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Conducting Polymers from Polybutadiene: Molecular Configuration Effects on the Iodine-Induced Conjugation Reactions

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ABSTRACT: The "doping" of *trans*-1,4-polybutadiene in the solid state with iodine has been reported to convert this polymer into a semiconductor at room temperature, but an analogous conversion is not observed on iodine doping of *cis*-1,4-polybutadiene. In this study, the reactions of 1,4-polybutadienes with iodine have been investigated in solution. UV/vis, IR, and NMR spectroscopic measurements, photosensitized cis–trans isomerization studies, and molecular orbital calculations indicate that the "I_2 doping" of *trans*-1,4-polybutadiene results in the formation of sequences of conjugated double bonds, which confer conductivity. In contrast, the I_2 doping of *cis*-1,4-polybutadiene does not lead to the formation of conjugated sequences at room temperature, due to an unfavorable combination of electronic and steric interactions associated with the polymer backbone geometry. The marked difference between the results of I_2 doping of *cis*-1,4-polybutadiene and those of *trans*-1,4-polybutadiene is thus interpreted in terms of differences in their *intramolecular* structure, rather than differences in *intermolecular* packing as previously proposed by others.

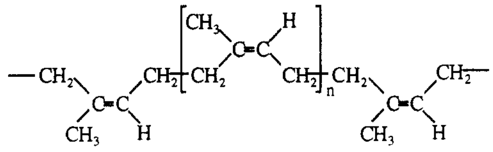
Introduction

In 1988 Thakur reported that the conductivity of *cis*-1,4-polyisoprene can be increased by about 10 orders of magnitude upon "doping" with iodine.[1] This observation generated considerable interest,[2-7] and various other polymers with isolated (nonconjugated) double bonds, such as *trans*-1,4-polyisoprene, 1,4-poly(2,3-dimethylbutadiene), and *trans*-1,4-polybutadiene, were found to become dark in color and conductive when "doped" with iodine in the solid state. Surprisingly, however, *cis*-1,4-polybutadiene does not change color or become conductive upon "iodine doping".[1,2,5] The mechanism of "I_2 doping" of 1,4-polybutadienes and the effects of double-bond configuration on this mechanism are still not fully understood, although the different behavior of *cis*- and *trans*-1,4-polybutadiene films toward I_2 doping has been proposed to be related to possible differences in their intermolecular packing.[5]

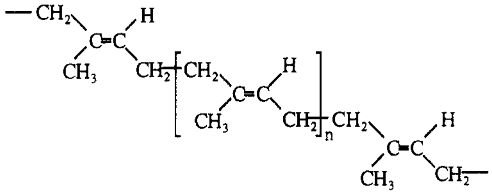
The cis configuration of double bonds is not inherently incapable of conversion to a conducting polymer, as exemplified by *cis*-1,4-polyisoprene which, on I_2 doping, produces conjugated sequences of unsaturated double bonds in the polyisoprene backbone.[8,9] This conjugation of double bonds is believed to be responsible for the markedly increased conductivity of "I_2-doped" *cis*-1,4-polyisoprene. This prompted us to investigate the effects of I_2 doping of *cis*- and *trans*-1,4-polybutadienes in solution, in light of the I_2-induced conjugation reactions proposed for 1,4-polyisoprene,[8,9] using spectroscopic measurements and molecular orbital calculations. The results of this study suggest reinterpretation of the different behavior of *trans*- and *cis*-1,4-polybutadienes upon I_2 doping in terms of intramolecular properties rather than intermolecular packing.

Experimental Section

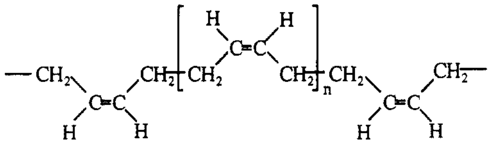
Materials and Characterization. The polymer samples used were purchased from Aldrich. Their molecular backbone configurations are shown in Figure 1. Relevant properties of the polymers, supplied by the manufacturer and/or obtained by NMR, are listed in Table 1. Note that the *cis*-polybutadiene sample contains 98% cis-1,4-addition structural units but that the nominal *trans*-1,4-polybutadiene sample consists of only 55% trans-1,4-addition units; no samples with a higher trans-1,4-addition content could be sourced commercially.



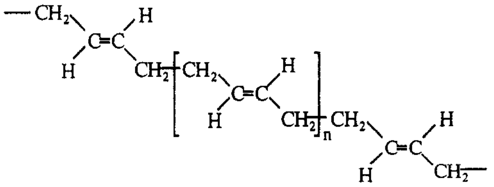
Cis-1,4-polyisoprene



Trans-1,4-polyisoprene



Cis-1,4-polybutadiene



Trans-1,4-polybutadiene

Figure 1. Molecular structure of the polymers used in this study.

Analytical grade cyclohexane and benzene (BDH) and reagent grade diphenyl disulfide (Aldrich) were used as received, as was reagent grade iodine (General Chemical Co.), which was stored over silica gel in a desiccator.

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Table 1. Molecular Characteristics of the Polymer Samples Used in This Study

sample	percentage content of isomer	mol wt (M_w)
cis-1,4-polyisoprene	97% cis	800 000
trans-1,4-polyisoprene	100% trans[a]	410 000
cis-1,4-polybutadiene	98% cis	2 500 000
trans-1,4-polybutadiene	55% (trans); 36% (cis); 9% 1,2-addition	420 000

[a] Determined by NMR.

Spectroscopy. Nuclear magnetic resonance (NMR) measurements were performed on a Bruker AC-200 NMR spectrometer at room temperature (20 °C) using deuterated chloroform (99.8% D) as solvent. Polymer samples, dissolved in cyclohexane, were collected at various stages of the conjugation reaction and dried by pumping under a dynamic vacuum (~10^{-5} Torr) until a constant weight was achieved. The dried polymer samples were then redissolved into a known volume of $CDCl_3$ for NMR measurements. ^{13}C chemical shifts were measured with respect to that of the central carbon peak of $CDCl_3$ (76.99 ppm downfield from tetramethylsilane (TMS)).

Fourier transform infrared (FTIR) spectra were measured on polymer samples cast onto a AgBr (400–4000 cm^{-1}) disk, using a Mattson Alpha Centauri unit. Ultraviolet/visible (UV/vis) spectra of the polymer solutions were recorded on a Hewlett-Packard HP-8451A spectrophotometer, using a quartz UV cell of 1-cm optical path length, unless otherwise stated. Solutions of the as-received polyisoprene and polybutadiene samples in cyclohexane were transparent between 300 and 800 nm. Fluorescence measurements were recorded from cyclohexane solutions of the polymers with and without iodine using a Perkin-Elmer MPF-4 fluorescence spectrophotometer. An excitation wavelength of 420 nm was used.

