Macromolecules

Volume 29, Number 20 September 23, 1996

Synthesis and Optical Characterization of Polydiacetylenes Containing Carboxylic Acid, Carbamate, Phosphonium, and Quaternary Ammonium Functionalities

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Received February 22, 1996; Revised Manuscript Received July 11, 1996[⊗]

ABSTRACT: Symmetrically substituted 1,3-diynes, $X(CH_2)_nC{\equiv}C{-}C{\equiv}C(CH_2)_nX$ ($X = Et_2N$; $n = 4, 9$; **1d,e**) have been prepared from the appropriate bis-tosylates ($X = OSO_2C_6H_4Me$-*p*; **1b,c**) and diethylamine, and one such derivative has been converted into a bis-quaternary ammonium salt ($X = N^+Et_2MeI^-$; $n = 4$; **1f**) and an ammonium sulfonate inner salt ($X = N^+Et_2(CH_2)_3SO_3^-$; $n = 4$; **1g**), respectively. Three bis-phosphonium salts, $X(CH_2)_nC{\equiv}C{-}C{\equiv}C(CH_2)_nX$ ($X = P^+Ph_3Br^-$; $n = 4, 9, 3$; **1h**−**j**), were synthesized from 1,4-bis(bromoalkyl)-1,3-diynes and the appropriate phosphine derivative. The new diyne derivatives did not polymerize on exposure to γ-irradiation or electron beam irradiation in a Van der Graff linear accelerator. The tosylated polydiacetylene (PDA) derivative (**2a**, "PTS-12") derived from **1b** was treated with diethylamine to yield a tertiary amine-functionalized PDA derivative (**2b**), and the latter was allowed to react (separately) with methyl iodide and 1,3-propanesultone to give ionomeric PDAs **2c** and **2d**, respectively. The phosphinated PDA (**2e**) was synthesized from PTS-12 (**2a**) and diphenylphosphinyllithium or -potassium, and this material was used to prepare the PDA phosphonium salt **2f**. The nonlinear optical properties of selected new PDAs (**2c,d,f**), as well as some known PDAs, were evaluated by means of the *z*-scan technique. The magnitudes of two-photon absorption coefficients (β) were determined and are discussed.

Introduction

The pioneering work of Wegner on the topochemical polymerization of conjugated diacetylenes[1] has generated wide interest in polydiacetylenes, with particular regard to third-order nonlinear optical properties.[2,3] There is also interest in chromic effects in polydiacetylenes induced by heat,[4] solvent variations,[5] and pH changes; the hypsochromic shifts observed in aqueous solutions of PDA carboxylic acids in passing from low to high pH have been investigated by Patel *et al.*[6] and ourselves,[7] and related chromic effects have been harnessed in PDA-based liposomes for the colorimetric detection of influenza virus.[8] The origin of such PDA dichroism has been speculated upon[6,9] and probably relates to either a change of "effective chain conjugated length" [6] or, for certain PDAs, aggregation effects.[9]

In the light of the unusual behavior of PDA carboxylic acids, we decided to synthesize ionomeric analogues, and we now describe new PDAs containing quaternary ammonium and sulfonate inner salt functionalities. We also describe an investigation of nonlinear optical properties of the new materials as well as some related PDAs in solution, using the *z*-scan method.

Experimental Section

Techniques. Reactions involving phosphines were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. Diphenylphosphinylpotassium was purchased from Aldrich. Solvents used were dried under reflux and freshly distilled under a dry nitrogen atmosphere before use. Drying agents were Na/benzophenone (for 60−80 °C petroleum ether, diethyl ether, tetrahydrofuran (THF), and toluene) and P_2O_5 (for dichloromethane). Infrared (IR) spectra were recorded on a Perkin Elmer FT 1600 instrument and calibrated against polystyrene. ^1H and ^{13}C NMR spectra in solution were recorded at 200.13 and 50.32 MHz, respectively, on a Bruker WP 200 SY spectrometer; chemical shifts are reported relative to tetramethylsilane as reference. ^{31}P NMR were recorded at 161.98 MHz on a Bruker DP X 400 instru-

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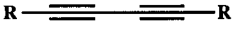
[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1996.

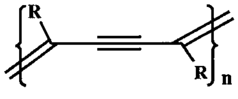
S0024-9297(96)00294-X CCC: $12.00

Chart 1



(1)

	R
a	$(CH_2)_3OSO_2C_6H_4Me$-*p*
b	$(CH_2)_4OSO_2C_6H_4Me$-*p*
c	$(CH_2)_9OSO_2C_6H_4Me$-*p*
d	$(CH_2)_4NEt_2$
e	$(CH_2)_9NEt_2$
f	$(CH_2)_4\overset{+}{N}(Me)Et_2\ I^-$
g	$(CH_2)_4\overset{+}{N}(Et_2)(CH_2)_3SO^-_3$
h	$(CH_2)_4\overset{+}{P}Ph_3\ Br^-$
i	$(CH_2)_9\overset{+}{P}Ph_3\ Br^-$
j	$(CH_2)_3\overset{+}{P}Me_2Ph\ Br^-$
k	$(CH_2)_4PPh_2$



(2)

