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POLYMERS WITH PENDANT FUNCTIONAL GROUP. III. POLYSULFONES CONTAINING VIOLOGEN GROUP

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ABSTRACT

The chloromethylation reaction of polysulfone and the amination reaction with 4,4'-bipyridyl or some monoquaternized derivatives of this in order to obtain polysulfone with viologen groups were analyzed. A kinetic study of amination reaction of a chloromethylated polysulfone with 4,4'-bipyridyl and Nbenzylbipyridinium chloride in dimethylsulfoxide is also reported.

INTRODUCTION

Functional polymers represent an important class of polymeric materials which contain the functional groups in the main or side chains. Their synthesis is performed by means of classical methods such as: polymerization or polycondensation of functional monomers, as well as by the chemical modification of some polymers. However, in many instances the chemical modification is the most frequently used method [1,2].

It is well known that polysulfones are outstanding polymer membranes with T_g of 195°C, an amorphous glassy state, thermal oxidative stability with excellent strength and flexibility, and resistance to extremes of pH and low creep [3-5].

Also, the chemical transformations of polysulfones as: chloromethylation [6], sulfonation[7,8], metalation [9] and quaternization [10] led to important functional membranes, coatings, ion-exchange resins, ion-exchanger fibers, selectively permeable films,etc. The first chemical transformation was performed with chloromethyl methyl ether, 1chloromethoxy-4-chlorobutane and 1,4-bis(chloro-methoxy)-butane [6]; as well as with chloromethyl octyl ether [11,12]. The last one used the amination with tertiary alkyl or hydroxyalkyl amines of chloromethylated polysulfones [10].

Another aspect well known from the literature data is that the viologens (1,1'- dimethyl-4,4'-bipyridinium dibromide and its analogues) are compounds with inter-esting electrochemical properties [13,14]. The polymers such as polystyrene and. some acrylic copolymers containing viologen groups also display special properties, [15,16].

For all above mentioned reasons, we have taken into account the chemical modification of polysulfone.

The goal of this study is to report the synthesis of polysulfones containing several viologen groups. For this, the common method namely the chloromethylation reaction of the polysulfone [poly(oxy-1,4-phenylensulfonyl:1,4-phenylenoxy-1,4-phenylene (1-methylethylidene)-1,4-phenylene] followed by the amination reaction of the chloromethylated product with monoquaternized compounds of 4,4'-bipyridyl was used.

The chloromethylation reaction was performed with paraformaldehyde: chlorotrimethylsilane mixture as chloromethylation agent and stannic chloride as catalyst [17]; this method being used only in the case linear and crosslinked polystyrene.

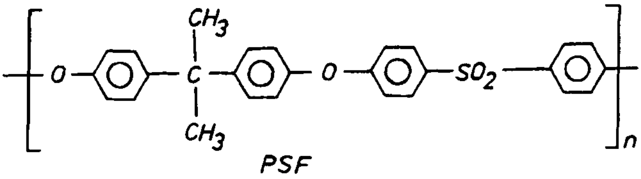
Also, the kinetic aspects of the amination reaction were analyzed.

In addition, the amination with 4,4'-bipyridyl, nonsubstituted compound, was investigated. The amination of chloromethylated polysulfone with the above mentioned amine, followed by the quaternization of the second nitrogen atom with a low molecular weight halogenated compound, can be another method leading to polysulfone with viologen groups.

EXPERIMENTAL

Materials and Methods

Polysulfone UDEL-1700 (Union Carbide) (PSF) commercial product with the structural unit shown in Scheme 1, was purified by dissolving in chloroform: precipitation with methanol, and finally it was dried in vacuum at 40°C before used.



Scheme 1.

The IR absorption spectra were obtained from KBr pellets on a SPECORD M 80 spectrophotometer and ^{1}H-NMR spectra were recorded on a BRUKER 80 AW spectrometer under standard measurement conditions.

Chloromethylation of Polysulfone

The mixture of commercial paraformaldehyde: chlorotrimethylsilane ($ClSiMe_3$) from Merck as chloromethylation agent, and stannic chloride from Fluka as catalyst were used for the chloromethylation reaction.

