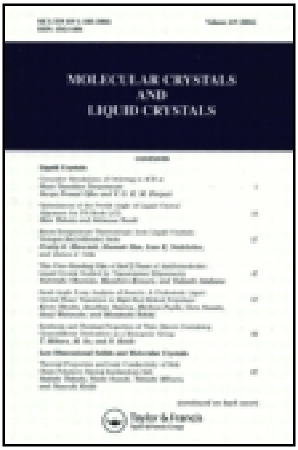

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Surface Chemistry of Polyacetylene: Adhesion to Silica, Derivatization With Nickel And Catalytic Activity

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SURFACE CHEMISTRY OF POLYACETYLENE: ADHESION TO SILICA, DERIVATIZATION WITH NICKEL AND CATALYTIC ACTIVITY

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Abstract Adhesion of $(CH)_x$ film prepared by the Luttinger method to glass can be improved by silylation in order to more closely match dispersive surface energies. Treatment of n-type $(CH)_x$ films with $NiBr_2$/HMPA/THF affords $(CH)_x$-supported Ni° which shows selectivity in hydrogenation of phenylacetylene.

INTRODUCTION

The use of polymeric materials as catalyst supports has been studied extensively in the past several years [1, 2]. A significant advantage gained by the use of supported catalysts is ease of separation although more elegant functions are offered by the support itself. Supports have been shown to contribute stereochemical control [3] and substrate selectivity [4,5] as well as improved activity and stability [6]. While a great deal of work has been done with polymer-modified electrodes containing catalytic species [7], only recently have electrically conductive polymers [8, 9] been considered as candidates for incorporation of catalysts. We consider the following characteristics of polyacetylene (and many other conducting polymers) to be particularly attractive for typical support materials: (1), $(CH)_x$ films have high surface areas (ca. 60 m^2/g) [10]; (2), the $(CH)_x$ surface, being organic, is easily derivitized by simple chemical reactions; and (3), $(CH)_x$ is neither solvated nor swelled in common reaction medica which can be desirable in the sense that the number of accessable catalyst sites will not change with solvent. Single crystals of polyethylene [11] offer a similar advantage to case (3). In addition to these points, however, electroactive polymers such as $(CH)_x$ allow the additional capability of introducing catalytic species via redox chemistry and maintaining (through an applied potential) a transition metal center, for example, in a particular oxidation state whereas otherwise the center would be rendered non-active after one chemical event. Oxidative coupling reactions involving metal catalysts, for example, result in an irrevsibly altered and inactive metal oxidation state. Additionally, an electrically conductive support may be able to conduct heat away from a catalyst site where an exothermic reaction occurs.

A goal of our research is to develop a tandom support system depicted qualitatively in Figure 1. We envision anchoring (via primary and/or secondary bonds) a thin layer of $(CH)_x$ to a high surface area inorganic support such as SiO_2. This would significantly enhance the number of catalytic sites available on a weight basis of $(CH)_x$.

Preliminary work on adhesion of polyacetylene to glass is discussed below. For initial experiments using $(CH)_x$ as a catalyst support we have chosen to incorporate nickel onto $(CH)_x$ for hydrogenation experiments by the reduction of Ni^{2+} using n-type $(CH)_x$. The choice was based on the extensive literature available on organonickel chemistry [12], and for comparative purposes, the fact that a similar system has been prepared and characterized using graphite , a relative of $(CH)_x$. Preliminary data on the use of "$(CH)_x$/Ni" as a hydrogenation catalyst are reported herein.

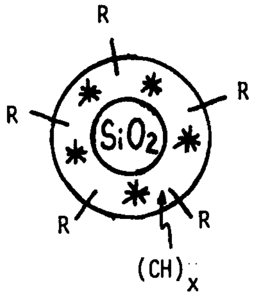


FIGURE 1

✱ ≡ catalyst sites

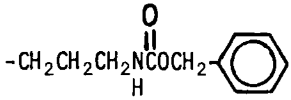
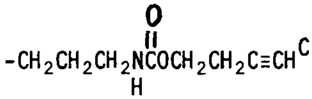
R ≡ groups to confer selectivity (for example, chiral species)

