

SURFACE CHEMISTRY OF POLYACETYLENE

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Résumé - La mouillabilité du polyacétylène sous forme de membranes et son rôle dans le transport ionique sont étudiés.

Abstract - Wettability and its role in ion transport through (CH)_x membranes are explored.

I

INTRODUCTION

The large surface area of polyacetylene, (CH)_x, (50 - 60 m² g⁻¹)/l/ and its unique redox properties suggests potential applications of (CH)_x as a mediating electroactive polymer in the protection of reactive semiconductor surfaces/2/ and as a photoelectrode for H₂ generation/3/. The non-wetting nature of hydrophobic (CH)_x has however limited its efficiency in such applications. Our objective has been to explore the value of polyacetylene as an electrode material in aqueous media. In this paper we report on the determination of wettability and surface energy characteristics of pristine, iodine-doped and surface functionalized (CH)_x and on the ion transport properties of these materials.

II

BACKGROUND

The empirical approach developed by Zisman/4/ for the study of substrate wettability uses a series of probe liquids for which the equilibrium contact angles, θ_e, are determined on a homogeneous, isotropic, flat surface. The cosine of the equilibrium contact angle is plotted against the surface tension of the probe liquid, γ_l, to produce a straight line. The intercept of this line at cos θ_e¹ = 1 (θ_e = 0) is defined as the critical surface tension (γ_c) for wetting of the substrate. γ_c is an empirically determined characteristic of the substrate and is related/5/ to the substrate surface energy, γ_s, via:

$$\gamma_c = \phi_{sl}^2 \gamma_s \tag{1}$$

where φ_{sl} is the substrate/liquid interaction parameter. It is more common in a fundamental approach to substrate surface energy to combine the modified Youngs equation/6/

$$\gamma_s - \sigma_e = \gamma_{sl} + \gamma_{lv} \cos \theta_e \tag{2}$$

and the Girifalco and Good approach to interfacial tension/7/

$$\gamma_{sl} = \gamma_s + \gamma_l - 2\phi_{sl}(\gamma_s\gamma_l)^{1/2} \tag{3}$$

to yield

$$\cos \theta_e = -1 + \frac{2\phi_{sl}(\gamma_s\gamma_l)^{1/2}}{\gamma_{lv}} - \frac{\sigma_e}{\gamma_{lv}} \tag{4}$$

Here the subscripts s and l refer to substrate (solid) and liquid respectively and γ is a surface or interfacial tension. Assuming $\theta_e = 0$, a condition which applies for all liquids which make a finite contact angle with the substrate/l, then equation (4) reduces to

$$\cos \theta_e = -1 + 2\phi_{sl}\gamma_s^{1/2} \gamma_l^{-1/2} \quad (5)$$

A plot of cosine θ_e vs $\gamma_l^{-1/2}$ produces a straight line through -1,0 of slope $2\phi_{sl}\gamma_s^{1/2}$ and intercept at $\cos \theta_e = 1$ of $\phi_{sl}\gamma_s^{1/2} = \gamma_c^{1/2}$ (compare with equation (1)). The slope and intercept therefore provide independent checks of the substrate surface energy. In the application of equations (1) and (5) for the determination of substrate surface energy, ϕ_{sl} may be justly assumed to be unity. This is true if the probe liquids and the substrate both derive their surface energies from similar components of the surface tension. This truism does not apply for the probe liquids used in this study but the approximation provides a reasonable estimate of (CH)_x surface energies.

III

EXPERIMENTAL

Cis-polyacetylene was synthesized as films at -78°C by techniques similar to those developed by Shirakawa *et al*/8/. Elemental analyses of the pristine polymer indicated (CH) contents of >99%. Wettability of (CH)_x films was studied at 20°C by contact angle measurements using a Rame Hart NRL Contact Angle Goniometer equipped with a Rame Hart environmental chamber. Films were mounted in a dry box onto glass slides using double sided Scotch Tape adhesive and placed in the environmental chamber before being transferred to the Goniometer. The chamber was first purged with purified argon before a 11.7 μl sessile drop of the probe liquid was applied from a teflon and glass screw microsyringe.

