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Polyene sequences in iodinated polyisoprene

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The presence of polyene sequences, introduced into polyisoprene by interaction with molecular iodine in the solid phase and in chloroform solution has been established using fluorescence emission and excitation spectroscopy. Changes in the electrical conductivity of polyene films following the interaction have been measured and the mechanism of polyene formation is discussed. The results support the conclusions of other workers that the presence of conjugated sequences are a pre-requisite for conducting materials rather than the intersite hopping between carbocation centres derived from oxidation of isolated double bonds which has been suggested. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Since the discovery some twenty years ago that the electrical conductivity of intrinsically insulating or semiconducting materials containing conjugated π-electron systems could be increased by several orders of magnitude by a relatively simple chemical or electrochemical process, the mechanism by which the conduction occurs has been the subject of intense research interest. In attempts to clarify the most likely structural requirements for conductive behaviour, a number of π-conjugated polymers have since been prepared and investigated by a variety of techniques[1]. These include the synthesis of 'precursor polymers' which are not conjugated but into which π-electron structures can be introduced in a controlled way[2]. This procedure has the potential to overcome the processing difficulties associated with the insolubility and infusibility of fully conjugated polymers and seems to offer an attractive route to a commercially exploitable material, particularly when the precursor in question is a readily available and well characterized polymer such as poly(vinyl chloride) (PVC).

Polymers in which the π-electron sequences extend through the whole chain length have been found, not surprisingly, to be reactive towards atmospheric oxygen and one aspect on which attention has recently been focused[3,4] is the optimum length of uninterrupted polyene sequences which are required for conductivity to reach a useful level without causing a dramatic reduction in environmental oxidative stability.

In 1988, a suggestion was made by Thakur[5] which challenged the previously held assumption that long conjugated polyene sequences were a pre-requisite for the formation of conductive materials. Evidence was presented which indicated that polyisoprene or poly(dimethyl butadiene) but not polybutadiene, containing isolated double bonds could be doped with I_2 to form a material with a conductivity in the range 10^{-2}–10^{-1} S cm^{-1}, more than ten orders of magnitude higher than that of the polymer in its pristine state. The mechanism proposed involved intersite hopping between carbocation centres derived by oxidation of isolated double bonds. In a Raman spectroscopic study of the same system, Williams[6] showed that the spectrum of iodine doped polyisoprene contained strong resonances which were clearly analogous to those obtained previously for degraded PVC[7] or iodine doped polyethylene[8] and which could be assigned with confidence to polyene sequences $-(CH{=}CH)_n-$, with n in the range 8–11. These were accompanied by resonances attributed to I_3^- anions. The mechanism suggested in this case involved addition of iodine to the double bond followed by dehydrohalogenation. The formation of conjugated polyene structures by double bond shifting reactions was also reported by Dai and White[9] in an ultraviolet-visible and n.m.r. study.

An alternative explanation put forward by Suh and Wnek[10] which did not include the formation of polyenes attributed the conductivity to a transport process involving polyiodide chains[11]. A considerable literature exists describing the existence of such structures which include the well known complexes between iodine and amylose or related carbohydrates[12]. An earlier quantitative study of 'donor–acceptor' complexes between iodine and rubber, obtained by acetone extraction of pale crepe latex, showed that the values of the equilibrium constants and extinction coefficients of the complexes formed in n-heptane solution were similar to those of complexes with analogous simple olefinic molecules[13].

In view of the important role played by polyene sequences in this system and as part of our long standing interest in the presence of these structures in closely related polymers, we have studied their formation in polyisoprene following reaction with molecular iodine. In particular we have shown that their presence can be confirmed with confidence using fluorescence emission and excitation spectroscopy.

