



## Solvent and aqueous-borne polyolefin coatings obtained by catalytic polymerization

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### ABSTRACT

Copolymers of ethylene with various olefins such as hexadecene, undecene and norbornene were obtained by emulsion and solution catalytic polymerization, using a nickel-based catalytic system. Aqueous-based coatings could be produced from hexadecene-containing copolymers, however these coatings exhibited poor adhesion properties. Adhesion was improved by introducing polar groups, as in the case of poly(undecene-co-ethylene), but the resulting films were very tacky. Copolymers of ethylene and norbornene were prepared by palladium-catalyzed polymerization. Solvent-based coatings of ethylene–norbornene copolymers were obtained when the incorporation of norbornene in the polymer was higher than 15 mol%. Using EIS experiments, the resulting films were shown to exhibit promising applications as barrier coatings for anticorrosion applications.

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### 1. Introduction

Although it is used in a growing number of applications, high-density polyethylene (PE) is scarcely present in coatings formulations [1,2]. However, one can envision that the use of PE in barrier coatings formulations would present obvious advantages because of its intrinsic stability, hydrophobicity and chemical inertness. The prospect of using PE in a solvent borne formulation is limited because PE is insoluble in any organic solvent at room temperature. Aqueous latex-based coatings are becoming increasingly popular because of obvious environmental advantages [3]. Upon water evaporation, the latex particles dry up and eventually form a continuous film when the polymer from one particle interpenetrates into another particle. This film-formation mechanism implies that the polymer has a  $T_g$  close to room temperature, in order to permit chain diffusion [4]. Evidently, aqueous dispersions of high-density linear PE are not suitable for this process because chains of PE are crystallized [5] and diffusion from one particle to another cannot take place.

The crystallinity of PE can be broken by inserting branches along the backbone [6–8], resulting in an disruption of the crystalline packing, and a concomitant increase of  $T_g$  since long chain poly  $\alpha$ -olefins possess higher  $T_g$  comparatively to PE [6]. Thus, highly branched PEs are amorphous [7] with a  $T_g$  of approximately  $-70$  to  $-50$  °C. When small amounts of undecenoic acid and dimethylol-

tadiene are incorporated into such a polymer, the adhesion of the coating on a substrate is significantly improved [8].

This report presents our first attempts at preparing coating formulations which are either solvent borne or aqueous borne via the catalytic copolymerization of ethylene with hexadecene or norbornene. Although nothing is known about the properties of coatings derived from these copolymers, one expects they should be good candidates for the protection against corrosion [9]. Corrosion remains a fundamental problem in the preservation of various metallic structures and it is often moderated by the use of anticorrosion coatings [10]. An ideal organic barrier coating for such usage must possess several essential properties such as environmental suitability, high dielectric strength, chemical resistance, weather resistance, resistance to dirt pick up, extended life time, ease of application and above all, low water permeability. Mathematically, the coefficient of permeability can be expressed as the product of diffusion coefficient and solubility [11]. For PE, reported values of permeability range from 0.015 to 0.074 (g mm)/(m<sup>2</sup> day cmHg) at 25 °C [12]. These values are in the low range of water permeabilities for common organic polymers, as expected from the very low solubility of water in PE. In PE, water diffuses by a Fickian mechanism through the amorphous fraction and by channeling through micropores. Therefore, coatings based on linear and crystalline high-density PE are expected to have very low permeability due to the combination of the low solubility of water in the coating and the minimal amount of amorphous phase through which water could channel [11–13].

There exist several commercial materials that are loosely referred to polyolefin coatings. PE encasement is not a true coating

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per se, because it usually does not bond to the substrate, but it is a standard corrosion control method, especially for water pipes [14]. Typically, the pipes are wrapped in a 100  $\mu\text{m}$  thick high-density PE film which is taped every two feet. Pipes can be truly coated by polyolefins by extruding the polyolefin at high temperature over the pipe [15]. This method, which is obviously reserved to OEM parts, is now commonly used for many underwater pipes and offshore equipment. In most cases, the polyolefin is applied as a thick barrier layer (top-coat).

