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Novel polymer systems with very bulky organosilicon side chain substituents

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Abstract

Synthetic methods leading to novel polysiloxanes and polystyrene copolymers are described. Both types of polymer could be modified by incorporation of the highly sterically demanding tris(trimethylsilyl)methyl substituent $(Me_3Si)_3C$. The modification increases the rigidity of polymers as shown by d.s.c. analyses. The effect is especially dramatic in the case of silyl substituted polysiloxane copolymer. In that case the steric bulk of the tris(trimethylsilyl)methyl group renders 8% of Si–H bonds in poly(methylhydrosiloxane) (PMHS) unreactive towards the hydrosilylation process. The Si–H bonds of the resultant copolymer can be utilised in crosslinking of the linear polysiloxane.

Keywords: Silyl modified polysiloxane and polystyrene; Tris(trimethylsilyl) methyl substituent; Steric hindrance

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1. Introduction

The tris(trimethylsilyl)methyl group, $\{(Me_3Si)_3C-\}$, denoted in this paper by trisyl or T_{Si}, has been shown over the years to affect the properties of a number of organometallic systems [1,2]. Its steric requirements appear to be greater than those of t-Bu, or 2,4,6-i-$Pr_3C_6H_2$ and close to those of 2,4,6-t-$Bu_3C_6H_2$ [3]. Extensive studies in this area led to the characterization of novel stable compounds and new reaction mechanisms, but there have been few studies towards material applications [4].

Attaching the tris(trimethylsilyl)methyl group to a macromolecular chain should lead to important modifications of polymer properties such as gas permeability and permselectivity parameters, mechanical, thermal and surface properties, as well as photochemical reactivity. In the literature there are already examples of some interest in this area, as a number of polymers, modified by silyl groups of various steric bulk, were synthesized and their properties (mainly as gas permeable materials) were studied. Among those were polycarbosilanes (polysilabutanes) with Me_3SiCH_2 substituents [5], substituted poly(acetylenes) such as poly(1-trimethylsilyl-1-propyne) (PTMSP) [6] or its alkylsilylated analogues [7], poly(norbornenes) with pendant Me_3Si and $Me_3SiCH_2Me_2Si$ groups [8], poly(1,6-heptadiyne) with two t-$BuMe_2SiOCH_2$ groups per monomeric unit[9], poly[(silylmethyl)phenylphosphazenes], bearing RMe_2SiCH_2 groups [R = Me, Pr, $(CH_2)_2CF_3$, $(CH_2)_2(CF_2)_8F$] [10], trimethylsilyl and triphenylsilyl modified poly(phenyleneoxides) [11], tris(trimethylsiloxy)silylpropyl malonate based polyesters [12] and also polystyrenes [13] with mono- and bis-(trimethylsilyl)methyl groups. The $(Me_3Si)_2CH$ group is one of the largest substituents used hitherto. In the present work we describe two different synthetic routes to modified polystyrenes {poly(styrene-*co*-[tris(trimethylsilyl)methyl]methylene styrene)} and polysiloxanes {poly(methylhydrosiloxane-*co*-methyl[tris(trimethylsilyl)butyl]siloxane)}. The substituents having three organosilyl groups bound to the central carbon are larger than those used previously and their steric requirements can be expected to affect the free volume of the macromolecules and modify properties of standard polymers to a much larger extent than has been observed so far.

2. Experimental

Syntheses of organolithium reagents and hydrosilylations

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were carried out under argon to exclude oxygen and moisture from the reaction systems.

2.1. Materials

Substrates for preparation of tris(trimethylsilyl)methyllithium ($T_{Si}Li$) and 4-[tris(trimethylsilyl)]but-1-ene, viz bromoform (Aldrich), Me_3SiCl (ABCR), *n*-BuLi (Aldrich, 2.5 M in hexanes), MeLi (Aldrich) were used as received. Allyl bromide (Aldrich) and benzyl chloride (Aldrich) were distilled before use. Platinum tetramethyldivinyldisiloxane (PTDD) 3% in xylenes (ABCR) was applied as the hydrosilylation catalyst.

