Colloid Polym Sci (2004) 282: 1213–1221
DOI 10.1007/s00396-004-1178-0

ORIGINAL CONTRIBUTION

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Mechanical properties of poly(vinyl methyl ether) hydrogels below and above their volume phase transition

Received: 11 February 2004
Accepted: 3 June 2004

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Abstract The mechanical properties of radiation cross-linked poly(vinyl methyl ether) hydrogels below and above the volume phase transition (VPT) under isobar conditions were studied. The viscoelastic properties as a function of radiation dose, radiation source and polymer concentration at the state of irradiation were examined. Increased radiation doses led to higher cross-linking densities and higher moduli. Hydrogels irradiated with γ-rays were much harder than those obtained with electron beam irradiation at the same radiation dose. It was found that the modulus strongly increased by up to 1 order of magnitude at a temperature of the VPT of about 37 °C. In the collapsed state at temperatures well above the VPT a frequency dependence of the $E'(\omega)$ moduli in the range 0.1–22 Hz was detected, indicating viscoelastic behavior. To study the influence of solvent quality on the modulus of the hydrogels, rheological measurements were performed in water, 2-propanol and cyclohexane. A scaling exponent for the modulus according to de Gennes ($G' \propto \phi^{2.25}$) was not found. Possible reasons for deviations ($G' \propto \phi^{3.54}$) on poly(vinyl methyl ether) hydrogels were discussed in the context of deviations from ideal networks.

Keywords Poly(vinyl methyl ether) · Viscoelasticity of thermosensitive hydrogels · Volume phase transition · de Gennes scaling law

Introduction

Temperature-sensitive hydrogels are known for their large volume change when crossing a critical temperature called the volume phase transition (VPT) temperature, T_{VPT}, which may deviate from the cloud point temperature. Hydrophobic polymers dissolved in water often develop a phase transition on heating in contrast to common synthetic polymers in organic solvents. This behavior is caused by the hydrophobic interaction [1]. Because of unfavorable interaction of water molecules with a hydrophobic group the neighborhood of the hydrophobic polymer causes a perturbation of the water structure which results in a cooperative rearrangement and enhanced cluster formation of the water molecules around the polymer particles. This enhanced ordering of the water molecules creates an exothermic enthalpy and a negative entropy contribution. The latter overcompensates the common positive configurational entropy, which is the main driving force to dissolution of polymers in organic solvents. Phase separation on heating leads, as in common cases, to a dilute and a highly concentrated phase, where in the latter the chains adopt a fairly compact or collapsed conformation. The striking transition from a highly swollen conformation in the solution towards the collapsed conformation in the phase-separated fraction has aroused much interest.

VPT phenomena were reviewed by Shibayama and Tanaka [2], Wu and Zhou [3] and Shibayama and Nagai [4]. Such hydrogels have been discussed for possible application in medicine [5, 6]. Some examples are synthetic wound care coverings and drug delivery systems. Separation of biomolecules by size or affinity chromatography in combination with "intelligent" polymers has been considered. In combination with immobilized enzymes or cells corresponding bioprocesses may be used for the development of sensor/actuator systems [7]. Finally new superabsorbant systems [6] appear to be possible with these polymer gels.

All these cases require materials with a certain rigidity; however, comparatively little is known on the shear and bulk moduli near the phase transition although these mechanical properties will undergo a significant change for swollen hydrogels. Undoubtedly, the mechanical response is of considerable importance in applications. Under isobar conditions Hirotsu [8, 9] found a drastic softening of the bulk modulus when the VPT temperature was approached. He concluded that the softening near this transition is uniform and an isotropic volume-deformation process occurs. The shear modulus, on the other hand, displayed only a weak change at the transition in his experiment.

Other observations [10] under the constraint of isochore conditions indicated a sharp increase of the shear equilibrium modulus by 1 order in magnitude during the collapse of poly(*N*-isopropylacrylamide) [poly(NIPAM)] hydrogels. Shibayama et al. [10] suggested a collapse mechanism for poly(NIPAM) gels, under these stringent isochore conditions, which means in their case no volume change during the VPT. The samples were isolated from the water reservoir to keep the gel concentration. They related the sharp increase of the E' modulus in the first temperature range to the instantaneous formation of what they called a "macro network". In this picture a strongly heterogeneous network, consisting of bundles of network chains (polymer-rich domain), is surrounded by a polymer poor matrix. In the deswollen state, a gel is composed of this kind of macro network, immersed in a highly swollen network of poly(NIPAM) chains. On further heating, the stretched chain can relax, and the whole network approaches the equilibrium state, but the heterogeneity is kept. Shibayama et al. [10] found a frequency dependence above the VPT, indicating that the deswollen gel becomes viscoelastic.

In another study Shibayama and Nagai [11] followed the phase separation with time of thin network samples. In these experiments, however, isobar conditions were applied.

