Poly(sulphopropylbetaines):
1. Synthesis and characterization

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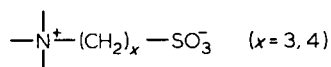Centre de Recherches sur les Macromolécules (CNRS), 6 rue Boussingault, 67083 Strasbourg, France
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The synthesis of aromatic and aliphatic poly(sulphopropylbetaines) is described within the series of vinylpyridines and tertiary amino-methacrylates. Two complementary strategies were used: (a) preparation and free radical polymerization in aqueous solution (60°C, 4,4'-azobiscyanovaleric acid) of the monomers; (b) heterogeneous quaternization of preformed poly(vinylpyridines) and poly(tertiary amino-methacrylates) by 1,3-propanesultone in propylene carbonate or tetramethylene sulphone solution (120°C). The high molecular weight poly(zwitterions) ($10^5 < \bar{M}_w < 5 \times 10^6$) were characterized by ultra-violet and ^1H nuclear magnetic resonance spectroscopy, and their water affinity at 20°C was estimated by water vapour absorption measurements.

Keywords Aliphatic and aromatic poly(sulphopropylbetaines); synthesis and characterization

INTRODUCTION

One of the major drawbacks of the use of high molecular weight hydrolysed polyacrylamides in enhanced oil recovery is the drastic decrease of the viscosity of their aqueous solutions when increasing the ionic strength, especially in the case of divalent cations[1]. For instance, concentrations of about 10^{-2} mol l^{-1} in $CaCl_2$ induce phase separation for dilute aqueous solutions ($4 g l^{-1}$) of such copolymers ($M_w \simeq 4 \times 10^6$, 29 wt% of potassium acrylate units)[2]. Such a general trend may be reasonably expected for any anionic polyelectrolyte[3], with only minor modulation due to the chemical structure of the polymeric chains and to the nature of the salts. In quite the opposite way, poly(zwitterions) of the sulphobetaine type,

$$-\overset{|}{\underset{|}{N^+}}-(CH_2)_x-SO_3^- \quad (x = 3, 4)$$

show improved solubility and greater chain expansion when increasing the salt concentration of their aqueous solutions, even in the presence of divalent cations[4]. A brief survey of literature[5-7] shows that sulphobetaine monomers were most often considered as functional monomers[8,9] used as minor components for copolymers in various fields, such as synthetic textile fibres, hydrophilic and charged dispersing agents and protective colloids, and so on. In spite of their potential versatility and of their emergence 25 years ago[10], the preparation and the characterization of sulphobetaine homopolymers has been scarcely detailed[8], especially in the vinylimidazole series[11]. We report in this investigation the major features of the synthesis and the characterization of aromatic and aliphatic poly(sulphopropylbetaines) within the two more easily accessible series of vinylpyridines and tertiary amino-methacrylates. Two complementary strategies were involved: (a) preparation and consecutive free radical polymerization of the zwitterionic monomers, and (b) quaternization of preformed tertiary amino polymers by 1,3-propanesultone.

EXPERIMENTAL

Solvent, monomer and reagent purification

After convenient drying and purification treatments according to literature[12] (see below), solvents were directly distilled and stored under argon and over 4 or 3 Å molecular sieves in Schlenk vessels. Benzene and tetrahydrofuran (THF) were distilled from the corresponding disodium-benzophenone dianion solutions; tetramethylene sulphone (TMSO$_2$), propylene carbonate (PGC) and ethylacetate were distilled over CaH$_2$; acetonitrile (ACN) was twice distilled over CaH$_2$ and then over P$_2$O$_5$; 2-vinylpyridine (2VP), 2-methyl-5-vinylpyridine (SM5VP), 4-vinylpyridine (4VP) and dimethylamino-ethylmethacrylate (DMAEMA) were vacuum distilled over CaH$_2$ just before use; 2-(2-diethylaminoethoxy)-ethanol (DEAEE) and 1,3-propanesultone (PS) were purified by vacuum distillation; 4,4'-azobis-4-cyano-valeric acid (ACVA) was recrystallized according to a literature procedure[13].

General experimental device for the various syntheses and polymerizations

Most experiments were carried out under a slight pressure of argon in an all-Pyrex glass double-wall reactor (temperature monitored by external thermostat regulated to ±0.1°C) fitted with a magnetic or mechanical stirrer, and allowing the use of vacuum and argon sweeping cycles. Solvents and reagents may be introduced under argon from Schlenck vessels, or through self-sealing rubber caps using a syringe technique.

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Synthesis of the sulphopropylbetaine monomers

Diethylaminoethoxyethylmethacrylate. First, 17 g (0.35 moles) of NaH (50% by weight in paraffin) are washed twice with benzene and put in suspension in 200 ml of benzene. Under continuous stirring, 51.4 ml (0.30 moles) of freshly distilled DEAEE are added dropwise with external cooling in order to avoid temperatures higher than 30°C. At the end of the addition, the suspension is heated at 50°C until hydrogen evolution stops (about 2 h). Then 0.1 g of 1,3-dinitrobenzene is added to the reaction mixture, which is cooled to 10°C. Following this, 30.9 ml (0.31 moles) of methacryloyl chloride are added dropwise at such a rate that the temperature never exceeds 20°C. At this stage, gelation of the reaction medium may take place in spite of the continuous stirring. The mixture is left overnight at room temperature. After separation of NaCl by centrifugation, the solvent and the benzene washings of the NaCl are stripped off by rotary evaporation, and the residual yellow mixture is distilled under vacuum. The desired monomer is recovered as the last fraction and its purity checked by gas chromatography. Yield = 80%. 1H n.m.r. (neat liquid) δ 5.75 and 5.20 (2s, 2H, CH_2=); 3.95 (t, 2H, $COOCH_2$); 3.30 (m, 4H, CH_2OCH_2); 2.25 (m, 6H, $N(CH_2)_3$); 1.65 (s, 3H, CH_3—C=); 0.70 (t, 6H, $N(CH_2$—$CH_3)_2$). Anal. calc. for $C_{12}H_{23}O_3N$: C, 62.94%; H, 10.10%; N, 6.10%. Found: C, 63.04%; H, 10.25%; N, 6.12%.

