

The preparation and characterization of phosphorus-terminated poly-1,3-butadiene: new telechelic ionomers

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Polybutadienyllithium systems, with high 1,4-microstructure, low polydispersity and \bar{M}_n in the range $(2-10) \times 10^3$, have been produced in hydrocarbon solvents by using *n*-butyllithium or 3-dimethylamino-propyllithium as initiator. Termination of these 'living' polymers with chlorophosphine, ClPR_2 ($\text{R} = \text{Ph}$, Et or Cy), occurs to give oxidatively unstable phosphine derivatives $\text{Y}-(\text{C}_4\text{H}_6)_n-\text{PR}_2$, in up to 93% efficiency. Oxidation products include the related phosphine oxides. Quaternization of the phosphinated polymers *in situ* with iodomethane gives a quantitative conversion into the cationomeric polymers $\text{Y}'-(\text{C}_4\text{H}_6)_n-\text{PR}_2\text{Me}^+\text{I}^-$, including the novel dicationic telechelic systems with $\text{Y}' = ^-\text{I}^+\text{NMe}_3(\text{CH}_2)_3$, which show thermoplastic elastomeric properties.

The products have been characterized by gel permeation chromatography, end-group analysis and ^1H , ^{13}C and ^{31}P nuclear magnetic resonance spectroscopy. Model quaternary phosphonium derivatives, *trans*- and *cis*- $\text{t-BuCH}_2\text{CH}=\text{CHCH}_2\text{PR}_2\text{Me}^+\text{I}^-$ and $\text{t-BuCH}_2\text{CH}(\text{CH}=\text{CH}_2)\text{PR}_2\text{Me}^+\text{I}^-$, are reported and help establish the terminal geometry of the quaternary phosphonium-capped polybutadienes: the addition of phosphorus to the terminal butadienyl follows the order *cis*-1,4 > *trans*-1,4 > 1,2 with the amount of 1,2-termination being smallest when R is the bulky cyclohexyl group.

(Keywords: telechelic poly-1,3-butadiene; phosphonium group; cationomer; anionic polymerization; n.m.r.)

INTRODUCTION

Functionally terminated polymers are of considerable current interest¹. Terminal functional groups modify the properties of the polymer chain and may also be susceptible to transformation reactions, often useful in the production of novel block copolymer systems². Of particular interest are elastomeric polymers with ionic terminal groups, since Coulombic interactions between ion pairs at the chain ends create polar micelles within the hydrophobic polymer matrix and the resulting physical crosslinking of chains may produce a thermoplastic elastomer³.

Anionically terminated elastomers with carboxylate^{3,4} or sulphonate^{3,5} groups have been subjected to a number of studies. Such anionomeric telechelic polymers show interesting variations in viscoelastic properties, which are dependent on the type of neutralizing counter-cation. The only cationomeric telechelic elastomers to have been reported have been derived from amine-terminated polybutadienes after reaction with alkyl halides, and the resulting polymers, with quaternary ammonium ions, do exhibit properties of thermoplastic elastomers⁶.

In this paper we present the synthesis and characterization of polybutadienes with terminal quaternary phosphonium groups, including new examples of cationic, telechelic elastomers.

EXPERIMENTAL

All reactions were performed under argon in clean, dry glassware using Schlenk-type techniques⁷. Reagents were handled under argon, nitrogen or in a vacuum system. Solvents were purified and dried as in previous work^{6,8} and were freshly distilled.

1,3-Butadiene (>99.5%, Union Carbide) was passed over molecular sieves, collected over CaH_2 or *n*-BuLi and distilled from graduated tubes, under vacuum, into reaction vessels. Dry 3-dimethylaminopropyl chloride was prepared from the hydrochloride (Aldrich), as previously described⁶, and converted into $\text{Me}_2\text{N}(\text{CH}_2)_3\text{Li}$ by using lithium metal (1% Na, Aldrich) in hexane^{9,10}. Solutions of *n*- and *t*-butyllithium in hexane and pentane (Aldrich), respectively, were transferred by syringe and standardized before use by titration with diphenylacetic acid. Iodomethane (BDH) was distilled from CaH_2 before use; chlorodiphenylphosphine (Fluka) was also distilled before use; but other chlorophosphines (Strem) were used as supplied.

