Polymerization of pyrrole by cationic photoinitiators

J. F. Rabek*
Polymer Research Group, Department of Dental Materials and Technology, Karolinska Institutet, Box 4064, S-141 04 Huddinge, Sweden

and J. Lucki
Department of Polymer Technology, Royal Institute of Technology, S-100 44 Stockholm, Sweden

and M. Zuber
Institute of Chemistry, University of Wroclaw, Wroclaw, Poland

and B. J. Qu and W. F. Shi
China University of Science and Technology, Heifei, Anhui, China

(Received 23 April 1991; revised 23 January 1992; accepted 2 March 1992)

A new method of polymerization of pyrrole in the presence of cationic photoinitiators such as iron–arene salts (η-C_5H_5)Fe(η-arene) under visible or ultraviolet irradiation has been described. The synthesized polypyrroles have low conductivity in the range of 10^{-5} S cm^{-1} and rather poor electrochemical properties. The polymerization reaction occurs only in the presence of oxygen and is inhibited by the addition of 1,10-phenanthroline. It is initiated by the Fe(III) species formed by the oxidation of Fe(II) fragments formed during the photolysis of the photoinitiators used.

(Keywords: polymerization; pyrrole; photoinitiators; characterization)

INTRODUCTION

It is well known that deoxidized pyrrole remains unchanged during u.v. or visible (vis.) irradiation. However, very long u.v. irradiation (15 h) in solution of $HClO_4$ or tetraethylammonium tetrafluoroborate causes its polymerization[1]. Recently two photosensitized polymerizations of pyrrole using Ru(bpy)$_3^{2+}$ and CuI(dpp)$^{2+}$, where bpy = bipyridine and dpp = 2,9-diphenyl-1,10-phenanthroline, have been reported[2,3].

Despite the extensive results obtained and published on chemical and electrochemical polymerization of pyrrole and its derivatives[4–6], reports on the photochemical polymerization of pyrrole are relatively scarce. It can be expected that the radical cations formed during photolysis of some cationic photoinitiators may initiate the polymerization of pyrrole. In the present work on the polymerization of pyrrole with iron–arene salts (η-C_5H_5)Fe(η-arene), cationic photoinitiators have been investigated. This forms part of a longer study of transition-metal-catalysed photoreactions carried out in our group.

EXPERIMENTAL

Iron–arene salt cationic photoinitiators such as (η^5-2,4-cyclopentadien-1-yl)[(1,2,3,4,5,6-η)-(1-methylethyl)-benzene]-iron(1+)-hexafluorophosphonate(1−) (Irgacure 261, Ciba-Geigy) and (η^5-2,4-cyclopentadien-1-yl)-[(1,2,3,4,5,6-η)-naphthalene]-iron(1+)-hexafluorophosphonate(1−) (Komplex KM 1144, Ciba-Geigy) were kindly provided by Dr G. Eugster (Ciba-Geigy). Both these photoinitiators were additionally purified by crystallization from nitromethane.

Nitromethane (CH_3NO_2) (Carl Roth GmbH, Germany) and pyrrole (Merck, Germany) have been purified by vacuum distillation.

U.v./vis. and i.r. absorption spectra were recorded with Perkin–Elmer 575 u.v./vis. and Perkin–Elmer 580B *FT*i.r. spectrometers, respectively. Mössbauer (recoil-free nuclear resonance absorption) spectra were recorded with an Oxford MS500 spectrometer, using a 50 mCi ^{57}Co/Rh source. The transmitted radiation was detected with a proportional counter. The simulation of the measured spectra was performed using the Gauss–Newton method by supposing that a single peak has a Lorentzian lineshape. Electron spin resonance (e.s.r.) spectra were measured with a Brüker ER 2000 e.s.r. spectrometer, using an ST cavity. N.m.r. spectra were made with a Brüker AM 400 spectrometer (400 MHz for ^{1}H). Conductivities of polypyrroles were measured using a four-point resistivity probe and a solid state electrometer (type 610C, Keithley Instrument). Measurements were recalculated with equations published elsewhere[7–9]. Cyclic voltammograms were performed on

---

*To whom correspondence should be addressed

0032-3861/92/224838-07

an EG&G Princetown Applied Research model 173 potentiostat/galvanostat in dry acetonitrile solutions of 0.1 M tetra-n-butylammonium perchlorate (TBAP) at room temperature in a two-compartment cell with an Ag/AgCl reference electrode at 20 mV s^{-1}. For u.v. and vis. irradation, UV HPK 125 W (Philips) and Wolfram Photolite 100 W (Philips) lamps, respectively, were used.

RESULTS AND DISCUSSION

The photoinitiators Irgacure 261 and Komplex KM 1144 are easily soluble in organic solvents such as ethanol, chlorinated solvents, acetonitrile and nitromethane, as well as in pyrrole. At concentrations of 10^{-3} M they have a strong absorption in the visible region at 350–550 nm (*Figure 1*). They are quickly photolysed by both vis. (>400 nm) (*Figure 1*) and u.v. (254 nm) (*Figure 2*) irradiation. However, the observed changes in the spectra during irradiation differ significantly for both photoinitiators. For the photoinitiator Irgacure 261 spectral intensity increases, whereas for the photoinitiator Komplex KM 1144 spectral intensity decreases. These changes are strongly dependent on the solvent in which photolysis has been carried out. Prolonged irradiation causes precipitation of a red-coloured colloidal deposit, containing iron(II), which with 1,10-phenanthroline gives a red–orange complex of the $Fe(phen)_3^{2+}$ ion. Irradiation of both photoinitiators in pyrrole solution causes precipitation of a black colloidal polypyrrole. The diameter of these colloidal particles is in the range of 20 μm, and it is very difficult to separate them from the solution. They pass easily through even the most dense filters. After centrifugation and drying, they give conglomerates (*Figure 3*).

