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Independent Electrocyclization and Oxidative Chain Cleavage along the Backbone of *cis*-Poly(phenylacetylene)

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ABSTRACT: *cis*-Poly(phenylacetylene) (PPA) and *cis*-poly(pentadeuteriophenylacetylene) (PPA-d_5) undergo similar thermally induced transformations in bulk and solution. The structures identified in thermally treated samples include *cis*−*trans* isomerization of the backbone, cyclohexadiene repeat units in the main chain, and extruded 1,3,5-triphenylbenzene (1,3,5-$C_6H_3Ph_3$). Among these structures, cyclohexadiene sequences along the backbone formed by intramolecular cyclization are the principal products in all solvents regardless of temperature and the presence or absence of ambient light or O_2. We propose that cyclohexadiene structures form via 6π electrocyclization of triene sequences and, therefore, are an unavoidable consequence of *cis*-alkene units of the polyene backbone. Concurrent with cyclization, decrease of molecular weight and increase of molecular weight distribution are observed. Traces of acid lead to a dramatic increase in cyclization. Extrusion of 1,3,5-$C_6H_3Ph_3$ results from cyclohexadiene repeat units and is slower than electrocyclization, even in the presence of acid, light, or O_2. In the presence of ambient light, O_2 accelerates the rate of cyclization and extrusion of 1,3,5-$C_6H_3Ph_3$, the decrease of molecular weight, and the formation of carbonyl-containing products detected in a 5:1 molar ratio to extruded 1,3,5-$C_6H_3Ph_3$. Under these conditions, the most dramatic changes in molecular weight and molecular weight distribution are observed.

Introduction

Poly(phenylacetylene) (PPA), a soluble analogue of polyacetylene, has been of interest for its electrical conductivity,[1] photoconductivity,[2] and nonlinear optical properties,[3,4] especially in liquid crystalline phases.[5−11] *Cis*-cisoidal, *cis*-transoidal, *trans*-cisoidal, and *trans*-transoidal PPA can each adopt a helical conformation,[1] and circular dichroism confirmed that *cis*-transoidal PPA is a dynamic helical polymer.[12,13] Subsequently, most research is directed toward PPAs as biological mimics,[10,11,14−19] sensors to measure chirality,[17,20−31] and chiral stationary phases for enantioselective separation.[32]

Thermally induced reactions of PPA consist of isomerization of *cis*-PPA to *trans*-alkenes and formation of several cyclic sequences: 1,3-cyclohexadiene, 1,2-terphenylene, 1,3-terphenylene, and 1,4-terphenylene.[1,33−36] Terphenylene sequences form by the aromatization of the 1,3-cyclohexadiene units with elimination of benzene. The extrusion of triphenylbenzene ($C_6H_3Ph_3$) occurs by aromatization of the 1,3-cyclohexadiene sequences and concomitant chain cleavage.[1,33,34] Scheme 1 outlines the formation of 1,3-terphenylene units and the extrusion of 1,3,5-$C_6H_3Ph_3$ from a stereoregular head-to-tail *cis*-transoidal PPA. Alternate isomers result from head-to-head defects and stereoirregularity. Decrease of molecular weight supports this mechanism.[37,38] Development of metathesis[35,39−41] and of Rh(I)-based catalysts[42−44] raised questions regarding the generality of the above observations.[38,45−47] A general framework has emerged from bulk and solution samples investigated in anaerobic (vacuum, Ar, or N_2) and ambient atmosphere.

In the absence of air, cyclization and aromatization are the only observed processes. Loss of the *cis*-polyene takes place with an activation energy of ∼29 kcal/mol in bulk.[34,48] Little change is observed by ^{1}H NMR, IR, or UV−vis for as long as 2 years in the solid state at 20−25 °C.[49] Even at 120−130 °C, cyclization occurs without 1,3,5-$C_6H_3Ph_3$ formation and a small decrease of M_n.[1,34,35,37] In solution, the activation energy depends on the initial *cis*-content and ranges from 13 to 24 kcal/mol.[34,48] In purified THF solution, the same has been observed, and M_n is unchanged for samples up to 50 days.[49] Above 160 °C, extrusion of 1,3,5-$C_6H_3Ph_3$ is significant in bulk and solution. Samples undergo large decrease of M_n,[37,38] depletion of the long wavelength absorption in UV−vis spectra,[50] cyclization,[38] and extrusion of 20−25% of 1,3,5-$C_6H_3Ph_3$.[50] Complete loss of the *cis*-polyene is observed by ^{1}H NMR spectroscopy together with a significant decrease of M_n (by GPC) and formation of 10% 1,3,5-$C_6H_3Ph_3$ (1 h, 180 °C, bulk).[51] For a liquid crystalline polyarylacetylene, structural changes were observed above 180 °C where 1,3,5-triarylbenzene was found to be the only aromatic product.[6]

More complex results have been reported for thermal treatments in air.[49,51−55] The focus of such experiments has been on changes in molecular weight and spectral evidence for oxidation. Almost all reports agree that molecular weight decreases for bulk and solution samples. Vohlidal, Sedlacek, and co-workers have shown that the decrease of molecular weight in THF solution can bias the determination of absolute and relative molecular weights.[56] Short residence times (i.e., less than 1 h with THF as eluent) on the GPC column provide reproducible results. The cumulative time spent in solution appears to be the most significant factor related to the decrease of molecular weight. Air accelerates the decrease of *cis*-polyene sequences and molecular weight compared to samples in inert atmosphere. Similar to anaerobic experiments, the decrease of relative molecular weight for solutions of PPA in $CHCl_3$,

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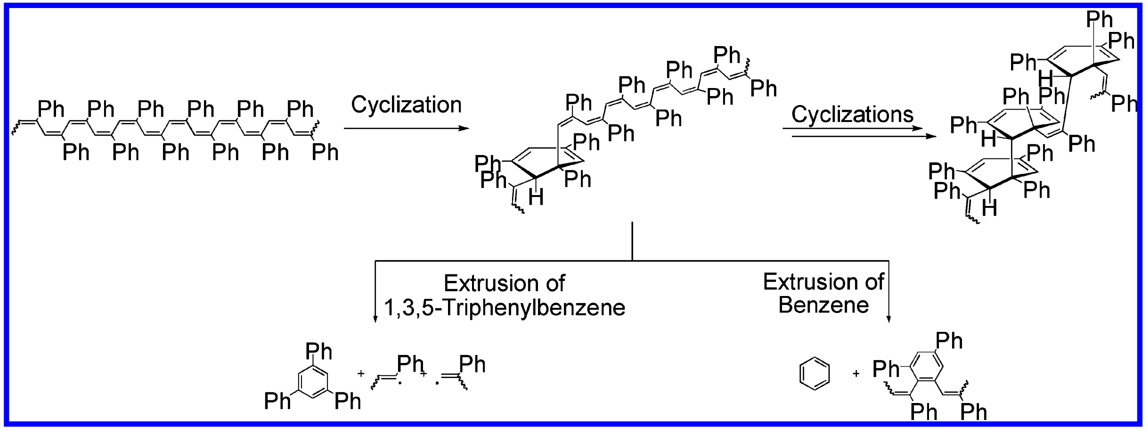
Scheme 1. Thermal Reactions of Stereoregular Head-to-Tail *Cis*-transoidal Poly(phenylacetylene) (PPA)



