ESR Studies of Chemically Modified and Photocrosslinked Poly(vinyl alcohol) Gels

THOMAS UHLICH,* MATHIAS ULBRICHT, GEORG TOMASCHEWSKI, and REINHARD STÖSSER

Humboldt Universität, Institut für Chemie, Invalidenstr. 42, D-10115 Berlin, Germany

SYNOPSIS

The hydrophilicity of poly(vinyl alcohol) (PVA) was lowered by acetalization with propionic aldehyde. After UV irradiation of pendent styrylpyridinium groups, these prepolymers form networks of different hydrophobicity depending on the degree of acetalization. PVA films containing different amounts of propionic acetals were doped with 4-hydroxy-2,2,6,6-tetra-methylpiperidine-1-oxyl. Then, the ESR spectra of the spin probe entrapped in the polymeric network were monitored while allowing different solvents to diffuse into the polymer. The rate of spin probe mobilization depends on the hydrophilicity/hydrophobicity of both the polymer network and the solvent. However, the modified polymers, even the more hydrophobic ones, are hydrophilic in comparison to "really" hydrophobic polymers. This is probably caused by the character of the parent polymer (PVA), unreacted hydroxy groups. Simulations of the ESR spectra have shown that in polymers with a higher degree of acetalization domains of different hydrophobicity are built in which the spin probes have a different mobility. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The described polymers are to be used for the entrapment of enzymes by photochemical crosslinking. The formed network containing the entrapped enzyme is employed for enzymatic reactions in organic media. Starting with poly(vinyl alcohol) (PVA), the hydrophilicity of the polymer should be lowered, guaranteeing a higher diffusivity of hydrophobic substrates and products. For that purpose, certain amounts of the polymer's hydroxy groups are blocked by acetalization with propionic aldehyde. Therefore, the synthesized polymers are expected to have a varied hydrophobicity that depends on the degree of hydroxy group conversion with the aldehyde.

An interesting subject is to monitor these differences in hydrophobicity of the polymers. Integral methods for the determination of bulk hydrophilicity/hydrophobicity are, e.g., swelling experiments or sorption kinetics. Contact angle measurements provide information about the hydrophilicity/hydrophobicity of the outer surface. In this article, we report on ESR spectroscopy using the spin probe technique to determine differences in the hydrophobicity of the synthesized polymers. This technique has several advantages, e.g., the sensitivity and selectivity of the spin probe to changes in its microenvironment, providing the possibility to detect local differences in solvent absorption as well as a high time resolution during the measurements.

The spin probe technique has found many applications in polymer research. The mainly used spin probes are stable organic nitroxides. They show an easily identifiable three-line spectrum that sensitively reflects the molecular motion of the radical. In a solid amorphous matrix (e.g., at temperature below the T_g of a polymer), the ESR spectrum corresponds to randomly distributed radicals with slow motion. If the motion increases (e.g., by rising temperature or solvent penetration into the polymer), the spectrum changes to that of a mobile spin probe in a more or less fluid solvent. Additionally, intermediate states of mobility are detectable.

Several authors reported on the penetration of solvents or nonsolvents into polymers observed by

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* To whom correspondence should be addressed.

ESR spectroscopy. Veksli and Miller studied the influence of solvent and temperature on the motion of nitroxide free radicals covalently bound to and incorporated in polystyrene and poly(methyl methacrylate).[1,2] Watanabe et al. observed the nitroxide motion in PVA gels produced by γ-irradiation.[3] They found an effect of the pore size on the rotational diffusion and the interaction of the nitroxide with the surrounding matrix. This interaction is due to a hydrogen bond between the spin probe and a hydroxy group of the PVA. Mäder et al. investigated the penetration of water into poly(hydroxyacetic acid-co-lactic acid) using ESR spectroscopy of various spin probes.[4] A fast diffusion of water was observed; however, other small molecules did not diffuse and, in general, the release of the nitroxide was low.

The morphology of hydrogels and polymer–polymer blends was studied by Pitt et al.[5,6] They examined poly(2-hydroxyethyl methacrylate) (PHEMA), PVA, and poly(acryl amide) (PAAm) blends of PVA with two other polymers, as well as block copolymers of poly(ethylene glycol) and poly(lactic acid). The line shape of the ESR spectra was dependent on the porosity of the hydrogels as well as on the composition of the tested polymer–polymer blends. For nonporous PHEMA (polymerized using a standard procedure and containing 40 wt % water), PVA, and PAAm, no separate domains of water and polymer with selectivity for a solute could be detected. However, ESR spectra of the spin probes in macroporous PHEMA (68–74 wt % water) were measured and could be simulated as the superposition of the spectra in nonporous polymer and in water, respectively. Several other conclusions could be drawn from such ESR experiments. Depending on the components, the polymer blends showed complete miscibility or phase separation. For the cited copolymer system, partial separation of the components was detectable at a certain polymer–polymer ratio.

Pekcan and Demir investigated the time dependence of spin probe penetration into sterically stabilized (with PHEMA) colloidal poly(vinyl acetate) (PVAc) particles.[7] It was reported that diffusion follows Fick's law. The diffusion coefficients D of spin probes were found to be inversely proportional to the viscosity of the solvent within the polymer particles. There was also an inverse proportionality between the absorbed solvent amount and the polymer–solvent interaction.

