

Reactive Blending via Metal-Olefin Coordination in Diene Polymers. Solid-State Properties That Support the Concept of a Network Structure

Francis Bossé, Pronab Das, and Laurence A. Belfiore*

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

*Received December 14, 1994; Revised Manuscript Received April 7, 1995**

ABSTRACT: This study focuses on the properties of solid films formed from tetrahydrofuran solutions containing diene polymers, polybutadiene or polyisoprene, and an inorganic salt, bis(acetonitrile)-dichloropalladium(II). Upon mixing, effective cross-links are formed, because the acetonitrile ligands of the palladium salt are displaced by olefinic pendant groups of the polymers. Infrared data measured herein and previous studies of the chemistry of palladium compounds suggest that a Heck-like mechanism is operative to generate chemical cross-links via palladium-catalyzed reactions. The swelling behavior of polybutadiene and polyisoprene was studied in various solvents. In both cases, equilibrium swelling ratios decrease with an increase in salt content, indirectly supporting the concept of a network structure. Using the Flory-Rehner relation, the number-average molecular weight between cross-link junction points (M_c) was calculated from the swelling data. Relative to the undiluted polymers, the mechanical properties of polybutadiene and polyisoprene solid films show a dramatic increase of 3 orders of magnitude in Young's modulus of elasticity when the palladium salt content is 4 mol %. Thermogravimetric measurements show that an increase in the transition-metal salt (PdCl_2) content, as well as annealing at 80 °C, enhances the thermal stability of solid films. The glass transition temperatures (T_g) of solid films determined by differential scanning calorimetry increase with PdCl_2 content until the thermal plateau is achieved between 1 and 3 mol % palladium salt, where the increase in T_g (i.e., ΔT_g) is approximately 100 °C relative to the undiluted polymer.

1. Introduction

The main objective of this study was to modify diene polymers via square-planar transition-metal salts that contain labile ligands and to determine the effects of this modification on swelling, thermal, and mechanical properties of the composite materials. The modifier was an inorganic salt, bis(acetonitrile)dichloropalladium(II), which has a strong affinity for the olefinic groups in the polymer matrix. When an organic polymer is mixed with an inorganic reinforcing filler or cross-linking agent, good wetting between the constituents must occur to promote continuous phase boundaries. The strength across the phase boundaries, or adhesion, usually affects the physical behavior of the composite materials. This modification is even more drastic for highly cross-linked material. Early studies of composite materials have shown that fracture toughness, ultimate tensile strength, elastic modulus, and ultimate elongation depend on the degree of adhesion¹ or the cross-link density between the constituents.

Adhesion between the filler and the matrix leads to the formation of a second phase in the vicinity of the phase boundaries. This is due to the difference in mobility between the matrix chain segments in the interlayer in contact with the filler.² The presence of this "interphase" usually modifies the structure and morphology of the polymeric matrix. Consequently, when this second phase is present, the average properties of the material are usually different from the bulk properties of the pure polymer. These effects can be observed experimentally by measuring macroscopic properties of the composite relative to those of the unmodified polymer, which indicate the effectiveness of

the interaction between phases or the strength of the cross-links.

For filled rubber systems, the effects of adhesion on the thermodynamic³ and mechanical properties⁴ of composite materials have been known for more than 4 decades. Similar effects were also observed for filled thermoplastic materials.⁵ In general, these studies showed that an increase in filler concentration leads to an increase in the glass transition temperature (T_g) of the matrix, as well as an increase in selected mechanical properties (e.g., elastic modulus). Analogous effects on thermodynamic and mechanical properties have been found for partially crystalline polymers.⁶ In this case, an increase in T_g accompanies an increase in crystallinity. Semicrystalline polymers mimic the behavior of filled polymer matrices in which good wetting between the phase boundaries is present, since the dispersed crystalline regions can act as filler particles. However, other studies have shown that exceptions to the general trend may exist and that T_g does not always increase with an increase in filler loading.⁷

It should be emphasized that the T_g of a composite is the temperature at which one observes a change in thermodynamic properties of the amorphous matrix only, since over that temperature range, an inorganic filler or cross-linking agent does not experience discontinuities in its thermodynamic properties. Hence, the glass transition temperature depends on the adhesive strength of the filler/matrix interface, and, for cross-linked materials, it is directly related to mechanical reinforcement. Thus, because precise measurements of the glass transition temperature can be performed, the variation in T_g of the matrix can be used as a probe of distinct regions of restricted mobility created by the introduction of cross-links. In the past, this type of scheme has been used successfully to determine qualitatively the extent of chain overlap in composite materials.⁸

* Author to whom correspondence should be addressed.

† Abstract published in *Advance ACS Abstracts*, August 15, 1995.

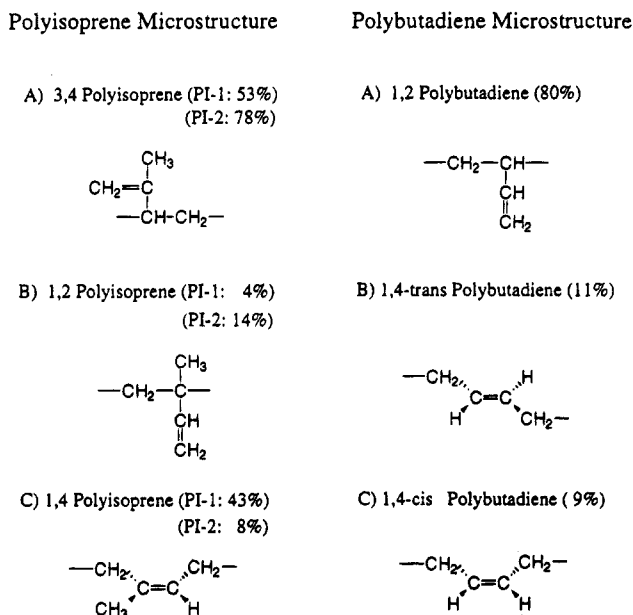


Figure 1. Chemical structures of the diene polymers.

Very few studies have dealt with solid-state property measurements for polymer-salt complexes in which thermally irreversible cross-links are present.⁹ To the best of our knowledge, most studies that address complexation have been performed in aqueous solution containing low-molecular-weight polymers and metal salts. All of these studies suggest that either reversible or irreversible specific interactions are present. Other types of hybrid organic-inorganic materials can be prepared by the addition of a metallic salt to a linear polymer, and this has given rise to the study of ionomers. However, most of the resulting ionomers are phase separated, and no irreversible chemical cross-links are present.

This paper is divided into three sections. In the first part, mechanical testing is employed to analyze the solid-state properties of films generated from tetrahydrofuran solutions. The investigated parameters are the structure of the polymer chains, the concentration of palladium chloride, and the addition of lithium chloride. In the second part, the results from swelling experiments are discussed, which support the hypothesis that effective cross-links are present in these films. Finally, the last section summarizes results from calorimetry and thermogravimetry. These results provide further indirect evidence that cross-linking reactions occur between PdCl_2 and the olefinic pendant groups of the diene polymers. The discussion also focuses on plausible reaction mechanisms for Pd-catalyzed chemical cross-links and structure-property relations for these novel materials.

2. Experimental Section

Materials. Atactic 1,2-polybutadiene (PBU) and 3,4-polyisoprene were supplied by Goodyear Tire & Rubber Co. (Akron, OH), courtesy of Dr. Adel F. Halasa. These samples were used as received without any additional purification. The microstructure for polybutadiene is 80% 1,2-vinyl, 11% 1,4-trans, and 9% 1,4-cis. Polyisoprene (PI-1) contains 43% 1,4-cis, 53% 3,4-vinyl, and 4% 1,2-, while PI-2 is composed of 8% 1,4-cis, 78% 3,4-vinyl, and 14% 1,2-. The chemical structures of the diene polymers are given in Figure 1. Lithium chloride (99.99+%) was obtained from Aldrich Chemical Co., Inc., and used as received. Bis(acetonitrile)dichloropalladium(II) was purchased from Strem Chemicals in Newburyport, MA. It was used as received, also.

Table 1. Molecular Weight Characterization for Polybutadiene and Polyisoprene Samples

polymer sample	label	$M_w \times 10^{-3}$	polydispersity index
polybutadiene	PBU	500	1.6
polyisoprene	PI-1	80	1.5
polyisoprene	PI-2	400	1.5

Size-Exclusion Chromatography. Molecular weight characterization of the polymer samples was performed by size-exclusion chromatography (SEC) on a Varian 5000 LC at 50 °C. The solvent used for the standardization curve was tetrahydrofuran (THF; Chemlab spectroscopic grade). The analyses were performed in duplicate, and the results were averaged. The weight-average molecular weight (M_w) and the polydispersity index for each sample are given in Table 1. The average deviation in the molecular weight determination is about 2%.

Sample Preparation Methods. The polymers (polybutadiene or polyisoprene) 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/100 mL. The fresh salt and polymer solutions were then mixed in an air-tight vial (20 mL). No further stirring was performed after the initial homogenization of the two solutions. Using this procedure, solutions containing 0.3–1.75 g of solids/100 mL of solvent were prepared, while the molar concentration of $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ relative to the polymer ranged from 0.5 to 10 mol %. Films were prepared from THF solutions by pouring the highly viscous ternary mixtures, before gelation, into a Petri dish to facilitate evaporation of the solvent in a fume hood at ambient temperature. In order to obtain a slower evaporation rate and more uniform films, the Petri dish was covered with aluminum foil.

Physical Property Measurements. Stress-strain measurements were performed at ambient temperature using an Instron Model 8501 servohydraulic mechanical testing system. The strain rate was 50 mm/min.¹⁰ Samples were cut into rectangular strips with average dimensions of 45 mm (length) by 6.5 mm (width) and a thickness ranging from 0.25 to 0.65 mm. Using this procedure, at least four solid films were tested at each salt concentration. Young's modulus of elasticity was calculated via Series IX software from Instron, using the original stress-strain data without smoothing.

Thermal stability studies on solid films were performed using a Seiko thermogravimetric/differential thermal analyzer (TGA/DTA 220). The temperature range in these experiments encompassed 30–400 °C at a heating rate of 20 °C/min using a dry nitrogen purge at a flow rate of 250 mL/min.

