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Vapor-Sorption Equilibria for 4-Vinylpyridine-Based Copolymer and Cross-Linked Polymer/Alcohol Systems. Effect of "Intramolecular Repulsion"

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ABSTRACT: Solvent activity data were obtained for three alcohols (methanol, 2-propanol, *tert*-butyl alcohol) in 4-vinylpyridine (4VP)-based polymers using a classical isothermal gravimetric-sorption method. The polymers were linear poly(4-vinylpyridine) ($M_w = 160\,000$), cross-linked poly(4-vinylpyridine) with 2 and 25 wt % divinylbenzene as cross-linking agent, random copolymers poly(4-vinylpyridine-*co*-styrene) (P4VP-*co*-S) (10 and 50 wt % styrene), and block copolymer P4VP-*b*-S (50 wt % styrene). The temperature range was 55−70 °C. Sorption in P4VP-*co*-10%S copolymer is significantly higher than that in the respective homopolymers. Sorption in P4VP-*co*-50%S is close to that in linear P4VP, while the sorption curve (solvent activity vs solvent weight fraction) for P4VP-*b*-50%S lies in between those for the two parent homopolymers. For cross-linked P4VP, the amount of solvent absorbed by the polymers strongly depends on the weight fraction of the cross-linking agent. When solvent activity is plotted as a function of solvent weight fraction for various degrees of cross-linking, there is an unexpected crossover among the curves. At low solvent activity, the largest sorption was for the 25% cross-linked polymer and the lowest for the linear polymer; however, at high solvent activity the curves switch position, and the linear poly(4-vinylpyridine) absorbs more than the cross-linked poly(4-vinylpyridine). This unusual behavior may be explained by "intramolecular repulsion" between bonded unlike segments (4-vinylpyridine and styrene/divinylbenzene in un-cross-linked/cross-linked copolymers, respectively) and by elastic contributions to the solvent chemical potential in cross-linked P4VP. In block copolymers, segregated sequence of the unlike monomers minimizes the effect of "intramolecular repulsion".

Introduction

Polymer−solvent equilibria are needed for a variety of applications in polymer production and purification processes, including, for example, recovery of organic compounds from waste air streams using a polymeric membrane;[1,2] pervaporation[3] and other membrane separation processes; surface acoustic-wave vapor sensor,[4,5] vapor-phase photografting;[6] polymer devolatilization;[7,8] and for optimum formulation of paints and coatings.[9] Moreover, experimental equilibrium data are required to develop or test molecular thermodynamics models for polymer solutions.

Reliable experimental vapor−liquid equilibrium (VLE) data for polymer solutions are not plentiful, and many literature data are frequently available for only a limited concentration range of sorbed solvent. Experimental VLE data are particularly rare for copolymers,[10−19] for cross-linked polymers,[20−28] and for polymers with unusual or well-defined architecture, as brush[29] and comb polymers,[30] arborescent,[31] starlike polymer,[32] and dendrimers.[33,34] However, copolymers and polymers with unusual structure are currently of increasing commercial interest because of their particular chemicophysical properties for potential applications.

The purpose of this work is to extend our knowledge of vapor-sorption behavior of copolymers and cross-linked polymers. For copolymer−solvent systems, we examine the effect of copolymer "intramolecular repulsion" by comparison with the properties of the parent homopolymers; for cross-linked polymer−solvent systems, we examine the effect of elastic forces by comparison with the solution properties of corresponding linear polymers.

The terms "repulsion", "intramolecular repulsion", and "repulsion effect" are used in this paper to refer to an unfavorable A−B interaction between unlike bonded segments in a copolymer molecule, described by a positive Flory−Huggins parameter χ_{AB}. We follow here the terminology used by others.[35−38] However, some authors[39] discourage use of this terminology because no repulsive interaction exists between the neighboring pairs of unlike segments within random copolymers, except for charged segments. All interaction energies ϵ_{AB} are attractive (negative), while the Flory−Huggins interaction parameter χ_{AB}, proportional to $(2\epsilon_{AB} - \epsilon_{AA} - \epsilon_{BB})$, is positive in the majority of those cases where specific A−B interactions do not occur.

To our best knowledge, no previous studies have been reported on the effect of "intramolecular repulsion" on VLE of cross-linked polymers, and only a few papers have been published concerning "intramolecular repulsion" in copolymer/solvent systems.[12,30] However, much attention has been given to the influence of "intramolecular repulsion" on miscibility in polymer blends.[35,36,39−42] Miscibility studies have shown that, when at least one component is a statistical copolymer, miscibility in copolymer−homopolymer blends can occur for a defined copolymer composition window even if none of the parent homopolymers are mutually miscible. The condition necessary to reach miscibility is that "intramolecular repulsion" between bonded unlike segments in the copolymer is sufficiently large to produce an exothermal enthalpy of mixing when polymers are blended. The mixing process causes a dilution of the unfavorable