Knörgen et al. [12] tried to realize the predicted structures by ^{1}H NMR imaging during the VPT under isobar conditions, with poly(NIPAM) hydrogels. The results show that the shrinking process proceeds in two steps. In one step, the elastic modulus of the gel increases very rapidly. The soft polymer changes to a more solidlike structure owing to the formation the previously mentioned macro network. The degree of swelling is constant. In the second step—after longer times—the shrinking process takes place. The sample volume decreases with a typical time constant determined by the cooperative diffusion coefficient of the polymer chains. Since the volume change in isobar gels is governed by mutual diffusion of the network chains and the solvent molecules, the rate of equilibration is inversely proportional to the square of the gel size.

Moerkerke et al. [13] carried out a fairly detailed study with cross-linked poly(vinyl methyl ether) (PVME) samples. In combination with a special theoretical model they concluded from their experiments that the collapse of radiation cross-linked PVME swollen in water is discontinuous and thermodynamically is a well-defined phase-transition process. The authors also showed that PVME displayed very complex lower critical solubility temperature behavior.

The PVME hydrogels in our study were cross-linked in water by an electron beam and these were compared with those by cross-linked by γ-ray irradation [13, 14, 15, 16, 17]. The rate of cross-linking by irradiation with an electron beam is a rather fast process and occurs within minutes. The γ-ray irradiation, on the other hand, requires long cross-linking times of several hours. Cross-linking via irradiation has a major advantage over chemical cross-linking because it allows the control of cross-linking at a defined temperature. The good temperature control permitted the preparation of well-defined hydrogels even close to the phase-separation temperature. In both cases the cross-linking reaction is accomplished by radicals which were produced by the cleavage of water into H• and OH• radicals [18, 19]. No cross-linking agents or initiators are needed.

The aim of this work was to examine a hydrophobic gel with PVME and to check whether similar mechanical properties (e.g., frequency dependence of the modulus in the deswollen state under isobar conditions) are found with this material as was observed by Shibayama and Hirotsu, respectively. It was also a task to check a relation derived under isochore conditions for the calculation of the modulus of deswollen gels above the VPT from the modulus below the VPT (in the homogeneous state) under isobar conditions like in this given case. The validity of the relation $E'/G' = 3$ and the scaling law according to de Gennes ($G' \propto \phi^{2.25}$) for radiation cross-linked PVME hydrogels should be examined. The influence of solvent quality on mechanical properties is also in the scope of the investigation.

Experimental

Materials

Eight PVME hydrogel networks of different cross-linking densities and polymer concentration were prepared by applying different radiation doses: These samples were given the notation PVME 20/60, PVME 20/80, PVME 20/100, PVME 20/120, PVME 30/60, PVME 30/80, PVME 30/100 and PVME 30/120. The two numbers at the end of PVME denote the polymer concentration and the dose of the electron beam irradiation in kilograys. For example, PVME 20/60 means a 20 wt % (w/v) aqueous PVME solution that was irradiated by an electron beam of 60 kGy. The γ-ray irradiated samples are defined separately in Fig. 5.

Preparation of the samples

PVME in a 50 wt % aqueous solution was purchased from Aldrich and was used without further modifications. The molar-mass distribution and the averages M_w and M_n were determined by size-exclusion chromatography in tetrahydrofuran at 30 °C [20]. The columns used were a system consisting of an Ultrastyragel 10^5-Å column and a μStyragel HT 10^3-Å column from Waters. The flow rate was 1 ml/min. A polystyrene calibration curve was used. The corresponding molar masses were $M_w = 13.9$ kg/mol and $M_n = 5.86$ kg/mol with a polydispersity of $M_w/M_n = 2.4$. The molar mass used by Moerkerke et al. [13] for the network formation was 60.5 kg/mol and was about 4.5 times larger in our work. Compared with literature values, the intrinsic viscosity of the present sample was found to be somewhat lower. Weak branching of about 4–5 branches per macromolecule in butanone was concluded [21] from the intrinsic viscosity and this was somewhat lower than that calculated from the relationship $[\eta] = 9.2 \times 10^{-4}$ $M^{0.58}$ dl/g by Manson and Arquette [22].

Prior to irradiation, the concentrations indicated were prepared by dilution with bi-distilled water. Oxygen was removed by bubbling argon for 5 h through the continuously stirred solutions and this was followed by degassing. The degassed solutions were poured into Petri dishes (for electron-beam irradiation) or polyethylene flasks (for γ-ray irradiation) and were then irradiated. The solution were kept under an argon atmosphere. The vessels were sealed with PARAFILM to inhibit and reduce the oxygen uptake in the uncross-linked polymer solution. For electron-beam irradiation the sample thickness was chosen to be smaller than 4 mm to minimize the inhomogeneity in cross-linking density. The electron-beam irradiation caused a slight increase of the temperature ($\Delta T \approx 2.5$ K/10 kGy) and probably also a higher heterogeneity, in particular near the lower critical solution temperature. After irradiation, the sol fraction was extracted with water for 1 week. A lower concentration (10 wt %) in the state of irradiation led to a higher value of the gel-content than for a 30 wt % solution at the same radiation dose. The higher the radiation dose, the higher the gel content, but for electron-beam irradiation doses above 100 kGy the gel-content decreased again. For further details see Ref. [21].