Differential scanning calorimetry (DSC) data were recorded on a Perkin-Elmer DSC 7 after calibration with indium. The samples were scanned under helium and nitrogen purges at a heating rate of 20 °C/min from 30 to 400 °C. All samples were heated once to remove differences in thermal history and to complete the crosslinking reactions. After the first heating scan, samples were annealed at 250 °C for 15 min and then quenched at the maximum cooling rate of the instrument (320 °C/min). A 15-min delay was used before recording data from the second heating trace to measure the glass transition temperature. Analyses were performed in duplicate, and the reproducibility in T_g , ΔH , and ΔC_p values was $\approx 1\%$.

Fourier transform infrared spectroscopy (FTIR) measurements were performed on a Galaxy series Model 5020 from Mattson Instruments. The optical bench is interfaced to a 486/50 MHz PC for data acquisition and control. FTIR measurements were performed under a dry air purge at ambient temperature. The FTIR spectrum of bis(acetonitrile)dichloropalladium(II) was obtained from a powder dispersed in dried KBr. The transition-metal complex between 1,2-polybutadiene and 10 mol % PdCl_2 was tested as a thin film deposited from THF on a KBr crystal. Each interferogram was generated by averaging 64 scans at a resolution of 1 cm^{-1} .

3. Results and Discussion

General Considerations. Previous studies of the reactions of low molecular weight model compounds of palladium(II) chloride containing acetonitrile ligands

Table 2. Swelling and Stress–Strain Results for Polybutadiene Solid Samples Containing Palladium(II) Chloride

sample	PdCl ₂ concn (mol %)	elastic modulus (N/m ²)	M_c^a	equilibrium V_{eq}/V_0 (%)	M_c^b	M_c^c
PBu	0.00	1.4×10^6		1280	87000	
PBu	0.50	4.9×10^6	2800	510	15000	820
PBu	1.00	4.9×10^6	3200	510	15000	370
PBu	2.00	7.4×10^7	100	180	980	370
PBu	3.00	2.3×10^8	32	145	410	350
PBu	3.50	5.0×10^8	15	145	410	330
PBu	4.00	1.4×10^9	5	145	410	380

^a M_c' values calculated from eq 1, using Young's elastic modulus.^b M_c values calculated from eq 4, using V_{eq}/V_0 parameters determined from the experimental swelling results in heptane. ^c M_c values calculated from eq 5, using T_g values determined via the second DSC heating trace.

indicate that acetonitrile is a weak ligand and that it can be easily displaced by olefinic groups.^{11,12} In an earlier publication,¹³ results from molecular spectroscopy (FTIR and high-resolution carbon-13 solid-state NMR) revealed that acetonitrile ligands are absent in solid films of atactic 1,2-polybutadiene (1,2-PBu) with bis(acetonitrile)dichloropalladium(II). Furthermore, an infrared signal at 1100 cm⁻¹ suggests that a three-membered ring is present when the salt content is 10 mol %. Coordination of the double bond in the polymeric side group to the palladium metal center offers an effective mechanism to generate networklike structures. If this scheme is operative, it should not be surprising that the mechanical properties of these "blends" will be enhanced relative to the parent polymers. This claim is supported herein via the calculation of M_c from stress–strain data and equilibrium swelling results for both diene polymers with bis(acetonitrile)dichloropalladium(II) at various salt concentrations.

Calculation of the Number-Average Molecular Weight between Cross-Link Junctions (M_c) Based on Various Experimental Techniques. The degree of cross-linking in each sample was characterized via two methods: by the swelling ratio at equilibrium and the experimental modulus of elasticity (κ) for nonequilibrium materials.

Calculation of M_c from Stress–Strain Measurements. Assuming that the kinetic or statistical thermodynamic theory of rubber elasticity is valid to analyze the stress–strain data for these complexes, the effective molecular weight between cross-links, M_c' , can be calculated from eq 1, which accounts for free ends but not molecular entanglements.¹⁴ The effect of free ends and loops on polymer networks is described elsewhere.¹⁵

$$M_c' = \left(\frac{\kappa}{3\rho_0 RT} + \frac{2}{M_0} \right)^{-1} \quad (1)$$

In eq 1, ρ_0 is the density of the elastomer (in g/cm³), R is the gas constant, T is the test temperature, M_0 is the number-average molecular weight of the polymer, and κ is measured experimentally from the initial slope of the stress–strain curve. M_c' values calculated from eq 1 and Young's modulus of elasticity (κ) are reported in Tables 2 and 3 for PBu and PI, respectively.

Calculation of M_c from Swelling Experiments. Triplicate samples were cut into strips of 1 cm² with an average thickness of 0.05 cm (≈ 0.1 g). The films were placed in 10 mL of solvent in an air-tight vial. Solvent uptake was calculated by removing the swollen films from the remainder of the solvent and weighing these films after gently wiping off the excess solvent. Results

Table 3. Swelling and Stress–Strain Results for Polyisoprene Solid Samples Containing Palladium(II) Chloride

sample	PdCl ₂ concn (mol %)	elastic modulus (N/m ²)	M_c^a	equilibrium V_{eq}/V_0 (%)	M_c^b	M_c^c
PI-1	0.00	2.0×10^6				
PI-1	1.00	4.9×10^6	5600			820
PI-1	2.00	7.6×10^6	4300	1200	55000	370
PI-1	3.00	1.0×10^7	3900	1200	55000	370
PI-1	4.00	1.1×10^7	4200	1200	55000	390
PI-2	0.00	8.3×10^5				
PI-2	1.00	3.4×10^7	1900	380	4800	1300
PI-2	2.00	2.1×10^8	760	250	1800	640
PI-2	3.00	9.2×10^8	8.0	245	1600	400
PI-2	3.50	9.0×10^8	8.0	230	1200	410
PI-2	4.00	1.0×10^9	8.0	230	1200	400

^a M_c' values calculated from eq 1, using Young's elastic modulus.^b M_c values calculated from eq 4, using V_{eq}/V_0 parameters determined from the experimental swelling results in heptane. ^c M_c values calculated from eq 5, using T_g values determined via the second DSC heating trace.

from this study confirm that equilibrium swelling is achieved after 150 h of contact between the film and the solvent. The volume fraction of the polymer, v_{2m} , in the swollen specimen was calculated assuming additivity of the volumes of polymer and solvent

$$V_0 = \frac{W_0}{\rho_0} \quad \text{and} \quad V_{eq} = \left(\frac{W_0}{\rho_0} + \frac{W_s}{\rho_s} \right) \quad (2)$$

$$v_{2m} = V_0/V_{eq} \quad (3)$$

where V_0 is the volume of the polymer prior to swelling and V_{eq} is the equilibrium volume of the swollen polymer. W_s is the weight of solvent (in grams), ρ_s is the solvent density (in g/cm³), and W_0 and ρ_0 are the weight and the density, respectively, of the polymer sample prior to swelling.

For a perfect network, M_c is calculated using the Flory–Rehner equation for swollen network structures. The parameter M_c , or the average number of repeat units between cross-link junctions, $\langle x \rangle$, can be expressed as:

$$M_0 \langle x \rangle = M_c = \left[\frac{V_s \rho_0 \left(v_{2m}^{1/3} - \frac{v_{2m}}{2} \right)}{-[\ln(1 - v_{2m}) + v_{2m} + \chi_1 v_{2m}^2]} \right] \quad (4)$$

where V_s is the molar volume of the solvent (cm³/mol), and χ_1 is the polymer–solvent energetic interaction parameter. In this analysis, the polymer–solvent interaction parameter corresponds to $\chi_1 = 0.38 + 0.27v_{2m}$ for polybutadiene in heptane¹⁶ and $\chi_1 = 0.39 + 0.04v_{2m}$ for polyisoprene in heptane.¹⁷ For each diene polymer with PdCl₂, the v_{2m}^{-1} parameters in heptane (V_{eq}/V_0), and the M_c values calculated from eq 4, are reported in Tables 2 and 3.

I. Elastic Moduli of Polymeric Palladium Complexes. Using the procedure described in the Experimental Section, stress–strain curves were acquired for solid films containing between 0.5 and 6 mol % palladium chloride. Young's modulus of elasticity was calculated via Series IX software from Instron, using the original stress–strain data without smoothing. Figure 2 summarizes the results obtained for polybutadiene (PBu) and polyisoprene (PI) films. The dramatic increase in modulus for PBu and PI-2, at rather low salt concentrations, can only be rationalized by palladium-catalyzed chemical cross-linking of the olefinic side

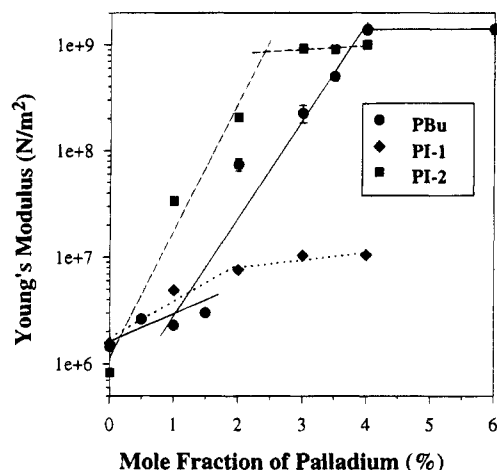


Figure 2. Semilog plots of Young's modulus vs palladium chloride concentration for two diene polymers. The filled circles (●) represent polybutadiene samples; the filled diamonds (◆) and squares (■) are assigned to polyisoprenes PI-1 and PI-2, respectively. When the concentrations of both palladium and the olefinic side groups are sufficient, the modulus enhancement reaches a plateau which is 3 orders of magnitude higher than the undiluted polymers.

groups to generate a network structure. If one focuses on the elastic moduli for polybutadiene films, it is obvious that there is a threshold in the vicinity of 1 mol % PdCl_2 . When the palladium salt concentration is greater than or equal to 4 mol %, moduli reach a glassy state plateau at $\approx 2 \times 10^9 \text{ N/m}^2$. This is not the case for the two polyisoprene matrices, since no threshold values are detectable at low palladium salt concentration. Both PI matrices do not exhibit a percolation threshold on the modulus–composition graph in Figure 2. When the palladium salt concentration is $\approx 2 \text{ mol } \%$, the elastic moduli for PI-1 complexes reach a rubbery state plateau at $1 \times 10^7 \text{ N/m}^2$. For PI-2 complexes, the plateau modulus is 2 orders of magnitude higher. In comparison to PI-1, the higher moduli obtained for PI-2 can be related to the fact that PI-2 has a greater proportion of olefinic groups residing in the side chain (PI-1 $\approx 57\%$ and PI-2 $\approx 92\%$). Thus, the difference in cross-link density for PI-1/ PdCl_2 vs PI-2/ PdCl_2 films can be explained by the microstructural differences between the two diene polymers.

