# Nonlinear Stress Relaxation in Palladium(II) Complexes with Triblock Copolymers of Styrene and Butadiene

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**ABSTRACT:** Above 200% strain, the mechanical response of triblock copolymers which contain styrene and butadiene is modified significantly by complexation with dichlorobis(acetonitrile)palladium(II). This pseudosquare-planar transition metal salt forms $\pi$-complexes with, and catalyzes the dimerization of, alkene groups in the main chain and the side group of Kraton's butadiene midblock. Between 10 and 100% strain, the plastic flow regime is similar for undiluted Kraton™ and its $Pd^{2+}$ complexes, but the level of engineering stress is approximately twofold larger for the complex that contains 4 mol % palladium(II) [Pd(II)]. Nonlinear stress relaxation measurements in the plastic flow regime (i.e., beyond the yield point but before the large upturn in stress) are analyzed at several different levels of strain. Transient relaxation moduli were modeled by a three-parameter biexponential decay with two viscoelastic time constants. The longer relaxation time for Kraton™ increases at higher strain, and in the presence of 4 mol % palladium chloride. A phenomenological model is proposed to describe the effect of strain on relaxation times. This model is consistent with the fact that greater length scales are required for cooperative segmental reorganization at larger strain. The resistance $\Omega$ to conformational reorganization during stress relaxation is estimated via integration of the normalized relaxation modulus versus time data. This resistance increases at higher initial jump strain because conformational rearrangements are influenced strongly by knots and entanglements at larger strain. The effect of strain on $\Omega$ is analyzed in terms of time-strain separability of the relaxation modulus. Linear behavior is observed for $\Omega$ versus inverse strain (i.e., $1/\varepsilon$), and the magnitude of the slope [i.e., $-d\Omega/d(1/\varepsilon)$] is threefold larger in the absence of $PdCl_2(CH_3CN)_2$. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1329–1336, 2004

**Key words:** Kraton™ rubber; palladium chloride; mechanical properties; nonlinear stress relaxation; effect of strain on viscoelastic time constants

## INTRODUCTION

Palladium(II) [Pd(II)] coordination in macromolecules which contain alkene functionality in the main chain or side group produces a variety of network topologies with crosslink densities that depend on polymer microstructure and metal cation concentration.[1,2] Characterization of these networks in terms of defect structures (i.e., branching, ineffective crosslinks, loops, etc.) is critically important to understand fracture properties and toughness. Recent studies of $Pd^{2+}$ complexation in polybutadienes and polyisoprenes[1] have resulted in reactive blends with significant enhancement in fracture stress and the resistance to deformation at large strain (i.e., above 200%). This response is most likely due to the presence of crosslinks and entanglements in the polymeric matrix, resulting from Pd-catalyzed dimerization of alkenes[3] that couples different chains and increases their effective molecular weight. For example, polybutadiene/$PdCl_2$ mixtures in THF or toluene below the gelation threshold exhibit light-scattering-detected average aggregation numbers (i.e., AN = $M_{w,complex}/M_{w,pure\ polymer}$ via Zimm-plot intercepts) of 2 for low-viscosity solutions, whereas AN $\approx$ 9 for viscous THF solutions.[4]

A polymer network can be modeled as an assembly of macromolecules interconnected by chemical or physical crosslinks.[5,6] Network characterization is achieved by monitoring these crosslinks, entanglements, and clusters in terms of the molecular weight between junction points, especially when viscoelastic properties are being measured. The classic approach to describe the stress–strain behavior of rubberlike materials in the linear viscoelastic regime is based on an analysis of polymer network strands that exhibit a Gaussian distribution of end-to-end chain dimensions within the framework of equilibrium thermodynamics.[7] However, theory does not predict an upturn in stress at moderate-to-large deformations. It was postulated that this significant increase in stress is due to strain-induced crystallization of network strands.[5]

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Surprisingly, this upturn in stress is observed in experiments with model poly(dimethylsiloxane) networks where chain segments cannot crystallize.[5] Hence, one postulates that chains exhibit limited extensibility in which their non-Gaussian nature and nonaffine deformation are not predicted by the classical theory of rubber elasticity.[7] This theory has been improved to capture the high-strain regime much better via the treatments of Flory and Erman.[8] However, the number of model parameters increases and the parameters become more difficult to quantify experimentally because nonlinear viscoelastic constitutive relationships are complex.

