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Synthesis and characterization of α,ω- and α-functionalized hydrogenated polybutadienes: telechelic and semi-telechelic amine and phosphite terminated polymers

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Polymers with terminal amine or phosphite groups (X) were synthesized from tosylated derivatives of hydrogenated α-hydroxy- and α,ω-dihydroxy-poly-1,3-butadienes, produced by anionic techniques. Products are semi-telechelic and telechelic polymers with X = NH_2 (**5**), NHPh (**6**), $NHPr^n$ (**7**), $NH(CH_2)_3NMe_2$ (**8**), $O(CH_2)_2NH_2$ (**9**), $O(CH_2)_2NH(CH_2)_2NH_2$ (**10**), NMe_2 (**13**), $OPO_2C_6H_4$ (**14**) of varying ethyl side-group content, controlled molar mass ($\bar{M}_n$ = 600–3000) and low polydispersity. Characterization of polymers by n.m.r. and i.r. spectroscopy is reported, with comparative studies on short chain model systems. Thermal properties and viscosities have been investigated in relation to molar mass, backbone structure and terminal functionality; comparisons are made with related saturated and unsaturated systems, and with polymers containing terminal ionic functionalities, formed by alkylation, protonation, or coordination with Cu(II), Ni(II) and Fe(III) chlorides. Effects of end-groups on variations in T_g, higher thermal transitions and on melt viscosities are discussed. Oxidation of phosphite end-groups is also observed. © 1997 Elsevier Science Ltd.

(Keywords: hydrogenated polybutadiene; telechelic; amine-termination)

INTRODUCTION

Attachment of terminal functional groups to linear polymers produces materials with modified physico-mechanical properties and such telechelic systems can also undergo further chemical interactions which may lead to the formation of extended polymer systems and networks[1]. Hydroxyl groups have proved to be interesting terminal functionalities, as exemplified by hydroxy-terminated polybutadienes, which have found several industrial applications[2–7]. Such hydroxy-polybutadienes are generally formed commercially by radical polymerizations of 1,3-butadiene with hydrogen peroxide yielding telechelic materials of functionality close to 2.0 but these polymers contain differing types of hydroxylalkyl groups and have a mixed backbone stereochemistry with relatively wide molecular weight distributions.

The hydroxyl function can alternatively be introduced in a quantitative procedure by anionic polymerization techniques, either via a termination step with ethylene oxide[8–12] or by using a suitably functionalized initiator[13]. Anionic polymerizations of 1,3-butadiene give polymers of low polydispersity and the extent of 1,2 vs 1,4 additions can be largely controlled by the choice of solvent[1,14]. Hydroxy-telechelic 1,4-polybutadiene has also been synthesized indirectly by the ring opening metathesis polymerization of 1,5-cyclooctadiene[15]. Hydrogenation of hydroxy-terminated polybutadienes to form saturated telechelic polymers has been reported[9]; related hydroxy-polymers with an isomeric saturated backbone have been formed by hydroboration of cationically produced polyisobutylenes[1,16,17] and it is also of interest that a mixture of products, including saturated terminal alcohols, is formed by oxidation of living oligo(ethylene) species[18].

Hydroxyl groups are precursors for a variety of other functionalities and such chemical transformations are conveniently achieved via intermediate tosyl derivatives; by such procedures, tosyl-telechelic polyisobutylene[16,19] and poly(oxyethylene)[20,21] have been prepared and converted into other terminally functionalized systems, including some amine-telechelic polymers[20,22]. Previous studies in this laboratory have involved quaternary ammonium[23] and phosphonium[24] terminated polybutadiene ionomers, synthesized by anionic techniques. We now report the synthesis and properties of some saturated hydrocarbon oligomers/polymers ($\bar{M}_n$ = 600–3000) with terminal amine or phosphite groups, obtained by reactions of hydrogenated hydroxy-terminated polybutadienes with selected backbone stereochemistries. Such terminally functionalized saturated polymers have potential as fuel and lubricant additives or as components of blends with commercial polyalkenes.

EXPERIMENTAL

All reactions and manipulations of air-sensitive materials were carried out under an atmosphere of dry nitrogen or

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argon or *in vacuo*, using carefully dried Schlenk-type glass apparatus (cf. refs 23 and 24). Solvents (Aldrich or Rhône-Poulenc) were pre-dried and freshly distilled under nitrogen or vacuum before use and 1,3-butadiene was handled and purified as previously described[24]. 3-Dimethylaminopropyllithium[23,25,26] and 5,5-dimethylhex-2-enyllithium[27,28] were prepared as reported; butyllithium solutions (Aldrich) were standardized before use[29]: naphthalene–lithium (LiNp) was prepared by stirring naphthalene (12.8 g, 0.1 mol) and lithium metal (2.1 g, 0.1 mol) in THF (100 cm^3) for *ca.* 4 h and standardized by acid titration. Other reagents were commercial materials (Aldrich, BDH or Fluka) which were distilled or recrystallized, as necessary, and dried before use.

N.m.r. spectra were obtained in $CDCl_3$ with Bruker WP 200 SY and WP 400 spectrometers using frequencies of 200.13 and 400.13 MHz for ^{1}H 50.32 and 100.60 MHz for ^{13}C{^{1}H}, and 81.0 MHz for ^{31}P{^{1}H}, with chemical shifts (δ ppm), referenced to TMS for ^{1}H and ^{13}C and to external 85% H_3PO_4 for ^{31}P. I.r. spectra were recorded on a Perkin–Elmer FT 1600 spectrometer and mass spectra (EI and FAB) on an updated VG MS9 instrument. G.p.c. measurements employed various Waters instruments using THF as solvent and a refractive index detector; initial analyses against polystyrene standards were converted to values for polybutadienes using appropriate Mark–Houwink parameters[30,31]. $\bar{M}_n$ values were also obtained for some samples in toluene using a Knauer Vapour Pressure Osmometer (VPO), calibrated against squalane. D.t.a. measurements were made on a DuPont 900 Thermal Analyser in the temperature ranges −100°C to 0°C (T_g measurements) and 0–200°C, at a heating rate of 20°C min^{-1}. Polymer viscosity was measured using a Haake cone and plate viscometer at 40°C. D.m.t.a. measurements utilized a PL instrument in the shear mode, range −40 to +150°C at 1 Hz, with a heating rate of 4°C min^{-1}. Elemental analyses were carried out at UMIST, Manchester, UK. All prepared polymers were stored at −15°C under nitrogen and were dried under vacuum at 85°C for 48 h before physical testing.

Hydroxy-terminated polybutadienes

α-Lithiopolybutadienes and α,ω-dilithiopolybutadienes, with differing backbone stereochemistry and molar mass, were prepared anionically by the general methods described previously[24,32], using the following initiators and solvents: *high 1,2 α-lithiopolybutadiene*: *n*-butyllithium and THF; *high 1,4 α-lithiopolybutadiene*: *n*-, *s*- or *t*-butyllithium and hexane: *high 1,2 α,ω-dilithiopolybutadiene*: naphthalene lithium (LiNp) and THF (see *Table 1*). A portion (*ca.* 10%) of each living polymer was quenched with methanol to yield proton terminated material for comparative studies. The remaining living polymer was terminated by addition of ethylene oxide (20% excess) to yield corresponding α-hydroxy or α,ω-dihydroxy terminated polybutadienes with 85–100% termination (cf. refs 9–11). All isolated polymer samples were purified by reprecipitation from methanol. Selected spectral data: n.m.r., ^{1}H, δ: 3.6 (*t*, CH_2O); ^{13}C{^{1}H}, δ: 61.1 and 62.4 (CH_2O); i.r. (bulk) cm^{-1}: *ca.* 3600 and 3400 vbr (νOH).

Reaction of 5,5-dimethylhex-2-enyllithium with ethylene oxide

5,5-Dimethylhex-2-enyllithium was prepared in pentane from 1,3-butadiene (4 cm^3, 0.048 mol) and *t*-butyllithium (32 cm^3, 1.7 mol dm^{-3})[27,28]. Ethylene oxide (3.6 cm^3, 0.058 mol) was distilled into this solution at −78°C and after 2 h the reaction mixture was left to warm to ambient temperature over 16 h. Methanol (40 cm^3), and then distilled water (4 cm^3), was added to the stirred solution. Extraction into hexane and evaporation of solvent gave the product as a yellow oil. G.c. and g.c./m.s. indicated two main constituents of formula $Bu^tC_4H_6CH_2CH_2OH$, mol ratio *ca.* 1 : 3, accompanied by smaller amounts of higher molar mass species. ^{13}C and ^{1}H n.m.r. were consistent with the presence of overall 62% 1,4- and 38% 1,2-linkages of butadiene units in the combined products. End group ^{13}C{^{1}H) n.m.r. resonances, δ: 61.0 (CH_2O, 1,2-addition, rel. int. 3) and 62.4 (CH_2O, 1,4-addition, rel. int. 7).

Hydrogenation of polybutadienes

Polybutadiene (4–20 g) in cyclohexane (60–300 cm^3) and 5% Pd/C (0.4–2 g; *ca.* 10% of polymer mass) were placed in a stirred autoclave (180 or 500 cm^3). Hydrogen (50–100 atm) was introduced and the temperature of the autoclave raised to 70°C for *ca.* 48 h, until hydrogenation was complete. Solutions of hydrogenated polybutadiene were separated from catalyst by centrifugation (high-1,2 polymer) or by filtration, after addition of toluene and heating to 75°C (high-1,4 polymer), and solvent was evaporated to give product in yields up to 98%. 100% hydrogenation was indicated by the complete absence of ethylenic resonances in ^{1}H and ^{13}C n.m.r., and by the absence of CH=CH and $CH{=}CH_2$ and presence of 1380 cm^{-1} (CH_3) vibrational bands in the i.r. spectra. Terminal OH or $N(CH_3)_2$ groups were unchanged.

