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International Journal of Polymer Analysis and Characterization

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646643>

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To cite this Article Villar, V. , Opazo, A. , Gargallo, L. , Radić, D. , Rios, H. and Clavijo, E.(1998) 'Poly(complexes) Stabilized by Acid-Base Interactions: Poly(4-vinylpyridine) and Poly(ethylene-co-maleic acid)', *International Journal of Polymer Analysis and Characterization*, 4: 4, 333 – 343

To link to this Article: DOI: 10.1080/10236669808009721

URL: <http://dx.doi.org/10.1080/10236669808009721>

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Poly(complexes) Stabilized by Acid-Base Interactions: Poly(4-vinylpyridine) and Poly(ethylene-co-maleic acid)

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(Received 19 September 1997; Revised 06 October 1997)

Interpolymer complex (IC) formation between poly(ethylene-co-maleic acid) and poly(4-vinylpyridine) (P4VPy) has been observed and characterized. Data from viscosity, infrared spectroscopy and thermogravimetric analysis show the presence of an interpolymer complex depending on the composition and pH of the solution. The driving force for poly(complex) formation seems to be the specific acid-base interactions between free carboxylic groups of the copolymer and the pyridine nitrogen of P4VPy.

Keywords: Interpolymer complex, poly(ethylene-co-maleic acid), poly(4-vinylpyridine), gain in viscosity, thermogravimetric analysis, Fourier-Transform infrared, hydrogen-bond formation

INTRODUCTION

Interpolymer complexes formation between complementary polymers is an interesting topic from both technological^[1-3] and fundamental point of view.^[4,5] These systems have attracted much attention due to the formation of

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Presented at the 10th International Symposium on Polymer Analysis and Characterization, Toronto, Ontario, Canada, August, 1997.

compatible polymer blends.^[4,6] The strength of the cooperative interaction between linear polymers is determined by the nature of the segments involved in the poly(complex). Effectively, poly(complexes) can be stabilized by ion pairs, coulombic interactions between poly(electrolytes) containing opposite charges,^[1,5,7,8] hydrogen bonds among a polybase and a polyacid,^[9-13] or by means of hydrophobic interactions in aqueous solutions.^[14]

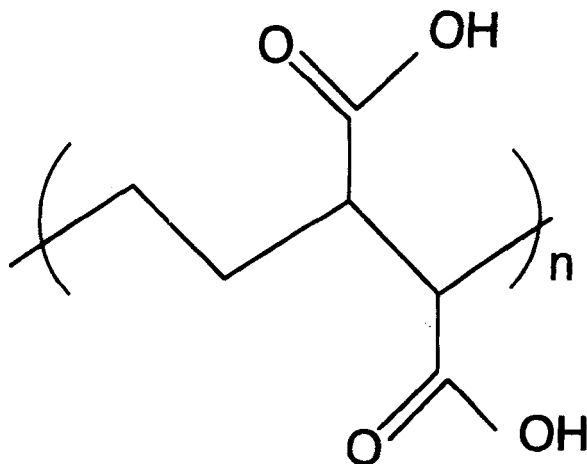
Among the works reported in literature on poly(complexes) stabilized by acid-base interactions, particularly interesting are the polymer blend between poly(4-vinylpyridine) (P4VPy), a weakly self-associated basic polymer, and poly(ethylene-*co*-methacrylic acid)^[4] (PE-*co*-MAc), a strong self-associated poly(electrolyte) through the formation of intermolecular carboxylic acid dimers. Strong association among these polymers occurs by the intermolecular hydrogen bonds between the carboxylic acid and the pyridine groups and the results were discussed in terms of competing equilibria. Similar behavior was described for the system poly(4-vinylpyridine) (P4VPy) and poly(acrylic acid) (PAA) in solution, where the poly(complex) is largely stabilized through hydrogen bonds with some degree of proton transfer as well.^[11]

In the present work the interaction of poly(4-vinylpyridine) (P4VPy) and poly(ethylene-*co*-maleic acid) (PE-*co*-MA) (See Scheme 1) was studied in aqueous solution as a function of the pH of the solution by viscometry measurements. IR spectroscopy, and thermogravimetric analysis (TGA) in the solid state was also performed. The behavior observed can be interpreted as an association between P4VPy and PE-*co*-MA. Spectroscopic reasons for the formation of soluble and insoluble interpolymer complexes are discussed.