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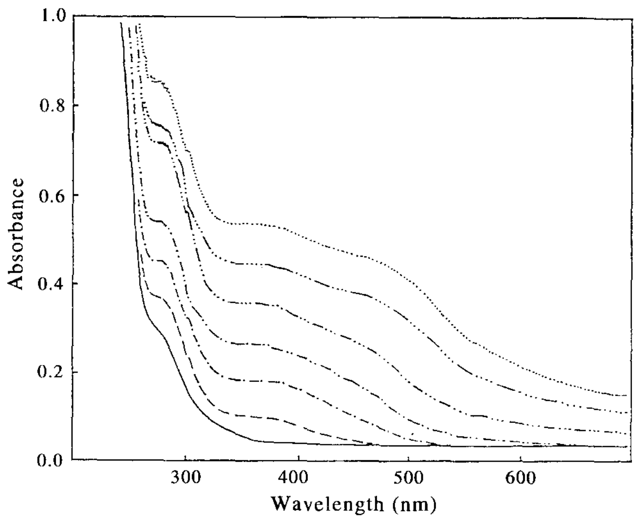


Figure 1 Development of absorptions for polyisoprene films in contact with iodine vapour. Increasing absorbances correspond with contact times of 0, 5, 10, 15, 20, 50, and 70 min

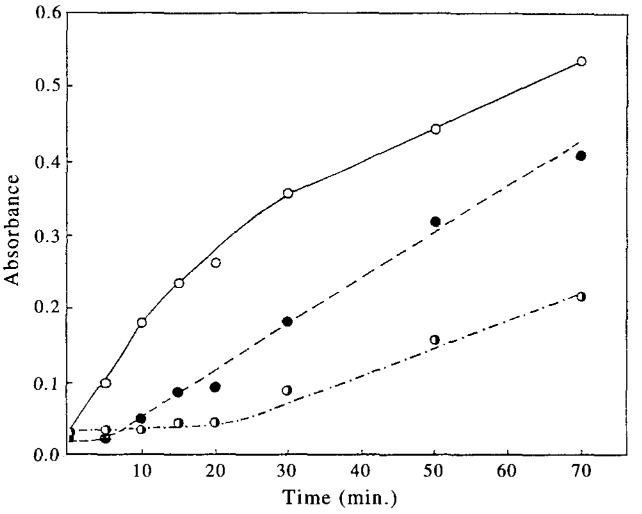


Figure 2 Changes in absorbances at 360 (–○–○–), 500 (–●– –●–) and 600 (–◑– ·◑–) nm