Molecular Orbital Calculations. Model structures were generated using the building capabilities of the Sybyl (version 6.0, Tripos Associates, St. Louis, MO) molecular modeling package. The MAXIMIN optimizer was used to obtain initial energy-minimized geometries used as input to the molecular orbital calculations. Molecular orbital calculations were performed using the MOPAC package and the PM3 parametrization. Full geometry optimization was undertaken, and the PRECISE keyword was used.[10] The calculations were run on a Silicon Graphics 4D/30G workstation.

Photosensitized Cis–Trans Isomerization. The photosensitized cis–trans isomerization of 1,4-polybutadiene was carried out following the procedure reported by Golub and Parkinson,[11] in benzene using diphenyl disulfide as sensitizer. Typically, 30 mg of diphenyl disulfide was added to 10 mL of benzene containing 100 mg of *cis*-1,4-polybutadiene, in a 1-cm-path-length quartz cuvette. The sample was flushed with nitrogen and exposed to a 354-nm UV illumination source (Varian 300W Illuminator, operated at a current of 16 A) for 1 h. Prior to NMR analyses and I_2-doping reactions, the isomerized polymeric material was separated from the reaction mixture by precipitation with methanol followed by centrifugation and dried under a dynamic vacuum (~10^{-5} Torr) at room temperature until a constant weight was achieved.

Iodine-Induced Conjugation Reactions. The I_2-doping reaction of the as-received and photoisomerized polymers was carried out by dissolving the polymer sample and iodine at a determined ratio in cyclohexane in a 1-cm-path-length (unless otherwise stated) quartz UV cell, which was sealed under nitrogen. UV/vis spectra were recorded *in situ* after various reaction times. Table 2 lists the reaction conditions used for each of the experiments.

Results

Reaction of the Polymers with Iodine at Room Temperature. Figure 2 shows typical series of UV/vis spectra recorded in the course of the reaction between iodine and *cis*- and *trans*-1,4-polyisoprenes in cyclohexane at ambient temperature. These spectra are closely analogous to those reported by Dai and White for the same reaction in toluene.[8] Accordingly, the reaction mechanism proposed in the earlier study[8] for the iodine-induced conjugation of polyisoprene in toluene is also considered to apply to the reaction taking place between polyisoprene and iodine in other solvents, such as cyclohexane.

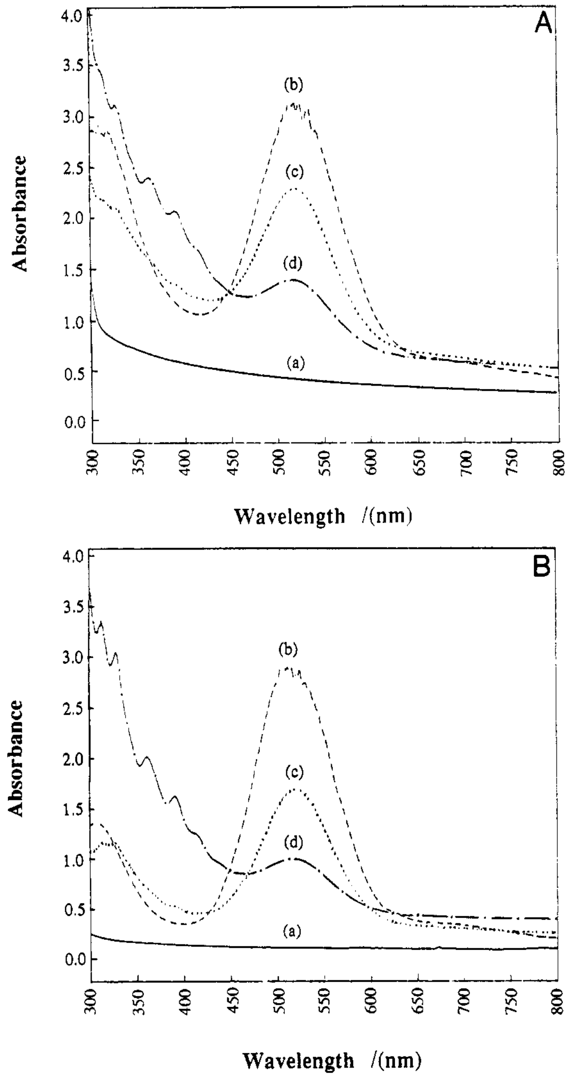


Figure 2. UV/vis spectra of (A) *cis*-1,4-polyisoprene and (B) *trans*-1,4-polyisoprene on reaction with I_2 in cyclohexane, measured after dilution by a factor of 2, at different reaction times under the conditions of expt. nos. 1 and 2, respectively (see Table 2). Curves: (a) before reaction; (b) immediately after mixing with I_2; (c) I_2-reacted for 14 h; (d) I_2-reacted for 96 h.

The UV/vis spectra for the reaction between iodine and *trans*-1,4-polybutadiene, shown in Figure 3A, are also characterized by a monotonically decreasing optical absorbance of the molecular iodine band at 520 nm. After reaction for 24 h, several weak bands at shorter wavelengths were observed; these bands are attributed to conjugated double bond sequences of various lengths.[8] Again, the close similarity between the spectra of Figure 3A and those of Figure 2 and other polymer/iodine reaction mixtures[8] suggests that the reaction between *trans*-1,4-polybutadiene and iodine proceeds by a mechanism related to that of the I_2-induced conjugation of polyisoprene. Scheme 1 details the reactions proposed to occur in the course of I_2 doping of *trans*-1,4-polybutadiene, a reaction sequence which, rather than doping, would be better termed an iodine-mediated conjugation reaction.

Figure 3B shows the UV/vis spectra for the reaction between *cis*-1,4-polybutadiene and an equivalent molar amount of iodine in cyclohexane at ambient temperature. As for the trans isomer, a substantial decrease in the optical

Table 2. Experimental Conditions for the Reactions between Polymer Samples and Iodine[a]

expt. no.	sample	C_{polym}/(g/mL)	$C_{\mathrm{I_2}}$/(g/mL)	[C=C]/[I_2]	temp/°C	UV irradiation
1	*cis*-1,4-PI	0.0150	0.0018	31	20	no
2	*trans*-1,4-PI	0.0150	0.0018	31	20	no
3	*cis*-1,4-PB	0.0075	0.0009	39	20 (70 h) → 60	no
4	*trans*-1,4-PB	0.0075	0.0009	39	20 (70 h) → 60	no
5	*cis*-1,4-PB	0.0150	0.0088	8	20 (48 h) → 60	no
6	*trans*-1,4-PB	0.0150	0.0088	8	20 (48 h) → 60	no
7	*cis*-1,4-PB	0.0075	0.0009	39	20	yes
8	*trans*-1,4-PB[b]	0.0075	0.0009	39	20	yes
		0.0150	0.0088	8	20	

[a] PI: polyisoprene. PB: polybutadiene. [b] Photoisomerized from the cis isomer using diphenyl disulfide as sensitizer (see text).

