Chemically Modified Polysulphones with (N-phenacyl and N-alckylacetate) -4,4'-Bipyridinium Bromide Derivatives as Pendent Groups

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New chemically modified polysulphones with both N-phenacyl-4, 4'-bipyridinium bromide and N-alkylacetate-4, 4'-bipyridinium bromide derivatives, have been synthesized by chemical modification reaction of chloromethylated polysulphones with various N-substituted monoquaternary-4, 4'-bipyridinium bromides. The structure of the modified polysulphones was confirmed by elemental analysis and ^{1}H-NMR spectroscopy. Various reaction conditions were checked in view to obtain soluble polymers.

Key words: chemically modified polysulphone, chloromethylated polysulphone, N-phenacyl-4, 4'-bipyridinium bromide, N-alkylacetate-4, 4'-bipyridinium bromide, viologen

The preparation of functional polymers is of great interest since they can be used in a large variety of applications as supports, reagents or catalysts for various reactions [1]. Applications for new reactive polymers containing functional groups continued to grow since Merrifield's pioneering work on solid phase synthesis [2]. Thereafter a significant work on reactive polymers has been focused on polystyrene derivatives obtained by chemical modification.

Aromatic polysulfones are high performance thermoplastic polymers which are largely recognized as excellent materials for membranes. Many chemical modification of polysulfones, such as sulfonation [3, 4], chloromethylation [5-8], methalation [9, 10], besides many structural variation of bisphenolic monomers, led to significant improvement of membrane performances.

The N, N-diquaternary-4, 4'-bipyridinium salts, called "*viologens*", are known for their use in interesting applications like electro chromic display [11, 12], electron mediation [13], thin-film mediator electrochemistry [14-18].

In a previous paper [19] we reported that chloromethylated polystyrene was transquaternized with N-phenacyl-4, 4'-bipyridinium bromide derivatives, resulting cross linked networks of polystyrene chains bridged by viologen linkages.

These results determined us to use polysulphone instead of polystyrene in view to prepare soluble polymers having viologen pendent groups. Due to their solubility, these polymers could be promising candidates for membranes. The influence of the synthesis parameters (time, temperature, reagents ratio) on the solubility of the final polymers was discussed.

Experimental Part

Materials and Methods

Polysulphone (Aldrich) was used as received. 4, 4'-Bipyridyl (Merck) was recrystallized from diethyl ether (mp. 110 °C). 2-Bromoacetophenone, 2-bromo-4'-nitroacetophenone, 2-bromo-4'-chloroacetophenone (Merck) were recrystallized from benzene and petroleum ether. Methyl bromacetate and ethyl bromacetate (Merck) were distilled under vacuum. Analytical grade acetone was distilled over anhydrous potassium carbonate.

^{1}H-NMR spectra were recorded on a JEOL 90 MHz spectrometer, using $CDCl_3$ or DMSO-d_6 as solvent and TMS as internal standard. Average number molecular weight ($\overline{M}_n$) and polydispersity index ($\overline{M}_w/\overline{M}_n$) of polymers have been determined with a GPC-PL-EMD.950 instrument (Polymer Laboratories), by using polystyrene as standard.

The total chlorine content was determined by Schöninger modified method [20]. The molar degree of chloromethylation (DCm) was calculated using the following equation:

$$DCm = \frac{442.51 \times Cl_t}{35.45 \times 100 - 48.45 \times Cl_t} \qquad (1)$$

where: 442.51 is molecular weight of structural unit of PSF; 35.45 is atomic weight of chlorine; 49.45 is molecular weight of CH_2Cl group and Cl_t is chlorine concentration, determined analytically.

Synthesis of chloromethylated polysulphones (CMPSF1-CMPSF4)

The chloromethylated polysulphones with various degrees of chloromethylation have been prepared by the chloromethylation reaction of Udel Polysulphone as described [7].