Surface functionalization of the pristine polymer was achieved by a 30s treatment in aqueous, deaerated, neutral, saturated (0.40M) KMnO_4 solution at room temperature. These conditions were optimized to produce a wettable substrate which retained the doping and conductivity characteristics of the pristine polymer.

D.C. ionic transport of the (CH)_x films was studied by making the film the separating membrane of a Hittorf-type two compartment cell using 0.5M KCl and Ag/AgCl, Cl^- electrodes at 2.0V.

IV

RESULTS AND DISCUSSION

In Table 1 are shown the surface tensions and equilibrium contact angles of the various probe liquids on the "smooth" (silvery) surface of pristine cis-(CH)_x. From the Zisman plot (Figure 1) the critical surface tension for wetting, γ_c , is found to be 42mN m^{-1} and the surface energy, γ_s , estimated by equation (1) is therefore also 42mN m^{-1} .

TABLE 1 EQUILIBRIUM CONTACT ANGLES, θ_e , FOR VARIOUS PROBE LIQUIDS ON THE SMOOTH SURFACE OF PRISTINE cis-POLYACETYLENE.

LIQUIDS	γ_c mN m^{-1}	θ_e	$\cos \theta_e$
WATER	72.75	70.80 \pm 1.60	0.33 \pm 0.03
GLYCEROL	63.40	58.03 \pm 7.23	0.53 \pm 0.11
FORMAMIDE	57.02	46.45 \pm 1.69	0.69 \pm 0.02
ETHYLENE GLYCOL	48.43	32.80 \pm 5.60	0.84 \pm 0.03
DIETHYLENE GLYCOL	45.21	26.00 \pm 1.26	0.90 \pm 0.01
NITROBENZENE	43.90	18.35 \pm 5.20	0.95 \pm 0.02

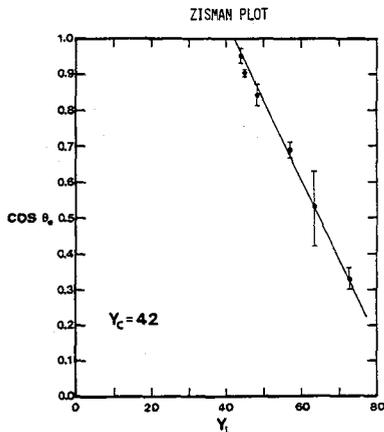


FIGURE 1. ZISMAN PLOT OF $\cos \theta_c$ VS $\gamma_L^{1/2}$ FOR VARIOUS PROBE LIQUIDS ON THE SMOOTH SURFACE OF PRISTINE cis-POLYACETYLENE.

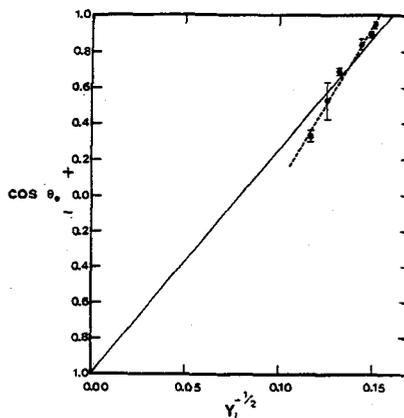


FIGURE 2. $\cos \theta_c$ VS $\gamma_L^{1/2}$ FOR VARIOUS PROBE LIQUIDS ON THE SMOOTH SURFACE OF PRISTINE cis-POLYACETYLENE.

