Soluble conducting polymers from polyisoprene

Liming Dai and J. W. White*
Research School of Chemistry, The Australian National University, PO Box 4, Acton 2601, Australia
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Recently, 1,4-polyisoprene has been reported to be a prototype of electrically conducting polymers having non-conjugated backbones. In this paper we demonstrate for the first time that 'I_2-doping' of 1,4-polyisoprene yields soluble conjugated conducting polymers through double bond shifting reactions. These reactions, in both solution and the solid state, are described. The formation of conjugated sequences of unsaturated double bonds in the polyisoprene backbone is followed by ultraviolet/visible and magnetic resonance spectroscopy. The sequences are stable and, resembling polyacetylene, they are probably responsible for the high conductivity of 'I_2-doped' polyisoprene.

(Keywords: soluble conducting polymers; polyisoprene; conjugation; charge-transfer complexes; spectroscopic studies)

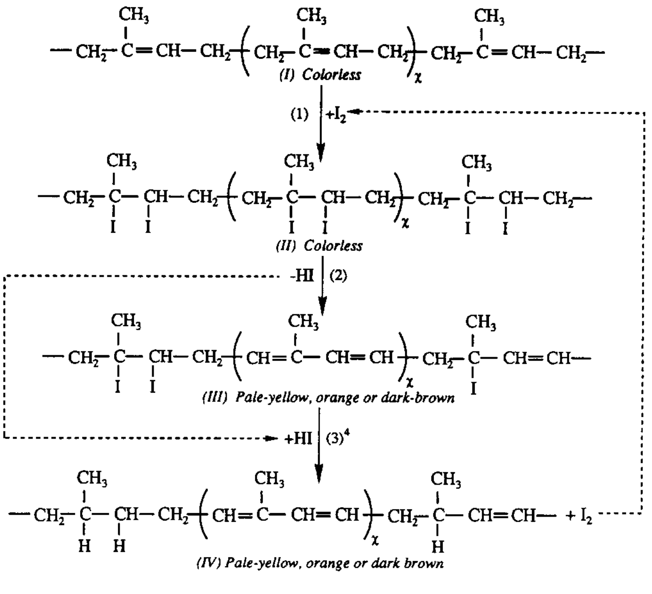
INTRODUCTION

Having a π-electron conjugated backbone has been widely believed to be a necessary condition for a polymer to be electrically conducting[1]. Recently, Thakur argued that in association with appropriate substituents and dopants some non-conjugated polymers may also become electrically conducting[2,3]. In particular, he demonstrated that 1,4-polyisoprene, a prototype of so-called conducting polymers having non-conjugated backbones, can be doped by I_2 to become a semiconductor having conductivity in the range 10^{-2}–$10^{-1}\,\Omega^{-1}\,cm^{-1}$. On this basis, he concluded that a conjugated backbone is not always necessary for a polymer to be electrically conducting. The results in this paper show for the first time that 'I_2-doping' of polyisoprene produces, by double bond shift reactions[4,5], conjugated sequences of unsaturated double bonds in the polyisoprene backbone. The polymer so transformed thus has the narrow molecular weight distribution of its precursor, is soluble in most organic solvents and closely resembles the soluble polyacetylenes made by copolymerization[6,7]. Thakur's conclusion should therefore be treated with some caution. In the following, we set out some of the chemistry of the transformation. Evidence for double bond shifting with reagents like I_2 has been recently reviewed[5] and a possible mechanism for the formation of conjugated sequences of unsaturated double bonds in the polyisoprene backbone in the presence of I_2 is shown in *Scheme 1*.

EXPERIMENTAL

Materials

1,4-addition polyisoprene (1,4-PI) was synthesized by anionic polymerization of isoprene with butyllithium in toluene at 300 K. All solvents used, both in the synthesis and subsequent reactions, were first distilled from P_2O_5 under N_2 and further purified by distillation from calcium hydride under high vacuum (10^{-7} kPa). All operations were conducted in vacuum or under pure argon. The concentration ratio of n-butyllithium to monomer determines the molecular weight of the polyisoprene produced. The polymerization reaction was followed by ultraviolet/visible (u.v./vis.) spectrosocopy. The reaction in the closed system was allowed to go to completion, and then the living polymer was killed by addition of a stoichiometric amount of methanol to produce the polyisoprene. The termination was clearly indicated by the immediate colour change from pale yellow to colourless for the reaction solution. Polymers were coagulated and dried under high vacuum at room temperature in a manner similar to recovering polyisoprene samples from anionic polymerization products for microstructure analyses[8], except for addition of antioxidant. Before use, the



Scheme 1 Reaction of polyisoprene with I_2 leading to the formation of conjugated sequences

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* To whom correspondence should be addressed

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1,4-polyisoprene samples thus obtained were stored under argon in a refrigerator and protected from light as much as possible.

Reagent grade I_2 from General Chemical Company was stored over silica gel in a desiccator and used without further treatment and chloroform-D (99.8% D with 0.05% TMS) was used for nuclear magnetic resonance (n.m.r.) analyses of the polyisoprene and subsequent reaction products.

Characterization of polyisoprene

The polyisoprene synthesized by the above method was characterized by gel permeation chromatography (g.p.c., Waters Associates g.p.c. system), small angle X-ray scattering (SAXS, Huxley–Holmes slit-collimated SAXS)[9] and n.m.r. (Varian XL-200). The g.p.c. and SAXS measurements give molecular weights in close agreement, with a relatively narrow molecular weight distribution (typically $M_w/M_n < 1.10$) as expected for polyisoprene prepared by anionic polymerization[10].

