Syntheses of New Amino-Functionalized Methacrylates and Their Use in Free Radical Polymerizations

JOHN M. GEURTS, CHRISTIANNE M. GÖTTGENS, MARCO A. I. VAN GRAEFSCHEPE, ROB W. A. WELLAND, J. J. G. STEVEN VAN ES, ANTON L. GERMAN

Department of Polymer Chemistry and Technology, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Received 21 September 1999; accepted 3 December 1999

ABSTRACT: For use in emulsion and solution copolymerization a series of novel amino-functional methacrylates has been synthesized, most of which have seldom, or never, been described in the literature before. In this investigation, the preparation of the hydrochloric and/or tosylate salt of the monomers aminoethyl, 3-amino-1-propyl, 5-amino-1-pentyl, 6-amino-1-hexyl and 11-amino-1-undecyl methacrylate will be described, along with the characterization of the parameters water solubility, pK_a and chemical stability. The homopolymers of these monomers have been prepared and characterized. Results show the occurrence of an acyl migration upon neutralization of the monomers aminoethyl- and 3-amino-1-propyl methacrylate. This migration does not occur in the monomer 5-amino-1-pentyl methacrylate, which makes it possible to synthesize the neutralized monomer although, after neutralization, a Michael addition occurs, resulting in a limited lifetime. Copolymerizations have been performed in emulsion. The monomer aminopentyl methacrylate especially proved to be suitable for emulsion copolymerizations when used under controlled conditions. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 1401–1415, 2001

Key words: ω-amino alkyl methacrylates; aminoethyl methacrylate; 3-amino-1-propyl methacrylate; 5-amino-1-pentyl methacrylate; 6-amino-1-hexyl methacrylate; 11-amino-1-undecyl methacrylate; amino-functional latexes; emulsion polymerization

INTRODUCTION

Functional polymer latexes are latexes which, after polymerization, still contain functional groups. These functional groups can be used in a wide variety of applications. The main ones are in the field of biological applications and in the field of coatings. Especially in the field of coatings and paints the interest in functional latexes is still increasing, mainly due to the stricter regulations concerning volatile components. In this case, the functional groups can act as crosslinking sites by which mechanical properties can be improved.[1–6]

Over the years many different functional groups have been introduced in latexes. The introduction of electrophilic groups like epoxy-, acetoacetoxy- or isocyanato groups is sometimes difficult, because they are sensitive to hydrolysis.[7–9] However, these groups have the advantage that, because of their high activity, they can react with several kinds of nucleophilic groups at low temperature. Nucleophilic groups like carboxylic[2] or hydroxylic[3] groups can also be incorporated via emulsion polymerization. These nucleophilic groups can react with highly active electrophilic groups added as external multifunctional crosslinkers at low temperature. However, these

Correspondence to: J. M. Geurts, Avecia NeoResins B.V., P.O. Box 123, 5140 AC Waalwijk, The Netherlands.

Journal of Applied Polymer Science, Vol. 80, 1401–1415 (2001)

crosslinkers have disadvantages concerning toxicity. Less active crosslinkers with a better toxicity profile do not react sufficiently or fast enough at ambient temperatures. Ambient temperature crosslinking is preferred, because it prevents the need of external devices like ovens (for temperature induced crosslinking) or UV-banks (for UV induced crosslinking). A well-known electrophilic group that could overcome both problems concerning stability and activity could be an amino group.

Primary amino-functional latexes have been prepared for many years. Amino-functionality can be incorporated into a latex by means of chemical modification of functionalized latexes, for instance, by treatment of a carboxyl-functional latex with aziridines[10] or by flushing a chloro-functional latex with ammonia.[11] However, the preparation of these latexes is in most cases very laborious and/or dangerous, thus preventing their wide-spread use.

Direct incorporation of primary amino-functional monomers in a latex has seldomly been reported, mainly because of the lack of amino-functional monomers. The use of the amino-functional monomer m,p-vinylbenzylamine in an emulsion polymerization was investigated by Pichot et al.[12–16] Other monomers like N-ethenyl formamide,[17] which has the ability to provide amino-functional polymers after hydrolysis of the formamide, cannot be used in an aqueous environment, because of premature hydrolysis of the formamide group and the resultant high water solubility. It is mainly used to synthesize amino-functional polymers that can provide a polymer in water dispersion. Another method reported is the dispersion of amino end-functionalized telechelic butadiene.[18] However, this method prevents any control of particle morphology.

The monomers of the group of the ω-aminoalkyl methacrylates are seldomly used in emulsion polymerizations and only then when a cationic latex was required. The one commonly described, 2-aminoethyl methacrylate (available as the HCl salt, AEMA · HCl) is completely water soluble, hence, difficult to incorporate into a latex. Furthermore, it has to be polymerized at low pH (<4), because when the amino group is deprotonated, there is a quick rearrangement of the monomer due to an acyl migration (Fig. 1[19]).

However, it was also reported that, although the monomer gives rapid acyl migration, the polymer itself is resistant to this acyl migration, thus in principle, enabling the preparation of amino-functional polymers.[19] The monomer has been used to prepare amino-functional polymers and dispersions,[20] and has also been used in emulsion polymerizations to prepare cationic latexes.[15,16,21–23] However, because of the disadvantages mentioned, the monomer never found widespread use. The emulsion polymerization of higher homologues, which are not commercially available, has never been reported in the literature.

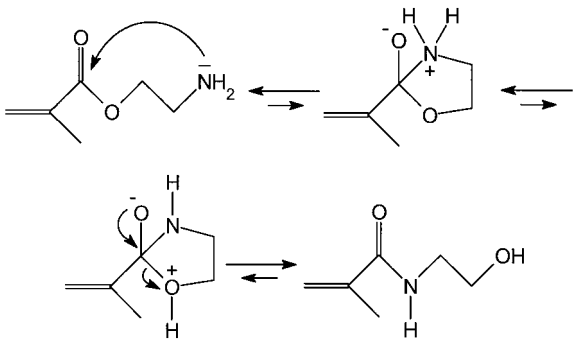

Figure 1 Acyl migration of aminoethyl methacrylate (AEMA).

Nonetheless, the use of higher homologues of AEMA · HCl may be worthwhile to investigate. Elongation of the alkyl chain between ester- and amino functionalities in ω-amino-1-alkyl methacrylates is expected to result in decreased water solubility and, as a result of that, a better incorporation during emulsion polymerization. Also, because the acyl migration occurs via cyclic intermediates (Fig. 1), elongation of the alkyl chain between ester- and amino-functionalities is expected to disfavor the acyl migration, which makes the deprotonation of ω-amino-1-alkyl methacrylate acid salts possible. This, in turn, implies that these neutralized monomers can be used directly in emulsion polymerization.

When working with acrylic monomers containing free primary amino groups, another problem can arise, i.e., the Michael addition (Fig. 2).

This reaction can occur after neutralization of the monomer. It is a nucleophilic attack of the amino group on, in this case, the α,β-unsaturated ester part of another molecule of amino-functional methacrylate. Because this reaction can be expected to be even more significant when working with acrylates, it was decided to work only with the methacrylate type of functional and main backbone monomers. However, even when working with amino-functional methacrylates, Michael addition cannot be completely prevented.

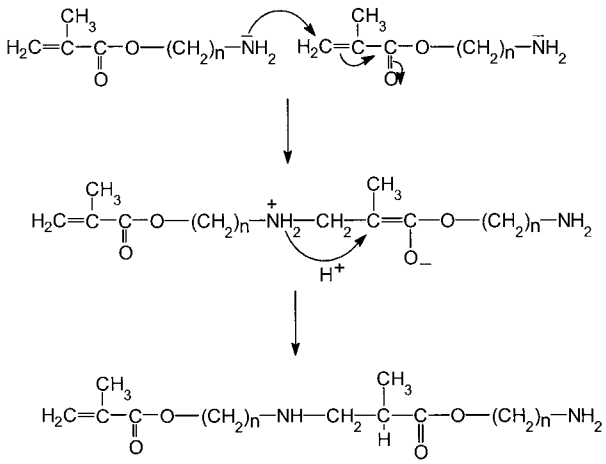

Figure 2 Michael addition of ω-aminoalkyl methacrylates.

