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On the Polarity of the Microenvironment of Polymers in Solution. 3. Poly[4(5)-vinylimidazole] in One-Component and Binary Mixtures

F. Mikeš,*[1a] P. Štrop,[1b] Z. Tuzar,[1c] J. Labský,[1c] and J. Kálal[1c]

Department of Polymers, Prague Institute of Chemical Technology, Prague 6, Czechoslovakia, Department of Proteins, Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, Prague 6, Czechoslovakia, and Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague 6, Czechoslovakia.

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ABSTRACT: Solution properties of poly[4(5)-vinylimidazole] (PVIm) were studied. Polyelectrolyte behavior of PVIm in methylcellosolve and mixtures of ethanol/water and dioxane/water and the suppression of the polyelectrolyte behavior by lithium chloride were studied viscosimetrically. The molecular weight of PVIm was determined by light scattering. Titration behavior of PVIm was measured and the dissociation constant of the solvatochromic compound was determined. For the estimation of the polarity of the microenvironment of PVIm, two differently labeled PVIm's were prepared. On the basis of the shift of the charge-transfer absorption band of the solvatochromic form of the 1-[β-(methacryloyloxy)ethyl]-4-(3-ethoxy-4-hydroxystyryl)pyridinium chloride (MSC) and 1-(δ-bromobutyl)-4-(3-ethoxy-4-hydroxystyryl)pyridinium bromide (BSB) it has been found that the polarity of the microenvironment of the polymer chains of PVIm in binary mixtures of alcohol/water and dioxane/water is lower than that of the solvent. At a low content of water in the mixture, selective sorption of water on the polymer coil yields a detected polarity in the neighborhood of the polymer even higher than that of the solvent used. In PVIm where a solvatochromic label is bound near the polymer chain, a lower polarity of the microenvironment of the polymer has been found than that of the polymer possessing a solvatochromic label farther from the polymer chain. Hydrophobic sorption of the compounds with a long aliphatic chain on the polymer chain of the PVIm in binary mixtures of ethanol/water with a low content of ethanol has been revealed.

Introduction

Polymers carrying imidazole substituents have been studied intensively in view of their catalysis of solvolytic reactions. The catalytic efficiency of polymers possessing pendant imidazole residues on reactions of low molecular weight compounds can be generally influenced[2] by a change of the local concentration of a compound in the neighborhood of the polymer due to electrostatic or hydrophobic forces, by steric factors, and by cooperative effects.

Poly[4(5)-vinylimidazole], the polymer studied most extensively from this point of view, exhibits a number of interesting properties. It possesses a hydrophobic aliphatic backbone and pendant amphiphilic groups. The electrostatic and hydrophobic interactions and the steric and cooperative effects have been studied in detail as to their effect on the catalytic activity of the polymer.[3] The hydrophobic interactions of PVIm with the neutral esters possessing a long aliphatic chain are probably most effective in increasing its catalytic efficiency. It seems reasonable to suppose that, besides the catalytically active hydrophilic part of the polymer, the hydrophobic character of the polymer chain backbone plays an important role.

In mixed solvents with a different affinity of the components of the solvent medium toward the polymer, one component of the mixture may be selectively bound to the polymer chain. The composition of the solvent in the polymer domain where the catalytic reaction occurs can then be considerably different from the bulk composition. This may influence the evaluation of the effect of high molecular character of the catalyst on the activity of imidazole residues in PVIm. For this reason we have tried to obtain by use of a polarity indicator some information concerning the polarity of the microenvironment of PVIm in solution where binding and conversion of the substrate takes place.

The quantitative evaluation of the sorption of compounds possessing long alkyl chains on PVIm from an ethanol/water mixture would also aid the interpretation of the increased solvolysis rate of active esters with similar alkyl groups.

In parts[4] 1 and 2 of this series the method proposed by Kosower[5] for semiempirical determination of the solvent polarity was employed to measure the polarity of the microenvironment of synthetic vinyl polymers. Small concentrations of monomer residues with pyridinium betaine side chains characterized by a sensitive solvatochromic charge-transfer band in the visible spectrum were embedded in the polymer chain and the spectrum of the charge-transfer band was compared with that of the free monomer in the same solvent. The polarity of the polymer microenvironment and solvent was expressed by the charge-transfer band energy.

In spite of complications arising from incorporation of such bulky foreign groups[6] in the polymer chain of synthetic polymers, it is our opinion that this method can give reasonable results in comparison with results obtained for more complicated biological macromolecules.

Experimental Section

A. Syntheses. 1. 4(5)-Vinylimidazole (VIm). VIm was prepared according to the procedure described by Overberger and Vorchheimer starting from histidine.[7] The crude product was purified by sublimation at 70–75 °C (3×10^{-4} mmHg).

