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Incorporation of acid polymethacrylates into temperature sensitive hydrogels using electron beam irradiation

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Summary

In this work, electron beam irradiation was used to prepare hydrogels from aqueous solutions of monomers and/or linear polymers. Poly(*N*-isopropylacrylamide) (PNIPAAm) and polymers of methacrylic acid derivatives were used to generate the different temperature sensitive hydrogels. The effects of irradiation dose and *N,N*'-methylenebisacrylamide (BIS) crosslinking agent were also studied. The polymethacrylate content in co-polymeric hydrogels was varied (5, 10, 15 and 20 mol%). The temperature dependence of the swelling behavior of the hydrogels was characterized. The influence of polymethacrylate content on the swelling characteristics of the hydrogels was investigated. The incorporation of polymers from methacrylic acid derivatives into hydrogels was effectively achieved under optimum conditions.

Introduction

The synthesis of hydrogels and other biomaterials by irradiation has attracted much attention in recent times due to the fact that this method can be performed without additives yielding sterilized super-clean biomaterials in one step [1-3].

The preparation of temperature-sensitive *N*-isopropylacrylamide (NIPAAm)-gels by irradiation methods hat been extensively studied recently [4-6]. In dilute aqueous NIPAAm-solution the radicals generated by the radiation are mainly a result of the radiolysis of water [5]:

$$H_2O \xrightarrow[\text{Radiation}]{\text{Ionizing}} e^-_{aq},\ {}^{\bullet}OH,\ {}^{\bullet}H,\ H^+,\ H_2O_2\ ,\ H_2 \uparrow$$

Depending on the experimental conditions selected, either hydrated electrons, $^{\bullet}OH$ or $^{\bullet}H$ radicals can be preferably generated. These primary radicals react with NIPAAm yielding different monomer-radicals which can undergo polymerization, branching and finally crosslinking [5]. In higher concentrated solutions (≥ 10 weight%) or by irradiation of pure NIPAAm, radicals are generated also directly in the monomer. These lead to simultaneously occurring processes of polymerization, cross-linking and degradation of NIPAAm [4]. The radiation type (γ-rays or electron-beam), the radiation dose, dose rate, and temperature employed yield NIPAAm-hydrogels with different microstructures [6]. Although the irradiation of monomers to form hydrogel works well, there are some intrinsically drawbacks:

-Since many of the monomers are harmful or even toxic (unlike the corresponding polymers), special care has to be taken to ensure that either all the monomer has reacted or its residues have been fully extracted afterwards (important in biomedical applications) [2].

-Since the irradiation of monomers produces consecutive and parallel reactions, the system is rather complicated and difficult for qualitative description [2].

The irradiation of polymers in aqueous solution is easier to control and study, since the polymers can be fully characterized and a lower number of unwanted processes occur [2].

Another very important class of sensitive polymers is the polyacids which show pH- and ionic strength-sensitivity. Hydrogels prepared from these are components of, so called “intelligent” biomaterials. The hydrogel formation via radiation cross-linking of two of the most common polyacids: polyacrylic acid (PAA) [7-9] and polymethacrylic acid (PMAA) [8-10] has also been studied. From the irradiation experiments on PAA in aqueous solutions, it was concluded that high gel fractions were only found at low pH-values whereas above pH ~ 4 no gel was formed unless a salt was added. The gelation results were explained in terms of ionic interactions. To form crosslinks, macro-radicals need to migrate and combine. The approach of two macro-radicals can be inhibited by electrostatic repulsion and is usually the case with PAA at high pH [7]. In a comparative study, both PAA and PMAA were irradiated in the solid state. In this case, the PAA was crosslinked whereas PMAA was depolymerized to lower molecular weights [8]. Irradiation in water-solution and at high pH, both PAA and PMAA revealed a remarkable increase of the radical lifetime. This minimized the recombination reactions and allowed the radical transfer-reactions to occur. For example, the intramolecular H-transfer and β-fragmentation (depolymerization) [9], see Figure 1. However in the case of PMAA the β-fragmentation (depolymerization) was considerably faster [9]. If the irradiation conditions are chosen to allow maximum $^{\bullet}OH$-yield (N_2O-saturated aqueous solutions) it is impossible to crosslink PMAA at high pH-values and the rate of chain-scission for PMAA-radicals is ca. 70 times faster than that for the PAA-radicals [10]. In a 10 weight% aqueous solution at the natural pH of PMAA, even at 200 kGy irradiation dose no macroscopic gel extending through the solution, was obtained [10]. These results show that the preparation via irradiation of hydrogels of PMAA or polymethacrylic ester-derivatives is much more difficult to achieve than that of the corresponding PAA or polyacrylic ester derivatives. Nevertheless, the generation of hydrogels via irradiation in aqueous solution of a methacrylic ester derivative was achieved, although at a much higher irradiation dose than for the corresponding acrylic ester derivative [11]. All this suggest that at low pH (non-charged polymer) and high irradiation dose, the hydrogel formation of PMAA and polymethacrylic acid-derivatives should be feasible.

