Tailored copolymers via coupled anionic and ring opening metathesis polymerization. Synthesis and polymerization of bicyclo[2.2.1]hept-5-ene-2,3-*trans*-bis(polystyrylcarboxylate)s

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The preparation of polystyrene macromonomers containing a norbornene unit and their living ring opening metathesis polymerization (ROMP) to produce comb graft copolymers is described. The ROMP was initiated by the well defined Schrock initiators, Mo(=CHR)(=NAr)(OR$'$)$_2$, where R is (CH$_3$)$_3$C– or C$_6$H$_5$C(CH$_3$)$_2$–, Ar is 2,6-diisopropylphenyl and R$'$ is (CH$_3$)$_3$C–. Well characterized macromonomers and comb graft copolymers with polystyryl grafts with average degrees of polymerization (*DP*s) of 4, 7, and 9 were successfully produced. The graft copolymers exhibit single mode molecular weight distributions and narrow polydispersities. Attempts to prepare copolymers with longer polystyryl grafts gave products which exhibited bimodal molecular weight distributions in which one component of the distribution had the same retention time as that of the macromonomer, this observation is rationalized in terms of steric inhibition of the ROMP of such macromonomers.

(Keywords: polystyrene macromonomers; ROMP; comb graft copolymers)

INTRODUCTION

Living chain growth methods allow the synthesis of polymers with control over molecular weight, molecular weight distribution and, in favourable cases, chain microstructure[1]. In this paper we report the first stage of a programme of work in which we are exploring the potential of combining the capabilities of living anionic and ring opening metathesis methods to prepare polymers with well defined structures and unusual topologies. The work reported here involves the synthesis of macromonomers via the reaction of living polystyrene capped with propylene oxide with bicyclo[2.2.1]hept-5-ene-2,3-*trans*-dicarbonyl chloride to give bicyclo[2.2.1]hept-5-ene-2,3-*trans*-bis(polystyrylcarboxylate)s. These macromonomers have then been polymerized via living ring opening metathesis using the well defined initiators introduced by Schrock[2], namely Mo(=CHR)(=NAr)(OR$'$)$_2$, where R is (CH$_3$)$_3$C– or C$_6$H$_5$C(CH$_3$)$_2$–, Ar is 2,6-diisopropylphenyl and R$'$ is (CH$_3$)$_3$C–. The process is summarized in *Schemes 1* and *2*.

The macromonomer synthesis (*Scheme 1*) involves the capping of polystyryllithium (I) with propylene oxide to give the lithium alkoxide (II) which is then reacted with bicyclo[2.2.1]hept-5-ene-2,3-*trans*-dicarbonyl chloride to give the required macromonomer (III). *Scheme 2* summarizes the polymerization of III to give a living polynorbornene derivative carrying two polystyrene grafts on each cyclopentane ring in the polymer backbone (IV). The living polymer is terminated by addition of benzaldehyde to give V. Related work has been reported by Norton and McCarthy[3], who used the classical ring opening metathesis polymerization (ROMP) initiator WCl$_6$/Me$_4$Sn, for the copolymerization of a mixture of a bicyclo[2.2.1]hept-5-ene-2-polystyrylcarboxylate macromonomer, norbornene and oct-1-ene; the acyclic olefin being included as a chain transfer reagent to limit the product molecular weight and minimize the tendency to gelation often observed in polymerization of norbornene with such active initiator systems. The grafted polynorbornenes obtained in this earlier work carry one polystyryl graft on each grafted cyclopentane unit and the grafted rings are statistically distributed along the polynorbornene backbone; by contrast, in the current work every cyclopentane ring of the polynorbornene backbone carries two polystyryl grafts and as a consequence the extent of steric crowding both in the monomer and at the propagating chain end is considerably increased. Although this approach would be expected to yield novel comb graft copolymers with a high density of grafts, it seemed likely that such a high level of steric crowding might present practical problems in the assembly of the polymers. With such considerations in mind we have investigated, in the first instance, the

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possibilities and limitations of the overall process depicted in *Schemes 1* and *2*. This work has established that comb graft copolymers of structure V can be prepared for relatively low molecular weight materials with relatively short grafts. In the process of making such polymers all the steps in the synthesis and all the features of the structures depicted in *Schemes 1* and *2* have been unambiguously demonstrated, together with the limitation to success of the process as described.

