# Synthesis and properties of polyelectrolytes based on dimethylaminoethyl methacrylate quaternary salt

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The quaternary salt of *N,N'*-dimethylaminoethyl methacrylate with dimethyl sulfate has been synthesized and its polymerization has been studied in aqueous solutions, using $K_2S_2O_8$ as initiator, as well as in dimethylformamide, dimethyl sulfoxide and ethanol in the presence of azobisisobutyronitrile. Exponents expressing the dependency of initial polymerization rate on monomer and initiator concentrations at 60°C were 1.6 and 0.5, respectively and the overall activation energy in the temperature range 40–60°C was 92.8 kJ $mol^{-1}$ (for aqueous systems). Polymeric quaternary salts (PQS) synthesized in various solvents differ in their intrinsic viscosity and the initial rate of polymerization is found to decrease with decreasing dielectrical constant of the solvent. By means of viscometry, conductometry and electrochemical analysis, PQS have been characterized as strong polyelectrolytes.

**(Keywords: dimethylaminoethyl methacrylate quaternary salt; radical polymerization; cationic polyelectrolytes; polymeric quaternary salts)**

## INTRODUCTION

Cationic polyelectrolytes have increasing applications in areas such as flocculation, especially for water and wastewater treatment, adhesives, emulsion stabilizers, corrosion inhibitors and dye improvers, as well as in the preparation of antistatic and cosmetic agents[1–5]. Cationic water-soluble polymers are also known as efficient ion-exchangers and catalyst matrices[6,7].

Depending on the position of the N atom in the polymer chain, cationic polymers are divided into two groups: polybases with the N atom in the main chain and polybases with the N atom in the branching groups (pendant polybases)[6]. Poly(aminoalkyl methacrylates), as well as poly(vinyl amine)s and poly(vinyl pyridine)s, belong to the second group of cationic polymers. The presence of a reactive primary, secondary and tertiary amino group in the chain of these polymers makes it possible to obtain strong polyelectrolytes by means of their chemical modification.

Another way to obtain strong pendant-type polyelectrolytes is by direct synthesis from polymerizable quaternary N-containing monomeric salts. Recently, a technological procedure for obtaining cationic water-soluble flocculants as products of the polymerization of the quaternary salts of 2-methyl-5-vinylpyridine with $C_2H_5Br$ or $(CH_3)_2SO_4$ has been described[8]. The polymers based on *N,N'*-dimethylaminoethyl methacrylate (DMAEMA) and its derivatives also belong to the relatively new group of ionic polymers suitable for current industrial applications[9]. Among the other areas of application, quarternary salts of poly(dimethylaminoethyl methacrylate) (PDMAEMA) have proved to be efficient initiator carriers in the radical polymerization of vinyl monomers[10,11].

However, there have been relatively few detailed studies of the radical polymerization of quaternary salts of DMAEMA[9,12–14].

The aim of the present work was to investigate the kinetics of polymerization of the quaternary DMAEMA salt with dimethyl sulfate in aqueous solutions, as well as in some organic solvents, and to determine the basic properties of the resulting polymers.

## EXPERIMENTAL

### *Materials*

*N,N*-dimethylaminoethyl methacrylate (DMAEMA) and dimethyl sulfate (DMS), both Merck products, were purified by vacuum distillation prior to use. The initiators, azobisisobutyronitrile (AIBN) and potassium peroxodisulfate ($K_2S_2O_8$) were used without further purification (Merck). Acetone, used for polymer precipitation and in the DMAEMA quaternary salt synthesis, was distilled once. Polymerization was carried out in distilled water, DMSO, DMF and ethanol (all p.a. grade, CarloErba R.P. products).