α,ω-Ditosylalkanes (model derivatives)

Derivatives $4\text{-}MeC_6H_4SO_3(CH_2)_nO_3SC_6H_4Me\text{-}4$ (n = 8, 12, 16) were prepared from α,ω-diol and *p*-tosyl chloride by standard literature procedures[21,33]: $n = 8$ (mp 72–74°C; lit.[33] ~70°C); n.m.r., ^{1}H, δ: 1.2 and 1.6 ($C\mathbf{C}\mathbf{H}_2C$, 12H), 2.45 (s, $\mathbf{CH}_3C_6H_4$, 6H), 4.05 (*t*, $C\mathbf{H}_2OS$, 4H), 7.45 (2 *d*, $C_6\mathbf{H}_4$, 8H); ^{13}C{^{1}H}, δ: 21.4 ($\mathbf{C}H_3C_6H_4$), 24.9, 28.4 and 28.5 ($C\mathbf{C}H_2C$), 70.4 ($\mathbf{C}H_2OS$) 127.6, 129.6, 133.1 and 144.5 ($\mathbf{C}_6H_4$); m.s. (EI) *m/z*: 454 (2%) [$M\cdot^+$], 173 (100%), 155 (80%), 91 (100%), 55 (94%); $n = 12$ (mp 73–75°C; lit.[33] 75°C); $n = 16$ (mp 84–85°C; lit.[34] 84–85°C).

Tosylation of hydroxy terminated hydrogenated polybutadienes (cf. ref. 21)

Hydrogenated, hydroxy-terminated polybutadiene was dissolved in dry toluene (*ca.* 1 g polymer per 20 cm^3 toluene) under nitrogen. A stoichiometric amount of *n*-butyllithium in hexane (HO : LiBu^n, 1 : 1) was added to the vigorously stirred solution at 5°C and the stirred mixture left for 2 h. *p*-Tosyl chloride (*ca.* 25% excess) in dry toluene was added and the reaction left stirring at ambient temperature for 16 h (overnight). The viscous solution was washed well with distilled water, followed by extraction of the organic layer into dichloromethane. The dichloromethane/toluene mixture was dried over anhydrous sodium sulfate and the solvents evaporated to leave tosylated polymer which was dried *in vacuo*; yield 75–97%; conversion to tosylate 95–100% (n.m.r. analysis). Selected spectral data: n.m.r., ^{1}H, δ: 2.45 (*s*, $C\mathbf{H}_3C_6H_4$), 4.05 (*m*, $C\mathbf{H}_2OS$), 7.35 and 7.8 (2 *d*, $C_6\mathbf{H}_4$); ^{13}C{^{1}H}, δ: 21.5 ($\mathbf{C}H_3C_6H_4$),

Table 1 Properties of poly-1,3-butadienes and some corresponding terminally functionalized and hydrogenated oligomers/polymers

Poly-1,3-butadiene	Initiator[a]/solvent	% 1,4[b]	$\bar{M}_n^c$	$\bar{M}_w/\bar{M}_n^d$	T_g^e (°C)	η^f (Pa.s)	Hydrogenated poly-1,3-butadiene	T_g^e (°C)	η^f (Pa.s)
I	LiBu^n/THF	14	820	1.13	−39	0.90	**HI**	−47	1.4
I-α-OH	LiBu^n/THF	14	810	1.09	−37	1.0	**HI**-α-OH	−46	1.8
II	LiBu^n/THF	12	1030	1.13	−36	1.5			
II-α-OH	LiBu^n/THF	11	940	1.12	−34	1.6	**HIII**-α-OH	−44	2.6
III	LiBu^n/THF	12	1080	1.16					
III-α-OH	LiBu^n/THF	10	1360	1.15	−27		**HIII**-α-OH		
IV	LiBu^n/THF	13	2410	1.06	−24	13.1	**HIV**	−45	13.6
IV-α-OH	LiBu^n/THF	8	2440	1.05	−22	15.6	**HIV**-α-OH	−35	16.6
V	LiBu^n/THF	14	2610	1.09	−23	14.3			
V-α-OH	LiBu^n/THF	8	2670	1.05	−22	16.0	**HV**-α-OH	−36	18.6
VI	LiBu^t/hexane	69	590	1.12	−91	0.042			
VI-α-OH	LiBu^t/hexane	65	660	1.07	−80	0.094	**HVI**-α-OH	−65	0.47
VII	LiBu^n/hexane	66	690	1.39	−94		**HVII**	−77	
VII-α-OH	LiBu^n/hexane	68	660	1.43	−86				
VIII	LiBu^n/hexane	72	900	1.48	−96				
VIII-α-OH	LiBu^n/hexane/THF^g	50	930	1.53	−79		**VIII**-α-OH	−69	
IX	LiBu^s/hexane	87	1660	1.05	−98	0.15			
IX-α-OH	LiBu^s/hexane	87	1770	1.06	−96	0.23	**IX**-α-OH	(104)^h	
X	LiBu^s/hexane	87	1680	1.10	−98	0.13	**HX**	(96)^h	
X-α-OH	LiBu^s/hexane	86	1710	1.10	−93	0.22	**HX**-α-OH	(102)^h	
XI	LiBu^t/hexane	87	2190	1.06	−95	0.30	**HXI**	(102)^h	
XI-α-OH	LiBu^t/hexane	87	2300	1.05	−93	0.37	**HXI**-α-OH	(102)^h	
XII-α-NMe_2	DMAPLi/hexane	58	1730	1.18			**HXII**-α-NMe_2	−66	
XIII-α-NMe_2	DMAPLi/hexane	50	2690	1.17			**HXIII**-α-NMe_2	−64	4.9
XIV	LiNp/THF	17	1020	1.19	−26	5.5			
XIV-α,ω-$(OH)_2$	LiNp/THF	15	1070	1.16	−20	10.9	**HXIV**-α,ω-$(OH)_2$	−40	14.1
XV	LiNP/THF	17	1100	1.20	−28	5.4	**HXV**	−51	5.5
XV-α,ω-$(OH)_2$	LiNp/THF	12	1140	1.16	−20	11.6	**HXV**-α,ω-$(OH)_2$	−35	17.9
XVI	LiNp/THF	13	1140	1.26	−25				
XVI-α.ω-$(OH)_2$	LiNp/THF	14	1090	1.27	−20				
XVII	LiNp/THF	13	2980	1.13	−23	28.3	**HXVII**	−32	28.5
XVII-α,ω-$(OH)_2$	LiNp/THF	12	2990	1.08	−19	36.2	**HXVII**-α.ω-$(OH)_2$	−27	47.1
XVIII	LiNp/THF	14	3130	1.12	−21	37.6			
XVIII-α,ω-$(OH)_2$	LiNp/THF	12	3110	1.12	−16	41.6	**HXVIII**-α,ω-$(OH)_2$	−28	53.6

[a] DMAPLi = 3-diethylaminopropyllithium, LiNp = naphthalenelithium
[b] Determined by ^{1}H n.m.r.
[c] Determined by g.p.c. and (in some cases) VPO
[d] Determined by g.p.c.
[e] From d.t.a.
[f] Melt viscosity at 40°C
[g] THF added to hexane before termination
[h] Melt temperature (T_m)

70–72 (2 *s*, CH_2OS), 127.7, 129.6, 133.1 and 144.5 (C_6H_4); i.r. cm^{-1}: 1170–1190 (νSO).

Synthesis of α, ω-diaminoalkanes (model derivatives)

Reaction of α, ω-ditosylalkanes with aniline. In a typical reaction, aniline (4.5 cm^3, 0.032 mol) and 1,12-ditosyldodecane (6 g, 0.012 mol) were heated for 3 h at 130–145°C. The solid formed on cooling to room temperature was dissolved in aqueous 40% NaOH and the product extracted into diethyl ether. After separation, the ether was removed by evaporation and the resulting oil was crystallized from petroleum ether to give the *N*, *N*′-diphenyl-1,12-diaminododecane as a white powder. Yield 62% (mp 67°C). $C_{24}H_{36}N_2$; found C 81.6, H 10.1, N 7.9%, calcd. C: 81.8, H 10.3, N 8.0%. M.s. (EI) *m*/*z*: 352 (85%) [$M\cdot^+$], 106 (100%). N.m.r., ^{1}H, δ: 1.3 and 1.6 (CCH_2C, 20H), 3.1 (*t*, CH_2N, 4H), 3.6 (*s*, NH, 2H), 6.6 and 7.2 (*m*, C_6H_5, 10H); ^{13}C{^{1}H}, δ: 27.0, 29.2 and 29.5 (CCH_2C), 43.9 (CH_2N), 112.6, 116.9, 129.1 and 148.4 (C_6H_5). I.r. (KBr) cm^{-1}: 3405 (νNH). Similarly prepared: *N*, *N*′-diphenyl-1,8-diamino-octane, 58% (mp 61°C). $C_{20}H_{28}N_2$; found C 80.9, H 9.2, N 9.5%, calcd. C 81.0, H 9.5, N 9.5%. M.s. (EI) *m*/*z*: 296 (89%) [$M\cdot^+$], 106 (100%). *N*, *N*′-Diphenyl-1,16-diaminohexadecane 14% (mp 81°C). $C_{28}H_{44}N_2$; found C 82.3, H 0.6, N 6.9%, calcd. C 82.3, H 10.9, N 6.9%. M.s. (EI) *m*/*z*: 409 (32%); 408 (100%) [$M\cdot^+$], 106 (30%).

