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Synthesis of well-defined graft copolymers via coupled living anionic polymerization and living ROMP

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Well-characterized polystyrene macromonomers containing a norbornene unit at the chain end were prepared by capping living polystyrene with *exo*-5-norbornene-2-carbonyl chloride. The macromonomers were then ring opened polymerized using well-defined Schrock molybdenum initiators, Mo(N-2,6-i-$Pr_2C_6H_3$)($OCMe_3$)$_2$(CHR) where R is CMe_3 or CMe_2Ph, to produce well-defined graft copolymers. Well-characterized graft copolymers with polystyryl grafts of average degrees of polymerization 15, 22, 35, 50, 100 and 130 were successfully prepared. Ring opening metathesis polymerization (ROMP) of macromonomers with a molecular weight of 1550 ($\overline{DP} = 13$) goes to completion at a macromonomer:initiator molar ratio of 200:1. Ring opening metathesis polymerization of macromonomers with molecular weights of 3500 and 4900 ($\overline{DP}$s of 32 and 46, respectively) also goes to completion even at comparatively high macromonomer:initiator molar ratios of 100:1. This produces relatively long polynorbornene backbone chains with relatively short polystyrene grafts. On the other hand, macromonomers with number average molecular weights of 10 200 and 13 200 ($\overline{DP}$s of 96 and 127) are completely polymerized only up to macromonomer:initiator molar ratios of 20 and 10:1, respectively. Beyond this stage polymerization stops without destruction of the living chain ends before complete consumption of macromonomers, giving short polynorbornene backbone chains with relatively long polystyrene grafts.

(Keywords: synthesis; graft copolymers; anionic polymerization)

INTRODUCTION

There is considerable interest in developing synthetic methodologies capable of giving structurally well-defined macromolecules with unusual topologies. This paper reports extensions of our earlier work on the synthesis of well-defined comb–graft copolymers in which the lengths of the grafts and the backbone chains are controlled through the use of living polymerization methods.

Previously, we reported the synthesis of well-characterized 5-norbornene-2,3-*trans*-bis(polystyrylcarboxylate) macromonomers and their ring opening metathesis polymerization (ROMP), using well-defined Schrock molybdenum initiators, Mo(N-2,6-i-$Pr_2C_6H_3$)($OCMe_3$)$_2$(CHR), where R is CMe_3 or CMe_2Ph, to produce well-defined graft copolymers[1,2]. The graft copolymers produced consisted of a polynorbornene backbone carrying two polystyrene grafts on each cyclopentane ring. Well-characterized macromonomers and comb graft copolymers with polystyryl grafts with average degrees of polymerization ($\overline{DP}$s) of 4, 7 and 9 were successfully produced[1]. The graft copolymers exhibited single mode molecular weight distributions and narrow polydispersities, typically in the range 1.09–1.16. Ring opening metathesis polymerization of macromonomers of different molecular weights, i.e. different polystyrene graft lengths, revealed a limit to the length of the polynorbornene backbone attainable in the graft copolymer which was related to the length of polystyrene graft in the macromonomer[2]. The results indicated that the living ROMP of macromonomers with different polystyrene graft lengths go to complete consumption of macromonomer only up to a certain molar ratio of macromonomer to initiator, in these cases the graft copolymers obtained exhibited single mode molecular weight distributions. However, when the molar ratio of macromonomer to initiator is greater than a threshold value, two peaks appear in the gel permeation chromatography (g.p.c.). The lower molecular weight peaks are narrow and, in each case, have the same retention volume as the starting macromonomers; the higher molecular weight peaks also have narrow molecular weight distribution and are due to the product graft copolymer. These results suggested that the graft copolymer backbone chain grows up to a certain length, beyond which the ROMP reaction becomes sterically hindered and eventually stops. As the length of polystyrene graft in the macromonomer was increased, the length of polynorbornene backbone attainable in the graft copolymer decreased. The polymerization reactions were demonstrated to be living by producing block and tapered copolymers with the sterically undemanding monomer 2,3-bis trifluoromethylnorbornadiene[2].

