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Synthesis and characterisation of novel methyl methacrylate-2-(dimethylamino)ethyl methacrylate copolymer salts containing polymerisable anions

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Abstract

A series of copolymers containing different ratios of methyl methacrylate and 2-(dimethylamino)ethyl methacrylate has been synthesised by conventional free radical polymerisation. These copolymers have been converted into a series of novel salts by reaction with the acid monomers, methacrylic acid, methacryloyloxyethyl phosphate and vinyl phosphonic acid. The copolymers and the corresponding salts have been characterised fully by a range of spectroscopic and thermal analysis techniques. The nature of the salt has a characteristic effect on the thermal degradation of the polymer. The presence of the phosphorus monomers leads to formation of residual char, even at temperatures as high as 1000 °C.

Keywords: Methacrylate copolymer; Free radical polymerisation; Monomeric salts

1. Introduction

Methacrylate polymers are among the most important commercial polymers, with a very wide range of applications in products as diverse as glazing, lighting housings, bath tubs and structural adhesives. The success of these polymers in many of the applications is dependent on the versatility of the acrylic monomers in copolymerising to produce a wide diversity of structures, which can be tailored to produce the desired properties. Of particular interest is the synthesis of copolymers with specific functionality, which can act as a locus for further reactions, or furnish the copolymer with specific chemical and/or physical characteristics. A system which has been studied extensively involves copolymers based on 2-(dimethylamino)ethyl methacrylate (DMAEMA) and methacrylates such as methyl methacrylate (MMA) [1–11].

The basic character of the tertiary amino side chain in MMA-DMAEMA copolymers has inevitably led to studies of the acid–base behaviour of the polymers using, for example, pH titration [1,2]. Efimova et al. [1] have studied the acid–base properties of both monomeric and polymeric DMAEMA salts in aqueous and aqueous-ethanolic conditions. Monomeric and polymeric salts of DMAEMA were made by reaction with the acids HCl, HNO_3, H_2SO_4 or H_3PO_4. The ionisation constants of the monomeric and polymeric ammonium salts were calculated and, from this, the electrostatic free energies of ionisation, ΔG_{el}. The structural features of the anions (size, element, e.g. carbon or phosphorus) were observed to have a significant effect on the ionisation constants and ΔG_{el} of the salts. It was also noted that the ionisation constants for the monomers and polymers were reduced in an aqueous environment compared to an aqueous-ethanolic environment.

pH titrations of copolymers containing MMA, DMAEMA and methacrylic acid (MA) units have been analysed by Patrickios et al. [2], who characterised colloidal polyampholytes over varying pH, polymer concentration and salt type. The authors concluded that both the attractive and repulsive forces, which oppose precipitation of the copolymer in solution, are pH dependent, especially between blocks of oppositely charged moieties. Studies of the compatibility of blends of poly[styrene-*co*-(cinnamic acid)] with poly[(ethyl methacrylate)-*co*-(2-(dimethylamino) ethyl methacrylate)], PSCA/PEMADEA, by Bouslah et al.

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[3] showed that as the amount of PEMADEA within the blend increased, the band at 1703 cm^{-1}, attributed to acid dimerisation of the PSCA, decreased.

We were interested in the possibility of synthesising salts by reaction of the copolymers with a range of acidic monomers, in particular MA and the phosphorus monomers, methacryloyloxyethyl phosphate (MOEP) and vinyl phosphonic acid (VPA). These salts are of interest as speciality adhesive systems. To date, no studies have been reported of the formation of salts from reaction of MMA-DMAEMA copolymers with acidic monomers. Monomers based on phosphorus acids are known for their adhesion promoting qualities [12,13], while some recent publications have illustrated the versatility offered by MOEP and VPA polymers [14–18]. For example, MOEP has been used as a functional monomer in molecular imprinting [14], while VPA homopolymer forms biocompatible composites with calcium phosphates [15,16]. VPA copolymers have also found use as pervaporation membranes [17].

In this paper, the synthesis of MMA-DMAEMA copolymers and their corresponding salts is described, along with their characterisation by nuclear magnetic resonance (NMR) and Fourier transform infra-red (FTIR) spectroscopy and thermal analysis techniques.

2. Experimental

Glassware was dried overnight at 70 °C and cooled in a desiccator before assembly. The monomers MMA (Aldrich) and DMAEMA (Aldrich) were distilled before use. MOEP was donated by Lord Corporation (USA). Other monomers were standard laboratory reagents and used as received. 2,2′-Azo*bis*(2-methylpropionitrile) (AIBN; Aldrich) was used as received. Solvents were standard laboratory grade and used as received.

2.1. Synthesis of methyl methacrylate and 2-(dimethylamino) ethyl methacrylate copolymers (P[MMA-DMAEMA])

A typical synthesis of poly[MMA-DMAEMA] copolymer is as follows. All other copolymerisations were carried out in a similar way, varying the monomer ratios. The molar ratios of MMA:DMAEMA used were ca. 100:0, 80:20, 70:30, 60:40 and 50:50 Actual copolymer ratios were determined post-synthesis using ^{1}H NMR spectroscopy (Table 1).

2,2′-Azo*bis*(2-methylpropionitrile) (0.049 g, 0.30 mmol, 0.0012 mol%) was dissolved in ethanol (20 ml) in a three neck round bottom flask fitted with condenser, thermometer and rubber septum. The solution was stirred continuously at 200 rpm and this remained constant for the duration of the reaction. Methyl methacrylate (2.6 ml, 2.44 g, 24 mmol) and 2-(dimethylamino)ethyl methacrylate (4.2 ml, 3.92 g, 25 mmol) were injected into the flask via a septum stoppered neck. The solution was degassed with nitrogen

Table 1
Typical theoretical and actual monomer ratios calculated from ^{1}H NMR spectra of P[MMA-DMAEMA] copolymer with varying monomer ratios

Copolymer	Theoretical MMA:DMAEMA ratio	Actual MMA:DMAEMA ratio
JE8020	80:20	76.2:23.8
JE7030	70:30	73.7:26.3
JE6040	60:40	61.4:38.6
JE5050	50:50	52.6:47.4

for 10 min and the reaction flask was heated in an oil bath until the internal solution temperature of the flask was 70 °C. The reaction was stirred for 24 hours at this temperature. The polymer solution was concentrated on a rotary evaporator to remove excess ethanol and the resulting product was dissolved in dichloromethane and pipetted into rapidly stirred petroleum ether (60–80 °C), forming a white precipitate. The solvent was decanted and the precipitate purified by dissolving in dichloromethane (30 ml) and re-precipitated by pipetting the solution into petroleum ether (60–80 °C) (300 ml). The solvent was again decanted and the solid dried overnight in a desiccator under vacuum at room temperature. Yield = 5.09 g; 97%.