Although there are numerous reports on the spin probe technique in polymer research, no article could be found in the literature concerning the influence of a chemical modification of the polymer on solvent penetration measured by the mobilization of a nitroxide. In this article, we report on the characterization of changes in hydrophilicity/hydrophobicity of chemically modified and photochemically cross-linked PVA. We used the above-mentioned technique to follow the penetration of different solvents into the polymeric networks. The embedded spin probe was mobilized depending on the hydrophobicity of the polymer and the penetrating solvent. The rotational correlation time of nitroxide probes in completely swollen networks offers the possibility to differentiate between the hydrophobicities of the various matrices.

EXPERIMENTAL

Prepolymer Synthesis

PVA used for our investigations was a commercial product of BUNA, Germany. It has a molecular weight of $M_v = 80,000$ g/mol and an acetate content of 11–14%. Chemicals and solvents (all of analytical grade) used for synthesis of the photosensitive compound and for polymer modification were purchased from Fluka (Buchs, Switzerland).

The photosensitive compound 1-methyl-4-[2-(4-formylphenyl)ethenyl]pyridinium–methosulfate (SbQ-4) was synthesized according to Ichimura and Watanabe.[8] For synthesis of the photosensitive prepolymer, 150 g of a 10 wt % solution of PVA in water was prepared. To this solution, 2.01 g of SbQ-4 dissolved in a small amount water and 1.8 g of phosphoric acid as a catalyst were added. The mixture was stirred at room temperature for at least 6 h. Then, propionic aldehyde in appropriate amounts was added and the reaction mixture was further stirred for several hours. For preparation of the more hydrophobic polymers, the PVA solution had a lower initial concentration (5 wt %) to prevent a too rapid gel formation. After finishing the reaction, the water phase was discarded and the gel-like photosensitive prepolymer was thoroughly washed with weakly alkaline water to remove phosphoric acid and, finally, dried in vacuo. All manipulations with the photosensitive compound were carried out with prevention of UV exposure.

The content of the photosensitive compound was determined spectrophotometrically using a Philips/Unicam PU 8735 UV/vis spectrophotometer. The absorption coefficient of a model compound for the polymeric acetal groups (33,600 L/mol^{-1} cm^{-1} in DMSO) prepared by reaction of SbQ-4 and propane-

1,3-diole was used assuming the same absorption coefficient of the chromophore in the model compound and in the synthesized prepolymers. The degree of propionic acetal formation was determined by quantitative ^{13}C-NMR spectroscopy on a Bruker AM 300. Analytical data for the different prepolymers are summarized in Table I.

Swelling Measurements

For the swelling experiments, polymer networks were prepared similar to the procedure described for the spin probe embedding (without adding the nitroxides) as stated below. Then, the films were immersed in the solvents for about 1 week. After this, the films were dried *in vacuo* again. The weight swelling ratio was calculated as the quotient of the weight of the solvent absorbed and the weight of the dried polymers. The weight of the dried polymers (and not the initial weight) was used because a certain amount of the polymer is still soluble after irradiation. Weight measurements were performed on a Sartorius balance R160P (Sartorius; Göttingen, Germany).

Spin Probe Embedding

The spin probe 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPOL) was obtained from Aldrich, Germany. The solvents used for the ESR measurements were all of spectroscopic grade and purchased from Merck, Germany.

A 10 wt % solution of the prepolymer in water or ethanol/water mixtures (depending on the degree of hydrophobization) was prepared and TEMPOL was added in a concentration of about 10^{-4} M. This solution, 0.5 g, was spread out on a 10 cm^2 glass plate and allowed to dry. The produced films had a thickness of about 30–40 μm. Finally, they were irradiated for 30 min on both sides through a glass

filter using an HBO 350 (Osram, Germany). The crosslinked films were stored in a desiccator over calcium chloride.

ESR Measurements

A Varian E4 spectrometer (Varian Associates Inc., USA) and an ERS 300 (ZWG, Berlin-Adlershof, Germany) were used for the ESR measurements (at room temperature) operating at a microwave frequency of about 9.4 GHz with 1 mW power. The modulation amplitude was 0.1 mT, and the spectra were recorded around 330 mT.

The TEMPOL-doped films were cut into round pieces of 5 mm diameter and placed on a flat ESR tissue holder covered with a Teflon sheet. For the solvent penetration studies, 100 μL of the liquid was put onto the polymer film and the covered holder was then placed in the spectrometer's cavity. For the investigations of spin probes in swollen polymers, the pieces were fixed on the tissue holder with adhesive tape to prevent evaporation of the swelling agent. The measurements with water vapor were performed as shown in Figure 1. A nitrogen stream was passed at room temperature and with constant flow rate (measured with a flow meter FP-1/8-12-G-5, floating body SA-18; Fischer & Porter, Göttingen, Germany) first through a washing bottle containing water, then through the tissue holder and over the polymer sample. In this way, the nitrogen was saturated with water vapor.

RESULTS AND DISCUSSION

Prepolymer Synthesis and Polymer Network Formation

PVA with pendent styrylpyridinium acetals as the crosslinking component shows a high hydrophilicity.