Similar studies on the "rough" surface produced dubious results as the surface roughness led to significant wicking resulting in time varying contact angles. Similar treatment of the "smooth" surface of iodine-doped $(CH)_x$ at $(CHI)_{0.20}$ showed increased wettability with the critical surface tension for wetting rising to 44.5 mN m^{-1} . Following surface functionalization in aqueous $KMnO_4$ the contact angle of water on the "smooth" surface fell from 70.8° to 12.0° showing that significant improvement in hydrophilicity was achieved. The contact angle of water on iodine-doped $(CH)_x$ at $(CHI)_{0.20}$ was 49.6° . In Figure 2 is shown a plot of $\cos \theta_c$ vs $\gamma_L^{1/2}$ based on equation (5) for the "smooth" surface of pristine cis-polyacetylene. From this plot both slope and intercept gave, for an assumed value of $\phi_{s1} = 1$, a value of $\gamma_s = 39.1 \text{ mN m}^{-1}$. The good agreement between γ_s determined by both methods suggests that surface roughness and the use of unmatched liquids were not significant in influencing the equilibrium contact angles.

The surface functionalized polymer showed a new IR band of weak to medium intensity at 3400 cm^{-1} on both its "rough" and "smooth" surfaces. This new band is associated with -OH stretch and except for this the ATR-IR spectrum unchanged from that shown in Figure 3. XPS analysis using $Mg K\alpha_{12} = 1253.7 \text{ eV}$ showed 1s at 534.4 eV and 533.0 eV resulting from MnO_2 and -OH. The syn-addition scheme for the production of the diol is shown in Figure 4.

FIGURE 3. ATR-IR (60) SPECTRUM OF THE SMOOTH AND ROUGH SURFACES OF PRISTINE POLYACETYLENE, $(CH)_x$, PREPARED AT -78°C .

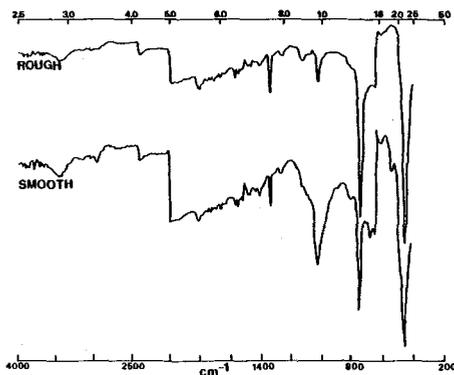
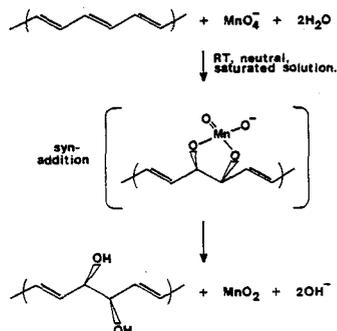
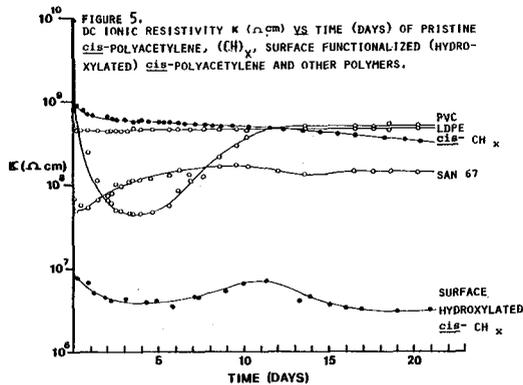


FIGURE 4. SURFACE FUNCTIONALIZATION REACTION OF POLYACETYLENE VICINAL ALCOHOL FORMATION BY NEUTRAL, SATURATED $KMnO_4$.



Interestingly, pristine predominantly cis-(CH)_x analysed by ATR-IR(60) showed that its smooth surface contained a higher trans content than its rough surface (Figure 4) (judged from intensities at 1040 cm⁻¹). No explanation can be advanced for this observation at present. Transmission IR, however, produced spectra similar to those observed by Shirakawa et al/9/ for cis-(CH)_x and were exactly the same as the rough surface ATR-IR spectrum. Figure 5 shows D.C. ionic resistivity of pristine cis-(CH)_x compared with surface hydroxylated cis-(CH)_x. The D.C. ionic resistivity is significantly lowered by the increased wettability of the membrane. When doped with iodine to (CHI_{0.20})_x the membranes become transparent to ions and contribute no resistance to the cell. The possibility of controlled electrochemical oxidation to modulate ionic resistivity, as was recently demonstrated for polypyrrole/10/, is presently being explored.



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