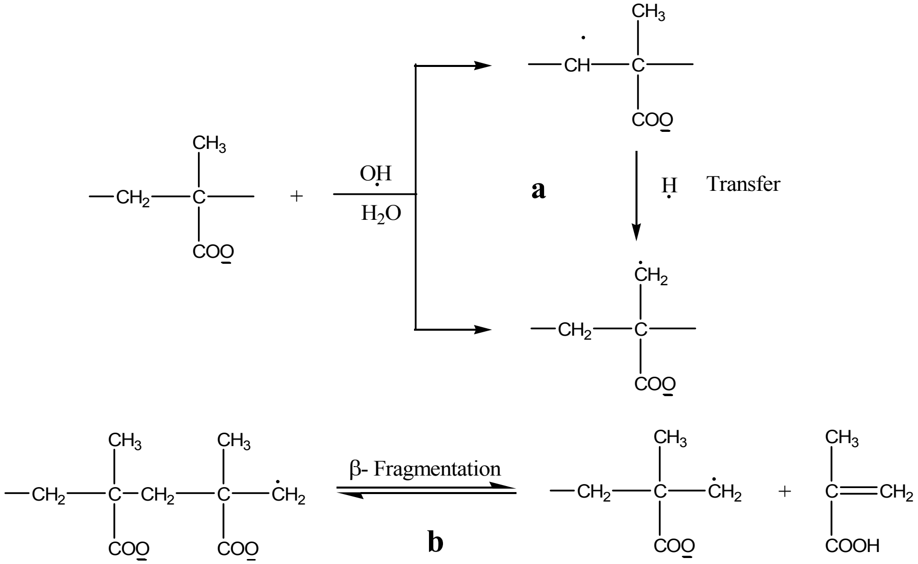
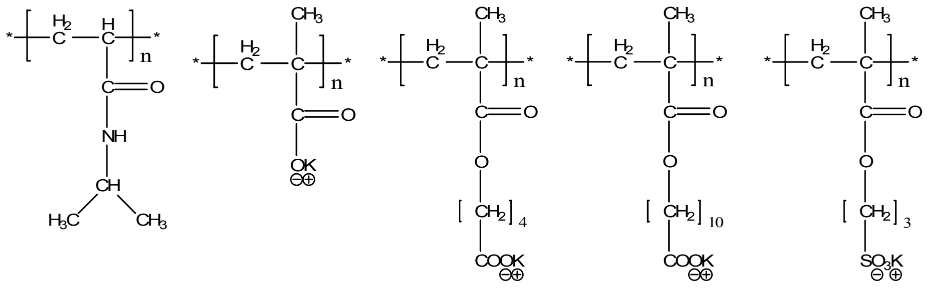


Figure 1. Radical reactions of PMAA after irradiation in conditions selected to produce a maximum yield of OH radical. a).-Intramolecular H-transfer, b).-Depolymerization