Chloroform purified by the usual method was used as solvent.

The chloromethylation reaction was performed in a glass flask equipped with stirrer and reflux condenser, then heated in a water bath at controlled temperature.

Typically, the chloromethylation agent and the catalyst are added to a polymer solution heated at the 50-52°C. Once the reaction is completed, the mixture is poured into methanol under stirring and the separated polymer is filtered, then washed well with methanol, and finally dried in vacuum at 40°C.

The total chlorine content of the chloromethylated polysulfones was determined by the modified Schoninger method [18].

Amination of Chloromethylated Polysulfone

For the amination reaction, the chloromethylated polysulfone CMPSF-8 (Table 1) was used.

4,4'-Bipyridyl(4,4'-Bpy) from Fluka was recrystallized from diethylether.

Monoquaternized derivatives of 4,4'-bipyridyl were performed by us according to a previous study [19].

The solvent N,N-dimethylformamide (DMF) and dimethylsulfoxide (DMSO) were puried by conventional methods.

The amination of chloromethylated polysulfone was performed in a glass flask equipped with stirrer, cooler and heated in a water bath at a controlled temper-

TABLE 1. Chloromethylation Reaction of the Polysulfone

Polymer Code	Catalyst $SnCl_4$ (mole)	Time (h)	C14.16 %	Substitution degree (DS)	Observation
CMPSF-1 a)	0 50	24	11.86	1.82	crosslinked
CMPSF-2	0.50	24	8.32	1.27	crosslinked
CMPSF-3	0.20	5	2.69	0.41	soluble
CMPSF-4	0 20	15	4.16	0.63	soluble
CMPSF-5	0.20	28	5.20	0.80	soluble
CMPSF-6	0.20	72	7.85	1.20	soluble
CMPSF-7 b)	0 20	72	10.35	1.58	soluble
CMPSF-8 b)	0 10	72	12.47	1.85	soluble

The reactions were carried out at 50°C, polymer structural unit: paraformaldehyde chlorotrimethylsilane molar ratio being 1:3:3 and polysulfone concentration in $CHCl_3$ of 2%.

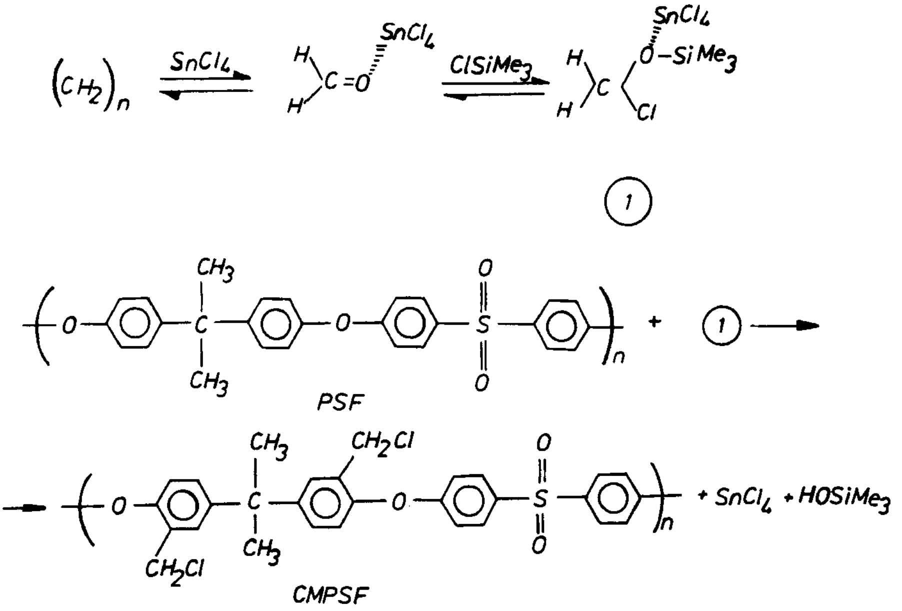
a) polysulfone concentration in $CHCl_3$ is 5% .