## STRESS RELAXATION

Coordination between reactive functional groups in the main chain or side group of selected polymers and transition metal centers has the potential to produce a variety of structures that range from loosely crosslinked rubberlike materials to densely crosslinked glasses.[2,3] Characterization of these materials in terms of defect structures, such as branching, ineffective crosslinks, loops, etc., allows one to correlate fracture properties and toughness via chain microstructure. Industrially important macromolecule–metal complexes described in this research contribution exhibit remarkable high-strain mechanical response,[1] as illustrated in Figure 1. Loops, entanglements, and, most importantly, chemical crosslinks are responsible for the significant increase in high-strain mechanical response when Kraton™ thermoplastic elastomers are complexed with palladium chloride. When materials exhibit large strains at failure, obvious questions arise that address potential energy dissipation mechanisms associated with the deformation process. Stress relaxation measurements that focus on viscous flow at constant strain provide a well-controlled macroscopic probe of the viscoelastic time constants that are associated with energy dissipation processes,[9,10] particularly at high levels of strain.[11,12] The Boltzmann superposition principle is not applicable when the response is nonlinear,[9,13,14] but stress relaxation experiments with strain-dependent time constants qualitatively simulate energy dissipation at large strains.[12,15] Brueller[16] has extended the Boltzmann superposition principle to nonlinear viscoelasticity by using creep experiments, not stress relaxation.

In general, stress relaxation can be viewed as the reorientation of chain segments via rotation about single bonds in the backbone that increases the conformational entropy of network strands.[17] If entanglements are present, then they will function as topological knots and enhance mechanical properties at large strain. The coupling model of Ngai et al.[14] describes relaxation phenomena rather successfully for a wide range of materials, including glass-forming viscous

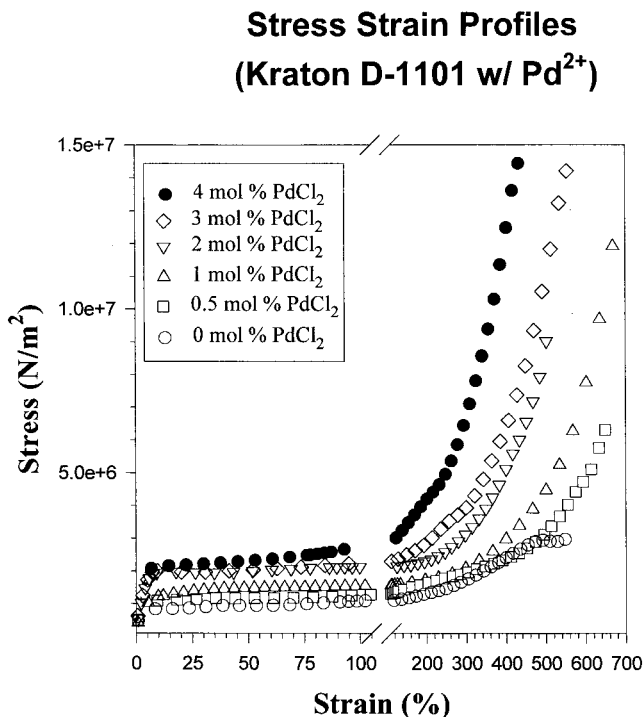## Stress Strain Profiles
## (Kraton D-1101 w/ Pd²⁺)



**Figure 1** Ambient temperature engineering stress–strain response of Kraton™ D-1101 complexes with palladium chloride at a strain rate of 50 mm/min (i.e., 2 in./min). The molar concentration of $PdCl_2(CH_3CN)_2$ is indicated in the legend. In each case, the polymeric palladium complex exhibits reinforced ductile mechanical response with an ultimate strain of 400% or greater. Reprinted with permission from ref. 1.

