

High-temperature infrared kinetics of transition-metal-catalyzed chemical reactions in solid state complexes of polybutadienes with palladium chloride

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Abstract

High-temperature infrared spectroscopy to 180°C identifies irreversible chemical changes that occur in solid state complexes of 1,2-polybutadiene and palladium chloride, prior to the onset of oxidation. The decrease in infrared absorption intensities at 910, 994, 1418 and 1640 cm⁻¹ signifies the consumption of carbon–carbon double bonds in the polymer whose microstructure is 80% 1,2-vinyl. The loss of C=C functionality in the sidegroup at elevated temperatures can be explained by palladium-catalyzed dimerization reactions. Transient experiments between 100°C and 140°C reveal that the reduction in the C=C infrared signal at 1640 cm⁻¹ follows an approximate 1st-order rate law which is consistent with a previous calorimetric study of exothermic kinetics over the same temperature range. Characteristic *n*th-order chemical reaction time constants for solid films of 1,2-polybutadiene with 4 mol% palladium chloride have been calculated at 100°C, 125°C and 140°C via infrared spectroscopy. These reaction time constants decrease at higher temperature with an apparent Arrhenius activation energy of ≈ 43 kJ/mol. Palladium complexes with *cis*-polybutadiene reveal that π back-donation of electron density from the metal center into the antibonding orbitals of the alkene group in the main chain shifts the C=C absorption from 1653 to 1543 cm⁻¹. The uncomplexed signal at 1653 cm⁻¹ is insensitive to high-temperature annealing whereas the palladium- π -complexed signal at 1543 cm⁻¹ is severely attenuated after annealing for a few minutes at 150°C. This suggests that the formation of a π -complex is required before high-temperature irreversible chemical reactions. Infrared-determined characteristic *n*th-order chemical reaction time constants for solid films of *cis*-polybutadiene with 4 mol% palladium chloride at 100°C, 125°C and 140°C are five-fold longer than the corresponding reaction time constants for 1,2-polybutadiene with 4 mol% PdCl₂. This kinetic mismatch is consistent with the trend in reaction rates for mono-substituted vs. di-substituted small-molecule alkenes, and suggests that a mixing strategy is required to compatibilize 1,2-polybutadiene and *cis*-polybutadiene via PdCl₂ at high temperatures. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The addition of palladium chloride to linear diene polymers containing olefinic sidegroups, followed by high temperature annealing, generates networks with greatly enhanced thermal and mechanical properties [1]. Solid films of these materials are insoluble in the original solvent used during the preparation step [2]. Macroscopic thermal and mechanical property modifications of atactic 1,2-polybutadiene (1,2-PBD) can be explained by palladium-

catalyzed addition reactions of alkene sidegroups that produce a chemically crosslinked network [3]. Motivation for this research is based on the organometallic literature of small molecules [4], where it has been demonstrated that selected transition metals form π -complexes and metallocycles with the carbon–carbon double bond in tetrafluoroethylene. Palladium(II) also forms coordination complexes with alkenes via displacement of weakly bound ligands such as acetonitrile [5,6]. Bis(acetonitrile)dichloropalladium(II) [PdCl₂(CH₃CN)₂] is employed in this investigation because previous studies in our laboratory [7–9] have shown that 1,2-polybutadiene forms covalent gels with PdCl₂(CH₃CN)₂ in a variety of solvents without stirring during a time span of 18 min to 18 h. Greater gelation times are observed in low-dielectric-constant solvents like toluene or benzene relative to high-dielectric-constant solvents such as tetrahydrofuran

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(THF) or chloroform [8]. These gels are classified as covalent chemical gels because even in the presence of a good ligand like triphenylphosphine, which should displace the alkene group(s) coordinated to palladium, the gels remain insoluble in all common solvents. Infrared spectroscopy and X-ray crystallography suggest that $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ exhibits a *trans*-square-planar geometry with D_{2h} symmetry [10]. After alkene sidegroups in the polymer displace both weakly bound acetonitriles and coordinate to palladium, there are a variety of high-temperature pathways [3,11], including (i) Heck-like dimerization reactions [12], and (ii) Pd^0 -catalyzed chemical crosslinking reactions that proceed via allylic intermediates, which lead to polymeric transition-metal complexes with enhanced thermal and mechanical properties.

The following significant physicochemical property modifications occur when $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ is added to atactic 1,2-polybutadiene. (i) Young's modulus of elasticity of the polymeric palladium complexes is three orders of magnitude higher than the undiluted solid polymer [2,3] when the palladium salt concentration is only 4 mol%, based on the moles of polymeric repeat units. (ii) Solid state carbon-13 NMR spectroscopy confirms that diamagnetic polymeric palladium complexes are glassy when the salt concentration is 4 mol% [2,9]. (iii) Swelling experiments reveal that solid films imbibe a variety of solvents, and the degree of swelling decreases as the concentration of palladium chloride increases [2,3]. (iv) Thermogravimetric analysis and differential scanning calorimetry indicate that diene polymers, including 1,2-polybutadiene and *cis*-polybutadiene (*cis*-PBD), are thermally stabilized by palladium chloride [3,13]. It is important to emphasize that items (i)–(iii) represent characteristics of solid complexes that have not been subjected to high temperature.

The primary objectives of this study are to (i) identify coordination complexes between PdCl_2 and polybutadienes via infrared spectroscopy, (ii) demonstrate that the kinetics of palladium-catalyzed dimerization reactions at high temperature proceed faster when olefinic functionality exists in the sidegroup (i.e. 1,2-PBD) relative to the main chain (i.e. *cis*-PBD), and (iii) develop a mixing strategy to compatibilize diene polymer blends via coordination and subsequent palladium-catalyzed chemical reactions when there is a kinetic mismatch as described in (ii).

2. Experimental considerations

2.1. Materials

Atactic 1,2-polybutadiene and 99% *cis*-1,4-polybutadiene were supplied by Goodyear Tire and Rubber Company (Akron, Ohio), courtesy of Dr. Adel F. Halasa. These samples were used as received without any additional purification. Size-exclusion chromatography at 50°C using spectroscopic grade tetrahydrofuran (THF) produced the

following data. The weight-average molecular weight of atactic 1,2-polybutadiene is 500 K with a polydispersity index of 1.6. Chromatographic calibration was based on narrow molecular weight polystyrene standards dissolved in THF. An intrinsic viscosity correction factor was employed to determine the absolute molecular weight of 1,2-polybutadiene. The microstructure of atactic polybutadiene is 80% 1,2-vinyl, 11% 1,4-*trans*, and 9% 1,4-*cis* [14]. The relatively weak infrared absorption at 967 cm^{-1} (see Fig. 4) is a signature of the *trans*-configuration, and signals between 670 and 740 cm^{-1} are characteristic of the *cis*-configuration [15]. Independent measurements of the number-average molecular weight of 99% *cis* 1,4-polybutadiene yielded 125 K [14]. The average molecular weights, polydispersities and microstructures of both polybutadienes are summarized in Table 1 for completeness, but no attempt is made to perform an in-depth study of these structural parameters on the physical properties that are presented in the Results and Discussion section. Bis(acetonitrile)dichloropalladium(II) was purchased from Strem Chemicals in Newburyport, Massachusetts. It was used without further purification.

2.2. Sample preparation methods

The polybutadienes and bis(acetonitrile)dichloropalladium(II) were dissolved separately while stirring in THF. The solubility of the palladium salt in THF is on the order of 0.5 g per 100 mL. The salt solution and polymer solutions were mixed in 20-mL air-tight vials. No further stirring was performed after the initial homogenization of the two solutions. Mole fractions of $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ are reported with respect to the repeat unit of the polymer, not relative to the polymer's average molecular weight. Thin films for transmission infrared spectroscopy were prepared from THF by solution casting onto KBr crystals prior to gelation. After most of the solvent evaporated in a well-ventilated fume hood, the films were dried further under vacuum in a desiccator for one hour to minimize residual solvent and water absorption. The absence of an infrared signal at 1076 cm^{-1} in all solid films (see Fig. 4), which is a signature of the antisymmetric C–O–C stretch for five-membered cyclic aliphatic ethers like THF [16,17], indicates that the residual level of THF is below the detection limit of the FTIR spectrometer. Even though some of the films are glassy at ambient temperature, high-temperature drying was not considered because this type of sample history would shed doubt on the validity of the subsequent infrared temperature study.

2.3. Differential thermal analysis and weight loss via thermogravimetry

Exothermic transitions coupled with weight-loss measurements of solid films were detected using a Seiko Thermogravimetric/Differential Thermal Analyzer (TGA/DTA 220). The temperature range in these experiments

Table 1
Physicochemical characterization of the polybutadienes investigated in this study

Polymer (source)	Microstructure	Molecular weight	Polydispersity
Polybutadiene (Goodyear)	80% 1,2-vinyl, 11% 1,4- <i>trans</i> , 9% 1,4- <i>cis</i>	$M_w \approx 500$ K	1.6
Polybutadiene (Goodyear)	99% 1,4- <i>cis</i>	$M_n \approx 125$ K	not available

encompassed 30°C–470°C at a heating rate of 20°C/min using a dry nitrogen purge at a flow rate of 250 mL/min.

2.4. Variable-temperature FTIR spectroscopy

Infrared spectra were measured using thin films cast from THF solution onto KBr crystals. A Galaxy™ series model 5020 FTIR from Mattson Instruments was employed to perform the desired task. The optical bench is interfaced to a 486/50 MHz personal computer for data acquisition and control. A heated transmission cell for solid films from Spectra-Tech (model HT-32) provides high-temperature capabilities within the sample chamber. Temperature control was accomplished via a Eurotherm 818P15 programmable microprocessor with an accuracy of $\approx 1^\circ\text{C}$. Each spectrum was generated by signal averaging 64 interferograms at a resolution of 2 cm^{-1} , and a triangular apodization smoothing function was employed prior to Fourier transformation. The spectrometer exhibits a signal-to-noise ratio of ≈ 300 at ambient temperature, based on 4 scans at 2 cm^{-1} resolution, using a thin polystyrene film cast from THF onto a KBr crystal. The signal-to-noise ratio was determined from peak-height measurements on the 1493 cm^{-1} signal of atactic polystyrene, which exhibits a full-width-at-half-height of 6.3 cm^{-1} .