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Table 1. Polymer Properties[a]

homopolymer	M_W	T_g (°C)	lot no.	supplier
P4VP	160 000	154.0	12338MS	Aldrich
PS	382 100	107.5	11538MS	Aldrich

copolymer	M_W	wt % styrene	T_g (°C)	lot no.	supplier
P4VP-*co*-10%S	1 200 000−1 500 000	10	149.4 (148.8)[b]	03001HN	Aldrich
P4VP-*co*-50%S	60 000	50	128.2 (129.4)[b]	03	Sp^2
P4VP-*b*−50%S	47 600[c]	50	107.0; 151.0[d]		Polymer Source

cross-linked	wt % DVB	T_g (°C)	lot no.	supplier
c-P4VP/2% DVB	2	156.6	16312LR	Aldrich
c-P4VP/25% DVB	25		03505AQ	Aldrich

[a] P4VP = poly(4-vinylpyridine); PS = polystyrene; S = styrene; DVB = divinylbenzene. [b] Glass transition temperature in parentheses calculated by eq 1. [c] M_n: PS (21 400), P4VP (20 700); $M_w/M_n = 1.13$ [d] Two glass transition temperatures: $T_{g,p1} = 107.0$ °C for PS block, $T_{g,p2} = 151.0$ °C for P4VP block.

Table 2. Solvent Properties

solvent	T^{exp} (°C)	P^{sat} (Torr)	supplier	lot no.	purity (%)
methanol	55	515	Fisher	992326	99.9
methanol	70	938	Fisher	992326	99.9
2-propanol	70	455	Fisher	992487	99.9
tert-butyl alcohol	70	458	J.T. Baker	8210519	99.9

interaction between the two copolymer units; the contribution of this dilution to the total enthalpy of mixing reduces the conventional endothermic enthalpy of solution that prevents miscibility. Moreover, it has been shown that the extent of the "intramolecular repulsion" effect is closely related to repeat-unit sequence: miscibility improves with alternating sequence distribution and decreases with polymer blockiness.[37,38]

To study the "intramolecular repulsion" effect and the effect of elastic forces on VLE for binary polymer/solvent mixtures, we chose some 4-vinylpyridine (4VP)-based polymers and alcohol solvents (methanol, 2-propanol, and *tert*-butyl alcohol). The polymers were P4VP and PS, random copolymers P4VP-*co*-10%S and P4VP-*co*-50%S, block copolymer P4VP-*b*-50%S, and cross-linked poly(4-vinylpyridine) with 2% (c-P4VP/2%DVB) and 25% (c-P4VP/25%DVB) divinylbenzene as cross-linking agent.

P4VP and its cross-linked form with divinylbenzene are useful as ion-exchange resins,[43−46] for gas-separation membranes,[47,48] for wastewater-treatment membranes,[43,49] and for recovery of organic compounds such as aliphatic alcohols,[50] phenols,[51,52] carboxylic acids,[53,54] and inorganic acids.[55] Copolymers P4VP-*co*-S are useful for enzyme immobilization and for biosensors,[56−58] while block copolymers P4VP-*b*-S serve as compatibilizers for polymer blends.[59,60]

Experimental Section

Materials. All polymers were supplied by Aldrich, except copolymers P4VP-*co*-50%S and P4VP-*b*-S, which were obtained respectively from Scientific Polymer Products and from Polymer Source. Table 1 gives weight-average molecular weights of linear P4VP and polystyrene PS and copolymers P4VP-*co*-S; cross-linking-agent weight percents for cross-linked P4VP; styrene content for P4VP-*co*-S; and glass-transition temperatures for each polymer. With the exception of PS and P4VP-*b*-S, both copolymers and linear P4VP are polydisperse; provided that the polymer is not glassy or crystalline and provided that $M_w > 10\,000$,[17,61] polymer molecular weight has little effect on VLE. For random copolymers, polydispersity of chemical composition also has little effect on VLE.[61] All the polymers are in powdered form.

Table 2 gives solvent characteristics: supplier, purity, and vapor pressures at the experimental temperatures. Pure-solvent vapor pressures P_1^{sat} are calculated using the equation suggested by Daubert and Danner.[62] The solvents, degassed with a standard freeze−thaw procedure described by Panayiotou and Vera,[16] were used without further purification.

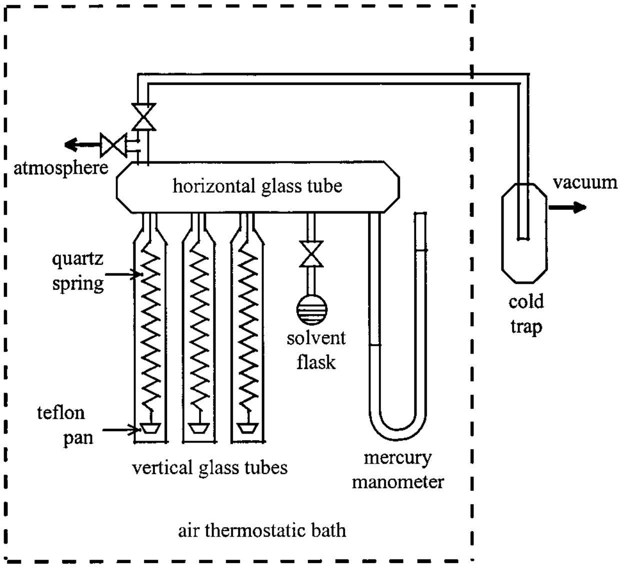

Figure 1. Schematic diagram of the experimental apparatus for VLE measurements.