Reaction of α, ω-ditosylalkane with n*-propylamine.* In a typical reaction, 1,12–ditosyldodecane (2 g, 3.9 × 10^{-3}

mol) and *n*-propylamine ($0.34\,cm^3$, 0.012 mol) were heated at 100°C for 4 h under a nitrogen atmosphere. Cooling and isolation of product as above gave white crystals—principally *N*,*N'*-di-*n*-propyl-1,12-diaminododecane, $Pr^nNH(CH_2)_{12}NHPr^n$ ($M = 284.3$), but also containing some coupled product $Pr^nNH(CH_2)_{12}NPr^n(CH_2)_{12}NHPr^n$ ($M = 509.6$). M.s. (FAB) *m/z*: 509 (14%), 297 (15%), 285 (33%) $[M+H]^+$, 283 (24%) $[M-H]^+$, 73 (63%), 72 (100%), N.m.r., ^1H, δ: 0.9 (*t*, $C\mathbf{H}_3$), 1.3 and 1.4–1.7 (*m*, $C\mathbf{C}H_2C$), 2.4 and 2.6 (*m*, $C\mathbf{H}_2N$); $^{13}C\{^1H\}$, δ: 11.8 and 12.0* ($\mathbf{C}H_3$); 20.2* and 23.2 ($CH_3\mathbf{C}H_2$); 27.0*, 27.4, 27.6*, 29.5 and 30.2 ($C\mathbf{C}H_2C$); 50.1, 51.9, 54.3* and 56.3* ($\mathbf{C}H_2N$) {*minor resonances associated with coupled product}.

Reaction of α,ω-ditosylalkane with 3-(dimethylamino)-propyl amine. By a similar procedure to that above 1,12-ditosyldodecane (2 g, 3.93×10^{-3} mol) and 3-(dimethylamino)propylamine ($1.28\,cm^3$, 0.012 mol) were heated to 100°C for 3 h to form *N*,*N'*-bis(3-dimethylaminopropyl)-1,12-diaminododecane as a low melting, white solid; yield 43%. $C_{22}H_{50}N_4$; found C 70.3, H 14.0, N 14.4%, calcd. C 71.3, H 13.6, N 15.1%. M.s. (EI) *m/z*: 370 (18%) $[M^{\cdot +}]$, 312 (11%), 85 (100%). N.m.r., ^1H, δ: 1.2 and 1.4 ($C\mathbf{CH}_2C$, 20H), 1.6 (m, $NCH_2\mathbf{CH}_2CH_2N$, 4H), 2.15 (*s*, $C\mathbf{H}_3$, 12H), 2.2 (*t*, $Me_2NC\mathbf{H}_2$, 4H), 2.5 (*m*, $C\mathbf{H}_2NC\mathbf{H}_2$, 8H); $^{13}C\{^1H\}$, δ: 27.3, 28.1, 29.4 and 30.0 ($C\mathbf{C}H_2C$), 45.4 ($\mathbf{C}H_3N$); 48.3, 50.0 and 58.0 ($N\mathbf{C}H_2$).

Preparation of 1,8-diamino-alkane. 1,8-Diazido-octane was prepared from 1,8-ditosyloctane and sodium azide by the general method described in ref. 35 {i.r. cm^{-1}: 2095 (ν_{asym} N_3); 1460 (CH, def); 1251 (ν_{sym} N_3)}. Reduction of 1,8-diazido-octane (2 g, 0.010 mol) in cyclohexane ($15\,cm^3$) with hydrogen (15 atm) and 5% Pd/C (0.2 g) in a stirred autoclave for 24 h at ambient temperature gave the product, 56%, mp 51°C (lit.[36,37] 50–52°C). M.s. (FAB) *m/z*: 149 (28%); 146 (5%), 145 (18%) $[M+H]^+$, 143 (6%) $[M-H]^+$, 69 (100%). N.m.r., ^1H, δ: 1.2 and 1.4 ($C\mathbf{CH}_2C$, 12H), 2.7 (*t*, $C\mathbf{H}_2NH_2$, 4H). I.r. (KBr) cm^{-1}: 3350–3300 (νNH).

Reaction of terminally tosylated hydrogenated polybutadienes with aniline

Aniline ($7.5\,cm^3$, 0.080 mol) and tosyl polymer (e.g. 4 g, 1.3×10^{-3} mol, $\bar{M}_n = 3000$, telechelic) were heated at 120°C with stirring for 24 h. After cooling, the reaction mixture was added to a large excess of stirred methanol containing a few drops of triethylamine. The precipitated polymer was collected, dissolved in THF, reprecipitated by addition to methanol and dried. Selected spectral data: n.m.r., ^1H, δ: 3.1 (*t*, $C\mathbf{H}_2N$), 6.7 and 7.2 ($C_6\mathbf{H}_5$); $^{13}C\{^1H\}$, δ: 42.0 and 44.0 ($\mathbf{C}H_2N$), 112.6, 117.0, 129.1 and 148.4 ($\mathbf{C}_6H_5$); i.r. (bulk) cm^{-1}: 3420 (νNH).

Reaction of terminally tosylated hydrogenated polybutadienes with n*-propylamine*

A mixture of *n*-propylamine ($6.8\,cm^3$, 0.080 mol) and tosyl polymer (e.g. 4 g, 1.3×10^{-3} mol, $\bar{M}_n = 3000$, telechelic) was heated to reflux and stirred for 24 h. The product was isolated as described for the previous reaction. Selected spectral data: n.m.r., ^1H, δ: 2.6 (*m*, $C\mathbf{H}_2\mathbf{N}$); $^{13}C\{^1H\}$, δ: 50.4, 51.8 and 51.9 ($\mathbf{C}H_2N$); i.r. (bulk) cm^{-1}: 3400–3350 (νNH).

Reaction of terminally tosylated hydrogenated polybutadienes with 3-dimethylaminopropylamine

As above, dimethylaminopropylamine ($10.5\,cm^3$, 0.080 mol) and tosyl polymer (4 g, 1.34×10^{-3} mol, $\bar{M}_n = 3000$, telechelic) were heated to reflux and stirred for 24 h. On cooling, the brown solution was worked up as described above. Selected spectral data: n.m.r., ^1H, δ: 2.1 (*s*, $C\mathbf{H}_3$), 2.3 (*t*, $(CH_3)_2NC\mathbf{H}_2$) 2.65 (*m*, $C\mathbf{H}_2NC\mathbf{H}_2$); $^{13}C\{^1H\}$, δ: 45.5 ($\mathbf{C}H_3$), 47.9–48.6 (2 *s*, $N\mathbf{C}H_2$), 50.1 $\{(CH_3)_2NCH_2CH_2\mathbf{C}H_2N\}$, 58.0 $\{(CH_3)_2N\mathbf{C}H_2\}$; i.r. (bulk) cm^{-1}: 3300–3290 (νNH).

Preparation of α-amino- or α,ω-diamino-polymer

Terminal azido-polymer. Excess sodium azide and terminally tosylated hydrogenated polybutadiene (*ca.* 6 g) in dimethylformamide ($50\,cm^3$) and toluene ($25\,cm^3$) were stirred at 50°C for 24–168 h (reaction followed by monitoring of tosyl and azido i.r. bands). On completion, the reaction mixture was filtered and the solid residue washed with toluene. Toluene was evaporated from the combined filtrate and washings; the polymer separated from the dimethylformamide and was collected, washed and dried *in vacuo*. I.r. (bulk) cm^{-1}: 2090 and 1261 (νN_3).

Reduction of polymeric azide. The polymeric azide (3 g), dissolved in cyclohexane ($25\,cm^3$), was hydrogenated with H_2 (50 atm) and 5% Pd/C (0.3 g) in a stirred autoclave for 5 days at room temperature. Solutions of the product in cyclohexane were isolated either by centrifugation (high 1,2 materials) or by filtration using large quantities of cyclohexane (high 1,4 materials). Polymer was isolated from solution as previously described. Selected spectral data: n.m.r., ^1H, δ: 2.7 (*t*, $C\mathbf{H}_2NH_2$); $^{13}C\{^1H\}$, δ: 40–42 (2 *s*, $\mathbf{C}H_2NH_2$); i.r. (bulk) cm^{-1}: 3400–3300 (νNH_2).

Reaction of terminally tosylated hydrogenated polybutadienes with ethanolamine

By a method similar to that described in ref. 22, ethanolamine ($0.9\,cm^3$, 0.013 mol) in dry toluene ($80\,cm^3$) was added to stirred potassium *t*-butoxide (2.4 g, 0.021 mol) dissolved in dry *t*-butanol ($40\,cm^3$). The solution was heated to reflux to form a yellow solution and then, over 10 min, the tosyl polymer (e.g. 4 g, 1.3×10^{-3} mol, $M_n = 3000$, telechelic), dissolved in toluene ($60\,cm^3$), was added dropwise. The orange/yellow solution was refluxed overnight. The solution was allowed to settle for 24 h, filtered and the filtrate washed with aqueous potassium hydroxide ($2 \times 100\,cm^3$) followed by distilled water ($1-2\,dm^3$) until neutral. After drying with anhydrous sodium sulfate, solvent was evaporated from the filtered solution to give the polymer. Selected spectral data: n.m.r., ^1H, δ: 2.85 ($C\mathbf{H}_2N$), 3.4 (*m*, $C\mathbf{H}_2OC\mathbf{H}_2$); $^{13}C\{^1H\}$, δ: 41.9 ($\mathbf{C}H_2N$), 69.5, 71.2 and 71.9 ($\mathbf{C}H_2O\mathbf{C}H_2$); i.r. (bulk) cm^{-1}: 3300–3200 (νNH).