	R
a	$(CH_2)_4OSO_2C_6H_4Me$-*p*
b	$(CH_2)_4NEt_2$
c	$(CH_2)_4\overset{+}{N}(Me)Et_2\ I^-$
d	$(CH_2)_4\overset{+}{N}(Et_2)(CH_2)_3SO^-_3$
e	$(CH_2)_4PPh_2$
f	$(CH_2)_4\overset{+}{P}(Me)Ph_2\ I^-$
g	$(CH_2)_4PO(Ph)_2$

ment and referenced to external 85% aqueous H_3PO_4. Solid state CPMAS ^{13}C NMR spectra (75.43 MHz) were run at the University of Durham, UK. ^{60}Co γ-irradiations were carried out at the SURRC, East Kilbride, Scotland, and electron beam irradiations were done using an "L" band (1300 MHz) electron linear accelerator at Christie Hospital, Manchester, UK. The machine was operated in the 8 MeV linear mode with a peak beam current of 500 mA at 50 Hz repetition frequency and pulse width of 2 μs. The dose per pulse at the sample was 51 rad, giving a mean dose rate of 9.18 Mrad h^{-1} (total dose, 10.8 Mrad). DSC (30−150/200 °C) and TGA measurements were made on samples under a nitrogen atmosphere, using Perkin Elmer DSC-4 and TGS-2 instruments, respectively, with a heating rate of 20 °C/min. Elemental analyses were performed at UMIST, Manchester, UK.

Syntheses. Preparation of Bis(tosylate) Derivatives 1a−c. The following compounds were made in 70% yield according to a known procedure.[10]

1a: ^1H NMR ($CDCl_3$) δ (ppm) 1.8 (m, 4H, CH_2), 2.3 (t, 4H, J = 7 Hz, $CH_2C{\equiv}C$), 2.4 (s, 6H, CH_3), 4.1 (t, 4H, J = 6 Hz, CH_2O), 7.3 and 7.75 (dd, 8H, J = 8.5 Hz, C_6H_4); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ (ppm) 15.4, 21.6, 27.5, 65.9 ($\mathit{C}{\equiv}C$), 68.6 ($\mathit{C}H_2O$), 75.3 ($C{\equiv}\mathit{C}$), 127.8, 129.8, 132.6, 144.9; MS *m/z* (relative intensity) (FAB) 475 (3) [M + 1]$^+$. Anal. Calcd for $C_{24}H_{26}O_6S_2$: C, 60.7; H, 5.5; S, 13.5. Found: C, 60.8; H, 5.6; S, 13.2.

1b: mp 56−57 °C; ^1H NMR ($CDCl_3$) δ (ppm) 1.65 (m, 4H, $C\mathit{H}_2$), 1.85 (m, 4H, $C\mathit{H}_2$), 2.3 (t, 4H, J = 6.7 Hz, $C\mathit{H}_2C{\equiv}C$), 2.5 (s, 6H, $C\mathit{H}_3$), 4.1 (t, 4H, J = 6.1 Hz, $C\mathit{H}_2O$), 7.4 and 7.8 (dd, 8H, J = 8.3 Hz C_6H_4); MS *m/z* (relative intensity) (FAB) 503 (4) [M + 1]$^+$, 349 (11), 331 (4).

1c: mp 73−75 °C; ^1H NMR ($CDCl_3$) δ (ppm) 1.25 (br s, 20H, $C\mathit{H}_2$), 1.5 (m, 8H, $C\mathit{H}_2$), 2.25 (t, 4H, J = 6.8 Hz, $CH_2C{\equiv}C$), 2.45 (s, 6H, $C\mathit{H}_3$), 4.0 (t, 4H, J = 6.5 Hz, $C\mathit{H}_2O$), 7.3 and 7.8 (dd, 8H, J = 8.5 Hz, $C_6\mathit{H}_4$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ (ppm) 19.3, 21.8, 25.4, 25.8, 28.4, 28.8, 28.9, 29.0, 29.3, 65.4 ($\mathit{C}{\equiv}C$), 70.8 ($\mathit{C}H_2O$), 77.6 ($C{\equiv}\mathit{C}$), 127.9, 129.9, 133.3, 144.8 (C_6H_4); MS *m/z* (relative intensity) (FAB) 643 (6) [M + 1]$^+$, 551 (8), 471 (11). Anal. Calcd for $C_{36}H_{50}S_2O_6$: C, 67.3; H, 7.8; S, 10.0. Found: C, 67.0; H, 8.1; S, 9.6.

Preparation of Bis(aminoalkyl)diacetylenes 1d,e. The appropriate bis(tosylate) derivatives (*ca.* 9 mmol) were heated under reflux with excess diethylamine (10 cm^3) for 24 h. The products were cooled and evaporated to low volume under reduced pressure. A 1 M aqueous sodium hydroxide solution (50 cm^3) was added, and the mixture was extracted with diethyl ether (3 × 10 cm^3). The ether extract was dried ($MgSO_4$) and evaporated to leave the product as a pale yellow oil. The following compounds were prepared.

1,12-Bis(diethylamino)dodeca-5,7-diyne (1d, 93%): ^1H NMR ($CDCl_3$) δ (ppm) 0.9 (t, 12H, J = 6.9 Hz, $C\mathit{H}_3CH_2N$), 1.5 (br s, 8H, $C\mathit{H}_2C\mathit{H}_2CH_2C{\equiv}$), 2.2 (br t, 4H, J = 6 Hz, $C\mathit{H}_2C{\equiv}C$), 2.35 (m, 12H, $CH_3C\mathit{H}_2NC\mathit{H}_2$); $^{13}C\{H\}$ NMR ($CDCl_3$) δ (ppm) 11.5, 19.0 ($\mathit{C}H_2C{\equiv}C$), 28.0, 28.3, 46.7, 52.1, 65.3 ($CH_2C{\equiv}\mathit{C}$), 77.1 ($CH_2\mathit{C}{\equiv}C$); MS *m/z* (relative intensity) (FAB) 305 (100) [M + 1]$^+$, 278 (91), 204 (24). Anal. Calcd for $C_{20}H_{36}N_2$: C, 78.9; H, 11.9; N, 9.2. Found: C. 78.7; H, 12.0; N, 9.3.

