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Chemical Reactions in Solid State Complexes of 1,2-Polybutadiene and Palladium Chloride: High Temperature Infrared Study

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Fourier transform infrared (FTIR) temperature studies were performed to examine the microstructural changes that occur in annealing process of the thin films of 1,2-polybutadiene (1,2-PBu)/palladium chloride (PdCl₂) complex. The disappearance of the infrared absorption intensities at 1640, 1418, 994 and 910 cm⁻¹ signifies the consumption of 1,2-vinyl groups of 1,2-PBu. The progressive loss of unsaturation and production of methyl groups as a function of temperature were identified by the enhanced infrared absorption intensities at 1447 and 1375 cm⁻¹. The loss of pendent carbon-carbon double bond is considered to involve both palladium-catalyzed addition reaction and thermally induced cyclization.

Introduction

In a recent paper,¹ a reactive blending through transition metal-olefin coordination complex formation in diene polymers was presented. Upon mixing these diene polymers with a *trans*-square-planar transition metal salt, *i.e.*, bis(acetonitrile) dichloropalladium(II), PdCl₂(CH₃CN)₂, effective coordination cross-links formed because the acetonitrile ligands of the palladium salt are displaced by olefinic pendent groups of the polymers. The addition of palladium chloride to linear diene polymers containing olefinic side groups followed by high temperature annealing generated networks with greatly enhanced thermal and mechanical properties. The macroscopic results could be explained by palladium-catalyzed addition reactions that chemically crosslink linear chains through olefinic side groups. It was proposed that a Heck like reaction mechanism is operative to produce linear chemical

cross-links between main chains. The reaction mechanism has been discussed in somewhat plausible manner based on the previous studies of the chemistry of palladium compounds in which the palladium catalyzed chemical cross-links occur in solid state complexes of 1,2-polybutadiene (1,2-PBu) and palladium chloride (PdCl₂) under annealing process.

FTIR spectroscopy has been useful as a diagnostic probe of the various types of chemical reactions that could occur in these solid films. In this report, we will present the above mentioned chemical reactions in more detail in the temperature range from room temperature to 200 °C by *in-situ* high temperature infrared spectroscopy.

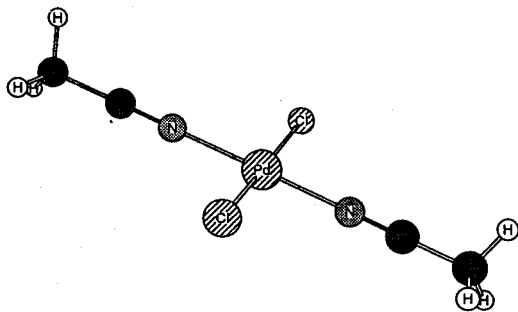
Experimental Section

Atactic 1,2-PBu was supplied by Goodyear Tire & Rubber Co. (Akron, OH), by the courtesy of Dr. Adel F. Halasa. The sample was used as received without any additional purification. The microstructure of 1,2-PBu investigated in this study

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is 80% 1,2-vinyl, 11% 1,4-*trans*, and 9% 1,4-*cis*.

Bis(acetonitrile)dichloropalladium(II) was purchased from Strem Chemicals Co. Molecular model illustrating the *trans*-square-planar configuration of PdCl₂(CH₃CN)₂ was shown below:



The molecular weight (Mw) of 1,2-PBu was 500,000 as determined by size-exclusion chromatography. Details of the characterization of Mw for 1,2-PBu have been reported elsewhere.^{1,2}

The 1,2-PBu and palladium chloride salt (PdCl₂) were dissolved separately in tetrahydrofuran (THF). The concentration of 1,2-PBu in THF was 2% (w/v). The fresh salt and polymer solutions were then mixed in an air-tight vial (20 mL). The concentration of PdCl₂ in the mixture was 4 mole % relative to the 1,2-PBu molar concentration. No further stirring was performed after the initial homogenization of the two solutions.

Thin films prepared for transmission FTIR spectroscopy were cast from the solution of 1,2-PBu/PdCl₂ onto potassium bromide windows. After the majority of the solvent had evaporated under a well-ventilated fume hood, the films were further dried under vacuum in a desiccator for an hour to minimize residual solvent and water adsorption.