EXPERIMENTAL

General

All manipulations of air and/or moisture sensitive materials were performed on a conventional vacuum/inert atmosphere (nitrogen) line using standard Schlenk and cannular techniques, or in an inert atmosphere (nitrogen) filled glove box. N.m.r. spectra were recorded using a Varian VXR400S (^1H at 399.95 MHz and ^{13}C at 100.58 MHz). Chemical shifts are reported in parts per million with respect to the internal reference tetramethylsilane (TMS). G.p.s. traces were recorded for solutions in chloroform using a Waters 590 HPLC pump, a Waters R401 RI detector and three PL gel columns with pore size of 10^2, 10^3 and 10^5 Å (flow rate $1\,cm^3\,min^{-1}$). Solutions (0.1–0.3% w/v) were filtered through a Whatman WTP type $0.2\,\mu m$ filter to remove particulates before injection. The columns were calibrated using polystyrene standards (Polymer Laboratories Ltd) ranging from 162 to $2.31 \times 10^6\,g\,mol^{-1}$. I.r. spectra were recorded on a Perkin–Elmer 1720-X series FTIR.

Reagents

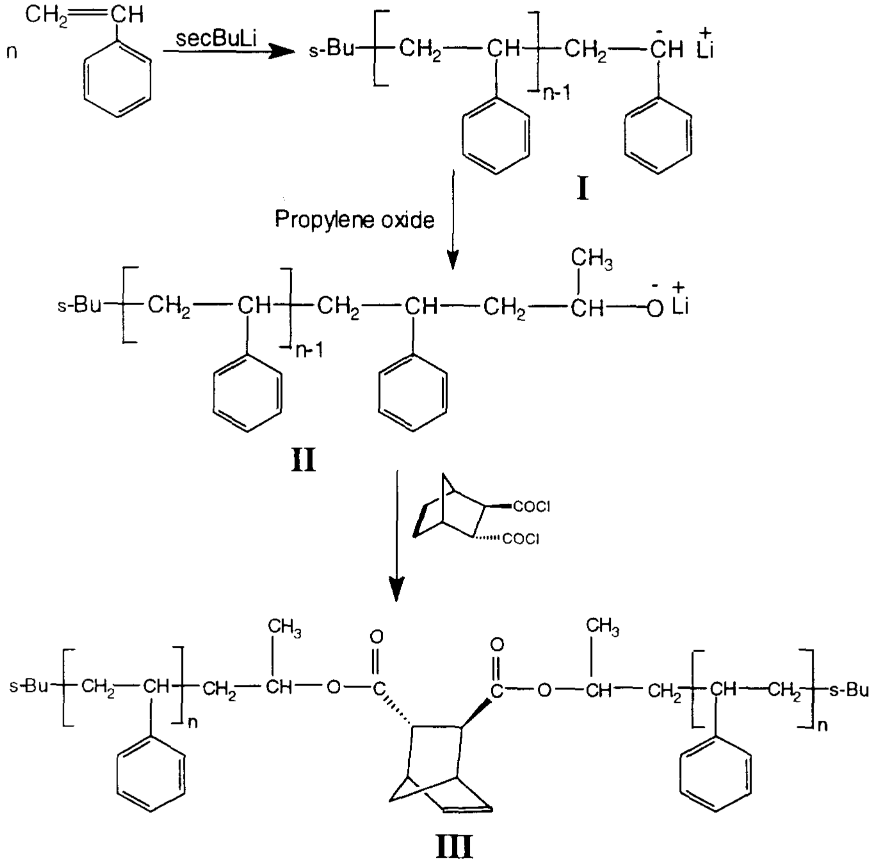
Deuterated solvents were stirred over the appropriate drying agent and vacuum distilled immediately prior to use. Polymerization solvents (drying agent in parentheses) were dried by prolonged reflux over the appropriate drying agent, freshly distilled and degassed before use: benzene (calcium hydride), benzene-d_6 (phosphorus pentoxide), toluene (sodium metal), tetrahydrofuran (THF; potassium benzophenone ketyl), cyclohexane (calcium hydride). Styrene was washed with 10% sodium hydroxide solution followed by distilled water and stored over calcium chloride overnight. It was distilled under reduced pressure from calcium hydride immediately prior to use. Bicyclo[2.2.1]hept-5-ene-2,3-*trans*-dicarbonyl chloride (Aldrich Chemical Co. Ltd) was used without further purification. Propylene oxide (Aldrich Chemical Co. Ltd) was stirred over calcium hydride overnight and distilled under reduced pressure prior to use.