1,22-Bis(diethylamino)docosa-10,12-diyne (1e, 79%): ^1H NMR ($CDCl_3$) δ (ppm) 0.9 (t, 12H, J = 7.2 Hz, $C\mathit{H}_3CH_2N$), 1.3 (br s, 20H), 1.4 (m, 8H), 2.2 (t, 4H, J = 6.8 Hz, $C\mathit{H}_2C{\equiv}C$) 2.3−2.5 (m, 12H, $CH_3C\mathit{H}_2NC\mathit{H}_2$); $^{13}C\{H\}$ NMR ($CDCl_3$) 11.5, 19.0 ($\mathit{C}H_2C{\equiv}C$), 26.8, 27.5, 28.2 28.7, 28.9, 29.3, 29.4,46.7, 52.8, 65.1 ($CH_2C{\equiv}\mathit{C}$), 77.3 ($CH_2\mathit{C}{\equiv}C$); MS *m/z* (relative intensity) (FAB) 445 (5) [M + 1]$^+$, 416 (5), 111 (14).

Reaction of 1,12-Bis(diethylamino)dodeca-5,7-diyne (1d) with Methyl Iodide. 1,12-Bis(diethylamino)dodeca-5,7-diyne (**1d**) was stirred with a molar excess of methyl iodide. The bis-quaternary ammonium compound **1f** was formed rapidly as a colorless solid in quantitative yield in an exothermic process. The product was triturated with dry diethyl ether and then filtered to give the bis-quaternary salt **1f**: ^1H NMR (D_2O) δ (ppm) 1.3 (t, 12H, J = 7.2 Hz, $C\mathit{H}_3CH_2N$), 1.6 (m, 4H, $C\mathit{H}_2$), 1.9 (m, 4H, $C\mathit{H}_2$), 2.4 (t, 4H, J = 6.7 Hz, $C\mathit{H}_2C{\equiv}C$), 3.0 (s, 6H, $NC\mathit{H}_3$), 3.2−3.4 (m, 12H, $CH_3C\mathit{H}_2N^+(C\mathit{H}_2)$: $^{13}C\{H\}$ NMR (D_2O) δ (ppm) 6.8, 17.8, 20.4, 23.9, 48.8, 58.1, 59.1, 65.1, 77.3; MS *m/z* (relative intensity) (FAB) 461 (15) [M − I]$^+$, 320 (67), 305 (32). Anal. Calcd for $C_{22}H_{42}N_2I_2$: C, 44.9; H, 7.2; N, 4.8; I, 43.1. Found: C 45.7; H, 7.2; N, 4.7; I, 42.2.

Reaction of 1,12-Bis(diethylamino)dodeca-5,7-diyne (1d) with 1,3-Propanesultone. The bis(diethylamino) derivative **1d** (2.0 g, 6.6 mmol) and 1,3-propanesultone (2.44 g, 20 mmol) were heated under reflux in tetrahydrofuran (50 cm^3) for 2 h. The product was cooled, and anhydrous acetone (100 cm^3) was added to precipitate the inner salt (**1g**, 3.3 g, 91%) as a pinkish white solid: mp 200 °C dec; ^1H NMR ($(CD_3)_2SO$) δ (ppm) 1.16 (t, 12H, J = 7 Hz, CH_3), 1.5, 1.7 and 1.9 (br m, ~16H, CH_2), 2.4 (~t, 4H, J = 6.7 Hz, $C\mathit{H}_2C{\equiv}C$), 3.2 (m, ~16H, $C\mathit{H}_2N^+$); MS *m/z* (relative intensity) (FAB) 549 (35) [M + 1]$^+$, 428 (30), 390 (30), 372 (40), 354 (20), 307 (40). Anal. Calcd for $C_{26}H_{48}N_2O_6S_2{\cdot}2H_2O$: C, 53.4; H, 9.0; N, 4.8; S, 11.0. Found: C, 53.0; H, 8.9; N 4.7; S 11.2.

General Procedure for the Preparation of Bis-Phosphonium Salts 1h−j: The appropriate bis(bromoalkyl) derivative[7] (6.25 mmol) and triphenylphosphine (25 mmol) were heated under reflux in acetonitrile (10 cm^3) for days. The product was cooled, and anhydrous diethyl ether (50 cm^3) was added to precipitate the salt. The solvents were evaporated under reduced pressure, and the residue was dried *in vacuo* for several hours. The solid was then redissolved in acetonitrile (10 cm^3) and reprecipitated by addition of anhydrous diethyl ether (50 cm^3). The product was filtered and again dried *in vacuo* to give the bis-phosphonium salt in *ca.* 95% yield.

1h: mp 247−251 °C; ^1H NMR (DMSO-d_6) δ (ppm) 1.6 (br s, 8H, $C\mathit{H}_2C\mathit{H}_2CH_2C{\equiv}C$), 2.4 (br t, 4H, J = 6.5 Hz, $C\mathit{H}_2C{\equiv}C$), 3.7 (br t, 4H, $PC\mathit{H}_2$), 7.7−7.9 (m, 30H, Ar-H); $^{13}C\{^1H\}$ NMR (DMSO-d_6) δ (ppm) 18.0, 20.2 (d, $J_{^{31}P-^{13}C}$ = 50 Hz, $P\mathit{C}H_2$), 21.3, 28.65 (d, $J_{^{31}P-^{13}C}$ = 17 Hz, $PCH_2\mathit{C}H_2$), 66.1 ($CH_2C{\equiv}\mathit{C}$), 78.0 ($CH_2\mathit{C}{\equiv}C$), 118.9 (d, $J_{^{31}P-^{13}C}$ = 85 Hz, *ipso*-C of Ph), 130.7 (d, $J_{^{31}P-^{13}C}$ = 12 Hz), 134.1 (d, $J_{^{31}P-^{13}C}$ = 10 Hz), 135.3 (*o*-, *m*-, and *p*-C of Ph); $^{31}P\{^1H\}$ NMR (DMSO-d_6) δ (ppm) 25.4; MS *m/z* (relative intensity) (FAB) 765 (14) [M − Br]$^+$. Anal. Calcd for $C_{48}H_{46}Br_2P_2$: C, 68.3; H, 5.5; P, 7.3. Calcd for $C_{48}H_{46}Br_2P_2{\cdot}H_2O$: C, 66.8; H, 5.6; P, 7.2. Found: C, 67.0; H, 5.7; P, 7.1.