General procedure

PS (0.11 mole) is added to a solution of 0.1 mole of a given monomer in a selected solvent in the presence of 6×10^{-4} mole of 1,3-dinitrobenzene. The medium is heated at a constant temperature T for a given time t under continuous stirring. The zwitterionic monomers are recovered as a precipitate (except for monomer V) by filtration, thoroughly washed with acetone and dried under vacuum at 50°C. In all cases, the absence of residual inhibitor was checked by thin-layer chromatography (t.l.c.): Merck silica gel 60 F_{254}, methanol as eluant. Analytical samples may be obtained by recrystallization from absolute ethanol or methanol–ethanol mixtures, but with drastic losses. The quoted yields are related to the crude monomers.

2-Vinyl-1-(3-sulphopropyl)pyridinium hydroxide inner salt (I). Solvent: PGC, T = 80°C, t = 7 days, yield = 90%, m.p. = 237.5–238.5°C. N.m.r. (D_2O) δ 8.60–7.80 (m, 4H, C_5H_4N); 7.40–6.00 (m, 3H, CH_2=CH); 4.70 (t, 2H, $^+NCH_2$); 2.95 (t, 2H, $CH_2SO_3^-$); 2.30 (m, 2H, $^+NCH_2CH_2$). Anal. calc. for $C_{10}H_{13}O_3NS$: C, 52.85%; H, 5.76%; O, 21.11%; N, 6.16%; S, 14.10%. Found: C, 53.14%; H, 5.92%; O, 20.90%; N, 6.13%; S, 14.14%.

2-Methyl-5-vinyl-1-(3-sulphopropyl)pyridinium hydroxide inner salt (II). Solvent: ACN, T = 75°C, t = 68 h, yield = 87%, m.p. = 280.9–286.3°C, basicity equiv. $(-SO_3^-)$ = 0.992. N.m.r. (D_2O) δ 8.50–7.20 (m, 3H, C_5H_3N); 6.90–5.30 (m, 3H, CH_2=CH); 4.50 (t, 2H, $^+NCH_2$); 2.90 (t, 2H, $CH_2SO_3^-$); 2.70 (s, 3H, $C_5H_3NCH_3$); 2.20 (m, 2H, $^+NCH_2 - CH_2$). Anal. calc. for $C_{11}H_{15}O_3NS$: C, 54.75%; H, 6.26%; O, 19.89%; N, 5.80%; S, 13.29%. Found: C, 54.64%; H, 6.30%; O, 20.24%; N, 5.73%; S, 13.67%.

4-Vinyl-1-(3-sulphopropyl)pyridinium hydroxide inner salt (III). Solvent: C_6H_6, T = 77°C, t = 20 h, yield = 89%,

m.p. = 250.8–255.4°C. N.m.r. (D_2O) δ 8.70–7.50 (m, 4H, C_5H_4N); 7.10–5.50 (m, 3H, CH_2=CH); 4.50 (t, 2H, $^+NCH_2$); 2.85 (t, 2H, $CH_2SO_3^-$); 2.30 (m, 2H, $^+NCH_2-CH_2$). Anal. calc. for $C_{10}H_{13}O_3NS$: C, 52.85%; H, 5.76%; O, 21.11%; N, 6.16%; S, 14.10%. Found: C, 51.89%; H, 6.01%; O, 21.65%; N, 6.27%; S, 14.02%.

Dimethyl-(2-methacryloxyethyl)-1-(3-sulphopropyl) ammonium hydroxide inner salt (IV). This was prepared according to the literature[9]. Basicity equiv. $(-SO_3^-)$ = 0.985. N.m.r. $(D_2O)\delta6.05$ (s, 1H, CH_2=C—CH_3); 5.70 (s, 1H, CH_2=C—CH_3); 4.55 (m, 2H, $COOCH_2$); 3.7 (m, 2H, $COOCH_2$—CH_2); 3.45 (m, 2H, $^+NCH_2(CH_2)_2$—SO_3^-): 3.1 (s, 6H, $^+N(CH_3)_2$); 2.9 (t, 2H, $CH_2SO_3^-$); 2.3 (m, 2H, CH_2—$CH_2SO_3^-$); 1.85 (s, 3H, CH_2=C—CH_3). Anal. calc. for $C_{11}H_{21}O_5NS$: C, 47.29%; H, 7.57%; O, 28.63%; N, 5.01%; S, 11.48%. Found: C, 47.08%; H, 7.48%; O, 28.78%; N, 5.53%; S, 11.66%.

Diethyl-(2-methacryloyloxyethoxy-2-ethyl)-1-(3-sulphopropyl) ammonium hydroxide inner salt (V). Solvent: ACN, T=78°C, t = 16.5 h. After rotary evaporation of the solvent under vacuum, the residual oil was triturated and crystallized in methylacetate. Yield = 87%, m.p. = 135.0–137.1°C. N.m.r. (D_2O), see text. Anal. calc. for $C_{15}H_{29}O_6NS$: C, 51.26%; H, 8.31%; O, 27.31%; N, 3.98%; S, 9.12%. Found: C, 51.30%; H, 8.41%; O, 27.67%; N, 3.84%; S, 9.23%.

