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Polysulfones on the Base of New Diallylaminophosphonium Salts

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Summary: Methods for the synthesis of new diallylaminophosphonium salts have been developed. The reactivity of tris(diethylamino)diallylaminophosphonium tetrafluoroborate (DAAP-BF_4) and chloride (DAAP-Cl) through free-radical copolymerization with sulfur dioxide have been studied. Diallylaminophosphonium salts do not undergo free radical homopolymerization but copolymerize at a low rate with vinyl monomers. DAAP-BF_4 and DAAP-Cl show high activity in copolymerization with sulfur dioxide. The structure of the polysulfones obtained has been identified by NMR ^{13}C. The investigations carried out have shown that DAAP-BF_4 and DAAP-Cl copolymerize with sulfur dioxide, both double bonds participating with formation of cis-, trans-stereoisomeric pyrrolidine structures in a cyclolinear polymer chain. The new polysulfones possess a broad spectrum of bactericidal effect.

Keywords: biological activity of polymers; diallylaminophosphonium salts; polysulfones; radical polymerization; synthesis

Introduction

The range of nitrogen- and phosphorous-containing allyl compounds for the synthesis of linear high molecular weight polymers through radical homo- and copolymerization is rather narrow. Actually, among allyl monomers only quaternary diallylammonium salts have found application as monomers for the synthesis of polyfunctional polymers.[1] Pioneering works of Butler and coworkers[2–4] led to the cyclopolymerization of a variety of diallyl quaternary ammonium salts to yield water-soluble homo- and copolymers. The polymerization proceeds via alternating intra-inter-molecular chain propagation, termed cyclopolymerization, involving the kinetically preferred five-membered cyclic structure[5] instead of thermodynamically most stable six-membered ring. Poly(diallyldimethylammonium chloride) alone accounts for over 1000 patents and publications. Dialkyldiallylammonium salt/sulfur dioxide copolymers[6–9] are useful as textile furnishes, polymer additives, coagulants, thickeners,[6] catalysts of chemical reaction and bactericides.[1] Cross-linked polysulfones are used as ion exchange beds. Tri- or tetraallylammonium salts have been used for desalination of brackish water and for the extraction of uranium.[10] As polymers based on quaternary salts of diallylammonium have large number of applications due to their useful properties, studying of nitrogen- and phosphorous-containing allyl monomers of new structural types is quite advisable.

Phosphoric polymer derivatives are of significant interest because they are used as extractants and complexing agents. Due to high selectivity phosphorylated polyamines can be used in the isolation of cations which are in hardly separable combinations. Complexation ability of aminopolyphosphonium compounds in reactions with different metals (copper, beryllium, uranium, lead) opens the possibility for their use in the removal of metal from organisms.[11,12]

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The results of investigations concerning synthesis of new polysulfones on the basis of diallylaminophosphonium salts are presented in this article.

Experimental Part

Materials

Tris(diethylamino)diallylaminophosphonium tetrafluoroborate (DAAP-BF_4) and chloride (DAAP-Cl) were obtained as described in our previous publication.[13]

To obtain tris(diethylamino)diallylaminophosphonium chloride the reaction flask was loaded with tris(diethylamino)phosphazohydride (1.5 mol, 392 g) and freshly distilled allylchloride (7.5 mol, 600 g) was added drop wise to the reaction mixture with stirring until the reaction temperature stopped rising. Then sodium hydroxide (6.4 mol of 50% aqueous solution) was added drop wise under stirring and the mixture was heated on a water bath at 38 °C for 30-45 min then for 10-12 hr with stirring at a boiling temperature. After cooling and the middle layer was separated. DAAP-Cl was extracted with dichlormethane, the extract was evaporated under vacuum at 100 °C. The yield of DAAP-Cl was 86.5% (490 g). ($C_{18}H_{40}ClN_4P$) (378.5): Calcd. C 57.07, H 10.57, N 14.79.; Found C 56.82, H 11.06, N 14.55.