The following standard polymers were used in modification reactions — copolymer containing 92% of styrene and 8% of chloromethylated (m/p mixture) units (Dow Chemicals), poly(methylhydrosiloxane) (PMHS) (Merck).

2.2. Instrumentation

Infra-red (i.r.) spectra were obtained using a Vector 22 Bruker spectrometer. Nuclear magnetic resonance (n.m.r.) spectra were obtained in solution (C_6D_6 or $CDCl_3$) using Bruker AM 200S and AC 200 spectrometers. Molecular weight of polymers was measured by size-exclusion chromatography (s.e.c.) in THF on Waters Mixed PL columns using a Waters apparatus with refractive index detection. The system was calibrated using monodisperse polystyrene standards. The d.s.c. scans were recorded on a Perkin Elmer DSC7 at 20°C min^{-1}. Mass spectra were obtained by the use of a Finnigan MAT95 spectrometer.

2.3. Synthesis of a model compound — tris(trimethylsilyl)(benzyl)methane

$T_{Si}Li$ was prepared in the usual way [14] from 0.78 g (3.4 mmol) of $T_{Si}H$ and 4.4 mmol of MeLi (2.7 ml, 1.6 M solution in Et_2O) in 16 ml of THF. After the lithiation of $T_{Si}H$ was complete (^1H n.m.r. analysis), the reaction mixture was transferred into a Schlenk flask, containing a solution of benzyl chloride (0.096 g, 0.76 mmol) in 25 ml of THF and the mixture was stirred for 24 h at room temperature. Then the THF was removed under vacuum, pentane (10 ml) was added and the suspension of LiCl was filtered off. The pentane was evaporated to leave 0.18 g of $(Me_3Si)_3CCH_2Ph$ (yield 73%).

M.p.: 45°C; n.m.r. [in C_6D_6 with tetramethylsilane (TMS) as a reference]: 0.12 (s, $SiMe_3$), 3.2 (s, CH_2), 7.1–7.3 (m, Ph) ppm; g.c.m.s. (*m*/*z*): 322 (M^+, 4%), 307 (M–Me, 41%), 248 (M–Me_3Si, 27%), 234 (M–Me_4Si, 100%), 161 (M–Me_3Si–Me_4Si, 82%), 135 (Me_2PhSi, 46%), 73 (Me_3Si, 95%).

2.4. Modification of poly(styrene-co-chloromethyl styrene)

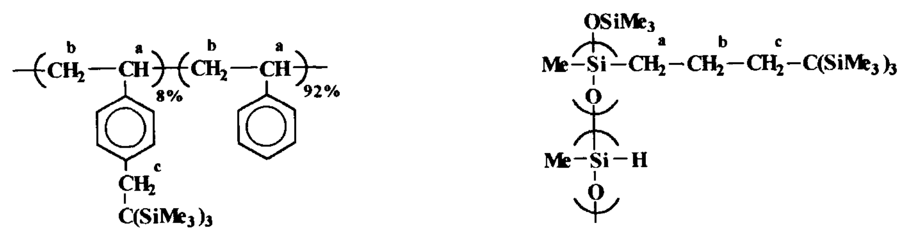
$T_{Si}Li$ (5.6 mmol), prepared as described above, was added dropwise to a solution in THF (30 ml) of 0.44 g of styrene copolymer (92% polystyrene–8% chloromethylated polystyrene, M_n = 187 000), with 0.33 mmol of chlorine-containing monomeric units. The stirred solution turned yellow after 5 min at room temperature and became pale brown after 30 min under reflux. The reaction mixture was stirred for a further 3 h at 70°C. ^1H n.m.r. analysis, run after that time, revealed no resonance characteristic of the CH_2Cl protons at 4.45 ppm. The resulting copolymer, containing T_{Si} substituents in the side chains, was precipitated with methanol and dried under vacuum (0.45 g, 89% yield, M_n = 200 000).