I.r. spectra of polypyrroles obtained in the presence of photoinitiators Irgacure 261 and Komplex KM 1144 (*Figure 4*) show the presence of the band at 838 cm^{-1}, which belongs to the PF_6^- anion, characteristic in the i.r. spectra of pure photoinitiators (*Figure 5*). This result supports the assumption that polypyrroles have as a counterion PF_6^- anions. Both polypyrrole samples show the existence of a polypyrrole ring and NH stretching vibrations at 1305, 1456, 1651 cm^{-1} and 3451, 3465 cm^{-1} respectively. A number of authors report in polypyrrole samples a broad and unstructured strong band in the region 4000–2000 cm^{-1}, which has been attributed to the tail of an electronic absorption in the near i.r.[6]. In contrast to these results, all our polypyrroles have a broad absorption band at 3600–2800 cm^{-1}, which precludes the observation of the expected NH (3451, 3465 cm^{-1}) and CH (3100–2940 cm^{-1}) stretching modes.

Mössbauer spectra show that both polypyrrole samples contain $^{57}Fe^{3+}$ ($3s^23p^63d^5$) atoms (*Figures 6a* and *6b*), whereas in pure photoinitiators Irgacure 261 and Komplex KM 1144 iron exists as $^{57}Fe^{+}$ ($3s^23p^63d^6$) ions (*Figures 6c* and *6d*, respectively). The Mössbauer spectra of both photoinitiators are quite similar to the Mössbauer spectra published for unsubstituted ferrocene[10]. However, they consist of a large temperature-independent quadrupole splitting: 1.809 mm s^{-1} for Irgacure 261 and 1.804 mm s^{-1} for Komplex KM 1144, in comparison to that in ferrocene, 0.237 mm s^{-1} (ref. 11). The Mössbauer spectra of both polypyrroles (*Figures 6a* and *6b*) are identical to the Mössbauer spectra published previously by us for polypyrroles polymerized on polyether–$FeCl_3$ complexes[12].

Polypyrroles, in both their neutral-insulating and oxidized states, exhibit a strong e.s.r. signal[13–16]. The e.s.r. spectra of polypyrroles obtained in the presence of photoinitiators Irgacure 261 and Komplex KM 1144 (*Figure 7*) show the presence of a single line of width

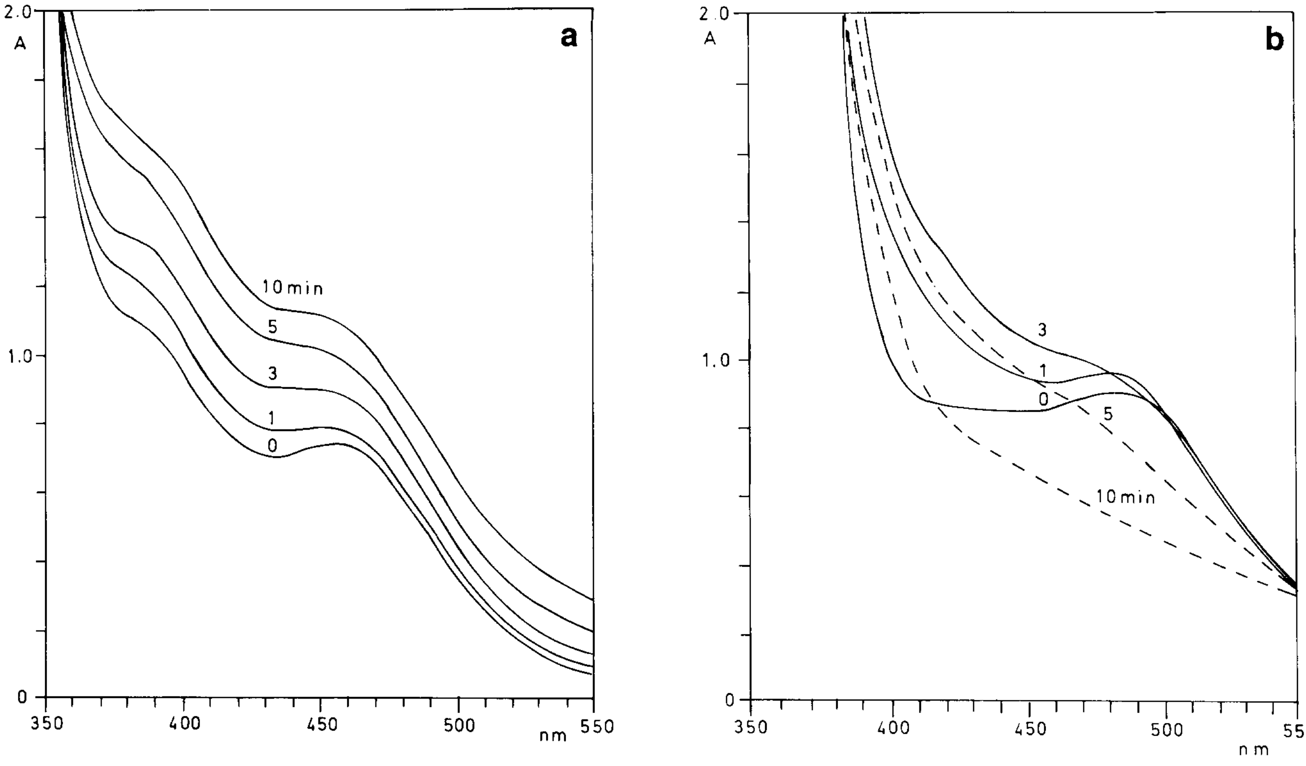


Figure 1 Change of absorption spectra of iron–arene salt photoinitiators in pure pyrrole: (a) Irgacure 261 (1 × 10^{-3} M) and (b) Komplex KM 1144 (3 × 10^{-3} M), during visible light (>400 nm) (1, 3, 5 and 10 min) irradiation