The aim of this work was to find appropriate conditions for the hydrogel formation via electron beam high energy irradiation to yield simultaneously temperature- and pH-sensitive gels from the following chemical structures (see Figure 2): NIPAAm as temperature-sensitive part and methacrylic acid derivatives as pH-sensitive parts. According to the literature reports discussed above, irradiation of polymers in aqueous solution, at high concentration, low pH-value and using a high irradiation dose, seemed to be the most favorably conditions to obtain hydrogels. Nevertheless other approaches were also tested including:



Poly(*N*-isopropyl-acrylamide)	Poly(potassium methacrylate)	Poly(potassium-5-methacryloyl-oxy-pentanoate)	Poly(potassium-11-methacryloyl-oxy-undecanoate)	Poly(3-sulfopropyl potassium methacrylate)
PNIPAAm	PMAAK	Pn4K	Pn10K	PSPMAK

Figure 2. Polymers used for irradiation experiments

-The use of polymethacrylic polymers of different pKa (carboxylic acid groups and sulfonyl groups, see Figure 2).
-Irradiation into solutions with salt addition (increased ionic strength).
-Irradiation in non-aqueous solution (methanol).
-Irradiation of NIPAAm monomer with polymethacrylic polymers.
-Irradiation of solutions of NIPAAm polymer with polymethacrylic polymers using *N,N′*-methylene bisacrylamide (BIS) as additive.
The use of additives to increase grafting yields is a common practice in radiation grafting of monomers onto polymeric substrates [12-16]. It is worth to mention that the grafting polymerization by irradiation of methacrylic acid onto cotton [12] and polypropylene [16] using additives has been successful, as opposed to the hydrogel formation by irradiation of polymethacrylic acid.

Experimental

Synthesis of Poly(N-isopropylacrylamide) (PNIPAAm)
NIPAAm monomer (Aldrich) was recrystallized from hexane. A free radical solution polymerization of NIPAAm (3.0 M) in 1-4-dioxane (Aldrich, HPLC-grade) was performed using 2,2'azobisisobutyronitrile (AIBN, 0.5 mol% with respect to NIPAAm) at 70°C for 6 h. The obtained PNIPAAm was precipitated with diethylether and purified by re-dissolution in acetone and re-precipitation in ether. (Yield: 87%, M_w = 173 000 g/mol by light scattering (LS) in THF).

Synthesis of Poly(potassium methacrylate) (PMAAK)
The potassium salt of methacrylic acid was obtained by reaction of methacrylic acid (Aldrich) with a methanolic 6 N KOH solution under cooling. The polymerization of this monomer was performed using the following procedure:
In 20 mL bi-distilled water, 40 mmol of potassium methacrylate and 0.4 mmol of ammonium persulfate as initiator were dissolved by stirring. The polymerization mixture was degassed and argon was added by the freeze-thaw technique. Afterwards 0.4 mmol of *N,N,N`N`*tetramethyleneethylenediamine (TEMED) as an accelerator was added using a syringe. The polymerization was run at room temperature for 24 h. After that time the polymer was precipitated using THF and washed with ethanol several times. (Yield 89%, M_w= 304 000 g/mol by LS in aqueous 0.05 M NaCl).

Synthesis of Poly(3-sulfopropyl potassium methacrylate) (PSPMAK)
The potassium salt of 3-sulfopropylmethacrylate (Aldrich) was used as received. The polymerization procedure was the same as for the synthesis of PMAAK with the exception that after 24 h reaction the polymer was precipitated using cold ethanol and washed with hot ethanol (45°C) to remove unreacted monomer.
(Yield 87%, M_w= 344 000 g/mol by LS in aqueous 0.05 M NaCl).

Synthesis of Poly (potassium-5-methacryloyloxy-pentanoate) (Pn4K) and Poly(potassium-11-methacryloyloxy-undecanoate) (Pn10K)
The potassium-5-methacryloyloxy-pentanoate was obtained by reaction of 5-methacryloyloxy-pentanoic acid with a methanolic 6 N KOH solution under cooling . The free radical polymerization of this monomer was carried out in methanol using

AIBN (1 mol%) as initiator at 60°C for 24 h. The polymer was precipitated in THF and washed with propanol (3x 40 mL).
(Yield ~60%, M_w= 37 300 g/mol by LS in methanol).
The potassium-11-methacryloyloxy-undecanoate was obtained from 11-methacryloyloxy-undecanoic acid. The polymerization procedure was the same except that the ethanol was used to wash the polymer.
(Yield ~50%, M_w= 52 700 g/mol by LS in methanol).

