Poly (vinyl methyl ether) Hydrogel Formed by High Energy Irradiation

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SUMMARY: Poly(vinyl methyl ether) shows a lower critical solution temperature behavior in water. The dimension of the polymer molecules depends on the temperature. A thermo-sensitive hydrogel was synthesized by irradiation of an aqueous solution of poly(vinyl methyl ether) with electron beam and γ-rays. At high polymer concentration a bulk gel was formed. The structure of the gel in the dry, swollen and shrunken state was investigated by field emission scanning electron microscopy (FESEM). It could be shown, that the gel synthesized by electron beam has a sponge-like structure consisting of cavities (≈1 μm) separated from each other by a polymer layer full of holes (≈10 nm). The macroscopic gel is characterized by several techniques, e.g. determination of the M_c-value by NMR-relaxation measurements.

Introduction

An aqueous solution of poly(vinyl methyl ether), PVME, has a lower critical solution temperature (LCST) at about 37°C. At high temperatures thermal motion of water molecules decompose the hydrogen bonds. The dehydrated PVME molecules collapse and micro-phase separation occurs.

When an aqueous solution of PVME is irradiated with electron beams or γ-rays the solution becomes a hydrogel. The reason for the cross-linking process is the formation of radicals from water molecules, which attack PVME molecules. The hydrogel is thermo-sensitive similar to the polymer solution. It swells at temperatures below the LCST and shrinks above this temperature. Stimuli-responsive hydrogels that undergo abrupt changes in volume in response to external stimuli such as temperature, have potential application in the creation of "smart" material systems, e.g. hydrogels made of hydrophobic polymers that undergo transitions near 37 °C have been considered as drug delivery systems, and materials for tissue reconstruction. The mechanical properties of gels undergoing a volume phase transition have been studied by S. Hirotsu [1] (isobar gel) and M. Shibayama et al. [2] (isochore gel). The mechanical properties

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change at the phase transition temperature. The reason for this is the formation of a macronetwork consisting of bundles of molecules (polymer rich phase) and large pores (polymer poor phase). In opposite to the volume change the increase of the modulus is very fast. After formation of the bundles of molecules (isochore process) the process of deswelling starts.

The kinetic of volume change is determined by diffusion processes, at least by the cooperative diffusion coefficient of the polymer chains (about 10^{-7} cm²/s). Since the diffusion time scales with the square of dimension, decreasing the characteristic dimension of the network will increase the swelling/deswelling rates dramatically. In former works (see ref. [3]) we investigated thin layers (thickness in the µm-range) of photo cross-linked T- and pH-sensitive hydrogels. A gel body with porous microstructure is expected to give rise to faster volume change, since the effective diffusion distance can be controlled by the average distance between neighboring pores.

Our interest in studying radiochemical cross-linked PVME was sparked by the report by M. Suzuki and O. Hirasa [4] of PVME gels (cross-linking by γ-irradiation) with a fine porous gel structure to obtain quick response gels. They founded, the higher the temperature of the aqueous PVME solution at cross-linking, the higher the mean cross-sectional area of the pores formed by the phase separation. The pore sizes became smaller with increasing PVME concentration. Typical dimensions of the pores are several µm. The porous gels swelling or shrinking is in order of magnitude faster than any other responsive gels of comparable dimension.

Another advantage of the radiochemical cross-linking is that we are able to produce large gel sheets, with electron beam irradiation, at least, of infinite length, in less than one minute. A disadvantage of e-beam irradiation procedure is the heat absorption during irradiation. It was not possible to prevent an increase in polymer solution temperature. The increase of temperature depends on the dose. We found about 2.5 °C per 10 kGy for our experimental conditions. For this reason at higher irradiation dose the polymer solution is heated above the volume phase transition temperature and therefore phase separation occurs. Another disadvantage of using e-beam irradiation is the inhomogeneity of the samples. In opposite to γ-radiation the electron beam is partially absorbed in the sample. This results in a gradient of radiation dose and, hence, in a gradient of cross-linking density. This effect become much more important with increasing radiation dose.