The ^1H and ^{13}C n.m.r. spectra of the polyisoprene solutions show the characteristic resonances of the 1,4-addition isomer. Following Chen[11] and Grant's[12] assignments of ^1H and ^{13}C n.m.r. spectra for polyisoprene, respectively, the composition of the polyisoprene was estimated to be 1,4-PI>95% with a relatively small amount of the 3,4-addition isomer.

RESULTS AND DISCUSSION

Reactions in solution

Conjugation reaction. As an initial approach, we carried out the conjugation reactions shown in *Scheme 1* simply by dissolving a fixed ratio of polyisoprene to I_2 in vacuum-distilled toluene in a 1 mm thick quartz u.v. cell sealed with a stopper and parafilm. The effects of temperature and polyisoprene molecular weight were studied. In order to exclude oxygen, all the manipulations were done in a glove-bag under high purity argon atmosphere. The u.v./vis. absorption spectrum of the solution was measured *in situ* on a HP48000 spectrometer at intervals. The reaction conditions for each of the experiments are summarized in *Table 1*.

The characteristic decolourization of I_2 upon reaction with polyisoprene occurs at low mole ratios of I_2 to double bonds. As can be seen in *Table 1*, for more concentrated solutions and elevated temperatures colour changes occurred from purple, characteristic of I_2 in toluene, to pale green and other colours with reaction progress. The observed colour change resembles that previously reported for dehydrohalogenation of poly(vinyl chloride) (PVC)[13], suggesting that structures of various conjugated sequences, $(\text{–CH=CH–})_n$, are responsible for the development of pale yellow ($n=3$) to orange ($n=4$ –7) and dark brown ($n \geqslant 8$) in the polyisoprene–I_2 solutions during the conjugation reaction. These changes were analysed spectrophotometrically.

Figure 1 shows the u.v./vis. spectra recorded *in situ* for a solution of 15 mol double bonds in PI_{8000} ($M_w = 8000$)/ mol I_2 at room temperature. At the start of the reaction (trace a) there is a monotonously decreasing optical absorbance below 400 nm (due to the polyisoprene) and an absorption band at 500 nm characteristic of molecular I_2 in toluene (the I_2–toluene charge-transfer spectrum). As the reaction proceeds, the I_2 band drops indicating that polar addition of I_2 to polyisoprene chains occurred, and the continuous shift in the edge of the polyisoprene absorption to lower wavelengths may reflect an associated decreasing in the average length of the polyisoprene segments.

The disappearance of the strong peak at 500 nm is accompanied by the emergence of several weak bands at shorter wavelengths, attributable to various $(\text{–CH=CH–})_n$ sequences (*Figure 1d*).

The initial rates of reaction can be measured from the time dependence of the absorbance at 500 nm. This has been done at several temperatures to get an indication of the activation energy. As shown in *Figure 2*, the optical

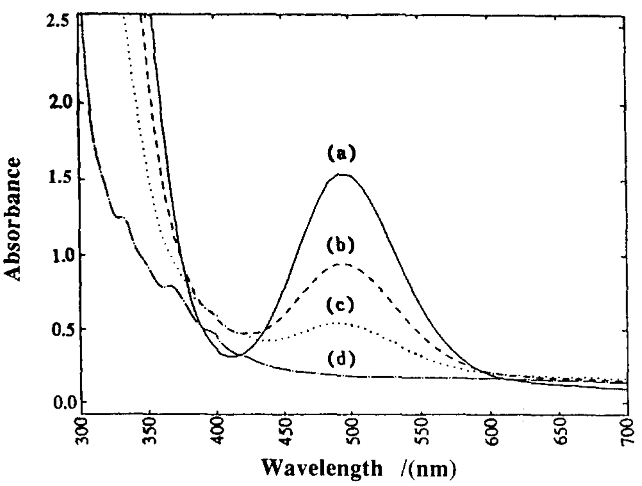


Figure 1 Ultraviolet/visible spectra of 1,4-polyisoprene–I_2 in toluene under the conditions of experiment 3: (a) before reaction; (b) 20 h; (c) 27 h; (d) 44 h

Table 1 Experimental conditions for conjugation of polyisoprene

Expt no.	M_w of PI	Conc. of PI (g ml^{-1})	Conc. of I_2 (g ml^{-1})	[C=C]/[I_2]	Temp. (°C)	Observations
1	8000	0.015	0.0037	15	0	Purle → pale green
2	8000	0.015	0.0037	15	10	Purple → pale green
3	8000	0.015	0.0037	15	22 → 60	Purple → pale green (colourless) → pale yellow → orange → dark brown
4	8000	0.015	0.0037	15	40	Purple → pale green → pale yellow
5	8000	0.015	0.0037	15	60	Purple → pale green (colourless) → pale yellow → orange → dark brown
6	16000	0.15	0.037	15	22	Purple → pale green → pale yellow