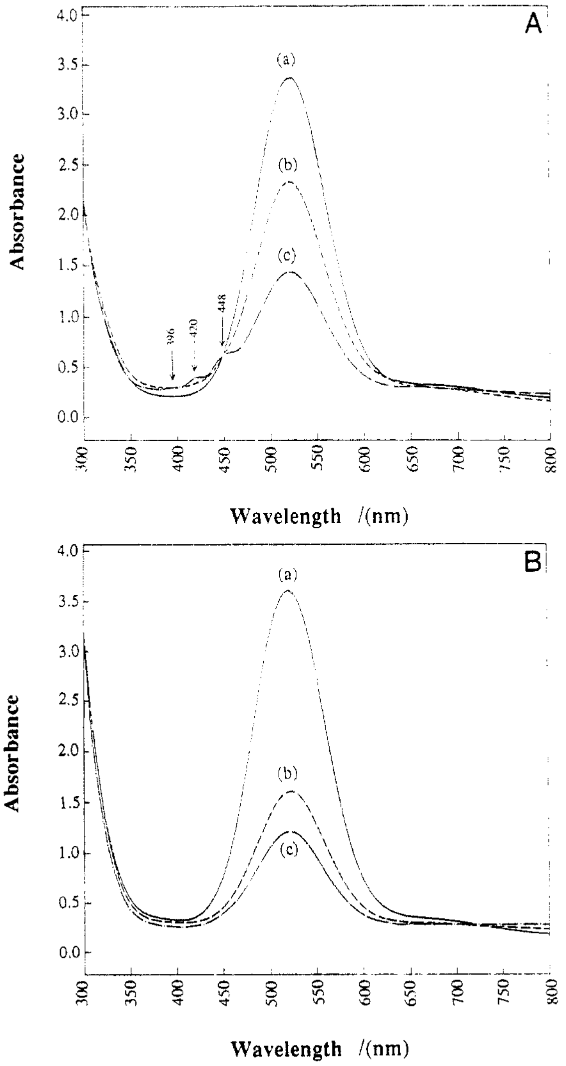


Figure 3. UV/vis spectra of (A) *trans*-1,4-polybutadiene and (B) *cis*-1,4-polybutadiene on reaction with I_2 in cyclohexane at different reaction times under the conditions of expt. nos. 4 and 3, respectively (see Table 2). Curves: (a) immediately after mixing with I_2; (b) I_2-reacted for 14 h; (c) after 23 h.

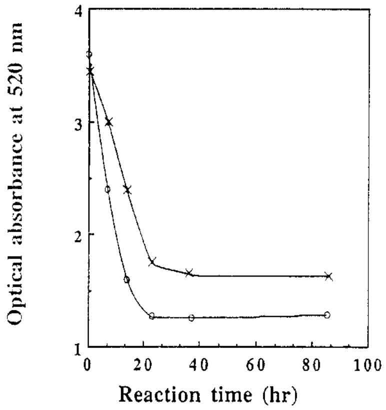
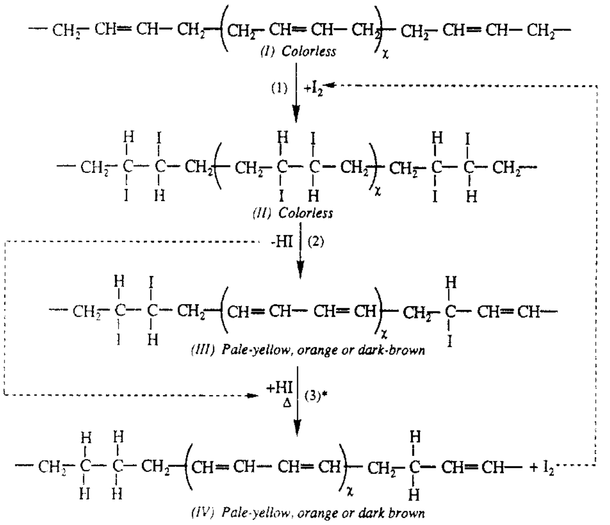


Figure 4. Optical absorbance at a wavelength of 520 nm as a function of the reaction time for the addition of I_2 to 1,4-polybutadienes at 20 °C under the conditions of expt. nos. 3 and 4 of Table 2: (○) *cis*-1,4-polybutadiene; (×) *trans*-1,4-polybutadiene.

Scheme 1. Reactions Leading to the Formation of Conjugated Sequences in Polybutadienes following Treatment with Iodine



absorbance of the I_2 absorption band at 520 nm is observed during the initial stage of the reaction. The optical absorbance at 520 nm decreases in fact faster when reacting iodine with *cis*-1,4-polybutadiene than with the trans isomer (Figure 4). In marked contrast, however, in the case of *cis*-1,4-polybutadiene the spectra (Figure 3B) do not show the emergence of bands attributable to conjugated polyene sequences, even after the reaction has proceeded for more than 2 weeks. The spectral differences between parts A and B of Figure 3 thus suggest that for *cis*-1,4-polybutadiene the reaction with iodine stops after the addition step; the elimination of HI (i.e., reaction 2 of Scheme 1) does not occur for the cis isomer, whereas it does for the trans isomer. The absence of formation of conjugated sequences of double bonds, which are necessary structural elements for a polymer to be electrically conductive,[12,13] renders the cis isomer incapable of attaining conductivity upon I_2 doping at room temperature. The UV/vis spectra thus suggest a mechanistic reason for the different effects of I_2 doping on *cis*- and *trans*-1,4-polybutadienes but do not indicate why the elimination of HI should be ineffective for the former isomer. We shall return to this point in the Discussion section.

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* Reaction (3) most likely proceeds by the free radical mechanism:
(see: Benson, S.W.; Bose, A.N. *J. Am. Chem. Soc.* 1963, 85, 1385 and references therein)

$$I_2 \rightleftharpoons 2I$$
$$I + RI \rightleftharpoons R + I_2$$
$$R + HI \rightleftharpoons RH + I$$

where, RI and RH represent Polymer (III) and Polymer (IV), respectively.