Gel preparation by irradiation

All irradiation experiments were performed in solution. For these the polymers prepared, PNIPAAm, PMAAK and PSPMAK; and also NIPAAm-monomer, were dissolved in different solutions. The solutions used were: bi-distilled water, aqueous 0.006 N HCl, aqueous 0.3 M KCl, aqueous 0.1 M KCl and methanol (p.a.). All solutions were prepared by the following methodology:
The amounts of polymer, monomer or combination of both (see Tables 1 and 2), were dissolved by magnetic stirring in 10 mL of the liquid chosen. The times required for dissolution varies greatly from one system to the another and ranges from 15 min (NIPAAm-monomer) up to 24 h (systems with PMAAK or PSPMAK) because the solutions are fairly concentrated (10 – 20 weight%). After complete dissolution, argon was bubbled into the solution using a needle trough a septum. A second needle served as valve for the evolved gas. Argon was bubbled under stirring for 4 h to drive away oxygen from the solution. After that time, the second needle (valve) was removed; the flask was filled with argon and sealed. The irradiation experiments were performed using an electron accelerator facility (ELV-2, INP, Novosibirsk, Russia) located at the Institute of Polymer Research, Dresden (IPF-Dresden). The acceleration voltage was maintained at 1 MeV and a linear conveyor has been used to transport the sample to and from the irradiation zone. The typical absorbed dose rate is 3000 kGy/h and irradiation doses of either 50 or 100 kGy per single pass were accomplished by varying the conveyor speed. For these experiments the argon filled flasks containing the solutions to be irradiated were opened, the solutions poured into Petri-dishes of 8 cm diameter at a liquid level of approx. 3 mm and the dishes covered with Parafilm^{TM}. By irradiation of the solutions the hydrogel forms either instantly or failed to form in some cases. In most cases the high energy used resulted in a temperature rise of the solution. This effect could not be avoided for the experiments and lead to the precipitation of polymers in some solutions and to the formation of trapped bubbles in other cases. Most gels obtained are turbid. The so obtained gels were removed in the swollen state from the Petri-dishes and were extracted for 24 h in refluxing methanol (Soxhlet).
To prepare hydrogels of PNIPAAm containing Pn4K and Pn10K, aqueous solutions of mixtures of polymers (10 weight%) were prepared. The polymers and BIS (3 mol%) were dissolved in deionized water in a round bottom flask while stirring with a magnetic bar and the flask was sealed with a septum. After that, the same procedure was followed as described above. Two series of copolymeric hydrogels were prepared containing PNIPAAm and Pn4K (or Pn10K) at different nominal molar compositions (5, 10, 15 and 20 mol %). For irradiation experiments the acceleration voltage was maintained at 1 MeV and a irradiation dose of 100 kGy was used. The swollen hydrogels were taken out from the Petri-dishes and washed extensively in deionized water changing the water several times within two days in order to remove unreacted BIS and non-crosslinked polymers.

Gel characterization

The gels were characterized by appearance, equilibrium swelling degree (Q) in methanol and in bi-distilled water, the swelling behavior in different temperature and pH and by elemental analysis. For visual appearance, we considered the overall shape, handling possibilities, color, trapped bubbles and stability in liquids. The degree of swelling was determined by weighing swollen and dry gel samples of he original gels after Soxhlet-extraction. From each gel three samples were cut and each sample was weighed by taking it out from the liquid, taping excess liquid from the gel surface with filter-paper and recording the weight; afterwards the gel sample was submerged again in the liquid for two minutes and the weighing procedure repeated. This procedure was repeated until a constant weight was measured, at least five times. The results given in the Tables 1 and 2 are average-values of the three samples. The swollen sample weight was recorded after the gel stayed for 24 h immersed in the given solvent, while the whole solvent content was changed every 4 h. The dry sample weight was recorded after the gel was dried using the following procedure: first the solvent was decanted and the gel left standing in the ambient for 24 h; then dried in an oven at 60°C for 4 h and finally in a vacuum-oven at 30°C. This formula was used for calculation of the Equilibrium Swelling degree Q:

