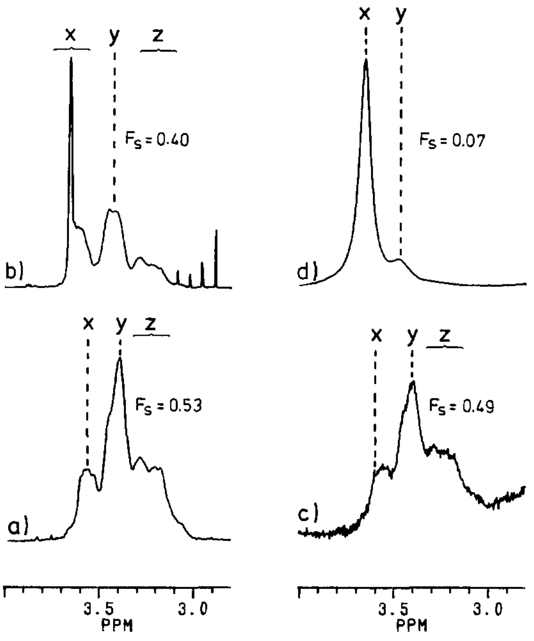


Figure 12 Expanded 400 MHz ^{1}H n.m.r. spectra of the methoxy region of (a) SMA-f 22.3% conversion, (b) SMA-f 94.9% conversion, (c) SMA-g 22.3% conversion and (d) SMA-g 94.9% conversion

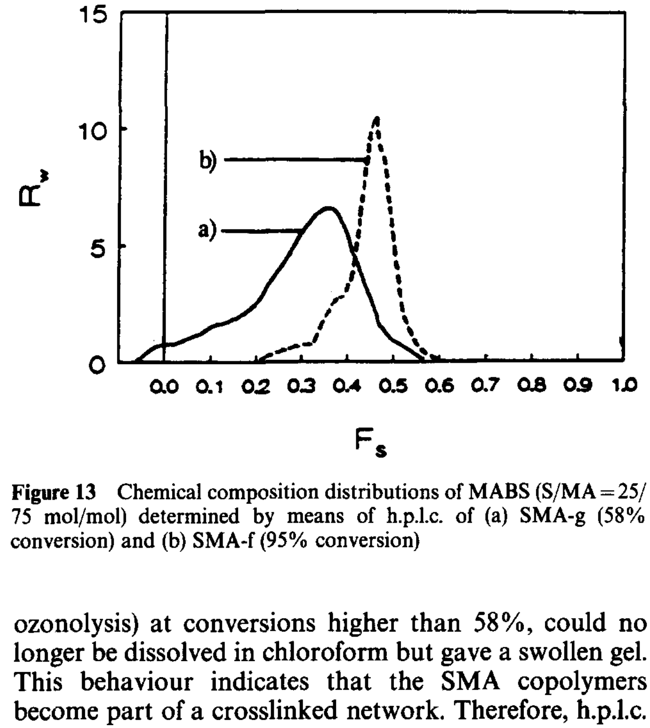


Figure 13 Chemical composition distributions of MABS (S/MA = 25/75 mol/mol) determined by means of h.p.l.c. of (a) SMA-g (58% conversion) and (b) SMA-f (95% conversion)

ozonolysis) at conversions higher than 58%, could no longer be dissolved in chloroform but gave a swollen gel. This behaviour indicates that the SMA copolymers become part of a crosslinked network. Therefore, h.p.l.c. could only be applied to the samples till 58% conversion.

The CCDs shown in *Figure 13* are in agreement with the composition drift over the 58% conversion range of the average copolymer composition as listed in *Table 6*. It is obvious from *Figure 13* that the CCD of SMA-f (95% conversion) and the CCD of SMA-g till 58% conversion are both monomodal, in contrast to the conventional batch process of SMA[30]. However, the CCD of SMA-g is very broad. It can be concluded that it is likely that at high conversion bimodality will occur in SMA-g, especially because S is practically depleted at ~60% conversion. This composition drift towards homopolymer MA directly shows up from the S-centred sequences and also the MA-centred sequences presented in *Table 6*.

Two main differences between MMA and MA exist. First, the chemical structure is different which can lead to different transfer mechanisms. It is known that grafting can take place onto a poly(butyl acrylate) seed, the so-called ASA type of graft polymers[31]. The chemical structure of butyl acrylate is similar to MA (except for the alkoxy group) leading to the assumption that grafting can take place due to the abstraction of a hydrogen atom from the polymer backbone in both systems. Second, the respective homopolymers have different glass transition temperatures (T_g). The polymerization of S and MA at 323 K probably takes place above the T_g of all copolymer fractions formed, which can lead to higher GE values[32].

CONCLUSIONS

The grafting of S and MMA onto PB seed particles, stabilized by sulfate end groups, gives stable composite particles. By using emulsifier free grafting processes high DG values were achieved, while neither coagulation nor formation of a new crop of particles occurred.

The intramolecular microstructure of SMMA-g copolymer shifts more strongly to higher MMA contents than that of SMMA-f. The CCD of SMMA-g is broad but not bimodal. Moreover, the lower fractions of S in the grafted copolymer are believed to be caused by the dominant grafting on the PB backbone of polymeric free radicals originating from the aqueous phase or by particle precursor coagulation. This mechanism will of course depend on the monomer type and its water solubility in combination with the monomer to polymer ratio and reaction temperature, and gains its importance as S becomes depleted.

The initiator type, on the other hand, has no influence on the copolymer microstructure, but affects the latex stability and through its intrinsic radical activity the DG.

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