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Synthesis of novel block and statistical methacrylate-based ionomers containing acidic, basic or betaine residues

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Group-transfer polymerisation (GTP) has been used to synthesise a range of statistical and block methacrylate copolymers containing a small fraction (10–30 mol%) of ionic residues. More specifically, *n*-butyl methacrylate (*n*BuMA) and benzyl methacrylate (BzMA) were copolymerised using GTP. The precursor copolymers were then deprotected *via* catalytic hydrogenolysis to selectively remove the benzyl groups, giving a range of statistical and block copolymers containing carboxylic acid groups. Similarly, copolymerisation of *n*BuMA with 2-(dimethylamino)ethyl methacrylate (DMAEMA) directly yielded copolymers containing tertiary amine groups. Zwitterionic and cationic derivatives of these copolymers were obtained by betainisation and quaternisation of the DMAEMA residues, respectively. Gel permeation chromatography was used to determine copolymer molecular weights and polydispersities, while proton n.m.r. spectroscopy was used to assess their composition. In all cases, the final copolymers were near-monodisperse ($M_w/M_n < 1.15$) and good molecular weight control was achieved. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Group transfer polymerisation (GTP) was first discovered by workers at Du Pont more than a decade ago[1,2]. Despite considerable controversy regarding its precise mechanism[3–5], GTP has become recognised as an excellent method for the synthesis of controlled-structure methacrylate (co)polymers of narrow molecular weight distribution. A wide range of architectures is accessible, including statistical[6,7], block[8–10], graft[11,12] and star[13–15] copolymers.

The resulting methacrylate copolymers have many potential applications. For example, workers at Du Pont have filed patents[16–18] describing the use of various methacrylate copolymers as pigment dispersants. Protein separation applications for ABC triblock copolymers comprising methyl methacrylate (MMA), methacrylic acid (MAA) and 2-(dimethylamino)ethyl methacrylate (DMAEMA) have been suggested by Patrickios *et al.*[19]. Al-Lami *et al.* reported[20] that *n*-butyl methacrylate–methacrylic acid statistical copolymers are efficient dispersants for alumina particles in toluene, which is a key to the fabrication of high quality green tapes and ceramics. Rannard[21] used *n*-butyl methacrylate–methacrylic acid block copolymers to prepare ion-selective membranes. Baines *et al.*[22] have reported the use of DMAEMA–MMA block copolymers as non-micellising steric stabilisers for the preparation of micrometer-sized polystyrene latex particles in alcoholic media. Finally Ober *et al.*[23,24] have demonstrated that *t*-butyl methacrylate-based copolymers can be used in u.v. lithography applications.

Compared to classical anionic polymerisation, GTP is reasonably tolerant of certain functionalities such as tertiary amines[25], epoxides[26], styrenic groups[27] and allylic groups[28,29]. Methacrylate monomers which contain other functional groups such as –OH or –COOH can be successfully polymerised using protection–polymerisation–deprotection methods. For example, (co)polymers containing methacrylic acid residues have been prepared using several different protected monomers, including trimethylsilyl methacrylate[30], *t*-butyl methacrylate[31], tetrahydropyranyl methacrylate[32], and benzyl methacrylate[33]. Quantitative deprotection to yield the desired acid residues can be achieved *via* hydrolysis, thermolysis or catalytic hydrogenolysis.

Recently we reported a facile two-step route for the synthesis of polybetaine homopolymers of narrow molecular weight distribution[34]. First, 2-(dimethylamino)ethyl methacrylate (DMAEMA) was polymerised *via* GTP to yield homopolymer precursors of varying molecular weights. These homopolymers were then quantitatively derivatised using 1,3-propanesultone under mild conditions (THF, room temperature) to yield polysulfopropylbetaines. Subsequent analysis of these polybetaines using aqueous gel permeation chromatography confirmed their narrow molecular weight distributions. Preliminary results suggested that this approach could also be used to obtain betaine block copolymers[35,36].

Ionomers are hydrophobic (co)polymers which contain a small percentage of ionic groups. Eisenberg and co-workers have studied the synthesis of various block copolymer ionomers by anionic polymerisation[37–40]. These copolymers can exhibit complex micellisation behaviour in aqueous solution. West[16] has described the synthesis of a

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series of methacrylate-based ionomers via GTP; these materials were shown to be effective dispersants for various pigments in non-aqueous media.

In the present work we report the synthesis of a series of novel *n*-butyl methacrylate-rich statistical and block ionomers containing either acidic, basic, or betaine residues. The acidic residues were incorporated using benzyl methacrylate as a protected monomer for methacrylic acid. The basic residues were obtained by direct copolymerisation with DMAEMA. Sulfobetaine residues were introduced by the post-polymerisation functionalisation of these tertiary amine groups using 1,3-propanesultone[34] according to the procedure described by Lowe *et al.*[34]. In contrast, carboxybetaine residues were obtained by reacting the DMAEMA residues with an excess of acrylic acid *via* Michael addition, as recently described by Barboiu *et al.*[41].

In each case the copolymer compositions and molecular weight distributions were assessed using ^{1}H n.m.r. spectroscopy and gel permeation chromatography, respectively.