b) polymer structural unit: paraformaldehyde: chlorotrimethylsilane molar ratio is 1:10:10.

ature. First, the chloromethylated polysulfone was dissolved in DMF and then the 4,4'-Bpy monoquaternized derivative was poured into the reactor. The stirring was continued for 10 hours at 70°C, and then the reaction product was precipitated into anhydrous diethylether. The product was filtered, then dried under vacuum over P_2O_5 at 20°C. The unreacted low molecular weight compound was isolated by washing the quaternized polysulfone with methanol 3-4 times understirring (the low molecular weight compounds are soluble in methanol). After purification, the polymers were again dried in vacuum at 40°C.

The aminated polysulfones are yellow powders.

Kinetic measurements, by the analytical method, were carried out according to a previously reported technique [20]. Thus, approximately 0,6-chloromethylated polysulfone was dissolved in 100 ml solvent. After thermosetting, a quantity of 4,4'-Bpy or 4,4'-Bpy monoquaternized derivative corresponding to an amine: chloromethylated group molar ratio of 5:1 was added. The temperature of the reaction mixture was maintained within ±0.2°C. The experiments were carried out in a reaction flask equipped with a stirrer and a condenser. At certain time intervals, 2



Scheme 2.

mL aliquots of the reaction mixture were removed, poured in bidistilled water, then immediately neutralized with 0.5 N nitric acid in order to stop the reaction, after which the amount of chlorine ions was potentiometrically determined with 0.02 M silver nitrate.

All reactions were carried out in air.

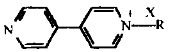
RESULTS AND DISCUSSION

Chloromethylation of Polysulfone

The chloromethylation reaction takes place according to Scheme 2:

It is possible to expect a crosslinking reaction (due to methylenic bridges between the macromolecular chains) which would effect the insolubilization of polysulfone. To avoid this side reaction, certain reaction conditions must be respected: as one can see from the data listed in Table 1.

The values from Table 1 show that an increase in the catalyst content, regardless of the dilution of the polymer solution, determines the crosslinking of the polysulfone. The soluble chloromethylated polysulfones can be obtained when the

TABLE 2. Characteristics of Monoquaternizated Derivatives of 4,4'-Bpy with  **structure**

R	X^-	Elemental analysys				IR (KBr)	^{1}H-NMR
		C (%) calcd/found	H (%) calcd/found	N (%) calcd/found	X (%) calcd/found	cm^{-1}	(δ -ppm)
-$CH_2C_6H_5$	Cl	72.23/72.15	5.31/5.03	9.91/9.69	12.55/12.27	3050, (ν C=C) 2800-3000, (ν CH_2) 1640, (ν C=O, C=N)	(D_2O) (s, 2H-CH_2-) 5.9 (s, 5H, C_6H_5) 7.6 (m, 8H, $C_5H_4N^+$, C_5H_4N) 7.9-9.3
-C_3H_7	Cl	66.54/66.34	6.40/6.12	11.94/11.57	15.12/14.94	2880, 2970, (ν alchil) 3030, 1600, (ν C=C, C=N)	(D_2O) (N^+-CH_2) 4.7; (t, 3H, CH_3) 1.1 (m, 2H, -CH_2CH_3) 2.2 (m, 8H, NC_6H_4) 7.7-9.3
-$CH_2COC_6H_5$	Br	60.84/61.11	4.22/4.31	7.88/7.82	22.54/22.34	1690, (ν C=O) 1637, 1598, 1540, 1493, (ν C=C, C=N)	(DMSO) (s, 2H, CH_2) 8.8 (2H, Bpy) 9.3; (2H, Bpy) 8.15 (2H, Bpy) 8.9; (2H, Bpy) 7.8-8.1
-$CH_2COC_6H_4NO_2$	Br	54.00/54.25	3.50/3.73	10.50/10.77	20.00/19.86	1703, (ν C=O) 1635, 1596, 1481, (ν C=C, C=N) 1528, 1346, (ν NO_2)	
-$CH_2COC_6H_4OCH_3$	Br	59.22/59.38	4.41/4.85	7.27/7.62	20.78/20.54	1666, (ν C=O) 1250, 1035, (ν -O-C-O-) 1637, 1597, 1540, 1514, 1478, (ν C=C, C=N)	