The polymerisation reactions were subsequently scaled up, using total monomer quantities of ca. 250 mmol.

2.2. Synthesis of salts using P[MMA-DMAEMA] and acid monomers

The experiment below describes the acid–base reaction (salt formation) between P[MMA-DMAEMA] (50:50) and MOEP. The same method was followed for the synthesis of each salt using the four different copolymers with only the quantities of the monomer being altered.

Poly[methyl methacrylate-*co*-*N*,*N*-2-(dimethylamino) ethyl methacrylate] (2.00 g, 18.14 mmol) was dissolved in dichloromethane/ethanol (50:50 v/v) (15 ml) and was constantly stirred at 200 rpm. MOEP (1.960 g, 9.32 mmol) was dissolved in dichloromethane/ethanol (50:50 v/v) (15 ml). The solution containing the monomer was pipetted into the copolymer solution and the solution was stirred for 2 h at room temperature, at no greater than 30 °C. The dichloromethane and ethanol solvents were removed by rotary evaporation, with the water bath temperature no greater than 40 °C. The salt was dried overnight at room temperature over phosphorus pentoxide, under vacuum. The crude product was dissolved in distilled water (30 ml), then the solution was vacuum filtered through a sinter funnel containing Celite®. Unreacted copolymer and unreacted MOEP were easily removed from the salt solution by filtration, as they are insoluble in water. The solution was freeze-dried for 2 days and a very fine white powder was produced.

Salts were formed in a similar way between P[MMA-DMAEMA] and MA, but in this case, the work up was

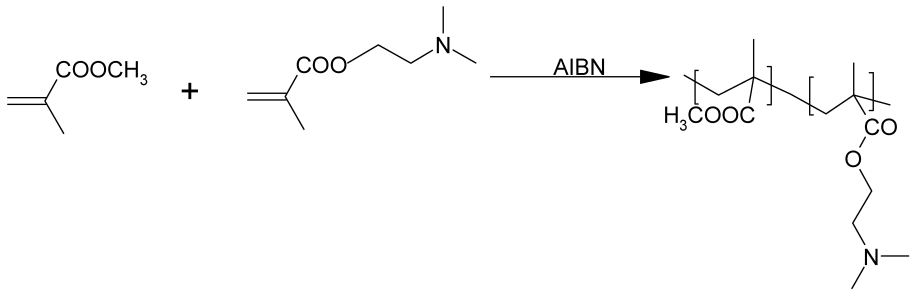

Fig. 1. Reaction scheme of the free radical initiated copolymerisation of methyl methacrylate and *N*,*N*-2-(dimethylamino)ethyl methacrylate.

modified. Purification of the salt was achieved by suspending the salt in hexane (200 ml). A mechanical high-speed stirrer (Ultraturrax) was used to break the salt into small particles to release any impurities or unreacted MA. The salt was insoluble in hexane while the monomer was soluble. Additional hexane was added, as necessary, due to solvent evaporation caused by the heat generated by the high-speed mechanical stirrer. The solvent was decanted and the salt was dried overnight at room temperature over phosphorus pentoxide under vacuum. A similar purification method was used for the salts formed between VPA and P[MMA-DMAEMA].

2.3. Characterisation methods

All samples were analysed by ^{1}H NMR spectroscopy using a Jeol GHX-270 spectrometer operating at 270 MHz, at 21 °C. Samples were analysed using three different types of solvents, depending on the solubility of the copolymer and the three types of salts: copolymers and P[MMA-DMAEMA]$^+$[MA]$^-$ salts in $CDCl_3$ with tetramethylsilane (TMS) as internal reference; P[MMA-DMAEMA]$^+$[VPA]$^-$ salts in CD_3OD with TMS as internal reference; P[MMA-DMAEMA]$^+$[MOEP]$^-$ salts in D_2O with no internal reference.

FTIR Spectroscopy was performed using a Perkin–Elmer System 2000 Fourier transform infrared spectrometer, with a resolution of 4 cm^{-1}. The samples were analysed as KBr discs, pressed for 15 minutes under a constant pressure of 9 ton.

Elemental analyses (C, H, N) were carried out using a Leeman CE440 Elemental Analyser.

Gel permeation chromatography (GPC) was carried out using a PL-GEL Mixed-D 5 μm 60 mm long column, a Waters 510 Pump and a ERMA ERC-7510 RI detector. The solvent was THF, with a flow rate of 1.0 ml min^{-1}. Molar masses are quoted against polystyrene standards (EasiCAl PS-2).

Modulated differential scanning calorimetry (MDSC) was performed using a TA Instruments 2920 MDSC instrument. Powdered samples (7–11 mg, except in the case of the MOEP salts, where ca. 2–5 mg were used) were analysed in unsealed aluminium pans, under an inert atmosphere of nitrogen (flow rate 40 ml min^{-1}), at a ramp rate of 3 K min^{-1}.

Powdered samples (ca. 1.5–11 mg, depending on the physical form of the sample) were analysed by thermogravimetric (TG) analysis, using a Perkin–Elmer Thermogravimetric Analyser 7. The copolymers and salts were heated at a rate of 10 K min^{-1} from 30 to 600 °C, under nitrogen (flow rate 40 ml min^{-1}), and 100 K min^{-1} from 600 to 1000 °C under air (flow rate 40 ml min^{-1}) for the salts. The heating rate was modified to 50 K min^{-1} from 600 to 1000 °C for VPA and MOEP salts, due to the presence of phosphorus within the samples, which caused side reactions and created degradation by-products during the analysis.

