ELSEVIER

Polymer 42 (2001) 8873–8881

polymer

www.elsevier.com/locate/polymer

Thermomechanical property modifications via reactive blending in polymeric complexes with palladium(II)

Pronab K. Das, Jin-Koo Lee, Izolda Y. Ruzmaikina[1], Laurence A. Belfiore*

Polymer Physics and Engineering Laboratory, Department of Chemical Engineering, Colorado State University, Fort Collins, CO 80523, USA

Received 16 July 2000

Abstract

Two organometallic strategies produce significant enhancements in the glass transition temperature and elastic modulus of polymer–polymer and polymer–ionomer blends. Reactive blending occurs via (i) olefin coordination and Zn/Pd transmetallation for zinc-neutralized sulfonated polystyrene with 3,4-polyisoprene, and (ii) direct nucleophilic attack on transition metal complexed organic substrates for sulfonated polystyrene or ethylene/methacrylic-acid random copolymers with 3,4-polyisoprene. The transition metal complex which facilitates chemical modification in each case is dichlorobis(acetonitrile)palladium(II). A 50/50 blend of lightly sulfonated polystyrene (4.8% sulfonation, 100% neutralized with zinc acetate) and 3,4-polyisoprene with 1 mol% Pd^{2+} exhibits reinforced rubbery response with a modulus of 1.4×10^8 N/m^2 and a fracture strain of 40%, whereas the binary polymer–ionomer blend without Pd^{2+} does not form a solid film that is cohesive enough for stress–strain testing. The T_gs and elastic moduli of these ternary complexes increase at higher concentrations of Pd^{2+}. A 50/50 complex of poly(ethylene-co-methacrylic acid) (i.e. Nucrel™ with 5.4 mol% acid) and 3,4-polyisoprene with 0.5 mol% Pd^{2+} exhibits a 5-fold increase in elastic modulus relative to the binary polymer–copolymer blend without Pd^{2+}. The same ternary complex with 2 mol% Pd^{2+} exhibits a 15-fold increase in elastic modulus. Infrared spectroscopy provides qualitative support for the proposed chemical modification mechanisms. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: 3,4-Polyisoprene; Zinc-neutralized sulfonated polystyrene; Nucrel™

1. Introduction

This research contribution focuses on the development of novel methods to modify the thermal and mechanical properties of polymer–polymer and polymer–ionomer blends. The global objective is to design polymeric materials that can withstand larger forces before failure occurs and higher temperatures prior to viscous flow or thermal degradation. This objective can be accomplished with assistance from transition metal chemistry because metal complexes from the d-block coordinate to ligands in the sidegroup of functional polymers via acid–base interactions [1–4]. Hence, these metal cations act like magnets that induce immiscible polymers to occupy vacant sites in the 1st shell coordination sphere of a single metal center. In some cases, the inorganic component catalyzes the formation of new chemical bonds that provide mechanical integrity by increasing elastic moduli and fracture stresses.

Previous studies of compatibilization of polymer–ionomer blends have focused on ion–dipole interactions. Weiss et al. investigated miscibility in polyamides [5–7] and bisphenol A polycarbonate [8] with metal-neutralized sulfonated polystyrene. Ha et al. have reported that the miscibility of polypropylene and ethylene/propylene/diene copolymer (EPDM) binary blends could be enhanced by adding ethylene/acrylic-acid ionomers [9]. Compatibilization can also be achieved by acid–base interactions. Eisenbach et al. [10] have utilized interactions between pyridine sidegroups in functionalized polydiacetylene and hydroxyl groups in sulfonated polystyrene to generate miscible blends. Molnar and Eisenberg [11] have induced miscibility between polyurethanes and sulfonated polystyrene, and Bazuin and Eisenberg [12] have complexed sulfonated polystyrene with tertiary amine-terminated oligomers of styrene via ionic interactions.

The following elementary reactions in low-molecular-weight organometallic compounds [1] are useful for chemical compatibilization of functional polymers. These are; (i)

---

* Corresponding author. Tel.: +1-970-491-5395; fax: +1-970-491-7369. *E-mail address:* belfiore@engr.colostate.edu (L.A. Belfiore).

[1] Permanent address: Institute of Macromolecular Compounds, St Petersburg, Russia.

PII: S0032-3861(01)00330-5

oxidative addition and reductive elimination, (ii) migratory insertion and β-hydride elimination, (iii) nucleophilic attack on transition metal complexed organic substrates, such as chloropalladation and hydropalladation, and (iv) transmetallation. By choosing polymers with the appropriate functional groups, preferably in the side chain, and combining some of these reactions, two dissimilar polymers can be linked via a coordination bridge or a chemical bond. Successful organometallic sequences for reactive blending rely on the following facts [1]; (a) organic functional groups coordinate to most transition metals via p–d overlap of ligand p-orbitals with partially filled metal d-orbitals, and (b) complexation drastically alters the reactivity of organic functional group that reside in the 1st-shell coordination sphere due to σ-donation and π-back-donation of electron density.

The specific objectives of this research are to modify the thermal and mechanical properties of (i) 3,4-polyisoprene (3,4-PI) and zinc-neutralized sulfonated polystyrene via olefin coordination and transmetallation, and (ii) 3,4-PI with either lightly sulfonated polystyrene or ethylene/methacrylic-acid random copolymers via nucleophilic attack on transition metal complexed organic substrates. In all cases investigated herein, the polymers are commercially available from Goodyear, DuPont and Exxon. Consequently, a minimal amount of preparative work is required to generate compatibilized organometallic complexes.

