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Conjugated phosphonium polyacetylenes

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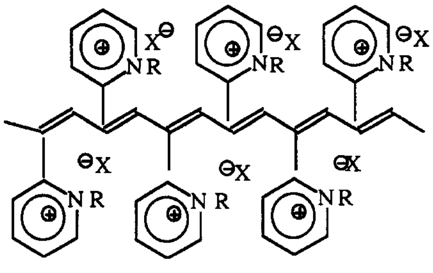
Several substituted phosphonium phenylacetylene monomers and the corresponding polymers were prepared through quaternization of trimethyl (or phenyl) phosphines with phenylacetylene bromide and subsequent polymerization of quaternized monomers. A nitrogen analogue, poly(1-triethyl ammonium bromide 2-phenylacetylene) was prepared for comparison. In contrast to the phosphonium monomers the quaternary ammonium analogue polymerized spontaneously and could not be isolated from its polymer. Spectroscopic and thermal properties of these polymers were studied. Ionic phosphonium polyacetylenes are characterized by higher u.v. absorption shifts toward the visible than the ammonium polyphenylacetylene and the non-ionic polyphenylacetylene and polyphenylacetylene bromide. The extent of conjugation in the main chain of the phosphonium polymers increases with the decreasing size of the substitutent, as does the thermal stability of the monomers and polymers. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: phosphonium polyacetylenes; conjugation; ionic polyacetylenes)

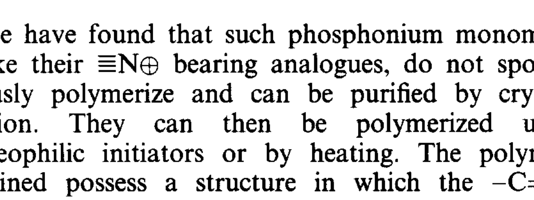
INTRODUCTION

In a series of publications, we have described the synthesis of a new class of mono- and di-substituted ionic polyacetylenes with extensively conjugated backbones[1–7]. These polymers were prepared through quaternization of mainly ethynylpyridines but also of tertiary ethynylalkylamines using various quaternizing agents such as bromine[1], concentrated HCl[2], methyl triflate[3], and alkyl bromide[4,5]. Such reaction, leading to the opening of the adjacent acetylenic triple bonds, is universal and can be used to introduce a sequence of conjugated double bonds into structures containing quaternizable nitrogen atoms[6,7]. Except for the methyltriflate, most quaternizing agents were found to lead to an overlap between the quaternization and the ensuing polymerization of quaternized monomers. In polymers obtained by the above method the quaternized nitrogen atom is in α to the –C=C– double-bond sequence of the backbone.



R--- H or alkyl group
X---halogen, CF_3SO_4

In this paper we report on the synthesis of novel ionic polyacetylenes in which the phosphonium group replaces the quaternary nitrogen. In the phosphonium monomer the triple bond is directly adjacent to the quaternized phosphorous atom as shown in *Scheme 1*.



Scheme 1

We have found that such phosphonium monomers, unlike their ≡N⊕ bearing analogues, do not spontaneously polymerize and can be purified by crystallization. They can then be polymerized using nucleophilic initiators or by heating. The polymers obtained possess a structure in which the –C=C– double bonds of the main-chain are in the α position to the quaternized charge-bearing phosphorous atom.

EXPERIMENTAL

Materials

Phenylacetylene (PA), and bromine (Br_2), trimethylphosphine (TMP), dimethyl phenylphosphine (DMPP), triphenylphosphine (TPP), triethylamine (TEA) were purchased from Aldrich Chemical Co. PA and TEA were purified by vacuum distillation under N_2. THF (h.p.l.c. grade) was dried over $CaCl_2$ and KOH for 2 days then

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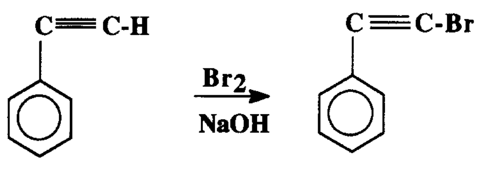
distilled over CaH_2. Toluene (h.p.l.c. grade) was refluxed over CaH_2 for 8 h and distilled before use. Other chemicals such as TPP and Br_2 were certified 98% pure and used without further purification.

Preparation of phenylacetylene bromide (PAB)

Phenylacetylene bromide was prepared by reacting phenylacetylene with an alkaline solution of bromine[8] (*Scheme 2*)



Scheme 2

The procedure is as follows. A solution of 30 g of NaOH in 80 ml of H_2O was prepared at 0°C in a 250 ml container covered with black tape. It was added to 16.0 g (5.2 ml) of bromine with stirring. PA (8.54 g or 9.2 ml) was then added to this solution (always with stirring) while the temperature was maintained at 0°C. The container was sealed and shaken mechanically for 72 h at room temperature. The crude product was then extracted with ethyl ether (3 × 60 ml). The combined ether layers were dried over $CaCl_2$ for 48 h in a refrigerator. The solvent (ethyl ether) was evaporated under reduced pressure to leave a pale yellow oil. Vacuum distillation of the oil (5 torr, 60–65°C, N_2) yielded 12.5 g (yield 51%) of a colourless product. It was stored at −15°C.

Preparation of quaternized phosphonium phenylacetylene monomers

Stable, quaternized monomer salts of phenylacetylene bromide were prepared by using trimethylphosphine (TMP), dimethylphenylphosphine (DMPP), and triphenyl phosphine (TPP). The reaction is shown in *Scheme 3*.

