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Electrical conductivity of poly(acrylic acid) gels

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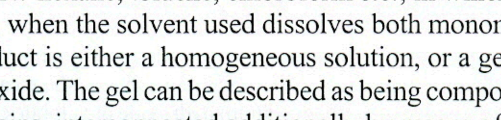
Complete solution transformation into ionically conducting hydrophilic rubber-like gels occurs on γ-ray polymerization of 1.5 – 10 M aqueous solutions of acrylic acid. Both the hydrophilicity and conductivity of this material are due to the volume distributed carboxylic groups. The conductivity of the gels was improved by addition of strong electrolytes, either sulphuric acid or sodium hydroxide, to the initial monomer solution. With the addition of sulphuric acid conductivities exceeding 10^{-1} S cm^{-1} were achieved.

Key words: poly(acrylic acid), electrical conductivity, gels.

Acrylic acid, $CH_2 = CHCOOH$, as an unsaturated compound of the vinyl type, is able to polymerize. The kinetics of its polymerization in various media have been investigated by many authors.[1-9] Under mild polymerization conditions, the monomer molecules build up chain-like polymer molecules of the form:



The form of the polymer product depends on the nature of the solvent.[1,7-9] When pure monomer is used as the reaction medium, the product precipitates as a powder, since the polymer is insoluble in its own monomer. Similar results are observed on polymerization from *n*-hexane, toluene, chloroform *etc.*, in which the polymer is also insoluble. However, when the solvent used dissolves both monomer and polymer, the polymerization product is either a homogeneous solution, or a gel, soluble in concentrated sodium hydroxide. The gel can be described as being composed of entangled (but not cross-linked) chains, interconnected additionally by means of hydrogen bonds.[1,8]

Since acrylic acid is a weak acid (its dissociation constant is 5.66×10^{-5}), predominantly neutral molecules participate in the polymerization process. However, if the acid is neutralized to form its well dissociated alkali salt, the polymerization process can be considerably attenuated due to the electrostatic repulsion of the monomer anions.[2-6]

Mercaptoethanol[2] or the dinitrile of azoisooleic acid,[3] which are able to form acrylic acid monomer radicals, can be used as polymerization initiators. However, it is known that the polymerization also occurs under γ-irradiation.[1,7-9]

Due to the presence of many carboxylic groups along the polymer molecules, poly(acrylic acid) behaves as an electrolyte, mentioned in the literature as a polyelectrolyte[10] or ionomer.[11] There are a few publications relating to the conductivity and transference numbers of dilute aqueous solutions of poly(acrylic acid).[12,13] It is noteworthy that the transference number of poly(acrylic acid) anions in aqueous solution, when the polyions were mobile, was found to amount to approximately 0.5.

Recently, non-liquid (solid, gel-polymeric) electrolytes have become attractive due to the possibility of their application as replacements for liquid electrolytes in electrochemical power sources and other electrochemical devices. A typical synthesis procedure involves the dissolution of a polymer (poly(ethylene oxide), poly(acrylonitrile), poly(vinyl chloride), *etc.*) together with an ionic salt, in a polar solvent (acetonitrile, propylene carbonate, dimethylsulphoxide, tetrahydrofuran *etc.*) followed by the partial or total evaporation of the solvent.[14,15] In the literature on non-liquid polymer electrolytes, poly(acrylic acid) is also mentioned, but only as a copolymer improving the electrical conductivity of poly(ethylene oxide).[16] Among the investigations concerning the systems similar to that investigated in this work, the attention should be paid to a series of papers by the authors Despić and Hills.[17-19] Namely, these authors investigated the ionic transport through poly(methacrylic acid), cross-linked by copolymerization with ethylene glycol dimethacrylate.

In accordance with the recent trends, an attempt was made in this work to produce a gel-type electrolyte by a γ-ray polymerization of concentrated aqueous solution of acrylic acid. A radiation dose was defined which enables an insoluble, transparent, elastic, ionically conducting product to be obtained. The ionic conductivity of this product is either due to the mobile protons originating from the dissociated carboxylic groups, or due to the conductivity of modifying additives.

EXPERIMENTAL

Synthesis[20]

For the synthesis, solutions of acrylic acid (Merck p.a. purity) within the concentration range 1.5 – 10 M, were used. Most samples were aqueous solutions, but in some cases methanol or ethanol were used as solvents. A controlled quantity of sodium hydroxide or sulphuric acid was added to some of the aqueous solutions prior to irradiation.

The samples were placed into glass tubes and irradiated with the γ-rays of a ^{60}Co source having an activity of 9.25×10^{14} Bq. After preliminary investigations in the dose interval 10 – 60 kGy, it was concluded that a dose of 20 kGy was always sufficient to obtain a product of maximum homogeneity and elasticity. Therefore, a constant dose of 20 kGy was subsequently used for the synthesis. During the irradiation the solutions are completely transformed into a transparent rubbery mass.