Reaction of terminally tosylated hydrogenated polybutadienes with 2-(2-aminoethylamine)ethanol

By a similar method to that above, 2-(2-aminoethylamino)ethanol (1.4 g, 0.013 mol) in dry toluene ($80\,cm^3$) was deprotonated with potassium *t*-butoxide (2.4 g, 0.021 mol) in dry *t*-butanol ($40\,cm^3$) and reacted with tosylated polymer to give the terminated polymer.

Selected spectral data: n.m.r., ^{1}H, δ: 2.8 (*t*, $C\mathbf{H}_2NH_2$), 2.9 (*m*, $C\mathbf{H}_2NC\mathbf{H}_2$), 3.4 and 3.5 (2*t*, $C\mathbf{H}_2OC\mathbf{H}_2$); $^{13}C\{^1H\}$, δ: 41.6 ($\mathbf{C}H_2NH_2$), 49.3 and 52.3 ($\mathbf{C}H_2N\mathbf{C}H_2$), 69.6, 70.0 and 71.2 ($\mathbf{C}H_2O\mathbf{C}H_2$); i.r. (bulk) cm^{-1}: 3400–3200 (νNH).

Formation of ionic derivatives of amine terminated hydrogenated polybutadienes

(i) Amino or mono- or di-alkyl amino terminated polymer (1 g) was dissolved in dichloromethane (25 cm^3) under nitrogen. To this solution was added a 30% stoichiometric excess (per N atom) of bromomethane in diethyl ether (2 mol dm^{-3}). The solutions were stirred for 16–24 h under nitrogen and then evaporated to dryness. The very viscous liquid or solid ionomeric product was washed with petroleum ether and dried *in vacuo*. Characteristic n.m.r. resonances: ^{1}H, δ: 3.45 ($C\mathbf{H}_3N^+$), 3.5–3.6 ($C\mathbf{H}_2N^+$) {exception: 3.0 ($C\mathbf{H}_2NH_2CH_3^+$)}; $^{13}C\{^1H\}$ δ: 52–55 ($\mathbf{C}H_3N^+$), 65–67 ($\mathbf{C}H_2N^+$).

(ii) Polymer with terminal phenylamino groups (1 g) was dissolved in dichloromethane (25 cm^3) and hydrogen bromide gas was bubbled through this solution for 2 min. The very viscous ionomer was isolated as above. Selected n.m.r. resonances: ^{1}H, δ: 3.3 ($C\mathbf{H}_2N^+$), 7.4 and 7.7 ($C_6\mathbf{H}_5N^+$); $^{13}C\{^1H\}$ δ: 53 ($\mathbf{C}H_2N^+$), 123.6, 129.5, 130.0 and 135.0 ($\mathbf{C}_6H_5N^+$).

Preparation of metal containing amine terminated hydrogenated polybutadienes

Hydrogenated polybutadienes ($\bar{M}_n > 2000$) with terminal groups $NH(CH_2)_3N(CH_3)_2$ or $O(CH_2)_2NH(CH_2)_2NH_2$ were reacted with $CuCl_2.2H_2O$, $NiCl_2.6H_2O$ or $FeCl_3.6H_2O$, in the stoichiometric ratio $MCl_{2/3}$: polymer end group of 1 : 2. Polymer (1.5 g) was dissolved in toluene (30 cm^3) and the metal chloride, dissolved in methano (0.2 mol dm^{-3}), was added dropwise to the polymer solution with vigorous stirring. After 24 h, the solvent was removed *in vacuo* and the product dried as described previously.

Formation of α,ω-phosphorus(III) alkanes (model derivatives)

Reaction of α,ω-alkanediol with 1,2-phenylene phosphochloridite. In a typical reaction, 1,2-phenylene phosphochloridite (1.6 cm^3, 0.014 mol) and pyridine (1.1 cm^3, 0.014 mol) was dissolved in THF in a Schlenk tube and cooled to 0°C. To this stirred solution was added, under argon, 1,8-octanediol (1 g, 6.9 × 10^{-3} mol) in THF (30 cm^3) and the mixture stirred for 24 h. The white precipitate was filtered off and washed with more THF. The solvent was evaporated from the filtrate and combined washings, leaving the product as a white solid that was vacuum dried; yield 73%. $C_{20}H_{24}O_6P_2$: found C 55.2, H 6.3, P 14.2%; calcd. C 56.9, H 5.7, P 14.7%; calcd. for $C_{20}H_{24}O_6P_2.H_2O$: C 54.6, H 6.0, P 14.1%. M.s. (EI) *m/z*: 422 (2%) [$M^{\cdot +}$], 172 (22%), 156 (31%), 139 (78%), 83 (100%). N.m.r. ($CDCl_3$) ^{1}H, δ: 1.2 and 1.6 ($CC\mathbf{H}_2C$, 12H), 3.5 (*m*, $C\mathbf{H}_2OP$, 4H), 6.9 and 7.1 (*m*, $C_6\mathbf{H}_4$8H); $^{13}C\{^1H\}$, δ: 25.3, 29.3 and 30.4 ($\mathbf{C}H_2$), 64.1 ($\mathbf{C}H_2OP$), 111.2, 122.5, 145.9 ($\mathbf{C}_6H_4$); $^{31}P\{^1H\}$, δ: 128.2.

Reaction of 1,8-octanediol with diethylchlorophosphite. By a similar preparative method to that above, diethylchlorophosphite (1.98 cm^3, 0.0137 mol), pyridine (1.1 cm^3, 0.0137 mol) and 1,8-octanediol (1.0 g, 6.85 × 10^{-3} mol) in THF gave $(EtO)_2PO(CH_2)_8OP(OEt)_2$, 43%; n.m.r. ($CDCl_3$) ^{1}H, δ: 1.1 (*t*, $C\mathbf{H}_3CH_2O$, 12H); 1.2 and 1.6 ($CC\mathbf{H}_2$,C 12H); 3.8 (*m*, $C\mathbf{H}_2OP$, 12H); $^{31}P\{^1H\}$, δ: 140.0.

Reaction of hydroxy terminated hydrogenated polybutadiene with phosphorus(III) reagents

1,2-Phenylene phosphochloridite (0.19 cm^3, 1.6 × 10^{-3} mol) and pyridine (0.13 cm^3, 1.6 × 10^{-3} mol) were dissolved in THF (30 cm^3) in a Schlenk tube and cooled to 0°C. To this stirred solution was added under argon a mixture of hydroxy terminated polymer (e.g. 4 g, 1.6 × 10^{-3} mol, $\bar{M}_n = 2440$, semi-telechelic) in THF (30 cm^3) and the mixture stirred for 4 days. The fine white precipitate was removed by filtration and the filtrate was evaporated to dryness to give the polymer which was dried *in vacuo* and stored at −15°C under argon. (For high 1,4 polymers, toluene rather than THF was used as solvent.) Selected spectral data: n.m.r., ^{1}H, δ: 3.55 (*m*, $C\mathbf{H}_2O$), 6.9 and 7.1 (2*m*, $C_6\mathbf{H}_4$); $^{13}C\{^1H\}$, δ: 62.3 and 63.9 ($\mathbf{C}H_2OP$), 111.6, 122.5 and 145.9 ($\mathbf{C}_6H_4$); $^{31}P\{^1H\}$, δ: 128.2; i.r. (bulk) cm^{-1}: 1230 and 1010 (POC). {Reactions of hydroxy terminated hydrogenated polybutadiene with diethyl chlorophosphite employed the same method; impure product was obtained: $^{31}P\{^1H\}$ n.m.r. δ: 139.4 (+other resonances in range −12 to +32)}.

RESULTS AND DISCUSSION

Synthesis and structural characterization

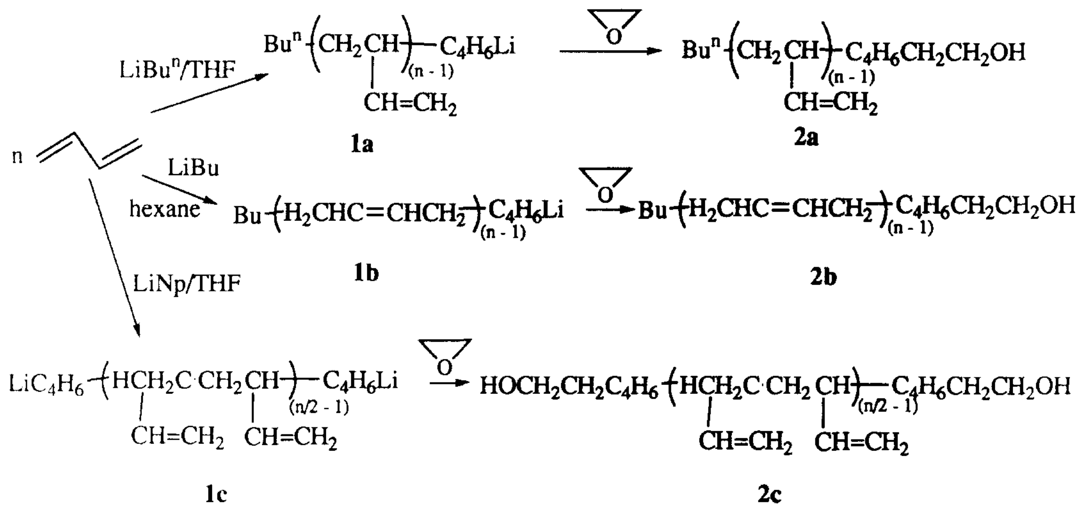
Hydroxy-terminated hydrogenated polybutadienes. Polymerization of 1,3-butadiene with *n*-butyllithium in tetrahydrofuran (THF) forms living poly(butadienyl)-lithium **1a** with a high proportion of 1,2-linkages and a degree of polymerization which can be controlled quite closely by use of the appropriate initiator : monomer concentrations, giving a product of low polydispersity[14]. Termination by reaction with ethylene oxide followed by protonation affords α-monofunctional (semi-telechelic) hydroxy-polybutadiene (**2a**, see *Scheme 1*). Some properties of representative products ($\bar{M}_n$ 600–3000) obtained by this procedure are given in *Table 1* (labelled **I**-α-OH to **V**-α-OH); properties of the corresponding, non-functionalized polybutadienes, formed by protonation of the living anions are also listed (**I**–**V**). The oligomers/polymers have been characterized by ^{1}H and $^{13}C\{^1H\}$ n.m.r. and i.r. spectroscopy (see Experimental); integrations of end-group n.m.r. signals, combined with $\bar{M}_n$ measurements, indicate 95–100% hydroxy-termination of the functionalized products. The 1,2-content of the semi-telechelic polybutadienes is 86–92% and values for $\bar{M}_w/\bar{M}_n$ lie around 1.1. It may be noted that these relatively low molecular weight products have slightly higher polydispersities than found for similarly produced polymers of higher molecular weight.

