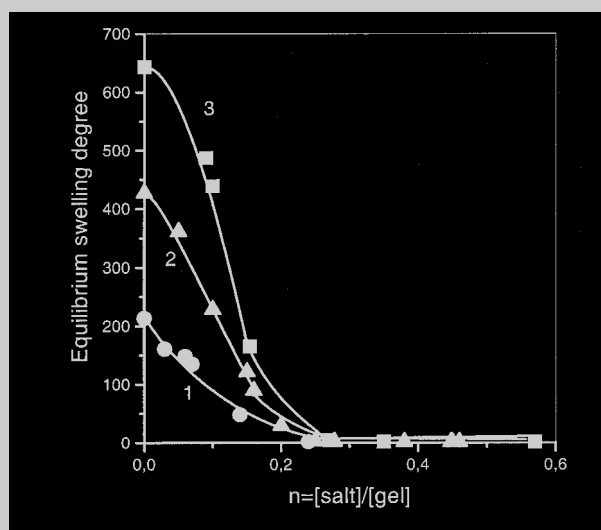**Full Paper:** Linear and crosslinked poly[2-(methacryloyl-oxy)ethyl]trimethylammonium chloride was synthesized by γ-irradiation polymerization in aqueous solutions. Interactions between linear poly[2-(methacryloyloxy)ethyl]trimethylammonium chloride and low molecular coordination compounds $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ have been studied in aqueous solutions by viscometric and turbidimetric measurements. The formation of complexes with certain stoichiometry depending on the nature of the low molecular ion was detected. Hydrogels of poly[2-(methacryloyloxy)ethyl]trimethylammonium chloride absorb these salts and undergo contraction. The stability of the complexes formed in different ionic strength media has been evaluated.

Swelling of PMADQUAT hydrogels in aqueous solutions of $K_4[Fe(CN)_6]$.

Radiation Synthesis of Linear and Crosslinked Poly[2-(methacryloyloxy)ethyl]trimethylammonium Chloride and Complex Formation with Potassium Hexacyanoferrates (II, III) in Aqueous Solutions

Vitaliy V. Khutoryanskiy,[1] *Piotr Kujawa,*[2] *Zauresh S. Nurkeeva,*[1] *Janusz M. Rosiak*[*2]

[1] Kazak State National University, Department of Macromolecular Compounds,
  Karasai Batyra Str. 95, 480012 Almaty, Kazakhstan
[2] Technical University of Lodz, Institute of Applied Radiation Chemistry, Wroblewskiego Str. 15, 93590 Lodz, Poland

Introduction

Complex formation between polyelectrolytes and low molecular ions is of considerable interest because it may be used successfully for the development of drug-delivery systems, and selective sorbents as well as in purification technologies.[1–5]

Poly[2-(methacryloyloxy)ethyl]trimethylammonium chloride (PMADQUAT) is an amphiphilic polyelectrolyte containing both hydrophobic groups (methyl groups and backbone chain) and hydrophilic positively charged tertiary amine groups in every elementary unit. Solution properties of PMADQUAT have been thoroughly studied by Stickler[6] and Griebel.[7]

Kim[8] demonstrated the ability of PMADQUAT and its copolymers with alkyl methacrylates and acrylates to form complexes with some anionic drugs (sodium sulfathiazole and sodium diclofenac). The solubility of these complexes in water was dependent on the copolymer composition. Homopolymer PMADQUAT formed complexes that were not stable and were destroyed upon dilution.

In the present work we report radiation synthesis and complex formation reactions between linear and cross-linked PMADQUAT and two inorganic coordination compounds $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$. We demonstrate that the stability of poly-complexes in respect to dilution can be enhanced if the low molecular ions have a higher negative charge.

Experimental Part

Radiation polymerization of MADQUAT was conducted in the gamma-cell BK-1000. The dose rate was determined with the help of a Fricke dosimeter and was equal to 1.8 Gy/min.

The conversion of MADQUAT was determined spectrophotometrically at 240 nm. The synthesized polymer was purified by double precipitation from water to isopropyl alcohol and dried at 50 °C to constant weight. The average viscosity molecular weight of PMADQUAT was determined using the relationship $[\eta] = 6 \times 10^{-3} \bar{M}_w^{0.72}$.[7]

Viscometric measurements have been carried out using an Ubbelohde viscometer, having the flow time for pure water of 92 s at 25 ± 0.1 °C.

Turbidimetric titration was conducted in spectrophotometer SPECORD (Germany) at the wavelength 500 nm. The normalized turbidity was calculated by dividing the turbidity values by the concentration of the titrated component expressed in M.