Free radical polymerization of the sulphopropylbetaine monomers (I to V)

Polymerizations were carried out at 60°C in triply distilled water degassed by previous boiling and cooling under argon atmosphere, in the presence of ACVA as initiator. The concentrations of monomer and initiator, the polymerization time and yields are given in *Tables 1* and *2*. In all cases the reaction medium (homogeneous or heterogeneous) is precipitated into a large excess of

Table 1 Free radical polymerization of the vinylpyridine–sulphopropylbetaine monomers[a]

Run	$[I] \times 10^3$ (mol l^{-1})	$[M]$ (mol l^{-1})	Time (h)	Yield (%)	$\bar{M}_w \times 10^{-5}$
I-1	2.20	0.44	24	30.0[b]	0.520
I-2	4.82	0.49	18	40.0[b]	0.530
I-3	19.0	0.49	18	54.5[b]	0.343
I-4	7.50	1.50	19	42.0[b]	0.910
I-5[d]	7.52	1.50	19	41.4[b]	0.783
I-6[e]	7.56	1.87	24	21.6[b]	0.700
I-7	0.30	3.20	21.5	16.4[b]	0.380
I-8[f]	redox	2.27	4	9.0[b]	0.200
II-1	2.14	0.50	24	49.0[c]	1.33
II-2	1.07	0.99	24	24.7[c]	1.60
II-3[d]	1.05	0.99	24	21.6[b]	3.14
II-4[d]	0.27	0.99	24	13.6[b]	3.74
II-5[g]	2.20	0.50	24	12.0[b]	0.345
III-1	7.50	1.50	19	75.0[c]	27.6

[a] All polymerizations were carried out in water solution at 60°C unless otherwise specified
[b] Homogeneous polymerization
[c] Heterogeneous polymerization
[d] Sodium salt of 4,4-azobis-4-cyanovaleric acid as initiator
[e] Polymerization at 50°C
[f] Redox initiation: $[KClO_3]$ = 1×10^{-2} mol l^{-1}, $[NaHSO_3]$ = 1×10^{-1} mol l^{-1}
[g] Polymerization in formamide solution

Table 2 Free radical polymerization of the sulphopropylbetaine methacrylates[a]

Run	[I] × 10³ (mol l⁻¹)	[M] (mol l⁻¹)	Time (h)	Yield (%)	$\bar{M}_W \times 10^{-6}$
IV-1[d]	4.20	0.716	18	95[c]	2.62
IV-2	10.20	0.511	18	96[b]	6.15
V-1[e]	7.50	1.50	19	[b]	1.15
V-2	3.0	0.60	19	76.5[b]	6.23
V-3	5.0	0.50	19	79.6[b]	5.00

[a] All polymerizations were carried out in water solution at 60°C unless otherwise specified
[b] Homogeneous polymerization
[c] Heterogeneous polymerization
[d] Polymerization solvent: 5 vol. DMAC + 2 vol. CH₃OH
[e] Polymerization solvent: DMSO

Figure 1 ¹H n.m.r. spectrum of poly(III) in D₂O–NaCl 0.6 M at 80°C

methanol, a good solvent of the monomers; the polymer recovered by filtration is thoroughly washed twice with methanol in a Waring blender, and finally dried under vacuum at 60°C. The lack of any residual monomer was checked by t.l.c. as previously described.

Poly(I). Anal. calc. for $C_{10}H_{13}O_3NS$: C, 52.85%; H, 5.76%; O, 21.11%; N, 6.16%; S, 14.10%. Found: C, 53.01%; H, 5.68%; O, 20.81%; N, 6.10%; S, 13.04%. N.m.r. (D₂O) δ 9.20–7.40 (m, 4H, C_5NH_4); 4.55 (s, 2H, $^+NCH_2$); 3.90–1.00 (m, 7H, $(CH_2CH + CH_2SO_3^- + {}^+NCH_2-\underline{CH}_2)$).

Poly(II). Anal. calc. for $C_{11}H_{15}O_3NS$: C, 54.75%; H, 6.26%; O, 19.89%; N, 5.80%; S, 13.29%. Found: C, 54.66%; H, 6.07%; O, 19.80%; N, 5.70%; S, 13.80%. N.m.r. (D₂O) δ 8.70–7.50 (2s, 3H, C_5H_3N); 4.60 (s, 2H, $^+NCH_2$); 3.25–2.55 (2s, 5H, $(CH_2SO_3^- + C_5H_3N\underline{CH}_3)$); 2.55–1.58 (2s, 5H, $(CH_2CH + {}^+NCH_2-\underline{CH}_2)$).

Poly(III). Anal. calc. for $C_{10}H_{13}O_3NS$: C, 52.85%; H, 5.76%; O, 21.11%; N, 6.16%; S, 14.10%. Found: C, 52.37%; H, 5.63%; O, 21.10%; N, 6.20%; S, 14.10%. N.m.r. (D₂O), see *Figure 1*.

Poly(IV). Anal. calc. for $C_{11}H_{21}O_5NS$: C, 47.3%; H, 7.57%; O, 28.63%; N, 5.01%; S, 11.48%. Found: C, 47.01%; H, 7.48%; O, 28.43%; N, 5.24%; S, 11.51%. N.m.r. (D₂O) δ 4.54 (s, 2H, COOCH₂); 4.00–3.47 (m, 4H, (OCH₂— CH₂⁺N + ⁺NCH₂(CH₂)₂SO₃⁻)); 3.26 (s, 6H, N(CH₃)₂); 3.00 (t, 2H, CH₂SO₃⁻); 2.60–1.71 (m, 4H, (CH₃—C—CH₂ + NCH₂—CH₂)); 1.49–0.72 (m, 3H, CH₃ - -C - -CH₂).