^1H n.m.r. (in $CDCl_3$ with TMS as a reference): 0.10 (s, Me_3Si), 1.42 (m, $CH_{2(a)}$), 1.59 (m, $CH_{2(b)}$), 1.84 (m, CH), 3.00 ($CH_{2(c)}$), 6.6–7.1 (m, Ph) ppm (see Fig. 1).

2.5. Synthesis of 4-[tris(trimethylsilyl)]but-1-ene

MeLi (0.08 mol) (50 ml of a 1.6 M solution in Et_2O) was transferred to a Schlenk flask, the Et_2O was removed in vacuum, and a solution of $T_{Si}H$ (17.4 g, 0.075 mol) in 80 ml of THF was added. The reaction mixture was heated under reflux for 2 h. Allyl bromide (14 g, 0.116 mol) was added dropwise at 0°C and the mixture was stirred at 0°C for 1 h. Then it was poured on to ice, extracted into Et_2O and the etheral solution was dried with anhydrous Na_2SO_4. The solid, after evaporation of Et_2O, was sublimed at 70°C per 0.1 mm Hg, to yield 14.4 g (71%) of $(Me_3Si)_3CCH_2CH{=}CH_2$.

^1H n.m.r.(in $CDCl_3$ with TMS as a reference): 0.14 (s, Me_3Si), 2.50 (m, $-CH_2-$), 5.00 (m, $=CH_2$), 6.04 (m, CH) ppm; ^{13}C n.m.r.: 2.67 (Me_3Si), 35.0 ($-CH_2-$), 115.7 ($=CH_2$), 140.2 (CH) ppm; ^{29}Si n.m.r.: 3.0 (Me_3Si) ppm;



A B

Fig. 1. Assignment of the respective n.m.r. shifts in modified polymers: (A) copolystyrene, (B) polysiloxane.

g.c./m.s. (m/z): 272 (M^+, 3%), 257 (M–Me, 1%), 169 (M–Me–Me_4Si, 100%), 73 (Me_3Si, 86%).

2.6. Hydrosilylation of PMHS

The reaction was carried out according to the standard procedure, described previously [15]. A solution of 0.204 g of PMHS (M_n = 1900, 3.2 mmol of SiH) and 0.964 g of $(Me_3Si)_3CCH_2CH{=}CH_2$ in toluene (5 ml) was stirred at 60°C with PTDD (2×10^{-4} mol Pt per mol of Si–H) for 17 h. The IR analysis showed that only a small fraction of Si–H bonds remained unreacted. Doubling the amount of the platinum catalyst and heating the reaction mixture for 20 h had no effect on the degree of conversion. The resulting polymer was precipitated with 500 ml of methanol, separated and dried in vacuum, to give 0.852 g of a white solid (M_n = 8700, yield 73%). ^1H and ^{29}Si n.m.r. analyses revealed unreacted methylhydrosiloxane monomeric units in the modified polysiloxane.

^1H n.m.r. (in $CDCl_3$ with TMS as a reference): 0.08 (s, $OSiMe_3$), 0.12 (s, $CSiMe_3$ + SiMe), 0.50 (m, $CH_{2(a)}$), 1.70 (m, $CH_{2(b+c)}$), 4.70 (m, SiH) ppm; ^{13}C n.m.r.: −0.25 (SiMe), 2.5 ($CSi\underline{Me}_3$ + $OSiMe_3$), 6.86 (C_q), 19.97 ($CH_{2(a)}$), 23.87 ($CH_{2(b)}$), 35.7 ($CH_{2(c)}$) ppm; ^{29}Si n.m.r.: −37.4 (MeHSiO), (−23.0, −21.8, −21.0) (OSiMe), 2.34 ($CSiMe_3$), 7.51 ($OSiMe_3$) (see Fig. 1).

3. Results and discussion

We have modified two well-known types of polymers by incorporation of very bulky $(Me_3Si)_3C$ groups (Fig. 2). Polymers based on polysiloxane chains, were long ago recognised as potentially useful for separation of fluids [16], but here, for the first time, we have succeeded in preparing polymers having side chains containing carbon atoms with three attached trimethylsilyl groups, that strongly affect the properties of the polymer. Bulky $(Me_3Si)_3C$ groups have also been attached to the poly(styrene-*co*-chloromethyl-styrene), which is easily available from commercial polystyrene.