EXPERIMENTAL

Materials

All monomers were obtained from Aldrich; inhibitors were removed using basic alumina columns. Each monomer was dried by stirring over calcium hydride and stored at −20°C until required. Benzyl methacrylate was filtered into a graduated schlenk flask and stirred with bis(dimethylamino)methylsilane (ABCR) for at least 2 h prior to use. All other monomers were freshly distilled prior to use. The initiator, 1-methoxy-1-trimethylsiloxy-2-methyl-1-propene (MTS) was obtained from Aldrich, distilled and stored at −5°C prior to use. Tetrahydrofuran (Fisons) was dried over sodium wire for 3 days and then refluxed over potassium for a further 3 days. The dried solvent was stored over 4 Å molecular sieves prior to use. The tetrabutylammonium bibenzoate (TBABB) catalyst was prepared by the method of Dicker *et al.*[42].

Copolymer syntheses

Polymerisations were performed under dry nitrogen using standard schlenk techniques. All glasssware was oven-dried overnight at 175°C before use. The assembled glassware was then flamed out under vacuum to eliminate surface moisture. In a typical synthesis, TBBAB (about 20 mg, 2 mol% based on the initiator) and MTS (0.40 ml) were added to THF (120 ml). Freshly distilled *n*-butyl methacrylate (*n*BuMA) monomer (8.5 ml) was added dropwise at an approximate rate of 1 ml min^{-1} *via* a double-tipped needle. The reaction exotherm (around 10°C) was measured using a contact thermocouple. The reaction mixture was stirred at room temperature for 2.5 h before the dropwise addition of purified benzyl methacrylate (BzMA) (or DMAEMA) comonomer (4.0 ml). A second exotherm (around 5°C) was observed. The reaction mixture was stirred for a further 2.5 h before being quenched by the addition of methanol (2 ml). The block copolymer was recovered by precipitation into a tenfold excess of water. Solvent was removed by decantation, and the precipitate was dried in a vacuum oven for 3 days at 60°C. This procedure resulted in a block copolymer containing 69.5 mol% *n*BuMA, with an M_n of around 8200 g mol^{-1} by g.p.c. (*versus* PMMA standards). Copolymers of different composition were prepared by varying the comonomer ratio at a fixed initiator concentration. A series of copolymer molecular weights was obtained by varying the comonomer/initiator ratio. Statistical copolymers were synthesised by simply mixing the two comonomers prior to addition.

Catalytic hydrogenolysis

Catalytic hydrogenolyses of BzMA-based (co)polymers were performed in a solvent mixture in which the copolymer remained soluble throughout the derivatisation. Thus, copolymer (15 g) was dissolved in 330 ml of ethyl acetate–methanol (10:1) and 4.0 g of 10% Pd/C catalyst were added to this solution under nitrogen. The reaction solution was stirred under hydrogen (1 atm) at room temperature for at least 8 days. Finally, the catalyst was filtered off and the (co)polymer was recovered using a rotary evaporator, before drying *in vacuo* for 2 days at room temperature.

Betainisation

Betainisation of the DMAEMA-containing (co)polymers (5–11 g) were carried out at room temperature in THF (50–100 ml). For the DMAEMA homopolymer, either a stoichiometric or a substoichiometric (based on the number of DMAEMA residues) amount of either 1,3-propanesultone or 1,4-butanesultone (0.5–6.0 ml) was added under nitrogen *via* a syringe. These reagents were used in stoichiometric amounts for the derivatisation of the copolymers. The reaction was either stirred for 3 days (1,3-propanesultone) or refluxed under nitrogen for 1 week (1,4-butanesultone). The resulting solution became viscous if the DMAEMA copolymer content was greater than 30 mol%. The product was dried in the vacuum oven for 2 days at room temperature. For lower DMAEMA contents, the solvent was removed using a rotary evaporator prior to drying. In order to remove excess 1,3-propanesultone, the *n*BuMA–DMAEMA copolymers were purified by precipitation and Soxhlet extraction in H_2O. The 10 and 30 mol% betainised DMAEMA homopolymers were dialysed against H_2O, while the 100% betainised DMAEMA was precipitated and Soxhlet-extracted with THF.

The analogous carboxybetaines were obtained by reacting the copolymers (2.0 g) with a tenfold excess of acrylic acid (0.9–2.8 ml) in acetonitrile (50 ml) at 60°C. The reaction was stirred for around 72 h and then precipitated three times into cold isopropanol (−20°C) from THF to remove the excess acrylic acid. In order to completely remove the acrylate salt formed during the reaction, the products were washed and Soxhlet-extracted with water. Finally, the carboxybetaines were dried under vacuum for 2 days at room temperature.

Quaternisation

Quaternisation reactions were carried out at 45°C in about 50 ml of a THF–water (50:10 (% (v/v)) solvent mixture. The reaction of the DMAEMA copolymer (4–10 g) with CH_3I (0.3–6.5 ml) gave an exotherm of around 7°C. The reaction was stirred for a further 2 h before the solvent mixture was removed by evaporation and the resulting copolymer was dried in a vacuum oven for 2 days at 60°C. Copolymers with high degrees of quaternisation were further purified by Soxhlet extraction using THF and acetone in turn to remove excess CH_3I and then dried under vacuum for 2 days at room temperature.

Gel permeation chromatography

Molecular weights and molecular weight distributions of all the copolymers were determined using g.p.c. The g.p.c.

set-up consisted of a Perkin-Elmer l.c. pump, an r.i. detector, and a PLgel 3 μm Mixed 'E' column (Polymer Labs). Calibration was carried out using a series of poly(methyl methacrylate) (PMMA) standards (Polymer Labs), with M_n values ranging from 29 400 to 625. The eluent was h.p.l.c. grade THF and the flow rate was 1 ml min^{-1}.