Initiators

Sec-butyllithium (Aldrich) was used as supplied. The ROMP initiators, $Mo(=N\text{-}2,6\text{-}i\text{-}Pr_2\text{-}C_6H_3)(=CHR)(OR')_2$ (where $R = CMe_2Ph$ and $R' = Me_3C$), were prepared following the published methods[2].

Synthesis of macromonomers

The synthesis is outlined in *Scheme 1*. Styrene was anionically polymerized at room temperature in cyclohexane or benzene using sec-butyllithium as initiator. A sample of the living polymer (I) was withdrawn, terminated by addition of methanol and the resulting polystyrene was analysed by g.p.c. The concentration of active ends



Scheme 1 Macromonomer synthesis

in the polystyryllithium solution was calculated from the number average molecular weight (M_n) obtained. An equimolar proportion of propylene oxide was transferred from a graduated vessel directly attached to the reaction flask into the living polystyryllithium solution. This reaction was carried out in order to cap the strongly basic polystyryl anion[4–6]. The resulting lithium 2-polystyrylisopropyl alkoxide (II) is less reactive than polystyryllithium and this procedure eliminates the possibility of side reactions resulting from polystyryl anion attack on the carbonyl functions present in the product of the initial reaction with bicyclo[2.2.1]hept-5-ene-2,3-*trans*-dicarbonyl chloride. The propylene oxide capping reaction was complete within 5 min and was monitored by the disappearance of the red colour associated with the propagating polystyryl chain ends. Since the rate of reaction of lithium alkoxide with propylene oxide is much slower than that of polystyryllithium, this procedure is expected to give II in which the product results almost exclusively from the addition of only one propylene oxide unit. Neat bicyclo[2.2.1]hept-5-ene-2,3-*trans*-dicarbonyl chloride was added to the solution of II using an air-tight syringe and the resulting mixture was stirred at room temperature for 30 min. The product (III) was precipitated by addition to excess methanol, recovered by filtration and purified by three cycles of dissolution in THF followed by reprecipitation in methanol. The product was finally dried in a vacuum oven at 40°C for 3 days.

ROMP of the macromonomers

Polymerizations were studied by n.m.r. prior to attempting syntheses on a larger scale. In a typical n.m.r. scale polymerization the monomer (10 equivalents) in benzene-d_6 (400 μl) was added to a stirred solution of initiator (0.010 g) in the same solvent (400 μl). In a typical preparative scale polymerization macromonomer (0.5–1.5 g) in a solvent (10 ml) was added dropwise to a stirred solution of initiator (0.010–0.020 g) in the same solvent (10 ml). The reactions were terminated by addition of benzaldehyde (a 10-fold excess). The volume of the mixture was reduced by ~70% by vacuum transfer of solvent and the resulting solution was added dropwise to 10-fold excess of methanol (non-solvent) with vigorous stirring. The polymer precipitated as a white powder which was recovered by filtration, washed several times with methanol and dried in a vacuum oven at 40°C. The polymeric samples were purified by reprecipitation from THF into methanol and finally dried under vacuum at 40°C for 3 days.