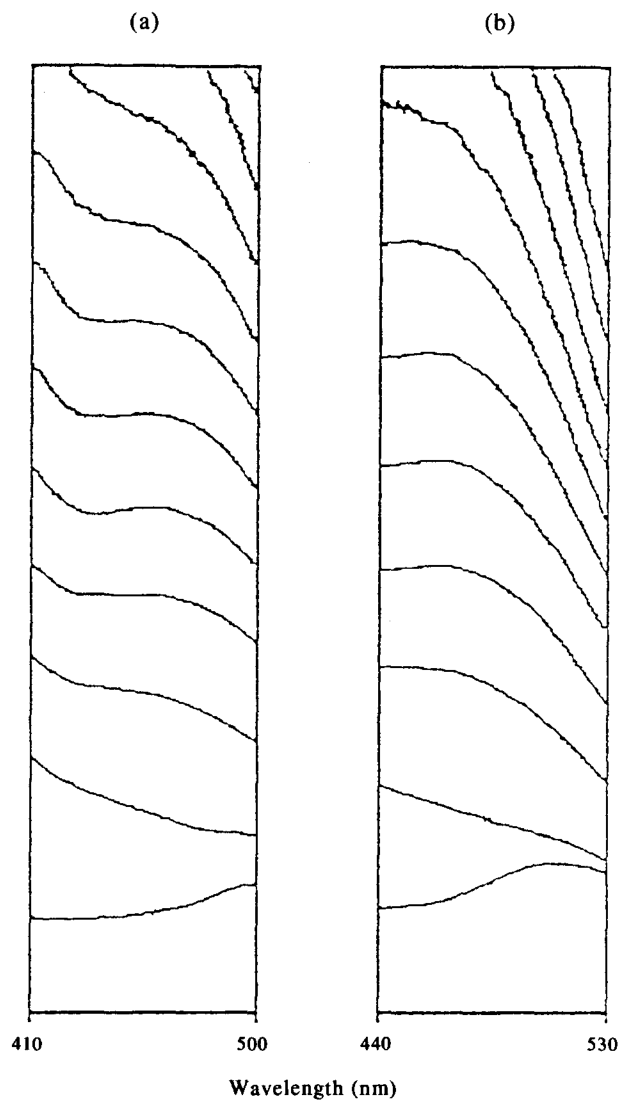


Figure 3 Absorption spectra for polyisoprene films in continuous contact with iodine vapour. Increasing absorbances correspond to scans at 1 min intervals over the ranges 410–500 and 440–530 nm

EXPERIMENTAL

Cis-polyisoprene (Aldrich), and all other reagents were used as received or purified by standard procedures. Polyisoprene films were cast from 1% (w/v) chloroform solutions on glass plates or KBr discs or from 1% (w/v) toluene solutions on a water surface.

U.v.-visible and *FT*i.r. spectra were measured on Perkin–Elmer models 559 and 1600 spectrophotometers respectively, and fluorescence emission and excitation spectra on a Perkin–Elmer model LS 50B spectrofluorimeter.

Film resistivities were measured by the standard four point probe technique using a Keithley 614 electrometer and a resistivity chamber.

E.s.r. experiments were carried out, with valuable assistance from Dr C. C. Rowlands, using a JEOL X-band spectrometer fitted with a JES-RE2X electromagnet and an ESPRIT 330 data station, and d.s.c. measurements used a Perkin–Elmer Series 7 thermal analysis system.

RESULTS

Polyisoprene films cast on quartz plates from $CHCl_3$ solutions were placed in contact with I_2 vapour in air at room temperature and the u.v.-visible spectra measured by removing samples at intervals. The resulting rapid (1 h) changes in absorbance (*Figure 1*) were characterized by initial increases around 280 and 360 nm which developed into broad structures extending over the whole spectral region. Rates of change in absorbance measured at 360, 500 and 600 nm showed that the longer wavelength increases in absorbance followed an induction period as the rate of increase at 360 nm declined (*Figure 2*). When samples were placed in a gas cell and the absorbances measured at 5 min intervals without removal from the iodine atmosphere, the rate of increase in absorbance was greater by a factor of about eight and no structure could be discerned, but when smaller wavelength ranges were scanned at 1 min intervals a shallow maximum around 460 nm was apparent which rapidly became submerged in the increases at longer wavelengths (*Figure 3*).

