

Synthesis and aqueous phase behaviour of homo- and copolymers of 1,1-diallyl-4-formylpiperazinium chloride

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The quaternary ammonium salt, 1,1-diallyl-4-formylpiperazinium chloride (**3**) on cyclopolymerization in water solution in the presence of *t*-butylhydroperoxide gave water soluble polymer (**5**). The copolymers of (**3**) with sulfur dioxide have been prepared in DMSO solvent using ammonium persulfate as the initiator. The composition and phase diagram of the aqueous two-phase systems of the homopolymer (**5**) and copolymer (**8**) has been studied for the first time for this class of polymers. Synthesis of the polymer (**8**) paves the way for the preparation of a new class of polymers with a basic trivalent nitrogen as well as a quaternary nitrogen. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Pioneering works by Butler and coworkers¹ led to the copolymerization of a variety of diallyl quaternary ammonium salts (**1**) via an intra-molecular chain propagation through the five-membered cyclic structure² to yield linear water soluble polymers (*Scheme 1*). Homo- and copolymers of diallyldialkylammonium salts have found extensive industrial and commercial applications^{4,5}. Polydiallyldimethylammonium chloride alone accounts for over 200 patents and publications. The dialkyldiallylammonium salts–sulfur dioxide copolymers are also manufactured commercially and are useful as textile finishes, polymer additives, coagulants and thickeners. Recently, we have reported⁶ the homopolymerization of 1,1-diallyl-4-formylpiperazinium chloride (DAFPC) (**4**). The piperazine moiety occurs in a wide range of compounds having interesting biological activities⁷. Piperazine is inexpensive and is used as an intermediate for various pharmaceuticals, polymers, dyes, corrosion inhibitors and surfactants. Here we report on the synthesis and solution properties of copolymers of DAFPC and sulfur dioxide. Obtainment of copolymer (**8**) would pave the way to its conversion to **9**, a unique dicationic polymer, and **10**, a bifunctional polymer with quaternary ammonium as well as basic trivalent amine groups. We also report the study of aqueous two-phase system of poly(DAFPC) (**5**) and poly(DAFPC–SO₂) (**8**).

EXPERIMENTAL

Materials

The monomer DAFPC was prepared as described⁶. Ammonium persulfate (APS) from BDH Chemical Co. (Poole, UK) and *t*-butylhydroperoxide (TBHP) (80% in di-*t*-butylperoxide) from Fluka Chemie AG (Buchs, Switzerland) were kept in the refrigerator and used without further purification. Deionized distilled water was used for the polymerization reactions. Dimethyl sulfoxide (DMSO) was dried over calcium hydride overnight and then distilled under reduced pressure at b.p. 64–65°C (4 mmHg). Sulphur dioxide gas was bubbled gently to a known quantity of DMSO and the final weight of the solution gave the wt% of the sulfur dioxide in DMSO. All glassware was cleaned using deionized water.

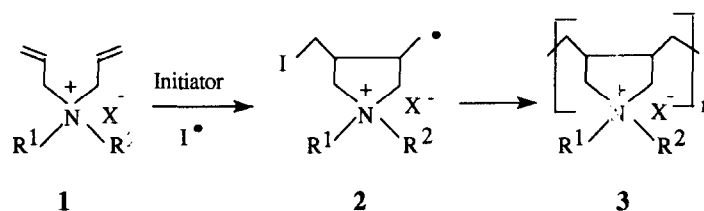
Physical methods

Elemental analyses were carried out on a Carlo-Erba Elemental Analyzer Model 1106. I.r. spectra were recorded on a Nicolet Model 5DX FT i.r. spectrophotometer and are reported in wave numbers (cm⁻¹). ¹H and ¹³C n.m.r. spectra were measured in D₂O using dioxan as internal standard on a Varian XL 200 spectrometer. Viscosity measurements were made by Ubbelohde viscometer (K 0.005989).

General procedure for the polymerization reactions of DAFPC (**4**)

In a 25 cm³ round-bottom flask containing a magnetic stirrer, was taken the monomer (**4**) (15.00 g). The

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Scheme 1

Table 1 Effect of concentrations of monomer, initiator (TBHP) on cyclocopolymerization^a of DAFPC in water solution^b

Entry no.	DAFPC conc. (%w/w)	Initiator (mg g ⁻¹ DAFPC)	Yield (%)	Intrinsic viscosity (dl g ⁻¹)	Unreacted ^d DAFPC (%)
1	60	1.0	76	0.805	20
2	60	2.0	86	1.12	9
3	60	3.0	92	0.850	5
4	60	5.5	87	0.665	11
5	62.5	3.0	91	1.68	6
6	65	3.0	–	Gel	–
7	70	3.0	–	Gel	–

^a Polymerization time: 24 h at 50°C followed by 24 h at 75°C in a closed vessel^b Prepared in deionized water^c Viscosity of 0.5–0.03125% polymer solution in 0.1 N NaCl at 30°C was measured in Ubbelohde viscometer at 30°C^d Determined by integration of ¹H signals of olefinic protons of unreacted DAFPC and NCHO proton signal of the DAFPC and poly(DAFPC)

required concentration of the monomer as specified in *Table 1* was achieved by adding deionized water. The flask was flushed with nitrogen. The appropriate amount of the initiator TBHP (see *Table 1*) was added with a syringe to the magnetically stirred monomer solution. The reaction mixture was then stirred for 24 h each at 50°C and 75°C. At 75°C rotation of the magnetic stirrer stopped completely in the viscous colourless solution. While hot, the slurry of the polymer in methanol (75 cm³) was transferred to a flask containing acetone (150 cm³). The white powder of the polymer was filtered and the sequence of slurry making and precipitation was carried out once more in order to ensure complete removal of the unreacted monomer DAFPC (4). The polymer was dried under high vacuum at 70°C for 10 h (or until constant weight of the polymer was achieved). Polymers started to turn brownish at ~350°C and melted with decomposition to a black material at 360–365°C (closed capillary). Most of the polymers (5) gave satisfactory elemental analysis [for instance polymer for entry no. 2 (Found: C, 56.3; H, 8.6; N, 11.9.