The degree of swelling was determined gravimetrically. To achieve equilibrium swelling the irradiated samples were kept in water for 2 days at room temperature.

Irradiation conditions

The irradiation was made at 20 °C. The electron beam of the electron accelerator ELV-2 (Budker Institute for Nuclear Physics of Novosibirsk) generated electron energies of 0.6–1.5 MeV with a beam power of 20 kW (60–120 kGy). The γ-ray irradiation was performed at 25 °C with a ^{60}Co source of 2 kGy/h (40–100 kGy).

Rheology

Thin disks of the polymer hydrogel (diameter 20 mm) were held between two parallel plates of porous rheometer fixtures (diameter 25 mm). These fixtures were made of porous glass glued with epoxy to the original rheometer fixtures. The open pores of the fixtures permitted the access of water (or solvent) to the sample surfaces and prevented drying of the sample during measurement. Sample and fixtures were mounted in a Rheometrics mechanical spectrometer (Rheometrics dynamic spectrometer linear actuator) by which the compression moduli $E'(\omega)$ were measured. The shear moduli, $G'(\omega)$ and $G''(\omega)$, were measured with a Rheometrics ARES rheometer. Again porous glass fixtures of 25 mm in diameter were used. In both types of rheological measurements the porous fixtures together with the hydrogel samples were immersed in a temperature-controlled water bath. After several hours, for temperature equilibration and a waiting time for complete deswelling of the hydrogel above the VPT, the measurements were started.

Measuring conditions

The $E'(\omega)$ moduli were measured in a frequency range of 0.1–22 Hz at a strain amplitude of $\epsilon = \ln(h/h_0) = 0.05$, under a preload force of 0.5 N. The temperature range applied was 19–62 °C. At each temperature, the diameter of the samples was measured with a ruler to normalize the force by the corresponding sample area.

In the measurements of $G'(\omega)$ and $G''(\omega)$ the frequency range was 0.2–80 Hz at a strain of 5%. Setting of the zero gap was repeated when advancing to the next-highest temperature.

Generally, the experimental uncertainty of all the mechanical data was around ±7%.

Results and discussion

$E'(\omega)$ of the hydrogel samples in water at different temperatures

The results of the E' moduli are shown in Figs. 1 and 2. The highly cross-linked samples, obtained with high radiation doses of 100 and 120 kGy, gave higher $E'(\omega)$ moduli than the other samples over the entire temperature range. There is no significant influence of the polymer concentration on the E' moduli at all temperatures.

For the frequency- and temperature-dependent measurements and all further investigations in other swelling agents PVME 30/80 was selected.

Below the VPT, i.e., in the swollen state, the $E'(\omega)$ modulus showed no frequency dependence, (Fig. 1). Above the VPT, at 42 and 45 °C, however, a slight frequency dependence occurred, indicating a noticeable viscous contribution to the modulus of the deswollen PVME hydrogel. The $E'(\omega)$ moduli were about 2.5 times higher at 64 rad/s than those at 0.628 rad/s. A similar frequency dependence was reported by Shibayama et al. [10] with cross-linked poly(NIPAM) gels, but under isochore conditions. The temperature dependence of $E'(\omega)$ for the various PVME hydrogel samples in water at the selected frequency of 20.1 rad/s is shown in Fig. 2. These data were compared with the temperature-shrinking behavior of PVME 20/80.

The degree of swelling is not influenced by the nature of the radiation: it depends only on the total dose. Higher radiation doses led to higher cross-linking densities and consequently to lower degrees of swelling. For further swelling data see Refs. [13, 20]. The temperature of the VPT is not influenced by the radiation dose [13].

The swelling decreased to the value of $Q=2$ with increasing temperature and then remained constant if the hydrogel was heated beyond 37 °C. At the same temperature the sample became turbid and the modulus increased further. All measurements were carried out for the samples in complete swelling equilibrium. This was checked with an example at 45 °C by repeating the experiments 2 h after the first measurement had finished. No change in behavior was found. The reproducibility of the measured data was given.