“Wax Emulsions” are very low molecular weight low-density polyethylene polymers that have been dispersed in water or in a solvent via an emulsification process. They are used as additives in varnishes and paints and for anticorrosion purposes [16]. This product is easily applicable (brush or spray) but its barrier properties are lower because polyolefin waxes are constituted of highly branched and amorphous materials which have often been modified with reactive groups (maleates, etc.) during a reactive processing step.

Since 2001, our group [5,17] and the group of Mecking [18,19] has been interested in preparing novel materials based on PE, either in solution or in emulsion. This report presents our first attempts to utilize these materials for the preparation of coatings, and to assess their anticorrosion properties. In a first section, the formation of coatings from poly(ethylene-co-hexadecene) will be presented. Unfortunately, in our hands, these coatings appear to be of low value, because of their inherent tackiness and poor adhesion. In a second section, coatings prepared from poly(ethylene-co-norbornene) will also be presented. Preliminary measurements indicate that these coatings are promising candidates for the formation of novel barrier coatings with anticorrosion properties.

## 2. Experimental part

### 2.1. Materials

Ethyl-4,4,4-trifluoro-2-(triphenylphosphoranylidene)acetoacetate (keto-ylide **1**) and nickel dicyclooctadiene  $\text{Ni}(\text{COD})_2$  were purchased from Aldrich. The synthesis of ligand **A** (2-[bis(2-methoxy-phenyl)phosphanyl]-4-methyl-benzenesulfonic acid,  $\text{P}(o\text{-OMe-C}_6\text{H}_4)_2(o\text{-SO}_3\text{H-C}_6\text{H}_3)$ , was based on the procedure detailed in Ref. [20]. Water was ultrapure grade (18.2 M $\Omega$ ) and degassed by boiling for 120 min, followed by sparging with Ar for several hours. Norbornene (NBE, Aldrich) was purified by passing it at 50 °C over a bed of activated basic alumina and activated molecular sieves. All other chemicals were purchased from Aldrich, used without further purification, but were dried and degassed using standard Schlenk techniques. All manipulations were done using standard inert atmosphere procedures. Steel coupons (6"  $\times$  12"  $\times$  1/8") were cold-rolled ANSI 1018 steel (UNS G10180) from the Metal Samples Company. The epoxy coating (MIL P2444) was kindly provided by the Office of Naval Research.

### 2.2. Typical miniemulsion copolymerization procedure

In a Schlenk flask, 9.2 mg (0.033 mmol) of  $\text{Ni}(\text{COD})_2$  and 7.4 mg (0.017 mmol) of keto-ylide **1** were mixed in 13 ml of toluene in a nitrogen filled dry box. The mixture was introduced into 100 ml of water containing 15 g/l of surfactant sodium dodecyl sulfate (SDS) and 15 g/l of hydrophobe hexadecene under stirring. The mixture was emulsified using a Branson sonifier 450 W for 4 min under magnetic stirring and under argon. Finally the resulting emulsion was cannula-transferred into a 300 ml stainless steel reactor equipped with mechanical stirrer and heated at 55 °C. Ethylene was introduced immediately at 300 psi (20 atm). Ethylene was continuously fed into the reactor at the set pressure. After 2 h, the reactor was degassed by slowly releasing ethylene, and the reaction medium was collected. The latex was filtered (if needed) to separate the floc.

Activity of the reaction was calculated from the pressure drop from the feed reservoir. Solid content was analyzed by gravimetry.

### 2.3. Typical solution polymerization

In a Schlenk tube, 2.1 mg of ligand **A** ( $5.57 \times 10^{-3}$  mmol) and 2.0 mg of  $\text{Pd}_2(\text{dba})_3$  ( $2.18 \times 10^{-3}$  mmol) were suspended in 90 ml of toluene. Separately, NBE (10 g) was dissolved in 10 ml of toluene. The catalyst solution and the NBE solutions were then introduced into the 300 ml Parr reactor, immediately pressurized with 100 psi ethylene, and heated to 100 °C. When this temperature was reached, ethylene was supplied continuously at 300 psi, and the conversion of ethylene was monitored on-line. After 90 min, the reaction was stopped, and the polymer collected by precipitation in 4 volumes of methanol, filtered and dried under vacuum.