Table 2 Effect of solvents and concentrations of monomers, initiator and temperature on DAFPC/SO₂ cyclocopolymerization^a

Entry no.	DAFPC conc. ^b (%w/w)	Solvent ^c	Molar ratio DAFPC/SO ₂	APS ^d (mg)	Temp (°C)	Yield ^e (%)	Intrinsic ^f viscosity (dl g ⁻¹)
1	23	A	1/2	3.0	33	8	0.0535
2	23	A	1/1	3.0	33	28	0.120
3	23	A	2/1	3.0	33	104	0.315
4	23	A	2/1	2.0	50	87	0.950
5	23	A	2/1	3.0	50	90	1.11
6	23	A	2/1	4.0	50	98	1.06
7	43	A	2/1	8.0	50	98	1.01
8	17	A	1/1	3.0	50	84	0.870
9	23	A	1/1	3.0	50	89	0.884
10	34	A	1/1	3.0	50	85	0.920
11	53	A	1/1	3.0	50	83	0.612
12	13	A	1/2	3.0	50	18	0.0667
13	18	A	1/2	3.0	50	22	0.0808
14	20	B	1/1	2.0	50	61	0.00750
15	50	B	1/1	2.0	50	93	0.00430
16	65	B	1/1	3.0	50	93	0.0101
17	50	A/B(1/1)	2/1	2.0	50	109	0.00915

^a Polymerization time: 36 h^b Concentration is expressed as (mass DAFPC/(mass DAFPC + mass solvent)) × 100^c A = DMSO, B = H₂O^d APS (ammonium persulfate), the amount in mg indicates the quantity used for every mmol of 1/1 complex of DAFPC/SO₂^e Based on 1/1 monomer complex of DAFPC/SO₂^f Viscosity of 0.5–0.03125% polymer solution in 0.1 N NaCl at 30°C was measured in Ubbelohde viscometer at 30°C

Table 3 Phase compositions of the P-PS-H₂O^a system at 23.5°C

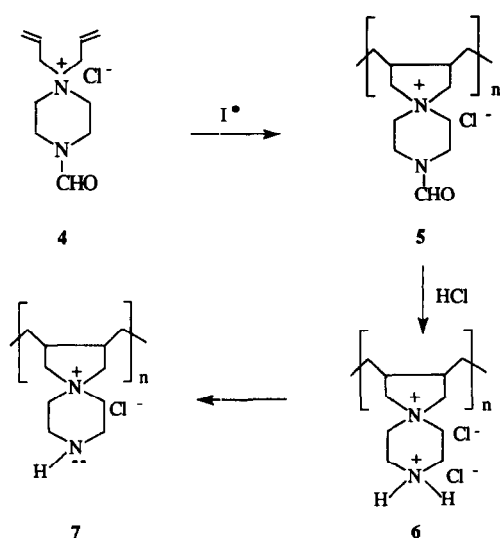
System	Total system			Top phase			Bottom phase		
	P %w/w	PS %w/w	H ₂ O %w/w	P %w/w	PS %w/w	H ₂ O %w/w	P %w/w	PS %w/w	H ₂ O %w/w
1	9.890	11.12	78.99	17.1	3.36	79.5	2.18	19.5	78.3
2	8.950	10.05	81.00	15.7	4.12	80.2	2.24	16.0	81.8
3	8.013	8.990	83.00	13.4	4.38	82.2	2.72	13.5	83.8
4	7.068	7.922	85.01	11.6	4.25	84.2	2.68	11.5	85.8
5	6.123	6.877	87.00	9.72	4.37	85.9	2.80	9.19	88.0

Dilution method

	Total system (two-phase)			Total system (one-phase) ^b		
	P %w/w	PS %w/w	H ₂ O %w/w	P %w/w	PS %w/w	H ₂ O %w/w
6	4.602	5.162	90.24	7.997	8.971	83.03
7	3.080	6.681	90.24	5.142	11.14	83.72
8	6.541	4.582	88.88	10.34	7.245	82.42

^a P = poly(DAFPC) (sample taken from entry 2, Table 1). PS = poly(DAFPC-SO₂) (sample taken from entry 5 Table 2)

^b Total system in entries 6–8 (two-phase system) was diluted with water until a one-phase system was obtained

**Scheme 2**

C₁₁H₁₉N₂OCl requires C, 57.26%; H, 8.30%; and N, 12.14%). Due to the hygroscopic nature the percentage of hydrogen is usually found to be more than the calculated value. I.r. and n.m.r. data of these polymers are identical to those prepared using the APS initiator in our earlier work⁶.

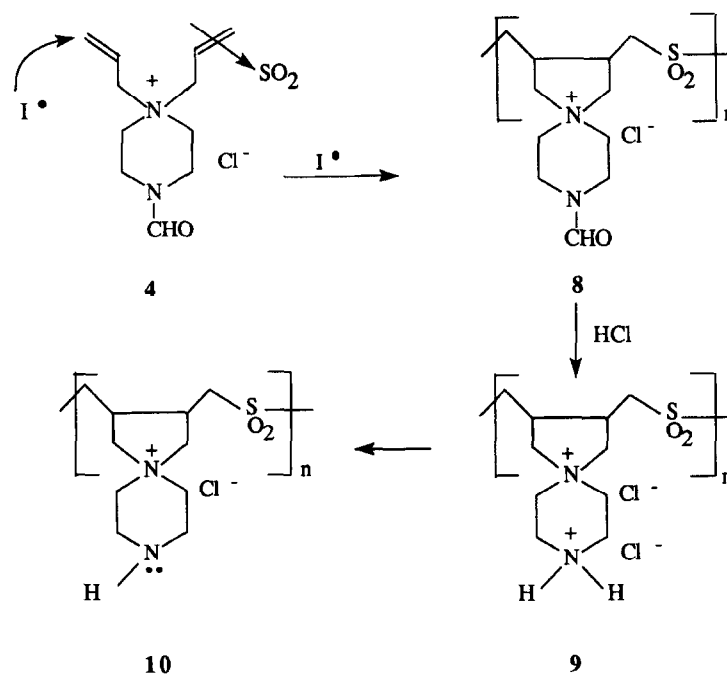
General procedure for the copolymerization reactions of DAFPC (**4**) with SO₂