VIm: mp 81–82 °C (lit. mp 83.2–84.5,[7] 81.5–83.0[8] °C). Anal. Calcd for $C_5H_6N_2$: C, 63.81; H, 6.43; N, 29.77. Found: C, 64.10; H, 6.56; N, 29.53.

2. 1-[β-(Methacryloyloxy)ethyl]-4-(3-ethoxy-4-hydroxystyryl)pyridinium Chloride (MSC). MSC was prepared by quaternization of (3-ethoxy-4-hydroxystyryl)pyridine (SP) with β-(methacryloyloxy)ethyl tosylate (METs).

β-(Methacryloyloxy)ethyl Tosylate (METs). METs was prepared by reaction of 2-hydroxyethyl methacrylate with tosyl chloride in anhydrous ether in the presence of pyridine. The product was homogeneous by TLC [Silufol R UV_{254}, toluene–acetone (9:1, v/v)].

METs: yield 75%; mp 15–20 °C. Anal. Calcd for $C_{13}H_{16}SO_5$: C, 54.91; H, 5.67; S, 11.28. Found: C, 54.69; H, 5.73; S, 11.22. The presence of hydroxyl groups was not revealed in the IR (neat) spectrum.

(3-Ethoxy-4-hydroxystyryl)pyridine (SP). SP was prepared by a modification of the procedure of Chiang and Hartung[9] by condensation of ethylvanillin with 4-methylpyridine in the presence of acetic anhydride at 165 °C.

SP: yield 17% based on ethylvanillin; mp 163–164 °C; IR (KBr) ν(C=C) 1625, γ(CH, trans) 965 (s) cm^{-1}; NMR ($CDCl_3$) τ_{Me_4Si} 8.6 (3 H, t, CH_3C), 5.85 (2 H, q, CCH_2O), 3 (8 H, m, aromatic H, pyridine subs 3, CH=CH, HO), 1.5 (2 H, d, pyridine subs 2). Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.68; H, 6.27; N, 5.80. Found: C, 74.61; H, 6.36; N, 5.73.

MSC was prepared by reaction of 20 g of SP with 25 g of METs in 550 mL of anhydrous methanol (inhibitor, 0.05 g of octyl pyrocatechol). The reaction was carried out at 50 °C for 4 h. The solution was concentrated under vacuum and the solid residue was filtered off. The filtrate was poured into 2.5 L of water, the solution was adjusted to pH 7 by addition of sodium hydroxide, and the precipitate which formed was filtered off. The solution was extracted seven times by 250 mL of chloroform and the water phase was lyophilized. The yellow solid product (10 g) was extracted by anhydrous acetone. The residue remaining after evaporation of acetone was dissolved in water, and this solution was poured through a column packed with Dowex 1X2 in the chloride form (pH ~5). The product was isolated by lyophilization. The purity of the compound was checked by TLC, continuous electrophoresis, and ion-exchange chromatography.

MSC: mp 207–209 °C; IR (KBr) ν(OH) 3650 (s), ν_s(C=C—C=O) 1720 (s), ν_{as}(C=C—C=O) 1640 (s), 1615 (s), 1583 (s), ν(C=C), benzene, pyridine 1555 (m) cm^{-1}; UV λ_{max} 197, 390 (H_2O) nm; NMR (methanol-d_4) τ_{Me_4Si} 8.6 (3 H, t, CH_3C), 8.1 (3 H, s, CH_3C=C), 6.65 (2 H, q, CH_2N^+), 5.85 (2 H, CH_2O). Anal. Calcd for $C_{21}H_{24}NO_4Cl$: C, 64.69; H, 6.20; N, 3.59; Cl, 9.10. Found: C, 64.51; H, 6.47; N, 3.39; Cl, 9.29.

3. 1-(δ-Bromobutyl)-4-(3-ethoxy-4-hydroxystyryl)pyridinium Bromide (BSB). SP was dissolved in a mixture of acetone and 1,4-dibromobutane; the mixture was heated for 17 h at 35 °C and for 7 h at 55 °C. The orange precipitate which formed was filtered off and recrystallized twice from methanol/acetone.

BSB: yield 55%; mp 188.5 °C. Anal. Calcd for $C_{19}H_{23}NO_2Br_2$: C, 49.91; H, 5.07; N, 3.06; Br, 34.95. Found: C, 49.81; H, 5.04; N, 3.47; Br, 34.87.

4. 4-(Dodecanoylamino)benzoic Acid (C_{12}BA). C_{12}BA was prepared by reaction of the acid chloride with 4-aminobenzoic acid in dioxane in the presence of triethylamine. C_{12}BA was crystallized from methanol and heptane/dioxane (1:1 by volume).