The aims of our work were

- investigation of the influence of experimental conditions on the cross-linking process induced by electron radiation;

- comparison of e-beam and γ-irradiation in view of the properties of the formed networks;
- determination of properties of the formed networks.

Experimental

PVME was obtained as a 50 wt.% aqueous solution from Aldrich Chemical Co. The molecular weight was determined by static light scattering in butanone to M_w = 46,000 g/mol. The glass transition temperature of the polymer was found to T_g = 242 K by DSC. The measured intrinsic viscosity in butanone was smaller than the calculated value ($[\eta] = 9.2\ 10^{-4}\ M^{0.58}$, $[\eta]$ in dl/g, see ref. [5]). From the comparison of both values it can be concluded that the used PVME is branched. The number of branches per molecule was estimated to 4...5 from the ratio of viscosity.

M_w in water was always higher (up to 20 times) than M_w in organic solvent, even for aqueous PVME solutions of low concentration and at temperatures lower than the LCST. The measured molecular weight in water depends on the condition of preparation of the solution. From these results follow, that PVME-molecules are not mono-molecularly dissolved, even in the dilute state. A consequence of this is, that the structure of the network must be influenced by two effects: The aggregation structure and, if phase separation occurs, the structure determined by the micro-phase separation.

Dynamic light scattering measurements of an aqueous PVME solution in dependence on temperature show the formation of particles in the 10^2 nm range, which hydrodynamic radius is temperature dependent (see Fig. 1).

Static light scattering measurements were performed on a modified static light scattering apparatus FICA 50 (SLS Systemtechnik G. Baur, Freiburg, Germany) using a laser light source (633 nm) at scattering angles $15° \leq \theta \leq 145°$ in steps of 5°. The solutions were filtered directly into the optical cells through 0.2 μm PTFE (butanone) membrane filter or 0.45 μm CME (water) membrane filter, respectively. The optical cells were brought to the right temperature in the light scattering equipment for 30 minutes before starting the measurements. The refractive index increment was measured by a DLS 1 (SLS Systemtechnik G. Baur, Freiburg, Germany) at 25 °C to 0.08953 cm^3/g (butanone) and to 0.1438 cm^3/g (water).

The dynamic light scattering measurements were performed with a DLS 700 (Otsuka, Japan) at $\theta = 90°$ and a concentration $c_B = 4.9$ g/l. An apparent (no extrapolation to $\theta \rightarrow 0$ and $c_B \rightarrow 0$) value of the hydrodynamic radius $R_{h,app}$ was calculated by using the Stokes-equation.

For irradiation, solutions of different concentrations were prepared by dilution of the high concentrated PVME solution with bi-distilled water. Oxygen can interfere with a free-radical polymerization. Therefore it was necessary to remove all of it by degassing the homogenized polymer solution before starting the irradiation. For this purpose argon was blowing (for 5 h) through the solution under stirring. After degassing, the prepared solutions were poured in petri dishes (e-beam) or poly(ethylene) flasks (γ-rays) and irradiated. Purging the solution with argon and sealing with PARAFILM® helps to reduce the rate of oxygen uptake in the uncross-linked polymer solution. At e-beam irradiation the thickness of the solution was smaller than 4 mm to minimize the inhomogeneity of the cross-linking density.

The irradiation conditions were:

e-beam:	electron accelerator ELV 2, 1.0 MeV; 20 – 250 kGy; starting at 20 °C
γ-ray:	^{60}Co; 2 kGy/h; 20 – 80 kGy; 25 °C and 35 °C

After irradiation the uncross-linked polymer (sol content) must be removed by extraction. For this, a soxhlett with the solvent acetone was used (5 days each 10 h). The gel content was determined by weighting the dried samples before and after extraction.