3. Results and discussion

The rationale behind the work reported here was the desire to synthesise novel methacrylate copolymer salt systems with potential applications as new high performance adhesives. For this reason, work was concentrated on MMA-rich copolymers (maximum DMAEMA content of 50 mol.%) as greater proportions of salt were expected to adversely affect the compatibility with, and adhesion properties of, the final adhesive formulation. The adhesion performance of the salt products will be reported elsewhere.

3.1. Copolymer synthesis and characterisation

A range of MMA-DMAEMA copolymers was synthesised successfully by free radical polymerisation using AIBN as the initiator. The copolymerisation reaction is represented in Fig. 1. Radical copolymerisations involving MMA and DMAEMA have been studied previously [10,11] and the results obtained here are consistent with earlier findings. The NMR and GPC results indicate successful copolymerisation of MMA and DMAEMA at all monomer ratios.

The ratio of the two monomers present in the polymer was determined from the ^{1}H NMR spectra by comparison of the integrals attributed to the N-$(CH_3)_2$ group of the DMAEMA side chain, and the CH_3O group from the MMA side chain (Fig. 2) [11]. Typical theoretical and actual

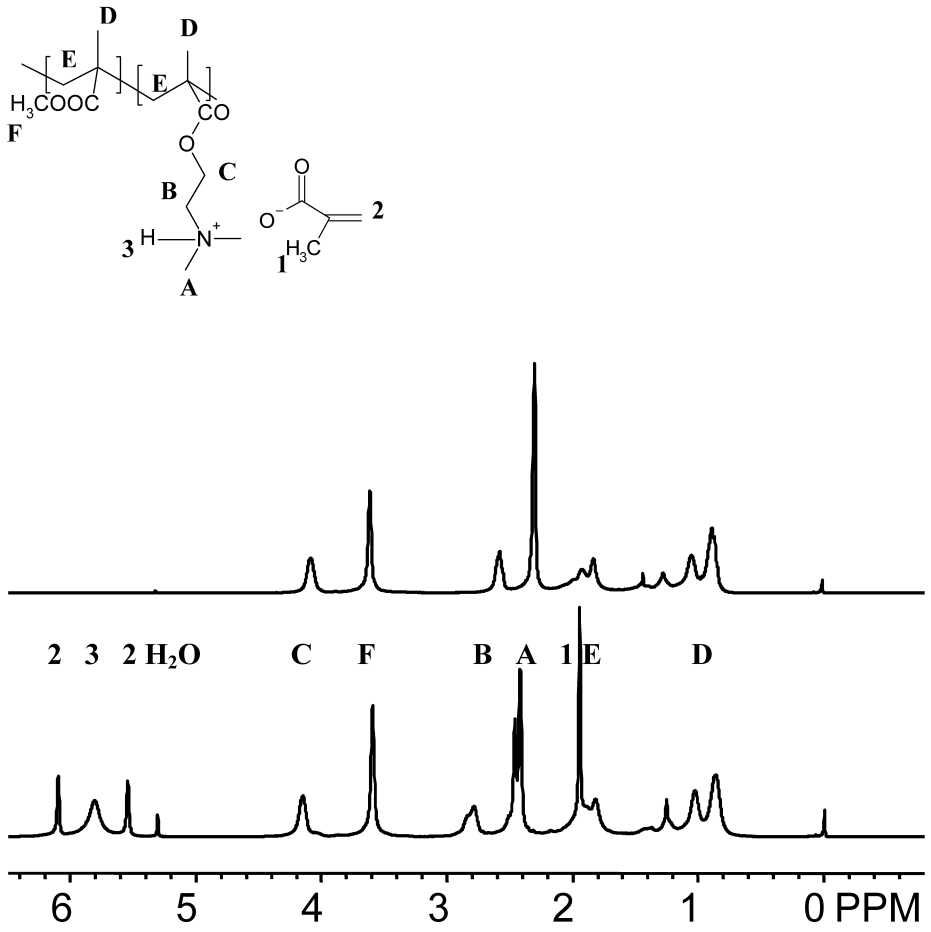

Fig. 2. ^{1}H NMR spectrum of [top] P[MMA-DMAEMA] (50:50), and [bottom] P[MMA-DMAEMA]$^{+}$[MA]$^{-}$ (50:50) in $CDCl_3$.