Still, these monomers were thought to represent the best compromise between chemical stability and good copolymerization behavior during batch and semicontinuous (emulsion) polymerization.

Aiming at the preparation of amino-functional polymers in solution and emulsion, the polymerization behavior and characterization of ω-amino-1-alkyl methacrylates and their acid salts will be described. It includes the preparation of the hydrochloric (HCl), or *p*-toluenesulfonic acid (*p*TsOH-) salts of the monomers aminoethyl, 3-amino-1-propyl, 5-amino-1-pentyl, 6-amino-1-hexyl and 11-amino-1-undecyl methacrylate. The monomers were characterized by measuring the water solubility, the pK_a of the ammonium group, and the chemical stability of the monomers and homopolymers. The monomers aminoethyl and 5-amino-1-pentyl methacrylate were used to synthesize amino-functional latexes via emulsion polymerization.

EXPERIMENTAL

Preparation of ω-Aminoalkyl Methacrylates

The amino-functional monomer aminoethyl methacrylate · HCl (AEMA · HCl, Eastman, USA) was obtained commercially, but was also synthesized using methacryloyl chloride and ethanolamine.HCl as described by Artursson et al.[24] (Fig. 3).

Aminopropyl, -pentyl, -hexyl, and -undecyl methacrylate.HX (HX = HCl or *p*-toluenesulfonic acid) were prepared using the same reaction as used for AEMA · HCl.

Materials

For the synthesis of the monomers, the following chemicals were used. Methacryloyl chloride (Acros, Brussels, Belgium) was distilled prior to use. Ethanolamine hydrochloride (Acros, Brussels, Belgium), 3-amino-1-propanol (Aldrich, Bornem, Belgium), 5-amino-1-pentanol (Acros, Brussels, Belgium), 6-amino-1-hexanol (Fluka, Bornem, Belgium), thionyl chloride, copper powder, 4 *M* hydrogen chloride in dioxane, and *p*-toluenesulfonic acid (all Aldrich) were used in the syntheses without purification. The 11-amino-undecanol was synthesized from 11-bromo-1-undecanol (Fluka, Bornem, Belgium) by substitution with sodium azide (Aldrich, Belgium), followed by reduction with triphenylphosphine (Aldrich, Belgium). Where the use of dry solvents is indicated, these were purified according to procedures reported elsewhere.[25] All other solvents were used as received.

All monomers prepared were characterized using ^{1}H- and ^{13}C-NMR (Varian 300 MHz).

Preparation of Aminoethyl Methacrylate · Hydrochloride (AEMA · HCl)[24]

To a rapidly stirred mixture of 94.5 g (0.90 mol) of ethanolamine · HCl, 8.8 mL (0.06 mol) of thionyl chloride and 0.2 g of copper powder at 90–100°C, 202 mL (1.80 mol) of methacryloyl chloride was added over a period of 2 h. The mixture was cooled to 60°C and 600 mL of ethyl acetate was added, and cooling was continued slowly to room temperature. The formed crystals were collected and the crude product was recrystallized using an ethyl acetate/ isopropanol (1 : 1) mixture (30% yield).

m.p. 116°C (lit.[20] 117–119°C); ^{1}H-NMR (DMSO-d_6) δ 1.90 (dd, 3 H, CH_3), 3.10 (t, 2 H, CH_2N), 4.27 (t, 2 H, CH_2O), 5.73 and 6.22 (each dd, 1 H, $=CH_2$), 8.35 (br s, 3 H, NH_3); ^{13}C-NMR (DMSO-d_6) δ 18.0 (CH_3), 37.7 (CH_2N), 61.1 (CH_2O), 126.9 ($CH_2=$), 135.6 (q-C, =C), 166.4 (q-C, C=O).

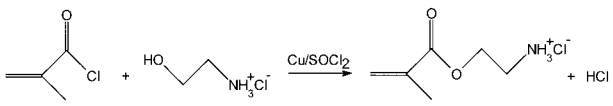

Figure 3 Preparation of AEMA · HCl.

Preparation of 3-Amino-1-propyl Methacrylate · *p*TsOH (APrMA · *p*TsOH)

To a solution of 199 g (1.05 mol) of *p*-toluenesulfonic acid monohydrate in 200 mL of ethanol, 75 mL (1.0 mol) of 3-amino-1-propanol was slowly added over a period of 1 h. Ethanol was removed by means of a rotary evaporator. The white cristals were dried in a vacuum oven at 50°C (74% yield).

m.p. 66°C; ^{1}H-NMR (DMSO-d_6) δ 1.70 (m, 2 H, CH_2), 2.31 (s, 3 H, CH_3), 2.88 (t, 2 H, CH_2N), 3.50 (t, 2 H, CH_2O), 7.15 and 7.50 (each d, 2 H, Ts), 7.68 (br s, 3 H, NH_3); ^{13}C-NMR (DMSO-d_6) δ 18.5 (CH_3), 30.0 (CH_2), 37.0 (CH_2N), 57.9 (CH_2O), 125.5 and 128.1 (each C-H, Ts), 137.8 and 146.0 (each q-C, Ts).

Next, the same procedure was followed as for the preparation of aminoethyl methacrylate hydrochloride. A mixture of 54.4 g (0.22 mol) of 3-amino-1-propanol · *p*TsOH, 0.1 g of copper powder and 1.1 mL of thionyl chloride was heated to 90–100°C. To this mixture 44 mL of methacryloyl chloride (0.4 mol) was added over a period of 2 h. Ethyl acetate (150 mL) was added, and the mixture was slowly cooled to 4°C. The formed crystals were collected and washed with ethyl acetate (90% yield).

m.p. 114°C; ^{1}H-NMR (DMSO-d_6) δ 1.91 (m, 5 H, CH_2 and CH_3), 2.30 (s, 3 H, Ts), 2.90 (t, 2 H, CH_2N), 4.15 (t, 2 H, CH_2O), 5.72 and 6.05 (each br s, 1 H, =CH2), 7.15 and 7.50 (each d, 2 H, Ts), 7.80 (br s, 3 H, NH_3); ^{13}C-NMR (DMSO-d_6) δ 17.9 and 20.8 (each CH_3), 26.3 (CH_2), 36.2 (CH_2N), 61.5 (CH_2O), 125.5 and 128.2 (each CH, Ts), 135.8 (q-C, C=), 138.0 and 145.1 (q-C, Ts), 166.4 (q-C, C=O).

Preparation of Aminoethyl Methacrylate · *p*TsOH (AEMA · *p*TsOH)

For comparison it was necessary to have the monomer aminoethyl methacrylate · *p*TsOH. To a solution of 190 g (1.00 mol) of *p*-toluenesulfonic acid monohydrate in 300 mL of ethanol, 62 mL (1.0 mol) of ethanolamine was added over a period of 1 h. Ethanol was removed by means of a rotary evaporator. The white crystals were dried in a vacuum oven at 50°C (94% yield).

m.p. 92°C; ^{1}H-NMR (DMSO-d_6) δ 2.30 (s, 3 H, CH_3), 2.85 (t, 2 H, CH_2N), 3.60 (t, 2 H, CH_2O), 7.15 and 7.50 (each d, 2 H, Ts), 7.78 (br s, 3 H, NH_3); ^{13}C-NMR (DMSO-d_6) δ 20.5 (CH_3), 40.8 (CH_2N), 58.9 (CH_2O), 122.9 and 124.2 (each C-H, Ts), 139.0 and 145.0 (each q-C, Ts).

Next, a mixture of 51.3 g (0.22 mol) of aminoethanol · *p*TsOH, 0.05 g of copper powder and 1.1 mL of thionyl chloride was heated to 90–100°C. To this mixture 44 mL of methacryloyl chloride (0.4 mol) was added over a period of 2 h. Ethyl acetate–hexane (1 : 1) (300 mL) was added and the mixture was slowly cooled to 4°C. The formed crystals were collected and washed with ethyl acetate (65% yield).

m.p. 114°C; ^{1}H-NMR (DMSO-d_6) δ 1.90 (s, 3 H, CH_3), 2.30 (s, 3 H, Ts), 3.18 (t, 2 H, CH_2N), 4.15 (t, 2 H, CH_2O), 5.72 and 6.05 (each br s, 1 H, =CH_2), 7.15 and 7.45 (each d, 2 H, Ts), 7.90 (br s, 3 H, NH_3); ^{13}C-NMR (DMSO-d_6) δ 17.9 and 20.8 (each CH_3), 36.2 (CH_2N), 61.5 (CH_2O), 125.5 and 128.2 (each C-H, Ts), 135.8 (q-C, C=), 138.0 and 145.1 (each q-C, OTs), 166.4 (q-C, C=O).