Infrared spectra were recorded on a Galaxy series Model 5020 from Mattson Instruments at a resolution of 2 cm⁻¹. The optical bench is interfaced to a 486/50 MHz PC for data acquisition and control. A minimum of 64 scans was signal averaged, and the spectra were stored on a magnetic disc system for further spectral analysis. Spectra recorded at elevated temperatures were obtained using a Spectra Tech Demountable high temperature cell mounted in the spectrometer. The temperature of the cell was controlled by Eurotherm 818 p15 programmable microprocessor that receives feedback from a thermocouple placed inside the cell. This device has a reported accuracy of ±0.1 °C.

Thermal analysis was performed on a Perkin-Elmer DSC 7 differential scanning calorimeter. The details of the thermal analysis of the 1,2-PBu/PdCl₂ were reported elsewhere.^{1,3}

Results and Discussion

Infrared Spectra Recorded at Room Temperature.

Figure 1 represents the infrared spectra of 1,2-PBu (b) and 1,2-PBu/PdCl₂ (a) in the region of 1800-800 cm⁻¹ recorded at room temperature, together with a difference spectrum (c) obtained by digitally subtracting the spectrum (b) from the spectrum (a). Even though the spectra of pure 1,2-PBu and 1,2-PBu/PdCl₂ complex look mostly the same at a first

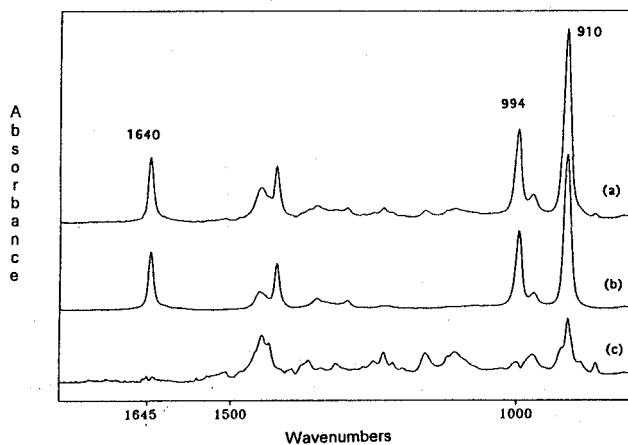


Figure 1. Scale expanded room temperature FTIR spectra of 1,2-PBu and 1,2-PBu/PdCl₂: (a) 1,2-PBu/PdCl₂ (4 mol %); (b) pure 1,2-PBu; (c) difference spectrum, (a)-(b).

glance, the difference spectrum (Figure 1c) dramatically demonstrates the spectral changes observed in 1,2-PBu/PdCl₂ complex before high temperature annealing. There are many new peaks appeared in the region of 1300-1000 cm⁻¹ in the difference spectrum. We interpreted these spectral changes as a perturbation of skeletal deformation mode of 1,2-PBu due to the transition metal coordination complex formation. The absorption peak at 1106 cm⁻¹ has been assigned to the three membered dihapto coordination complex with respect to the metal center in PdCl₂.¹ There is also a further indication of the perturbation of vinyl groups in 1,2-PBu/PdCl₂ through the coordination complex formation at room temperature. The absorption band width at 910 cm⁻¹ was somewhat broadened therefore there are some residual peaks appeared in the difference spectrum. These spectral changes observed in the difference spectrum may not be a conclusive evidence for the coordination complex formation between 1,2-vinyl C=C double bond and PdCl₂. However, we assumed that these all spectral changes could be attributed to the formation of 1,2-PBu/PdCl₂ coordination complex at room temperature.

One may expect to see more significant spectral change of the peak at 1640 cm⁻¹ due to the C=C double bond stretching mode of 1,2-PBu. We will discuss the spectral changes observed in this region later when we discuss on the spectra of 1,2-PBu/PdCl₂ complex obtained as a function of temperature.

The possible coordination complexes that could be present in 1,2-PBu/PdCl₂ solid film are illustrated in Figure 2. Form I represents intramolecular coordination complex formed between the neighboring pendent vinyl groups in the same chain.⁴ Forms II and III are well-known palladium coordination complex forms that generate effective coordination cross-links in the presence of olefinic groups.⁵ Having the possible palladium coordinations to the pendent carbon-carbon double bonds formed in the solid state complexes at room temperature, we are now in a position to characterize the chemical reactions that may occur in these polymer complexes by *in-situ* high temperature infrared spectroscopy.

