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AB_2 Hyperbranched polymers derived from amino-methacrylate monomers

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The synthesis and characterisation of AB_2 hyperbranched homopolymers prepared from *N*-methacryloyl-1,2-diaminoethane hydrochloride and a series of AB_2 copolymers derived from different molar ratios of acryloyl- and methacryloyl-1,2-diaminoethane hydrochlorides are described. The reactivity and properties of these materials are contrasted with those previously reported for AB_2 and AB_2/B_n hyperbranched systems based on *N*-acryloyl-α,ω-diaminoalkane hydrochloride monomers.

Introduction

The field of dendritic polymers is now well established and a series of highly branched materials characterised in terms of both structure and physical properties have been reported.[1,2] In order to be able to tailor these polymers to the requirements of specific applications, a considerable research effort is being directed towards obtaining a fundamental understanding of structure–property correlations in these highly branched materials.[1–4] It has been demonstrated that a slight change in the structure of an AB_2 monomer can produce dramatic effects in terms of both reactivity towards polymerisation and the physical properties of the resultant hyperbranched materials.[3,4] For example, in the synthesis of the hyperbranched aliphatic polyesters polymerisation of the diol acid, 2,2-bis(hydroxymethyl)propionic acid proceeds successfully to give polymers,[5] whereas the hydroxy diester, diethyl 3-hydroxyglutarate gives only oligomers even at prolonged reaction times in the presence of effective transesterification catalysts such as titanium tetrabutoxide.[6]

Results and discussion

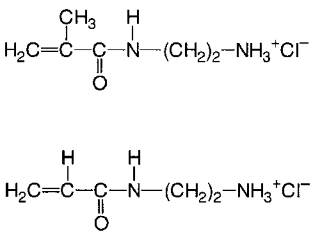
Previously we reported that, in contrast to *N*-acryloyl-α,ω-diaminoalkane hydrochlorides, the AB_2 monomer *N*-methacryloyl-1,6-diaminohexane hydrochloride does not polymerise readily, even at elevated temperatures.[7] However, our observations that in the amino-acrylate monomer series, $CH{=}CH(CH_2)_nNH_3^+Cl^-$ ($n = 2$ to 6), reactivity decreased with increasing internal oligomethylene spacer length from a maximum where $n = 2$[8] led us to reinvestigate the reactivity of methacrylates. We have examined the melt behaviour of three *N*-methacryloyl-α,ω-diaminoalkane hydrochlorides derived from α,ω-diaminoethane, butane and hexane respectively. The α,ω-diaminobutane and hexane derived monomers do not undergo polymerisation in the melt; however, *N*-methacryloyl-1,2-diaminoethane hydrochloride, see Fig. 1, undergoes homo- and co-polymerisations in the melt at 210 °C.

It is postulated that polymerisation occurs *via* Michael addition of the N–H unit of the amine group across the methacrylate double bond, a process analogous to that established for the polymerisation of *N*-acryloyl-α,ω-diaminoalkane hydrochloride monomers.[8] This hypothesis is supported by the results of ^1H and ^{13}C NMR spectroscopy, both techniques showing a reduction in the intensity of the vinylic signals of the methacrylate unit and generation of new methylene signals as the reaction proceeds. The integrated ^1H NMR spectra allow calculation of number average molecular weight and degree of polymerisation from the relative intensity of the vinylic ^1H signals. In conformity with the analogous polymers prepared from the *N*-acryloyl-α,ω-diaminoalkane hydrochloride monomers,[8,9] the hyperbranched materials derived from *N*-methacryloyl-1,2-diaminoethane hydrochloride lost no HCl during polymerisation in the melt at 210 °C, giving a polyelectrolyte product with an approximate composition of one HCl group for every polymer repeat unit.