The reaction conditions for the copolymerization reactions are included in the Table 2. In a flame-dried 25 cm³ round-bottom flask containing a magnetic stirrer, was taken the dry monomer (**4**) (10.00 g). Appropriate concentration of the monomer (**4**) and SO₂ was achieved by adding DMSO-SO₂ stock solution with known wt% of SO₂ (see Materials). Fresh DMSO was added in order to achieve the monomer concentrations as shown in the Table 2. All these additions were carried out under N₂ to exclude the absorption of

moisture. The required amount of initiator APS was then added (see Table 2). The reaction mixture in the closed flask was then stirred magnetically at the specified temperature. Within 10–15 min white polymers started to precipitate out. At the end of the specified time the polymers were taken in liberal excess of methanol and filtered and washed with methanol several times in order to ensure complete removal of the unreacted monomer (**4**). The polymer was dried under high vacuum at 60°C for 10 h (or until constant weight of the polymer was achieved). Polymers (**8**) started to turn brownish ~300°C and decomposed to black material at 350–360°C. Most of the polymers (**8**) gave satisfactory elemental analysis [for instance polymer for entry no. 5 (Found: C, 43.9; H, 6.9; N, 9.3; S, 10.6. C₁₁H₁₉N₂O₃SCl requires C, 44.81; H, 6.50; N, 9.51; and S, 10.88%)]. Due to the hygroscopic nature the percentage of hydrogen is usually found to be more than the calculated value. I.r. data is as follows: ν_{\max} (KBr) 3400, 2925, 1662, 1448, 1402, 1298, 1267, 1220, 1041 and 1005 cm⁻¹.

Phase compositions and phase diagram

To a mixture of 671.6 mg of poly(DAFPC) (**5**) (sample from entry 2, Table 1) and 753.7 mg of poly(DAFPC-SO₂) (entry 5, Table 2) was added 6.0780 g of water. The mixture was shaken occasionally (24 h) to complete the solution process. Phase separation took place within 20 min after thorough shaking. The mixture was kept at 23.5°C for 48 h. The volume of the top and bottom layers was found to be 3.57 and 3.48 cm³, respectively. Density of the top and bottom layer was determined to be 1.048 and 1.079 g cm⁻³, respectively. The ¹H n.m.r. spectra of the top and bottom layer were measured in D₂O (after removal of water by a gentle stream of nitrogen and repeating the process after adding some D₂O to the residue). The top layer was found to contain P (polyDAFPC) and PS (polyDAFPC-SO₂) in a respective ratio of 83.0/17.0 and that of the bottom layer 15.2/84.8, respectively. Using equations as described in Results and Discussion the % w/w of the



Scheme 3

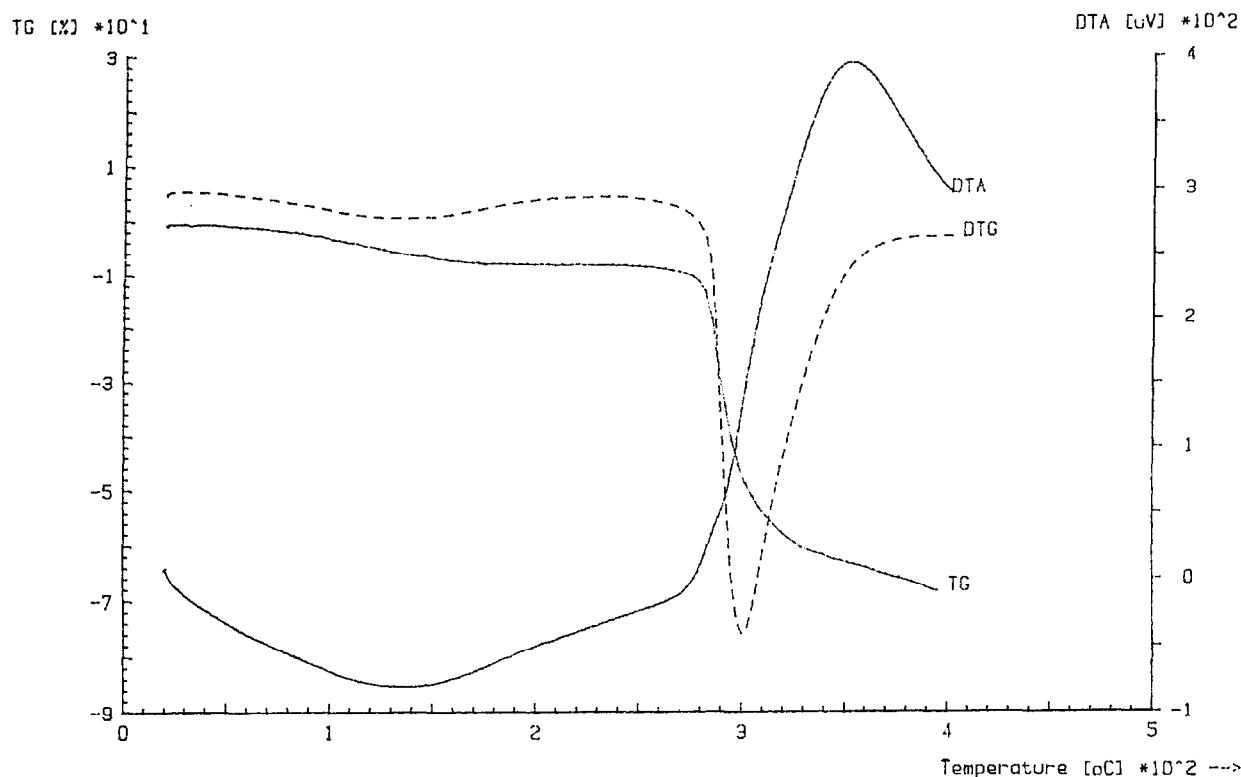


Figure 1 Differential thermal and thermogravimetric analysis of poly(DAFPC-SO₂) (8) (Sample: Entry 5, Table 2) with scanning rate of 10°C min⁻¹

polymers in each phase was calculated. The results just described represent system 2 in Table 3. Likewise phase compositions of other total systems were calculated and included in Table 3 and Figure 4.