The reactivity of many tris(trimethylsilyl)methyl derivatives is lower than that of compounds bearing less bulky substituents. For the purpose of modifying polymers a starting material must fulfil two basic requirements: it must be sufficiently reactive to effect substitution on a polymer chain and it must be isolable in a good yield by a simple procedure. Tris(trimethylsilyl)methyllithium, made in almost quantitative yield from the reaction between tris(trimethylsilyl)methane and methyllithium, was shown to be sufficiently reactive towards benzyl chloride to give tris(-trimethylsilyl)(benzyl) methane in > 70% yield (Fig. 2a) and towards partly (8%) chloromethylated styrene with replacement of all the chlorine to give a polystyrene

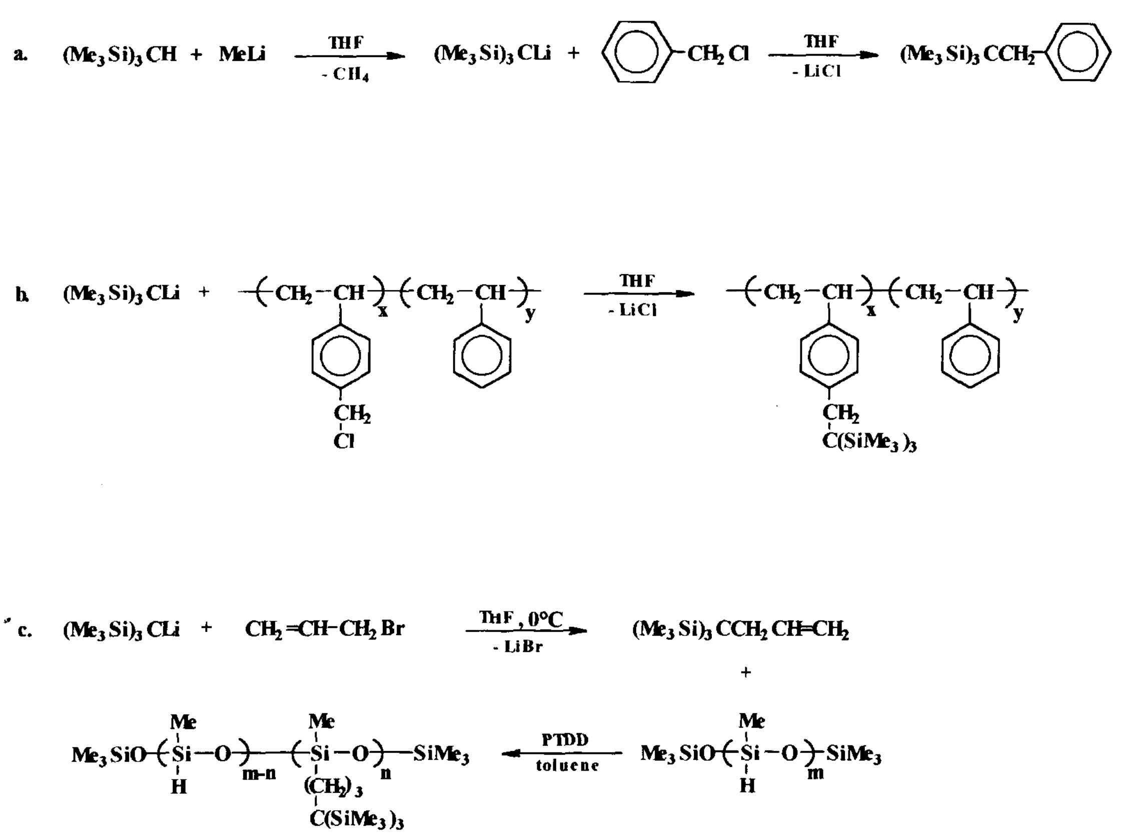


Fig. 2. Synthetic routes for substitution of trisyl groups at: (a) benzyl moiety-model structure, (b) poly(styrene-*co*-chloromethylstyrene), (c) polysiloxane.