C_{12}BA: mp 233.5 °C. Anal. Calcd for $C_{19}H_{29}NO_3$: C, 71.47; H, 9.09; N, 4.39. Found: C, 71.14; H, 9.35; N, 4.74.

5. Poly[4(5)-vinylimidazole] (PVIm). 4(5)-Vinylimidazole (10 g, 0.1 mol) and 2,2′-azobis(2-methylpropionitrile) (0.2 mol % based on VIm) were dissolved in 200 mL of benzene. The ampule was sealed after three freeze–thaw cycles under nitrogen. Polymerization was carried out at 65 °C for 24 h. The polymer was precipitated four times from methanol in benzene.

PVIm: yield 65%; [η] 0.63 dL/g (methylcellosolve/0.045 M KCl, 25 °C). Anal. Calcd for $(C_5H_6N_2)_x$: C, 63.80; H, 6.43; N, 29.77. Found: C, 61.74; H, 6.82; N, 26.41.

For measurement of the sorption properties of PVIm by means of equilibrium dialysis, low molecular weight PVIm was removed by gel filtration on Sephadex LH 20 and by dialysis.

6. Copolymerization of VIm with MSC. Copolymerization of VIm with MSC was carried out in methanol (copolymer PVIm-I) in the same way as the homopolymerization of VIm. The polymer formed was precipitated twice from methanol into acetone and finally dialyzed from methanol/water (1:1 by volume) and isolated by precipitation in acetone.

7. BSB-Modified PVIm (PVIm-II). Alkylation of the imidazole residues in PVIm was carried out analogously to the preparation of *N*-alkyl-substituted imidazoles.[10] A solution of PVIm (0.7 g) and BSB (0.05 g) in a mixture of dioxane (8 mL), water (2 mL), and 0.2 mL of 2 N KOH was heated for 2 h at 55 °C. The polymer was precipitated in acetone and purified like polymer PVIm-I.

B. Molecular weights, $\bar{M}_w$, were determined by light scattering. Intensities of the scattered light were measured on a Photo-Gonio-Diffusomètre Sofica, using unpolarized light, λ 546 nm. The refractive index increments, d*n*/d*c*, were measured at 25 ± 0.2 °C on a Brice-Phoenix differential refractometer Model BP-2000-V, calibrated at λ 546 nm. For the evaluation of the true molecular weight of the polymer in mixed solvents refractive increments were measured after attaining dialysis equilibrium between the polymer solution and the mixed solvent[11,12] $(dn/dc)_\mu$. Equilibrium dialysis and determination of $(dn/dc)_\mu$ were described elsewhere.[13]

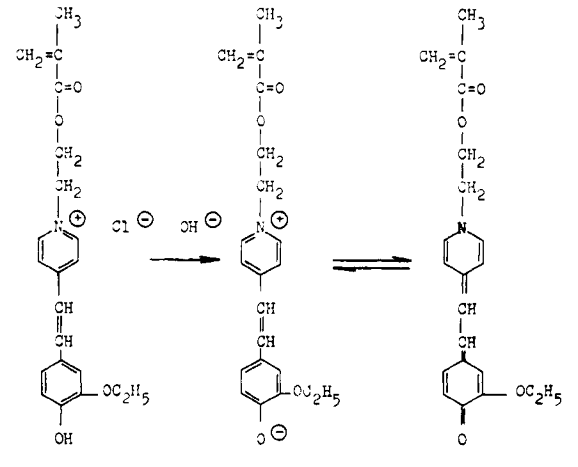
The coefficient of selective sorption γ was calculated by $\gamma = [(dn/dc)_\mu - dn/dc]/(dn/dc_s)$, where dn/dc_s is the refractive index increment of the solvent component whose sorption is followed in the absence of the polymer. In the case of the mixtures methylcellosolve/0.05 M LiCl and methylcellosolve/0.1 M LiCl, $dn/dc_s = 0.27$ mL/g.

Viscosity measurements were carried out in an Ubbelohde viscometer at 25 °C.

C. Potentiometric Titrations. Solutions of PVIm in methanol/51.5 vol % H_2O (0.02 g of PVIm, 25 mL of 8×10^{-3} M KCl, ionic strength 0.05 M) were titrated with 1 N HCl and 1 N KOH in the same solvent at 25 °C under a nitrogen atmosphere. The pa_H* was measured on a Radelkis OP-205 (Hungary) pH meter after stirring for at least 5 min so that electrode equilibrium was attained. The results obtained in this way were equal to results of titrations when a solution of PVIm with hydrochloric acid was retitrated with potassium hydroxide. The glass electrode response was checked against buffers[14] in methanol/51.5 vol % H_2O in the region of 1.7–11.3 units[15] pa_H*. The glass electrode was equilibrated in methanol/water of the same composition.