Experimental Apparatus and Procedure. Solvent activities were measured using a classic gravimetric sorption technique. Because the experimental pressure is always lower than 1.5 bar, we consider the vapor phase as ideal gas. The solvent activity in the vapor phase is the ratio of solvent pressure (P) to the pure-solvent vapor pressure at the experimental temperature.

Figure 1 shows a schematic diagram of the apparatus. The apparatus and the experimental procedure have been described in detail by Panayiotou and Vera[16] and by Gupta and Prausnitz.[14]

The amount of solvent absorbed by a polymer is measured at increasing solvent pressure, typically through steps of 1/10 of solvent vapor pressure (P_1^{sat}). To avoid solvent condensation in the system, all experimental data are below $0.90{-}0.95P_1^{sat}$. The solvent pressure is read from a mercury manometer with an uncertainty of 1 Torr. The solvent weight fraction is calculated by measuring the elongation of calibrated quartz springs with sensitivity of about 1 mm/mg using a cathetometer (model KM274, Heerbrugg, Switzerland) with a precision of 0.1 mm. Uncertainty in the solvent weight fraction w_1 is 2−5% above $w_1 = 0.1$ and increases to 5−10% below $w_1 = 0.1$. The temperature is controlled with an air bath within 0.3 °C.

A small amount of polymer (15−25 mg) is loaded in each Teflon pan that hangs from the calibrated spring. Before solvent is admitted, the glass chambers containing the polymer

Table 3. Systems Studied

polymer	solvent	*T* (°C)
homopolymer		
P4VP	methanol	55
P4VP	methanol, 2-propanol, *tert*-butyl alcohol	70
PS	methanol, 2-propanol	70
copolymer		
P4VP-*co*-10%S	methanol, 2-propanol	70
P4VP-*co*-50%S	methanol, 2-propanol	70
P4VP-*b*-50%S	methanol, 2-propanol	70
cross-linked polymer		
C-P4VP/2%DVB	methanol	55
C-P4VP/2% DVB	methanol, 2-propanol, *tert*-butyl alcohol	70
C-P4VP/25% DVB	methanol	55
C-P4VP/25% DVB	methanol, 2-propanol, *tert*-butyl alcohol	70

samples are evacuated to remove volatile low-molecular-weight impurities including air. The capacity of the apparatus to keep the desired vacuum is tested before each experiment: the apparatus is acceptable if the pressure reading does not change within the experimental error in 24 h.

Table 3 lists the binary systems studied, and the Supporting Information gives experimental results.

Glass-Transition Temperature. The glass-transition temperature T_g for each polymer was measured with a differential scanning calorimeter (Seiko DSC6200). First, the polymers were heated to 150 (PS), 200 (P4VP, P4VP-*b*-50%S, P4VP-*co*-10%S, and P4VP-*co*-50%S), and 250 °C (c-P4VP/2%DVB) using a heating rate of 10 °C/min. The polymers were held at these temperatures for 10 min, cooled at room temperature, and heated again over the glassy transition temperature at the same rate. Recorded glass transitions are for the second heating step.

No glass transition was detected in the 25% cross-linked P4VP in the range 25−350 °C; the latter temperature is close to the thermal degradation temperature ($T_{deg} = 330-380$ °C) of P4VP.[63−65] For random copolymers P4VP-*co*-S, T_g was also calculated using the Flory−Fox[66] equation:

$$\frac{1}{T_g} = \frac{w_{p1}}{T_{g,p1}} + \frac{w_{p2}}{T_{g,p2}} \qquad (1)$$

where T_g is the glass-transition temperature of the copolymer, $T_{g,p1}$ and $T_{g,p2}$ are the glass-transition temperatures of the parent homopolymers, and w_{p1} and w_{p2} are the mass faction of the parent monomers. Table 1 shows measured glass-transition temperatures. Measured T_g and those calculated by eq 1 are in very good agreement.

Results and Discussion

To present our data, we plot solvent activity a_1 as a function of the solvent weight fraction in the polymer phase w_1.

Copolymers P4VP-*co*-S and P4VP-*b*-S. Figure 2 shows VLE for five P4VP-*co*-S random copolymers + methanol; the polymers have different percent styrene content, %S. The two limiting cases %S = 0 and %S = 100 correspond to homopolymers P4VP and PS, respectively. As discussed later, the good affinity of the polar segments of P4VP for methanol determines the high solvent sorption in this polymer. Because methanol is not a solvent for PS, the PS solvent sorption curve is close to the vertical axis. Intuitively, one might expect that the solvent sorption in P4VP-*co*-S copolymers is the average of P4VP and PS sorption, weighted by the comonomer unit content, as reported for some other copolymer + solvent systems.[14] However, P4VP-*co*-10%S absorbs more methanol than either of the two homopolymers.