PhCl, and THF in air is not influenced by light.[49,55] Masuda and co-workers have questioned the generality of these results, observing an accelerated decrease of molecular weight of PPA in THF and toluene solutions.[55] Both IR and ^{1}H NMR spectroscopy support the formation of oxidation products in PPA solutions (i.e., THF, PhCl, and $CHCl_3$) thermally treated in air.[49,51,55] Bulk thermal treated PPA produced oxidation products.[52,57] By contrast, bulk samples annealed at 180 °C for 1 h in air are indistinguishable from those under vacuum.[51]

Additives and impurities complicate efforts to draw connections between experiments. Stable free radicals and radical trapping agents retard the rate of molecular weight decrease in THF, PhCl, and $CHCl_3$ but do not prevent it.[49,53,55] Using reagent grade solvents without purification, M_w of PPA determined by light scattering (20 °C) increases with time in THF solution, remains constant in toluene solution, and decreases for a $CHCl_3$ solution.[54] A contrasting report, which does not specify the quality or purification of THF, found M_w of PPA determined by light scattering (25 °C) to decrease in time. Addition of HCl to a $CHCl_3$ solution of PPA accelerates the rate of molecular weight decrease while K_2CO_3 retards the process.[55]

To clarify the role of O_2 in thermal transformation of PPA and provide a clear understanding of the general process, we have undertaken mechanistic and structural studies. Herein we will confirm the microstructural changes in PPA prepared with Rh(I)-based catalysts, demonstrate that the intramolecular cyclization rate is solvent independent, and isolate the effects of ambient light and O_2. Thermal treatment of PPA-d_5 clearly shows that formation of cyclohexadiene repeat units is the most prominent reaction, although it is accompanied by extrusion of 1,3,5-$C_6H_3Ph_3$ and *cis*−*trans* isomerization. We clarify the role of base and radical scavengers in $CDCl_3$ solutions of PPA to confirm that the rate of cyclization is solvent independent. Taken with the general scheme above, the process is best described as a 6π electrocyclization of triene sequences along the polyene backbone. This description becomes more complex when samples are thermally treated in acidic media or in the presence of both O_2 and ambient light.

Experimental Section

Materials. Diethyl ether (Et_2O, Fisher) and tetrahydrofuran (THF, Fisher, Certified A.C.S.) were distilled from Na/benzophenone ketyl under argon. Glacial acetic acid (Fisher) was used as received. Methanol (MeOH, Fisher, Certified A.C.S.) and ethanol (100%, EtOH, Pharmco) were each distilled from Mg turnings under argon. $RhCl_3 \cdot xH_2O$ (Lancaster), bicyclo[2.2.1]hepta-2,5-diene (nbd, Aldrich), *n*-butyllithium (2.5 M in hexanes, Aldrich), hexachloro-1,3-butadiene (C_4Cl_6, Acros), and anhydrous potassium carbonate (K_2CO_3, Fisher) were used as received. Triphenylphosphine (99%, PPh_3, Acros) was recrystallized from hexanes. Phenylacetylene (98%, PA) was vacuum-distilled from CaH_2 (both from Acros). 4-(Dimethylamino)pyridine (DMAP, Lancaster) was recrystallized from toluene. Carbon tetrachloride (CCl_4, Acros) was fractionally distilled from P_2O_5 under argon. 2,2,6,6-Tetramethyl-1-piperidinyloxy free radical (TEMPO, Acros) was sublimed under vacuum. $[Rh(nbd)Cl]_2$ was prepared according to a literature procedure.[59] $Rh(C{\equiv}CPh)(nbd)(PPh_3)_2$ (Noyori's catalyst) was prepared according to a literature procedure[60,61] and used *without* recrystallization. Deuterated solvents $CDCl_3$ (99.98% D), C_6D_6 (99.6% D), and THF-d_8 (99.5% D) (all from Cambridge Isotope Laboratories) were used as received. In $CDCl_3$, trace acid and its removal by storage over K_2CO_3 were qualitatively confirmed using pH paper (Whatman).

Techniques. ^{1}H (500 MHz) NMR spectra were recorded on a Bruker DRX-500 or Bruker DMX-600 spectrometer. Sealed NMR sample tube experiments were performed in NMR sample tubes equipped with a Schlenk-adapted Teflon screw cap (New Era Enterprises). UV−vis spectra were recorded using a Shimadzu UV-1601 spectrophotometer. Relative molecular weights were determined using a Shimadzu LC-10AT liquid chromatograph equipped with a CTO-10A column oven (40 °C), a Nelson Analytical 900 Series integrator data station, and two Polymer Laboratories PL gel columns of 5×10^2 and 10^4 Å with THF as the eluent at 1 mL/min. Detection was by UV absorbance at 254 nm. Under a N_2 atmosphere THF is distilled into the reservoir that supplies the GPC pump to eliminate oxygen and peroxide contaminants. Relative weight-average (M_w) and number-average (M_n) molecular weights were calculated using a calibration plot constructed from polystyrene standards. Air-sensitive procedures were performed under argon using standard Schlenk techniques.

Typical Polymerization of Phenylacetylene (PA) Using $Rh(C{\equiv}CPh)(nbd)(PPh_3)_2$. An oven-dried, argon-filled round-bottom flask equipped with a Teflon-coated magnetic stir bar was charged with 37.1 mg (0.045 mmol) of $Rh(C{\equiv}CPh)(nbd)(PPh_3)_2$ and 56.4 mg (0.46 mmol) of DMAP. The solids were degassed by three cycles of evacuation followed by backfilling with argon. Via a glass syringe, 50 mL of dry THF was added under argon and stirred until all solids were dissolved. Another oven-dried, argon-filled Schlenk tube was charged with 1.0 mL (9.01 mmol) of PA and 10 mL of dry THF. This solution was degassed by three freeze−pump−thaw cycles. The THF solution of PA was transferred to the catalyst solution at 21 °C under argon using a glass syringe. The reaction was stirred under argon for 3 h and quenched with 2 mL of glacial acetic acid. The reaction mixture was precipitated into 500 mL of cold MeOH. The polymer was collected by filtration and dried under vacuum to yield 780 mg (85%) of PPA. $M_n = 5.6 \times 10^4$ g/mol; $M_w/M_n = 1.54$. ^{1}H NMR ($CDCl_3$, δ, ppm): 6.94 (m, 3H), 6.64 (d, J = 6.89 Hz, 2H), 5.85 (s, 1H).