$E'(\omega)$ of hydrogel PVME 30/80 in 2-propanol and cyclohexane at various temperatures

PVME is also soluble in organic solvents. It appeared of interest whether a phase separation and corresponding

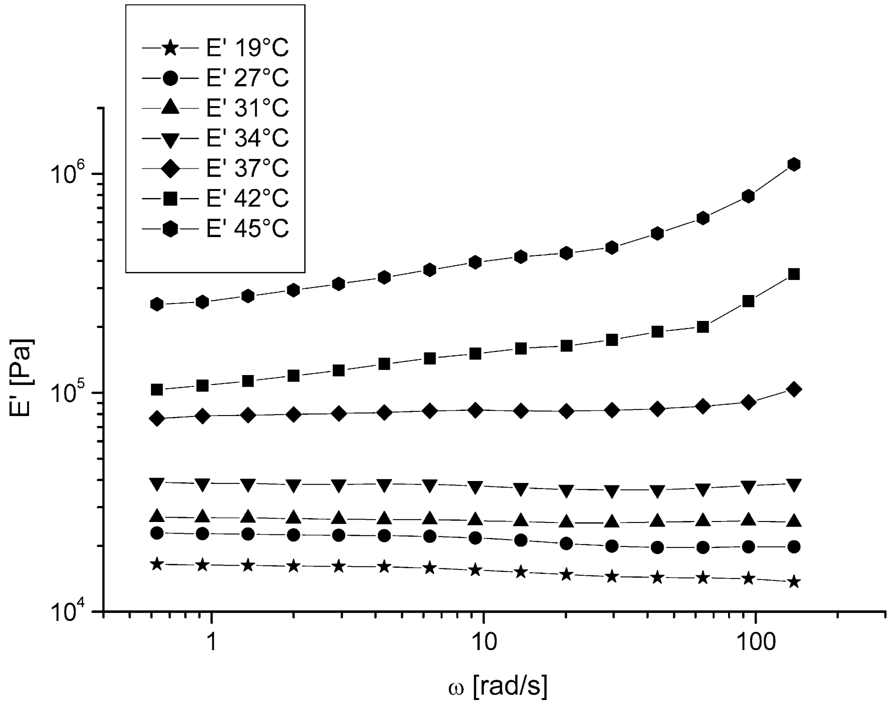

Fig. 1 Frequency dependence of the moduli $E'(\omega)$ of PVME 30/80 as an example at various temperatures in water

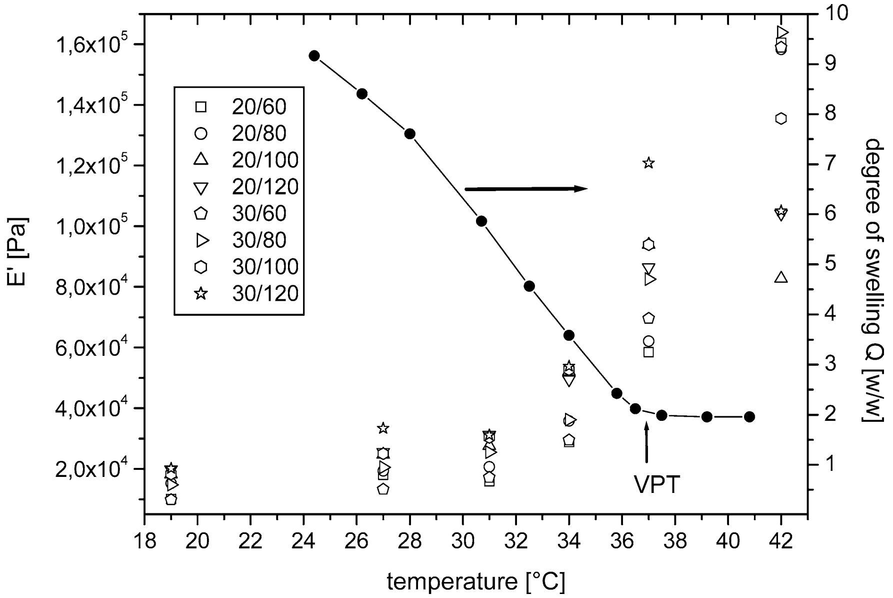

Fig. 2 Temperature dependence of $E'(\omega)$ of all poly(vinyl methyl ether) (*PVME*) hydrogels in water at $\omega = 20.1$ rad/s (*open symbols*). For comparison the degree of swelling $Q = m_q/m_{dry}$ as a function of temperature is also shown for the selected hydrogel PVME 20/80 as an example (*solid symbols*). m_q is the weight of the sample in the fully swollen state and m_{dry} is that in the dry state. The volume phase transition (*VPT*) temperature is emphasized in the figure

gel shrinking would also be observed in such nonaqueous media. We chose 2-propanol and cyclohexane as examples and investigated the swelling behavior and the change of the compression modulus with temperature.

2-Propanol is a fairly good solvent for PVME, and it swelled the hydrogels in a similar manner as water (at room temperature $Q\approx 9$ for 2-propanol and $Q\approx 9$ for water [20]). However, no noticeable change in the degree of swelling was observed as the temperature was increased. Up to 35 °C the storage modulus increased in almost the same manner as in water, but then passed through a maximum at about 37 °C (Fig. 3). No VPT occurred; the sample diameter remained nearly constant over a wide temperature range. These observations gave, as expected, evidence for a different solvation mechanism.