Nuclear magnetic resonance spectroscopy

Copolymer compositions were determined using ^{1}H n.m.r. spectroscopy by comparing peak integrals assigned to the different comonomers. For example, the peak integral of the $-OCH_2-$ protons in the *n*BuMA residues at $\delta = 3.8$–4.0 was ratioed to that of the aromatic protons at $\delta = 7.2$–7.4 for benzyl methacrylate containing copolymers (or to that of the dimethylamino group protons at $\delta = 2.2$–2.4 for the DMAEMA-containing copolymers). All ^{1}H n.m.r. spectra were recorded using a Bruker 250 MHz instrument, using either CD_2Cl_2 or $CDCl_3$ as solvents for the poly(*n*BuMA-BzMA) and poly(*n*BuMA–DMAEMA) copolymers, respectively. The degree of deprotection of the *n*BuMA–MAA copolymers was assessed using their proton n.m.r. spectra recorded in either DMSO-d_6 or DMF. Proton n.m.r. spectra of the betainised DMAEMA-based statistical copolymers were obtained in D_2O/DCl, while deuterated trifluoroethanol (CF_3CD_2OD) was used as a solvent for the *n*BuMA–betaine copolymers in order to solubilise both the hydrophilic and hydrophobic residues. The carboxybetaine copolymers were insoluble in this latter solvent; a mixture of DMF-d_7 and D_2O/DCl was used instead. The proton n.m.r. spectra of the cationic derivatives were recorded using D_2O for the quaternised homopolymers and either DMSO-d_6 or DMF-d_7 for the quaternised *n*BuMA–DMAEMA block and statistical copolymers, respectively.

Elemental microanalyses

C, H, N and S elemental microanalyses were carried out by MEDAC Ltd., Brunel University, UK.

Table 1 Copolymer compositions, number-average molecular weights and polydispersities for both the poly(*n*BuMA–DMAEMA) and poly(*n*BuMA–BzMA) statistical/block copolymers

Copolymer[a]	Theoretical *n*BuMA content (mol%)	*n*BuMA content by ^{1}H n.m.r. (mol%)	Polymer yield (%)	Theoretical M_n of block copolymer	M_n of block copolymer by GPC[b]	M_w/M_n^b
Poly(*n*BuMA)	100.0	100.0	100.0	6200	7900	1.05
Poly(BzMA)	–	–	99.5	5800	6400	1.12
Poly(DMAEMA)	–	–	100.0	6100	5900	1.07
*n*BuMA-*stat*-BzMA	89.5	87.0	99.0	6200	6700	1.12
*n*BuMA-*stat*-BzMA	70.0	69.0	100.0	6100	8600	1.11
*n*BuMA-*b*-BzMA	90.0	90.0	99.5	6000	7500	1.06
*n*BuMA-*b*-BzMA	70.0	70.0	100.0	6100	7500	1.07
*n*BuMA-*stat*-DMAEMA	90.0	90.0	100.0	6000	7600	1.10
*n*BuMA-*stat*-DMAEMA	70.0	70.0	100.0	6000	6900	1.09
*n*BuMA-*b*-DMAEMA	90.0	90.0	100.0	6000	6800	1.11
*n*BuMA-*b*-DMAEMA	70.0	70.0	99.5	6200	7200	1.07

[a] Statistical and block copolymers are denoted by *stat* and *b*, respectively

[b] As determined by g.p.c. (calibrated with poly(methyl methacrylate) standards)

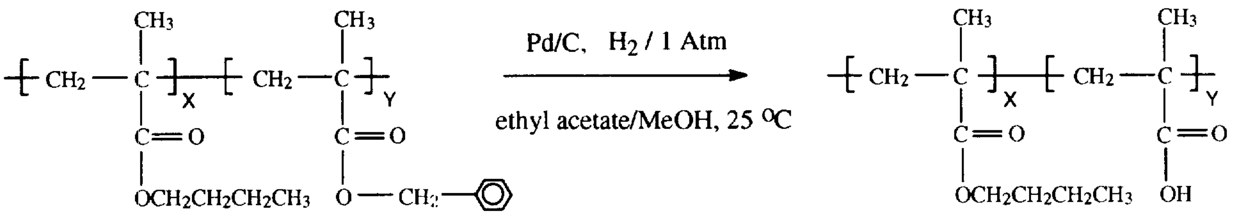


Figure 1 Reaction scheme for the catalytic hydrogenolysis of BzMA-based copolymers

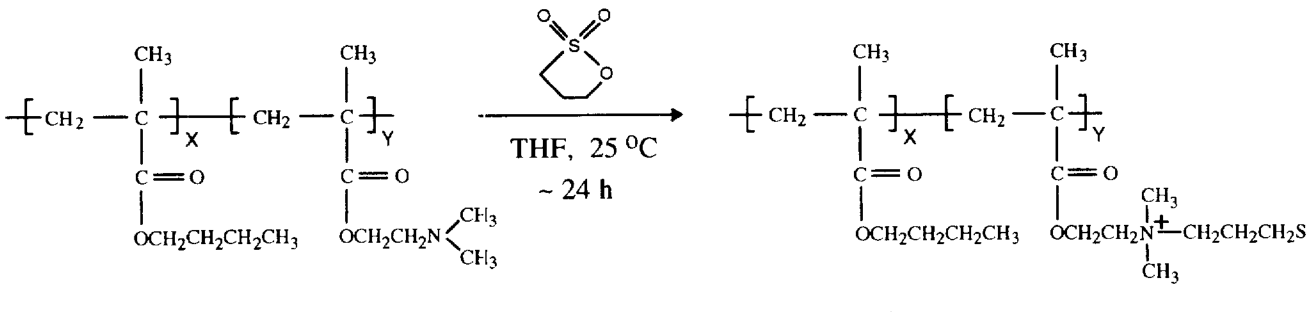


Figure 2 Reaction scheme for the betainisation of DMAEMA-based copolymers using 1,3-propanesultone