Typical Polymerization of PA Using [Rh(nbd)Cl]$_2$. A flame-dried, argon-filled round-bottom flask equipped with a Teflon-coated magnetic stir bar was charged with 39.2 mg (0.009 mmol) of [Rh(nbd)Cl]$_2$. The solid was degassed by three cycles of evacuation followed by backfilling with argon. Via a glass syringe, 6.0 mL of dry NEt$_3$ was added under argon and warmed to 30 °C. In a flame-dried, argon-filled Schlenk tube, 1.0025 (9.81 mmol) of PA was degassed by three freeze−pump−thaw cycles. Addition of 7.0 mL of dry NEt$_3$ produced a yellow solution, which was immediately transferred via glass syringe to the catalyst solution. The reaction was stirred under argon for 20 h, and the resulting precipitate was collected by filtration. Consecutive washings of the solid material with THF separated the desired *cis*-transoidal fraction. Precipitation of the THF washings into cold MeOH provided 240 mg (24%) of PPA. $M_n = 9.4 \times 10^4$ g/mol; $M_w/M_n = 2.09$.

Thermal Treatment of *Cis*-Transoidal PPA Solutions at 60 °C in NMR Sample Tubes Sealed in Vacuum (in the Dark). A solution of ~7 mg of *cis*-PPA in 0.5 mL of CCl$_4$ (or other solvent) was prepared while taking no precaution to exclude to air. Samples were subjected to three freeze−pump−thaw cycles, and the NMR sample tube was sealed. Degassed samples were introduced into an NMR spectrometer at 60 °C. After appropriate time intervals, spectra were measured at 60 °C.

Thermal Treatment of *Cis*-Transoidal PPA Solutions at 60 °C in NMR Sample Tubes Sealed in Vacuum (in the Dark). A solution of ~7 mg of *cis*-PPA (or *cis*-PPA-d_5) in 0.5 mL of CCl$_4$ (or CDCl$_3$) was prepared while taking no precaution to exclude to air. Samples were subjected to three freeze−pump−thaw cycles, and the NMR sample tube was sealed. Degassed samples were introduced into an oil bath equilibrated at 60 °C. After appropriate time intervals, ^{1}H NMR spectra were measured at 30 °C. In some cases, the sample was opened and diluted with THF after obtaining the ^{1}H NMR spectrum. The THF solution was used for GPC measurements.

Thermal Treatment of *Cis*-Transoidal PPA in C$_4$Cl$_6$ Solutions at 120 or 160 °C in an NMR Sample Tube Sealed in Vacuum (with Light). A solution of ~26 mg of *cis*-PPA in 3.0 mL of C$_4$Cl$_6$ was prepared while taking no precaution to exclude to air. Portions were distributed among several NMR sample tubes. Samples were subjected to three freeze−pump−thaw cycles, and the NMR sample tube was sealed. Degassed samples were introduced into an oil bath equilibrated at the desired temperature. After appropriate time intervals, ^{1}H NMR spectra were measured at 60 °C.

Thermal Treatment of *Cis*-Transoidal PPA in O$_2$-Saturated Solutions at 60 °C in Sealed NMR Sample Tubes (in the Dark). Carbon tetrachloride (or CDCl$_3$) was sparged with O$_2$ for 30 min prior to preparing the sample solution. A solution of ~7 mg of *cis*-PPA was dissolved in 0.5 mL of CCl$_4$ (or other solvent) was prepared while taking no precaution to exclude to air. The NMR sample tube was sealed and introduced into an NMR spectrometer at 60 °C. Spectra were measured at appropriate time intervals.

Thermal Treatment of *Cis*-Transoidal PPA in Solution with TEMPO at 60 °C in an NMR Sample Tube Sealed in Vacuum (in the Dark). A solution of ~8 mg of *cis*-PPA and 4.5 mg (0.03 mmol) of TEMPO in 0.5 mL of CDCl$_3$ was prepared while taking no precaution to exclude to air. Samples were subjected to three freeze−pump−thaw cycles, and the NMR sample tube was sealed. Degassed samples were introduced into an NMR spectrometer at 60 °C. Spectra were measured at appropriate time intervals.

Thermal Treatment of *Cis*-Transoidal PPA Solutions in CCl$_4$ at 60 °C (with Light and O$_2$). Approximately 23 mg of *cis*-PPA was dissolved in 1.5 mL of CCl$_4$ with no precaution for the exclusion of air. Portions were distributed among several NMR sample tubes. The NMR sample tubes were then capped with a Teflon screw cap valve, but the valve was left open to ambient atmosphere. Samples were introduced into an oil bath equilibrated at 60 °C. After appropriate time intervals, ^{1}H NMR spectra were measured at 30 °C. The sample was subsequently diluted with THF and used for GPC measurements.

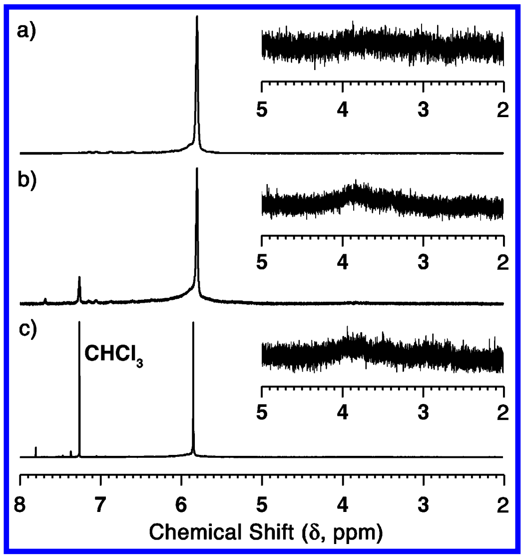


Figure 1. ^{1}H NMR spectra of PPA-d_5 measured at 28 °C: (a) as-prepared in CCl$_4$, (b) following thermal treatment at 60 °C for 8 h in CCl$_4$, and (c) following thermal treatment at 60 °C in CDCl$_3$. Thermal treatments were performed on degassed samples in NMR sample tubes sealed under vacuum. Heating was performed in an oil bath with no precaution to exclude ambient light.

In a similar experiment, CCl$_4$ was sparged with O$_2$ for 30 min prior to sample preparation. The NMR sample tubes were sealed under an ambient atmosphere before heating.

Results and Discussion

Numerical Model for Kinetic Analyses. In a previous report[51] we took for granted that *cis*-transoidal PPA prepared with Noyori's arylacetylene polymerization catalyst[60,61] undergoes the same thermal transformations as PPA prepared with Ziegler−Natta type or ill-defined metathesis catalysts. To develop a quantitative measure for the observed transformations, we prepared poly(pentadeuteriophenylacetylene) (PPA-d_5) and investigated its structure after thermal treatment. Figure 1 presents ^{1}H NMR spectra for the as-prepared sample in CCl$_4$ as well as samples sealed under vacuum and thermally treated at 60 °C for 8 h in CCl$_4$ and CDCl$_3$. Evident from the as-prepared sample is the lone resonance at δ 5.80 ppm assigned to the *cis*-transoidal stereostructure.[1,33,61] Downfield from this resonance are very weak resonances from incomplete deuteration of the aromatic ring. Three new resonances are observed in the thermally treated samples. At δ 7.68 ppm in CCl$_4$ and δ 7.80 ppm in CDCl$_3$ is the resonance for 1,3,5-C$_6$H$_3$-(Ph-d_5)$_3$. At δ 7.26 ppm in CCl$_4$ and δ 7.36 ppm in CDCl$_3$ is the resonance for *trans*-alkene residues along the polyene backbone.[1,33] Finally, a broad resonance at δ 3.90 ppm in CCl$_4$ and δ 4.00 ppm in CDCl$_3$ is the methine proton of the cyclohexadiene structures formed along the backbone.[1,33,38,45,46] Neither sample exhibits resonances inconsistent with that previously described for PPA prepared using other catalysts.