Petri et al. [23] studied PVME in cyclohexane by light scattering. At 51 °C a Θ temperature and endothermal solution properties with an upper critical solution temperature were found. At 19 °C the E' modulus in

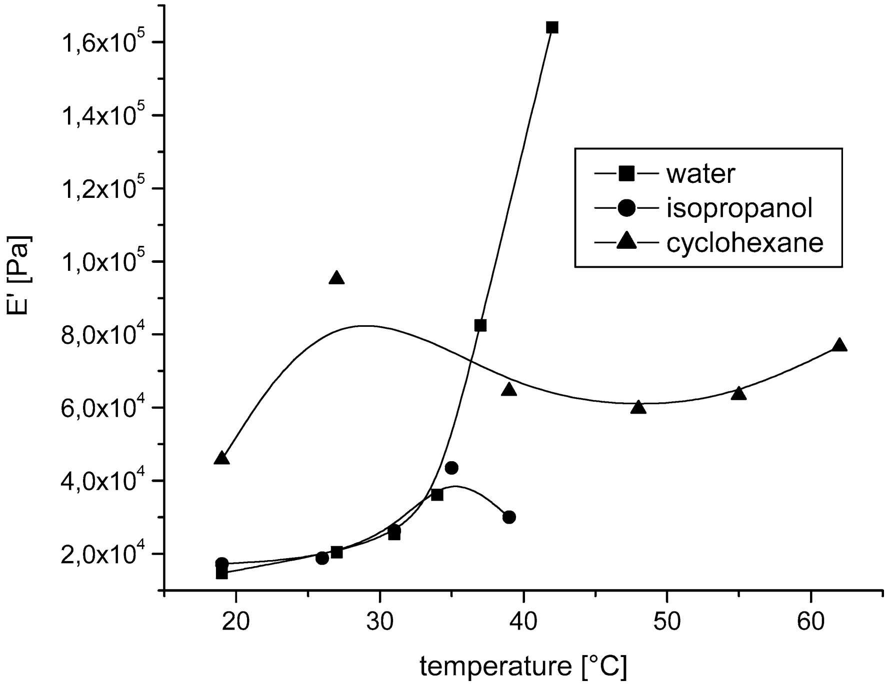

Fig. 3 Temperature dependence of $E'(\omega)$ at $\omega = 20.1$ rad/s in water and two organic solvents (2-propanol and cyclohexane) of the sample PVME 30/80

cyclohexane was twice as large as in water or 2-propanol. The values passed a maximum and then ran through a flat minimum near the Θ temperature of 51 °C. The behavior at low temperature resembled that of PVME in 2-propanol but the maximum occurred here about 10 °C lower than in 2-propanol (Fig. 3). In spite of temperatures considerably below the Θ temperature no phase separation was observed. A phase transition may be expected to occur below 19 °C. The sample diameter decreased somewhat with increasing temperature but approached a constant value at 51 °C and higher.

Note that no frequency dependence of the samples swollen in 2-propanol and cyclohexane at all temperatures was observed.

$G'(\omega)$ and $G''(\omega)$ of all hydrogel samples in water and of PVME 30/80 in 2-propanol at 19 °C

Unfortunately, the available rheometer was not equipped with a temperature-control system for temperatures higher than room temperature; therefore only measurements at 19 °C could be carried out.

The shear moduli $G'(\omega)$ and $G''(\omega)$ of PVME hydrogels in water were found to be virtually constant over the entire frequency range (Fig. 4). Similar behavior was observed in 2-propanol at the same temperature. PVME 30/80 had a shear modulus around 2.5 times lower in 2-propanol than in water. The loss modulus $G''(\omega)$ was about 2 decades smaller than the storage modulus and again showed no frequency dependence. Thus, also tanδ remained constant. Such behavior would be indicative for homogeneous networks.

The same trend as found for the compression modulus $E'(\omega)$ was observed for $G'(\omega)$. The values of $G'(\omega)$ increased with increasing cross-linking density, but there was a slight influence of the polymer content on the mechanical properties (Fig. 5).

The 20 wt % electron-beam cross-linked samples (60, 100, and 120 kGy) had slightly but significant higher (around 20%) G' moduli than the 30 wt % electron-beam irradiated samples. This effect was not observed on the E' moduli (compare with the section $E'(\omega)$ of the hydrogel samples in water at different temperatures). An explanation could be that at lower concentrations of the polymer chains in the state of irradiation their mobility is higher. The macroradicals formed can then diffuse better to each other and the portion of the chain-termination reaction is lower. The γ-ray irradiated samples have 3 times higher storage moduli values in comparison with electron-beam irradiated samples at the same irradiation dose. A much more compact network structure was obtained by the higher cross-linking density as a result of the larger penetration depth in comparison with electron beam irradiation.