D. Spectrometric Titration of MSC. Spectrometric titration methods were used to determine pK_a and $(pK_a)a_H$* of the solvatochromic compound (MSC) in water and in methanol/51.5 vol % H_2O. The solvatochromic compound possesses in aqueous buffers two absorption maxima, λ_{MSC} 384.7 nm (neutral form, MSC at pH ≤6) and λ_{SB} 465 nm (basic form, SB at pH ≥11) with an isosbestic point at λ 412 nm (Scheme I). A solution of the solvatochromic compound MSC in water solution of Tris buffer was titrated with concentrated hydrochloric acid or sodium hydroxide. The degree of ionization of the solvatochromic compound MSC was calculated according to Stenström and Goldsmith[16] and the p*K* value was evaluated by the Henderson–Hasselbach equation by plotting log $[(1 - \alpha)/\alpha]$ vs. pH. In the same way the

Scheme I



MSC SB

$(pK_a)a_H$* value of the solvatochromic compound MSC was determined in methanol/51.5 vol % H_2O.

E. Polarity of Solvents and Polarity of the Microenvironment of Polymers. The determination of the polarity of the solvents and the polarity of the microenvironment of the synthetic polymers was described elsewhere.[4] Solvents used were of the same quality.

F. Characterization of Monomers and Polymers. IR spectra were taken on a Perkin-Elmer 325 and UV-visible spectra were taken on a Cary 14 and a Specord UV-VIS (Zeiss Jena, GDR). NMR spectra were taken on a Varian XL-100.

Results and Discussion

Solution Properties of PVIm. The viscosity behavior of poly[4(5)-vinylimidazole] in one-component and especially in binary mixtures of alcohol/water can give basic information regarding the behavior of this polymer in solution and its interactions. PVIm is soluble in methanol and methylcellosolve; in ethanol and in propanol it is soluble only at elevated temperatures. At 25 °C the polymer is soluble in dioxane/33-87 vol % H_2O, ethanol/5-70.5 vol % H_2O, and 1-propanol/7-87 vol % H_2O.

PVIm behaves in methylcellosolve, in ethanol/water, and in dioxane/water like a polyelectrolyte. The polyelectrolyte effect was wholly eliminated by addition of lithium chloride or potassium chloride. The molecular weights were determined by light scattering in methylcellosolve and in the binary mixtures ethanol/water in the presence of lithium chloride, using refractive index increments measured at dialysis equilibrium between the polymer solution and solvent. The average value of $\bar{M}_w$ from data in different media (Table I) is 170 × 10^3.

In solutions of polyelectrolytes, low molecular weight salt is excluded from the polymer domain by the Donnan equilibrium.[11] The positive value of the coefficient of selective sorption of lithium chloride on the polymer in the system PVIm/MSC/LiCl (Table I) suggests a specific interaction between lithium chloride and the polymer, involving probably the imidazole residues.

The dependence of the intrinsic viscosity of PVIm on the composition of ethanol/water mixtures in the presence of lithium chloride (Figure 1) is typical of cosolvent systems. In analogy with similar systems[13,17] we suppose that, while at the composition corresponding with the maximum of the dependence in (Figure 1) ethanol/35 vol % water selective sorption does not take place, at other compositions of the mixture, the component present at lower concentration is selectively sorbed. A similar dependence of the specific viscosity on the composition of ethanol/water mixtures (without salt) possessing a maximum for the mixture ethanol/40 vol % water was described elsewhere.[8] The quantitative determination of the coefficient of selective sorption of water or ethanol on PVIm (as in the case of MSC/LiCl mixture) is not possible. The indices of refraction of water and ethanol are too similar and the presence of lithium chloride introduces an additional complexity.

Table I
Light Scattering and Refractometric Data for Poly[4(5)-vinylimidazole]

solvent	dn/dc	$(dn/dc)_\mu$[a]	γ_{LiCl}[b]	$10^{-3}\bar{M}_w$
methylcellosolve/0.05 M LiCl	0.167	0.177	0.036	148
methylcellosolve/0.010 M LiCl	0.165	0.175	0.037	185
ethanol/20 vol % water/0.01 M LiCl	0.195	0.195		148
ethanol/40 vol % water/0.1 M LiCl	0.189	0.181		169
ethanol/60 vol % water/0.1 M LiCl	0.195	0.195		194

[a] Refractive index increment at conditions of equilibrium dialysis between polymer solution and solvent.
[b] Coefficient of selective sorption (g/g).