Here, we report an extension of this programme to the synthesis of well-defined graft copolymers with a polynorbornene backbone chain carrying only one polystyrene graft on each cyclopentane ring. It was anticipated that this would provide a basis for comparison with our earlier results

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on the synthesis of graft copolymers with two polystyrene grafts in each cyclopentane ring, with only one graft per norbornene repeat unit, the steric hindrance effect was expected to be lower allowing the formation of graft copolymers with longer grafts and backbone chains.

Fontanille *et al.*[3] have reported the synthesis of graft copolymers via ROMP of *exo*/*endo*-5-norbornene-2-(polystyrylcarboxylate) macromonomers using the 'Schrock hexafluoro' molybdenum alkylidene initiator, Mo(N-2,6-i-$Pr_2C_6H_3$)(OC$(CH_3)(CF_3)_2)_2$(CHC$(CH_3)_3$). They reported that for macromonomers with $\overline{Mn}$ of up to 2700 ($\overline{DP} = 24$) complete consumption of macromonomer is achieved at a monomer-to-initiator molar ratio of up to 100. In another approach *exo*/*endo*-5-methylene lithium norbornene was synthesized and used as an initiator for anionic polymerization of styrene to produce ring open polymerisable macromonomers with no ester linkages[4]. Macromonomer with $\overline{Mn} = 2600$ ($\overline{DP} = 22$) synthesized by this method was subjected to ROMP using the 'Schrock hexafluoro' molybdenum alkylidene initiator and complete consumption of macromonomer was obtained at a monomer-to-initiator molar ratio of 100.

The work reported here involves synthesizing pure *exo*-5-norbornene-2-carbonyl chloride and using it as an end capping reagent for living anionic polystyrene to produce well-defined *exo*-5-norbornene-2-(polystyrylcarboxylate) macromonomers, and subsequent ROMP of these macromonomers to produce well-defined graft copolymers. Thus, a range of macromonomers with $\overline{Mn}$ of 1550–13 200 ($\overline{DP}$s of 13–127) were synthesized. These macromonomers were then subjected to ROMP using well-defined Schrock initiators. The effects of the macromonomer molecular weight and the macromonomer-to-initiator molar ratio on the course of the polymerization were systematically studied in order to establish the limits of this approach to synthesis and the effect of steric hindrance at the living chain end.

EXPERIMENTAL

General experimental procedures

All manipulations involving polymerization reactions were carried out in an inert atmosphere (dry nitrogen) filled glove box or a conventional high vacuum line. ^1H and ^{13}C n.m.r. spectra were recorded using a Varian VXR 400 n.m.r. spectrometer at 399.953 MHz (^1H) and 100.577 MHz (^{13}C). Deuterated chloroform or deuterated benzene were used as solvents with TMS as internal standard. Infrared spectra of macromonomers were recorded on solvent (chloroform) case films using a Perkin Elmer 1600 series *FT* i.r. spectrometer. G.p.c. analyses were performed on chloroform solutions using a Knauer h.p.l.c. pump (Model 64), Waters Model R401 differential refractometer detector and 3 PLgel columns with pore sizes of 10^2, 10^3 and 10^5 Å (column packing PLgel 5 μm mixed styrene–divinyl benzene beads). The sample solutions (concentration 0.2%) were filtered through a Whatman WTP type 0.2 μm filter to remove any particulates before injection. The system was calibrated using Polymer Laboratories polystyrene standards (162–770 000 amu). Differential scanning calorimetry (d.s.c.) was carried out using a Perkin Elmer d.s.c. 7 differential scanning calorimeter over the temperature range of 25–200°C (heating rate 10°C min^{-1}). Thermagravimetric analysis (t.g.a.) was performed using a Stanton Redcroft TG 760 thermobalance. T.g.a. traces were recorded by increasing the sample temperature from 20°C to 650°C at 10°C per minute under a nitrogen atmosphere and the 2% weight loss temperature was recorded.