To obtain tris(diethylamino)diallylaminophosphonium tetrafluoroborate a reaction flask was loaded with DAAP-Cl (1.3 mol, 490 g) dissolved in water (2 L) and 20% aqueous solution of sodium tetrafluoroborate (1.7 mol, 960 g) was added drop wise with intensive stirring. Stirring was continued for 24 hr at 25 °C, then the mixture was filtered. The precipitate was thoroughly washed with distilled water and dried under vacuum at 80 °C to constant weight. The yield of DAAP- BF_4 was 70.1% (390 g). ($C_{18}H_{40}F_4N_4PB$) (430): Calcd. C 50.23, H 9.30, N 13.02; Found C 49.72, H 10.03, N 12.83.

Sulfur dioxide was dried by passing through concentrated sulfuric acid and freshly-sintered $CaCl_2$.

All applied initiators (potassium persulphate (PP), 2,2'-azobisisobutyronitrile (AIBN)) and solvents (DMSO, methanol, tetrahydrofurane) were purified using standard laboratory methods.

Copolymerization

The monomers were mixed in suitable molar proportions and copolymerization of DAAP-BF_4 and DAAP-Cl with SO_2 was conducted in bulk and in solution in the presence of initiator AIBN ($3 \cdot 10^{-2}$ mol L^{-1}) by performing the reaction in bulk and in organic solvent and initiator PP ($2 \cdot 10^{-2}$ mol L^{-1}) in aqueous medium. Kinetic investigations were carried out at initial conversions by the gravimetric method at 60–90 °C.

The copolymerization experiments of DAAP-BF_4 and DAAP-Cl with SO_2 were carried out in a glass reactor according to the following technique. A desired quantity of SO_2 was introduced into a liquid nitrogen-cooled reactor via condensation, then the necessary quantity of monomer, initiator and solvent were added. The reactor was sealed and the reaction was carried out at the chosen temperature. The reaction was allowed to proceed to an extent not passing 10% conversion, at which point the reaction was stopped. Copolymers were precipitated in tetrahydrofurane and purified by three-fold reprecipitation from methanol. The purified copolymers were dried under vacuum at 50 °C to constant weight. The copolymer composition was calculated from the elemental analysis.

Measurements

UV-spectra were recorded on a Shimadzu UV-VIS-NIS-NIR 3100 spectrometer. The complexation was studied depending on deviations from additivity of absorbance differences of the monomer mixture solutions and the sums of absorbances of each comonomer at the same concentrations. The complex composition was determined by the method of isomolar series.[14]

NMR^{13}C spectra were recorded on a Bruker AM-300 spectrometer operating at

75,47 MHz using a broad-band proton decoupling and in the JMOD (J-modulated) spin echo mode. DMSO-d_6 and tetramethylsilane (TMS) were used as solvent and internal standard, respectively.

The reduced η_{red} and intrinsic $[\eta]$ viscosity measurements were performed in a Ubbelohde capillary viscometer at $25 \pm 0,1\,^{\circ}C$.

The molecular weight of copolymers was determined by centrifugation method[15] in methanol at 25 °C.

The precipitation of $HAuCl_4$ by polysulfones was conducted in the following way. The measuring flask (25 ml) was loaded with 0.5 ml $5 \cdot 3 \cdot 10^{-3}$ M solution of $HAuCl_4$ (Au initial concentration = 20.9 mg L^{-1}) and with different volume of polysulfone solution in water. Then hydrochloric acid (0.3 M) was added in order to reach the volume of 25 ml. The solution was stored for 10 min and then filtered. The concentration of gold was determined by spectrophotometry.[16]

Sorptive ability of polysulfones in 0.3 M HCl was determined by the static sorption method (initial Au concentration 20.9 mg L^{-1}). The measuring flask (25 ml) was loaded with $6.95 \cdot 10^{-3}$ g copolymer and 0.5 ml $5.3 \cdot 10^{-3}$ M solution of $HAuCl_4$ (Au initial concentration is 20.9 mg l^{-1}). The solution was stored for 1 day and then filtered. The residual concentration of gold was determined by spectrophotometry. The value of copolymer static sorption capacity on gold was estimated as the difference between metal concentrations before and after sorption.