chloromethylation is performed at the high dilution and low catalyst amounts. In the case of the soluble polymer, one can see: (1) as expected, the increase of the reaction time, as well as of the polymer structural unit: chloromethylation agent molar ratio improves the content of the chloromethylated groups of the functionalized polysulfone, (2) at the same reaction conditions, a lower catalyst content leads to a higher DS value.

Amination of Chloromethylated Polysulfone

The monoquaternized derivatives of 4,4'-Bpy used in the amination reaction have the structures shown in the Table 2.

The reactions of chloromethylated polysulfone with the products mentioned in Table 2 take place according to Scheme 3 and the characterization of the performed polymers (Q_2-Q_6) is presented in Table 3.

Kinetic Aspects

It is known that the reaction between a halogenated derivative and a tertiary amir nucleophilic substitution SN_2 with a second -order kinetic.

The formation of a charged transition state is favored by more polar solvent, solvate the developing charge.

For the reactions with second-order kinetics, the integrated form of rate expression is:

$$f(x) = 1/a\text{-}b \ln (1\text{-}\alpha/1\text{-}\beta) = kt \quad (1)$$

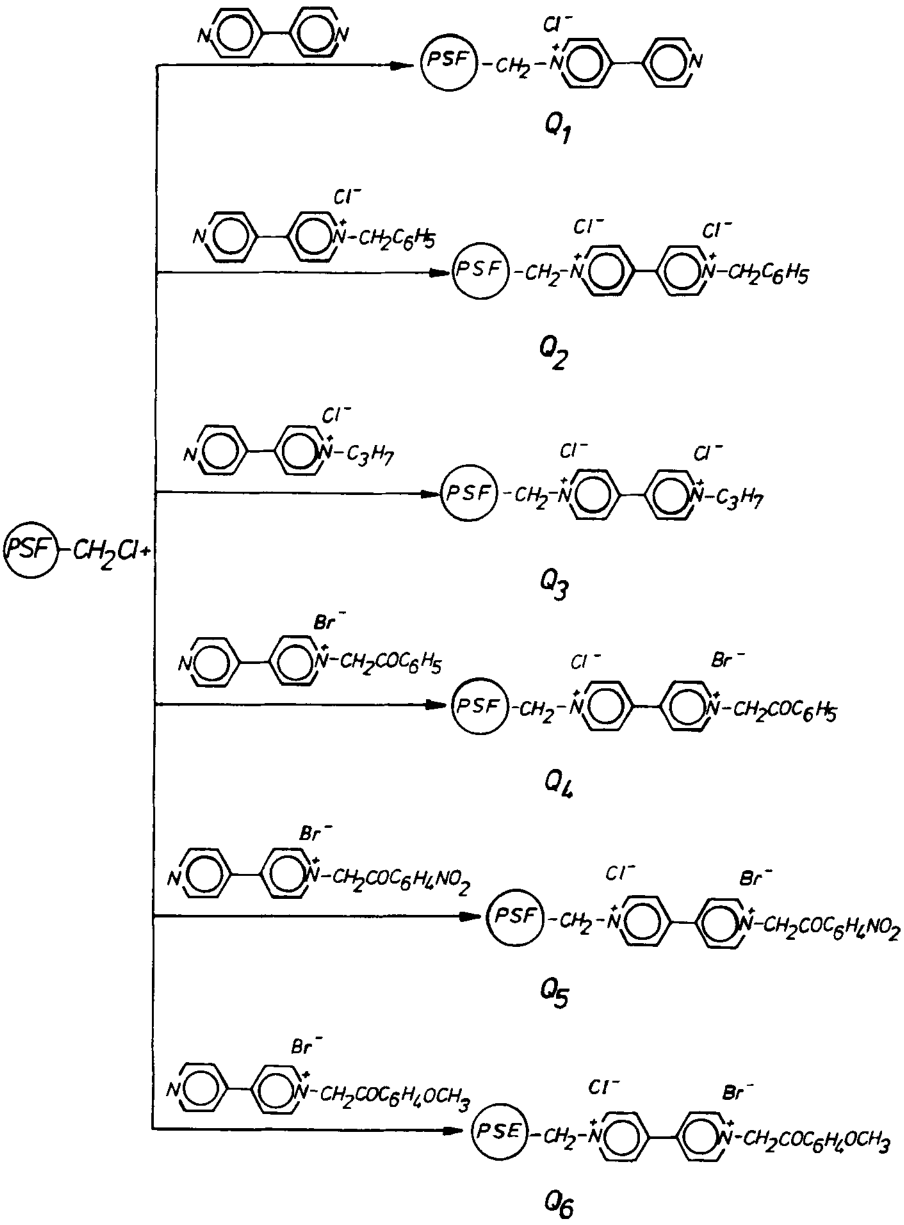
where: $\alpha = x/a$ and $\beta = x/b$ (molar transformation degree), x is the concentration of halogens at time t, in mol/L and a and b are the initial concentration of the reactants in mol/L.

