The dissymmetry at $c = 9.6 \times 10^{-3}$ g cm^{-3} was determined from $g(r)$ values derived by Kirkwood and Boggs[16] for what they termed an idealized liquid structure in which the average distance between the centre of a sphere and the centre of its nearest neighbours was 1.15D.

Better agreement between experiment and theory could undoubtedly be obtained by choosing a slightly different effective size for the micelles. The present analysis is sufficient to show that the micelles remain colloidally stable even when packed at relatively high number densities. If however we increased the concentration somewhat further, a transition from a liquid-like to a more highly ordered mesomorphic type structure would eventually occur.

Recently we found that other micellar systems show a similar dependence of angular dissymmetry on concentration to that described here. A full report on these studies will be presented later.

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Lithium doping of *cis* polyacetylene $(CH)_x$

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n-Type doping of polyacetylene $(CH)_x$ has been performed using benzophenone–lithium solutions in THF. It is shown that doped *cis*-rich films can reach the metallic level, as evidenced by e.p.r. Raman spectroscopy shows that during the doping process, isomerization from *cis* to *trans* occurs. Preliminary results show that for short doping times the distribution of the dopant in thick films is strongly inhomogeneous.

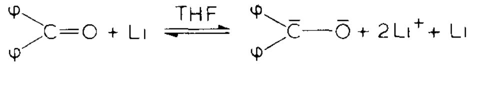
Keywords Polymer, polyacetylene, spectroscopy; Raman; doping; lithium; isomerization

A great deal of experimental work has focused on the chemical and physical properties of polyacetylene films doped with electrons acceptors such as I_2, AsF_5,[1] $NOHSO_4$,[2] $FeCl_3$,[3] etc.

Much less work has been done on the subject of doping with electron donors such as alkali metals. Interest concerning this type of doping comes from the potential ability of polyacetylene films being used as electrodes in electrochemical processes. For instance $(CH)_x$ can be electrochemically doped with Li^+ or with ClO_4^- by using a solution of $LiClO_4$ in propylene carbonate[4]. Only a few experiments have been performed using chemical doping with Li[5], Na[5-7], and K[5]. The extreme reactivity of the system with air and moisture does not permit easy handling of the samples. Nevertheless some combined e.p.r., i.r. and visible spectroscopies and conductivity measurements have shown that, by doping with Na, polyacetylene could be brought to the metallic state and that isomerization occurred during the doping process[6,7].

In this communication we present the chemistry of the Li doping using benzophenone–lithium complexes in THF, as well as preliminary e.p.r. and Raman spectroscopies experiments. A careful analysis of the results suggests that for short doping times the dopant distribution is strongly inhomogeneous and varies with time.

Polyacetylene films have been obtained using the standard procedure of Ito *et al.*[8]. A solution of benzophenone and Li in very dry and clean THF was prepared with excess Li in order to favour the following reaction:



$$\varphi_2C{=}O + Li \overset{THF}{\rightleftharpoons} \varphi_2\bar{C}{-}\bar{O} + 2Li^+ + Li$$

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*Laboratories associated with CNRS

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The whole procedure was performed in sealed Pyrex tubing, without stopcocks, to avoid any contact with air or moisture. The doping was achieved by immersing the $(CH)_x$ film in the solution over a given time, then removing the solution and washing the sample with pure THF distilled from the solution. After washing, the system was dried by constant cryogenic pumping which was persisted during the e.p.r. experiments. All the present measurements have been performed using a concentration $c \sim 0.05$ mol/litre of benzophenone in THF. The samples were 2 mm x 8 mm x 0.1 mm pieces of *cis*-rich $(CH)_x$ (85% as determined by Raman spectroscopy).

E.p.r. spectra have been recorded at room temperature, using an ER10 Bruker spectrometer, working at a low power level (< 1mW). A typical spectrum of a *cis*-rich $(CH)_x$ film presented the characteristics in good agreement with standard results[9]. A highly doped $(CH)_x$ (the Li content has not been determined) presented a spectrum with a g value close to 2.00 and an assymetric shape (*Figure 1*).

The Raman spectroscopy was performed at room temperature using standard equipment (Ramanor HG2S equipped with holographic gratings) with the excitation laser wavelength $\lambda_{exc} = 600$ nm. *Figure 2a* shows the Raman spectrum of the *cis*-rich $(CH)_x$ sample that we started with. After doping with Li under the conditions described above, significant changes occurred in the observed spectrum (*Figure 2b*). The Raman lines characteristic of the *cis*$-(CH)_x$ are no longer seen and two main bands are observed at 1090 and 1480 cm^{-1} characteristic of the *trans* isomer.