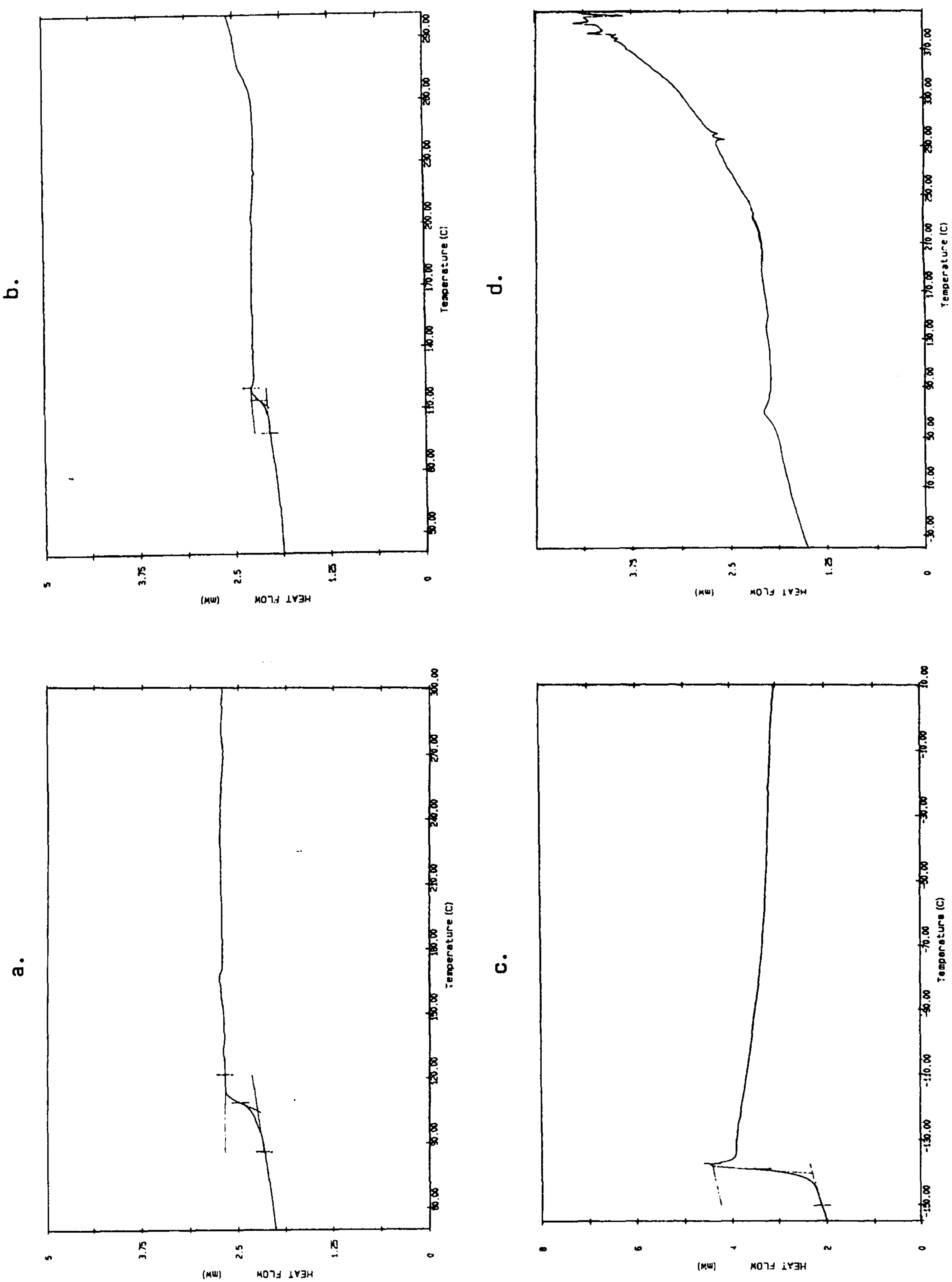


Fig. 3. The d.s.c runs of (a) poly(styrene-*co*-chloromethylstyrene), (b) trisyl modified poly(styrene-*co*-chloromethylstyrene), (c) polysiloxane, (d) trisyl modified polysiloxane.