Preparation of 5-Amino-1-pentyl methacrylate · *p*TsOH (APMA · *p*TsOH)

A solution of 103.0 g (1.0 mol) of 5-amino-1-pentanol in 300 mL of anhydrous dioxane was heated to 100°C. A solution of 192.2 g (1.05 mol) of *p*-toluenesulfonic acid in 700 mL of anhydrous dioxane was added dropwise and the solution was refluxed for 30 min. To the mixture 0.24 g (3.8 mmol) of copper powder was added. Next, 223 mL (2.0 mol) of methacryloyl chloride was added over a period of 2 h, and the mixture was refluxed for 3 h. To the refluxing mixture 300 mL of *n*-heptane was added. The temperature was slowly lowered to 4°C. The white crystals were filtered and dried (yield 86%).

m.p. 122°C; ^{1}H-NMR (DMSO-d_6) δ 1.29–1.42 (m, 2 H), 1.49–1.70 (m, 4 H), 1.88 (dd, 3 H, CH_3), 2.30 (s, 3 H, Ts), 2.78 (t, 2 H, CH_2N), 4.10 (t, 2 H, CH_2O), 5.68 and 6.05 (each dd, 1 H, =CH_2), 7.12 and 7.48 (each d, 2 H, Ts), 7.65 (br s, 3 H, NH_3); ^{13}C-NMR (DMSO-d_6) δ 18.4 (CH_3), 21.1 (CH3, Ts), 22.7, 26.9 and 27.9 (each CH2), 39.1 (CH_2N), 64.4 (CH_2O), 126.0 (=CH_2), 125.9 and 128.5 (each C-H, Ts), 136.3 (q-C, =C), 138.2 and 146.0 (each q-C, Ts), 166.9 (q-C, C=O).

Isolation of 5-Amino-1-pentyl Methacrylate (APMA)

In 100 mL of dichloromethane, 10 g (0.03 mol) of 5-amino-1-pentyl methacrylate · *p*TsOH was dissolved. To this solution 40 mL of an aqueous 1 *M* NaOH solution was added. The two layers were separated and 100 mL of brine was added to the water layer. Next, the water layer was extracted

three times with 100 mL portions of dichloromethane. The collected organic layers were dried over sodium sulfate and filtered. The solvent was removed using a rotary evaporator, resulting in a clear oil (yield 80%).

^{1}H-NMR ($CDCl_3$) δ 1.18 (br s, 2 H, NH_2), 1.28–1.48 (m, 2 H, CH_2), 1.53–1.70 (m, 4 H, CH_2), 1.86 (s, 3 H, CH_3), 2.61 (m, 2 H, CH_2N), 4.07 (t, 2 H, CH_2O), 5.46 and 6.00 (each br s, 1 H, $=CH_2$); ^{13}C-NMR ($CDCl_3$) δ 18.8 (CH_3), 23.8, 29.0, and 33.9 (each CH_2), 42.5 (CH_2N), 65.1 (CH_2O), 125.6 ($=CH_2$), 137.0 (q-C, =C), 167.9 (q-C, C=O).

Preparation of 6-Amino-1-hexyl Methacrylate · *p*TsOH (AHMA · *p*TsOH)

To a solution of 5.1 g (43.5 mmol) of 6-amino-1-hexanol in 60 mL of anhydrous dioxane a solution of 8.5 g (77.8 mmol) of *p*-toluenesulfonic acid in 25 mL of anhydrous dioxane was added dropwise. The solution was refluxed for 30 min. Then, 9.5 mL (85.0 mmol) of methacryloyl chloride was added slowly at reflux and the mixture was heated for 3 h. Next, 60 mL of *n*-heptane was added at reflux. After slowly cooling to room temperature and then to 4°C, a small portion was crystalline, the major part was an oil. The mixture was heated again and 20 mL of dioxane was added. After slowly cooling to room temperature and then to 4°C, 1.5 g (16% yield) of 6-amino-1-hexyl methacrylate · *p*TsOH was obtained.

m.p. 80°C; ^{1}H-NMR (DMSO-d_6) δ 1.21–1.68 (m, 8 H), 1.85 (dd, 3 H, CH_3), 2.30 (s, 3 H, Ts), 2.78 (t, 2 H, CH_2N), 4.10 (t, 2 H, CH_2O), 5.75 and 6.05 (each dd, 1 H, $=CH_2$), 7.12 and 7.48 (each d, 2 H, Ts), 7.75 (br s, 3 H, NH_3); ^{13}C-NMR (DMSO-d_6) δ 18.4 and 21.1 (each CH_3), 25.3, 25.7, 27.2, and 28.3 (each CH_2), 39.1 (CH_2N), 64.5 (CH_2O), 125.8 ($=CH_2$), 125.8 and 128.5 (each C—H, Ts), 136.7 (q-C, =C), 138.0 and 145.8 (each q-C, Ts), 167.0 (q-C, C=O).

Preparation of 11-Amino-1-undecyl Methacrylate · Hydrochloride (AUMA · HCl)

Because 11-amino-1-undecanol is not commercially available, it was prepared from 11-azido-1-undecanol, which was prepared from 11-bromo-1-undecanol. A solution of 99.6 g (0.40 mol) of 11-bromo-1-undecanol and 38.8 g (0.60 mol) of sodium azide in 800 mL of acetonitrile was refluxed for 32 h. The mixture was cooled to room temperature and water was added until saturation. The two layers were separated and the acetonitrile still dissolved in the water layer was removed by means of a rotary evaporator. The residue together with the original water layer was extracted three times with dichloromethane. The dichloromethane layers were washed with water and brine and dried over magnesium sulfate. Next, the product was filtered and the dichloromethane was removed by means of a rotary evaporator. The product 11-azido-1-undecanol consisted of white crystals (yield 93%) and was sufficiently pure for further use.

^{1}H-NMR ($CDCl_3$) δ 1.18–1.38 (m, 14 H), 1.44–1.62 (m, 4 H), 3.18 (t, 2 H, CH_2N_3), 3.63 (t, 2 H, CH_2OH); ^{13}C-NMR ($CDCl_3$) δ 25.7, 26.6, 28.8, 29.3, 29.3, 29.4, 29.5, and 32.7 (each CH_2), 51.4 (CH_2N_3), 62.9 (CH_2OH).

To a solution of 212.6 g (1.00 mol) of 11-azido-1-undecanol in 27 mL of water and 1.3 L of THF was added portionwise 287.5 g (1.10 mol) of triphenylphosphine at room temperature (cooling in water bath) in 1 h. This mixture was stirred for 4 h. Aqueous 2 *M* hydrochloric acid was added until pH < 3. Dichloromethane (ca. 400 mL) was added, and the layers were separated. The water layer was washed once with dichloromethane and then treated with sodium hydroxide until pH > 13. The basic water layer was extracted three times with dichloromethane. Next, the combined organic layers were washed with water and brine, dried over sodium sulfate, and filtered. The solvent was removed using a rotary evaporator. The product consisted of slightly yellow crystals (yield 85%), which were generally of sufficient purity for further use.

^{1}H-NMR ($CDCl_3$) δ 1.26–1.30 (m, 14 H), 1.42–1.56 (m, 4 H), 2.68 (t, 2 H, CH_2N), 3.64 (t, 2 H, CH_2OH); ^{13}C-NMR ($CDCl_3$) δ 25.5, 26.5, 29.1, 29.1, 29.2, 29.2, 32.2, and 32.8 (each CH_2), 41.3 (CH_2N), 62.0 (CH_2OH).