EXPERIMENTAL

Adhesion of $(CH)_x$ to glass was studied using $(CH)_x$ films prepared via the Luttinger [13] method on glass slides following a procedure similar to that of Wegner, et al [14], although the catalyst concentrations used here were greater by a factor of five and the $Co(NO_3)_2/NaBH_4$ ratio was approximately 50% greater. Several slides were silylated (for general review see [15]) with the organofunctional silanes shown in table 1 by treatment of a slide with a 1% solution of silane in 95% ethanol (with acid catalyst added), followed by drying at 100°C for 1 hour. Critical surface tensions for wetting (γ_c's) of the treated slides were determined from Zisman plots [16] and listed in table 1. Prior to glass treatment slides were rigorously cleaned and used only if a drop of water subsequently wet the surface indicating that the critical surface tension of the cleaned glass was greater than the surface tension of purified water (72 $\frac{\text{dynes}}{\text{cm}^2}$). Also, it should be noted that the polar forces (vs. dispersion forces) account for the majority of the critical surface tension of glass whereas the opposite is true with silanes 1a-c.

Table 1

$(CH_3O)_3Si-R$

	R	γ_c(dyne/cm)
1a	$-CH_3$[A]	29.3
1b	 [B]	39.6
1c	 $-CH_2CH_2CH_2\underset{H}{N}\overset{O}{\overset{\|}{C}}OCH_2CH_2C\equiv CH$[C]	40.6

A: Purchased from Petrarch Systems, Inc.; B: prepared from isocyanatopropyl trimethoxysilane (IPTMS) (Petrarch) and benzyl alcohol; C: prepared from IPTMS and 3-butyn-1-01 (Farchan Labs.

Adhesion of $(CH)_x$ to the treated and untreated slides was compared qualitatively by immersion in deionized, distilled water. The $(CH)_x$-coated slides were immersed for 72 hours in room-temperature water, and 2 hours in boiling water and the percentage of film retention was observed.

Experiments involving "$(CH)_x$/Ni" employed $(CH)_x$ film prepared by the modified Shirakawa method [17]. The films were n-type doped by immersion in 0.5 M sodium naphthalide/THF solution in a dry box, followed by washing with dry THF (distilled from sodium/benzophenone) until the washings were colorless. Compositions of $[(CH)Na_{0.14-0.24}]_x$ were calculated from weight uptake analysis and elemental analysis. Conductivities of the resulting films (measured by two-point method) were on the order of $10^{1}\ \mathrm{cm}^{-1}\ \Omega^{-1}$. The films were then treated with a solution of $NiBr_2$[4]. The Ni^{2+} solution was prepared at a concentration of 0/.25 M in THF/HMPA (15:1, v/v). The amount of solution used for Ni deposition was based on a stoichiometric balance of n-type charge carrier concentration and Ni^{2+} concentration, although in all cases the Ni salt solution was not completely decolorized.

A typical hydrogenation experiment was performed as follows. After allowing doped $(CH)_x$ and $NiBr_2$ solution to react 30 minutes the hydrogenation substrate, phenylacetylene, was added directly to the reaction flask, which consisted of a 100 ml, three-neck round bottom flask (one neck having a serum stopper). The apparatus was then connected to a vacuum line, evacuated, and refiled with purified (deoxygenated and dried) hydrogen gas. Based on the amount of Ni on the $(CH)_x$ film (ca. 8 wt. % by elemental analysis) the amount of phenylacetylene added was a 50:1 mole ratio excess. Hydrogen uptake was followed with a mercury leveling bulb [18] which also allowed for maintainance of ca. 1 atm. H_2. Aliquots of the reaction mixture were removed via syringe at regular intervals and analyzed by gas-liquid chromatography.