We previously reported the successful determination of degree of branching for hyperbranched acryloyl-α,ω-diaminoalkane hydrochloride polymers and copolymers[8–10] by quantitative ^{15}N NMR spectroscopy. Unfortunately this analytical approach was not successful with these relatively low molecular weight methacrylate analogues because of low signal intensity; however we were able to detect and assign different nitrogen environments from the spectra obtained, see Table 1. The number of signals and the chemical shifts observed are consistent with a polymerisation process strictly analogous to that reported previously for structurally related monomers.[7–10]

These aminomethacrylate hyperbranched polymers, although prepared under the same conditions, showed different properties to their aminoacrylate counterparts, in terms of both reactivity and solubility. For example, in contrast to the AB_2 hyperbranched poly(amidoamine)s previously reported,[7–9] the materials prepared from *N*-methacryloyl-1,2-diaminoethane hydrochloride retain their solubility as the corresponding free bases. This improved solubility is presumably due to the disruption of hydrogen bonding and/or packing consequent on the replacement of a C–H unit by a methyl group. Also there is a marked reduction in reactivity on going from acryloyl to methacryloyl monomer, see Table 2, which may be due to a combination of steric and electronic effects on the Michael addition step.

The polymerisation of *N*-methacryloyl-1,2-diaminoethane


$H_2C{=}C(CH_3){-}C({=}O){-}N(H){-}(CH_2)_2{-}NH_3^+Cl^-$

N-methacryloyl-1,2-diaminoethane hydrochloride
Fw. = 150

$H_2C{=}C(H){-}C({=}O){-}N(H){-}(CH_2)_2{-}NH_3^+Cl^-$

N-acryloyl-1,2-diaminoethane hydrochloride
Fw. = 164

Fig. 1 AB_2 Monomer structures.

Table 1 ^{15}N NMR chemical shifts for polymers of *N*-methacryloyl-1,2-diaminoethane hydrochloride [MA·HCl] in comparison with those derived from *N*-acryloyl-1,2-diaminoethane hydrochloride [AC·HCl]

Polymer	Terminal (ppm)	Branched/Linear (ppm)	Amide (ppm)
MAC·HCl[b]	38.38	48.98	122.45[a]
AC·HCl[c]	31.54	43.44	116.66

[a]Broad peak 119.5–124.5 ppm, centred at 122.45 ppm. [b]Results based on analysis of material prepared at 210° C for 4 h, spectrum recorded at pH ~3. [c]Results based on analysis of material prepared at 210° C for 4 h, spectrum recorded at pH ~1.

hydrochloride appeared to attain a limited plateau value at an average DP of 11, $M_n \sim 1800$, Fig. 2, a phenomenon reported for other AB_2 polymerisations.[6,11] This is in contrast to the polymerisation of *N*-acryloyl-1,2-diaminoethane hydrochloride which under similar conditions gave rise to higher molecular weight polymers, *e.g.* 2 h at 210 °C gives DP = 130, $M_n \sim 19\,500$, and showed no tendency to reach a plateau in molecular weight.

The melt polymerisation of mixtures of *N*-acryloyl-1,2-diaminoethane hydrochloride and *N*-methacryloyl-1,2-diaminoethane hydrochloride was studied with respect to the effect of monomer molar ratio and reaction time on molecular weight and product solubility. The monomer structures are shown in Fig. 1 and the results are collected in Table 3.

The "as-made" AB_2 hyperbranched polyelectrolytes derived from *N*-acryloyl-1,2-diaminoethane hydrochloride are water soluble, but after washing with aqueous base to release the free base become insoluble in water or organic solvents. Clearly the relatively minor perturbation resulting from the introduction of $\geqslant 10\%$ methacryloyl-1,2-diaminoethane hydrochloride into the polymerisation of *N*-acryloyl-1,2-diaminoethane hydrochloride causes sufficient disruption in the structure and organisation of the resultant AB_2 hyperbranched polymers to render them soluble. This somewhat surprising observation indicates the subtle factors at play in determining the properties of these systems. Since we have previously reported that addition of a B_n core terminating unit (where $n \geqslant 2$) to the melt polymerisation of *N*-acryloyl-1,2-diaminoethane hydrochloride allows the resultant polymer to remain water soluble as the free base,[8,9] it appears that solubility in these systems is determined by a subtle interplay of repeat unit structure and overall topology.