The acute toxicity was measured on mongrel white male mice weighing 18-20 g, using intraperitoneal doses. Each group consisted of six animals. LD_{50} values were calculated according to the method described in.[17]

The microbiological tests were performed by serial dilution of preparations in meat-peptone broth followed by inoculation of meat-peptone agar. Test cultures were *Staphylococcus aureus* strain 906, *Staphylococcus saprophyticus*, ATCC 15305, *Micrococcus luteus*, ATCC 4698, *Escherichia coli* strain 25922, *Bacillus antracoides* strain 1312, *Bacillus subtilis, ATCC 663, Bacillus proteus* strain «Tsvetkov», *Candida albicans*, *264/624, Salmonella spp.* Bacteria were grown for 20 h or 7 days. Microbial loads were $2.5 \cdot 10^5$ cells in 1 ml of preparation-containing liquid growth medium.

The protection effect of gastric ulcers was measured on rats and it was determined in the following way. The compounds were introduced in dose of 100 mg kg^{-1}. Ulcers were obtained by the application of indometacine in a dose of 20 mg kg^{-1} in 1 hour after the introduction of compounds.

Results and Discussion

It is well known that allyl monomers polymerize only with difficulty and yield polymers with low molecular weight. These effects are the consequence of degradative monomer chain transfer.[18–22] Therefore, the first stage of our investigation was to find out if the involvement of new diallylaminophosphonium salts in the processes of radical polymerization is possible.

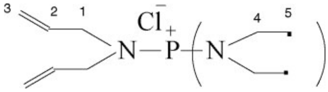
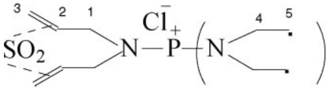
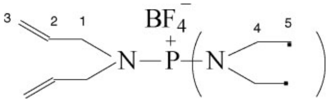
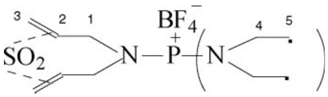
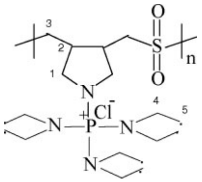
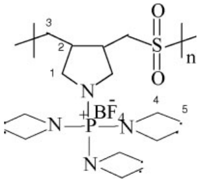
Homo- and Copolymerization of Tris(diethylamino)diallylaminophosphonium Tetrafluoroborate and Chloride

It was found that diallylaminophosphonium salts do not homopolymerize according to free radical mechanism in the presence of PP and AIBN at 60–90 °C. Their activity increases a bit in the case of reaction conducted in the presence of protic acides. However in this case particularly at polymerization in the presence of HCl (90 °C, 30 hours), the polymer yield does not exceed 10%. Diallylaminophosphonium salts were found to be copolymerized at a low rate with vinyl monomers, the copolymers being characterized by statistical distribution of monomer units.

Diallylaminophosphonium salts are active in copolymerization with sulfur dioxide exhibiting high electron-acceptor activity. The study of diallylaminophosphonium salt copolymerization with SO_2 showed that the composition of copolymers obtained did not depend on the monomer ratio in the initial mixture nor on the reaction conditions (nature of a solvent and initiator, temperature, conversion level). The uniformity of composition regardless of the monomer ratio in the reaction mixture suggests that copolymerization of diallylaminophosphonium salts with SO_2 proceeds via complex formation (Table 1) which was supported by NMR –spectroscopy data. Analysis of ^{13}C NMR spectra of DAAP−BF_4 and DAAP−CI with SO_2 mixtures shows a significant shift of signals of allyl group carbon atoms (as compared to monomers) which indicates the formation of donor-acceptor complexes of the monomers with SO_2 (Table 1). However, the values of these shifts are much greater than with diallylacylhydrazines.[23] Perhaps, in the case of diallylaminophosphonium salts P and N atoms of electrodonor groups P-$(N\text{-}C_2H_5)_2$ take part in complexation.