The $E' = 3G'$ relation of PVME hydrogels at 19 °C

For ideal elastic networks, which contain no solvent, the familiar relationship between the compression and the shear moduli $E' = 3G'$ is valid. Since highly swollen gels consist of more than 90% of solvent and liquids are very incompressible, this relation seems to be easily met [24]. For this PVME hydrogel system, the $E'(\omega)$ values deviated from the $3G'(\omega)$ ones. For all the electron-beam

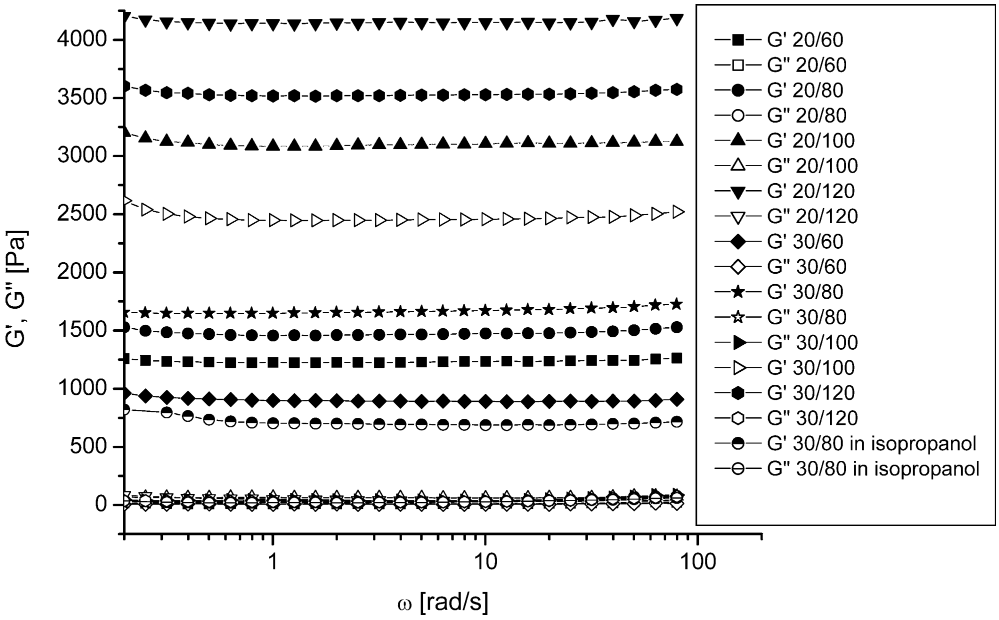

Fig. 4 Frequency dependence of the moduli $G'(\omega)$ and G''rime;(ω) of all the hydrogels in water and of the PVME 30/80 in 2-propanol. The temperature was 19 °C in all cases

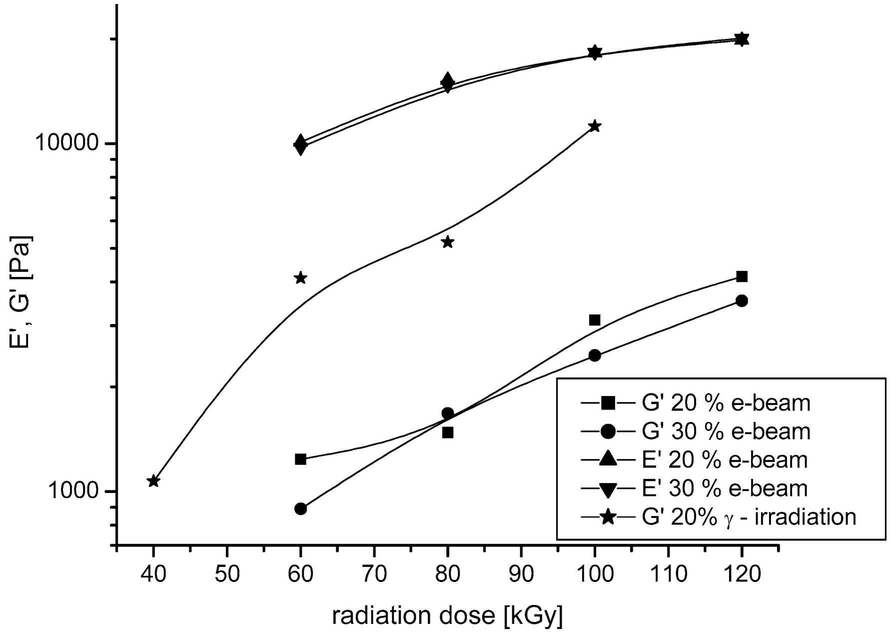

Fig. 5 Comparison of $E'(\omega)$ and $G'(\omega)$ at $\omega = 20.1$ rad/s and 19 °C for each sample cross-linked with electron-beam (polymer concentration of the irradiated samples is 20 and 30 wt %) and γ-ray irradiation (polymer concentration of the irradiated samples is 20 wt %)