### *Synthesis of the quaternary salt of DMAEMA*

Alkylation of DMAEMA with DMS was carried out in acetone at 0°C by adding DMS dropwise during 120 min with vigorous stirring. The expected product of quaternization, according to *Scheme 1*, is the quaternary

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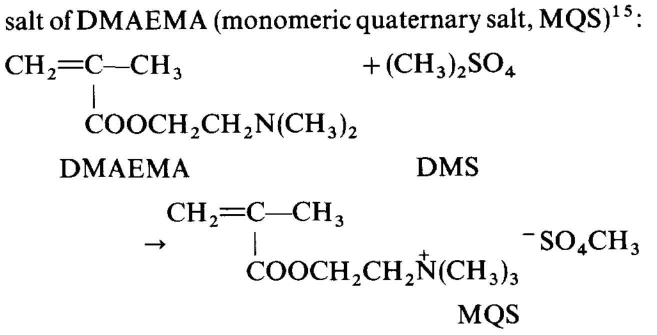
salt of DMAEMA (monomeric quaternary salt, MQS)[15]:



$$\underset{\text{DMAEMA}}{\mathrm{CH_2{=}C(CH_3)\!-\!COOCH_2CH_2N(CH_3)_2}} + \underset{\text{DMS}}{\mathrm{(CH_3)_2SO_4}} \rightarrow \underset{\text{MQS}}{\mathrm{CH_2{=}C(CH_3)\!-\!COOCH_2CH_2\overset{+}{N}(CH_3)_3\ {}^{-}SO_4CH_3}}$$

**Scheme 1**

MQS was precipitated twice from the reaction medium by the addition of a sufficient amount of cold acetone at 0°C. The precipitated product was then washed several times with ice-cold acetone and dried in a vacuum desiccator overnight. MQS, a white crystalline powder, was stored in a vacuum dessicator over $P_2O_5$ and kept in a refrigerator until use. Identification of MQS was performed by elementary analysis and infra-red spectroscopy (KBr-technique).

### *Polymerization*

Polymerization of MQS was carried out in 50 $cm^3$ glass polymerization ampoules in the temperature range 40–60°C at various concentrations of monomer (0.4–1.3 mol $dm^{-3}$). Polymerization was initiated by $K_2S_2O_8$ when water was used as a solvent, and by AIBN when DMSO, DMF and ethanol were used as solvents for MQS. The polymer (PQS) was isolated by slowly pouring the reaction mixture into excess ice-cold acetone. Conversion was measured gravimetrically after precipitation and drying *in vacuo* overnight. On the basis of kinetic experiments with conversions usually $<10\%$, the initial rates of polymerization were calculated.

### *Viscometry*

The intrinsic viscosities of aqueous solutions of the polymers, synthesized by polymerization of MQS in different solvents, were determined with an Ostwald viscometer at $25 \pm 0.1$°C. Aqueous solutions were prepared with double-distilled water and the measurements were performed after storage for 24 h.

### *Electrochemistry*

*Conductometry.* Aqueous solutions of PQS and MQS in double-distilled water (1.0–9.2 g $dm^{-3}$) were used for determining the electrical conductivity. The experiments were carried out at 22°C and the specific conductivity, $\kappa$, was measured 2 min after the electrode was dipped into the aqueous solution, i.e. constant values for $\kappa$ were obtained. The equivalent conductivity, $\lambda$, was calculated from the equation:

$$\lambda = \frac{1000\kappa}{C}$$

where $C$ is the concentration of the PQS solution.

### *Adsorption isotherms*

Adsorption of the PDMAEMA quaternary salt on the surface of an Au electrode has been investigated in the classical thermostated electrochemical cell as a function of the electrochemical potential (from 0 to 2 V $she^{-1}$) under potentiodynamic conditions with the potential rate, $dE/dt = 2$ mV $s^{-1}$, at 20 and 30°C.

Adsorption isotherms were measured in aqueous solutions of 0.5 M $H_2SO_4$ in a standard electrochemical cell with three electrode systems: Au wire as a working electrode, Pt or Au foil as an auxiliary electrode and a saturated calomel electrode as a reference.

### *Infra-red spectroscopy*

I.r. spectra of MQS and PQS were measured using a Perkin-Elmer i.r. spectrophotometer, applying the KBr technique and liquid-phase techniques for DMS.

## RESULTS AND DISCUSSION

### *Quaternization of DMAEMA*

In order to confirm the structure of the product of quaternization, an elementary analysis (*Table 1*) and i.r. spectroscopy (*Figure 1*) were performed.

According to the results given in *Table 1*, it can be deduced that the expected product of quaternization of DMAEMA is MQS, as shown in *Scheme 1*.

