Molecular Mass Control in Methacrylic Copolymer Latexes Containing Glycidyl Methacrylate

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SYNOPSIS

Results are presented on the preparation and characterization of batch emulsion copolymers of butyl methacrylate and glycidyl methacrylate (GMA). The two main problems occurring during an emulsion copolymerization with GMA are partial hydrolysis of the epoxy groups and internal crosslinking of the latex particles formed. The influence of chain transfer agents (CTA) on the degree of crosslinking was investigated. Furthermore, the effect of reaction temperature and the addition of methacrylic acid on the sol/gel content of the polymer formed and on the rate of epoxy hydrolysis were investigated. It was found that lowering the reaction temperature did not increase the sol content; however, it significantly decreased the extent of hydrolysis. The addition of a CTA (especially CBr_4) increased the sol content of the polymer, and good control over the molecular mass was achieved. The addition of methacrylic acid showed that this monomer can be used without any complications with respect to the control of the sol content of the polymer formed. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Latexes containing epoxy groups have been prepared and investigated for many years. These latexes find their application especially in waterborne coatings,[1–4] but their use has been investigated for a wide variety of other applications as well.[5–8] In coatings, epoxy groups can act as crosslinking sites by which mechanical properties can be improved.[1–3,8]

The monomer commonly used to incorporate an epoxy group is glycidyl methacrylate (GMA). The epoxy group is sufficiently stable to hydrolysis to allow its incorporation in latex particles by means of emulsion polymerization. However, although it is known that a major part of the epoxy groups remains intact during an emulsion polymerization, the minor part that has hydrolyzed may give rise to side reactions.[1,2] Furthermore, the hydrolysis product of GMA itself, 1,2-dihydroxypropyl (or glyceryl) methacrylate, is a water-soluble monomer that might have an influence on the emulsion polymer-

ization process. One of the possible consequences is that hardly any significant extent of epoxy functionality is located at, or close to, the surface of the particles.

Another problem when using GMA may be the occurrence of crosslinking inside the latex particles.[2,9] This intraparticle crosslinking prevents proper control of the molecular mass and may have an adverse effect on the final properties of the latex.

Our incentive to investigate the preparation of epoxy-functional latexes is that the latter will be studied in their crosslinking behaviour toward amino-functional latexes.[10] For this purpose, it is important to control the amount and position of the epoxy groups in the latex and to control the molecular mass of the copolymer. To this end, the influence of several parameters was investigated, especially the influences of chain transfer agents and of reaction temperature on the molecular mass and the degree of intraparticle crosslinking. Furthermore, the degree of hydrolysis of the epoxy groups was determined to get an impression of the amount of epoxy groups left for post-crosslinking.

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Table I   Results of the Emulsion Polymerizations

Code	T (°C)	CBr_4 (g)	NDM (g)	Methacrylic Acid (g)	D_w (nm)	Sol Content (%)	Epoxy Content NMR (%)	Epoxy Content Titr. (%)	$M_n \times 10^{-3}$ (g/mol)	$M_w \times 10^{-3}$ (g/mol)	M_w/M_n
1	60	—	0	—	73.4	8	—	67	—	—	—
2	60	—	0.5	—	77.1	79	83	93	64	892	13.9
3	60	—	1	—	69.9	100	69	96	112	993	8.8
4	60	—	5	—	65.1	105	85	87	27	260	9.7
5	60	0.5	—	—	93.0	92	58	68	89	308	3.5
6	60	1	—	—	93.9	104	94	83	30	157	5.2
7	60	5	—	—	93.7	100	99	91	7	24	3.4
8[a]	20	0	—	—	93.9	2	—	95	—	—	—
9[a]	20	0.5	—	—	79.6	26	100	94	282	796	2.8
10[a]	20	1	—	—	75.7	36	100	98	346	917	2.7
11[a]	20	2	—	—	79.5	44	63	66	182	1030	5.6
12[a]	20	4	—	—	87.8	70	52	59	48	137	2.8
13[a]	20	5	—	—	80.5	102	53	56	38	99	2.6
14[b]	60	5	—	0.5	74.4	100	59	—	4	20	5.0
15[b]	60	5	—	1	74.5	101	86	—	4	20	5.0
16[b]	60	5	—	2	74.4	101	77	—	3	16	5.3

[a] Redox initiator.

[b] An equimolar amount of $NaHCO_3$ was added to compensate for the effect of added methacrylic acid (so in these cases sodium methacrylate is polymerized).

EXPERIMENTAL

Materials

Butyl methacrylate (BMA, Merck, Darmstadt, Germany), GMA (Janssen Chimica, Brussels, Belgium), and methacrylic acid (Fluka AG, Bachs, Switzerland) were cleaned of their inhibitor by passing them through an inhibitor-removing column (Aldrich, Brussels, Belgium) before use. The emulsifier sodium dodecyl sulfate (SDS, Janssen Chimica), the initiator sodium persulfate (SPS, Fluka AG), or a redox initiator system, consisting of SPS, sodium hydrogen sulfite ($NaHSO_3$, Janssen Chimica) with iron sulfate ($FeSO_4$, Janssen Chimica) complexed with ethylenediamine-tetraacetic acid tetrasodium salt hydrate (EDTA, Fluka AG), the buffer sodium hydrogen carbonate ($NaHCO_3$, Janssen Chimica) and the chain transfer agents n-dodecyl mercaptan (NDM, Merck) and carbon tetrabromide (CBr_4, Merck) were obtained commercially and used without further purification. Water was doubly distilled and deionized (Millipore Super Q).

