Intermolecular Crosslinking of Poly(acrylic acid) in Aqueous Solution by Electron Beam Irradiation

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ABSTRACT: Poly(acrylic acid) (PAA) was dissolved in water, and the solution was irradiated with high-energy electrons. The formation of macroscopic gel was studied as a function of the radiation dose, the pH of the aqueous solution, and the concentration of added salt. Gelation by intermolecular crosslinking was found at low pH values of 2–4, whereas at pH greater or equal to 5, no gel was formed by electron beam irradiation. Nevertheless, by adding monovalent salt the gel formation was enhanced at intermediate pH values. The intermolecular crosslinking was assumed to be inhibited by electrostatic repulsive forces when the macromolecules of PAA are negatively charged and the ionic strength of the solution is low. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 3113–3116, 2011

Key words: poly(acrylic acid); polyelectrolytes; electron beam irradiation; crosslinking; gelation

INTRODUCTION

Since over 40 years, there is a growing interest in crosslinked, water-swellable polymer structures—hydrogels.[1] Radiation-based techniques can be used effectively for the preparation of hydrogels. As the properties of hydrogels are strongly affected by crosslinking density and structure, the radiation is advantageously used for the control of crosslinking.[2] The method of radiation-induced crosslinking has been used for the preparation of hydrogels based on different polymer systems, as for instance polyvinyl pyrrolidone,[3] carboxymethyl cellulose/acrylamide,[4] carboxymethyl cellulose/chitosan,[5] and blends of poly(lactic acid) and poly(butylene terephthalate-co-adipate).[6]

Some of the hydrogels are capable of reacting to various environmental stimuli as temperature, pH, ionic strength, so forth.[7] One type of these stimuli-sensitive gels can be prepared by crosslinking of a weak polyelectrolyte, such as poly(acrylic acid) (PAA), which demonstrates remarkable pH responsiveness.[2,8]

When a solution of a polymer is subjected to ionize radiation, reactive sites are formed on the macromolecules. This can result from direct action of radiation on the polymer chains and from indirect effect.[7] The action of ionizing radiation on polymers in aqueous solutions occurs mainly through an indirect effect. Most part of the energy is absorbed by water molecules. Ionization of water molecules and subsequent reactions lead to the formation of reactive species such as hydroxyl radicals, hydrogen atoms, and hydrated electrons. Subsequently, hydroxyl radicals and hydrogen atoms react rapidly with the polymer by hydrogen abstraction. Macroradicals are formed.[9]

The irradiation of PAA in solution has been studied briefly.[7–17] It was described that PAA can be effectively crosslinked by irradiation, provided the irradiation is performed in acidic solution (e.g., pH 2) so that most of the carboxylate groups are protonated.[7]

The exact amount of the gel depends on conditions such as pH, salt concentration, polymer concentration, polymer molecular weight, absorbed dose, and dose rate. The objective of this work was to explore the influence of radiation dose, pH, and added salt on the gel formation, when a dilute aqueous solution of PAA is irradiated with high-energy electrons using an industrial electron beam accelerator.

EXPERIMENTAL

Materials

A PAA powder having molecular weight of 450,000 g/mol was supplied by Polysciences (Warrington, PA) and used as received. Stock solutions of PAA with a concentration of 1 wt % in Milli-Q-filtered (Millipore) water were prepared by stirring overnight at room temperature. The pH was adjusted with HCl or NaOH solution. In some experiments, NaCl was added to the solution, which results in salt concentrations c_{NaCl} from 0.05 to 0.50 mol/L.

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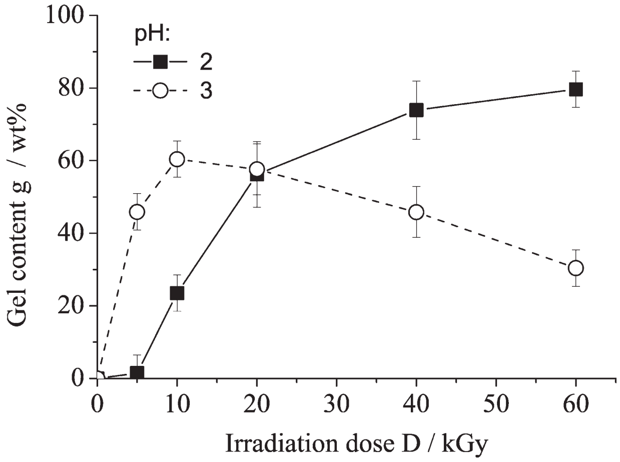

Figure 1 Gel content g of poly(acrylic acid) solution as a function of irradiation dose D.