The enhancement in modulus with increasing PdCl_2 concentration suggests that a similar behavior for the glass transition temperature of the polymeric complexes is operative. One can calculate the number-average molecular weight between cross-link junctions (M_c') from the modulus of elasticity (κ) via eq 1. However, eq 1 is only valid for samples at equilibrium.¹⁸ This is not the case here because the glass transition temperatures of the undiluted diene polymers are close to room temperature (PBu $\approx 5^\circ\text{C}$ and PI $\approx 45^\circ\text{C}$). Thus, application of eq 1 should lead to an overestimation of the cross-link density or an underestimation of M_c or M_c' . Tables 2 and 3 summarize the κ and M_c' values for polybutadiene and polyisoprene films issued from THF solutions, respectively. The unrealistically small values of M_c' obtained for PI-2/ PdCl_2 and PBu/ PdCl_2 when the salt concentration is greater than 2 mol % suggest that T_g has increased dramatically relative to the undiluted polymers. The glass transition temperature behavior is discussed in more detail later (i.e., part IV).

Support for the claim that palladium chloride catalyzes chemical cross-links is based on an attempt to inhibit these reactions. Lithium chloride is known to disrupt or greatly reduce the rate of charge transfer,

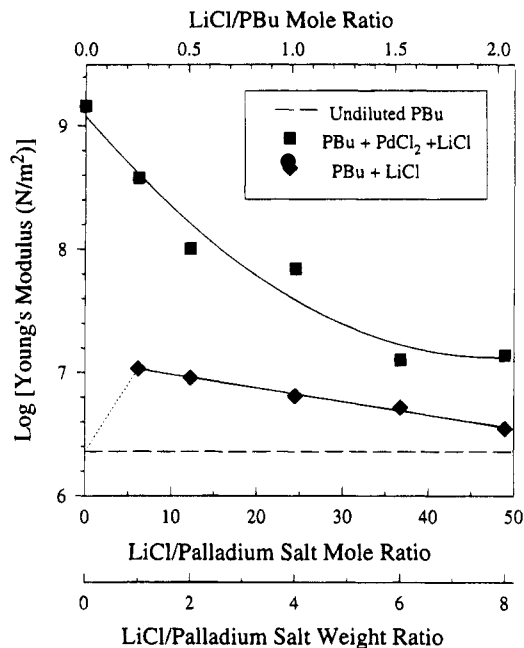


Figure 3. Effect of lithium chloride on Young's modulus of elasticity for 1,2-polybutadiene, with and without 4 mol % PdCl_2 relative to the polymer. The LiCl/ PdCl_2 weight and molar ratios are indicated on the lower horizontal axis. The LiCl/polybutadiene ratio is indicated on the upper horizontal axis and applies to binary and ternary systems. The lower horizontal axis is applicable only for the data plotted as squares where 4 mol % palladium chloride is present in ternary mixtures with LiCl and the polymer. The horizontal dashed line represents the elastic modulus for undiluted atactic 1,2-polybutadiene.

ligand exchange,¹⁹ and polymerization.²⁰ Addition of LiCl to PBu/ PdCl_2 in THF reduces the rate at which the palladium salt coordinates to the olefinic pendant group. Thus, the elastic modulus of ternary solid-state films should decrease when the concentration of LiCl increases. In order to verify the effect of lithium chloride on elastic moduli, LiCl was added to THF solutions containing 4 mol % PdCl_2 with respect to PBu. Films issued from THF solutions were prepared and analyzed using the procedure described earlier in the Experimental Section. The LiCl/PBu molar ratio in these films was varied from 0.25 to 2.0. Additionally, films without palladium chloride were prepared using the same LiCl/PBu molar ratios. The results obtained from stress–strain measurements are shown in Figure 3. The horizontal dashed line represents the modulus of undiluted polybutadiene. The LiCl/PBu molar ratio range applies to the two types of films, i.e., with or without 4 mol % PdCl_2 .

It is obvious from Figure 3 that the elastic modulus of both types of films decreases when the LiCl concentration increases. The decrease in elastic modulus is more dramatic for films that contain 4 mol % PdCl_2 and LiCl (■) compared to those containing only LiCl (◆). This behavior is consistent with the fact that the LiCl phase separates from the polymer matrix and forms aggregates that could act as physical cross-link centers. However, these cross-links due to adhesion and entanglements are much weaker than chemical cross-links. This is illustrated by the relatively higher value of Young's modulus for a chemically cross-linked network. For the films containing only LiCl, the initial increase in Young's modulus of elasticity relative to undiluted PBu is mainly due to a filler effect. The subsequent decrease in modulus with increasing LiCl content is due to two well-known effects, i.e., the

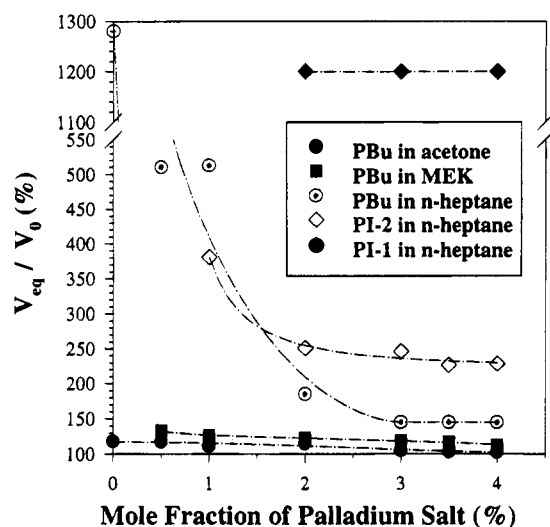


Figure 4. Equilibrium swelling data for solid polymeric complexes as a function of PdCl_2 concentration. The horizontal axis represents the mole fraction of palladium chloride relative to the diene polymer. The vertical axis represents the volume of the solid film and the imbibed solvent relative to the initial volume of the solid film. The PBU films are swollen in acetone (●), methyl ethyl ketone (■), and heptane (○), while heptane was used as the swelling agent for PI-1 (◆) and PI-2 (◇).

increase in aggregate size without good wetting, which results in reduced adhesion at the LiCl /polymer interface, and an increase in the number of defects.^{3–5,21}

For ternary solid-state films that contain both PdCl_2 and LiCl , the reduction in Young's modulus is about 2 orders of magnitude when the $\text{LiCl}/\text{PdCl}_2$ molar ratio is 40 (see Figure 3). This significant decrease in modulus suggests that LiCl reduces the exchange rate of acetonitrile and the olefinic group via destabilization of the intermediary complex required for ligand exchange. However, the presence of LiCl does not completely disrupt ligand exchange because the ligands involved in the process are neutral. Thus, the presence of lithium chloride reduces the rate at which chemical cross-links are formed, but cross-link formation is not completely inhibited. When the LiCl/PBU molar ratio is greater than 1, lithium chloride could act as a plasticizer and effectively reduce the elastic modulus as illustrated in Figure 3. In addition to the palladium salt content that enables one to tailor films with a wide range of mechanical properties, it is clear that LiCl can be used as an additive which will permit greater control of these properties.

II. Equilibrium Swelling of Solid Films. Indirect Evidence for Cross-Linked Networks. The swelling behavior of polybutadiene and polyisoprene solid films in a variety of solvents is illustrated in Figure 4. In all cases investigated, swelling ratios decrease with increasing PdCl_2 concentration and exhibit a plateau at about 2 mol % salt. At constant PdCl_2 concentration, comparison of the swelling behavior of PI-1 and PI-2 in heptane clearly shows that the cross-link density is greater for PI-2, because the swollen volume of the polymer complex is smaller.

Quantitative determination of the number-average molecular weight was performed using the formalism described above (see eq 4). The absolute M_c values obtained from swelling data are more reliable and accurate than those determined via eq 1 based on stress-strain data. The calculated M_c values for polyisoprene and palladium chloride in heptane are summarized in Table 3. Evidently, for both polyisoprenes, the M_c values obtained from swelling experiments are

much larger relative to M_c' obtained via eq 1. Clearly, M_c values for PI-1/ PdCl_2 are quite high because the cross-link density is low. Surprisingly enough, at 2 mol % PdCl_2 the relatively low cross-link density of PI-1 renders the solid complex soluble in heptane and leads to the formation of a gel which does not exhibit steady-state flow. This is definitely not the case for PI-2, since the cross-link density is high enough in films containing 1 mol % PdCl_2 to make them insoluble.

Table 2 summarizes the swelling results for polybutadiene complexes, which exhibit trends that are similar to those discussed above for PI-2 complexes in Table 3. The following characteristics are common to both PBU/ PdCl_2 and PI-2/ PdCl_2 : (i) cross-link density increases at higher palladium salt concentration, (ii) M_c values calculated via swelling are at least 1 order of magnitude higher than those estimated via eq 1, (iii) the concentration threshold for vitrification is in the vicinity of 2 mol % PdCl_2 , which corresponds to $M_c < 2000$, and (iv) the cross-link density in these films is much higher than one would predict for palladium/olefin coordination complexes, because M_c should be $\approx 30\,000$ when the PdCl_2 concentration is 4 mol %, characteristic of a rubbery material. Thus, the material properties of these solid films strongly suggest that PdCl_2 catalyzes a cross-linking reaction after coordination to the olefinic side group. Additionally, PBU films containing 4 mol % PdCl_2 are slightly soluble in heptane when lithium chloride is added in the same proportions as discussed above (see Figure 3). In contrast, PBU films containing only LiCl are completely soluble in heptane. This clearly indicates that the presence of lithium chloride leads to a major reduction in cross-link density in these diene complexes.