The chemical modification reaction proceeded in chloroform at 50-52°C, using paraformaldehyde trimethylchlorosilane as chloromethylation reagent and $SnCl_4$ as catalyst. The main characteristics of these polymers are presented in table 1.

Synthesis of N-phenacyl and N-alkyl acetate-4, 4'-bipyridinium bromides (3a-3e)

The 4,4'-bipyridinium bromide derivatives have been prepared by reacting 4,4'-bipyridyl (**1**) with corresponding phenacyl bromides (**2a-2c**) or alkyl acetate bromides (**2d, 2e**) in a 1/1 molar ratio (scheme 1).

The synthesis of N-phenacyl-4, 4'-bipyridinium bromide (**3a)** is given below as an example. A solution of 1.99g (10 mmol) **2a** in 10 mL anhydrous acetone was added to a stirred solution of 1.57g (10.1 mmol) **1** in 10 mL anhydrous acetone, at room temperature. The mixture was stirred for

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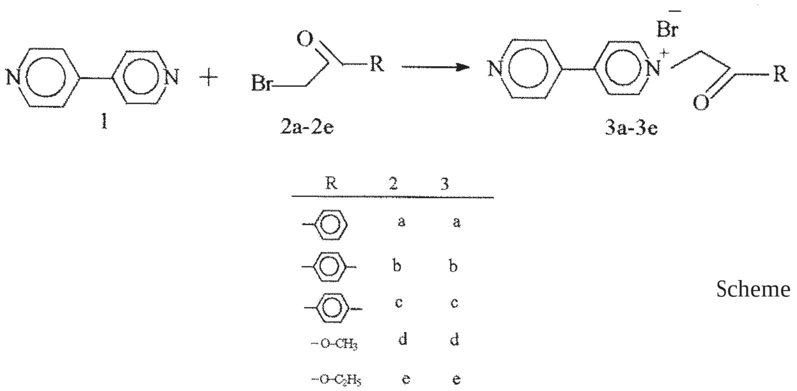
Table 1
CHARACTERIZATION OF UDEL POLYSULPHONE AND CHLOROMETHYLATED POLYSULPHONES

Sample	Cl[a], (%)	DCm[b]	$\overline{M_n}$ [c]	$\overline{M_w}/\overline{M_n}$
PSF	0.18	0.00	28 600	1.64
CMPSF1	3.34	0.44	27 500	1.77
CMPSF2	5.90	0.80	28 600	1.84
CMPSF3	8.85	1.26	29 800	1.90
CMPSF4	12.97	1.97	30 800	1.95

a Chlorine content found from elemental analysis;
b Degree of chloromethylation calculated from the chlorine content with formulas (1);
c Average number molecular weight measured by GPC.



Scheme 1

3 h, then kept at room temperature for 12 h without stirring. The resulted precipitate was filtered and washes three times with anhydrous diethyl ether, to recover the unreacted reagents. Finally, the product was kept over phosphorous pentoxide under vacuum at room temperature for 48 h.

Analysis:

N-phenacyl-4, 4'-bipyridinium bromide (3a): White-blue crystals yield 88 %, mp. 203 °°C. $C_{18}H_{15}N_2OBr$: calculated (%): C 60.84; H 4.22; N 7.88; Br 22.54; found (%): C 61.11; H 4.30; N 7.82; Br 22.34. IR (KBr, cm^{-1}): 3050 ($\nu_{C\text{-}H\ aromatic}$); 1693 ($\nu_{C=O}$); 1637, 1598, 1540, 1493 ($\nu_{C=C}$, $\nu_{C=N\ aromatic}$). ^{1}H-NMR (DMSO-d_6, TMS) δ: 9.216 (d, 2H, ortho >N$^+$<); 8.90-8.65 (m, 4H, Ph-Ph); 8.175-7.65 (m, 5H, -Ph, 2H, ortho >N); 6.55 (s, 2H, -CH_2-).