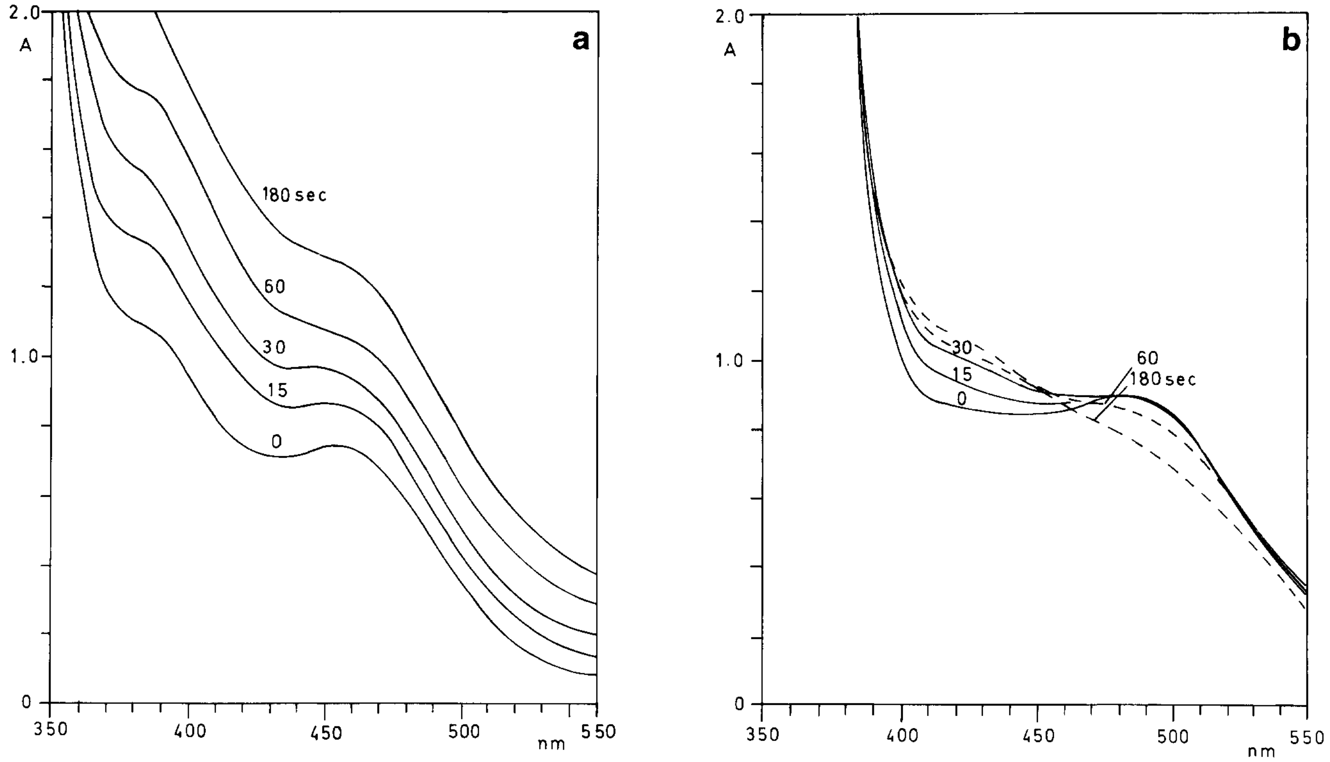


Figure 2 Change of absorption spectra of iron–arene salt photoinitiators in pure pyrrole: (a) Irgacure 261 (1×10^{-3} M) and (b) Komplex KM 1144 (3×10^{-3} M), during u.v. (254 nm) (15, 30, 60 and 180 s) irradiation

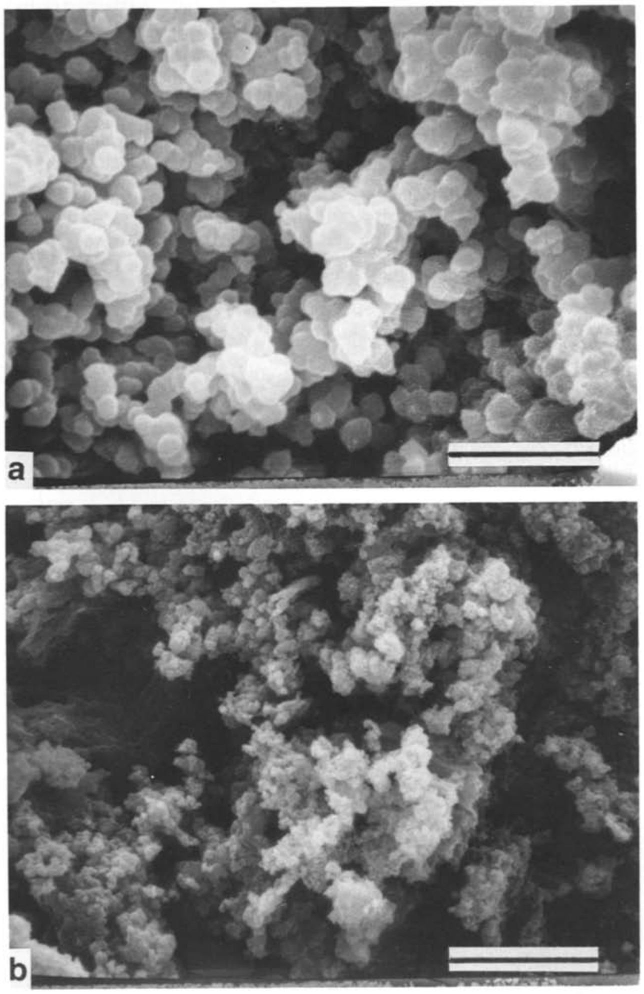


Figure 3 SEM photomicrographs of polypyrrole colloidal aggregates (powder) obtained in the presence of iron–arene salt photoinitiators: (a) Irgacure 261 and (b) Komplex KM 1144. Scale bars are 10 μm

10 G (peak-to-peak) and a g-value of 2.0026, which indicates a high number of free spins (10^{19} spins g^{-1}).

The conductivities of polypyrroles obtained in the presence of photoinitiators Irgacure 261 and Komplex KM 1144 are 2.2×10^{-5} and 5.0×10^{-5} S cm^{-1}, respectively. The low conductivities of the samples may be due to the obtained polypyrroles existing in the form of small colloidal grains (*Figure 2*), which are difficult to press into tablets for conductivity measurements. For that reason electrodes in the measuring cell do not achieve good contact with polypyrrole grains. The conductivity between electrodes and measured materials depends on differences in charge resulting from microstructural and morphological properties of the product. On the other hand conductivities can depend on chemical structures, defects in conjugated bonds, molecular weights, etc.