$$Q = \frac{W_{swollen} - W_{dry}}{W_{dry}} \tag{1}$$

For the hydrogels with PNIPAAm, Pn4K (or Pn10K) and BIS, deswelling experiments were carried out by measuring the diameter of the gels while the temperature increased. Cylindrical gels were cut and placed in a cuvette immersed in a jacketed beaker connected to a thermostated circulating water bath. The gels were kept at a constant temperature until they reached equilibrium, at least for 20 min. Measurements of the gel diameters at different temperatures (from 5 to 60°C, in intervals of 5°C) were taken using a microscope equipped with a CCD video camera. The temperature of the water bath was set using the temperature inside the cuvette measured with a thermocouple.

The swelling degree ratio (r) is calculated and then plotted versus temperature, where d_0 is the diameter of the swollen gel at start of the experiment, and d is the diameter of the gel at a given temperature.

$$r = \frac{d}{d_0} \tag{2}$$

The incorporation of each component in the resulting gel was determined by elemental analysis after soxhlet extraction or extensive washing procedures. For this, gel-samples were dried at room temperature overnight and under vacuum at 30°C for 24 h. Afterwards the samples were pulverized and filled in a vial and again left for 24 h in a vacuum oven at room temperature to equilibrate before the analysis.

Results and discussion

In Table 1, the main parameters of the prepared polymers used for hydrogel preparation, are listed. Static light scattering measurements were used to characterize the linear polymers and the results show that the molecular weights obtained for Pn4K and Pn10K are an order of magnitude lower than for the other polymers prepared. Nevertheless these molecular weights are high enough for irradiation experiments.

Table 1. Characterization results of linear polymers using Static Light Scattering

Polymer	M_w (10^3 g/mol)	Solvent	R_g* (nm)	A_2@ (10^{-4} mol mL/g^2)
PNIPAAm	166	Methanol	27	5.50
PMAAK	304	0.05 M NaCl	42	19.6
Pn4K	37	Methanol	-	23.3
Pn10K	53	Methanol	15	89.4
PSPMAK	344	0.05 M NaCl	35	42.2

* Radius of gyration @ Second virial coefficient

The results on Table 2 were obtained from irradiation experiments using monomers and polymers in solution. The results on Table 3 were obtained from irradiation experiments using only polymers in solution. The reaction parameters varied were: irradiation dose, solvent and the combination of compounds.

Table 2. Irradiation experiments using a combination of monomers and polymers

Description	Dose (kGy)	Appearance	Q in Methanol
NIPAAm*(100mol%) 20weight% in H_2O	2 x 50#	White gel not very stable	15.9 17.1@
NIPAAm (77mol%)+MAAK (23mol%) 20weight% in H_2O	2 x 100#	Viscous liquid	-
NIPAAm*(75mol%)+PMAAK(25mol%) 20weight% in H_2O	2 x 50#	White gel, by extraction destroyed	-
NIPAAm(74.7mol%)+PMAAK(25.3mol%) 20weight% in H_2O	100	White parts, by extraction destroyed	-
NIPAAm*(75mol%)+PSPMAK(25mol%) 20weight% in H_2O	2 x 50#	Viscous liquid	-

* Non recrystallized NIPAAm @ in Water # Irradiated for 50 or 100 kGy, then exposed to air for 5 min and irradiated again for the same dosage (50 or 100 kGy)

All the irradiation experiments using NIPAAm-monomer in combination with methacrylic-polymers or monomers failed to yield a hydrogel. Only pure NIPAAm-monomer could be crosslinked at the conditions used. The results were better when polymers were used, however, not all experiments succeeded. From these we conclude that:

1.-Experiments in methanol solution did not worked, this confirms that the main radicals responsible for the hydrogel formation came from water-radiolysis.

2.-Salt addition (KCl) in two different concentrations did not produce a better gel in the case of PMAAK, contrary to the expectation from literature reports [7].