Anionic polymerization of 1,3-butadiene in hexane generates polymer with a high 1,4-content[14]. This can be achieved using *n*-, *s*- or *t*-butyllithium as initiator and termination of the living poly(butadienyl)lithium, **1b**, with ethylene oxide affords the corresponding α-hydroxy-terminated polymers, **2b**. Properties of typical examples of these products, **VI**-α-OH to **XI**-α-OH, and of corresponding non-functionalized polybutadienes, **VI–XI**, are given in *Table 1*. 1,4-Contents of 87% are achieved for polybutadienes with $\bar{M}_n$ values 1500–3000 but more 1,2-links are present in oligomers of lower $\bar{M}_n$ since 1,2-additions are favoured during initial propagation steps, even in hydrocarbon solvents[28,38]. Initiation is a slower process with *n*-butyllithium than with *s*- or *t*-butyllithium and this leads to greater polydispersity with the former reagent (see *Table 1*) so that the latter are more suitable as initiators of controlled polymerizations in non-polar solvents, giving products with $\bar{M}_w/\bar{M}_n \leq 1.1$. Termination of the living anion by ethylene oxide in hexane is also slow and most reactions in this work were accelerated by introducing an aliquot of THF to the system after addition of terminating agent, giving hydroxyethylated polymer with 85–100% terminal functionalization, as determined by n.m.r. integrals, combined with $\bar{M}_n$ measurements. If THF was added to the incompletely polymerized system before addition of ethylene oxide, a product with a higher proportion of 1,2-linkages was formed (e.g. sample **VIII**-α-OH).

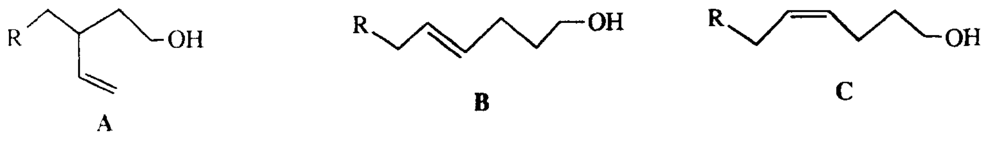
By using the 1 : 1 addition compound, naphthalene-lithium (NpLi) in THF as initiator, 1,3-butadiene is polymerized in a difunctional propagation mode[9,14,32] to form α,ω-dilithium living anions, **1c**, which yield telechelic α,ω-dihydroxy-polybutadiene, **2c**, after reaction with ethylene oxide. Properties of typical samples **XIV**-$\alpha\omega$-$(OH)_2$ to **XVIII**-$\alpha\omega$-$(OH)_2$ and of the corresponding non-functionalized polymers, **XIV–XVIII**, are given in *Table 1*. These low polymers ($\bar{M}_n = 1$–3×10^3) have predominantly 1,2-structures (83–88%) and $\bar{M}_w/\bar{M}_n$ values of 1.1–1.2, with the difunctional growth giving rise to slightly higher polydispersities than found for semi-telechelic products formed under similar conditions. Terminal hydroxyl group functionality, determined from n.m.r. integrals and $\bar{M}_n$ measurements, was 1.90–1.95.

The absence of any resonances in the region $\delta = 70$–73 ppm in the $^{13}C\{^1H\}$ n.m.r. spectra of all hydroxy-terminated polymers indicate that no ether linkages, CH_2OCH_2, have been formed and that only one ethylene oxide unit adds to a living end of poly(butadienyl)lithium species in a ring-opening reaction. This inability of the initially formed alkoxylithium centre to cause oligomerization of excess ethylene oxide has also been reported for reactions of poly(styryl)lithium with ethylene oxide[12]. However, the terminal CH_2OH groups of all hydroxyethylated polymers show two distinct ^{13}C resonances at *ca.* 61.1 and 62.4 ppm with relative intensities 1: (0.5–0.9), arising from differing modes of ethylene oxide addition to the terminal butadienyl group. C–C Bond formation at the allylic position (1,2 addition) generates a product of stereochemistry **A**, whereas terminal C–C bond (1,4 addition) produces either *trans*- or *cis*-isomers, **B** or **C** (see *Scheme 2*). To identify these addition modes, the model compound 5,5- dimethylhex-2-enyllithium[27,28] was reacted with ethylene oxide. The resulting alcohols were mainly **A**, **B** and **C** (R = Bu^t), accompanied by some higher butadiene oligomers, and g.c., g.c.m.s., i.r. and ^1H and $^{13}C\{^1H\}$ n.m.r. studies indicate that species $Bu^tC_4H_6CH_2CH_2OH$ comprise *ca.* 30% **A** (1,2-addition product) and *ca.* 70% **B/C** (1,4-addition products) with respective ^{13}C resonances of CH_2OH groupings at 61.0 and 62.4 ppm. Thus, it can be deduced that hydroxyethylation of poly(butadienyl)lithium in THF or hexane/THF forms functionalized polymer with **A** as the major terminal structure, with relative amounts **A** : (**B/C**) of 1 : (0.5–0.9).

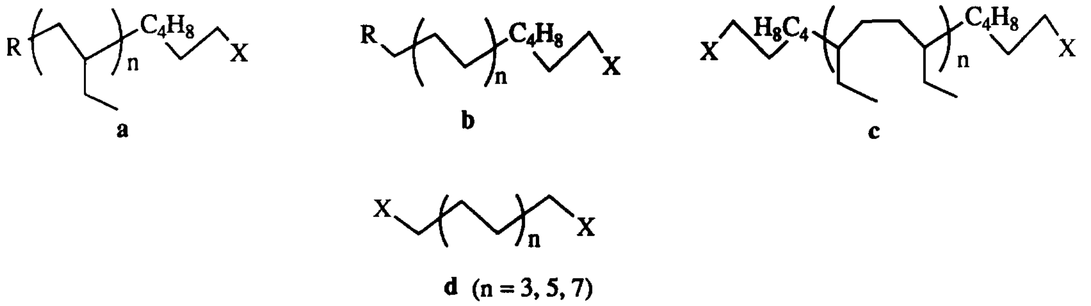
Hydrogenation of all types of hydroxy-terminated polybutadienes in cyclohexane was achieved using 5%Pd/C as a heterogeneous catalyst (cf. ref. 9) under 50–100 atm hydrogen gas at 70°C. N.m.r. and i.r. spectra indicated that complete hydrogenation of all unsaturated bonds had occurred and that hydroxyl groups were



Scheme 1



Scheme 2



3, X = OH; **4**, X = OTs; **5**, X = NH_2; **6**, X = NHPh;
7, X = $NHCH_2CH_2Me$; **8**, X = $NHCH_2CH_2CH_2NMe_2$; **9**, X = $OCH_2CH_2NH_2$;
10, X = $OCH_2CH_2NHCH_2CH_2NH_2$; **14**, X = OPO_2-1,2-C_6H_4; **15**, X = $OP(OEt)_2$

Scheme 3

retained. Hydrogenated samples are denoted by the prefix **H** in *Table 1*; hydrogenated high-1,4 polybutadienes are saturated polymers approaching polyethylene in structure, with **3b** representing the idealized hydroxy-terminated species; hydrogenated high-1,2 polybutadienes resemble poly-1-butene, with structures approaching **3a** and **3c** for semi-telechelic and telechelic hydroxy-polymers, respectively (see *Scheme 3*).

Amine-terminated hydrogenated polybutadienes. Hydrogenated hydroxy-terminated polybutadienes, prepared as described above, were transformed into amine functionalized polymers, **5–10**, by reactions of azide, amines or amino-alkoxides with intermediate tosylated derivatives, **4**. Semi-telechelic and telechelic tosyl polymers were prepared by reaction of tosyl chloride with the corresponding lithiated hydroxy polymers, a method similar to that reported for poly(oxyethylene) systems[21].