liquids, polymer melts, and vitreous ionic conductors.[18] The experimental methodologies of Ngai et al.,[14,18–23] Rendell et al.,[14,19] and Yee et al.,[19] which describe nonlinear viscoelasticity in glass-forming materials, include (1) imposing a level of strain that induces nonlinear response, and (2) measuring stress relaxation after application of a small 0.5% perturbation in strain. In these studies,[14,18–23] relaxation spectra were analyzed by using a coupling model that includes one fractional exponential function, as suggested by Kohlrausch, Williams, and Watts[24] (i.e., the KWW model). One of the most important parameters in this coupling model is the fractional exponent in eq. (1)

$$E_R(t) = E_R(t = 0) \exp\left\{ -\left(\frac{t}{\lambda}\right)^{1-n} \right\} \qquad (1)$$

where $E_R$ is the relaxation modulus, $\lambda$ is the effective (i.e., average) viscoelastic time constant, and $1 - n$ is the fractional exponent (i.e., $0 \leq n \leq 1$). A smaller exponent, with $n$ closer to unity, is consistent with a broader spectrum of relaxation times for real materials, whereas exponents that approach unity as $n$ tends

toward zero describe a system that exhibits a much narrower distribution of viscoelastic time constants. McKenna and Zapas[25] impose a large deformation initially and then apply incremental strains at selected time intervals. Askadskii et al.[17,26] use a nonlinear integral expansion representation of time-dependent stress to model nonlinear stress relaxation based on the rate of entropy generation. Yoshioka[27] employs a nonlinear model with one relaxation time to predict yielding in glassy polymers at large deformation. There are several examples where the relaxation modulus[28-35] or the viscoelastic strain energy function[36] exhibits time-strain separability at large deformations. Osaki et al.[30] conclude that time-dependent reptation based on the tube model and time- and strain-dependent retraction along the tube axis are uncoupled below 700% strain, but the factorability of time and strain is not possible at higher strains. Watanabe et al.[29] conclude that time-strain separability can be applied to styrene–isoprene diblock copolymers in the terminal relaxation regime, where terminal relaxation times are strain-independent below 200% strain. Ionic interactions in molten ionomers[28] do not invalidate the separability of time and strain. The strain-dependent damping function reveals strain softening of ethylene/methacrylic acid copolymers at high degrees of $Na^+$ and $Zn^{2+}$ neutralization[28] in the nonlinear viscoelastic regime. Randomly dispersed rubber particles have a considerable effect on strain-dependent damping functions in molten acrylonitrile–butadiene–styrene terpolymers,[32] but the validity of time-strain separability of the nonlinear relaxation modulus is not challenged. However, Tanaka and Edwards[37] demonstrate that the underlying physical basis of time-strain separability is questionable in their transient study of physically crosslinked gels. Kwon and Cho[38] conclude that several well-known viscoelastic constitutive equations exhibit dissipative instabilities because of the hypothesis of time-strain separability. This hypothesis is violated during the short time response immediately after imposing a jump strain.[38,46]

## EXPERIMENTAL

### Materials

Styrene–butadiene–styrene triblock copolymers (Kraton™ D-1101) with an unsaturated midblock were supplied by Drs. Rick Gelles and Mike Grogan at Shell Development (Houston, TX). The overall molecular weight of the triblock copolymer is $1.13 \times 10^5$ Da, and that of the butadiene midblock is $8 \times 10^4$ Da. The mole fraction of styrene repeat units is 32%, and at least 80% of the chains are linear. Dichlorobis(acetonitrile)palladium(II) was purchased from Strem Chemicals (Newburyport, MA). It was used without further purification. Reagent grade tetrahydrofuran (THF, >99% pu-

rity) was obtained from Aldrich Chemical Co. (Milwaukee, WI) for sample preparation.

### Sample preparation methods

The polymer (Kraton™ D-1101) and dichlorobis(acetonitrile)palladium(II) were dissolved separately while stirring in THF. The solubility of $PdCl_2(CH_3CN)_2$ in THF is on the order of 0.5 g/100 mL. The fresh salt and polymer solutions were mixed in a 125-mL Erlenmeyer flask. No further stirring was performed after the initial homogenization of the two solutions. Solid films were prepared from THF solutions by pouring the highly viscous ternary mixtures into a Petri dish to facilitate evaporation of the solvent in a fume hood at ambient temperature, followed by vacuum drying at ambient temperature for 12 h. The absence of an infrared signal at $1076 \, cm^{-1}$ in all solid films, which is a signature of the antisymmetric C—O—C stretch for five-membered cyclic aliphatic ethers[39,40] such as THF, indicates that the residual level of THF is below the detection limit of Mattson's Galaxy™ 5020 FTIR spectrometer (Madison, WI). To achieve a slower evaporation rate during solvent evaporation and more uniform films, the Petri dish was covered with perforated aluminum foil.

