Molecular weight and stability of the charge transfer complex of poly(2-vinylpyridine) and 1,4-benzoquinone

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(Received 27 October 1989; revised 2 June 1990; accepted 11 June 1990)

The interaction between monodisperse poly(2-vinylpyridine) ($\bar{M}_w/\bar{M}_n = 1.1$–$1.5$) and 1,4-benzoquinone was examined in aqueous alcohols. The presence of charge transfer interactions was examined spectrophotometrically by Benesi–Hildebrand plots. It was found that a negative molecular weight effect does exist whereby the level of interaction between poly(2-vinylpyridine) and benzoquinone decreases with increasing molecular weight. However, considerable time is required for the interaction to achieve equilibrium, with the kinetics of 'complexation' varying with the molecular weight of the polymer. An extensive spectroscopic investigation of the phenomenon confirms, however, that benzoquinone reacts over time with alcohols to form primarily 1,4-hydroquinone. Our results show that the molecular complex formed in these systems is probably due to the well documented quinhydrone complex between 1,4-hydroquinone and 1,4-benzoquinone.

(Keywords: charge stability interactions; molecular weight effects; chemical stability; equilibrium constant; time dependencies)

INTRODUCTION

In recent years a considerable amount of information has accumulated regarding macromolecular charge transfer associations[1–3]. Interest is due, in part, to the many significant changes in both solution and solid state properties which are known to occur as a result of this interaction. These properties (e.g. electrical conductivity, enhanced tensile properties and blend compatibility) are all directly related to the association of electron donating and electron accepting moieties within the polymer.

The impact of the polymer chain on charge transfer complexation is well documented as polymer bound donor and acceptor functionality can display either an increased or decreased interaction. Enhanced complexation is typically recognized as a positive polymer effect and decreased interaction as a negative polymer effect.

Generally, when the charge transfer functionality is a strong fluorophore (i.e. carbazole) in a closely packed arrangement directly bound to the polymer backbone, a decrease in complexation is usually observed[4]. Rather than participate in an intermolecular complex (i.e. charge transfer), the carbazolyl group in the polymer forms intramolecular aggregates or excimers with adjacent carbazolyl functionality. Generally, these excimers are more strongly associated ($E \approx 3$–10 kcal mol^{-1}) than ground-state donor–acceptor complexes ($E \approx 1$–3 kcal mol^{-1})[5] and may be the reason why a negative polymer effect is observed.

In cases where negative polymer effects exist, molecular weight effects have sometimes been observed whereby the level of charge transfer interaction (as measured by an equilibrium constant K_{ct}) decreases with increasing molecular weight. For example, the relationship between K_{ct} and molecular weight of poly(N-vinylcarbazole) has been demonstrated[6]. K_{ct} possesses a rather strong dependence at low molecular weights (10^2–10^4 g mol^{-1}), becoming invariant at high molecular weight ($>10^4$ g mol^{-1}).

Interestingly, when the same donor functionality (carbazolyl) is sufficiently spaced from the polymer backbone, existing as flexible, moderately mobile pendants, an enhanced donor–acceptor intermolecular interaction (charge transfer) results[4]. Presumably, the steric constraints are significantly reduced, as are the intramolecular associations. Furthermore, these polymers are known to possess enhanced interactions (higher K_{ct}) with electron acceptors compared with their monomeric analogues. For example, polyesters containing ω-(9-carbazolyl)butyl pendants display positive polymer effects[6]. This is believed to result from multiple donor interactions with the electron accepting species whereby an electron acceptor, once taken into the polymer environment, becomes encapsulated in a microdomain of donor moieties. The result is an enhanced donor–acceptor interaction. This positive polymer effect as a function of molecular weight has also been documented, as K_{ct} was found to increase with increasing molecular weight[6,7].

These phenomena are of key importance when designing or blending charge transfer (i.e. associating) polymers for potential use. In consideration of molecular weight effects, for example, the molecular weight distribution of a blended donor and acceptor polymer may significantly affect the degree of charge transfer interaction.