RESULTS AND DISCUSSION

Two series of *n*BuMA-based block and statistical copolymers with either BzMA or DMAEMA were synthesised, as well as the corresponding homopolymers (see *Table 1*). The comonomer composition was varied, while the overall molecular weight was kept approximately constant. The BzMA-containing copolymers were then deprotected by catalytic hydrogenolysis to selectively remove the benzyl groups, giving statistical and block copolymers containing carboxylic acid groups (see *Figure 1*).

Similarly, copolymerisation of *n*BuMA with DMAEMA yielded copolymers containing tertiary amine groups directly. These precursor copolymers were further functionalised by either betainisation (*Figure 2* and *Figure 3*) or quaternisation (*Figure 4*) of these amine groups to produce zwitterionic and cationic copolymers, respectively.

Block copolymers were prepared by first polymerising *n*BuMA, followed by either BzMA or DMAEMA. The *n*BuMA content was kept constant at either 70 or 90 mol% and the overall copolymer molecular weight was maintained at around 6000 g mol^{-1} (*Table 1*; *Figure 5*). The absence of a low molecular weight tail in the g.p.c. trace of the first block (not shown) indicated minimal homopolymer contamination. Most of the copolymers were easily isolated by precipitation into water. However, water proved to be a surprisingly poor non-solvent for the 70:30 *n*BuMA–DMAEMA copolymers; instead these were recovered by removing excess THF using a rotary evaporator and then drying the resulting viscous solution in a vacuum oven. Excellent yields were obtained in all cases. Copolymer molecular weights and molecular weight distributions were determined by g.p.c. and are summarised in *Table 1*. In general, good agreement between the theoretical and g.p.c. molecular weights was observed and polydispersities were low ($M_w/M_n < 1.15$). The relative copolymer compositions determined by ^{1}H n.m.r. spectroscopy (see *Table 1*) were in good agreement with the expected values.

Poly(BzMA) homopolymers and copolymers were deprotected by catalytic hydrogenolysis (see *Table 2*). Debenzylation was indicated by the complete disappearance of the aromatic and benzylic proton signals observed in the n.m.r. spectra of the precursor (co)polymers. The actual degree of debenzylation was determined by comparing the peak integral of the un-ionised carboxylic acid proton (around δ = 12.5 in DMSO-d_6 or DMF-d_7) of the deprotected copolymer to that of the $-OCH_2-$ protons of the *n*BuMA residues (δ = 3.8–4.0) (see *Figure 6*). Our observations are in excellent agreement with those reported earlier by both Mykytiuk *et al.*[33] and Rannard *et al.*[31], who achieved complete debenzylation of poly(benzyl methacrylate) homopolymers and poly(benzyl methacrylate-*b*-methyl methacrylate) copolymers, respectively. In order to verify that debenzylation had not resulted in any side reactions, Mykytiuk *et al.*[33] remethylated a poly(methacrylic acid) homopolymer using diazomethane to obtain a poly(methyl methacrylate) homopolymer, which was then analysed by g.p.c. (THF eluent). This confirmed that the narrow molecular weight distribution of the poly(benzyl methacrylate) precursor was retained in the final poly(methacrylic acid). Since the same mild debenzylation conditions were used in the present study, no side reactions, such as chain scission or cross-linking, were anticipated.

Quantitative derivatisation of the DMAEMA homopolymers and copolymers was achieved with 1,3-propanesultone to give betaine-based (co)polymers. The degree of

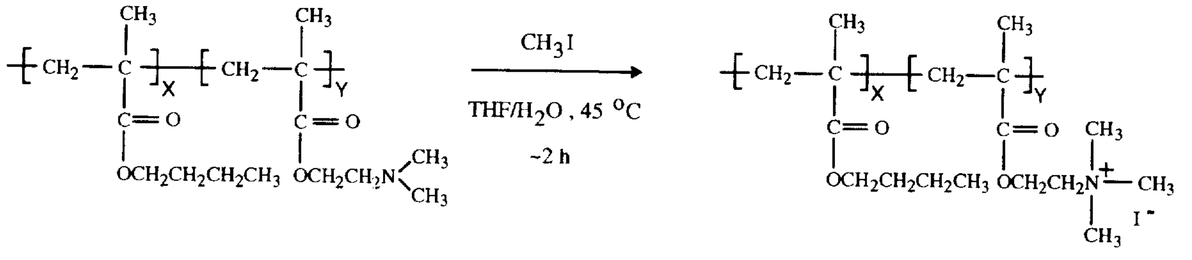


Figure 3 Reaction scheme for the carboxybetainisation of DMAEMA-based copolymers using acrylic acid (see Ref. [41])