In order to establish the best conditions for these reactions and to provide spectral data of well defined model systems for use in characterization of functionalized polymers, the linear α,ω-alkanediols, $HO(CH_2)_nOH$ ($n = 8$, 12, 16) were converted to α,ω-ditosylalkanes, **4d**, and subsequently to representative α,ω-diamines, **5d–8d**. α,ω-Ditosyl species, $TsO(CH_2)_nOTs$ ($n = 8$, 12, 16; $Ts = O_2SC_6H_4CH_3$-4), were successfully prepared by several literature procedures[21,33] but pure product was easiest to isolate in a high yield from reaction of lithiated diol and tosyl chloride and this method was adapted for use on the hydrogenated hydroxypolybutadienes. Compounds $TsO(CH_2)_nOTs$ ($n = 8$, 12, 16) have been reported previously[33,34] and new spectroscopic data listed in the Experimental section include characteristic ^1H and ^{13}C n.m.r. resonances of CH_2OSO_2 and aromatic C_6H_4 groupings. Tosylation of hydrogenated hydroxy-terminated polybutadienes afforded terminally functionalized polymers, **4a–c** (idealized structures), generally in isolated yields >80%, and n.m.r. and i.r. spectral analyses indicated an essentially quantitative conversion of CH_2OH groupings to $CH_2OSO_2C_6H_4CH_3$-4. Properties of some α- and α,ω-tosylated polymers are given in *Table 2*: sample codes correspond to those of hydroxy-precursors listed in *Table 1*.

Heating model ditosyl compounds, **4d**, with 30–40% excess of neat aniline, *n*-propylamine or 3-(dimethylamino)propylamine (cf. refs 20, 39) affords the α,ω-diamino products **6–8d**. Reactions with aniline gave fully characterized derivatives $PhNH(CH_2)_nNHPh$ ($n = 8$, 12, 16) as the only isolated products; it may be noted that $PhNH(CH_2)_8NHPh$, prepared by a different route, has been reported previously but without characterization data[40]. 3-(Dimethylamino)propylamine with the diols also gave $Me_2N(CH_2)_3NH(CH_2)_nNH(CH_2)_3NMe_2$ as the only isolable product. In reactions with *n*-propylamine, a by-product was the coupled species, $Pr^nNH(CH_2)_nNPr^n(CH_2)_nNHPr^n$, which was not separated from the main product, $Pr^nNH(CH_2)_nNHPr^n$, but the n.m.r. resonances of the two species could be distinguished. The simple α,ω-diamino compound $H_2N(CH_2)_8NH_2$[36,37] was produced from $TsO(CH_2)_8OTs$ by initial reaction with sodium azide followed by reduction of the resulting 1,8-diazido-octane[29] with hydrogen gas over 5%Pd/C catalyst. ^1H and ^{13}C n.m.r. spectra of all amine containing products included distinctive resonances for the introduced funtionalities, including bands for structural units CH_2N, CH_3N and C_6H_5, if present (see Experimental).

The general procedures employed for conversion of model α,ω-ditosylalkanes into amines were adapted for the tosyl-terminated hydrogenated polybutadienes, however, it was desirable to eliminate the formation of coupled by-products found in the model reaction with *n*-propylamine. Such coupling was expected to be less likely with the high molecular weight reactants and, to suppress any tendency to chain extension, a high (*ca.* 100:1) stoichiometric excess of the reacting amine was used in these reactions. In this way amine-terminated polymers of types **6–8 a–c** were obtained. N.m.r. studies of the reprecipitated products indicated a quantitative conversion of tosyl to amino groups and an absence of coupled material; see *Table 2* for properties of such polymers. Primary amine-terminated hydrogenated polybutadienes of types **5a–c** (see *Table 2*) were formed via the corresponding azide as in the preparation of 1,8-diamino-octane except that a two phase system of dimethylformamide/toluene was employed in the conversion of tosyl- to azido-polymer and longer times (24–168 h) were necessary for complete reaction.

Using a method developed by Kennedy and coworkers for transformation of hydroxy-telechelic polyisobutylenes to amine[22], the tosylated hydrogenated polybutadienes were reacted with the potassium salt of ethanolamine $H_2NCH_2CH_2OK$ to introduce H_2NCH_2-CH_2O as a terminal group. N.m.r. spectroscopic investigations of the product indicated 100% displacement of the tosyl groups and new end-group resonances and integration of signals supported high conversion to the

Table 2 Properties of some terminally functionalized hydrogenated poly-1,3-butadienes

Terminally functionalized hydrogenated poly-1,3-butadiene	X = $OSO_2C_6H_4Me$-*p*		X = NH_2		X = $NHCH_2CH_2Me$		X = NHPh		X = $NHCH_2CH_2CH_2NMe_2$		X = $OCH_2CH_2NH_2$		X = $OCH_2CH_2NHCH_2CH_2NH_2$	
	T_g (°C)	η^a (Pa.s)	T_g (°C)	η^a (Pa.s)	T_g (°C)	η^a (Pa.s)	T_g (°C)	η^a (Pa.s)	T_g (°C)	η^a (Pa.s)	T_g (°C)	η^a (Pa.s)	T_g (°C)	η^a (Pa.s)
HI-α-X	−46	1.3	−44	2.4	−47	1.5	−45	1.7	−47	1.5	−45	1.9	−46	1.5
HIII-α-X	−49	2.6					−49	3.4	−55	3.1				
HIV-α-X									−39				−38	
HV-α-X	−37	13.5	−34	18.9	−36	14.2	−35	17.5	−36	14.7	−36	16.3	34	16.1
HVI-α-X	−61	0.30			−67	0.30	−60	0.33	−67	0.32				
HVIII-α-X	−68		−62	0.75			−60	1.4						
HX-α-X	(98)[b]										(55)[b]		(58)[b]	
HXCIV-α,ω-X_2	−44	6.55	−36	22.1	−44	7.1	−36	12.0	−44	7.2				
HXV-α,ω-X_2	−55										−40	9.7	−40	8.7
HXVI-α,ω-X_2	−50										−44		−45	
HXVII-α,ω-X_2	−32	28.8	−28		−33	29.4	−30	34.8	−33	30.0	−32	35.6	−32	35.0
HXVIII-α,ω-X_2									−32				−30	

[a] Melt viscosity at 40°C
[b] Melt temperature (T_m)

2-aminoethyloxy-polymers, of idealized types **9a–c**. A similar high conversion reaction of $H_2N(CH_2)_2$-$NH(CH_2)_2OK$ with tosylated hydrogenated polybutadienes, afforded polymers with 2-(2-aminoethylamino) ethyloxy groups attached as terminal groups (structural types **10a–c**; see *Table 2* for properties of typical examples).

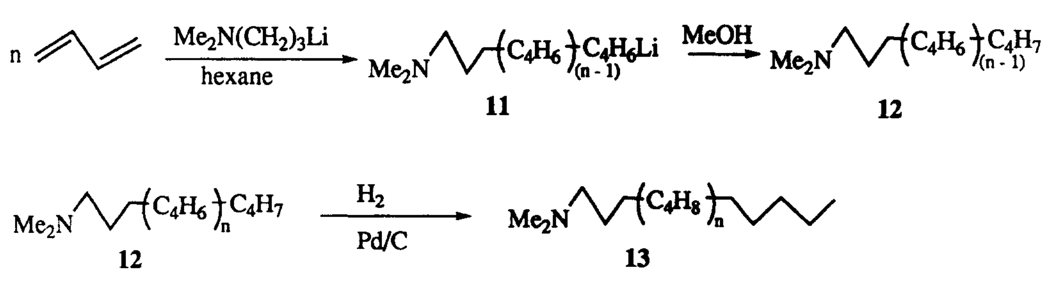
The fully alkylated dimethylamino group was introduced as a terminal function by polymerization of butadiene with 3-dimethylaminopropyllithium in hexane, as in previous work[23–26,41]. Termination of living α-dimethylamino polymers **11** with methanol afforded semi-telechelic products (**12**, e.g. **XII-** and **XIII**-α-NMe_2 in *Table 1*) with 50–70% 1,4 linkages (see *Scheme 4*). Subsequent hydrogenation, using the procedure adopted for hydroxy-terminated polybutadienes, gave saturated α-dimethylamino-terminated polymers (**13**, e.g. **HXII-** and **HXIII**-α-NMe_2 in *Table 1*) in 100% conversion. A related hydrogenation of an α-dimethylamino-polyisoprene, using $Pd/CaCO_3$ as catalyst, has been reported[42].

Formation of ionomers from amine-terminated hydrogenated polybutadienes. Methylation of polymers of types **5**, **7–10** and **13** by reaction of excess methyl bromide produced ionomers with alkylammonium terminal groupings, including MeH_2N^+, $MePr^nHN^+$ and Me_3N^+, identified by n.m.r. spectroscopy, i.e. secondary, tertiary and quaternary ammonium salts. In reactions of polymers of types **8** and **10**, containing terminal diamine functionalities, n.m.r. spectra indicated that both nitrogen centres were methylated, as occurs in simple diamines, $RR'N(CH_2)_nNRR'$ ($n = 2$–6)[43], although it is possible that the conversion of amine to ammonium groups was <100% in some cases since quantitative analysis of n.m.r. data was inconclusive. Methylation of phenylamino-terminated polymers **6** did not proceed with methyl bromide under various reaction conditions and ionization of these polymers to systems containing PhH_2N^+ terminal groups was achieved by reaction with HBr. Semi-telechelic and telechelic hydrogenated polybutadiene ionomers produced by these methods (see *Table 3* for examples) varied in form from viscous liquids to solids, with materials of high ethyl side-chain content and with quaternary ammonium centres being more solid. α,ω-Diquaternary ammonium polybutadienes[23,44] and polyisoprenes[44–46] and organic acid salts of an α,ω-dimethylamino-polybutadiene[47] have been previously reported and studied.