Water Solubility Determination

The water solubilities of BMA and GMA were measured using a Hewlett Packard 8451A diode array UV-vis spectrometer, according to a method described by Nowicka-Jankowska.[11] For BMA a wavelength of 232 nm and for GMA a wavelength of 268 nm were used. The calibration curve was prepared with nonsaturated solutions as standards.[11] Next, the saturated solution was prepared; to ensure saturation of the water phase, a drop of monomer was placed on top of the water phase in the cuvette. The cuvette was thermostated and the absorption was measured. The concentration was then determined by extrapolation of the calibration curve. This procedure was repeated for several temperatures. Although GMA has a higher density than water, the drop of GMA remained on top of the water layer due to the surface tension of water.

Emulsion Copolymerization

The emulsion copolymerizations were varied according to the formulations given in Table I. All recipes contained 900 g of water, 90 g of butyl methacrylate, and 10 g of glycidyl methacrylate and were 10 mM in initiator, 10 mM in surfactant (SDS) and 20 mM in buffer ($NaHCO_3$). Emulsion polymerizations performed at 60°C were initiated with SPS, those performed at 20°C were initiated by means of a redox initiator system, consisting of SPS (10 mM)

and sodium hydrogen sulfite (10 mM) with iron sulfate (1.5 · 10^{-3} mM) complexed with an equimolar amount of EDTA.

All emulsion polymerizations were carried out in a 1.2-L stainless steel tube reactor containing a six-blade turbine stirrer and baffles. The reactor could be thermostated between 20 and 80°C. The water and monomers were cleared of oxygen by flushing with nitrogen before use. The pressure in the reactor was maintained by nitrogen at 1.5 bar. The latexes obtained were cleaned of any salts and oligomers by means of dialysis (Visking 9-36/32″, Medicell Ltd., UK).

Determination of the Sol Content

To determine the sol content of the latex copolymers (meaning the fraction of soluble free polymer compared with the fraction of insoluble polymer having an infinite molecular mass), a modified version of an extraction method described by Weerts[12] was used. The copolymer was obtained from the cleaned latex by freeze drying. One gram of the dry copolymer was then put into a flask together with 50 g of 1,4-dioxane p.a. (Merck). The flask was emersed in an ultrasonic bath for 5 min and placed in a shaker for 24 h. During this procedure, the free polymer dissolved, whereas the insoluble polymer swelled. The insoluble polymer was separated from the solution by means of ultracentrifugation (2 h, 50,000 rpm). An exact amount of sample was taken from the clear liquid and dried. By measuring the dry solids content of this solution, the total amount of dissolved polymer and, thus, the sol content of the copolymer could be calculated. This procedure was repeated five times for each latex, and the results were averaged. The whole procedure was checked by varying the residence time in the ultrasonic bath, the time of shaking, and the time of ultracentrifugation. No influence on the sol content was found when increasing the ultrasonification time up to 20 min. After 6 h of shaking, an influence on the gel content was no longer found (checked up to 7 days). No effect was observed when increasing the duration of ultracentrifugation from 2 to 6 h. The accuracy of the method was estimated to be 5%.

Polymer Characterization

Molecular Mass Distribution

The free polymer obtained by the extraction method in the sol determinations was analyzed by means of gel permeation chromatography (Waters Millipore).

The molecular mass distributions were measured using tetrahydrofuran as the continuous phase and a pBMA calibration curve.

Glass Transition Temperature (T_g)

After the dialysis and freeze drying of the latex, the T_g of the copolymer was measured using differential scanning calorimetry (Perkin Elmer DSC 7, heating rate 10°C/min, range 0–100°C).

Determination of the Epoxy Content

The epoxy content[13–16] was determined using a titration method derived from the literature.[5,14,15] First, 0.5 g of polymer was swollen or dissolved (depending on the sol content) in 25 mL of dioxane. Then, 5 mL of a 0.2M solution of HCl in dry 1,4-dioxane was added. This mixture was stirred for 24 h. The excess of HCl was then titrated back with a 0.1M methanolic NaOH solution. The whole titration was performed in an argon atmosphere and followed conductometrically. Recent literature[15] showed that this method gives accurate results.

As a check on some of the results of the titrations, ^{1}H-NMR spectra (Varian 300 MHz) were recorded in CDCl$_3$. For GMA, the integrals of two of the three epoxy peaks were taken (δ 2.82; δ 3.18) and compared with the total resonance belonging to the methacrylic esters (δ 3.7–4.4). From the peak ratio, the epoxy content could be calculated. NMR was only used when the copolymer was completely or partially soluble.