Materials

Cyclopentadiene was obtained by pyrolysis of dicyclopentadiene at 180°C. Benzene-d_6 used in n.m.r. scale polymerizations was dried over phosphorus pentoxide and vacuum transferred. Benzene used in preparative scale polymerizations was dried over CaH_2 and vacuum transferred. Benzaldehyde was distilled directly into an ampule containing molecular sieves (type 4A). *Exo*/*endo*-5-norbornene-2-carboxylic acid was prepared by carrying out a Diels–Alder reaction between acrylic acid and cyclopentadiene[5]. The product contained approximately 24% *exo*-acid as determined by ^{13}C n.m.r. spectroscopy. *Exo*/*endo*-5-norbornene-2-carboxylic acid was also prepared by carrying out a Diels–Alder reaction between acrylic acid and dicyclopentadiene in a high-pressure reaction vessel[6]. Product obtained by this method contains 47% *exo*-acid. The *exo*/*endo* product mixture was used in the following step without any further purification. *Exo* and *endo* acids were separated via synthesis of the *endo*-iodolactone following established procedures[7–9]. *Exo*-5-norbornene-2-carbonyl chloride was synthesized by reacting crude *exo*-5-norbornene-2-carboxylic acid with oxalyl chloride and purified by fractional distillation[10]. The ROMP initiators, Mo(N-2,6-i-$Pr_2C_6H_3$)$(OCMe_3)_2$(CHR), where R is CMe_2Ph or CMe_3, were prepared following the published method[11]. *Exo*-5-norbornene-2-(polystyrylcarboxylate) macromonomers were synthesized following the method described previously for the synthesis of 5-norbornene-2,3-*trans*-bis(polystyrylcarboxylate) macromonomers[1,2].

A typical n.m.r. scale ring opening metathesis polymerization

The initiator Mo(N-2,6-i-$Pr_2C_6H_3$)$(CHCMe_2Ph)(OCMe_3)_2$ (12.7 mg, 0.023 mmol) and *exo*-5-norbornene-2-(polystyrylcarboxylate) macromonomer ($\overline{Mn} = 1460$, 335.8 mg, 10 equivalents) were dissolved in benzene-d_6 (400 μl and 600 μl respectively) in separate sample vials. The macromonomer solution was added to the initiator solution and stirred for 25 min. The mixture was transferred into a screw-cap n.m.r. tube and analysed by ^1H n.m.r. spectroscopy. The polymerization reactions were terminated by addition of benzaldehyde (a 10-fold excess). The reaction mixture 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 for 72 h.

A typical preparative scale ring opening metathesis polymerization

The initiator Mo(N-2,6-i-$Pr_2C_6H_3$)$(CHCMe_3)(OCMe_3)_2$ (41.8 mg, 0.086 mmol) was dissolved in benzene (3 ml) in a sample vial and the solution was transferred to a single-neck round-bottom flask (250 ml). The vial was washed with benzene (30 ml) which was added to the initiator solution. *Exo*-5-norbornene-2-(polystyrylcarboxylate) macromonomer ($\overline{Mn} = 3500$, 30 g, 100 equivalents) was dissolved in benzene (80 ml) and added to the initiator solution in 5 equal portions at 15–20-min interval under vigorous stirring. After adding all the macromonomer, the mixture was stirred for a further 3 h. The polymerization reactions were terminated by the

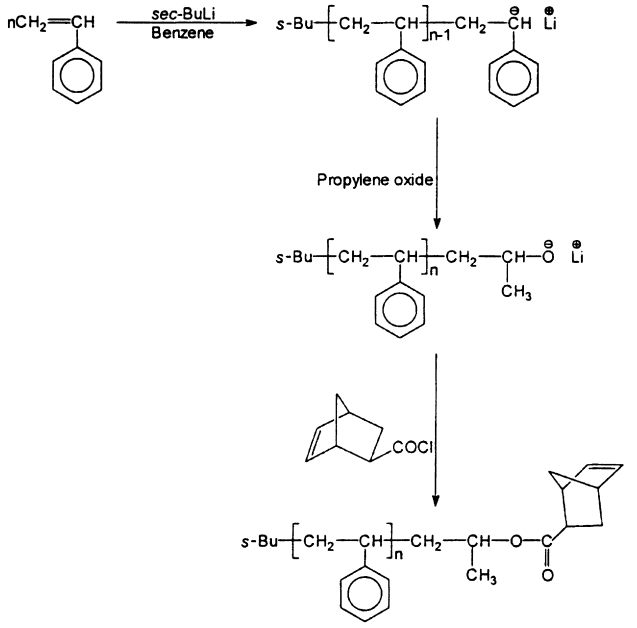

Figure 1 Reaction scheme for *exo*-5-norbornene-2-(polystyrylcarboxylate) macromonomer synthesis