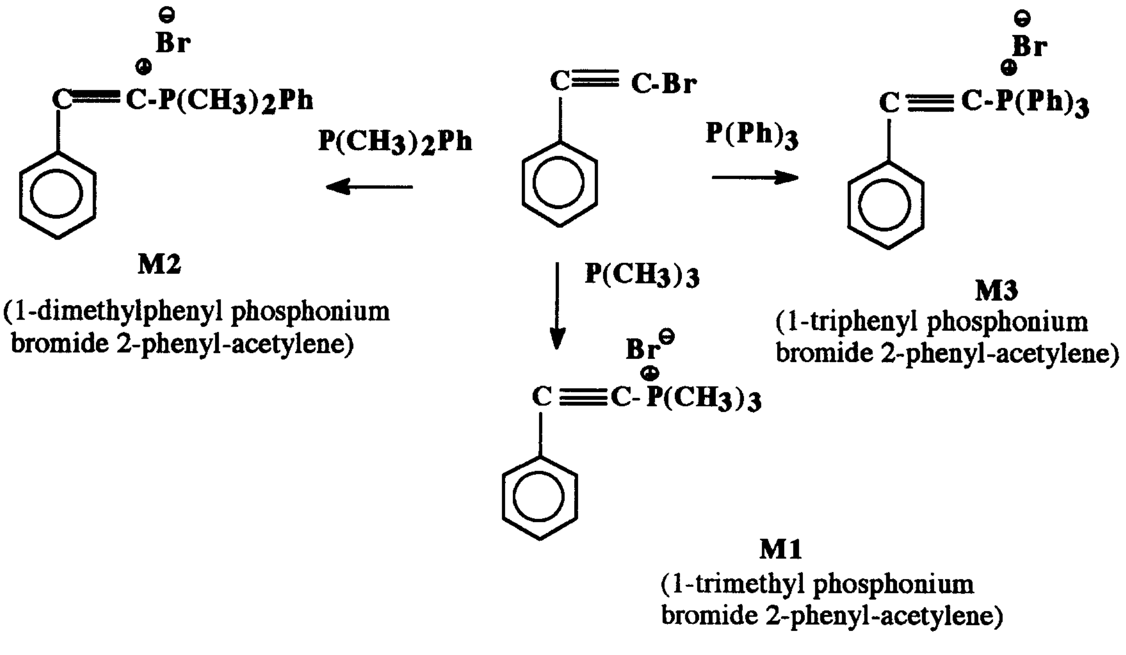
(1) Preparation of M1: A typical example of preparation of the monomer salt M1 is as follows: 5.6 ml (5.6×10^{-3} mol) of a 1 M solution of TMP in THF was added under N_2 to a flask containing 10 ml of toluene and 10 ml of THF. To this clear solution, a solution containing 1.0 g (5.52×10^{-3} mol) of PAB in a mixture of 10 ml of toluene and 5 ml of THF was added dropwise under N_2, with vigorous stirring at room temperature. The reaction was strongly exothermic and a white precipitate formed immediately. The mixture was stirred for another 12 h at room temperature. It was then heated to 40°C and allowed to stand overnight at 40°C. The white precipitate composed of quaternized M1 was collected. It was purified by dissolution in methanol and precipitation by adding the solution to toluene. The precipitate was washed with THF. The yield was 90%. The white product was soluble in MeOH, acetonitrile, and $CHCl_3$, and insoluble in THF, toluene, and acetone. It was recrystallized from a mixture of 1-propanol and ethyl ether(1 : 1 v/v). Melting point 218–221°C (d.s.c., heating rate at 10°C min^{-1}).

*FT*i.r. (cm^{-1}): 3052 (=C-H aromatic stretching) 2964, 2893 ($-CH_3$ stretching), 2186 ($-C{\equiv}C-P(CH_3)_3$ stretching); 1287 ($P-CH_3$ asymmetric deformation).

N.m.r. ($CDCl_3$, δ): 2.80 (9H, *d*, $P-CH_3$); 6.9–7.3 (5H, *m*, aromatic protons).

Analysis: calculated for $C_{11}H_{14}PBr$ (MW 257): C, 51.36%; H, 5.45%; Br, 31.13%. Found: C, 50.66%; H, 5.60%; Br, 31.00%.

(2) Preparation of M2. The compound was prepared similarly to M1. It decomposed at 200°C (before melting). Yield: 45.7%. *FT*i.r. (cm^{-1}): 3052 (=C–H aromatic stretching); 2964, 2893 ($-CH_3$ stretching); 2182 ($-C{\equiv}C-P(CH_3)_2(Ph)$ stretching); 1439(P-phenyl links); 1287 ($P-CH_3$ asymmetric deformation). N.m.r. ($CDCl_3$, δ): 2.80 (6H, *d*, P-CH3); 6.9–7.3 (5H, *m*, aromatic protons); 8.2–8.6 (5H, *m*, P–Ph aromatic protons).



Scheme 3

Analysis: calculated for $C_{16}H_{16}PBr$ (MW = 319): C, 60.19%; H, 5.02%; Br, 25.08%. Found: C, 58.94%; H, 5.06%; Br, 26.50%.

(3) Preparation of M3. The preparation of M3 was similar to M1. The compound decomposed at 200°C (before melting). Yield: 37.0%. *FT*i.r. (cm^{-1}): 3052 (=C–H aromatic stretching); 2175 ($-C{\equiv}C-P(Ph)_3$ stretching); 1439 (P–phenyl links). N.m.r. ($CDCl_3$, δ): 6.9–7.3 (5H, *m*, aromatic protons); 7.5–8.2 (15H, *m*, P–Ph aromatic protons).

Analysis: calculated for $C_{26}H_{20}PBr$ (MW = 443): C 70.43%; H, 4.51%; Br, 18.06%. Found: C, 68.70%; H, 5.16%; Br, 14.93%.

The results of elemental analysis are not in complete agreement with the calculated values. This discrepancy is not surprising in view of the well known difficulty of determining the exact bromine and phosphorus contents in the presence of both elements[9,10]. An additional difficulty is the hygroscopic nature of phosphonium salts. The values for C are systematically lower and those for H higher than the calculated ones. This is consistent with the presence of some water. Examples of such discrepancies are given in the literature and are treated using the water content as an adjustable parameter[9]. Here we preferred to report such results for the anhydrous state. N.m.r. and *FT*i.r. spectra for all of the above monomeric compounds were in qualitative and quantitative agreement with the proposed structures.

Polymerization of quaternized phosphonium phenylacetylene monomers

Zwitterionic/anionic polymerization. Quaternized monomers can be polymerized at 50–70°C as shown below by using a weak base (pyridine, picoline) as initiator. A typical polymerization procedure is given below: 0.5 g of monomer M1 was dissolved in 6.0 g of $CHCl_3$, 0.3 ml of pyridine (or picoline) was added to this solution under stirring. The container was then sealed under N_2 and placed at 60°C. The colourless solution became black in 5 min and the sealed container was left at 60°C for 5 days in order to complete the polymerization. A black precipitate appeared in 8 h. The polymerization was terminated by pouring the content of the container into toluene. The black solid obtained was purified by dissolution in MeOH and precipitated with toluene. This process was repeated twice. The lustrous black solid was vacuum dried at 60°C to constant weight. The yield of P1 (poly(M1)) was 90%. The product dissolved readily in MeOH, and only slightly in $CHCl_3$. It was insoluble in THF and toluene.