To quantify the extent that each transformation takes place during thermal treatment, we define the mole fraction of alkene residues ($F_{a.r.}$) for each component structure. Each *cis* or *trans* double bond constitutes a single alkene residue. The cyclic structures cyclohexadiene and 1,3,5-C$_6$H$_3$Ph$_3$ each account for three alkene residues. From the spectra for PPA-d_5 in Figure 1 these

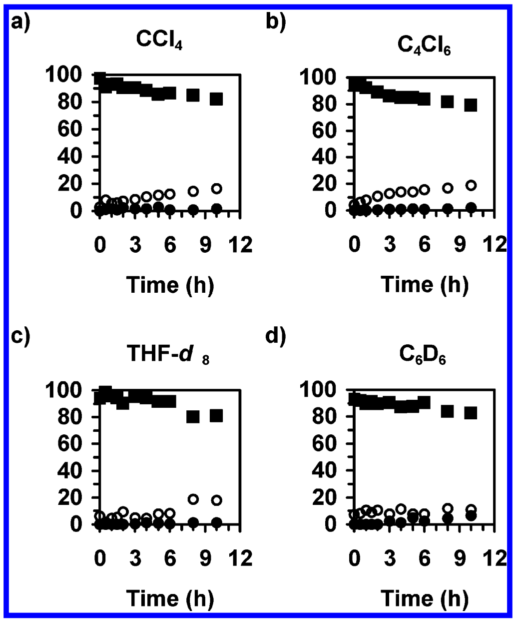


Figure 2. Plots of the mole percentage of alkene residues ($F_{a.r.} \times 100\%$) attributed to PPA (■), cyclohexadiene moieties (○), and extruded 1,3,5-$C_6H_3Ph_3$ (●) for (a) CCl_4, (b) C_4Cl_6, (c) THF-d_8, and (d) C_6D_6 solutions thermally treated at 60 °C. Thermal treatments were performed on degassed samples in NMR sample tubes sealed under vacuum. Heating was performed in the NMR spectrometer.

values for 1,3,5-$C_6H_3(Ph\text{-}d_5)_3$ and *trans*-PPA-d_5 are directly measurable from the integrated area for each assigned resonance. The cyclohexadiene structure contains two vinyl protons that overlap with the *cis*-PPA resonance.[38,45,46] The integrated area for the methine resonance is, therefore, proportional to $(1/3)F_{a.r.}$. Determination of $F_{a.r.}$ for *cis*-PPA from the integration of the assigned resonance requires subtraction of the area due to the vinyl protons of the cyclohexadiene structure. From sample thermally treated in CCl_4 these values are

$$F_{a.r.}(trans\text{-PPA-}d_5) = \frac{A_{\delta 7.26}}{A_{\delta 7.68} + A_{\delta 7.26} + A_{\delta 5.80} + A_{\delta 3.90}} = 0.07$$

$$F_{a.r.}(C_6H_3(Ph\text{-}d_5)_3) = \frac{A_{\delta 7.68}}{A_{\delta 7.68} + A_{\delta 7.26} + A_{\delta 5.80} + A_{\delta 3.90}} = 0.03$$

$$F_{a.r.}(\text{cyclohexadiene}) = \frac{3A_{\delta 3.90}}{A_{\delta 7.68} + A_{\delta 7.26} + A_{\delta 5.80} + A_{\delta 3.90}} = 0.13$$

$$F_{a.r.}(cis\text{-PPA-}d_5) = \frac{A_{\delta 5.80} - (2A_{\delta 3.90})}{A_{\delta 7.68} + A_{\delta 7.26} + A_{\delta 5.80} + A_{\delta 3.90}} = 0.77$$

For the sample thermally treated in $CDCl_3$, the values are $F_{a.r.}(trans\text{-PPA-}d_5) = 0.04$, $F_{a.r.}(C_6H_3(Ph\text{-}d_5)_3) = 0.02$, $F_{a.r.}(\text{cyclohexadiene}) = 0.36$, and $F_{a.r.}(cis\text{-PPA-}d_5) = 0.57$. The disagreement between experiments in CCl_4 and $CDCl_3$ was also noted in kinetic experiments described below. Nonetheless, both observations validate our qualitative assessment that PPA prepared using Rh(I)-based catalysts undergo the same transformations as previously described for samples prepared with alternate catalysts.[1,6,33−35,37,38,47−56]

To extend this analysis to nondeuterated polymers, the aromatic ring protons need to be considered. It was found empirically that the *cis*-PPA and *trans*-PPA could not be calculated independently. Broadening of the resonances for the aromatic ring protons in thermally treated PPA and overlap with resonances from 1,3,5-$C_6H_3Ph_3$ prevents identification and integration of a unique resonance for *trans*-alkene residues in PPA. As such, there are too few independent variables to solve the above system of equations. Consequently, we will calculate $F_{a.r.}(\text{PPA}) = F_{a.r.}(trans\text{-PPA}) + F_{a.r.}(cis\text{-PPA})$. The proton resonances for the 1,3,5-$C_6H_3Ph_3$ core and the cyclohexadiene methine are readily isolated and integrated ($A_{C_6H_3Ph_3}$ and A_{Methine}, respectively) in all solvents. The *cis*-polyene resonance is well-resolved but is overlapped by the vinyl resonances from the cyclohexadiene ($A_{cis-\text{PPA+diene}}$), as noted above. Taking each of these into consideration, the following expressions were employed to monitor $F_{a.r.}$ for each component:

$$F_{a.r.}(\text{PPA}) = 1 - F_{a.r.}(\text{cyclohexadiene}) - F_{a.r.}(C_6H_3Ph_3)$$

$$F_{a.r.}(\text{cyclohexadiene}) = \frac{3A_{\text{Methine}}}{(A_{C_6H_3Ph_3} + A_{\text{aromatic}} + A_{cis-\text{PPA+diene}} + A_{\text{methine}})/6} = \frac{18A_{\text{methine}}}{A_{\text{total}}}$$

$$F_{a.r.}(C_6H_3Ph_3) = \frac{\left[6 - \left(\frac{1}{3}\right)F_{a.r.}(\text{cyclohexadiene})\right]A_{C_6H_3Ph_3}}{A_{C_6H_3Ph_3} + A_{\text{aromatic}} + A_{cis-\text{PPA+diene}}}$$

Role of Solvent. Degassed solutions of PPA in CCl_4, C_4Cl_6, C_6D_6, and THF-d_8 (Figure 2) were thermally treated at 60 °C in the NMR spectrometer (i.e., in the dark). The plots in Figure 2 illustrate the experimentally determined mole fraction of alkene residues expressed as percentages for each reaction component over time. The decrease of the polyene backbone is similar in all four solvents. Concurrent with the loss polyene backbone, an equivalent amount of cyclohexadiene formed and only a trace of 1,3,5-$C_6H_3Ph_3$ can be identified.

