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Conjugated ionic polyacetylenes: 8. Amphiphilic poly(*N*-octadecyl-2-ethynylpyridinium bromide)

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An amphiphilic, ionic, conjugated polymer, poly(*N*-octadecyl-2-ethynylpyridinium bromide) (PNO2EPB), was prepared by two different synthetic processes. One involved a direct reaction of 2-ethynylpyridine (2EPY) with 1-bromooctadecane (1-BO), the other involved quaternization of the uncharged poly(2-ethynylpyridine) (P2EPY) with 1-BO. A fully quaternized PNO2EPB homopolymer was produced in the former reaction, but a copolymer of 2EPY and *N*-octadecyl-2-ethynylpyridinium bromide (NO2EPB) was obtained in the latter due to partial quaternization of P2EPY. The structure and properties of these polymers were investigated. The study of PNO2EPB formation using differential scanning calorimetry and ultraviolet–visible spectrophotometry indicated that quaternization of 2EPY monomer by 1-BO preceded polymerization of quaternized 2EPY monomer. Fully quaternized PNO2EPB displays a longer conjugation length and an enhanced thermal stability compared with the partially quaternized P2EPY-q-octa and the non-quaternized P2EPY. The study of compression isotherms of monolayers of the fully quaternized polymer leads to the conclusion that the alkyl (octadecyl) chains of the repeating unit are perpendicular to the water interface while the conjugated polymer chains are in the plane of the interface. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polyacetylenes; synthesis; properties)

INTRODUCTION

In previous papers from this laboratory we have reported on the synthesis and characterization of conjugated, ionic, substituted polyacetylenes based on ethynylpyridine (EPY)[1–3]. These polyacetylenes were obtained through activation of the acetylenic bond in EPY by quaternization of the pyridine nitrogen. The reaction mechanism in this spontaneous polymerization was ionic, since free-radical inhibitor did not affect the polymerization.

In this work, the synthesis and characterization of a poly(*N*-alkylpyridinium acetylene bromide) with a long alkyl octadecyl chain attached to the quaternized nitrogen is reported. Polymers (or oligomers) characterized by a rigid and strongly charged backbone and a long, non-polar, alkyl side group are expected to display amphiphilic properties and hence a tendency to self-organization. Stable liquid-crystalline arrays as well as Langmuir–Blodgett multilayers may thus be obtained.

The synthesis of poly(*N*-octadecyl-2-ethynylpyridinium bromide) (PNO2EPB) was achieved by two different polymerization processes. In the first, 2-ethynylpyridine (2EPY) was quaternized by 1-bromooctadecane (1-BO) and spontaneously polymerized (*Scheme 1*, route a). In the second, the synthesis was carried out by using poly(2-ethynylpyridine) (P2EPY) previously prepared by thermal polymerization[4]. The polymer (P2EPY) was then quaternized using 1-BO (*Scheme 1*, route b).

Such an approach provides a comparison between two polymers prepared by polymerization of the ionic monomer and the quaternization of a polymer obtained by free-radical polymerization. The amphiphilic polymer with long hydrophobic chains and a rigid, conjugated backbone is of interest in the preparation of ultrathin polymer films using both Langmuir–Blodgett and alternating layer-by-layer self-assembly techniques[5].

EXPERIMENTAL

Synthesis

2-Ethynylpyridine (2EPY) and 1-bromooctadecane (1-BO) were provided by Lancaster and Aldrich Co.; 2EPY was purified by vacuum distillation under N_2 atmosphere. Toluene and tetrahydrofuran (THF) were distilled over CaH_2 under N_2 before use.

Synthesis of PNO2EPB by direct reaction of 2EPY with 1-BO. PNO2EPB was prepared by reacting the 2EPY monomer with 1-BO in solution or in bulk (50–90°C, 72–150 h). This resulted in spontaneous polymerization of *N*-octadecyl-2-ethynylpyridinium bromide (NO2EPB).

A typical synthesis of the polymer PNO2EPB is as follows: 1-BO (0.68 g) was melted at 35°C in a glass tube and then 2EPY (0.22 g) was transferred into it by means

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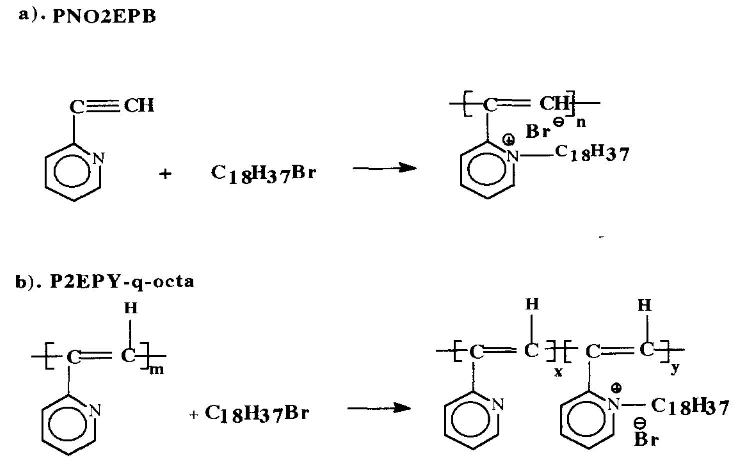

Scheme 1

of a syringe under N_2 and sealed. The mixture of 2EPY and 1-BO was heated to 80°C (oil bath) and magnetically stirred. It was observed that the system changed from a light yellow colour to black in 15 min. The system was kept for 120 h under the above reaction conditions. The dark solid product was purified by dissolving it in THF and then precipitated into petroleum ether. This process was repeated twice. The lustrous dark solid was vacuum dried at 60°C for 24 h until constant weight (0.79 g). The yield of polymer was 87% and the number-average molecular weight (M_n) was approximately 3500 as measured by vapour pressure osmometry (v.p.o.). The black polymer (PNO2EPB) readily dissolved in THF, chloroform and methanol. It was slightly soluble in acetone and acetonitrile. It was not soluble in toluene and water.