3. Results and discussion

3.1. Overview of palladium complexes with atactic 1,2-polybutadiene

Measurements of aggregation below the gelation threshold [18] in THF and toluene solutions of atactic 1,2-polybutadiene and bis(acetonitrile)dichloropalladium(II) reveal an increase in the apparent molecular weight of the chains via static light scattering. Aggregation is the process that occurs in solution prior to gelation when the transition metal salt forms a coordination bridge between two different polymer chains. Based on Zimm-plot intercepts for high-viscosity mixtures of 1,2-polybutadiene/PdCl₂ in THF that were equilibrated for more than seven days [18], the weight-average molecular weight is approximately 9-fold larger than that of the original polymer. Scaling analysis of the weight-average molecular weight dependence of the root-mean-square size of these aggregates yields an effective exponent of 0.7 for polymer/metal–salt complexes at infinite dilution (i.e., $\langle s^2 \rangle^{0.5} \approx M_w^{0.7}$, where s is the radius of

gyration) [18,19]. This experimental light-scattering-based scaling law agrees with literature values for crosslinked polymer networks [20–22]. These results from previous solution studies [18,19] are consistent with solid state measurements described later.

3.2. High-temperature infrared spectra of undiluted 1,2-polybutadiene in the solid state

Before presenting an infrared temperature study of undiluted 1,2-polybutadiene and its complexes with palladium chloride, it is necessary to monitor weight loss and possible microstructural changes in the undiluted polymer as a result of high-temperature heat treatment. Ambient temperature spectra of 1,2-polybutadiene (not shown) before and after annealing [23] at 200°C for 15 min suggest that there are no significant irreversible modifications in chemical structure because of thermal oxidation [24] or configurational rearrangements [25]. In the process of annealing 1,2-polybutadiene at 200°C for 15 min, the sample was exposed to temperatures above 100°C for about 1.5 h during the heating/cooling cycle. Thermogravimetric (TGA) and differential thermal analysis (DTA) data in Fig. 1a reveal that the undiluted polymer exhibits no weight loss below 200°C. Decomposition occurs above 300°C accompanied by a relatively sharp exothermic DTA peak at 350°C. When infrared spectra are obtained during heating and cooling between 40°C and 200°C, the data in Fig. 2 reveal that the C=C stretch in undiluted 1,2-polybutadiene near 1640 cm^{-1} exhibits thermally reversible changes in peak position and absorption intensity. Temperature-dependent conformational changes in this particular polymer thin film are, most likely, responsible for the decrease in absolute absorbance from 0.15 at 40°C to 0.13 at 200°C. The C=C peak position shifts from 1640 cm^{-1} at 40°C to 1637 cm^{-1} at 200°C (Fig. 2a). Upon cooling, the peak position and absolute absorbance of the C=C stretch return to their original values, as illustrated in Fig. 2b.

3.3. High-temperature infrared spectra of 1,2-polybutadiene complexes with palladium chloride

The objective of this section is to present molecular-level evidence in the solid state that palladium chloride chemically modified 1,2-polybutadiene at elevated temperatures. This evidence from infrared spectroscopy is lacking at 25°C, even though 4 mol% palladium chloride transforms the polymer into a glass and increases the elastic modulus by

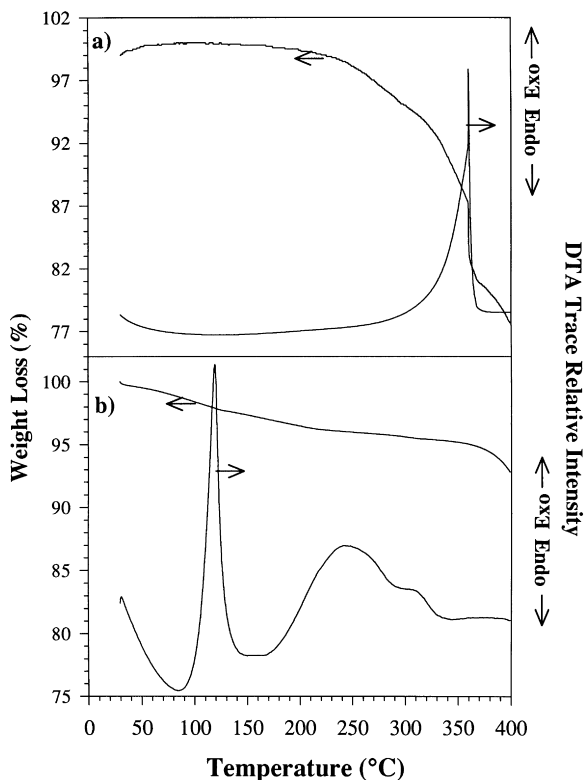


Fig. 1. Initial heating traces from thermogravimetric and differential thermal analyses of (a) atactic 1,2-polybutadiene and (b) the polymeric complex that contains 2 mol% palladium chloride.

three orders of magnitude without high-temperature annealing [2,3,9]. Differential thermal analysis data in Fig. 1b identify three exotherms at 115°C, 250°C and 310°C prior to decomposition of 1,2-polybutadiene with 2 mol% PdCl₂. Thermogravimetric analysis data in Fig. 1b reveal that thermal decomposition accompanied by weight loss does not occur below 400°C in the presence of palladium chloride. FTIR data in Figs. 3–5 reveal that major irreversible changes in infrared absorption intensities occur when complexes containing 4 mol% PdCl₂ are heated from ambient to 180°C. These infrared spectral changes correlate directly with the DTA exotherm at 115°C in Fig. 1b. The C=C stretch at 1640 cm⁻¹ in Fig. 3 decreases at higher temperature because palladium(II) catalyzes an exothermic dimerization reaction of alkene sidegroups [3,11,12]. For this particular thin film, the absolute C=C absorbance in Fig. 3 decreases from 0.28 at ambient to 0.12 at 180°C. This decrease of 0.16 in relative absorbance is much stronger than the reversible decrease of 0.02 absorbance units upon heating undiluted 1,2-polybutadiene to 200°C in Fig. 2a.

High-temperature FTIR spectral changes for the C=C stretching vibration are accompanied by increases in absorption intensities at 1375 cm⁻¹ and 1447 cm⁻¹ in Fig. 3, and decreases in the signals at (i) 1418 cm⁻¹ in Fig. 3 and (ii) 910 and 994 cm⁻¹ in Fig. 4. Aliphatic CH₂ deformations at 1447 cm⁻¹ and CH₃ bending at 1375 cm⁻¹, the latter being unique to a three-carbon linear chemical crosslink with a methyl substituent (i.e., -HC=CH-CH(CH₃)-), are

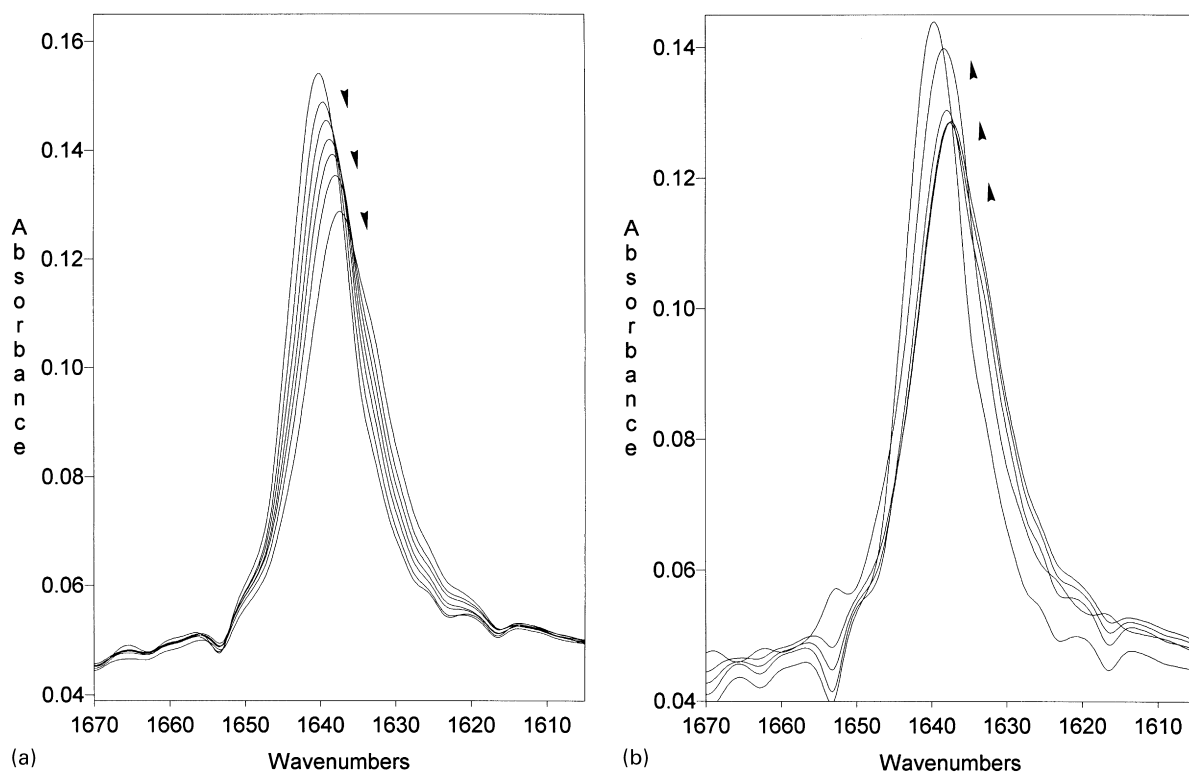


Fig. 2. Infrared spectra of undiluted atactic 1,2-polybutadiene in the vicinity of the carbon-carbon double bond stretching vibration near 1640 cm⁻¹ during (a) heating from 40°C to 200°C and (b) cooling from 200°C to 65°C.