The strong assymetry of the e.p.r. spectrum characterized by $A/B \sim 7$ (*Figure 1*) indicates that the highly Li doped $(CH)_x$ has reached the metallic state. If an assymetry of the e.p.r. spectra is usually observed for highly doped $(CH)_x$ films[2,6,7,11], the A/B value reported here is particularly high. As, all other conditions being unchanged, A/B increases with increasing conductivity of the sample[10], we deduce from the comparison with AsF_5 doped $(CH)_x$[11] that in the present case the electrical conductivity is probably higher than 100 $(\Omega\ cm)^{-1}$.

From Raman data we can conclude that starting from a 85% *cis*-rich film of $(CH)_x$, we have achieved, by Li doping, an apparently complete isomerization (*Figure 2*). Nevertheless $(CH)_x$ films are highly absorbant and therefore mainly the surface of the sample is investigated by the Raman technique. This point is clearly so as exactly similar Raman spectra are observed after two very different doping times (15 min and 15 h) while e.p.r. spectra of the same samples present very different features. On the one hand a long doping time (15 h) yields a single e.p.r. line, suggesting a quasi homogeneous distribution of the dopant while on the other, two superposed e.p.r. lines with similar g values, but different linewidths, are observed after a short doping time (15 min) (*Figure 3*), probably assignable to a very inhomogeneous distribution of the dopant.

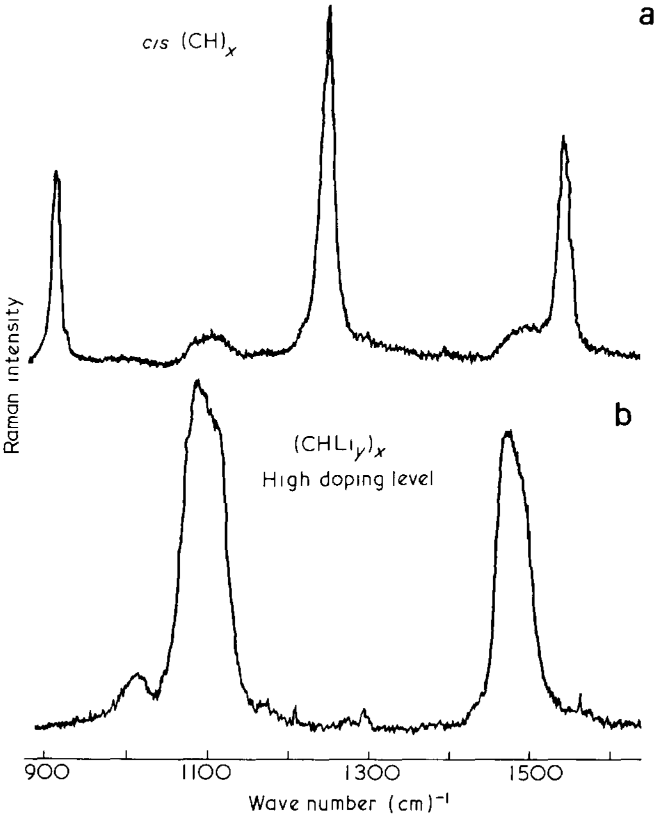

Figure 2 Raman spectra of $(CH)_x$ with $\lambda_{exc} = 600$ nm at room temperature: (a) *cis*-rich film before doping; (b) same sample after a long Li doping process

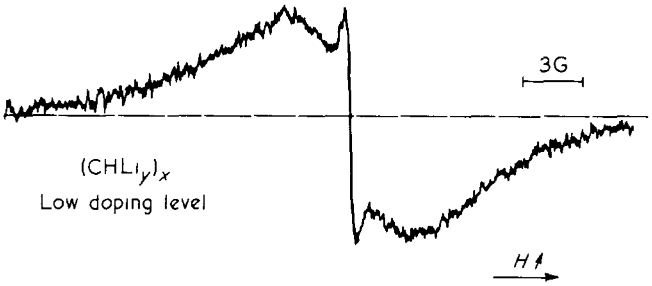

Figure 3 E.p.r. spectrum of *cis*-$(CH)_x$ film doped with Li during a short time (15 min) showing the superposition of two lines with same g values and different widths