Previous research in our laboratory [13,14] has established that dichlorobis(acetonitrile)palladium(II) forms η^2-coordinated π-complexes with atactic 1,2-polybuta-diene and 3,4-PI [i.e. $R(CH_3)C{=}CH_2$]. Transmetallation [1] involves ligand exchange, as illustrated below, where R′, initially bound to a main group metal cation (i.e. Zn^{2+}), exchanges with a halide and coordinates to Pd^{2+};

$$R'ZnCl + PdCl_2(CH_3CN)[R(CH_3)C{=}CH_2]$$

$$\leftrightarrow R'PdCl(CH_3CN)[R(CH_3)C{=}CH_2] + ZnCl_2$$

The palladium complex on the right side of the previous transmetallation reaction contains two different polymer chains, denoted by R and R′, in its 1st shell coordination sphere. Zinc-to-palladium transmetallation proceeds favorably because this palladium intermediate, $R'PdCl(CH_3CN)[R(CH_3)C{=}CH_2]$, is consumed irreversibly in a subsequent reaction. There is substantial precedence in the organometallic literature of small molecules that organozinc halides are the most efficient main group halides in transmetallation reactions with palladium(II) [15,16]. Unfortunately, zinc chloride is thermodynamically unfavorable for neutralization of sulfonated polystyrene. To circumvent this difficulty, zinc acetate was chosen as the neutralizing agent. Reactive functional groups in the side-chains of zinc-neutralized sulfonated polystyrene and 3,4-PI can be linked together via olefin coordination and Zn/Pd transmetallation. The first part of this manuscript addresses chemical modification of this polymer–ionomer blend.

Next, modification of 3,4-PI and either (i) lightly sulfonated polystyrene without zinc neutralization or (ii) ethylene/methacrylic-acid random copolymers is accomplished using Pd^{2+}. The mechanism for reactive blending is based on the fact that Pd-coordinated alkene sidegroups in 3,4-PI are susceptible to nucleophilic attack, [17,18] due to (i) σ-donation of electron density from π-bonding orbitals of the alkene to the z^2 and x^2–y^2 d-orbitals of the metal cation, and (ii) π-back-donation of electron density from d_{xy} on the metal to antibonding π^* orbitals of the alkene via the Dewar–Chatt model [19]. Nucleophilic attack is favored at the more substituted olefinic carbon [1] in low-molecular-weight systems. This approach is feasible only for monosubstituted and 1,1-disubstituted olefins [1], like 1,2-polybutadiene and 3,4-PI, respectively. The techniques employed to characterize these ternary complexes include mechanical property measurements, differential scanning calorimetry and infrared spectroscopy.

2. Experimental considerations

2.1. Materials

3,4-PI was obtained from Goodyear Tire and Rubber Company in Akron, OH, courtesy of Dr Adel F. Halasa, with a weight-average molecular weight of 4×10^5 daltons and a polydispersity index of 1.5. The microstructure of polyisoprene is 78% 3,4- (i.e. vinyl), 14% 1,2- and 8% 1,4-*cis*. Random copolymers of ethylene and methacrylic acid (Nucrel™) were obtained from DuPont in Wilmington, DE, courtesy of Drs George Hoh and Donna L. Visioli, with 5.4 mol% (i.e. 15 wt%) methacrylic acid and a melting (i.e. peak) temperature of 94°C. Polystyrene was purchased from Scientific Polymer Products with a weight-average molecular weight of 3.5×10^4 daltons, and T_g is 61°C. Zinc(II) acetate dihydrate and dichlorobis(acetonitrile)palladium(II) were purchased from Strem Chemicals. Tetrahydrofuran, methanol, 2-butanol, 2-propanol, toluene, xylene and dichloroethane were purchased from Aldrich Chemical Company.

2.2. Sulfonation and neutralization of polystyrene

Lightly sulfonated polystyrene was prepared via a procedure that is described in the research [20] and patent [21] literature. The sulfonating agent was acetyl sulfate at 50°C in dichloroethane. The reaction was terminated by adding 2-propanol, and the product was recovered in methanol. Approximately 80–90% yield was achieved. The sulfonation content of polystyrene employed in this study is 4.8%, as determined by titration of the sulfonic acid pendant groups using 0.02N NaOH in methanol, with a phenolphthalein indicator. The presence of sulfonic acid pendant groups was verified by infrared absorptions at (i) 1033 cm^{-1} for in-plane stretching of the sulfonate anion and (ii) 1126 cm^{-1} for in-plane skeletal vibrations of sulfonated benzene [22]. Next, lightly sulfonated polystyrene was dissolved in a 90/10 mixture of toluene and methanol, and the solution was neutralized with 0.02-molar zinc(II) acetate in methanol. The indicator dye titration method suggests that approximately 100% neutralization was obtained. An infrared signal at 1259 cm^{-1}, due to asymmetric stretching [22] of SO_3Zn supports the neutralization procedure that was employed.

2.3. Sample preparation methods

Polymer/metal solid complexes were prepared by mixing appropriate amounts of polymer and metal-complex solutions in a 250-ml airless flask under reflux and a slight positive pressure of argon. Blends of sulfonated polystyrene and 3,4-PI were prepared in a 90/10 (v/v) mixture of THF/methanol. The cosolvent for Nucrel™ was 90/10 (v/v) xylene/2-butanol. Blends of Nucrel™ and 3,4-PI were prepared under reflux and slight positive pressure of argon at 100°C for 1 h. The solvents (i.e. xylene and 2-butanol) were removed at 80°C under vacuum for 3 days. Binary polymer–polymer blends described below as 50/50 (i.e. equimolar) indicate the repeat unit mole fraction of each polymer as a percentage. Sample compositions for polymer/polymer/Pd^{2+} complexes employ the same ratio mentioned above for the two polymers (i.e. 50/50) and include the molar ratio of Pd^{2+} with respect to the total moles of both polymeric repeat units. Since reactive blending is operative for chemical compatibilization, mole fractions are the preferred concentration variables instead of weight fractions.

2.4. Physical property measurements

Mechanical. Engineering stress–strain response was measured at ambient temperature using an Instron model 8501 servohydraulic mechanical testing system. The strain rate was 25 mm/min (i.e. ≈1 inch/min). Samples were cut into rectangular strips with average dimensions of 45 mm (length), 3.2 mm (width), and a thickness varying from 0.25 to 0.65 mm. At least three solid films were tested for reproducibility of each material. The elastic modulus was calculated from the initial slope of the stress–strain curve.