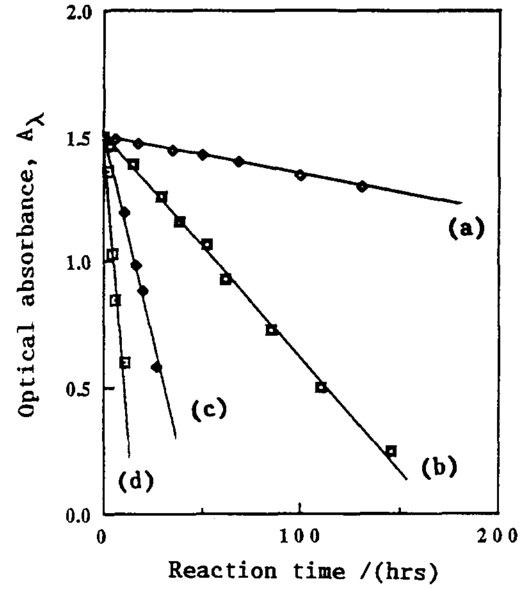


Figure 2 Dependence of optical absorbance at a wavelength of 500 nm upon the reaction time for addition of I_2 into 1,4-PI_{8000} at various reaction temperatures: (a) 0°C; (b) 10°C; (c) 22°C; (d) 40°C

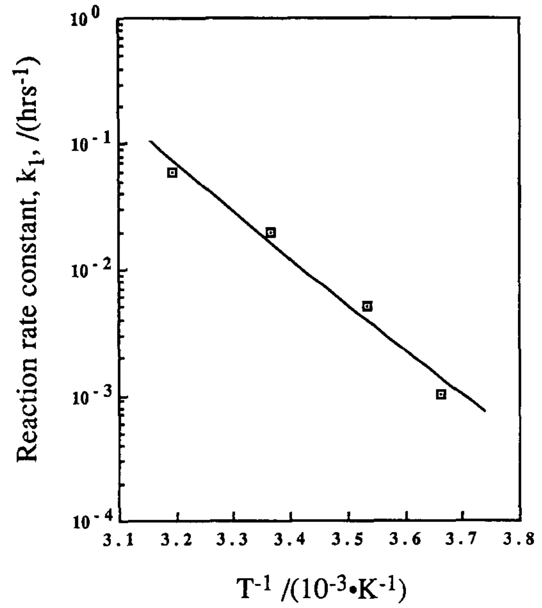


Figure 3 Arrhenius plot for addition of I_2 into 1,4-polyisoprene chain with molecular weight of 8000

absorbance at 500 nm decreases linearly with reaction time in the temperature range covered. The pseudo first-order initial reaction rate constants, k_1, were in the range 0.001–0.06 (h^{-1}). By plotting $\log k_1$ against $1/T$ (*Figure 3*) the good linear relation gives 52.3 kJ mol^{-1} for the activation energy, ΔE_a, of the polar addition reaction. The low activation energy thus obtained may indicate that the direct addition of I_2 to olefinic double bonds occurred quickly presumably due to the presence of electron repulsive groups of $-CH_3$ on the $-C{=}C-$ bonds. In fact, such a reaction has been suggested by Benson and Bose[4].

Further evidence for the polar addition of I_2 to polyisoprene comes from the infra-red (i.r.) spectra of thin polymer films vacuum-cast from a polyisoprene solution onto a CsI disc. The spectra before and after reacting with I_2 in solution are shown in *Figure 4*. The bands at 840 cm^{-1} and 1670 cm^{-1} correspond to bending and stretching vibrations of isolated C=C bonds of the native polyisoprene chains. These decrease rapidly with iodination, a new band developing at 439 cm^{-1} which is assigned to the C–I stretching vibration (465 cm^{-1}) altered somewhat as a result of interactions with neighbouring groups[14]. The i.r. spectra for polyisoprene heavily reacted with I_2 will be discussed below.

The evolution in time of a reaction between higher molecular weight polyisoprene ($M_w = 16\,000$) and an equivalent amount of I_2 is shown in *Figure 5*. All peaks in the u.v./vis. spectrum (*Figure 5*) can be assigned by comparing their peak positions to wavelengths for the strongest absorption bands of various $H{-}(CH{=}CH)_n{-}H$ model compounds[13] as listed in *Table 2*. The excellent coincidence between the band positions shown in *Figure 5*

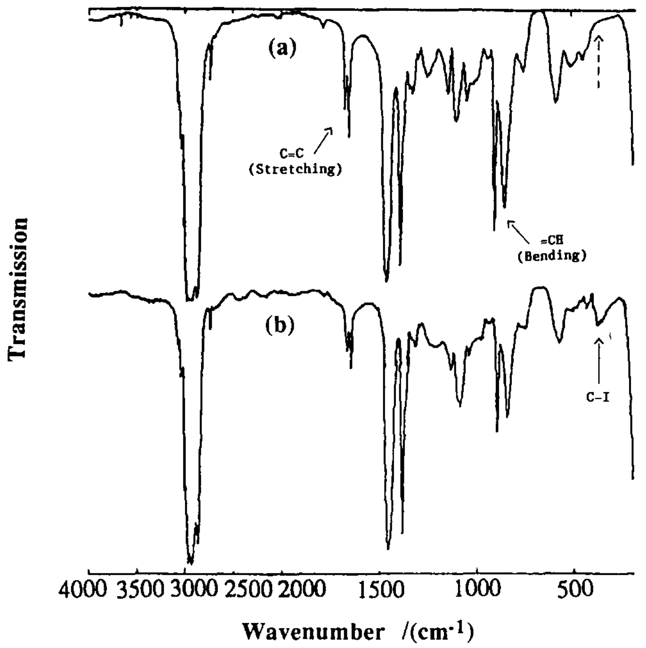


Figure 4 Fourier transform infra-red spectra of 1,4-PI_{8000} before and after reacting with I_2 under the conditions of experiment 3: (a) pristine 1,4-polyisoprene; (b) reacted with I_2 for 30 h