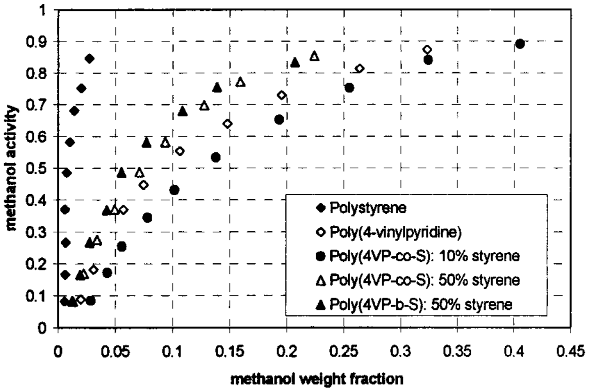

Figure 2. Solvent activities for binary solutions of linear poly(4VP-*co*-S) copolymers in methanol at 70 °C. Effect of "intramolecular repulsion".

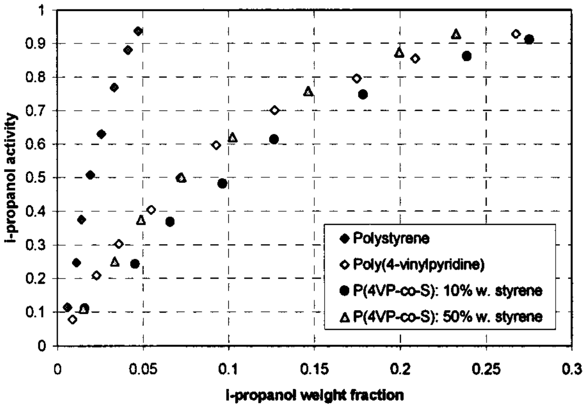

Figure 3. Solvent activities for binary solutions of poly(4VP-*co*-S) copolymers in 2-propanol at 70 °C. Effect of "intramolecular repulsion".

Figure 3 shows similar behavior for four P4VP-*co*-S polymers with 2-propanol. Again, the P4VP-*co*-10%S sorption curve lies to the right of the P4VP curve, while P4VP-*co*-50%S shows almost the same sorption as P4VP homopolymer. Analogous results were obtained by Gupta and Prausnitz[12] for poly(butadiene-*co*-acrylonitrile) + acetonitrile and poly(butadiene-*co*-acrylonitrile) + methyl ethyl ketone.

This nonintuitive behavior may be explained by "intramolecular repulsion" between unlike segments in a random copolymer. The addition of styrene units in P4VP changes the chemical affinity of the polymer for alcohol. Two competitive factors affect the VLE: (1) the poor affinity of styrene for methanol and 2-propanol; (2) the solvent-screening effect of unfavorable intramolecular interaction ("repulsion") between 4VP and styrene units in the copolymer.

For the binary system P4VP-*co*-S/alcohol, a measure of affinity is provided by the Flory−Huggins interaction parameter $\chi_{(AB)C}$,[67] where AB stands for copolymer and C for solvent (or homopolymer):

$$\chi_{(AB)C} = \chi_{AC}\phi_A + \chi_{BC}\phi_B - \chi_{AB}\phi_A\phi_B \qquad (2)$$

where χ_{AC}, χ_{BC}, and χ_{AB} are Flory interaction parameter for A−C, B−C, and A−B, respectively (A = 4VP, B = S, C = alcohol); ϕ_A and ϕ_B represent the volume faction of monomer A and B, respectively.

The parameter $\chi_{(AB)C}$ provides an inverse measure of affinity: the lower the parameter, the higher the affinity.

Table 4. Flory χ Parameters from Vapor Pressure Data[a]

solvent temp	methanol (70 °C)	2-propanol (70 °C)
$\chi_{\text{styrene/solvent}}$	2.47	2.0
$\chi_{\text{4-vinylpyridine/solvent}}$	0.56	0.81
$\chi_{\text{4-vinylpyridine/styrene}}$		
10% S	4.82	3.4
50% S	2.90	2.3
$\chi_{\text{copolymer/solvent}}$		
10% S	0.31	0.62
50% S	0.81	0.85

[a] The homopolymer/solvent interaction parameters are calculated using Flory−Huggins theory. These χ's are then introduced into eq 2 for the copolymer/solvent system; the remaining intramolecular interaction parameter is obtained by fitting experimental data for the corresponding copolymer/solvent system with the same theory.

Table 4 presents Flory parameters obtained from our data. For PS/alcohols systems, Gòndòz and Dincer[68] measured Flory−Huggins interaction parameters by inverse-gas chromatography in the temperature range $162 < T < 229.5$ °C. At the lowest temperature, the reported χ values are 2.19 and 1.74 for methanol and 2-propanol, respectively. Those values are somewhat lower than ours (2.47 for methanol and 2.0 for 2-propanol), as expected because of the lowest experimental temperature in our work. We recognize, however, that our calculated χ's cannot be accurate because the sorption of alcohols in PS is very low and the experimental error in vapor-sorption measurements is high at small solvent concentrations. Boyes and Strauss[69] measured osmotic second virial coefficients for P4VP in methanol and 2-propanol at 25 °C by light scattering. The χ value is related to the second virial coefficient B_{22} by[70]

$$B_{22} = \frac{v_2^{\,2}}{\nu_1}\left(\frac{1}{2} - \chi\right) \tag{3}$$

where v_2 is the specific volume of P4VP (here 0.917 cm^3/g, measured by pycnometry) and v_1 is the solvent molar volume, cm^3/mol. Applying eq 3, we obtain $\chi = 0.48$ for methanol and $\chi = 0.47$ for 2-propanol at 25 °C, lower than our results from vapor-sorption measurements. This difference is probably due to the χ concentration dependence and temperature dependence. In particular, because of the role played here by attractive specific interactions (see later discussion), we expect that χ increases when temperature increases.