Table I   Analytical Data for the Synthesized Prepolymers

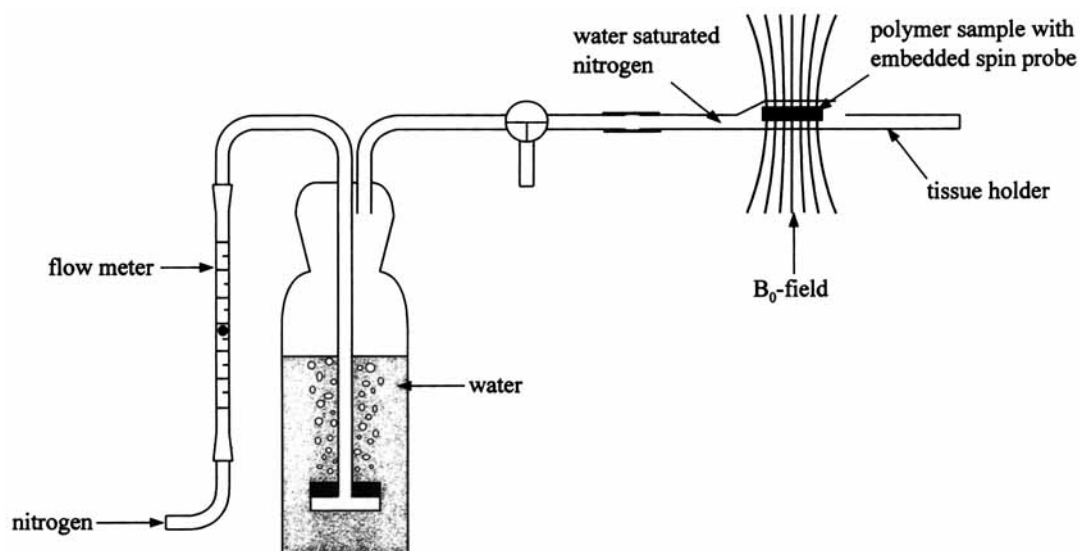| Polymer	Elementary Analysis (%)		Propionic Acetal Content (mol %)	Content of Photosensitive Compound (wt %)
PVA	C: 52,48	H: 9,86	0	0
PVA-0PA	C: 51,59	H: 8,65	0	9.1
PVA-5PA	C: 52,66	H: 8,22	4–5	9.8
PVA–12PA	C: 53,42	H: 8,94	10–12	9.3
PVA-20PA	C: 55,02	H: 8,83	17–20	9.0
PVA-50PA	C: 58,76	H: 8,56	45–50	8.9

Figure 1 Experimental setup for exposition of the polymer sample to a water-saturated vapor phase.

By chemical reaction with propionic aldehyde, this hydrophilicity can be lowered. Chemical synthesis of the prepolymers is shown in Figure 2. The analytical data for the prepolymers are summarized in Table I. An almost similar content of the photosensitive compound for all prepolymers is ensured by stepwise reaction, first with SbQ-4 and then with propionic aldehyde. The resulting hydrophobic character of the polymer depends on the degree of propionic acetal formation.

PVA with a very low content of residual acetate groups (0–5%) usually shows a certain level of crystallinity which influences its diffusivity. However, in PVA polymers with higher acetate contents (12%), those prevent the formation of regular structures in the polymer, especially at lower annealing temperatures (<60°C) and, thus, no crystallites can be found.[9] So, we conclude that in our polymer systems (containing 11–14% acetate groups and additionally modified with propionic aldehyde) no crystalline regions occur.

The formation of the network occurs through a [2 + 2]-cycloaddition of styrylpyridinium moieties in the polymer induced by UV irradiation through a glass filter (Fig. 3). The formed network provides insolubility in various organic solvents. However, it remains swellable, and the diffusion of solvent molecules as well as substrates and products (for enzymatic reactions) is preserved. The procedure for the embedding of the spin probe is described in Figure 4. It is similar to that employed in enzyme entrapment.
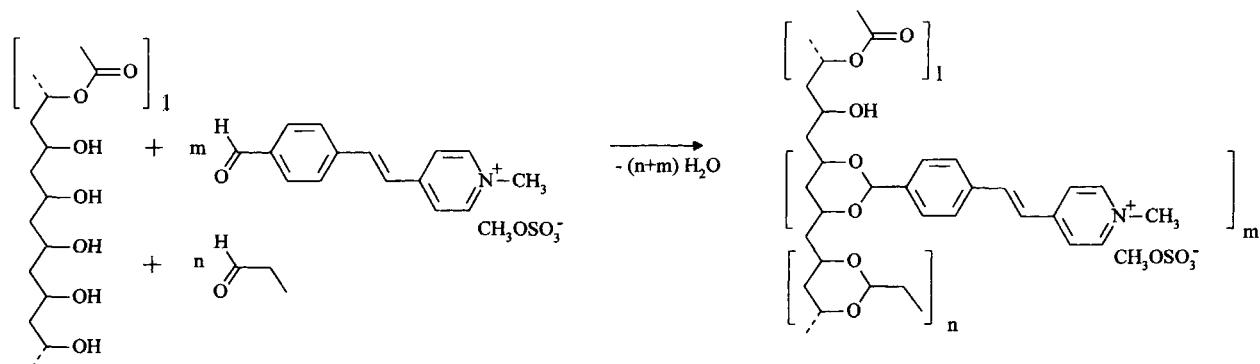