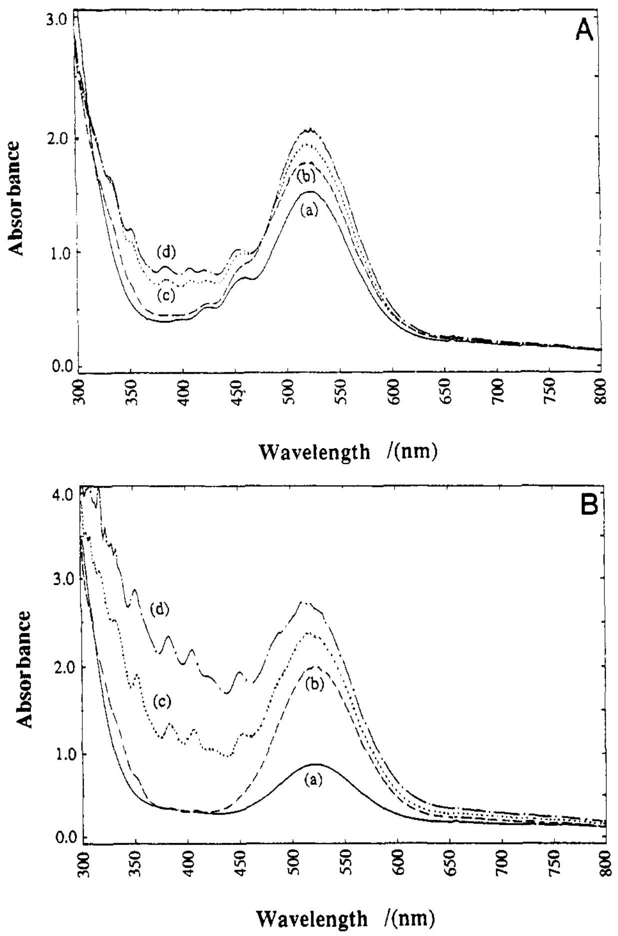

Figure 5. UV/vis spectra of (A) *trans*-1,4-polybutadiene and (B) *cis*-1,4-polybutadiene on heating at 60 °C following reaction with I_2 in cyclohexane at 20 °C under the conditions of expt. nos. 4 and 3, respectively (see Table 2). Curves: (a) reacted with I_2, no heating; (b) 60 °C for 22 h; (c) 60 °C for 93.5 h; (d) 60 °C for 144 h.

Effect of Temperature on the Reactions. The iodine-induced conjugation of 1,4-polyisoprene can be enhanced by heating the polymer/iodine solution to a higher temperature.[8] Consequently, we also investigated the reactions of *cis*- and *trans*-1,4-polybutadienes with iodine by heating the I_2-reacted polybutadienes obtained at room temperature to 60 °C. The changes in the UV/vis spectra upon heating are shown in parts A and B of Figure 5 for *trans*- and *cis*-1,4-polybutadiene, respectively. As can be seen, a number of additional absorption bands appeared after heating either isomer at 60 °C for about 20 h; the intensity of these new bands then increased further with time. These bands are assigned to conjugated polyene sequences, formed by thermally activated, additional double-bond conjugation reactions. The similarity of the newly observed spectral features in parts A and B of Figure 5 indicates that the two isomers participate in the same thermally induced conjugation reactions. Thus, while ineffective at room temperature, the iodine-induced conjugation of *cis*-1,4-polybutadiene can proceed at 60 °C.

The spectra also show an increase in the iodine optical absorbance, at 520 nm, upon heating. This is consistent with reaction (3) of Scheme 1 which provides a mechanism for the generation of I_2 upon heating.

The optical absorbance in the region 350–450 nm is significantly stronger after heating for the cis isomer (Figure 5), indicating a higher density of conjugated structures. This might seem inconsistent with the more facile formation of conjugated sequences in *trans*-1,4-polybutadiene at room temperature. However, the addition of iodine at ambient temperature proceeds faster in *cis*-1,4-polybutadiene compared with the trans isomer (Figures 3 and 4). The difference in the initial optical absorbance at 520 nm, shown in curve a of parts A and B of Figure 5, indicates that the I_2-reacted *cis*-1,4-polybutadiene starting material had undergone more extensive iodine addition than its trans counterpart. Consequently, the higher yield of conjugation in the *cis*-1,4-polybutadiene at 60 °C is related to the greater iodine content of the precursor obtained from the room-temperature addition of iodine. This suggests that heating enhances the elimination of hydrogen iodide more significantly with respect to the addition of iodine.

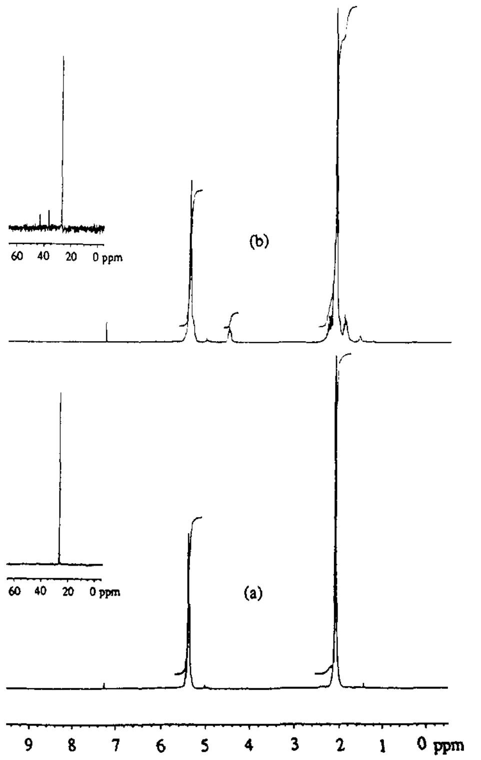

Figure 6. ^1H NMR spectra of *cis*-1,4-polybutadiene in $CDCl_3$ (a) before and (b) after reaction with I_2 under the conditions of expt. no. 3 of Table 2. The insets show the corresponding ^{13}C NMR spectra in the aliphatic carbon region: (a) pristine *cis*-1,4-polybutadiene; (b) I_2-reacted for 24 h.