### 2.4. Coating preparation

Aqueous-borne latexes such as ethylene-hexadecene coatings were prepared by applying the latex of copolymer (~3 g, based on the latex, approximately 600 mg based on the polymer) to the steel plate. Water was left to evaporate overnight, generating films of approximately 200  $\mu\text{m}$  thickness, based on the amount of polymer deposited. Because of the low solid content and low viscosity of these latexes, there were no differences between films prepared using a draw-bar (Microm-II, Gardco) or film prepared by brush application.

Solvent borne coatings such as ethylene-norbornene copolymers were prepared by applying a 10 wt% solution of the polymer dissolved in xylene.

### 2.5. Latex characterization

Particle size distribution was assessed by transmission electron microscopy (TEM) and dynamic light scattering (DLS). TEM measurements were effected on a Leo 922 using uranyl acetate as negative contrast agent. Particle size measurements were carried out using a capillary hydrodynamic fractionation instrument, CHDF 2000 from Matec Applied Sciences and by dynamic light scattering using a Nanotrak S/N:U1730 or a Microtrac VSR S3000 instrument.

#### 2.5.1. Analysis of the polymer microstructure

NMR spectra were recorded in  $d^4$ -*o*-dichlorobenzene (ODCB) at 115 °C using NMR Varian 400 MHz (Mercury) and 500 MHz (Inova). Polymers were first washed in water in order to remove most of the adsorbed surfactant and unreacted monomer (when present). When residual surfactant was observed by  $^1\text{H}$  NMR, the integrals of the polymer peaks were corrected to account for the presence of residual surfactant buried under the resonances of the polymer.

#### 2.5.2. Pure PE

NMR  $^1\text{H}$  (ODCB): 0.83 (t,  $J=6.30$  Hz,  $\text{CH}_3$ ), 1.26 (m,  $\text{CH}_2$  “PE”), 1.56 (m, CH), 1.96 (m,  $\text{CH}_2$  allyl), 4.71 (s,  $\text{CH}_2=\text{CR}_2$ ), 4.86 (d,  $J=9.67$ ,  $\text{H}^1\text{H}^2\text{C}=\text{CH}$ - *trans*), 4.92 (d,  $J=17.23$ ,  $\text{H}^1\text{H}^2\text{C}=\text{CH}$ - *cis*), 5.35 (m,  $-\text{CH}=\text{CH}-$ ), 5.73 (m,  $\text{CH}_2=\text{CH}-\text{CH}_2-$ ).

#### 2.5.3. Poly(ethylene-hexadecene) (expt. 9)

NMR  $^1\text{H}$  (ODCB): 0.82 (m,  $\text{CH}_3$ ), 1.26 (m,  $\text{CH}_2$  “PE”), 1.54 (m, CH), 1.96 (m,  $\text{CH}_2$  allyl), 4.71 (s,  $\text{CH}_2=\text{CR}_2$ ), 4.86 (d,  $J=10.15$ ,  $\text{H}^1\text{H}^2\text{C}=\text{CH}$ - *trans*), 4.92 (d,  $J=17.24$ ,  $\text{H}^1\text{H}^2\text{C}=\text{CH}$ - *cis*), 5.37 (m,  $-\text{CH}=\text{CH}-$ ), 5.73 (m,  $\text{CH}_2=\text{CH}-\text{CH}_2-$ ).

Molecular weight of a copolymer ( $M_n$ , g/mol) was assessed as  $M_n = I_{\text{total}}(14/2)/[I(-\text{CH}=\text{CH}_2) + I(-\text{CH}=\text{CH}-)/2]$  where  $I$  is the integral of the corresponding peak. The percentage of hexadecene units incorporation ( $X_{\text{hd}}$ ) was calculated as  $X_{\text{hd}} = \{28(r-1-y)/[M_n - 197(r-1-y)]\} \times 100\%$  where  $r$  is the

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