III. Evidence for Palladium-Catalyzed Reactions That Produce a Chemically Cross-Linked Network. For small molecules, palladium salts are known to catalyze various reactions in heterogeneous and homogeneous media.²² These reactions involve the condensation or coupling of aromatic amines²³ and nucleophilic alkylation of allylic compounds. In the absence of a nucleophile, palladium(II) or Pd^0 induces 1,3-transposition of allylic acetates or sigmatropic rearrangements of heteroatoms ($\text{S} \rightarrow \text{N}$). However, the reactions that pertain to the olefinic systems under investigation in this study are the Heck reaction, cyclization of dienes, and dimerization. It should be emphasized that none of the last three reactions have been observed in macromolecular systems, but coupling of polymers containing aromatic amines and nucleophilic alkylation have been reported.²⁴

The Heck reaction, which leads to the coupling of olefins via palladium catalysis, requires the presence of an organic halide, while a cocatalyst (CuCl) must be present for these systems to undergo cyclization. Thus, the most probable scheme is a dimerization or addition reaction. Usually, nucleophiles (e.g., NH_3) must be present to initiate both reactions, but they are not essential, as illustrated by two classical reactions, i.e., dimerization of acetylene and Diels–Alder-like reactions.²⁵ Both schemes imply that double bonds should be transformed chemically into single bonds. Infrared spectroscopy enables one to probe the occurrence of these reactions by monitoring the $\text{C}=\text{C}$ stretching vibration at 1650 cm^{-1} . Thus, comparison of undiluted polybutadiene with polymeric palladium complexes should reveal a reduction of the $\text{C}=\text{C}$ infrared absorption if dimerization or addition reactions are operative. However, Diels–Alder additions require a concerted mechanism. In a disorganized, viscous medium such

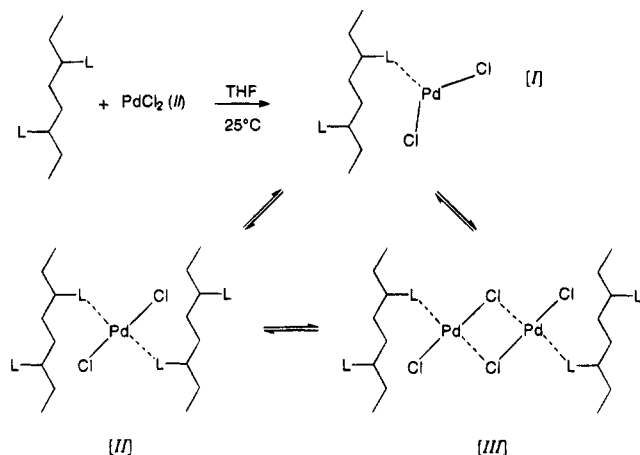


Figure 5. Illustration of possible palladium complexes that could be present in the polymer matrix at room temperature. Form I represents a three-coordinate complex which is lacking a second olefinic ligand, while forms II and III represent four-coordinate square-planar complexes that are known to exist in solution or at the surface of polymeric materials.

as a polymer matrix, only a small fraction of the palladium metal centers should participate in the Heck and/or the Diels–Alder reactions at ambient temperature. Hence, one expects that a few double bonds in the vicinity of the metal center will undergo these reactions. Furthermore, it is speculated that, during the time frame required for solvent evaporation, PdCl_2 metal centers can form at least three coordination complexes with olefinic side groups in these diene polymers (see Figure 5).²⁴

Figure 5 illustrates three types of coordination complexes that could be present in PBU/ PdCl_2 solid films. Form I represents a three-coordinate palladium metal center that does not lead to the formation of coordination cross-links, due to the absence of a second side-chain double bond in the vicinity of the metal salt. Forms II and III are well-known four-coordinate palladium complexes²⁴ that generate effective coordination cross-links in the presence of olefinic groups. At room temperature and in the absence of a stabilizing ligand like triphenylphosphine, palladium(II) will not form allylic complexes. In this respect, the electron density will remain mostly localized between palladium and the side-group carbon–carbon double bonds and give rise to an infrared signal for three-membered rings at 1100 cm^{-1} . Furthermore, any mechanisms that lead to chemical cross-linking reactions between ambient temperature and 120°C must proceed without the formation of an allylic complex.

IR spectroscopy is useful as a diagnostic probe of the various types of chemical reactions that could occur in these solid films. For PBU complexes containing low concentrations of PdCl_2 (up to 4 mol %), no major change was observed in the intensity of the $\text{C}=\text{C}$ vibrational absorption¹³ at 1650 cm^{-1} . Figure 6a represents the infrared spectrum for undiluted polybutadiene, while Figure 6b shows the polymeric palladium complex with 10 mol % PdCl_2 . The increase in the intensity of the aliphatic $\text{C}-\text{H}$ modes ($1200\text{--}1350\text{ cm}^{-1}$ region) in the lower spectrum indicates that a palladium-catalyzed reaction is operative. The $\text{C}=\text{C}$ vibrational absorption at 1650 cm^{-1} suggests that, at most, only a few double bonds in the vicinity of the metal center undergo chemical reactions.

Figure 7a illustrates the postulated Diels–Alder-like reaction, while Figure 7b depicts the Heck-like reaction that primarily occurs above ambient temperature. Pal-

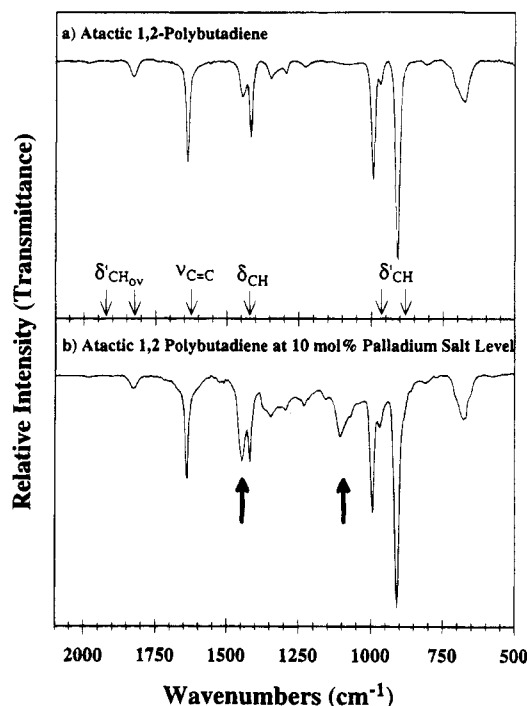


Figure 6. Fourier transform infrared spectra between 2100 and 500 wavenumbers: (a) undiluted atactic 1,2-polybutadiene; (b) polymeric palladium complex which contains 10 mol % PdCl_2 . The $\text{C}=\text{C}$ stretching vibration of the polymer and various CH deformation modes in the backbone and the side group, including overtone bands, are highlighted on the frequency (horizontal) axis.

ladium chloride should exist primarily as one of the coordination complexes illustrated in Figure 5, at ambient temperature. At higher temperature, deviations from these complexes are possible and one expects that this would favor the Heck-like addition reaction. If adducts IV and/or V are formed, a characteristic band due to aliphatic $\text{C}-\text{H}$ deformation modes should be present in the $1440\text{--}1460\text{ cm}^{-1}$ (sharp/strong) region of the infrared spectrum. Furthermore, for the four-membered ring which is characteristic of adduct IV, a band in the $1050\text{--}1070\text{ cm}^{-1}$ region (wide/medium) and two or three additional low-intensity bands in the $820\text{--}980\text{ cm}^{-1}$ region should be visible,²⁶ but these signals are difficult to identify because the spectrum contains a few strong signals in this region.

In a previous publication,¹³ the 1100 cm^{-1} signal was assigned to a fingerprint vibration of three-membered rings and dihapto coordination between the PBU side-group double bond and the palladium metal center. This previous assignment is consistent with the mechanisms described above. Unfortunately, three- and four-membered rings give rise to fingerprint absorptions in the same region of the infrared spectrum. Visual inspection of the 1100 cm^{-1} signal in Figure 6b reveals the presence of a shoulder at lower wavenumber (1050 cm^{-1}). It is reasonable that this composite infrared signal could contain two distinct contributions, which would substantiate the proposed mechanisms that give rise to either three- or four-membered rings. For adduct V, the presence of a weak shoulder assigned to a $\text{C}-\text{Cl}$ stretching model centered at 2800 cm^{-1} (not illustrated) supports the possibility of reductive halogenation of the polymer double bond at ambient temperature. As mentioned above, the absence of a distinct signal for $\text{C}-\text{Cl}$ aliphatic deformation modes in the $500\text{--}800\text{ cm}^{-1}$ region could be due to the fact that they are obscured by the medium-strength signal in that region of the