Thermal. Differential scanning calorimetry was performed on a Perkin Elmer DSC-7 after calibration with indium and zinc. Samples were heated under nitrogen purge at a rate of 20°C/min from −40 to 250°C. After the 1st heating scan, samples were quenched to −40°C using dry-ice/acetone as the coolant. T_g was measured during the 2nd, 3rd or 4th heating traces. Of particular concern, here, is that solid state chemical reactions in the presence of Pd^{2+} during the 1st DSC heating could affect the measurement of T_g during subsequent heating scans. Due to the presence of exotherms and endotherms prior to major melting in ternary complexes of Nucrel™, 3,4-PI and Pd^{2+}, the melting transition in Nucrel™ was measured during the 2nd heating scan, which occurred immediately after the first cooling to ambient temperature because recrystallization of the ethylene segments occurs rapidly.

Infrared spectroscopy. Fourier transform infrared spectroscopy was performed on a Galaxy™ series model 5020 from Mattson Instruments. The optical bench is interfaced to Mattson's WinFIRST v.3.5 software on a personal computer for data acquisition and control. Transition metal complexes were tested as thin films deposited on KBr crystals acquired from International Crystal Labs. Each spectrum was generated by signal averaging 32 interferograms at a resolution of 2 cm^{-1}, and a triangular apodization smoothing function was implemented prior to Fourier transformation. A heated transmission cell from Spectra-Tech (model HT-32) was employed to obtain infrared spectra at 200°C. Temperature control was accomplished via a Eurotherm 818P15 programmable microprocessor with an accuracy of ≈1°C.

3. Results and discussion

3.1. Thermomechanical properties of SPS/3,4-PI binary blends, with and without zinc neutralization

The glass transition temperatures of 3,4-polyisoprene (3,4-PI) and sulfonated polystyrene (4.8% sulfonation), SPS, are 14°C and 98°C, respectively. At 6.7% sulfonation, for example, the glass transition temperature of 35 K polystyrene increases to 111°C. When 2.4 mol% zinc(II) acetate is employed to neutralize sulfonated polystyrene (i.e. 4.8% sulfonation), T_g increases from 98°C to 117°C. This is due to the formation ionic clusters that are characteristic of ionomers [23]. Mechanical data in Fig. 1 reveal that 3,4-PI is rubbery with an elastic modulus of 1.2×10^7 N/m^2 and a fracture strain greater than 660%. Sulfonated polystyrene is glassy, and it does not form films that are cohesive enough for stress–strain testing. The 50/50 blend of lightly sulfonated polystyrene and 3,4-PI exhibits an elastic modulus of 4.8×10^7 N/m^2 and a fracture strain of 180%, as illustrated in Fig. 1 and summarized in Table 1. Hence, the low-molecular-weight nature of polystyrene used herein does not preclude measurements of its mechanical properties in blends with rubbery polymers, like 3,4-PI. However, the 50/50 blend of zinc-neutralized sulfonated polystyrene and 3,4-PI is opaque, and could not be removed from a Teflon™ petri dish for mechanical testing.

3.2. Thermomechanical properties of SPS/3,4-PI/Pd^{2+} ternary complexes, with and without zinc neutralization

Immiscible blends of 3,4-PI and the sulfonated polystyrene ionomer are chemically modified by rather low concentrations of Pd^{2+} at 65°C under argon. A 50/50 blend of zinc-neutralized sulfonated polystyrene and 3,4-PI with 1 mol% Pd^{2+} exhibits a modulus of 1.4×10^8 N/m^2 and a fracture strain of 40%. At 5 mol% Pd^{2+}, the elastic

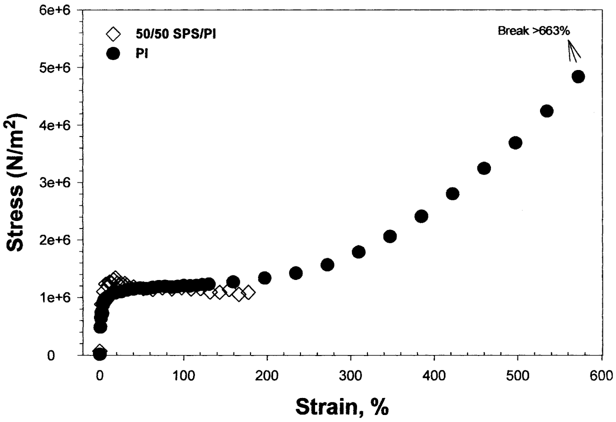

Fig. 1. Stress–strain response of 3,4-polyisoprene and a 50/50 blend of sulfonated polystyrene with 3,4-PI.

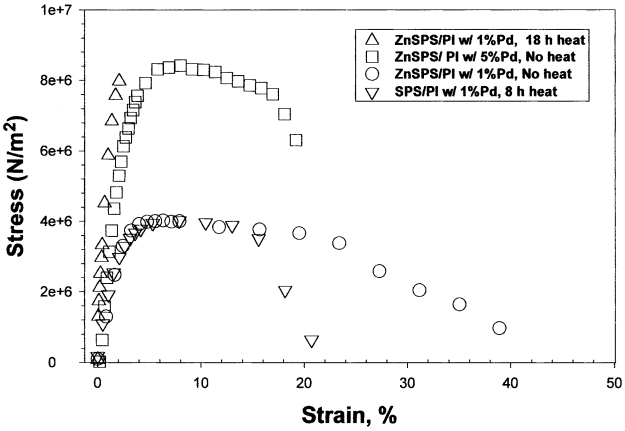

Fig. 2. Stress–strain response for complexes of 3,4-PI and zinc-neutralized sulfonated polystyrene with Pd^{2+}.