From the i.r. spectrum one can see that the bands at 1300 and 1100 $cm^{-1}$, which are present in the DMAEMA spectrum obscured by the tertiary N atom, are not present in the MQS spectrum. The possibility that the product of quaternization is a mixture of DMAEMA and DMS or MQS is also eliminated, because in the spectrum of MQS, the band at 2750 $cm^{-1}$ which is characteristic in the spectrum of DMAEMA[16] is not present.

In the spectrum of MQS at 1060 $cm^{-1}$, the band that comes from the $SO_4^{2-}$ group ionic bonding is marked; this band is not apparent in the spectrum of DMS.

Obviously, after the alkylation reaction there are no changes in the C=C and C=O bonds of the monomer; i.e. $\nu_{C=C}$ and $\delta_{C=C}$ vibrations at 1635–1640 $cm^{-1}$ and above 3500 $cm^{-1}$ are both present in the spectra of DMAEMA and MQS. In both spectra, $\nu_{C=O}$ vibrations at 1718 $cm^{-1}$ (MQS) and at 1720 $cm^{-1}$ (DMAEMA) are apparent. The ratio of intensities $\nu_{C=O}/\nu_{C=C}$ is unchanged after the alkylation of DMAEMA, as can be seen from the spectra of DMAEMA and MQS.

MQS is polymerizable and shows good solubility in water, ethanol, DMF and DMSO, solvents in which the product of polymerization is also soluble. In aqueous solutions, MQS acts as a surface-active substance; thus, the surface tension of its 0.5% and 1% solutions is $71 \times 10^{-7}$ and $69 \times 10^{-7}$ J $cm^{-2}$, respectively, compared to $73 \times 10^{-7}$ J $cm^{-2}$ for pure distilled water at 20°C.

### *Polymerization of MQS in aqueous solutions*

The polymerization of MQS was investigated in various solvents (water, DMSO, DMF and ethanol) at

**Table 1** Elementary analysis data for the product of quaternization of DMAEMA

| | | Product of quaternization | |
|---|---|---|---|
| Element | DMAEMA (%) | Theor. (%) | Exp. (%) |
| C | 61.15 | 42.40 | 42.45 |
| H | 9.55 | 7.42 | 8.50 |
| N | 8.92 | 4.95 | 6.30 |
| S | – | 11.30 | 12.00 |