For experiments with complex formation we used the sample of PMADQUAT with $\bar{M}_w = 1.2 \times 10^6$, obtained at an irradiation dose 257 Gy for 80% conversion. The solutions of PMADQUAT and inorganic salts used for measurements both had the concentration 0.001 M.

The equilibrium swelling degrees (DS) of hydrogels were determined gravimetrically and calculated using the formula: $DS = (m - m_0)/m_0$, where m and m_0 are weights of gel in the swollen and dry states, respectively.

Complexes of PMADQUAT hydrogels with salts were prepared by placing PMADQUAT hydrogels into an excess of 0.001 M solution of salt and storing them over several days.

Results and Discussion

Synthesis of Linear and Crosslinked PMADQUAT

Previous reports have detailed the synthesis of linear PMADQUAT by free-radical polymerization in aqueous solutions[6−8] as well as by inverse microemulsion polymerization initiated by radical initiators.[9, 10]

Recently the early stages of polymerization of MADQUAT in irradiated aqueous solutions were studied by pulse radiolysis.[11] In the present work we synthesized linear PMADQUAT by gamma-irradiation polymerization of 10 wt.-% aqueous solutions of monomer saturated with argon prior to irradiation.

Figure 1 shows the dependence on the absorbed dose of the degree of monomer conversion and average viscosity molecular weight of polymer formed. It can be seen that an increase of absorbed dose considerably decreases the molecular weight of the resultant polymer. Probably this is connected with the scission of newly formed linear chains at higher doses, because PMADQUAT belongs to the group of methacrylic polymers that usually undergo degradation processes upon irradiation.[12, 13]

As discussed above, PMADQUAT undergoes scission and cannot be crosslinked by irradiation treatment of its solution without a crosslinking agent. Therefore we synthesized hydrogels of PMADQUAT by gamma-irradiation polymerization of 10 wt.-% aqueous solutions of the monomer in the presence of N,N'-methylenebis(acrylamide) as the crosslinking agent. The concentration of
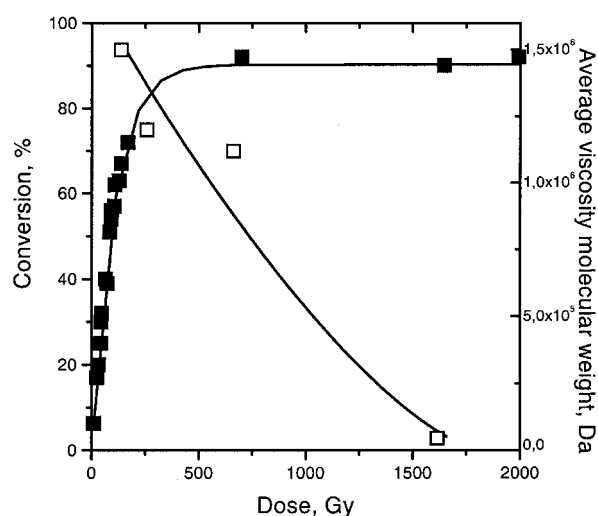

Figure 1. Dependence of MADQUAT conversion (■) and average viscosity molecular weight (□) of PMADQUAT on irradiation doses.

Table 1. Dependence of equilibrium swelling degrees of hydrogels on the irradiation dose.

Sample	Dose Gy	DS g/g
Gel#1	382	213 ± 2
Gel#2	205	427 ± 15
Gel#3	171	644 ± 12

crosslinking agent was equal to 3.84×10^{-3} g/mL in each experiment. Synthesized hydrogels were washed with deionized water over a 2 week period under continuous stirring. The washing water of the bath was changed every 12 h. The equilibrium swelling degrees of the synthesized hydrogels are shown in Table 1.

Interaction of Potassium Hexacyanoferrates (II, III) with Linear Poly[2-(methacryloyloxy)ethyl]trimethylammonium Chloride

Specific interactions of polyelectrolytes with oppositely charged complementary polymers,[14−16] surfactants,[5] drugs[17] and metallic ions[2−4] lead to considerable conformation changes of macromolecules. Usually these interactions are accompanied by the formation of compact poly-complex particles in solutions.