In addition to thermal treatment in the NMR spectrometer, we have investigated how light influences PPA solutions in CCl_4 thermally treated at 60 °C. Comparison of the results in Figure 2a to those values determined for thermally treated PPA-d_5 in CCl_4 shows good agreement. In the latter experiment, heating was performed in an oil bath exposed to ambient light. The amounts of PPA ($F_{a.r.} = 0.85$), cyclohexadiene ($F_{a.r.} = 0.14$), and 1,3,5-$C_6H_3Ph_3$ ($F_{a.r.} = 0.01$) after 8 h at 60 °C in CCl_4 almost exactly match those observed in the above experiment with PPA-d_5. The first four entries of Table 1 offer a second point of comparison. Anaerobic CCl_4 solutions of PPA thermally treated at 60 °C in light show quantitative agreement with in the dark. It is important to note that the cyclization phenomenon, accompanied by marginal amounts of 1,3,5-$C_6H_3Ph_3$ extrusion, results in measurable decreases of M_n and

Table 1. Structural Composition, Molecular Weight, and Molecular Weight Distribution of PPA in CCl_4 Solutions at 60 °C under Various Atmospheres in Light

		$F_{a.r.} \times 100\%$				
time (h)	treatment	PPA	cyclohexadiene	1,3,5-$C_6H_3Ph_3$	$M_n \times 10^{-3\,a}$	M_w/M_n
b	*b*	96	4	0	62.3	1.44
1	vacuum[c]	96	4	0	51.3	1.56
4	vacuum	92	6	2	41.5	1.64
8	vacuum	87	10	3	30.0	1.93
1	ambient[d]	92	5	2	11.3	2.9
4	ambient	83	12	5	2.8	2.7
8	ambient	77	15	8	2.2	2.3
1	O_2[e]	86	13	2	8.8	3.3
4	O_2	79	17	3	3.5	2.6
8	O_2	76	18	6	2.5	2.3

[a] Relative molecular weight determined by GPC in THF (1 mL/min) calibrated using polystyrene standards. [b] As-prepared sample of PPA. [c] Samples were degassed by freeze−pump−thaw cycles and sealed under vacuum. [d] Samples were open to air during thermal treatment. [e] Samples were prepared in O_2-saturated CCl_4 and sealed in air.

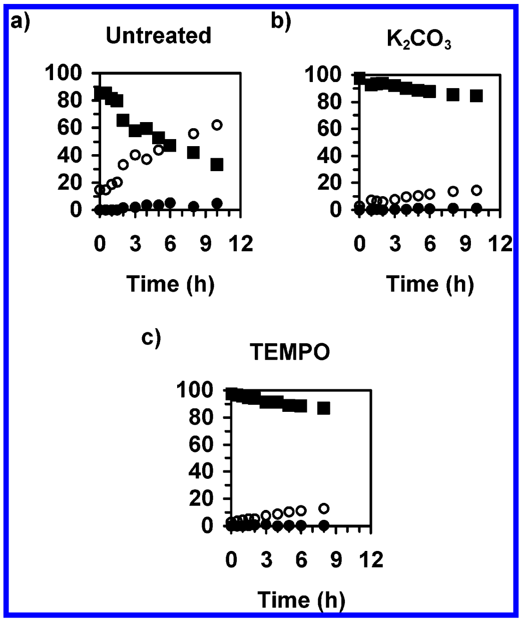


Figure 3. Plots of the mole percentage of alkene residues ($F_{a.r.} \times 100\%$) attributed to PPA (■), cyclohexadiene moieties (○), and extruded 1,3,5-$C_6H_3Ph_3$ (●) for solutions in (a) $CDCl_3$, (b) $CDCl_3$ pretreated with K_2CO_3, and (c) $CDCl_3$ containing 33 mol % TEMPO thermally treated at 60 °C. Thermal treatments were performed on degassed samples in NMR sample tubes sealed under vacuum. Heating was performed in the NMR spectrometer.

broadening of the molecular weight distribution. The cyclization process is independent of solvent and light.

Anomalous behavior is observed upon thermal treatment of degassed solutions of PPA in $CDCl_3$ (Figure 3a). The transformation of the polyene backbone to cyclohexadiene structures is significantly accelerated. In addition to the increased rate of cyclization, there is an increase in the amount of 1,3,5-$C_6H_3Ph_3$ formed. The amount of extruded benzene may be greater because of the significant amount of cyclization. While the acceleration was consistently observed, there was noticeable variation in the amount of cyclization between experiments. This variance is evident when comparing the kinetic data in Figure 3a and the numerical analysis from Figure 1c.

Unspecified amounts of HCl, K_2CO_3, and the stable free radical TEMPO have been added to open-air solutions of PPA in $CHCl_3$ and the effects on the change in M_n assessed.[55] While acid accelerates the decrease of M_n, K_2CO_3 and TEMPO show slower decreases of M_n.[55] The inhibition observed in the TEMPO-containing solution was used to substantiate a radical-based oxidation mechanism.[55] Addition of radical scavenging agents to THF and PhCl solutions of PPA inhibits the decrease of molecular weight.[49] In light of the accelerated rate of cyclization in $CDCl_3$ compared to all other solvents, we considered that acidity might be a critical factor to influence the rate of cyclization. To validate our observation, we investigated the effect of K_2CO_3-pretreated $CDCl_3$ and addition of TEMPO in degassed solutions of PPA. The results are illustrated in Figure 3b,c. In the absence of O_2, both additives inhibit the rate of cyclization. In fact, both experiments display kinetic behavior similar to that observed in CCl_4 and other solvents. As both additives are competent to consume the acidic deuteron,[62] acceleration due to acid is eliminated.

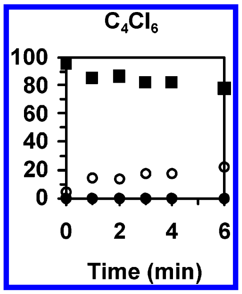


Figure 4. Plots of the mole percentage of alkene residues ($F_{a.r.} \times 100\%$) attributed to PPA (■), cyclohexadiene moieties (○), and extruded 1,3,5-$C_6H_3Ph_3$ (●) for a C_4Cl_6 solution thermally treated at 120 °C. Thermal treatments were performed on degassed samples in NMR sample tubes sealed under vacuum. Heating was performed in an oil bath with no precaution to exclude ambient light.

No new molecular fragments are observed in ^1H NMR spectra of C_4Cl_6 solutions of PPA at 120 or 160 °C. Figure 4 illustrates kinetics for the observed structural transformations of PPA at 120 °C. Transformation of PPA to cyclohexadiene repeat units is rapid, while no more 1,3,5-$C_6H_3Ph_3$ is formed than for experiments at 60 °C. Even after 8 h at 120 °C in C_4Cl_6, we observed $F_{a.r.}(C_6H_3(Ph\text{-}d_5)_3) = 0.07$, $F_{a.r.}(\text{cyclohexadiene}) = 0.37$, and $F_{a.r.}(\text{PPA}) = 0.56$. After only 3 min at 160 °C in C_4Cl_6 the sample had the following composition: $F_{a.r.}(C_6H_3(Ph\text{-}d_5)_3) = 0.07$, $F_{a.r.}(\text{cyclohexadiene}) = 0.28$, and $F_{a.r.}(\text{PPA}) = 0.65$. Comparing the formation of 1,3,5-$C_6H_3Ph_3$ at 120 and 160 °C indicates that the activation energy for the extrusion process is dramatically higher than that for cyclization. At 60 and 120 °C, extrusion of 1,3,5-$C_6H_3Ph_3$ is not significant.