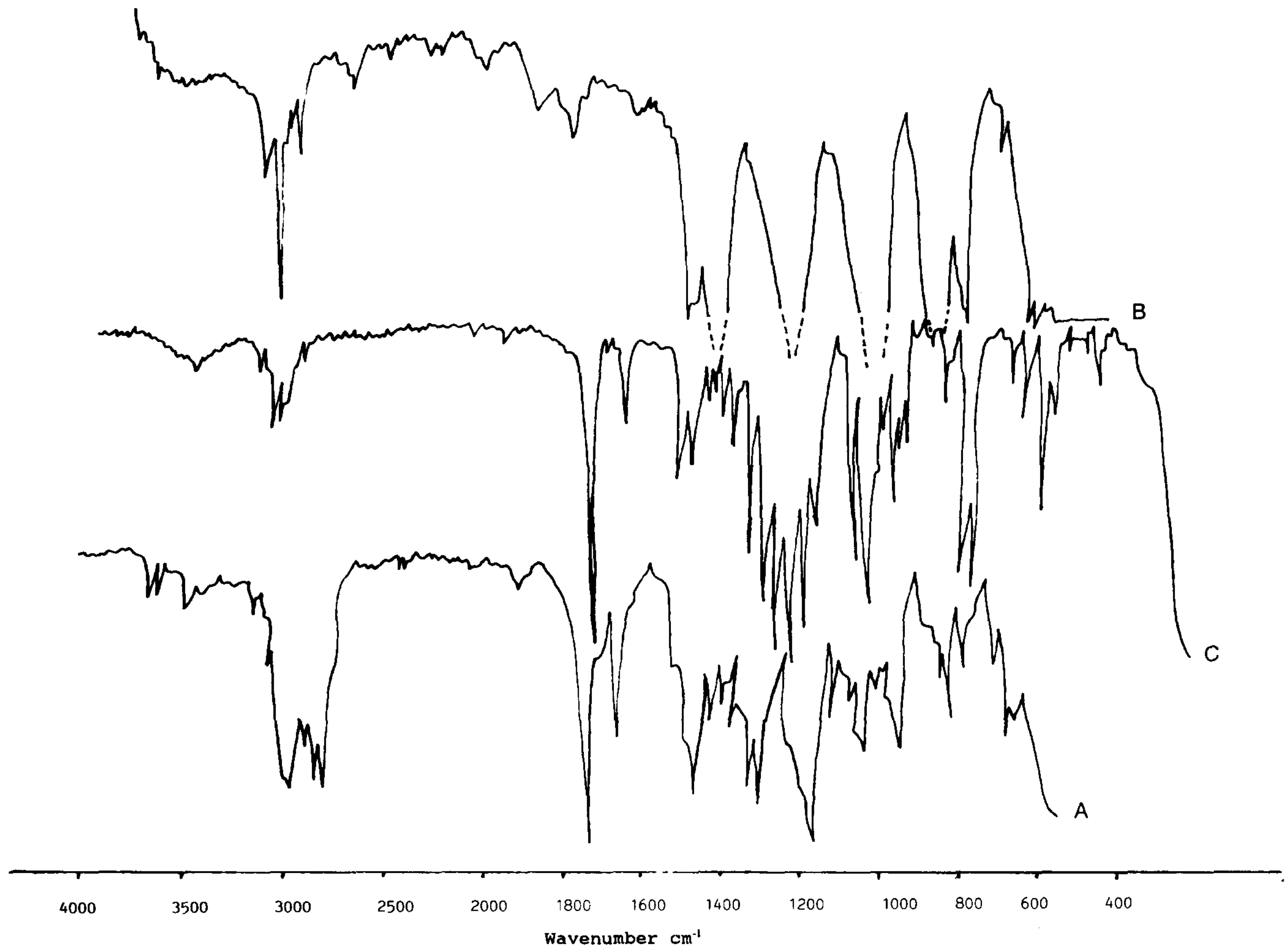


**Figure 1** Infra-red spectra of DMAEMA (A), DMS (B) and the product of quaternization (C)

40–60°C. The reaction proceeds without an induction period at 50 and 60°C.

Conversion–time curves for the kinetics of polymerization of MQS in aqueous solutions, initiated by $K_2S_2O_8$ at 60°C, are shown in *Figure 2*.

The initial rate of polymerization, $R_{po}$, was found to increase from $2.16 \times 10^{-4}$ to $9.30 \times 10^{-4}$ mol dm$^{-3}$ s$^{-1}$ with the monomer MQS concentration in the range 0.6–1.3 mol dm$^{-3}$ (see *Table 2*). The order of the reaction with respect to the monomer was found to be 1.6, that is higher than the theoretical value predicted by the simplest kinetic scheme for radical polymerization. The order of the reaction with respect to $K_2S_2O_8$ was found to be 0.5. The kinetic results can be summarized in the empirical overall rate expression:

$$-\mathrm{d}[M]/\mathrm{d}t = K[M_o]^{1.6}[I]^{0.5}$$

The effect of temperature on the reaction kinetics of MQS was studied for the polymerization in aqueous solutions.

In the examined temperature range 40–60°C, an overall activation energy of 92.8 kJ mol$^{-1}$ was calculated.

It is well known that radical polymerizations in aqueous media with $K_2S_2O_8$ as initiator usually take place with an appropriate measureable rate at temperatures higher than 50–60°C[17]. However, the polymerization of MQS proceeds even at 30–40°C, when thermal decomposition of $K_2S_2O_8$ in the aqueous reaction medium is very slow or completely excluded[18].