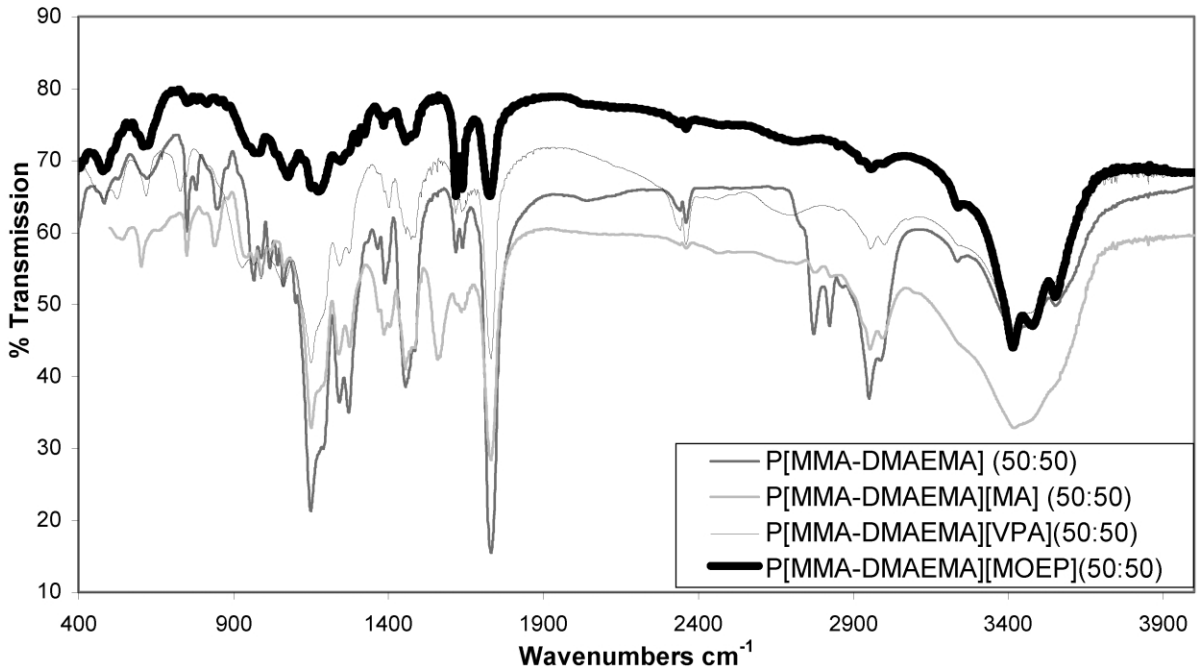

Fig. 3. FTIR spectra of an MMA-DMAEMA copolymer and representative salts.

Table 2
GPC data on P[MMA-DMAEMA] copolymers with varying monomer ratios

Sample number/name	Monomer molar ratio (MMA:DMAEMA)	Retention time (min)	M_n (g mol^{-1})	M_w (g mol^{-1})	Polydispersity
1 PMMA	100:0	13.62	24100	34100	1.41
2	50:50	13.72	13800	23400	1.69
3	60:40	14.25	8800	14700	1.67
4	70:30	13.50	15400	30600	1.99
5	80:20	13.55	14900	30200	2.03
6 JE8020	80:20	14.71	6900	10800	1.57
7 JE7030	70:30	13.08	17000	38500	2.26
8 JE6040	60:40	13.82	10200	21300	2.08
9 JE5050	50:50	13.83	12800	21100	1.64

M_n = number average molar mass of the polymer; M_w = weight average molar mass of the polymer; polydispersity = M_w/M_n.

copolymer compositions are given in Table 1. The polymers have been systematically named according to the theoretical monomer ratio, rather than the actual calculated ratio. The spectra clearly show chemical shifts arising from the methyl groups at δ 0.86–1.27, and methylene group at δ 1.7–2.1, resulting from the tacticity of the polymers, with syndiotactic dominating, as expected [10,11]. The FTIR spectra for the four copolymers were essentially identical (Fig. 3). An absorption band at 3418–3419 cm^{-1}, indicative of an O–H stretching vibration, could be due to hydrogen bonding interactions with atmospheric water. The absorption bands at 1731–32 cm^{-1} indicate the presence of the ester carbonyl. A good correlation was observed between the theoretical CHN values and the experimental values, reflecting the precision of the determination of the DMAEMA content by ^{1}H NMR spectroscopy.

The GPC data are tabulated in Table 2, samples 2–5 being the products of small scale synthesis, while samples 6–9 are produced by scale-up. Only one well-defined peak is observable in each case, suggesting that no homopolymerisation of the monomers had occurred. The GPC data showed a random variation in the chain lengths of the copolymers. Compared to PMMA, all copolymers exhibited lower molar mass values and higher polydispersities. Scaling up of the copolymer synthesis produced changes in M_n and M_w, JE5050 and JE8020 both having lower M_n and M_w for the scaled up products compared to the original reactions. Conversely, JE6040 and JE7030 had higher M_n and M_w values for the scale-up reactions. This was also translated into changes in the polydispersity of the copolymers.

3.2. Salt synthesis and characterisation

In the synthesis of the salts (e.g. Fig. 4), the amount of acidic monomer required was determined using the ratio of MMA to DMAEMA calculated by ^{1}H NMR spectroscopy and a 1:1 stoichiometric ratio of DMAEMA to acid monomer. This does not take into consideration amino side chains which are unavailable for protonation owing to

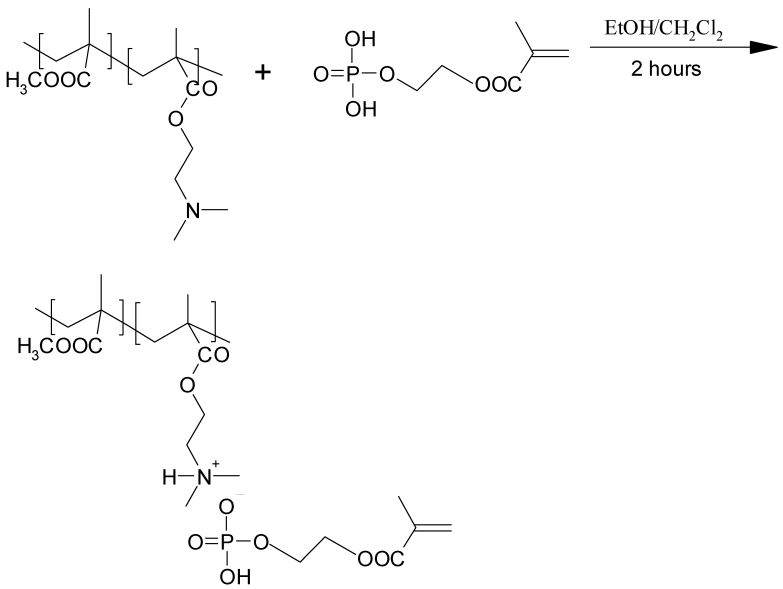

Fig. 4. Reaction scheme for formation of the salt between poly[methyl methacrylate-*co*-*N*,*N*,-2-(dimethylamino)ethyl methacrylate] and methacryloyloxyethyl phosphate.