RESULTS AND DISCUSSION

Characterization of the macromonomers

Figure 1 shows typical g.p.c. traces recorded for samples of the living polystyryllithium (I) quenched with methanol or capped with propylene oxide and reacted with bicyclo[2.2.1]hept-5-ene-2,3-*trans*-dicarbonyl chloride, i.e. III from experiment 4 of *Table 1* (see below).

Within the limits of experimental error the value of M_n for the macromonomer is consistent with expectation, that is twice the mass of the initial living polystyryllithium plus the mass of the capping and coupling units. The degrees of polymerization (*DP*s) calculated for the polystyrene blocks are, respectively, 9.5 from the quenched polystyryllithium M_n and 9.0 from the macromonomer M_n. *Figure 2* compares the i.r. spectra of the macromonomer and the quenched polystyrene homopolymer samples produced in the same experiment. As expected, the macromonomer exhibits absorptions due to an ester C=O stretching mode at 1729 cm^{-1} and an ester C–O stretch at 1181 cm^{-1}. The ^{1}H n.m.r. spectrum of the macromonomer shows resonances due to polystyrene and the substituted norbornene residue, integration of either the aromatic or methine protons of the polystyrene

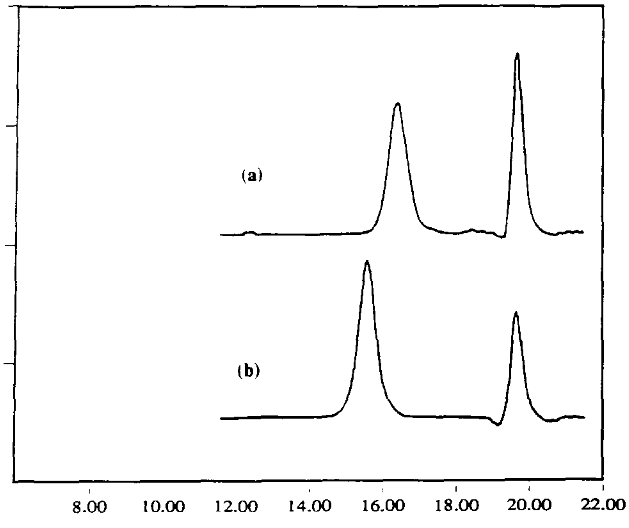


Figure 1 G.p.c. traces for (a) living polystyryllithium quenched in methanol (M_n = 1050, M_w/M_n = 1.06) and (b) the same sample capped with propylene oxide and reacted with bicyclo[2.2.1]hept-5-ene-2,3-*trans*-dicarbonyl chloride (M_n = 2260, M_w/M_n = 1.09); experiment 4, *Table 1*

Table 1 G.p.c. data for macromonomer III

	Homopolymer I		Macromonomer III			Average *DP* polystyrene block	
Experiment	M_n	PDI[a]	M_n theory[b]	M_n found	PDI	From quenched sample M_n	From macromonomer M_n
1	490	1.15	1240	1200	1.06	4	4
2	810	1.11	1880	1670	1.12	7	6
3	790	1.10	1840	1700	1.10	7	6.5
4	1050	1.06	2360	2260	1.09	9.5	9
5	1020	1.07	2300	2130	1.07	9	8.5