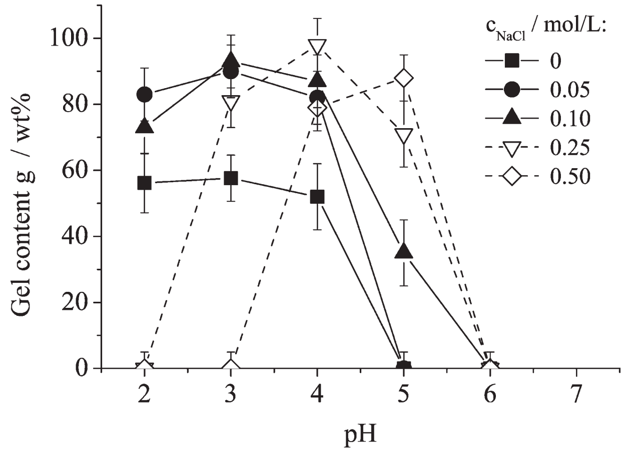

Figure 3 Gel content g of poly(acrylic acid) solution irradiated with a dose of 20 kGy in the presence of added NaCl salt as a function of pH.

Irradiation

Before irradiation, the PAA stock solutions were deoxygenated by nitrogen bubbling for 30 min. In each case, 25 mL of the PAA solution was poured in a Petri dish. It results in a maximal thickness of the sample of 4.5 mm, which is smaller than the penetration depth of the accelerated electrons. After repeated nitrogen bubbling, the dishes were sealed with Parafilm®. The samples were irradiated with accelerated electrons using an ELV-2 electron accelerator (Budker Institute of Nuclear Physics, Novosibirsk, Russia) installed in the Leibniz Institute of Polymer Research Dresden. The energy of the electrons and the beam current were 1.5 MeV and 4 mA, respectively. The irradiation facility is described in detail in Ref. 18. The absorbed irradiation dose D was varied in the range from 5 to 60 kGy and applied at room temperature. Total doses D greater than 10 kGy were realized on a step-by-step basis with a dose of 10 kGy per pass.

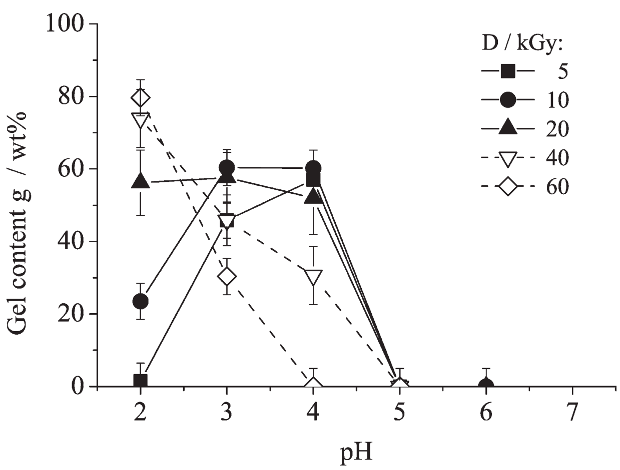

Figure 2 Gel content g of irradiated poly(acrylic acid) solution as a function of pH.