Because of its interaction with a host of commercial polymers, the charge transfer interactions of poly(vinylpyridine) homopolymers and copolymers have also been of interest. Sugiyama[8] and co-workers made a detailed study of the charge transfer interaction between

0032-3861/91/112060–04

pyridine-containing polymers and 1,4-benzoquinone in aqueous ethanol. Studies of donor–acceptor equilibrium constants of monomeric and polymeric pyridines with 1,4-benzoquinone suggest that the polymer bound pyridine (poly(2-vinylpyridine), poly(4-vinylpyridine) etc.) does possess enhanced degrees of interaction (i.e. positive polymer effect). This work has been cited[6] as a prime example in which positive polymer effects are operative.

The present work includes a detailed investigation examining the overall stability of 1,4-benzoquinone in aqueous alcohol solutions and determining its level of interaction with polymer bound pyridine functionality.

EXPERIMENTAL

Materials

1,4-Benzoquinone (98%) was sublimed before use (Aldrich). Fractionated poly(2-vinylpyridine) ($\bar{M}_w/\bar{M}_n$ = 1.1–1.5) was used as received (Pressure Chemical Company). Reagent grade isopropanol, ethanol and deionized water were used without further purification.

Spectrophotometric analyses

All spectrophotometric data were obtained on a Perkin-Elmer lambda 7 u.v./vis. spectrophotometer using 1 cm quartz cells. Desired concentrations for sample analysis were obtained by weighing out the appropriate amounts of donor and acceptor into a flask followed by quantitative transfer (with solvent) into an appropriately sized volumetric flask.

Since the optical density of the complex solution varied with polymer molecular weight, donor concentrations varied for each molecular weight fraction, so that absorbance was maintained between approximately 0.2 and 1.0. In all instances, however, the polymer concentration was below the critical overlap concentration.

In all measurements, the optical density of 1,4-benzoquinone was subtracted from the complex solution containing donor and acceptor. Poly(2-vinylpyridine) does not absorb significantly in the absorption region of the charge transfer complex.

Optical density measurements were made 7 h after solution preparation. All solutions were kept in the dark before analysis.

Proposed equilibrium constants (K_{ct}) and molar extinction coefficients (ε) were calculated by using a method originally described by Benesi and Hildebrand[9] employing a least-squares analysis.

If the donor–acceptor complex is 1:1 in donor and acceptor, the equilibrium constant may be written as

$$K_{ct}=[\mathrm{C}]/[\mathrm{D}][\mathrm{A}] \qquad (1)$$

where [C], [D] and [A] are the molar concentrations of complex, donor, and acceptor, respectively.

In sample preparation, $[\mathrm{D}]>[\mathrm{A}]$ so $[\mathrm{D}]-[\mathrm{C}]\approx[\mathrm{D}]$. The actual concentration of free acceptor is then $[\mathrm{A}]-[\mathrm{C}]$. The absorbance ($d$) of the complex is related to its concentration by

$$d=\varepsilon b[\mathrm{C}] \qquad (2)$$

Substituting the absorbance terms in (2) into equation (1), the following expression is obtained:

$$\frac{[\mathrm{A}]l}{d}=\frac{1}{K_{ct}\varepsilon[\mathrm{D}]}+\frac{1}{\varepsilon} \qquad (3)$$

where l is optical path length in cm. A plot of $[\mathrm{A}]l/d$ *versus* $1/[\mathrm{D}]$ should be linear, giving $K_{ct}\varepsilon$ as the reciprocal of the slope and ε as the reciprocal of the y intercept.

^{13}C nuclear magnetic resonance (n.m.r.) was measured on a Bruker GX-400 or a Jeol using D_2O as solvent. Chemical shifts are reported in ppm using tetramethylsilane (TMS) as reference.