The course of polymerization of MQS is affected

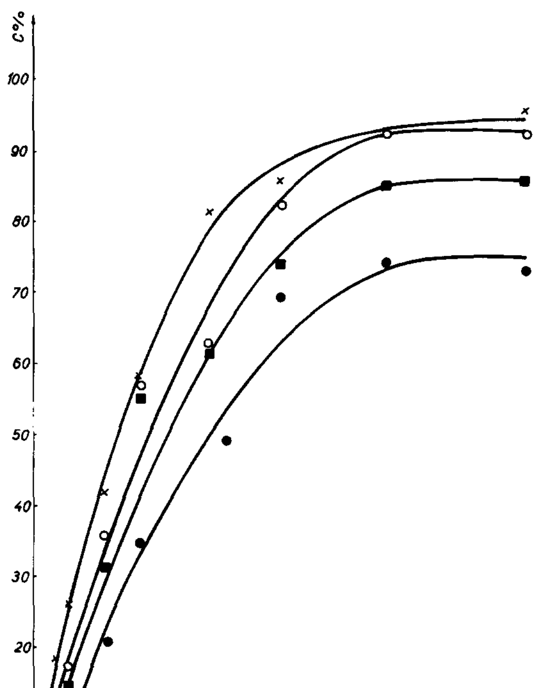


**Figure 2** Percentage conversion (*c*) *versus* polymerization time (τ) for MQS aqueous solutions at 60°C at various MQS concentrations: (●) 0.6; (■) 0.8; (○) 1.0; (×) 1.3 mol dm$^{-3}$. 1.25% $K_2S_2O_8$ as initiator

**Table 2** Dependence of the initial rate of polymerization, $Rp_o$, on monomer concentration (1.25%[$K_2S_2O_8$], 60°C, $\tau = 10$ min)

| $C$ (mol dm$^{-3}$) | $Rp_o$ ($\times 10^4$) (mol dm$^{-3}$ s$^{-1}$) | $-\log C$ | $-\log Rp_o$ |
|---|---|---|---|
| 0.6 | 2.16 | 0.2218 | 3.66 |
| 0.8 | 4.68 | 0.0970 | 3.33 |
| 1.0 | 5.24 | 0.0000 | 3.28 |
| 1.3 | 9.30 | −0.1139 | 3.03 |

considerably by addition of hydroquinone, sharply decreasing the rate of polymerization. This indicates the free-radical mechanism of the process.

The fact that the reaction order with respect to the monomer is 1.6 and the overall activation energy is lower than for usual radical polymerizations initiated by the thermal decomposition of initiators, suggests a possible mechanism for the reaction. Specific interaction of the monomer and complexing between the positively-charged N atoms of the monomer and the $S_2O_8^{2-}$ ions of the initiator could be the reason for easier decomposition of the initiator, thus taking place at lower temperatures[9]:

$$\underset{\text{complex}}{[MQS^+ \ldots S_2O_8^{2-}]} \rightarrow MQS^+ + 2SO_4^{-\bullet}$$

In this way, the monomer has been involved in the act of initiation, in which primary $SO_4^{-\bullet}$ ion radicals, responsible for starting the polymerization process, are generated. A similar mechanism has been proposed for the liquid-phase graft polymerization of some monomers onto a polyamide matrix, pretreated with polymeric initiators based on polyquaternary salts of DMAEMA and peroxodisulfates[19].

It should be noted that under the same reaction conditions, $K_2S_2O_8$ does not initiate the polymerization of the DMAEMA monomer (40°C, 1 mol dm$^{-3}$ DMAEMA; 1.25% $K_2S_2O_8$).

*Polymerization of MQS in organic solvents*

Solvent effects are particularly apparent in the polymerization of polar monomers[17]. Therefore, an attempt was made to correlate the quality of the solvent with the initial rate of polymerization of MQS and with the intrinsic viscosity of the observed polymers.

*Table 3* shows that the rate of polymerization of MQS increases rapidly with increasing dielectric constant ($\varepsilon$) of the solvent. The intrinsic viscosities of corresponding polymers change in the same manner: the highest value for $[\eta]$ is 58.42, found for the PQS synthesized in aqueous media.

It is well established that monomer–solvent association is one of the reasons for change in the reactivity of the monomers and their increasing macroradicals in radical polymerizations[20]. Grigiryan *et al.*[20] have noted that the rate of polymerization and the molecular weight of the polymer increase on going from DMFA and FA to aqueous polymerization systems of DMAEMA. Similar effects are found for the polymerization of hydrochlorides of DMAEMA and are explained by conformational and electrostatic factors[21].

Change of conformation of polymer chains with changing quality of solvents may influence interactions of growing macroradicals in chain termination and may also affect the formation of intramolecular associate structures[20,22].