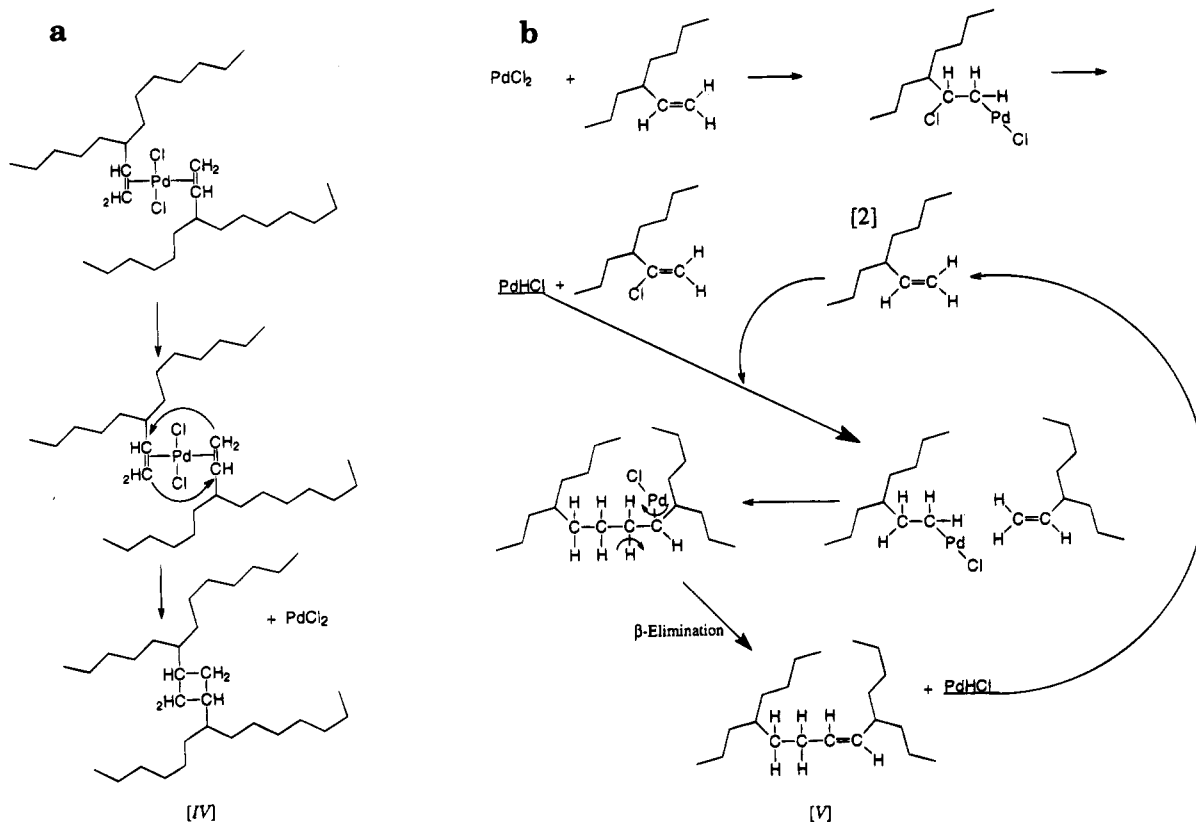


Figure 7. Two schemes that illustrate possible palladium-catalyzed chemical reactions of the olefinic side groups in diene polymers: (a) concerted Diels–Alder-like reaction; (b) Heck-like addition reaction.

spectrum. In Figure 6b the 1100 cm^{-1} signal is clearly visible. There are no overlapping signals between 1050 and 1200 cm^{-1} for undiluted PBU or bis(acetonitrile)dichloropalladium(II), while the increase in intensity for the 1450 cm^{-1} signal relative to the 1415 cm^{-1} signal indicates that additional aliphatic C–H deformation modes are present in the polymeric palladium complex. Hence, IR results support both palladium-catalyzed reactions, but, intuitively, adduct V is favored relative to adduct IV. Molecular mechanics simulations suggest that there is considerable torsional and bond-angle strain energy for the four-membered ring in the cyclic structure of adduct IV relative to the straight-chain cross-link illustrated by adduct V. Hence, the most probable mechanism is Heck-like, illustrated in Figure 7b, and this mechanism leads to the formation of linear chemical cross-links.

IV. Thermal Properties of Solid Films Obtained from THF Solutions. In this section, results from thermogravimetric analysis, differential thermal analysis, and differential scanning calorimetry are presented to support the claim that PdCl_2 induces exothermic chemical reactions in solid films, leading to vitrification of the rubbery polymers. Figure 8 illustrates the thermal behavior of undiluted polybutadiene and a PBU complex containing 2 mol % palladium chloride.

In Figure 8a, the TGA trace reveals that undiluted PBU is thermally stable to temperatures as high as $\approx 250^\circ\text{C}$, while DTA reveals that exothermic decomposition (chain scission) of the matrix starts $\approx 300^\circ\text{C}$ and reaches a maximum at 360°C . At 360°C , polybutadiene loses 17% of its initial weight, while undiluted PI-2 loses 13% (not illustrated). Figure 8b depicts the thermal behavior of PBU containing 2 mol % PdCl_2 . The thermal behavior in Figure 8b is quite different from that of the parent polymer in Figure 8a. The TGA data for the polymeric palladium complex reveal a much smaller weight loss relative to the undiluted polymer.

The DTA trace in Figure 8b indicates that three exothermic processes occur at 120 , 250 , and 320°C . Figure 8c shows the first DSC heating scan of the same material that is illustrated in Figure 8b. This DSC scan in Figure 8c clearly reveals that the three exothermic peaks are also observed over the same temperature range. The concomitant TGA trace in Figure 8b suggests that these three processes occur without major weight loss. Hence, these exothermic events most likely involve spatial or bond rearrangement via chemical reaction. Moreover, Figure 8b does not exhibit an exothermic peak at 360°C , and this suggests that either (i) few double bonds survive these high-temperature processes at 120 , 250 , and 320°C or (ii) the decomposition temperature is now outside of the experimental temperature range ($>400^\circ\text{C}$). Similar exothermic peaks are also observed when elastomers are cured under an oxidative atmosphere with cross-linking agents like sulfur or peroxides.²⁷ However, these exothermic peaks, which are indicative of cross-linking reactions, are rarely observed when the experiment is performed under an inert atmosphere such as nitrogen or helium. The second DSC heating scan in Figure 8d shows that these reactive processes are completed because no exothermic behavior is observed. The second DSC heating scan also reveals the presence of a distinct T_g in the vicinity of 110°C . This rather high glass transition temperature suggests that the PBU/ PdCl_2 matrix contains a relatively high cross-link density. For comparison, the glass transition temperature of undiluted atactic 1,2-polybutadiene is $\approx 5^\circ\text{C}$ via dynamical mechanical testing at 1 Hz coupled with a heating rate of $2^\circ\text{C}/\text{min}$.

Characterization of the Exothermic Processes Observed by DTA and DSC. The objective of this section is to identify the origin of the three exothermic processes observed via calorimetry and illustrated in

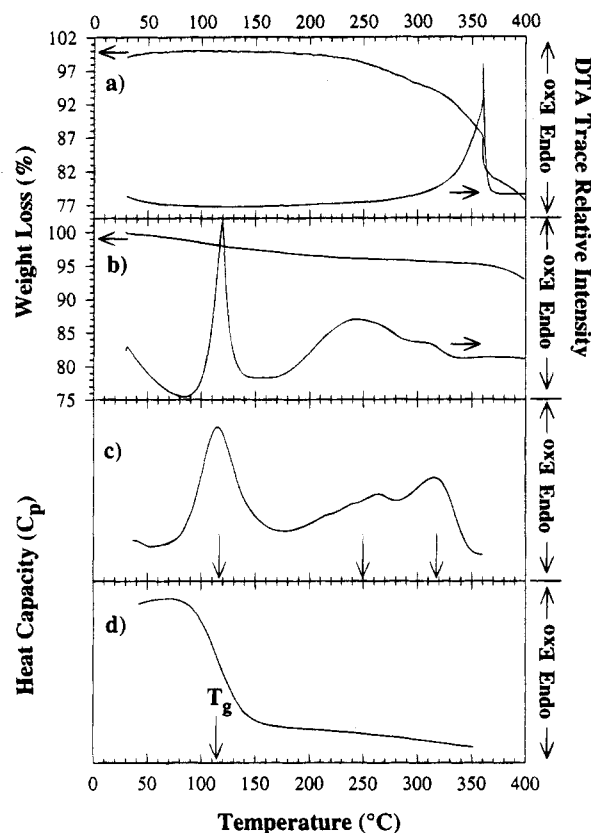


Figure 8. Summary of the thermal properties for polymeric complexes of atactic 1,2-polybutadiene: (a) TGA/DTA scan for undiluted PBU; (b) TGA/DTA scan for a film containing 2 mol % PdCl_2 ; (c) first DSC scan for PBU containing 2 mol % PdCl_2 ; (d) second DSC scan for the polymeric complex containing 2 mol % PdCl_2 . In parts c and d, processes of interest are highlighted on the temperature axis.

parts b and c of Figure 8 for PBU/ PdCl_2 complexes. The relatively narrow temperature range ($\Delta T \approx 30\text{--}35^\circ\text{C}$) of the exothermic peak at 120°C suggests that the first process involves only one reaction. However, the other two exothermic processes at higher temperatures (250 and 320°C) are quite broad, which indicates that they could be diffusion controlled²⁸ or that they could involve more than one reaction. Dynamic mechanical thermal analysis of undiluted PBU indicates that this material starts to flow during a reasonable experimental time scale above 130°C , where it behaves mostly as a nonpolar viscous liquid. Furthermore, due to the presence of effective cross-links, the addition of PdCl_2 to polybutadiene increases the temperature at which this material flows. It is worth mentioning that TGA/DTA data for polyisoprene (PI-2) films containing 2 mol % PdCl_2 reveal exactly the same thermal behavior relative to the data in Figure 8 for polybutadiene, i.e., three exothermic peaks which are located at 120 , 250 , and 320°C .

In an attempt to identify these processes, a polybutadiene film containing 2 mol % PdCl_2 was cut into pieces, and each sample was annealed under vacuum at either 100 , 120 , or 160°C for 1 day. Annealed samples were pulverized in liquid nitrogen using a freezer/mill apparatus from SPEX Industries, Inc. The powdery samples were dried for 1 day under reduced pressure in a vacuum oven at room temperature. Compressed pellets for infrared spectroscopy were prepared from 5 mg of the cryogenically pulverized polymer in 100 mg of KBr at ambient temperature. It is imperative to exercise caution during the analysis of infrared signals when annealing investigations are performed. The

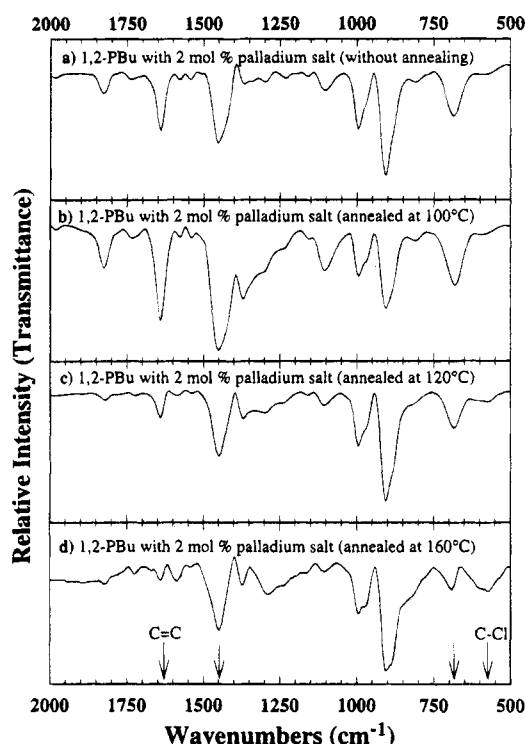


Figure 9. Fourier transform infrared spectra between 2000 and 500 wavenumbers for polymeric complexes of atactic 1,2-polybutadiene containing 2 mol % PdCl_2 : (a) without annealing; (b) annealed at 100°C for 1 day; (c) annealed at 120°C for 1 day; (d) annealed at 160°C for 1 day. The $\text{C}=\text{C}$ stretching vibration of the polymer and two CH deformation modes in the backbone and the side group, including the gauche $\text{C}-\text{Cl}$ band, are highlighted on the frequency (horizontal) axis.

samples experience a change in color after annealing, and this affects the intensity of an infrared absorption. The original film is yellow, while, after annealing at 100 , 120 , and 160°C for 1 day, the solid samples become dark yellow, yellow-orange, and green, respectively. The 680 cm^{-1} signal, which is a combination of skeletal vibrations due to the connectivity of CH and CH_2 groups in long alkane chains, was selected as the standard for comparison of the infrared spectra in Figure 9 because this signal is affected only mildly by cross-linking reactions. It is worth mentioning that the weak signal assigned to $\text{C}-\text{Cl}$ stretching (2800 cm^{-1}) is also present in these spectra, but it only becomes significant when the samples are annealed at 160°C . Moreover, palladium does not induce polymer chain scission because no additional CH_3 stretching modes (2962 and 2872 cm^{-1}) or CH_3 symmetric bending modes (1380 cm^{-1}) are present in the IR spectra.