Table 3
Composition of salts made from P[MMA-DMAEMA] copolymers and acid monomers, determined by ^{1}H NMR spectroscopy

Sample	Acid monomer (mol.%)	MMA (mol.%)	DMAEMA (mol.%)	Mol.% protonation [molar ratio of acid:DMAEMA]
MA5050	29	39	32	91
MA6040	25	46	29	86
MA7030	19	58	23	83
MA8020	19	61	20	95
VPA5050	44	28	28	157
VPA6040	34	43	23	148
VPA7030	32	56	12	267
VPA8020	25	53	22	114
MOEP5050				101
MOEP6040				88
MOEP8020				45

steric hindrance of the amino group. Intramolecular interactions could inhibit the acid–base reaction between the side chains and the acidic monomer, through cyclisation of the tertiary amino side chain, as highlighted by Prádný et al. [6–8]. Other studies of DMAEMA polymers have shown that the amine groups can also be readily quaternised using methylating agents such as methyl iodide [19,20], although the reactivity is dependent on the polarity of the solvent [19].

Salt yields (assuming 100% protonation) ranged from 25 to 55% (MOEP salts), 31 to 61% (MA salts) and 53 to 74% (VPA salts). The MOEP salt readily dissolved in water, while the unreacted MOEP monomer and unreacted (or partially reacted) copolymer separated out of solution, allowing easy purification. Note that it is unlikely that entirely unreacted copolymer remains in the product, but individual polymer chains are likely to show varying degrees of protonation. The MOEP method could not be used for the salts containing MA and VPA because both monomers are soluble in water. Hexane was used to dissolve unreacted monomer.

A typical ^{1}H NMR spectrum of a salt is shown in Fig. 2, for P[MMA-DMAEMA]$^+$[MA]$^-$ (50:50), together with the spectrum of the corresponding copolymer. This shows clearly resonances for the copolymer and the MA monomer. Evidence for salt formation was provided by the presence of a broad N–H$^+$ peak. A trend of increasing upfield shift was observed for the N–H$^+$ peak with a decrease in the amount of MA and the corresponding molar ratio of DMAE-MA:MMA. The N–H$^+$ shift is caused by a decrease in the deshielding of the amino side chain as the degree of protonation by the acid monomer decreased. Similar shifts were not observed for the VPA salts. JEMA6040 was the exception to the trend where a shift downfield of δ 0.86 to δ 6.65 was observed. The precise reason for this is unknown. A noticeable downfield shift of the resonances due to protons **A** and **B** occurs on protonation and is consistent with the deshielding which occurs on protonating the nitrogen atom. No N–H$^+$ resonance could be observed for the MOEP salts, since these were dissolved in D_2O, which would exchange with the protons.

The NMR spectra permit the composition of the salts to be determined by comparing the relative ratios of the integrals for the protons identified as **2**, **A** and **F** in Fig. 2 (Table 3). In the case of the MOEP salts, the region around δ 3.6, where the signals for the **F** protons are found, is too complex to allow accurate integration and so only the ratio of anions to cationic side chains is given. In most cases, the data show degrees of protonation approaching 100%; however, the data for the VPA salts suggest well in excess of quantitative incorporation of the VPA. This may arise from hydrogen bonding of unreacted VPA within the salt, although it is unclear why this should occur with VPA but not, for example, MOEP. No evidence is observed from the NMR spectra for the presence of excess VPA monomer, but this may be a consequence of rapid exchange of ionised and unionised VPA species. In the case of MOEP salts, clear integrals could not be obtained for MOEP7030, while MOEP8020 shows a relatively low degree of protonation.

Typical IR spectra of the salts are shown in Fig. 3. The methyl C–H stretch at 2953–2958 cm^{-1} shifted to lower frequency from JE5050 to JE8020 for both the MOEP and VPA salts. This was not observed for the copolymers or the MA salts. The spectra of the VPA salts showed absorptions at 2685–2664 cm^{-1}, which were not observed for any other salt or copolymer. This absorption decreased in frequency from 2685 cm^{-1} (50:50) to 2664 cm^{-1} (80:20). This could be due to either $\equiv$NH$^+$ or phosphonate or both [21]. The presence of H-bonded monomer, suggested by NMR spectroscopy, could also contribute to this absorption. The absorption at 1558 cm^{-1} was only observed for the salts and was not seen in the spectra of the monomers or copolymers. This band is due to N–H$^+$, and confirms salt formation. The C–N tertiary bend at 1310–1360 cm^{-1} was seen in the copolymer spectra, but disappeared in the spectra of the salts. The MOEP salts have an absorption at 1176 cm^{-1} (PO$^-$), a single absorption at 1299 cm^{-1} (P=O), and a P–O–C absorption at ca. 1075 cm^{-1}. This last absorption was not observed for the VPA and MA salts. The spectrum of

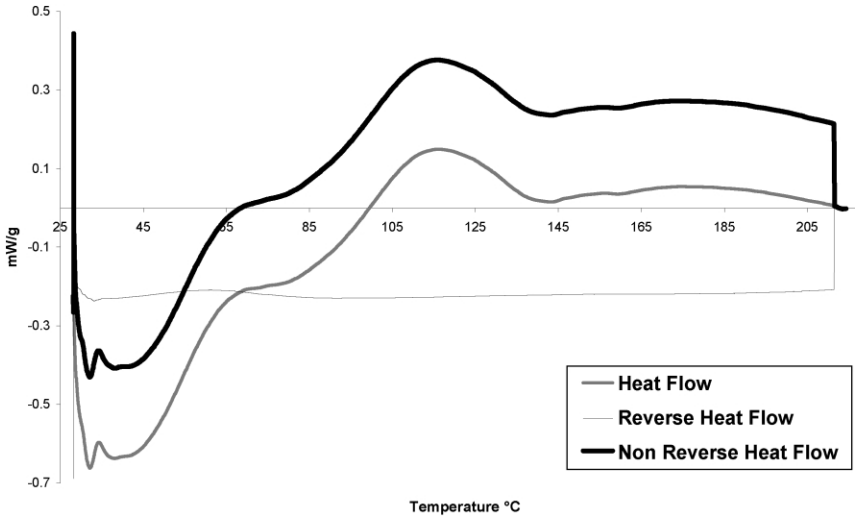

Fig. 5. MDSC thermogram of P[MMA-DMAEMA]$^{+}$[MOEP]$^{-}$ (50:50).