The contribution of styrene affinity to the total copolymer affinity for methanol or 2-propanol is represented by the second term in eq 2, while the contribution of “intramolecular repulsion” is given by the third term. Equation 2 shows that even if the added comonomer units lower the average segmental affinity ($\chi_{AC}\phi_A + \chi_{BC}\phi_B > \chi_{AC}$) for the solvent, a sufficiently large χ_{AB} can overcome this effect and globally produce an enhanced favorable solvent/copolymer interaction (small or negative $\chi_{(AB)C}$) for some copolymer compositions.

This enhanced favorable interaction is observed for P4VP-*co*-S random copolymer + alcohol systems. The interaction parameter P4VP−PS χ_{AB} has been measured by Clarke et al.[71] by three different methods. Clarke et al. were not able to give a well-defined value of χ_{AB} but only a range (from 1.4 to 7.5); they pointed out that the lower limit is an order of magnitude greater than the largest value of χ_{AB} reported for other nonionic systems. More recently, Alberda van Ekenstein et al.[72] demonstrated, on the basis of experimentally determined phase behavior of PS/P4VP-*co*-S blends, that the Flory intramolecular interaction parameter satisfies $0.30 < \chi_{AB} < 0.35$. This value is substantially smaller than the range reported by Clarke et al. but still relatively large. By fitting our experimental data for copolymer/solvent using Flory−Huggins theory, where the interaction parameter is expressed by eq 2, we obtained $2.3 < \chi_{AB} < 4.82$ at 70 °C, inside the range reported by Clarke et al. Table 4 shows that the fitted χ_{AB} are solvent and copolymer composition dependent. These values of the Flory intramolecular interaction parameter can be only qualitative, because Flory−Huggins theory does not strictly apply when polymer/solvent specific interactions are significant, as in our systems (see later discussion). Once again we observe that χ_{AB} depends on the experimental method chosen for its estimation. Because of the broad range of values of Clark's and of our calculation and because of disagreement with Alberda van Ekenstein et al.'s results, additional study will be necessary to obtain a reliable value of χ_{AB}.

The strong “repulsion” between 4VP-and-S-bonded segments determines the VLE behavior in P4VP-*co*-10%S, while the poor affinity of PS for alcohol balances the “intramolecular repulsion” effect in P4VP-*co*-50%S + 2-propanol ($\chi_{(AB)C} \approx \chi_{AC}$) and determines the VLE in P4VP-*co*-50%S + methanol. From our data, we expect a maximum in alcohol affinity for P4VP-*co*-S, for %S < 50%.

Figure 2 shows also VLE data for P4VP-*b*-50%S block copolymer + methanol. The sorption curve lies to the left of the P4VP-*co*-50%S sorption curve and between the two homopolymer curves. In a block copolymer the “intramolecular repulsion” between unlike bonded segments is much reduced because of the segregated distribution sequence $[A]_n[B]_m$ (n, m large). Block copolymers minimize the unfavorable A−B interaction by microphase separation and micelle formation.[37] The microstructure (lamellae, cylindrical, or spherical shape) is governed by the relative block lengths.[71]

Cross-Linked P4VP. Previously reported VLE for solutions of cross-linked polymers has shown that the introduction of cross-links in polymeric linear chains lowers the amount of sorption at fixed solvent activity. Experimental data for cross-linked poly(dimethylsiloxane) (PDMS)[21,24] and styrene−butadiene rubber (SBR) with various solvents[26,27] showed this decrease in sorption. Moreover, as shown by gel-swelling data, increasing the degree of cross-linking reduces solvent sorption and swelling.[73,74] This reduction follows because, during vapor sorption, the solvent mixes with the polymer chains in an entropically driven process; as the polymer imbibes more solvent, the volume increases. In a polymer network, this sorption-swelling process forces the polymer molecules to assume an extended, less-probable configurations. The entropic gain due to mixing is accompanied by a decrease in entropy of the elongated polymer strands in the network that retains the solvent. Equilibrium is reached when the effect of elastic expansion of the polymer chains balances that of mixing. For linear polymers, there is no elastic effect because the polymer chains are not connected by cross-links, and volume increase due to addition of solvent is not accompanied by a significant deformation of the polymer chains. Introduction of cross-links in polymeric linear chains reduces solvent sorption because of the elastic