The study of kinetic regularities of diallylaminophosphonium salts copolymerization with SO_2 showed a strong dependence of reaction rate on the monomer ratio. The maximum rate was observed at equimolar ratio of monomers (Figure 1). The deviation of the comonomer ratio from equimolar both to higher and lower values

Table 1.
NMR^{13}C spectra of DAAP-Cl (1), DAAP-BF_4 (3), their complexes (2,4) and copolymers (5,6) with SO_2 (DMSO-d_6, TMS, 25 °C)

№	Compounds	Chemical shift values and signals multiplets of the atoms (δ, ppm)					
		stereo-isomers	C_1	C_2	C_3	C_4	C_5
1			49.65 t	134.08 d	119.65 t	41.02 t	13.73 q
2			43.01 t	136.00 d	115.48 t	39.44 t	12.75 q
3			49.27 t	132.54 d	119.58 t	40.58 t	13.09 q
4			43.10 t	135.67 d	115.66 t	40.25 t	13.25 q
5		cis trans	52.60 53.34 t	36.71 38.77 d	51.98 54.82 t	41.27 40.37 t	13.94 13.94 q
6		cis trans	50.57 51.04 t	34.90 36.94 d	50.42 52.14 t	39.40 39.35 t	12.93 12.43 q

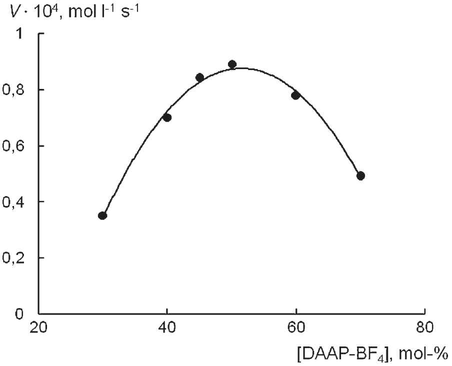


Figure 1.
Rate of copolymerization of DAAP-BF$_4$ (M$_1$) with SO$_2$ vs. monomer ratio. Methanol, $[M_1 + M_2] = 2$ mol L^{-1}, $[AIBN] = 3.0 \cdot 10^{-2}$ mol L^{-1}, T = 80°C.

of one of comonomers results in reaction rate reduction; this can be explained by the change of the reactive complex concentration in the system.

As a result of kinetic investigation of DAAP-BF$_4$ copolymerization with SO$_2$ in methanol at low conversion a reaction order 0.75 for the initiator was found. The reaction order with respect to the monomer was 1.35. Such high values of the reaction orders with respect to the initiator and monomer (as compared to characteristic of radical polymerization) are related, probably, to the fact that copolymerization proceeds via complex formation and viscosity of the system is high even at low conversion.

The reaction rate in the range from 60–90°C increases with the temperature independently on the media. The value of the total activation energy of DAAP-BF$_4$ copolymerization with SO$_2$ in methanol, calculated from Arrhenius equation, is 91.0 ± 2.0 kJ mol^{-1} (Figure 2).

The reaction conditions significantly influence the reaction rate and copolymer yield (Table 2). Analysis of data obtained suggest as optimum conditions for copolymer synthesis bulk or solution polymerization (methanol chloroform) in the presence of AIBN (2.0–3.0 wt.-%) between 70–90 °C.