NMR Studies. The addition of iodine was also evident in ^1H NMR spectra, as exemplified by Figure 6 for *cis*-1,4-polybutadiene. The ratio of olefinic protons to aliphatic protons was assessed by integration of the resonance peaks at 5.40 and 2.08 ppm;[14] the ratio was reduced from 0.50 to 0.46 upon reaction with iodine. A new peak was observed centered at 1.92 ppm and assigned to $-CH_2CI-$ structures. Another new peak was located at 4.46 ppm, consistent with an expected $-CHI$ resonance. The area ratio between the peaks at 1.92 and 4.46 ppm was close to 2. These features all indicate the production of saturated $-CH_2CHI-$ structures consequent upon iodine addition to some of the C=C double bonds. A small peak at 7.25 ppm was attributed to the $CHCl_3$ impurity in the solvent used for the NMR measurements. The conjugated sequences formed by further reaction were not observable by NMR, presumably due to aggregation associated with the conjugated structure, as is the case for the conjugated sequences from the I_2-induced conjugation of polyisoprene or those produced by copolymerizations.[8,15–17]

The corresponding resonances of aliphatic carbons are shown in the insets of parts a and b of Figure 6. Two new peaks at 37.00 and 43.48 ppm (inset of Figure 6b), which

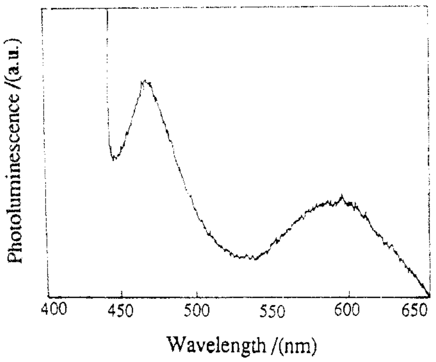

Figure 7. Fluorescence emission (excitation wavelength: 420 nm) of *trans*-1,4-polybutadiene after reaction with I_2 for 216 h under the conditions of expt. no. 4 of Table 2.

we assign to aliphatic carbons based on literature data,[18,19] were observed as expected from the addition of iodine. As for the ^1H NMR, the resonances characteristic of conjugated sequences were also absent from the ^{13}C NMR spectra.

No evidence was found for carbonyl groups (C=O), expected between 160 and 200 ppm,[19] which might form if air had entered the reaction systems.

Fluorescence Spectra. No emission was observed between 450 and 800 nm from the as-received 1,4-polybutadienes dissolved in cyclohexane. Nor was emission detected in an iodine-containing cyclohexane solution of the polymers after short contact times. After prolonged reaction with iodine, however, two emission peaks centered at 470 and 590 nm, respectively, emerged, for instance, after 216 h as shown in Figure 7. Thus, the emission peaks appear to be linked to the newly formed conjugated sequences.[20-23]

The structure of the individual emission bands is vibrationally unresolved and very broad, which is indicative of a wide distribution of geometries and "sites" of the emitting molecular structures (inhomogeneous line broadening).

Reactions with High Molar Ratios of Iodine. A higher molar ratio of iodine was used in further I_2-induced conjugation reactions in an attempt to obtain longer conjugated sequences. Parts A and B of Figure 8 illustrate the time evolution of the UV/vis spectra of *cis*- and *trans*-polybutadienes treated with iodine in cyclohexane at a molar ratio of 8 ([C=C]/[I_2]). As before, the temperature was raised from 20 to 60 °C after the initial reaction. Comparison of the spectra of Figure 8 with Figure 5 suggested that different mechanisms for the elimination of hydrogen iodide operated at the higher molar ratio of [I_2]/[C=C]. Under these conditions short polyenes can form charge-transfer complexes exhibiting two strong, broad absorption bands centered at ~400 and 520 nm.[8,9] Although absorption at 520 nm can also be assigned to molecular I_2 produced by reaction (3) of Scheme 1, the stronger intensity of the 520-nm band in curves c and d relative to curve a in Figure 8A indicates that charge-transfer complexes contribute significantly to this band.

The spectra in Figure 8 contain, after heating to 60 °C, considerable intensity at wavelengths larger than 600 nm, indicating the formation of charge-transfer complexes involving longer polyene chains, analogous to the case of conjugated polyisoprene.[8] Prolonged heating may also cause a sol–gel transformation, as observed occasionally in the case of reactions with high molar ratios of iodine, probably due to an intermolecular cyclization of polybutadiene chains in the presence of I_2.[24,25]

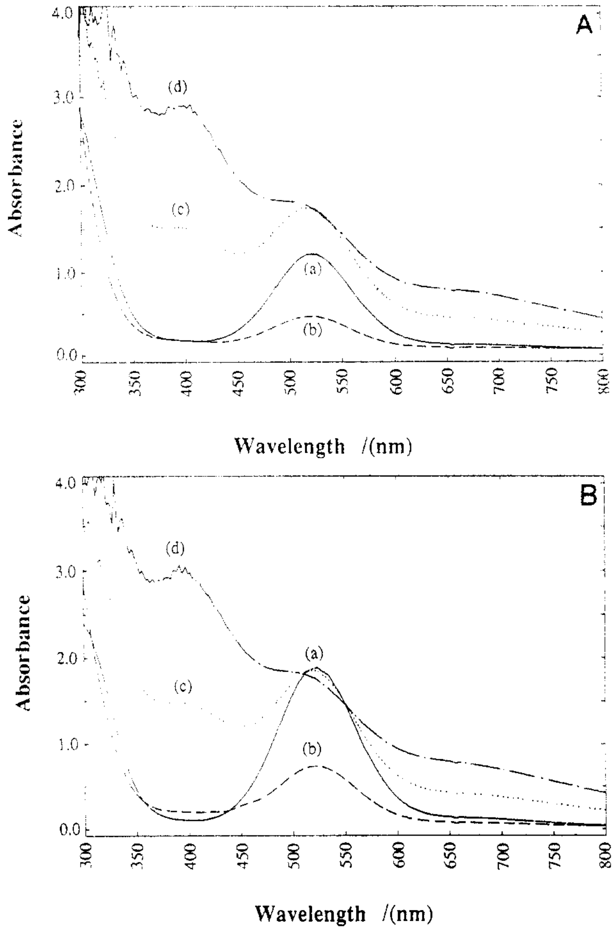

Figure 8. UV/vis spectra of (A) *cis*-1,4-polybutadiene and (B) *trans*-1,4-polybutadiene reacted with I_2 in cyclohexane under the conditions of expt. nos. 5 and 6, respectively (see Table 2), measured in a 1-mm cell. Curves: (a) before reaction; (b) I_2-reacted for 48 h at 20 °C; (c) then held at 60 °C for 31.5 h; (d) 60 °C for 72 h.