Gel permeation chromatography (g.p.c.) was carried out principally at RAPRA, Shawbury, UK, but also at RARDE, Waltham Abbey, UK, using differential refractive index detectors; four columns of divinylbenzene crosslinked polystyrene beads (10 μm) of porosities 10^2 – 10^5 Å were employed and molecular weights were determined from a universal polystyrene calibration by using the reported Mark-Houwink coefficients ($a = 0.693$; k varied between $(4.28-4.57) \times 10^{-4}$ for polymers with

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48–92% 1,4-content, as appropriate¹¹. N.m.r. spectra were recorded on a Bruker WP 200 SY spectrometer operating at 200.1 MHz (¹H), 81.0 MHz (³¹P) and 50.3 MHz (¹³C); CDCl₃ was employed as solvent and chemical shifts are quoted relative to tetramethylsilane (¹H and ¹³C) or external 85% orthophosphoric acid (³¹P). I.r. spectra were obtained on a Perkin–Elmer 580 instrument. Dynamic mechanical thermal analysis was carried out on a Polymer Laboratories DMTA instrument operating in the shear mode at 10 Hz with a heating rate of 10°C min⁻¹. Elemental analyses were carried out by the analytical service at UMIST, Manchester, UK.

Preparation of phosphinated polybutadienes

Typical preparations are described below. Variations in 1,3-butadiene and initiator concentrations produce polymers with differing molecular weights.

n-Butyllithium as initiator. 1,3-Butadiene (40 cm³, 0.55 mol) was slowly distilled into hexane (200 cm³), under argon at -78°C, in a three-necked polymerization flask fitted with a septum and an argon inlet/outlet and containing an efficient stirrer. The solution was warmed to ca. -30°C and *n*-butyllithium, in hexane (1.6 mol dm⁻³, 6.5 cm³), was introduced by injection in order to initiate polymerization. The flask was warmed to -10 to 0°C and polymerization proceeded for 18–20 h, during which time the reaction mixture slowly attained ambient temperature. At this stage a 10 cm³ sample was removed by syringe and terminated by addition to methanol to provide a sample for comparative n.m.r. and g.p.c. studies. Tetrahydrofuran (50 cm³) was added to the remaining living polymer solution and this was cooled to ca. -20°C. An equimolar amount (0.010 mol) of the appropriate chlorophosphine, PClR₂ (R = Ph, Et or Cy), was introduced by syringe and, although the resulting termination appeared to be quite rapid, the system was left for ~24 h to ensure complete reaction. At this stage, in some preparations, an aliquot of the polymer solution was withdrawn and the polymer isolated by precipitation with methanol: this neutral polymeric phosphine invariably underwent some oxidation on subsequent purification by reprecipitation. Iodomethane (0.015 mol) in dichloromethane (40–50 cm³) was added to the bulk of the phosphinated polymer in solution under argon and the quaternization reaction left for 24–48 h (the longer times being used for R = Cy). The solvent and volatiles were removed under vacuum and the product was thoroughly washed with hexane. Purification of the resulting viscous polymer was effected by dissolution in the minimum amount of dichloromethane and subsequent precipitation by addition to methanol; in many cases this procedure caused formation of an emulsion, which was difficult to separate, but centrifugation and/or long standing enabled the polymer to be isolated, although sometimes in reduced yield. The viscous polymer was finally dried under high vacuum and stored at -15°C.

3-Dimethylaminopropyllithium as initiator. The polymerization procedure was analogous to that above, with the following modifications: (i) A standardized solution of Me₂N(CH₂)₃Li in benzene (~0.2 mol dm⁻³) was used as initiator. (ii) The quaternization, involving both tertiary amine and phosphine functions, required 2 mol of MeI. The quaternized polymer was isolated as a rubbery semi-solid at room temperature.