Poly(V). Anal. calc. for $C_{15}H_{29}O_6NS$: C, 51.26%; H, 8.31%; O, 27.31%; N, 3.98%; S, 9.12%. Found: C, 51.48%; H, 8.27%; O, 27.57%; N, 3.75%; S, 9.12%. N.m.r. (D₂O), see *Figure 2*.

Synthesis of tertiary amine containing polymers

These polymeric precursors were prepared according to classical methods as follows.

Poly(2-vinylpyridine). THF/diphenylmethylsodium, −70°C, 1 h: yield = 100%, $\bar{M}_w = 4.95 \times 10^4$.

Poly(2-methyl-5-vinylpyridine). [2M5VP] = 3 mol l⁻¹, [AIBN] = 1 × 10⁻³ mol l⁻¹, dioxane, 60°C, 70 h: yield = 16%, $\bar{M}_w = 1.02 \times 10^5$.
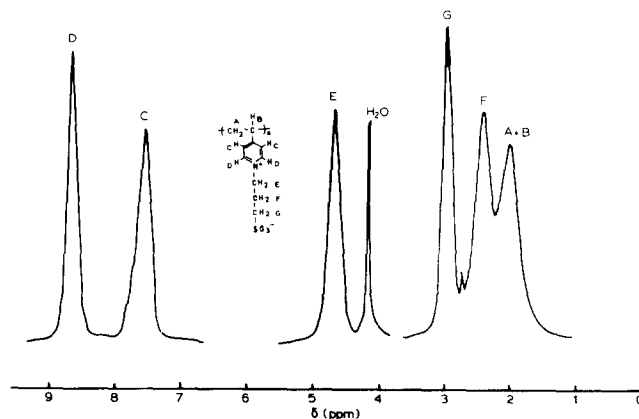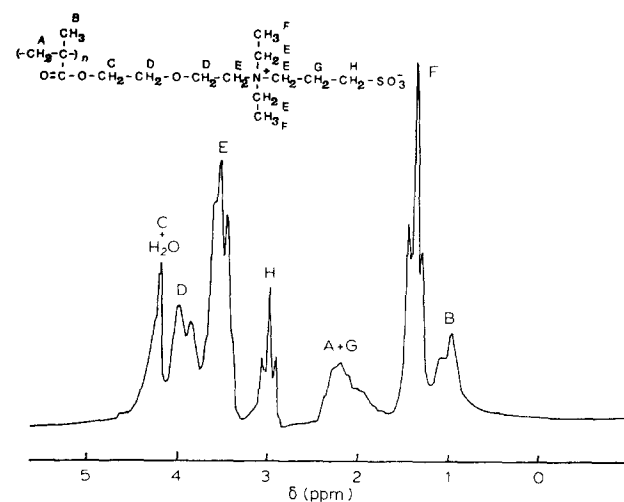

Figure 2 ¹H n.m.r. spectrum of poly(V) in D₂O–NaCl 0.6 M at 80°C

Poly(4-vinylpyridine). [4VP] = 2 mol l⁻¹, [AIBN] = 4 × 10⁻² mol l⁻¹, MeOH, 60°C, 72 h: yield = 77%; $\bar{M}_w = 7.23 \times 10^5$.

Poly(2-dimethylaminoethylmethacrylate). [M] = 1.5 mol l⁻¹, [AIBN] = 1.5 × 10⁻² mol l⁻¹, benzene, 60°C, 21 h: yield = 81%, $\bar{M}_w = 1.19 \times 10^5$.

Poly[2-(2-diethylaminoethoxy)ethylmethacrylate]. [M] = 1 mol l⁻¹, [AIBN] = 5 × 10⁻³ mol l⁻¹, benzene, 60°C, 17 h: yield = 44%, $\bar{M}_w = 1.37 \times 10^5$.

Quaternization of tertiary amine containing polymers

Quaternizations were carried out at 120°C in PGC or TMSO₂, eventually in the presence of (Bu)₄N⁺SO₄H⁻, using a stoichiometric ratio of [PS]/[amine] = 1.1. In all cases the heterogeneous medium was precipitated into a large excess of acetone: the polymer recovered by filtration was thoroughly washed with acetone in a Waring blender, and finally dried under vacuum at 60°C. See *Table 3* for detailed experimental conditions and polymer characterization.

Physical measurements

¹H n.m.r. spectroscopy. Spectra of low molecular weight reagents were recorded at 30°C on a 60 MHz Hitachi–Perkin Elmer R-24 A apparatus. Spectra of po-

Table 3 Quaternization of poly(vinyl pyridines) and poly(dimethylaminoethylmethacrylate) by 1,3-propanesultone at 120°C

Polymeric precursor	Solvent	Quaternization degree			$k_i \times 10^3$ (l mol s^{-1})	$k_f \times 10^5$ (l mol s^{-1})
		First cloud point[a]	$t = 18$ h	$t = 24$ h		
P2VP	TMSO$_2$	0.52 (18)	0.62	0.65	1.1	0.93
0.774 mol l^{-1}	PGC	0.37 (13)	0.50	0.53	0.86	0.69
	PGC + salt[b]	0.42 (3)	0.71	0.76	4.6	2.8
P2PV[c]	PGC			0.42		
P2M5VP	PGC	0.68 (1)	0.79	0.81	42	2.6
0.692 mol l^{-1}	PGC + salt[b]	0.69 (1)	1.0		44	
P4VP	PGC	0.71 (<1)	0.85	0.88	>43	4.6
0.774 mol l^{-1}	PGC + salt[b]	0.95 (<1)	1.0		>220	
PDMAEMA						
0.495 mol l^{-1}	PGC	0.92 (<1)	1.0		>240	

[a] The time at the first cloud point is quoted in minutes within brackets
[b] $[(n\text{-}Bu)_4N^+HSO_4^-]$/[amine group] = 1.5
[c] 1,4-Butanesultone as quaternizing reagent

lymers were recorded at 80°C on a 90 MHz Brucker spectrometer, using 5–10% by weight solution in 0.6 M NaCl–D$_2$O. In all cases the chemical shifts were measured with respect to hexamethyl-disiloxane as external reference (δ ppm).