High Temperature Infrared Spectra of 1,2-PBu/PdCl₂. Before we continue to the infrared temperature

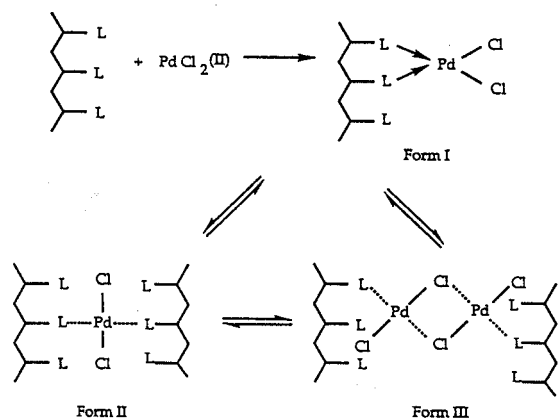


Figure 2. Schematic illustration of possible palladium chloride complexes that could be present in the polymer matrix at room temperature.

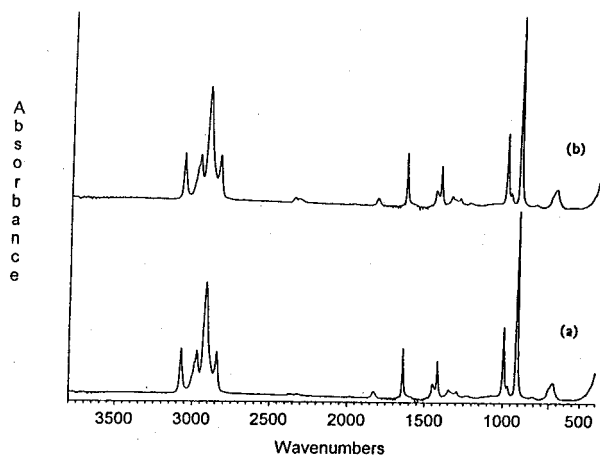


Figure 3. Scale expanded room temperature FTIR spectra of 1,2-PBu: (a) before heat treatment; (b) after heat treatment up to 200 °C.

study of the 1,2-PBu/PdCl₂ complex, it is worth confirming if there is any significant change in the microstructure of undiluted 1,2-PBu sample while the sample is heat treated in the temperature range under study. Figure 3 illustrates the infrared spectra of undiluted 1,2-PBu film recorded at room temperature and of the same film after heat treatment up to 200 °C in the temperature cell. No significant change in the chemical structure due to the thermal autoxidation⁶ or configurational change⁷ in the microstructure of 1,2-PBu can be observed in the temperature range under study.

By contrast, the presence of PdCl₂ in the 1,2-PBu/PdCl₂ complex does change the microstructure of 1,2-PBu significantly as the palladium catalyzed chemical reactions proceed. The subsequent thermal treatment of 1,2-PBu/PdCl₂ complex resulted in gross structural change in the microstructure of 1,2-PBu. Figure 4 shows representative infrared spectra of the 1,2-PBu/PdCl₂ (4 mole %) complex in the region of 1700-1200 cm⁻¹ recorded as a function of temperature from room temperature to 180 °C. Most noticeably, the absorption intensity of the C=C double bond stretching mode at 1640 cm⁻¹ decreased as a function of temperature. Briefly, it confirmed

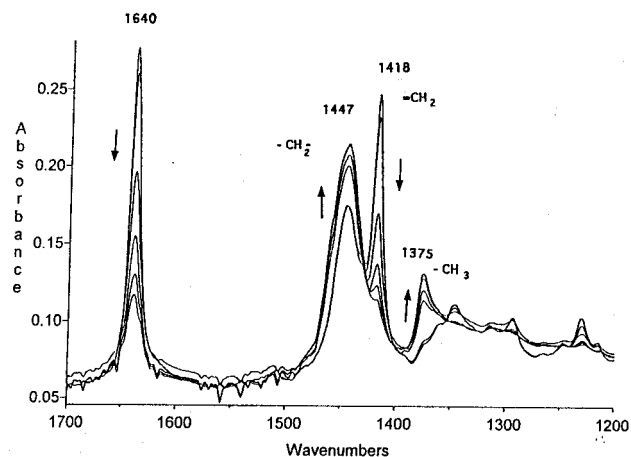


Figure 4. FTIR spectra of 1,2-PBu/PdCl₂ complex in the region of 1700-1200 cm⁻¹ recorded as a function of temperature: (a) room temperature; (b) 80 °C; (c) 90 °C; (d) 120 °C; (e) 150 °C; (f) 180 °C.