Polymerization of M2 and M3 was carried out under similar conditions. The yields of P2 (poly(M2)) and P3 (poly(M3)) were 85% and 75%, respectively. The black polymers obtained were soluble in MeOH and $CHCl_3$ and insoluble in THF and acetonitrile.

Thermal polymerization. Quaternized monomers such as those described here can be polymerized also by heating under N_2: 0.5 g (2.76×10^{-3} mol) of purified PAB was placed into a thick-walled glass tube containing 5 ml of THF and 10 ml of toluene, together with 2.8 ml of a 1 M solution of TMP in THF. The mixture was maintained at 40°C with stirring under N_2. A white precipitate of M1 formed immediately. The polymerization of M1 was carried out by raising the temperature to 70°C under N_2 for overnight then to 140°C for 48 h. The polymerization was terminated by pouring the content of the tube into toluene. The yield was 83% using the polymer purification described in the previous section.

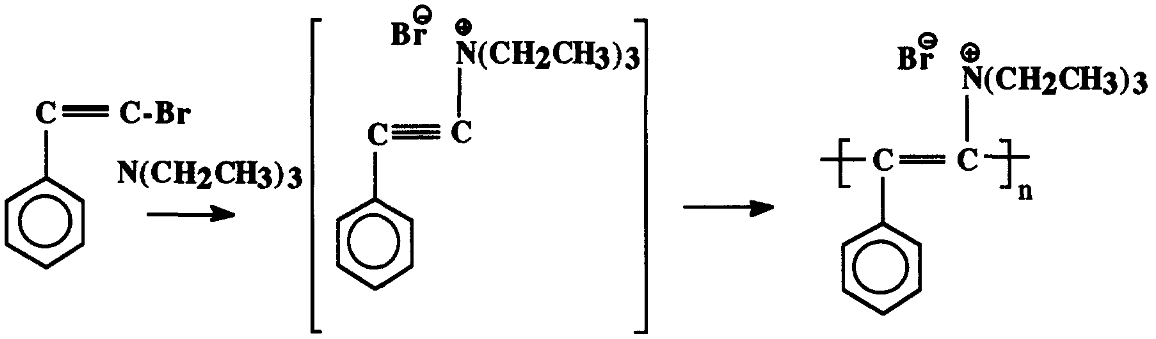
Thermal polymerization of M2 and M3 can be carried out similarly. Yields of P2 and P3 were 86% and 90%, respectively. The black polymers obtained were soluble in MeOH and $CHCl_3$ and insoluble in THF and acetonitrile.

Synthesis of poly(1-triethyl ammonium bromide 2-phenyl acetylene)

Poly(1-triethyl ammonium bromide 2-phenyl acetylene) (PTABPA) was prepared by reacting the phenylacetylene bromide (PAB) with triethyl amine (TEA) in solution or in bulk. This resulted in a spontaneous polymerization of 1-triethyl ammonium bromide 2-phenyl acetylene (TABPA) (*Scheme 4*).

A typical synthesis of the polymer PTABPA is as follows: 0.50 g (2.75×10^{-3} mol) of PAB was kept at 35°C in a glass tube then 0.38 ml (2.75×10^{-3} mol) of TEA was added under N_2 and sealed. The mixture of PAB and TEA was heated to 75°C (oil bath) and magnetically stirred. The colour of the mixture changed from light yellow to black in 10 min. The system was kept for 72 h under the above conditions. A dark precipitate formed and was purified by repeated dissolution in THF and precipitation in petroleum ether. The lustrous dark solid was vacuum dried at 60°C for 24 h to constant weight (0.65 g). The yield of polymer was 84%. Its inherent viscosity at a concentration of 0.5 g dl^{-1} in methanol at 25°C was 0.15 dl g^{-1}. The black polymer (PTABPA) readily dissolved in THF, chloroform and MeOH. It was insoluble in toluene and water. The number average molecular weight of PTABPA was $M_n = 3000$.

*FT*i.r. (cm^{-1}): 2982, 2932 ($-CH_3$ and $-CH_2$ stretching);



Scheme 4

3052 (=C–H aromatic stretching); 1575, 1492 (=C stretching of aromatic ring); 765, 697 (monosubstituted aromatic ring). Triple bond stretching at 2187 cm^{-1} owing to –C≡C–N(C_2H_5)$_3$ was replaced by a new peak at 1625 cm^{-1} due to the conjugated –C=C– double bond.

^{1}H n.m.r. ($CDCl_3$, δ): 0.8–1.9 (9H, *m*, –CH_3); 3.00–4.0 (6H, *m*, N–CH_2); 7.0–8.2 (5H, *m*, aromatic protons). ^{13}C n.m.r. ($CDCl_3$, δ): 30, 38 (–CH_3, –CH_2); 100–105 (–C=C– aliphatic conjugated double bond); 145–150 (–C= aromatic carbons).

Characterization

Direct measurements of the molecular mass of these conjugated polymers were not possible using optical methods given the high degree of light absorption of their solutions. However an estimation of Mn can be made by using colligative methods such as vapour pressure osmometry (v.p.o.) given the solubility of these polymers in nonionizing solvents. This method was already used successfully in the case of poly(octadecyl 2-ethynyl-pyridinium bromide)[2] and was also used here (see *Figure 1*).

*FT*i.r. spectra of films of polymers deposited on a KBr crystal from MeOH solution were recorded using a Perkin–Elmer 1600 series *FT*i.r. spectrometer. U.v. spectra were recorded by means of a u.v./vis 916 spectrometer (GBC Scientific Equipment Pty Ltd) with a temperature control and a computer-aided data analysis software program. It was used to measure the u.v. absorption of conjugated –C=C– double bonds of polymers in absolute methanol or THF.

The number average molecular mass (M_n) of polymers was determined in anhydrous MeOH at 45°C, using a UIC Inc., 070 VPO Osmometer. Benzil was used as a calibration standard (*Figure 1*). The inherent viscosities of P1, P2, and P3 in MeOH (0.5 g dl^{-1} at 25 ± 0.1°C) were measured using a Canon Ubbelohde dilution viscometer.

^{1}H, ^{13}C and ^{31}P n.m.r. spectra of quaternized monomers (solvent $CDCl_3$) and polymers (solvent MeOH-d_4) were recorded by a Bruker 270 MHz n.m.r. spectrometer model WP270SY. For ^{31}P n.m.r. an external reference H_3PO_4 was used.