[a] PDI, polydispersity index
[b] Calculated from M_n of I, see text

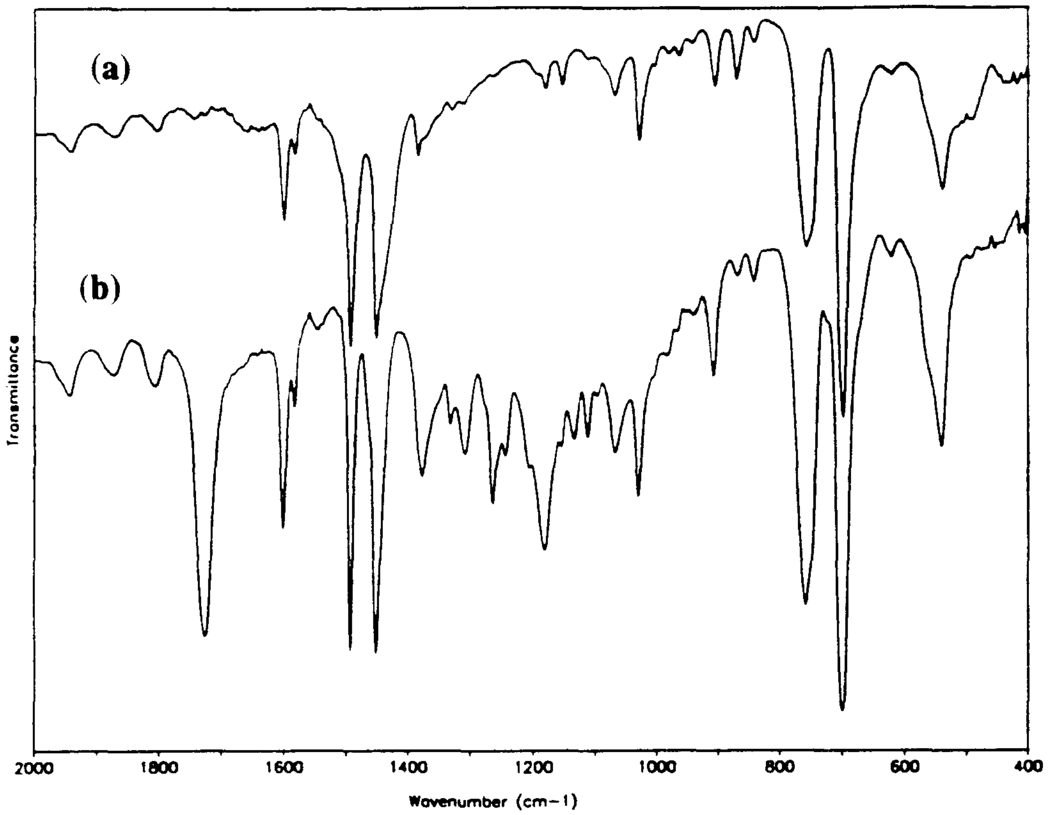


Figure 2 I.r. spectra of (a) quenched polystyrene homopolymer I and (b) macromonomer III. Samples discussed in the text; experiment 4, *Table 1*

blocks and the olefinic protons of norbornene residues yields a value for the molar ratio of styrene:norbornene of 15:1, which is consistent within experimental error with the 18:1 ratio obtained from the g.p.c. analysis (see below). A series of macromonomers with different polystyrene block lengths were prepared and characterized. Illustrative results are collected in *Table 1*, which also indicates the reproducibility of the procedures.