Electrical conductivity measurements

Electric conductivity was measured at a constant frequency of 10 kHz using a Wayne Kerr model B224 conductance bridge equipped with an external function generator. For testing of liquid solutions, a dipping type conductometric cell with platinum foil electrodes was used. Polymerized samples, obtained as the rods within the glass tubes, were cut into discs and fastened between platinum foils by means of a micrometric screw.

All measurements were carried out at a room temperature of 20 °C.

RESULTS AND DISCUSSION

As already mentioned in a paper published by Chapiro *et al.*,[9] not only chain-like polymerization but also the cross-linking, followed by degradation of the polymer molecules can occur under drastic γ-irradiation. In this work, considering the earlier reports, the concentrated acrylic acid solutions were irradiated with doses sufficient to obtain maximum homogeneity and elasticity of the final product. Proof that not the usual[1] but a cross-linked gel was obtained was the fact that the product was elastic and insoluble in a concentrated (2 M) aqueous solution of sodium hydroxide. The product retains the form of the vessel, which means that a foil could also be obtained if, for example, one irradiates a spot of initial solution on a flat surface.

There are interesting questions to be considered on the mechanism of polymerization under the γ-ray dose used, for example the nature of the radicals participating in the polymerizatin process, the degree of damage to the carboxylic groups, the chain length, the type and number of cross-linking bonds. However, the primary aim of this work was the synthesis and conductance study of gel electrolytes based on poly(acrylic acid), and the data obtained in this work are insufficient for a deeper discussion on the mechanistic and structural aspects of the polymerization.

The conductivity of the materials obtained by polymerization of acrylic acid dissolved in pure water are presented in Fig. 1. Contrary to liquid polymer solutions,[12,13] in our case, as also in the similar ionically conducting resins,[17] it is unlikely that the polymer molecules are mobile, *i.e.*, the only possible current carriers are the protons originating from the dissociated carboxylic groups. The magnitude of the conductivity is in accordance with the fact that acrylic acid is a

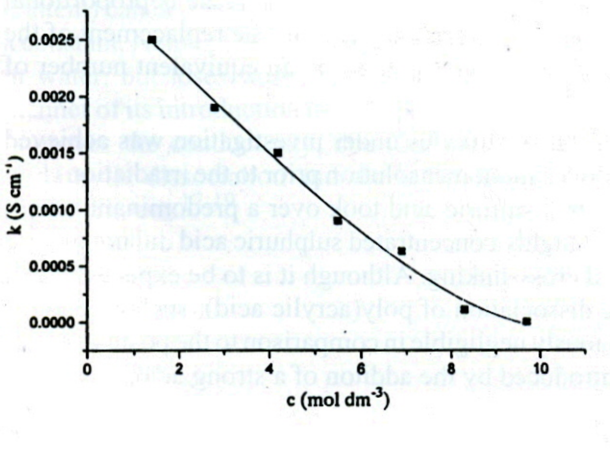


Fig. 1. Specific electric conductivity of gel electrolyte obtained by γ-ray polymerization of aqueous acrylic acid solution, in dependence on the initial monomer concentration.

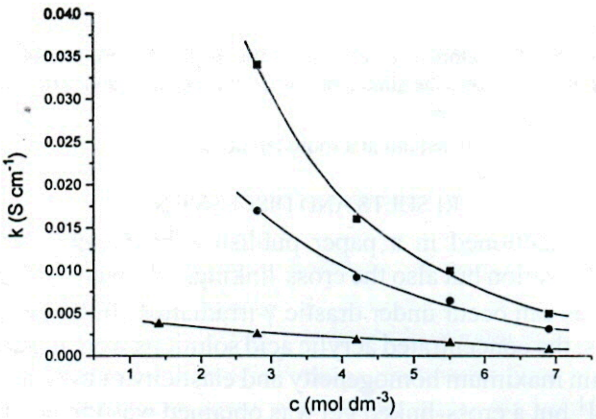


Fig. 2. Specific electric conductivity of gel electrolyte obtrained by γ-ray polymerization of partially neutralized aqueous solution of acrylic acid, in dependence on the initial monomer concentration. The concentration of NaOH added to the initial monomer solution: (▲) – 0.1 M, (●) –1 M and (■) – 2 M.

weak acid. The intrinsic role of the dielectric constant of the solvent is visible from the Table I. Namely, when a solvent of lower dielectric constant than water is used for the polymer electrolyte preparation, the conductivity is lower as a consequence of the suppressed dissociation of the carboxylic groups.