U.v. spectrometry. All the measurements were carried out in trifluorethanol solution either on a Beckman Acta V or a Shimadzu UV-240 spectrometer.

Molecular weight measurements. The refractive index increments were measured at room temperature on a Brice-Phoenix BP-10004 differential refractometer fitted with a neon laser beam, $\lambda = 6320$ Å: dn/dc (ml g^{-1}) = 0.254, 0.250, 0.157 and 0.163 for P2VP, P2M5VP, PDMAEMA and PDEAEEMA in CH$_3$OH respectively; dn/dc (ml g^{-1}) = 0.153 for P4VP in DMF; dn/dc (ml g^{-1}) = 0.185, 0.187, 0.187, 0.0713 and 0.146 for poly(I), (II), (III), (IV) and (V) in H$_2$O–NaCl 1 M respectively. Light scattering experiments were performed at 25°C on a Fica PGD 420.0 M apparatus, at the same wavelength.

Potentiometric measurements. Potentiometric measurements were carried out on an automatic Mettler device (DK-11 and DK-14) fitted with a joint calomel–glass electrode Metrohm EA 121-H. Titration of residual pyridine or tertiary amino units in the polymers was performed according to a modification of a literature procedure[14]: titrating reagent, HClO$_4$ in CH$_3$CO$_2$H; solvent, HCO$_2$H:(CH$_3$CO)$_2$O 4:3 by volume; titration of the sulphopropylbetaine function, see text.
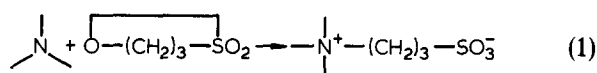
Water absorption measurements. The water uptake at 20°C from the gas phase by finely powdered polymers was determined after equilibration of the samples to constant weight ($\simeq$ 2–3 days) in closed desiccators where the water vapour pressure was controlled using various saturated salt solutions in the presence of a large excess of salt[15]. Relative humidity: 90.7, 79.5, 63 and 47 for Na$_2$CO$_3$.10H$_2$O, NH$_4$Cl, NH$_4$NO$_3$ and KSCN at 20°C. The reproducibility was generally better than ±8%.
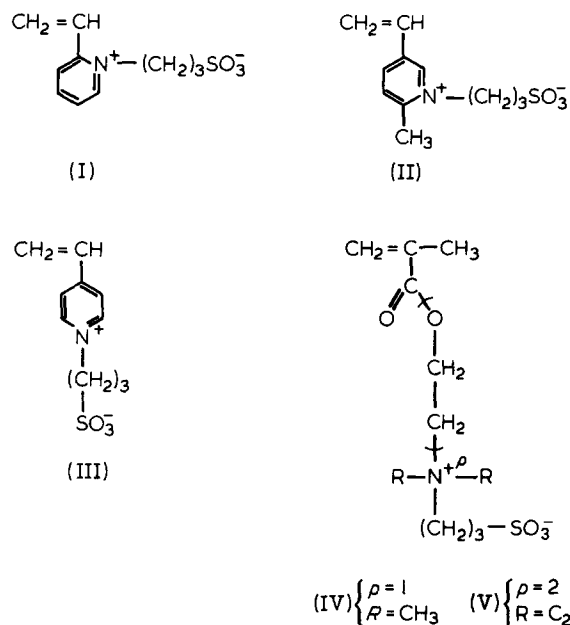
RESULTS AND DISCUSSION

Monomer synthesis and characterization

It rests upon the quaternization of tertiary amines by

1,3-propanesultone (PS) according to the general scheme[16]:

$$\ce{N + O-(CH2)3-SO2 -> N+-(CH2)3-SO3-} \quad (1)$$

We transposed this reaction to the three isomeric vinylpyridines and to two tertiary aminomethacrylates to obtain the corresponding vinylic and methacrylic sulphopropylbetaines (I) to (V):
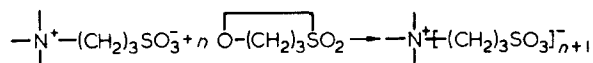

(I)   (II)

(III)

(IV) $\begin{cases} \rho = 1 \\ R = CH_3 \end{cases}$ (V) $\begin{cases} \rho = 2 \\ R = C_2H_5 \end{cases}$

Most quaternizations were performed at 75°C, using a stoichiometric ratio [PS]/[amine] = 1.1, in aprotic solvents of various polarity (C$_6$H$_6$, Ac$_2$OEt, ACN, PGC) where the sulphopropylbetaines are insoluble: see experimental section. These straightforward syntheses may suggest the following comments:

(a) In the presence of *m*-dinitrobenzene or phenothiazine as free radical polymerization inhibitors, yields greater than 85% are currently obtained.
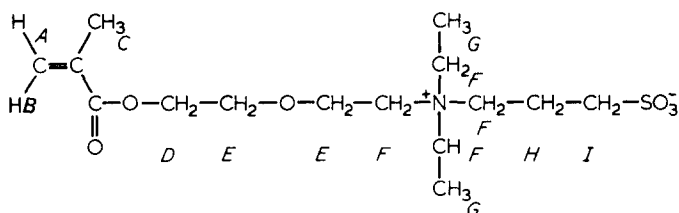
(b) For such quaternization, highly dipolar aprotic solvents are expected to enhance significantly the reaction

rates[17], and this is of special interest for 2VP: under otherwise similar conditions (60°C, 85 h), the yield increases from 17 to 76% when going from ethylacetate to propylene carbonate.