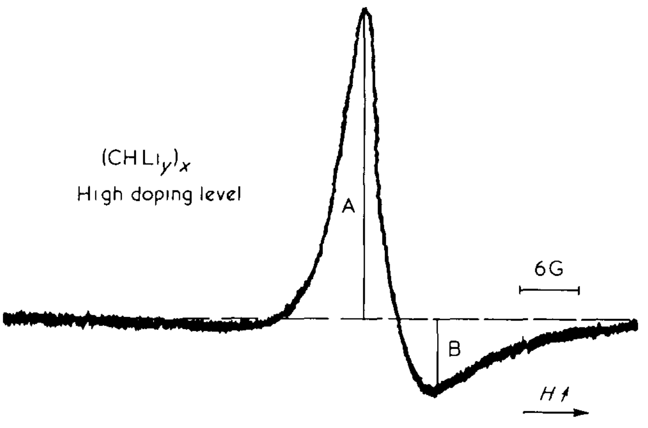

Figure 1 E.p.r. spectrum of a highly Li doped $(CH)_x$ showing the strong assymetry of the line characteristic of the metallic state[10]

From all these preliminary results it seems that Li is a very efficient dopant in $(CH)_x$, probably because of the small size of the Li^+ ion. We have pointed out that the kinetics of the doping process must be taken into account in order to control the homogeneity of the samples. Careful studies with this purpose are underway.

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Polarization of excimer emission in solution

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Polarization of fluorescent emission of excimer structures for polystyrene and poly (α-methyl styrene) has been examined in cyclohexane solution. No depolarization was observed resulting in the conclusion that energy migration does not take place under the experimental conditions studied.

Keywords Optical properties; polarization; excimer; fluorescence; energy transfer

Introduction

Observation of polarized emission from excimer structures in thin films of polystyrene at room temperature led to the conclusion that either energy migration was not an efficient process or, if it were, the migrating exciton was retaining spatial identity as it moved into the excimer traps[1]. Provided they are aligned such that their transition moments interact with the incident radiation all phenyl units have an equal probability of excitation and consequently each step in the migration process, including the final transfer into the excimer structure, would proceed under strict control of orientation of chromophores. None of the accepted theories of energy transfer have been shown to impose such strict conditions of orientation of transition moments. In order to extend the investigation of the photophysical behaviour of poly(vinyl arenes)[2] polarization measurements have been made on solutions of both polystyrene and poly(α-methyl styrene). Under such conditions anisotropy or orientation of the macromolecules can be discounted.

Experimental

The polymers were prepared by anionic polymerization using purified monomers. Molecular weights, measured viscometrically were: polystyrene 1.2×10^5, and poly (α-methyl styrene), 8×10^4. Freshly distilled cyclohexane was used as solvent and measurements were made over a range of temperatures. De-oxygenated solutions, 10^{-2}M in repeat unit, were examined using a Perkin Elmer MPF2 with polarizers supplied by the instrument makers. The usual correction was applied for anisotropy of the optics of the instrument. The results are shown in *Table 1*.

Discussion

The fluorescent emission of excimer for both polystyrene and poly(α-methyl styrene) is polarized in solution as well as in the solid state. The solvent chosen, cyclohexane, is a poor solvent for both polymers and consequently the interphenyl separation in the macromolecules will be minimized. Such a condition should favour inter unit energy transfer. Orientation of chromophores and anisotropy of the samples, conditions which can be realized for solid solutions, cannot be relevant factors for observations made on solutions of the polymers, therefore it must be concluded that for these two polymers formation of the excimer involves the phenyl unit which makes the initial photon capture and very little energy migration takes place. Furthermore the resultant excimer structure undergoes no spatial relaxation during its life-time of approximately 20 ns. Such a situation is surprising since the excimer involves

Table 1 Polarization of excimer emission for solutions of polystyrene and poly(α-methyl styrene). Excitation – 265 nm, emission – 330 nm

Polymer	Polarization	Temperature
Polystyrene (film)	0.20	295K
Poly(α-methyl styrene) (film)	0.25	295K
Polystyrene (solution)	0.22	295K
Poly(α-methyl styrene) (solution)	0.19	308K
"	0.21	311K
"	0.21	314K
"	0.22	317K
"	0.23	320K
"	0.22	323K
"	0.23	329K

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