*FT*i.r. spectra of polyisoprene films showed the

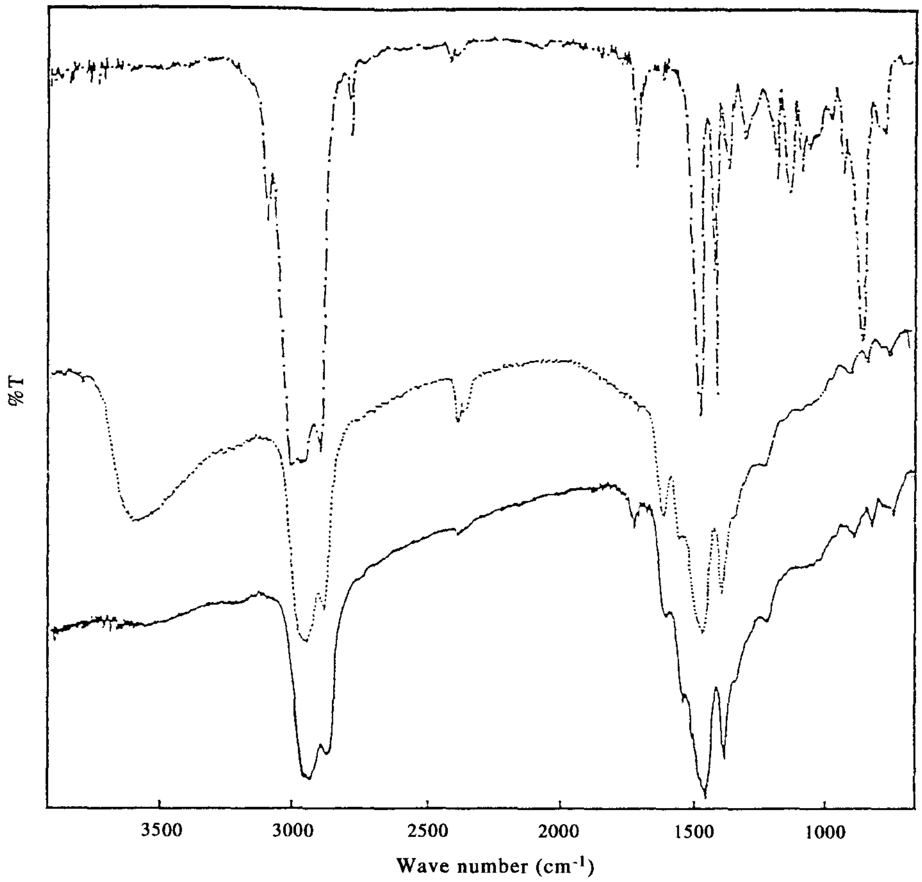


Figure 4 *FT*i.r. spectra of polyisoprene films, before contact with iodine vapour (— · — ·), after 72 h contact (· · ·) and after 72 h contact followed by 22 h pumping under vacuum (——)

expected pattern of absorptions which, in addition to the usual range of C–H modes, included a low intensity resonance at 1664 cm^{-1} characteristic of the $-C=C-$ stretching vibration as well as that of the $=C-H$ bending mode at 836 cm^{-1}. After exposure to iodine vapour for 3 days, the pattern changed to that shown in *Figure 4* which was dominated by the strong band centered at 3439 cm^{-1} characteristic of the –O-H stretching vibration. In addition, an absorption of moderate intensity developed at 1599 cm^{-1} but the one present at 835 cm^{-1} before treatment with iodine was absent. When the film was pumped under vacuum for 24 h and the spectrum re-measured, both the broad absorption centered at 3439 cm^{-1} and the sharp one at 1599 cm^{-1} were reduced to almost zero intensity and a low intensity peak at 1710 cm^{-1} attributable to a carbonyl chromophore was present. When the experiment was repeated using iodine in an atmosphere of nitrogen neither the broad –O–H absorption at 3439 cm^{-1} nor the carbonyl absorption at 1710 cm^{-1} appeared. The film could be cycled many times through the sequence of iodination in air followed by pumping under vacuum without any significant change in the pattern.

Fluorescence emission and excitation spectra of iodine doped polyisoprene films which had been exposed to iodine vapour for 30 min, are given in *Figure 5*. The emission, *A* ($\lambda_{ex} = 370$ nm), which had a broad, undulating structured appearance in the range 400–600 nm was similar to those obtained previously for polyene sequences in poly(vinyl chloride)[14] and in poly(vinyl alcohol)[15]. Excitation spectra (C, D and E) for different emission wavelengths had maxima and shoulders in the range 300–400 nm, the relative intensities of which varied in a way which was also reminiscent of polyenes in PVC.

When the reaction between iodine (2×10^{-3} M) and polyisoprene (0.1–0.3%) was carried out in chloroform solution, strong absorptions developed but more slowly than in the case of the solid films, and in a way which was strongly influenced by the presence of light. Under room light conditions, the iodine absorption around 500 nm, which was accompanied by the appearance of two peaks around 280 and 360 nm which are characteristic of I_3^-, decreased gradually to zero. When the same reaction was carried out in the dark, strong development of the I_3^- absorptions occurred (*Figure 6*), which, due to the approximately 27-fold larger extinction coefficient of I_3^- relative to I_2, eventually overwhelmed the decrease in absorbance at 500 nm and extended over the whole of the visible spectrum.