Preparation of model quaternary phosphonium iodides

(*t*-BuC₄H₆PPh₂Me)I. 5,5-Dimethylhex-2-enyllithium (0.041 mol) was prepared from equimolar amounts of *t*-butyllithium and 1,3-butadiene in pentane (24 cm³)¹². This solution was cooled to -78°C and chlorodiphenylphosphine (7.2 cm³, 0.040 mol) was added. The stirred solution was left to warm slowly to room temperature over 18 h. To this solution, dichloromethane (20 cm³) and iodomethane (2.5 cm³, 0.040 mol) were injected and the quaternization reaction left for 24 h. Evaporation of volatiles under vacuum and preparative t.l.c. (silica gel. G-200) using chloroform/methanol 9:1 gave the product as a mixture of three geometrical isomers: *trans*(*E*)-1,4, **A** (71%); *cis*(*Z*)-1,4, **B** (18%); and 1,2, **C** (11%). Elemental analysis: calc, C₂₁H₂₈PI, C 57.5%, H 6.4%, P 7.1%; found, C 57.5%, H 6.6%, P 7.0%. ¹H n.m.r. (CDCl₃) selected bands (ppm): 0.67 (s) **A**, 0.76 (s) **B**, 0.89 (s) **C**, ((CH₃)₃C); 2.75 (d, 13.5 Hz) **A**, 2.77 (d, 13.4 Hz) **B**, 1.99 (d, 13 Hz) **C**, CH₃P; 4.15 (dd, 15.1, 7.2 Hz) **A**, 4.06 (dd, ~16, 7.6 Hz) **B**, CH₂P; 3.67 (m) **C**, CHP; other bands (ppm): 1.2–1.8, *t*-BuCH₂; 4.8–6.1, alkene-H; 7.4–8.1, phenyl-H. ¹³C {¹H} n.m.r. (CDCl₃) selected bands (ppm): 7.7 (d, 57 Hz) **A**, 8.4 (d, 55 Hz) **B**, ~7 (d) **C**, CH₃P; 27.7 (d, 50 Hz) **A**, 23.7 (d, 51 Hz) **B**, CH₂P; 46.7 (s) **A**, 40.9 (s) **B**, *t*-BuCH₂; 115.4 (d, 10 Hz) and 139.3 (d, 13 Hz) **A**, 114.2 (d) and 136.8 (d) **B**, CH=CH; 125.0 **C**, =CH₂ and 128.2 **C**, =CH; main phenyl resonances (ppm): 118.5 (d, 84 Hz), 129.7 (d, 13 Hz), 132.4 (d, 10 Hz), 134.3 (d, ~2 Hz); other bands (ppm): 28.9–30.6 alkyl-C.

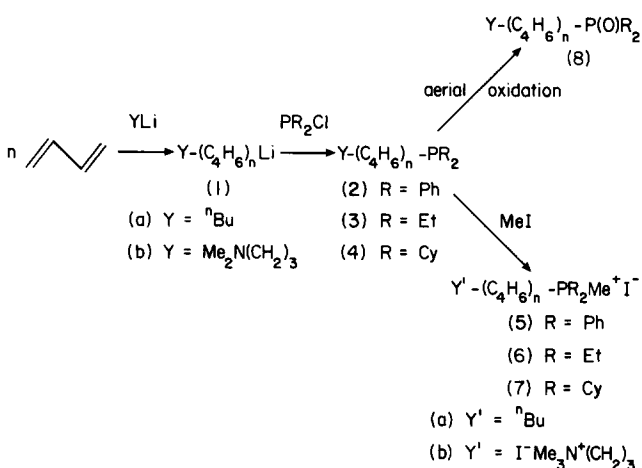
(*t*-BuC₄H₆PEt₂Me)I. In a similar procedure to above, chlorodiethylphosphine (2.0 g, 0.016 mol) was added to 5,5-dimethylhex-2-enyllithium (0.017 mol) in pentane/hexane (35 cm³) at -78°C and the reaction mixture warmed to room temperature. After stirring for 1 h at room temperature, tetrahydrofuran (10 cm³) and iodomethane (11 cm³) were added and the quaternization reaction left for 48 h. After evaporation of the volatile components, column chromatography of the residue (silica gel 80–200 mesh) using chloroform/methanol 95:5, followed by recrystallization and drying under vacuum, gave the product as mixture of isomers: *trans*(*E*)-1,4, **A** (72%); *cis*(*Z*)-1,4, **B** (11%); and 1,2, **C** (17%). Elemental analysis: calc, C₁₃H₂₈PI, C 45.6%, H 8.2%, P 9.05%; found, C 44.6%, H 8.0%, P 9.3%. ¹H n.m.r. (CDCl₃) selected bands (ppm): 0.64 (s) **A**, 0.70 (s) **B**, 0.76 (s) **C**, (CH₃)₃C; 1.84 (d, 13.3 Hz) **A**, 1.80 (d, 12.9 Hz) **B** or **C**, CH₃P; 1.08 (dt, 18.8, 7.7 Hz) **A**, ~1.1 (dt) **B** and/or **C**, CH₃CH₂; 2.30 (dq, 13.0, 7.7 Hz) **A**, ~2.3 (dq) **B** and **C**, CH₃CH₂; 3.21 (dd, 15.3, 7.5 Hz) **A**, ~3.2 (dd) **B**, CH₂P; other bands (ppm): 1.47 (m) and 1.73 (m), *t*-BuCH₂; 5.0–5.9, alkene-H. ¹³C {¹H} n.m.r. (CDCl₃) selected bands (ppm): 114.9 (d, 10 Hz) and 136.2 (d, 12 Hz) **A**, 113.8 (d, 9) and 134.4 (d, 12 Hz) **B**, CH=CH; 121.6 (d, 12 Hz) **C**, =CH₂; 130.5 (d, 9 Hz) **C**, =CH; other bands (ppm): 3–46, alkyl-C.