FTIR Studies. FTIR spectra of polybutadiene films cast from *cis*- and *trans*-1,4-polybutadiene solutions in cyclohexane with and without reaction with iodine are shown in parts A and B of Figure 9. For the polybutadiene films not treated with iodine, the bands at 715 and 960 cm^{-1} are characteristic of the =CH out-of-plane (bending) deformation for *cis*- and *trans*-polybutadiene, respectively.[18,26] Also, the cis and trans isomers can be distinguished by their characteristic $-CH_2-$ and $-CH-$ stretching bands in the region of 2700–3000 cm^{-1}.[26] Following reaction with iodine, a new band was observed at 495 cm^{-1} (parts A and B of Figure 9, curves b); it was attributed to the C–I stretching vibration.[8,26] The bands at 715 and 960 cm^{-1} decreased in intensity with respect to the $-CH_2-$ deformation vibration at 1445 cm^{-1}. These changes in the FTIR spectra are consistent with the addition of iodine to C=C bonds along the polybutadiene backbones.

When heating the solutions at 60 °C, the C–I stretching mode at 495 cm^{-1} became weaker, consistent with elimination of HI (parts A and B of Figure 9, curves c). Additional intensities emerged in the range of 800–1350 cm^{-1}. These broad, indistinct bands resemble those observed for conjugated 1,4-polyisoprene.[8]

Furthermore, heating also changed the structure of the absorption bands in the range 2700–3000 cm^{-1}. As shown in Figure 9A, absorption bands characteristic of the cis isomer (curve a) changed shape considerably on heating (curve c), assuming a shape more indicative of the trans isomer, as is evident by comparison with Figure 9B, curve a. This spectral result suggests an iodine-induced cis to

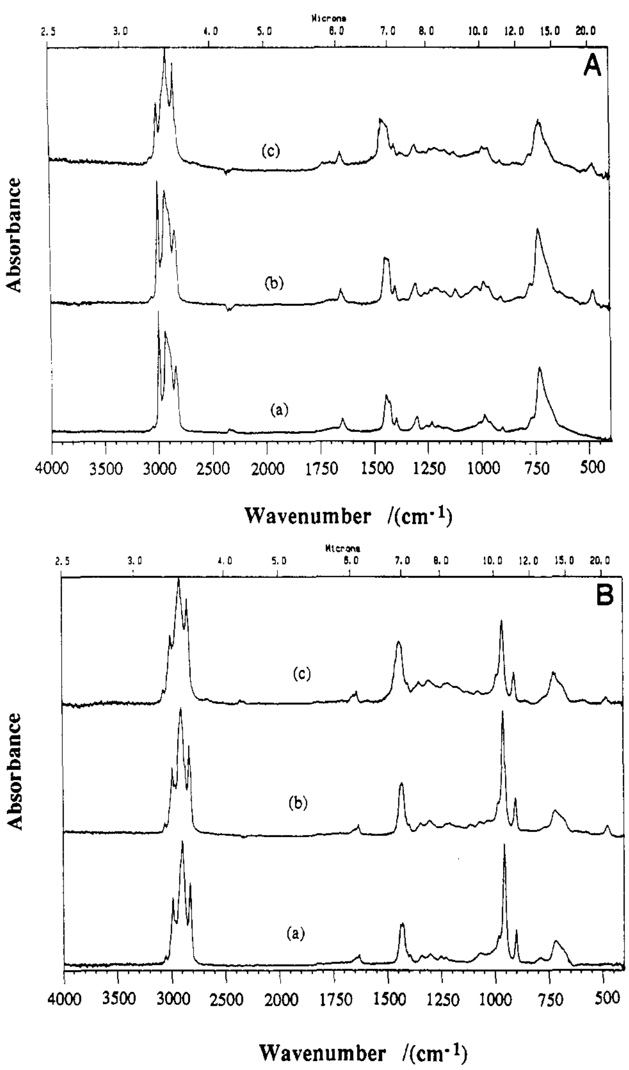

Figure 9. FTIR spectra of (A) *cis*-1,4-polybutadiene and (B) *trans*-1,4-polybutadiene before and after reaction with I_2 for different times under the conditions of expt. nos. 5 and 6, respectively (see Table 2). Curves: (a) pristine polybutadienes; (b) I_2-reacted for 50 h; (c) I_2-reacted for 192 h.

trans isomerization of polybutadiene at 60 °C. Iodine is known to catalyze both the thermal and the photoisomerization of some olefins and halogenated alkenes.[27-30] Non-iodine-induced thermal isomerization of *cis*-polybutadiene has also been reported to occur, albeit under much more severe conditions.[31]

Effects of UV Irradiation. A *cis*-1,4-polybutadiene/iodine solution in cyclohexane was exposed to UV irradiation (without using diphenyl disulfide as the photosensitizer) to further demonstrate the I_2-enhanced cis–trans isomerization. Figure 10 shows the UV/vis spectra before and after UV irradiation. It is evident that UV exposure brought about an increase in the optical absorbance, accompanied by the emergence of several weak bands below 450 nm characteristic of various short polyene sequences. Prolonged UV exposure of a *cis*-1,4-polybutadiene/I_2 solution, however, caused the absorbances corresponding to polyene structures to diminish, indicating decomposition of the conjugated structures.

Also, an important check on the intramolecular origin of the different behavior of *cis*- and *trans*-1,4-polybutadienes upon I_2 doping was made by carrying out the photosensitized cis–trans isomerization of *cis*-1,4-polybutadiene in a more controlled fashion: Using diphenyl disulfide as the photosensitizer, *cis*-1,4-polybutadiene was isomerized as described in the Experimental Section, and the resultant material, I_2-doped at room temperature. The ^{13}C NMR spectra (Figure 11) demonstrated the extent of the photosensitized cis–trans isomerization. Figure 11a shows the ^{13}C NMR spectrum of as-received *cis*-1,4-polybutadiene, a spectrum which is characterized by two peaks at 129.56 and 27.38 ppm assignable to the olefinic and aliphatic carbons, respectively. The ^{13}C NMR spectrum of the photoisomerized polybutadiene (Figure 11b) showed a marked loss of intensity from the resonances characteristic of *cis*-1,4-polybutadiene, while two new peaks appeared at 129.97 and 32.68 ppm, which were assigned to the olefinic and aliphatic carbons of *trans*-1,4-polybutadiene, respectively, on the basis of published data.[18,31] The intensity of the peaks at 27.38 and 32.68 ppm in Figure 11b suggests a conversion to about 79% trans-1,4 isomer. No signals were observed between 160 and 200 ppm, a region where carbonyl groups would be found, which indicates that photooxidation is not of significance.