The cyclic voltammograms for different polypyrroles obtained in the presence of photoinitiators Irgacure 261 and Komplex KM 1144 (*Figure 8*) show the low electrochemical activity of these polymers, which can be the result of non-equivalent electroactive sites in the polymer chain. These non-equivalent sites may arise from defects due to the β–β linkages as a result of polymerization, during which reactive fragments from photolysed initiators may disrupt the conjugation along the backbone. An inverse relation between the chain length and the anodic peak is a general feature of conjugated systems and leads to polymers with a range of formal potentials and thus a broad peak. The peak shapes of cyclic voltammogram curves also depend on the presence of the PF_6^- anion, which influences in a wide range the kinetics of redox processes. The size of the anion used during the synthesis has an enormous influence on the electrochemical characteristics[17].

The gravimetrically measured kinetics of pyrrole polymerization in the presence of photoinitiators Irgacure 261 and Komplex KM 1144 using 254 nm u.v.

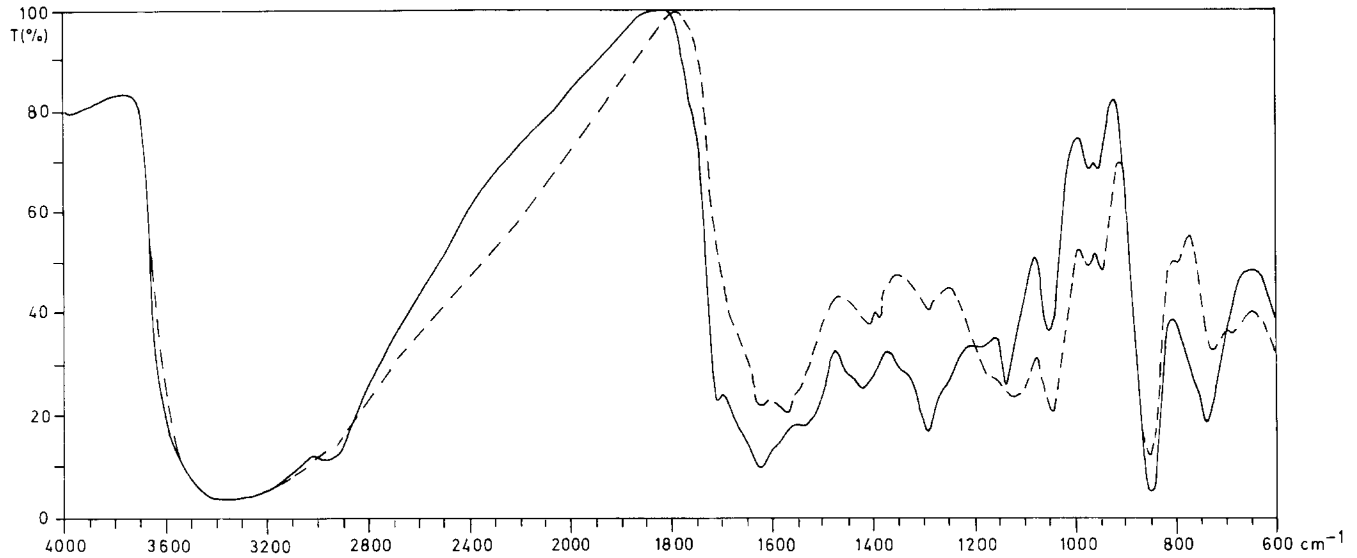


Figure 4 I.r. spectra of polypyrroles obtained in the presence of iron–arene salts: (——) Irgacure 261 and (– – –) Komplex KM 1144