(*t*-BuC₄H₆PCy₂Me)I. In a procedure identical to that immediately above, this product was obtained as a mixture of geometrical isomers. However, the material separated by chromatography also contained some CHCl₃, shown by analysis. Isomer content: *trans*(*E*)-1,4, **A** (74%); *cis*(*Z*)-1,4, **B** (18%); 1,2, **C** (8%). Elemental analysis: calc, C₂₁H₄₀PI·0.5 CHCl₃, C 50.6%, H 8.0%, P 6.1%, I 24.9%; found, C 50.3%, H 8.0%, P 5.5%, I

24.4%. ^1H n.m.r. (CDCl_3) selected bands (ppm): 0.70 (s) **A**, 0.75 (s) **B**, 0.82 (s) **C**, $(\text{CH}_3)_3\text{C}$; 3.16 (dd, 14.3, 7.5 Hz) **A**, ~ 3.1 (dd) **B**, CH_2P ; other bands (ppm): 1.0–2.6 (complex), alkyl-H; 4.7–5.9, alkene-H. ^{13}C $\{^1\text{H}\}$ n.m.r. selected bands (ppm): 116.7 (d, 9 Hz) and 137.5 (d, 12 Hz) **A**, 115.5 (d, 8 Hz) and 135.0 (d, 11 Hz) **B**, $\text{CH}=\text{CH}$; ~ 123 and ~ 130 **C**, $\text{CH}=\text{CH}_2$; 1.42 (d, 50 Hz) **A** (+**B**+**C**) CH_3P ; other bands (ppm): 17.6–46.6, alkyl-C.

RESULTS AND DISCUSSION

Living polybutadienyllithium systems **1a** or **1b** were produced anionically¹³ in hydrocarbon solutions by using, respectively, either *n*-butyllithium or 3-dimethylaminopropyllithium⁹ as initiator. Such polymerizations produce material with a low polydispersity ($\bar{M}_w/\bar{M}_n = 1.1$ –1.3, cf. Table 1) and enable the degree of polymerization to be controlled by introducing appropriate initiator and butadiene concentrations: \bar{M}_n values in the range $(2$ – $10) \times 10^3$ were obtained, but mainly $\sim 3 \times 10^3$. The hydrocarbon solvent promotes the formation of 1,4-linkages in the polybutadiene (80–90% 1,4 from *n*-BuLi as initiator in hexane; 60–70% 1,4-linkages from $\text{Me}_2\text{N}(\text{CH}_2)_3\text{Li}$ as initiator in hexane:benzene 7:1) and so improves the elastomeric properties of the polymer. Aliquots of the living polymer were terminated at this stage by addition to methanol to give non-functionally terminated polybutadiene for comparative studies.