Figure 9 summarizes the IR spectra obtained for PBU containing 2 mol % PdCl_2 . Comparison of the spectrum in Figure 9a with the one in Figure 6b reveals that the same characteristic bands are present in both spectra. The $\text{C}=\text{C}$ stretching vibration is observed at 1650 cm^{-1} . In-phase and out-of-phase CH_2 deformation is observed at 1450 cm^{-1} . Out-of-plane CH wagging of the olefinic side group is identified at 1000 and 900 cm^{-1} . Finally, the 1100 cm^{-1} signal has been assigned to a three-membered dihapto coordination complex that includes the palladium metal center. Cryogenic pulverization must be responsible for the decreased resolution of the spectrum in Figure 9a relative to the spectrum in Figure 6b because the sample for the spectrum in Figure 6b was prepared by depositing the residue from dilute THF solution on a KBr crystal. The intensity of the 680 cm^{-1}

a) *In-situ* generation of Pd⁰ (T ≥ 160 °C):



b) Pd catalyzed processes (T ≥ 160 °C):

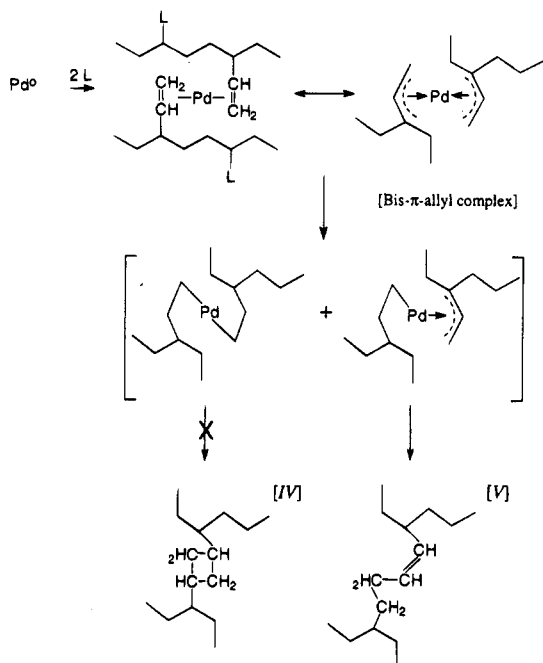


Figure 10. Illustration of the reaction pathways that can occur when a 1,2- or 3,4-diene polymer is annealed in the presence of PdCl₂: (a) *in-situ* reduction of Pd(II) to Pd⁰ due to the antiaddition of chlorine at the double bond, yielding a gauche adduct; (b) reactive schemes for palladium-catalyzed additions. The pathway yielding adduct IV is not observed for the annealed samples, while adduct V is produced via Pd(II) or Pd⁰.

signal in Figure 9b is not affected much when the sample is annealed at 100 °C, which is a temperature slightly lower than the first exothermic peak (see Figure 8b,c). The $\nu_{\text{C}=\text{C}}$ absorption is also unaffected by annealing at 100 °C, while all of the signals in the 1100–1450 cm⁻¹ region increase significantly. This provides further evidence that, at temperatures below 100 °C, palladium(II) selectively leads to the formation of Pd-catalyzed chemical cross-links via Heck-like addition reactions. However, these linear cross-links are present in a small quantity since the intensity of the C=C vibrational absorption at 1650 cm⁻¹ and the intensity of the C–Cl stretch at 2800 cm⁻¹ (not shown) remain essentially unaffected.

The IR spectrum of a PBU/PdCl₂ film annealed at 120 °C is illustrated in Figure 9c. The intensities of the 1650 cm⁻¹ ($\nu_{\text{C}=\text{C}}$) and 1100 cm⁻¹ bands decrease significantly. This confirms that palladium(II) catalyzes a Heck-like addition reaction between the olefinic side groups at 120 °C. As mentioned earlier, PdCl₂ cannot catalyze addition reactions of olefinic functional groups via π -allyl intermediates because this metal center does not stabilize the intermediary complex required for the reaction.²⁹ Figure 10 illustrates the mechanism for a Pd⁰ cyclization or addition reaction via the π -allyl intermediate. However, the color of the film and the relatively low intensity of the C–Cl band at 2800 cm⁻¹ rule out the presence of Pd⁰ as a catalyst after annealing at 120 °C. Thus, between room temperature and 120 °C, the addition proceeds via the Heck-like mechanism illustrated in Figure 7b.

As illustrated in Figure 8, the temperature of the first exothermic peak via DSC (120 °C) for solid films of

polybutadiene with palladium chloride is similar to the upper limit of the glass transition (T_g) process. This correlation between the first exothermic peak and T_g is also observed for polyisoprene, which implies that (i) interchain cross-links are required to achieve the final macroscopic thermomechanical properties of the material and (ii) these cross-links form at relatively low temperature. This has been confirmed by stress–strain results for PBU films containing 0.5 mol % PdCl₂ that were annealed at three temperatures (80, 120, and 160 °C) for 3 h. Annealing at 120 and 160 °C generates glassy materials which exhibit similar elastic moduli and ultimate elongations. Moreover, the moduli of these annealed films containing only 0.5 mol % PdCl₂ approach the modulus of PBU containing 6 mol % PdCl₂ (1.4×10^9 N/m²), which is the upper limit of mechanical response. The mechanical behavior of annealed samples will be described in greater detail in a subsequent paper.

The trends illustrated in Figure 9c become even clearer for the film that was annealed at 160 °C (see Figure 9d). The $\nu_{\text{C}=\text{C}}$ signal is almost nonexistent in the spectrum in Figure 9d, while the 1100 cm⁻¹ signal remains constant relative to the absorption at 680 cm⁻¹. Furthermore, all signals arising from aliphatic C–H bending modes at 1300, 1250, 1000, 900, and 825 cm⁻¹ increase. In addition to the greenish color of the film, the presence of a characteristic band for a gauche C–Cl stretch centered at 575 cm⁻¹ supports *in-situ* generation of Pd⁰ at high temperature (i.e., ≈160 °C). This mechanism is illustrated in Figure 10. The gauche or skewed conformation has a torsional angle of 60° between two specific substituents. Moreover, a broad intense signal due to the C–Cl stretch is present at 2725 cm⁻¹ (not shown). Hence, the transformation of PdCl₂ to Pd⁰ at ≈160 °C leading to antiaddition of the chlorine atoms in the main-chain double bond is consistent with typical S_N2 mechanisms for the halogenation of alkenes, and this is a significant oxidative exothermic process. Moreover, since the halogenation rate increases dramatically with increasing alkylation at the double bond, at such low concentrations of Pd(II) one expects that chlorination of the olefin will mostly occur in the main polymer chain, leaving the side-chain double bonds untouched. Thus, at 160 °C the cross-linking reaction proceeds via the bis(π -allyl) intermediate illustrated in Figure 10. Moreover, IR results indicate that this mechanism leads exclusively to the formation of linear chemical cross-links, illustrated by adduct V in Figure 10.

Thus, during the DSC or DTA heating trace, a wide variety of addition reactions can occur. At temperatures below the first exothermic peak (<120 °C), only coordination cross-links (Pd → C=C) and a small quantity of Heck-like linear chemical cross-links are produced (see Figure 7). The first exothermic peak at 120 °C is due to a palladium-catalyzed addition reaction of double bonds in the side chain via a Heck-like mechanism. The second exothermic peak at 250 °C is most probably due to the antiaddition of chlorine in the main-chain double bonds, which in turn leads to the *in-situ* generation of Pd⁰. Finally, the presence of Pd⁰ will promote addition, coupling, or cross-linking of the few remaining recalcitrant double bonds left in the matrix. This latter process is detected via calorimetry as the exotherm centered at 320 °C.

Glass Transition Temperature Enhancement as an Indicator of Network Formation. As mentioned earlier, polymer glass transition temperatures increase at higher cross-link density. Using the semiempirical equation suggested by Muroyama and Bell,³⁰ which was

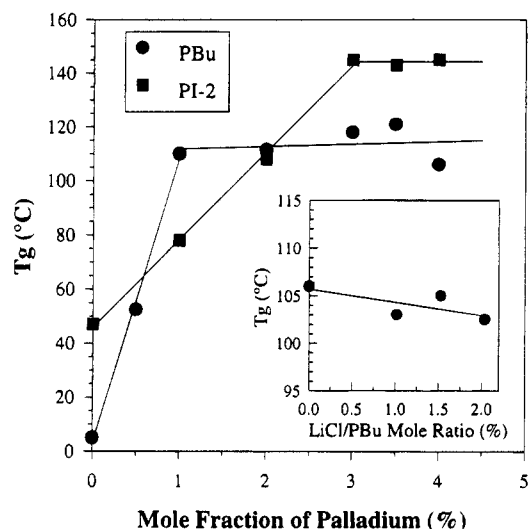


Figure 11. Glass transition temperatures determined by DSC for polybutadiene (●) and polyisoprene (■) polymeric complexes vs palladium salt content. The inset shows that, for films containing 4 mol % PdCl_2 relative to PBu, T_g is not affected much when LiCl is present.

confirmed experimentally for a variety of rubbery polymers, including PBu and PI, by Glans and Turner,³¹ one can estimate the number-average molecular weight between cross-link junctions from the T_g values obtained by DSC:

$$M_c = K/\Delta T_g \quad (5)$$

where K is a constant ($3.9 \times 10^4 \text{ K} \cdot (\text{g/mol})$), and ΔT_g is the difference between the glass transition temperature of the cross-linked matrix and the undiluted polymer. When the concentration of PdCl_2 is 2 mol %, application of eq 5 to T_g values determined via DSC (see Figure 8d) yields M_c values of 370 and 640 for PBu and PI-2, respectively. These M_c values compare well with those reported in Tables 2 and 3.