1i: ^1H NMR (DMSO-d_6) δ (ppm) 1.1−1.6 (br m, 28H), 2.25 (t, 4H, J = 6.3 Hz, $C\mathit{H}_2C{\equiv}C$), 3.6 (br t, 4H, $PC\mathit{H}_2$), 7.7−8.0 (m, 30H, Ar-H); $^{13}C\{^1H\}$ NMR δ (ppm) 18.7, 20.2, 21.5, 22.2, 28−30 (complex region), 65.8 ($CH_2C{\equiv}\mathit{C}$), 78.4 ($CH_2\mathit{C}{\equiv}C$), 119.0 (d, $J_{^{31}P-^{13}C}$ = 85 Hz, *ipso*-C), 130.7 (d, $J_{^{31}P-^{13}C}$ = 12 Hz), 134.1 (d, $J_{^{31}P-^{13}C}$ = 10 Hz), 135.3 (*o*-, *m*-, and *p*-C of Ph); $^{31}P\{^1H\}$ NMR (DMSO-d_6) δ (ppm) 25.4; MS *m/z* (relative intensity) (FAB) 985 (6) [M + 1]$^+$, 905 (22) [M − Br]$^+$. Anal. Calcd for $C_{58}H_{66}Br_2P_2$: C, 70.7; H, 6.7; P, 6.3. Calcd for $C_{58}H_{66}Br_2P_2{\cdot}4H_2O$: C, 65.9; H, 7.1; P, 5.9. Found: C, 65.1; H, 5.8; P, 6.2.

1j: ^1H NMR (DMSO-d_6) δ (ppm) 1.6 (~d, 4H, $J_{^{31}P-^1H}$ = 15 Hz, PCH_2), 2.25 (d, 12H, $J_{^{31}P-^1H}$ = 15 Hz, $PC\mathit{H}_2$), 2.4 (t, 4H, $C\mathit{H}_2C{\equiv}C$), 2.65 (m, 4H, $CH_2C\mathit{H}_2CH_2$, 7.55−8.15 (m, 10H, Ar-H); $^{31}P\{^1H\}$ NMR (DMSO-d_6) δ (ppm) 27.7; $^{13}C\{^1H\}$ NMR δ (ppm) 6.9 (d, $J_{^{31}P-^1H}$ = 54 Hz, $P\mathit{C}H_3$), 19−25 (CH_2), 66.6 ($C{\equiv}C$), 77.3 ($C{\equiv}C$), 121.5 (d, $J_{^{31}P-^{13}C}$ = 84 Hz, *ipso*-C), 129.9 (d, $J_{^{31}P-^{13}C}$

Table 1. Two-Photon Absorption Coefficients of PDA Solutions

entry	R group in structure **2**	λ_{max} (nm)	solvent	concn[a] (mol/L)	β (cm GW^{-1})
1	$(CH_2)_2COOK$[7]	410	H_2O (1 M KOH)	0.055	0.07
2	$(CH_2)_2COOH$[7]	554	DMF[b]	0.044	0.06
3	$(CH_2)_4OCONHCH_2CO_2K$[30]	567	H_2O	0.007	0.64
4	$(CH_2)_4OCONHCH_2CO_2H$[6d]	520	DMF[b]	0.023	0.19
5	$(CH_2)_4OCONHCH_2COOBu$	470	$CHCl_3$	0.014	0.75
6	$(CH_2)_4OCONHCH_2OBu$	526	$CHCl_3$	0.040	0.19
7	$(CH_2)_4N^+(Et_2)Me$ (I^-) (**2c**)	510	H_2O (1 M LiCl)	0.010	0.48
8	$(CH_2)_4N^+Et_2(CH_2)_3SO_3^-$ (**2d**)	520	H_2O (1 M LiCl)	<0.007	0.17
9	$(CH_2)_4P^+Ph_2Me$ (I^-) (**2f**)	385	DMF[b]	0.071	<0.01[c]

[a] Molar concentrations are calculated on the basis of the monomer repeat unit. [b] *N,N*-Dimethylformamide. [c] The same value for β was obtained by monitoring at 595 nm.

= 13 Hz), 132.2 (d, $J_{^{31}P-^{13}C}$ = 10 Hz), 134.4 (*o*-, *m*-, and *p*-C_6H_5); MS *m/z* (relative intensity) (FAB) 489 (29) $[M - Br]^+$. Anal. Calcd for $C_{26}H_{34}Br_2P_2$: C, 54.95; H, 6.0; P, 10.9. Found: C, 54.9; H, 6.2; P, 10.9.