Chlorophosphines, PClR_2 ($\text{R} = \text{Ph}$, Et , Cy (cyclohexyl)) in tetrahydrofuran (THF) solution were reacted with the polybutadienyllithium in hydrocarbon solution at *ca.* -10°C to form phosphinated polymers **2**–**4**. These polymeric phosphines were easily oxidized on exposure

to the air so that full characterization was not carried out at this stage: purification procedures, including reprecipitations by methanol, invariably caused some oxidation and the primary species detected by ^{31}P n.m.r. and by i.r. spectroscopy were phosphine oxides (**8**) (e.g. (**8**) $\text{Y} = n\text{-Bu}$; $\text{R} = \text{Ph}$: i.r. $\nu(\text{PO})$ 1180 cm^{-1} , ^{31}P n.m.r. 33.6, 33.2, 30.4 ppm; $\text{R} = \text{Cy}$: i.r. $\nu(\text{PO})$ 1160 cm^{-1} , ^{31}P n.m.r. 51.7, 50.8 ppm). The relatively high lability to oxidation, even of the diphenylphosphinated polymer **2**, may be a consequence of the unsaturated allylic linkage of phosphorus(III) to the polymer chain and it may be noted that the simple phosphine $\text{PPh}_2(\text{CH}_2\text{CH}=\text{CH}_2)$ is also quite air-sensitive¹⁴.

To avoid oxidation the phosphines **2**–**4** were quaternized *in situ* by addition of iodomethane in dichloromethane, giving the ionic polymers **5**–**7**: note that polymers **5b**, **6b** and **7b** also contain quaternized amine initiating groups so that these are telechelic, dicationic polymers. Investigations of these quaternized polymers by a combination of n.m.r., g.p.c. and elemental analysis indicated that, although quaternization was quantitative, the termination reaction with PClR_2 had occurred with variable efficiency, 50–93% (Table 1). A by-product of this termination was the coupled polymer $\text{Y}'-(\text{C}_4\text{H}_6)_{2n}-\text{Y}'$, monitored by g.p.c., and this may result from a single electron transfer (SET) mechanism for reaction of **1** with PClR_2 , giving rise to some radical coupling of chains. The coupling was particularly evident with PClPh_2 and this is consistent with the phenyl groups favouring the transfer of an electron from **1**.

^{31}P n.m.r. spectra of the quaternized polymers **5**–**7** show three groups of resonances assignable to quaternary ^{31}P atoms (cf. Figure 1). These three resonances may be assigned to PMeR_2^+ groups bonded to a terminal C_4H_6 unit with *cis*(*Z*)-1,4, *trans*(*E*)-1,4 or 1,2 geometry, resulting from the three possible modes of termination. In order to characterize the regiochemistry of the termination reaction, model studies were undertaken. 5,5-Dimethylhex-2-enyllithium (neopentylallyllithium) was prepared from *t*-butyllithium and butadiene in pentane¹² and reaction of this with PClR_2 , followed by quaternization, afforded the phosphonium salts **9**–**11**, which were isolated after chromatography. The salts comprise mixtures of isomers **A**, **B** and **C** ($\text{X} = t\text{-Bu}$) which are distinguishable by ^1H , ^{13}C (including DEPT) and ^{31}P n.m.r. spectroscopy (Table 2). The relative amounts of **A**:**B**:**C** varied somewhat with preparations but **A**, i.e. *trans*-1,4 addition to

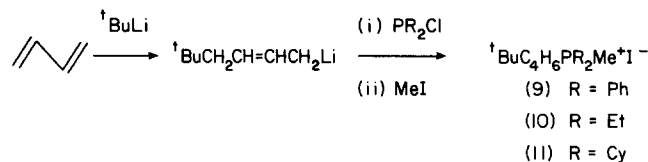


Table 1 Properties of some representative examples of quaternary phosphonium-terminated polybutadienes, $\text{Y}'-(\text{C}_4\text{H}_6)_n-\text{PR}_2\text{Me}^+\text{I}^-$

Y'	R	1,4 (%)	\bar{M}_n	\bar{M}_w/\bar{M}_n	PR_2Me^+ (%)	Terminal configuration (%)		
						<i>cis</i> -1,4	<i>trans</i> -1,4	1,2
<i>n</i> -Bu	Ph	86	3300	1.17	50	50	22	28
<i>n</i> -Bu	Et	83	4400	1.21	~ 50	71	16	13
<i>n</i> -Bu	Cy	86	2900	1.25	73	58	42	–
$\text{I}^+\text{NMe}_3(\text{CH}_2)_3$	Ph	63	7600	1.25	70	~ 43	~ 30	27
$\text{I}^+\text{NMe}_3(\text{CH}_2)_3$	Et ^a	60	2300	1.18	71	41	41	18
$\text{I}^+\text{NMe}_3(\text{CH}_2)_3$	Cy ^a	60	4100	1.15	93	~ 65	27	~ 8