The equilibrium degree of swelling was measured by weighting the swollen and dried sample (mass degree of swelling, Q_m) or by determination of the dimension (volume degree of swelling, Q_V) of a sample in both states (for further details of experimental procedures see ref. [6]). These measurements were done on a 500 μm thick sample with a microscope (Hund, Wetzlar, Germany) and a CCD-camera (JVC, Japan).

The cross-linking density of a hydrogel can be determined by measuring its compression modulus (RET-equation). A pre-condition of this method is the homogeneity of the network. Bastide et al.[7] showed that the presence of pendant chains in the network affected the compression modulus. They found that the modulus decreases drastically with increasing concentration of dangling chains. It is shown later, that our network do not satisfy the basic assumptions of RET. It is porous and because of the branching of the uncross-linked chain it contains a lot of dangling chains.

Another possibility for network characterization is based on the Flory-Rehner-equation. But the prerequisites are rather the same to that of RET. Another problem in connection with FR-equation is the need of the concentration dependence of the Huggins interaction parameter.

The magnetic relaxation of protons attached to a polymer has proven to be a suitable tool for investigating properties of networks. To get an idea on the cross-linking density we use a NMR method based on the measurement of transverse ^{1}H-NMR relaxation well above the glass transition temperature. An introduction into the method is given in ref. [8-10]. The presence of topological hindrances due to the junction points leads to an an-isotropic motion of segments of network chains. This results in a non-zero average of the dipolar coupling and a residual dipolar magnetic interaction of protons. The total transverse magnetization decay *M(t)* is composed of three contributions:

$$M(t) = A\,M(t)_{network} + B\,M(t)_{dangling\ end} + C\,M(t)_{sol} \qquad (1)$$

The fractions A, B and C represent the parts of magnetization of protons in intercross-link chains, dangling ends and uncross-linked chains (sol content), respectively. A mathematical expression is derived for each part of the magnetization decay (see ref. [10]). By a fit procedure of the experimental data the parameters describing the sol content and concentration of dangling ends as well as the molecular weight of the network chains M_c can be calculated.
The measurements were performed with a Varian Unity 400 spectrometer operating at 400 MHz proton frequency in the dry state at 60 °C, and in the swollen state (swelling agent D_20) at 23 °C (high degree of swelling) and at 40 °C (low degree of swelling).
Besides of cross-linking densities of hydrogels also the structure is of great importance to understand their specific behavior, especially in the case of a porous (sponge-like) hydrogel. A new method for investigation thermo-sensitive hydrogels is the field emission SEM at low voltage [11]. The structure of a radio-chemically cross-linked hydrogel in different states was investigated with an “in-lens” field emission scanning electron microscope (FESEM) S-5000 (Hitachi Ltd., Japan). Briefly, the sample preparation was as follows: 20 wt.% PVME solution were dropped onto a small piece of clean aluminum and covered with mica platelet. The Al-support was irradiated with 0.5 MeV electron beam (dose: 50 kGy). The gel-coated aluminum was immersed in distilled water for 15 min to remove non-crosslinked PVME. The secondary electron micrographs were taken on samples in the dry and in the swollen state (swollen at room temperature and at 40 °C, see Fig. 4). The structure formed during swelling was fixed by rapid cooling with liquid ethane (cooled to ≈ 77 K). Under these conditions, the ice was in an amorphous state and did not destroy the network structure. The frozen water was remove by freeze-drying at ≈ 190 K for 6 h at about 5 10^{-6} torr. The samples were rotationally coated with 2 nm Pt/C at an elevation angle of 65°.

Results and discussion

The dimension of the PVME molecules solved in water depends on the temperature. Figure 1 shows the temperature dependence of the apparent hydrodynamic radius $R_{h,app}$. Because of the formation of aggregates and the high concentration of PVME the values represent not the dimensions of single macromolecules. The change of dimension occurs between 32 °C and 36 °C. As expected, the degree of swelling is temperature dependent. The temperature dependencies of $R_{h,app}$ and Q_v are comparable. In comparison with other thermo-sensitive hydrogels, the degree of swelling at temperatures above the volume phase transition temperature is rather high (about 2). This indicates the sponge-like structure of the hydrogel.