ROMP of the macromonomers

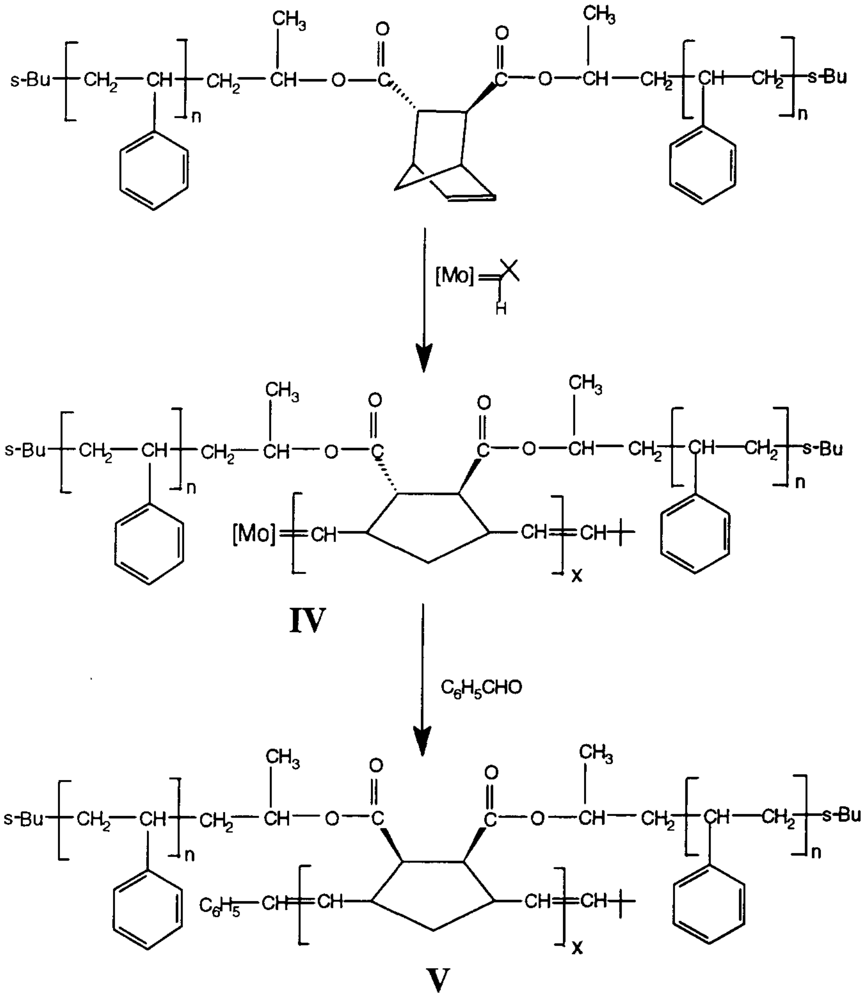
The well defined macromonomers were subjected to ROMP using the Schrock molybdenum initiator and the products were capped with benzaldehyde (*Scheme 2*). The ROMP reaction was first investigated on an n.m.r. tube scale, and then scaled up to obtain sufficient polymeric material for characterization.

The n.m.r. scale experiments were carried out in benzene-d_6. Typical ^{1}H n.m.r. spectra of a polymerization mixture show a broad unresolved signal at 11.38 ppm characteristic of the propagating alkylidene[7] and broad resonances due to both polystyrene and polynorbornene. The broad unresolved nature of the n.m.r. signals is consistent with either or both low molecular mobility and a multiplicity of slightly differing environments for the nuclei representative of nominally similar structural features in an atactic or low tacticity material. After quenching the living alkylidene by addition of benzaldehyde, g.p.c. analysis revealed that the product had a narrow polydispersity ($M_w/M_n = 1.16$) but otherwise yielded no useful quantitative information since the numerical values for molecular weight are computed with reference to calibration with linear polystyrene standards and the hydrodynamic volume to molecular weight relationship for this comb graft copolymer structure is, as yet, unknown. The composition of the sample was determined by integration of the aromatic and olefinic ^{1}H resonances in the ^{1}H n.m.r. spectrum yielding a styrene:norbornene molar ratio of 15:1, which is in good agreement with the value obtained for the macromonomer prior to ROMP as required. *Tables 2* and *3* summarize the g.p.c. and ^{1}H n.m.r. based analyses of the process of synthesis and ROMP of macromonomers (III) from experiments 5 and 1 in *Table 1*. The data are internally self-consistent for these macromonomers and comb graft copolymers with polystyrene blocks of *DP* 4 and 9, respectively, and underline that for systems of this size the process is entirely regular and well behaved.

The carbonyl chloride substituents in the capping reagent are *trans* with respect to each other (i.e. *endo*, *exo*) and the polystyrene blocks in the comb copolymer have the same configuration. The polymer microstructure is represented diagrammatically in *Figure 3*. The possibility of *cis* or *trans* vinylene units, *meso* or *racemic* dyads and *syn* or *anti* dispositions of adjacent grafts on adjacent rings means considerable microstructural variety is possible and the spectroscopic data available, while being entirely consistent with the broad features described above, are not sufficiently well resolved to be interpreted in terms of microstructural detail as is often possible for polymers produced by ROMP[8].