TABLE I. Specific electric conductivity (S cm^{-1}) of gel electrolyte obtained by γ-ray polymerization of various concentrations of acrylic acid in different solvents

Solvent c/mol dm^{-3}	6.9	8.3	9.7
Water	6.3×10^{-4}	1.1×10^{-4}	4.4×10^{-6}
Methanol	3.88×10^{-7}	1.1×10^{-7}	8.4×10^{-8}
Ethanol	8.0×10^{-8}	2.2×10^{-8}	1.4×10^{-8}

Partial neutralisation of the poly(acrylic acid), by addition of sodium hydroxide (0.1, 1 and 2 M) to the monomer solution prior to irradiation, generally leads to a conductivity increase, as compared to the conductivity of pure poly(acrylic acid) obtained at the same initial monomer concentration. This increase is proportional to the neutralisation degree, and arises as a consequence of the replacement of the protons of the slightly dissociated carboxylic groups, by an equivalent number of free and mobile sodium cations.

A highest conductivity of the electrolytes under investigation was achieved when sulphuric acid was added to the monomer solution prior to the irradiation (Fig. 3), as a consequence of the fact that sulfuric acid took over a predominant role in the conductivity. The presence of highly concentrated sulphuric acid did not disturb the radiation polymerization and cross-linking. Although it is to be expected that a strong acid would suppress the dissociation of poly(acrylic acid), such a negative effect on the conductivity is obviously negligible in comparison to the positive effect of the numerous mobile ions introduced by the additon of a strong acid. However,

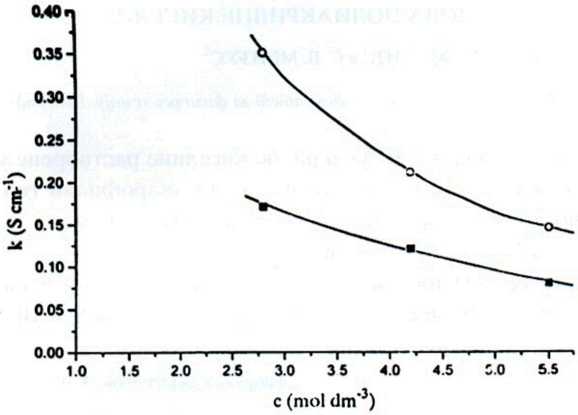


Fig. 3. Specific electric conductivity of gel electrolytes obtained by γ-ray polymerization of aqueous solution of acrylic acid in dependence on the initial monomer concentration, when sulphuric acid in concentrations of 1.2 (■) and 4.1 M (o) was added prior to polymerization.

by comparing the conductivity of the poly(acrylic acid) impregnated with aqueous solution of sulphuric acid, to the conductivity of pure aqueous solution of sulphuric acid, one can notice a non-additive behaviour. Namely, from the handbooks relating to the electrolyte solutions, the conductivity of 1.2 M and 4.1 M sulphuric acid in pure water at 20 °C is 0.41 and 0.75 S cm^{-1}, respectively. Within the poly(acrylic acid) obtained with the initial monomer concentration of 2.75 M, which occupies approximately 20% of sample volume, the conductivities of 1.2 M and 4.1 M sulphuric acid amount however 0.175 and 0.35 S cm^{-1}, respectively. The conclusion imposes itself that the polymer matrix displays an additional suppressing effect to the ion movement, overrating that of liquid volume fraction decrease. This effect is most probably the consequence of an overall decrease of the dielectric constant in the presence of poly(acrylic acid), which indicates that in this sense the sample under investigation displays the behaviour of a homogeneous solution rather than that of a heterogeneous two-phase system composing of the mutually independent phases.

In the concentration range studied (1.5 – 10 M), the conductivity decreases with the increase in initial monomer concentration (*i.e.*, with the decrease in solvent content) can be observed (Figs. 1– 3). The solvent content of the final product is not a constant. Namely, as a hydrophilic material, poly(acrylic acid) swells when placed in water, but loses water when placed in a dry atmosphere. Independent of the manner of its introduction into the polymer matrix, an increase in the solvent content improves the conductivity, due to its favorable influence on both the degree of electrolytic dissociation and the ion mobility, as already found elsewhere for a similar system.[17-19]

И З В О Д

ЕЛЕКТРИЧНА ПРОВОДЉИВОСТ ГЕЛОВА ПОЛИАКРИЛНЕ КИСЕЛИНЕ

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Полимеризацијом помоћу γ-озрачивања 1,5-10 M акрилне киселине растворене у води, комплетан раствор је преведен у еластичан јонски проводан хидрофилан гел. Хидрофилност и јонска проводљивост гела потичу од запремински распоређених карбоксилних група. Проводљивост гела је додатно побољшана додавањем јаких електролита: сумпорне киселине или натријум хидроксида, у полазни раствор мономера. Додатком сумпорне киселине постигнуте су високе проводљивости које превазилазе 10^{-1} S cm^{-1}.

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