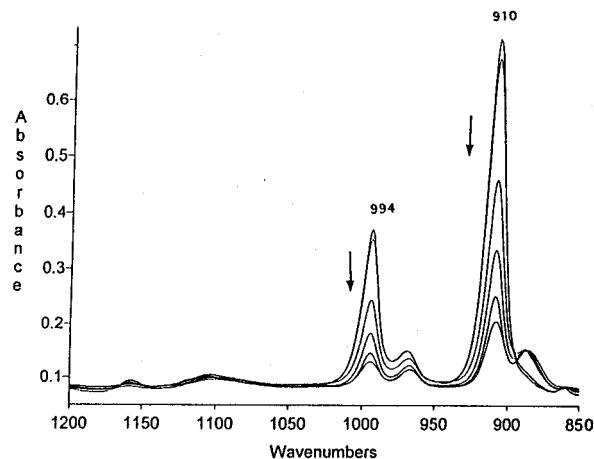


Figure 5. FTIR spectra of 1,2-PBu/PdCl₂ complex in the region of 1200-850 cm⁻¹ recorded as a function of temperature: (a) room temperature; (b) 80 °C; (c) 90 °C; (d) 120 °C; (e) 150 °C; (f) 180 °C.

that the olefinic diene of the 1,2-PBu was involved in a chemical reaction in the presence of PdCl₂ as the temperature is elevated. In accordance with the spectral change observed in the C=C bond stretching region, there are corresponding spectral changes as the chemical reactions occur in the solid state of 1,2-PBu/PdCl₂ complex. The absorption intensities of the peaks at 1447 and 1375 cm⁻¹ due to the aliphatic -CH₂- deformation and the -CH₃ bending modes at the end of the side group, respectively, increased as a function of temperature. This indicates that 1,2-vinyl groups undergo some chemical reactions to produce both aliphatic -CH₂- and -CH₃ groups. At the same time, the absorption peak at 1418 cm⁻¹ that has been assigned to the in-plane scissoring modes of the olefinic =CH₂ side group decreased as the reaction proceeds.

Figure 5 shows the infrared spectra of 1,2-PBu/PdCl₂ complex in the regions of 1200-850 cm⁻¹ recorded as a function

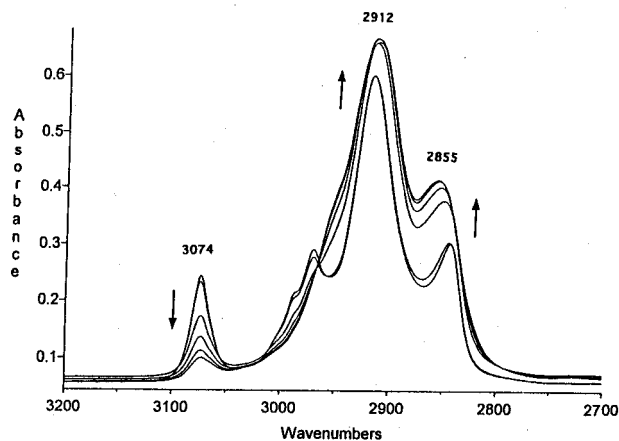


Figure 6. FTIR spectra of 1,2-PBu/PdCl₂ complex in the region of 3200-2700 cm⁻¹ recorded as a function of temperature: (a) room temperature; (b) 80 °C; (c) 90 °C; (d) 120 °C; (e) 150 °C; (f) 180 °C.

of temperature. Both absorption intensities of out-of-plane deformation vibrational mode of the hydrogen atoms of the 1,2-vinyl group at 994 and 910 cm⁻¹ decreased as the temperature is elevated up to 180 °C. This observation strongly suggests that 1,2-PBu undergoes a palladium catalyzed chemical reaction in which the 1,2-vinyl groups -CH=CH₂ are consumed to produce aliphatic -CH₂- groups.