Thermal properties of monomers and polymers were studied by differential scanning calorimetry (d.s.c.) and thermogravimetric analysis (t.g.a.) using a Perkin–Elmer DSC 7 and a TGA 2950 (TA Instruments). D.s.c. scans were made on cooling and on heating using 10 mg samples with repeated scans from room temperature to 200°C at a scanning rate of 10°C min^{-1} under N_2 atmosphere. T.g.a. testing was carried out from room temperature to 600°C in air and N_2 with a scanning rate of 10°C min^{-1}.

RESULTS AND DISCUSSION

^{1}H n.m.r. and *FT*i.r. spectra of PA and PAB were obtained. The monosubstituted PA shows the characteristic

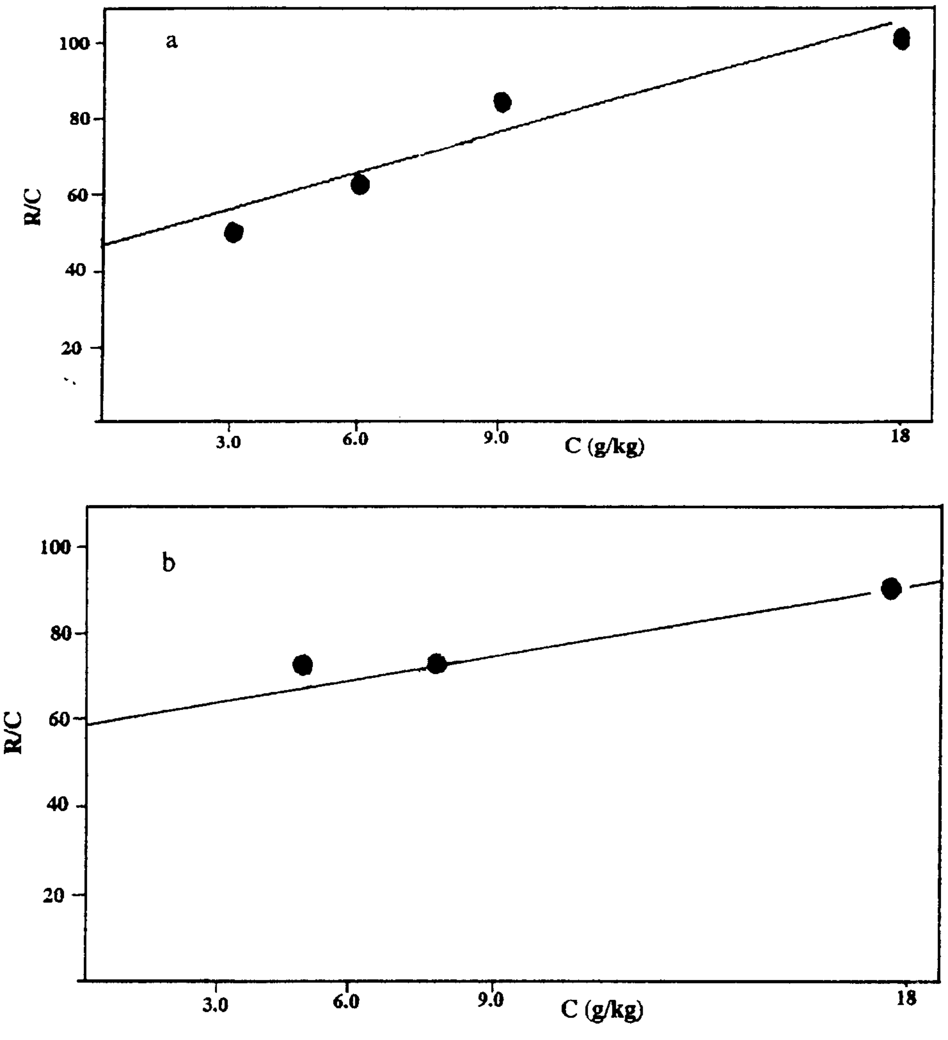


Figure 1 Plots of v.p.o. data of PTABPA, M_n = 3000 (a); and P2, M_n = 2400 (b). (Solvent anhydrous MeOH, 45°C)

absorption of $-C{\equiv}C-$ stretching at 2109 cm^{-1}. After the substitution of the H in $\equiv$C-H by Br the characteristic absorption of the disubstituted triple bond shifts from 2109 to 2209 cm^{-1}. The proton n.m.r. spectrum of PA displays a single peak at 3.1 ppm, which is absent in the PAB spectrum. Both the *FT*i.r. and n.m.r. spectra indicate that PA was completely converted to PAB.

Poly(phosphonium phenylacetylenes)

*FT*i.r. absorption bands characteristic of M1, M2, and M3 are given in the Experimental section. The peak positions of substituted triple bonds of quaternized monomers shifted to lower wave numbers with increasing size of the substituent: from 2186 cm^{-1} for $-C{\equiv}C-P(CH_3)_3$, through 2182 cm^{-1} for $-C{\equiv}C-P(CH_3)_2(Ph)$, to 2175 cm^{-1} for $-C{\equiv}C-P(Ph)_3$.

*FT*i.r. spectra of monomers (using picoline as an initiator) were taken at different polymerization times and temperatures. The spectra show that monomers can be polymerized completely in the temperature range of 50–70°C for 3–7 days. The peak of the triple bond of the monomer such as M1 (2812 cm^{-1}) disappears completely and a peak corresponding to a conjugated double bond (1625 cm^{-1}) appears. The polymers obtained display a relatively high degree of polymerization (20–25) as determined by v.p.o. In contrast to P1, the DP of P2