(c) In our experimental conditions we never observed the ring-opening polymerization of 1,3-propanesultone, where anionic propagation occurs according to the scheme[18,19]:
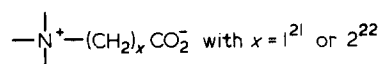
$$-\overset{|}{\underset{|}{N}}{}^{+}\!\!-\!(CH_2)_3SO_3^- + n \;\; \overset{\boxed{}}{O\text{-}(CH_2)_3SO_2} \longrightarrow -\overset{|}{\underset{|}{N}}{}^{+}\!\!\text{\textonehalf}(CH_2)_3SO_3]_{n+1}^-$$

This feature may be attributed to the specific initial ratio [PS]/[amine] = 1.1 and to the greater rate constant of the initiation (formation of the betaine structure, equation (1)) with respect to the propagation (equation (2))[19]. The hygroscopic zwitterionic monomers were characterized by elemental analysis, [1]H n.m.r. spectroscopy and potentiometry, as detailed in the experimental section. A typical [1]H n.m.r. pattern (D_2O solution) is illustrated below for monomer (V):

H	A	B	C	D
δ ppm	s, 5.60	s, 6.00	s, 1.80	t, 4.25

E	F	G	H	I
m, 3.73	m, 3.35	t, 1.20	m, 2.05	2.80

The characteristic chemical shifts of the various methylenic groups of the sulphopropylbetaine zwitterion are in good agreement with that already observed in the vinylimidazole series[11]. With respect to PS^{20}, the H_F in α to the quaternary nitrogen atom is the most shifted upfield by more than 1 ppm.

In sharp contrast with carboxylic betaines

$$-\overset{|}{\underset{|}{N}}{}^{+}\!\!-\!(CH_2)_x CO_2^- \;\; \text{with } x = 1^{21} \text{ or } 2^{22}$$

perchloric acid in acetic acid does not afford any clear equivalence point with the sulphobetaines. We found however that trifluoromethanesulphonic acid[23] in acetic acid allows a quantitative and accurate titration of these very weak bases (1 equivalent CF_3SO_3H for 1 zwitterion) when dissolved in a binary mixture of acetic anhydride:acetic acid 9:1 by volume. Such a potentiometric titration is impossible in pure acetic acid currently used as solvent with trifluoromethanesulphonic acid[24]. The sulphopropylbetaine monomers are soluble in protic solvents such as water, formamide and the lower alcohols, and insoluble in dipolar aprotic solvents (dimethylformamide, dimethylacetamide, N-methylpyrrolidone, dimethylsulphoxide, tetramethylene sulphone or propylene carbonate) except monomer (V).

Free radical polymerization of the vinyl and methacrylic sulphopropylbetaines

In most cases free radical polymerization of the mo-

nomers (I) to (V) was carried out in aqueous solution at 60°C, in the presence of 4,4'-azobis-4-cyanovaleric acid (ACVA) as initiator. Some representative results are collected in *Tables 1* and *2*.

Homogeneous versus *heterogeneous* *polymerization*. For monomers (I) and (V) polymerization occurs entirely in homogeneous solution, the corresponding polyzwitterions being water soluble. Poly(II), poly(III) and poly(IV) are only swelled in the reaction medium, and polymerization thus occurs under heterogeneous conditions. However, the use of the sodium salt of ACVA as initiator, of the same decomposition rate constant as its acid form[25], does allow the polymerization of (II) to proceed in homogeneous phase and to yield higher molecular weights: compare runs II-2 and II-3 in *Table 1*. Such an effect is obviously not observed for monomer (I), as illustrated by the nearly identical results of runs I-4 and I-5. The simultaneous increase of water solubility of poly(sulphopropylbetaines) with salt concentration will be discussed in a following paper[26]. Finally, homogeneous polymerization of monomer (II) in formamide solution leads to lower yield and molecular weight than heterogeneous polymerization in water, as illustrated by runs II-1 and II-5.

Molecular weight ranges. The experimental $\bar{M}_w$ data suggest the following order of decreasing monomer reactivity:

$$(III) \simeq (IV) \simeq (V) > (II) > (I)$$

The methacrylic and the 4-vinylpyridinium monomers easily lead to molecular weights of about 10^6 or more with very high yields (75%), while the 2-vinylpyridinium monomer leads to drastically lower $\bar{M}_w$, not over 10^5. In identical reaction conditions, the yield and the molecular weight are increased by a factor of about 2 and 30 respectively when going from the homogeneous polymerization of (I) to the heterogeneous polymerization of (III): compare runs I-4 and III-1. In the absence of any transfer reaction, it may be easily deduced from Tobolsky's calculation[27] that the initial reactant concentrations $[M]_0$ and $[I]_0$, the $\overline{DP}_w$, the monomer conversion α and time t are correlated through a relation of the form:

$$\overline{DP}_w \frac{2[I]_0\{1 - \exp(-k_d t)\}}{[M]_0 \alpha} = \frac{u\lambda}{2f}$$

where k_d is the decomposition rate constant of the initiator ($k_d = 7.24 \times 10^{-6} \, s^{-1}$ at 60°C[25]), f is the initiator efficiency, $u = \bar{M}_w / \bar{M}_n$ is the polydispersity index and λ is a factor depending on the mode of termination: $\lambda = 2$ or 1 and $u = 1.5$ or 2 for combination and dismutation respectively. Assuming in a first approach that the variations of u and f are negligible within a wide conversion range, this straightforward relation may be used to check the self-consistency of the various polymerization runs. In fact it actually holds only for runs I-1, 2, 4 and 5 carried out at 60°C within the rather narrow concentration ranges $2 \times 10^{-3} < [I]_0 \, mol \, l^{-1} < 8 \times 10^{-3}$ and $0.4 < [M]_0 \, mol \, l^{-1} < 2$: the constancy of the $u\lambda/2f$ value, 1.95 ± 0.2, may be considered fairly satisfactory taking into account the previous assumptions. An attempt to obtain higher molecular weights using very low and very high initiator and monomer concentrations respectively as in run I-7 proved to be quite disappointing. The low reactivity of the