modulus increases to 3.4×10^8 N/m^2 and the fracture strain decreases to 19%. These results are illustrated in Fig. 2 and summarized in Table 1. The measurement of T_g in reactive blends is complicated by the fact that the addition of thermal energy in the calorimeter triggers solid state reactions which could increase T_g. Hence, samples with ambient-temperature elastic moduli that are characteristic of reinforced rubbery solids might exhibit a glass transition well above ambient if three or four DSC heating scans are required to obtain a reproducible T_g from two successive experiments. For the 50/50 blend of zinc-neutralized sulfonated polystyrene and 3,4-PI with 1 mol% Pd^{2+}, one glass transition at 104°C was measured during the 3rd and 4th heating scans after all of the exothermic processes were completed. At higher Pd^{2+} concentrations, the single T_g of these ternary complexes increases to 131°C at 2 mol% Pd^{2+} and 202°C at 3 mol% Pd^{2+}. T_g is not detected by DSC when the Pd^{2+} concentration is greater than 3 mol% in these ternary complexes because the discontinuous change in specific heat at T_g decreases considerably, and the glass transition becomes more diffuse, at higher crosslink density.

The ternary solid state complexes discussed above were generated by mixing the polymer and Pd^{2+} solutions at 65°C under argon for about five minutes, and evaporating the

Table 1
Thermal and mechanical properties of polymer blends and complexes with Pd^{2+}

Material	Preparation	Tg (°C)	Elastic modulus (N/m^2)	Fracture strain (%)
3,4-Polyisoprene	dissolved at ambient	14	1.2×10^7	> 660
Nucrel™	dissolved at 100°C		6.2×10^7	400
50/50 blend				
Nucrel™	mixed 1 h at 100°C		2.8×10^7	240
3,4-Polyisoprene	> 48 h at ambient			
50/50 blend				
3,4-Polyisoprene	mixed at 65°C		4.8×10^7	180
Sulfonated polystyrene				
50/50 complex				
3,4-Polyisoprene	mixed 8 h at 65°C		1.8×10^8	22
Sulfonated polystyrene	> 24 h at ambient			
1 mol% Pd^{2+}		87,127		
50/50 complexes				
3,4-Polyisoprene				
Zn-sulfonated polystyrene				
(a) 1 mol% Pd^{2+}	mixed 5 min at 65°C	104	1.4×10^8	40
(b) 1 mol% Pd^{2+}	mixed 18 h at 65°C	101	6.2×10^8	2
(c) 5 mol% Pd^{2+}	mixed 5 min at 65°C	202	3.4×10^8	19
50/50 complexes				
Nucrel™				
3,4-Polyisoprene				
(a) 0.5 mol% Pd^{2+}	mixed 1 h at 100°C		1.5×10^8	274
(b) 2 mol% Pd^{2+}	mixed 1 h at 100°C		4.2×10^8	8

solvents at ambient temperature in a fume hood. When a 50/50 blend of zinc-neutralized sulfonated polystyrene and 3,4-PI with 1 mol% Pd^{2+} is refluxed for 18 h at 65°C under argon, a glassy solid is obtained upon solvent evaporation at ambient temperature with a modulus of 6.2×10^8 N/m^2, a fracture strain of 2%, and T_g is 101°C. Hence, reactive blending at 65°C for much longer times induces an approximate 4-fold increase in elastic modulus (i.e. from 1.4×10^8 to 6.2×10^8 N/m^2) and a considerable decrease in fracture strain (i.e. from 40 to 2%). However, single T_g response is essentially unchanged (i.e. 104 vs. 101°C) because samples not exposed to prolonged refluxing at 65°C were subjected to three or four DSC heating scans and isothermal soaks in the molten state at 250°C prior to the measurement of T_g. The stress–strain response of all SPS/PI/Pd^{2+} blends and complexes that can be tested via Instron™ is illustrated in Fig. 2 and summarized in Table 1.

Ternary complexes of lightly sulfonated polystyrene, 3,4-PI and Pd^{2+} exhibit thermomechanical properties that are modified by reactions which proceed in the coordination sphere of the transition metal cation. When an equimolar blend of both polymers with 1 mol% Pd^{2+} is refluxed for 8 h at 65°C under argon, a reinforced rubbery solid is obtained after solvent evaporation at ambient temperature with an elastic modulus of 1.8×10^8 N/m^2, a fracture strain of 22%, and two T_gs near 87 and 127°C. The stress–strain response of this complex is illustrated in Fig. 2 and summarized in Table 1. In this case, reactive blending at 65°C for extended times with 1 mol% Pd^{2+} induces an approximate 4-fold increase in elastic modulus relative to the binary polymer–polymer blend without Pd^{2+} (i.e. 4.8×10^7 N/m^2 vs. 1.8×10^8 N/m^2), with significantly lower fracture strain (i.e. 180 vs. 22%). Since sulfonated polystyrene is not neutralized and transmetallation should not occur, mechanical property modification might proceed by direct nucleophilic attack of the polystyrene sulfonate anion on a palladium-coordinated alkene sidegroup in 3,4-PI, as discussed below.

3.3. A proposed mechanism for thermomechanical property modifications of zinc-neutralized sulfonated polystyrene and 3,4-PI via Pd^{2+}

When sulfonated polystyrene is neutralized with Zn^{2+}, a possible explanation for chemical modification in ternary complexes with 3,4-PI and Pd^{2+} is based on a multi-step sequence of organometallic reactions which include olefin coordination and transmetallation. Two slightly different final products are envisioned in which both polymers are linked to adjacent alkene carbons (i.e. step 4) or one tetrahedral carbon (i.e. step 5(b-(iv)). The complete sequence is described below and in Fig. 3.