*N-(p-chloro)-phenacyl-4,4'-bipyridinium bromide (3b)***:** Pink-lilac crystals, yield 91%, mp. 270 °°C. $C_{18}H_{14}N_2OBrCl$: calculated (%): C 55.45; H 3.59; N 7.19; found (%): C 55.73; H 3.81; N 7.33. IR (KBr, cm^{-1}): 3050 ($\nu_{C\text{-}H\ aromatic}$); 1666 ($\nu_{C=O}$); 1637, 1597, 1540, 1514, 1478 ($\nu_{C=C,\ C=N\ aromatic}$); 1090 ($\nu_{C\text{-}Cl\ aromatic}$). ^{1}H-NMR (DMSO-$d_6$, TMS) δ: 9.425 (d, 2H, ortho >N$^+$<); 8.950-8.675 (m, 4H, Ph-Ph); 8.125-8.025 (m, 2H, 2H ortho>N:); 7.225 (d, 2H); 6.525 (s, 2H, CH_2), 4.0 (s, 3H, -OCH_3).

*N-(p-nitro)-phenacyl-4,4'-bipyridinium bromide (3c)***:** Blue crystals, yield 93%, mp. 148 °°C. $C_{18}H_{14}N_3O_3Br$: calculated (%): C 54.00; H 3.50; N 10.50; Br 20.00; found (%): C 54.25; H 3.73; N 10.77; Br 19.86. IR (KBr, cm^{-1}): 3040 ($\nu_{C\text{-}H\ aromatic}$); 1703 ($\nu_{C=O}$); 1635, 1596, 1481 ($\nu_{C=C}$, $\nu_{C=N\ aromatic}$); 1528($\nu_{NO2\ asym}$.), 1346 ($\nu_{NO2\ sym}$.). ^{1}H-NMR (DMSO-d_6, TMS) δ: 9.212 (d, 2H, ortho >N$^+$<); 8.90-8.675 (m, 4H, Ph-Ph); 8.375 (m, 4H, -Ph); 8.05 (m, 2H, ortho>N:); 6.725 (s, 2H, -CH_2-).

*N-[1-(2-methoxy-2-oxo)ethyl]-4,4'-bipyridinium bromide (3d)***:** Beige crystals, yield 78%, mp. 176 °°C $C_{13}H_{13}N_2O_2Br$: calculated (%): C 50.42; H 4.20; N 9.06; Br 25.89; found (%): C 50.52; H 4.34; N 9.12; Br 26.02. IR (KBr, cm^{-1}): 3040 ($\nu_{C\text{-}H\ aromatic}$); 1730 ($\nu_{C=O}$); 1636, 1584, 1541, 1482, ($\nu_{C=C}$, $\nu_{C=N\ aromatic}$); 1238, 1178 ($\nu_{C\text{-}O\text{-}C\ ester}$). ^{1}H-NMR (DMSO-$d_6$, TMS) δ: 9.17 (d, 2H, ortho >N$^+$<); 8.67 (m, 4H, Ph-Ph); 7.90 (m, 2H, ortho >N:); 5.87 (s, 2H, -CH_2-); 3.85 (s, 3H, -CH_3).

*N-[1-(2-ethoxy-2-oxo)ethyl]-4,4'-bipyridinium bromide (3e)***:** Beige crystals, yield 72%, mp. 198°°C. $C_{14}H_{15}N_2O_2Br$: calculated (%): C 52.01; H 4.64; N 8.67; Br 24.76; found (%): C 51.78; H 4.71; N 8.72; Br 24.85. IR (KBr, cm^{-1}): 3050 ($\nu_{C\text{-}H\ aromatic}$); 1722 ($\nu_{C=O}$); 1635, 1597, 1580, 1478, ($\nu_{C=C}$, $\nu_{C=N\ aromatic}$); 1240, 1182 ($\nu_{C\text{-}O\text{-}C\ ester}$). ^{1}H-NMR (DMSO-$d_6$, TMS) δ: 9.17 (d, 2H, ortho >N$^+$<); 8.65 (m, 4H, Ph-Ph); 7.92 (m, 2H, ortho>N:); 5.82 (s, 2H, -CH_2-); 4.30 (m, 2H, -CH_2-, ethyl); 1.30 (s, 3H, -CH_3, ethyl).