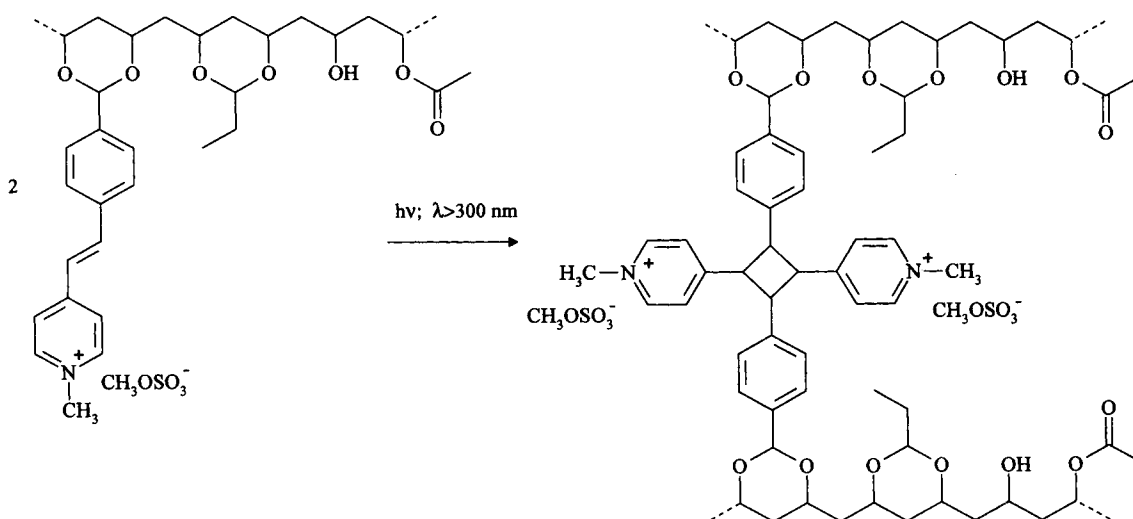**Figure 2** Synthesis of photocrosslinkable PVA prepolymers with variable amount of propionic acetals.

Figure 3 Network formation by UV irradiation of PVA prepolymers containing styryl-pyridinium groups.

Swelling Experiments

The swelling of the described polymers in solvents of different hydrophobicity is shown in Figure 5. It can be seen that the higher degree of acetalization with propionic aldehyde causes less swelling in water. In all other cases investigated, more solvent was absorbed with increasing degree of acetalization. Hence, the swelling experiments show that the acetalization causes the desired hydrophobization of the polymer. A gradation in the hydrophobicity can be obtained by a variation of the degree of acetalization. However, the polymers formed after modification are not entirely hydrophobic, which is a result of the remaining hydroxy groups in the polymer chain.

ESR Experiments

ESR spectra of the spin probes in the polymer networks are by the effect of immobilization similar to those of nitroxide radicals as polycrystalline solid (see Fig. 6) at room temperature. The probes have a statistical orientation in the polymer and, thus,

the spectrum represents the envelope of all values for the g-factor and the hyperfine splitting constants. In comparison, penetration of solvents into the polymer causes a mobilization of the spin probe. If the solution has a low viscosity, the rotational correlation time is shorter than is the time scale of the x-band. Then, the anisotropy of the g-factor and the hyperfine splitting constant is averaged and the resulting spectrum contains no information about the orientation of the spin probe.

The dynamic processes of spin probe mobilization by penetrating solvent molecules have been followed as a function of time. As a measure of nitroxide mobilization, the ratio of the height of the low field and the central line of the mobile component was used.

Investigations with Water

Sorption Studies

Although the polymers had been hydrophobized (in comparison to the PVA) by formation of propionic acetals, they still remain hydrophilic to some extent (see swelling experiments). The reduced hydrophi-
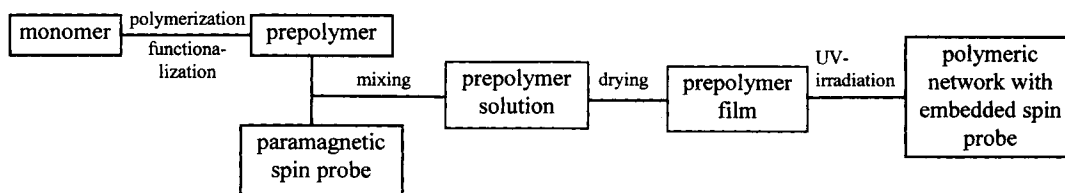