RESULTS AND DISCUSSION

Even though the homopolymerization of DAFPC under different conditions using ammonium persulfate (APS) as an initiator proceeds smoothly to give poly(DAFPC) (5),

there remained a considerable amount of unreacted monomer (20–25%) at the end⁶. To improve the polymer yields we investigated the polymerization reactions in water using *t*-butylhydroperoxide (TBHP) as the initiator (Scheme 2). The effects of concentration of monomer, initiator on the polymerization are given in Table 1. Using 3 mg of TBHP per gram of monomer, homopolymers are obtained in excellent yields with very little amount (~5%) of the unreacted monomer (4) as indicated by the proton n.m.r. spectra of the crude

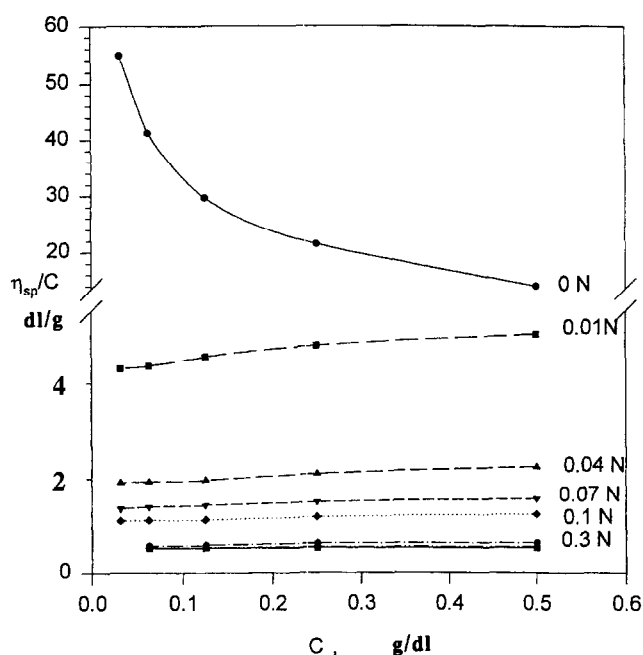


Figure 2 Viscosity behaviour of poly(DAFPC-SO₂) (8) (Sample: Entry 5, Table 2) water at 30°C at different NaCl concentration at a shear rate of $\sim 7.5 \times 10^3 \text{ s}^{-1}$

polymerization products. Highest intrinsic viscosity was obtained at 62.5% monomer concentration (entry 5). Further increase in the monomer concentration however resulted in the formation of gels (entries 6 and 7). The highest intrinsic viscosity of 1.68 dl g^{-1} is obtained for the polymer in entry 5. The polymer was found to be insoluble in various organic solvents including methanol but readily soluble in water. The aqueous solution remained stable for months with no discoloration and very little change in their viscometric behaviour.

Copolymerization of DAFPC (4) with sulfur dioxide was carried out in dimethyl sulfoxide (DMSO) and water using APS as the initiator (Scheme 3). The effects of concentration of monomers, initiator, temperature, and solvents on the polymeric yields and viscosities are included in Table 2. While at 33°C low molecular mass polysulfones (8) are obtained (entries 1–3), and at 50°C copolymers of high molar masses are obtained as indicated by their very high intrinsic viscosities (entries 4–11). The molar ratio of DAFPC and SO₂ in the feed has a profound effect on the intrinsic viscosity and yield of the copolymers. Polymerization using 1/2 ratio of DAFPC/SO₂ afforded copolymers in very low yields as well as very low viscosities (entries 12 and 13). Monomer (DAFPC) concentration seems to have very little effect on the viscosity and yield (entries 8–10). The cyclopolymerization in water or water–DMSO mixture afforded copolymers in excellent yields but with extremely low viscosities. The copolymers are found to be insoluble in methanol but readily soluble in water. The aqueous solution of the copolymers remained colourless for months with no appreciable change in their viscosities. The copolymers are white amorphous and hygroscopic solids and do not melt but decompose at around 300°C to a black material. The differential thermal analysis and the thermogravimetric analysis of a copolymer sample (entry 5, Table 2) are shown in Figure 1. The polymer shows some predecomposition

weight loss, which is attributed to the loss of water. Initial decomposition starts at 290°C and the polymer melts at 300°C. There is a chemical reaction at 350°C presumably the breakdown of the polymer to SO₂. The elemental analyses of the copolymers indicated that DAFPC and SO₂ were incorporated in the polymer backbone in a 1/1 ratio, regardless of the molar ratio of the starting monomers. The i.r. spectra of the polysulfones were virtually identical. The hygroscopic nature of the polymers is indicated by the presence of strong hydroxyl absorption around 3400 cm^{-1} . The presence of strong bands at 1298 and 1123 cm^{-1} are indicative of the presence of SO₂ unit in the polymeric backbone. Viscosity curves of the copolymer (8) (entry 5, Table 2) are presented in Figure 2. The plots are typical for polyelectrolytes in general, unlike the behaviour of nonionic linear polymers. Figure 2 also displays the reduced viscosity behaviour of the copolymers in different concentrations of added NaCl. In the presence of added salt the viscosity curves become linear as expected. The intrinsic viscosity decreases with increase in the NaCl concentration and converge to a minimum at 0.3 N NaCl. The viscosity remains the same thereafter in 0.4 and 0.5 N NaCl solution.