Table 3. Irradiation experiments using polymers only

Description	Dose (kGy)	Appearance	Q (MeOH)	Mol% NIPAAm (gel)
PNIPAAm 10weight% in H_2O	50	Transparent gel with bubbles	14.6 20.6^b	100
PNIPAAm 10weight% in H_2O	2 x 50^a	White gel in parts but stable	12.1 18.8^b	100
PNIPAAm(73.8mol%) + PMAAK: 10weight% in H_2O	50	White stable gel	45.3 82.0^b	85.8*
PNIPAAm(76.6mol%) + PMAAK: 10weight% in H_2O	100	White stable gel	37.1 49.6^b	88.3*
PNIPAAm(76.9mol%) + PMAAK: 10weight% in 0.3 M KCl	2 x 50^a	White parts swimming in liquid	-	-
PNIPAAm(77.2mol%) + PMAAK: 10weight% in 0.1 M KCl	2 x 100^a	Small gel parts, non stable	-	-
PNIPAAm(76.5mol%) + PMAAK: 10weight% in 0.006 N HCl	2 x 50^a	White stable gel	28.4 36.8^b	88.7*
PNIPAAm(75.9mol%) + PMAAK 10weight% in Methanol	2 x 50^a	White viscous liquid	-	-
PNIPAAm(76.9mol%) + PMAAK: 10weight% in MeOH	2 x 100^a	White viscous liquid	-	-
PNIPAAm(72.1mol%) + PSPMAK: 10weight% in H_2O	50	White gel by extraction destroyed	-	-
PNIPAAm(74.6mol%) + PSPMAK: 10weight% in H_2O	100	White stable gel	23.0 113.1^b	91.8*
PNIPAAm(100mol%) +BIS: 10weight% in H_2O	100	White stable gel	n.d.	100
PNIPAAm(95mol%) +Pn4K + BIS: 10weight% in H_2O	100	White stable gel	n.d.	99.6$^\#$
PNIPAAm(90mol%) +Pn4K + BIS: 10weight% in H_2O	100	White stable gel	n.d.	94.4$^\#$
PNIPAAm(85mol%) +Pn4K + BIS: 10weight% in H_2O	100	White stable gel	n.d.	87.5$^\#$
PNIPAAm(80mol%) +Pn4K + BIS: 10weight% in H_2O	100	White stable gel	n.d.	n.d.
PNIPAAm(95mol%)+Pn10K + BIS: 10weight% in H_2O	100	White stable gel	n.d.	n.d.
PNIPAAm(90mol%)+Pn10K + BIS: 10weight% in H_2O	100	White stable gel	n.d.	94.6$^\#$
PNIPAAm(85mol%)+Pn10K + BIS: 10weight% in H_2O	100	White stable gel	n.d.	91.2$^\#$
PNIPAAm(80mol%)+Pn10K + BIS: 10weight% in H_2O	100	White stable gel	n.d.	79.9$^\#$

[a] Irradiated for 50 or 100 kGy, then exposed to air for 5 min and irradiated again for the same dosage (50 or 100 kGy); [b] in Water; *Calculated from Elemental Analysis (%C/%N) in dry sample; [#] Calculated from Elemental Analysis (%C/%N) in dry sample considering 3 mol% of BIS; n.d. (not determined)

3.-The irradiation dose is crucial role in gel formation since:

-PNIPAAm decreases its swelling degree (Q) with higher irradiation dose as a result of increased cross-link density (Q=20.6 at 50 kGy; Q=18.8 at total of 100 kGy).

-In solutions with PMAAK also higher irradiation dose results in lower Q of the gels more dramatically (Q=82 at 50 kGy; Q=49.6 at 100 kGy).

-In solutions with PSPMAK a higher irradiation dose was needed for gel formation at all (at 50 kGy, no gel; at 100 kGy gel with Q=113.1).

4.-Irradiation of PMAAK at low pH (acid media) gave a better gel in agreement with the expectations from literature [7] (pure water, total of 100 kGy, Q=49.6; 0.006 N HCl, 100 kGy, Q=36.8).