It must be pointed out that the polymerization of MQS in DMF and DMSO (initiated by AIBN) also proceeds at a lower temperature (40°C), as in the case of aqueous polymerization systems where $K_2S_2O_8$ was used as initiator.

*Basic properties of polymers synthesized from MQS*

In *Figure 3* the data of the viscometric analysis of polymers, synthesized from MQS with polymerization in aqueous solutions, have been plotted in a graph $\eta_{sp}/c = f(c)$ and $c/\eta_{sp} = f(c)^{1/2}$. The viscosity of the polymers is independent of the time of polymerization (see *Table 4*).

The viscosity–concentration dependence (*Figures 3* and *4*), i.e. decreasing $\eta_{sp}/c$ with increasing concentration, is typical for polymeric electrolytes[6,9]. Decreasing the concentration of the solution leads to an increase in the linear dimensions of the macromolecules, i.e. an increase in the size of the polymer coil in solution. In fact, the intrinsic viscosity of the polymer increases with the decrease in the polymer solution concentration and a poor, but significant Fuoss–Strauss correlation between $c/\eta_{sp}$ and $c^{1/2}$, characteristic of polymeric electrolytes[23], is found (*Figure 3*).

**Table 3** Influence of the solvent in the radical polymerization of MQS on the initial rate of polymerization and the intrinsic viscosity of synthesized polymers (1 mol dm$^{-3}$ MQS; 1.25% AIBN; 60°C; 10 min)

| Solvent | $\varepsilon$ | $Rp_o$ ($\times 10^4$) (mol dm$^{-3}$ s$^{-1}$) | $[\eta]$ (dl g$^{-1}$) |
|---|---|---|---|
| EtOH | 24.30[a] | 0.62 | 2.70 |
| DMF | 38.00[b] | 1.95 | 9.07 |
| DMSO | 45.00[b] | 3.80 | 17.39 |
| $H_2O/K_2S_2O_8$ | 78.54[a] | 5.24 | 58.42 |

[a] At 25°C
[b] At 20°C

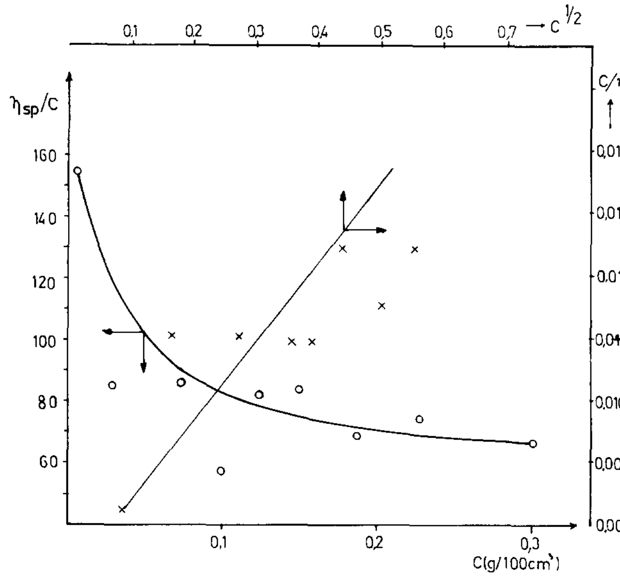


**Figure 3** Dependence of reduced specific viscosity on concentration for PQS in water at 25°C (○) and corresponding Fuoss–Strauss function $C/\eta_{sp} = f(C)^{1/2}$ (×). (PQS synthesized by polymerization of MQS (0.8 mol dm$^{-3}$) with 1.25% $K_2S_2O_8$ as initiator at 60°C for 70 min)

**Table 4** Dependence of the viscosity of aqueous solutions of synthesized polymers (1.25% $K_2S_2O_8$; 60°C) on the time of polymerization

| $C_{MQS}$ (mol dm$^{-3}$) | $t$ (min) | $\eta_{rel}$ | $[\eta]$ |
|---|---|---|---|
| 0.6 | 10 | 12.80 | 57.49 |
| | 25 | 12.76 | 57.38 |
| | 70 | 12.07 | 55.40 |
| 1.0 | 10 | 3.12 | 37.40 |
| | 25 | 3.11 | 37.39 |
| | 70 | 3.05 | 36.58 |
| 1.3 | 10 | 5.01 | 58.50 |
| | 25 | 5.14 | 59.78 |
| | 70 | 4.71 | 55.56 |