Chemical modification of polysulphones

The reaction was performed in a glass flask fitted with stirrer, condenser and controlled temperature bath. To a solution of 1,0 g (2 mmol) **CMPSF2** in 15 mL DMF were added 2.1 mmol of bromide derivatives **3a-3e**. The stirring was maintained for 6 h at 40 °C, then the reaction mixture was poured into absolute methanol. The resulting precipitate was filtered and washed three times on the filter with absolute methanol. Then, it was dried at 40°C under vacuum for 48 h.

Results and discussion

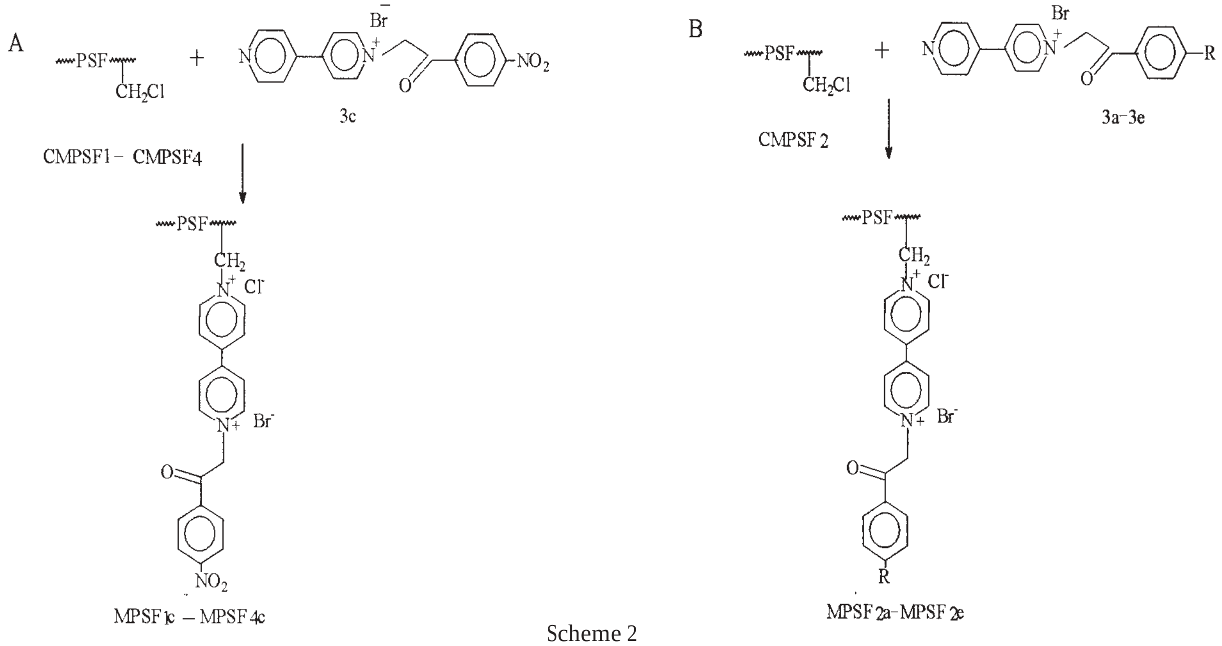
Various reaction conditions (temperature, time, molar ratio of reagents) have been tested to obtain soluble chloromethylated polysulphones, with variable degree of substitution. The obtained data are presented in Table 1.

As one can see from Table 1, while samples CMPSF1 and CMPSF2 are monosubstituted, having the chlorine content lower than 7.22 (high limit of monosubstitution), samples CMPSF3 and CMPS4 are disubstituted, i.e. they had two –CH_2Cl groups per S.U. Their corresponding DCm values, calculated from chlorine content by formula presented in the experimental section, ranged between 0.44 and 1.97. The $\overline{M}_n$ values, measured by GPC in chloroform ranged between 27500 and 30800, with corresponding polydispersity indexes ranging between 1.77 and 1.95.