A solution of 5 g of 11-amino-1-undecanol (26.7 mmol) in 50 mL of anhydrous dioxane was heated to 100°C. Thirteen milliliters of a 4*M* solution of HCl in dioxane (52 mmol) was added dropwise and the solution was refluxed for 30 min. Then 3.7 mL of methacryloyl chloride (33 mmol) was added dropwise and, next, the reaction mixture was refluxed for an additional 3 h. Next, 200 mL of *n*-heptane was slowly added at reflux and the solution was cooled very slowly first to room temperature and then to 4°C. The product obtained after filtration consisted of slightly yellow crsytals (yield 57%).

^{1}H-NMR (DMSO-d_6) δ 1.12–1.62 (m, 18 H), 1.85 (dd, 3 H, CH_3), 2.72 (t, 2 H, CH_2N), 4.08 (t, 2

H, CH_2O), 5.74 and 5.95 (each dd, 1 H, $=CH_2$), 7.93 (br s, 3 H, NH_3); ^{13}C-NMR (DMSO-d_6) δ 18.4 (CH_3), 25.8, 26.2, 27.3, 28.4, 28.9, 29.0, 29.2, and 29.2 (each CH_2), 39.1 (CH_2N), 64.6 (CH_2O), 125.8 ($=CH_2$), 136.4 (q-C, =C), 166.8 (q-C, C=O).

Characterization of the Amino-Functional Monomers

The amino-functional monomers were characterized regarding the parameters of water solubility, pKa, and chemical stability.

Water Solubility

The water solubility of the various amino-functional monomers, in their protonated form and, when possible, also in their neutralized form, was measured using a UV-VIS spectrometer. For calibration purposes several nonsaturated aqueous solutions were prepared. The absorption of these solutions was between 0.1 and 0.9, resulting in a linear calibration curve. Next, a saturated solution was prepared. A sample of this solution was taken and diluted, until the absorption was in the range of the calibration curve.

pKa

The pKa of the monomer was measured using a standard potentiometric titration method as described by Hand and Blewitt.[26] A 0.01*M* solution of the aminoalkyl methacrylate salt was prepared in 25 mL of water. This solution was titrated with an aqueous 0.1 *M* NaOH solution at 20°C (thermostated). Air was excluded by working in an argon atmosphere. The pH was monitored potentiometrically with an accurately calibrated pH-meter (Orion).

By using eq. (1), one can calculate at each pH the pK_a of the monomer:

$$pK_a = pH + \log\left(\frac{C - [K^+] - [H_3O^+] + [OH^-]}{[K^+] + [H_3O^+] - [OH^-]}\right) \quad (1)$$

where [H3O$^+$], [OH$^-$], [K$^+$], and C are the proton, hydroxyl, counter-ion, and total monomer concentration, respectively. The pK_a was taken as the average over the whole range of deprotonation (between a relative deprotonation of 0.1 and 0.9).

Chemical Stability

The occurrence of an acyl migration was checked by dissolving 0.01 mol of monomer in 100 mL of dichloromethane. Next, 10 mL of a 1 *M* aqueous solution of NaOH was added while stirring. After different time intervals a sample of 10 mL of the mixture was taken, and 40 mL of dichloromethane and 40 mL of brine were added. After separation, the water layer was extracted three times with 40 mL of dichloromethane. The organic layers were collected and dried over sodium sulfate. After filtration, the solvent was removed with a rotary evaporator and the product was immediately analyzed using ^{1}H-NMR. This procedure was followed for aminoethyl, -propyl and -pentyl methacrylate.

The extent of Michael addition was checked for the monomer 5-amino-1-pentyl methacrylate. For this purpose, 4 g of the amino-functional monomer was prepared and stored at 20°C and −10°C, respectively. Samples were taken after different time intervals, and the amount of Michael adduct was measured, using ^{1}H-NMR ($CDCl_3$).

Polymerization

Chemicals

Butyl methacrylate (BMA, Merck, Germany) was cleaned of the inhibitor by passing it through an inhibitor-removing column (Aldrich, Belgium) prior to use. The emulsifier nonylphenyl poly(ethylene oxide)$_{30}$ (Antarox CO-880, Rhône Poulenc, France), the initiators α,α'-azoisobutyronitrile (AIBN, Fluka, Switzerland) and α,α'-azobis(2-amidinopropane)dihydrochloride (AAPH, Polysciences, UK), and the chain transfer agent carbon tetrabromide (CBr4, Merck, Germany) were obtained commercially and used without further purification. Water was doubly distilled and deionized (Millipore Super Q). All the amino-functional monomers were used as obtained in the syntheses.

Equipment

All polymerizations were carried out in a 300-mL glass reactor, equipped with a mechanical stirrer, baffles, and a cooler. During the reaction the gas volume above the reaction mixture was constantly flushed with nitrogen. The temperature and pH of the reaction mixture were constantly monitored. In the semicontinuous emulsion polymerizations the reactor was additionally equipped with a peristaltic pump to control monomer dosage.

Solution Homopolymerization

The homopolymers were prepared by dissolving 5 g of monomer in 100 mL of a suitable solvent. In

Table I Formulations of the Batch Emulsion Polymerizations[a]

	H_2O (g)	Ethanol (g)	BMA (g)	AEMA · HCl (g)	APMA · TsOH (g)	CBr_4 (g)
A1	300	—	20	2.5	—	—
A2	275	25	20	2.5	—	—
A3	250	50	20	2.5	—	—
A4	200	100	20	2.5	—	—
A5	150	—	13	—	3.6	—
A6	150	—	13	—	3.6	0.15
A7	150	—	13	—	3.6	0.75

[a] All reactions were 10 m*M* in emulsifier (Antarox Co-880) and 10 m*M* in initiator (AIBN).

the case of the ammonium salts of aminoethyl-, -propyl- and -pentyl methacrylate the solvent was methanol. In the case of the neutral aminopentyl- and -undecyl methacrylate the solvent was ethanol. The initiator concentration was in all cases 10 m*M*. In all cases the polymerization was initiated by α,α'-azoisobutyronitrile.

pK_a

The homopolymers of aminoethyl methacrylate · HCl and aminopropyl methacrylate · *p*TsOH are still water soluble. For these polymers the pKa was determined using the same method as described for the monomers. The determination of the pKa of the other homopolymer salts was not performed, because of the insolubility of these polymers in water.

T_g

The T_g of the homopolymers, both in their free amine form and in their fully protonated form, was determined using a Perkin-Elmer DSC 7 (heating range dependent on polymer, heating rate 20°C/min). In principle, the T_g should be measured as an average of three runs with the same sample. However, in many cases this proved not to be possible, due to reactions during the heating of the polymer. Because of the high T_g of pAEMA · HCl and pAPrMA · TsOH, first-run measurements were taken: these measurements were performed twice for the homopolymers (prepared in different batches). A T_g measurement for pAPM was difficult to interpret, probably due to the occurence of crosslinking during heating.

Amino-Functional Latexes

To prepare amino-functional latex particles, several emulsion polymerization techniques were used. The first technique involved a batch emulsion copolymerization in the presence of surfactants. The second technique involved an emulsifier-free emulsion copolymerization, resulting in a particle surface covered with amino groups. The third technique involved a semicontinuous emulsion copolymerization.

Batch Emulsion Polymerization

The recipes of the emulsion polymerization experiments are given in Table I.

The reactor was the same as that used for solution polymerization. The emulsion copolymerizations of butyl methacrylate and aminoethyl methacrylate · HCl were performed at 60°C for 24 h. Because of the instability of AEM · HCl, the pH of the aqueous phase was kept within the range of pH 2 to 6. The pH of the solution was measured on-line, and was stable during the reaction at pH 4.8. After the reaction the polymer was separated from the aqueous phase by means of an ultracentrifuge, both the polymer phase and the aqueous phase were analyzed by means of ^{1}H-NMR.

The emulsion polymerizations of aminopentyl methacrylate were performed by addition of the monomer salt (APM · TsOH). Prior to the addition of initiator, the pH of the reaction mixture was adjusted to pH = 12 using an aqueous 3 *M* NaOH solution. During the reaction, the pH was adjusted when necessary. The reaction time was 24 h in all cases.