Preparation of Polydiacetylenes. PTS-12 (2a). This was prepared in 85% or 50% conversion from TS-12 (**1b**) either by ^{60}Co γ-irradiation (*ca.* 10 Mrad at 0.1 Mrad h^{-1}, ambient temperature) or by irradiation in an electron linear accelerator (see experimental techniques). The crude product was purified by stirring in THF for several hours to dissolve the material and then reprecipitating it by pouring the solution into stirred methanol. The orange material was then triturated with petroleum ether (bp 40−60 °C) and finally dried to leave the orange, gummy PTS-12 (**2a**): ^1H NMR ($CDCl_3$) δ (ppm) 1.4−1.8 (br s, 8H, CH_2), 2.25−2.5 (br s, 10H, CH_3 and $CH_2C{=}$), 4.0 (br s, 4H, CH_2OTos), 7.3 and 7.7 (A_2B_2 system of C_6H_4); $^{13}C\{H\}$ NMR ($CDCl_3$) δ (ppm) 21.6 (CH_3), 24.5, 28.3 and 34.5 (CH_2), 70.5 (CH_2O), 99.3 ($C{\equiv}C$), 127.8 (C_6H_4), 129.3 ($C{=}C$), 129.9, 132.9 and 144.9 (C_6H_4). Typical GPC [material from γ-irradiation procedure] ($CHCl_3$ solvent) molecular mass values: $\bar{M}_w = 9.6 \times 10^5$; $\bar{M}_n = 2.7 \times 10^5$; $\bar{M}_w/\bar{M}_n = 3.5$.

Diethylamino-Substituted Polymer 2b Derived from PTS-12 (2a). PTS-12 (2.0 g) and tetrahydrofuran (100 cm^3) were stirred at room temperature until a solution was obtained (*ca.* 24 h). Diethylamine (50 cm^3) was added, and the solution was heated under reflux for 24 h. The product was cooled, and volatile materials were evaporated under reduced pressure. The residual orange gel was treated with 1 M aqueous sodium bicarbonate (100 cm^3), and the mixture was stirred for 1 h. The product was then extracted with chloroform (100 cm^3) and the chloroform layer separated, dried ($MgSO_4$), and evaporated to low volume. Reprecipitation with *n*-hexane gave polymer **2b** (1.2 g) as an orange solid: ^1H NMR ($CDCl_3$) δ (ppm) 1.0 (t, 12H, CH_3CH_2N), 1.3−1.7 (br s, ~8H), 2.1−2.8 (m, ~16H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ (ppm) 11.5 (CH_3), 25.7, 26.7 and 35.1 (CH_2), 46.7 ($MeCH_2N$), 52.8 (CH_2N), 99.4 ($C{\equiv}C$), 129.4 ($C{=}C$).

Diethyl(methyl)ammonium-Substituted Polymer 2c. The diethylamino-substituted polymer **2b** (0.5 g) and methyl iodide (0.5 g) were stirred in chloroform (2 cm^3) for 24 h; an orange precipitate formed after 1 h. *n*-Hexane was added, and the precipitate was filtered and dried *in vacuo* to give the bisquaternary ammonium polymer **2c** quantitatively. The material was insoluble in organic solvents including DMSO but was sparingly soluble in water to give yellow solutions: ^{13}C CPMAS NMR δ (ppm) 10 (CH_3CH_2N), 24, 26 and 35 ($NCH_2CH_2CH_2CH_2$), 49 (CH_3N), 57 and 61 (CH_2NCH2), 101 ($C{\equiv}C$), 130 ($C{=}C$). Anal. Calcd for $C_{22}H_{42}N_2I_2$: C, 44.9; H, 7.1; N, 4.7; I, 43.2. Found: C, 43.5; H, 6.4; N, 3.9; I, 33.2.

Preparation of the Polydiacetylene Inner Salt 2d. The diethylamino-substituted polymer **2b** (0.50 g, 1.95 mmol) was stirred in tetrahydrofuran (100 cm^3) until a clear solution was obtained (*ca.* 12 h). 1,3-Propanesultone (0.50 g, 4 mmol) was added, and the mixture was heated under reflux for 5 days. The product was cooled, and anhydrous acetone (150 cm^3) was added to cause precipitation of the title material as a hygroscopic reddish-orange solid. The polymer was insoluble in common organic solvents including DMSO and also in water, except in the presence of lithium chloride. **2d**: ^{13}C CPMAS NMR δ (ppm) 8.6 (CH_3CH_2N), 26, 30−40, 49, 54 and 68 (CH_2), 101 ($C{\equiv}C$), 130 ($C{=}C$). Anal. Calcd for $C_{26}H_{48}N_2S_2O_6$: C, 56.9; H, 8.8; N, 5.1; S, 11.7. Found: C, 49.6; H, 9.5; N, 4.2; S, 9.9.

Preparation of the Phosphinated Polydiacetylene 2e. PTS 12 (**2a**, 0.749 g, 1.49 mmol) was dissolved in tetrahydrofuran (150 cm^3) by stirring for 24 h at room temperature. Diphenylphosphinylpotassium (9 cm^3 of 0.5 M solution in hexane; 4.47 mmol) was added dropwise to the polymer solution held at 0 °C, during which time the color changed from orange to dark red. [The phosphinated polydiacetylene **2e** could also be prepared using diphenylphosphinyllithium (prepared[11] from Ph_2PH and *n*-BuLi in tetrahydrofuran at 0 °C).] The mixture was stirred for 3 days at room temperature. Methanol (250 cm^3) was then added, and the solvents were evaporated under reduced pressure to leave a dark brown-yellow solid. This solid was washed with diethyl ether (20 cm^3) and then dissolved in chloroform (20 cm^3). The chloroform solution was washed with water (50 cm^3), the organic layer was separated and dried ($MgSO_4$), and the chloroform was then evaporated under reduced pressure to leave a dark yellow waxy solid. The solid was finally triturated with methanol to leave the title material **2e** (0.64 g, 81%) as a yellow waxy solid: ^1H NMR ($CDCl_3$) δ (ppm) 0.5−2.5 (br, 8H, CH_2), 6.5−8.0 (br, 10H, Ar-H); $^{31}P\{^1H\}$ NMR δ (ppm) −16 (br, PPh_2). There was also evidence [δ 33 ppm (br), $-P(O)PPh_2$] for the presence of oxidized material **2g** (<10%).