For these reactions, the plot of f(x) against time should be linear, with a slope equal to k.

It is known that the amination of the model compound of the chloromethylated.polysulfone with tertiary amines in DMSO proceeded to completion with no deviation from second-order kinetics [8].

Since 4,4'-Bpy is a bifunctional compound, experiments with different molar ratios CMPSF: 4,4'-Bpy were performed in order to obtain linear polymers. Crosslinking does not occur for a CMPSF: 4,4'-Bpy molar ratio of 1:5.

Figures 1 and 2 show the kinetic behavior of the CMPSF reactions with 4,4'-Bpy and N-benzylbipyridinium chloride in DMSO.



Scheme 3.

TABLE 3. Characteristics of Q_2 - Q_6 Polymers[a]

Polymer Code	Nitrogen content, %		% b	IR (KBr) cm^{-1}
	Calculated	Found		
Q_2	5.07	3.65	72	1640 (ν >N^+-)
Q_3	5.55	4.50	81	1640 (ν >N^+-)
Q_4	4.48	3.50	78	1710 (ν C=O)
Q_5	6.27	5.32	85	1720 (ν C=O) 1356 (ν NO_2)
Q_6	4.28	2.70	63	1612 (ν C=O)

a) All amination reactions were carried out in DMF, at 70°C, time 10 hs.

b) Molar conversion calculated from nitrogen content.

One can observe that the amination of CMPSF with 4,4'-Bpy in DMSO is characterized by a slight deceleration which appears at ß = 0.15, while the amination of the chloromethylated polysulfone with N-benzylbipiridinium chloride is characterized by an sensible acceleration appearing at ß = 0.12. The magnitude of the deceleration or acceleration phenomenon is represented by k_2/k_1 ratio value.

The kinetic paramter values (Table 4) were calculated by using the following: the rate constants with Equation (1), E_a from the slope of lines in graphs of log k against 1/T, and A with Equation (2).

$$\log k = \log A - E_a/2.303\ RT \qquad (2)$$

We consider that the kinetic behaviors of the two amination reactions depend on the Ea values. This supposition is in good agreement with the results listed in Table 4. Thus, the amination with 4,4'-Bpy has close values of Ea for the two reaction steps characterized by k_1 and k_2 rate constants, whereas the amination with