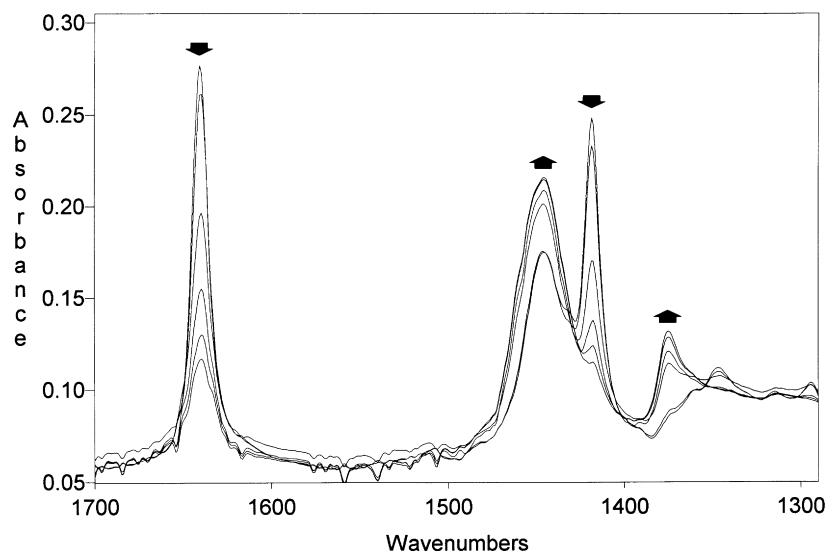


Fig. 3. High-temperature infrared spectra of atactic 1,2-polybutadiene and 4 mol% palladium chloride between 1300 and 1700 cm^{-1} . Arrows indicate the trend for each absorbance as the temperature is increased from 25°C to 180°C. The actual temperatures are; ambient, 80°C, 90°C, 120°C, 150°C and 180°C. Assignments of four significant signals are; C=C stretching at 1640 cm^{-1} , aliphatic CH_2 deformation at 1447 cm^{-1} , in-plane scissoring of olefinic $=\text{CH}_2$ sidegroups at 1418 cm^{-1} and CH_3 bending at 1375 cm^{-1} .

stronger at higher temperature in Fig. 3 when alkene sidegroups undergo dimerization addition. In-plane scissoring of olefinic $=\text{CH}_2$ sidegroups at 1418 cm^{-1} in Fig. 3 becomes weaker at higher temperature. The infrared spectra in Fig. 4 reveal that out-of-plane deformations of vinylic hydrogens in the polybutadiene sidegroup at 910 and 994 cm^{-1} decrease at high temperature. The CH stretching region from 2700 to 3200 cm^{-1} is illustrated in Fig. 5 as a function of temperature from ambient to 180°C. This region of the spectrum contains overtone contributions from CH_2 deformations and CH_3 bending vibrations. In the presence of 4 mol% palladium chloride, CH stretching of 1,2-vinyl side-

groups at 3074 cm^{-1} decreases at higher temperature, whereas the asymmetric (2912 cm^{-1}) and symmetric (2855 cm^{-1}) stretching vibrations of aliphatic CH_2 and CH_3 groups [26] increase at higher temperature. All of these concerted infrared spectral changes in Figs. 3–5 are consistent with the transformation of alkenes to alkanes.

3.4. Infrared measurements of the kinetics of high-temperature chemical crosslinking

The carbon–carbon double bond stretch at 1640 cm^{-1} in 1,2-polybutadiene and 4 mol% palladium chloride has been

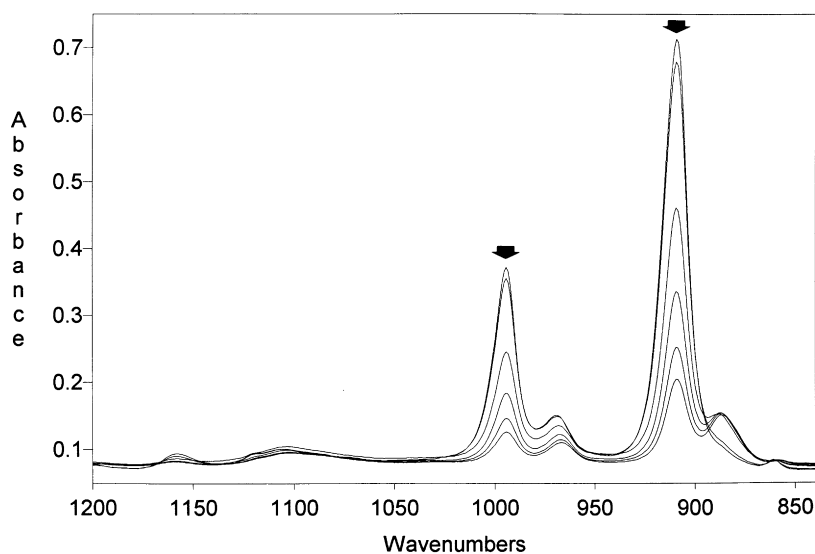


Fig. 4. High-temperature infrared spectra of atactic 1,2-polybutadiene and 4 mol% palladium chloride between 850 and 1200 cm^{-1} . Both out-of-plane deformations of vinylic hydrogens exhibit a decrease in absorbance as the temperature is increased from 25°C to 180°C. The actual temperatures are; ambient, 80°C, 90°C, 120°C, 150°C and 180°C.

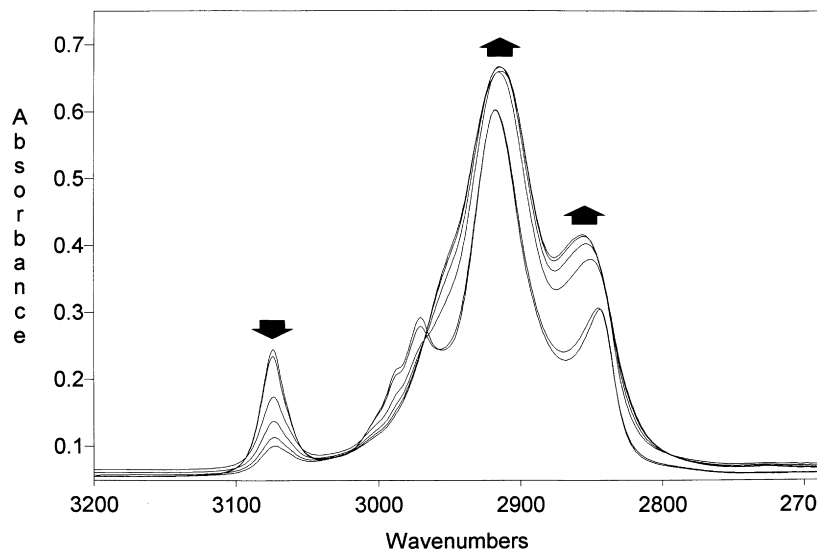


Fig. 5. High-temperature infrared spectra of atactic 1,2-polybutadiene and 4 mol% palladium chloride between 2700 and 3200 cm^{-1} . Arrows indicate the absorbance trend for each CH stretching mode as the temperature is increased from 25°C to 180°C. The actual temperatures are; ambient, 80°C, 90°C, 120°C, 150°C and 180°C. Assignments of three significant signals are; olefinic CH stretching of 1,2-vinyl sidegroups at 3074 cm^{-1} , asymmetric stretching of aliphatic CH_2 and CH_3 groups at 2912 cm^{-1} and symmetric stretching of aliphatic CH_2 and CH_3 groups at 2855 cm^{-1} .

monitored as a function of time to probe isothermal kinetics of the irreversible changes that occur in these complexes at high temperature. Spectral data at 100°C are illustrated in Fig. 6 and a simple kinetic analysis is presented in Fig. 7. For this particular sample, the C=C absolute absorbance is 0.38 at ambient temperature. At 100°C, the “initial” C=C absorbance of the same sample is 0.35, indicative of the fact that reactions occur to a limited extent when the film is heated from ambient to 100°C. Even though the decrease of 0.03 absorbance units is comparable to the reversible changes that occur in the undiluted polymer (see Fig. 2a), palladium-catalyzed chemical crosslinking reaction

probably hinder some conformational rearrangements that are responsible for the 13% decrease in absolute absorbance illustrated in Fig. 2a upon heating. In other words, it is difficult to determine whether the 13% decrease in absolute absorbance of the undiluted polymer should be subtracted from the transient decay of 1640 cm^{-1} signal when palladium-catalyzed reactions occur at elevated temperatures. Reactions also occur during the 1.5-min span required to obtain the first spectrum at 100°C. The transient intensity of the C=C absorbance at 1640 cm^{-1} decreases continuously until it achieves an asymptotic absolute absorbance of 0.23 after approximately 20 min at 100°C. The fact that

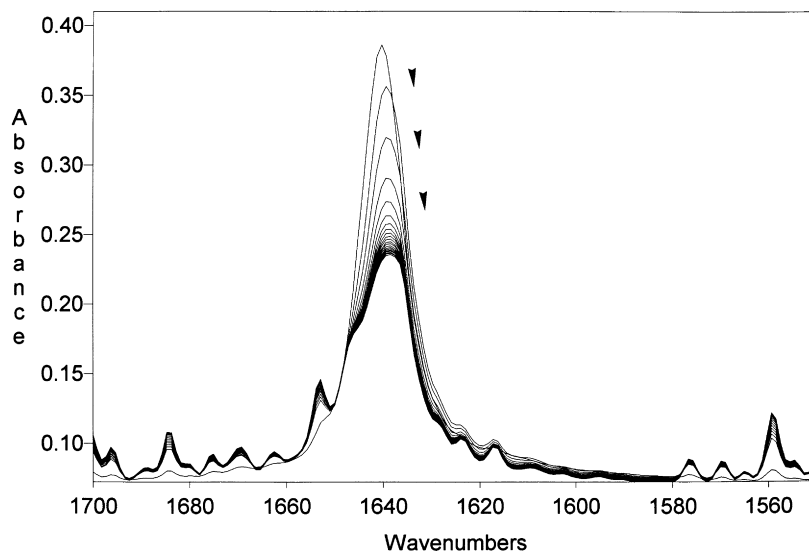


Fig. 6. High-temperature infrared spectra of atactic 1,2-polybutadiene and 4 mol% palladium chloride at 100°C illustrating the transient decrease in C=C signal intensity near 1640 cm^{-1} . The isothermal experiment encompassed a time span of ≈ 30 min.

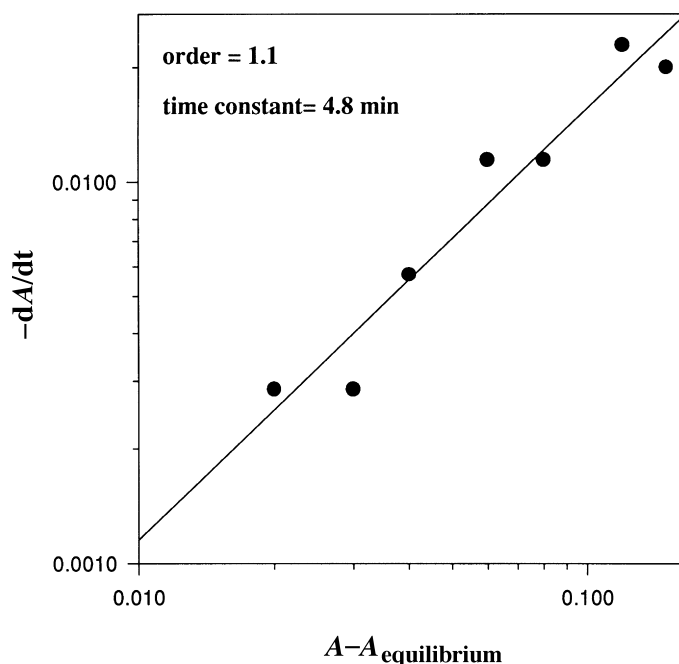


Fig. 7. Kinetic analysis of infrared absorbance data at 100°C for atactic 1,2-polybutadiene and 4 mol% palladium chloride, suggesting that the solid state chemical reaction follows an approximate 1st-order rate law. When the kinetics are dominated by the molar density of one species in the mixture, then the differential method of reaction rate data analysis indicates that; $\log\{-dA/dt\}$ is a linear function of $\log\{A - A_{\text{equilibrium}}\}$, with slope n (i.e., the order of the reaction) and an intercept given by $-\log\{\lambda(T)\}$.