Quaternization of P2EPY with 1-BO (P2EPY-q-octa). P2EPY obtained by thermal polymerization of 2EPY was quaternized by 1-BO (equimolar ratio) in a solvent mixture of THF and toluene (1:3 volume ratio). A clear solution of P2EPY and 1-BO in the mixture of THF and toluene was kept at 80°C for 150 h (oil bath) under N_2 atmosphere and magnetic stirring (total concentration of P2EPY and 1-BO was 20 wt%). A deep brown product was obtained by adding this solution to petroleum ether. The product was purified by dissolving it in THF. It was then precipitated by petroleum ether again. Finally, the precipitate was washed with toluene and vacuum dried.

P2EPY-q-octa readily dissolved in THF, chloroform and methanol. It was slightly soluble in water, acetone and acetonitrile. It was not soluble in toluene.

To determine the amount of quaternization that took place in the reaction of 1-BO with P2EPY and to separate P2EPY-q-octa from unreacted 1-BO and P2EPY, a mixture of P2EPY and 1-BO was made by dissolving P2EPY and 1-BO (equimolar ratio) in THF at room temperature. The solvent was then evaporated. The film was dried *in vacuo* at room temperature until constant weight. The mixture was separated by alternating extraction using petroleum ether (solvent for 1-BO) and toluene (solvent for P2EPY). The insoluble residue was the quaternized product. No quaternization reaction was found to occur at room temperature.

PNO2EPB and P2EPY-q-octa were iodine-doped using the vapour absorption method[4].

Characterization

Fourier transform infra-red (*FT*i.r.) spectra were obtained on films of PNO2EPB and P2EPY-q-octa deposited on a KBr crystal from THF solution (Perkin–Elmer 1600 series FTIR spectrometer). An ultraviolet–visible (u.v.–vis.) spectrophotometer (GBC, UV/VIS 918) with temperature control and a computer-aided data analysis software program was used to measure the absorption of conjugated –C=C– double bonds of PNO2EPB and P2EPY-q-octa in absolute methanol or THF.

The number-average molecular weight (M_n) of PNO2EPB and P2EPY-q-octa was determined by v.p.o. in THF at 45°C (UIC, 070 Vapor Pressure Osmometer), using benzil and polystyrene (PS) of $M_n = 2000$ (Polysciences Inc.) as calibration standards. The inherent viscosities of PNO2EPB and P2EPY-q-octa were measured in THF using a Canon Ubbelohde dilution viscometer (concentration $0.5\,\mathrm{g\,dl^{-1}}$, 25 ± 0.1°C).

^1H, ^{14}N and ^{13}C nuclear magnetic resonance (n.m.r.) spectra of PNO2EPB and P2EPY-q-octa were recorded by a Bruker 270 MHz NMR spectrometer (model WP270SY), using $CDCl_3$ as solvent and TMS and CH_3NO_2 as internal references.

Thermal analysis of PNO2EPB and P2EPY-q-octa was carried out by differential scanning calorimetry (d.s.c.) and thermogravimetric analysis (t.g.a.). D.s.c. was performed using a Perkin–Elmer DSC 7 series instrument; t.g.a. was performed using a TGA 2950 (TA Instruments). D.s.c. measurements were made on cooling and on heating using repeated scans from room temperature to 200°C at a scanning rate of $10\,°\mathrm{C\,min^{-1}}$ under N_2 atmosphere using 10 mg samples. T.g.a. testing was carried out from room temperature to 600°C with a scanning rate of $10\,°\mathrm{C\,min^{-1}}$. Experiments were performed in air and N_2 separately.

Compression isotherms of polymers at the air–water interface were obtained on a Langmuir trough (Lauda Langmuir Filmwaage FW-2). About $100\,\mu l$ of the polymer solution (10^{-4} M, in $CHCl_3$) was spread on the water surface (MilliQ water) with the aid of a syringe.

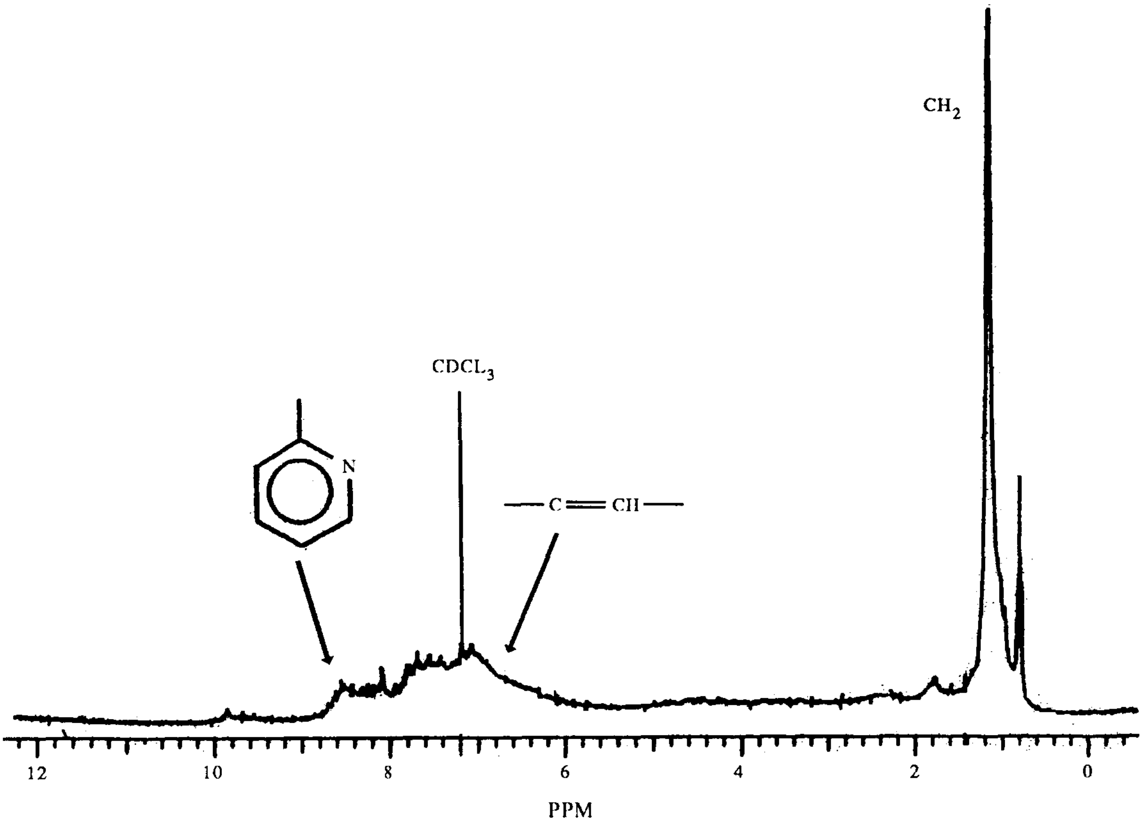

Figure 1 ^{1}H n.m.r. spectrum of PNO2EPB

After spreading and stabilization of the obtained monolayer, the surface area was gradually decreased using a compression barrier and the surface pressure was recorded against the surface area.