2-vinylpyridinium monomer may be tentatively attributed to the greater steric hindrance in the close vicinity of the double bond, and transfer to monomer cannot be completely ruled out. Moreover, the simultaneous decrease of molecular weight with temperature when going from 60° to 50°C, as in the otherwise identical runs I-4 and I-6, is also unexpected since most free radical polymerizations lead to opposite effects[28].

Chemical stability of the zwitterionic polymethacrylates. The very low acidity detected by potentiometric measurements on both vinylpyridinium and methacrylic polymers (15–60 m Eq kg^{-1} for poly(I) and 2–10 mEq kg^{-1} for poly (IV)) is a decreasing function of molecular weight, and it merely arises from the acid initiator fragments incorporated as end-groups in the chain. In the polymerization conditions we used (60°C, pH $\simeq 3.2$) eventual acidic hydrolysis of the ester functions does not occur even to low extent.

Quaternization of preformed polymeric tertiary amines by 1,3-propanesultone

As an alternative strategy to the synthesis of poly(sulphobetaines) we briefly analysed the quaternization of polymeric amine precursors by PS in a reaction process quite similar to that previously involved in the monomer preparation. The experiments deal with poly(2-vinylpyridine) (P2VP), poly(2-methyl-5-vinylpyridine) (P2M5VP), poly(4-vinylpyridine) (P4VP) and poly (N,N-dimethylaminoethyl methacrylate) (PDMAEMA). The reactions were carried out at 120°C in dipolar aprotic solvents of high dielectric constant such as propylene carbonate ($\varepsilon(25°C) = 61.7$) or tetramethylene sulphone ($\varepsilon(25°C) = 42.3$) which have been shown to be the best medium for quaternization of polymeric amines[29]. The most representative results are collected in *Table 3*.

Composition and structure. The agreement observed between the results derived from sulphur elemental analysis and potentiometric titration of the residual amine functions (see experimental section) was always better than 8%: this is a strong argument in favour of a simple binary structure of unreacted amine and sulphopropylbetaine units, without any grafts of poly(1,3-propanesultone). This feature may be readily explained in a quite similar way as for the monomer synthesis (initial ratio [PS]/[amine] = 1.1), and especially by the fact that the propagation of the PS polymerization is actually negligible at 120°C since its ceiling temperature has been estimated to about 110° $\pm$ 5°C[18].

Quaternization yields and polymeric amine reactivities. In all cases quaternization occurs in two consecutive steps: the first and the faster in homogeneous solution, and the second in heterogeneous phase due to the insolubility of the highly quaternized chains in dipolar aprotic medium. The first step is quite rapid for P2M5VP, P4VP and PDMAEMA, leading to high conversion of about 70% or more in 1 min. In the absence of added salt, PDMAEMA is the only precursor to be nearly quantitatively modified, in good agreement with the lowest steric hindrance and the highest nucleophilicity of the aliphatic tertiary amino function. The addition of tetrabutylammonium hydrogen sulphate, as a non-nucleophilic salt inert towards PS, does improve the reaction rate and allows quantitative conversion except in the case of P2VP: its highest steric hindrance and lowest nucleophi-

licity may account for such a low reactivity. Assuming a bimolecular mechanism of order 2 for the reaction process[18,19], the experimental results may be tentatively interpreted to afford estimates of an apparent initial rate constant k_i (homogeneous phase) and of an apparent final rate constant k_f (heterogeneous phase): the figures quoted in *Table 3* should be considered obviously as very rough semi-quantitative values, but they are nevertheless of interest to quantify polymer reactivities. Thus, k_i and k_f differ by two orders of magnitude for P2VP, but only by one order of magnitude for the more reactive P2M5VP and P4VP. The addition of salt increases the rate constants by a factor of about 5, except for P2M5VP. PDMAEMA is about two orders of magnitude more reactive than P2VP. TMSO$_2$ seems to be a slightly better solvent than PGC. Most of these general trends are in good agreement with literature data related to the quaternization of polyvinylpyridines by alkyl halides[29], or to the initiation step of the PS polymerization by tertiary amines[19]. Quaternization of the P2VP block of a styrene–2VP block copolymer by ethylbromide in TMSO$_2$ may be quantitative[30] ($t = 80°C$, time = 92 h, pressure = 5 bar, [EtBr]$_0$/[P2VP]$_0$ = 10), and the maximum conversion observed for the system P2VP/PS of about 0.65 has not to be considered as the limiting conversion: it may probably be enhanced using longer reaction times and excess of PS.

Degradation as a side reaction. The apparent molecular weight $\bar{M}_w$ of P2VP quaternized to 0.65 is a function of the selected solvent for light scattering measurements, as illustrated by the following data:

H–CO–NH–CH$_3$(dn/dc = 0.097 ml g^{-1}): $\bar{M}_w$ = 1.29 × 10^5;
H$_2$O (dn/dc = 0.168 ml g^{-1}): $\bar{M}_w$ = 1.27 × 10^5;
H$_2$O – NaCl 1 M (dn/dc = 0.175 ml g^{-1}): $\bar{M}_w$ = 1.33 × 10^5;
CF$_3$–CH$_2$OH (dn/dc = 0.222 ml g^{-1}): $\bar{M}_w$ = 0.922 × 10^5.