We have previously shown[51] that annealing bulk samples of PPA at 180 °C for 1 h in argon or air produces comparable changes in structure and molecular weight. In those experiments, ~10% 1,3,5-$C_6H_3Ph_3$ was identified in GPC chromatograms. Similar experiments are reported in Table 2 for bulk samples annealed at 100 °C for 1 h. No evidence of 1,3,5-$C_6H_3Ph_3$ formation is observed by ^1H NMR spectroscopy. The transformations in bulk are the same as in solution.

Role of Molecular Oxygen (O_2). Figure 5 illustrates kinetic data for samples thermally treated in O_2-saturated CCl_4 and $CDCl_3$ solutions. Again, heating was performed in the dark. Surprisingly, the CCl_4 solution of PPA behaved just like the degassed solution. Cyclization of PPA in O_2-saturated $CDCl_3$ solution is dramati-

Table 2. Influence of Atmosphere on the Structural Composition, Molecular Weight, and Molecular Weight Distribution of PPA Thermally Treated for 1 h at 100 °C in Bulk in Light

	$F_{\mathrm{a.r.}} \times 100\%$				
treatment	PPA	cyclohexadiene	1,3,5-$C_6H_3Ph_3$	$M_n \times 10^{-3\,a}$	M_w/M_n
b	95	5	0	6.7	1.34
ambient[c]	90	10	0	6.2	1.38
argon[d]	94	6	0	5.6	1.51

[a] Relative molecular weight determined by GPC in THF (1 mL/min) calibrated using polystyrene standards. [b] As-prepared sample of PPA. [c] Samples were annealed in air. [d] Samples were degassed by freeze−pump−thaw cycles and sealed in argon.

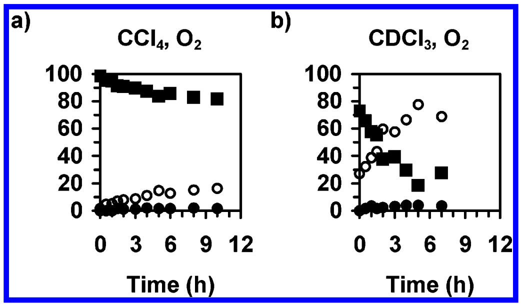


Figure 5. Plots of the mole percentage of alkene residues ($F_{\mathrm{a.r.}} \times 100\%$) attributed to PPA (■), cyclohexadiene moieties (○), and extruded 1,3,5-$C_6H_3Ph_3$ (●) for solutions in (a) CCl_4 and (b) $CDCl_3$ saturated with O_2. Thermal treatments were performed on samples in NMR sample tubes sealed under an ambient atmosphere. Heating at 60 °C was performed in the NMR spectrometer.

cally accelerated compared to degassed $CDCl_3$ and CCl_4. Decomposition of $CDCl_3$ (or $CHCl_3$) to form DCl (or HCl) is accelerated by the presence of O_2.[63] While the cyclization step is accelerated under conditions that promote decomposition of $CDCl_3$ to DCl, there is no apparent increase in the amount of 1,3,5-$C_6H_3Ph_3$ compared to the degassed sample. This suggests that acid exclusively promotes the cyclization step. The enhanced quantities of 1,3,5-$C_6H_3Ph_3$ in both $CDCl_3$ solutions of PPA compared to the CCl_4 solutions are more likely a consequence of larger concentrations of cyclized triene sequences and resulting steric strain.

While O_2 or light does not directly affect the rate of cyclization, we observe that in combination they result in accelerated cyclization and decrease of molecular weight. Table 1 provides comparative composition and molecular weight data for thermally treated solutions in CCl_4 in light. As noted above, degassed solutions thermally treated at 60 °C in an oil bath show the same composition as a sample in the NMR spectrometer. Samples open to air and in O_2-saturated solvent sealed in air undergo more rapid cyclization, extrusion of 1,3,5-$C_6H_3Ph_3$, and decrease of M_n when exposed to light. A modest acceleration is noted between the ambient and O_2-saturated solutions.

Structural differences are also noticeable between the different thermally treated samples. Figure 6 illustrates ^{1}H NMR spectra for PPA in CCl_4 thermally treated at 60 °C for 8 h and compares the impact of light, O_2, and the combination of them. The appearance of resonances between δ 10−9 ppm is indicative of aldehyde functionalities due to oxidation. Integration of the two resonances observed in Figure 6d (assuming that each is the result of one proton) demonstrates that this oxidative chain cleave occurs 5 times more frequently than extrusion of 1,3,5-$C_6H_3Ph_3$ in the same sample. After 72 h, several resonances in the same region were found in spectra of a thermally treated PPA-d_5 sample in $CDCl_3$. The relative intensity of these resonances changed upon removal of solvent and drying under vacuum. After drying under vacuum, the sample was precipitated from $CHCl_3$ into MeOH. ^{1}H NMR spectra of both the MeOH-soluble and MeOH-insoluble fractions contained resonances attributable to aldehyde moieties. The oxidation, therefore, involves the polyene carbon chain and results in oxidized residues in the cleaved polymer chain and low molecular weight materials.

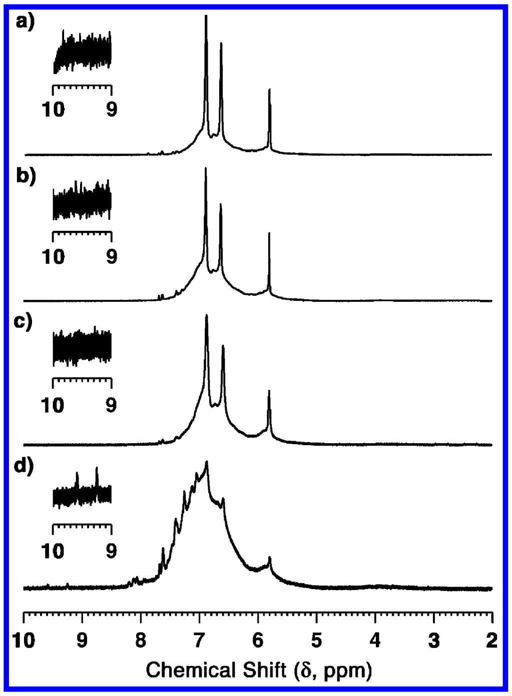


Figure 6. Comparison of ^{1}H NMR spectra of PPA in CCl_4 thermally treated at 60 °C for 8 h. (a) Degassed sample was sealed under vacuum and heating was performed in the NMR spectrometer. (b) O_2-saturated solution sealed under ambient atmosphere and heating was performed in the NMR spectrometer. (c) Degassed sample was sealed under vacuum and heating performed in an oil bath. (d) O_2-saturated solution sealed under ambient atmosphere. No precaution was taken to exclude ambient light from samples during heating in an oil bath.