Sol-gel analysis

The irradiated PAA samples were kept closed for 24 h. Subsequently, the samples were poured in Erlenmeyer flasks, mixed with 50 mL of 0.1 mol/L HCl, and stirred overnight at room temperature. The solutions were filtered under vacuum and washed using 20 mL 0.1 mol/L HCl solution and 100 mL methanol to remove the sol fraction. The gels were dried under vacuum at 50°C for at least 5 days to constant weight. The gel content g was calculated using eq. (1):

$$g = m_{gel}/(m_{gel} + m_{sol}) \times 100\% \qquad (1)$$

RESULTS AND DISCUSSION

Figure 1 shows the gel content g produced by the irradiation of the PAA solution in dependence of the absorbed dose for two low pH values. At pH 2, the gel content increases with increasing dose up to about 80 wt % at a dose of 60 kGy. At pH 3, the gel formation shows a maximum at a dose of 10 kGy. Then the gel content decreases with increasing dose again. Already at a dose as low as 5 kGy a gel content of more than 40 wt % was achieved compared with nearly no gel formation for the PAA solution with pH 2.

The influence of the pH in the range from 2 to 6 on the gel formation is illustrated in Figure 2. At pH 4, the gel content also shows a maximum at a dose of 10 kGy. At pH values greater or equal to 5 a gel was formed at no dose at all. The gel content at doses of 5–40 kGy drastically decreases when the pH was raised from 4 to 5. The irradiation with a dose of 60 kGy, the highest dose applied in the study, already results in no gel formation at pH 4.

Furthermore, a series of PAA solutions containing NaCl salt with a concentration from 0 to 0.50 mol/L were irradiated. Figure 3 shows the influence of the

NaCl concentration on the gel content as a function of pH for an irradiation dose of 20 kGy. Under certain conditions, the gel formation was enhanced by the adding of NaCl. The addition of NaCl resulting in concentrations c_{NaCl} of 0.05 and 0.10 mol/L raises the gel content of solutions with pH 2–4 significant. At pH 5, the gel content dramatically increases with salt addition up to 0.5 mol/L. No increase in gel content was observed by salt addition at higher pH. Adding NaCl at pH 6 did not yield any gel. At high salt concentrations, no macroscopic gel was also formed at low pH values. Macroscopic gel was absent at pH 2 for NaCl concentrations of 0.25 and 0.5 mol/L as well as at pH 3 for 0.5 mol/L. Radiation-induced reactions, which result in intramolecular crosslinking, are assumed to be the dominant process under these conditions.

In summary, it can be stated that PAA gel formation was especially enhanced by adding NaCl at intermediate pH values.

It is known that the polyelectrolyte PAA offers an other behavior than nonionic macromolecules upon irradiation of their aqueous solutions.[7] With increasing pH of the solution the PAA reveals their specific properties as a polyelectrolyte. At intermediate and alkaline pH values the PAA molecules are increasingly charged because of the dissociation of the carboxylic acid groups attached on the chain. The negative charges induce electrostatic repulsion between the chain segments. As a consequence, the molecules have a rod-like, relatively stiff conformation. During irradiation, the macroradicals generated on charged chain segments of neighboring macromolecules must overcome the electrostatic repulsive forces to recombine. Therefore, the rate of the recombination reactions goes down with increasing density of negative charges on the chain. Competitive reactions, such as chain scissions proceed with higher yield than crosslinking reactions (Fig. 4). The macroradicals initiate β-scission resulting in end-chain radicals and unsaturated terminal structures.[7] It is known from low-angle laser light-scattering measurements that the average molecular weight of the PAA decreases by irradiation at intermediate and alkaline pH.[9] As a result of the change in the ratio of reaction rates, no gel is formed. Under the particular conditions of this study, the macroscopic gel formation is completely inhibited at pH greater or equal to 5. At low pH values the PAA molecules are nearly uncharged and there is hardly any electrostatic inhibition of intermolecular crosslinking. The electron beam irradiation in the range of pH from 2 to 4 resulted in macroscopic gel formation in this study, whereas the exact gel content was found to depend on the pH and the absorbed dose. At pH 2, the gel content increases with increasing dose as expected. On the other hand, at pH 3 and 4, the gel content shows a maximum at a dose of 10 kGy. At higher absorbed doses chain scissions are assumed to become increasingly important. The fraction of chains incorporated in the three-dimensional network decreases, which means lower gel content.