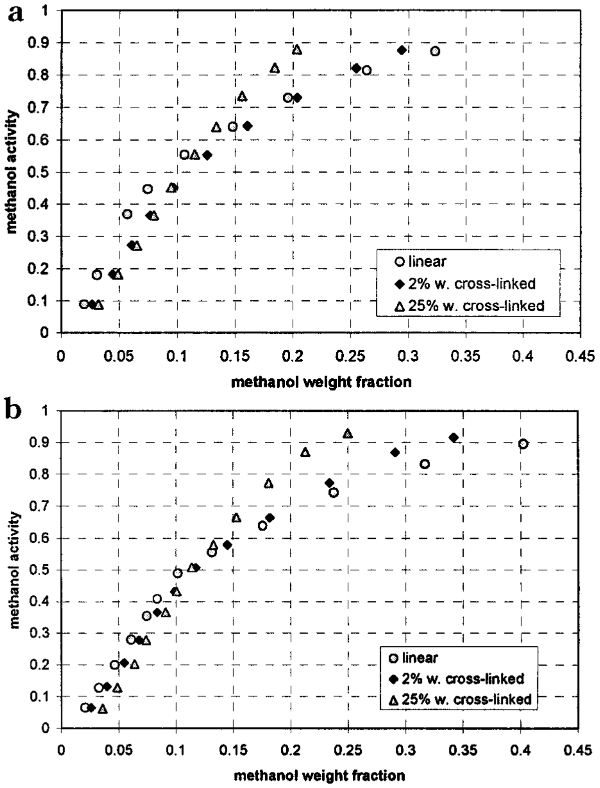

Figure 4. Solvent activities for binary solutions of cross-linked poly(4-vinylpyridine) in methanol (a) at 70 °C and (b) at 55 °C. Effect of cross-linking concentration.

contribution; the magnitude of this effect is proportional to the number of polymer-chain links.

Our experimental data show unexpected VLE for cross-linked P4VP compared with that for linear P4VP. At low solvent activity, the trend in the amount of sorption with degree of cross-linking is exactly the opposite of that predicted by the discussion above. The expected behavior is recovered only at high solvent activity.

Figure 4a compares VLE for linear P4VP, c-P4VP/2%DVB, and c-P4VP/25%DVB with methanol at $T = 70$ °C. At low methanol activity ($a_1 < 0.7$), solvent sorption increases with degree of cross-linking, while for $a_1 > 0.7$, sorption is a decreasing function of cross-linking concentration. At low activity, the difference in sorption between c-P4VP/2%DVB and c-P4VP/25%DVB is only slightly greater than the experimental error, but data for the same systems at 55 °C confirm the observed trend at 70 °C, as shown in Figure 4b. The experimental measurements shown in Figure 4b were repeated twice; the indicated results for the respective polymer/solvent couples were reliably reproducible. Other data were not repeated.

Additional evidence for this unexpected behavior is shown in Figure 5a where data are shown for 2-propanol sorption in the same polymers at 70 °C. When 2-propanol is the solvent, the dependence of solvent sorption on the degree of cross-linking is much stronger, erasing any doubt about the sorption curve crossover. Again, at $a_1 < 0.8$, c-P4VP/25%DVB exhibits the highest sorption and linear P4VP the lowest. However, when the solvent activity is raised above 0.8, the curves switch relative position; the greatest solvent affinity is then observed for the linear polymer.

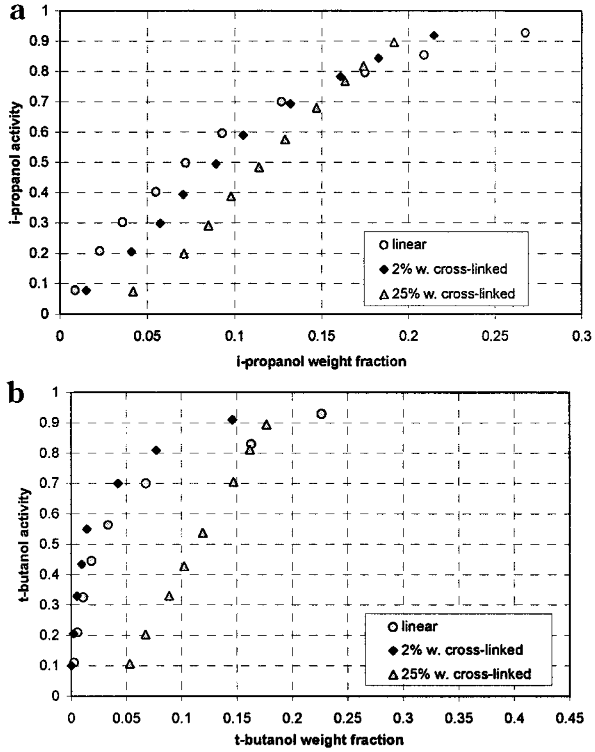

Figure 5. Solvent activities for binary solutions of cross-linked poly(4-vinylpyridine) (a) in 2-propanol and (b) in *tert*-butyl alcohol at 70 °C. Effect of cross-linking concentration.

Figure 5b shows sorption of *tert*-butyl alcohol in linear and cross-linked P4VP. Comparing the sorption curves for linear P4VP and P4VP/25%DVB, we reach similar conclusions concerning the cross-linking effect. At low solvent activity, the sorption curves for linear P4VP and P4VP/2%DVB overlap. Because of the very small sorption of *tert*-butyl alcohol due to the low affinity of P4VP for this solvent and because of the high experimental error at very low amount of sorbed solvent, crossover of these two sorption curves cannot be detected.

The apparent disagreement between our results and those reported by others at low solvent activity may be resolved upon considering the results presented in the previous section where it was shown that the sorption of methanol (or 2-propanol) for random P4VP-*co*-10%S is much higher than that for P4VP homopolymer, despite the poor affinity of styrene for a low-molecular-weight alcohol. The increase in the amount of sorbed solvent follows from the solvent-screening effect of “intramolecular repulsion” between unlike segments that constitute the copolymer.