RESULTS AND DISCUSSION

Water Solubilities

The results of the water solubility measurements are shown in Figure 1. The water solubility of BMA shows a linear dependency on the temperature in the measured range. For GMA, a deviation from a straight line is observed for the water solubility as a function of temperature. It was unclear whether this was a real "nonlinear" dependency or caused by concomitant hydrolysis, resulting in the formation of 2,3-dihydroxypropyl methacrylate (glyceryl methacrylate). It is known from the literature that glyceryl methacrylate has a high water solubility or, better, miscibility.[16,17] The deviation from the straight line could exclusively be caused by the extra UV absorption of glyceryl methacrylate, dissolved in the aqueous phase. Another possibility of the deviation, as noticed by Refojo,[16] could be the fact that
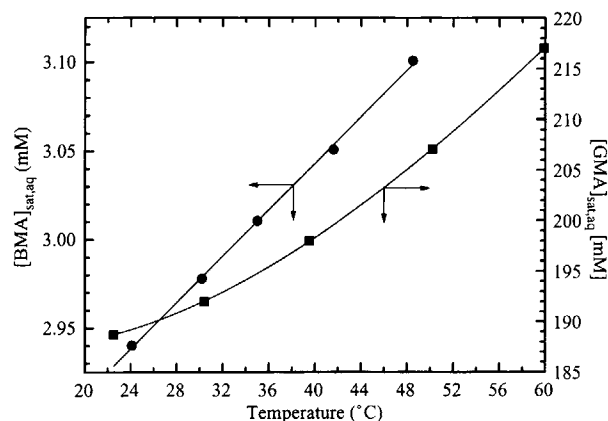
Figure 1   Water solubilities of GMA (■) and BMA (●) as a function of temperature. The lines represent the best curve fit through the data points: BMA, $[M]_{aq}$ = 2.781 + $6.55 \cdot 10^{-3}$ T; GMA, $[M]_{aq}$ = 185.492 − $9.515 \cdot 10^{-2}$ T + $1.040 \cdot 10^{-2}$ T^2.

GMA has a higher solubility in a water/glyceryl methacrylate mixture. This would imply that the deviation is only partly caused by the hydrolysis to give glyceryl methacrylate.

The hydrolysis of GMA to glyceryl methacrylate is important because of two reasons. First, it causes a loss of epoxy functionality during an emulsion polymerization and, second, the presence of glyceryl methacrylate in an emulsion polymerization may lead to water-soluble polymer or incorporation of glyceryl methacrylate in the particles (mainly at or near the surface). Therefore, it is of great importance to know what the extent of hydrolysis of GMA would be during an emulsion polymerization.

Some model experiments were performed to measure this hydrolysis rate. Because the emulsion polymerizations performed took maximally 5 h, hydrolysis was followed for 8 h. The rate of hydrolysis was followed by means of ^{1}H-NMR. For this purpose, two aqueous solutions of GMA were prepared ($[GMA]_{aq}$ = 0.15M). The solutions were thermostated at 20 and 60°C, respectively. After 8 h the amount of hydrolysis was checked in both solutions. ^{1}H-NMR showed no trace of glyceryl methacrylate after these 8-h periods, indicating that hydrolysis had not occurred to any significant extent [a later analysis by gas chromatography-mass spectroscopy (GC-MS) showed traces of glyceryl methacrylate, but these could not be quantified]. From these experiments, it could be concluded that the nonlinear dependency of the water solubility of GMA on the temperature was not caused by glyceryl methacrylate formation.

The experiment was repeated in the presence of NaHCO$_3$ (10 mM), which can be used as a buffer in the emulsion polymerizations. After 8 h at 20°C, a very small amount of glyceryl methacrylate was formed. However, at 60°C after 2.5 h, more than 90% of the GMA was hydrolyzed. No quantitative results were obtained with this method concerning the rate of hydrolysis; however, it was clear that the rate of hydrolysis of GMA in an emulsion polymerization is strongly influenced by the temperature and by the presence of other components (in the emulsion polymerizations performed especially the buffer NaHCO$_3$). The effect of the formation of glyceryl methacrylate will be further elaborated in the section on emulsion copolymerization.

Emulsion Copolymerization

To exclude any effect of intermolecular heterogeneity on the final properties, the aim was to avoid composition drift. From the known r values of BMA/GMA (r_{BMA} = 0.85, r_{GMA} = 0.94)[18] and the experimentally determined water solubilities, it was expected that the copolymer formed would show only minor compositional heterogeneity. The reactions 1 (at 60°C) and 8 (at 20°C) were followed over time. The partial conversions of GMA and BMA were monitored by means of gas chromatography. Figure 2(a) and (b) shows the partial conversions as a function of the overall conversion. By combining the r values from the literature with the measured water solubilities, the theoretical partial conversions as a function of total conversion could be calculated using a method described by Schoonbrood.[19] From Figure 2(a) and (b), it follows that the experimentally determined partial conversions of BMA were equal to the theoretical ones. However, the experimentally determined partial conversions of GMA were somewhat higher than the calculated ones. This may be explained by the observation that part of the GMA was hydrolyzed during the emulsion polymerization, as evidenced by GC analysis.