Figure 11 summarizes the glass transition temperatures obtained via DSC during the second heating trace for PBu and PI-2 at various PdCl_2 concentrations. The inset in Figure 11 illustrates the fact that when lithium chloride is added to polybutadiene films containing 4 mol % PdCl_2 , the decrease in T_g is insignificant relative to the effect of LiCl on the elastic modulus in Figure 3. For polybutadiene films, T_g reaches a plateau at about 1 mol % PdCl_2 . In contrast, a minimum amount of 3 mol % PdCl_2 is required to reach the plateau in thermal behavior for polyisoprene (PI-2). This difference in T_g response for both polymers is related to their chemical structure. PI-2 side chains have a methyl group that is electron withdrawing, and it may destabilize the intermediary complex required for addition of the double bonds. Consequently, a greater concentration of palladium chloride is required to fully cross-link polyisoprene. Higher concentrations of palladium chloride will not stabilize the intermediary complex, but they will increase the probability that a cross-linking reaction occurs. For both polymers, the plateau value of ΔT_g is about the same ($\approx 100^\circ\text{C}$), and this implies that both matrices are fully cross-linked in their respective regimes of PdCl_2 concentrations.

The large increase in T_g ($\Delta T_g = 100^\circ\text{C}$) relative to the undiluted diene polymers is somewhat surprising but not inconsistent with other systems which undergo curing reactions.³² The first DSC heating trace cures the polymer via palladium-catalyzed addition reactions.

Hence, one expects a higher cross-link density in the cured sample relative to the one determined via swelling measurements. By extension, the network which is generated via curing should be quite different from the one which is present in the uncured samples. If one could determine the glass transition temperature without inducing curing reactions, the increase in T_g would be smaller than the enhancement reported in this study. Thus, using T_g to evaluate M_c via the semiempirical equation by Muroyama and Bell should yield smaller M_c values relative to those determined via swelling. Similarly, the cross-link density determined via T_g is systematically larger than the one obtained via swelling. This suggests that the network which is formed via high-temperature curing reactions is more closely related to vulcanized rubber, i.e., a complex hyperbranched network.³³ However, based on the data contained in this research investigation and the shortage of literature that addresses these polymeric palladium complexes, it would be specious to postulate a structure for the uncured material.

In comparison to the results shown in Figure 3, the addition of LiCl to PBu does not have a major influence on the glass transition temperature when the samples are annealed during the first and second DSC heating traces. This is consistent with the previous claim that LiCl hinders the rate at which palladium complexes form (Figure 5) or chemical cross-linking reactions occur (Figures 7 and 10), but LiCl does not completely eliminate these reactions, particularly when the samples are annealed at elevated temperatures.

Thermal Stabilization of Polymeric Palladium Complexes via Annealing at 80°C . Thin films of PBu and PI-2 containing various amounts of PdCl_2 were analyzed thermogravimetrically to illustrate the fact that palladium-catalyzed chemical cross-links result in thermal stabilization of these diene polymers. These samples were prepared and tested as described in the Experimental Section. For both polymers and their complexes with PdCl_2 , the maximum weight loss via TGA was evaluated at 360°C , which corresponds to the temperature of the exothermic peak via DTA analysis of the undiluted polymers. The theoretical maximum weight loss was calculated as follows. First, spectroscopic evidence suggests that both acetonitrile ligands are not present in solid films. Hence, weight loss due to acetonitrile does not occur during the TGA experiment. PdCl_2 loses less than 0.2% of its weight over the experimental temperature range ($30\text{--}400^\circ\text{C}$). Hence, its contribution to the total theoretical weight loss was neglected. Second, the weight losses for undiluted PBu and PI-2 are 17% and 13%, respectively, at 360°C . Multiplication of those percentages by the weight fraction of polymer used to prepare solid films yields the reported theoretical weight loss, which is indicated by dashed lines in Figure 12. During the annealing step at 80°C under vacuum, films containing PdCl_2 lose less than 0.3% of their initial weight over 3 h. Thus, the trends illustrated in Figure 12 are not due to weight loss that could have occurred during annealing at 80°C .

Figure 12a summarizes weight loss for PBu/ PdCl_2 complexes. In the absence of annealing, the experimental weight loss increases slightly with increasing PdCl_2 concentration, but thermal stabilization is obvious relative to the undiluted polymer. However, weight loss remains constant as a function of palladium salt concentration when samples are annealed at 80°C for either 30 or 180 min. For an annealing period of 30 min, the weight loss is constant at about 4%. When

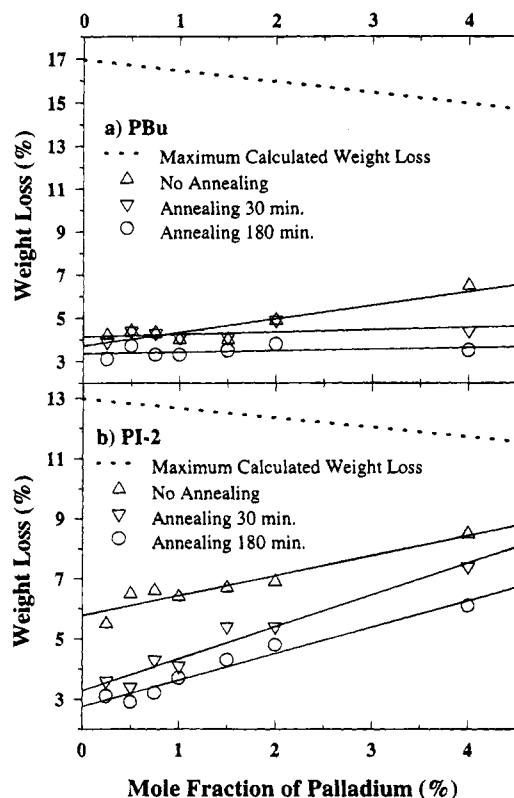


Figure 12. Weight loss at 360 °C for polybutadiene (a) and polyisoprene (b) films vs PdCl_2 concentration for sample annealed at 80 °C: (Δ) without annealing; (∇) annealed 30 min; (\circ) annealed 180 min. For both polymers, the dashed line represents the theoretical weight loss, assuming additivity.

samples are annealed for 180 min, the constant weight loss is reduced to $\approx 3\%$. In all cases, it is obvious that the weight loss is less than expected. For example, weight loss for the 180-min annealed sample is only 20% of the predicted value when the PdCl_2 concentration is 2 mol %. Annealing does not affect the temperatures of the three exothermic processes observed by DTA, which are illustrated in Figure 8. However, the relative intensities of the three exothermic processes change. The intensity of the first exothermic process, at ≈ 120 °C, increases at the expense of the two other exotherms at 250 and 320 °C. As discussed above, temperatures below 100 °C do not promote extensive chemical cross-linking reactions that involve addition or halogenation of the olefinic groups. Thus, one might speculate that annealing at 80 °C generates greater concentrations of form II or form III polymeric coordination complexes illustrated in Figure 5. Furthermore, form III is most likely transformed into form II during annealing at 80 °C. This transformation from one coordination geometry to another generates a greater concentration of favorable sites that could lead to the formation of interchain cross-links via double-bond addition (see Figures 7b and 10). This is consistent with the fact that a Heck-like mechanism (Figure 7b) is favored above room temperature.

Figure 12b summarizes weight loss for PI-2/ PdCl_2 complexes. In all cases, the experimental weight loss increases with increasing PdCl_2 concentration for annealed and unannealed samples, but thermal stabilization is obvious relative to the undiluted polymer. Once again, the experimental weight loss is less than theoretical predictions for all PI-2/ PdCl_2 samples. At 2 mol % PdCl_2 , polyisoprene loses 30% of its theoretical weight loss after 180 min of annealing at 80 °C. At 4 mol % PdCl_2 , polyisoprene loses 50% of its theoretical weight

loss after 180 min of annealing at 80 °C. Clearly, annealing has a smaller effect on polyisoprene weight loss relative to that for polybutadiene. As mentioned earlier, this could be related to the lower stability of the transition state for chemical reactions involving polyisoprene, relative to polybutadiene. Thus, greater annealing times are required for palladium chloride to induce coordination cross-links (form II in Figure 5) and chemical cross-linking reactions (adduct IV and/or V in Figure 7) in polyisoprene.

4. Conclusions

Previous research in our laboratory on strongly interacting polymer blends and transition-metal coordination complexes has evolved into the present study where blending concepts have been replaced by transition-metal-catalyzed chemical reactions. In the early stages of these reactions, transition-metal coordination is probably operative. The overall objective was to modify diene polymers via the addition of bis(acetonitrile)dichloropalladium(II), because research on low-molecular-weight analogs in the organometallic literature documents the fact that ethylene coordinates to this *trans*-square-planar transition-metal salt $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ by displacing weakly bound acetonitrile ligands. Palladium-catalyzed chemical reactions of the olefinic side groups in atactic 1,2-polybutadiene and 3,4-polyisoprene must be operative to explain the following macroscopic results:

(1) Young's modulus of elasticity for the polymeric palladium complexes is 3 orders of magnitude higher relative to the undiluted polymers when the palladium salt concentration is only 4 mol %. Rather low concentrations of palladium chloride have transformed a weak rubbery-type material into a glassy one, where T_g is well above 100 °C after thermal treatment (or curing). The enhancement in peak stress and elastic modulus cannot be explained by the presence of crystallized salt particles, a filler effect, or antiplasticization.