Large scale polymerization

Macromonomers with a range of molecular weights have been subjected to ROMP. The polymerization reactions were carried out in benzene or a toluene/THF mixture (80/20, v/v) as solvent. Comb graft copolymers (V) with polystyrene block *DP*s of 4, 7 and 9 were successfully prepared. The comb copolymers exhibit narrow mode molecular weight distributions (*Table 4* and *Figure 4*).



Scheme 2 Graft comb copolymer synthesis

Table 2 Summary of g.p.c. and ^{1}H n.m.r. analysis of ROMP of the macromonomers (III) described in *Table 1*, experiment 1

	G.p.c. analysis			^{1}H n.m.r. analysis	
System	M_n	PDI	Ratio ST:NBE[a]	Resonances observed	Ratio ST:NBE
Polystyrene homopolymer (I)	1020	1.10	–	–	–
Macromonomer (III)	2130	1.07	18:1	Polystyrene Norbornene	15:1
Comb graft copolymer (V)	13000	1.16	–	Propagating alkylidene Polystyrene Polynorbornene	15:1

[a] ST:NBE, styrene:norbornene

Table 3 Summary of g.p.c. and ^{1}H n.m.r. analysis of ROMP of the macromonomers (III) described in *Table 1*, experiment 5

	G.p.c. analysis			^{1}H n.m.r. analysis	
System	M_n	PDI	Ratio ST:NBE[a]	Resonances observed	Ratio ST:NBE
Polystyrene homopolymer (I)	490	1.15	–	–	–
Macromonomer (III)	1200	1.07	12:1	Polystyrene Norbornene	14:1
Comb graft copolymer (V)	13000	1.16	–	Propagating alkylidene Polystyrene Polynorbornene	13:1

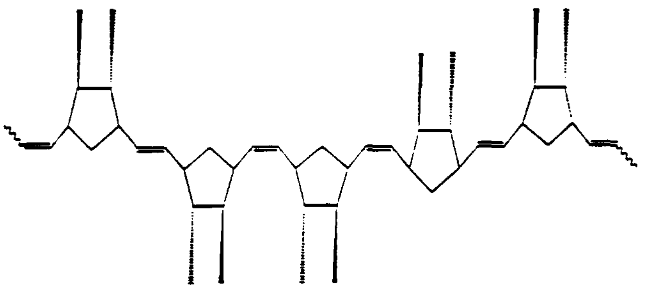


Figure 3 Schematic diagram of a section of the chain of the comb graft copolymers prepared in this work, illustrating the multiplicity of microstructural possibilities

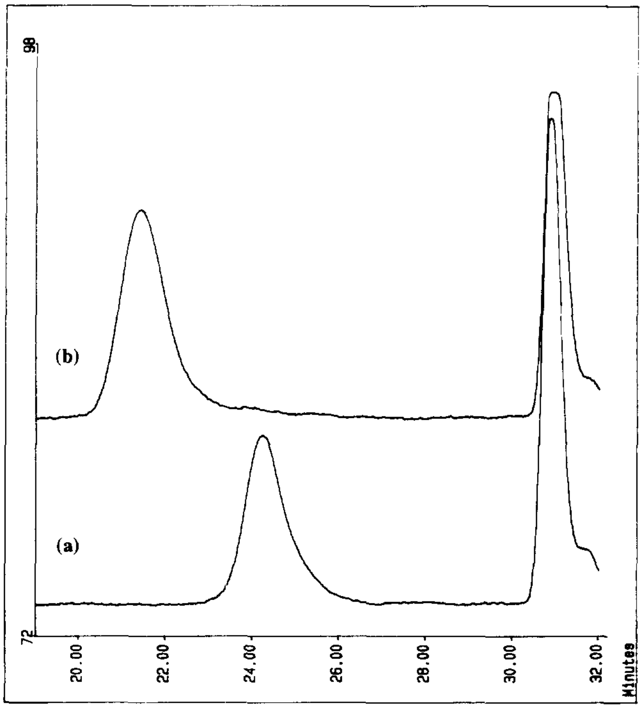


Figure 4 Illustrative g.p.c. traces for (a) a macromonomer and (b) the comb graft copolymer derived from it. Samples refer to experiment 4, *Table 4*