EXPERIMENTAL

Polymers

Linear poly(4-vinylpyridine), P4VPy, with a weight-average molecular weight of 50,000 from Polysciences Inc. (Warrington, Penn.) was used. Poly(ethylene-*co*-maleic anhydride), (PE-*co*-MAH), with weight-average molecular weight ranging from 1×10^5 to 5×10^5 was purchased from Aldrich Chemicals Co. (Milwaukee, Wisconsin). PE-*co*-MAH was hydrolyzed in distilled water by refluxing aqueous dispersions for 48 h. A pale-yellow aqueous solution was obtained which was lyophilized to obtain a white hygroscopic solid of poly(ethylene-*co*-maleic acid) (PE-*co*-MA).



PE-co-MA

Scheme 1

Preparation of the Mixtures

Mixtures of PE-co-MA and P4VPy were prepared by dissolving both polymers in a water/methanol mixture 1:1 at three different compositions:

$\tau = 0.5$, $\tau = 1$, and $\tau = 2$ where τ is defined by:

$$\tau = \frac{[PE-co-MA]}{[P4VPy]} \quad (1)$$

Viscosity and pH Determinations

Viscosity measurements were performed at all the compositions in a Desreux Bischoff dilution viscometer^[15] with negligible energy corrections to obtain the reduced viscosity of each solution. All measurements were carried out at $25 \pm 0.01^\circ\text{C}$. The pH of the solution were adjusted with dilute HCl or NaOH in the acid and basic range, respectively.

IR Measurements

The IR spectra were obtained using an FT-IR 2000 Perkin Elmer spectrophotometer with the solid blends obtained from solutions at pH = 1.8, 6.0, and 9.0, respectively.

Thermal Analysis

Dynamic thermogravimetric analysis was performed in a Mettler TA-3000 calorimetric system equipped with a TC-10A processor and a TG-50 thermobalance with a Mettler MT5 microbalance. The samples were heated on Al₂O₃ pans. Measurements were carried out between 300 and 800 K at 5° min⁻¹ under N₂.

RESULTS AND DISCUSSION

Solution Behavior

Figure 1-A is a representation of the reduced viscosity (η_{sp}/c) in water/methanol (50% v/v) of the pure polymers against pH. η_{sp}/c for PE-co-MA increases monotonically with pH values indicating charge repulsion among neighboring anionic groups. This effect is reflected in an increased hydrodynamic volume of the polymer. The curve reaches a maximum and then diminishes probably caused by an increased ionic strength of the media because of the addition of NaOH to adjust the pH. As would be expected, η_{sp}/c for P4VPy increases slightly at low pH values where P4VPy is protonated.

Figure 1-B represents the variation of η_{sp}/c as a function of the pH for three mixtures containing PE-co-MA and P4VPy ($\tau = 0.5$, $\tau = 1.0$, and $\tau = 2$). For pH ≤ 2 , polymers remain in solution. At intermediate pH values η_{sp}/c cannot be determined because of insoluble poly(complex) formation. For pH ≥ 6 , η_{sp}/c is sharply increase for the different τ values.

It is well known^[11] that poly(complex) formation can be observed viscometrically if the hydrodynamic volume of the complex is different from the sum of the hydrodynamic volumes of their individual constituents. The concept of gain in viscosity, g , is usually employed for this comparison:

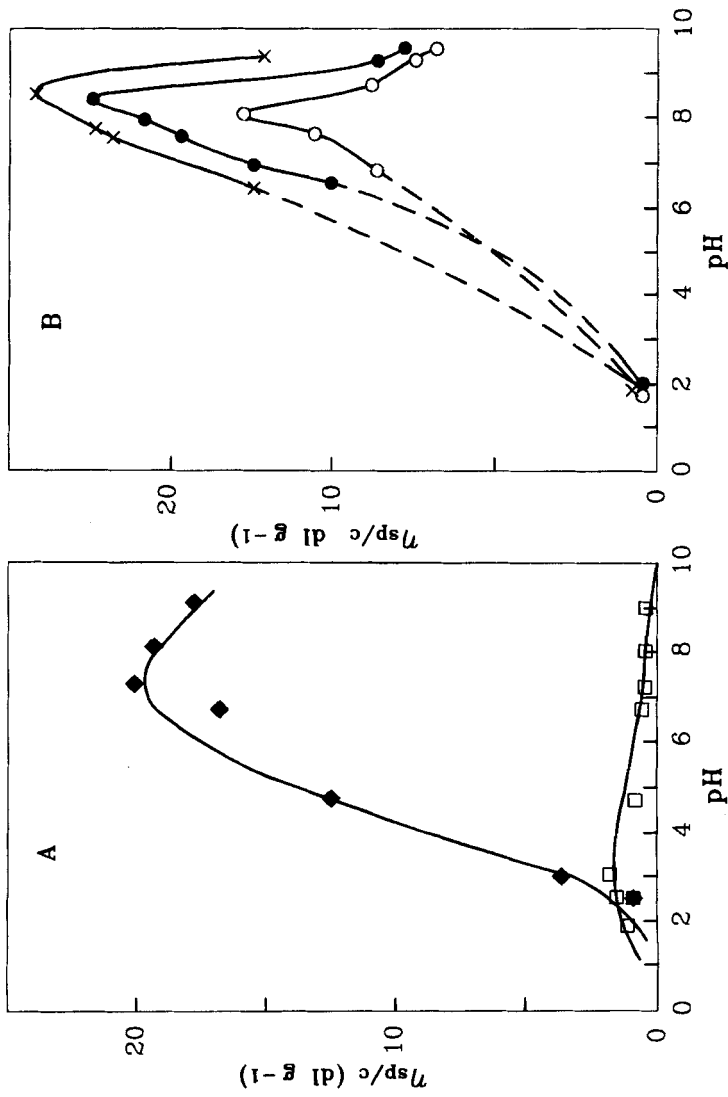


FIGURE 1. Variation of the reduced viscosity (η_{sp}/c) as a function of the pH. A: ♦ PE-co-MA; □ P4VPy. B: PE-co-MA/P4VPy Blends (○) $\tau = 0.5$; (●) $\tau = 1.0$; (X) $\tau = 2$.

$$g = \frac{(\eta_{sp})_{PC}}{[(\eta_{sp})_{PA} + (\eta_{sp})_{PB}]} \quad (2)$$

where PC, PA, and PB are the poly(complex), the polyacid, and the polybase, respectively. Thus $g < 1$ indicates a certain degree of interaction of the polymers, whereas $g = 1$ indicates that the polymers are practically indifferent to each other, at least viscometrically.

Figure 2 shows the dependence of g with τ . For $\text{pH} \geq 6$, g values approach unity as the pH increases. g values lower than unity means that some kind of interaction between the components takes place. If $g \rightarrow 1$, polymers become mutually indifferent at a certain pH value; at g values less than 1 the poly(complex) is very compact. The gain in viscosity increases as the pH of the solution increases at constant τ value. However, g also increases sharply as τ increases (see Fig. 2). According to these results, at larger τ values g may even become larger than 1 indicating that poly(complex) particles could be highly branched (microgel) under those conditions.^[12] Therefore, this behavior could be attributed to the fact that each polyacid chain joins to several chains of polybase. The volume and structure of the poly(complex) would depend mainly on the ratio of polyacid/polybase.

Infrared Analysis

In order to characterize the poly(complex), FT-IR spectra were measured from 1800-1500 cm^{-1} . Figure 3A shows the IR spectra for three solid blends at $\tau = 1$ obtained from solutions at three different pH values: At $\text{pH} = 1.8$ (curve a), a band at 1640 cm^{-1} corresponds to protonated vinylpyridine ($\equiv\text{N}\cdots\text{H}$) by HCl and a second band at 1725 cm^{-1} corresponds to the carboxylic group. At $\text{pH} = 6.0$ (curve b), the same two bands are observed but in this case the protonation of the vinylpyridine $\equiv\text{N}\cdots\text{H}$ group is due to hydrogen bonding by the carboxylic group from PE-*co*-MA, because this is a neutral pH value. At $\text{pH} 9.0$ (curve c), both bands are not observed because the carboxylic groups are in the carboxylate form, and vinylpyridine is in its normal state.