The proton-decoupled ¹³C n.m.r. spectra of the homopolymer (5) and the copolymer (8) are shown in Figure 3, excepting the carbonyl resonance which is observed around 164.7 ppm. The monomer ¹³C spectrum shows the carbons in the piperazine ring (C-a, C-a' and C-b, C-b') to be non-equivalent with equal populations, due to the slow amide N–C bond rotation at ambient probe temperatures. In the polymer, the C-a, C-a' and C-b, C-b' are made further non-equivalent in the *cis* isomer. So we observe two equal intensity peaks for each of the piperazine ring carbons in the *cis* isomer and a single peak each in the *trans* isomer. The assignments are shown in Figure 3.

The splitting of the methine carbon (C-2) in the *cis*-isomer of the homopolymer into two peaks of approximately equal intensity peaks can be clearly seen. The splitting is apparently small in the *trans* isomer, giving only a broad, single peak. This splitting may be explained as arising from a configurational difference between the adjacent rings; the adjacent ring can add in two ways (*R* or *S*) with equal probabilities. The *cis* isomer of the copolymer does not show this splitting for the C-2 carbon; presumably the intervening S atom can mask the configurational differences between adjacent rings.

The presence of significant amounts of six-membered piperidinium rings in the homopolymer can be ruled out as the C-4 absorption for the six-membered ring, predicted³ in the range 35–41 ppm, is not observed. However, in the copolymer some weak peaks are evident in the 35–41 ppm range, showing the presence of small amounts ($\sim 8\%$) of the piperidinium rings. Integration of relevant peaks of the homopolymer spectrum yields the *cis/trans* ratio to be 80/20, while in the copolymer the ratio is 75/25.

Both the homo- (5) and copolymers (8) on acidic hydrolysis (7% HCl, 20°C, 12 h) afforded the dicationic polymers (6) and (9) in almost quantitative yields (Schemes 2 and 3). Subsequent basification with sodium bicarbonate provided the polymers (7) and (10) containing quaternary as well as trivalent nitrogen in the same polymer. We shall report in due time the properties and possible application of these interesting polymers.

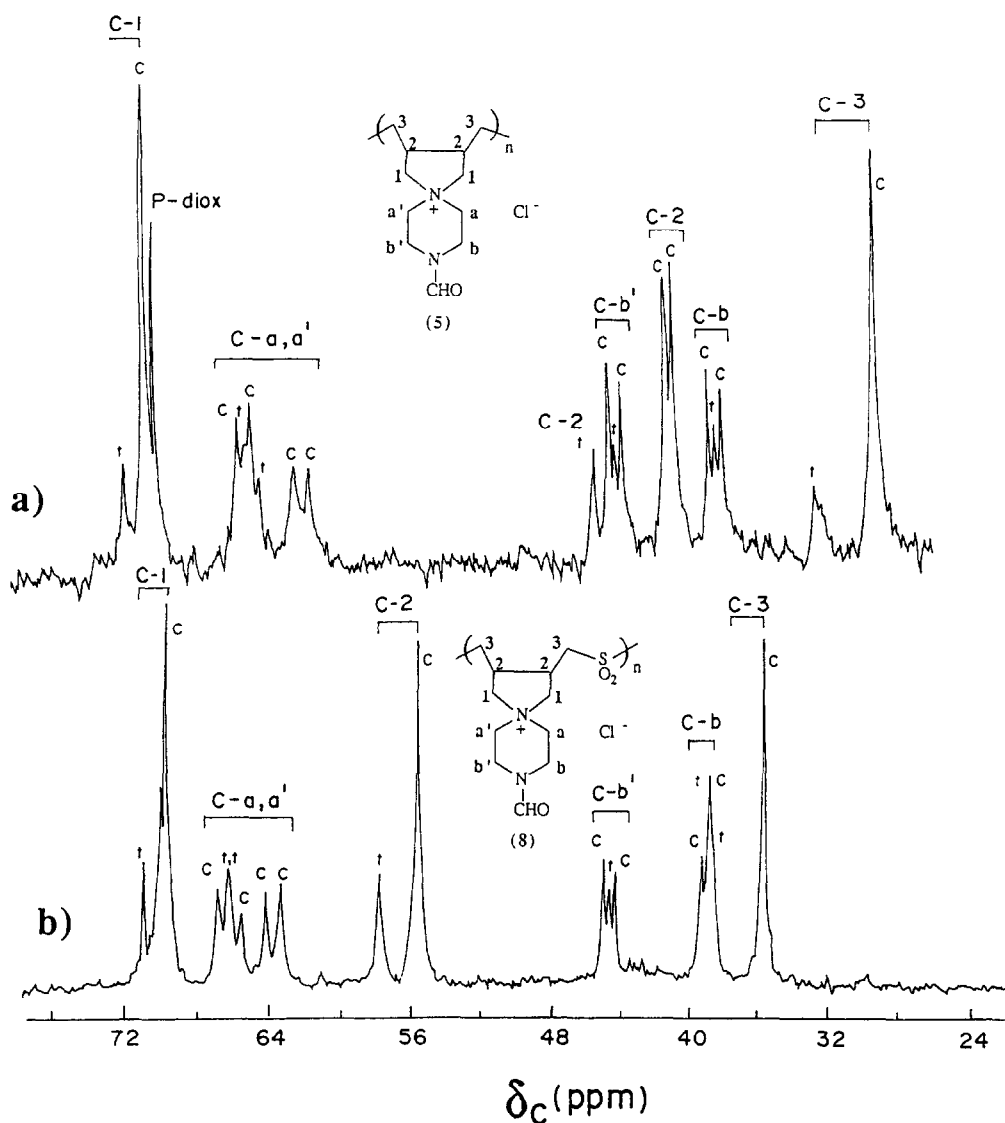


Figure 3 ^{13}C n.m.r. spectrum in D_2O of: (a) homopolymer (5); (b) copolymer (8)