1. An alkene sidegroup in 3,4-PI displaces weakly bound acetonitrile and coordinates to Pd^{2+}, forming an η^2 π-olefin complex,
2. Nucleophilic attack by the polystyrene sulfonate anion (Y) occurs on Pd^{2+}, and the polymeric ion attached to Zn^{2+} exchanges with one of the chlorides coordinated to Pd^{2+} via Zn/Pd transmetallation,
3. If sulfonated polystyrene occupies a site in the coordination sphere of Pd^{2+} such that the polymeric anion is *cis* to the coordinated alkene, then sulfonated polystyrene migrates and inserts at the *less* substituted end of the terminal alkene,
4. β-hydrogen elimination links these two immiscible polymers via a carbon–oxygen single bond and generates $HPdCl(CH_3CN)$(solvent). There are three possibilities for β-hydrogen elimination. The final product illustrated in step 4 of Fig. 3 is based on β-hydride elimination from the olefinic CH_2 sidegroup in 3,4-PI. An overall summary of these four elementary steps yields;

$$\begin{aligned} & R(CH_3)C{=}CH_2 + PdCl_2(CH_3CN)_2 + CH_3COOZnY \\ & \quad \rightarrow R(CH_3)C{=}CHY + HPdCl(CH_3CN)_2 \qquad (1) \\ & \quad + CH_3COOZnCl \end{aligned}$$

   where the first structure on the right represents the final product of interest, with enhanced glass transition temperature and elastic modulus.
5. At most, the cycle continues once more because $HPdCl(CH_3CN)$ (solvent) either;
   (a) Reductively eliminates to Pd(0) and HCl and the process is completed, because there are no more anionic chloride ligands in the coordination sphere of Pd(0) that are required for transmetallation,
   or $HPdCl(CH_3CN)$ (solvent);
   (b) (i) coordinates to another alkene sidegroup in 3,4-PI via displacement of acetonitrile or the solvent,
   (ii) hydropalladates the coordinated alkene (i.e. migratory insertion of coordinated H at the *less* substituted end of the terminal alkene), which proceeds much faster than chloropalladation,
   (iii) transmetallates with zinc-neutralized sulfonated polystyrene, which is favored relative to reductive elimination, and
   (iv) reductively eliminates to Pd(0), generating a covalent linkage between these two immiscible polymers which is different from the product in step 4. Sulfonated polystyrene and 3,4-PI are tetrahedrally attached to the same carbon in the final product.

An overall summary of the last four elementary steps in 5(b) yields;

$$\begin{aligned} & R(CH_3)C{=}CH_2 + HPdCl(CH_3CN)(THF) + CH_3COOZnY \\ & \quad \rightarrow R(CH_3)_2CY + Pd(0)(CH_3CN)(THF) \\ & \quad + CH_3COOZnCl \qquad (2) \end{aligned}$$

where the first structure on the right represents the final

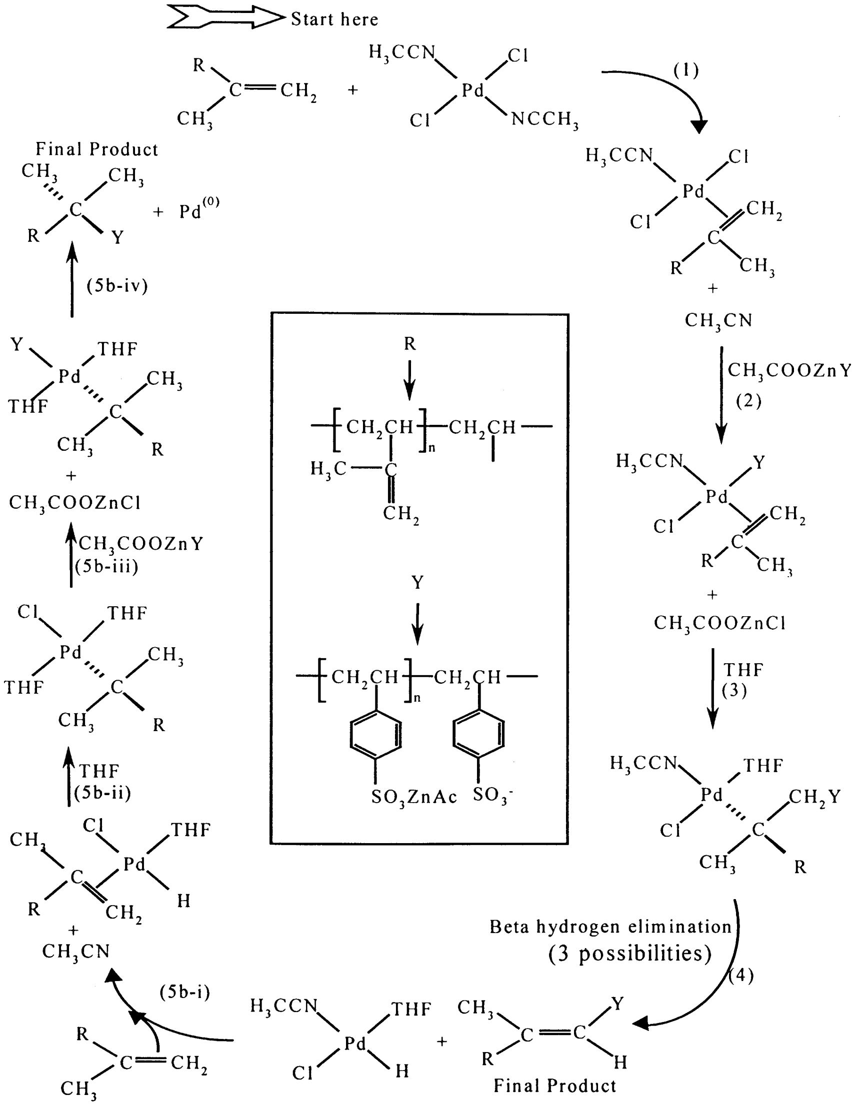

Fig. 3. A proposed mechanism for chemical modification of zinc-neutralized sulfonated polystyrene and 3,4-PI via palladium(II), based on transmetallation between Zn^{2+} and Pd^{2+}.

product of interest. Since the mechanism is not catalytic, there will be only a few covalent linkages between the two dissimilar polymers at very low palladium chloride concentrations. This is consistent with the fact that the elastic modulus of zinc-neutralized sulfonated polystyrene and 3,4-PI experiences only moderate increases due to Pd^{2+}. If the mechanism were catalytic, then one should expect more than one order of magnitude increase in elastic modulus at 2 mol% Pd^{2+}, even though only ≈5% of the sidegroups in polystyrene are sulfonated and neutralized. The presence of C–O–S stretching [22] in the infrared spectrum at 1192 cm^{-1} supports the final products in steps 4 and 5(b-(iv)), suggesting that reactive blending via transmetallation is operative.