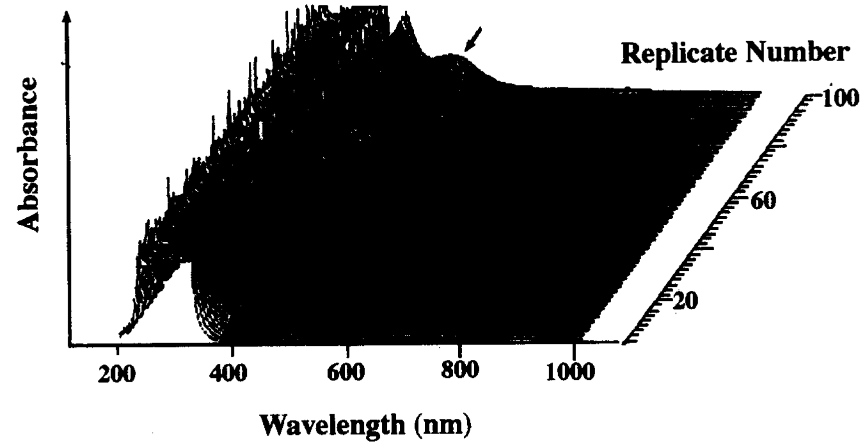
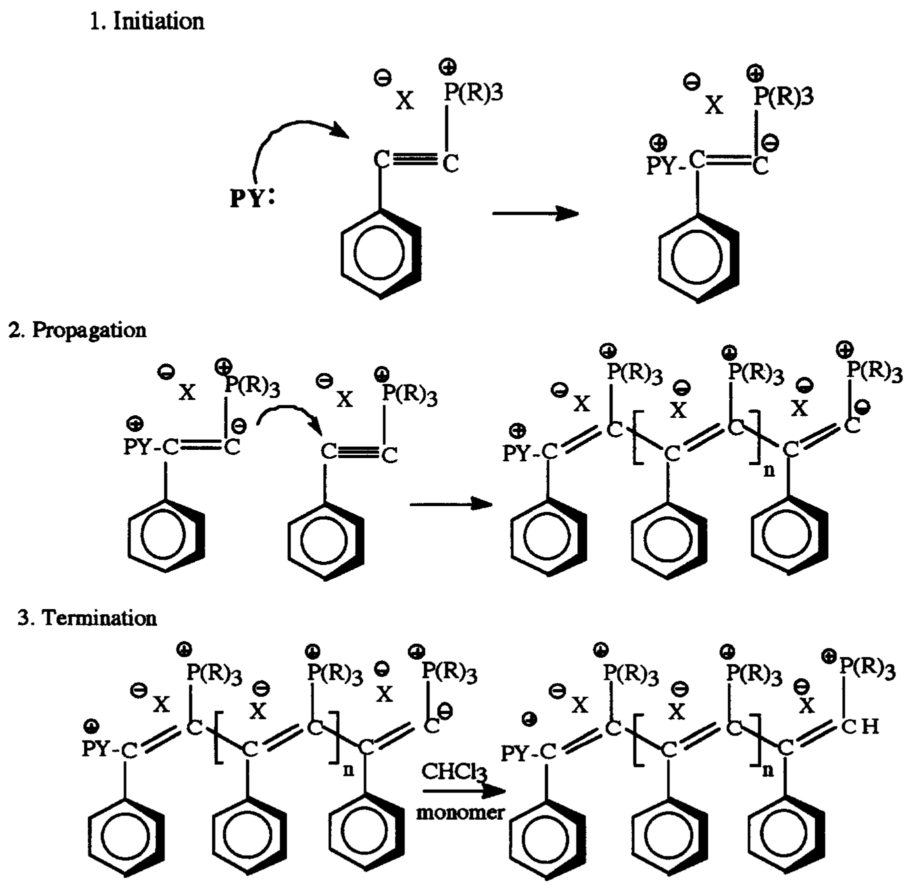


Figure 2 Time monitored of u.v./vis spectra of formation of P1 at 50°C, using picoline as an initiator and solvent $CHCl_3$



Scheme 5

and P3 prepared under similar conditions were found to be low (8–10 and 4–6, respectively).

Figure 2 shows time-monitored u.v./vis spectra of the P1 formation using picoline as initiator (50°C, in $CHCl_3$). It can be clearly seen that the characteristic peak due to the conjugated –C=C– double bond at $\lambda_{max} = 460$ nm appears after approximately 2 h (20 runs). This peak continuously intensifies with increasing reaction time, and trails to more than 700 nm ($\lambda_{max} = 580$ nm and trailing to above 700 nm). This results in a deepening colour, eventually giving a black solution.

This polymerization can be compared to that of *N*-methyl-2-ethynylpyridinium trifluoromethanesulfonate monomer in aprotic polar solvents such as DMF or DMSO using pyridine as initiator. The polymerization of these monomers follows a complex zwitterionic/anionic mechanism[3]. A general polymerization scheme is shown in *Scheme 5*.

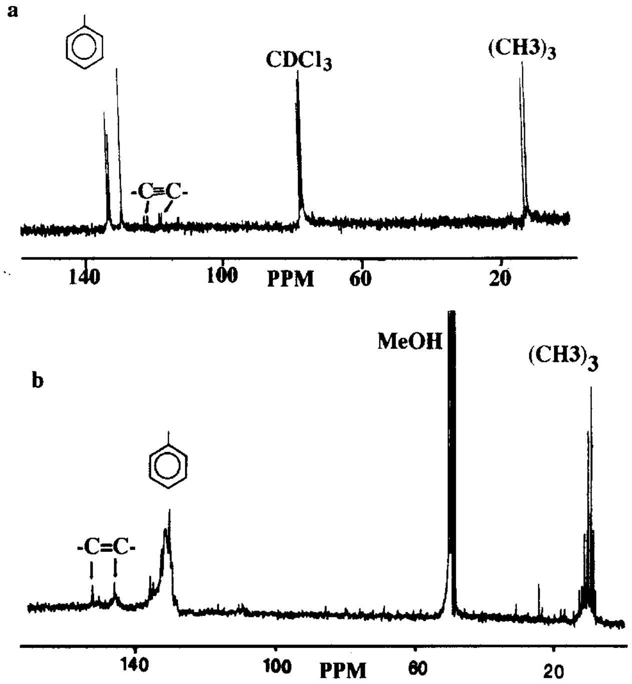


Figure 3 ^{13}C n.m.r. spectra of (a) the monomer M1; (b) polymer P1. (Solvent d_4-MeOH)

The termination can proceed by proton transfer from solvent ($CHCl_3$) or monomer to the nucleophilic chain end of the polymer. The degree of polymerization of phosphonium polymers is relatively low, suggesting that the termination steps compete effectively with chain propagation.