U.v.–vis. and d.s.c. studies of PNO2EPB formation. The u.v.–vis. spectrophotometer was used to monitor the reaction of 2EPY with 1-BO in THF (equimolar ratio) at 50 ± 1°C. The method and instrument parameters were as follows: automatic replicate number, 100; time between replicate measurements, 180 s; wavelength scan from 800 to 200 nm; scan speed, 3000 nm min^{-1}; slit width, 2.0 nm; lamp change wavelength, 350 nm; double beam. The experimental results are plotted as two- and three-dimensional modes.

D.s.c. was also used to study the formation of PNO2EPB. Scanning and isothermal modes were used. In the scanning mode the rate profile *versus* temperature was recorded, and in the isothermal mode the exothermic reaction rate *versus* time at constant temperature was followed. Details of the method and the assumptions made for the isothermal kinetics studied by d.s.c. have been described elsewhere[6].

A typical procedure of a d.s.c. isothermal experiment is as follows: 1-BO (0.68 g) was melted at 35°C and then mixed with 2EPY (0.22 g). The mixture was stirred vigorously until all chemicals dissolved completely. A clear solution was obtained, a sample (~10–15 mg) of which was then transferred to a sample pan. A stream of dry N$_2$ was used to purge the air and moisture that may have been present inside the sample holder, which was then sealed under N$_2$. The second scanning from room temperature to 220°C was conducted immediately following the isothermal experiment to ensure completeness of the reaction.

RESULTS AND DISCUSSION

*FT*i.r. spectra of PNO2EPB show that the absorption at 2109 cm^{-1} due to stretching of the carbon–carbon triple bond in 2EPY is absent in the polymer. The strong new absorption peaks at 1620 and 1510 cm^{-1} in the polymer are indicative of the extensively conjugated double-bond structure, and new peaks at 2920 and 2838 cm^{-1} are due to $-CH_2$ stretching of the alkyl chain of the octadecyl group. The ^{1}H n.m.r. spectrum of PNO2EPB confirms the *FT*i.r. measurements (*Figure 1*). Two strong peaks between 0.8 and 1.5 ppm are due to the aliphatic chain of the octadecyl group, while the broad peak between 6 to 9 ppm is characteristic of the pyridinium ring and of the conjugated $-C{=}CH-$ main chain.

The u.v.–vis. spectra of PNO2EPB give more evidence for the existence of the conjugated sequence of double bonds (*Figure 2*). In *Figure 2* the u.v.–vis. spectra of four polymer samples are superimposed: a sample of the unquaternized monomer 2EPY (a) and three polymers of different molecular weight prepared through quaternization of 2EPY with 1-BO in three different solvents (b, c and d). One can see the development in the polymer species of an absorption peak at $\lambda_{max} = 480$ nm (indicated by the arrow) trailing to 620 nm. This peak does not depend significantly on molecular mass M_n. Assuming that the Lewis–Calvin equation[7] is valid for substituted polyenes, these polymers appear to possess a similar distribution of conjugation lengths, indepen-

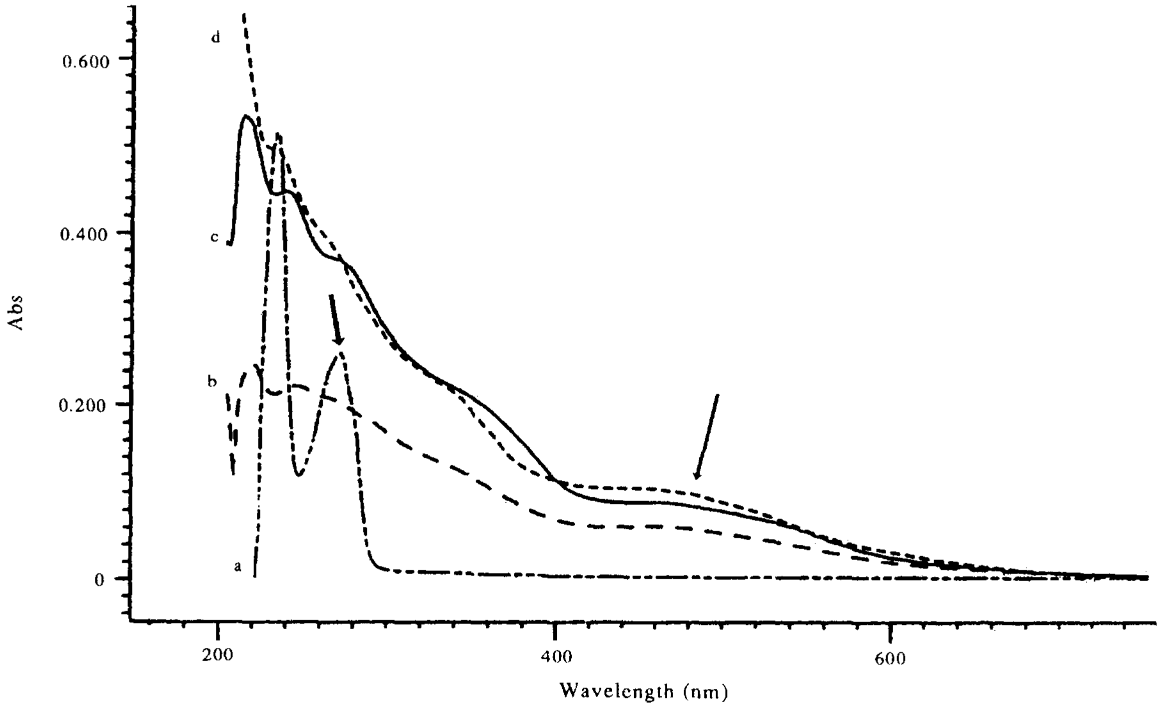

Figure 2 U.v.–vis. spectra in methanol of: (a) 2EPY; (b) PNO2EPB prepared in toluene, $M_n = 2500$; (c) PNO2EPB prepared in bulk, $M_n = 3500$; (d) PNO2EPB prepared in THF, $M_n = 3000$

dent of M_n. The average conjugation length appears not to exceed 6–8 monomer units in all cases. This is somewhat smaller than expected from λ_{max} but is in agreement with the value of the conjugation length found previously for a similar polymer[2]. It indicates that structural defects occasionally disrupt the conjugation sequence, on average every 6–8 monomer units, making the degree of polymerization smaller than that of the chain but substantially larger than the conjugation length of 2–3 repeat units found for non-ionic substituted polyacetylenes[8].