Figure 3 shows the conversion vs. time curve of DAAP-BF$_4$ copolymerization

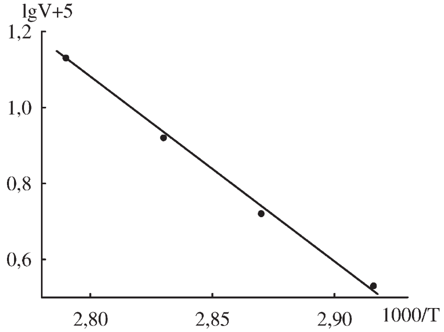


Figure 2.
Rate of copolymerization of DAAP-BF$_4$ (M$_1$) with SO$_2$ vs. the temperature. Methanol, $[M_1 + M_2] = 2$ mol L^{-1}, $[M_1]: [M_2] = 1: 1$, $[AIBN] = 3.0 \cdot 10^{-2}$ mol L^{-1}.

Table 2.
Influence of copolymerization conditions on the DAAP-BF$_4$ with SO$_2$ copolymer yield. $[M_1 + M_2]$: [solvent] = 50: 50 (wt.-%), $[M_1]: [M_2] = 1: 1$, t = 7 hours hours (* - t = 10.5 hours).

Copolymerization conditions			
T, °C	[AIBN], wt.-%	Medium	Yield, %
70	2	In bulk	34.6
70	3	In bulk	39.1
80	2	In bulk	46,1
80	3	In bulk	58.7
80	3	Methanol	62.9
90	2	In bulk	60.0
90	3	In bulk	61.8
90	3	Methanol	70.7
90	3	Methanol *	76.7
90	3	Chloroform*	71.4

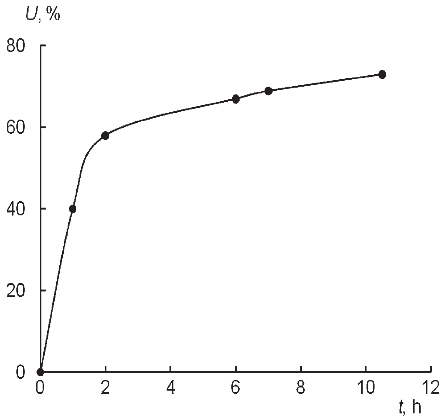


Figure 3.
Kinetic curve of copolymerization of DAAP-BF$_4$ (M$_1$) with SO$_2$, U – copolymer yield. Methanol, $[M_1 + M_2] =$ 2 mol L^{-1}, $[M_1]: [M_2] = 1: 1$, $[AIBN] = 3.0 \cdot 10^{-2}$ mol L^{-1}, T = 90 °C.

with SO_2 in methanol. Reaction rate has high values up to 60% conversion (approximately 30% per hour), after that the reaction rate decreases significantly. The same behaviour has been found for DAAP-Cl copolymerization with SO_2.

Structure of New Copolymers

The structure of the polymers obtained was investigated by NMR ^{13}C. In the NMR ^{13}C spectra of polysulfones (Table 1) are two pairs of weak field triplet signals of cis/trans-isomeric C_1, C_1' and C_3, C_3' atoms and a pair of doublet signals of C_2, C_2' atoms. Content of cis-stereoisomeric units in polysulfones (DAAP-BF_4 with SO_2 and DAAP-Cl with SO_2) is higher than that of trans-units (7: 1 and 5: 1, respectively). The analysis of the values of chemical shifts of the signals and their multiplets shows that diallylaminophosphonium salt copolymerization with SO_2 proceeds with participation of both double bonds, this phenomenon is consistent with data on polymerization of other diallylamonium salt – N,N- diallyl -N,N- dimethylammonium chloride.[5,24,25]

Viscosity and Molecular Weight

The polysulfones obtained are soluble due to intramolecular cyclization of diallylaminophosphonium salts during formation of the polymer chain and to the absence of intermolecular crosslinks. Polysulfones are soluble in DMSO, DMFA, methanol, acetone and chloroform; they are insoluble in other common solvents. Due to the polyelectrolyte effect, the reduced viscosity of copolymer solutions increases with dilution. DAAP-Cl polysulfones are soluble also in water. The adding of low-molecular polyelectrolyte (1N NaCl) allows to suppress the polyelectrolyte effect. The value of intrinsic viscosity of DAAP-Cl polysulfone solution (water with 1N NaCl) is 0,05 dl g^{-1}.