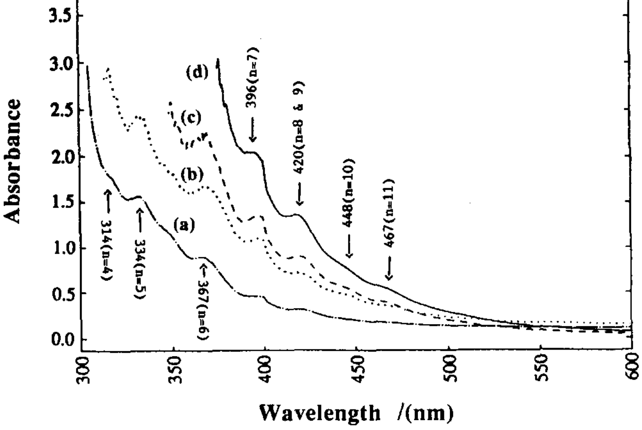


Figure 5 Ultraviolet/visible spectra of 1,4-PI_{16000}–I_2 in toluene at different reaction times under the conditions of experiment 6: (a) 18 h; (b) 26 h; (c) 54 h; (d) 958 h

Table 2 Molar absorption coefficient of $H{-}(CH{=}CH){-}H$[13]

Number of conjugated double bonds, *n*	Wavelength where the strongest absorption occurs, λ (nm)	Molar absorption coefficient, $\varepsilon_\lambda \times 10^3$
3	268	34.6
4	304	73.0
5	334	121.0
6	364	138.0
7	390	174.0
8	410	203.5
9	428	233.0
10	447	261.0

and those of *Table 2* strongly suggests that conjugated sequences with up to 10 double bonds have been introduced into the polyisoprene chains. Moreover it appears that for this higher molecular weight starting material the average length of the conjugated sequence is greater than for PI_{8000} and that this length increases with reaction time.

A literature survey shows that similar u.v./vis. spectra have been reported by several investigators for PVC after dehydrohalogenation[13,15,16]. Clearly, therefore, one question which needs to be answered is what kind of polymer (pure conjugated polymer, random or block copolymers) has resulted from I_2-induced bond shift conjugation of polyisoprene.

From *Figure 5* several main points emerge. By plotting the *n* value *versus* the square of the wavelength for each of the absorption bands shown in *Figure 5* a straight line was obtained for all of the points (except the band at 420 nm which is intermediate in position between the band positions for $n=8$ and 9). This indicates that the Lewis–Calvin equation, $\lambda^2 = kn$, is obeyed fairly well[17] and implies that the properties of the conjugated sequences formed in polyisoprene–I_2 solution resemble those of the corresponding dimethylpolyenes, from which the Lewis–Calvin equation was deduced. Thus, the absorption positions of conjugated sequences obtained from polyisoprene–I_2 were calculable from a single value of *k*. A correlation of expected and found value for $k=17\,532$ is shown in *Figure 6*.

A molecule with different conjugated sequences isolated from one another will show separated absorptions[17]. Given the known ratio of the molar extinction coefficients the wave-like shape of the spectra of *Figure 5* may allow the number distribution of polyenes as a function of *n* to be deduced.

The evolution of the spectrum of *Figure 5* with time has two interesting aspects. There is a general intensification at short wavelength, compared to the starting material, and this eventually makes the short wavelength bands invisible without dilution. There is also an apparent continued growth in conjugation length illustrated by the appearance of bands at 448 ($n=10$) and 467 nm ($n=11$) after 950 h at 22°C.

The observed red-shifting can be explained by assuming that elimination of HI proceeds by the 'zipping' mechanism proposed for dehydrohalogenation of PVC by Tsuchida *et al.*[18]. This mechanism suggests that as soon as a double bond is formed on the polymer chain through the elimination reaction, the α-position relative to the double bond becomes activated allowing succeeding double bonds to be easily formed. Thus, the first double bond acts as the key of a zip fastener and leads to propagation of the polyene. Therefore, the short conjugated sequences formed in the initial stage of the elimination reaction should increase in chain length with reaction time.

Figure 7 shows how the concentrations of various conjugated sequences, $(-CH{=}CH-)_n$, calculated by Beer's law evolve relative to the concentration of $n=6$ as the reaction proceeds at 22°C. The steeper slope of the straight lines in *Figure 7* for smaller *n* indicates a higher molar concentration for the $(-CH{=}CH-)_n$ with smaller *n*. This may imply that long conjugated sequences could retard the zipping reaction making the longer conjugated sequences more difficult to form. In fact, Shindo and Hirai have reported that 21 kJ mol^{-1} is necessary to add one more double bond to the long sequence of conjugated polyene obtained by dehydrohalogenation of PVC[13].

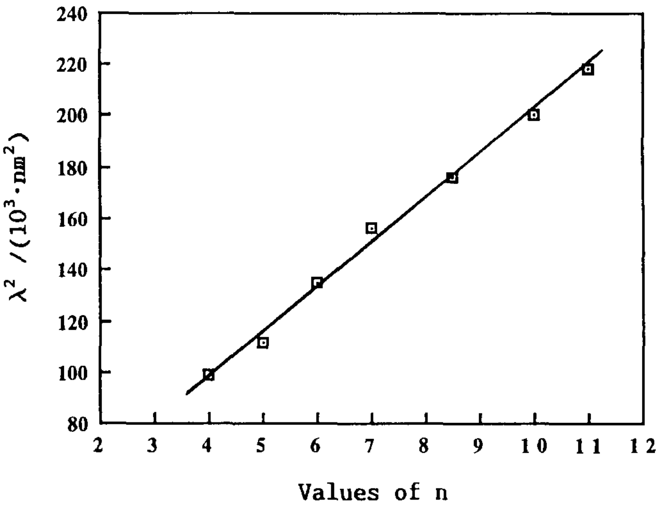


Figure 6 Relationship between the wavelength squared and the value of *n* for each of the absorption bands shown in *Figure 5*