Emulsifier-Free Batch Emulsion Copolymerization

The reaction was performed in the same reactor as used in the other polymerizations. The recipe of this polymerization is: water 98 g, AEM · HCl 0.7 g, BMA 9.3 g, H_2O_2 (30 wt % in water) 2 mL,

Table IIA Formulation of the Semicontinuous Emulsion Copolymerizations

Initial Reactor Charge	Preemulsion
H_2O : 144 g	H_2O : 6.26 g
Antarox CO-880 : 1.85 g	Antarox CO-880 : 0.46 g
AAPH : 0.41 g	$CBrCl_3$: 0.46 g
	BMA : 11.91 g
BMA shot : 1.32 g	APMA · pTsOH or APMA (Table IIB)

$Fe(NO_3)_3 \cdot 9H_2O$ 0.081 g , pH 2.7 (addition of HCl), T = 70°C, 500 rpm, reaction time 12 h.

To create a latex with neutral amino-groups on the surface, the surface of the particles had to be covered with Antarox Co-880 prior to neutralization. The amount of surfactant necessary to cover the surface of the particles was determined using a surfactant titration while measuring the surface tension as a function of the added amount of surfactant solution. The difference between the amount of surfactant to be added to reach the critical micelle concentration (CMC) in pure water and in the presence of latex, gave the amount of surfactant needed for a complete coverage of the surface. After the addition of the surfactant, the latex could be neutralized by adding a 1*M* aqueous solution of NaOH until a pH of 12 was reached.

Semicontinuous Emulsion Copolymerization

The semicontinuous reactions were performed in the same reactor as used for the batch reactions. However, in this case a preemulsion was added to the reaction mixture in 2 h by a peristaltic pump. After addition of the preemulsion, the reaction was continued for another 22 h to garantee full conversion of the monomers. The recipes of the preemulsion and total recipe are described in Table II.

The preemulsion was prepared by slowly adding the monomer BMA to a rapidly stirred solution of the amino-functional monomer and emulsifier in water over a period of 3 h. The preemulsion was cooled in an ice bath during the preparation and the addition.

As can be seen in Table IIB, in some experiments the pH of the reaction mixture was controlled. The control took place by addition of an aqueous 3 *M* NaOH solution to keep the pH above 11 (usually the pH was around 12).

Characterization Methods

The latexes were characterized regarding particle size, M_w, and amino content. The particle size was determined using dynamic light scattering (DLS, Malvern Autosizer II, Malvern, UK). The molecular weight of the copolymers was determined using gel permeation chromatography (GPC, Waters Millipore) using THF/acetic acid as the eluent and a pBMA calibration curve. The polymer was obtained from the latex by freeze drying.

The amino content was determined using ^{1}H-NMR. For this purpose the polymer was dissolved in a suitable deuterated solvent (in most cases CD_3OD). The polymer was separated from the aqueous phase by means of ultracentrifugation. Both the aqueous- and the polymer phase were then analyzed by NMR. For the amino-functional monomer the integral of the CH_2N groups was taken and compared with the total resonance belonging to the methacrylic esters (δ 3.7–4.4). From the peak ratio the amino content could be calculated. Titrations of the amino groups were also tried, but this method was abandoned due to difficulties with the solubility of the copolymers.

RESULTS AND DISCUSSION

Properties of the Amino-Functional Monomers

Synthesis of the Monomers

One of the problems in monomer synthesis was that after the reaction between methacryloyl chloride and the amino-functional alcohol, ^{1}H-NMR always showed the presence of difunctional impurities (a side reaction of the amino group with methacryloyl chloride, Fig. 4) in the crude product.

By means of recrystallization the difunctional impurities were removed to such extent that ^{1}H-

Table IIB Formulation of the Semicontinuous Emulsion Copolymerizations

	APMA · TsOH (g)	APMA (g)	pH[a]
A8	3.55	—	5.9^s, 3.3^e
A9	3.55	—	>11
A10	—	1.77	8.7^s, 8.2^e
A11	—	1.77	>11

[a] When pH was not controlled, the pH at the start (s) and end (e) of the reaction is given.

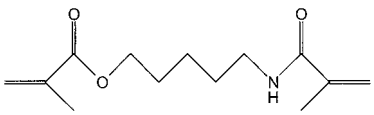

Figure 4 Difunctional monomer [5-(methacrylamido)-1-pentyl methacrylate] present in the monomer APMA · TsOH.

NMR no longer revealed their presence. Every batch of amino-functional monomer should be expected to contain a varying but low amount of difunctional monomer, which can influence the polymer properties.

In the syntheses of the amino-functional methacrylates, copper was used as an inhibitor to prevent premature polymerization of the methacrylates. The syntheses were conducted under atmospheric conditions. Because the scale of the syntheses in case of AHMA · *p*TsOH and AUMA · HCl were small, it was assumed that oxygen inhibition from the air would be sufficient to prevent any polymerization, and therefore, copper was not added. No radical polymerization has been observed in these cases. When these syntheses would be conducted on a bigger scale, copper addition would be advisable to prevent polymerization.

The monomer 6-amino-1-hexyl methacrylate was synthesized according to the procedure as described. However, the yield of this synthesis was very low, and the reproducibility was poor. Therefore, AHMA was only used for monomer characterization, but not in polymerizations.

Physical Properties

To understand the polymerization behavior and reactivity of the amino-functional monomers, they were characterized regarding the properties pK_a, [M]aq and chemical stability. Table III shows these important physical parameters of the monomers.

Some important observations can be derived from the table. First of all, the water solubility of the monomer salts decreases drastically when elongating the aliphatic chain between the ester and the pendant amino group. Upon deprotonation of the ammonium group in the monomer acid salts, the water solubility is expected to decrease. For AEMA · HCl and APrMA · TsOH, deprotonation is not possible because of the acyl migration. For APMA · TsOH, deprotonation is possible, and as can be seen in Table III, this decreases the water solubility of APMA to an even lower value. In emulsion polymerizations, this water solubility should be sufficiently low to allow the incorporation of the amino-functional monomer without significant problems concerning the possible aqueous phase polymerization.

Also noticeable in Table III is the decrease in acidity (pKa) of the ammonium group when elongating the aliphatic chain. This behavior is obviously caused by the electron withdrawing ester group, which decreases the nucleophilicity of the amino group. The effect becomes weaker when the number of CH_2 units between the ester and the amino group increases. When neutralization of the amino group is required, the pH should be at least two units higher, implying a pH > 12.

The only monomer deviating from the above trend is AUMA, which shows unusual behavior when determining the pKa. First of all, the pKa of a 0.01 *M* aqueous solution of the monomer AUMA · HCl was considerably lower (pKa = 9.4) than expected. The determination was complicated by the observation that during the titration the aqueous solution became cloudy, indicating that the monomer became insoluble when neutralized. This behavior resulted in a deviating value of the pKa at higher deprotonation values (neutralization was possible until a value of ca. 0.6). The pKa determination was repeated on a 1 m*M* aqueous AUMA · HCl solution, i.e., a concentration below the solubility of the monomer. In this case, a pKa value of 10.2 was found; however, the experimental error in this value is expected to be higher than for the other monomers.

Table III Physical Properties of the Amino-Functional Monomers

Monomer	n[a]	M_w (g/mol)	pK_a	$[M]_{aq}^{25°C}$ (m*M*)
AEMA · HCl	2	165.61	8.1	1200
APrMA · TsOH	3	315.38	9.3	466
APMA · TsOH	5	343.43	10.2	195
AHMA · TsOH	6	357.46	10.7	162
AUMA · HCl	11	291.85	9.4[b]	69
			10.2[c]	
APMA	5	171.23	—	53
AHMA	6	185.26	—	—
AUMA	11	255.39	—	<2

[a] $H_2C{=}C(CH_3)C(O)O(CH_2)_nNH_2(\bullet HX)$.
[b] $[M]_{aq}$ = 10 m*M*.
[c] $[M]_{aq}$ = 1 m*M;* see text.