5.-The pKa of the acid group in the irradiated polymer plays an important role for gel formation: the lower the pKa (higher acidity), the higher the Q obtained and the higher the irradiation dose needed for gel formation (compare results on solutions with PSPMAK, a strong acid, with solutions with PMAAK, a weak acid, under comparable conditions).

6.-For the case of the gels that contain Pn4K (4 methylenes) and Pn10K (10 methylenes) the addition of BIS resulted in a more stable gel and a higher incorporation of acid polymethacrylate into the hydrogel (15 and 20%) than without using BIS where there was poor incorporation of PMAAK and PSPMAK.

The temperature dependent deswelling experiments of selected hydrogels are shown in Figures 3, 4 and 5. In Figure 3 the well documented transition temperature (T_{tr}) of PNIPAAm in Water is clearly seen at around 30°C. The deswelling behaviour of hydrogels containing PMAAK from two different preparation conditions, are also shown in the same Figure 3. The presence of PMAAK in the hydrogels, results in a slightly higher transition temperature and a higher swelling ratio in the collapsed state ($T > T_{tr}$). In the case of the hydrogels prepared using Pn4K and Pn10K the differences in the swelling ratio (see Figures 4 and 5) and in the transition temperature are more clearly seen.

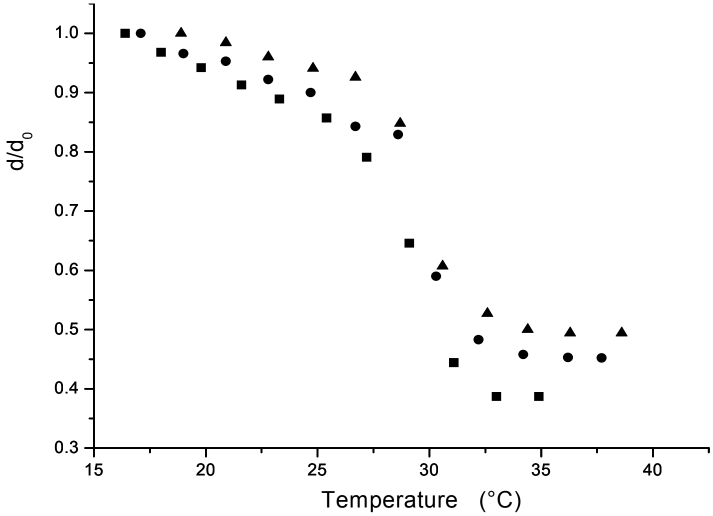


Figure 3. Deswelling behavior as a function of temperature for copolymer gels without crosslinker. (▲) PNIPAAm+PMAAK at 100 kGy (HCl), (●) PNIPAAm+PMAAK at 100 kGy and (■) PNIPAAm at 100 kGy

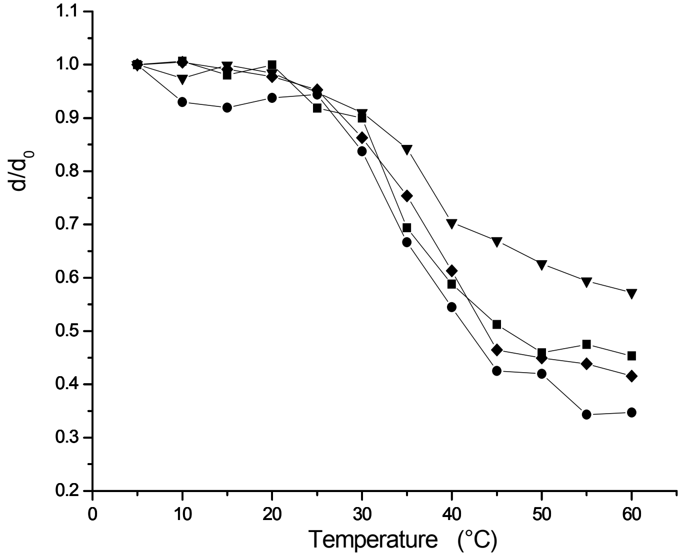


Figure 4. Deswelling behavior as a function of temperature for copolymer gels of PNIPAAm with Pn4K in water. (▼) PNIPAAm:Pn4K(80:20) at 100 kGy, (■) PNIPAAm:Pn4K(85:15) at 100 kGy, (♦) PNIPAAm:Pn4K(90:10) at 100 kGy and (●) PNIPAAm:Pn4K(95:05) at 100 kGy