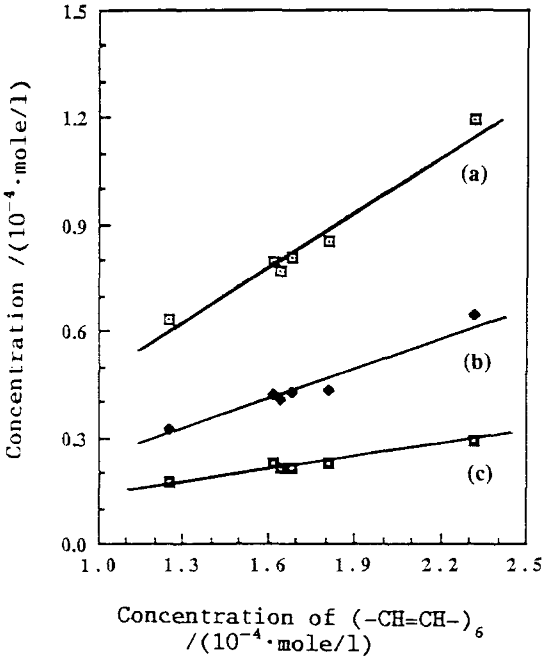


Figure 7 Plot of molar concentrations for various $(-CH{=}CH-)_n$ against that of $(-CH{=}CH-)_6$ at various stages of the conjugation reaction under reaction conditions of experiment 6: (a) $n=7$; (b) $n=8$ and 9; (c) $n=10$

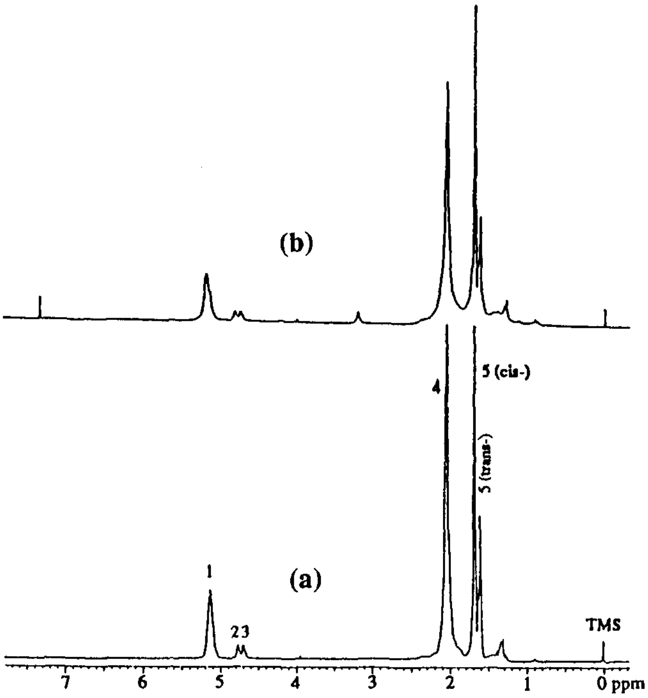


Figure 8 ^1H n.m.r. spectra of 1,4-polyisoprene before and after reacting with I_2 under the conditions of experiment 6: (a) pristine 1,4-PI_{16000}; (b) after reacting with I_2 for 11 days

Taking only the chains of length $6<n<10$ we estimate that about 3% of double bonds in the original 1,4-polyisoprene are converted to these sequences. We believe that there is even higher conversion to shorter sequences.

Further details of the conjugation reaction come from n.m.r. studies of the polyisoprene–I_2 solution. The ^1H n.m.r. spectra in *Figure 8* demonstrate the extent of reaction; the resonances characteristic of the protons in native 1,4-polyisoprene at 2.06, 4.79 and 5.15 ppm were greatly reduced in intensity. A new peak at 7.25 ppm, although near the expected shift for protons in a conjugated chain[19,20] is very narrow, close to the resonance expected for any $CHCl_3$ impurity in the solvent and so is attributed to the impurity. The ^{13}C n.m.r. spectra in *Figure 9* also show a progressive loss of intensity from the resonances characteristic of native polyisoprene as the reaction proceeds. The new bands at 128 and 129 ppm which increase in intensity with reaction time, though close to the expected shifts for polyacetylene[20,21], are provisionally assigned to trapped toluene released from the polymer during the measurements. They were much weaker when the reaction was repeated with polyisoprene in cyclohexane. The newly produced polymer is thus unobserved in these spectra possibly due to long correlation times associated with aggregation.