Compression Treatment of PPA. Compression of several substituted PPAs has been reported to induce *cis*−*trans* isomerization of the polyene backbone.[64−68] Because of the reactions described above, thermal isomerization is not the method of choice for preparing *trans*-PPA. Characterization of compressed samples has focused on bulk analysis. Given the promiscuity of the cyclization reaction, we have investigated a sample of PPA compressed at 1500 kg/cm^2 for 10 min. The polymer was prepared by polymerization of PA using $[Rh(nbd)Cl]_2$ in NEt_3 at 20 °C. Effort was made to remove the THF insoluble fraction (*cis*-cisoidal PPA). Table 3 tabulates relevant structural and molecular weight characteristics for the as-prepared and compressed samples.

Compression of the initially orange powder produced a deep-red disk. The compressed pellet was dissolved in THF or $CDCl_3$. Not all the material was soluble, which suggests that *cis*-transoidal PPA crystallizes into the *cis*-cisoidal form during compression.[1,69] ^{1}H NMR spectra of the soluble portion of the compressed pellet

Table 3. Influence of Compression on the Structural Composition, Molecular Weight, and Molecular Weight Distribution of PPA

$F_{a.r.} \times 100\%$				
PPA	cyclohexadiene	1,3,5-$C_6H_3Ph_3$	$M_n \times 10^{-3\,a}$	M_w/M_n
95[b]	5	0	94.0	2.09
90[c]	10	0	89.1	2.12

[a] Relative molecular weight determined by GPC in THF (1 mL/min) calibrated using polystyrene standards. [b] As-prepared sample of PPA. [c] Soluble fraction of PPA sample compressed at 1500 kg/cm^2 for 10 min.

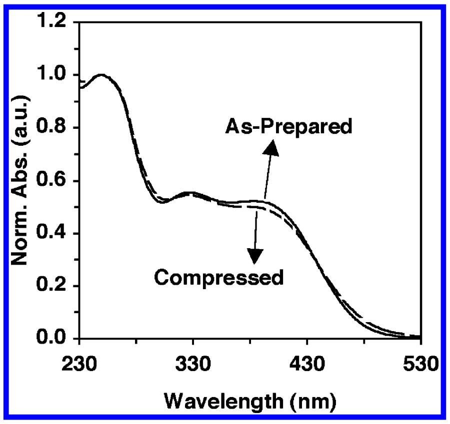


Figure 7. UV–vis spectra in THF of (a) PPA (1.03 × 10^{-4} M) and (b) the soluble fraction of PPA after compression (less than 7.87 × 10^{-5} M).

and original polymer sample were indistinguishable. Only a nominal difference in M_n and molecular weight distribution are observed. Figure 7 illustrates UV–vis spectra of the as-prepared and compressed PPA samples as solutions in THF.

The lack of evidence for thermally induced transformations in the soluble portion of compressed PPA confirms that this is a mild processing method. Crystallization of *cis*-transoidal PPA into *cis*-cisoidal PPA leaves uncertainty in structural characterization. Because no 1,3,5-$C_6H_3Ph_3$ is identified in the compressed samples, we can employ previously developed methods for assessing the *cis*-content.[1,35,48] The small change in *cis*-content[1,35,48] from 96% to 92% indicates that very little *cis*–*trans* isomerization occurs, which contrasts the structural assignments based on Raman, ESR, and diffuse reflectance UV–vis spectra of ring-substituted polyarylacetylenes.[64,65,67,68] Furthermore, we have shown the sensitivity of molecular weight in PPA to small structural changes. Such changes are not apparent from our investigations of compressed samples of PPA.

Scope and Limitations. Given the solvent independence of this process and the previously reported activation energy,[34,48] we envision cyclization to occur via 6π electrocyclization (Scheme 2). This is based on analogy to kinetic investigations of such reactions in *cis*-1,3,5-trienes. The experimentally determined activation energy for conversion of 1,3,5-hexatriene to 1,3-cyclohexadiene is 29.9 kcal/mol.[70] Substituted analogues have comparable activation parameters.[71,72] Substitution of the triene shows small electronic influence, although substitution at the terminal carbons imposes a steric penalty on the rate of cyclization.[73] Computational efforts validate this observation.[74] This mechanistic pathway offers an explanation for the observation that *ortho*-substituents on the aromatic ring inhibit the loss of *cis*-content and decrease of molecular weight.[75,76] Furthermore, it has been demonstrated that the rate of cyclization and its activation parameters are solvent independent.[71] Cyclization along the polyene backbone of PPA appears to be the same.

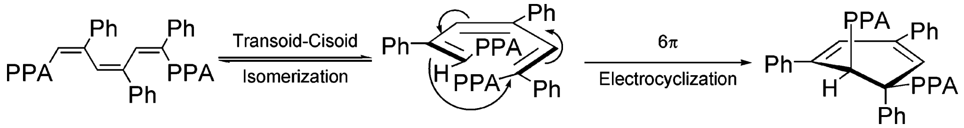
In the limit of a purely concerted reaction mechanism, 6π electrocyclization reactions are expected to be stereospecific and abide by the Woodward–Hoffmann rules.[77,78] Theoretical approaches to such reactions affirm that the process is concerted, though not necessarily synchronous. In the absence of a stereochemical bias, dynamic helical polymers undergo rapid isomerization between *P*- and *M*-helical conformations.[13] Helical triene sequences are predisposed to cyclization. Evident from the experiments described above, cyclization occurs even in the absence of light and air. As a consequence, this process may serve to distort the observed dynamic helical behavior in helical PPAs. The cyclohexadiene structures are capable of conformational inversion, but not stereochemical inversion. Furthermore, the newly generated stereocenter adjacent to the main chain may impart a strong thermodynamic input to the adopted helical conformation.

In acidic media, cyclization may proceed as described above. To our knowledge, there are no examples of acid-catalyzed 6π electrocyclization reactions. As an alternative to explain the accelerated cyclization, we can invoke an electrophilic reaction pathway (Scheme 3). This pathway, though, is inconsistent with other observations. As pointed out above, there are no apparent structural differences between degassed samples thermally treated in CCl_4 and $CDCl_3$. The promiscuity of carbocations to react with adventitious water and undergo hydride abstraction is not apparent in the ^1H NMR spectrum of PPA-d_5 thermally treated at 60 °C in $CDCl_3$ (Figure 1c).