Fluorescence excitation and emission spectra of reacted solutions of polyisoprene and iodine were similar to those obtained for reactions of the solids (*Figure 7*). Emissions F ($\lambda_{ex} = 270$ nm) and G ($\lambda_{ex} = 393$ nm), were the extremes in that spectra excited below 270 nm were identical to F and those excited above 393 nm resembled G. Those excited at intermediate wavelengths showed features of both F and G. Similarly the excitation spectra, which extended over the 300–450 nm range, could be assigned to the absorptions of at least two emitting species. Spectrum H was characteristic of emissions below

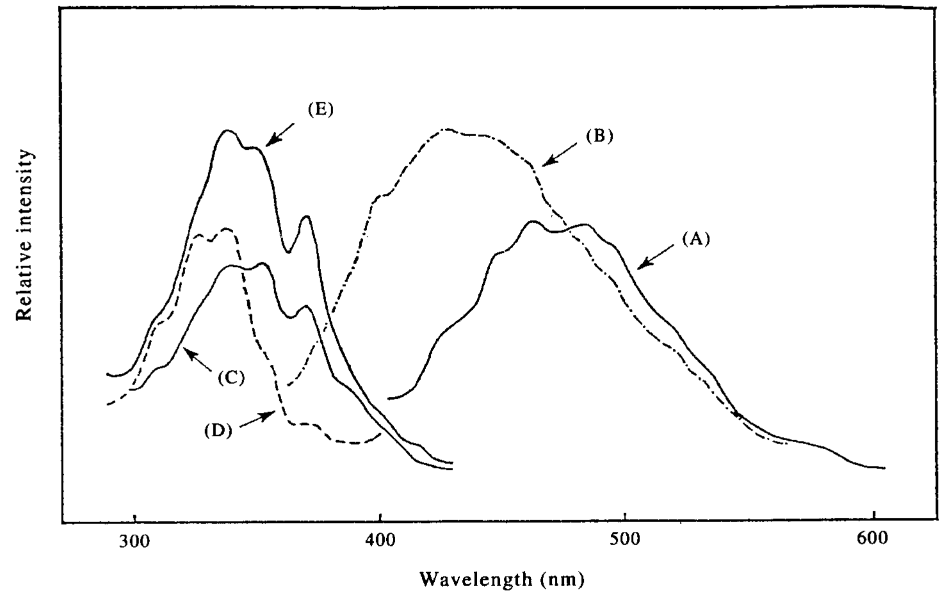


Figure 5 Fluorescence emission and excitation spectra of a polyisoprene film after contact with iodine vapour for 30 min. Emission wavelengths: (D) 422 nm, (E) 496 nm and (C) 520 nm. Excitation wavelengths: (B) 330 nm and (A) 370 nm