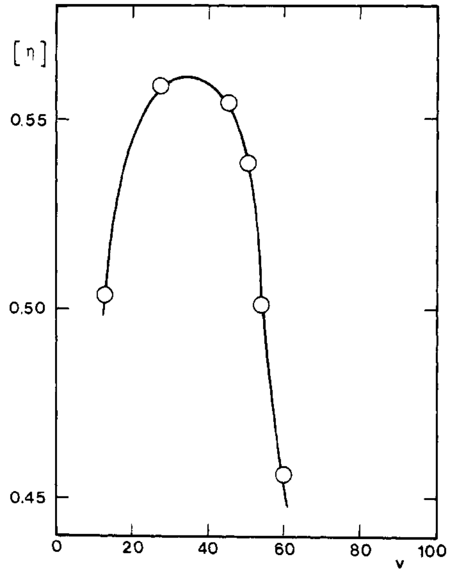
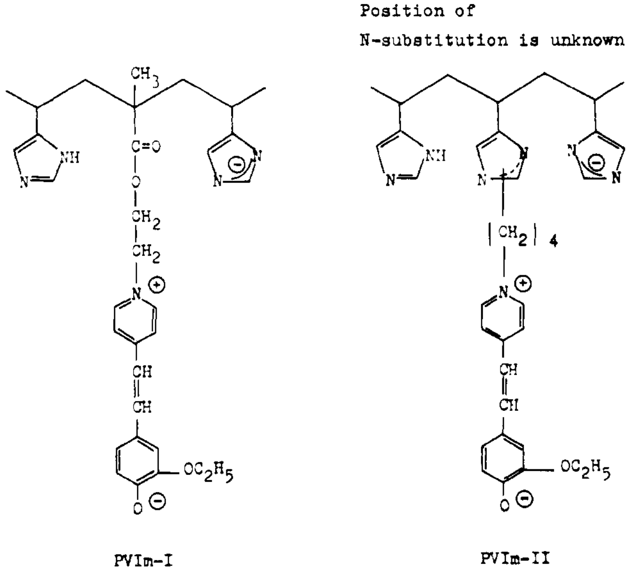


Figure 1. Dependence of the intrinsic viscosity [η] (dL/g) on the composition (v) of the ethanol/water/0.1 M LiCl mixture. v is the volume percent of water.

The selective sorption of water on PVIm in ethanol/water mixtures containing more than 65 vol % of the ethanol is more likely to be the reason for the relative increase of the rate of p-nitrophenyl acetate and p-nitrophenyl heptanoate hydrolysis catalyzed by PVIm and imidazole than a conformational change of the PVIm.[8] The selective sorption of water on PVIm causes a relative increase in the polarity of the microenvironment of PVIm (see following section) as compared with the ethanol/water mixture, leading to a relative increase of the rate of hydrolysis. The rate of hydrolysis catalyzed by imidazole itself is strongly dependent on the water content in the reaction medium.[8]

Potentiometric and Spectrometric Titrations. In order to determine the degree of ionization of PVIm during the estimation of the polarity of the microenvironment of PVIm, we determined the apparent dissociation constants, Scheme II



$(pK_1')a_H{}^*$ and $(pK_2')a_H{}^*$, for PVIm and pK of the solvatochromic indicator of polarity. The dependence of log $[(1 - \alpha_1)/\alpha_1]$ vs. $pa_H{}^*$ for PVIm in methanol/51.5 vol % H_2O at 25 °C is linear and obeys the modified Henderson–Hasselbach equation,[18] where α_1 is the fraction of the neutral imidazole residues in the polymer. The $(pK_1')a_H{}^*$ for the dissociation of the protonated form determined under these conditions is 6.20, $n' = 2.0$. Similarly $(pK_2')a_H{}^*$ was determined as 7.3. In this case the Henderson–Hasselbach plot was not linear.

The location of the absorption maximum of the solvatochromic compound is sensitive to the polarity of the environment only in the SB form (Scheme I).

The solvatochromic compound is essentially an acid–base indicator. For this compound a dissociation constant $pK_a = 8.55$ was determined in water and $(pK_a)a_H{}^* = 9.30$ in methanol/51.5 vol % H_2O.

Estimation of the Polarity of the Microenvironment of PVIm. In a number of reactions, including solvolytic reactions, the reaction rate is influenced by the polarity of the medium.[5] However, the catalytic activity of the polymer as compared with that of a low molecular weight catalyst can also be influenced by preferential sorption of one component of the binary mixture on the polymer and a restricted solvation in the neighborhood of the polymer chain. These effects can be detected semiquantitatively by microenvironment polarity labels bound on polymers,[4] where the polarity of the microenvironment of the polymer in a solvent and the polarity of the same solvent are compared by the energy of the solvatochromic label in the visible region of the spectrum. Two different modified polymers, PVIm-I and PVIm-II, were prepared for the estimation of the polarity of the microenvironment of PVIm (Scheme II).