(2) Swelling experiments reveal that solid films of these polymeric palladium complexes imbibe a variety of solvents, and the degree of swelling decreases as the concentration of palladium chloride increases. The concept of a more compact network with a higher cross-link density is borne out by Flory–Rehner calculations of the number-average molecular weight of network strands. At higher concentrations of the transition-metal salt, the molecular weight between cross-link junctions decreases.

Thermogravimetric analysis and differential scanning calorimetry indicate that (i) both diene polymers are thermally stabilized by palladium chloride and (ii) a variety of exotherms between 120 and 320 °C occur without weight loss, signifying exothermic chemical reactions. When results from infrared spectroscopy and calorimetry are analyzed together with well-known reactions of palladium chloride in low-molecular-weight systems, the following reaction mechanisms seem reasonable:

(1) Heck addition reactions produce linear chemical cross-links between main chains. Reactions of this nature occur to a limited extent at room temperature. It is believed that the strong exotherm at 120 °C in Figure 8 is due to Heck-like coupling of olefinic side groups. This mechanism is illustrated in Figure 7b.

(2) Above 160 °C, the presence of Pd^0 could catalyze reactions of the olefinic side groups that must proceed via an allylic intermediate. Once again, linear chemical cross-links bridge main chains as a consequence of these reactions that are illustrated in Figure 10.

(3) Four-membered rings could be produced via Diels-Alder cyclization reactions as illustrated in Figures 7a and 10. However, the probability of that event is remote because a concerted mechanism is required. Moreover, these cyclic cross-link structures are highly strained with rather large bond-angle and torsional energies, as suggested by molecular mechanics calculations.

In summary, the addition of palladium chloride to linear diene polymers with olefinic side groups generates networks with greatly enhanced thermal and mechanical properties. The macroscopic results can be explained by palladium-catalyzed addition reactions that chemically cross-link linear chains via carbon-carbon side-group double bonds, characteristic of 1,2- and 3,4-diene polymers. Transition-metal-catalyzed reactions of this nature are consistent with earlier gelation studies of these diene polymers with palladium chloride in dilute solution.

Acknowledgment. This research described herein is supported by the National Science Foundation, Division of Materials Research (Polymers Program), through Grant No. DMR-9214022, and the donors of the Petroleum Research Fund, administered by the American Chemical Society. Professor Adi Eisenberg, Director of Polymer McGill in the Department of Chemistry at McGill University (Canada), is gratefully acknowledged for providing facilities to prepare samples and perform TGA/DTA experiments on polymeric palladium complexes. The authors benefitted from many helpful discussions with Professor Mark Bradley in the Physics Department at Colorado State University related to applications of percolation theory for the description of elastic moduli in the vicinity of the threshold concentration. Professor Louis S. Hegedus, in the Department of Chemistry at Colorado State University, is gratefully acknowledged for enlightening discussions about the complexation and reaction schemes that generate catalytically induced chemical cross-links in these polymeric palladium complexes.

References and Notes

- Wambach, A. D.; Trachte, K. L.; Dibeneditto, A. T. *J. Compos. Mater.* **1968**, 3, 266. Kenyon, A. S.; Duffey, H. J. *Polym. Eng. Sci.* **1967**, 7, 189.
- Ogale, A. A. *Compos. Mater. Ser.* **1991**, 7, 205. Paipetis, S. A. *Dev. Compos. Mater.* **1982**, 2, 39.
- Baccareda, M.; Butta, E. *J. Polym. Sci.* **1961**, 57, 617. Landel, R. F. *Trans. Soc. Rheol.* **1958**, 2, 53. Martin, G. M. *J. Res. Natl. Bur. Stand.* **1959**, 62, 141.
- Bueche, A. M. *J. Polym. Sci.* **1957**, 25, 139. Stearns, R. S.; Johnson, B. L. *Ind. Eng. Chem.* **1951**, 3, 146.
- Kunungi, T.; Watanabe, H.; Hashimoto, M. *J. Appl. Polym. Sci.* **1979**, 24, 1039. Lipatov, Y. S. *Trans. J. Plast. Inst. (London)* **1966**, 34, 83. Kargin, V. A.; Sogolova, T. I.; Shaposhnikaya, T. K. *Vysokomol. Soedin.* **1962**, 4, 601. Uskov, I. A.; Tarasenko, Y. G.; Kusnitsyna, T. A. *Vysokomol. Soedin.* **1961**, 3, 37. Nielsen, L. E.; Wall, R. A.; Richmond, P. G. *SPE J.* **1955**, 11, 22.
- De Porter, J. K.; Baird, D. G.; Wilkes, G. L. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1993**, 33, 1. O'Reilly, J. M.; Karasz, F. E.; Bair, H. E. *Bull. Am. Phys. Soc.* **1964**, 9, 285. Newman, S.; Cox, W. P. *J. Polym. Sci.* **1960**, 46, 29. Nagamatsu, K. Z. *Kolloid* **1960**, 172, 141. Woods, D. W. *Nature* **1954**, 74, 753.
- Theocaris, P. S.; Spathis, G. *J. Appl. Polym. Sci.* **1982**, 27, 3019. Paipetis, S. A. *Colloid Polym. Sci.* **1980**, 258, 42.
- Iisaka, K.; Shibayama, K. *J. Appl. Polym. Sci.* **1978**, 22, 1321. van der Wal, C. W.; Bree, H. W.; Schwarzl, F. R. *J. Appl. Polym. Sci.* **1965**, 9, 2143. Kummins, C. A.; Roteman, J. *J. Polym. Sci.* **1963**, 1A, 527.
- Droste, D. H.; Dibeneditto, A. T. *J. Appl. Polym. Sci.* **1969**, 13, 2149.
- Asloun, El. M.; Nardin, M.; Schultz, J. *J. Mater. Sci.* **1989**, 24, 1835. Boyarskii, G. Y.; Babich, V. F.; Paramonova, Y. M. *Kompoz. Polim. Mater.* **1981**, 10, 25. Fabulyak, F. G. *Probl. Polim. Kompoz. Mater.* **1979**, 28.
- Peiffer, D. G.; Agarwal, P. K.; Duvdevani, I.; Lundberg, R. D. *Plast. Eng.* **1987**, 43, 35.
- Maitlis, P. M.; Espinet, P.; Russel, M. J. H. In *Comprehensive organometallic chemistry—synthesis, reactions, and structures of organometallic compounds*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1986; Vol. 6, Chapter 38.6, pp 363–384.
- Andrews, M. A.; Chang, T. C. T.; Cheng, C. W. F.; Emge, T. J.; Kelly, K. P.; Koetzle, T. F. *J. Am. Chem. Soc.* **1984**, 106, 5913.
- Belfiore, L. A.; Bossé, F.; Das, P. *Polym. Int.* **1995**, 36, 165.
- Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; Chapter 6.
- Bastide, J.; Boué, F.; Buzier, M. In *Molecular Basis of Polymer Networks*; Springer Proceedings in Physics Vol. 42; Baumgärtner, A., Picot, C. E., Eds.; Springer-Verlag: Berlin, 1989; p 48.
- Carpenter, R. L.; Kan, H.-C.; Ferry, J. D. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, 18, 165.
- Allen, G.; Kirkham, M. J.; Padjet, J.; Price, C. *Trans. Faraday Soc.* **1971**, 67, 1278.
- Sperling, L. H. *Introduction to Physical Polymer Science*, 2nd ed.; Wiley-Interscience: New York, 1992; Chapter 7.
- Hartley, F. R. *The Chemistry of Platinum and Palladium*; John Wiley & Sons: New York, 1973; Chapter 11, p 308.
- Varshney, S. K.; Gao, Z.; Zhong, X. F.; Eisenberg, A. *Macromolecules* **1994**, 27, 1076 and references therein.
- Kim, J.-S.; Jackman, R. J.; Eisenberg, A. *Macromolecules* **1994**, 27, 2789.
- Black, T. H. *Adrichim. Acta* **1982**, 15 (1), 13 and references therein.
- Perry, R. J.; Turner, R. S.; Blevins, R. W. *Macromolecules* **1994**, 27, 4058.
- Mani, R.; Mahadevan, V.; Srinivasan, M. *React. Polym.* **1991**, 14, 263. Mani, R.; Mahadevan, V.; Srinivasan, M. *Br. Polym. J.* **1990**, 22, 177.
- Ternay, A. L. *Contemporary Organic Chemistry*, 2nd ed.; W. B. Saunders Co.: Philadelphia, PA, 1979; Chapter 13, pp 506–522.
- Ternay, A. L. *Contemporary Organic Chemistry*, 2nd ed.; W. B. Saunders Co.: Philadelphia, PA, 1979; Chapter 28, pp 1187–1194.
- Maurer, J. J. In *Thermal Characterization of Polymeric Materials*; Turi, E. A., Ed.; Academic Press Inc.: New York, 1981; Chapter 6.
- Struick, L. C. E. *Physical Aging in Amorphous Polymers and Other Materials*; Elsevier: Amsterdam, The Netherlands, 1978.
- Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer-Verlag: New York, 1980; p 91.
- Muroyama, T.; Bell, J. P. *J. Polym. Sci., Polym. Chem. Ed.* **1969**, 7, 1059.
- Glans, J. H.; Turner, D. T. *Polymer* **1981**, 22, 1540.
- See, for example: Ma, S. C.; Lin, H. L.; Yu, T. L. *Polym. J.* **1993**, 49, 897. Fitzgerald, J. J.; Landry, C. J. T. *J. Appl. Polym. Sci.* **1990**, 40, 1727. Peng, X.; Gillham, J. K. *J. Appl. Polym. Sci.* **1985**, 30, 4685.
- See, for example: Malmstrom, E.; Johansson, M.; Hult, A. *Macromolecules* **1995**, 28 (5), 1698. Kim, Y. H.; Beckerbauer, R. *Macromolecules* **1994**, 27 (7), 1968. McKenna, G. B. *Polymer Properties*. In *Comprehensive Polymer Science*; Booth, C., Price, C., Eds.; Pergamon Press: Oxford, U. K., 1989; Vol. 2, p 311.

MA9463829