Finally, we were interested in the phase behaviour of aqueous polymer mixtures of the homo- and copolymers of DAFPC. Mixing aqueous solution of two different polymers may lead to phase separation regardless of whether the polymers are ionic or nonionic⁸⁻¹⁰. Depending on the nature of the polymers three kinds of result can be obtained. Polymer incompatibility will lead to phase separation in a segregative way where two polymers are collected mainly in different phases, i.e. each phase is rich in one of the polymers. The second type of phase separation, called associative phase separation, results when both the polymers are concentrated in one phase while the other phase contains mainly the solvent. In the third type, compatible polymers would lead to complete miscibility and a homogeneous solution is obtained. Polymer mixtures with both polymers either ionic with similar charges or nonionic lead to segregative type of phase separation, whereas mixtures with one polymer having cationic backbone and the other with anionic backbone results in associative phase separation. Segregative phase separation occurs if the effective interaction between the polymers is repulsive or if the two differ in their interaction towards the solvent.

The aqueous two phase systems have a horizontal

interface with the test tube held in a vertical position and the interface forms a 90° angle with the tube walls. The interfacial tension is known⁸ to be low, between 0.0001 and 0.1 dyne cm^{-1} compared with $1-20 \text{ dyne cm}^{-1}$ for conventional systems. As such, the aqueous two-phase polymeric systems provide an efficient separation method for water-soluble substances which as proteins and nucleic acids which partition unequally to the different phases. A mild system with low interfacial tension does not damage the secondary structure or biological activities of such delicate biomolecules. The interesting phase behaviour of a mixture of two similarly charged polyelectrolytes, although recognized early by Albertson^{8,9}, has received very little attention. With all this in mind we set out to study the phase diagram of the poly(DAFPC) (5) and poly(DAFPC- SO_2) (9) system. Needless to say, the availability of a variety of cheap water soluble quaternary ammonium polymers, including the ones reported here, make it imperative to look into their phase behaviours.

A phase diagram can be constructed in many different ways. In one such way concentrated solution of polymer A is added dropwise onto a concentrated solution of polymer B until it causes turbidity, hence

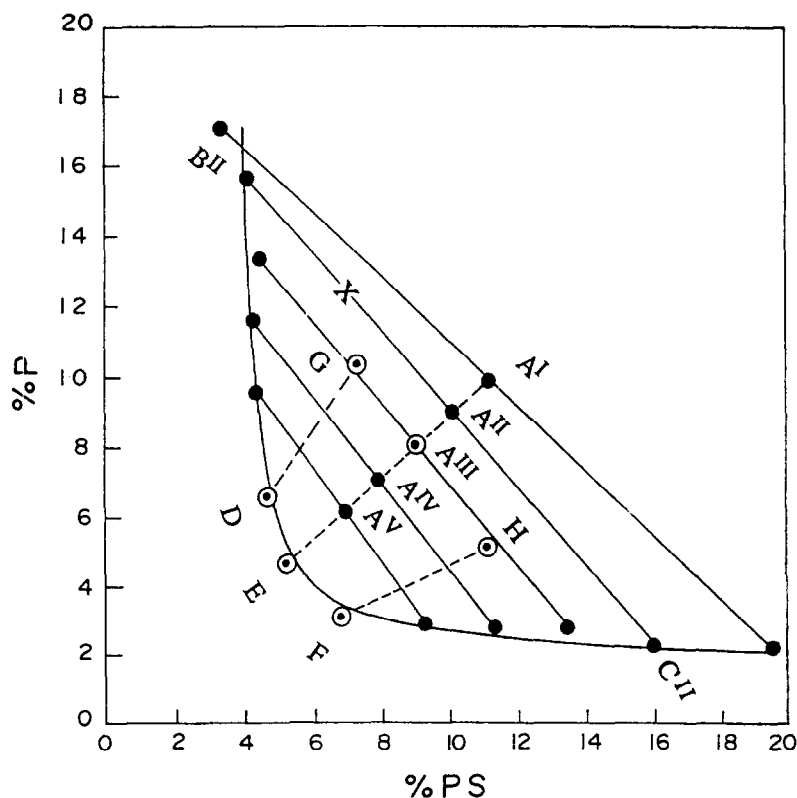


Figure 4 Phase diagram of P-PS-H₂O system at 23.5°C

separation into two phases. The composition (%w/w) of this mixture is then calculated. Sufficient water is then added to make the mixture clear again. More solution of polymer **B** is again added until turbidity reappears. The composition of this mixture is noted and so on. If the concentration of polymer **A** is plotted against that of **B**, a binodial curve is obtained. The curve line separates the two areas. Mixtures having composition below and above the binodial will give rise to homogeneous and two-phase systems, respectively. However, we faced problems in the construction of the phase diagram of our poly(DAFPC) (P)-polyDAFPC/SO₂ (PS) system using the above-mentioned turbidity method. The polymers under study have, presumably, a wider distribution of molar masses and as expected there is not a sharp change from a clear solution to a turbid mixture with these polydisperse polymers. Hence we decided to analyse the different phases by ¹H n.m.r. spectroscopy to determine the composition of each polymer. By trial and error a two-phase system with almost equal volume of the two phases is obtained. As shown in Table 3 a total system represented by the point A^I in the phase diagram (Figure 4) with a composition of 9.89% P, 11.12% PS and 78.99% water gave two phases with almost equal volume. While the ratio of the weight fractions were kept constant, the amount of water was varied to achieve a total system with composition of A^{II}, A^{III}, A^{IV} and A^V. All of these five 'total-systems' gave two phases each with almost equal volumes at the top and bottom phases. The tie lines (e.g. B^{II}-A^{II}-C^{II}) are obtained by analysing the composition of the top and bottom phases by ¹H n.m.r. spectroscopy as detailed in the Experimental section. The system with total composition represented by A^{II} (Table 3, system 2) gave the top and bottom phase with composition of B^{II} and C^{II}, respectively. The composition of several total