The dilute aqueous solutions of PMADQUAT are characterized by relatively high values of reduced viscosity due to the polyelectrolyte effect. The addition of even small amounts of $K_4[Fe(CN)_6]$ or $K_3[Fe(CN)_6]$ to aqueous solutions of PMADQUAT leads to a considerable decrease in reduced viscosity of polyelectrolyte up to the precipitation, indicating complex formation (Figure 2). The viscometric curve showing the dilution of PMADQUAT solution by pure water, added at the same amount
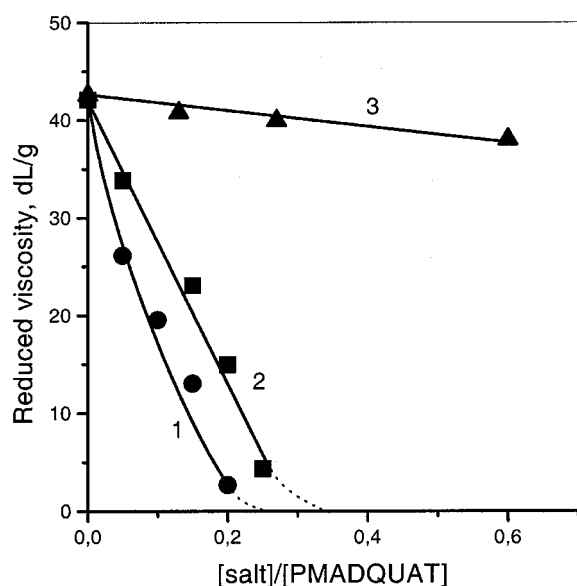
Figure 2. Viscometric titration curves of 0.001 M PMADQUAT by 0.001 M $K_4[Fe(CN)_6]$ (1), $K_3[Fe(CN)_6]$ (2), and pure water (3).

Figure 3. Turbidimetric titration curves of 0.001 M $K_4[Fe(CN)_6]$ (1) and $K_3[Fe(CN)_6]$ (2) by 0.001 M PMADQUAT.

as solutions of salts, is depicted for comparison. The precipitation of poly-complex particles occurred within the interval of [salt]/[PMADQUAT] concentration ratio 0.2:0.25 and 0.25:0.3, for $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$, respectively. It is probable that the complex formation is accompanied by inter- and intramolecular bridging of PMADQUAT by inorganic salts, and formation of insoluble crosslinked poly-complex aggregates.

In order to determine the compositions of complexes formed we studied these interactions by turbidimetric titration. Turbidimetric titration is a very simple and useful tool for the determination of the composition of poly-complexes, if their formation is accompanied by the appearance of turbidity.[18] The results of reverse turbidimetric titration are plotted in Figure 3. We used the normalized turbidity values in order to eliminate the influence of dilution in the course of titration. The increase of normalized turbidity is caused by the formation of poly-complexes. The appearance of a plateau on the turbidimetric curve indicates the stoichiometry of the poly-complexes formed. Further addition of PMADQUAT solution does not influence the turbidity values, indicating the stability of the poly-complexes with respect to dilution. A similar result was obtained for forward turbidimetric titration. According to the data obtained, the interaction between PMADQUAT and $K_4[Fe(CN)_6]$ leads to the formation of a polymer complex in which the $[Fe(CN)_6]^{4-}$ ion is linked with 4 monomeric units of PMADQUAT. The composition of the complex between PMADQUAT and $[Fe(CN)_6]^{3-}$ is close to the ratio 2.5:1. The binding of negatively charged molecular coordination ions by the cationic polyelectrolyte occurred due to the electrostatic
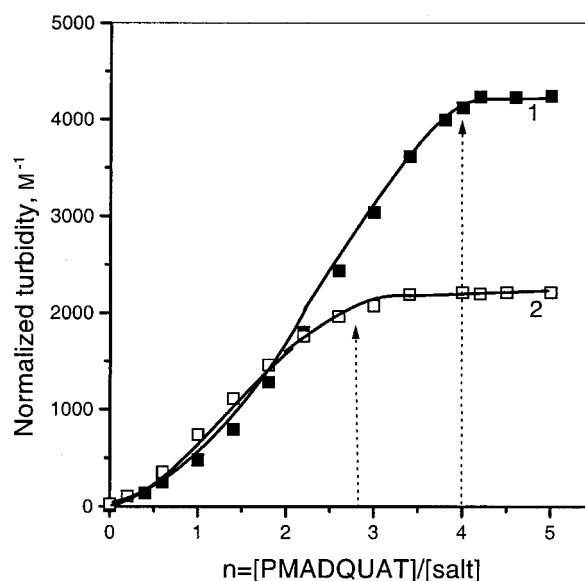
interactions. Complexes of PMADQUAT with hexacyanoferrate (II, III) ions are stable in aqueous solutions and are not destroyed upon dilution unlike the complexes reported by Kim et al.[8] Probably, the higher stability of the complexes can be explained by the higher charge density of molecular ions connected to PMADQUAT.