RESULTS AND DISCUSSION

Solutions of poly(2-vinylpyridine) and 1,4-benzoquinone were examined in a variety of solvents. One analysis was made in an 80:20 (v/v) mixture of isopropanol and water. *Figure 1* shows a typical Benesi–Hildebrand plot for the solution ($\bar{M}_w$ = 105 000 g mol^{-1}). Good correlation was obtained for all optical density plots. Absorption maxima, proposed K_{ct} and extinction coefficients are shown in *Table 1*.

Time dependency studies

Although K_{ct} values are reported here and elsewhere[8] for the poly(2-vinylpyridine)–1,4-benzoquinone 'complex', a substantial amount of time is required to reach the donor–acceptor 'complexation' equilibrium. *Figure 2* illustrates the influence of time on the optical density of the complex ($\bar{M}_w$(poly(2-vinylpyridine)) = 309 000 g mol^{-1}). The data show that at least several hours are necessary to achieve a state of equilibrium. It also appears that the rate at which this occurs depends on polymer molecular weight (*Figure 3*). For example, while lower molecular weight poly(2-vinylpyridine) ($\bar{M}_w$ = 13 000–105 000 g mol^{-1}) appears to reach a state of equilibrium in ≈7 h, a somewhat longer time is required for a higher molecular weight fraction (e.g. $\bar{M}_w$ = 309 000 g mol^{-1}). Another striking feature is the increase in optical density with decreasing molecular weight of poly(2-vinylpyridine). As shown in *Figure 3*, the absorbance of the complex is substantially greater for lower molecular weight fractions.

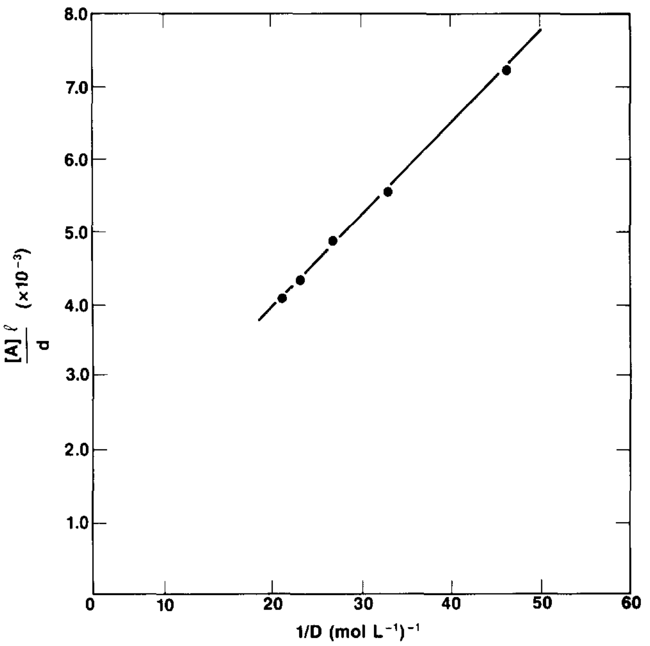


Figure 1 Benesi–Hildebrand plot for a poly(2-vinylpyridine)–benzoquinone solution in aqueous isopropanol ($\bar{M}_w$ = 105 000 g mol^{-1})

Table 1 Postulated equilibrium constants and molar extinction coefficients of the poly(2-vinylpyridine)–1,4-benzoquinone 'complex' in aqueous isopropanol

$\bar{M}_w$ (g mol^{-1})	Donor concentration[c] (mol l^{-1}) ($\times 10^{-2}$)	Acceptor concentration (mol l^{-1}) ($\times 10^{-3}$)	λ_{max} (nm)	ε	K (l mol^{-1})
13 000[a]	0.47–0.82	1.9	360	888	100
43 700[a]	0.82–1.62	2.8	363	722	73
105 000[a]	2.15–4.59	5.5	362	710	11
309 000[b]	2.50–4.42	5.5	366	754	9