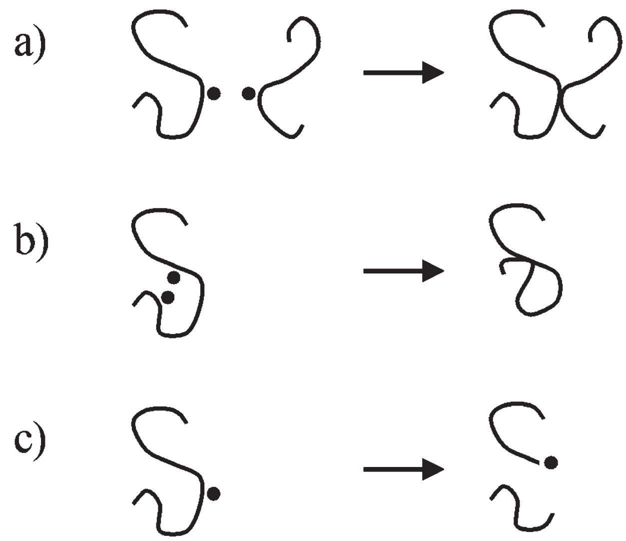

Figure 4 Schematic representation of (a) intermolecular crosslinking, (b) intramolecular crosslinking, and (c) degradation by chain scission.

In the case of weak polyelectrolytes such as PAA the density of charges depends on the pH as well as the ionic strength. In contrast to a small molecule of a weak acid, the pK value for the weak PAA is not a constant.[16] The origin of this behavior is that the presence of charged groups on a polymer chain makes it more difficult to dissociate neighboring carboxylic acid groups because of high local electrostatic potentials. Added salt attenuates the electrostatic interactions.[16] The adding of NaCl in this study results in a less charged polymer chains at intermediate pH. Crosslinking becomes the predominant process at pH 5. The gel content increases with increasing concentration of NaCl. At higher pH values the density of charges is high and electrostatics effects cannot be eliminated by adding NaCl salt.

In this study, no macroscopic gel was also formed at low pH of 2–3 and high salt concentration. On the contrary, it was described in Ref. 16 that the addition of salt at very low pH of 1 did not influence the high gel content of PAA, which was crosslinked via gamma irradiation. The irradiation with gamma-rays from isotope sources is known to be characterized by significantly lower dose rate than irradiation using an electron beam accelerator. Because of the low dose rate the number of radicals generated in a short period of time is low in the case of gamma irradiation. Consequently, the averaged number of radicals simultaneously present at the same PAA molecule is very low. A recombination of radicals is only possible between radicals, which are localized on two different macromolecules. This intermolecular crosslinking results in macroscopic gel formation. The higher dose rate of electron beam irradiation causes a higher steady-state concentration of radicals. The probability that several radicals are generated at the same molecule at the same time is increased. This has an influence on the competition between inter- and intramolecular recombination. Using accelerated electrons with high dose rate the intramolecular crosslinking is promoted rather than the macroscopic gel formation by intermolecular crosslinking. In this study, the high salt concentration, which enhances the coiling of the macromolecules at low pH, leads along with the high dose rate to the fact that the conditions for the intramolecular recombination of macroradicals are fulfilled. The intermolecular crosslinking plays a minor part and macroscopic gel was not formed at pH 2 and concentrations c_{NaCl} of 0.25 and 0.5 mol/L as well as at pH 3 and c_{NaCl} of 0.5 mol/L.

CONCLUSIONS

The formation of macroscopic gels upon electron beam irradiation of PAA in aqueous solution was investigated as a function of irradiation dose, pH, and salt concentration. It was found that at pH 2, the gel content increases with increasing irradiation dose. On the contrary, at pH 3 and 4, it shows a maximum at a absorbed dose of 10 kGy. At pH values greater or equal to 5 no gel was formed at all doses investigated.

By adding NaCl salt, the gel formation was enhanced at intermediate pH values. The intermolecular crosslinking is concluded to be inhibited by electrostatic repulsive forces when the ionic strength of the solution is low, and the macromolecules are charged because of the dissociation of the carboxylic acid groups. Through the high dose rate of the electron beam used the intramolecular crosslinking is supposed to be an important reaction if the PAA is irradiated at low pH and high salt concentration.

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