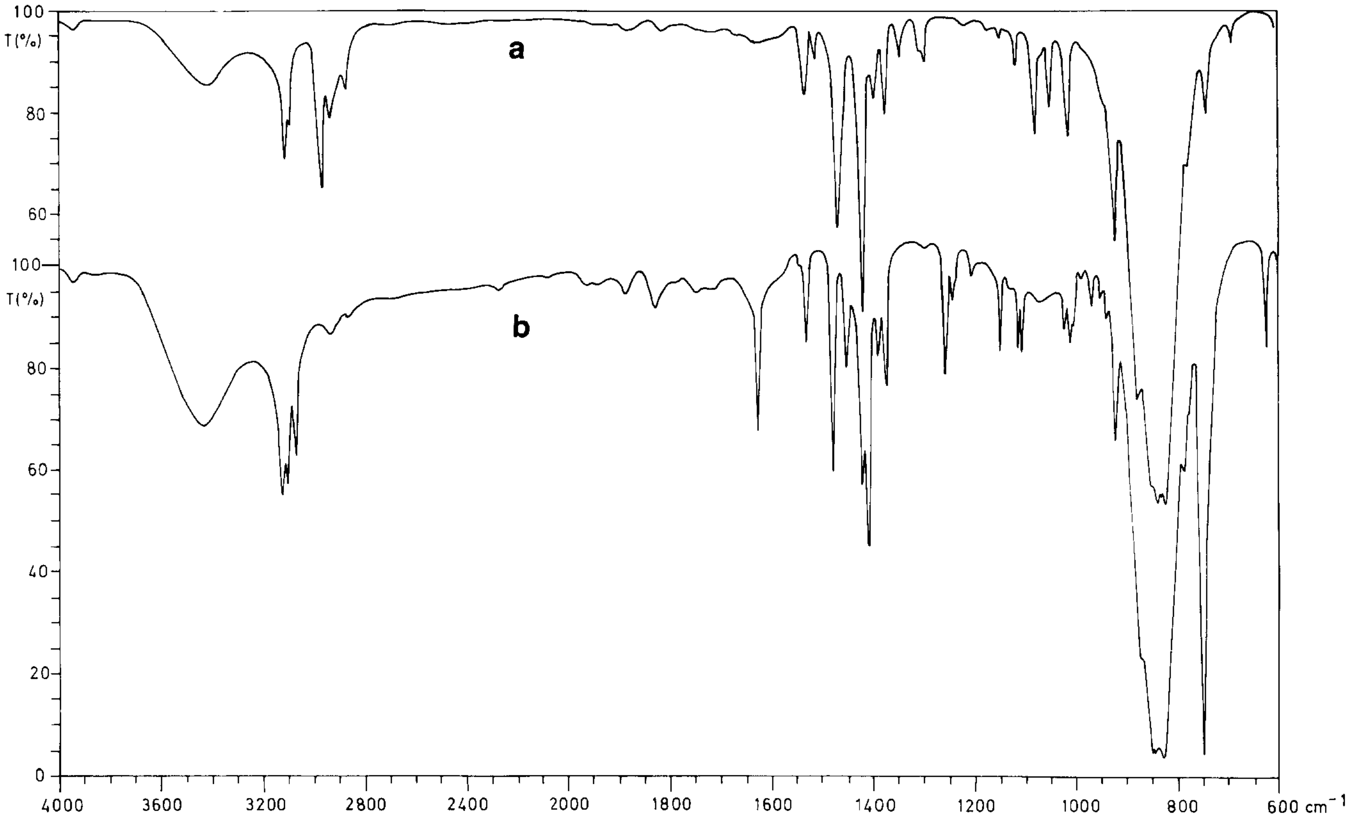


Figure 5 I.r. spectra of iron–arene salt photoinitiators: (a) Irgacure 261 and (b) Komplex KM 1144. The bands at 838 cm^{-1} belong to the anion PF_6^-

irradiation shows that the reaction proceeds rapidly during the first 60 min of irradiation and then reaches a plateau (*Figure 9*). Prolonged irradiation, even for 24 h, does not increase the weight per cent of monomer conversion. The reaction is complete after 60 min of irradiation. The kinetic measurements of pyrrole (wt%) as a function of photoinitator concentration (*Figure 10*) show a good linear dependence. However, even at high concentration of photoinitiators Irgacure 261 or Komplex KM 1144, the percentage of monomer conversion does not exceed 8–10%. These results suggest that the polymerization reaction occurs only with direct contact between pyrrole and the polymerization initiating species. When the polymer grows around such a centre, new monomer molecules are less likely to approach it, and finally the reaction is complete. The character of such a pyrrole polymerization species requires consideration of the reactions that occur during the photolysis of photoinitiators Irgacure 261 and Komplex KM 1144.

It is well known that iron–arene compounds (I) are

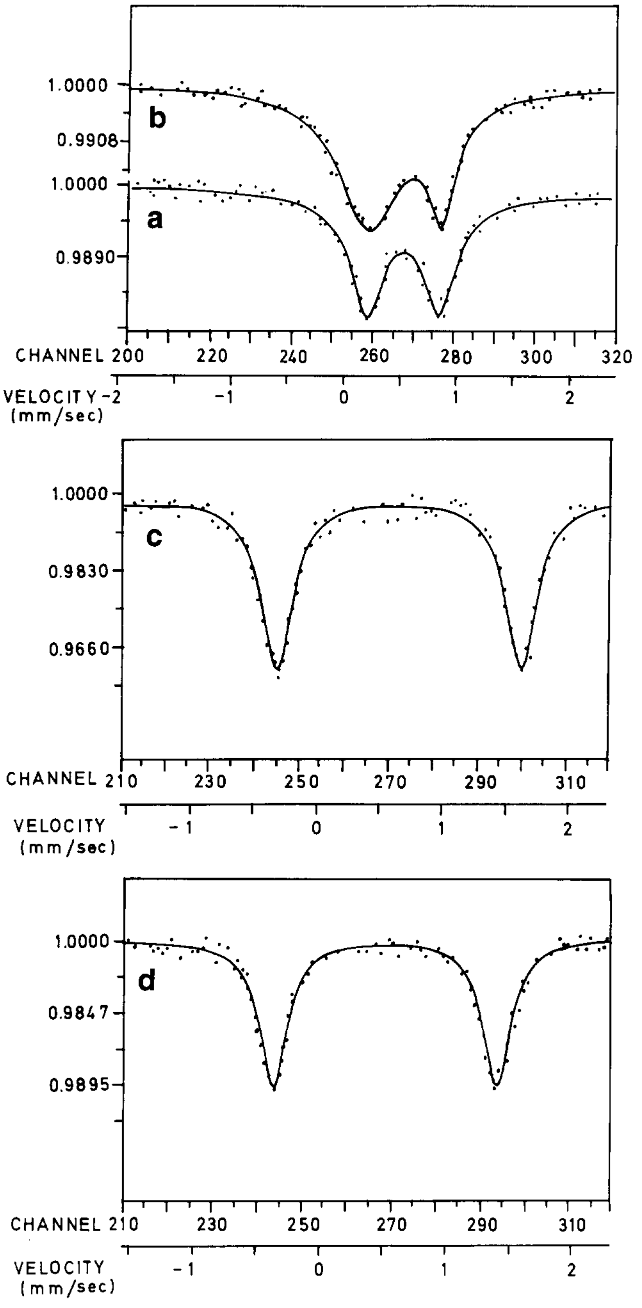


Figure 6 Mössbauer spectra of: polypyrroles obtained in the presence of iron–arene salts, (a) Irgacure 261 and (b) Komplex KM 1144; and of (c) pure Irgacure 261 and (d) pure Komplex KM 1144, measured at 77 K

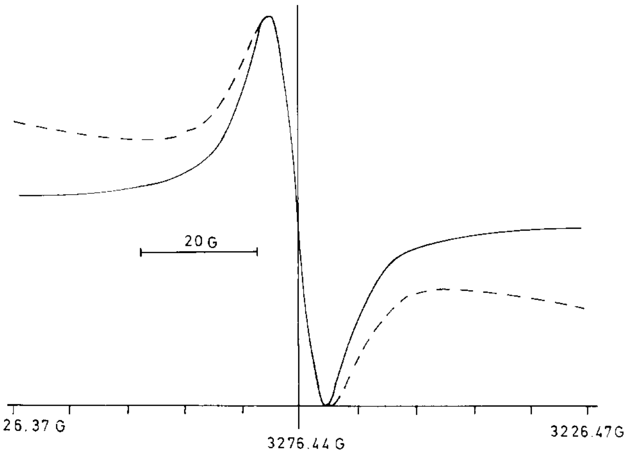


Figure 7 E.s.r. spectra of polypyrroles obtained in the presence of iron–arene salts: (- - -) Irgacure 261 and (——) Komplex KM 1144, measured at 77 K