Effects of temperature on the conjugation reaction. The process of elimination of HI and the regeneration of I_2 through reaction III in *Scheme 1* were enhanced by heating. Upon heating at 60°C, the pale green solution from experiment 3 changed colour from pale green passing through pale yellow to orange and dark brown. *Figure 10* illustrates changes of the u.v./vis. spectra for the pale green solution (i.e. *Figure 1d*) upon heating at 60°C. Two distinct aspects of the change are noticeable: evolution of the band at 480 nm and then its reduction, with an isobestic point near 500 nm, as the strong absorption at 560 nm develops; comparing the spectra shown in *Figure 10* with those in *Figure 5* suggests that different mechanisms for the elimination of HI operate at different temperatures. An immediate effect of temperature is to generate some of the molecular I_2–toluene complex. The band at 480 nm is associated with a polyene charge-transfer complex with the extra I_2 being provided by elimination in the final step of *Scheme 1*. With further heating this evolves to a charge-transfer complex of an

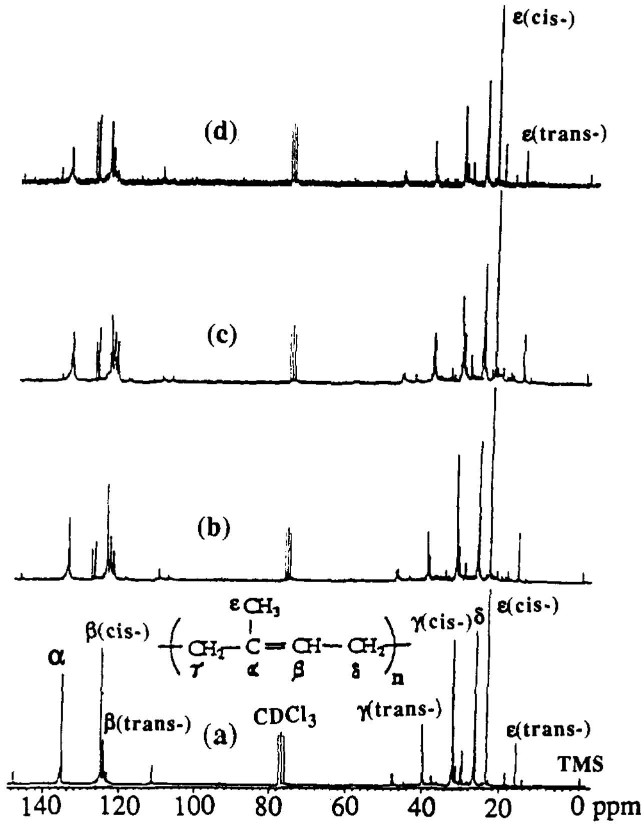


Figure 9 ^{13}C n.m.r. spectra of 1,4-polyisoprene before and after reacting with I_2 for different periods under the conditions of experiment 6: (a) pristine 1,4-PI_{16000}; (b) 4 days; (c) 11 days; (d) 16 days

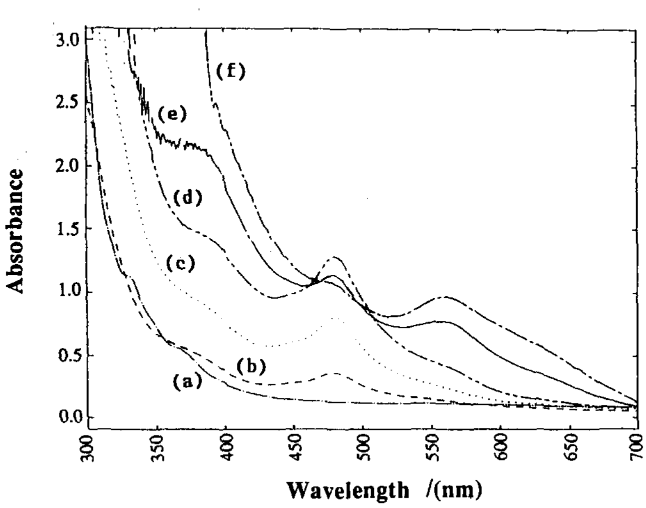
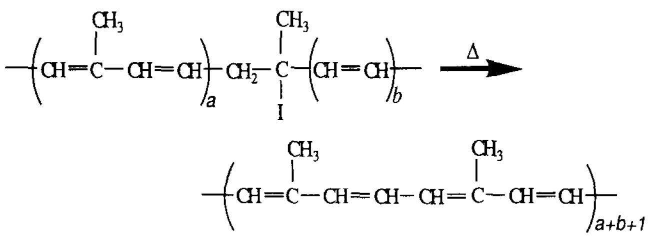


Figure 10 Ultraviolet/visible spectra of a pale green 1,4-PI_{8000}–I_2 solution in toluene at different reaction times upon heating at 60°C under the conditions of experiment 3: (a) before heating (i.e. *Figure 1d*); (b) 60°C for 80 h; (c) 60°C for 120 h; (d) 60°C for 190 h; (e) 60°C for 455 h; (f) 60°C for 730 h



Scheme 2 Transition of short to long conjugated sequences at high temperature

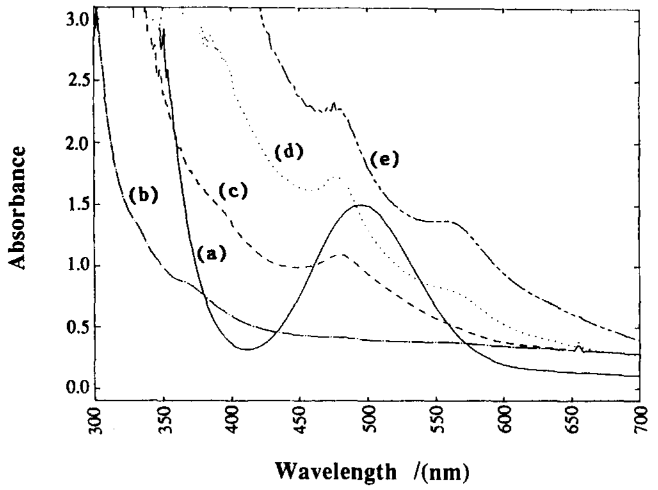


Figure 11 Ultraviolet/visible spectra of 1,4-PI$_{8000}$–I$_2$ solution in toluene at different reaction times at 60°C under the conditions of experiment 5: (a) before reaction; (b) 6 h; (c) 72 h; (d) 140 h; (e) 290 h

even longer polyene (absorption at 560 nm), possibly through the mechanism of *Scheme 2*. It should be noted that the charge-transfer bands are much stronger than the π–π^* polyene bands. The conjugated sequences finally obtained at high temperature (say at 60°C) may thus be longer with narrower distribution in conjugated chain lengths than those obtained at lower temperatures.