At both 60 and 20°C, the partial conversions of BMA and GMA showed that both monomers reacted almost equally fast, indicating that practically no composition drift occurs. In both cases, the T_g of the copolymer was 35°C, and no indication of phase separation was found. In the case of reactions 7 (60°C) and 11 (20°C), which were performed in the presence of 5% CBr$_4$, the copolymer could be easily dissolved. High-performance liquid chromatography analysis (Waters Millipore HPLC) showed that the copolymers formed had a narrow chemical composition distribution, so it may be concluded that no
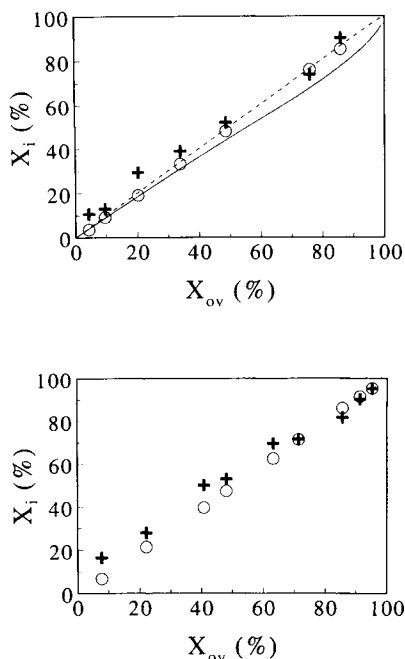
Figure 2 Partial conversion of BMA (O) and GMA (+) as a function of the overall conversion. (a) For reaction 1 at 60°C, the lines represent the simulated partial conversions of BMA (---) and GMA (———) as a function of the overall conversion; (b) for reaction 8 at 20°C, the line represents the ideal situation of a copolymer formed without any composition drift.

significant composition drift had occurred during any of the emulsion copolymerizations.

For all emulsion copolymers, the amount of epoxy groups, the sol content, and the molecular mass distribution of the free polymer were determined. With respect to the determination of the epoxy content, there were some problems concerning the insolubility of crosslinked copolymers. The titration technique chosen[14,15] was found to be preferable over other techniques, which are performed in an aqueous environment.[1,2,13] In the latter cases, there is always the risk of concurrent hydrolysis of the epoxy group. It should be realized that the addition of HCl to an epoxy ring is not an instantaneous reaction, although the activation of the epoxy ring by a proton is.[14] So in the presence of water in an environment not saturated with Cl⁻, addition of H_2O to the epoxy ring will compete and will result in an apparently lower epoxy content. NMR analysis was used as a check for the titration method. The technique was especially useful when the polymer-contained components that could influence the titration (like methacrylic acid). The used methods showed in most cases comparable epoxy contents. However, some

deviations occurred, in particular when the polymer was only partly soluble.

The influence of several parameters (chain transfer agent, temperature, methacrylic acid addition) on the sol content, on the extent of hydrolysis of the epoxy groups, and on the molecular mass distribution were determined. Table I shows all the determined sol contents and epoxy contents of the final latexes. Comparing reactions 1 (performed at 60°C) and 8 (performed at 20°C), it is striking that the epoxy content of copolymer formed at 60°C equals 67% and the epoxy content of the reaction performed at 20°C equals 95%. In both cases, however, the emulsion copolymers formed were almost completely crosslinked, indicating that the hydrolysis of GMA was not the main cause of the crosslink reaction. In our opinion the internal crosslinking of the particles is mainly caused by the presence of small amounts of dimethacrylates in the monomer GMA. This was confirmed by performing GC-MS on GMA. GC-MS showed that GMA contains small amounts (100–200 ppm) of dimethacrylates. These dimethacrylates only cause problems when preparing high-molecular-mass material, as in regular emulsion polymerizations. The dimethacrylates can be removed by distillation, but upon storage of the monomer or during the emulsion polymerization they may be formed again. Therefore, we preferred to reduce the molar mass to such an extent that the crosslinking of the copolymer by the dimethacrylates was effectively avoided.

Influence of Chain Transfer Agents on the Sol Content

Because the particles formed during the emulsion polymerizations 1 (60°C) and 8 (20°C) were internally crosslinked, we tried to completely prevent crosslinking by lowering the molecular mass of the copolymer. For this purpose, emulsion polymerizations at 60°C were performed in the presence of chain transfer agents.

A semiquantitative estimation of the effect of a chain transfer agent on the sol content can be made by looking at the effect of a chain transfer agent on the theoretical gel point. For a chain-reaction polymerization, this gel point (P_{gel}) can be calculated using eq. 1[20]:

$$P_{gel} = \frac{1 - q}{q(f - 2)\alpha_f S} \quad (1)$$

where the value of q is given by

$$q = \frac{R_p}{R_p + R_t + R_{tr}} \qquad (2)$$

S is the probability that the multivinyl monomer (in this case the dimethacrylate) does not cyclize (S is assumed to be 1), f is the functionality of the dimethacrylate ($f = 4$), α_f is the mole fraction of double bonds in the dimethacrylate in the polymerizing mixture, R_p is the rate of propagation, R_t is the rate of termination, R_{tr} is the rate of termination by transfer.

To calculate the gel point, one has to know the complete reaction kinetics of an emulsion polymerization. In the case of the emulsion polymerizations performed, a simple zero-one mechanism is assumed that is justified by the size of the particles (Table I). In this case, termination is instantaneous when a radical enters a particle, already containing another radical and termination solely depends on the rate of entry (ρ).[21] This results in particles only containing one or no radical. Transfer can occur to the monomer or to a chain transfer agent (when present). So in case of the emulsion polymerizations, eq. 2 can be written as

$$q = \frac{k_p C_{m,p}}{k_p C_{m,p} + \rho + C_{m,p} k_{tr,M} + k_{tr,CTA} C_{CTA}} \qquad (3)$$

where ρ is given by[22]

$$\rho = \frac{2 k_d [I] N_a}{N_c} \left(\frac{\sqrt{k_d [I] k_{t,aq}}}{k_{p,aq} C_{m,w}} + 1 \right)^{1-z} \qquad (4)$$

k_p is the propagation rate coefficient, $k_{tr,M}$ and $k_{tr,CTA}$ are the transfer rate coefficients to monomer and chain transfer agent, respectively, $C_{m,p}$ and C_{CTA} are the concentration of monomer and chain transfer agent inside the particles, respectively. In eq. 4 k_d is the dissociation rate constant of the initiator, $k_{p,aq}$ and $k_{t,aq}$ are the propagation and termination rate coefficients in the aqueous phase, respectively, [I] is the initiator concentration, $C_{m,w}$ is the concentration of monomer in the aqueous phase, N_c is the number of particles, and N_a is Avogadro's number.