### Stress relaxation measurements

Uniaxial tensile deformation measurements were performed at ambient temperature by using an Instron™ model 8501 servohydraulic mechanical testing system (Canton, MA) equipped with pneumatic grips from Lloyd Instruments (Fareham, UK). Mechanical data in Figure 1 are presented in terms of engineering stress versus engineering strain. The strain rate was 50 mm/min. The discontinuity on the horizontal strain axis in Figure 1 is employed to illustrate better resolution in the low-strain regime, as well as high-strain response using only one graph. Stress relaxation experiments were performed at several different jump strains between 5 and 55% that were achieved by using a strain rate of 254 mm/min (i.e., 10 in./min). Data acquisition proceeded for a 15-min interval after achieving the desired strain at $t = 0$. Waveform generation in position-control mode and digital data acquisition were accomplished via Series™ IX software from Instron and an IEEE-488 instrumentation interface on a personal computer. All samples for stress relaxation measurements had the following approximate dimensions: 6.5 mm (width) and 0.25 mm to 0.65 mm (thickness). The lengths of the samples, which varied from 45 to 76 mm, were adjusted to equalize the time required to reach the desired levels of strain prior to stress relaxation. Measurements of stress versus time were analyzed after waiting 10 times the duration of the ramp required to achieve the desired strain. Relaxation moduli were calculated via division of the

time-dependent engineering stress by the magnitude of the jump strain in each experiment. This procedure to calculate the stress relaxation modulus is consistent with the methodology of Watanabe et al.[29] Chen et al.[41] suggest that true stress is more accurate than engineering stress, particularly in the nonlinear regime.

## RESULTS AND DISCUSSION

### Effect of palladium chloride on the stress–strain behavior of triblock copolymers containing styrene and butadiene

Previous research on $Pd^{2+}$ complexes with cis-polybutadiene,[1] 1,2-polybutadiene,[2] and 3,4-polyisprene[3] suggests that polymers containing alkene functionality in either the main chain or the side group can be modified chemically via dichlorobis(acetonitrile)palladium(II). This methodology was employed to induce a significant upturn in the stress–strain response of Kraton™ D-1101, above 200% strain,[1] as illustrated in Figure 1. Relative to the undiluted triblock copolymer, the engineering fracture stress is more than fivefold larger in complexes that contain either 3 or 4 mol % palladium chloride. Hence, significant modifications in the mechanical properties of an important engineering thermoplastic[1] have been achieved at ambient temperature via $Pd^{2+}$ catalyzed dimerization of alkenes.[3] These materials are lightly crosslinked, but the crosslink density increases when the $Pd^{2+}$ concentration is larger.[1,3]

### Stress relaxation measurements

Stress relaxation moduli $E_R(t,\varepsilon)$ were obtained at jump strains between 5 and 55% in the plastic flow regime. These data are illustrated in Figure 2 for Kraton™ D-1101, and Figure 3 for complexes of Kraton™ D-1101 with 4 mol % $PdCl_2(CH_3CN)_2$. At the same level of strain, relaxation moduli are larger for the Kraton™/$Pd^{2+}$ complex relative to the undiluted polymer. In the plastic flow regime where engineering stress does not increase significantly at larger strain, the corresponding relaxation moduli are smaller when experiments are performed at larger jump strain, because the relaxation modulus was calculated via division of the time-dependent engineering stress by the magnitude of the constant jump strain. The data in Figures 2 and 3 are qualitatively consistent with an increase in creep compliance for nylons and cellulosic fibers at higher jump stress.[15,42] Watanabe et al.,[29] Osaki et al.,[30] and Merriman and Caruthers[43] report decreasing stress relaxation moduli at larger strain in the nonlinear regime above 10% strain. For comparison with the stress relaxation data of Kraton™ D-1101 in Figure 2, Merriman and Caruthers measured non-
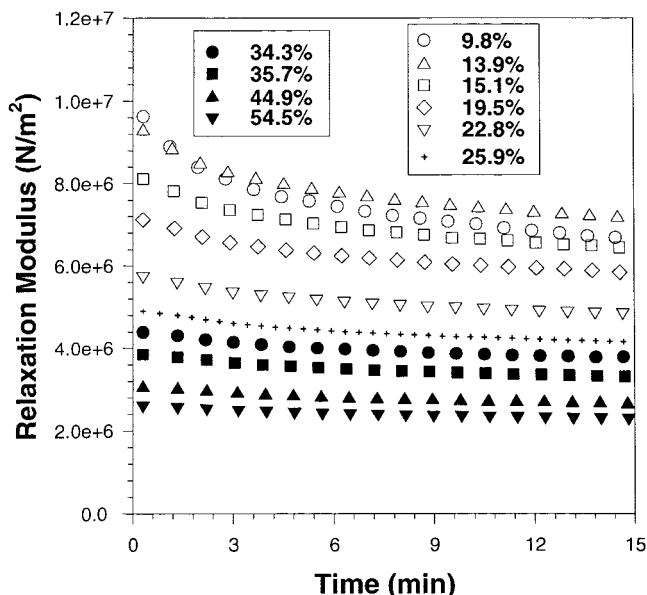
## Relaxation modulus for
### Kraton D-1101