The polymer prepared by copolymerization (PVIm-I) or by modification of PVIm (PVIm-II) contained a small quantity (less than 0.1 mol %) of the solvatochromic label. The polarity of solvents was expressed by the energy of the CT absorption band of the solvatochromic form of monomer MSC and compound BSB. The spectral properties of the reporter SB were previously described.[4] It was found that the energy of the solvatochromic CT absorption band is identical in compounds BSB and MSC in the same solvent.

Table II
Polarity of the Microenvironment of PVIm in One-Component Solvents

	E_T, kcal/mol			
	model compound			
solvent	MSC	BSC	PVIm-I	PVIm-II
methanol	54.38	54.33	53.18	54.32
methylcellosolve	52.15	52.21	52.20	52.38
ethylcellosolve	51.23	51.38	52.20	

The difference in the type of substituent on the nitrogen atom of the solvatochromic compound does not influence its spectral properties in the visible region of spectrum. The polarity of the microenvironment of PVIm-I and PVIm-II was studied in methanol, methylcellosolve, and ethylcellosolve (Table II) and in the binary mixtures methanol/water, ethanol/water, 1-propanol/water, *tert*-butyl alcohol/water, and dioxane/water.

The difference between the energy of the CT absorption band for solutions of polymer PVIm-I or polymer PVIm-II and the energy of the CT absorption band for solutions of the reporter in the same medium represents the difference between the polarity of the microenvironment of the polymer and the polarity of the polymer-free medium. For polymer PVIm-I the local polarity in the vicinity of the polymer chains was in all cases lower than that of the binary solvents used. In all cases the CT absorption band of the reporter in PVIm-II was shifted to shorter wavelengths in comparison with the CT absorption band for PVIm-I in the same solvent.

This demonstrates that the polarity of the medium surrounding the reporter in PVIm-II is higher. A great difference in E_T values for PVIm-I and PVIm-II was observed in methanol (Table II). The polarity of the microenvironment of PVIm-I in methylcellosolve is equal to the polarity of methylcellosolve itself, while in ethylcellosolve the polarity of the microenvironment of PVIm-I is higher than that of ethylcellosolve. The above results suggest that PVIm in the anionic form is relatively polar. Under the conditions employed during the study of the polarity of the microenvironment of PVIm, i.e., at $pa_H \sim$ 8.6–9.0, PVIm is partially in the anionic form (~70–80%). In ethylcellosolve PVIm-II was insoluble. The difference between the energy of the CT absorption band for PVIm-I and PVIm-II in particular solvents is caused by a different distance of the solvated reporter group from the polymer backbone.

In the case of PVIm-II, the dipole formed between the nitrogen and oxygen atoms of the reporter is bound to the imidazole ring through a tetramethylene link and is located there beyond the side chains of the polymer. Therefore the reporter group is more easily solvated, and shielding by the polymer side chains and the polymer backbone is less effective than in the case of PVIm-I. Selective sorption also plays an important role. The differences found between PVIm-I and PVIm-II suggest that the above-mentioned effects, which cause the microenvironment of the polymer to be different from the bulk solution, are limited to the immediate vicinity of the polymer chain.

PVIm behaves in all the above-mentioned solvents as a polyelectrolyte. The influence of the polymer expansion on the polarity of the microenvironment of PVIm was followed by suppression of the polyelectrolyte effect by an increase of the ionic strength. For PVIm-II and the solvatochromic form of BSB in ethanol/50 vol % H_2O and 1-propanol/50 vol % H_2O it was found that a suppression of the polyelectrolyte effect by addition of KCl (0.0–0.5 M) does not lead to a shift in the maximum of the CT solvatochromic band; i.e., it does not influence the polarity

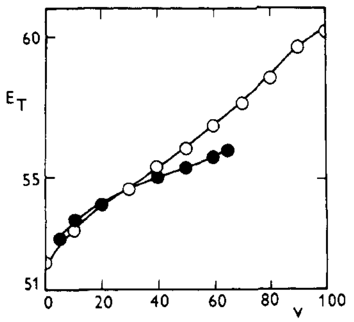


Figure 2. Dependence of the polarity (E_T) of the binary solvent ethanol/water (○) and the polarity of the microenvironment of PVIm-II (●) on the solvent composition (v). E_T is the energy of the CT absorption band of the solvatochromic chromophore (kcal/mol) and v is the volume percent of water.

of the microenvironment of the polymer. On this basis one may conclude that the polarity of the microenvironment of PVIm and also of the other polymers is not influenced by their expansion.[4]

In cosolvent mixtures (for example, ethanol/water) (Figure 2) containing a low fraction of water, where selective sorption of water on PVIm takes place, it was observed that the polarity of the microenvironment of PVIm-II is higher than the polarity of the solvent used. On the other hand, selective sorption of alcohol diminishes the polarity of the microenvironment of PVIm; at a lower content of alcohol in the binary mixture a higher difference between the polarity of the microenvironment of the polymer and the polarity of the solvent was observed.