In the case that chain transfer agents are present, the entry coefficient can be influenced by the chain transfer agent (small amounts are present in the aqueous phase). However, this effect will not be taken into account. Because the equations presented are only intended to illustrate the effect of small amounts of dimethacrylates and of the presence of chain transfer agents on crosslinking, homopolymerization kinetics of BMA is assumed, so GMA is

treated in the same way as BMA, despite the effect that the higher water solubility of GMA will have on its entry rate.

Table II gives the values of the different parameters as used in the calculations. Figure 3 represents the calculated gel points as a function of the chain transfer agent concentration for different contents of dimethacrylates in the total amount of monomer (the dimethacrylates are only present in GMA, which only represents 10% of the total amount of monomer).

What is most remarkable in these calculations is that extremely low amounts of dimethacrylates (<20 ppm on total monomer content) already can lead to the formation of a gel. Equally remarkable is that relatively low amounts of chain transfer agents can prevent the formation of a gel.

The effect of the addition of the chain transfer agents n-dodecyl mercaptan and carbon tetrabromide at 60°C on the gel content is presented in Table I (reactions 1–7) and in Figure 4. It can be seen in Figure 4 that the addition of small amounts of chain transfer agent led to a drastic increase in the sol content. This confirmed the trend obtained by the calculations as shown in Figure 3. Very low amounts of chain transfer agent postpone the gel point until no gel is being formed anymore. It is not exactly clear how much dimethacrylates are present in the monomer GMA and whether or not dimethacrylates are formed during the emulsion polymerization; however, the data show that the presence of dimethacrylates can lead to the formation of a gel and that small amounts of chain transfer agent can pre-

Table II Values for the Different Parameters Used to Calculate Figure 3

Constant	Value[(60°C)]	Value[(20°C)]
k_d[a]	$5.3 \cdot 10^{-6}$ mol L^{-1} s^{-1}	
[$S_2O_8^{2-}$]	$1.0 \cdot 10^{-2}$ mol L^{-1}	
$C_{w,aq}$	$3.2 \cdot 10^{-3}$ mol L^{-1}	$2.9 \cdot 10^{-3}$ mol L^{-1}
$C_{m,p}$[b]	3.8 mol L^{-1}	
N	$2.22 \cdot 10^{17}$ L^{-1}	
N_a	$6.022 \cdot 10^{23}$ mol^{-1}	
k_p[c]	1080 L mol^{-1} s^{-1}	393 L mol^{-1} s^{-1}
$k_{tr,M}$[d]	$1.5 \cdot 10^{-2}$ mol^{-1} s^{-1}	$5.5 \cdot 10^{-3}$ L mol^{-1} s^{-1}
k_t[e]	$3 \cdot 10^9$ L mol^{-1} s^{-1}	$1 \cdot 10^9$ L mol^{-1} s^{-1}
f	4	
k_{tr,CBr_4}[d]	292 L mol^{-1} s^{-1}	106 L mol^{-1} s^{-1}

[a] See reference 23.
[b] See reference 24.
[c] See reference 25.
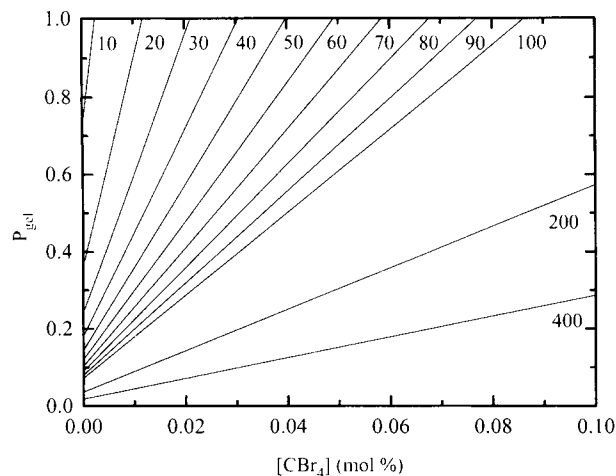[d] See reference 26.
[e] See reference 21.

Figure 3 Gel point as a function of the concentration CBr_4 (on total monomer base) as calculated using eqs. 1–4. The lines represent different amounts of dimethacrylates (in ppm on total monomer).
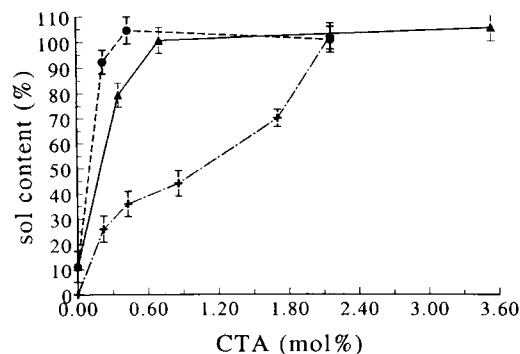

Figure 4 The sol content of the copolymer as a function of the molar amount of chain transfer agent (mol chain transfer agent on total amount of monomer), with NDM at 60°C (— ▲ —), CBr_4 at 60°C (---●---) and CBr_4 at 20°C (- · - + - · -).

vent this. The calculated gel points do not exactly match the gel points expected from the data (for the CBr_4 addition the gel point of 1 is reached at ca. 0.2 mol %, whereas the calculated gel point of 1, for 200 ppm dimethacrylates in GMA, is reached at about 0.02 mol %).