In view of the results at elevated temperatures, experiment 5 was run at 60°C to try and obtain long conjugated sequences with narrow distribution in segment length. As seen in *Figure 11*, this aim was realized. The final product solution was dark brown. The ^{1}H and ^{13}C n.m.r. spectra of this dark brown conjugated polyisoprene solution (*Figure 12*) show nearly complete loss of all the resonances characteristic of native polyisoprene except those corresponding to the $-CH_3$. This is presumably due also to the conjugation reaction and/or the subsequent aggregation mentioned above. Another significant feature shown by the ^{13}C n.m.r. spectra (*Figure 12b*) is the absence of any evidence for carbonyl groups (C=O) (between 160 ppm and 200 ppm), which might be introduced in the high temperature reaction if air had entered the cell.

Reactions in solid films

Standard procedures[2,21] have been adopted to carry out I_2 (gas) doping of polyisoprene film. As seen in *Figure 13*, prior to doping, the polyisoprene film is colourless[1]. As the doping proceeds, the optical density increases strongly but, with care, two broad bands can be observed. The colourless polyisoprene film turned

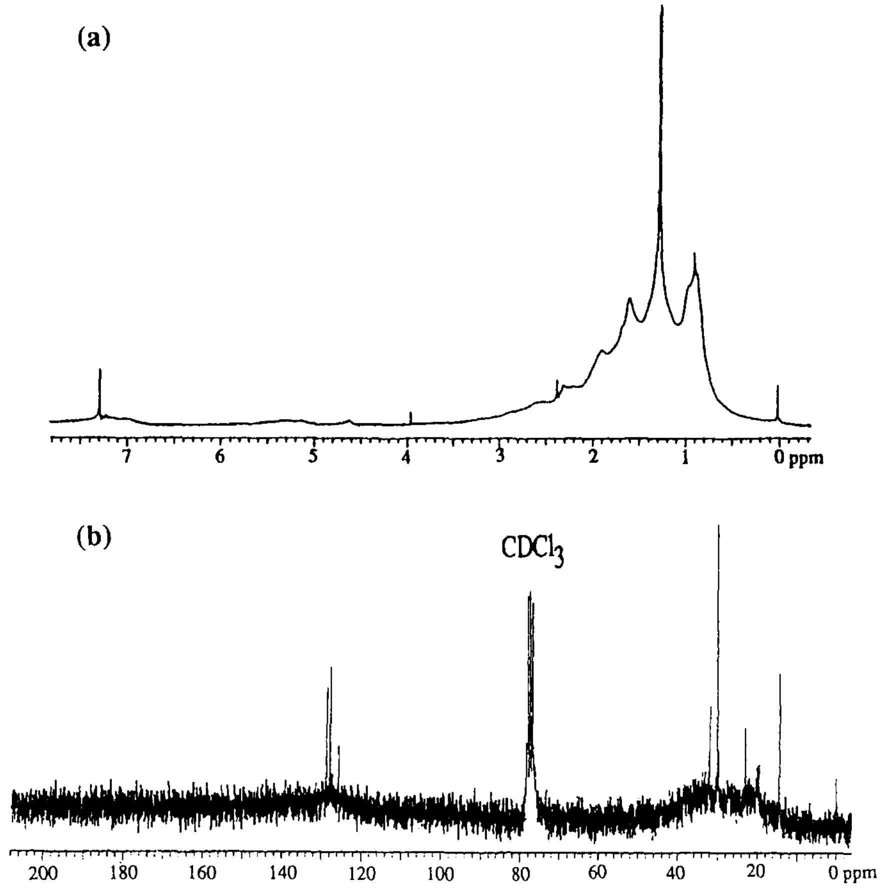


Figure 12 (a) ^{1}H and (b) ^{13}C n.m.r. spectra of the highly conjugated polyisoprene formed at 60°C under the conditions of experiment 5

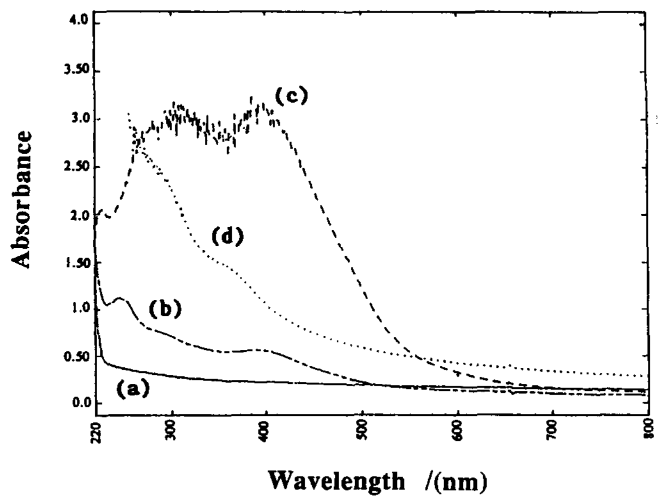


Figure 13 Ultraviolet/visible spectra of I_2(gas)-doped $1,4\text{-PI}_{8000}$ film: (a) undoped; (b) I_2-doped for 18 days; (c) I_2-doped for 40 days; (d) NH_3-compensated for 20 days