^a Ionic transition temperature from d.m.t.a.: 102°C ($\text{R} = \text{Et}$); 73°C ($\text{R} = \text{Cy}$)

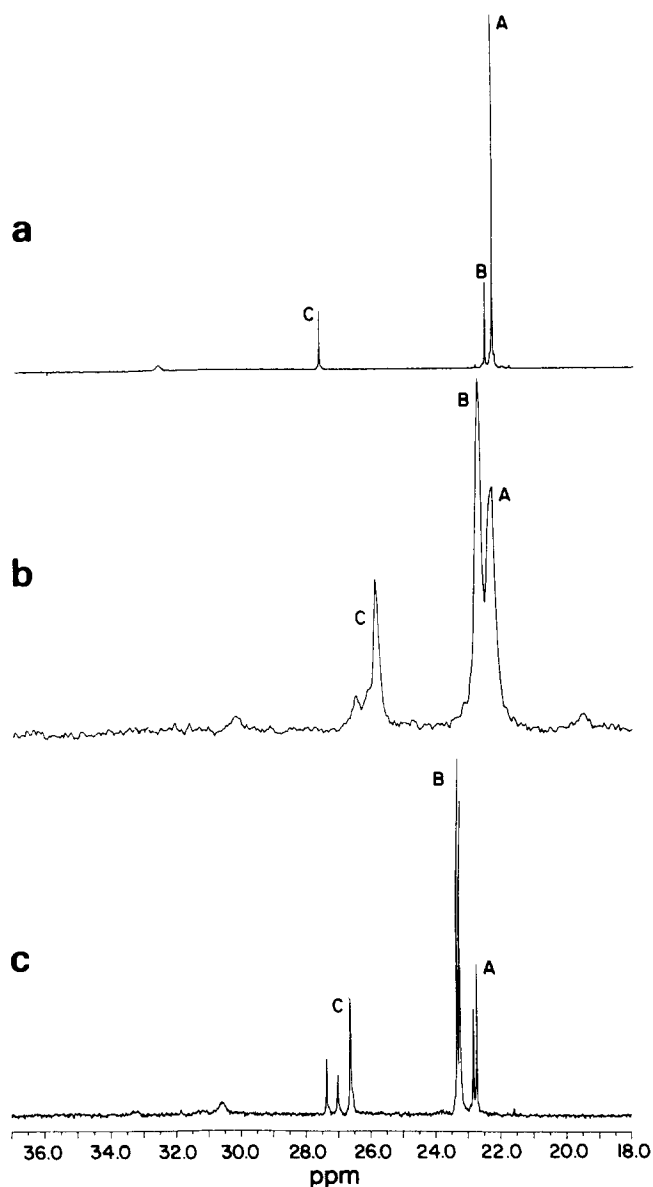


Figure 1 ^{31}P n.m.r. spectra in CDCl_3 at 22°C : (a) $(t\text{-BuC}_4\text{H}_6\text{PPh}_2\text{Me})^+\text{I}^-$; (b) $n\text{-Bu}(\text{C}_4\text{H}_6)_n\text{PPh}_2\text{Me}^+\text{I}^-$ ($\bar{M}_n = 3300$); (c) $^-\text{I}^+\text{Me}_3\text{N}(\text{CH}_2)_3(\text{C}_4\text{H}_6)_n\text{PPh}_2\text{Me}^+\text{I}^-$ ($\bar{M}_n = 7600$). Bands A, B and C are assigned, respectively, to *trans*-1,4, *cis*-1,4 and 1,2 terminal configurations