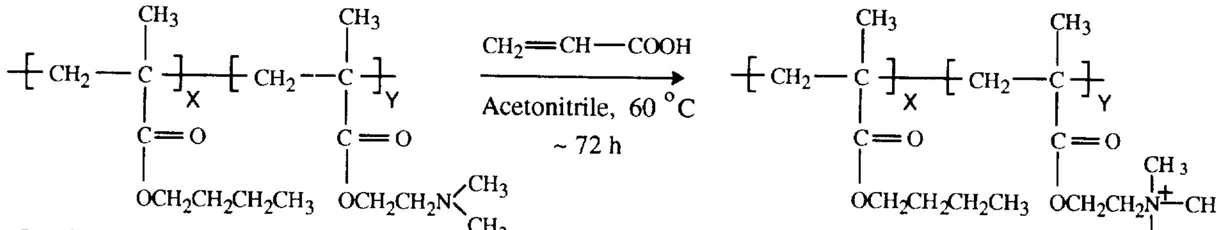


Figure 4 Reaction scheme for the quaternisation of DMAEMA-based copolymers using iodomethane

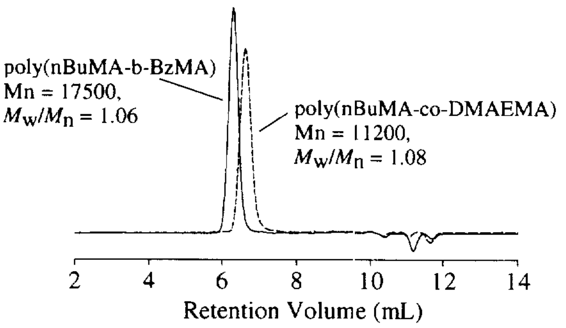


Figure 5 Typical gel permeation chromatograms for (a) a 90–10 poly(*n*BuMA-*stat*-DMAEMA) copolymer, and (b) a 90–10 poly(*n*BuMA-*b*-BzMA) copolymer

Table 2 Copolymer compositions of BzMA-based copolymers and their degrees of debenzylation after catalytic hydrogenolysis

Copolymer[a]	*n*BuMA content of copolymer (mol%)	% Debenzylation by ^{1}H n.m.r.	Reaction yield (%)[b]	Reaction time (days)
Poly(BzMA)	–	100	79	5
*n*BuMA-*stat*-BzMA	90	100	93	13
*n*BuMA-*stat*-BzMA	70	100	92	13
*n*BuMA-*b*-BzMA	90	100	92	13
*n*BuMA-*b*-BzMA	70	100	96	13

[a] Statistical and block copolymers are denoted by *stat* and *b*, respectively

[b] Some copolymer lost during filtration work-up

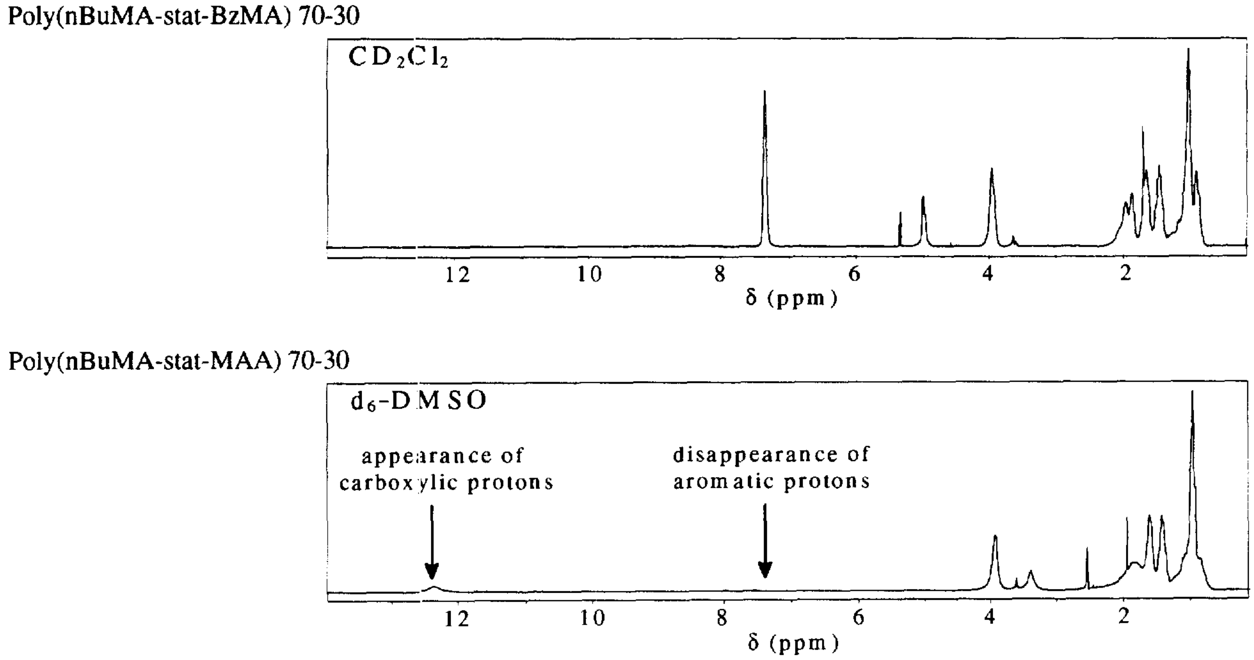


Figure 6 Typical ^{1}H n.m.r. spectra of a 70–30 *n*BuMA-*stat*-BzMA precursor copolymer (upper spectrum) and the final debenzylated *n*BuMA-*stat*-MAA copolymer (lower spectrum) obtained after catalytic hydrogenolysis

Table 3 Degrees of betainisation of DMAEMA-based copolymers as determined by ^{1}H n.m.r. spectroscopy and S/N microanalyses