When attempts were made to ROMP macromonomers with polystyrene block *DP*s of 14, 24 and 46 in the same way, two peaks were invariably observed in the g.p.c. traces. The lower molecular weight peaks all had the same retention time as the macromonomers and were accompanied by a higher molecular weight peak due to product. Illustrative examples are shown in *Figure 5*. It appears that as the length of the polystyrene block in the macromonomer is increased the metathesis reaction becomes sterically inhibited and eventually stops. Qualitatively, the intensity of the residual macromonomer peak is dependent on its molecular weight, the higher the molecular weight the bigger it is relative to the polymer peak at the time polymerization stops (*Figure 5*). It appears that the cessation of polymerization is dependent primarily on macromonomer molecular weight rather than reaction duration since, even for the macromonomer with polystyrene blocks of $DP = 14$, the macromonomer remains even after reactions of up to 3 weeks' duration in which the living chain ends were still detectable by ^{1}H n.m.r. spectroscopy.

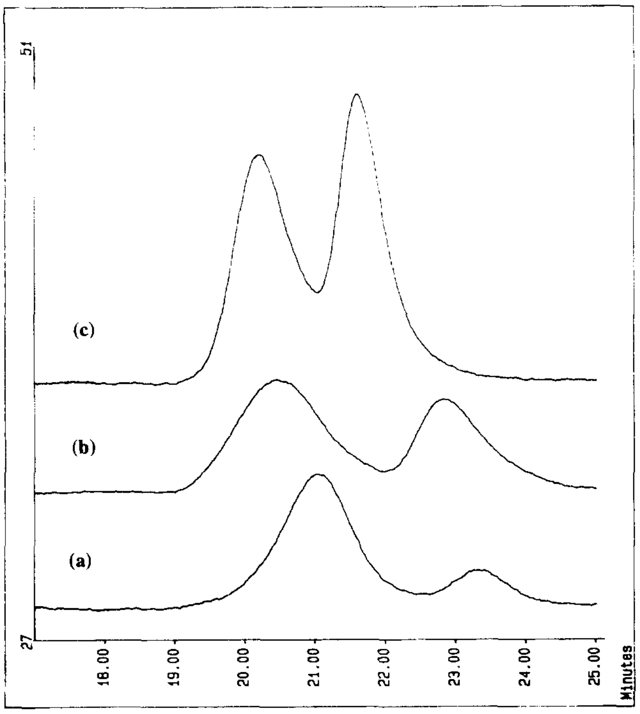


Figure 5 Illustrative g.p.c. traces for ROMP of macromonomers with polystyrene block *DPs* of (a) 14, (b) 24 and (c) 46

CONCLUSIONS

The results of the work presented here demonstrate that well defined comb graft copolymers can be made by a

Table 4 Polystyrene equivalent molecular weights for macromonomers (III) and the comb graft copolymers (V) derived from them

	Macromonomer III				Comb graft copolymer V	
Experiment	M_n	PDI	Polystyrene block *DP*	Ratio 'Mo':monomer	M_n	PDI
1	1200	1.06	4	1:10	6870	1.14
2	1200	1.06	4	1:27	17520	1.09
3	1670	1.12	7	1:15	13900	1.14
4	1700	1.10	7	1:13	11400	1.13
5	2260	1.09	9	1:16	16150	1.13
6	2130	1.07	9	1:7	12960	1.16

combination of (i) macromonomer synthesis using living anionic polymerization techniques and (ii) their subsequent polymerization by living ROMP. Comb graft copolymers with a polynorbornene backbone and polystyrene grafts with *DP*s of 4, 7 and 9 were successfully prepared and characterized. ROMP of macromonomers with longer polystyrene grafts was only partially successful and polymerization stopped before complete consumption of macromonomer, probably due to steric hindrance, the longer the graft length the less effective the macromonomer polymerization. Our investigations into the combining of living ROMP and living anionic polymerization methodologies as a route to polymeric materials with novel architectures are continuing.

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