Preparation of Polydiacetylene Phosphonium Salt 2f. The phosphinated polymer **2e** (0.1 g) was dissolved in chloroform (2 cm^3), and a few drops of methyl iodide were added. The mixture was stirred for 5 min, and then diethyl ether (10 mL) was added to cause precipitation of a yellow solid. This solid was filtered and dried *in vacuo* to give the yellow title material (0.98 g, 75%): ^1H NMR δ (ppm) 1.6 (br s), 3.0 (br s, CH_3), 7.8 (br, Ar-H); $^{31}P\{^1H\}$ NMR δ (ppm) 26 (br). The small resonance at δ 33 ppm was still present (see **2e** above).

Optical Experiments. The *z*-scan technique was employed, using a dye laser sychronously pumped by a Coherent Antares Nd:YAG mode-locked laser. The 76 MHz pulse train from the dye laser was amplified at 10 Hz in a three-stage dye cell system pumped by a regenerative amplifier. Pyridine-2 was used to provide 705 nm pulses of 0.4 ps (fwhm) duration and up to 1 mJ in pulse energy. Results were obtained with a spatially-apertured detector and with an unapertured detector as the sample was moved through the focal plane in the *z*-direction of beam propagation. Measurements were carried out on PDA solutions of 1 mm path length within cuvettes. Samples listed in Table 1 were investigated at the maximum concentration achievable without gel formation. All solutions had negligible linear absorption at 705 nm (<0.1 cm^{-1}); λ_{max} values for linear absorption of samples studied are given in the table. In addition, results were taken for the solvents themselves. Pulse energies used were in the range of 30−100 nJ. For the spot size (beam waist) of 11 μm, the corresponding irradiance levels were 30−100 GW cm^{-2}.

Results and Discussion

Monomer Synthesis. The target materials of the present study were ionomeric PDAs with quaternary ammonium side chains, as exemplified by the iodide (**2c**), the inner salt (**2d**), and phosphonium salts (e.g., **2f**). At the outset, it was hoped to synthesize the desired

PDAs in the standard manner by topochemcial polymerization of diacetylenes. A reported procedure[10] was used to convert the appropriate diol into bis-tosylates **1a**−**c**, full spectral characterizations for which are included in the Experimental Section. Two such compounds (**1b,c**) were transformed in high yields into oily bis(dialkylamino)diynes **1d,e**, respectively, by heating them under reflux with excess dimethylamine. Quaternization of one of the bis(dialkylamino)diynes (**1d**) was effected routinely by treating it with methyl iodide at room temperature to give the quaternary salt **1f**. The bis-sulfobetaine **1g** was synthesized by heating the bisamine **1d** with 1,3-propanesultone under reflux in tetrahydrofuran. It may be noted that novel micellar polymers incorporating the sulfobetaine functionality are of interest with respect to blend formation with inorganic salts[12] and aggregation in solution;[13] the sulfobetaine function has also been incorporated into bis(diacetylene) monomers by Ringsdorf *et al.* in their early studies on the polymerization of amphiphilic monomers.[14] Bis-phosphonium salts **1h**−**j** were prepared from the appropriate dibromides[7] and phosphines in acetonitrile solvent. It should be noted that the use of acetonitrile is essential because the reaction does not proceed in chloroform, dichloromethane, tetrahydrofuran, or diethyl ether/*n*-hexane.[7] All the new ionomeric diacetylenes were hygroscopic, and thorough drying was necessary.

Polymer Synthesis and Characterization. None of the new diacetylene monomers **1d**−**j** could be polymerized by the standard procedure of γ-irradiation (total dose, 50 Mrad at 0.1 Mrad/h) or, for **1f**−**j**, by electron beam irradiation in a Van der Graff linear accelerator (total dose, 20 or 50 Mrad).[15] The nonoily diacetylenes showed clear melting points (see Experimental Section). Simple thermal polymerization did not occur, although in some cases decompostion was observed above 200 °C; DSC thermograms up to 200 °C of diacetylenes showed no clear evidence of transitions other than melting and variable, broad endotherms associated with loss of traces of water.

Accordingly, it became necessary to approach the synthesis of PDAs (**2c, 2d**, and **2f**) by using "polymer analogous reactions". The bis-tosylate (**1b**, TS-12) was polymerized by γ-irradation to give, after reprecipitation from THF solution with methanol, a bright orange-red material, PTS-12 (**2a**), with $\bar{M}_w = 9.6 \times 10^5$, $\bar{M}_n = 2.7 \times 10^5$, and $\bar{M}_w/\bar{M}_n = 3.5$ (GPC in $CHCl_3$; cf. ref 10). This polymer was used for all the transformations described below, and it can be assumed that average molar masses of products **2c,d,f** can be calculated on the basis of data determined for this polymer, as it proved impossible to obtain reliable GPC measurements on the new highly polar or ionic PDAs.