3.4. Physical properties of Nucrel™/3,4-PI/Pd^{2+} complexes

Nucrel™ is a random copolymer of ethylene and methacrylic acid with an elastic modulus of 6.2×10^7 N/m^2, a fracture strain of 400%, and a melting peak at 94°C. If the carboxylate anion in the methacrylic acid segments of Nucrel™ functions similarly to the polystyrene sulfonate anion without zinc neutralization, then Pd^{2+} should induce significant physical property modifications in ternary complexes with 3,4-PI. A 50/50 blend of Nucrel™ and 3,4-PI exhibits an elastic modulus of 2.8×10^7 N/m^2 and stress–strain response which resembles that of 3,4-PI, but with considerably lower fracture strain (i.e. 240 vs. 660%) as illustrated in Fig. 4. When a 50/50 complex of Nucrel™ and 3,4-PI with 0.5 mol% Pd^{2+} is prepared under reflux in xylene and 2-butanol at 100°C for 1 h, the solid which is recovered after 48 h at ambient temperature and dried for 24 h at 90°C under vacuum exhibits reinforced ductile response with an elastic modulus of 1.5×10^8 N/m^2 and a fracture strain of 274%. This represents a 5-fold increase in elastic modulus relative to the polymer–polymer blend without Pd^{2+}, and slightly higher fracture strain (i.e. 274

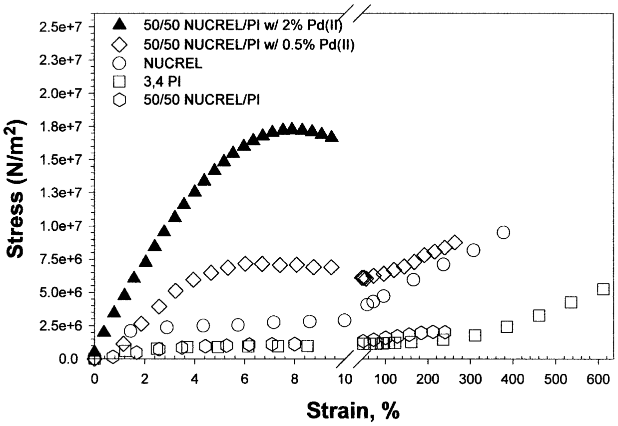

Fig. 4. Stress–strain response of 3,4-PI /Nucrel™ blends and complexes with Pd^{2+}.

vs. 240%). At 2 mol% Pd^{2+}, the ternary complex with Nucrel™ and 3,4-PI is glassy with 8% fracture strain and a 15-fold increase in elastic modulus relative to the polymer–polymer blend without Pd^{2+}. All of these stress–strain results are illustrated in Fig. 4 and summarized in Table 1. At higher Pd^{2+} concentrations, the solid ternary complexes are too brittle for stress–strain testing. The 50/50 binary polymer–polymer blend of Nucrel™ and 3,4-PI, and all of the ternary complexes with Pd^{2+}, exhibit ethylenic melting in the vicinity of 80°C.

3.5. A proposed mechanism for mechanical property modification of Nucrel™ and 3,4-PI via Pd^{2+}

As illustrated in Fig. 5, the following pathway represents a plausible mechanism for reactive blending of 3,4-PI with either lightly sulfonated polystyrene or ethylene/methacrylic-acid copolymers via dichlorobis(acetonitrile)-palladium(II). High temperature infrared data for the Nucrel™ complex in the following section are consistent with this sequence of elementary steps.

(1) An alkene sidegroup in 3,4-PI displaces weakly bound acetonitrile and coordinates to Pd^{2+}, forming an η^2 π-olefin complex.

(2a) Direct nucleophilic attack by the carboxylate anion of Nucrel™ (A) or the polystyrene sulfonate anion occurs at the more substituted carbon of the Pd-coordinated olefin. An aliphatic ester is produced via this pathway when the carboxylate anion of Nucrel™ participates in direct nucleophilic attack. β-Hydrogen elimination does not occur due to the presence of the methyl group in 3,4-PI, and neither does reductive elimination. Hence, Pd^{2+} remains coordinated to these two polymers as illustrated in Fig. 5. This pathway suggests that the concentration of C=C sidegroups in 3,4-PI should decrease. Since palladium remains in the +2 oxidation state, one of the anionic chloride ligands is displaced to the outer sphere and forms HCl with either the sulfonic acid proton of SPS or the carboxylic acid proton of Nucrel™. The vacant site in the 1st shell is occupied by acetonitrile or the solvent, THF.