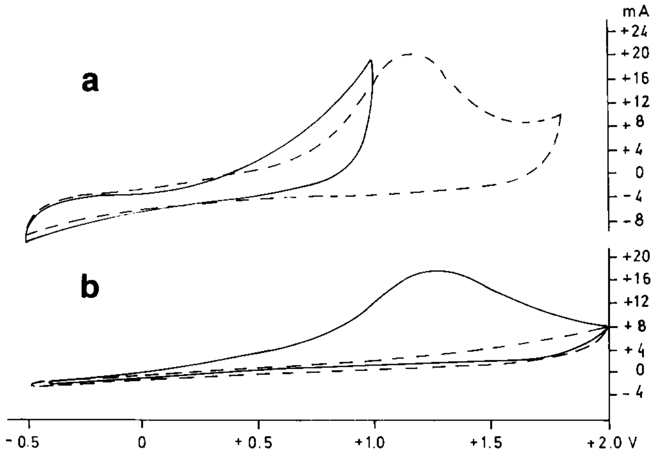


Figure 8 Cyclic voltammogramms of polypyrroles obtained in the presence of iron–arene salts: (a) Irgacure 261 and (b) Komplex KM 1144

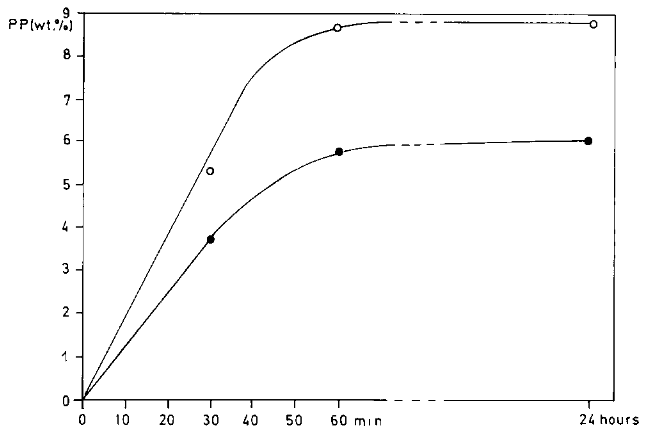
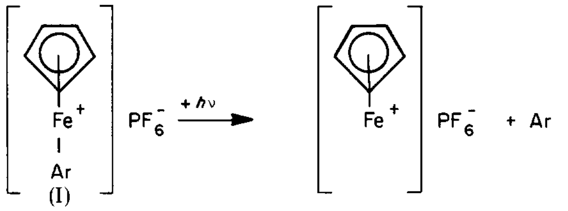


Figure 9 Kinetic curves of photoinitiated polymerization of pyrrole in the presence of iron–arene salts (molar ratio of monomer to photoinitiator 1:0.01) *versus* time of u.v. (254 nm) irradiation: (●) Irgacure 261 and (○) Komplex KM 1144

photolysed according to the mechanism[18]:



(1)

where Ar = isopropylbenzene, naphthalene, pyrene, etc. On the other hand, photolysis of iron–arene salts $(\eta\text{-C}_5\text{H}_5)\text{Fe}(\eta\text{-arene})^+$ in acetonitrile solution yields Fe(II) and ferrocene as the Fe-containing product[19]:

$$2(\eta\text{-C}_5\text{H}_5)\text{Fe}(\eta\text{-arene})^+ \xrightarrow[\text{CH}_3\text{CN}]{+h\nu} \text{Fe(II)} + (\eta\text{-C}_5\text{H}_5)_2\text{Fe} + 2(\text{arene}) \quad (2)$$

This mechanism has been established by others[20]. Ferrocene and Fe(II) species formed in acetonitrile can also be the result of two other independent mechanisms:

Mechanism I

$$(\eta\text{-C}_5\text{H}_5)\text{Fe}(\eta\text{-arene})^+ \xrightarrow[\text{CH}_3\text{CN}]{+h\nu} (\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CH}_3\text{CN})_3^+ + \text{arene} \quad (3)$$

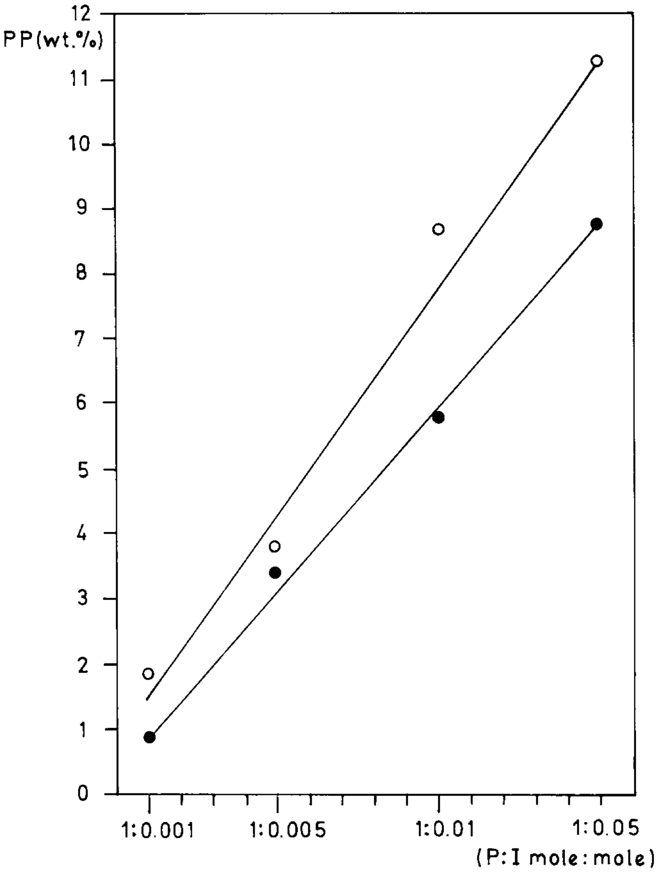


Figure 10 Kinetic curves of photoinitiated polymerization of pyrrole (P) in the presence of different molar concentrations of iron–arene salt photoinitiators (I): (●) Irgacure 261 and (○) Komplex KM 1144 after 60 min u.v. (254 nm) irradiation

$$(\eta\text{-}C_5H_5)Fe(CH_3CN)_3^+ \xrightleftharpoons{+CH_3CN} Fe(CH_3CN)_6^{2+} + C_5H_5^- \quad (4)$$

$$(\eta\text{-}C_5H_5)Fe(CH_3CN)_3^+ + C_5H_5^- \rightarrow (\eta\text{-}C_5H_5)_2Fe + 3CH_3CN \quad (5)$$