To corroborate this point further, the molecular mass distributions of the free polymer as a function of the chain transfer agent concentration are shown in Figure 5(a) (for NDM) and Figure 5(b) (for CBr_4). From these figures it follows that the molecular mass distribution narrowed upon addition of more chain transfer agent. Lowering the molecular mass did not prevent the occurrence of crosslink reactions, but it effectively prevented the formation of an infinite network. Also, when increasing the amount of chain transfer agent, the fraction of branched chains would be decreased, leading to a lower molecular mass and a more narrow molecular mass distribution.

Figures 4 and 5 and Table I indicate that CBr_4 was a more efficient chain transfer agent than NDM, for which there may be two reasons. The first reason is the possibility that CBr_4 has a higher chain transfer constant than NDM in this system, although it is known from the literature[23] that in a somewhat similar system the chain transfer constant (C_{rx}) of CBr_4 to methyl methacrylate $(C_{rx} = 0.27^{60°C})$ is somewhat lower than that of a thiol to methyl methacrylate $(C_{rx} = 0.66^{60°C})$. Another reason could be that part of the NDM is deactivated by addition of the thiol to an epoxy group. This reaction is catalyzed by base but may also occur in a neutral environment.[14] This would imply that during the

emulsion polymerization, some NDM may have reacted with epoxy groups. Because of this reaction, the effectiveness of NDM to act as a chain transfer agent would be decreased. This also implies a de-
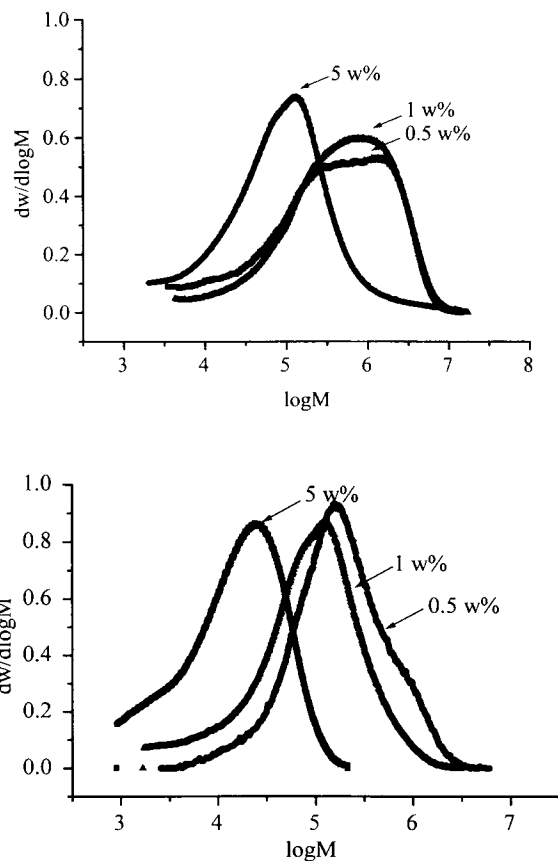

Figure 5 Molecular mass distributions of the sol part, (a) as a function of the NDM content at 60°C, and (b) as a function of the CBr_4 content at 60°C.

crease in the epoxy content, especially for the reaction containing the largest amount of NDM (reaction 4, mol GMA/mol NDM = 3.5). However, the epoxy content as measured by NMR and by titration (Table II) did not reveal such a correlation. Because of the hydrolysis, the extent of any possible reaction of epoxy groups with NDM is negligible as compared with the total amount of epoxy loss.

In a number of cases, very low values for the epoxy content were measured (e.g., in reactions 1 and 5). It is not clear whether the titration technique (^{1}H-NMR fails to give good quantitative results when the polymer does not completely dissolve) or the hydrolysis was the cause of this behavior.

Because in an emulsion polymerization all monomer has to pass through the aqueous phase to reach the locus of polymerization, it appears likely that the larger part of the epoxy group that hydrolyzes during the polymerization has been hydrolyzed in their monomeric state, resulting in the monomer glyceryl methacrylate, which was actually detected with GC during the emulsion copolymerizations. Glyceryl methacrylate is more hydrophilic than GMA and, when formed during the emulsion polymerization, will probably polymerize in the water phase or near the surface of the polymer particle. This leads to a surface bearing few epoxy groups. It has been shown[27,28] that in a seeded copolymerization of compositions poor in hydroxyethyl methacrylate (HEMA) with styrene on a styrene core, where the styrene/HEMA monomer mixture is slowly added, HEMA is localized on the surface of the particles, probably because most of the HEMA is incorporated through oligomers formed in the aqueous phase. Thus, it could very well be possible that the formed glyceryl methacrylate, which is also present in very low amounts, will show a similar behavior and will be localized at, or near, the surface of the particles.