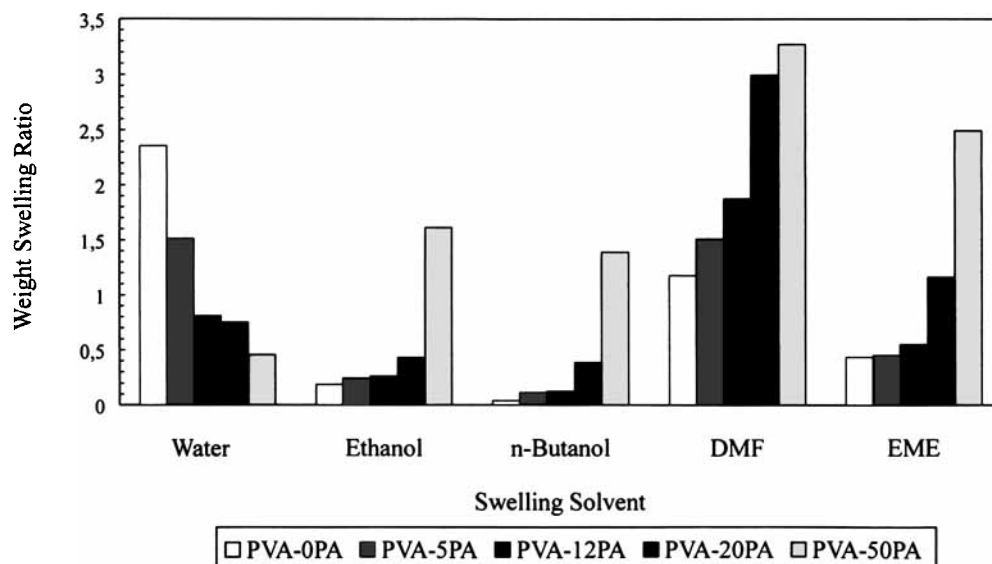**Figure 4** Schematic procedure for the spin probe embedding.

Figure 5 Swelling of hydrophobized PVA networks in various solvents (DMF: N,N-dimethylformamide; EME: ethylene glycol monomethyl ether).

licity causes slight differences in the spectra of the embedded spin probes recorded after 24 h of swelling (see Fig. 7). The mobility of a spin probe can be described by the rotational correlation time, which affects the line shapes and line widths. For their calculation, the following equation has been used[10,11]:

$$\tau_c = 6.6 \times 10^{-10} \times W_0 \times \left[\left(\frac{h_0}{h_{-1}}\right)^{1/2} + \left(\frac{h_0}{h_{+1}}\right)^{1/2} - 2\right]$$

where W_0 represents the line width of the midfield line (in G) and h_{-1}, h_0, and h_{+1} are the peak-to-peak heights of the low-, central-, and high-field lines, re-

spectively. The constant 6.6×10^{-10} has been calculated for di-tert-butylnitroxide,[12,13] but it was also used for other nitroxides.[14] The rotational correlation times of spin probes embedded in polymeric networks after saturation with water containing TEMPOL are summarized in Table II (data are taken from experimental spectra). It is seen that there is a dependence on the degree of hydrophobization. The values indicate a fast reorientation in all types of water-swollen networks except in the most hydrophobic one. However, the comparison with TEMPOL dissolved in a 10 wt % PVA solution indicates that the mobility of the spin probes even in the hydrophilic polymer is restricted. A similar
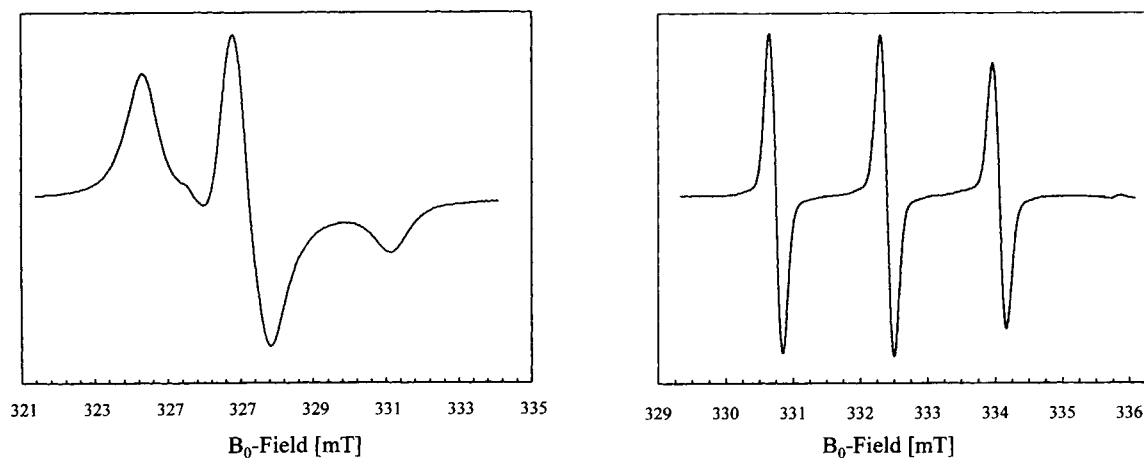