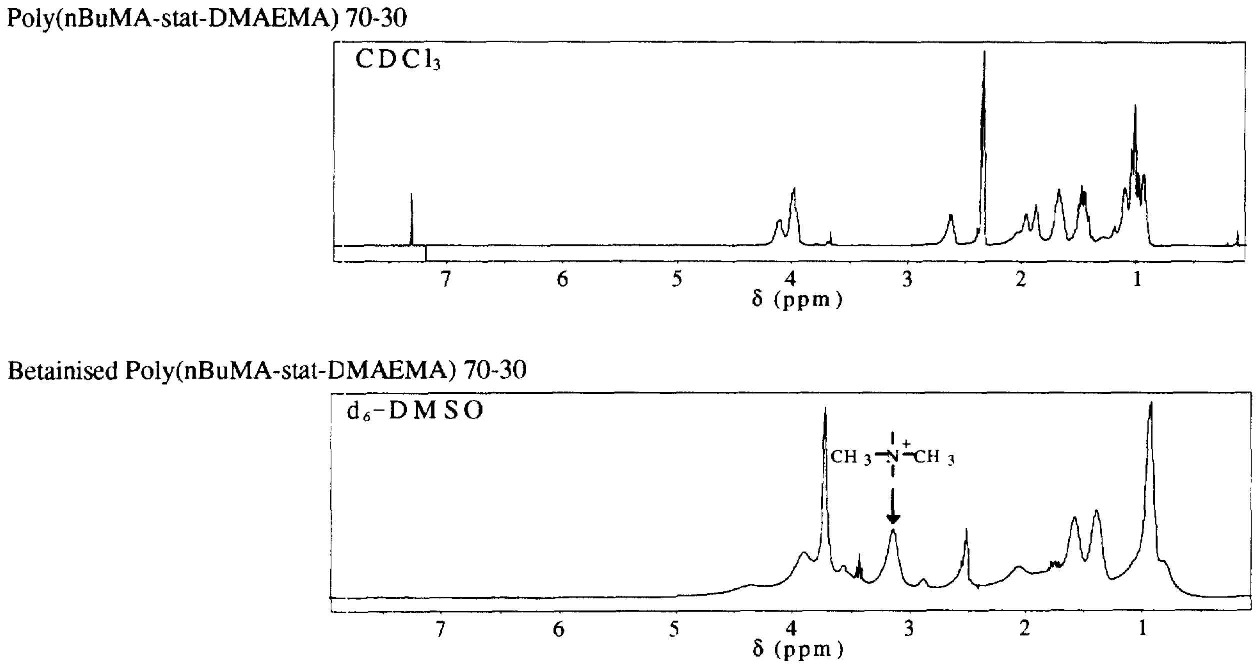
Copolymer[a]	*n*BuMA content of copolymer (mol%)	Calculated degree of betainisation (mol%)	Actual degree of betainisation by ^{1}H n.m.r. (mol%)	Actual degree of betainisation by elemental microanalysis (mol%)[c]
Poly(DMAEMA)	–	100.0	100.0	100.5
Poly(DMAEMA)	–	37.0	36.5	42.5
Poly(DMAEMA)	–	11.5	12.5	13.0
Poly(DMAEMA)[b]	–	100.0	100.0	101.0
*n*BuMA-*stat*-DMAEMA	90.0	10.0	10.0	9.5
*n*BuMA-*stat*-DMAEMA	70.0	30.0	29.5	28.5
*n*BuMA-*b*-DMAEMA	90.0	10.0	10.0	10.5
*n*BuMA-*b*-DMAEMA	70.0	30.0	29.5	28.5

[a] All yields are quantitative

[b] The betainising agent was 1,4-butanesultone rather than 1,3-propanesultone

[c] Calculated from the S/N ratio taking into account the DMAEMA content of the precursor copolymers obtained from ^{1}H n.m.r. spectroscopy

betainisation (see *Table 3*) was determined using ^{1}H n.m.r. spectroscopy (see *Figure 7*). For the betainised DMAEMA homopolymers, the peak integrals of the $-OCH_2-$ proton signals ($\delta = 4.3$–4.4 in D_2O/DCl) were ratioed to those of the betainised dimethylamino protons ($\delta = 3.3$–3.4). For the *n*BuMA–DMAEMA copolymers the peak integral of the $-OCH_2-$ proton signal due to the *n*BuMA residues ($\delta = 4.0$ in CF_3CD_2OD) was compared to that of the betainised dimethylamino group protons ($\delta = 3.3$–3.4). When substoichiometric amounts (e.g. 10 or 30 mol% based on DMAEMA residues) of 1,3-propanesultone were deliberately used to derivatise the DMAEMA homopolymer, statistical copolymers containing underivatised DMAEMA and betainised DMAEMA residues were obtained. On the


Poly(nBuMA-stat-DMAEMA) 70-30

Betainised Poly(nBuMA-stat-DMAEMA) 70-30

Figure 7 Typical ^{1}H n.m.r. spectra of a 70–30 *n*BuMA-*stat*-DMAEMA precursor copolymer (upper spectrum) and the resulting betainised copolymer (lower spectrum) after reaction with 1,3-propanesultone

Table 4 Degrees of quaternisation of iodomethane-derivatised DMAEMA copolymers as determined by ^{1}H n.m.r. spectroscopy

Copolymer[a]	*n*BuMA content of copolymer (mol%)	Calculated degree of quaternisation (mol%)	Actual degree of quaternisation by ^{1}H n.m.r. (mol%)
Poly(DMAEMA)	—	100.0	100.0
Poly(DMAEMA)	—	30.0	30.5
Poly(DMAEMA)	—	10.0	10.5
*n*BuMA-*stat*-DMAEMA	90.0	10.0	10.0
*n*BuMA-*stat*-DMAEMA	70.0	30.0	30.0
*n*BuMA-*b*-DMAEMA	90.0	10.0	10.0
*n*BuMA-*b*-DMAEMA	70.0	30.0	30.0

[a] All yields were quantitative (> 95%)

other hand, using stoichiometric amounts of 1,3-propanesultone produced polysulfobetaine homopolymers and betainised block or statistical *n*-butyl methacrylate copolymers with quantitative degrees of betainisation.