The dramatic rate-enhancing effect of a long aliphatic chain carried by esters on the esterolytic action of polymeric imidazole in binary mixtures with high contents of water is most probably caused by an increase in concentration of substrate at the reaction site due to the hydrophobic sorption of the substrate on the polymer chain.[3] We tried to prove independently the hydrophobic sorption of the compounds possessing the aliphatic long-chain moiety on this polymer mainly by measurement of the dialysis equilibria.

Hydrophobic Sorption of the Compounds with Aliphatic Long Chains on PVIm. In the course of the study of the polarity of the microenvironment of PVIm, we found that in some solvents the polarity of the microenvironment of PVIm can be lower than that of the solvent used. It may be assumed that in these systems the hydrophobic sorption of compounds with long aliphatic chains on PVIm takes place.

To establish unequivocally whether or not compounds with aliphatic long chains are sorbed on PVIm and to confirm the role of hydrophobic sorption of substrate on solvolysis, we prepared a compound with an aliphatic long-chain moiety similar to the substrate used for solvolytic measurements. 4-(Dodecanoylamino)benzoic acid ($C_{12}BA$) is not hydrolyzed under the conditions of equilibrium dialysis.

After removal of the low molecular weight fraction of PVIm from the sample used for the dialysis measurements, the hydrophobic sorption of $C_{12}BA$ on PVIm was proved. The sorption of $C_{12}BA$ on the polymer chain of PVIm was studied in aqueous ethanol containing 67, 50, and 30 vol % H_2O. It was found that sorption of $C_{12}BA$ on the dialysis membrane does not take place in the above-mentioned binary solvents. Figure 3 shows the dependence of the molar fraction of the sorbed $C_{12}BA$ on the concentration of PVIm for these binary mixtures. It can be seen that with increasing content of ethanol in the ethanol/water mixtures the sorption of $C_{12}BA$ on PVIm decreases and at 67 vol % ethanol in the mixture no sorption occurs. This is in agreement with a decreasing difference between the polarity of the microenvironment of PVIm and the polarity of the solvent (Figure 2).

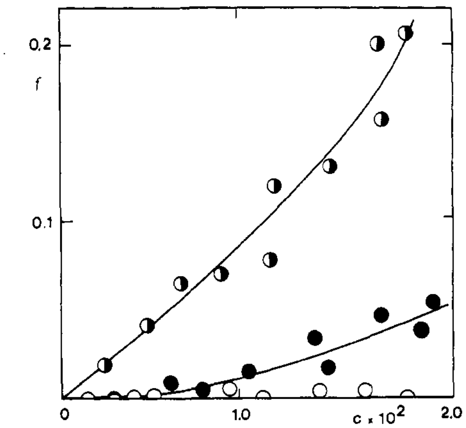


Figure 3. Dependence of the amount (f) of 4-(dodecanoylamino)benzoic acid ($C_{12}BA$) sorbed by the polymer on the concentration of PVIm (c) (mol of VIm/L) in ethanol/water mixture: (◐) 67, (●) 50, (○) 30 vol % water. f is the molar fraction; concentration of $C_{12}BA$, 5×10^{-5} M.

From the amount of sorbed $C_{12}BA$ on PVIm we tried to evaluate the increase of the local concentration of $C_{12}BA$ in the polymer domain where the catalyzed reaction takes place and to estimate the influence of this effect on the hydrolysis of hydrophobic-active esters catalyzed by PVIm.

The volume in which the increase of the concentration of $C_{12}BA$ caused by sorption on the PVIm occurs was approximated by the volume of a domain of the polymer chain $V = \pi r^2 L_{max}$, where r is the radius of the domain of the polymer chain and L_{max} is the length of extended chain with a valence angle of 109.5°.