Figure 6 ESR spectrum of a nitroxide spin probe embedded in a polymeric network before and after penetration of a solvent into the network.
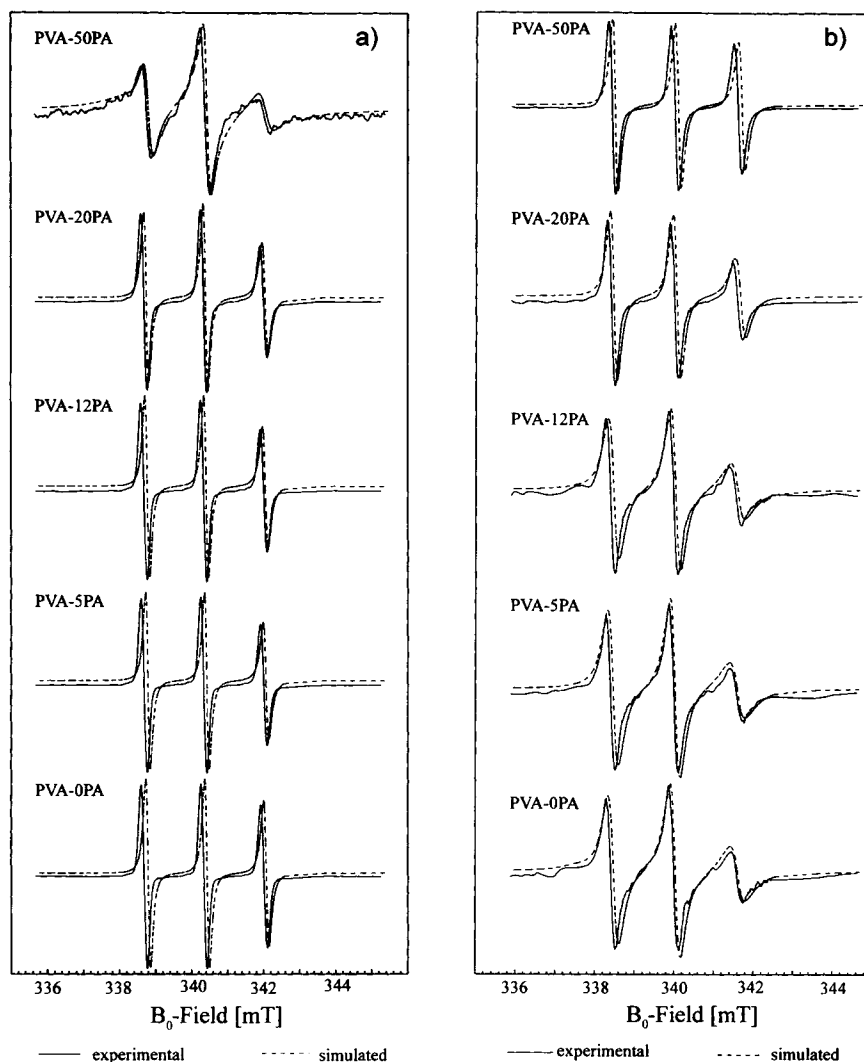
Figure 7   ESR spectra and simulations of TEMPOL in swollen polymer networks: (a) swollen in water; (b) swollen in ethanol.

Table II   Rotational Correlation Time of Spin Probes Embedded in Polymeric Networks After Diffusion of Water and Ethanol

Polymer	Rotational Correlation Time (ns) of Spin Probes Embedded in Polymers Which Were Swollen in	
	Water	Ethanol
In solution (10% PVA)	0.038	—
PVA-0PA	0.157	1.237
PVA-5PA	0.248	0.999
PVA-12PA	0.268	0.735
PVA-20PA	0.345	0.543
PVA-50PA	2.416	0.143

increase in the rotational correlation time has been found by Watanabe et al. for several substituted nitroxides in PVA crosslinked by γ-irradiation.[3]

To obtain more and quantitative information about the structure of the swollen polymer networks, simulations of the ESR spectra are compared with the experimental recorded spectra (see Fig. 7). The simulations of TEMPOL in the polymers PVA-0PA, PVA-5PA, PVA-12PA, and PVA-20PA correspond to spin probes in solution with slightly increasing line widths (according to the increasing hydrophobization). This indicates that these polymers absorb enough water to build up domains where the spin probe can rotate almost freely (see τ_c values in Table II). In contrast, the spectrum for the spin probe in the polymer PVA-50PA can be satisfactorily described as the superposition of the simulated spectra

of isotropic (with a high line width) and anisotropic species in a ratio of about 2 : 8. From this simulation, we conclude that there are domains in the polymer which are not accessible for the water molecules and domains which are—at least partially—accessible.

At this point, the overall degree of acetalization (45–50%) of the polymer PVA-50PA must be considered, meaning that about 30% of the hydroxy groups are still existing on the polymer chain. So, the question of distribution of the acetal groups (and, hence, the hydrophobicity) in the polymer has to be answered. If acetal and hydroxy groups are statistically distributed over the whole polymer chain, there is no possibility to build up those hydrophobic spheres, not even during the film formation. Thus, they should be formed as the acetalization reaction with propionic aldehyde proceeds. This phenomenon could be caused by a neighboring group effect. In the same way, Raghavendrachar and Chanda[15] explained acetalization degrees higher than those predicted by Flory's theory.[16]