($2b_1$) Steric hindrance of both polymeric chains (i.e. A and R) tetrahedrally attached to the same carbon atom in the final structure of step 2a might favor direct nucleophilic attack of either polymeric anion (i.e. A) at the *less* substituted carbon of the Pd-coordinated olefin. Once again, an anionic chloride ligand is displaced to the

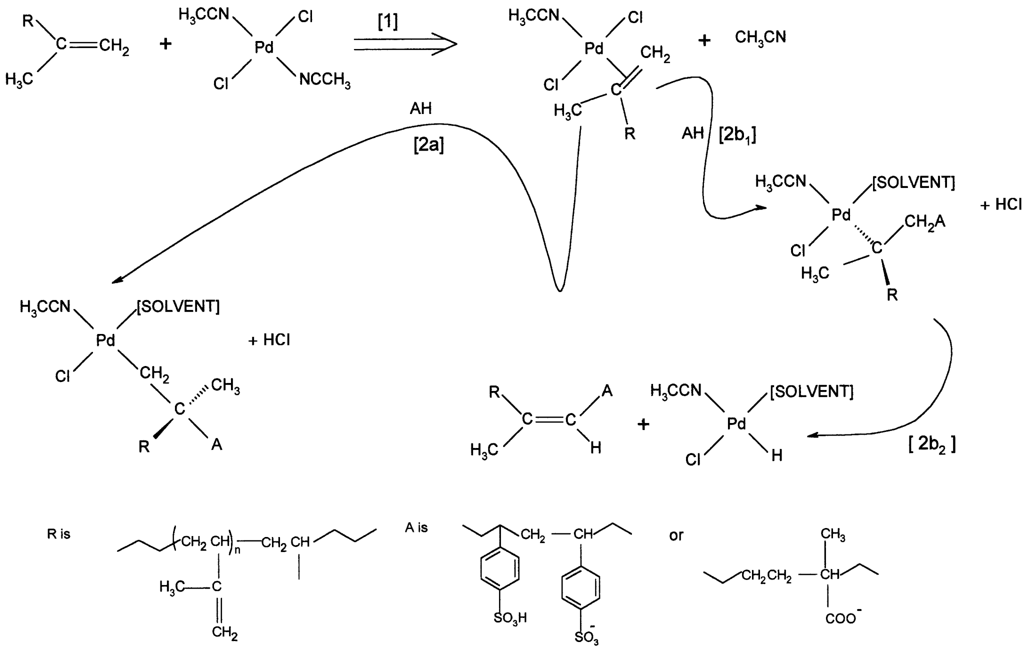

Fig. 5. A proposed mechanism for chemical modification of 3,4-PI and either sulfonated polystyrene or random copolymers of ethylene and methacrylic acid (i.e. Nucrel™) via Pd^{2+} coordination to alkenes.

outer sphere and forms HCl, while THF or acetonitrile occupies the vacant site in the 1st shell coordination sphere of Pd^{2+}.

($2b_2$) If step $2b_1$ occurs, then β-hydrogen elimination is feasible and the two polymers are linked by a carbon–oxygen single bond. This pathway does not convert alkene sidegroups in 3,4-PI to aliphatic functionality. There are three possibilities for β-hydrogen elimination based on the intermediate product from step $2b_1$. Of the three β-carbons in this intermediate product, one of them (i.e. R) contains one β-hydrogen, the β-carbon of choice contains two β-hydrogens, and the methyl group in the sidechain of 3,4-PI contains three β-hydrogens. All of the possible final products represent a compatibilized blend in which A and R are attached to adjacent carbons. The final product illustrated in step $2b_2$ is based on β-hydride elimination from the olefinic CH_2 sidegroup in 3,4-PI. This final product yields a vinyl ester when the carboxylate anion of Nucrel™ participates in direct nucleophilic attack at the *less* substituted end of the coordinated olefin.

3.6. High-temperature infrared spectroscopy of Nucrel™/3,4-PI/Pd^{2+} complexes

When a solid ternary complex of Nucrel™, 3,4-PI and 4 mol% Pd^{2+} is held isothermally at 200°C, the intensity of the C=C stretch in 3,4-PI at 1640 cm^{-1} decreases irreversibly, and C=O stretching in the methacrylic acid segments [24] of Nucrel™ between 1700 and 1750 cm^{-1} is redistributed with a superficial peak absorption at 1718 cm^{-1}, which increases at longer annealing times. The kinetics of this process are illustrated in Fig. 6. One of the pathways described above (i.e. step 2a) converts carbon–carbon double bonds in the sidegroup of 3,4-PI to aliphatic functionality. Hence, direct nucleophilic attack by the carboxylate anion of Nucrel™ at the *more* substituted carbon of the Pd-coordinated olefin without β-hydrogen elimination is operative at 200°C, because the intensity of 3,4-PI's C=C stretch at 1640 cm^{-1} decreases by about 30–40% after 2 h. When nucleophilic attack occurs via the carboxylate anion of Nucrel™, an aliphatic ester is generated via step 2a, as described in the previous section, which produces a C=O stretch [25] at 1735 cm^{-1}. This infrared signal appears as one of the shoulders between 1700 and 1750 cm^{-1} in Fig. 6. If step 2b is favored, then a vinyl ester is produced, and the C=O stretching frequency should increase [25] (i.e. between 1770 and 1800 cm^{-1}) relative to the carbonyl stretch of the aliphatic ester produced via step 2a. Chemical modification pathway 2a is favored at 200°C because (i) the C=C stretch in 3,4-PI decreases irreversibly, (ii) an aliphatic ester C=O absorption is observed near 1735 cm^{-1}, and (iii) there is no vinyl ester C=O signal. Hydrogen-bonded carboxylic acid dimers absorb [24] at 1702 cm^{-1}, and the weak C=O stretch in 'free' (i.e. non-hydrogen-bonded) methacrylic acid segments absorbs [24] at 1750 cm^{-1} on the far left side of Fig. 6.