Monitoring the [25 : 75], [50 : 50] and [75 : 25] copolymerisations by NMR spectroscopy (see Table 3) indicates that in these polymerisations the molecular weight increases as a function of reaction time with an apparent plateau in M_n being observed only for the methacryloyl monomer, Fig. 3.

The data in Fig. 3 also illustrate how the rate of reaction increases as the percentage of acrylate monomer used in the copolymerisation increases.

The products of polymerisation reactions using $\geqslant 10\%$ methacryloyl-1,2-diaminoethane hydrochloride in the monomer feed are water-soluble polyelectrolytes from which the free bases can be liberated by reaction with the aqueous potassium hydroxide solution. Separation of the resultant water-soluble polymeric free base from its water-soluble by-products, namely potassium hydroxide and potassium chloride, was demonstrated for the [50 : 50] copolymer using a benzoylated cellulose dialysis membrane. This technique also provides a method for removing low molecular weight oligomers (< 1200 amu) from the sample.

Table 2 Homopolymerisation of *N*-methacryloyl-1,2-diaminoethane hydrochloride

	N-Methacryloyl-1,2-diaminoethane HCl[a]	
Reaction time/h	DP	M_n
0.5	1.2	~200
1	3.2	~525
2	4.8	~790
3	7.0	~1150
4	11.2	~1840
5	11.0	~1800
6	10.1	~1660
7	11.3	~1850
8	11.9	~1940

[a]Average results calculated from ^{1}H NMR data, based on a 6 g melt polymerisation reaction at 210 °C.

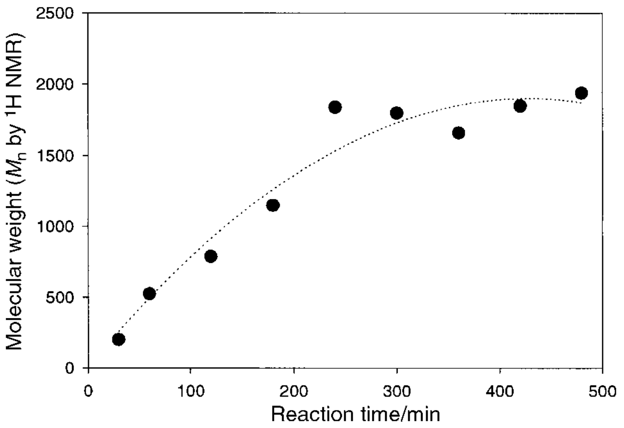


Fig. 2 Homopolymerisation of *N*-methacryloyl-1,2-diaminoethane hydrochloride.

Thermogravimetric analysis of the series of polymers recorded in Table 2 showed that these materials display fairly good thermal stability. When heated under dry nitrogen at 10 °C min^{-1} 2% weight loss occurred between 260–290 °C for all samples. Differential scanning calorimetry (Perkin Elmer, DSC7 at 10 °C min^{-1}) failed to reveal any crystalline melting points or glass transitions for any of these hyperbranched systems. The absence of melting points is in accord with expectation since similar results have been reported for a number of other hyperbranched and dendritic polymers.[12,13] The lack of crystallinity is usually attributed to disruption of packing in these highly branched structures; however, the lack of any evidence for a glass transition is more surprising since the analogous poly(aminoamide) AB_2 hyperbranched polymers displayed glass transition temperatures in the 15 to 130 °C range dependent on the monomer methylene spacer length sequence.[8] These polyelectrolytes are expected to be fairly stiff structures as a consequence of intramolecular ionic repulsions and it may be that the extra steric hindrance to segmental motion consequent on introduction of a methyl group is sufficient to account for the lack of any observable glass transition process.

Experimental

All chemicals were purchased from either Lancaster Synthesis or the Aldrich Chemical Company and used as received without further purification. Benzoylated cellulose dialysis tubing, 32 mm width, was obtained from the Sigma Chemical Company.