Mechanism II

$$(\eta\text{-}C_5H_5)Fe(CH_3CN)_3^+ + (\eta\text{-}C_5H_5)Fe(CH_3CN)_3^+ \rightarrow (\eta\text{-}C_5H_5)_2Fe + Fe(\text{II}) + 6CH_3CN \quad (6)$$

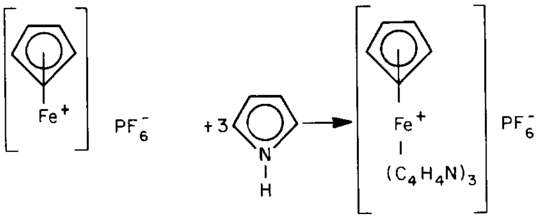
$$(\eta\text{-}C_5H_5)Fe(CH_3CN)^+ + (\eta\text{-}C_5H_5)Fe(\eta\text{-arene})^+ \rightarrow (\eta\text{-}C_5H_5)_2Fe + Fe(\text{II}) + \text{arene} + 3CH_3CN \quad (7)$$

The ^1H n.m.r. spectra obtained by us reconfirmed the formation of free arenes during photolysis of photoinitiators Irgacure 261 (*Figure 11*) and Komplex KM 1144 (*Figure 12*) in CD_2Cl_2. In the photoirradiated samples, there appear signals at $\delta = 7.29$ and 7.15 ppm (*Figure 11*) existing only in free isopropylbenzene and signals at $\delta = 7.86$ and 7.47 ppm (*Figure 12*) characteristic of free naphthalene.

The formation of Fe(II) has also been confirmed by us in the reaction of photolysed fragments with 1,10-phenanthroline.

It is very characteristic that polymerization of pyrrole in the presence of photoinitiators Irgacure 261 or Komplex KM 1144 under light irradiation occurs only in the presence of oxygen (it does not occur in argon or nitrogen atmospheres) and is completely inhibited by the addition of 1,10-phenanthroline. These results assume that the Fe(II) produced during the photolysis of photoinitiators Irgacure 261 or Komplex KM 1144 must be oxidized to Fe(III), which can initiate the polymerization of pyrrole. It is well known that Fe(II) is rapidly oxidized to Fe(III) in air. It is quite probable that polymerization of pyrrole can be caused by Fe(III), which is formed from Fe(II) produced in both mechanisms I and II. The presence of Fe(III) in polypyrroles has been proved by Mössbauer spectra (*Figure 6a*). The polymerization reaction continues until the monomer has reached the Fe(III) species, which initiate polymerization of pyrrole. When polypyrrole completely covers the initiation species, the reaction stops.

On the other hand, the cyclopentadiene–iron cation $(\eta\text{-}C_5H_5)Fe^+$ formed during the photolysis of initiators Irgacure 261 or Komplex KM 1144 (reaction (1)) probably has the ability to coordinate up to three molecules of pyrrole[21]:



(II)

(8)

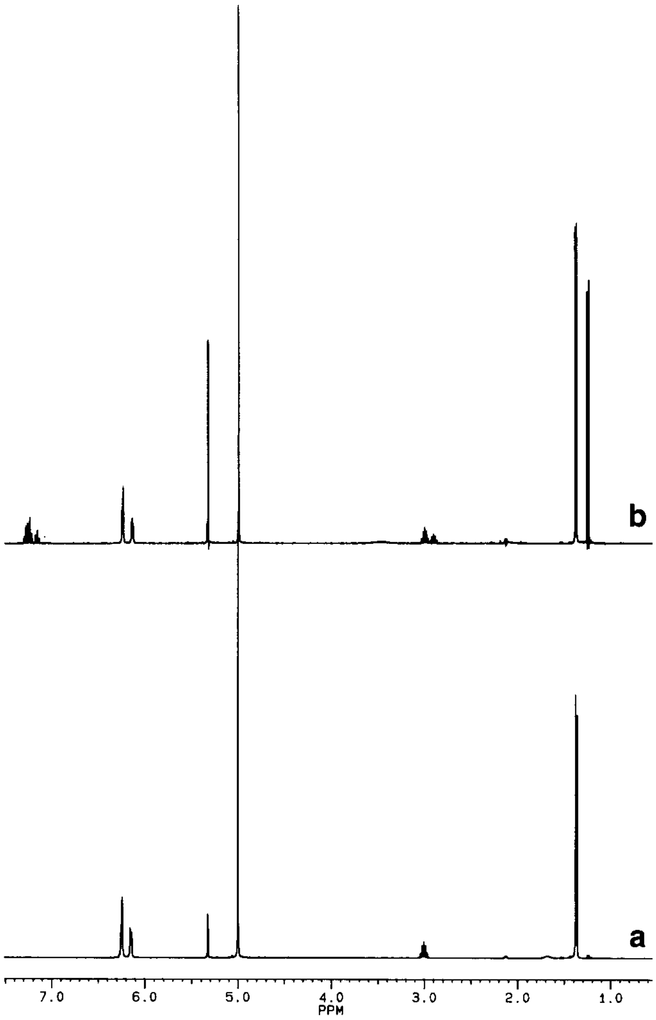


Figure 11 N.m.r. spectra of iron–arene salt photoinitiator Irgacure 261: (a) before irradiation and (b) after u.v. (254 nm) irradiation without previous separation of photolysis products