The chemical modification of chloromethylated polysulphones with 4, 4'-bipyridinium bromide derivatives (**3a-3e**) was performed in two ways: first, chloromethylated polysulphones CMPSF1-CMPSF4 have been reacted with nitro-derivative **3c** to establish optimum reaction parameters and to obtain soluble final product (Scheme 2A). In the second ideea, the CMPSF2 was reacted with derivatives **3a-3e** (scheme 2B). The obtained polymers were characterized by elemental analysis, ^{1}H-NMR spectroscopy and solubility tests.

To obtain soluble samples we monitored the reaction of chloromethylated polysulphones having various degree of chloromethylation (DCm) with N-*p*-nitrophenacyl-4.4'-bipyridinium bromide (**3c**) (scheme 2A). As can be seen from table 2, when the DCm of the chloromethylated polysulfone is greater than unity, the resulting modified polymers are insoluble, probably due to a secondary transquaternization reaction leading to cross linked moieties (scheme 3).

The modified polysulfones (scheme 2B) were characterized by elemental analysis, ^{1}H-NMR spectra and solubility tests. All the obtained polymers exhibited good solubility in N,N-dimethylformamide, N,N-dimethylacetamide, N-methylpyrrolidine-2-one, tetrahydrofurane and they are insoluble into water, methanol and ethanol. Their characteristics are listed in table 3.

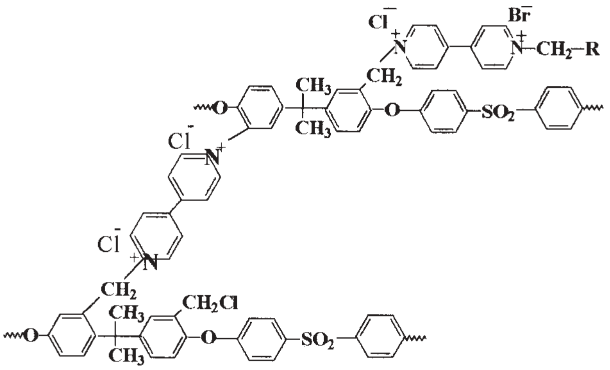


Scheme 2

Table 2
CONDITIONS OF QUATERNIZATION REACTION OF CMPSF WITH N-p-NITROPHENACYL-4, 4'-BIPYRIDINIUM BROMIDE IN DMF AS SOLVENT

Sample	CMPSF		Reaction conditions			N %	DS_1[d] %	Solubility
	Cl[a] %	DCm[b]	Temperature °C	Time h	Molar ratio[c]			
MPSF 1c	3.34	0.44	50	6	1:1.2	1.02	*	—
	3.34	0.44	40	6	1:1.2	0.46	3.58	+
	3.34	0.44	40	8	1:1.2	0.75	6.24	+
MPSF 2c	5.90	0.80	50	6	1:1.2	0.83	*	—
	5.90	0.80	40	6	1:1.2	3.14	71.60	+
	5.90	0.80	20	8	1:1.2	1.40	28.45	+
MPSF 3c	8.85	1.26	50	8	1:1.2	3.02	*	—
	8.85	1.26	40	6	1:1.2	2.95	*	—
MPSF 4c	12.97	1.97	50	12	1:1.2	5.23	*	— —
	12.97	1.97	50	8	1:1.2	5.07	*	— —
	12.97	1.97	50	4	1:1.2	3.25	*	— —
	12.97	1.97	50	2	1:1.2	2.32	*	— —
	12.97	1.97	40	1	1:1.2	1.58	*	— —

a- determined by modified Schöniger method [20];
b- molar degree chloromethylation of chloromethylated polysulphone;
c- molar ratio CMPSF2/ N-(*p*-nitro)phenacyl-4, 4'-bipyridinium bromide;
d- molar substitution degrees calculated from the nitrogen content analytically determined in polysulphone with pendent N-(*p*-nitro)phenacyl-4,4'-bipyridinium chloride, bromide group
* DS can't be calculated because of the cross linking;
\+ soluble;
— low degree of cross linking observed by the swelling of polymer in solvent;
— — high degree of cross linking observed by insolubilization of polymer.