Infrared spectra were recorded as thin films on NaCl plates,

Table 3 *N*-Acryloyl-, *N*-methylacryloyl-1,2-diaminoethane hydrochloride copolymers

Monomer composition/mol					
Methacryloyl-AB$_2$	Acryloyl-AB$_2$	Reaction time[a]/min	DP[b] (^{1}H NMR)	M_n[b] (^{1}H NMR)	Soluble in aqueous base
100	0	240	11	1850	✓
75	25	30	2.6	410	✓
		60	4.8	770	✓
		120	7.6	1220	✓
		180	19.6	3150	✓
		240	24.3	3900	✓
50	50	30	4	650	✓
		60	7	1180	✓
		120	11	1720	✓
		180	57	8950	✓
		240	97	15210	✓
25	75	30	12	1820	✓
		60	16	2500	✓
		120	39	5920	✓
		180	N/A[c]	N/A[c]	✓
		240	N/A[c]	N/A[c]	✓
10	90	240	N/A[c]	N/A[c]	✓
5	95	240	N/A[c]	N/A[c]	✗
0	100	240	116	17450	✗

[a] All reactions were carried out in the melt at 210 °C, under nitrogen with continuous stirring. [b] Calculated from vinyl group intensity in the ^{1}H NMR spectra, assuming an average monomer formula weight calculated from the initial ratio of monomers. [c] No vinylic signal visible in the ^{1}H NMR spectrum, *i.e. ca.* 100% extent of reaction.

unless otherwise stated, using a Perkin Elmer 1600 series spectrometer. ^{1}H, ^{13}C and ^{15}N NMR spectra were recorded using a Varian VXR400S spectrometer. Thermogravimetric analysis was carried out using a Rheometrics Scientific Ltd. TG760 thermobalance, 5–10 mg, 10 °C min^{-1}. Differential scanning calorimetry measurements were recorded using a Perkin Elmer DSC7, scanning at a rate of 10 °C min^{-1}. Elemental analysis was obtained using a Carlo-Erba instrument, some of the intermediates were marginally low on carbon probably due to the problem of water absorption in these hygroscopic materials.

Monomer synthesis

N-*tert*-Butoxycarbonyl-1,2-diaminoethane hydrochloride (95%) was prepared as previously described.[7,14]

N-Butoxycarbonyl-N′-methacryloyl-1,2-diaminoethane was prepared following the procedure described for *N*-butoxycarbonyl-*N′*-acryloyl-1,2-diaminoethane previously.[7] Calculated for $C_{11}H_{20}N_2O_3$: C, 57.89; H, 8.77; N, 12.28%; found: C, 57.50; H, 8.72; N, 12.11%. ^{1}H NMR ($CDCl_3$) $\delta = 1.42$ (s,9H, CH_3), 1.95 (s, 3H, CH_3), 3.35 (m, 2H, CH_2), 3.40 (m, 2H, CH_2), 5.32 (m, 1H, vinyl proton), 5.02 (br s, 1H, amide proton), 5.74 (m, 1H, vinyl protons), 6.76 (br s, 1H, amide proton); ^{13}C NMR ($CDCl_3$) $\delta = 18.51$, 28.30, 39.89, 41.58, 79.83, 119.92, 139.47, 157.30, 168.78.