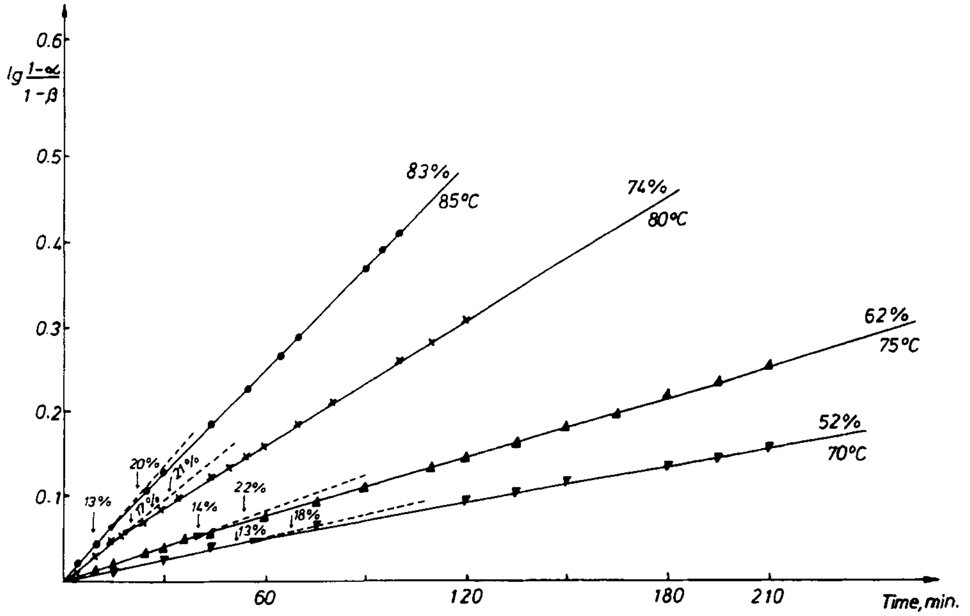


Figure 1. Conventional second-order plot for the quaternization of CMPSF-8 with 4,4'-Bpy in DMSO.

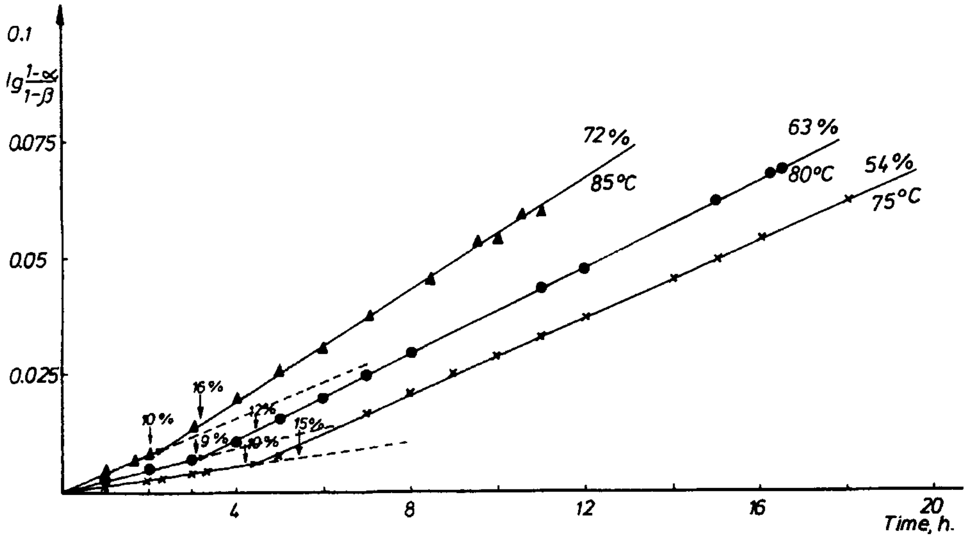


Figure 2. Conventional second-order plot for the quaternization CMPSF-8 with N-benzylbipyridinium chloride in DMSO.

The percentage values express the molar transformation degree (ß).