the C=C absorbance does not disappear completely is consistent with a previously proposed mechanism [3] of Heck-like dimerization addition of two alkene sidegroups catalyzed by palladium chloride [12]. The resulting four-carbon chemical bridge (i.e., crosslink) that is void of PdCl₂ contains a residual carbon-carbon double bond. There are at least two possibilities for this linear crosslink; (i) $-\text{HC}=\text{CH}-\text{CH}_2\text{CH}_2-$ or (ii) $-\text{HC}=\text{CH}-\text{CH}(\text{CH}_3)-$. Hence, one should not expect the C=C absorbance to disappear completely. In support of this claim, it is obvious that none of the olefinic infrared signals in Figs. 3–5 disappears completely at 180°C. The transient data in Fig. 6 have been analyzed via a kinetic model which accounts for the fact that the C=C absorbance does not disappear completely at equilibrium;

$$-\frac{d[\text{C}=\text{C}]}{dt} = k_n\{[\text{C}=\text{C}] - [\text{C}=\text{C}]_{\text{equilibrium}}\}^n$$

where [C=C] represents the carbon-carbon double bond concentration, n is the apparent reaction order, and k_n is the n th-order rate constant for a volumetric rate law with units of (volume/mole) ^{$n-1$} /time. Beer's law is used to relate [C=C] molar densities to spectral absorbance based on peak heights via $A = \epsilon\delta[\text{C}=\text{C}]$, where A is the net absorbance with respect to the baseline, ϵ is the molar absorption coefficient for the carbon-carbon double bond stretch, and δ represents path length. The product of molar absorption coefficient and path length has units of inverse concentration because spectral absorbance is dimensionless. When Beer's law is used to replace the carbon-carbon double

bond concentration by net absorbance in the kinetic model introduced earlier, the time dependence of spectral absorbance obeys the following ordinary differential equation based on a constant-volume unsteady state mass balance;

$$-\frac{dA}{dt} = (A - A_{\text{equilibrium}})^n/\lambda(T)$$

where;

$$\lambda(T) = (\epsilon\delta)^{n-1}/k_n(T)$$

is a characteristic reaction time constant for n th-order irreversible chemical kinetics. If the kinetics are 1st-order or pseudo-1st-order (i.e., $n = 1$), then λ and the 1st-order kinetic rate constant k_1 are related inversely. The absorbance data point at “ $t = 0$ ” (i.e., $A = 0.38$) was obtained from the ambient-temperature spectrum. Linear least squares analysis of the spectral absorbance data in Fig. 7 via the differential method of reaction rates indicates that $n = 1.1$ and λ (at 100°C) = 4.8 min, which is interpreted as an approximate 1st-order rate process in the solid state at 100°C. This infrared kinetic analysis of high-temperature induced chemical crosslinking is consistent with previous DSC kinetic analyses [1] of the exotherm at 115°C (see Fig. 1b). Reaction orders slightly less than unity were calculated at 65°C ($n = 0.90$), 75°C ($n = 0.89$), 85°C ($n = 0.96$), and 95°C ($n = 0.98$) from isothermal DSC measurements of the reaction exotherm in solid complexes of 1,2-polybutadiene with 4 mol% palladium

Table 2

Summary of kinetic parameters for 1,2-polybutadiene and *cis*-polybutadiene with 4 mol% palladium chloride. Characteristic *n*th-order chemical reaction time constants are reported in minutes and the corresponding reaction order is included in brackets. Arrhenius activation energies are reported in kJ/mol

Temperature (°C)	<i>cis</i> -PBD 4 mol% PdCl ₂ 1543 cm ⁻¹	25% 1,2-PBD 75% <i>cis</i> -PBD 4 mol% PdCl ₂ 1543 cm ⁻¹	25% 1,2-PBD 75% <i>cis</i> -PBD 4 mol% PdCl ₂ 1640 cm ⁻¹	1,2-PBD 4 mol% PdCl ₂ 1640 cm ⁻¹
100	24 {0.7}	19 {0.8}	51 {0.7}	4.8 {1.1}
125	13 {0.7}	15 {0.6}	26 {0.6}	2.7 {1.3}
140	5.7 {0.9}	5.9 {0.8}	13 {0.7}	1.2 {1.6}
<i>E</i> _{act} (kJ/mol)	45	34	42	43

chloride [1]. Interestingly enough, the apparent DSC reaction order increases slightly and approaches unity when the isothermal experiment is performed at higher temperature, albeit below 115°C. Hence, the apparent infrared reaction order (*n* = 1.1) at 100°C is consistent with isothermal DSC kinetic measurements in solid films [1]. High-temperature infrared kinetic data for 1,2-polybutadiene complexes with 4 mol% PdCl₂ yield;

1. *n* = 1.1 and λ = 4.8 min at 100°C,
2. *n* = 1.3 and λ = 2.7 min at 125°C, and
3. *n* = 1.6 and λ = 1.2 min at 140°C.

The characteristic reaction time constant decreases at higher temperature according to an Arrhenius activation energy of \approx 43 kJ/mole. All of these kinetic parameters are summarized in the 5th column of Table 2. When kinetic analysis is performed on the diminishing infrared signal at 910 cm⁻¹ (see Fig. 4) caused by out-of-plane deformations of vinylic hydrogens in the polybutadiene sidegroup, the characteristic chemical reaction time constant is 3.3 min at 125°C in the presence of 4 mol% palladium chloride. This compares well with λ = 2.7 min at 125°C based on the C=C stretching vibration at 1640 cm⁻¹. Further, when controlled oxidation experiments are performed at 140°C on 1,2-polybutadiene with 4 mol% PdCl₂, acid carbonyl signals in the infrared spectrum near 1700 cm⁻¹ do not appear for almost 500 min [27]. Hence, high-temperature oxidation processes should not affect the intensity of the C=C stretch at 1640 cm⁻¹ during the timescale of the kinetic measurements (i.e., \approx 20–30 min).

3.5. Overview of palladium complexes with *cis*-polybutadiene

Palladium chloride forms a π -complex with *cis*-polybutadiene, and high-temperature annealing activates the formation of a palladium-catalyzed network [13] via the same chemistry that is operative in 1,2-polybutadiene/PdCl₂. High-temperature infrared experiments are performed in conjunction with thermogravimetric measurements to provide convincing evidence that thermal degradation of

either PdCl₂ or the *cis*-polymer does not occur during annealing at temperatures up to 150°C.

3.6. Coordination complexes between *cis*-polybutadiene and PdCl₂ cannot be disrupted

Triphenylphosphine is a good ligand that should be capable of displacing alkenes which are coordinated to palladium. Hence, the introduction of triphenylphosphine to a solid film of *cis*-polybutadiene and palladium chloride should serve as a qualitative diagnostic probe of the interactions between main-chain olefins and PdCl₂. In this respect, a 1% (w/v) solution of triphenylphosphine was prepared in THF and a film of *cis*-polybutadiene with 4 mol% PdCl₂ that was not previously subjected to heat treatment was added to this solution. It was not possible to redissolve the polymeric palladium complex at a concentration of 2% (w/v) in triphenylphosphine/THF between ambient temperature and 70°C, where the experiment at 70°C was performed for at least 1 h. The triphenylphosphine/PdCl₂ molar ratio was 2.8 in these experiments. These observations suggest that the main-chain carbon-carbon double bond in *cis*-polybutadiene coordinates to and undergoes further irreversible chemistry with palladium chloride which cannot be nullified or reversed by triphenylphosphine.

3.7. High-temperature exothermic processes in *cis*-polybutadiene and PdCl₂

High-temperature annealing at 140°C for 1–2 h transforms *cis*-polybutadiene and 4 mol% PdCl₂ from a mechanically reinforced ductile material to a brittle glass [13]. This ductile-to-brittle transformation has also been observed in reactive blends of 1,2-polybutadiene with as little as 0.5 mol% PdCl₂ as a consequence of annealing for comparable times at similar temperatures [1]. Data from calorimetry (DTA) and thermogravimetry (TGA), illustrated in Fig. 8 for *cis*-polybutadiene with 4 mol% palladium chloride, reveal a broad exotherm that (i) is initiated at 150°C, (ii) peaks at 250°C, and (iii) is accompanied by approximately 5% weight loss. An incomplete

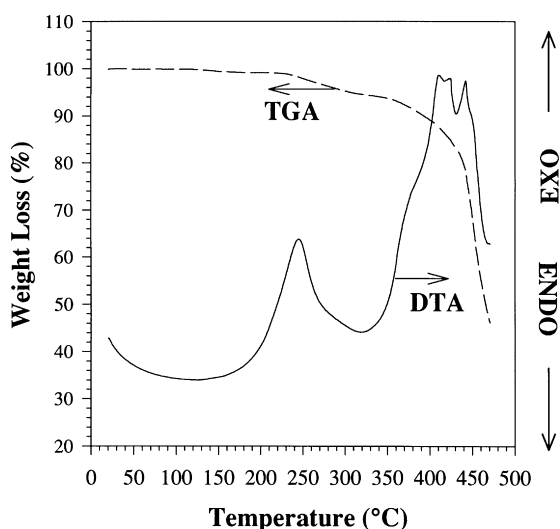
cis-Polybutadiene with 4 mol % PdCl₂

Fig. 8. Thermogravimetric analysis (dashed line, left vertical axis) and differential thermal analysis (solid line, right vertical axis) of *cis*-polybutadiene containing 4 mol% palladium chloride. The exotherm at 250°C, which occurs with $\approx 5\%$ weight loss, is consistent with a thermally activated palladium-catalyzed chemical crosslinking reaction. The exotherm above 350°C is characteristic of thermal degradation, which occurs in conjunction with major weight loss above 400°C.

cis- to-*trans* isomerization of undiluted *cis*-polybutadiene [15] occurs near 200°C where there is a strong exotherm in the DTA trace of the *cis*-polymeric palladium complex illustrated in Fig. 8. However, no exothermic or endothermic behavior has been reported for this transformation to *trans*-polybutadiene [15]. It is important to emphasize that the exotherm at 250°C in Fig. 8 is irreversible because it is

observed only during the first heating trace. For example, when a different sample of *cis*-polybutadiene and 4 mol% PdCl₂ is heated to 350°C in a differential scanning calorimeter and then cooled to ambient, the exotherm at 250°C is absent during the second heating trace [28]. Further, the second DSC heating reveals a weak glass transition at 63°C, which corresponds to an increase of approximately 100°C in T_g relative to undiluted *cis*-polybutadiene [28].