Increasing the ionic strength of the solution can readily destroy the poly-complexes. Thus, the complexes are soluble in 1 M NaCl solution, which confirms the electrostatic nature of the interaction.

Sorption of Potassium Hexacyanoferrates (II, III) by Hydrogels of Poly[2-(methacryloyloxy)ethyl]trimethylammonium Chloride

Polymer gels are excellent models for studying molecular interactions since a polymer network can be regarded as a single giant molecule. Any phenomena which lead to changes in the conformational size of the linear polymer molecule in homogenous solution will lead to directly measurable changes in the dimensions, i.e. the degree of swelling of the gel consisting of the same monomer units. With the polymer in the form of the gel, the binding may be studied directly by the equilibrium uptake of low molecular ions by the gel, which acts as its own semipermeable membrane.[1] Such interactions may be interesting from a practical point of view for designing selective membranes and sorbents.

Hydrogels of PMADQUAT immersed into aqueous solutions of $K_3[Fe(CN)_6]$ or $K_4[Fe(CN)_6]$ absorb these salts from the solution and undergo contraction. The dependencies of the equilibrium swelling degree of the
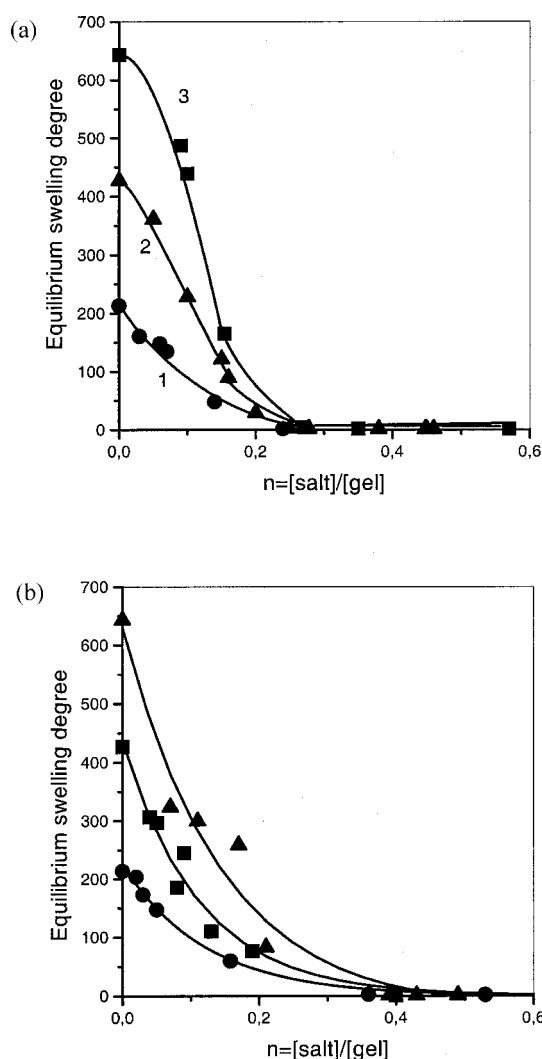
(a)

(b)

Figure 4. Swelling of PMADQUAT hydrogels in aqueous solutions of $K_4[Fe(CN)_6]$ (a), and $K_3[Fe(CN)_6]$ (b). Samples: Gel#1 (1), Gel#2 (2), Gel#3 (3).

hydrogels on the relative concentration of low molecular salts are plotted in Figure 4a and 4b. It can be seen from the figures that even an insignificant increase of the relative salt concentration considerably decreases the equilibrium swelling degree of the hydrogels. At a certain [salt]/[gel] ratio the hydrogels are characterized by their completely collapsed state and a further increase in this ratio does not influence the swelling of the hydrogels. It is interesting to note that the values of this ratio from which the gels attain the completely collapsed state are 0.25 and 0.4, for $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$ respectively. The contraction curves for hydrogels with different degrees of equilibrium swelling are distinguished from each other only by the amplitude of shrinking. These results are in good agreement with the compositions of complexes between these salts and linear PMADQUAT.