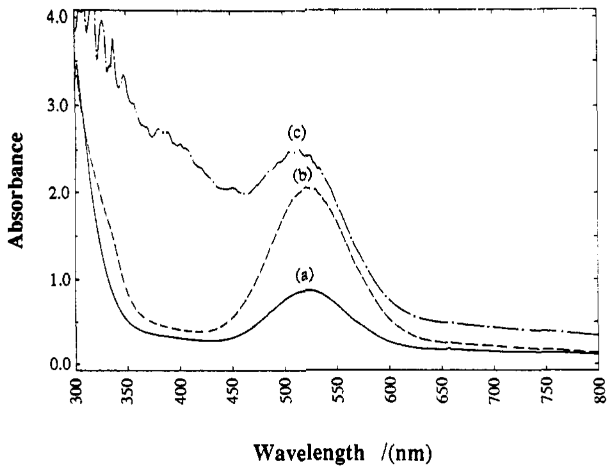

Figure 10. UV/vis spectra of a *cis*-1,4-polybutadiene/I_2 solution in cyclohexane at different UV irradiation times under the conditions of expt. no. 7 of Table 2: (a) not irradiated (i.e., curve a of Figure 5B); (b) after UV irradiation for 10 min; (c) after UV irradiation for 30 min.

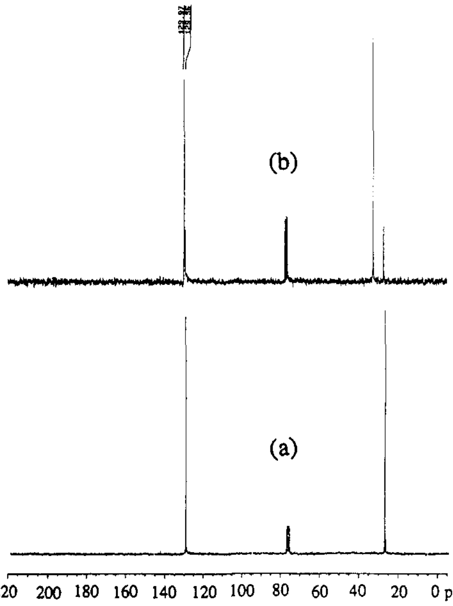

Figure 11. ^{13}C NMR spectra of *cis*-1,4-polybutadiene (a) before and (b) after 1 h of photosensitized cis–trans isomerization (see text): (a) pristine *cis*-1,4-polybutadiene; (b) after UV irradiation for 1 h.

The UV-isomerized 1,4-polybutadiene material was used for reaction with iodine at room temperature (see expt. no. 8 of Table 2). UV/vis spectra very similar to those of

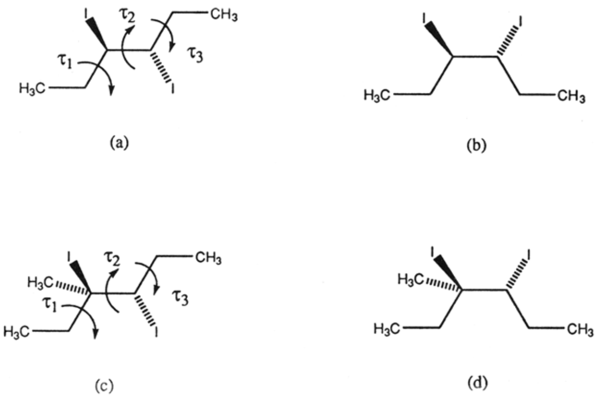

Figure 12. Model structures used for molecular orbital calculations: (a) I_2-reacted *trans*-1,4-polybutadiene structure unit; (b) I_2-reacted *cis*-1,4-polybutadiene structure unit; (c) I_2-reacted *trans*-1,4-polyisoprene structure unit; (d) I_2-reacted *cis*-1,4-polyisoprene structure unit.

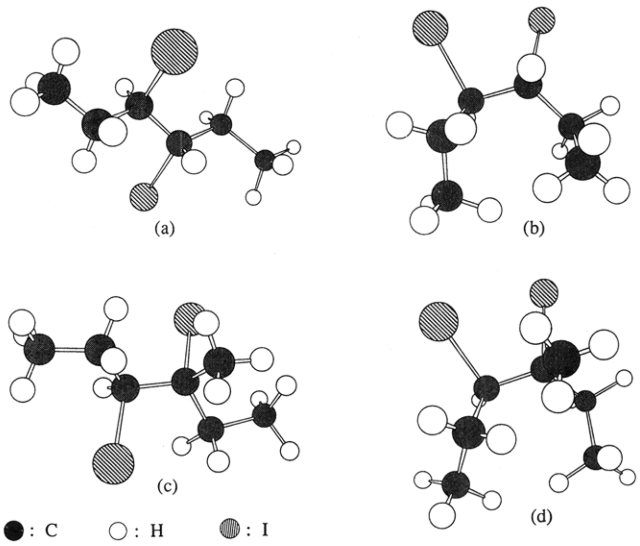

Figure 13. Lowest energy conformations from molecular orbital calculations: (a) I_2-reacted *trans*-1,4-polybutadiene structure unit; (b) I_2-reacted *cis*-1,4-polybutadiene structure unit; (c) I_2-reacted *trans*-1,4-polyisoprene structure unit; (d) I_2-reacted *cis*-1,4-polyisoprene structure unit.

reactions with the commercial *trans*-1,4-polybutadiene (Figures 3A and 8B) resulted.

Discussion

Previous studies[1–7] have documented that, whereas *trans*-1,4-polybutadiene can be made electrically conducting by iodine-doping, the cis isomer does not attain similar conductivity. Our results confirm these findings indirectly by showing spectroscopically that the reaction between *cis*-1,4-polybutadiene and iodine does not lead to the formation of conjugated double-bond structures—conductivity requires the presence of such structures. The question is, why does I_2 doping of *cis*-1,4-polybutadiene at room temperature not produce conjugated double-bond sequences when the doping of the trans isomer does.

Our results also show that iodine does become incorporated into the cis isomer and can be used to catalyze the formation of conjugated sequences when the sample is held at 60 °C. In fact, the addition of iodine to the cis isomer appeared to proceed at a faster rate. Evidently, the different conductivities attained at room temperature upon iodine doping of *trans*- and *cis*-1,4-polybutadienes are not caused by different reactivities of the polymers toward the addition of iodine but are related to the elimination of HI, an elimination which proceeds at room temperature in the case of the trans isomer but requires elevated temperatures for the cis isomer.