[a] Optical density measurements made 7 h after solution preparation

[b] Optical density measurements made 21 h after solution preparation

[c] Polymer concentration is less than the critical overlap concentration (c^*) as calculated[10] by the relationship $c^* = 0.7/[\eta]$, where $[\eta]$ is the intrinsic viscosity

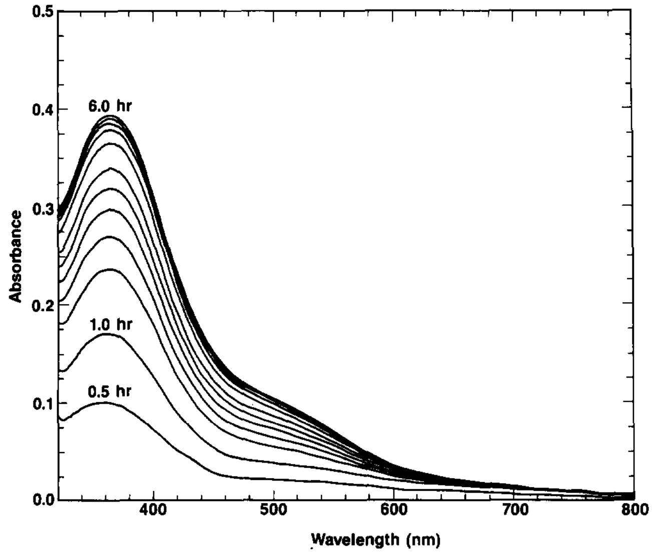


Figure 2 Increase in optical density over time for poly(2-vinylpyridine)–benzoquinone solution in aqueous isopropanol: $\bar{M}_w$ = 309 000 g mol^{-1} (donor, 3.8×10^{-2} M; acceptor, 5.5×10^{-3} M)

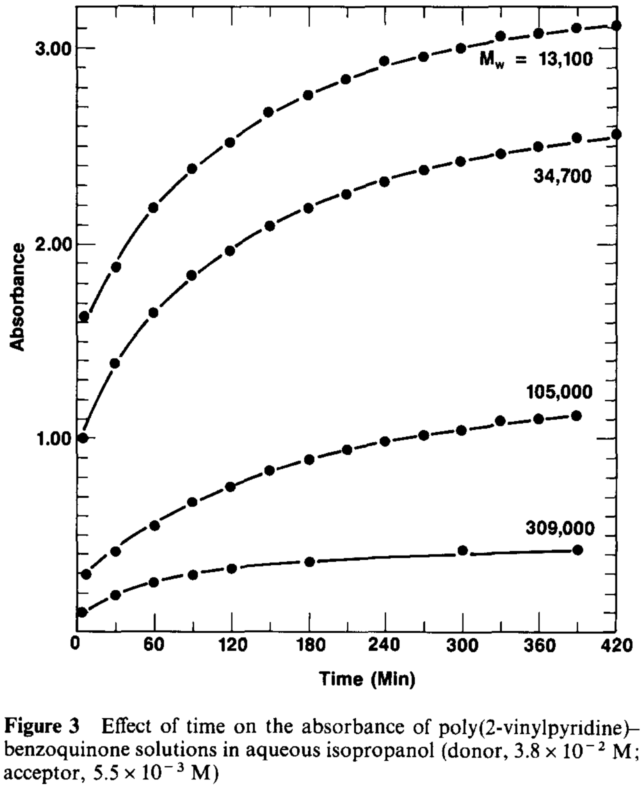


Figure 3 Effect of time on the absorbance of poly(2-vinylpyridine)–benzoquinone solutions in aqueous isopropanol (donor, 3.8×10^{-2} M; acceptor, 5.5×10^{-3} M)