This suggests rather strong compositional heterogeneity within the sample[31]. The apparent $\bar{M}_w$ value obtained in trifluoroethanol, the solvent of lowest refractive index, is the closest to the true molecular weight: its good agreement with the calculated value of 0.875 × 10^5, derived from the P2VP precursor value $\bar{M}_w$ = 0.495 × 10^5 and the reaction conversion, shows that no degradation nor crosslinking occurs in the selected reaction conditions. This is not the case however for quantitatively quaternized P2M5VP, $\bar{M}_w$ = 1.17 and 2.08 × 10^5 for the experimental and calculated $\bar{M}_w$ values respectively. The rather drastic reaction conditions of temperature and time required for P2VP could probably be smoothed to avoid this degradation without lowering the final conversion.

Properties of the poly(sulphopropylbetaines)

Solubility and water affinity. In organic solvents, solubility of the polyzwitterions is strictly restricted to protic solvents of high hydrogen bond donor strength such as formamide, fluorinated alcohols or strong acids such as formic and dichloracetic acids. Poly(I) and poly(V) do show water solubility at room temperature, a very unusual property for poly(sulphobetaines)[4,10,11]. Addition of monovalent or bivalent salts (NaCl, CaCl$_2$, LiClO$_4$,...) promotes water solubility for all the polymers as already observed in the vinylimidazole series[11]. Their solubility properties and their morphological and hydrodynamical behaviour in dilute solution will be criti-

cally discussed in a forthcoming paper[26]. All these amorphous polyzwitterions are characterized by excellent water affinity, as illustrated by the high values of their water vapour absorption at 20°C (*Table 4*). Poly(I) and poly(II) on the one hand and poly(IV) and poly(V) on the other show nearly identical behaviours.

U.v. spectroscopy. The u.v. spectra of the aromatic poly(sulphopropylbetaines) in trifluorethanol solution are characterized by two main absorption bands at about 205 ± 5 and 266 ± 8 nm: see *Table 5*. The well defined long-wavelength band, of interest for analytical purpose, shows definite bathochromic shift and hyperchromocity with respect to the spectrum of the precursor poly(vinylpyridines). In the case of P2VP and poly(I), especially where $\Delta\lambda \simeq 7$ nm is maximum, u.v. spectroscopy does not afford a straightforward method of composition determination of the partly quaternized P2VP, in contrast with the simple behaviour of poly(2-vinylpyridinium salts)[32]. On the other hand, poly(III) is characterized by a specific absorption band of high absorptivity ($\varepsilon = 67501 \, \text{mol}^{-1} \, \text{cm}^{-1}$) at 229 nm: such a new transition already observed in poly(4-vinylethylpyridinium bromide)[33] may arise from the symmetry of the chromophore.

^1H n.m.r. spectroscopy. ^1H n.m.r. spectra (D_2O, 80°C) obtained at 90 MHz were not sufficiently resolved to allow an accurate estimation of the polymer tacticities. However, they were in very good agreement with the expected quaternary ammonium salt structure[11]. Poly(III), for instance, shows typical patterns for the aromatic nucleus and the 1- and 4-methylenic groups are analogous to that observed on 1,4-diethylpyridinium iodide[34] (see *Figure 1*). Poly(V) on the other hand has no stereoregularity as suggested by the poor but definite resonance splitting of the backbone methyl group (see *Figure 2*).

Some remarks about the carcinogenity of 1,3-propanesultone

The very dangerous carcinogenic properties of PS were recently recognized[35,36]. For laboratory purposes, however, small quantities of this crystalline reagent may be safely used by avoiding any contact with the skin (systematic wearing of gloves); moreover, the vessels were cleaned and washed with concentrated sodium methoxide–methanol solutions, which afford fast and quantitative destruction of PS. The use of higher homologues such as 1,4-butanesultone, found to be much less carcinogenic[36], is of less interest due to its strongly decreased reactivity.

CONCLUSION

The nucleophilic ring opening of 1,3-propanesultone by substituted pyridines or tertiary amines readily leads to sulphopropylbetaine structures

$$-\overset{|}{\underset{|}{N}}{}^{+}\!-\!(CH_2)_3SO_3^{-}$$

This selective reaction is the key step of the synthesis of a series of aromatic or aliphatic polyzwitterions of high molecular weights. Monomer synthesis and consecutive free radical polymerization are straightforward processes, while quaternization of the related amino-polymeric precursors may offer a useful alternative strategy. These very stable polyzwitterions should be clearly differentiated from classical anionic or cationic polyelectrolytes, and their original specific properties are currently under investigation.

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Table 4 Equilibrium water uptake of the poly(sulphopropyl-betaines) at 20°C

Relative humidity (%)	Water absorption (%)[a]				
	Poly(I)	Poly(II)	Poly(III)	Poly(IV)	Poly(V)
13	11	12	13	11	10
47	18	17	27	19	20
63	24	26	34	30	30
90.7	44	49	47	60	62

[a] Water absorption (%) = 100 (wet weight − dry weight)/dry weight

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Table 5 U.v. transitions of poly(vinylpyridines) and of their sulphopropylbetaine derivatives in trifluoroethanol solution
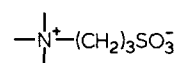
	P2VP	Poly(I)	P2M5VP	Poly(II)	P4VP	Poly(III)
λ_{max} (nm)	$\leqslant 190$		210	210	205	197
ϵ (l mol^{-1} cm^{-1})	[a]		4970	4020	3470	9470
λ_{max} (nm)	262	269	267.5	274	255	258
ϵ (l mol^{-1} cm^{-1})	3000	5220	3040	3790	1600	2790

[a] Non-measurable

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