The ease of elimination of HI can depend on the molecular weight of the polymer. It has been demonstrated that the iodine doping of polyisoprenes was more effective at higher molecular weights; this is due to a "zipping" mechanism for the elimination of HI, where the first double bond formed facilitates successive adjacent eliminations of HI.[8] In the present case, however, Table 1 shows that the *cis*-1,4-polybutadiene used has a higher molecular weight than the trans isomer and therefore should eliminate HI faster if a zipping mechanism dominated the rate.

The elimination of HI usually can be described in terms of an E-2 elimination mechanism.[32] E-2 eliminations proceed most readily when the groups being eliminated are situated trans to each other and coplanar with the two intervening carbon atoms. They also proceed more quickly and more completely when elimination is from a tertiary carbon.[33] This was investigated by molecular orbital calculations on model structures.

The model structures shown in Figure 12 were used to explore the conformational properties of *cis*- and *trans*-1,4-polybutadiene and -polyisoprene chains. For each model structure the three staggered conformations of the three rotatable torsion angles were optimized using molecular orbital calculations. This resulted in 27 conformational calculations for each model structure. The choice of three rotamers for each torsion angle was validated by preliminary molecular mechanics calculations of the conformational energy surface of the models.

Molecular orbital calculations on the *trans*-1,4-polybutadiene model showed that the all-trans conformation ($\tau_1 = -168°$, $\tau_2 = 180°$, $\tau_3 = 168°$) had the lowest energy. In this conformation the HCCI torsion angles were ±162° (see Figure 13a). In the *cis*-1,4-polybutadiene model the lowest energy conformation (Figure 13b) was gauche$^-$, gauche$^+$, gauche$^-$ ($\tau_1 = -91°$, $\tau_2 = 80°$, $\tau_3 = -96°$). The torsion angles deviated significantly from the normal ±60° observed for unhindered gauche conformations. In this conformation the HCCI torsion angles were −88° and −82°.

The lowest energy conformation which had a favorable geometry for HI elimination from the cis isomer was the trans, gauche$^-$, trans configuration, with an energy 2.4 kcal/mol above that of the global minimum in this model system. This suggests that a configurational mechanism could explain not only the lack of conjugated sequence formation in *cis*-1,4-polybutadiene at room temperature but also the formation of conjugated sequences at 60° from iodine-doped polymer, as the higher temperature allows the higher energy conformations with favorable HI elimination geometries to be populated.

Molecular orbital calculations on the *trans*-1,4-polyisoprene model showed that the all-trans conformation ($\tau_1 = 159°$, $\tau_2 = 164°$, $\tau_3 = 166°$) and the trans, trans, gauche$^+$ conformation ($\tau_1 = 163°$, $\tau_2 = 146°$, $\tau_3 = 69°$) had the lowest energy (0.2 kcal/mol difference in energy between the two conformations). In the all-trans conformation the HCCI torsion angles were 163° and 166° (see Figure 13c). The *cis*-1,4-polyisoprene model had a lowest energy conformation (Figure 13d) which was again gauche$^-$, gauche$^+$, gauche$^-$ ($\tau_1 = -71°$, $\tau_2 = 89°$, $\tau_3 = -111°$). Again the torsion angles deviated significantly from the normal ±60° observed for unhindered gauche conformations. In this case the HCCI torsion angles were −60° and −112°.

Conformational analysis of the *cis*-1,4-polyisoprene model suggests additional complexity in the mechanism of conjugated bond formation. The −112° torsion angle is nearer to trans geometry than is the lowest energy *cis*-1,4-polybutadiene model conformation. The −60° torsion angle involves a tertiary carbon to which is bound the isoprene methyl side group. HI elimination proceeds much faster, and to a greater extent, when tertiary carbons are involved. Consequently, it appears that, for the *cis*-1,4-polyisoprene case, conformational effects are not sufficient *per se* to promote HI elimination. It is likely that the more favorable HCCI torsion angle (−112° *cf.* −82° for the *cis*-1,4-polybutadiene) coupled with the greater rate and extent of HI elimination from a tertiary carbon is required to obtain HI elimination for *cis*-1,4-polyisoprene.

Thus, our molecular orbital calculations using models for *trans*-1,4-polybutadiene and *trans*-1,4-polyisoprene showed that the all-trans conformation had the lowest energy. In this conformation the HCCI torsion angles are close to the most favorable conformation for HI elimination via the E-2 mechanism. In contrast, however, in the case of the *cis*-1,4-polybutadiene model the lowest energy conformation had HCCI torsion angles nearly orthogonal to those required for optimal HI elimination. In this case the common trans geometry for E-2 elimination and the much less common cis-elimination geometry both were not accessible. These simplified models suggest that intramolecular, conformational effects may be invoked to rationalize the observed ready elimination of HI by the I_2-reacted *trans*-1,4-polybutadiene and the lack of HI elimination by the cis isomer at room temperature.

The results from *cis*-1,4-polyisoprene indicate that, while the molecular configuration is a key factor in the E-2 elimination of HI, it appears that side groups on the double-bond structures can also have a pronounced effect. Tertiary carbon atoms in *cis*-1,4-polyisoprene facilitate elimination; it appears that they may (partly) compensate for less favorable geometries. In the case of *cis*-1,4-polybutadiene, however, both a very unsuitable molecular geometry and the lack of tertiary carbon atoms mitigate against HI elimination at room temperature. By the same argument, HI should be readily eliminated from I_2-reacted *cis*- and *trans*-1,4-poly(2,3-dimethylbutadiene)s, since both carbons to which iodine may be bonded are tertiary. This is consistent with experimental observations.[1]

Clearly, therefore, experimental results and molecular orbital calculations indicate that differences in molecular properties, rather than intermolecular packing, can explain the differences observed between *cis*- and *trans*-1,4-polybutadienes following I_2 doping.

Conclusions

Our results provide a rationale for previous observations that *cis*-1,4-polybutadiene, unlike *trans*-1,4-polybutadiene and polyisoprenes, fails to become conductive on I_2 doping. This is a result of an unfavorable combination of electronic and steric interactions within the iodinated polymer backbone which inhibit the E-2 elimination of hydrogen iodide and thus halt the formation of conjugated sequences at room temperature. In contrast, the *trans*-1,4-polybutadiene/iodine addition product can readily adopt a favorable configuration, resulting in HI elimination and the formation of the conjugated sequences along the polymer backbone necessary to confer electrical conductivity on the I_2-reacted polymer. However, both heating and UV isomerization result in I_2-induced conjugation of *cis*-1,4-polybutadiene. The difference in behavior upon iodine doping between *trans*- and *cis*-1,4-polybutadiene macromolecular chains can thus be explained in terms of *intramolecular* rather than intermolecular (packing) interactions.

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