The study of polymer formation using u.v.–vis. spectrophotometry shows that the reaction of 2EPY with 1-BO can be divided into two stages. First, 2EPY is quaternized by the 1-BO, then the conjugated structure develops through polymerization of the quaternized monomer. One can see from *Figure 3a* that the characteristic peak due to 2EPY at $\lambda_{max} = 275$ nm (indicated by the arrow) gradually decreases, while a new peak at $\lambda_{max} = 400$ nm appears after ~1.5 h (20 runs). This peak continuously extends and intensifies with increasing reaction time. A deepening of the colour takes place, eventually producing a black solution. In contrast, the formation of a poly(*N*-octadecylvinylpyridinium bromide) by the quaternization of 4-vinylpyridine (4-VPY) produces no new peak since only quaternization takes place, i.e. no conjugated structure is produced and no colour changes accompany this reaction (*Figure 3b*).

Isothermal and dynamic studies of the formation of PNO2EPB by d.s.c. confirm the results obtained by u.v.–vis. spectrophotometry. *Figure 4* illustrates two consecutive heating scans made with a stoichiometric mixture of 2EPY and 1-BO. The first endothermic peak at ~25°C (curve a) is assigned to the melting of the unreacted 1-BO. A broad exothermic peak centred at ~175°C is assigned to the overlapping quaternization and polymerization reactions (total enthalpy 130 kJ mol^{-1}) (the arrow in *Figure 4* indicates the location of the quaternization reaction). The absence of the larger peak in the second run (curve b) indicates the completeness of the quaternization and polymerization processes. A d.s.c. scan of a mixture of pyridine and $C_{12}H_{25}Br$ (curve c) confirms that the quaternization process occurs at 100–130°C. An experimental quaternization enthalpy of -24.9 kJ mol^{-1} is obtained and exceeds the expected enthalpy of -21 kJ mol^{-1} calculated from the addition of bond energies of C–N and C–Br[9]. This discrepancy may be due to thermal gradient effects and the non-linear heating rates prevalent in the d.s.c. scanning mode[10,11].

A polymerization enthalpy of -105 kJ mol^{-1} was obtained from polymerization of quaternized 2EPY monomer, this value being smaller than the expected enthalpy of -121 kJ mol^{-1} obtained from summation of bond energies produced in the transformation of –C≡C– to –C=C– during the polymerization process[9]. This suggests that the triple bond of 2EPY is weakened by the introduction of a positive charge into the pyridine ring.

Figure 5A shows the d.s.c. curve corresponding to the isothermal reaction of PNO2EPB formation at 125°C (2EPY and 1-BO at equimolar ratio, in bulk). Two exothermic peaks are observed. The first, a narrow peak at 10 min (peak range from 2 to 20 min), is clearly associated with the quaternization of 2EPY by 1-BO. The enthalpy of quaternization in this case is about -13.5 kJ mol^{-1}, much less than the expected value of -21 kJ mol^{-1}. The discrepancy is probably due to the overlap with the polymerization peak (from 24 to 220 min) centred at ~145 min. The enthalpy corresponding to the second peak is approximately -90 kJ mol^{-1}. It