TABLE 4. Amination of Chloromethylated Polysulfone

Run	Solvent	T °C	a mol / l	b mol / l	a/b	$k_1 \times 10^3$ l/mol.sec	$k_2 \times 10^3$ l/mol.sec	k_2/k_1
	Amination with 4,4'-Bpy							
1	DMSO	70	0.07429	0.01486	5.00	0.474	0.451	0.96
2	DMSO	75	0.07429	0.01486	5.00	0.783	0.728	0.93
3	DMSO	80	0.07429	0.01486	5.00	2.071	1.960	0.94
4	DMSO	85	0.07429	0.01486	5.00	2.650	2.552	0.96
	For k_1, E_a = 18.82 Kcal/mol, log A = 11.59; for k_2, E_a = 17.89 Kcal/mol, log A = 12.18							
	Amination with N-benzylpyridinium chloride							
5	DMSO	75	0.06965	0.01393	5.00	0.293	0.854	2.91
6	DMSO	80	0.06965	0.01393	5.00	0.535	1.461	2.73
7	DMSO	85	0.06965	0.01393	5.00	0.863	2.071	2.40
	For k_1, E_a = 16.65 Kcal/mol, log A = 10.39; for k_2, E_a = 12.12 Kcal/mol, log A = 9.30							

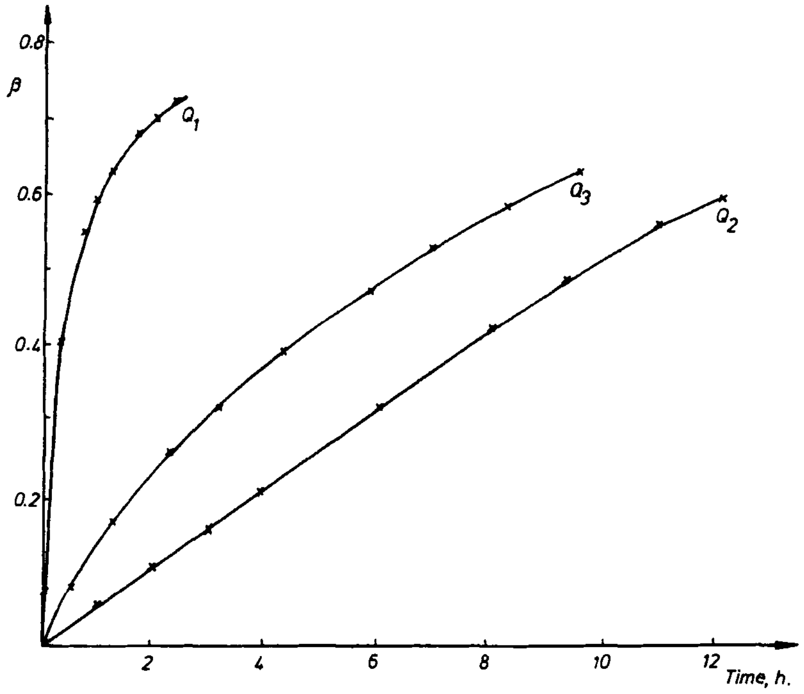


Figure 3. Transformation degree versus the time for the amination reaction of chloromethylated polysulfone with 4,4'-Bpy (Q_1), N-benzylbipyridinium chloride (Q_2) and N-propylbipyridinium chloride (Q_3) in DMSO at 85°C.

N-benzylbipyridinium chloride has a lower sensitive value for E_a in the second reaction step appearing at $ß = 0.12$.

We have also studied the influence of substituent nature on tertiary nitrogen atom of compounds utilized as nucleophiles, in the amination reaction of chloromethylated polysulfone by determining the transformation degree as a function of the reaction time (Figure 3).

As expected, the plots from Figure 3 show that the monoquaternized compounds of 4,4'-Bpy are less active nucleophiles than the nonquaternized compound. The stronger inductive effect (-I) of a quaternary ammonium group than of a tertiary amine group determines a greater decrease of the reactivity of the tertiary nitrogen atom from the monoquaternized compounds than from 4,4'-Bpy.

Also, it is observed that the nucleophylicity of the tertiary nitrogen atom of the monoquaternized compounds increases as the inductive effect (+I) of the substituent on the quaternary nitrogen atom increases. Thus, an alkyl has a higher inductive effect (+I) than that of an arylalkyl; these are the cases of propylbipyridinium chloride and N- benzylbipyridinium chloride, respectively.