**Figure 2** Non-normalized stress relaxation modulus versus time for Kraton™ D-1101 at ambient temperature, corresponding to jump strains between 10 and 55%, as indicated in the legend. The ratio of engineering stress to the initial jump strain is plotted on the vertical axis.

linear stress relaxation in lightly crosslinked styrene–butadiene random copolymers in the vicinity of the glass transition temperature.[43] The volume decrease during stress relaxation, that follows the instantaneous dilation upon deformation, was measured experimentally, and nonlinearity in the transient viscoelastic response was correlated with volume relaxation via fractional free volume.[43] Matsuoka et al.[44] report that polycarbonate dilates under tensile deformation in the glassy state, and Poisson's ratio decreases from 0.45 to 0.375 at higher strain.

### Effect of strain on stress relaxation

Based on the stress relaxation data in Figures 2 and 3, the area under the normalized stress relaxation modulus versus time curve provides an estimate of the resistance $\Omega$ to conformational reorganization in the polymer

$$\Omega(\varepsilon) = \int_{t_{start}}^{t_{final}} \left\{ \frac{E_R(t,\varepsilon)}{E_R(t=0,\varepsilon)} \right\} dt \qquad (2)$$

where the lower integration limit (i.e., $t_{start}$) is 0.3 min and the upper integration limit (i.e., $t_{final}$) is 15 min.

## Relaxation modulus for

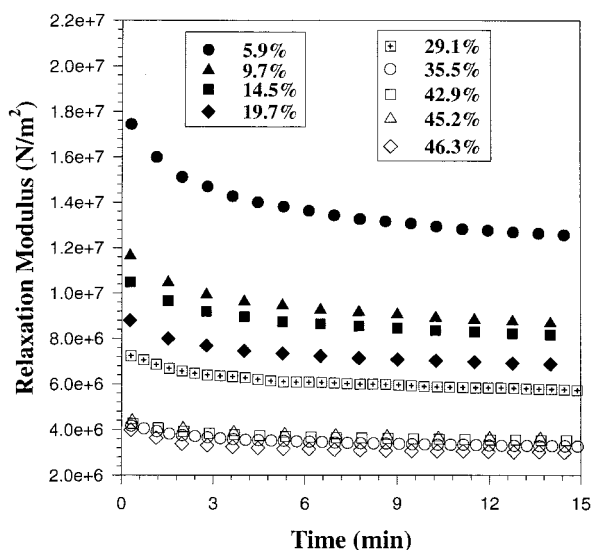## Kraton D-1101 w/ 4 mol% palladium chloride



**Figure 3** Non-normalized stress relaxation modulus versus time for complexes of Kraton™ D-1101 with 4 mol % palladium chloride at ambient temperature, corresponding to jump strains between 6 and 46%, as indicated in the legend. The ratio of engineering stress to the initial jump strain is plotted on the vertical axis.