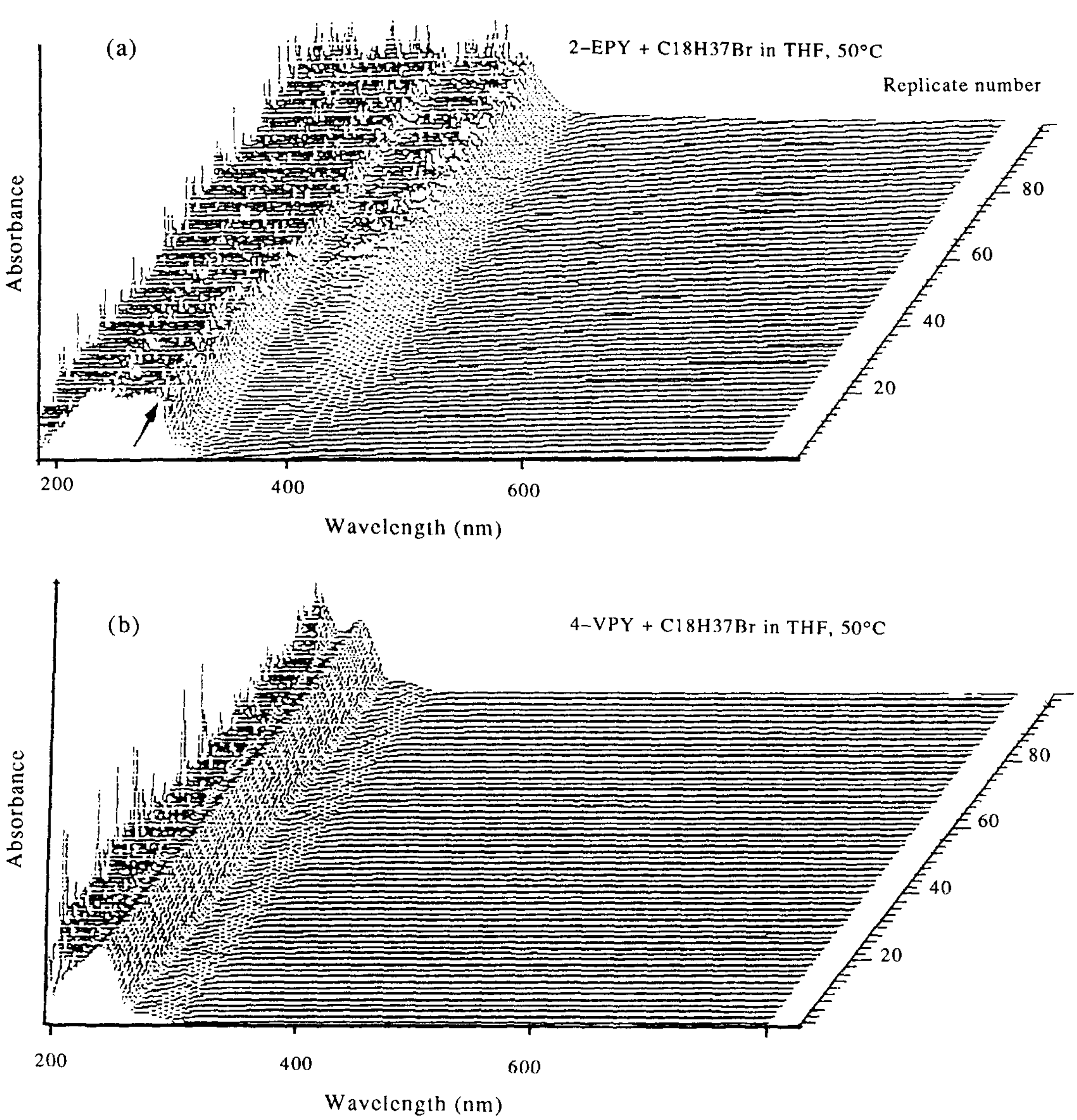

Figure 3 Time-monitored u.v.-vis. spectra of the reaction of: (a) 2EPY with $C_{18}H_{37}Br$ in THF; (b) r-VPY with $C_{18}H_{37}Br$

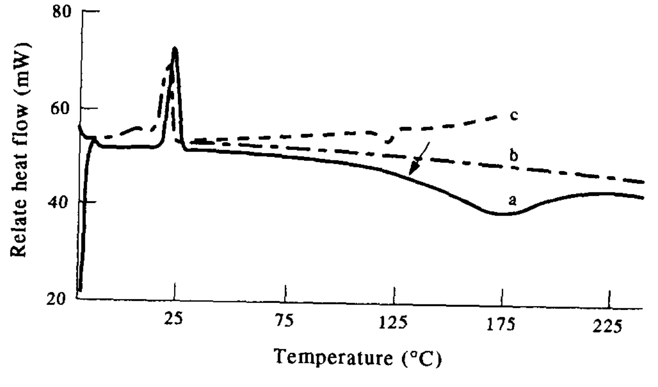

Figure 4 D.s.c. (5°C min^{-1}) traces of: (a) 2EPY with $C_{18}H_{37}Br$, first scan (arrow indicates quaternization); (b) second scan of a; (c) pyridine with $C_{12}H_{25}Br$

indicates that about 86% of the monomer has polymerized in this isothermal experiment.

In contrast to equimolar blends of 2EPY and 1-BO, an equimolar blend of P2EPY and 1-BO does not lead to a significant thermal effect at 125°C. A slight dip in the baseline indicates that only a very slow quaternization reaction occurs between the solid P2EPY and the liquid 1-BO (*Figure 5B*).

Another path to prepare PNO2EPB is through quaternization of the uncharged P2EPY with 1-BO[4]. The M_n of such a quaternized P2EPY (P2EPY-q-octa) is about 2000 (the M_n of the original P2EPY is 1100). It follows that the degree of quaternization of the P2EPY is ~25 to 30%. The formation of this partially quaternized polymer is confirmed by the ^{14}N n.m.r. spectrum, which shows a sharp peak at −74 ppm due to uncharged nitrogen and a broad peak from −140 to −200 ppm produced by a positively charged pyridinium nitrogen[12] (*Figure 6a*). The low intensity and breadth of the peak suggests that a random quaternization has occurred in the polymer. The quaternized P2EPY can therefore be considered a random copolymer of P2EPY and PNO2EPB. The low degree of quaternization of the polymer is probably due to steric repulsion between the pyridine ring and the long alkyl chain of 1-BO. The ^1H n.m.r. spectrum of P2EPY-q-octa is basically identical to that of PNO2EPB, showing a broad peak from 6 to 9.0 ppm (pyridinium ring and conjugated −C=CH− double bond) and strong multiple peaks