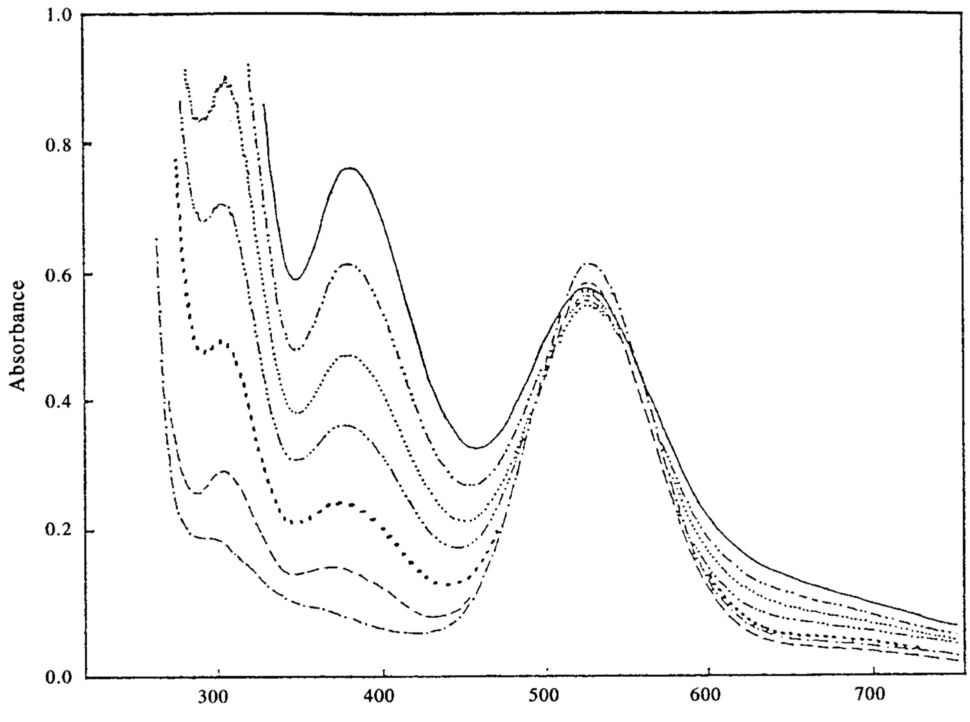


Figure 6 U.v.-visible spectra of chloroform solutions of iodine (2×10^{-3} M) and polyisoprene (7.4×10^{-3} M) under dark conditions. Increasing absorbances around 400 nm correspond to scans taken at 48 h intervals

393 nm and I for emissions above 462 nm although components of H were also present.

The electrical conductivity of 10^{-3} cm thick, freshly cast polyisoprene films was $<10^{-10}$ S cm^{-1}, which increased to 1.1 0.46×10^{-6} S cm^{-1} on contact with iodine but decreased to 1.04 0.78×10^{-8} S cm^{-1} after pumping under vacuum.

D.s.c. of the polyisoprene sample gave no indication of any phase change below 150°C which suggests that the sample was largely amorphous. No e.s.r. signal could be detected either before or after doping.

DISCUSSION

The broad structured absorptions which developed when I_2 vapour interacted with polyisoprene films were essentially similar to those described by Thakur[5]. The absorption maximum around 460 nm (*Figure 3*), which was clearly discernible in the early stages of the reaction but which became submerged by the more rapidly developing broader absorptions, was the first to emerge clearly. On the basis of its position and by analogy with related systems it may be assigned tentatively to a