P[MMA-DMAEMA]$^{+}$[MOEP]$^{-}$ (70:30) has two unique peaks at 1843 cm^{-1} and 1778 cm^{-1}, which are not observable for the other MOEP salts. The peaks are indicative of hydrogen bonding interactions, either P=O···HO–P or C=O···HO–P, or combinations thereof, similar to the peaks observed by Tretinnikov et al. [22].

The CHN results for the MA salts showed a fair correlation between the theoretical and experimental results, in line with the near-quantitative salt formation observed by NMR spectroscopy. A greater deviation from the calculated values was observed for both the VPA and the MOEP salts. This could result from non-stoichiometric salt formation in the case of the VPA and MOEP systems, as noted from the NMR results. There may also be an effect on stoichiometry of phosphate diester impurities present in the MOEP.

3.3. Thermal analysis of the salts

Modulated differential scanning calorimetry (MDSC) was performed on the salts. Fig. 5 shows the MDSC thermogram of P[MMA-DMAEMA]$^{+}$[MOEP]$^{-}$ (50:50), illustrating the complexity of the salt thermal behaviour. A large initial endotherm is followed by an exotherm in the overall heat flow curve. The endotherm is possibly a result of loss of hydrogen-bonded water molecules, while the exotherm around 110–115 °C may result from thermally initiated polymerisation of the MOEP double bond. The reversing heat flow shows a small inflection, which can be tentatively assigned to the T_g, at 72 °C. Difficulties in determining the glass transition temperature in quaternised polymer systems have been noted previously [20,23]. Allen et al. [20] found little effect of copolymer composition on the T_g values of quaternised isobutene–DMAEMA copolymer networks. Zhou et al. [23] observed that the glass transition temperature of the polyvinylphosphonic acid, PVPA–polyvinylpyridine, PVP, complex was suppressed by the electrostatic interactions between the two molecules. Tentative T_g values for each of the synthesised salts have been assigned in Table 4. The MA salts show a decreasing trend in T_g as the MMA content increases (i.e. as the proportion of salt decreases). The salts containing the phosphorus-containing monomers, VPA and MOEP, follow different trends. The T_g of the VPA system increases with an increase in MMA and a decrease in anionic monomer. This indicates that the amount of VPA in the salt is directly related to a reduction in the T_g of the salts, perhaps *via* a plasticisation effect on the matrix. This may also be influenced by the presence of hydrogen-bonded monomer, as noted above. The T_g values for the MOEP salts follow a more random pattern, allowing no definite conclusions to be drawn.

Thermogravimetic (TG) analysis was used to characterise the copolymers and salts, to assess the thermo-oxidative stability of the samples and determine whether the samples contained any residual solvents. The degradation of poly(methyl methacrylate), PMMA, has been studied by Kashiwagi et al. [24], Manring et al. [25–27] and summarised by Wilkie et al. [28], the main process being unzipping of the polymer backbone, initiated by various

Table 4
MDSC T_g assignments for the P[MMA-DMAEMA] copolymer salts

Sample	T_g (°C)	Energy (J g^{-1})
JEMA5050	107	0.17
JEMA6040	95	0.12
JEMA7030	55	0.20
JEMA8020	64	0.21
JEVPA5050	55	0.01
JEVPA6040	58	0.15
JEVPA7030	82 (162)	0.14 (0.04)
JEVPA8020	94	0.13
JEMOEP5050	72	0.14
JEMOEP6040	65 (103)	0.06 (<0.01)
JEMOEP7030	82	0.08
JEMOEP8020	75	0.19

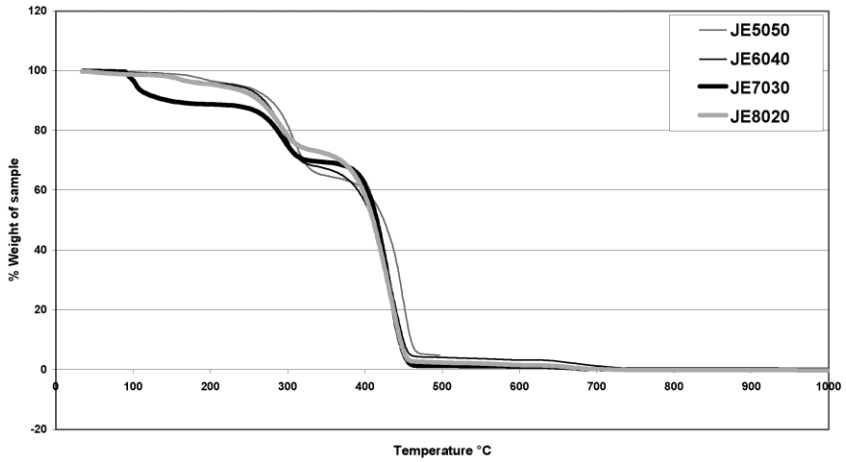

Fig. 6. Thermogravimetric degradation curves for P[MMA-DMAEMA], of varying monomer ratios.

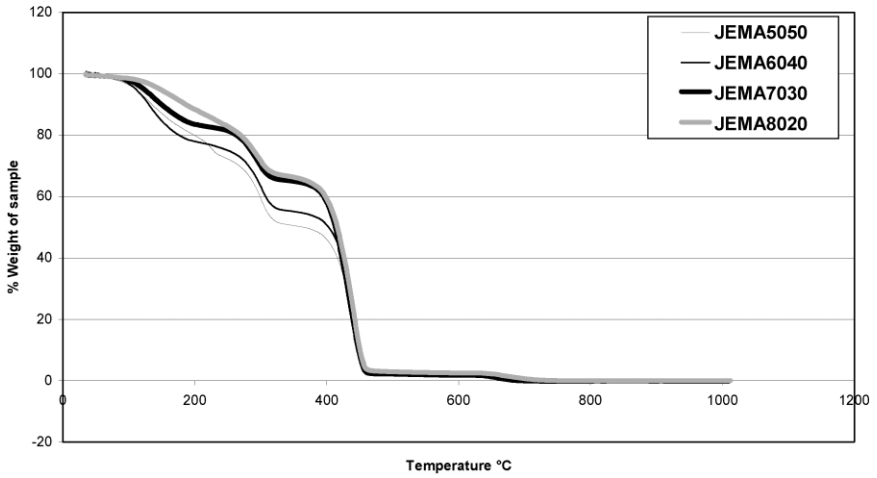

Fig. 7. Thermogravimetric degradation curves for P[MMA-DMAEMA]$^{+}$[MA]$^{-}$.