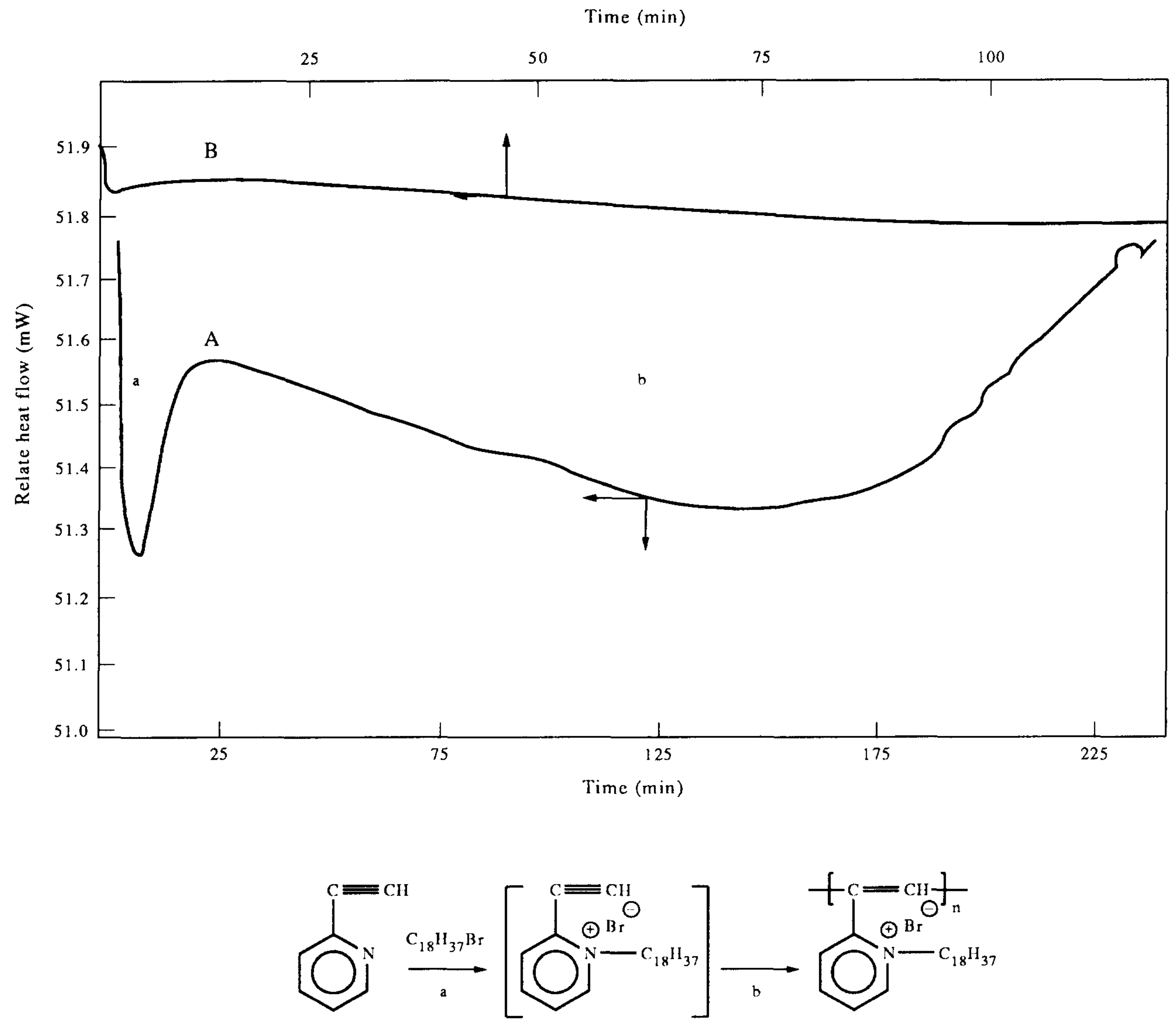

Figure 5 D.s.c. isothermal traces at 125°C of equimolar mixtures: (A) 2EPY and $C_{18}H_{37}Br$; (B) P2EPY and $C_{18}H_{37}Br$

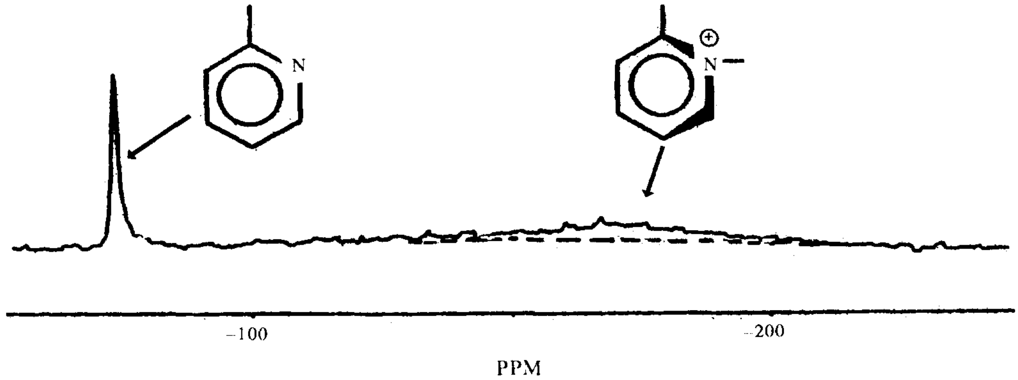

Figure 6 ^{14}N n.m.r. spectra of P2EPY-q-octa

between 0.8 and 1.5 ppm due to the methylene protons of the octadecyl group.

The *FT*i.r. spectrum of the quaternized copolymer P2EPY-q-octa is similar to that of PNO2EPB homopolymer. Peaks characteristic of the conjugated structure (–C=C– double bonds) at 1620 and 1510 cm^{-1} are less intense in the copolymer than in the homopolymer and increase with the degree of quaternization of the former. Similarly, peaks at 2920 and 2840 cm^{-1} due to the alkyl chain ($-CH_2$ stretching) are less intense in the copolymer than in the homopolymer.

Figure 7 illustrates the u.v.–vis. spectra of the copolymer solutions in MeOH at different pH values. The u.v. spectrum of the copolymer P2EPY-q-octa