systems, top and bottom phases are given in the Table 3. Total composition represented by any point, say X, on the tie line B^{II}-A^{II}-C^{II} will have the top and bottom phase represented by B^{II} and C^{II}, respectively, but the volume or mass ratio of the top and bottom phases will be determined by the ratio of length X-C^{II} and B^{II}-X, respectively. The mole ratio of the polymers in each phase was determined by a ¹H n.m.r. technique. As a check on the reliability of the integration of the n.m.r. signals the ¹H n.m.r. spectra of pure polyDAFPC (P) and poly(DAFPC/SO₂) (PS), and each containing 20 mol% of the other polymer, are displayed in Figure 5. Careful analysis revealed that the six protons of P appears at the δ0.90-3.05 ppm region, whereas the copolymer PS does not have any proton signal in that region. The NCHO proton of both the polymers appeared at δ8.15 ppm. The molar ratio by ¹H integration was found to be within 1-3% of the known ratio. Integration of these signal helped us to determine the molar ratio of the polymers in each phase. Weight percent of each polymer is determined by using the equations

$$[P_t]V_t + [P_b]V_b = P_o/MM_p \quad (1)$$

$$[P_t]V_t([PS]/[P])_t + [P_b]V_b([PS]/[P])_b = PS_o/MM_{PS} \quad (2)$$

where subscripts t and b represent top and bottom phase, respectively, [P] represents concentration of homopolymer P in mmol of repeat unit cm⁻³. P_o and PS_o represent total mass in mg of the homo- and copolymer, respectively, and V represents volume in cm³. MM_P and MM_{PS} represent molar mass of the repeat unit of homo- and copolymer which are 230.73 and 294.79, respectively. (PS/P) represents molar ratio of the copolymer and homopolymer as determined by ¹H n.m.r. integration. After multiplying equation (1) with

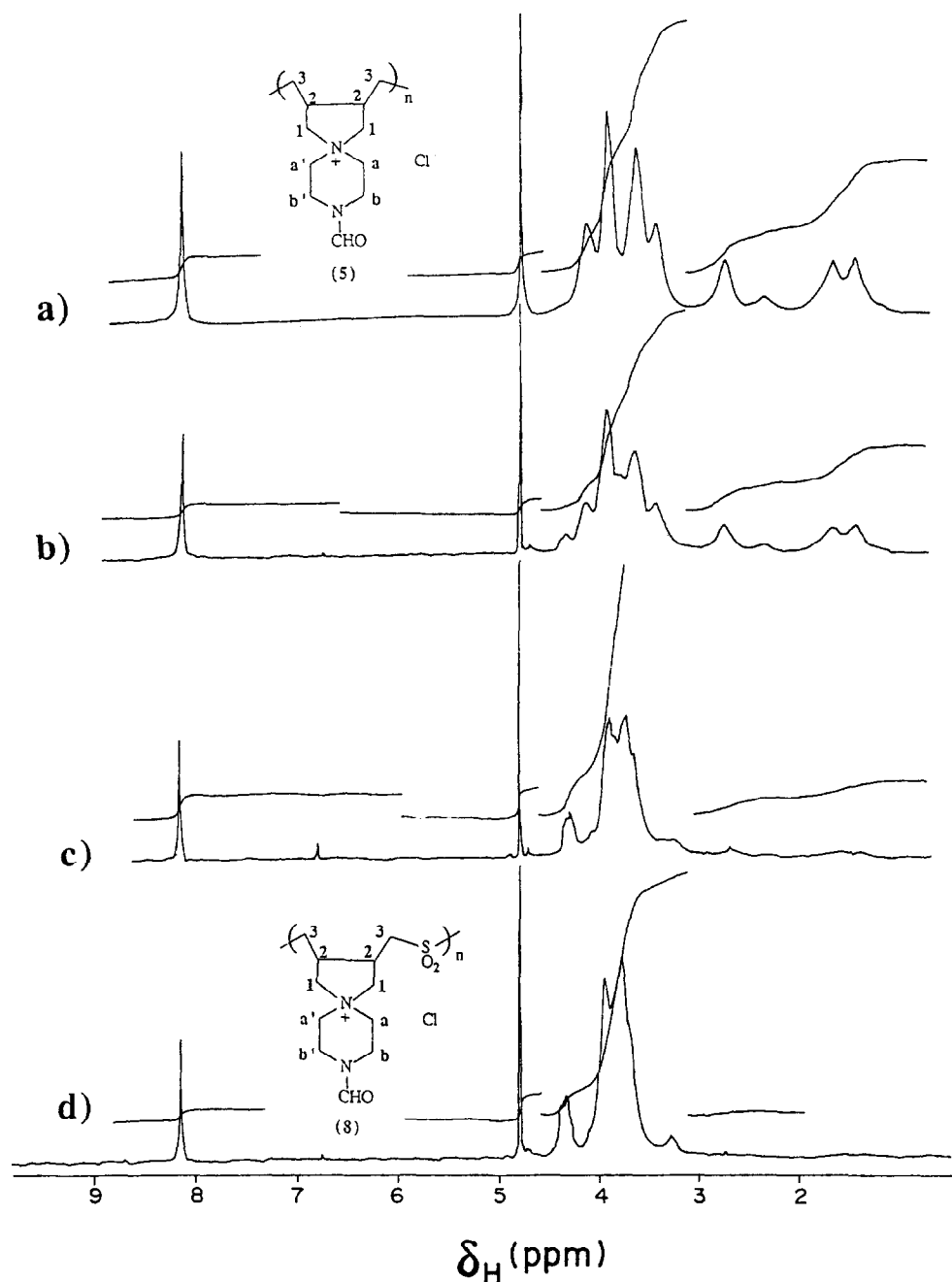


Figure 5 ^1H n.m.r. spectrum of D_2O of: (a) homopolymer (5); (b) homopolymer (5) and copolymer (8) in 80/20 mol ratio; (c) homopolymer (5) and copolymer (8) 20/80 mol ratio; (d) copolymer (8)