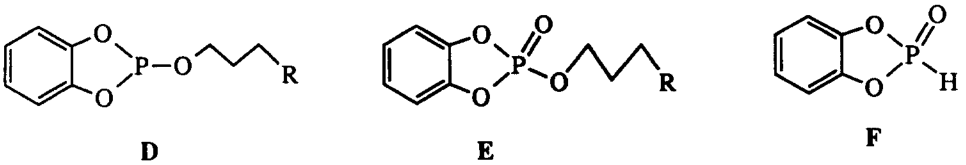
Hydrogenated polybutadienes with terminal diamine groups of types **8** and **10** (as semi-telechelic or telechelic polymers with high ethyl substituent content) were complexed with transition metal ions. The diamine functionalities are potential chelating ligands and in function **10** an additional O-donor site is also available. Metal chlorides, $CuCl_2.2H_2O$, $NiCl_2.6H_2O$ or $FeCl_3.6H_2O$, were mixed with the polymers in a metal ion : end-group stoichiometric of 1 : 2, i.e. four available N-donor sites per metal ion. The coloured metal-containing polymers produced were highly viscous semi-telechelic or solid telechelic systems in which metal ions interacted strongly with the end-groups, showing new i.r. bands in the region 1200–950 cm^{-1} as expected from chelating amine ligands[48], although the precise nature of the coordination modes was not determined. Similar complexes of this group of metal chlorides have been prepared with α,ω-dipiperazinopolybutadiene, in which the terminal amide-linked piperazine units may act as bidendate ligands[49–52].

Phosphite-terminated hydrogenated polybutadienes. Phosphorus(III) compounds are employed as polymer antioxidants and it was of interest to attach such derivatives chemically to the ends of saturated hydrocarbon polymers to introduce a relatively low concentration of fixed oxidizable sites. Also, hydrogenated polybutadienes with a high proportion of 1,4 backbone linkages are structurally related to polyethylene so that such phosphorus(III) functionalized systems of suitable chain length could act as effective antioxidants by blending with normal polyethylene.

Reactions of 1,2-phenylene phosphochloridite, C_6H_4-1,2-O_2PCl, with primary alcohols form structures of type **D** (see *Scheme 5*). By this method, the model α,ω-diols, $HO(CH_2)_nOH$ ($n = 8$, 12), were converted into the corresponding diphosphites, **14d**; the ^1H and ^{13}C n.m.r.spectra showed characteristic resonances for the C_6H_4 and CH_2OP groups and a distinctive $^{31}P\{^1H\}$ n.m.r. singlet resonance at 128.2 ppm. Using similar synthetic procedures, hydroxy-terminated hydrogenated polybutadienes were also transformed into phosphite-terminated derivatives of idealized structural types **14a–c**,



Scheme 4


D
E
F

Scheme 5

Table 3 Glass transition temperatures of some hydrogenated α or α,ω amino poly-1,3-butadienes and their related, ionized ammonium derivatives

Terminally functionalized hydrogenated poly-1,3-butadiene		X = NH_2 T_g (°C)	X = $NHCH_2CH_2Me$ T_g (°C)	X = NHPh T_g (°C)	X = $CH_2CH_2CH_2NMe_2$ T_g (°C)	X = $NHCH_2CH_2CH_2NMe_2$ T_g (°C)	X = $OCH_2CH_2NH_2$ T_g (°C)	X = $OCH_2CH_2NHCH_2CH_2NH_2$ T_g (°C)
HV-α-X	unreacted	−34	−36	−35		−36	−36	−34
	+ HBr			−32				
	+ MeBr	−32	−33			−33	−38	−29
HXII-α-X	unreacted				−66			
	+ MeBr				−60			
HXIII-α-X	unreacted				−64			
	+ MeBr				−58			
HXVIII-α,ω-X_2	unreacted	−28	−33	−30		−33	−32	−32
	+ HBr			−28				
	+ MeBr	−23	−27			−22	−32	−24

with n.m.r. spectra including bands analogous to those of low molecular weight models, e.g. a singlet $^{31}P\{^1H\}$ resonance at 128 ppm. All these phosphorus species are hygroscopic and sensitive to oxidative and hydrolytic attack: N.m.r. spectra of samples that had been exposed to air showed additional resonances assignable to P(V) oxides of type **E** ($^{31}P\{^1H\}$ $\delta = 8.2$ ppm), to compound **F** {$^{31}P\{^1H\}$ $\delta = 22.2$ ppm; ^1H including a doublet $\delta = 8.27$ ppm ($J_{P-H} = 760$ Hz, HP)} formed by hydrolysis and, in some cases, to other species including a $^{31}P\{^1H\}$ resonance at $\delta = -20.9$ ppm. Even spectroscopically pure samples of model compounds gave elemental analyses indicating the uptake of approximately one mole of water (or oxygen atom), which must have occurred during handling. In qualitative experiments, solutions in $CDCl_3$ of these phosphorus(III)-terminated derivatives were exposed to air over several days and monitored by ^{31}P n.m.r.; a decrease in the resonance at 128 ppm, at rates varying with the structure of the system, was accompanied by increasing intensities of resonances of decomposition products, in particular of oxides of type **E**.

Reactions of diethylchlorophosphite, $PCl(OEt)_2$, with 1,8-octanediol formed compound **15d** ($n = 3$) with a singlet $^{31}P\{^1H\}$ n.m.r. resonance at 140 ppm but this could not be obtained completely free of traces of other phosphorus by-products, or decomposition products, with minor $^{31}P\{^1H\}$ resonances at 8.2, −0.1 and −12.5 ppm. The amounts of these latter species increased on exposure to air. Attempts to prepare related diethylphosphite derivatives **15a–c** from hydroxy-terminated polybutadienes invariably led to impure products and the desired species, with a $^{31}P\{^1H\}$ resonance at 139.4 ppm, was accompanied by several oxidation/hydrolysis products with $^{31}P\{^1H\}$ resonances in the region −12 to +32 ppm.

Properties of terminally functionalized hydrogenated polybutadienes

Thermal properties. The data in *Table 1* illustrate the well established variation in glass transition temperatures for polybutadienes, with non-functionalized polymers **I–XVIII** having T_g values from −98°C for high-1,4 to −21°C for high-1,2 systems and, for polymers with the same backbone stereochemistry, T_g values show a small increase with increasing $\bar{M}_n$, in the range 600–3000. Introduction of terminal hydroxyethyl groups increases T_g values by 2–11°C relative to those of the parent polybutadiene. Smallest changes (*ca.* 2°C) occur for semi-telechelic hydroxy 1,2-polybutadienes, increases of *ca.* 6°C for telechelic hydroxy 1,2-polymers and largest increases for hydroxy semi-telechelic high-1,4 polymers. Thus, H-bonding interactions between terminal OH groups must cause some restriction of chain motion.

On hydrogenation of non-functionalized, high 1,2-polybutadienes the T_g values are lowered by 8–23°C, depending on other molecular parameters of polymer (see *Table 1*), and this may be attributed to the transformation of rigid vinyl substituents into more flexible ethyl groups. The addition of one or two terminal hydroxyl groups raises T_g values of the hydrogenated 1,2-polybutadienes by increments similar to those observed for the polybutadiene systems giving materials with glass transitions at lower temperatures than the corresponding hydroxy-terminated unsaturated polymers. Hydrogenated polybutadienes with >80% 1,4-linkages contain long segments of simple methylene units in the chain and give no glass transition observable by d.t.a., whereas these samples possess sufficient crystallinity to show clear T_m transitions around +100°C. Polybutadienes and α-hydroxy-polybutadienes with 50–70% 1,4-linkages undergo ≥ 10°C increases in T_g values on hydrogenation (*Table 1*).

Glass transition temperatures of tosyl-terminated hydrogenated polybutadienes do not vary significantly from those of the parent hydrocarbon polymers. Hydrogenated polybutadienes with the differing amine terminal groups employed in this study do show small variations in T_g values and the following trends may be noted (see *Table 2*). Each semi-telechelic or telechelic polymer shows highest T_g values for NH_2 and NHPh terminal groups which are generally similar or marginally higher than T_g values of the hydroxy-terminated species: this observation may be attributed to more effective H-bonding interactions between these end-groups, with the presence of a more rigid aromatic substituent probably also of significance for NHPh groups. Terminal groups $NHCH_2CH_2CH_3$ and $NHCH_2CH_2N(CH_3)_2$ give polymers with T_g values which are the lowest of the set of amine derivatives investigated, suggesting that the *n*-propyl and the 3-dimethylaminopropyl substituents have similar effects on the polymer flexibility. Terminal oxyalkylamine functionalities, $OCH_2CH_2NH_2$ and $OCH_2CH_2NHCH_2CH_2NH_2$, on hydrogenated polymers generally give materials with intermediate T_g values, probably the result of greater end-group flexibility opposing H-bonding interactions: however, attachment of these functionalities to hydrogenated, high 1,4-polybutadiene **HX** causes the melt temperature, T_m, to drop by >40°C (see *Tables 1* and *2*). It may also be noted that addition of a terminal phosphite group, **14**, to hydrogenated polybutadiene causes T_g to increase; e.g. **HVII** and **HVII**-α-X (X = **14**) have T_g values of −77 and −71°C, respectively.