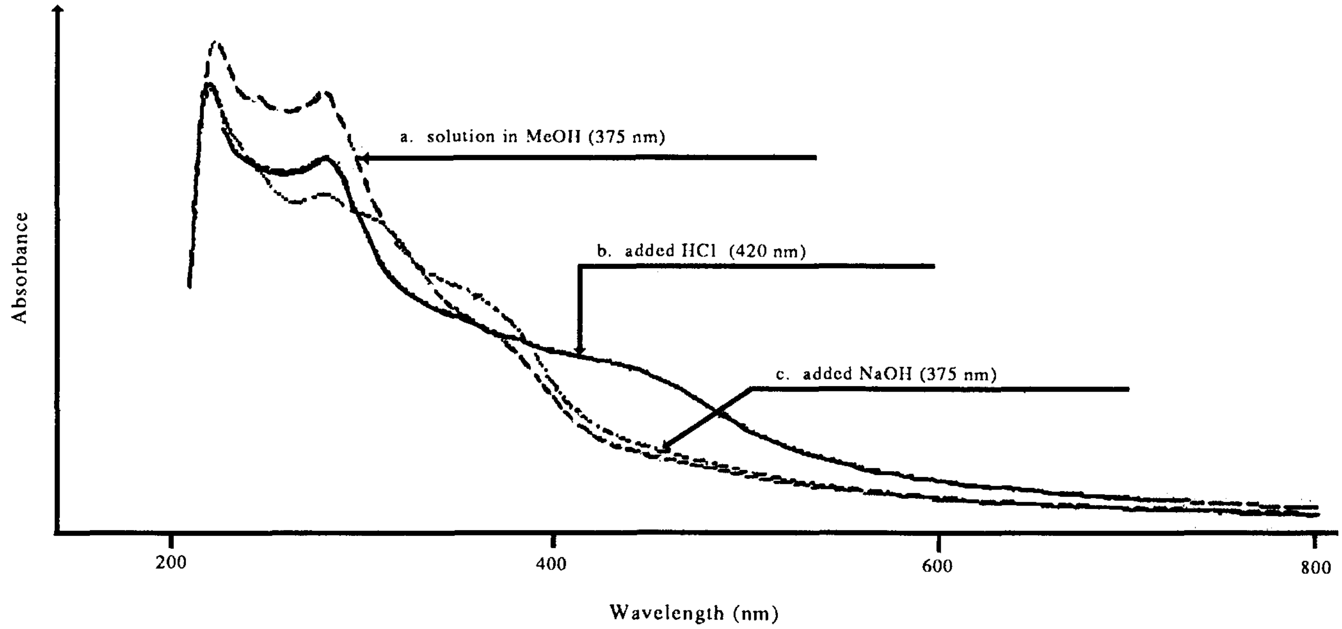

Figure 7 U.v.-vis. spectra of P2EPY-q-octa: (a) in methanol; (b) in methanol + HCl, pH < 2.0; (c) in methanol + NaOH, pH > 11

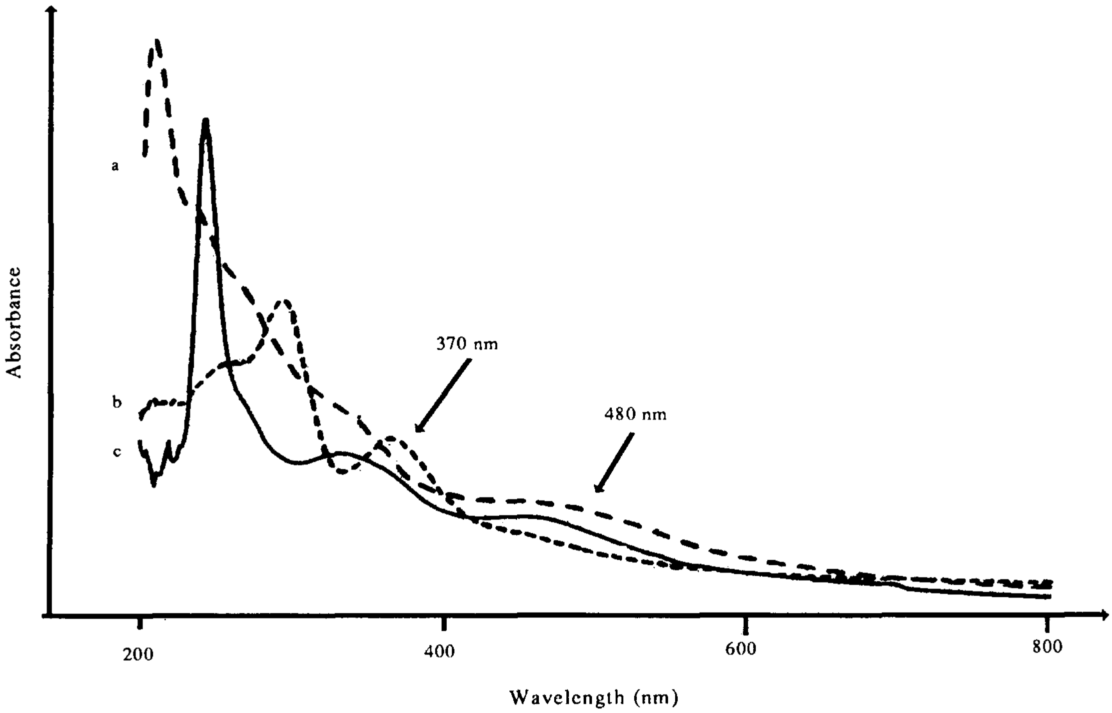

Figure 8 U.v.-vis spectra of: (a) PNO2EPB; (b) I_2-doped PNO2EPB; (c) b + HCl (solvent methanol)

(*Figure 7a*) shows $\lambda_{max} = 375\,nm$, quite near to that of the unquaternized P2EPY ($\lambda_{max} = 370\,nm$). A shift in λ_{max} from 375 to 420 nm was found on addition of HCl (*Figure 7b*). The same shift was observed on addition of HCl to the THF solution of P2EPY[4]. No shift was found on addition of base (*Figure 7c*). This shift with pH is reversible. No shifts were observed for solutions of P2VPY and a fully quaternized PNO2EPB subjected to similar treatment. This suggests that the conjugation length of the uncharged P2EPY and partially quaternized copolymer P2EPY-q-octa can be extended by additional protonation of the unquaternized or partially quaternized polymers. It additionally confirms the influence of ionic respulsion on the conjugation length[1-4,13].

A 'stretching' of the quaternized polyacetylenic chain can also take place on dilution. A significant polyelectrolyte effect of the fully quaternized PNO2EPB is indeed observed by following the inherent viscosity (η_{in}) as a function of concentration (*Table 1*). One can see that η_{in} of PNO2EPB increases significantly with dilution, in contrast to the η_{in} of the non-charged P2EPY or the weakly charged copolymer.

Iodine absorption of films of quaternized, partially quaternized and unquaternized polymers was carried out by exposing samples to iodine vapour. High iodine

Table 1 Inherent viscosity of PNO2EPB, P2EPY-q-octa and P2EPY in diluted solution (solvent THF, 25°C)

Polymer	η_{in} (dl g^{-1})	Conc. (g dl^{-1})
P2EPY	0.040	0.520
	0.036	0.047
P2EPY-q-octa	0.040	0.540
	0.113	0.015
PNO2EPB	0.091	0.510
	0.119	0.057