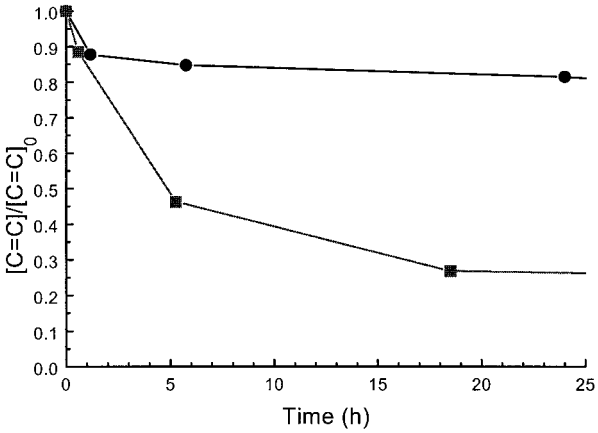

Figure 5 Disappearance of double bonds in the monomer APMA due to Michael addition when stored in bulk: ● −10°C, ■ 20°C.

Chemical Stability

After neutralization of the amino-functional monomers two types of unwanted side reactions can occur: acyl migration and Michael addition. The acyl migration has been described for AEMA.[19] However, the extent of this intramolecular rearrangement can be expected to be dependent on the chain length connecting the primary amine and ester functionalities. In the case of AEMA, the intramolecular rearrangement occurs via five-membered ring intermediates; for APrMA a six-membered ring has to be formed, while for APMA an eight-membered ring would have to be formed, which is energetically far less favorable.

The occurrence of the acyl migration was checked by neutralizing the monomers AEMA · HCl, APrMA · TsOH, and APMA · TsOH in diluted solution. Using ^{1}H-NMR the disappearance of AEMA was monitored by determining the ratio of the C$\underline{H}_2$NH$_2$ peak (2-aminoethyl methacrylate) at δ = 2.7 ppm with the C$\underline{H}_2$OH peak (2-hydroxyethyl methacrylamide) appearing at δ = 3.5 ppm. AEMA · HCl and APrMA · TsOH showed a fast rearrangement after deprotonation (80% in 1 h and 100% in 30 min, respectively). In the case of aminopentyl methacrylate, no rearrangement could be detected even after 4 days.

Michael addition occurs when the amino group of the monomer, for exmaple, APMA, attacks the double bond of another monomer. This occurs fastest after neutralization in concentrated solutions or when stored pure or dissolved in acrylates or methacrylates. The extent of Michael addition was measured using ^{1}H-NMR by determining the peak ratio of δ 5.46 (dd, 1 H, =CH$_2$) to that at δ 4.07 (t, 2 H, CH$_2$O) .

$$\frac{[\text{C}{=}\text{C}]}{[\text{C}{=}\text{C}]_0} = \frac{A_{\delta(=\text{CH}_2)}}{A_{\delta(\text{CH}_2\text{O})}/2} \quad (2)$$

Figure 5 represents the disappearance of APMA stored in bulk after neutralization at two temperatures (−10 and 20°C).

It is obvious that, at room temperature, APMA has only a limited stability (20°C, $t_{1/2} \approx$ 6.5 h). This prevents the monomer from being stored at room temperature after neutralization. In the cases where it cannot be used immediately after neutralization it is possible to store it for a somewhat longer period in the freezer (−10°C, $t_{1/2} \approx$ 220 h). The monomer APMA was normally used by neutralizing the monomer just prior to use. However, in all cases some APMA will be lost during the polymerization due to Michael addition.

Solution Homopolymerization

The monomers synthesized were homopolymerized in solution. The homopolymers of AEMA · HCl and APrMA · HCl were prepared in methanol, the homopolymers of APMA · TsOH and AUMA · HCl were prepared in ethanol. For all the homopolymers the T_g was measured. The results are summarized in Table IV.

The T_g of the homopolymer salts shows familiar behavior: the longer the alkyl chain, the lower the T_g of the polymer. The polymer salts have a much higher T_g than the deprotonated polymers, a behavior also shown by other ionic polymers, like poly(acrylic acid).

Also known from literature is the fact that the counter ion has a large effect on the T_g of the polymer.[27] For this purpose the homopolymer of AEMA.TsOH was prepared. As can be seen in Table IV, there is a difference of almost 100°C

Table IV T_g of the Amino-Functional Polymers

Polymer	T_g (°C)
pAEMA · HCl	174
pAEMA · TsOH	271
pAPrMA · TsOH	199
pAPMA · TsOH	137
pAUMA · HCl	24
pAPMA	92

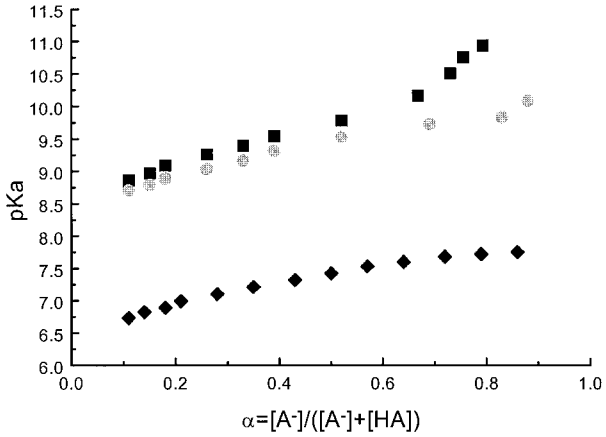

Figure 6 pK_a as a function of the relative deprotonation: ■ pAPMA.TsOH, ● pAPrMA · TsOH, ◆ pAEMA · HCl.

between the T_g of pAEMA · HCl and pAEMA · TsOH.

Figure 6 shows the pKa as a function of deprotonation of the homopolymers pAEMA · HCl, pAPrMA · TsOH, and pAPMA · TsOH.

As can be seen in this figure, the pKa does not have a constant value, but changes as a function of the degree of deprotonation. This behavior is comparable to that shown by ionic polymers like poly(acrylic acid) and poly(methacrylic acid).[28,29]

In these cases the ionic strength during the titrations was low (no extra salt was added). The behavior of the curves may change when the salt concentration becomes higher.[26] The pK_a determination of pAPMA became inaccurate when the extent of neutralization of the polymer was higher than 0.7, due to precipitation of polymer during the titration. This effect also prevented the pKa determination of the polymer pAUMA, which was almost completely insoluble in water. The increase in the pKa as a function of deprotonation is mainly caused by the decreasing extent of charge repulsion. The first protons can be easily titrated because the polymer chain is completely positively charged. This results in an apparently lower pKa. The more the chain gets deprotonated, the less pronounced this effect. Eventually, the single protons that are left on the polymer chain are no longer influenced by the rest of the polymer chain and the pKa will be close to the pKa of the monomer.

Amino-Functional Latexes

Batch Emulsion Copolymerization

Batch emulsion polymerizations were performed starting from several recipes. In all cases the water phase was separated from the polymer phase by ultracentrifugation and both phases were analyzed by means of ^{1}H-NMR.

The aim when working with the amino-functional monomers was to obtain as high an incorporation of the amino-functional monomer in the particles as possible. When working with water-soluble monomers it is known that water phase polymerization can occur, which may result in no or little incorporation of the water-soluble monomer in the particles. This problem is especially expected when working with the relatively water-soluble AEMA · HCl and, to a lesser extent, with APMA · TsOH.

The emulsion polymerizations to be described were all performed with a nonionic initiator (AIBN) and a nonionic surfactant (Antarox Co880). The use of anionic initiators and/or surfactants proved not to be possible, because in all cases investigated coagulation occurred. This point was verified by mixing an aqueous 0.01 *M* AEMA · HCl solution with an equivalent amount of sodium persulfate or sodium dodecyl sulfate. Both solutions became instantly cloudy, implying that the water solubility of the monomer salts consisting of ammonium and persulfate groups, is very low.

In the case of the emulsion copolymerization of AEMA · HCl and BMA (experiment A1), ^{1}H-NMR showed no trace of incorporation of AEMA · HCl in the particle phase (Fig. 7).

This figure shows the polymer present in the particle and in the aqueous phases after seperation by ultracentrifugation. It can be seen that in the polymer of the particle phase there is no visible trace of AEMA · HCl (no CH_2N at δ 3.4). However, this peak is visible in the spectrum of the aqueous phase polymer, indicating that AEMA · HCl polymerized predominantly in the aqueous phase. On the other hand, there is hardly any incorporation of BMA in the aqueous phase polymer (δ 1.4 and 1.6, Bu).