The cross-linked P4VP polymers used in this work are copolymers of 4-vinylpyridine (4VP) and divinylbenzene (DVB). These repeating units are the same constitutive units as those for P4VP-*co*-S, except for the double vinyl functional group in DVB monomer (that allows cross-linking) instead of the single bond in styrene. The unfavorable interaction between 4VP and DVB is the same as that between 4VP and styrene. Moreover, because the same DVB monomeric unit links together two P4VP chains, the number of 4VP units covalently bonded with a single DVB unit is twice that in the nonlinked copolymer. As a result, we expect that “intramolecular repulsion” in the cross-linked copolymers is stronger than that in the nonlinked copolymers at fixed copolymer composition.

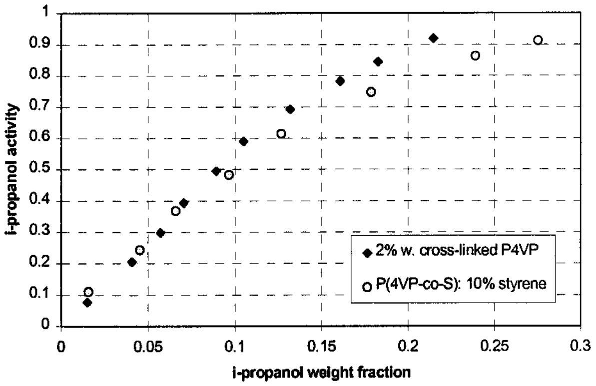

Figure 6. Comparison of 2-propanol sorption in cross-linked and nonlinked 4-vinylpyridine copolymers. Comonomers: divinylbenzene (2 wt %) for the cross-linked polymer; styrene (10 wt %) for the nonlinked polymer.

This expectation is confirmed upon comparing the data for P4VP-*co*-10%S + 2-propanol and for c-P4VP/2%DVB + 2-propanol at low solvent activity (Figure 6). Lower comonomer concentration in the cross-linked copolymer is able to produce the same increase in vapor sorption. Hence, "intramolecular repulsion" can explain why, at low solvent activity, the sorption rises with degree of cross-linking. However, at high solvent activity, recovery of the usual trend (higher sorption in linear homopolymer P4VP) follows from the contribution of elastic forces that are small at low solvent concentration but become increasingly important as more solvent enters the polymer.

Sorption Dependence on Solvent Quality. Figure 7a–e shows results similar to those presented above. However, in each part of Figure 7 there is only one polymer with three different solvents. Linear P4VP absorbs more methanol than 2-propanol; the sorption of *tert*-butyl alcohol is low compared to those of the other two alcohols, especially for $a_1 < 0.65$. These results are in agreement with data for osmotic second virial coefficient B and for viscosity η for P4VP in methanol and 2-propanol:[69] B and η increase in the direction 2-propanol < methanol, showing that P4VP has the greatest affinity for the smallest alcohol.