The *FT*i.r. was also used to monitor the thermal polymerization of phosphonium monomers at different polymerization temperatures and polymerization times. The intensity of the characteristic peaks for the –C≡C–P(R)3 triple bond stretching at 2186, 2182 and 2175 cm^{-1} was monitored for M1, M2, and M3, respectively. We found that these monomers, unlike ethynylpyridinium triflates[10], cannot be polymerized by u.v. irradiation (50°C, 1 week). However, surprisingly, they can be polymerized at high temperatures (145°C 2–5 days). Under these conditions peaks corresponding to the –C≡C– triple bond completely disappear. A new absorption peak appears at 1620 cm^{-1} and is due to the conjugated –C=C– double bond. The degree of polymerization is about 5–10 for all of the three phosphonium polymers (oligomers) obtained thermally. All of them show a λ_{max} in the vicinity of 300 nm.

The *FT*i.r. spectrum of P1 prepared with an ionic initiator (picoline) is basically the same as that of the thermal polymerization product. The only discernible difference is a more intense –C=C– double bond absorption at 1622 cm^{-1} in the polymer prepared ionically (picoline). The ratio of transmissions *T* at 2968 cm^{-1} (–CH_3 stretching) and 1622 cm^{-1} (–C=C– stretching) is 1.09 for the spectrum of the ionically prepared polymer and 0.88 for the thermally prepared polymer. This suggests that a more conjugated structure is present in the ionically prepared polymer.

^{13}C-n.m.r. spectra of M1 and P1 (initiator picoline) are given in *Figures 3a* and *b*, respectively. The spectrum

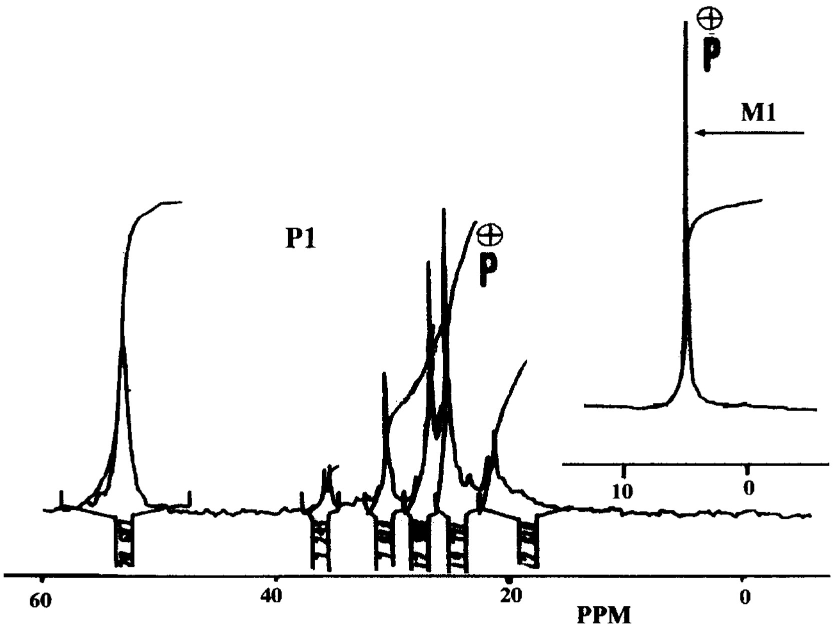


Figure 4 ^{31}P n.m.r. spectra of the monomer M1 (a) and the polymer P1 (b). (Solvent d_4-MeOH)

(*Figure 3a*) shows a doublet at 10–20 ppm to unequal --CH_3 splitting and multiple peaks at 120–140 ppm due to the aromatic ring. Two doublets at 120 ppm are due to the triple bond. In the ^{13}C polymer spectrum (*Figure 3b*) new peaks appear at 140–160 ppm. These peaks are absent in the monomer spectrum and are due to –C=C– conjugated double bonds. The ^{31}P spectra of M1 and of the corresponding ionically prepared polymer are shown in *Figure 4*. It can be seen that the chemical shift δ increases from 8.0 to 20–60 ppm when passing from monomer to polymer. It is known that phosphine derivatives such as uncharged $P(Me)_3$ and $P(Ph)_3$ display a shift of −62.2 and −5.4 ppm[11–13] respectively. The presence of peaks with positive shifts in both, the monomer and the polymer, and the absence of peaks with negative chemical shifts characteristic of the uncharged phosphorus, indicate that complete quaternization of the phosphorus in the monomers and polymers has occurred. An increase in charge density of the polymeric species may be responsible for the increase of the positive chemical shift when passing from M1 to P1. A broad distribution of chemical shifts of the polymer P1 (20–60 ppm) may also suggest a broad molecular weight distribution.

Figure 5 shows the u.v. spectra of M1 and of polymers P1, P2, P3 prepared by ionic initiation. It is interesting to note that λ_{max} increases with the decreasing size of the substituent of the polymer: 580 nm for P1, 460 nm for P2, and 300 nm for P3. The Calvin–Lewis equation ($\lambda^2_{max} = kn$) relating the shift in the u.v. absorption peak to the number of conjugated double bonds in a sequence n (conjugation length n) was originally applied to polyenes[13] and subsequently to various conjugated polyacetylenes[4,14]. Assuming that it holds for the system described here, the calculated conjugation length n of polymers is approximately 19, 12, and 5 for P1, P2, and P3, respectively. These results are in reasonably good agreement with the DP_n determined by v.p.o.

Molecular dynamic simulation of conjugated ionic polyacetylenes suggests that enhanced electrostatic repulsion of charged repeating units of the polymer are responsible for its extended configuration leading to high conjugation lengths[15]. Replacing $-CH_3$ with a much larger phenyl group could increasingly interfere with the overlap of π orbitals of the double bonds of the backbone.

In contrast to the charged phosphonium polymers uncharged polyphenylacetylene bromide (PPAB) and polyphenylacetylene (PPA) prepared by thermal polymerization display a λ_{max} in the vicinity of 300 nm. Such low values are characteristic of small conjugation lengths ($n = 2$–3). The low conjugation length of the non-ionic PPAB and PPA is due to a structure differing from the structure of substituted ionic polyacetylenes by a rapid loss of planarity of the polymer backbone[15]. Thus, nonionic substituted polyacetylenes display a short conjugation length (typically 2–3) irrespective of their DP[14]. Ionic polyethynylpyridines, in contrast, display large u.v. shifts characteristic of substantially higher conjugation lengths[1,2,4,10] which, at least in the range of DPs of 5–20, are related to the degree of polymerization. Only in the case of quasi-perfect continuity in the overlap of π orbitals can we expect n to approach DP_n. The experimentally determined DP_ns are almost always superior to the n obtained from u.v. spectra (assuming that the Calvin–Lewis relationship is valid). In substituted ionic polyacetylenes n (estimated from u.v. spectra) is larger than that of nonionic substituted polyacetylenes[5,14] but is always smaller than n expected from the value of DP_n.