Scheme 3

Table 3

CHARACTERISTICS OF POLYSULPHONES WITH PENDENT VIOLOGEN GROUPS (**MPSF2a-MPSF2e**) [a]

Sample	Nitrogen content (%)		^{1}H-NMR[b]	
	Calculated	Found	δ (ppm) (CH_2Cl)	δ (ppm) $(CH_3)_2C<$
MPSF2a	2.93	2.13	4.75	1.70
MPSF2b	5.24	3.14	4.62	1.76
MPSF2c	2.83	2.12	4.62	1.74
MPSF2d	3.06	2.47	4.60	1.74
MPSF2e	3.08	2.63	4.60	1.74

a -The modified polysulfones were obtained in same reaction conditions: CMPSF2, DMF as solvent, temperature of 40 °C, reaction time of 6 h and molar ratio CMPSF2/ N-monoquaternary bromides are 1/ 1.2;

b- DMSO-d_6 as solvent and TMS as internal reference.

Table 4

SUBSTITUTION DEGREE FOR **MPSF2a-MPSF2e**, CALCULATED FROM ELEMENTAL ANALYSIS AND ^{1}H-NMR DATA

Sample	Molar substitution degree, DS	
	Elemental analysis, DS_1	^{1}H-NMR, DS_2
MPSF2a	0.73	0.75
MPSF2b	0.72	0.75
MPSF2c	0.75	0.79
MPSF2d	0.77	0.79
MPSF2e	0.76	0.79

DS_1 - substitution degrees calculated from the nitrogen content analytically determined in polysulphones with viologen pendent groups;

DS_2 - substitution degrees of derivative polysulphones calculated from ^{1}H-NMR spectra with the formula:

$$DS_2 = 1 - \frac{3A_{CH2Cl}}{A_{(CH3)2C} \times 0.80}$$

Where: 0.80 = the substitution degree of starting chloromethylated polysulfone (CMPSF2);

A_{CH2Cl} = area corresponding to $-CH_2Cl$ protons (δ 4.45 ppm);

$A_{(CH3)2C}$ = area corresponding to $(CH_3)_2C <$ protons (δ 1.70 ppm).

This behaviour was also observed in the reaction of chloromethylated polystyrene with the same N-monoquaternary salts of 4, 4'-bipyridyl [19]. Also, long reaction times, temperature of 50°C and an excess of low molecular weight monomer led to cross linked product. The lower is the content of CH_2Cl groups, the higher the probability to obtain soluble polysulphone with pendent viologen groups will be. For example, when using a CMPSF with DCm of 0.80, after 8 h reaction time at 20°C, a soluble diquaternary sample was obtained, but having a low quaternization content (28.45 %).

Therefore it was concluded that a soluble, satisfactory product, could be obtained after 6 h reaction time, at reaction temperature of 40°C, using a molar ratio of the reagents of 1:1.2. Starting from CMPSF2 having DCm of 0.80, under the reaction conditions discussed above, soluble polysulphones having pendent viologen groups were obtained with various DS's (table 4).

Conclusions

New soluble modified polysulphones, with both N-phenacyl-4,4'-bipyridinium bromide and N-alkylacetate-4, 4'-bipyridinium bromide pendent groups, have been synthesized. The polymers showed good solubility in N,N-dimethylformamide, N,N-dimethylacetamide, N-methylpyrrolidine-2-one, tetrahydrofurane which recommended them as potential candidates for semi permeable membranes. When the DCm of the chloromethylated polysulfone is bigger than unity, the corresponding modified polymers are insoluble, probably due to a secondary transquaternization reaction leading cross linked moieties.

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