Table 5
Percentage weight loss from P[MMA-DMAEMA] samples during heating under a nitrogen atmosphere

Sample	% Weight loss solvent transition 45–98 °C	% Weight loss first transition 103–186 to 298–313 °C	% Weight loss second transition 298–313 to 450–460 °C
JE5050	3.4	32.1	59.0
JE6040	3.1	38.9	63.0
JE7030	11.4	19.4	67.6
JE8020	4.5	22.9	69.7

Table 6
Percentage weight loss of P[MMA-DMAEMA]$^{+}$[MA]$^{-}$ samples during each transition, on heating under a nitrogen atmosphere

Sample	% Weight loss first transition 70 to 205 °C	% Weight loss shoulder transition 205 to 254 °C	% MA (calc.)	% Weight loss second transition 210–226 to 345–358 °C	% Weight loss third transition 345–358 to 471–480 °C
JEMA5050	19.0	8.8	29	21.0	47.8
JEMA6040	23.2		25	21.3	30.7
JEMA7030	16.2		19	17.7	62.2
JEMA8020	15.4		19	17.7	63.6

calc. = calculated from NMR spectroscopy.

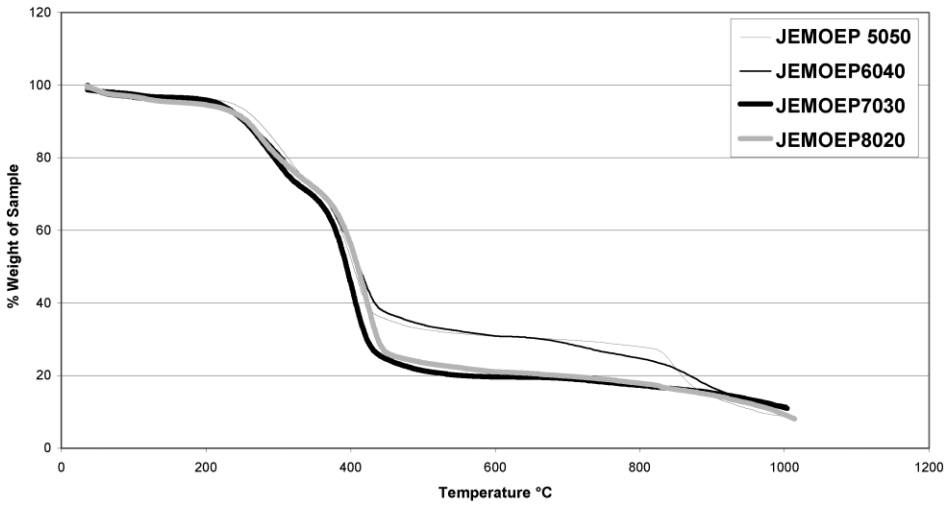

Fig. 8. Thermogravimetric degradation curves for P[MMA-DMAEMA]$^{+}$[MOEP]$^{-}$.

events including cleavage of the methoxycarbonyl side chain [27]. The TG degradation curves for the copolymers are shown in Fig. 6 and the results tabulated in Table 5. The initial weight loss from the P[MMA-DMAEMA] is probably due to the release of solvent trapped within the copolymer. The weight loss found in the first major transition is possibly due to loss of a vinylamine fragment by cleavage of the *N*,*N*-2-(dimethylamino)ethyl side chain. The weight loss during the second transition may occur via cleavage of the remnants of the DMAEMA side chains and some of the MMA side-chains, leaving the copolymer backbone to degrade almost totally by radical unzipping, as suggested by Manring [27] for the degradation of PMMA. A tiny residual weight loss may be due to some char, which is finally degraded at higher temperatures.

The TG degradation curves are shown for P[MMA-DMAEMA]$^{+}$[MA]$^{-}$ in Fig. 7 and tabulated in Table 6. The first transition partially mirrors the percentage MA monomer present within the salt (Table 3), which is indicative of the loss of the monomer on heating. The first transition has a shoulder between 205 and 254 °C for JEMA5050, perhaps demonstrating the presence of different methacrylic acid environments in this polymer containing a high proportion of salt. The second transition is attributed to loss of the DMAEMA side chain, as noted for the copolymers, but occurring at a higher temperature in the salts. This is supported by the results of Yan et al. [29] on the TG analysis of the cationic copolymers, poly[butylacrylate-*co*-3-(methacryloylamino)-propyltrimethylammonium chloride], P[BA-MAPTAC], where they attributed a transition from 230 to 360 °C to the thermal degradation of the MAPTAC content. The third transition is very sharp for the four salts and is very similar in shape to the final transition in the degradation of the copolymers. The almost complete weight loss observed is attributed to the ultimate unzipping of the chain. As above, a small residual weight loss is observed.

The four MOEP salts (Fig. 8, Table 7) showed three very distinct weight loss regimes. There is an initial weight loss (2–4%) assumed to be due to H-bonded water, followed by three major regions of weight loss. The first of these occurs over an identical temperature range to the second transition observed for P[MMA-DMAEMA]$^{+}$[MA]$^{-}$ and may also be due to DMAEMA side chain degradation. In this case, however, initial loss of the phosphate monomer appears not to have occurred (see below). The second major weight loss also occurs over an identical temperature range to the final degradative unzipping observed for P[MMA-DMAEMA]$^{+}$[MA]$^{-}$. This weight loss is greater for those polymers containing the higher proportions of MMA, indicating that degradation of MMA-rich chains and segments is more favourable than for those segments associated with the phosphate monomer. In contrast to P[MMA-DMAEMA]$^{+}$[MA]$^{-}$ where the polymer is completely degraded above 700 °C, in this case a significant proportion of the polymer remains intact at this temperature and even at 1000 °C, ca. 10% of the original mass remains.