The amorphous nature of P1, P2, and P3 is indicated on d.s.c. traces by absence of melting transitions. T.g.a. traces of these polymers and of the corresponding monomers under N_2 show that up to 300°C for M1 no appreciable loss occurs (*Figure 6*). M2 and M3 begin to degrade, however, around 200°C. The thermal stability of the monomer decreases with the increasing size of the substituent. Surprisingly, polymers are less thermally stable than the corresponding monomers. P1 begins to degrade at about 200°C, and its weight loss is approximately 20% at 250°C. An *FT*i.r. spectrum of a sample kept isothermally at 250°C for 1 h shows the presence of peaks corresponding to –C=C–, aromatic rings, and P-CH_3. In contrast to other peaks, C-H stretching of the CH_3 becomes weaker than in the original sample. This suggests that an abstraction of CH_3Br may have taken place at 250°C, in agreement with the weight loss of 35% found by isothermal t.g.a. (36.9% expected for a full cleavage of CH_3Br). The lower thermal stability of the

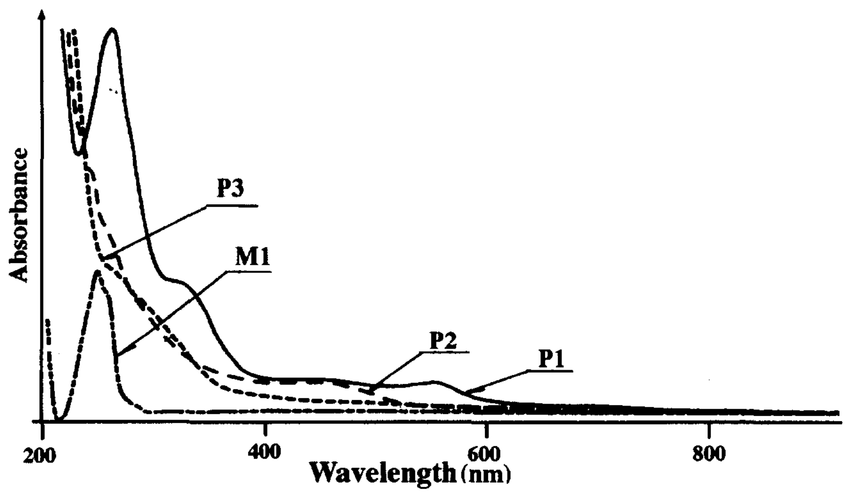


Figure 5 U.v. spectra of polymers P1, P2, P3 and of the monomer M1 (solvent MeOH)

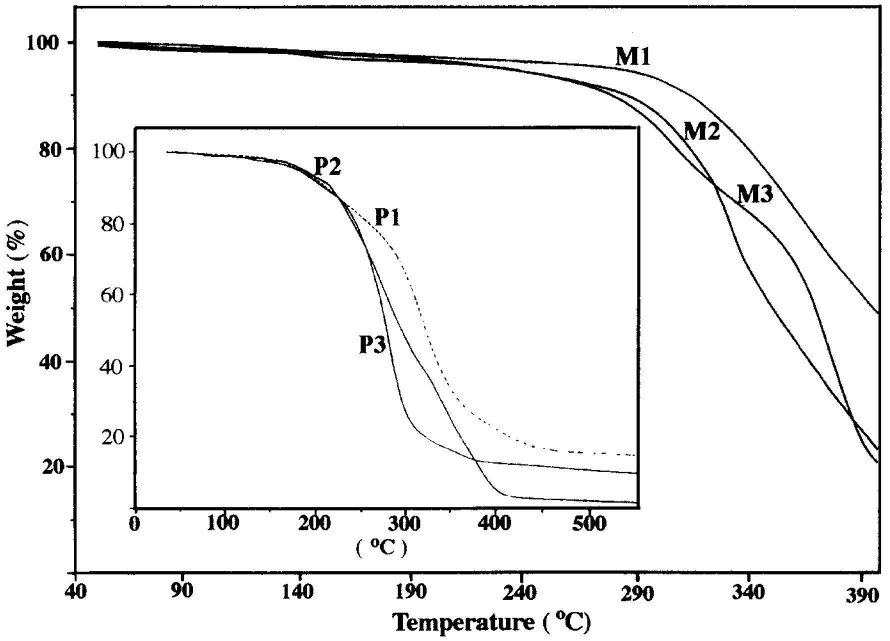


Figure 6 T.g.a. traces of polymers and monomers. (N_2, scanning rate 10°C min^{-1})