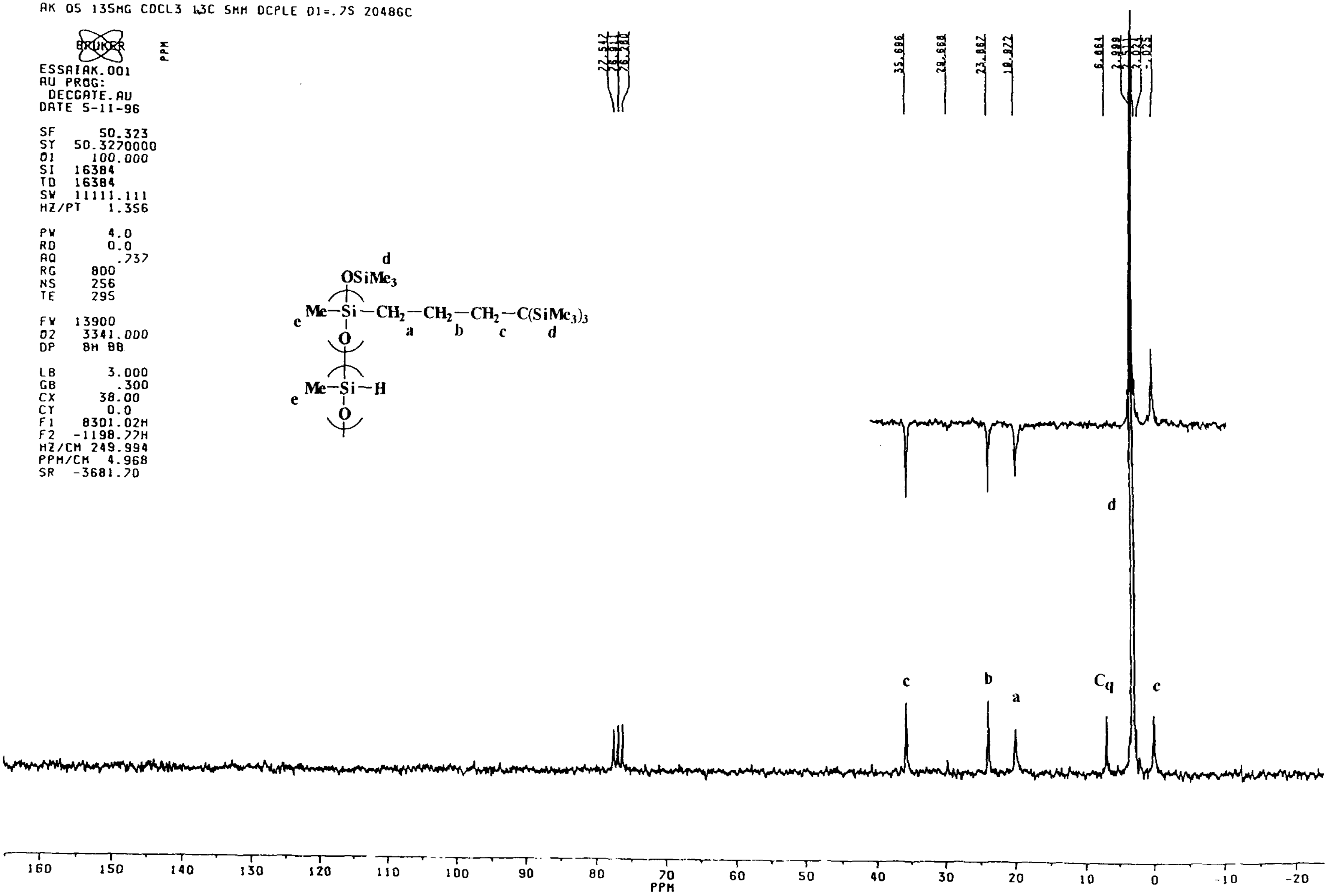


Fig. 4. ^{13}C n.m.r. spectrum of poly[(methyl)(tristrimethylsilylbutyl)-*co*-methyl-hydro]siloxane.

copolymer with tris(trimethylsilyl)methyl groups attached to phenyl rings via methylene spacers (Fig. 2b). The copolymer was isolated in better (89%) yield than the model compound, probably because of its low solubility in methanol.