cross-linked samples the $E'(\omega)/G'(\omega)$ ratio varied between 4.8 and 10.9 without detectable correlation to the radiation dose and the concentration. It could be expected from the short penetration depth of the electron beam radiation that these samples are clearly macroscopically inhomogeneous, probably with a relatively hard outer skin and a soft interior. For this reason, the limiting value of $E'/G' = 3$ for homogeneous incompressible solids does not apply. It must be pointed ou, that these results are not the consequence of a too long measuring time (e.g., solvent evaporation or escape).

The concentration dependence of the modulus

De Gennes [25] proposed the following scaling law between the elastic modulus E and the polymer concentration ϕ in the swollen gel:

$$E \propto k\varphi^{\alpha}, \qquad (1)$$

with $\alpha = 2.25$ for good solvents [26] and with $\alpha = 3$ for Θ solvents [27, 28].

These theoretical predictions have been confirmed by neutron scattering measurements of the coherence length in polymer solutions [29, 30], by direct mechanical measurements on gels in a good solvent [31, 32], and by inelastic light scattering for gels in a poor solvent [33].

Based on their macro-network model Shibayama et al. [10] discussed an equation for the modulus of the gel above the VPT, E_{VPT}, which is dependent on the modulus of the gel in the homogeneous state below the VPT, E_0, as follows,

$$E_{\mathrm{VPT}} = E_0 m^{\alpha-1}, \qquad (2)$$

with $m = \phi_{\mathrm{p}}/\phi_0$, where ϕ_{p} is the polymer concentration in the gel phase above the VPT and ϕ_0 is the gel concentration in the homogeneous state below the VPT.

For this given case of PVME hydrogels the assumption (as in Ref. [10]) of $\alpha \approx 2.5$ was made for the solvent. The ratio $m \approx 4.5$ is given by the measured values of ϕ_{p} and ϕ_0 : $\phi_{\mathrm{p}} \approx 50$ wt % (degree of swelling $Q \approx 2$ at and above the VPT, Fig. 2) and $\phi_0 \approx 11$ wt % (degree of swelling $Q \approx 9$ below the VPT at 24 °C, Fig. 2). Calculating according Eq. (2), we can obtain a ratio of $E_{\mathrm{VPT}}/E_0 \approx 9.7$.

For samples with a low radiation dose (PVME 20/60, PVME 20/80, PVME 30/60, PVME 30/80) the modulus rose to about 1.6×10^5 Pa at 42 °C (Fig. 2). The ratio E_{VPT}/E_0 is about 10 in these cases and confirmed the calculations. Also, this is in good agreement with Shibayama et al. [10]. They predicted simply a 1 order of magnitude increase in E' above the VPT. The upturn of the E' moduli of hydrogels PVME 20/100 and PVME 30/120 and the deviation of samples PVME 30/100 and PVME 20/120 is attributed to the high porosity (due to the high radiation dose, followed by a slight degradation of the network structure) and the strong phase separation. They are softer since the influence of the immersed water in the network cannot be neglected anymore. By using field emission scanning electron microscopy it was shown [21] that the gel synthesized using the electron beam has a spongelike structure consisting of cavities (about 1 μm) separated from each other by a polymer layer full of holes (about 10 nm). Here, in such cases this relation is not applicable anymore.

We note that the exact degree of swelling in the contracted state must be measured in each case. Shibayama et al. [10] assumed a value of $\phi_{\mathrm{p}} \approx 100$ wt %, but this was not possible for the PVME of this study, which only reached a value of $\phi_p \approx 50$ wt % ($Q \approx 2$) for the completely deswollen state. Furthermore the authors derived the equation based on the isochore macro network model, but as mentioned before, isochore conditions are not involved in this case and the macro network model maybe is not generally transferable to these conditions or, the shrinking process of PVME hydrogels cannot be described with this model. It must be noted that the porosity of the samples at higher radiation doses can prevent exact conclusions about this calculation based on his model. Shibayama et al. [10] mentioned that their calculation may be an exaggeration and this type of discussion is valid as long as the concentration dependence of the modulus is much stronger than that of the volume fraction. Nevertheless, it seems that this relation (Eq. 2) is valid and also applicable for isobar conditions.

Furthermore, it was tested to see if de Gennes' scaling law $G' \propto \phi^{2.25}$ is valid for these PVME hydrogels. In Ref. [34] it was concluded that the data from the shear modulus could be satisfactorily fitted to this power law, independently of the functionality. Generally, the power-law behavior fits more accurately the osmotic pressure data than the shear moduli data. This can be due to the difficulty in the preparation of networks with a negligible number of structural defects. When the cross-linking reaction is carried out in bulk or concentrated solutions, the formation of trapped entanglements is favored, which maybe depends on the molecular weight of the polymer precursor [34].