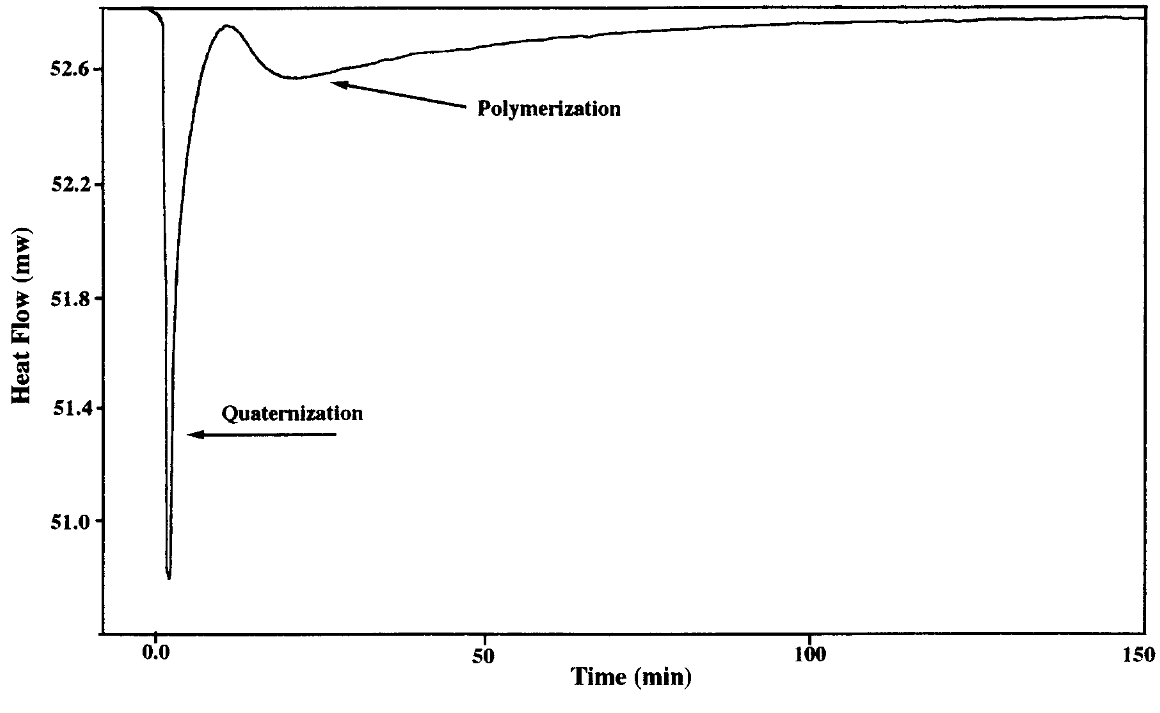


Figure 7 D.s.c. isothermal traces at 110°C of equimolar PAB and TEA (N_2)

polymers may be due to steric constraints introduced in the backbone by the bulky substituents[16].

Poly(ammonium phenylacetylene)

D.s.c. was carried out using a stoichiometric mixture of PAB and TEA. The peak representing the quaternization of PAB is centered around 90°C and partially overlaps with a second much broader peak (145°C) representing the polymerization of the quaternized monomer. Subsequent heating of the sample gave a flat curve, indicating the completeness of the reaction. This was corroborated by isothermal runs at 110°C. One can see clearly on *Figure 7* that a sharp peak due to the quaternization of PAB with TEA precedes and partially overlaps a broad peak due to subsequent polymerization of the quaternized monomer.

U.v./vis spectrophotometry was also used to monitor the reaction of PAB and TEA in THF (equimolar ratio) at 50.0°C. Similarly to the polymerization of quaternized ethynylpyridines[17], the quaternization of PAB with TEA occurred first, followed by the development of a conjugated structure through polymerization of the quaternized monomer. A new

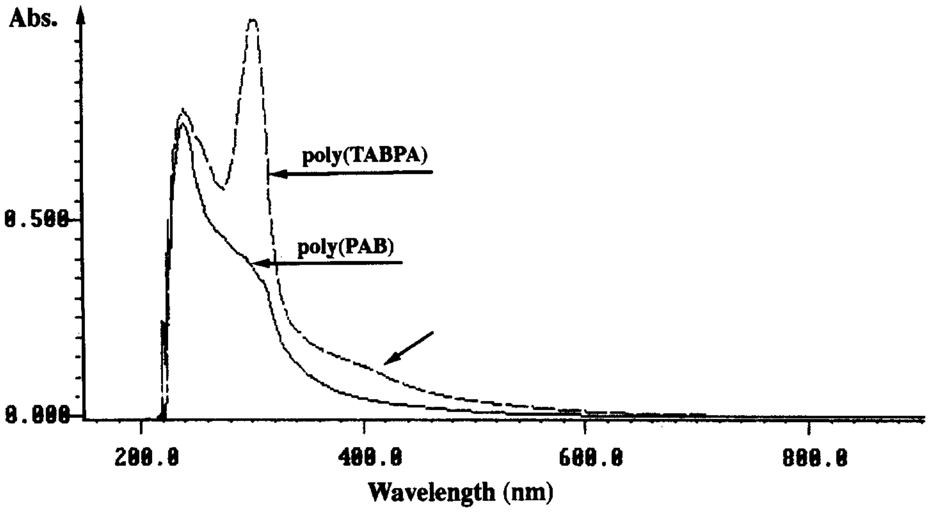


Figure 8 U.v. spectra of PTABPA and PPAB. (Solvent THF)

peak at λ_{max} 400 nm appeared approximately after 3.5 h (40 runs). This peak continuously extended and intensified with increasing reaction time. A deepening of the colour took place, eventually producing a black solution. However, the spectrum of unquaternized PAB in THF solution remained unchanged all other things being equal (concentration, 50°C, etc). No polymerization of PAB has taken place.

Figure 8 shows superimposed u.v./vis spectra of the polymer of PAB obtained by thermal polymerization and of the polymer of TABPA obtained by ionic polymerization (picoline). The polymer of TABPA exhibits a λ_{max} of 410 nm, trailing to 600 nm while the polymer of PAB gave a λ_{max} of 300 nm. Assuming again that the Calvin–Lewis equation is valid for this system, the conjugation length of the polymer of TABPA is 8–10 monomer units (while its DP_n as measured by v.p.o. was found to be 10–12) indicating a degree of conjugation substantially higher than that of the nonionic polyacetylene bromide (PAB).

The thermal stability of the polymer of TABPA was studied by t.g.a. Thermal behaviour of the polymer was similar to the polymer of 2-ethynylpyridinium analogues[17], which showed no significant weight loss up to 200°C.

CONCLUSION

Novel polyalkyl(aryl) phosphonium bromide phenylacetylenes and poly(1-triethylammonium bromide 2-phenylacetylene) have been synthesized. The synthesis proceeds through quaternization of alkyl-aryl-phosphines by the phenylacetylene bromide. In contrast to the ammonium polyacetylene in which the formation of the quaternized monomer overlaps with the polymerization process, in the phosphonium monomers the quaternization step does not lead to polymerization. Isolation and purification of the monomers are easy. Polymerization of these phosphonium monomers can be accomplished with a weak base or by heating. It is possible that the higher electron affinity of phosphorous is responsible for the rapid quaternization and stabilization of the monomer.

*FT*i.r. u.v./vis and n.m.r. spectroscopy suggest a structure in which the double bonds of the main chain are located α to the charge-bearing phosphorous atom of the above phosphonium polymers. Higher degrees of polymerization and longer conjugation lengths can be achieved using nucleophilic initiators rather than heat. Another factor influencing the molecular mass and the conjugation length is the size of the substituent group on the polymer chain. Smaller substituents favour higher *DP*s, longer conjugation lengths and higher thermal stability.

Permselectivities (P_{O2}/P_{N2}) of membranes based on poly(1-trimethylphosphonium bromide 2-phenylacetylene) and poly(1-triethylammonium bromide 2-phenylacetylene) have been studied and are found to be higher than those for uncharged analogues of similar molecular characteristics such as for example polyphenylacetylene bromide. They do not appear to differ significantly from gas permeation properties obtained with polyethynylpyridinium derivatives, this will be reported in a future publication.

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