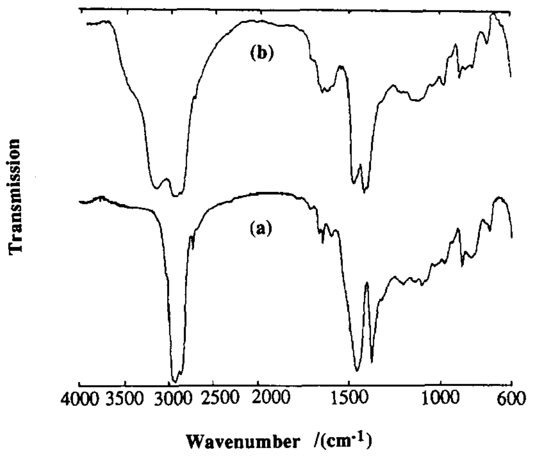


Figure 14 Fourier transform infra-red spectra of heavily I_2-doped and NH_3-compensated $1,4\text{-PI}_{16000}$ film: (a) heavily I_2-doped; (b) film (a) after NH_3 compensation

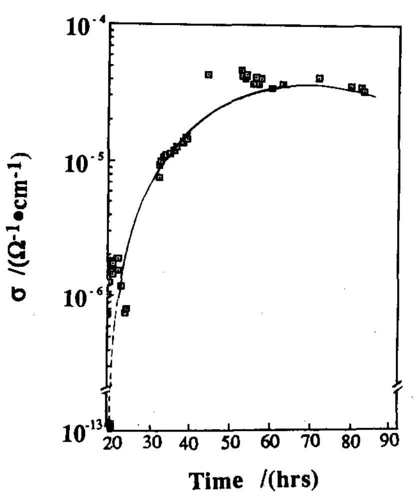


Figure 15 Electrical conductivity of $1,4\text{-PI}_{16000}$ film during the I_2 (gas) doping at 25°C. (The first point in this figure, the conductivity of the pristine polyisoprene, is from ref. 1. The limiting conductivity for our I_2-doped material is lower than that shown in ref. 1 presumably due to the different doping method used.)

successively pale yellow, dark brown and was black upon heavily doping with I_2. These changes agree with the observations made by Thakur[2,3].

At low doping levels, two broad bands at 243 and 400 nm are observed. Further doping caused the band at *c.* 243 nm to shift to *c.* 300 nm, which may reflect the transition from short polyene–I_2 charge-transfer compounds to I_2 charge-transfer complexes with longer polyenes, as mentioned above. However, the absorption band at 400 nm remained relatively unchanged in wavelength and may be attributed to the charge transfer between localized states, as pointed out by Thakur[2].

That explanation is supported by the u.v./vis. spectrum recorded after NH_3 compensation (*Figure 13d*), where the broad band centred on 400 nm is almost completely lost as the result of removal of the cation (hole) state. However, the increased intensity of the region between 240 nm and 380 nm remained with peaks corresponding to $n=4$ and 6, which unambiguously indicate that some conjugated structures have formed in the polyisoprene chains. The solid state reactions shown in *Scheme 1* were also confirmed by i.r. spectra (*Figure 14*), where the isolated C=C bend and stretch at 840 and 1670 cm^{-1} are almost completely lost upon heavily reacting with I_2. At the same time, the conjugated C=C stretching[16,22] appears at 1598 cm^{-1}. Upon compensating with NH_3, a band at 1000 cm^{-1} corresponding to C–H out-of-plane and a band at 3100 cm^{-1} appear (attributed to the stretching vibrations of C_{sp^2}–H in conjugated double bonds and to the N–H stretching vibrations). It has been reported that low molecular weight compounds of conjugated double bonds generally show multiplets in i.r. bands. In particular, the diene has two, the triene three and the tetraene four bands which are doublets or even higher multiplets[22], and an evaporated film of the hexaene gave four bands at 1567, 1611, 1635 and 1664 cm^{-1}. By analogy, therefore, the multiplet broad band centred at *c.* 1600 cm^{-1} most probably represents the sequences of conjugated double bonds in the I_2-doped polyisoprene.

A plot of the four probe electrical conductivity of a 1,4-polyisoprene film at 25°C during doping by I_2 shows that the conductivity increased by a factor of *c.* 10^8 (*Figure 15*). For this experiment I_2 powder was brought into contact with the perimeter of a vacuum-cast polymer film under an inert atmosphere. The observed kinetic curve is characterized by two features: a very long induction time (*c.* 20 h) and a very low overall doping rate. The doping curve resembles that for polyacetylene homopolymer in overall appearance[21,23] indicating diffusion-limited kinetics.

CONCLUSIONS

For the first time, we have demonstrated that soluble conjugated conducting polymers can be prepared from 1,4-polyisoprene either in solution or in solid state through double bond shifting induced by I_2. The effects of temperature, molecular weight of polyisoprene and concentration of polyisoprene on the conjugation reaction of 1,4-polyisoprene in the presence of I_2 have been investigated using u.v./vis., Fourier transform infra-red and n.m.r. spectroscopic techniques. The spectroscopic results show the formation of conjugated sequences of unsaturated double bonds in the polyisoprene backbone and from the magnetic resonance that these polyenes appear to be aggregated in some form. By extension, these results probably indicate that soluble conducting polymers could be obtained from many other polymers with isolated double-bond structures (e.g. poly(2,3-dimethylbutadiene), etc.) by double-bond shift reactions.

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