Table 7
Percentage weight loss of P[MMA-DMAEMA]$^{+}$[MOEP]$^{-}$ samples during each transition, on heating

Sample	% Weight loss solvent transition 64–79 to 123–131 °C	% Weight loss first transition 213–220 to 350–357 °C	% Weight loss second transition 350–357 to 470–483 °C	% Weight loss third transition 600–1000 °C
JEMOEP 5050	2.5	25.4	41.1	22.4
JEMOEP 6040	2.9	18.7	46.1	13.6
JEMOEP 7030	2.1	23.1	53.8	8.4
JEMOEP 8020	3.8	22.0	52.4	11.5

If the exotherm seen in the DSC trace of the MOEP salts is indeed caused by polymerisation of the phosphate monomer, the phosphorus species are trapped and can undergo (and catalyse) condensed phase degradation reactions at elevated temperatures. This leads to formation of the observed black char, which is thought to be due to the formation of phosphines and phosphine oxides, as demonstrated by Jiang et al. [30], who studied the degradation of polymeric phosphonic acids using TG analysis coupled to a FTIR spectrometer.

The general shapes of the degradation curves for the VPA salts are similar to those observed for the MOEP salts, but with some differences in the details of the weight losses found. The major transitions occur over broadly similar temperature ranges to those of the MOEP salts, although the residue remaining at 1000 °C is usually lower for the VPA salts. The first major transition occurs in the temperature range where degradation of the DMAEMA side-chain is expected [29]. Total weight loss is not achieved by 1000 °C for any of the four VPA salts, probably due to the presence of residual phosphines and phosphine oxides.

4. Conclusions

Synthesis of the copolymers, P[MMA-DMAEMA], and formation of their salts with three different acid monomers was undertaken successfully, as evidenced by FTIR spectroscopy, ^{1}H NMR spectroscopy (which also gave the stoichiometric ratio of the monomers in the products, in most cases), GPC and elemental analysis. Thermal analysis of the salts using MDSC showed some trends in the T_g values, although masking of the T_g by the ionic bonding made interpretation difficult. TG analysis of the copolymers and salts produced distinctive degradation curves, which were characteristic of the type of polymer under investigation. The weight losses showed a dependency on the monomer ratio in the copolymer. The salts containing phosphorus did not fully decompose by 1000 °C and a black char remained. This was attributed to the formation of phosphines and phosphine oxides *via* degradation catalysed by the phosphorus acids.

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References

[1] Efimova DY, Shilbalovich VG, Nikolaev AF, Tribo EN. Russian J Appl Chem 1998;71:1432–6.
[2] Patrickios CS, Sharma LR, Armes SP, Billingham NC. Langmuir 1999;15:1613–20.
[3] Bouslah N, Hammachin R, Amrani F. Macromol Chem Phys 1999; 200(4):678–82.
[4] Triftaridou AI, Vamvakaki M, Patrickios CS. Polymer 2002;43(10): 2921–6.
[5] Triftaridou AI, Hadjiyannakou SC, Vamvakaki M, Patrickios CS. Macromolecules 2002;35(7):2506–13.
[6] Prádný M, Ševcik S. Makromol Chem 1985;186:111–21.
[7] Prádný M, Ševcik S. Makromol Chem 1987;188:227–38.
[8] Prádný M, Ševcik S. Makromol Chem 1987;188:2875–83.
[9] Webber GB, Wanless EJ, Armes SP, Baines FL, Biggs S. Langmuir 2001;17:5551–61.
[10] Wen S, Yin X, Stevenson WKT. J Appl Polym Sci 1991;43:205–12.
[11] Camail M, Essaoudi H, Margaillan A, Vernet JL. Eur Polym J 1995; 31:1119–25.
[12] Ando H, Nakahara M, Yamamoto M, Itoh K. Langmuir 1996;12: 6399–403.
[13] Priola A, Gozzelino G, Ferraro F, Scarrone PG. Polym Paint Colour J 1987;177:408–14.
[14] Kugimiya A, Kuwada Y, Takeuchi T. J Chromatograph A 2001;938: 131–5.
[15] Greish YE, Brown PW. J Mater Sci Mater Med 2001;12:407–11.
[16] Greish YE, Brown PW. Biomaterials 2001;22:807–16.
[17] Park CH, Nam SY, Lee YM. J Appl Polym Sci 1999;74:83–9.
[18] Kato K, Eika Y, Ikada Y. J Biomed Mater Res 1996;32:687–91.
[19] Prádný M, Ševcik S. Makromol Chem 1985;186:1657–63.
[20] Allen AJ, Kennedy JP. Des Monomers Polym 1999;2:29–52.
[21] Williams DH, Fleming I. Spectroscopic methods in organic chemistry, 4th ed. London: McGraw-Hill; 1989.
[22] Tretinnikov ON, Ikada Y. Macromolecules 1997;30:1086–90.
[23] Zhou X, Goh SH, Lee SY, Tan KL. Polymer 1997;38:5333–8.
[24] Kashiwagi T, Inabi A. Polym Degrad Stabil 1989;26:161–84.
[25] Manring LE. Macromolecules 1991;24:3304–9.
[26] Manring LE, Sogah DY, Cohen GM. Macromolecules 1989;22: 4652–4.
[27] Manring LE. Macromolecules 1989;22:2673–7.
[28] Wilkie CA. Polym Degrad Stabil 1999;66:301–6.
[29] Yan Z, Yulin D, Zhang D, Yang CQ. J Polym Sci, Part A: Polym Chem 2001;39:1031–9.
[30] Jiang DD, Yao Q, McKinney MA, Wilkie CA. Polym Degrad Stabil 1999;63:423–34.