3.8. Variable-temperature FTIR spectroscopic evidence for complexation and chemical reactions in *cis*-polybutadiene and palladium chloride

Infrared data in Figs. 9 and 10 provide molecular-level support for the formation of transition-metal complexes between *cis*-polybutadiene and palladium chloride. These results are significant because they support the claim that the thermo-mechanical properties of diene polymers with alkene groups in the main chain can be modified via reactive blending [13]. The C=C stretch at 1653 cm⁻¹ is observed in the undiluted polymer (spectrum 9a) and in π -complexes with PdCl₂ (spectra 9b and 9c). Without subjecting these complexes to high-temperature heat treatment, spectra (b) and (c) in Fig. 9 reveal a signal at 1543 cm⁻¹, indicated by the asterisk, which is characteristic of a π -complex between palladium(II) and the carbon-carbon double bond [6,29]. The infrared absorption at 1543 cm⁻¹ is absent in the undiluted *cis*-polymer, as illustrated in spectrum 9a, and it is not a contribution from bis(acetonitrile)dichloropalladium(II) [10]. This palladium- π -complexed C=C stretch at 1543 cm⁻¹ exhibits a much stronger absorbance than the original uncomplexed C=C stretch at 1653 cm⁻¹, suggesting that the molar absorption coefficient for the C=C stretch at 1543 cm⁻¹ is much larger than ϵ for the free C=C stretch

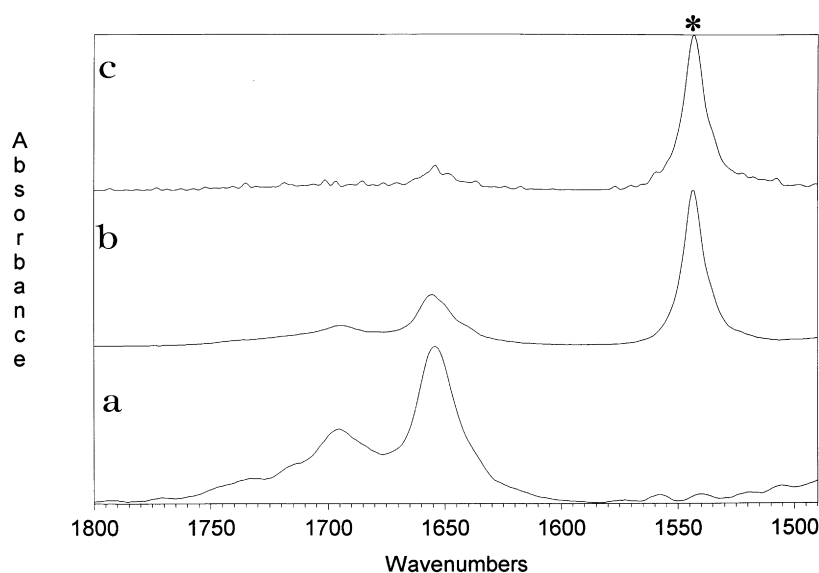


Fig. 9. Ambient-temperature infrared spectra between 1500 and 1800 cm⁻¹ for *cis*-polybutadiene and palladium chloride. The signal at 1543 cm⁻¹ (identified by the asterisk) is due to the formation of a coordination complex between palladium and the carbon-carbon double bond in the backbone of the polymer. (a) undiluted *cis*-polybutadiene, (b) *cis*-PBD with 4 mol% PdCl₂, (c) *cis*-PBD with 10 mol% PdCl₂.

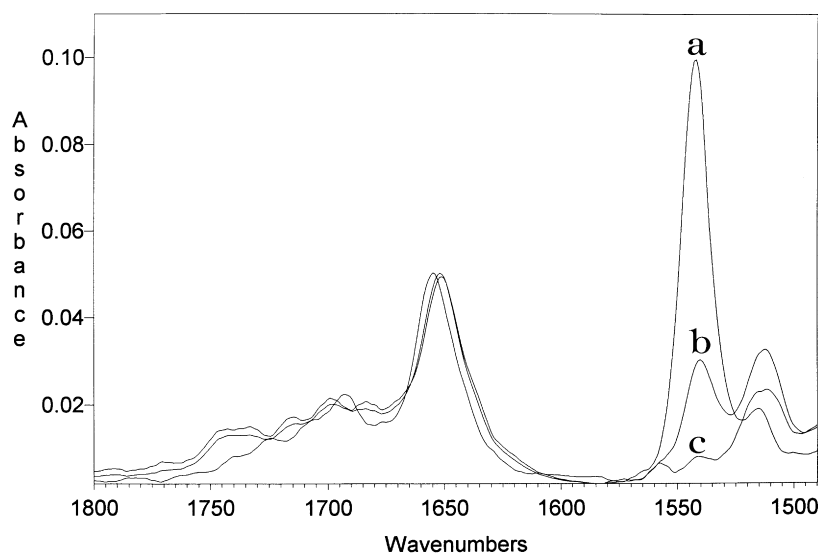


Fig. 10. Infrared spectra at 30°C and 150°C for *cis*-polybutadiene and 4 mol% PdCl₂, illustrating the elimination of the palladium- π -complexed C=C stretch at 1543 cm⁻¹. The uncomplexed C=C stretch in the polymer at 1653 cm⁻¹ shifts slightly to lower wavenumbers at 150°C in undiluted *cis*-polybutadiene and in the complex with palladium chloride. Spectra for the polymeric palladium complex are presented at (a) 30°C, (b) after 2 min at 150°C and (c) after 3.5 min at 150°C. The sample was heated from 30°C to 150°C at a rate of 20°C per min.

at 1653 cm⁻¹. Palladium(II) could form a di-hapto coordination complex with the alkene group in the main chain of *cis*-polybutadiene, analogous to the Dewar–Chatt model in small molecules [30]. As a consequence of π -back-donation and the flow of electron density from filled metal *d*-orbitals to the empty anti-bonding π^* orbitals of the alkene, (i) the C=C bond order is reduced, (ii) its bond strength is weakened, and (iii) the palladium- π -complexed C=C stretching frequency is lowered by more than 100 cm⁻¹ [6]. Palladium(II) should not form a tri-hapto π -allyl complex with *cis*-polybutadiene unless one of the methylene carbons adjacent to the double bond is deprotonated and electron density is delocalized over three carbon centers [29–31]. Spectra (b) and (c) in Fig. 9 suggest that (i) some carbon–carbon double bonds in the main chain of the *cis*-polymer form π -complexes with palladium(II) by occupying a square-planar site in the coordination sphere of the metal, and (ii) some C=C groups are not affected by the presence of PdCl₂ because there is a residual signal at 1653 cm⁻¹. The intensity of the *cis*-polybutadiene signal at 1543 cm⁻¹ increases, due to π -complexation, at the expense of the uncomplexed C=C stretch at 1653 cm⁻¹ when the concentration of PdCl₂ is larger. Palladium- π -complexes with polymers that contain alkene groups in the backbone have been proposed recently [32] to rationalize the fact that insoluble materials are produced when Pd(II) activates the carbon–carbon triple bond in ethynyl-trimethylsilane. The transition-metal catalyst is inserted into the growing chain and two vacant coordination sites on the metal allow Pd(II) to form π -complexes (i.e., coordination crosslinks) with carbon–carbon double bonds on neighboring chains [32].

Infrared spectra at 30°C (spectrum a) and 150°C (spectra b and c) are illustrated in Fig. 10 for *cis*-polybutadiene and 4 mol% palladium chloride. As shown in Fig. 8, thermal degradation of this material does not occur below 350°C. The heating profile and isothermal dwell to obtain the spectra at 150°C consumed less than 10 min. Formation of a π -complex between palladium(II) and alkene groups in the chain backbone should hinder the *cis*-to-*trans* isomerization. The palladium- π -complexed C=C stretch at 1543 cm⁻¹ should not be affected if uncomplexed C=C groups experience this transformation from *cis* to *trans* [15]. Further, cyclic Diels–Alder adducts are not favored because no signals are present in the 1050–1070 cm⁻¹ region after high-temperature heat treatment. The spectra in Fig. 10 reveal that the palladium- π -complexed C=C stretch at 1543 cm⁻¹ decreases dramatically at 150°C in spectrum (b), and it is nonexistent in spectrum (c) after the sample is exposed to this temperature for 3.5 min. There is a slight shift of the uncomplexed C=C stretch by about 4 wavenumbers to lower energy (i.e., 1649 cm⁻¹) at 150°C, but the intensity of this signal near 1650 cm⁻¹ does not change from 30°C to 150°C. The spectra in Figs. 9 and 10 suggest that only the carbon–carbon double bonds in the chain backbone which form π -complexes with palladium(II) at ambient temperature participate in chemical cross-linking at 150°C. Otherwise, one should measure a decrease in the uncomplexed carbon–carbon double bond signal at 1653 cm⁻¹ in Fig. 10. This observation in binary mixtures is significant because it suggests that elementary step 4 in the proposed mechanism, described later, probably does not occur in solid films at high temperature.

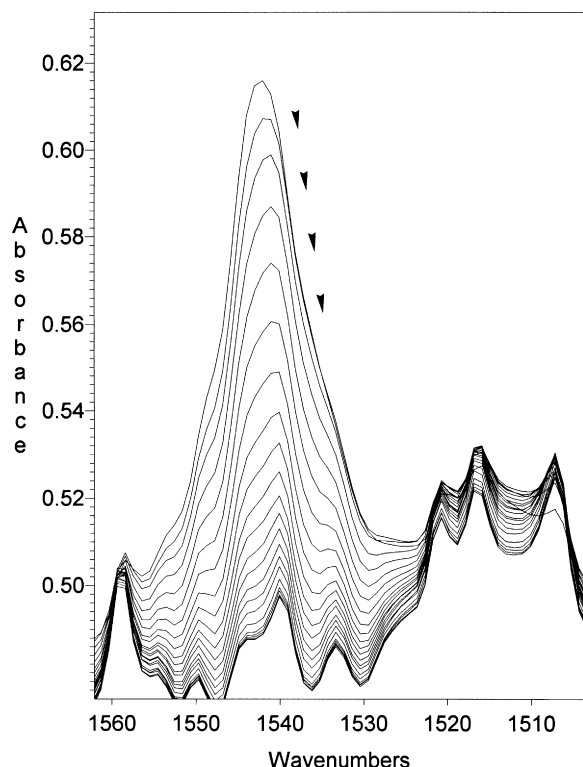


Fig. 11. High-temperature infrared spectra of *cis*-polybutadiene and 4 mol% palladium chloride at 100°C illustrating the transient decrease in the palladium- π -complexed C=C signal intensity at 1543 cm^{-1} . The isothermal experiment encompassed a time span of ≈ 40 min.