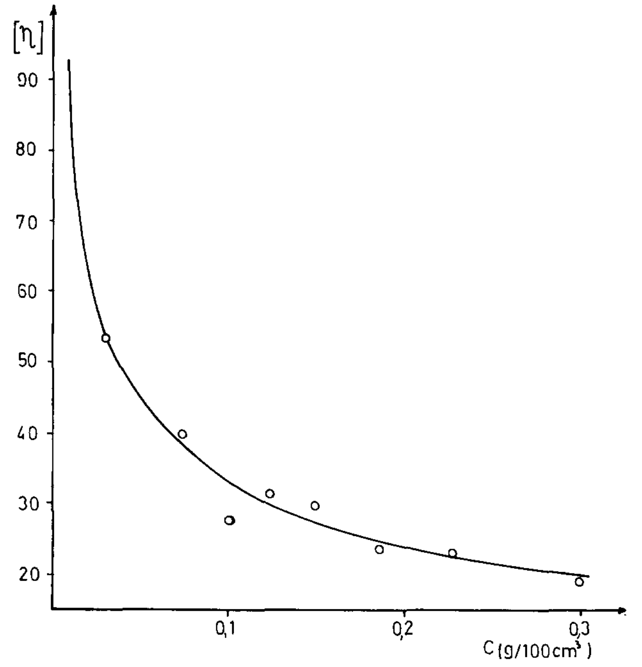


**Figure 4** Intrinsic viscosity–concentration relationship for PQS in water at 25°C

The polyelectrolytic character of the synthesized polymers is also confirmed by the results of conductometric measurements (*Figures 5* and *6*). The polyelectrolytic properties of PQS are higher than those of PDMAEMA, clearly as a result of the positively-charged quaternary N atoms present in the macromolecules of PQS, compared to the tertiary N atoms in PDMAEMA. Thus, values of the specific electrical conductivity, $\kappa$, for 0.5 g cm$^{-3}$ MQS, PDMAEMA and PQS are $9.85 \times 10^{-4}$, $1.52 \times 10^{-4}$ and $3.84 \times 10^{-4}\ \Omega^{-1}\ \mathrm{cm}^{-1}$, respectively, at 20°C (PDMAEMA was synthesized with polymerization of DMAEMA in aqueous solution (1 mol dm$^{-3}$; 1.25% $K_2S_2O_8$; 60°C).

Calculated values for the equivalent conductivity, $\lambda$, of synthesized PQS characterized PQS as strong polyelectrolytes (see *Figure 6*).

Investigations of the adsorption of PQS on metal surfaces have shown that the synthesized polymers have a high adsorption ability (*Figure 7*).

It was found that the adsorption process of PQS, analysed by capacity measurements using the two-condenser model[24,25], depends strongly on the electrode potential range. As can be seen from the results presented in *Figure 7*:

(i) In the potential range from 0 to 0.5 V she$^{-1}$ (when the metallic surface is neutral to low-cathodic charged), the capacity changes indicate a relatively thin adsorption film formation of ~0.6 nm (probably, complete coverage of the metal surface is not reached). The effect is especially pronounced at extremely low polymer concentrations in solution (5–20 ppm PQS).

(ii) Drastic capacity changes are noted at high anodic potentials, possibly as a result of achieving a nearly complete limiting-coverage value close to $\theta = 1$, with the thickness of the adsorbed layer ~0.9 nm.

(iii) At the same time, very poor adsorption is determined on the metallic surface oxidative phase.

It was confirmed that the thickness of the adsorbed layer for several series of PQS is strongly affected by their molecular mass.

However, the changes in the capacity ($\Delta C = 20$–$30$ mF cm$^{-2}$) indicate a good adsorption ability of the synthesized PQS towards the metal surface.