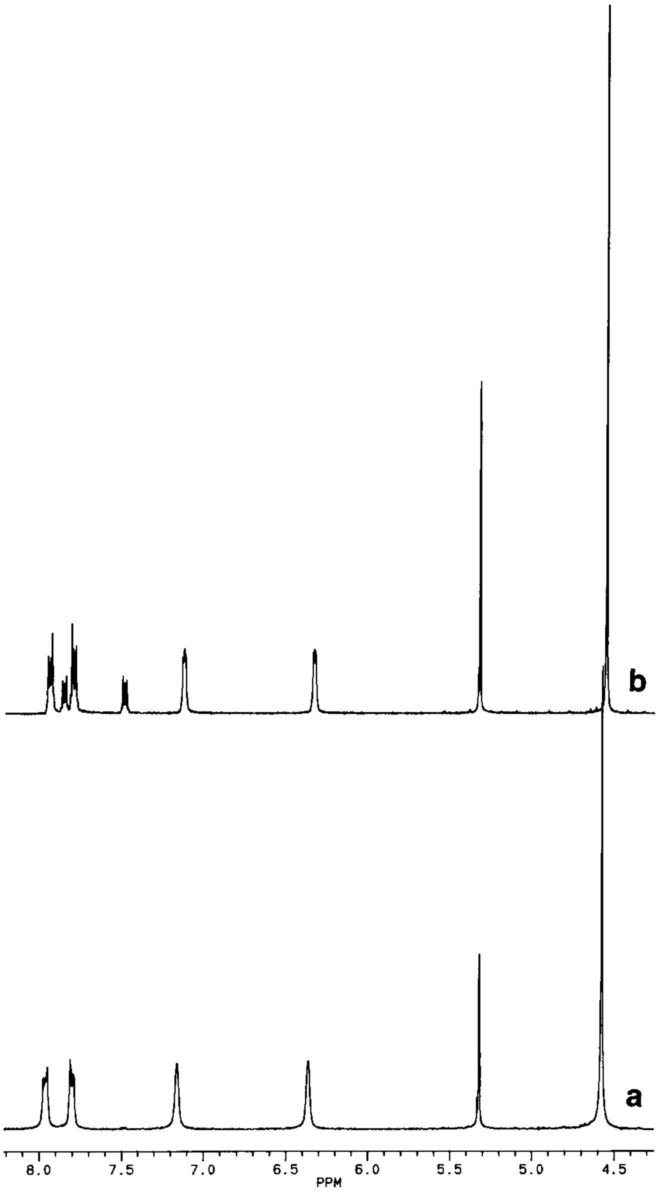


Figure 12 N.m.r. spectra of iron–arene salt photoinitiator Komplex KM 1144: (a) before irradiation and (b) after u.v. (254 nm) irradiation without previous separation of photolysis products

The role of cation (II), which is related to the arene(cyclopentadienyl)iron cation (I), in the polymerization mechanism of pyrrole is not yet clear, because the polymerization reaction occurs only in the presence of oxygen.

CONCLUSIONS

This new method of polymerization of pyrrole by the reactive species formed from the photolysis of photoinitiators Irgacure 261 and Komplex KM 1144 gives polypyrroles that differ structurally and electrochemically from those obtained by chemical or electrochemical methods as described elsewhere in the literature[4–6]. This reaction can also be performed when photoinitiators Irgacure 261 or Komplex KM 1144 are introduced onto the surface of a polymer matrix, e.g. poly(ethylene oxide), and placed in contact with pyrrole vapour and light. Polymerization occurs on such an activated polymer surface, and the polypyrrole formed is permanently bonded to it. These sandwich materials with both ionic and electronic conductivities can be considered as valuable materials for the construction of electrochemical devices.

REFERENCES

1 Rodrigues, T. and Gonzales-Velasco, J. *J. Chem. Soc., Chem. Commun.* 1990, 387
2 Segawa, H., Shimidzu, T. and Honda, K. *J. Chem. Soc., Chem. Commun.* 1989, 132
3 Kern, J. M. and Sauvage, J. P. *J. Chem. Soc., Chem. Commun.* 1989, 657
4 Diaz, A. F. and Kanazawa, K. K. in 'Extended Linear Chain Compounds' (Ed. J. S. Miller), Plenum, New York, 1982, Vol. 3, p. 417
5 Street, G. B., Geiss, R. H., Lindsey, S. E., Nazzal, A. and Pfluger, A. *Solid State Sci.* 1983, **49**, 242
6 Street, G. B. in 'Handbook of Conducting Polymers' (Ed. T. A. Skotheim), Dekker, New York, 1986, Vol. I, p. 265
7 Smith, F. M. *Bell Syst. Tech. J.* 1958, May, 712
8 Vaughan, P. E. *Br. J. Appl. Phys.* 1961, **12**, 414
9 Blythe, A. R. *Polym. Testing* 1984, **4**, 195
10 Collins, R. L. *J. Chem. Phys.* 1965, **42**, 1072
11 Wertheim, G. K. and Herber, R. H. *J. Chem. Phys.* 1963, **38**, 2106
12 Rabek, J. F., Lucki, J., Kereszti, H., Krische, B., Qu, B. J. and Shi, W. F. *Synth. Met.* 1992, **45**, 335
13 Scott, J., Pfluger, P., Krounbi, M. T. and Street, G. B. *Phys. Rev.* (*B*) 1983, **28**, 2140
14 Kaufman, J. H., Colaneri, N., Scott, J. C., Kanazawa, K. K. and Street, G. B. *J. Polym. Sci.* (*B*) 1983, **28**, 1005
15 Scott, J. C., Bredas, J. L., Yakushi, K., Pfluger, P. and Street, G. B. *Synth. Met.* 1984, **1**, 165
16 Nalwa, H. S. *J. Polym. Sci., Polym. Phys. Edn* 1988, **26**, 351
17 Marque, P., Roszczak, J. and Garnier, F. *J. Electroanal. Chem.* 1987, **218**, 107
18 Lohse, F. and Zweifel, H. *Adv. Polym. Ser.* 1986, **78**, 72
19 Nesmeyanov, A. N., Volkenan, N. A. and Shilortseeva, L. S. *Dokl. Akad. Nauk SSSR* 1970, **190**, 857
20 Gill, T. P. and Mann, K. R. *Inorg. Chem.* 1983, **22**, 1986
21 Kuhn, N., Horn, E. M. and Zauder, E. *Angew. Chem. Int. Edn. Engl.* 1988, **27**, 579