C, H, N and S elemental microanalyses was also carried out on all betaine (co)polymers in order to confirm the degree of betainisation determined by proton n.m.r. spectroscopy. In general, good agreement between proton n.m.r. and elemental microanalytical data was observed (see *Table 3*). These observations are in excellent agreement with the high degrees of betainisation previously reported for DMAEMA homopolymers by Lowe *et al.*[34]. These workers used aqueous g.p.c. to confirm that the narrow molecular weight distributions of the precursor DMAEMA homopolymers were retained in the final polysulfobetaines. Unfortunately, due to the hydrophobicity of the *n*-butyl methacrylate-rich copolymers, this technique was not suitable in the present study. However, with the exception of the 1,4-butanesultone reagent, we have used similarly mild conditions for betainisation; thus side reactions such as chain scission or cross-linking etc. are unlikely and the final derivatised copolymers are believed to retain the narrow molecular weight distributions of the precursor copolymers.

Quantitative analysis of the carboxybetaine copolymers by proton n.m.r. spectroscopy proved problematic. A new peak at $\delta = 2.4$ in the n.m.r. spectrum of a carboxybetaine statistical block copolymer containing 30 mol% DMAEMA residues was assigned to the methylene group protons adjacent to the carboxylic acid group. Comparison of this integral to that of the $-OCH_2-$ protons of the DMAEMA residues at $\delta = 4.4$ indicated that complete betainisation had occurred, but the experimental uncertainties in both integrals were rather large due to overlapping integrals.

Cationic block and statistical copolymers were obtained by quaternisation of the tertiary amine groups in the DMAEMA residues using iodomethane under mild conditions. For the DMAEMA homopolymers derivatised with substoichiometric amounts of iodomethane, the degrees of quaternisation (see *Table 4*) were calculated using ^{1}H n.m.r. spectroscopy by comparing the quaternary trimethylamino group proton signal ($\delta = 3.2$–3.4 in DMSO-d_6) to that of the unquaternised dimethylamino group protons ($\delta = 2.2$–2.3). The latter signal was absent when a stoichiometric amount of iodomethane was used, which is consistent with complete quaternisation of the DMAEMA residues. Similarly, quantitiative quaternisation was achieved with the *n*BuMA-DMAEMA copolymers. In this case, the $-OCH_2-$ protons due to the *n*BuMA residues ($\delta = 4.0$ in DMSO-d_6 or DMF-d_7) were compared to the trimethylamino group protons ($\delta = 3.2$ or $\delta = 3.5$).

Table 5 Degrees of carboxybetainisation of acrylic acid-derivatised DMAEMA copolymers as estimated by ^{1}H n.m.r. spectroscopy

Copolymer[a]	*n*BuMA content of copolymer (mol%)	Calculated degree of betainisation (mol%)	Actual degree of betainisation by ^{1}H n.m.r. (mol%)[b]
*n*BuMA-*stat*-DMAEMA	90.0	10.0	> 9.5
*n*BuMA-*stat*-DMAEMA	70.0	30.0	> 28.5
*n*BuMA-*b*-DMAEMA	90.0	10.0	> 9.5
*n*BuMA-*b*-DMAEMA	70.0	30.0	> 28.5

[a] All yields were quantitative

[b] Complete betainisation was indicated by ^{1}H n.m.r. specroscopy; however, experimental uncertainties are rather large due to overlapping integrals

CONCLUSIONS

Well-defined, near-monodisperse block and statistical copolymers of *n*-butyl methacrylate with either benzyl methacrylate or 2-(dimethylamino)ethyl methacrylate have been synthesised using GTP. The BzMA-containing copolymers can be selectively deprotected by catalytic hydrogenolysis to obtain the corresponding methacrylic acid copolymers. Complete deprotection was verified using proton n.m.r. spectroscopy. The DMAEMA-based copolymers were readily betainised using 1,3-propanesultone under mild conditions. Betainisation was also achieved using the less reactive 1,4-butanesultone, albeit under more aggressive conditions. Both proton n.m.r. spectroscopy and C, H, N and S elemental microanalyses indicated quantitative betainisation in all copolymers. Carboxybetainisation was also achieved via Michael addition using an excess of acrylic acid. In this case copolymer purification proved rather tedious and accurate degrees of betainisation were difficult to determine by proton n.m.r. spectroscopy due to overlapping signals (see *Table 5*). Very high degrees of quaternisation of the DMAEMA-based copolymers were obtained using iodomethane under relatively mild conditions.

In summary, facile synthetic routes have been developed for the preparation of ionomeric methacrylate block and statistical copolymers. Applications of these novel materials are currently being explored.