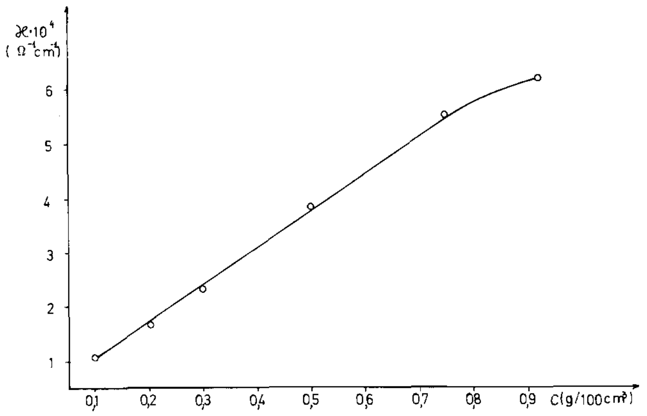


**Figure 5** Specific electrical conductivity of aqueous PQS solutions at 22°C

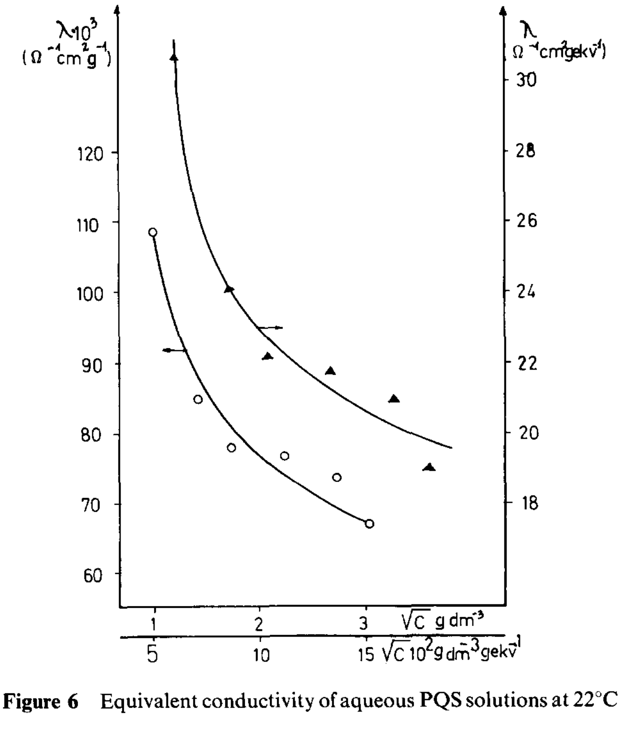


**Figure 6** Equivalent conductivity of aqueous PQS solutions at 22°C

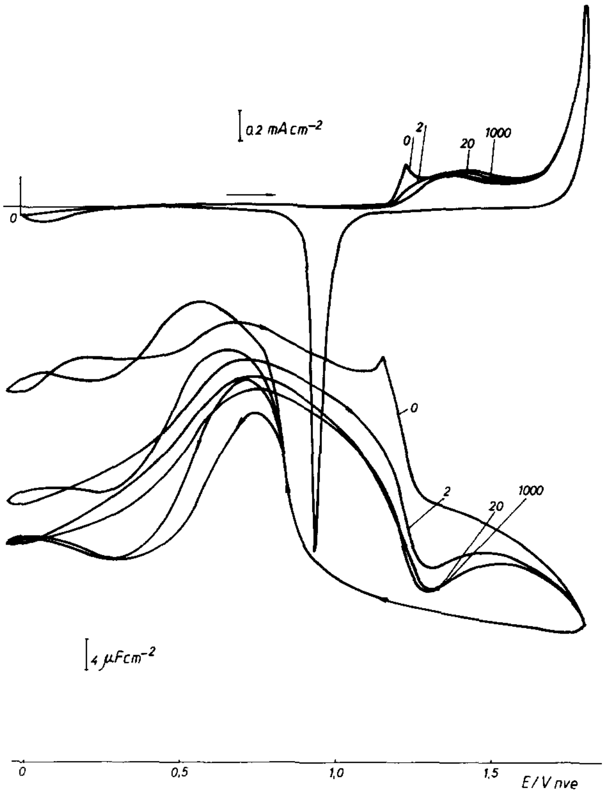


**Figure 7** Voltammograms and capacitance spectra for Au in 0.5 M $H_2SO_4$ and in the presence of PQS ($dE/dt = 100$ mV s$^{-1}$ at 20°C)

Investigations concerning the possible application of the synthesized PQS, based on their electrolytic properties and good surface adsorption ability are in progress and will be the subject of our next publication.

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