Figure 6 shows the infrared spectra of the aliphatic C-H stretching region (3200-2700 cm⁻¹) of 1,2-PBu/PdCl₂ complex recorded as a function of temperature. Even though it is very complicated to assign the C-H stretching modes precisely due to the overlaps with overtones and combinations of both aliphatic -CH₂- deformation (1447 cm⁻¹) and -CH₃ bending (1375 cm⁻¹) modes, we attempted to correlate the spectral changes observed in this region to the chemical reactions occurred in 1,2-PBu/PdCl₂ complexes. The absorption intensity of the peak at 3074 cm⁻¹ assigned to the C-H stretching mode of the 1,2-vinyl groups decreased as a function of temperature that resulted in increase of the intensity of the peaks at 2912 and 2855 cm⁻¹ assigned to the asymmetric and symmetric C-H stretching vibrational modes of -CH₂- and -CH₃, respectively.⁸ All of these concerted spectral changes reflect the consumption of 1,2-vinyl groups of 1,2-PBu via palladium catalyzed chemical reactions.

Characterization of the Exothermic Processes Observed by DSC.

In the previous publications¹² it was reported that there exist three exothermic processes in the DSC thermogram for 1,2-PBu/PdCl₂ (2 mole %) in the first DSC scan and the significant increase in *T_g* ($\Delta T_g \sim 100$ °C) was observed in the second DSC scan for the annealed sample. The objective of this section is to summarize our previous DSC results before we propose a reaction mechanism for the palladium catalyzed chemical reactions occur in the solid state 1,2-PBu/PdCl₂ complexes. The relatively narrow exothermic peak at 120 °C in the DSC thermogram indicates that the chemical reaction indeed occurred at that temperature. Upon heating the sample up to 350 °C broad exothermic peaks at 250 and 320 °C were observed which indicate that there are some other reactions occurring during the high temperature annealing process. We have suggested

that these high temperature reactions could be diffusion controlled reactions.¹ However, it is not a reasonable assumption since the PdCl₂ has been already uniformly coordinated to 1,2-PBu through solution mixing process. In an attempt to identify these high temperature exothermic reactions we will incorporate the thermal cyclization of 1,2-PBu with the palladium catalyzed chemical reaction.

Reactions of 1,2-vinyl Groups in 1,2-PBu/PdCl₂.

The objective of this section is to reexamine the chemical reaction mechanism that leads to the enhancement of mechanical and thermal properties of 1,2-PBu/PdCl₂ complexes during the high temperature annealing. We have proposed a Heck-like reaction mechanism is operative to the system based on the multiple exotherms in the DSC thermogram and the spectral comparison between the spectra obtained from the samples before annealing and after annealing in the high temperature vacuum oven.¹ We attributed the enhancement of the mechanical and thermal properties of the annealed 1,2-PBu/PdCl₂ complexes to the intermolecular linear chemical crosslinks via pendent double bonds.

It is well known that the presence of multiple carbon-carbon bonds in hydrocarbon polymers leads ultimately to an increase in reactivity of the polymers whereas the chemical bonds in saturated hydrocarbon polymers are relatively stable. Since the reactivity of the diene functional groups of the diene polymers depends on the microstructure of the polymer, it may vary considerably under different reaction conditions. Golub and his coworkers have reported in their series of papers that successive reactions of carbon-carbon double bonds in various diene polymers have occurred under different reaction conditions.^{7,9} One of the best examples of the possible reactions is *cis-trans* isomerization of the carbon-carbon double bond in the backbone of the diene polymers. The isomerization of 1,4-PBu depends on the initial and equilibrium amount of the isomers that depends on the structure of the diene polymer and the experimental conditions such as the mode of initiation, pressure, temperature, etc. On the other hand, irradiation of diene polymers also gives rise to *cis-trans* isomerization.^{10,11}

Besides the *cis-trans* isomerization described above, cyclization provides another route for the isomerization of diene polymers which reduces the unsaturation of the polymer. Strong acids (e.g., H₂SO₄, HCl, some Lewis acids, etc.) convert diene polymers to hard, non-rubber-like, thermoplastic materials of higher density than the parent rubbery polymers.¹¹ Raven and Heusinger reported that pendent double bonds are more reactive than double bonds in the backbone of the diene polymer for the radiation-induced crosslinking and cyclization.¹²