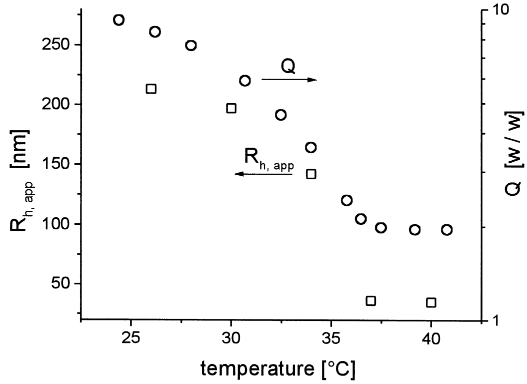


Fig. 1: Temperature dependence of the apparent hydrodynamic radius $R_{h,app}$ (□) and of the volume degree of swelling Q_v (○) of a PVME hydrogel cross-linked by e-beam (80 kGy)

The LCST of aqueous solutions of PVME can be changed by mixing water with organic solvents or by dissolving inorganic salts [12]. The phase transition temperature T_{vpt} of a 4.0 g/l PVME solution was determined by DSC (dT/dt = 5 K/min; DSC 2920, TA Instruments) for salt concentrations between 0.1 mol/l and 0.5 mol/l. Our experiments show a linear correlation between the volume phase transition temperature and the used salt concentration, eq. (2):

$$T_{vpt}(c) = T_{vpt}(H_2O) + A\,c \qquad (2)$$

For halides it is valid that the smaller the radius of the anion the lower the volume phase transition temperature at constant concentration. For values of A see table 1.

The cross-linking reaction of the PVME solution was monitored by sol-gel-analysis. The gel-content g depends on the concentration of the irradiated PVME solution. The measurements show, that the lower the polymer concentration, the higher the value of g. For higher polymer concentration the gel-content is strongly affected by the total dose. The maximum value of gel-content we got, was $g = 0.95$ for 10 wt.% PVME at 90 kGy. But, the gel formed under

Table 1: The influence of salt concentration on the volume phase transition temperature

salt	A / grd l mol^{-1}
NaCl	-14.3
NaBr	-7.6
NaI	+5.6
$NaNO_3$	-5.6
Na_2SO_4	-2.7
Na_2CO_3	-8.9
Na_3PO_4	-4.5
KCl	-16.7
KI	+8.5

these conditions was too brittle. For lower concentrations and low irradiation dose the gels were too soft for further analytical investigations. At irradiation dose above 100 kGy the gel-content decreases again.

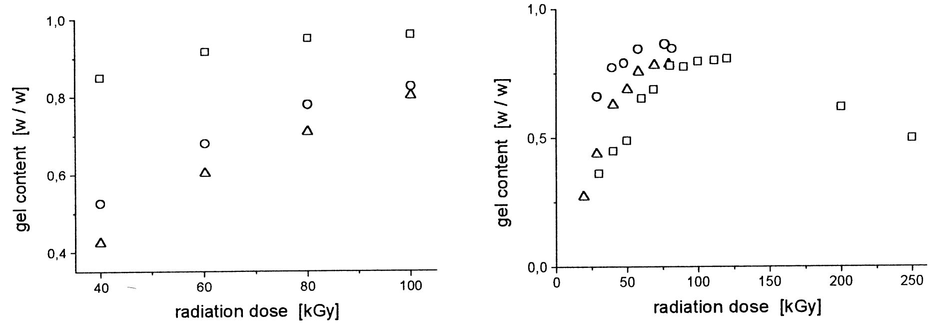


Figure 2: The gel content *g* (%) in dependence on total dose (kGy)
left: e-beam at different concentration of PVME in water; (□)10 wt.%; (○) 20 wt.%; (Δ) 30 wt.%; right: for irradiation of a 20 wt.% PVME solution;(□) e-beam; (○) γ at 25 °C; (Δ) γ at 35°C