3.9. Infrared studies of the kinetics of high-temperature chemical crosslinking in *cis*-polybutadiene and palladium chloride

The palladium- π -complexed carbon-carbon double bond stretch at 1543 cm^{-1} in *cis*-polybutadiene and 4 mol% palladium chloride has been monitored as a function of time to probe isothermal kinetics of the irreversible changes that occur in these complexes at 100°C, 125°C and 140°C. Spectral data at 100°C are illustrated in Fig. 11. The data have been modelled using the same n th-order kinetic rate law and unsteady state mass balance that were described before for 1,2-polybutadiene with 4 mol% PdCl_2 :

$$-\frac{dA}{dt} = (A - A_{\text{equilibrium}})^n / \lambda(T)$$

Isothermal infrared kinetic experiments yield the following results;

1. $n = 0.7$ and $\lambda = 24$ min at 100°C,
2. $n = 0.7$ and $\lambda = 13$ min at 125°C,
3. $n = 0.9$ and $\lambda = 5.7$ min at 140°C.

The characteristic chemical reaction time constant decreases at higher temperature with an apparent Arrhenius activation energy of 45 kJ/mol. More importantly, infrared data support the claim that the kinetics of palladium-

catalyzed dimerization reactions at high temperature proceed faster when olefinic functionality exists in the side-group relative to the main chain [33]. This is obvious from a comparison of chemical reaction time constants for both polymers at the same temperature:

1. $\lambda_{1,2\text{-PBD}/4\text{mol}\% \text{Pd}} = 4.8$ min at 100°C, whereas $\lambda_{\text{cis-PBD}/4\text{mol}\% \text{Pd}} = 24$ min;
2. $\lambda_{1,2\text{-PBD}/4\text{mol}\% \text{Pd}} = 2.7$ min at 125°C, whereas $\lambda_{\text{cis-PBD}/4\text{mol}\% \text{Pd}} = 13$ min;
3. $\lambda_{1,2\text{-PBD}/4\text{mol}\% \text{Pd}} = 1.2$ min at 140°C, whereas $\lambda_{\text{cis-PBD}/4\text{mol}\% \text{Pd}} = 5.7$ min.

On the average, the palladium-catalyzed dimerization reaction proceeds about five-fold faster in 1,2-polybutadiene relative to *cis*-polybutadiene, as summarized in the 2nd and 5th columns of Table 2. This is consistent with the relative trend in ligand displacement rates for mono-substituted (i.e., 1,2-PBD) vs. di-substituted (i.e., *cis*-PBD) small-molecule alkenes [6,34].

3.10. Consideration of the kinetic mismatch between 1,2-PBD/ PdCl_2 and *cis*-PBD/ PdCl_2 during transition-metal compatibilization of these two diene polymers

As the overall kinetics of (i) palladium coordination to the alkene group and (ii) subsequent dimerization addition proceed much faster in 1,2-polybutadiene relative to *cis*-polybutadiene, a mixing strategy must be developed to compatibilize both of these polymers. It should be obvious from the binary system kinetic studies discussed earlier that, if all three components are mixed simultaneously in THF, then 1,2-polybutadiene will occupy vacant sites in the coordination sphere of palladium and undergo dimerization addition at a much faster rate than *cis*-polybutadiene. Hence, the vinyl polymer will form a chemically cross-linked network at elevated temperatures. Only a small fraction of *cis*-polybutadiene should participate in the formation of this network. If this occurs, then palladium chloride will not be successful in compatibilizing the two diene polymers. To circumvent this difficulty in a realistic situation, *cis*-polybutadiene and PdCl_2 were mixed initially in THF for 2 h at ambient temperature before 1,2-polybutadiene/THF was added to this solution. A trial-and-error procedure was implemented to identify the 2-h mixing delay prior to introducing the vinyl polymer. A solid residue was cast on KBr within one minute after 1,2-polybutadiene/THF was added to the solution of *cis*-polybutadiene and PdCl_2 . The molar ratio of the *cis*-polymer to the vinyl polymer was 3 : 1 and 4 mol% PdCl_2 was present relative to the total moles of alkene functional groups in both polymers. As (i) there is an excess of *cis*-polybutadiene relative to the vinyl polymer and (ii) the *cis*-polymer is allowed to coordinate to PdCl_2 for 2 h prior to introducing the vinyl polymer in solution, a substantial fraction of sites vacated by acetonitrile in the coordination sphere of palladium are occupied by *cis*-polybutadiene. This claim is verified by the relatively strong

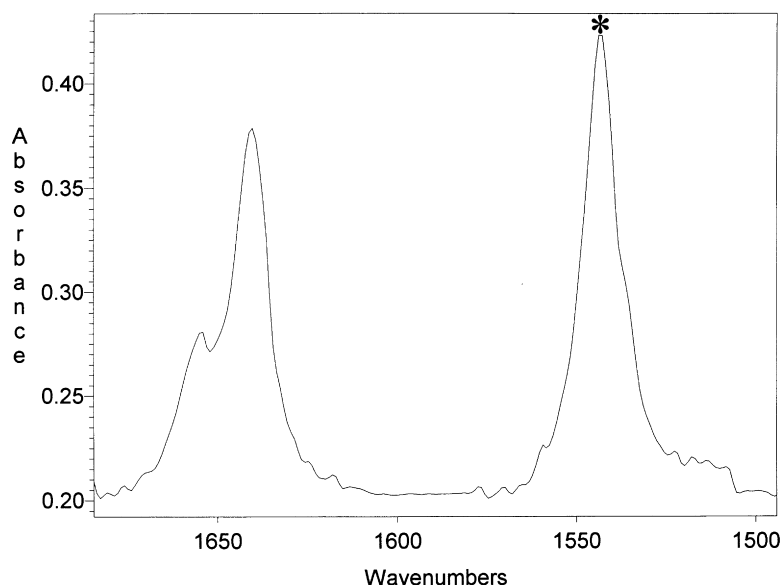
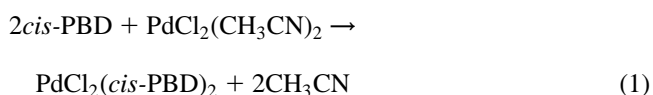


Fig. 12. Ambient-temperature infrared spectrum of a ternary solid state mixture that illustrates three different C=C stretching vibrations. The film contains a 3:1 molar ratio of *cis*-polybutadiene to 1,2-polybutadiene, and 4 mol% PdCl₂ relative to the total moles of both diene polymers. *Cis*-polybutadiene and palladium chloride were mixed in THF for 2 h prior to adding 1,2-polybutadiene/THF. For *cis*-polybutadiene, the “free” C=C stretch appears at 1653 cm⁻¹ and the palladium- π -complexed C=C stretch appears at 1543 cm⁻¹, identified by the asterisk. The intensity of this latter signal depends strongly on the mixing delay. Free and complexed C=C stretches in 1,2-polybutadiene appear at 1640 cm⁻¹.

palladium- π -complexed C=C stretch at 1543 cm⁻¹ in Fig. 12, which is indicated by the asterisk. Hence, there is experimental evidence that the mixing strategy allows a significant fraction of *cis*-polybutadiene to coordinate to PdCl₂, but it should be emphasized that the molar absorption coefficient of the C=C stretch is distorted when alkene groups in the *cis*-polymer coordinate to palladium(II).

3.11. A proposed kinetic mechanism that is consistent with transient high-temperature infrared data

The following sequence of elementary steps is postulated to model the infrared kinetics of ternary solid state mixtures containing palladium chloride and both diene polymers. This mechanism accounts for the fact that *cis*-polybutadiene and PdCl₂ are mixed in THF for 2 h prior to introducing a THF solution of 1,2-polybutadiene. No steps are included in the mechanism that lead to disagreement with the infrared data. Representative spectra at 125°C are presented in Fig. 13 and chemical reaction time constants for the ternary system are given in the 3rd and 4th columns of Table 2 at 100°C, 125°C and 140°C. In the first step, alkene groups in the main chain of the *cis*-polymer displace both acetonitrile ligands and coordinate to palladium(II).

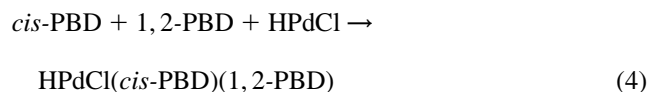


The polymeric palladium complex PdCl₂(*cis*-PBD)₂, which exhibits a C=C stretch at 1543 cm⁻¹, undergoes dimerization addition to increase the effective molecular

weight of the polymer chains and regenerate the palladium catalyst (i.e., HPdCl).



The second step occurs only at high temperature in the solid state. The palladium catalyst that is regenerated in reaction (2) could form coordination complexes with both diene polymers in the solid state, as illustrated by reactions (3) and (4).



Whereas reaction (3) occurs rather quickly in THF solutions of 1,2-polybutadiene and PdCl₂(CH₃CN)₂, it must be excluded from the mechanism when both diene polymers are present and a 2-h mixing delay is employed because it leads to erroneous predictions about the rate at which the 1640 cm⁻¹ C=C stretch in 1,2-polybutadiene decreases in binary vs. ternary solid state mixtures. Reaction (4) is suggested because the vinyl polymer coordinates to the transition metal ion much faster than *cis*-polybutadiene coordinates to PdCl₂, based on kinetic data for mono-substituted vs. di-substituted small-molecule alkenes [6,34]. However, high-temperature infrared data for binary complexes of *cis*-polybutadiene and PdCl₂ in Fig. 10 suggest that kinetic rate constant $k_4 \approx 0$ because the “free” C=C stretch at 1653 cm⁻¹ does not decrease. Hence, reaction (4) is neglected. In other words, when chemical crosslinks form

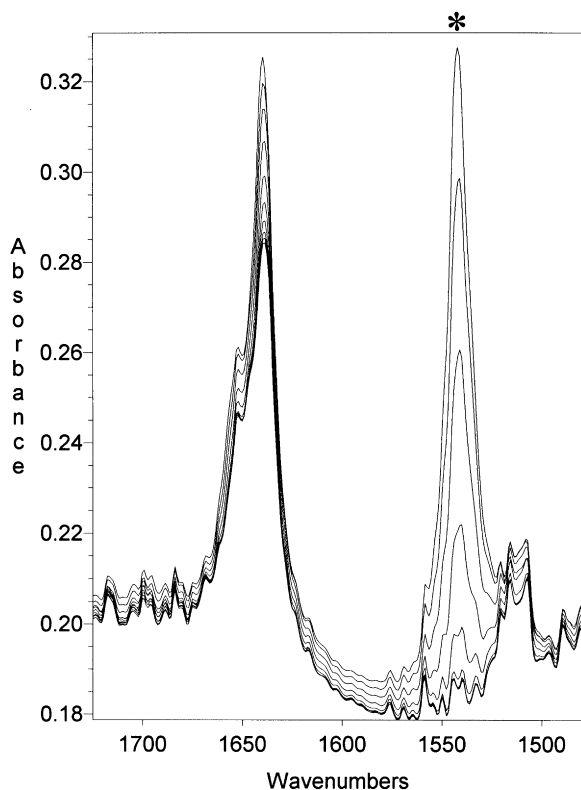
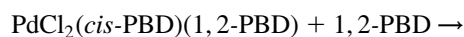
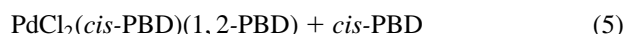
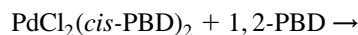


Fig. 13. High-temperature infrared kinetic study at 125°C for a ternary solid state mixture which contains a 3 : 1 molar ratio of *cis*-polybutadiene to 1,2-polybutadiene, and 4 mol% PdCl₂ relative to the total moles of both diene polymers. The C=C stretch in 1,2-polybutadiene at 1640 cm⁻¹ decreases to an equilibrium absolute absorbance of 0.29. The palladium- π -complexed C=C stretch in *cis*-polybutadiene at 1543 cm⁻¹ almost disappears completely after 10–12 min. The “free” C=C stretch in *cis*-polybutadiene at 1653 cm⁻¹ superficially decreases because it overlaps the decreasing C=C signal of 1,2-polybutadiene at 1640 cm⁻¹.