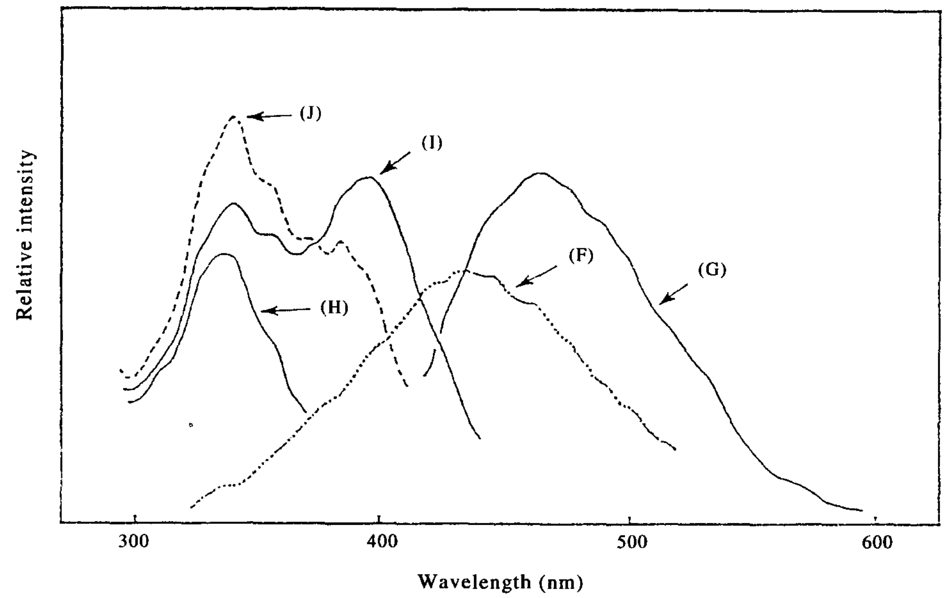
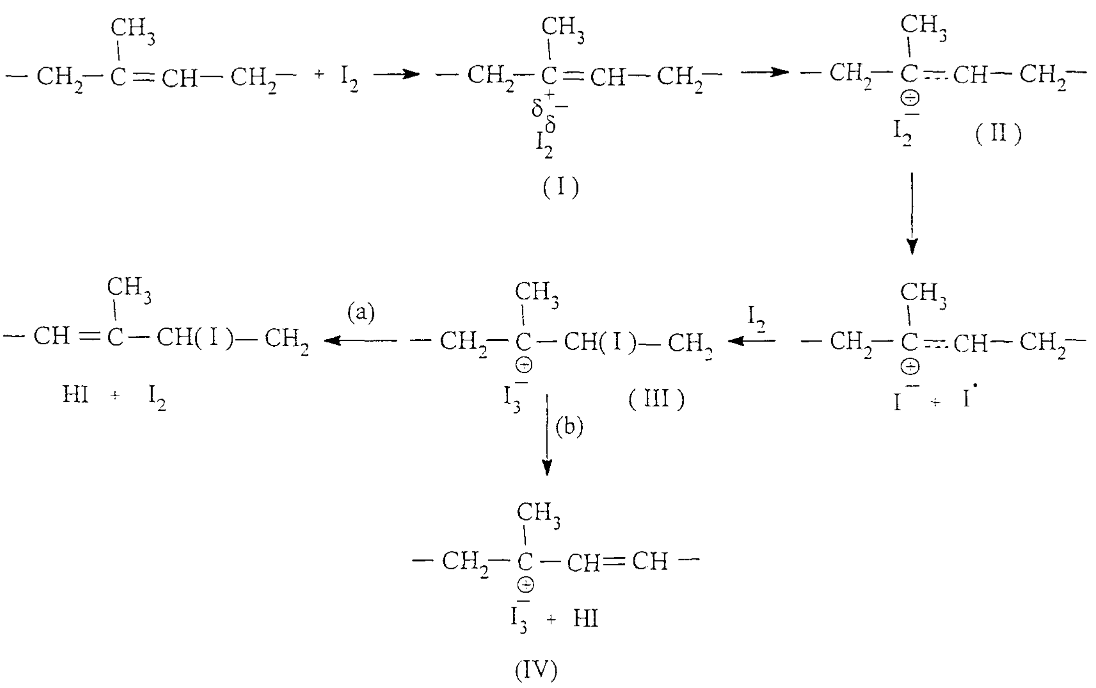


Figure 7 Fluorescence emission and excitation spectra of chloroform solutions of iodine (2.5×10^{-3} M) and polyisoprene (7.4×10^{-2} M), 15 days after mixing under dark conditions. Emission wavelengths: (H) 396 nm, (J) 430 nm, (I) 462 nm. Excitation wavelengths: (F) 270 nm, (G) 393 nm



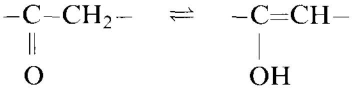
Scheme 1 Suggested mechanism for iodine catalysed introduction of unsaturation into the 1,2 and 3,4 positions in polyisoprene leading to polyene formation

polymer charge transfer complex $\overset{\delta+}{P}-\overset{\delta-}{I_2} \leftrightarrow P^+I_2^-$ but may also contain contributions from either the cation radical species $-\underset{+}{C}-C-$ suggested first by Thakur[5], the cationic iodine complex or the iodonium complex which have been suggested as more likely alternatives by Shang *et al.*[17] and by Suh and Wnek[10] respectively. Similar structures have been described for poly(phenyl acetylene)[18].