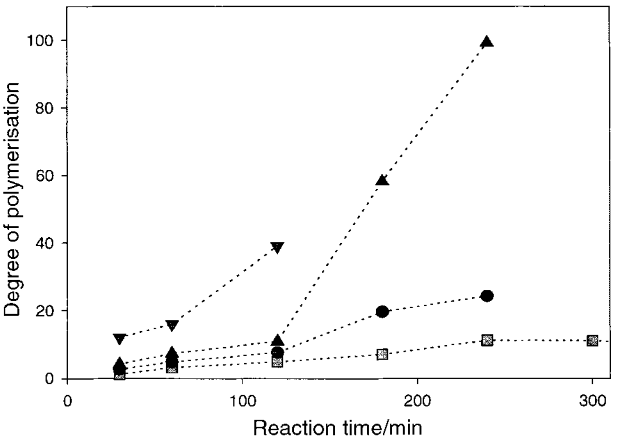


Fig. 3 Degree of polymerisation against reaction time for the polymerisation of *N*-methacryloyl-1,2-diaminoethane hydrochloride and its [25 : 75], [50 : 50] and [75 : 25] copolymers with *N*-acryloyl-1,2-diaminoethane hydrochloride. ▼ = [25 : 75] copolymer, prepared in the melt at 210 °C; ▲ = [50 : 50] copolymer, prepared in the melt at 210 °C; ● = [75 : 25] copolymer, prepared in the melt at 210 °C; ■ = methacryloyl-1,2-diaminoethane hydrochloride homopolymer, prepared in the melt at 210 °C.

N-Methacryloyl-1,2-diaminoethane hydrochloride was obtained from *N*-butoxycarbonyl-*N′*-methacryloyl-1,2-diaminoethane in 93% yield following the literature method.[7] Calculated for $C_6H_{13}N_2Cl$: C, 43.90; H, 7.93; N, 17.07%; found: C, 43.45; H, 7.86; N, 17.37%. ^{1}H NMR (D_2O) $\delta = 1.80$ (s, 3H, CH_3), 3.04 (m, 2H, CH_2), 3.44 (m, 2H, CH_2), 5.36 (m, 1H, vinyl proton), 5.63 (m, 1H, vinyl protons); ^{13}C NMR (D_2O) $\delta = 17.69$, 37.17, 39.40, 122.11, 138.60, 172.62.

Polymer syntheses

Polymerisations were carried out in the melt at 210 °C, unless stated otherwise.[7] The temperature of the reaction vessel was ramped at 10 °C min^{-1} from RT to 210 °C. The reaction times quoted are measured from the onset of 210 °C. All experiments are carried out under a constant nitrogen flow with constant stirring at 125 rpm.

Sample polymer characterisation. Poly(amidoamine)hydrochloride, prepared from the AB$_2$ monomer, *N*-methacryloyl-1,2-diaminohexane hydrochloride, by reaction at 210 °C for 60 min. Calculated for the monomer *N-methacryloyl-1,2-diaminoethane hydrochloride*, $C_6H_{13}N_2Cl$: C, 43.90; H, 7.93; N, 17.07; Cl, 21.34%: found for the polymer: C, 44.20; H, 7.78; N, 16.97%. ^{13}C NMR (D_2O): $\delta = 15.11$, 15.51, 17.65, 19.87, 23.86, 25.55, 35.55, 36.54, 36.77, 37.13, 42.583, 44.42, 44.64, 50.22, 50.46, 50.56, 50.72, 122.07, 138.58; ^{1}H NMR (D_2O): $\delta = 0.95$–1.20 (m, 3H, CH_3), 1.80–3.50 (m, 4H, CH_2), 3.60–3.95 (m, 4H, CH_2), 5.20–5.70 (m, 2H, vinylic protons). [DP = 9; Extent of reaction = 91%; M_n = 1480, all calculated from ^{1}H NMR data.]

Conclusion

Polymerisation of *N*-methacryloyl-1,2-diaminoethane hydrochloride occurs although homologues with longer methylene sequences between the functional groups are unreactive. *N*-Methacryloyl-1,2-diaminoethane hydrochloride is much less reactive than its acryloyl analogue and has been shown to produce only oligomers of a relatively low plateau molecular weight even after prolonged reaction at 210 °C. Addition of this AB_2 monomer to the polymerisation of *N*-acryloyl-1,2-diaminoethane hydrochloride has been shown to modify the properties of the resultant copolymer materials, in particular at $\geqslant 10$ mol% addition of this monomer to the copolymer feed renders the resultant copolymers soluble in water as their free bases. Thermal analysis, in particular the absence of any T_g process, suggests that these materials are more rigid at a molecular level than their acryloyl analogues; these subtle thermomechanical and solubility effects consequent on relatively minor structural changes are interesting in their own right and imply the possibility of tuning the properties of this class of material.

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