By adding ethanol to the continuous phase (Experiments A2–A4), we tried to incorporate AEMA · HCl in the polymer particles. Ethanol will partition between the polymer and water phase resulting in a more hydrophilic polymer phase. AEMA · HCl might then partition over the water and polymer phase and be incorporated. However, even when using up to 33% of ethanol on volume base of continuous phase, no visible incorporation of amino functionality took place (at higher percentages of ethanol no stable latex was formed).

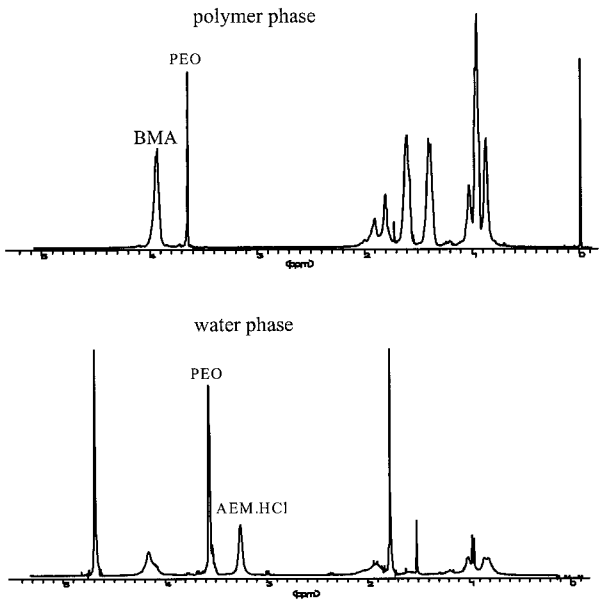

Figure 7 ^{1}H-NMR spectra for the emulsion copolymerization A1; top spectrum of the polymer phase, bottom spectrum of the material present in the aqueous phase.

To avoid the problem of aqueous phase polymerization when using AEMA · HCl and APMA · TsOH, batch emulsion copolymerization of APMA · TsOH with BMA was performed by neutralizing the monomer inside the reactor by adjusting the pH of the aqueous phase. The pH of the water phase could be adjusted during the reaction by addition of sodium hydroxide. The pH of the reaction mixture was kept as constant as possible (pH $\approx$ 12). In the case of the batch recipes, which were kept at a high pH, no trace of water phase polymerization was encountered (no polymer was encountered in the water phase after ultracentrifugation). However, when checking the polymer phase with ^{1}H-NMR, the incorporation of APMA · TsOH proved not to be affected. It was remarkable that the incorporation appeared to improve when the amount of chain transfer agent (CBr_4) in the recipe was increased (Experiments A5–A7, Table V).

Because, in principle, the CTA does not have an influence on the kinetics of the system, it was believed that the strange results obtained concerning the incorporation of APMA had something to do with solubility problems of the copolymer formed. This was confirmed when performing GPC. The molecular weight distributions of the copolymers were very broad, indicating that some kind of crosslinking had occurred during the emulsion polymerization. This crosslinking might have the same cause as encountered in the emulsion copolymerization with epoxy- or acetoacetoxy-functional monomers (glycidyl methacrylate and acetoacetoxyethyl methacrylate, respectively).[7,8] The cause of this crosslinking in these emulsion copolymerizations is the presence of traces of dimethacrylates in the functional monomers. In the case of the emulsion copolymerizations with APMA · TsOH it was known that, in the synthesis of the monomer, a difunctional monomer was formed (Fig. 4).

Another possible reason for the occurrence of crosslinking or branching of the amino-functional polymers might be chain transfer to the amino groups. It is known that the chain transfer activity of AEMA · HCl is high.[15] If this was also the case for APMA · TsOH, this could result in the occurrence of branching and crosslinking via an activated pendant amino group. It also leads to a decrease of the amount of amino groups. This effect might be decreased when adding another even more active chain transfer agent, like CBr_4.

So, besides the occurrence of composition drift during the polymerization, the copolymer formed can also become insoluble because of partial crosslinking. These features made it very difficult to determine the exact amount of amino-functional monomer incorporated. Therefore, to syn-

Table V Batch Emulsion Copolymerizations (APMA · TsOH/BMA) in Alkaline Medium

Exp.	CBr_4 (g)	$M_w * 10^{-3}$ (g/mol)	$M_n * 10^{-3}$ (g/mol)	M_w/M_n	d_p (nm)	$[A]/[A]_0$[a] (%)
A5[b]	—	296	48	6.2	73	—
A6	0.15	68	14	4.8	62	1.1
A7	0.75	27	9	3.0	64	13.5

[a] Percentage of monomer incorporated in the copolymer compared to the intake of monomer (^{1}H-NMR).
[b] Polymer only partially soluble.

Table VI Results of the Semicontinuous Emulsion Copolymerizations

	Monomer	pH[a]	$M_n * 10^{-3}$ (g/mol)	d_p (nm)	$[A]/[A]_0$ (%)
A8	APMA · TsOH	no control $pH_s = 5.9$, $pH_e = 3.3$	10.3	60	<5
A9	APMA · TsOH	control pH > 11	15.2	98	77
A10	APMA	no control $pH_s = 8.7$, $pH_e = 8.2$	11.5	126	<5
A11	APMA	control pH > 11	7.6	97	82

[a] The pH was controlled by addition of an aqueous 1*M* NaOH solution; in the cases where the pH was not controlled, the pH of the latex at the beginning (pH_s) and at the end (pH_e) is given.

thesize a homogeneous copolymer, semicontinuous emulsion polymerization was performed.

No formulations are presented of the copolymerization of APMA with BMA in batch. When performing this reaction, the Michael addition became a serious problem. The batch emulsion copolymerization was performed at 60°C, which results in a very fast Michael addition, probably mainly between APMA and BMA, resulting in an unacceptable loss of primary amino functionality. This was confirmed by a ^{1}H-NMR experiment on the monomer mixture.

Emulsifier-Free Batch Emulsion Copolymerization

In the case of the emulsifier-free emulsion copolymerization with AEMA · HCl, it was possible to incorporate amino functionality at the surface of the particle. This recipe did not contain any species that could stabilize the particles other than the monomer AEMA · HCl. The latex was still stable (d_p = 81 nm), leading to the conclusion that the particles were stabilized by the cationic monomer AEM · HCl. This point was confirmed by measuring the zeta-potential of the particles (Coulter Delsa 440), which resulted in a positive zeta potential of + 45 mV.

After the latex was prepared and dialysed, the surface coverage with Antarox Co880 was determined. The CMC of Antarox was determined to be $4.3 \cdot 10^{-4}$ mol/L in pure water. In the presence of the 1 wt % latex, $7.6 \cdot 10^{-4}$ mol/L of surfactant had to be added to reach the CMC, the difference resulting from surfactant being adsorbed on the latex. From this, the surface coverage per surfactant molecule was calculated to be 153 A^2. This value was taken to calculate the total amount of surfactant that should be added to the cationic latex. After this amount was added, the pH of the latex was raised to pH 12.1 using a 1*M* aqueous NaOH solution. The latex remained stable during this procedure. Determination of the zeta potential gave a value +1 mV, indicating that the surface had indeed been (practically) neutralized. Hence, one could conclude that primary amine-functional groups are present at the surface of the particles.

Semicontinuous Emulsion Copolymerizations

To prepare more homogeneous copolymers with the monomer APMA · TsOH, semicontinuous copolymerizations were performed under monomer-starved conditions. After trying several addition procedures, it was decided to add the monomer as a preemulsion rather than as pure compounds. This procedure solved both mixing problems (APMA · TsOH does not dissolve in BMA) and operational problems (separate addition of BMA and an aqueous solution of APMA · TsOH). Table VI gives the amount of incorporated amines, as measured by ^{1}H-NMR.

Figure 8 shows the ^{1}H-NMR spectrum of a BMA/APMA copolymer prepared semicontinuously: δ 2.65–2.75 (CH_2N, APMA), δ 3.85–4.05 (CH_2O, APMA + BMA). Also visible is a sharp signal of the surfactant used δ 3.6–3.7 (—$(C_2H_4O)_n$—, Antarox Co-880).