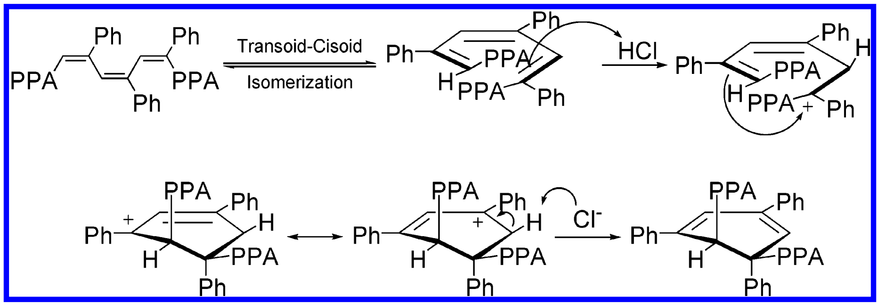
While light and O_2 do not independently affect the structural and molecular weight changes reported herein, ambient light and O_2 synergistically cause dramatic changes. Structural features observed by ^1H NMR spectroscopy suggest oxidative cleavage of the polyene backbone. The mechanism by which oxidation occurs is not clear. Photosensitization of singlet O_2 by PPA is consistent with the dependence on both O_2 and light. Reactions of singlet O_2 preferentially undergo an "ene"-type reaction with an allylic hydrogen.[79] We can envision the "ene" reaction at the methine associated with the cyclohexadiene, but this appears to preclude extrusion of 1,3,5-$C_6H_3Ph_3$. When the "ene" pathway is unavailable, [2 + 2] cycloaddition of singlet O_2 to an alkene occurs.[80] The resulting 1,2-dioxetane can rearrange to the corresponding dicarbonyl. These statements hold for conformationally unlocked dienes.[81] Cyclohexadiene is exclusively transformed to the endoperoxide, which further transforms into an epoxy ketone or diepoxide.[81] Among the described reactivity, the only path consistent with our observations is [2 + 2] cycloaddition of singlet O_2 with a backbone alkene to generate a transient 1,2-dioxetane. The 1,2-dioxetane further decomposes to generate aldehyde products (Scheme 4). In addition to the formation of aldehyde functionalities, ambient light and O_2 accelerate cyclization and extrusion of 1,3,5-$C_6H_3Ph_3$. The solvent dependencies reported previously are likely connected to these processes and not the electrocyclization pathway.

Solvent decomposition also affects the observed structural changes. The representative example of $CDCl_3$ has been shown herein. Other examples are evident in the

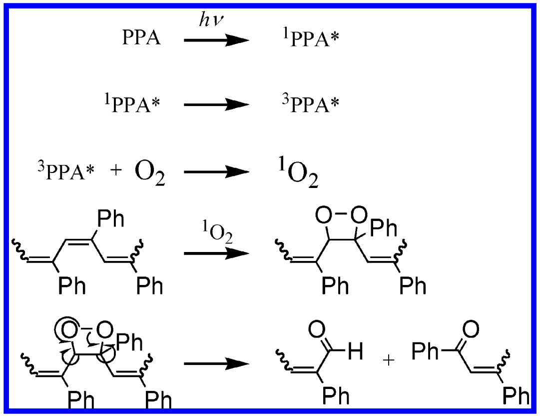
Scheme 2. Illustration of Transoid–Cisoid Conformational Isomerization Followed by Concerted 6π Electrocyclization of a Triene Sequence along the Polyene Backbone of PPA



Scheme 3. Illustration of Electrophilic Cyclization of a Triene Sequence along the Polyene Backbone of PPA in the Presence of Acid (HCl or DCl)



Scheme 4. Illustration of Photosensitized [2 + 2] Cycloaddition of Singlet O_2 to PPA Followed by Chain Cleavage Due to Decomposition of the 1,2-Dioxetane to an Aldehyde and Ketone



literature. Contradictory statements regarding results in $CHCl_3$, toluene, THF, and PhCl may find some explanation therein. The results described in Figures 3 and 5 and Table 1 shed light on the observation[55] that light does not influence the rate of molecular weight decrease of PPA in $CHCl_3$ solution. The rate of 6π electrocyclization is the same in all solvents, including neutral $CDCl_3$, and is independent of the presence of light in degassed samples. On the other hand, light influences the oxidative decomposition of $CHCl_3$ (and $CDCl_3$).[63] 6π Electrocyclization and acid-catalyzed cyclization in PPA may be more rapid than solvent decomposition. Similarly, autoxidation of THF[82] can lead to divergent data sets.

Experiments in air with and without light present have led to the presumption of a radical-based autoxidative mechanism for decrease of molecular weight.[49,52,53,55,56] Drawing on the speculative discussion about the autoxidation mechanism of poly(methylacetylene),[83] this view has gained acceptance. Some key distinctions can be made between the two polymers during oxidation. The initiation process for autoxidation of poly(methylacetylene) directly involves O_2.[83] Clearly, this is not the case for PPA where light is a necessary component. While it is acknowledged that poly(methylacetylene) can serve as a sensitizing agent to generate the excited singlet state, the authors suggest that the subsequent "ene" reaction pathway is insignificant.[83] The authors distinguish between a free radical autoxidation of poly(methylacetylene) and a photooxidation process. Free radical scavengers are found to inhibit and retard the autoxidation process but do not affect the photooxidation process in poly(methylacetylene).[83] As shown herein, the observed role of radical scavengers can be obscured by the influence of solvent. In the case of poly(methylacetylene), all experiments were performed in bulk to avoid complications due to adventitious solvent.[83]

Conclusions

Kinetic investigations of the structural and molecular weight changes undergone by *cis*-PPA and *cis*-PPA-d_5 in bulk and solution have been undertaken using a combination of ^{1}H NMR spectroscopy and GPC experiments. In the absence of light and O_2, the process is best described as formation of cyclohexadiene repeat units via cyclization of triene sequences along the polyene backbone. When exposed to either light or an O_2-containing atmosphere, the process is the same. Cyclization along the polymer backbone produces modest decreases in molecular weight and broadening of the molecular weight distribution. In the presence of O_2 or ambient light, or in the absence of both, the rate of cyclization is solvent independent, so this process is unavoidable. The cyclization event likely proceeds via 6π electrocyclization because of the overall solvent independence and activation energy.

In $CDCl_3$, which decomposes to form DCl, the rate of cyclization appears to be dramatically faster than other solvents. This phenomenon is the result of the acid formed by decomposition of the solvent. Since light and O_2 promote decomposition of $CDCl_3$ (or $CHCl_3$), such conditions should be avoided when handling PPA. We observed a marked increase in the rate of cyclization in O_2-saturated $CDCl_3$. Acid catalysis of electrocyclization is the likely cause of this observation, though an electrophilic cyclization mechanism has not been excluded. Oxidative decomposition of other solvents such as THF may account for other discrepancies between literature results.

When samples are exposed to both O_2 and light, yet another process dominates the observed behavior. Cyclization and extrusion of 1,3,5-$C_6H_3Ph_3$ are more rapid under these conditions, but not as fast as in acidic media. Decrease of molecular weight and broadening of molecular weight distribution are dramatically accelerated when light and O_2 are present. Reliable correlation of structure and function cannot be made under such conditions. In contrast to previous explanations for the transformations observed in light and air, we do not advocate a free radical autoxidation mechanism. Rather, we have noted distinct differences between PPA and poly(methylacetylene).[83] Most important is the necessity for both components. The results reported here provide correct strategies for manipulating *cis*-PPA during solution phase investigations at ambient temperature and solid state at elevated temperatures.

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Supporting Information Available: A full explanation of the equations used to determine the mole fraction of alkene residues ($F_{\mathrm{a.r.}}$) for each component observed in annealing experiments with PPA. This material is available free of charge via the Internet at http:\\pubs.acs.org.

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