Macromolecules are known to suffer cross-linking or degradation as a result of exposure to high-energy radiation. Only if the formation of cross-links is preferred a network can be formed. Charlesby and Pinner [13] derived a simple equation (3) which correlates the sol-content s ($s + g = 1$) and the total dose D. According to them the sol-content, resp. the gel-content, depends on the total dose D, the number-averaged molecular weight M_n, and on the ratio p_0 / q_0, where p_0 is the fracture density per unit dose, and q_0 represents the density of cross-linked units per unit dose. For cross-linking the ratio must be smaller than 1.

$$s+\sqrt{s}=\frac{p_0}{q_0}+\frac{1}{q_0\,M_n\,D} \qquad (3)$$

Plotting of ($s + s^{1/2}$) vs. $1/D$ allows the determination of both the ratio p_0 / q_0 and of the dosage D_g ($s = 1$) above which the gel formation starts (see table 2).

Table 2: Parameter of the Charlesby-Pinner-equation

sample	D_g /kGy Charlesby/Pinner	p_0/q_0
e-beam	21.10	0.36
γ-ray, 25 °C	10.93	0.25
γ-ray, 35 °C	14.42	0.37

It was found experimentally that ($s + s^{1/2}$) values for doses smaller than 30 kGy tended to diverge from the straight line passing through the higher dose points. For this reason the values of D_g are not absolutely correct. However, the values of D_g for γ-irradiation are smaller than that for e-beam irradiation. We checked by sol-gel analysis, that at $D \geq D_g$ a gel was formed. Not only the gel-content is influenced by the total dose. The higher the total dose, the lower the degree of swelling and the higher the cross-linking density. It makes no difference whether e-beam irradiation or γ-irradiation is used for cross-linking.

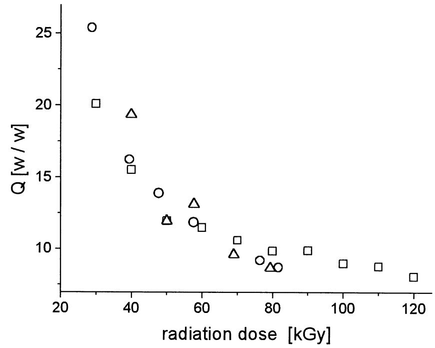
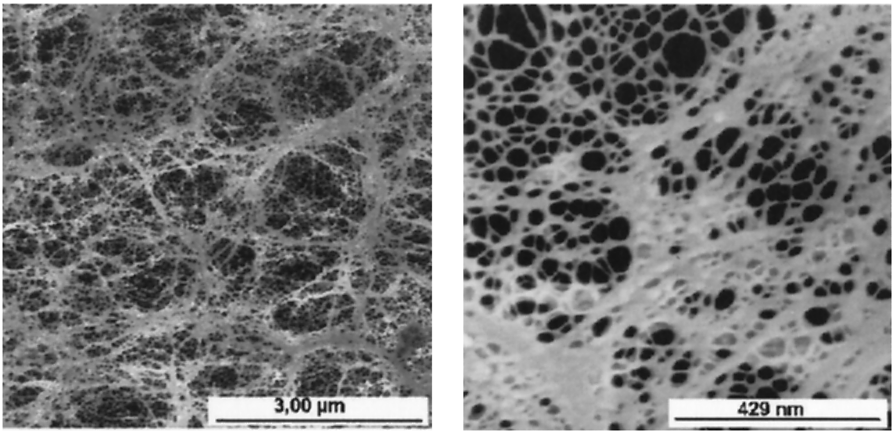