Compared with the batch emulsion copolymerization, the semicontinuous strategy aimed at monomer-starved conditions yields much better incorporation of APMA. It was not possible to add the preemulsion at a rate lower than 0.15 mL/min. Because of the small scale of the reaction, this leads to a preemulsion addition time of 2 h. This addition rate was probably not sufficiently

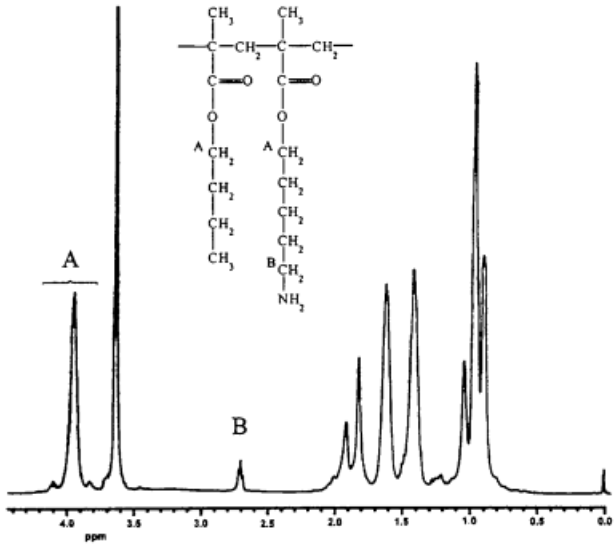

Figure 8 ^{1}H-NMR spectrum of the emulsion copolymer APMA/BMA.

low to strictly reach starved conditions (free monomer was present in the form of droplets during addition). However, in all the cases a stable latex was formed when using this method. The incorporation yield of the amino groups was high when the pH was controlled, i.e., when pH $>$ 11. In this case, the deprotonated APMA was incorporated in the polymer of the particles, as could be shown by ^{1}H-NMR. The water phase was separated from the polymer phase, and both phases were analyzed. No difference in incorporation yield of APMA was observed when the monomer was neutralized before the polymerization or during the addition (inside the reactor). In the latter case, the monomer was added as the tosylate salt but, by maintaining the pH $>$ 11 during the reaction, the monomer was deprotonated. Under starved conditions, the monomer will be polymerized almost instantly and so this method would effectively avoid Michael addition. A disadvantage of this method is the relatively high amounts of sodium hydroxide needed, which sometimes adversely affects storage stability of the latex.

In the experiments the initiator 2,2′-azobis-(2-amidinopropane) dihydrochloride (AAPH, Polysciences, Warrington, PA) was used. This initiator proved to be better than other initiators used (like AIBN or sodium persulfate). The main advantages of this water-soluble azo-initiator are that it has no influence on the stability of the latex and no effect on the amino-functional monomer itself (like sodium persulfate).

CONCLUSIONS

The amino-functional methacrylic monomers aminoethyl-, -propyl-, -pentyl-, and -undecyl methacrylate can be synthesized in good to excellent yields by reaction of the HCl, or *p*TsOH, salt of an ω-amino alcohol with methacryloyl chloride. Elongation of the alkyl chain between the ester group of the methacrylate and the amino group has two main effects; i.e., the water solubility of the monomer decreases, and the pKa (and thus the reactivity) of the monomer increases significantly. The amino-functional monomers have to be synthesized and stored with the amino group protonated (i.e., as the HCl or *p*TsOH acid salt). Upon deprotonation, side reactions can occur that prevent or limit the use of the monomers. The monomers 2-aminoethyl- and 3-aminopropyl methacrylate cannot be deprotonated before polymerization, because of the occurence of an acyl migration. 5-Amino-1-pentyl methacrylate · *p*TsOH and the higher homologues do not show acyl migration, probably because the transition state for acyl migration (eight-membered ring or higher) is energetically not favored. However, the longer amino-functional monomers still are susceptible to Michael addition after deprotonation.

For the homopolymers of the amino-functional monomer salts, it was shown that elongation af the aliphatic chain decreases the T_g of the polymer. Furthermore, the counter-ion of the ammonium group in the polymer salts has an influence on the T_g: a tosylate salt results in a higher T_g than a hydrochloride salt. The T_g decreases significantly when the polymer is neutralized.

Amino-functional latexes could be prepared by using a semicontinuous emulsion copolymerization of APMA · TsOH with BMA. By maintaining the pH of the aqueous phase above a value of 12, good incorporation of the amino-functional monomer was achieved. Because the reaction was performed under almost starved conditions, only a limited loss due to Michael addition occurred.

REFERENCES

1. Grawe, J. R.; Bufkin, B. G. J Coat Technol 1978, 50, 67.
2. Bufkin, B. G.; Grawe, J. R. J Coat Technol 1978, 50, 83.
3. Grawe, J. R.; Bufkin, B. G. J Coat Technol 1978, 50, 70.
4. Noomen, A. Prog Org Coat 1989, 17, 27.

5. Ooka, M.; Ozawa, H. Prog Org Coat 1994, 23, 325.
6. Müller, P. Proc. 20th FATIPEC Congress, 263 (1990).
7. Geurts, J. M.; Jacobs, P. E.; Muijs, M.; Van Es, J. J. G. S.; German, A. L. J Appl Polym Sci 1996, 61, 9.
8. Geurts, J. M. Ph.D. Thesis, Eindhoven University of Technology, Eindhoven, 1997.
9. Feng, J.; Winnik, M. A.; Geurts, J. M.; Zirkzee, H. F.; van Es, J. J. G. S.; German, A. L. J Coat Technol 1998, 70, 57.
10. Simms, J. A. Ger Offen 1,520,590 (1972).
11. Camps, M.; Chatzopoulos, M.; Monthéard, J. Rev Macromol Chem Phys 1982–83, C22, 343.
12. Charreyre, M.; Razafindrakoto, V.; Veron, L.; Delair, T.; Pichot, C. Makromol Chem Phys 1995, 195, 2141.
13. Charreyre, M.; Razafindrakoto, V.; Veron, L.; Delair, T.; Pichot, C. Makromol Chem Phys 1995, 195, 2153.
14. Ganachaud, F.; Mouterde, G.; Delair, T.; Elaïssari, A.; Pichot, C. Polym Adv Technol 1994, 6, 480.
15. Ganachaud, F.; Sauzedde, F.; Elaïssari, A.; Pichot, C. J Appl Polym Sci 1997, 65, 2315.
16. Sauzedde, F.; Ganachaud, F.; Elaïssari, A.; Pichot, C. J Appl Polym Sci 1997, 65, 2331.
17. Badesso, R. J.; Lai, T. W.; Pinschmidt, R. K.; Sagi, D. J.; Vijayendran, B. R. Polym Prep 1991, 32, 110.
18. Xu, J.; Dimonie, V. L.; Sudol, E. D.; El-Aasser, M. S. J Polym Sci Part A Polym Chem 1995, 33, 1353.
19. Smith, D. A.; Cunningham, R. H.; Coulter, B. J Polym Sci Part A-1 1970, 8, 783.
20. LeFevre, W. J.; Sheetz, D. P. U.S. 3,108,979 (1963).
21. Burke, E. A.; John, R. G. U.S. 2,973,285 (1961).
22. Brown, F. L. U.S. 3,419,507 (1968).
23. Scheffler, M. E.; Brown, F. L. U.S. 3,449,149 (1969).
24. Arthursson, P.; Brown, L.; Dix, J.; Goddard, P.; Petrak, K. J Polym Sci Part A Polym Chem 1990, 28, 2651.
25. Perrin, D. D.; Armarego, W. L. F. Purification of Laboratory Chemicals; Pergamon Press: Oxford, 1988, 3rd ed.
26. Hand, C. W.; Blewitt, H. L. Acid-Base Chemistry; Macmillan Publishing Company: New York, 1986, p. 215.
27. Kim, H.-B.; Winnik, M. A. Macromolecules 1994, 27, 1007.
28. Bloys van Treslong, C. J. Recl Trav Chim Pays-Bas 1978, 97, 13.
29. Davenport, J. N.; Wright, P. V. Polymer 1980, 21, 287.