Watanabe et al.[3] and Fujiwara et al.[17] discussed the relation between the critical volume (which is "the minimum volume of solution required for maintenance of free motion of the solute molecule in the solution") and the molecular motion of spin probes. They obtained a variation in the pore sizes and, thus, in the free volume (which is the volume fraction of swelling agent) by changing the degree of crosslinking. In contrast, the free volume in our investigations was changed by a chemical modification resulting in a lowered capability of swelling in water. However, we observed a similar effect. The higher the degree of hydrophobization, the less the amount of water absorbed by the network. Thus, the free volume is smaller than is the critical volume and, therefore, the motion of the nitroxide radicals is slower. As shown by the simulation for the most hydrophobic polymer network (PVA-50PA), about 80% of the spin probes embedded are immobilized. The calculation of the rotational correlation time for the other spin probes ($\approx$ 20%) in this polymer network shows that their motion is also comparatively slow (see Table II). This indicates that the free volume in the less hydrophobic domains must be smaller than is the critical volume of TEMPOL. For the other, more hydrophilic polymers, the lowered free volume is still higher than is the critical volume, causing only a line width broadening.

Experiments with an excess of water (polymers swollen in pure water) proved that the spin probes diffuse into the surrounding solution. Thus, the network formed after irradiation has no capability to retain small molecules. Also, small solute molecules are able to diffuse into the PVA networks. If ascorbic acid was used as the solute, penetration of these molecules is as fast as the diffusion of the solvent. As a result, reduction of the spin probes takes place and no spectrum of a nitroxide spin probe was observable.

Diffusion Studies with Water Vapor

To lower the solvent absorption rates and to obtain distinctions between the different polymer types, the amount of water offered should be reduced. This was achieved by passing a water-saturated nitrogen flow over the polymer sample (see Fig. 1) which reduces the water gradient between the surrounding volume and the polymer (in comparison to swelling in liquid water). In Figure 8, the ratio of the peak heights as a function of time for the penetration of water vapor into the polymer networks and an example of the measured ESR spectra are shown. The following dependence is observed: The higher the degree of acetalization, the lower the rate of water-vapor penetration into the polymer. The penetration process can be described by a first-order rate. Because crystallinity is assumed not to play an important role in these polymer systems, the unexpected high initial rate of solvent absorption for the most hydrophobic polymer is probably a result of the film preparation. It was cast from an ethanolic solution, which may produce a film with higher porosity or surface area in comparison to a film prepared from an aqueous solution of the other, more hydrophilic polymers. Again, the lower peak height ratio observed for the most hydrophobic polymer indicates an inhomogeneity already discussed above.

In contrast to water diffusion from a liquid phase, the lower amount of water offered from the vapor phase means that the—at least the initial—water fraction in the formed hydrogel is smaller than in the hydrogels swollen in water. This causes a limited mobilization of the spin probe for the less hydrophilic polymers.

Investigations with Ethanol

Sorption Studies

Studies of networks swollen for 24 h in ethanol containing TEMPOL and subsequent calculations of rotational correlation times are rather difficult. This is a consequence of the high vapor pressure of the solvent ethanol causing a fast drying of the polymer samples in the spectrometer's cavity. However, the
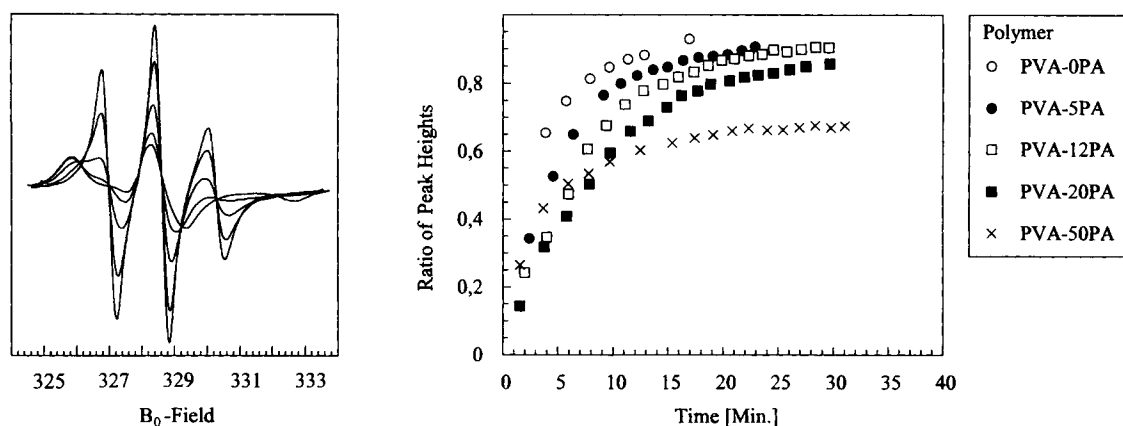
Figure 8   ESR spectrum (PVA-5PA) and time dependence of the ratio of peak heights for the diffusion of water vapor into PVA networks.

spectra obtained (see Fig. 9) reflect the results of the swelling experiments (see Fig. 5). For the more hydrophilic types, the reorientation time is higher, because there is very little absorption of ethanol by these polymers (see Fig. 5). Only the spin probes embedded in the most hydrophobic network are completely mobilized. The calculated rotational correlation times (see Table II) are in the range of the one obtained after swelling in water, but with an inverse order.