Having much information obtained from literature concerning about the reactivity of the diene functional groups of the polymer, we are now in a position to build our knowledge about the chemical reactions that occur in the solid state complexes of 1,2-PBu/PdCl₂. Before we proceed to construct our understanding of the reactions that occur in the polymeric palladium complexes, it should be mentioned that the microstructure of undiluted 1,2-PBu used for this research work contains three diene configurations as described in the experimental section. Therefore, each diene functional group may undergo different reactions even the sample is under the same reaction condition. However, we assumed that the

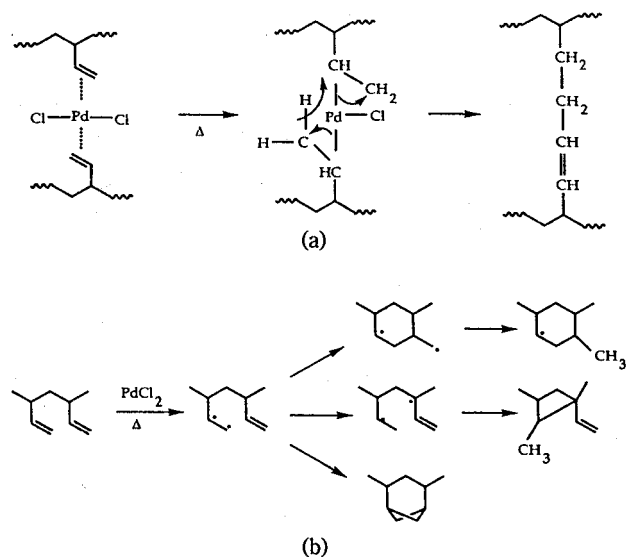


Figure 7. Schematic illustration of possible palladium catalyzed chemical reactions: (a) Heck like addition reaction; (b) thermal cyclization.

microstructure of our sample as solely 1,2-PBu to avoid extra complexity due to the minor *cis-trans* isomerization.

In the previous publication,¹ we proposed that a Heck-like addition reaction mechanism is operative for the palladium catalyzed reaction in which carbon-carbon double bonds should be transformed into single bonds leading to the increase of aliphatic $-\text{CH}_2-$ group. However, we could not clearly resolve our FTIR spectral data, especially in the region of $1500\text{--}1350\text{ cm}^{-1}$ associated with the change in concentration of $-\text{CH}_2-$ and $-\text{CH}_3$ groups. The palladium catalyzed addition reactions indeed occur in the 1,2-PBu/ PdCl_2 complexes leading to the increase in the concentration of aliphatic $-\text{CH}_2-$ group as evidenced by the increase of infrared absorption intensity at 1447 cm^{-1} . Summarized Heck like addition reaction scheme is illustrated in Figure 7 (a). *In-situ* high temperature infrared spectroscopy revealed that the progressive reduction of the double bonds occurred as the temperature is elevated as shown in Figure 4. We observed not only the increase of $-\text{CH}_2-$ band at 1447 cm^{-1} but also the increase of $-\text{CH}_3$ band at 1375 cm^{-1} . Therefore, in addition to cross linking reaction another reaction consuming double bonds must take place to produce $-\text{CH}_3$ groups.

This reaction should be a thermal cyclization. Our FTIR spectral data also indicated that thermal cyclization indeed occurs in 1,2-PBu when heated above $100\text{ }^\circ\text{C}$ in the presence of PdCl_2 leading to the development of $-\text{CH}_3$ groups with progressive loss of unsaturation (Figure 4). This thermal intramolecular cyclization may be further supported by the possible chelate complex formation (Form I) shown in Figure 2.

Golub⁷ has reported on the microstructural changes produced in 1,2-PBu during thermal cyclization under non-pyrolytic condition with the aid of infrared spectroscopy. His

infrared spectral results are the same as our current spectral data, even though the temperature range we studied for this investigation was lower than his non-pyrolytic condition.

Figure 7 (b) illustrates the possible thermal intramolecular cyclization in which 1,2-PBu could undergo to produce cyclic structures containing methyl groups. The reaction, which proceeds by a radical mechanism, is initiated by heating the polymer to above $100\text{ }^\circ\text{C}$.¹¹ The activation energy for the reaction may be lowered to some extent in the presence of the palladium catalyst. Cycloalkane structural units may also be produced by cycloaddition at high temperature.⁷

Conclusion

In summary, *in-situ* high temperature infrared spectroscopy revealed that solid state 1,2-PBu/ PdCl_2 complex undergoes not only palladium catalyzed Heck like addition reaction but also thermally induced cyclization.

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