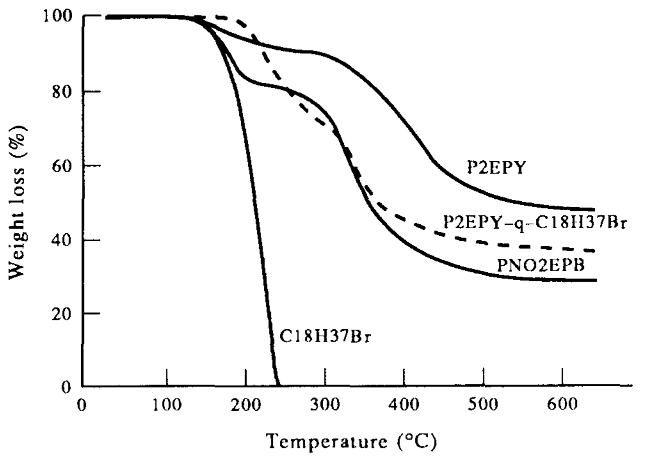

Figure 9 T.g.a. traces of P2EPY, P2EPY-q-octa, PNO2EPB and $C_{18}H_{37}Br$ (N_2, scanning rate 10°C min^{-1})

absorption yields of 320–450 wt% can be reached. The doped samples still retained 90% of iodine even after placing them in a vacuum oven (3 mmHg) for 24 h at room temperature. The order of iodine absorption is P2EPY > P2EPY-q-octa > PNO2EPB. This could be due to the interplay of the polar nature of iodine molecules capable of fixation on charged sites of the polymer chain and steric factors introduced by the voluminous octadecyl group[4]. Interestingly, *FT*i.r. and u.v.–vis. spectra of iodine-doped samples of PNO2EPB and P2EPY-q-octa still contained strong absorption peaks indicative of remaining conjugated –C=C– double bonds (e.g. *FT*i.r., –C=C–, 1622 cm^{-1}). However, the λ_{max} of iodine-doped PNO2EPB decreased from 480 to 375 nm (*Figure 8b*). Absorption of I_2 by the sample seems to reduce the conjugation length of the chain, possibly through steric effects (favouring a twist of the conjugated –C=C– sequence of bonds of the backbone out of its plane). One should note that the λ_{max} of doped PNO2EPB can be brought back to that corresponding to the undoped PNO2EPB (λ_{max} = 480 nm) by addition of HCl (*Figure 8c*).

Thermal stability of polymers was investigated by t.g.a. The fully quaternized PNO2EPB homopolymer exhibits enhanced thermal stability compared with P2EPY and P2EPY-q-octa (*Figure 9*). PNO2EPB is thermally stable up to 230°C and its weight loss is <2.0% at that temperature. In comparison, the weight loss of P2EPY and 1-BO is 9.0 and 50%, respectively, under the same conditions. The weight loss of P2EPY-q-octa is 20%. Higher charge density in the polymer is thus related to a higher thermal stability.

Figure 10 shows the compression isotherms of monolayers of PNO2EPB homopolymer and P2EPY-q-octa copolymer spread on a water surface. It can be seen that the monolayer of the homopolymer is highly expanded compared with that of the copolymer. Both form stable monolayers at high surface pressures.

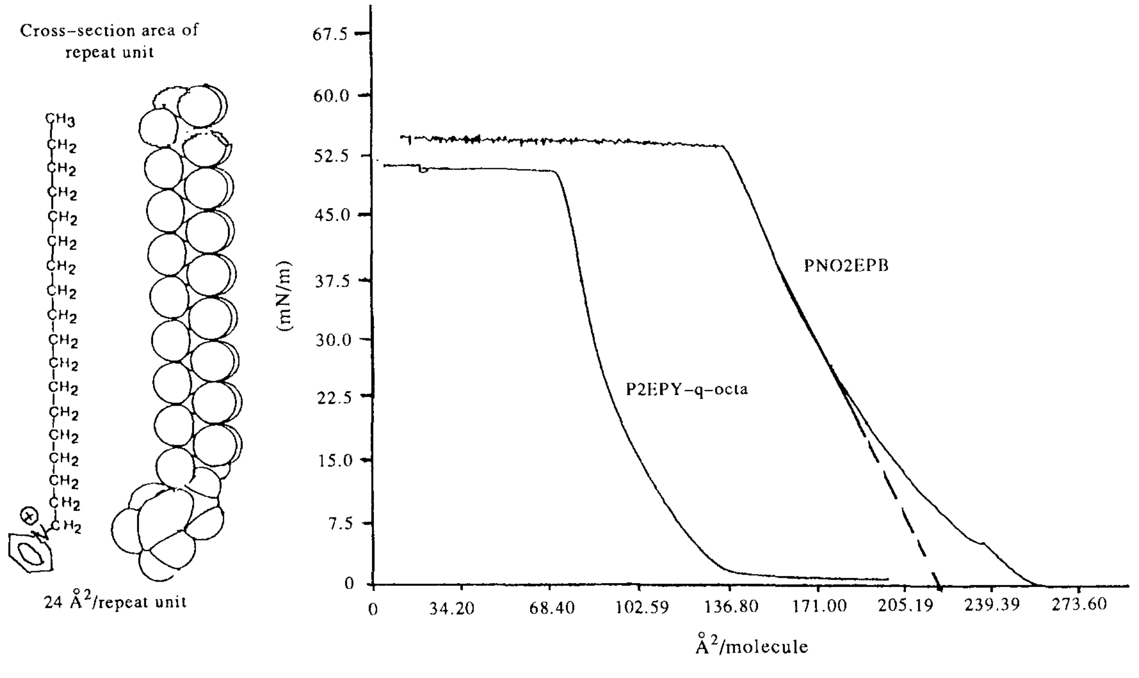

Figure 10 Compression isotherms of monolayers of PNO2EPB and P2EPY-q-octa at air–water interface (20°C)

From *Figure 10* it follows that the cross-sectional area per repeat unit of PNO2EPB is about 24 Å^2. This is not unreasonable for a cross-sectional area of an alkyl chain (20 Å^2) terminated by a pyridinium ring[14,15]. The octadecyl chains are hence perpendicular to the water surface with the conjugated polymer chain located in the plane of the surface.

CONCLUSIONS

Conjugated, ionic, poly(*N*-octadecyl-2-ethanylpyridinium bromide) can be prepared by direct reaction of 2-ethynylpyridine and 1-bromooctadecane. Quaternization of poly(2-ethynylpyridine) leads to only partially quaternized polymer which can be considered a random copolymer of 2EPY and NO2EPB. The study of the formation of PNO2EPB indicates that quaternization and polymerization steps are sequential. The conjugation length of the copolymer increases with increasing charge density and so does the thermal stability. Monolayers of such charged polymers are stable and can be easily prepared. Within these monolayers the alkyl chains are perpendicular to the water surface, while the conjugated polymer chains are located in the plane of the surface.

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