Poly(methylhydrosiloxane), PMHS, bearing reactive Si–H bonds at each silicon atom, was modified by the use of a tris(trimethylsilyl)methyl-terminated alkene (prepared by coupling of $T_{Si}Li$ with allyl bromide) via hydrosilylation of the silylbutene with the polymer (Fig. 2*c*). The reaction, as shown by ^{1}H and ^{13}C n.m.r. analyses of the resulting silylated polymer, involves an anti-Markovnikov addition to a double bond of the alkene, the bulk of the tris(trimethylsilyl)methyl substituent certainly promoting such a course of the addition process. The size of the side-chain substituent also affects the degree of hydrosilylation. ^{1}H and ^{29}Si n.m.r. analyses point to some Si–H bonds left (resonances at 4.70 and −37.4 ppm, respectively) that remained unreacted even after prolonged heating with an additional amount of Karstedt catalyst, evidently being trapped among sterically demanding T_{Si} groups in the polymer. The i.r. spectra allow one to estimate that the silylated polymer contains up to 8% of the Si–H bonds that are stable under reaction conditions.

The d.s.c. scans (Fig. 3) show that the presence of bulky T_{Si} groups leads to an increase in the glass transition temperature (T_g) from 108°C for poly(styrene-*co*-chloromethylstyrene) to 114°C for the trisyl-substituted copolymer, even though the percentage of modified monomeric units is only 8%. The increase of the T_g is much more pronounced for the main chain polysiloxane polymer. The glass transition temperature changes from −139°C for the starting PMHS to 70°C for the T_{Si} modified one, reflecting the substantial increase in rigidity of the new polysiloxane bearing very bulky substituents in side chains.

^{13}C n.m.r. spectrum (Fig. 4) of the modified polysiloxane shows a distinct resonance of the quartenary carbon atom in the 'trisyl' group, that is absent (due to a long relaxation time) from the spectrum of a simple alkene $-(Me_3Si)_3CCH_2CH{=}CH_2$ used for the hydrosilylation reaction with the parent polysiloxane. The restriction of motion of polymer segments [17] is reflected in the value of the spin-lattice relaxation time of quarternary carbon (T_{1q}). It has been calculated from ^{13}C n.m.r. experiment as 4.9 s. Anchoring of the molecule on the polysiloxane main chain thus leads to significant reduction in its flexibility.

4. Conclusion

Two new copolymers incorporating highly sterically hindered tris(trimethylsilyl)methyl (trisyl) groups were made from poly(methylhydrosiloxane) and poly(styrene-*co*-chloromethylstyrene). Reaction of the latter copolymer with $(Me_3Si)_3CLi$ led to complete substitution of chlorine, to yield the novel modified copolystyrene with 8% monomeric units having trisyl substituents bound to aromatic rings via a methylene group. The spacer separating trisyl groups from the backbone in novel polysiloxanes consisted of three methylene groups. However, hydrosilylation of the trisyl-terminated alkene ($T_{Si}CH_2CH{=}CH_2$) with PMHS resulted in the incorporation of the trisyl groups into side chain, but about 8% of the –Si(Me)(H)O– groups did not react. The formation of a random copolymer rather than a homopolymer during the course of prolonged hydrosilylation is a very good indication that the size of the trisyl groups renders the few remaining Si–H bonds resistant to further addition across the unsaturation site of the bulky ligand spacer. The unreacted Si–H bonds can, however, be exploited for crosslinking, as shown by preliminary experiments involving u.v.-initiated free radical coupling. The incorporation of the tris(trimethylsilyl)methyl group into polymer structure, creates macromolecules of novel architecture with potential use as membranes for fluid separation.

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