$(\text{PS}/\text{P})_t$ and then subtracting from equation (2), a simple rearrangement leads to

$$[\text{P}_b] = \frac{\text{PS}_o/294.79 - (\text{P}_o/230.73)([\text{PS}]/[\text{P}])_t}{V_b\{([\text{PS}]/[\text{P}])_b - ([\text{PS}]/[\text{P}])_t\}} \quad (3)$$

The mass of polymer P in the bottom phase is then calculated using

$$\text{P}_b = [\text{P}_b]V_b \times 230.73 \text{ mg} \quad (4)$$

Once one of the polymer concentrations is known in a phase, then the rest of the concentrations in the two phases are easily calculated from the known volume, density and mass of the two phases. Points D, E, and F in the binodial are obtained by a dilution method. Systems with total composition of G, A^{III} and H (entries 6–8, Table 3) were diluted with water, a few drops at a time,

and allowed to separate into two phases. This process was continued until the two phases became one. The composition of the diluted system (before the last drop makes the system homogeneous) was determined and these points along with the composition determined by ^1H n.m.r. analyses were used to construct the phase diagram (Figure 4). The polymers displayed segregative phase separation behaviour. The binodial was found to be symmetrical and this is not surprising since the two polymers are quite similar in nature and have almost similar intrinsic viscosities^{8,9}. While the top phase was found to be rich in the homopolymer (5), the copolymer (8) remains mostly in the bottom phase. Homo- and sulfur dioxide copolymers of dialkyldiallylammonium halides are an extremely important class of inexpensive polymers, and to the best of our knowledge, the phase diagram and composition studied in this work represent the first example among these polymers.

Table 4 Phase diagram data of P-PS-H₂O^a system at 23.5°C

System	Polymer	Top phase	Bottom phase	Partition coefficient		Difference in weight frac. ^d (w'' - w') × 100
		w/w ^b (w'')	w/w ^b (w')	$K = C_t C_b^c$	ln K	
1	P	0.171	0.0218	7.84	2.06	14.9
	PS	0.0336	0.195	0.172	-1.76	16.1
2	P	0.157	0.0224	7.01	1.95	13.5
	PS	0.0412	0.160	0.258	-1.35	11.9
3	P	0.134	0.0272	4.93	1.60	10.7
	PS	0.0438	0.135	0.324	-1.13	9.12
4	P	0.116	0.0268	4.33	1.47	8.92
	PS	0.0425	0.115	0.370	-0.994	7.25
5	P	0.0972	0.0280	3.47	1.24	6.92
	PS	0.0437	0.0919	0.476	-0.742	4.82

^a P = poly(DAFPC), PS = poly(DAFPC-SO₂)

^b w/w represents weight fraction = %w/w × 100

^c C_t and C_b are concentration of polymers in the top and bottom phase, respectively

^d w'' and w' represent polymer weight fractions in the top and bottom phase, respectively

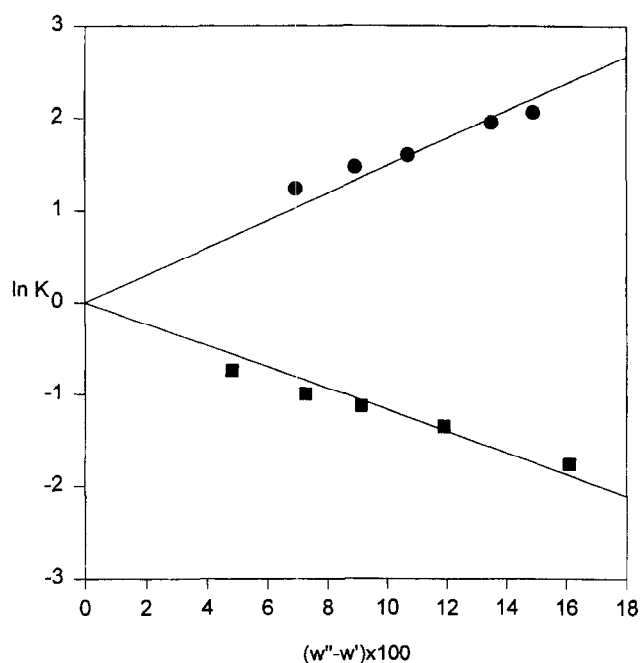


Figure 6 Correlation of the phase diagram of P-PS-H₂O system using the method of Diamond and Hsu¹¹

To check the consistency of the binodial curve of the P-PS-H₂O system, the following correlation developed by Diamond and Hsu¹¹ based on Flory-Huggins theory, is employed:

$$\ln(K_1) = A_1(W''_1 - W'_1) \quad (5)$$

and

$$\ln(K_2) = A_2(W''_2 - W'_2) \quad (6)$$

where W'' and W' are the polymer weight fractions in the top and bottom phase, respectively, the slopes A_1 and A_2 are functions of the polymer molecular weight and the interactions between the polymers and water, and the subscripts 1 and 2 represent polymer 1 and polymer 2. Equations (5) and (6) provide a means for correlating phase equilibrium data for an aqueous

polymer system. The correlation results are shown in Table 4 and Figure 6. Straight lines are obtained indicating satisfactory representation of the phase behaviour by this model phase separation characteristics.

CONCLUSION

Syntheses of piperazine-based homo- and copolymers with excellent yields and viscosity are achieved. We anticipate that the presence of trivalent basic nitrogen as well as cationic centre in (7) and (10) would make these polymers potential candidates for flocculation studies. Segregative phase separation of the homo- and copolymers does indeed open up a new avenue in separation technology for important biomolecules.

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