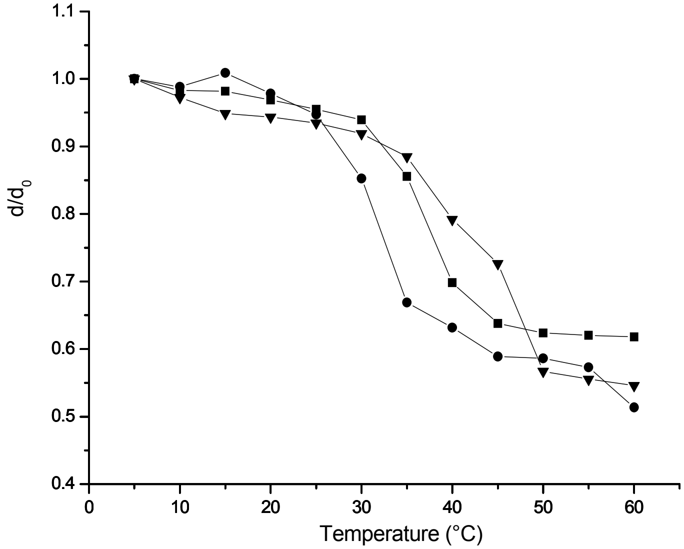


Figure 5. Deswelling behavior as a function of temperature for copolymer gels of PNIPAAm with P10nK in water. (▼) PNIPAAm:Pn10K(80:20) at 100 kGy, (■) PNIPAAm:Pn10K(90:10) at 100 kGy and (●) PNIPAAm:Pn10K(95:05) at 100 kGy

The hydrophobicity of the gel increases with the number of methylenes and therefore a decrease in the value of r is observed. On the other hand the transition temperature shifts to higher values with the amount of incorporated poly acid methacrylate.

In all cases, the temperature needed to achieve the swelling to collapsing transition is higher for hydrogels with acid polymethacrylates than for pure PNIPAAm. However, the water content after collapsing remains higher for hydrogels with acid polymethacrylates normalized by its content at swollen state (before collapsing). This suggests that the water molecules are held stronger in the hydrogel network when acid polymethacrylates are part of this network. This is the case even though the total water absorption capacity is lower for hydrogels containing Pn10K which results from the hydrophobic effect due to the spacer chain of 10 methylenes.

Conclusions

It was shown that hydrogel formation by electron beam high energy irradiation of polymethacrylic acid derivatives in aqueous solutions is possible. The best preparation conditions for a given polymethacrylic acid derivative to yield a hydrogel with good physical properties needs to be studied for each case in detail. The structure-property relations such as, temperature- and pH-sensitivity remains to be studied in more deep and compared with similar, chemically cross-linked, hydrogels.

1.-Experiments in methanol solution did not work, this confirms that the main radicals responsible for the hydrogel formation came from radiolysis of water.

2.-The irradiation dose plays a crucial role in gel formation since:

-PNIPAAm had less swelling degree (Q) with higher irradiation dose due to increased cross-link density (Q=20.6 at 50 KGy; Q=18.8 at total of 100 KGy).

-In solutions with PMAAK higher irradiation dose results in much lower Q of the gels (Q=82 at 50 KGy; Q=49.6 at 100 KGy).

3.-Irradiation at low pH (acid media) gave a better gel in agreement with the expectations from literature.

4.-Methacrylate based polymers are incorporated into the gel at a lower rate as that expected from composition in the feed. However, by addition of 3 mol% of a crosslinker, the incorporation was almost complete with 15mol% and above.

5.-It was demonstrated that irradiation of polymers of methacrylic acid derivatives yield hydrogels with properly selected experimental conditions.

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