Treatment of PTS-12 (**2a**) with diethylamine in tetrahydrofuran under reflux, followed by an alkaline workup, afforded the orange PDA derivative **2b**; the ^1H and ^{13}C NMR spectral data were in accord with structure **2b**. The latter was then transformed by methyl iodide into the orange PDA quaternary salt **2c** and by 1,3-propanesultone into the orange-red inner salt **2d**. Polymer **2d** is very insoluble in common organic solvents including DMSO and also in water, except in the presence of lithium chloride. The phosphinated PDA (**2e**) was prepared[16] by treating PTS-12 (**2a**) with diphenylphosphinyllithium or -potassium in tetrahydrofuran. In early experiments, even using a slight molar excess of the lithium reagent, it was clear that the product was only partially phosphinated: the ^{31}P NMR spectrum showed a broad resonance for the PPh_2 group at $\delta = -16$ ppm (cf. $\delta = -15.75$ ppm for **1k**),[7] but the ^1H NMR spectrum indicated the presence of residual PDA tosylate **2a**. It was also concluded (^{31}P NMR) that the phosphinated PDA **2e** slowly oxidized to the analogous phosphine oxide derivative **2g** when chloroform solutions were exposed to air ($\delta_{^{31}P} = 33$ ppm). The fully oxidized PDA was obtained after prolonged aerial oxidation.

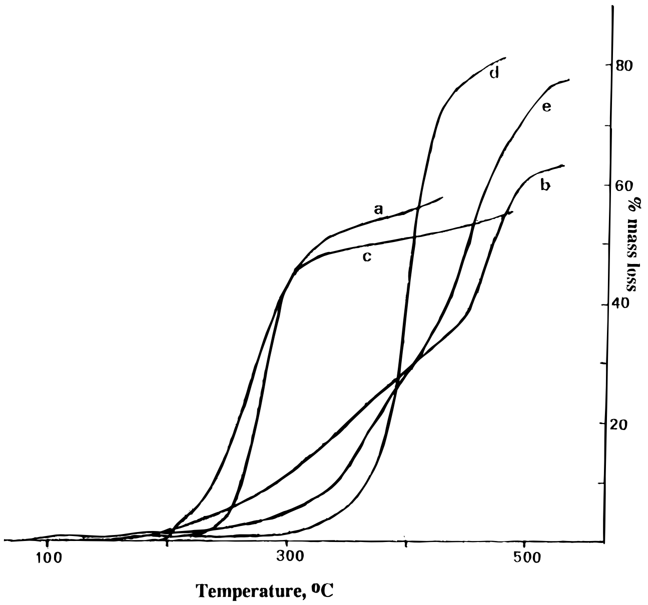


Figure 1. Thermogravimetric analyses (TGA) of polydiacetylenes $({=}CR{-}C{\equiv}C{-}CR{=})_n$: a, R = $(CH_2)_4OSO_2C_6H_4Me$-*p* (**2a**, PTS-12); b, R = $(CH_2)_4NEt_2$ (**2b**); c, R = $(CH_2)_4N^+MeEt_2I^-$ (**2c**); d, R = $(CH_2)_4P^+MePh_2I^-$ (**2f**); e, R = $(CH_2)_4PO(Ph)_2$ (**2g**).

The yellow PDA phosphonium salt **2g** was formed rapidly upon treating **2e** with methyl iodide in chloroform. The $^{31}P\{^1H\}$ NMR spectrum of this material indicated disappearance of the resonance at $\delta = -16$ ppm and the presence of a resonance at $\delta = 26$ ppm, characteristic of phosphonium salts.[17] All new polar and ionic PDAs were hygroscopic and were handled and stored in dry conditions; this caused problems in acquiring accurate data from elemental analysis.

Nonionic PDAs **2b** and **2g** showed the onset of melting around 70/90 °C and 110 °C, respectively, with visual evidence of decomposition above 150 °C, whereas ionic PDAs **2d** and **2f** showed visible thermal changes only in the range 200−300 °C. Thermogravimetric analyses (see Figure 1) indicate no significant mass loss below 200 °C, except for minor traces of water/solvent, but substantial losses occur between 200 and 500 °C, probably mainly from side-chain decompositions. The *ca.* 80% mass loss of the phosphonium salt **2f** around 400 °C can be attributed primarily to Hofmann-type elimination of HI and PPh_2Me. The smaller (*ca.* 50%) mass loss at <300 °C of the quaternary ammonium-functionalized PDA **2c** is not consistent with complete Hofmann elimination and may involve some primary loss of alkyl iodide. Apart from variable, nonreversible, broad endotherms from loss of traces of absorbed water, no reversible phase transitions were observed in DSC scans (30−150 °C), other than those associated with polymer melting.

Optical Studies. A number of polydiacetylene materials have previously been investigated for their nonlinear optical behavior. Single crystals, amorphous thin films, and solutions have been studied.[18−25] In

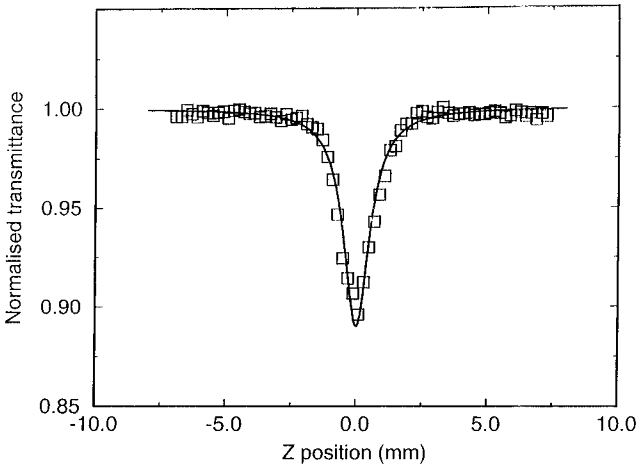


Figure 2. Open-aperture *z*-scan results obtained for sample 1 of Table 1 at a peak irradiance level of 80 GW cm^{-2}. The solid line is a theoretical fit using a two-photon absorption coefficient, β, of 0.07 cm GW^{-1}.

particular, the crystalline quasi 1-D material PTS-12 (**2a**) has one of the largest nonresonant third-order nonlinear refractive indexes known.[21] For device applications, such as optical switching and logic, it is essential that such nonlinearities exist under conditions of low background linear absorption and in the absence of increasing nonlinear absorption. The giant, resonant nonlinearities of PDAs have not to-date been exploited in devices because of the large linear and induced absorptions, although recent results on thin films indicate a narrow, near-resonant spectral window in which the required switching criteria are satisfied.[25] Off-resonance, the presence of strong two-photon absorption (TPA) can prevent application. For switching to be possible, it is necessary to satisfy the criterion[26]

$$|n_2| > \beta\lambda \qquad (1)$$

where n_2 is the nonlinear refraction coefficient, β the two-photon absorption coefficient, and λ the wavelength of operation.