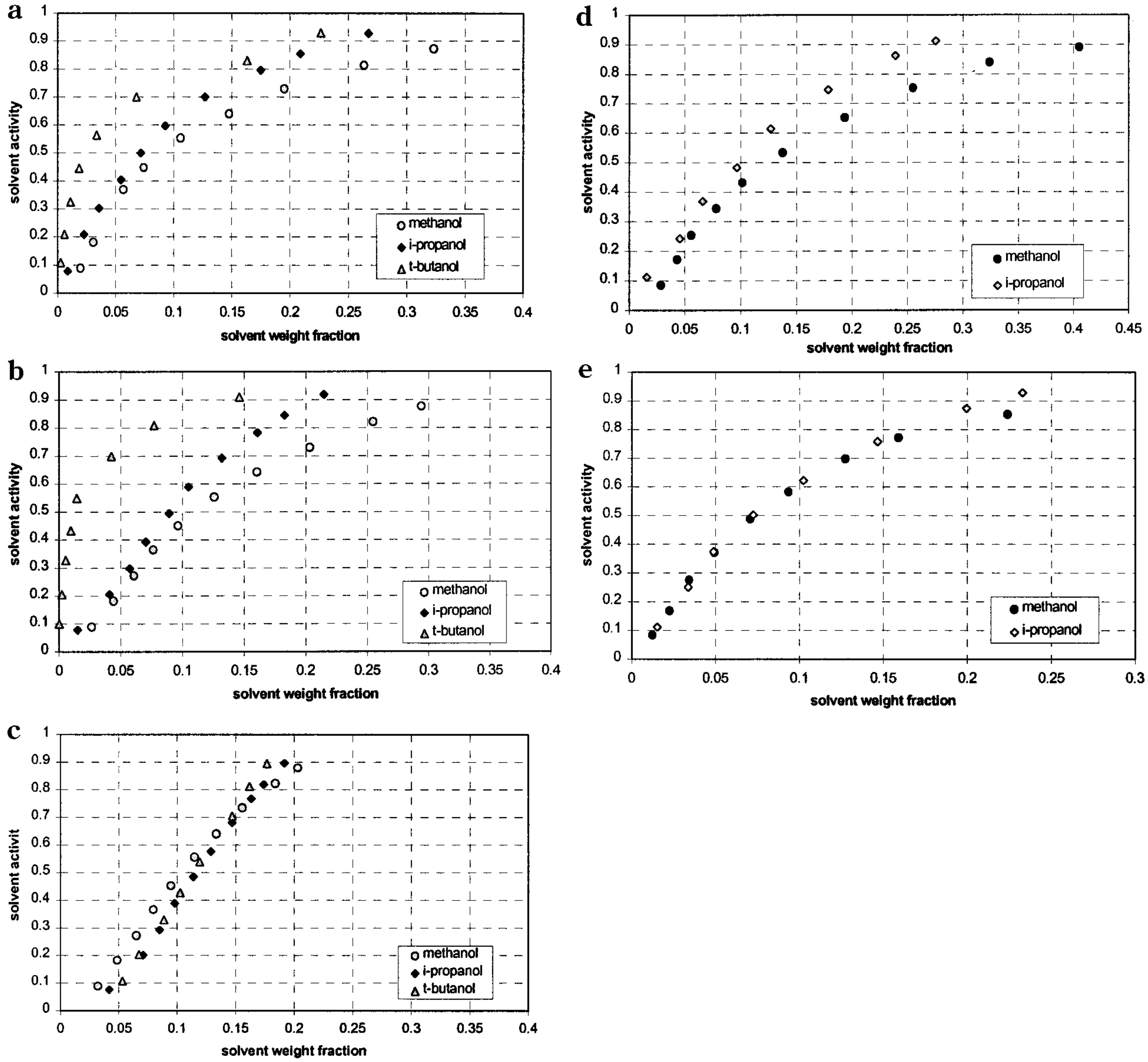

Figure 7. Activities of methanol, 2-propanol, and *tert*-butyl alcohol at 70 °C in (a) linear poly(4-vinylpyridine), (b) 2% cross-linked poly(4-vinylpyridine), and (c) 25% cross-linked poly(4-vinylpyridine). Activities of methanol and 2-propanol at 70 °C in (d) poly(4VP-*co*-10%S) and (e) poly(4VP-*co*-50%S).

The affinity of P4VP for alcohol probably follows from the formation of a specific interaction (hydrogen bond, acid−base interaction) between the −OH group in the alcohol and the basic nitrogen in the pyridine ring. Indeed, it has been shown experimentally that the absorption capacity of carboxylic acids and substituted phenols in P4VP increases with solvent acidity.[53,54] Moreover, Boyes and Strauss[69] recognized the existence of an H-bond in P4VP *tert*-butyl alcohol system because of the negative temperature coefficient of the solubility of this polymer in a *tert*-butyl alcohol/benzene mixture.

Steric hindrance in the formation of specific interaction may have some influence on the affinity of alcohol/P4VP: moving from methanol to 2-propanol and *tert*-butyl alcohol, the specific interaction of −OH with pyridine N become less probable because of the more restrictive orientation requirement. The role of steric hindrance is indicated by observed insolubility of *tert*-butyl alcohol in poly(2-vinylpyridine) where the interacting site in the polymer is in a position more hidden than that in P4VP.[75]

For the three alcohols studied here, similar affinity has been observed for c-P4VP/2%DVB: again, the highest sorption is observed with methanol and the lowest with *tert*-butyl alcohol. For c-P4VP/25%DVB, the sorption curves for the three alcohols do not show any significant difference. Similar behavior has been observed for P4VP-*co*-S: increasing %S from 10% to 50% cancels any difference in sorption between methanol and 2-propanol. At high comonomer concentration, the reduction of solvent affinity for P4VP in the direction methanol > 2-propanol > *tert*-butyl alcohol is probably balanced by the increased solvent affinity of styrene segments for higher aliphatic alcohols.

As expected, sorption at 70 °C is less than that at 55 °C when compared at the same solvent activity.

Conclusion

New VLE sorption data for alcohols have been obtained for cross-linked 4VP/DVB and for linear 4VP/S copolymers at 55−70 °C. Solvent sorption depends strongly on the comonomer (S or DVB) content. “Intramolecular repulsion” between unlike bonded segments enhances solvent sorption for some copolymer compositions. The effect of “intramolecular repulsion” appears to be larger in the cross-linked copolymers where a single DVB unit is covalently bonded to a higher number of 4VP segments. In block copolymers, the segregated sequence (blockiness) of unlike monomers minimizes “repulsive” interactions.

Surprisingly, at low solvent activity, the amount of sorbed solvent in cross-linked copolymers increases with cross-linker concentration (DVB) because of the “intramolecular repulsion” effect. However, at high solvent activity, where elastic forces hinder solvent sorption, sorption decreases with cross-linker concentration.

Comparing the sorption of methanol, 2-propanol, and *tert*-butyl alcohol in the same copolymer, the difference in the amount of sorbed alcohol decreases significantly upon increasing the percent S or DVB content in a 4VP-based copolymer: the reduction of solvent affinity for P4VP in the direction methanol > 2-propanol > *tert*-butyl alcohol seems to be balanced by the increased solvent affinity of S or DVB segments for aliphatic alcohols with longer hydrocarbon content.

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Supporting Information Available: Experimental solvent−activity data for solvent−polymer systems. This material is available free of charge via the Internet at http://pubs.acs.org.

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