RESULTS AND DISCUSSION

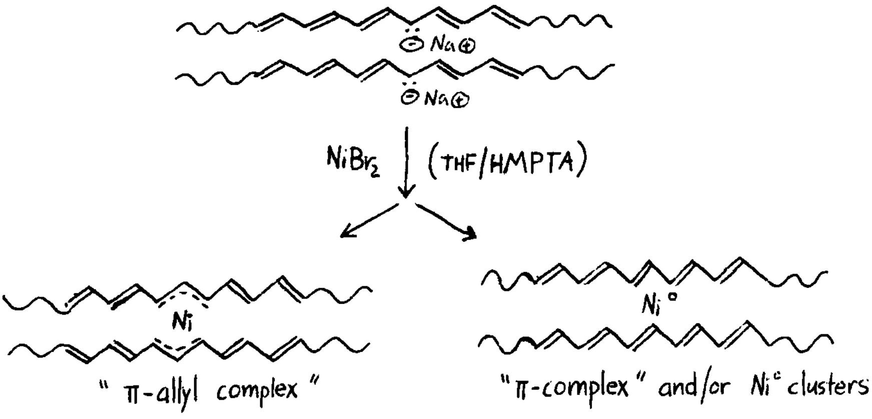
A. Adhesion to Glass

We find, as did Wegner et al. [13], that $(CH)_x$ film grown by the Luttinger method on untreated glass microscope slides easily "lift-off" when the slides are immersed in water. Slides treated with 1c prior to $(CH)_x$ growth showed no debonding even after submersion in water for several days. After two hours in boiling water slides treated with 1c had only *ca*. 5% of the $(CH)_x$ film debonded. While it is tempting to suggest that the terminal akyne functionality of 1c entered into copolymerization with C_2H_2, thus forming a covalent bond with the coupling agent, the actual explanation may not be this simple. Slides treated with 1b, which has a γ_c similar to that of 1c, but which could not react with the C_2H_2, afford $(CH)_x$ adhesion comparable to that of slides treated with 1c. Reactions of the carbamate moiety are ruled out as contributing to adhesion from model reactions. Slides treated with 1a similarly showed dramatically improved adhesion of $(CH)_x$ films compared to untreated glass although the water immersion results were not as good as with 1b and 1c. Therefore in addition to the possibility of covalent bond formation with 1c, a correlation appears to exist between surface energy equivalence (between that of the slide and the $(CH)_x$ film) and adhesion (where for polyacetylene $\gamma_c = 50 \frac{\text{dyne}}{\text{cm}}$ and has purely dispersive forces contributions). It should be mentioned, however, that dispersive forces provide the major contribution to γ_c's for 1a-c also. Thus by treating pristine glass with silanes, the γ_c is actually reduced, but the dispersive component of the surface energy (γ_D) is increased leading to a more favorable interaction with $(CH)_x$ *via* secondary bonds.

B. $(CH)_x$-Supported Nickel

We now turn to initial experiments with "$(CH)_x$/Ni," which are prepared as outlined in Figure 2. We believe that formation of Ni π-allyl complexes and/or π-complexes are possible, although the latter are more likely based on their anticipated higher (relative) stability [19]. It has not been established, however, if discrete clusters on Ni° exist on the $(CH)_x$ film or if π-complexes of the Ni° and polyacetylene unsaturation are predominantly formed (similar to $Ni[COD]_2$ or Ni[COT] complexes [19]).

Figure 2



The "$(CH)_x$/Ni" appears to be rather selective in the semihydrogenation of phenylacetylene. The fully hydrogenated product, ethylbenzene, is formed although for the most part when alkyne is present styrene is formed at the exclusion of ethylbenzene. Also the semihydrogenation reaction product (styrene) is formed much faster than the fully hydrogenated product (ethylbenzene) if the reaction is allowed to proceed to completion. Table 2 summarizes an experiment which complements the observations: (1) When styrene alone was added to the supported catalyst, a small amount was converted to ethylbenzene very slowly; (2) phenylacetylene was subsequently added (1:1 molar ratio with styrene) and is clearly converted to styrene while little hydrogenation of styrene occurs. Typically, more H_2 is consumed than theoretically expected from a mass balance which may be due to partial hydrogenation of the $(CH)_x$. Compared to the system of nickel deposited on graphite, our system showed similar selectivity towards semihydrogenation. As a final note, preliminary results indicate that "$(CH)_x$/Ni" has a somewhat greater activity than a similarly prepared "unsupported" Ni-dispersion, based on reaction rate per gram of nickel.

Table 2

procedure	sample	% ethylbenzene	% styrene	% pheylacet	*H_2-uptake (mol H_2/mol starting mat.)
1	1	8%	92%	--	--
2	2	4	50	46	0.14
	3	4	60	36	0.50
	4	5	62	33	0.56
	5	6	71	23	0.74

* For part (1) starting material is styrene; for part (2) starting material is assumed to be pheylacetylene alone so that H_2-uptake = 1.0 theoretically implies semihydrogenation.

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