CONCLUSIONS

The chloromethylation reaction of the polysulfone [poly(oxy-1,4-phenylensulfonyl-1,4-phenylenoxy-1,4-phenylene(1-methylethylene)-1,4-phenylene] followed by the amination reaction of chloromethylated product with several monoquaternized derivatives of 4,4'-bipyridyl is a method leading to polymers containing viologen groups.

The paraformaldehyde: chlorotrimethylsilane mixture is a chloromethyation agent as efficient as halogenated ethers; the results of chloromethylation by using the halogenated ethers are known from the literature data.

Comparative studies on the amination of chloromethylated polysulfone with 4,4'-bipiridyl and of some of its monoquaternized derivatives show that, as expected, the first amine has the highest reactivity. In the case of the monoquaternized compounds, the reactivity of tertiary nitrogen atom depends on the chemical nature of the substitute on the quaternary nitrogen atom.

Also, the comparison of the kinetic determinations made for two aminations of the chloromethylated polysulfone, namely, with 4,4'-bipyridyl and N-benzylbipyridinium chloride in DMSO shows: (1) a slight deceleration phenomenon for the first amination; (2) a sensitive acceleration phenomenon for the second one. Based on the kinetic parameter values, we consider that the value of E_a may be the major factor influencing the kinetic behavior.

REFERENCES

[1] D. C. Sherrington, in *Encyclopedia of Polymer Science and Engineering,* 2nd Edition, Vol. 14, Wiley & Sons, New York, 1988, p. 130.

[2] H. Ritter, in *Macromol. Eng.,* Munmaya Mishra, Ed., Plenum, New York, 1995, p. 291.

[3] R. N. Johnson, A. G. Farnham, R. A. Clenndinning, W. H. Hale, and C. N. Merriam, *J. Polym. Sci., A-1, 5,* 2399 (1967).

[4] A. Moshay and L. M. Rabeson, *J. Appl. Polym. Sci., 20,* 1885 (1976).

[5] A. Wnuk, T. T. Davidson, and J. E. McGrath, *J. Appl. Polym. Sci., Polym. Symp., 108* (1978).

[6] W. H. Daly, *J. Macromol. Sci. Chem., A 22*, 713 (1985).

[7] C. Arnold and R. Assink, *J. Membr. Sci., 38*, 71 (1988).

[8] C. Arnold and R. . Assink, *Polymer, 30*, 1137 (1989).

[9] M. D. Guiver, J. W. Apsimov, and O. Kutomy, *J. Polym. Sci. Polym. Lett. Ed., 26*, 123 (1988).

[10] W. H. Daly and S. J. Wu, *Modification of Polymers,* (B. V. Culbertson, Ed.), Amer. Chem. Soc., Washington, DC, 1983.

[11] A. Warshawsky, A. Deshe, and R. Gutman, *Brith. Polym. J., 16,* 234 (1984).

[12] A. Warshawsky, N. Kahana, A. Deshe, H. E. Gotlieb, and R. Arad-Yellin, *J. Polym. Sci. Polym. Chem. Ed., 28*, 2885 (1990).

[13] W. Slima, G. Matusiak, and A. Postawka, *Heterocycles, 23,* 1513 (1985).

[14] W. Stiwa and B. Mianowska, *Heterocycles, 29,* 557 (1989).

[15] I. Rubinstein, *J. Phys. Chem., 31, 235* (1987).

[16] Y. Okahata and G. En-na, *J. Phys. Chem., 92,* 4546 (1988).

[17] G. Itsuno, K. Uchiosh, and K. Ito, *J. Am. Chem. Soc., 112*, 8187 (1990).

[18] J. Haslan, B. Hamilton, and D. M. Squirell, *Analyst, 85,* 556 (1960).

[19] I. Druta, L. Smau, C. Cuciac, and R. Dinica, *An. St. Univ. "Al.I. Cuza"*, Iasi, T. III, S. Chim., 117 (1995).

[20] C. Luca, E. Avram, and M. N. Holerca, *J. Macromol. Sci.-Pure. Appl. Chem., A 33,* 233(1996).

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