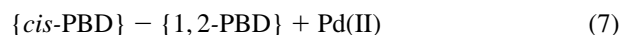
at high temperature between two repeat units of *cis*-polybutadiene that are coordinated to palladium(II) in solid films, the regenerated catalyst does not form complexes with the remaining main-chain alkene groups in the solid state during the timescale of the kinetic measurements (i.e., \approx 30–40 min).

The polymeric palladium complex with *cis*-polybutadiene that is generated in reaction (1), PdCl₂(*cis*-PBD)₂, undergoes the following sequential ligand displacement reactions in the presence of 1,2-polybutadiene.



Reactions (5) and (6) occur in THF as well as in the solid state at elevated temperatures. The polymeric palladium complexes on the right sides of reactions (5) and (6) undergo

palladium-catalyzed dimerization addition in the solid state to increase the effective molecular weight of the chains and regenerate the catalyst (i.e., HPdCl).



(8)

Reaction (7) represents a classic example of transition-metal compatibilization via reactive blending. Palladium chloride catalyzes the high-temperature dimerization of two diene polymers that are incompatible in the absence of the inorganic component. Reaction (7) is partially responsible for decreasing the palladium- π -complexed C=C absorbance at 1543 cm⁻¹ during the transient infrared experiment, but its effect on the signal at 1640 cm⁻¹ is questionable because a residual carbon-carbon double bond survives the dimerization reaction. Reactions (2), (7) and (8) are not truly elementary steps. Each one summarizes the following sequence of steps via detailed organometallic considerations [12,34]:

- an alkene functional group in polybutadiene displaces acetonitrile and coordinates to PdCl₂,
- nucleophilic attack by one of the anionic chloride ligands occurs at the more-substituted end of the coordinated alkene (i.e., chloropalladation of the alkene),
- β -hydrogen elimination generates HPdCl which participates in the following catalytic cycle,
- another alkene functional group in polybutadiene coordinates to HPdCl,
- migratory insertion of coordinated H at the less-substituted end of the coordinated alkene produces a palladium(II) σ -alkyl intermediate,
- another alkene functional group in polybutadiene coordinates to Pd(II), generating and η^1 σ -alkyl, η^2 π -olefin complex,
- migratory insertion of the σ -alkyl occurs at the less-substituted end of the coordinated alkene,
- β -hydrogen elimination generates HPdCl to continue the catalytic cycle at (d), and a 4-carbon chemical crosslink between two different chains or a 4-carbon bridge within the same chain.

The 4-carbon crosslink or bridge is $-\text{CH}(\text{CH}_3)\text{CH}=\text{CH}-$, as mentioned in a previous section. If migratory insertion of coordinated H in step (e) occurs at the more-substituted end of the coordinated alkene, then the 4-carbon crosslink or bridge is $-\text{CH}_2\text{CH}_2\text{CH}=\text{CH}-$.

The kinetic analysis described below treats reactions (2), (7) and (8) as elementary steps. If reaction (8) is solely responsible for decreasing the C=C absorbance of 1,2-polybutadiene at 1640 cm⁻¹ during the transient infrared

experiment for ternary solid state mixtures, then

$$\begin{aligned} d[\{1, 2\text{-PBD}\} - \{1, 2\text{-PBD}\}]/dt &= \{-dA_{1640}/dt\}_{\text{ternary}} \\ &= k_8[\text{PdCl}_2(1, 2\text{-PBD})_2] \end{aligned} \quad (9)$$

where k_i represents the kinetic rate constant for the i -th elementary step in the six-step sequence proposed above via reactions (1) through (8), excluding reactions (3) and (4). The following nomenclature is employed to represent molar densities of the various species that participate in the proposed mechanism:

- $x = \text{PdCl}_2(\text{cis-PBD})(1, 2\text{-PBD})$
- $y = \text{PdCl}_2(\text{cis-PBD})_2$
- $z = \text{PdCl}_2(1, 2\text{-PBD})_2$
- $V = 1, 2\text{-PBD}$
- $C = \text{cis-PBD}$
- $M = \text{PdCl}_2$ or HPdCl

The rate of decrease of the C=C infrared absorbance at 1640 cm^{-1} for 1,2-polybutadiene, given by Eq. (9), is rewritten as;

$$\{-dA_{1640}/dt\}_{\text{ternary}} = k_8z \quad (10)$$

The pseudo-steady state approximation is invoked for the polymeric palladium complexes (i.e., reactive intermediates) denoted by x , y and z .

$$dx/dt = k_5Vy - k_6Vx - k_7x \approx 0 \quad (11)$$

$$dy/dt = k_1C^2M - k_2y - k_5Vy \approx 0 \quad (12)$$

$$dz/dt = k_6Vx - k_8z \approx 0 \quad (13)$$

The solution to Eqs. (11)–(13) for the approximate molar densities of the three intermediate complexes, in the order in which they were solved, is;

$$y = \text{PdCl}_2(\text{cis-PBD})_2 = \frac{k_1C^2M}{k_2 + k_5V} \quad (14)$$

$$x = \text{PdCl}_2(\text{cis-PBD})(1, 2\text{-PBD}) = \frac{k_1k_5C^2VM}{(k_2 + k_5V)(k_7 + k_6V)} \quad (15)$$

$$z = \text{PdCl}_2(1, 2\text{-PBD})_2 = \left\{ \frac{k_6}{k_8} \right\} \frac{k_1k_5C^2V^2M}{(k_2 + k_5V)(k_7 + k_6V)} \quad (16)$$

The rate of decrease of the C=C infrared absorbance at 1640 cm^{-1} for 1,2-polybutadiene in ternary solid state mixtures, given by Eqs. (9) and (10), is;

$$\left\{ -\frac{dA_{1640}}{dt} \right\}_{\text{ternary}} = k_8z = \frac{k_1k_5k_6C^2V^2M}{(k_2 + k_5V)(k_7 + k_6V)} \quad (17)$$

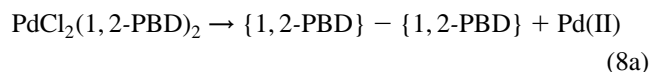
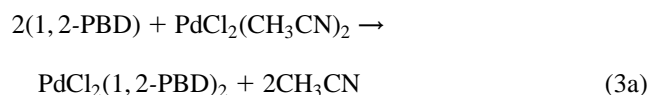
If (i) the vinyl polymer and the *cis*-polymer are present in excess relative to 4 mol% palladium chloride, (ii) $k_5V > k_2$, and (iii) $k_6V > k_7$, then the disappearance of the 1640 cm^{-1}

absorption obeys the following kinetic rate law;

$$\{-dA_{1640}/dt\}_{\text{ternary}} \approx k_1C^2M \quad (18)$$

which is 1st-order with respect to palladium chloride. Eq. (18) describes the rate of disappearance of the C=C absorbance at 1640 cm^{-1} for 1,2-polybutadiene in ternary solid state mixtures with *cis*-polybutadiene and PdCl_2 , subject to the mixing strategy employed.

For binary mixtures of 1,2-polybutadiene and palladium chloride, the reaction scheme is;



Reaction (8a) is solely responsible for the disappearance of the C=C stretch at 1640 cm^{-1} . Coordination of the vinyl sidegroup in 1,2-PBD to PdCl_2 does not affect the absorbance of this C=C stretch [2,3]. Hence;

$$\{-dA_{1640}/dt\}_{\text{binary}} = k_8z \quad (19)$$

Now, the pseudo-steady state approximation for $\text{PdCl}_2(1, 2\text{-PBD})_2$, based on reactions (3a) and (8a) in binary mixtures, is;

$$\begin{aligned} \{d[\text{PdCl}_2(1, 2\text{-PBD})_2]/dt\}_{\text{binary}} &= \{dz/dt\}_{\text{binary}} \\ &= k_3V^2M - k_8z \approx 0 \end{aligned} \quad (20)$$

Based on the pseudo-steady state approximation in Eq. (20), transient decay of the 1640 cm^{-1} signal for binary mixtures follows;

$$\{-dA_{1640}/dt\}_{\text{binary}} = k_3V^2M \quad (21)$$

which should be compared with Eq. (18) for ternary mixtures. Transient decay of the C=C stretch at 1640 cm^{-1} in binaries and ternaries follows 1st-order kinetics with respect to palladium chloride, which could be the dominant effect when the other components are present in excess. Pseudo-1st-order kinetic rate constants in Eq. (18) for the ternary (i.e., k_1C^2) and Eq. (21) for the binary (i.e., k_3V^2) differ by a factor of ≈ 10 , as illustrated by the chemical reaction time constants in the 4th and 5th columns in Table 2. When the total initial linear-polymer concentration is the same in binaries and ternaries and the C : V molar ratio is 3 : 1 in the ternary, as suggested by the mixing strategy, the pseudo-1st-order kinetic rate constants are proportional to $1k_3$ for the binary and $(3/4)^2k_1 \approx 0.56k_1$ for the ternary. Hence, the ratio of pseudo 1st-order kinetic rate constants (i.e., $k_{3,\text{binary}}/0.56k_{1,\text{ternary}}$) for the rate of disappearance of 1,2-polybutadiene's C=C stretch at 1640 cm^{-1} in binary and ternary complexes is approximately equal to 10.