Diffusion Studies

To obtain solvent penetration even into the more hydrophobic domains, the less polar solvent (in comparison to water) ethanol was used. For the investigations, the polymers were placed on an ESR tissue holder, then a small amount of ethanol was added, and, finally, the holder was covered with a Teflon sheet. The ESR spectra were recorded as

function of time. The observed dependence of the spin probe mobilization on the degree of acetalization is shown in Figure 9. In comparison to the water and water vapor diffusion studies, an inverse sequence of the initial rates of the solvent diffusion is observed. This is expected and agrees with the swelling experiments and sorption studies.

Investigations with n-Butanol

The most hydrophobic solvent used in our investigations was n-butanol. It was also chosen because of its higher molecular weight to obtain a better time resolution for the more hydrophobic polymers (see Fig. 10). However, the penetration of n-butanol is comparable to ethanol for the hydrophobic polymer, and there is almost no solvent absorption by the more hydrophilic polymers. This is consistent with the results of the swelling experiments in n-butanol (see Fig. 5).
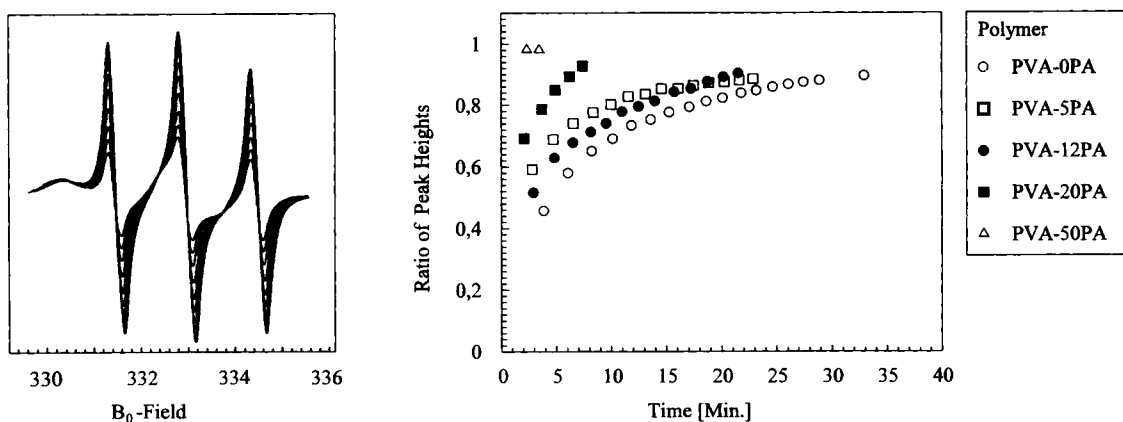

Figure 9   ESR spectrum (PVA-5PA) and time dependence of the ratio of peak heights for the diffusion of ethanol into PVA networks.
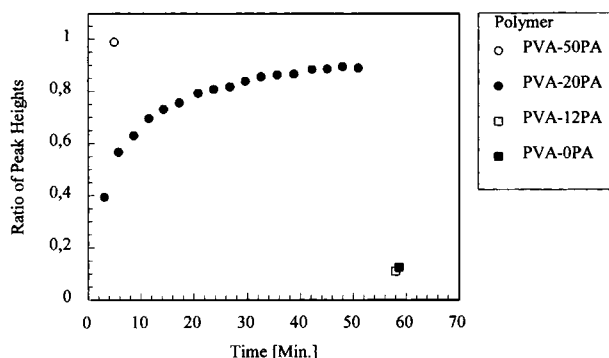
Figure 10 Diffusion of n-butanol into PVA networks (PVA-50PA: peak height corresponds to spin probes in liquids; PVA-12PA and PVA-0PA: no change in the peak heights during the measurement).

CONCLUSIONS

Acetalization of PVA with propionic aldehyde causes a hydrophobization of the polymer. Thus, the networks formed after cycloaddition of pendent styrylpyridinium groups become swellable in organic solvents. This allows reactions in organic media catalyzed with enzymes entrapped in these networks. However, they exhibit a considerable hydrophilic character as seen from the water uptake that is attributed to unreacted hydroxy groups of the parent polymer.

The ESR spectroscopy using the spin probe technique offers the possibility to detect differences in the solvent penetration into polymers of different hydrophilicity/hydrophobicity. If this process is slow, the rate of mobilization of the spin probe provides a tool for estimating qualitatively the hydrophilicity/hydrophobicity of the polymer network. The rotational correlation time of the spin probes embedded in networks of different hydrophilicity allows one to distinguish even between structurally similar, highly swollen polymers. Provided that the spin probe is homogeneously distributed in the different polymer domains, the shape of the ESR spectrum allows one to differentiate between spin probes of different mobility and, thus, by a simple model, between different locations in the polymer matrix. The results correspond to gravimetric experiments of swelling in different solvents. However, it is pos-

sible to obtain more detailed information about the microstructure of the polymer network.

For the described polymers, there is a dependence of the formation of hydrophobic domains on the degree of hydroxy group conversion by acetalization. At higher degrees of acetalization (40–50% blocked hydroxy groups), separate domains with higher hydrophobicity are formed which are less accessible for water but still remain accessible for ethanol. We postulate that a neighboring group effect during the acetalization is responsible for this phenomenon.

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