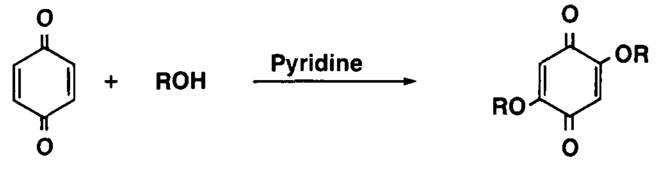
Stability of 1,4-benzoquinone

The unusually slow rate of interaction between pyridine functionality and benzoquinone prompted a spectrophotometric examination of 1,4-benzoquinone in 80:20 (v/v) isopropanol–water and ethanol–water mixtures. Results show that benzoquinone, itself, is not sufficiently stable in these solvents. The absorption maximum initially observed at ≈240 nm decreases over time, while corresponding increases in absorption are observed at higher wavelengths (360–450 nm). Also, coinciding with these changes, a distant colour change in the visible region is observed as the benzoquinone solution changes from yellow to red.

A ^{13}C n.m.r. analysis of 1,4-benzoquinone in isopropanol/D_2O solvent gave resonances at 137.3 and 189.8 ppm corresponding to the unsaturated and carbonyl carbons, respectively. However, resonances at 29.8 and 210.6 ppm and also 116.6 and 149.9 ppm also appear over time, suggesting formation of acetone and hydroquinone, respectively. Incidentally, the ^{13}C n.m.r. resonances of acetone in D_2O are observed at 29.8 and 210.6 ppm and those of 1,4-hydroquinone are observed at 116.5 and 149.9 ppm. G.c. analysis of 1,4-benzoquinone in isopropanol–water also indicates the production of acetone.

In summary, it appears that 1,4-benzoquinone is acting as a hydride acceptor, thereby oxidizing isopropanol to acetone and thus forming 1,4-hydroquinone. In fact, the use of benzoquinone to oxidize secondary alcohols to the corresponding ketone has been reported[11,12].

A ^{13}C n.m.r. study of 1,4-benzoquinone/aqueous ethanol and isopropanol mixtures containing pyridine also confirms the presence of 1,4-hydroquinone. In addition, other side reaction products are observed. ^{13}C n.m.r. analysis suggests possible nucleophilic attack of alcohol and water on benzoquinone to form products as shown in *Scheme 1*. In fact, this side reaction has been used to incorporate quinone moieties into polymers for charge-transfer applications[13]. Thus, it appears that the pyridine mediated side reaction is somewhat different.



Scheme 1

Presumably, the pyridine behaves as a hydrogen acceptor (i.e. base), thus facilitating the attack of alcohol on benzoquinone. However, a spectrophotometric study of these poly(2-vinylpyridine)–benzoquinone solutions in aqueous alcohol does suggest that strong molecular weight effects are operative. As a qualitative means of measuring reaction rate, the optical density at 360 nm was measured over time. These results are in qualitative agreement with previous measurements, i.e. *Figure 2*. It appears that the influence of the polymer bound pyridine moiety on the degradation of benzoquinone decreases with increasing molecular weight.

CONCLUSIONS

Although 1,4-benzoquinone has been used as a probe to investigate the charge transfer properties of a number of pyridine-containing polymers in aqueous alcohols, it is not sufficiently stable in these solutions. ^{13}C n.m.r. and g.c. analysis of 1,4-benzoquinone solutions in aqueous ethanol and isopropanol indicates that the benzoquinone reacts with these alcohols to form 1,4-hydroquinone. Further studies reveal that pyridine functionality facilitates this reaction, also introducing side reactions.

In conclusion, the increased absorptions and colour changes associated with these solutions are presumably due to the interaction between 1,4-benzoquinone and 1,4-hydroquinone, which is the well documented quinhydrone complex[14]. In addition, because of the acidic nature of 1,4-hydroquinone, acid–base interactions with the pyridine functionality are possible, which may also contribute to the enhanced absorptions observed in the range 360–450 nm.

Our studies have shown, however, that molecular weight effects are indeed operative. It appears that negative catalytic polymer effects exist whereby the accelerative effect of pyridine functionality in these side reactions decreases with increasing molecular weight of the polymer.

ACKNOWLEDGEMENT

Special thanks are due to Richard Ernst for his assistance and technical skill in our g.c. studies.

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