**TABLE I**
**Effect of Strain on the Resistance to Conformational Reorganization $\Omega$ and Viscoelastic Time Constants $\tau$ During Stress Relaxation**

| Kraton™ | | | Kraton™ (4 mol % PdCl$_2$) | | |
|---|---|---|---|---|---|
| Strain (%) | $\Omega$ (min) | $\tau$ (min) | Strain (%) | $\Omega$ (min) | $\tau$ (min) |
| 9.8 | 12.8 | 63 | 5.9 | 13.0 | 101 |
| 13.9 | 13.3 | 84 | 9.7 | 13.2 | 110 |
| 15.1 | 13.4 | 91 | 14.5 | 13.4 | 119 |
| 19.1 | 13.5 | 105 | 19.7 | 13.5 | 133 |
| 22.8 | 13.7 | 119 | 29.1 | 13.5 | 149 |
| 25.9 | 13.7 | 121 | 35.5 | 13.5 | 154 |
| 34.3 | 13.8 | 130 | 42.9 | 13.7 | 179 |
| 35.7 | 13.8 | 133 | 45.2 | 13.7 | 170 |
| 44.9 | 13.9 | 149 | 46.3 | 13.6 | 167 |
| 54.5 | 14.0 | 164 | — | — | — |

rability of time and strain[28–35] when reptation and retraction can be decoupled, is given by

$$\Omega(\varepsilon) = \frac{h(\varepsilon)}{\varepsilon} \int_{t_{start}}^{t_{final}} g(t)dt \qquad (3)$$

Sweeney et al.[45] discuss the effects of microstructural rearrangements as semicrystalline polymers are stretched, and they predict yielding and necking of isotactic polypropylene at 150°C via an inhomogeneously strained network model. Both the stress relaxation modulus $E_R$ and the resistance $\Omega$ depend on strain $\varepsilon$ in the nonlinear regime. In the linear viscoelastic regime, $\Omega$ is independent of strain. Normalization of the relaxation modulus prior to performing the integration via eq. (2) precludes any inconsistencies in using engineering stress instead of true stress in the nonlinear regime. The effect of strain on $\Omega$ is summarized in Table I for Kraton™ and its complex with 4 mol % palladium chloride.

These results are displayed in Figure 4, where $\Omega$ is correlated versus inverse strain. One concludes that (1) $\Omega$ increases when stress relaxation experiments are performed at larger jump strain; (2) $\Omega$ versus inverse strain exhibits linear behavior; and (3) the magnitude of the slope, $-d\Omega/d(1/\varepsilon)$, is threefold larger (i.e., 0.13 versus 0.04) for Kraton™ without PdCl$_2$(CH$_3$CN)$_2$.

### Time–strain separability

Strain dependence of the resistance to conformational reorganization in the nonlinear viscoelastic regime, based on the definition of $\Omega$ via eq. (2) and the sepa-
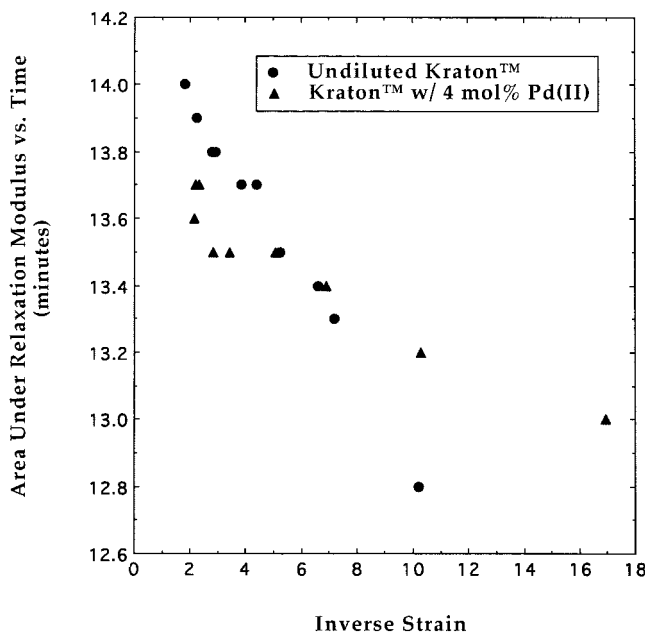
## Omega vs. Inverse Strain



**Figure 4** Effect of jump strain during nonlinear stress relaxation on the area under the curve of the normalized relaxation modulus versus time [i.e., $\Omega$ via eq. (2)] for Kraton™ D-1101 and its complex with 4 mol % palladium chloride. Approximate linear behavior is observed for $\Omega$ versus inverse strain, with a threefold larger slope when PdCl$_2$(CH$_3$CN)$_2$ is absent.

where $g(t)$ is the time-dependent part of the stress response that decays during the relaxation experiment (i.e., analogous to the normalized relaxation modulus for linear viscoelasticity), $h(\varepsilon)$ resembles a damping function,[28] and $h(\varepsilon)/\varepsilon$ approaches unity in the linear viscoelastic regime.[35] When $g(t)$ is analyzed in terms of a biexponential two-time constant model for the transient relaxation moduli in Figures 2 and 3, the longer relaxation time is reported in Table I as a function of strain. In general, one observes that the longer relaxation time constant increases at higher strain. This effect is described in the following section. The presence of palladium chloride also increases these longer relaxation times, relative to undiluted Kraton™. If the conformational rearrangements which give rise to stress relaxation occur over length scales that are comparable to the distance between network junction points at low crosslink densities, then it seems reasonable that the concentration of the low-molecular-weight transition metal complex should affect viscoelastic time constants.