It is very difficult not only to define the domain of the polymer chain where due to sorption the concentration of substrate is increased but also to estimate the dimension of this domain. The forces which participate in the hydrophobic interactions are largely short range.[19] For this reason we propose a small radius (6 Å) for the sorption domain of the polymer coil. The calculated local concentration of $C_{12}BA$ in the domain of PVIm with a molecular weight of 170×10^3 and a concentration of 5×10^{-4} mol./L (VIm), when 0.5% of $C_{12}BA$ present at an initial concentration of 5×10^{-5} M was sorbed from ethanol/67 vol % H_2O, is 2.9×10^{-3} M. This represents a 58-fold increase of concentration of $C_{12}BA$ from the bulk of the solution.

Thus, we may conclude that the increase of the concentration of the hydrophobic substrate in the domain of polymer chain is an important factor causing an increase in the rate of hydrolysis of active esters. The quantitative evaluation of this effect from a kinetic point of view is now being studied.

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Elongational Deformation by Shear Flow of Flexible Polymers Adsorbed in Porous Media

Ph. Gramain* and Ph. Myard

CNRS, Centre de Recherches sur les Macromolécules, 67083 Strasbourg-Cedex, France.
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ABSTRACT: We have studied the influence of a shear flow on the configuration of flexible polymers adsorbed in porous media. High molecular weight fractions of polyacrylamide and polystyrene were adsorbed from solution onto commerical filters of different nature and structure and the thickness of the adsorbed layers was studied by using a hydrodynamic method based on Poiseuille's law. An abrupt coil-stretch transition was observed when the velocity of the solvent flowing through the pores was increased. The observed hydrodynamic thickness increased by a factor of 3–6, depending on the molecular weight of the adsorbed polymers. We have deduced that the number of trains in contact with the surface is very low, about 3 or 4, leading to a model of spotwise adsorption with a low surface attraction, and that a net circulation of solvent exists in the layer. By studying the influence of the pore size, we have shown that the parameter governing the stretching is not the transverse velocity gradient but the average velocity of the solvent into the pores. We conclude that the acting velocity gradient is in the axial direction and results from the nonuniform structure of the adsorbed layer which can be viewed as a monolayer stacking of semipermeable prolate spheroids.

The increasing amount of work on the adsorption of macromolecules from solution onto solid surfaces can be well understood, considering the theoretical and practical interest of the subject. One of the most spectacular effects of such adsorption is the restriction of flow in capillaries due to the effective decrease in size. Such an effect influences many processes, such as filtration, ultrafiltration, liquid chromatography, and, more recently, oil recovery by injection of a polymer into the oil-bearing rock. On the other hand, this phenomenon is the basis of an interesting method with which to study the thickness of the adsorbed layer.[1-5] This method has been developed in our laboratory and leads to very interesting results based upon the iteraction of the flowing phase with the adsorbed polymer. Du[illegible] the tendency for a flexible macromolecule to adsorb with free loops of segments extended out into the solution phase, one can foresee that strong interaction with the flow can lead to a deformation of the adsorbed layer. Very little has been published on this subject. In 1978, Varoqui et al.[4] detected no effect of the applied pressure on the thickness of the adsorbed layers of polystyrene. However, their results are limited to the cases of intermediate molecular weights and a rather low pressure difference. Silberberg[6] observed a tremendous reduction of throughput at high applied pressure gradient for polyacrylamide gels coated on tubes.

The purpose of this paper is to present evidence of such deformation and to study the different parameters governing this phenomenon.

The basic experimental method used has already been described.[2] The permeability of a porous medium is measured before and after adsorption by solvent flow. If ϕ_0 and ϕ are the flow rates due to a given pressure drop, measured before and after adsorption, the permeability reduction is given by $R_k = \phi_0/\phi$. In the case where the size of the pores is known, the use of Poiseuille's law leads to the value L_H for the hydrodynamic thickness of the adsorbed layer

$$L_H = \bar{r}[1 - (\phi/\phi_0)^{1/4}]$$

where $\bar{r}$ is the radius of the pores or an appropriate average in case of a pore-size heterogeneity. The commercial filters used as porous media in this study present a nonnegligible pore-size heterogeneity and a complete analysis of this influence on the value of L_H demands an extensive characterization of the filters, but this is beyond the scope of this paper where we are mainly interested in the relative variations of L_H. However, a quick analysis of this problem[3] shows that the error becomes negligible for small values of $L_H/\bar{r}$ corresponding to $\phi/\phi_0 < 0.5$.

Experimental Section

Porous Media. Three different types of commerical filters have been used as porous media. Their characteristics are presented in Table I. Millipore filters are made of a mixture of cellulose esters, Sartorius filters are made of cellulose nitrate, and Nuclepore filters consist of polycarbonate. In contrast with the first two types, which have a spongy structure, Nuclepore filters offer nice cylindrical pores. All the filters were repeatedly washed

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