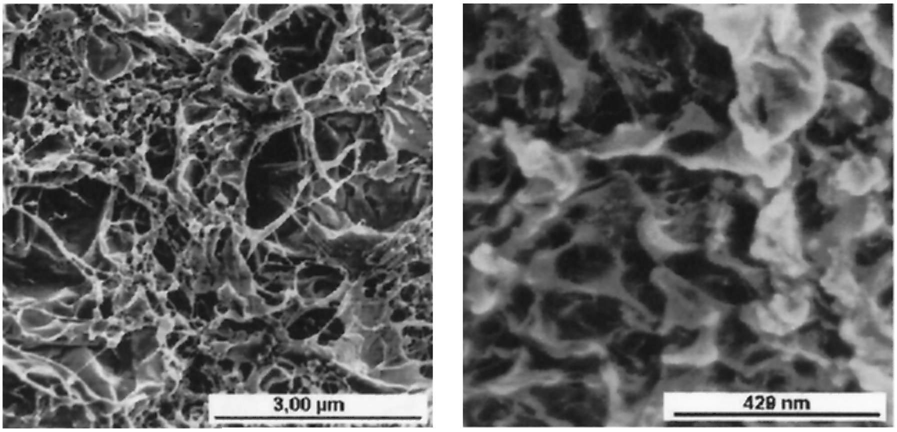
Figure 3: Mass degree of swelling Q_m as function of total dose
(□) e-beam irradiation; (○) γ-irradiation at 25 °C; (Δ) γ-irradiation at 35°C of a 20 wt.% PVME solution

To understand the behavior of the hydrogels their structure is of great importance. Both, the swollen state of the hydrogel at 25 °C and at 40 °C are characterized by three-dimensional sponge-like patterns, which consist of many small cavities ($10^2 ... 10^3$ nm) separated permeably from each other by a thin membrane-like layer. There structure can be observed by images at high magnification. The layer is porous with a typical pore-size of 10 nm.

After heating to 40°C, the gel collapses and shrinks. The micrographs show that the gel is porous, but that the polymer layers which separate the cavities are compact. The cavities (they are smaller than at 25 °C) contain water, which is the reason for the rather high degree of swelling even at temperatures above T_{vpt}.



swollen state at 25 °C



swollen state at 40 °C

Figure 4: Secondary electron micrographs of PVME hydrogel (e- beam irradiation, 50 kGy) in different states; the bars indicate the length scales.

With help of the NMR-relaxation measurements the molecular weight of network chains (M_c) and the concentration of dangling ends were determined. The results show, that the sol-content is negligible after the extraction procedure. The concentration of dangling ends is rather high and gives hints that the network structure is non-regular. Taking the numeric values of degree of swelling into account, the M_c-values are small. An explanation could be, that the majority of the solvent was in the cavities and not in the surrounded polymer layer.

The *M_c*–values depends on the swelling state, they are lower for the collapsed network because of formation of macro-network consisting of bundles of molecules.

Table 3: Network parameters determined by NMR
PVME concentration: 20 wt.%; 1: e-beam, 120 kGy; 2: e-beam, 80 kGy; swelling agent: D_2O

sample	condition	sol-content/%	content of dangling ends/%	M_c /g mol^{-1}
1	dry	0.4	63.8	1940
2	dry	0.4	57.8	2400
1	swollen, 23°C		62.8	2200
2	swollen, 23°C		67.7	3200
1	deswollen, 40°C		75.9	1000
2	deswollen, 40°C		78.2	730

The experiments have shown, that e-beam irradiation is a suitable procedure for synthesis of thermo-sensitive hydrogels. The degree of swelling is not influenced by the nature of radiation, it depends only on the total dose. By e-beam irradiation, a sponge-like structure of hydrogels with a polymer-poor phase (cavities in μm-range) and a polymer-rich phase (full of holes in nm-range) is typical. The NMR-relaxation measurements seem, in principle, to be an useful tool for characterization the porous and non-regular networks. Nevertheless, the reliability must be improved be further experiments with samples of different cross-linking densities.

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