Absorptions in this region are quite distinct from those around 360 nm which are clearly visible in the solution experiments and are invariably associated with I_3^- and a number which have been reported at longer wavelengths which have been attributed to $(\text{Pol-I})^+I^-$ structures formed by the addition of I_2 to polyene structures such as β-carotene[19].

The absorptions around 360 nm in the solution experiments developed slowly at first (*Figure 6*), but then at a rapidly increasing rate. During this time, the absorption due to I_2 did not change appreciably but was eventually submerged by the broad structureless absorption which extended over the whole region. This is consistent with a change of mechanism due perhaps to the change in polarity of the medium as HI is eliminated. Such a mechanistic dichotomy has been reported[9] for the interaction of I_2 with carefully characterized polyisoprene synthesized using an anionic catalyst where different u.v.-visible characteristics were apparent for reactions carried out at 22 and 60°C.

Changes in absorptions in the i.r. region are consistent with an iodine catalysed isomerization of the type:



$$-\underset{\underset{O}{\|}}{C}-CH_2- \rightleftharpoons -\underset{\underset{OH}{|}}{C}=CH-$$

which indicates that some oxygenation of the polymer has occurred and therefore that oxygen may play a part in some of the changes which have been described. This aspect is currently being investigated further.

The fluorescence excitation and emission spectra provide striking confirmation of the formation of polyene sequences, the characteristic absorptions of which are not discernible in the presence of the much stronger absorptions in the 300–400 nm region. The broad undulating emissions in the 400–600 nm region suggested the presence of more than one component and this was confirmed by the variation in the relative intensities of the maxima in the excitation spectra as the emission wavelength was changed. The positions of the two principal maxima at 334 and 368 nm suggest that values of n around 4 or 5 would seem most probable but these values are based on data for polyenes of the type $-(CH{=}CH)_n-$ whereas the sequences in question here would be methyl substituted, i.e. $-(CH{=}C(CH_3)-CH{=}CH)_n-$ with $n = 2$ or 3. However, the effects of methyl substituents are usually small.

Similar polyene distributions have been found in a number of thermally and photochemically degraded polymer systems[15,20] and recently in a soluble fraction isolated from a preparation of polyacetylene[21]. The presence of longer sequences is of course possible and likely, but fluorescence quantum yields of low molecular weight linear unsubstituted model polyenes indicated that only the octatetraene ($n = 4$), has an appreciable value ($\phi_f = 0.02$ in hexane at ambient temperature[22]).

A sequence of reactions which would lead to the formation of conjugated polyene sequences is suggested in *Scheme 1*. This consists of an oxidative route to species III, which would become more favourable with increasing medium polarity, which could then form HI from the 1,2 position by abstraction of a proton by I_3^-, additionally re-forming I_2 (route a), or eliminate HCl from the 3,4 position leaving the $-\overset{|}{\underset{|}{C}}{}^{+}I_3^{-}$ unit intact (route b). Either route alone would amount only to a double bond shifting reaction of a type which has been reviewed[23] and for which iodine is known to be an effective catalyst. It appears likely therefore that both routes are required to achieve the formation of long sequences of conjugation, i.e.

$$-(CH_2-C(CH_3){=}CH-CH_2)_r- + nI_2$$
$$\rightarrow -(CH{=}C(CH_3)-CH{=}CH)_n- + 2nHI$$

Our fluorescence data therefore confirm the conclusions drawn from u.v.-visible data of Dai and White[9] and the resonance Raman results of Williams and Gerrard[6]. Further quantification of the extent of the process or speculation about the conduction mechanism is complicated by the inhomogeneous nature of the material since amorphous and crystalline regions have been shown[24] to behave quite independently. The prominent photochemical reaction of iodine which may lead to more permanent iodination of the polymer is also a complication which would lead to a reduction in the conductivity of the material. It seems likely, however, that any mechanism proposed must take account of the possibility of the participation of charge carriers which may be delocalized over polyene sequences of varying lengths.

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