Ionization of the terminal amine groups by reaction with methyl bromide, or of NHPh groups by neutralization with HBr, generally produces polymers with higher T_g values (see *Table 3*), as a result of aggregation of ions and formation of ionic crosslinks between chains. Semi-telechelic high-1,2 polymers, **HV**-α-X, show smaller increases in T_g (≤ 5°C) on ionization than telechelic high-1,2 polymers of similar molar mass, **HXVII**-α, ω-X_2 (≤ 9°C), consistent with the formation of ions at both termini in the latter. Methylation of the diamine functions $NH(CH_2)_3NMe_2$ and $O(CH_2)_2NH(CH_2)_2NH_2$ causes the greatest changes, as might be expected from the formation of two ammonium ion centres per end-group; methylation of NH_2 and $NHPr^n$ or protonation of NHPh groups causes smaller increases; rather unexpectedly, methylation of $OCH_2CH_2NH_2$ produces a zero or small negative change in T_g. Hydrogenated α-dimethylamino-polybutadienes (**13**), **HXII**- and **HXIII**-α-X, with 50–60% 1,4-linkages show increases in T_g of 6°C on methylation to quaternary ammonium terminated systems.

T_g values of metal complexes of semi-telechelic, **HIV**, or telechelic, **HXVIII**, hydrogenated polybutadienes terminated with diamino functions, $NH(CH_2)_3NMe_2$ (**8**) or $O(CH_2)_2NH(CH_2)_2NH_2$ (**10**), are listed in *Table 4*. In all but one case {the Cu(II) complex of **HXVIII**-α, ω-X_2 (X = 8)}, T_g values increase on complexation, as might be expected with the formation of more polar end groups. The metal : end-group ratio of 1 : 2 used in the

Table 4 Glass transition temperatures of α and α,ω amino poly-1,3-butadienes and complexes with transition metal ions

Terminally functionalized hydrogenated poly-1,3-butadiene		X = $NHCH_2CH_2CH_2NMe_2$		X = $OCH_2CH_2NHCH_2CH_2NH_2$	
		Colour	T_g (°C)	Colour	T_g (°C)
HIV-α-X	uncomplexed	Colourless	−39	Colourless	−38
	+ $CuCl_2$	Brown	−32	Green	−34
	+ $NiCl_2$	Purple	−31	Purple	−36
	+ $FeCl_3$	Orange	−36	Orange	−37
HXVIII-α,ω-X_2	uncomplexed	Colourless	−32	Colourless	−30
	+ $CuCl_2$	Brown	−43	Dark green	−28
	+ $NiCl_2$	Light green	−28	Light green	−29
	+ $FeCl_3$	Brown	−22	Brown	−29

synthesis of these materials would permit two chain ends to bind to each metal centre, if uniform coordination occurred, and this could produce significant chain extension in telechelic systems. It should be noted that (**8**), as a bidentate ligand, forms 6-membered rings whereas (**10**) forms more stable 5-membered rings and also could act as tridentate ligand if the ether O-atom and the two N-atoms all act as donors. Complexes of both Ni(II) and Fe(III) with N or O ligands are normally 6-coordinate whereas Cu(II) tends to form distorted octahedral complexes with only four strongly bound N-ligands, but other coordination geometries are known for all metals. Associated chloride ions may also occupy sites and, although these products were thoroughly dried *in vacuo* at 85°C, it is possible that water molecules introduced from the hydrated metal chlorides could, in some cases, be retained in a coordinated form and that bands assignable to NH vibrations in i.r. spectra could include components from OH vibrations. Such possible variations in coordination modes between the metals and ligand systems utilized here could account for irregular variations in the T_g values and other properties of the metallated polymers, especially the anomalous behaviour of the Cu(II) complex with **HXVIII**-α,ω-X_2 (X = **8**). Qualitative d.m.t.a. investigations of these metal-coordinated polymers, their parent amine-terminated polymers, and also of ionized amine-terminated polymers **HV**-α-X and **HXVII**-α,ω-X_2 of *Table 3*, showed one or, in the case of some telechelic metallated or ionic systems, two maxima in tan δ values in the temperature range −6 to +50°C: single maxima may be related to the glass transition but occur *ca.* 40–50°C higher than the T_g values determined by d.t.a.; again it was notable that the Cu(II) complex of **HXVIII**-α,ω-X_2 (X = **8**) was anomalous with a single maximum in tan δ at −14°C.

Investigations of amine-terminated hydrogenated polybutadienes by d.t.a. over the temperature range 0–200°C revealed a transition at >100°C in some telechelic ionized or metal complexed polymers but not in the parent telechelic amines. Thus, metal complexes of polymer **HXVIII**-α,ω-X_2 (X = **8**) displayed a weak endothermic transition on heating at *ca.* 160°C and complexes of polymer **HXVIII**-α,ω-X_2 (X = **10**) showed a more intense endothermic transition in the region 110–150°C. On re-running d.t.a. scans of these samples within 30 min, the transitions were no longer evident, but on re-testing after 2 weeks they had reappeared with essentially the original intensity. These transitions are likely to be associated with the aggregation of metal complexed chain termini and with the break-up of these clusters at higher temperatures. Slow reformation of clusters at ambient temperature may explain the delayed reappearance of these transitions. Interestingly, it has been reported that Cu(II) complexes of the unsaturated polymer, telechelic α,ω-piperazino-polybutadiene, show transitions which have also been assigned to ionic clustering of coordinated Cu^{2+} and which show a similar slow reversibility in d.s.c. experiments but, in contrast to our observations, these transitions were stated to be exothermic[51,52].

Viscosity. Melt viscosities of non-ionic polymers, determined at 40°C, are listed in *Tables 1* and *2*. Viscosities of the simple polybutadienes of similar microstructure show the expected increase with $\bar{M}_n$, and high 1,2-polymers show η values more than an order of magnitude larger than high 1,4-polymers. On termination with hydroxyl groups the viscosities increase and the increase is more marked for telechelic systems, especially for systems of lower $\bar{M}_n$, and this must be attributed to H-bonding interactions between chain ends. On hydrogenation, the viscosities of unfunctionalized, high 1,2-polybutadienes show little change, indicating that vinyl and ethyl substituents have similar effects on shear mobility, whereas hydrogenated high 1,4-materials are very viscous waxes or solids with a degree of crystallinity and melt viscosities cannot be determined at 40°C. From data on samples amenable to study at 40°C, it appears that the introduction of terminal hydroxyl groups to the hydrogenated samples has a similar but greater effect on the viscosity as on the unsaturated polybutadienes, and telechelic hydrogenated α,ω-dihydroxypolybutadienes have particularly high η values.

Tosyl-terminated hydrogenated polybutadienes have viscosities virtually unchanged from the corresponding proton-terminated polymers. Amine terminated, hydrogenated polybutadienes all show higher viscosities than the unfunctionalized polymers. In general, $NHPr^n$ and $NH(CH_2)_3NMe_2$ functions give polymers with lowest η values, slightly above those of the parent hydrocarbons, and the NH_2 function produces the most viscous systems with η values above those of the hydroxy-terminated polymers. The terminal NHPh group, except when attached to **HVIII**-α-X with 50% 1,4-links, forms slightly less viscous materials than NH_2 or OH; aminoalkoxy or diaminoalkoxy groups, (**9**) and (**10**), give materials of intermediate viscosity, generally with η values less than the corresponding hydroxy systems.

Measurements at 60°C indicate that viscosities of high-1,2 semi-telechelic and telechelic hydrogenated polybutadienes with diamine terminal groups, (**8**) and (**10**), decrease less with temperature than viscosities of corresponding hydroxy-terminated polymers. Viscosity indices, evaluated by interpolation[53], are similar for polymers terminated by either diamine function and values increase with molecular weights ($\bar{M}_n$ 800–3000) in the ranges 65–110 for semi-telechelic and 85–120 for telechelic systems. Viscosity indices of high-1,2 hydroxy-terminated hydrogenated polybutadienes are slightly lower, but these are generally greater than indices of parent unsaturated hydroxy-terminated polybutadienes. These temperature/viscosity characteristics of the diamine terminated polymers, when combined with good dispersancy properties, should make them suitable as potential engine oil additives.

CONCLUSIONS

α-Hydroxy (semi-telechelic) hydrogenated polybutadienes, with side-chain ethyl group contents varying from *ca.* 3 to 43 per 100 CH_2 backbone units, can be obtained by catalytic hydrogenation of anionically polymerized 1,3-butadiene terminated with ethylene oxide. α,ω-Dihydroxy (telechelic) hydrogenated polybutadienes with high ethyl group content can be synthesized similarly using difunctional anionic propagation. These hydroxy-terminated polymers are transformable in high conversions and yields, via isolable tosyl derivatives, into semi-telechelic or telechelic hydrogenated polybutadienes with primary amines, secondary alkyl or aryl amines, tertiary alkyl amines or diamines as terminal groups, with overall structures approaching **5–10 a–c**. Tertiary amine terminated polymers with intermediate ethyl group content, are also formed by using 3-dimethylaminopropyllithium as initiator.

Small increases are noted in glass transition temperatures of amine terminated hydrogenated polybutadienes in comparison with related non-functionalized polymers, with highest transitions occurring for polymers containing NH_2 and NHPh terminal groupings, although terminal OH groups give similar T_g values. Variations in bulk viscosities of amine and hydroxyl terminated polymers reflect differences in the T_g values, with the most viscous systems possessing NH_2 functions, and effectiveness of H-bonding between chain ends appears to be an important factor. More viscous ionomers are obtained by the formation of ammonium salts or by complexation of transition metal ions with chelating diamine-terminated polymers.

Hydroxy terminated hydrogenated polybutadienes can also be converted into phosphite terminated polymers which are susceptible to oxidation, especially in solution. In the bulk polymers these covalently bound phosphorus(III) centres may function as inherent antioxidant sites.

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