Influence of Temperature

To decrease the extent of hydrolysis of GMA during emulsion polymerization, the polymerization temperature was lowered to 20°C. Also at this temperature, the copolymer formed (without chain transfer agent) was almost completely crosslinked (Table I, reaction 8). The gel content in this case was even higher than for the copolymer formed at 60°C. This can be explained by calculation of the gel point using eqs. 1–4 and the values in Table II. At 60°C, the gel points are usually higher than those at 20°C. However, it was harder to calculate the gel point because

not all parameters are known at 20°C (for instance, k_d of the redox initiator at 20°C).

To reduce the gel content, also at 20°C, CBr_4 was used in the formulation. In the reactions at 60°C, this chain transfer agent had proven to be the most effective. Figure 4 also shows the influence of temperature on the sol content when using CBr_4 as chain transfer agent. From this figure, it is obvious that at 20°C the effectiveness of CBr_4 to act as chain transfer agent is much lower than at 60°C. This is confirmed by the data in Table I, when comparing the molecular mass of the free polymer (reactions 9–13 at 20°C as compared with reactions 5–7 at 60°C). For a given chain transfer agent concentration, the molecular mass of the soluble polymers was much lower when the reaction was performed at 60°C than at 20°C. It appears that the chain transfer constant (C_{sx}) at 20°C is lower than at 60°C, resulting in a lower gel point. However, it is not clear what the real cause of the lower efficiency of CBr_4 is when looking at Figure 6(a) and (b).

Figure 6 shows the total conversion as a function of time for different chain transfer agent concentrations. At 60°C, the addition of CBr_4 had hardly any influence on the reaction rate [Fig. 6(a)]. However, at 20°C [Fig. 6(b)], it appears that CBr_4 does not only influence the chain length but also affects the reaction rate.

The effect of CBr_4 on the kinetics of seeded emulsion polymerizations of styrene has been described by Lichti et al.[29] They stated that CBr_4 may increase the entry rate of radicals into the polymer particles and decrease the exit rate of radicals from the particles. Figure 6(a) shows that at 60°C, CBr_4 has hardly any influence on the reaction rate (this was also observed by Lichti et al. at higher initiator concentrations). However, Figure 6(b) shows that at 20°C, the influence of CBr_4 on the kinetics is quite important. In the absence of CBr_4, one sees that the reaction is very fast, indicating a high radical flux. When adding CBr_4, the reaction is retarded and sometimes even inhibited. One possible explanation could be that at 20°C the reinitiation rate constant of the $CBr_3^{\cdot}$ radical has decreased dramatically, which would retard the reaction until the CBr_4 concentration starts to decrease. A lower reinitiation constant combined with a higher entry rate would mean that the chance of the $CBr_3^{\cdot}$ radical to terminate before it could initiate a novel polymer chain inside the particles increased, resulting in a lower radical concentration. In the recipes, the total concentration of initiator radicals is higher than the total
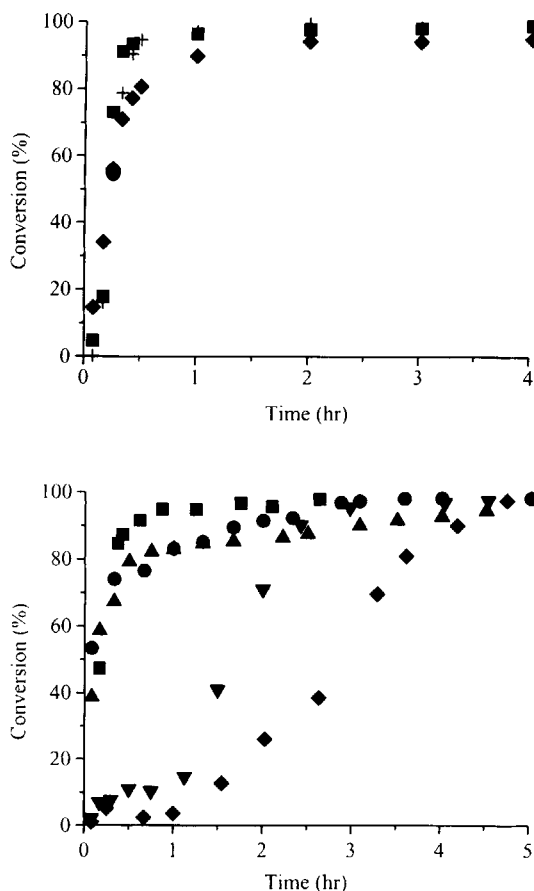
Figure 6 Conversion versus time plots (a) of reactions 5–7 performed at 60°C and (b) of reactions 8, 10–13 performed at 20°C using CBr₄ as CTA: ■, 0 wt % of CBr₄; +, 0.5 wt % of CBr₄; ●, 1 wt % of CBr₄; ▲, 2 wt % of CBr₄; ▼, 3 wt % of CBr₄; ◆, 5 wt % of CBr₄.

concentration of CBr₄. This explains why all reactions have reached 100% conversion.

One of the most remarkable results is the variety in epoxy content of the polymers formed at 20°C. Looking at the epoxy content in Table I, one sees that at 20°C the epoxy content is close to 100%, implying that at 20°C almost no epoxy groups are hydrolyzed when no or little CBr₄ is present. However, at higher CBr₄ concentrations, a considerable extent of hydrolysis occurs. As was already mentioned, these reactions showed a different kinetic behavior; the loss of epoxy functionality could be simply caused by the longer reaction time, in the presence of the initiator and the buffer.