Figure 3B shows the FT-IR spectra for pure P4VPy neutralized with HCl (curve d) and the blend at $\text{pH} 1.8$ (curve e). Clearly it can be observed that the band at 1640 cm^{-1} corresponds to protonated $\equiv\text{N}\cdots\text{H}$, which is similar to that observed at $\text{pH} = 1.8$.

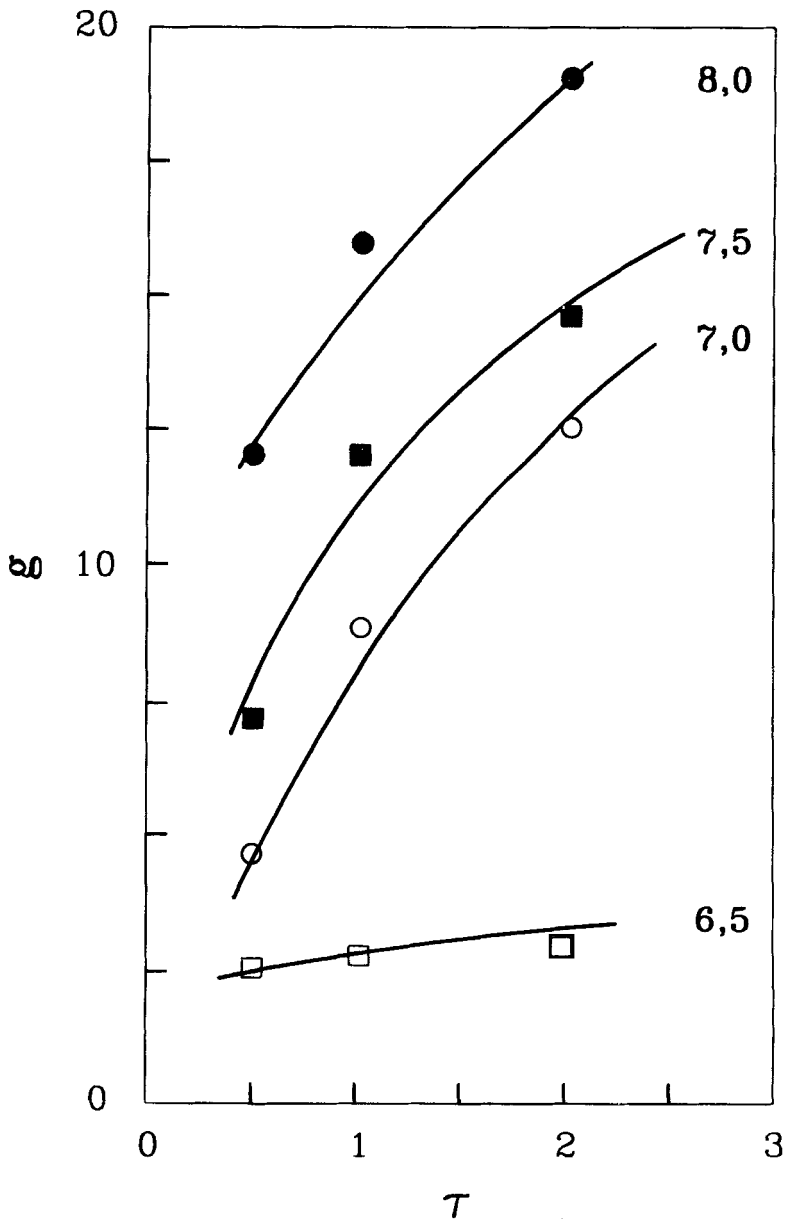


FIGURE 2 Dependence of the gain in viscosity (g) as function of τ at different pH values. (\square) pH = 6.5; (\circ) pH = 7.0; (\blacksquare) pH = 7.5; (\bullet) pH = 8.0.