To examine the nonlinearities of the polydiacetylenes described in the above sections, the *z*-scan technique was employed. This is a single-beam measurement technique in which the transmitted energy of a laser pulse is detected in the far field.[27] Results are taken with a spatially-apertured detector and an unapertured detector as the sample is moved through the focal plane in the *z*-direction of beam propagation. From the analysis of the apertured and nonapertured results, both nonlinear refraction and nonlinear absorption can be measured. Figure 2 shows the unapertured *z*-scan for sample 1 of Table 1, and is typical of all the the nine samples listed in Table 1.

All of the samples studied showed both nonlinear refraction and nonlinear absorption behavior. While the absorption was entirely due to the polymers in the solutions, the refraction was, however, dominated by the solvents. This is to be expected for the concentrations that can be achieved in solution. For example, the measured nonlinear refractive coefficients of chloroform ($CHCl_3$) and water (H_2O) are close to those previously reported, 1.1×10^{-12} and 1.3×10^{-13} esu, respectively.[28] It has been estimated recently that the n_2 value at 600 nm for a 4BCMU (the PDA in sample 5) solution of about twice the concentration of sample 5 is the same as that of the chloroform solvent.[29] At 705 nm, the n_2 value is smaller than that at 600 nm since the former is farther away from the resonance. This indicates why no significant nonlinear refraction was observed for the polymers in Table 1 as compared to that of the solvents. However, the nonresonant n_2 for 4BCMU has been measured as large as 5.6×10^{-11} esu (1.5×10^{-13} cm^2 W^{-1}) at the wavelength of 1.06 μm for thin-film material.[24] Hence, larger n_2 values may be achievable for thin films of the polymers shown in Table 1.

The observed nonlinear absorption is due to a two-photon mechanism, as opposed to excite-state-induced absorption, since the excitation wavelength is far from resonance. Results for the two-photon absorption coefficients of the polymers are presented in Table 1; the theoretical fit for sample 1 is shown in Figure 1 as the full line. The fitting parameters were found to be independent of the choice of laser pulse energy in the energy range used, indicating that the third-order nonlinear mechanisms (β and n_2) dominated. The magnitude of two-photon absorption coefficient, 0.75 cm GW^{-1}, obtained for sample 5 (4BCMU in chloroform), is comparable to the result of 0.3 cm GW^{-1} for 4BCMU in 1,4-dichlorobutane measured at 1.06 μm; the weight-volume concentrations are 7 and 5g L^{-1}, respectively.[23] The measured TPA coefficients shown in Table 1 vary significantly and cannot be correlated with the concentrations and the λ_{max} values of the samples. This indicates that the side chains (R) have a significant influence on the two-photon absorption behavior of the samples, although strong TPA effects in PDAs have been considered to result from the nature of the polymer backbone.[31] This has been previously shown in PTS (R is $-CH_2OSO_2C_6H_4CH_3$) and TCDU (R is $-(CH_2)_4-OCONHC_6H_5$); the TPA effect in the former was about an order of magnitude larger than that in the latter.[18] From a device viewpoint, samples 1, 2, and 9 appear to have the best prospects for switching. It will be necessary to study thin-film samples in order to measure PDA n_2 values and to check this prediction.

Conclusions

1,4-Disubstituted 1,3-butadiynes with ionic substituents, derived from amine or phosphine functionalities, can be prepared from the corresponding ditosylates, but transformation of these diacetylenes into polydiacetylenes by γ-irradiation or electron beam irradiation has been unsuccessful. On the other hand, related "polymer analogous" transformations of the tosylated polydiacetylene, $[{=}C\{(CH_2)_4X)C{\equiv}CC\{(CH_2)_4X){=}]_n$ ($X = OSO_2C_6H_4$-Me-4), afford polydiacetylenes with ionic or zwitterionic side chains [$X = N^+(Et)_2Me\ I^-$ (**2c**), $N^+Et_2(CH_2)_3SO_3^-$ (**2d**), or $P^+(Ph)_2Me\ I^-$ (**2f**)], by quantitative displacement of the tosyl groups. These newly prepared polymers show solubility in polar solvents, and the nonlinear optical properties of solutions of some of these materials have been investigated in a comparative study with related, soluble PDAs, with a view to assessing their applications for all-optical switching. The two-photon absorption coefficients of these polymers have been evaluated, and it has been shown that the side chains have a significant influence on two-photon behavior. These results indicate that the two-photon absorption effect in a PDA, which may prevent its application in all-optical switching,[26] can be reduced by modification of the side group of the polymer. We are presently investigating the synthesis and evaluation of a wider range of PDA substrates.

Acknowledgment. We thank EPSRC for support, Dr. D. C. Apperley (University of Durham) for measurement of solid-state NMR spectra, and Brian Hodgson (Christie Hospital, Manchester) for provision of access to a linear accelerator.

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MA9602942