The rate of disappearance of the palladium- π -complexed

Table 3
Summary of predicted kinetic rate laws for 1,2-polybutadiene and *cis*-polybutadiene with low concentrations of palladium chloride

Mixture	Pd- π -complexed C=C stretch in <i>cis</i> -polybutadiene at 1543 cm ⁻¹ { - dA ₁₅₄₃ /dt } ^{a,b,c,d,e}	C=C stretch in 1,2-polybutadiene at 1640 cm ⁻¹ { - dA ₁₆₄₀ /dt } ^{b,c,d,e,f}
Binaries with PdCl ₂	Reactions (1) and (2) 2k ₁ C ² M [Eq.(26)]	Reactions (3) and (8) k ₃ V ² M [Eq.(21)]
Ternaries w/3 : 1 molar ratio of <i>cis</i> -PBD/1,2-PBD and strategic mixing	Reactions (1)–(8) Excluding (3) 2k ₁ C ² M [Eq. (23)]	Reactions (1)–(8) Excluding (3) and (4) k ₁ C ² M [Eq.(18)]

^a A₁₅₄₃ = infrared absorbance of the Pd- π -complexed C=C stretch in *cis*-polybutadiene.

^b k_i = kinetic rate constant for the *i*th elementary step in the physical mechanism.

^c C = molar density of *cis*-polybutadiene.

^d V = molar density of 1,2-polybutadiene.

^e M = molar density of palladium chloride of HPdCl.

^f A₁₆₄₀ = infrared absorbance of the C=C stretch in 1,2-polybutadiene.

C=C stretch in *cis*-polybutadiene is predicted for (i) binary mixtures of the *cis*-polymer with PdCl₂, and (ii) ternary mixtures of both diene polymers with PdCl₂. Reactions (1) through (8), excluding (3) and (4), apply to ternary mixtures subject to the 2-h mixing delay. The rate of disappearance of the absorbance at 1543 cm⁻¹ is calculated by considering each elementary step that dissociates a di-hapto coordination bond between palladium(II) and the main-chain alkene. In light of the fact that reaction (1) occurs in THF solution prior to performing the solid state infrared experiments;

$$\{-dA_{1543}/dt\}_{\text{ternary}} = 2k_2y + k_5Vy + k_6Vx + k_7x \quad (22)$$

where 2k₂y accounts for the fact that dimerization addition reaction (2) dissociates two palladium-alkene coordination bonds. Eqs. (14)–(16) provide approximations for the molar densities of the desired polymeric palladium complexes in ternary mixtures via the pseudo-steady state approximation. These are employed to simplify the prediction given by Eq. (22). For example;

$$k_2y + k_5Vy = \{k_2 + k_5V\}y = k_1C^2M$$

Also;

$$\{k_7 + k_6V\}x + k_2y = k_1C^2M$$

Hence, transient decay of the palladium- π -complexed C=C stretch in *cis*-polybutadiene at 1543 cm⁻¹ should obey the following rate law in ternary mixtures

$$\{-dA_{1543}/dt\}_{\text{ternary}} = 2k_1C^2M \quad (23)$$

which is 1st-order with respect to palladium chloride. It is not necessary to exclude reaction (4) to arrive at Eq. (23). Infrared data in the 3rd and 4th columns of Table 2 reveal that the palladium- π -complexed C=C absorbance at 1543 cm⁻¹ in *cis*-polybutadiene decreases at a rate which is \approx 2-fold faster than the rate at which the 1640 cm⁻¹

signal decreases in 1,2-polybutadiene for the ternary solid state mixture under investigation. The predictions given by Eqs. (18) and (23) are consistent with these experimental data.

When 1,2-polybutadiene is absent in THF solutions of *cis*-polybutadiene and palladium chloride, only elementary steps (1) and (2) occur. In solid binary mixtures, reaction (2) is solely responsible for decreasing the absorbance of *cis*-polybutadiene at 1543 cm⁻¹. Hence;

$$\{-dA_{1543}/dt\}_{\text{binary}} = 2k_2y \quad (24)$$

Now, the pseudo-steady state approximation for PdCl₂(*cis*-PBD)₂ based on reactions (1) and (2) in binary mixtures is;

$$\begin{aligned} \{d[\text{PdCl}_2(\text{cis-PBD})_2]/dt\}_{\text{binary}} &= \{dy/dt\}_{\text{binary}} \\ &= k_1C^2M = k_2y \approx 0 \end{aligned} \quad (25)$$

Hence, transient decay of the C=C signal at 1543 cm⁻¹ for binary mixtures obeys the following rate law;

$$\{-dA_{1543}/dt\}_{\text{binary}} = 2k_1C^2M \quad (26)$$

which has the exact same functional form as Eq. (23) for ternary mixtures. In practice, the molar density of *cis*-polybutadiene [C] is slightly less in the 3 : 1 ternary solid state mixture relative to binary mixtures with PdCl₂. Chemical reaction time constants for $\{-dA_{1543}/dt\}_{\text{binary}}$ and $\{-dA_{1543}/dt\}_{\text{ternary}}$ in the 2nd and 3rd columns of Table 2 are very similar between 100°C and 140°C. This is consistent with the predictions given by Eqs. (26) and (23), respectively, as summarized in Table 3.

3.12. Analysis of pseudo-1st-order kinetic rate constants

Infrared kinetic data at 125°C are illustrated in Fig. 13 for the ternary solid state mixture which contains a 3 : 1 molar

ratio of *cis*-polybutadiene relative to the vinyl polymer, and 4 mol% PdCl₂. As mentioned before, the mixing strategy employs a 2-h delay prior to introducing 1,2-polybutadiene/THF to the solution of *cis*-polybutadiene and palladium chloride. Transition-metal coordination to the vinyl polymer is hindered by *cis*-polybutadiene via the mixing strategy. Chemical reaction time constants at 100°C, 125°C and 140°C in the 4th and 5th columns of Table 2 reveal that the C=C stretch of 1,2-polybutadiene at 1640 cm⁻¹ decreases at a rate which is ≈ 10-fold slower in the ternary solid state film relative to the binary system without *cis*-polybutadiene. This is consistent with the ratio of pseudo-1st-order kinetic rate constants mentioned before, for the rate of disappearance of the C=C stretch at 1640 cm⁻¹ in binary vs. ternary complexes via Eqs. (21) and (18) (i.e., $k_{3, \text{binary}}/0.56k_{1, \text{ternary}}$). A summary of predicted kinetic rate laws for the rates of disappearance of the C=C stretches at 1543 cm⁻¹ and 1640 cm⁻¹ is provided in Table 3 for binaries and ternaries that contain low concentrations of PdCl₂. The relative magnitudes of k_1 and k_3 can be estimated as follows. Binary kinetic rate laws in Table 3 reveal that k_3V^2 and $2k_1C^2$ represent pseudo-1st-order rate constants and, hence, inverse chemical reaction time constants, for 1,2-polybutadiene/4 mol% PdCl₂ and *cis*-polybutadiene/4 mol% PdCl₂, respectively. As the total polybutadiene concentration is the same in each binary complex (i.e., $[V]_{\text{binary}} = [C]_{\text{binary}}$), the predicted pseudo-1st-order rate constant ratio is;

$$\{k_3\}_{1,2\text{-PBD}/4 \text{ mol\% Pd}} / \{2k_1\}_{\text{cis-PBD}/4 \text{ mol\% Pd}}$$

According to data in the 2nd and 5th columns of Table 2, this pseudo-1st-order rate constant ratio is 5.0 at 100°C, 4.8 at 125°C and 4.8 at 140°C. Hence, the predicted average value of k_3/k_1 is 9.7 between 100°C and 140°C. Using this information from binary complexes, the predicted ratio of pseudo-1st-order rate constants for the rate of disappearance of the C=C stretch at 1640 cm⁻¹ in binary vs. ternary complexes is $k_{3, \text{binary}}/0.56k_{1, \text{ternary}} \approx 17$, averaged over the same temperature range. This prediction is valid because k_1 , which accounts for the rate at which *cis*-polybutadiene coordinates to palladium(II), should be the same in binaries and ternaries, particularly when the ternary mixing strategy provides 2 h of contact between the *cis*-polymer and PdCl₂ prior to introducing the vinyl polymer. Experimental data in the 4th and 5th columns of Table 2 reveal pseudo-1st-order rate constant ratios of 11 at 100°C, 10 at 125°C and 11 at 140°C for the rate of disappearance of the C=C stretch at 1640 cm⁻¹ in binaries and ternaries that should be compared with the predicted value of 17. Hence, the 6-step physical model described in the previous section via reactions (1)–(8), excluding (3) and (4), deserves merit because it predicts correct trends and, in some cases, correct numerical ratios of reaction velocities in binary and ternary polybutadiene complexes with palladium chloride.

4. Conclusions

Palladium chloride modifies the thermal and mechanical properties of atactic 1,2-polybutadiene and *cis*-polybutadiene at ambient and elevated temperatures. The infrared temperature study described herein sheds light on the irreversible chemical changes that occur. For example, alkene absorbances are reduced and alkane signals increase upon heating 1,2-polybutadiene with 4 mol% PdCl₂ to 180°C. This is consistent with a previously proposed Heck-like dimerization mechanism [3,12] of alkene sidegroups to produce linear 4-carbon chemical crosslinks between main chains of the vinyl polymer, prior to the onset of oxidation. Infrared kinetics of the decreasing C=C vibrational absorption at 1640 cm⁻¹ for 1,2-polybutadiene are consistent with (i) the Heck-like dimerization mechanism, and (ii) isothermal kinetics of the exothermic response measured via differential scanning calorimetry over the same temperature range. The carbon-carbon double bond in the main chain of *cis*-polybutadiene forms a π -complex with palladium chloride at ambient temperature, as suggested by the infrared signal at 1543 cm⁻¹. Formation of this π -complex is required before irreversible palladium-catalyzed reactions occur at higher temperatures. Only the main chain alkene groups in *cis*-polybutadiene that coordinate to the transition metal ion during solution preparation participate in the formation of chemical crosslinks. Binary system infrared kinetic measurements of the palladium- π -complexed C=C stretch in *cis*-polybutadiene agree with generalized reactivity trends for mono-substituted (i.e., 1,2-PBD) and di-substituted (i.e., *cis*-PBD) small-molecule alkenes. The infrared kinetics of *cis*-polybutadiene with PdCl₂ proceed about 5-fold slower than those for 1,2-polybutadiene with PdCl₂ in binary mixtures. A mixing strategy is required to overcome this kinetic mismatch and compatibilize the two diene polymers via palladium-catalyzed high-temperature chemical crosslinking reactions. Otherwise, palladium chloride will not function as a transition-metal compatibilizer. Infrared kinetic measurements in a ternary solid state mixture support the predictions based on a detailed 6-step physical mechanism and subsequent kinetic model.

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