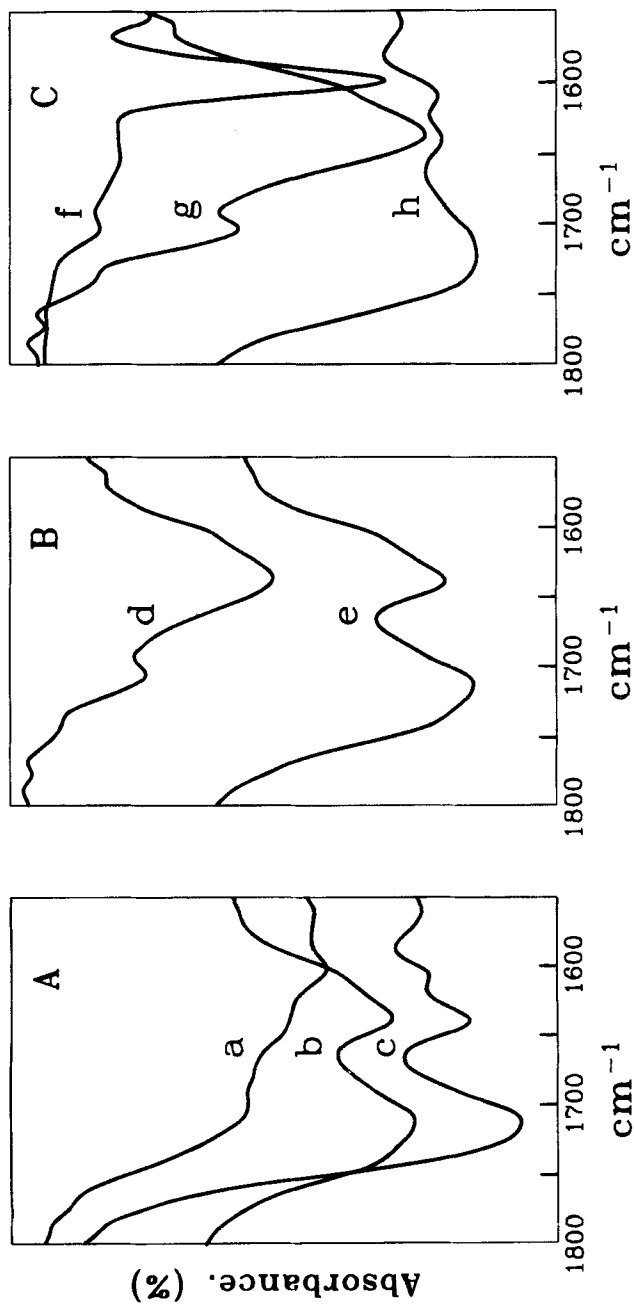


FIGURE 3. A: FT-IR spectra for a blend of $\tau = 1$ at three different pH values: (a) pH = 1.8, (b) pH = 6.0, (c) pH = 8.7. B: FT-IR spectra for P4VPy neutralized with HCl (d) and the blend at pH = 1.8 (e). C: FT-IR spectra for P4VPy (f), P4VPy neutralized with HCl (g) and P4VPy blended with succinic acid as a model monomeric molecule (h).

Figure 3C corresponds to the FT-IR spectra of P4VPy (curve f), P4VPy-HCl (curve g), and P4VPy with succinic acid (curve h), taken as a model small molecule of the MA moiety of PE-*co*-MA, which is considered as being responsible for the formation of the interpolymer complex. The spectrum corresponding to P4VPy-succinic acid (curve h) is quite similar to that of the blend of PE-*co*-MA/P4VPy at pH = 6.0 (curve b). Therefore, it is possible to assign the band at 1640 cm^{-1} to the protonated $\equiv\text{N}\cdots\text{H}$ group.