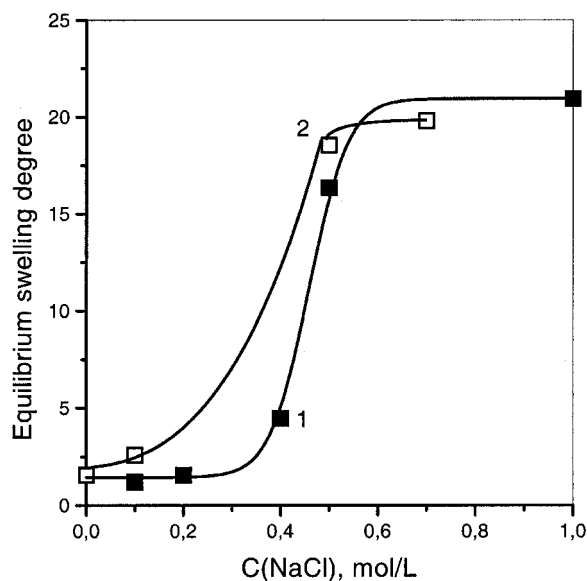The complexes of PMADQUAT hydrogels are stable and do not release the low molecular coordination com-

Figure 5. Swelling of complexes between PMADQUAT hydrogels with $K_4[Fe(CN)_6]$ (1) and $K_3[Fe(CN)_6]$ (2) in solutions of different NaCl concentration.

pounds even after immersion in pure water for some months. However, in solutions of NaCl starting from a certain concentration, we observed the release $K_4[Fe(CN)_6]$ or $K_3[Fe(CN)_6]$ and an increase in the equilibrium swelling degree of hydrogels (Figure 5). Probably, in the media of high ionic strength, the electrostatic interactions between polyelectrolytes and coordination compounds are screened by Na^+ and Cl^- ions, which causes the destruction of the poly-complexes.

Conclusion

Linear and crosslinked PMADQUAT form relatively stable complexes with potassium hexacyanoferrates. The interaction of linear PMADQUAT with $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$ is accompanied by a decrease in hydrodynamic volume of polyelectrolyte and precipitation of polymer complexes from solution. The composition of the complexes formed depends on the charge of the low molecular coordination ion. Hydrogels of PMADQUAT undergo sharp contraction in solutions of $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$ and absorb these salts from the solution. Complexes are stable in a wide range of concentrations and are destroyed only in media having a high ionic strength.

[1] P. Molyneux, *"Water-Soluble Synthetic Polymers: Properties and Behavior"*, Volume 2, CRC Press, 1982.

[2] E. Tsuchida, H. Nishide, *Adv. Polym. Sci.* **1977**, *24*, 1.

[3] M. Kaneko, E. Tsuchida, *J. Polym. Sci., Part D: Macromol. Rev.* **1981**, *16*, 397.

[4] B. L. Rivas, K. Geckeller, *Adv. Polym. Sci.* **1992**, *102*, 171.

[5] J. C. T. Kwak, *"Polymer-Surfactant Systems"*, Marcel Dekker, Inc., 1998.

[6] M. Stickler, *Angew. Makromol. Chem.* **1984**, *123/124*, 85.

[7] Th. Griebel, W.-M. Kulicke, A. Hashemzadeh, *Colloid Polym. Sci.* **1991**, *269*, 113.

[8] N. Konar, C.-J. Kim, *J. Appl. Polym. Sci.* **1998**, *69*, 263.

[9] A. Saenz de Buruaga, I. Capek, J. C. De La Cal, J. M. Asua, *J. Appl. Polym. Sci.* **1998**, *36*, 737.

[10] A. Saenz de Buruaga, J. C. De La Cal, J. M. Asua, *J. Appl. Polym. Sci.* **1999**, *72*, 1341.

[11] P. Kujawa, J. M. Rosiak, *Rad. Chem. Phys.* **2000**, *57,* 559.

[12] Y. Tabata, Y. Ito, S. Tagawa, *"CRC Handbook of Radiation Chemistry"*, CRC Press, 1991.

[13] V. S. Ivanov, *"Radiation Chemistry of Polymers"*, VSP BV Utrecht, The Netherlands 1992.

[14] E. A. Bekturov, L. A. Bimendina, *Adv. Polym. Sci.* **1981**, *41*, 99.

[15] E. Tsuchida, K. Abe, *Adv. Polym. Sci.* **1982**, *45*, 1.

[16] M. Jiang, M. Li, M. Xiang, H. Zhou, *Adv. Polym. Sci.* **1999**, *146*, 121.

[17] T. L. Lowe, J. Virtanen, H. Tenhu, *Polymer* **1999**, *40*, 2595.

[18] G. A. Mun, Z. S. Nurkeeva, V. V. Khutoryanskiy, *Macromol. Chem. Phys.* **1999**, *200*, 2136.