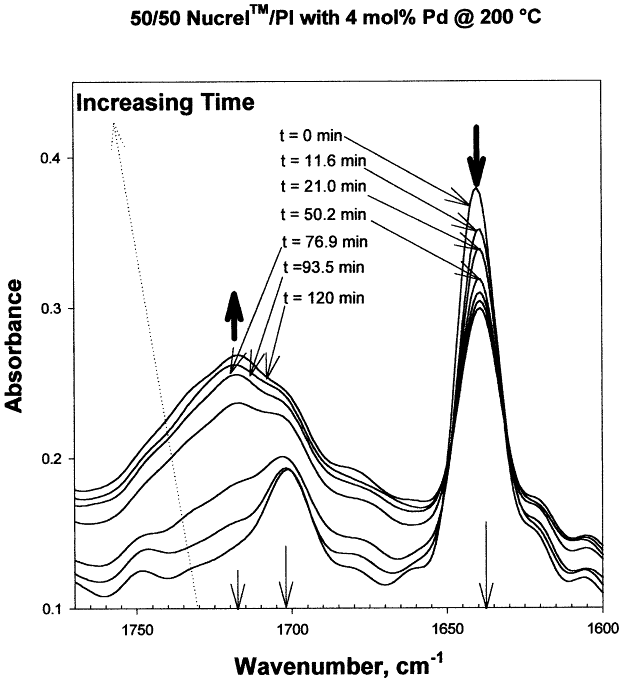

Fig. 6. Transient infrared spectra at 200°C for a ternary complex of 3,4-PI, Nucrel™ and 4 mol% Pd^{2+}. The C=C stretch in 3,4-PI is identified at 1640 cm^{-1}. The hydrogen-bonded and non-hydrogen-bonded carbonyl stretches in Nucrel™ absorb infrared radiation at 1702 and 1750 cm^{-1}, respectively. An aliphatic ester carbonyl appears as a shoulder at 1735 cm^{-1}.

4. Conclusions

The thermomechanical properties of 3,4-PI blends with either (i) lightly sulfonated polystyrene, (ii) zinc-neutralized sulfonated polystyrene, or (iii) random copolymers of ethylene and methacrylic acid are modified significantly by dichlorobis(acetonitrile)palladium(II). In each case, organometallic reactions which occur in the coordination sphere of Pd^{2+} link both polymers via chemical bonds. Both types of chemical modification strategies have been demonstrated using commercially available polymers. Olefin coordination and zinc-to-palladium transmetallation are operative when sulfonated polystyrene is neutralized with Zn^{2+}. Whereas zinc-neutralized sulfonated polystyrene is too brittle and cannot be tested mechanically, the ternary complex with 3,4-PI and dichlorobis(acetonitrile)palladium(II) exhibits an elastic modulus and glass transition temperature which increase at higher concentrations of Pd^{2+}. When sulfonated polystyrene is not neutralized, reactive blending with 3,4-PI occurs via nucleophilic attack of the sulfonate anion on the Pd-coordinated alkene sidegroup of 3,4-PI. The same mechanism is responsible for thermophysical property modifications of Nucrel™ with 3,4-PI. At 2 mol% Pd^{2+}, the ternary complex with Nucrel™ and 3,4-PI exhibits a 15-fold increase in elastic modulus relative to the polymer–copolymer blend without Pd^{2+}. Hence, two different organometallic strategies based on palladium(II) coordination to alkenes have been implemented to produce significant thermomechanical property modifications in commercially important polymers.

Acknowledgements

The research described herein is supported by the National Science Foundation's Division of Materials Research, Polymer program, through grant DMR-9902657. Aaron R. Goerke in the Department of Chemical Engineering at Colorado State University is acknowledged for synthesizing lightly sulfonated polystyrene.

References

[1] Hegedus LS. Transition metals in the synthesis of complex organic molecules. 2nd ed. Mill Valley, CA: University Science Books, 1999.
[2] Fu DK, Xu B, Swager TM. Tetrahedron 1997;53:15487.
[3] Peng Z, Charavi AR, Yu L. J Am Chem Soc 1997;119:4622.
[4] Maddix T, Li W, Yu L. J Am Chem Soc 1997;119:844.
[5] Feng Y, Schmidt A, Weiss RA. Macromolecules 1996;29(11):3909.
[6] Feng Y, Weiss RA, Karim A, Han CC, Anker JF, Kaiser H, Peiffer DG. Macromolecules 1998;31(2):484.
[7] Lu X, Weiss RA. Macromolecules 1992;25(23):6185.
[8] Lu X, Weiss RA. Macromolecules 1996;29(4):1216.
[9] Kim Y, Cho WJ, Ha CS. Polym Engng Sci 1995;35:1592.
[10] Eisenbach CD, Hofmann J, Göldel A, Noolandi J, Shi AC. Macromolecules 1999;32(5):1463.
[11] Molnar A, Eisenberg A. Macromolecules 1992;25:5774.
[12] Bazuin CG, Eisenberg A. Ind Engng Chem Prod Res Dev 1981;16:271.
[13] Bossé F, Das PK, Belfiore LA. Macromolecules 1995;28(20):6993.
[14] Belfiore LA, Bossé F, Das PK. Polym Int 1995;36:165.
[15] Kobayashi M, Negishi EI. J Org Chem 1980;45:5223.
[16] Negishi EI, Owczarczyk Z. Tetrahedron Lett 1991;32:6683.
[17] Hegedus LS, Akermark B, Zetterberg K, Olsson LF. J Am Chem Soc 1984;106:7122.
[18] Hegedus LS, Williams RE, McGuire MA, Hayashi T. J Am Chem Soc 1980;102:4973.
[19] Shriver DE, Atkins PW, Langford CH. Inorganic chemistry. New York: W.H. Freeman and Company, 1990 p. 520.
[20] Feng Y, Karim A, Weiss RA, Douglas JF, Han CC. Macromolecules 1996;29(11):3918.
[21] Makowski HS, Lundberg RD, Singhal GH. Flexible polymeric compositions comprising a normally plastic polymer sulfonated to about 0.2% to about 10% sulfonate. US Patent 3,870,841, 1975. Exxon Research and Engr.
[22] Zundel G. Hydration and intermolecular interaction: infrared investigations with polyelectrolyte membranes. New York: Academic Press, 1969.
[23] Eisenberg A. Macromolecules 1971;4(1):125.
[24] Painter PC, Coleman MM. Fundamentals of polymer science. Lancaster, PA: Technomic, 1994 p. 161–2.
[25] Pavia DL, Lampman GM, Kriz GS. Introduction to spectroscopy. 2nd ed. New York: Saunders College Publishing, 1996 p. 52–4.