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REFERENCES

1. Sogah, D. Y., Hertler, W. R., Webster, O. W. and Cohen, G. M., *Macromolecules*, 1988, **20**, 1473.
2. Webster, O. W., Hertler, W. R., Sogah, D. Y., Farnham, W. B. and Rajanbabu, T. V., *J. Am. Chem. Soc.*, 1983, **105**, 5706.
3. Webster, O. W., *Macromol. Chem. Macromol. Symp.*, 1993, **67**, 365.
4. Quirk, R. P. and Bidinger, G., *Polym. Bull.*, 1989, **22**, 63.
5. Jenkins, A. D., *Eur. Polym. J.*, 1991, **27**(7), 649.
6. Zou, Y. S., Lan, T., Dai, L. Z., Lin, G. L. and Pan, R. H., *Polymer*, 1996, **37**(5), 875.
7. Catalgil, H. and Jenkins, A. D., *Eur. Polym. J.*, 1991, **27**(7), 651.
8. Choi, W. J., Lim, K. T., Kwon, S. K. and Choi, S. K., *Polym. Bull.*, 1993, **30**(4), 401.
9. Masar, B., Vlcek, P., Kriz, J. and Kovarova, J., *Macromol. Chem. Phys.*, 1994, **195**(1), 289.
10. Spinelli, H. J., *Prog. Org. Coatings*, 1996, **27**(1-4), 255.
11. Takacs, A. and Faust, R., *J. Macromol. Sci.-Pure Appl. Chem.*, 1996, **A33**(2), 117.
12. Jenkins, A. D., Tsartolia, E., Walton, D. R. M., Horskajenkins, J., Kratochvil, P. and Stejskal, J., *Macromol. Chem. Macromol. Chem. Phys.*, 1990, **191**(10), 2511.
13. Simms, J. A., *Rubber Chem. Technol.*, 1991, **64**, 139.
14. Zhu, Z., Rider, J., Yang, C. Y., Gilmartin, M. E. and Wnek, G. E., *Macromolecules*, 1992, **25**, 7330.
15. Efstratiadis, V., Tselikas, G., Hadjichristidis, N., Li, J., Yunan, W. and Mays, J. W., *Polym. Int.*, 1994, **33**, 171.
16. West, M. W. J., US Patent No. 4 755 563, 1988.
17. Dicker, I. B., Hertler, W. R. and Ma, S.-H., US Patent No. 5 219 945, 1993.
18. Ma, S.-H., Dicker, I. B. and Hertler, W. R., Eur. Patent No. 0 556 649 A1, 1993.
19. Patrickios, C. S., Hertler, W. R., Abbott, N. L. and Hatton, T. A., *Macromolecules*, 1994, **27**, 930.
20. Al-Lami, H. S., Billingham, N. C. and Calvert, P. D., *Chem. Mater.*, 1992, **4**, 1200.
21. Rannard, S. P., D.Phil. Thesis, University of Sussex, UK, 1993.
22. Baines, F. L., Dionisio, S., Billingham, N. C. and Armes, S. P., *Macromolecules*, 1996, **29**, 3096.
23. Gabor, A. H., Pruette, L. C. and Ober, C. K., *Chem. Mater.*, 1996, **8**(9), 2282.
24. Gabor, A. H. and Ober, C. K., *Chem. Mater.*, 1996, **8**(9), 2272.
25. Baines, F. L., Billingham, N. C. and Armes, S. P., *Macromolecules*, 1996, **29**, 3416.
26. Hoad O., D.Phil. Thesis, University of Sussex, UK, 1993.
27. Asami, R., Kondo, Y. and Takaki, M., *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, 1986, **27**(1), 186.
28. Öncül-Koç, A. and Catalgil-Giz, H., *Macromol. Chem. Phys.*, 1995, **196**, 2475.
29. Catalgil-Giz, H., Uyanik, H. and Erbil, C., *Polymer*, 1992, **33**(3), 655.
30. Al-Lami, H. S., D.Phil. Thesis, University of Sussex, UK, 1989.
31. Rannard, S. P., Billingham, N. C., Armes, S. P. and Mykytiuk, J., *Eur. Polym. J.*, 1993, **29**(2/3), 407.
32. Lowe, A. B., D.Phil. Thesis, University of Sussex, 1997.
33. Mykytiuk, J., Armes, S. P. and Billingham, N. C., *Polym. Bull.*, 1992, **29**, 139.
34. Lowe, A. B., Billingham, N. C. and Armes, S. P., *Chem. Commun.*, 1996, 1555.
35. Lowe, A. B., Billingham, N. C. and Armes, S. P., *Macromolecules*, 1997, in preparation.
36. Tuzar, Z., Pospišil, H., Pleštil, J., Lowe, A. B., Baines, F. L., Billingham, N. C. and Armes, S. P., *Macromolecules*, 1997, **30**, 2509.
37. Gao, Z. S., Desjardins, A. and Eisenberg, A., *J. Polym. Sci., Polym. Phys. Ed.*, 1991, **29**(12), 1559.
38. Zhu, J. Y., Eisenberg, A. and Lennox, R. B., *J. Am. Chem. Soc.*, 1991, **113**(15), 5583.
39. Hird, B. and Eisenberg, A., *Macromolecules*, 1992, **25**(24), 5774.
40. Gronowski, A. A., Jiang, M., Yeager, H. L., Wu, G. and Eisenberg, A., *J. Membr. Sci.*, 1993, **82**(1-2), 83.
41. Barboiu, V., Streba, E., Luca, C. and Simionescu, C. I., *J. Polym. Sci., Polym. Chem. Ed.*, 1995, **33**, 389.
42. Dicker, I. B., Farnham, W. B., Hertler, W. R., Laganis, E. D., Sogah, D. Y., Del Pesco, T. W. and Fitzgerald, P. H., US Patent No. 4 588 795, 1986.