Thermogravimetric Analysis

The thermogravimetric profiles of the pure components and the poly(complex) for $\tau = 1$ are represented in Figure 4A. Three different degradation profiles can be observed. P4VPy follows a single one-stage decomposition process and PE-*co*-MA a three-stage profile. The blend corresponding to a composition of $\tau = 1$ shows a two-stage decomposition process. In order to show more clearly the different maxima, the first derivative of the weight loss (dM/dT) against temperature was constructed. Figures 4B and 4C show these plots for PE-*co*-MA and the poly(complex), respectively. This behavior can be explained in a quantitative way by assuming that in the case of PE-*co*-MA, the inflection point is around 12.5% weight loss; this corresponds to one water molecule released per mole of comonomer unit. According to the comonomeric structure, it is possible to calculate theoretically, that the weight loss for one water molecule corresponds exactly to a 12.5% weight loss. The result shown in this figure is in good agreement with this calculation. This phenomenon takes place at 410 K for PE-*co*-MA and probably can be attributed to a cyclization process of the polyacid to form a maleic anhydride moiety.

In the case of the blend of PE-*co*-MA/P4VPy at a composition of $\tau = 1$, the same inflection point is observed, but at a higher temperature (*c.a.* 450 K) than that for pure PE-*co*-MA. It is of interest to note that the temperature difference at which both PE-*co*-MA and the blend release a water molecule is caused by the acid-base interaction in the blend, and represents the driving force in the poly(complex) formation.

Acknowledgements

We express our thanks to Fondecyt, Project 8970011. V.V. thanks DIPUC for a Doctoral Fellowship. D.R. and A.O. also acknowledge the financial support from Cátedra Presidencial en Ciencias'95.

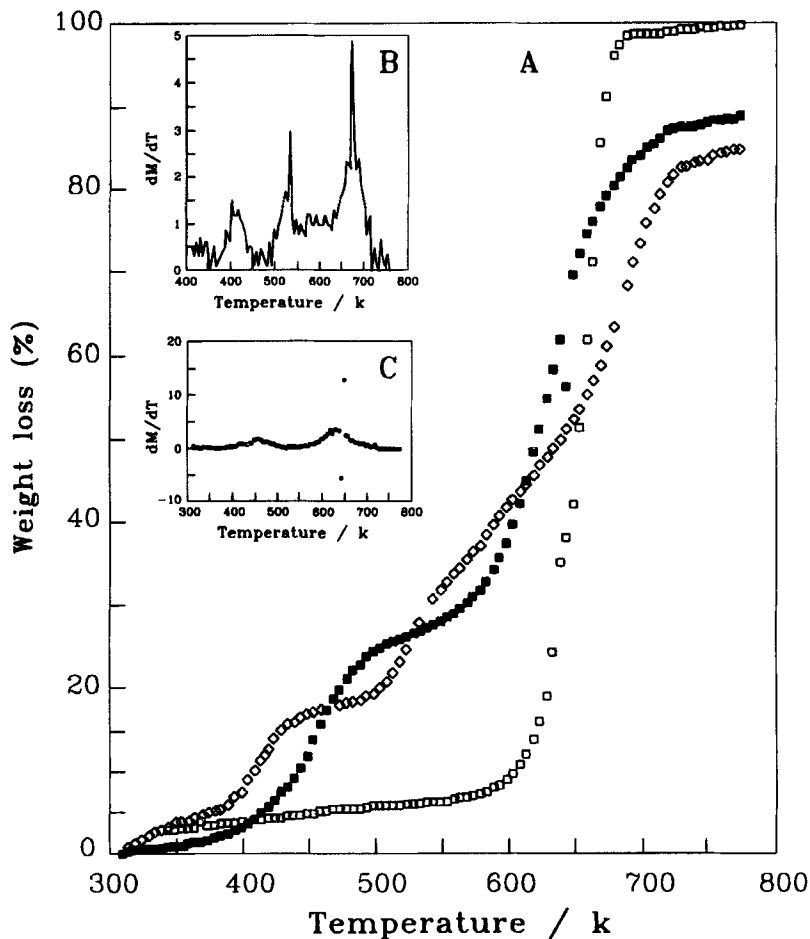


FIGURE 4 A: Thermogravimetric profiles for P4VPy (\square), PE-co-MA (\diamond) and P4VPy-PE-co-MA ($\tau = 1$) polycomplex (\blacksquare). B: First derivative of the weight loss (dM/dT) for PE-co-MA. C: First derivative of the weight loss (dM/dT) for the polycomplex formed at $\tau = 1$.

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