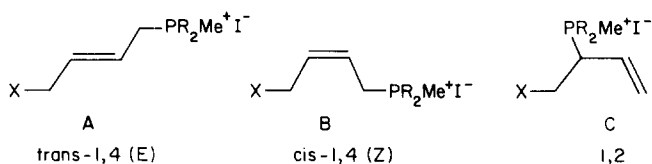


Table 2 ^{31}P n.m.r. resonances of quaternary phosphonium products

Compound	Terminal configuration (chemical shifts, ppm)		
	1,2	<i>cis</i> -1,4	<i>trans</i> -1,4
$t\text{-BuC}_4\text{H}_6\text{PPh}_2\text{Me}^+$	27.7	22.6	22.35
$t\text{-BuC}_4\text{H}_6\text{PEt}_2\text{Me}^+$	38.5	36.1	34.6
$t\text{-BuC}_4\text{H}_6\text{PCy}_2\text{Me}^+$	35.9	34.9	33.2
$n\text{-Bu}-(\text{C}_4\text{H}_6)_n\text{-PPh}_2\text{Me}^+$	27.37, 27.03, 26.64	23.34, 23.26	22.84, 22.73
$^+\text{NMe}_3(\text{CH}_2)_3-(\text{C}_4\text{H}_6)_n\text{-PPh}_2\text{Me}^+$	26.51, 25.87	22.7	22.3
$n\text{-Bu}-(\text{C}_4\text{H}_6)_n\text{-PEt}_2\text{Me}^+$	38.0, 37.9	36.38, 36.27	34.9
$^+\text{NMe}_3(\text{CH}_2)_3-(\text{C}_4\text{H}_6)_n\text{-PEt}_2\text{Me}^+$	38.08, 37.84, 37.49	36.22, 36.12	35.13, 35.02, 34.77, 34.63
$n\text{-Bu}-(\text{C}_4\text{H}_6)_n\text{-PCy}_2\text{Me}^+$	—	34.81, 34.72	33.21, 33.10
$^+\text{NMe}_3(\text{CH}_2)_3-(\text{C}_4\text{H}_6)_n\text{-PCy}_2\text{Me}^+$	—	35.27, 34.99, 34.90, 34.66	33.42, 33.27

butadiene, predominates with A $\sim 70\%$, B 15–20%, C 8–20% and the percentage of C (i.e. 1,2-addition) being smallest for the bulky dicyclohexyl group PCy_2^+ . The distinct ^{31}P chemical shifts of the resonances assigned to the three isomers of the model compounds may be utilized to identify the configuration of terminal PMeR_2^+ groups in polymers 5–7 by comparison of corresponding ^{31}P n.m.r. spectra (Table 2). For all polymers 1,4-termination predominates with *cis*-1,4 > *trans*-1,4 and the 1,2-termination mode is negligible for the sterically demanding PCy_2 functional group (see Table 1).

The additional complexity of resonances assigned to terminal types A, B and C in the polymers (see Table 2) must originate from secondary influences of the polymer geometry. Effects of the penultimate groups of the polybutadiene chain (i.e. *cis*-1,4; *trans*-1,4; (*R*) or (*S*)) 1,2 linkages) are the most probable cause. It may be noted that the complexity is most marked for polymers with terminal configuration C ($\text{X}=\text{Y}^-(\text{C}_4\text{H}_6)_{n-1}$) in which the ^{31}P atom is closest to the penultimate unit and in which chirality introduced by the 1,2-addition process may cause chemical-shift variations arising from tacticity effects. These secondary chemical-shift differences may also be enhanced by interpolymeric interactions between the terminal ionic groups.

The telechelic dicationic polybutadienes are highly viscous materials but become free flowing at higher temperatures. A transition associated with the interaction of the ionic groups can be monitored by dynamic mechanical thermal analysis, and is generally found in the range $70\text{--}120^\circ\text{C}$ (e.g. see footnote a, Table 1). These physical studies will be reported in detail in a comparative paper with related data for α,ω -diquaternary ammonium polybutadienes.

CONCLUSIONS

Living poly-1,3-butadiene with high 1,4-content, generated anionically by alkyl lithium initiators in hydrocarbon solvents, reacts with dialkyl- or diarylchlorophosphines to give new materials with terminal phosphine groups. These polymers are readily quaternized to form stable ionic phosphonium derivatives. Termination yields are dependent on the phosphine used and on the conditions of the reaction but, in suitable cases, can occur to >90%. By using a functionalized initiator, novel telechelic dicationic ionomers can be obtained.

Alternatively, if polybutadiene with a high 1,2-content is required, these studies indicate that a telechelic diquaternary phosphonium polymer could be produced by termination of living polybutadiene initiated by a

difunctional initiator (e.g. sodium- or lithium-naphthalene) in a polar solvent (e.g. tetrahydrofuran, cf. ref. 6).

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