In the works of Horkay and Zrinyi [35, 36, 37] a good comparison between experiment and theory for poly (vinyl acetate) gels, poly(vinyl alcohol) gels, and other systems was reported. On the other hand, in the work of Meyvis et al. [38] on dextran hydrogels a higher exponent of 3.4 was reported.

A scaling exponent of about 3.54 ± 0.74 for electron-beam irradiated PVME hydrogel samples at 19 °C was found (Fig. 6). The polymer volume fractions at equilibrium swelling ϕ were calculated from $\phi = 1/Q$. Owing to different radiation doses different values of the degrees of swelling were obtained; hence, the degrees of swelling were changed by changing the cross-linking density. The swelling data were taken from PVME 20/60, PVME 20/80, PVME 20/100 and PVME 20/120. Unfortunately a deeper interpretation is not possible, because only a few data points were available.

The irradiation with the electron beam and with γ-rays leads to branched structures in the network, which can give through their entanglements and dangling ends a nonnegligible contribution to the mechanical properties of such systems. Arndt et al. [21] also showed with NMR-relaxation measurements that the content of the dangling ends in radiation cross-linked PVME hydrogels is rather high and the results obtained gave hints that the network structure is nonregular.

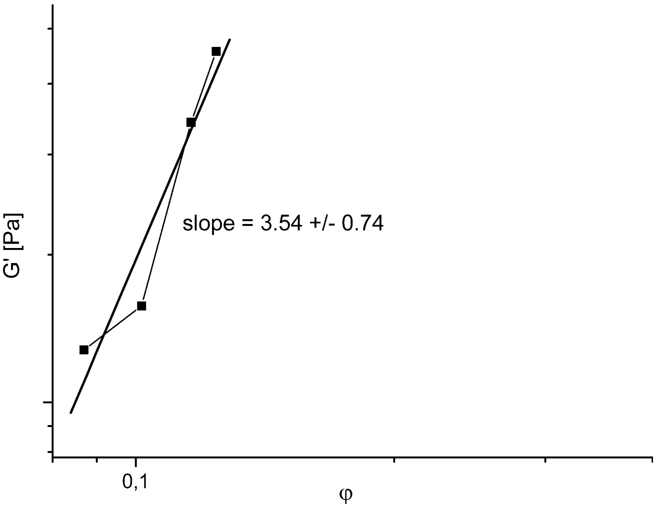

Fig. 6 Double-logarithmic plot of G' and the polymer volume fraction ϕ at equilibrium swelling (values were calculated from $\phi = 1/Q$) according to the de Gennes scaling behavior. A linear fit was applied to the data

Conclusions

Changes in the mechanical properties of radiation cross-linked PVME hydrogels above and below the VPT under isobar conditions were investigated. It was found that an increase of the storage elastic modulus E' was observed at the VPT. In the shrunken state a frequency dependence of the moduli in the range of 0.1–22 Hz was detected, indicating viscoelastic behavior. At temperatures well below the VPT in the homogeneous state the gel shows mainly pure elastic properties. Samples which were made by γ-rays have higher moduli than those obtained from electron-beam irradiation. The main reason is the more homogeneous structure in the gel. The porosity of the hydrogels, owing to the special conditions of manufacturing, has a large influence on their mechanical stability.

The influence of solvent conditions on the mechanical properties are important; changing the solvent from water to cyclohexane, we observed much higher moduli. For the PVME/cyclohexane system, the VPT is possibly shifted to temperatures lower than 19 °C; hence, by in situ rheology the VPT was not detectable. The hydrogel sample swollen in 2-propanol had a G' modulus 2.5 times lower than a similar sample swollen in water, possibly owing to different solvation behavior. As a result, the modulus in 2-propanol is smaller, despite the fact that the degrees of swelling are nearly the same in both solvents.

Acknowledgements For the possibility to work in his group the author thanks H.H. Winter (Department of Chemical Engineering and Department of Polymer Science and Engineering, University of

Massachusetts at Amherst, MA, USA). B.D. Chin and R. Horst (University of Massachusetts at Amherst) prepared the experiment in the linear rheometer and the ARES. T. Schmidt (TU Dresden) is acknowledged for helping with the preparation of the samples. The author thanks furthermore H. Dorschner (Institute of Polymer Research Dresden), for electron-beam irradiation and U. Gohs (Gamma-Service Radeberg), for γ-ray irradiation. Last but not least, the author especially expresses his gratitude to G. Heinrich (Institute of Polymer Research Dresden) for critical reading the manuscript and many fruitful discussions. This work was kindly supported by the Deutsche Forschungsgemeinschaft, grant nos. RI 1079/1-1 and RI 1079/1-2 to S.R.

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