To check whether the epoxy groups are hydrolytically stable or still hydrolyze when the latex is stored at room temperature, we followed the epoxy content of latex 8 during a year. Directly after the polymerization, the epoxy content was 95% of the original amount. After 3 months, the epoxy content

had decreased to 78%, and after 1 year 68% of the epoxy groups were still present. To look at the influence of the formulation on the epoxy content, one should keep in mind that latexes will always be susceptible to hydrolysis when stored. Because the cleavage of the epoxy groups is both acid- and base-catalyzed, storage should always occur at neutral pH.

Influence of Methacrylic Acid

A possible side reaction leading to intraparticle crosslinking may be the reaction between a carboxylic acid group and an epoxy group.[30] Methacrylic monomers may contain some methacrylic acid formed through hydrolysis of the ester, when stored over longer periods. Also, some methacrylic acid can be formed during the emulsion polymerization. To check this possible side reaction and whether it is possible to use methacrylic acid in formulations containing GMA without a significant influence on the sol content, a series of experiments was performed with different amounts of methacrylic acid in the formulation. In these experiments, 5% of CBr₄ was used as chain transfer agent. As can be seen in Table I (exp. 14–16), the sol content did not vary with the concentration of methacrylic acid. However, the molecular mass distribution (Fig. 7) and the molecular mass (Table I) showed that the presence of methacrylic acid has a considerable influence.

The main difference is the increase in the amount of low molecular mass material when adding methacrylic acid. Most likely, this material is methacrylic acid-rich polymer formed in the aqueous phase. Because of the presence of methacrylic acid, it was not possible to perform the titrations in this case and
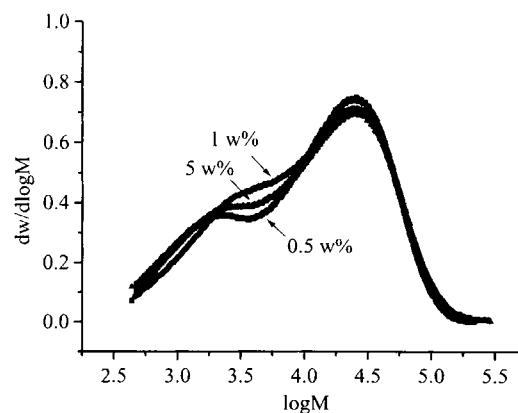

Figure 7 Molecular mass distributions as a function of the methacrylic acid (buffered at pH 7) content added, performed at 60°C in the presence of 5 wt % of CBr₄.

only NMR could be used. Looking at the epoxy content (Table I), it is difficult to determine the actual effect of the addition of methacrylic acid on the extent of hydrolysis of the epoxy groups. The data showed no consistent behavior. However, the epoxy content was considerably lower than the epoxy content of the reaction performed in the absence of methacrylic acid (reaction 7). Because there was no significant decrease in sol content, it appears that the reaction between a carboxylic acid and an epoxy group did not cause the intraparticle crosslinking and that methacrylic acid can be used in epoxy-functional latexes. The storage stability of these latexes has not been checked yet. However, one would expect that due to the presence of methacrylic acid, the rate of hydrolysis will be somewhat increased, mainly because the polymer will have become more hydrophilic, which will increase the water content inside the particles.

CONCLUSIONS

To obtain control over the hydrolysis rate and the molecular mass in a copolymerization of GMA and BMA, the influence of chain transfer agents, the temperature, and the addition of methacrylic acid on the sol content and the molecular mass distribution was investigated. The addition of a chain transfer agent dramatically increases the sol content, leading to a control over the molecular mass distribution. This implies that the crosslink density of the copolymer formed without chain transfer agent is very low, because when adding a chain transfer agent, the reaction leading to intraparticle crosslinking is not prevented. The main cause for the intraparticle crosslinking is the presence of dimethacrylates in the monomer GMA and the possible formation of these species during the emulsion polymerization.

At 60°C, CBr_4 is more effective in reducing the molecular mass than NDM. This can be caused by a higher chain transfer constant of CBr_4 or by reaction of part of the NDM with epoxy groups, resulting in a lower NDM concentration. At 20°C, the addition of CBr_4 is less effective in reducing the gel content than at 60°C. The exact reason for this behavior is difficult to specify, because it is obvious that especially at 20°C, high amounts of CBr_4 influence the kinetics of the emulsion polymerization, which was also found for the seeded emulsion polymerizations of styrene.[18] The rate of hydrolysis of GMA at 20°C is considerably lower than at 60°C. This makes reactions at 20°C preferable to reactions

performed at 60°C. However, at high CBr_4 concentrations, the epoxy content decreases probably due to a side reaction involving CBr_4. Because a chain transfer agent is needed to increase the sol content and control the M_w of the material, it is necessary to look for another chain transfer agent, which is more effective at low concentration at lower reaction temperatures.

Finally, the addition of methacrylic acid does not influence the sol content of the polymer. This implies that the reaction between a carboxylic acid and an epoxy group is not a main reason for the crosslink reaction and methacrylic acid can be used in emulsion polymerization recipes containing GMA without an influence on the sol content. An effect on the sensitivity to hydrolysis is expected but still needs to be investigated.

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