## Characteristic length scales for cooperative reorganization and the effect of strain on viscoelastic relaxation times

In the condensed state, polymer chain segments typically do not undergo conformational rearrangements without cooperativity from neighboring segments. Stress relaxation requires that nearest neighbor segments within the same chain or from different chains must move in synchronous fashion. Hence, barriers to segmental relaxation contain both intramolecular and intermolecular contributions. In general, chain segments between crosslink junctions respond to an applied deformation by reorganizing and dissipating stress. Free-energy dissipation occurs when segments rotate about single bonds in the chain backbone to increase their conformational entropy, with a corresponding decrease in free energy. Characteristic dimensions, or length scales for cooperative segmental relaxing units, have been discussed by Matsuoka,[13] yielding an expression for the stress relaxation modulus that is very similar to eq. (1), with much better physical significance of the model parameters. Viscoelastic time constants $\tau$ for cooperative rearrangements are directly related to the characteristic dimensions over which segmental relaxation occurs, such that $\ln \tau$ scales linearly with the number $z$ of cooperatively relaxing segmental units. As these length scales increase, the associated inertia reduces the relaxation frequencies and increases viscoelastic time constants. There is a critical strain, $\varepsilon_{critical}$, most likely in the linear regime, below which the segmental relaxation process is independent of conformational rearrangements from neighboring segments on different chains. In this regime, barriers to segmental relaxation

are dominated by intramolecular cooperativity and the corresponding relaxation times are rather short. At higher jump strain, there is a stronger coupling among all of the segmental relaxing units; the intermolecular contribution to the overall relaxation process increases at the expense of the intramolecular contribution, and viscoelastic time constants increase considerably. According to Matsuoka,[13] the probability that $z$ cooperative segments will relax simultaneously is given by the product of $z$ identical factors, where each factor represents the probability that one segment will relax. Hence, the apparent activation energy for this cooperative process is $z$-fold larger than the barrier that must be overcome for one segment to relax. If the temperature dependence of viscoelastic time constants $\tau$ is based on a thermally activated rate process in Arrhenius form, then the following scaling law is appropriate[13]

$$\ln \tau \approx \frac{z\Delta G}{k_B T} \tag{4}$$

where $\Delta G$ is the free-energy barrier for one segment to relax at temperature $T$, and $k_B$ is Boltzmann's constant. Based on results from the previous section, the effect of strain on viscoelastic time constants is proposed in eq. (5) for a rate process that is thermally and mechanically activated, requiring cooperativity when jump strain $\varepsilon$ is greater than $\varepsilon_{critical}$

$$\tau \approx f(\varepsilon) \exp\left\{\frac{z\Delta G}{k_B T}\right\} \tag{5}$$

where $f(\varepsilon)$ increases at larger strain and approaches a nonzero constant at zero strain. The time constants in Table I for Kraton™ and its complex with 4 mol % palladium(II) are presented graphically in Figure 5 to illustrate that $f(\varepsilon)$ in eq. (5) depends logarithmically on strain. For example, nonlinear least-squares analysis yields the following phenomenological result

$$\tau(\varepsilon) \approx a_0\{1 + a_1 \ln(1 + a_2\varepsilon)\} \tag{6}$$

where $a_0$, $a_1$, and $a_2$ are positive constants, and $a_0$ represents the relaxation time at zero strain. For undiluted Kraton™, the inverse Hessian method reveals that several combinations of $a_0$ and $a_1$ in eq. (6) satisfy the minimization procedure such that $a_0 a_1 \approx 68$ min, and $a_2 \approx 0.18$ when strain is reported in percent. For the complex between Kraton™ and 4 mol % $PdCl_2(CH_3CN)_2$, which produces a lightly crosslinked network, the method of steepest descent yields $a_0 = 83.3$ min, $a_1 = 1.17$, and $a_2 = 0.033$, when strain is reported in percent. Effects of strain on viscoelastic relaxation times for polymeric materials have not been discussed previously in much depth, either phenom-