The weight average molecular weight of DAAP – BF_4 polysulfone ($[M_1 + M_2] = 2$ mol/l, $[AIBN] = 0.6\%$, methanol, 80 °C) is 17800.

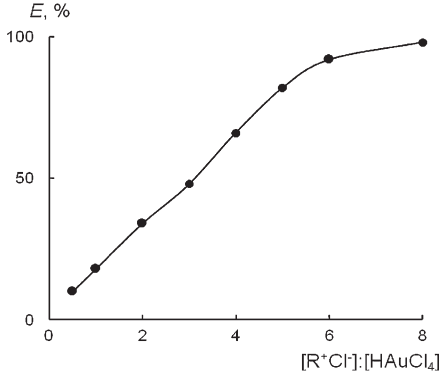


Figure 4.
Degree of $HAuCl_4$ precipitation (*E*) vs. [polysulfone]:[$HAuCl_4$] ratio. $C_{Au} = 20.9$ mg L^{-1}, t = 10 min.

Precipitation and Sorption Ability

It was found that DAAP – Cl polysulfone forms coloured precipitates with CrO_4^{2-}, $AuCl_4^-$, $PtCl_6^{2-}$. Investigation of the precipitation of $HAuCl_4$ by polysulfones showed that an eightfold excess of copolymer precipitates 98% $HAuCl_4$ (Figure 4). The ratio $[R + Cl\text{-}]:[HAuCl_4]$ in the precipitate is equal to 1:1. On the basis of these data the following scheme of the precipitation process can be presented:

$$RC1 + HAuC1_4 \rightarrow RAuC1_4 \downarrow + HC1$$

The water insoluble DAAP-BF_4 polysulfone sorbs the salts of precious metals from solutions. The static sorption capacity of gold is equal to 59.3 Au g^{-1}.

Microbiological Tests

All polysulfones are non-toxic and can be used for medical purposes (LD_{50} values were more than 1000 mg kg^{-1}). Studies of antimicrobial activity showed that the polysulfones of equimolar composition have a significant antimicrobial activity (Table 3). They are more active against Gram positive microflora. Moreover, polysulfones showed a protection effect of gastric ulcers, ulcer quantity reduces twofold compared to control test. These preliminary studies confirm that the new polysulfones can be used in medicine and biotechnology.

Table 3.
Antimicrobial activity of new polysulfones

№	Test cultures	Minimal bacteriostatic concentration (MBsC), μg/ml	
		DAAP – Cl with SO_2	DAAP – BF_4 with SO_2
1	*Escherichia coli*	62.5	62.5
2	*Staphylococcus aureus*	7.8	$<31.2 >15.6$
3	*Micrococcus luteus*	$>7.8 < 15.6$	$<15.6 > 7.8$
4	*Staphylococcus saprophyticus*	$<31.2 > 15.6$	15.6
5	*Candida albicans*	31.2	$<62.5 > 31.2$
6	*Bacillus antracoides*	$<500.0 > 250.0$	500.0
7	*Bacillus proteus*	$<1000.0 > 500.0$	$>250.0 < 500.0$
8	*Bacillus subtilis*	$<15.6 > 7.8$	$<62.5 > 31.2$
9	*Salmonella spp.*	<125.0	125.0

Conclusion

Ttris(diethylamino)diallylaminophosphonium tetrafluoroborate and chloride do not homopolymerize virtually in the presence of radical initiators. These new allyl monomers exhibit high activity in copolymerization with sulfur dioxide. Copolymerization proceeds via complexation, resulting in alternating copolymers independent of the monomer ratio in the initial mixture and of the reaction conditions. These diallylaminophosphonium salts copolymerize with sulfur dioxide, both double bonds participating, with formation of cis-, trans-stereoisomeric pyrrolidine structures in a cyclolinear polymer chain. The polysulfones obtained have shown good antimicrobial activity against Gram positive bacteria.

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