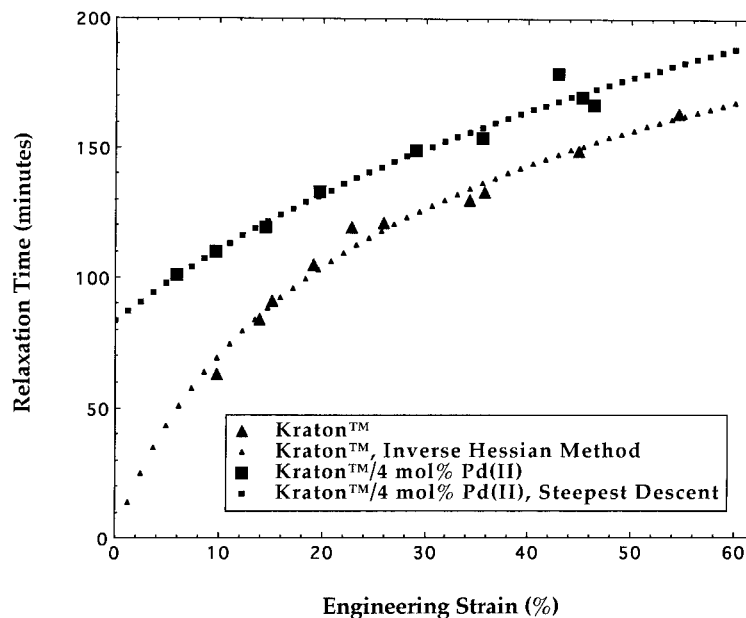## Viscoelastic Relaxation Times vs. Strain



**Figure 5** Effect of jump strain during nonlinear stress relaxation on the longer viscoelastic time constant for undiluted Kraton™ and its complex with 4 mol % palladium chloride. Each set of transient stress relaxation data in Figures 2 and 3 was modeled as a three-parameter biexponential decay with two time constants. The longer relaxation time is plotted on the vertical axis. The strain dependence of $\tau$ is given phenomenologically by eq. (6). For undiluted Kraton™, the product of $a_0$ and $a_1$ is $\approx 68$ min, and $a_2 \approx 0.18$ via the inverse Hessian method of nonlinear least-squares analysis, when strain is reported in percent. For the complex between Kraton™ and 4 mol % $PdCl_2(CH_3CN)_2$, $a_0 = 83.3$ min, $a_1 = 1.17$, and $a_2 = 0.033$ via the method of steepest descent.

enologically or theoretically. The dimensionless free-energy barrier (i.e., $z\Delta G/k_B T$) for stress relaxation in eqs. (4) and (5) is higher when the length scale over which segmental relaxation occurs is larger, due to intermolecular coupling among more cooperatively relaxing units.

## CONCLUSION

Nonlinear stress relaxation experiments on styrene–butadiene–styrene triblock copolymers and their complexes with palladium chloride have been analyzed in the plastic flow regime via time-strain separability, the resistance to conformational reorganization $\Omega$ in the polymer, and the effect of strain on viscoelastic time constants. Pseudosquare-planar dichlorobis(acetonitrile)palladium(II) forms $\pi$-olefin complexes with, and catalyzes the dimerization of, alkene groups in the main chain and the side group of Kraton's butadiene midblock. Consequently, the high-strain mechanical properties of Kraton™ are modified significantly by $PdCl_2(CH_3CN)_2$. Transient relaxation moduli were modeled by a three-parameter biexponential decay with two viscoelastic time constants. The longer relaxation time for Kraton™ increases at higher strain, and in the presence of 4 mol % palladium chloride. A

phenomenological model is proposed to describe the effect of strain on relaxation times. This model is consistent with the fact that greater length scales are required for cooperative segmental reorganization at larger strain. The resistance $\Omega$ to conformational reorganization during stress relaxation is estimated via integration of the normalized relaxation modulus versus time data. This resistance, denoted by $\Omega$, increases at higher jump strain, which is consistent with the fact that knots, entanglements, and low crosslink densities have a stronger influence on mechanical properties at larger strain.

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