Table 1 G.p.c. analysis results of the macromonomers prepared

Run	Polystyrene homopolymer		Macromonomer		
	$\overline{Mn}$	PDI	$\overline{Mn}$	PDI	$\overline{DP}$ of PS
1	1300	1.10	1450	1.08	12
6	1300	1.07	1550	1.05	13
3	2100	1.10	2250	1.05	20
4	2400	1.06	2590	1.05	22
5	3400	1.04	3500	1.04	32
10	—	—	4750	1.08	44
14	4800	1.06	4900	1.08	46
7	—	—	10 200	1.13	96
15	—	—	13 200	1.08	127

addition of benzaldehyde (a 10-fold excess). The recovery procedure used for the polymer was similar to that described above.

RESULTS AND DISCUSSION

Synthesis of macromonomers

The synthesis of *exo*-5-norbornene-2-(polystyrylcarboxylate) macromonomer was carried out in close analogy to the method described previously[1] and the reaction scheme is outlined in *Figure 1*.

All the macromonomers were characterized by g.p.c., ^{1}H n.m.r. spectroscopy and i.r. spectroscopy. *Table 1* gives the g.p.c. analysis results for polystyrene homopolymers and the macromonomers. The g.p.c. results indicate that these macromonomers have a very narrow molecular weight distributions (PDI).

The end capping reaction of living polystyrene homopolymer with pure *exo*-5-norbornene-2-carbonyl chloride was confirmed by ^{1}H n.m.r. and i.r. spectroscopy. The ^{1}H n.m.r. spectra of the macromonomers are similar to those described in the literature[1,12], and show olefinic resonances around 6.0–6.2 ppm, due to the norbornenyl unit, which are resolved from the aromatic hydrogens due to polystyrene (6.35–7.35 ppm). The styrene:norbornene

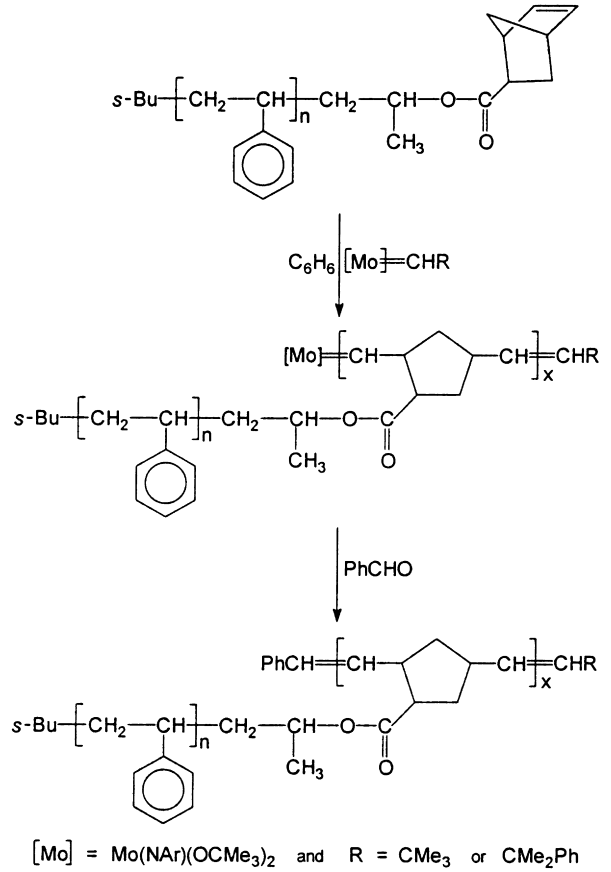

Figure 2 Reaction scheme for the synthesis of graft copolymers

molar ratios calculated from the integration of the olefinic and aromatic proton resonances for low molecular weight macromonomers (up to $\overline{Mn} = 3500$) agree, within experimental error, with that calculated from g.p.c. analysis.

The i.r. spectra of the macromonomers exhibit ester C=O stretching at 1726 cm^{-1} and ester C–O stretching at 1179 cm^{-1} and agree with those of analogous materials described in the literature[1,12].

Ring opening metathesis polymerization of macromonomers

The well-characterized *exo*-5-norbornene-2-(polystyrylcarboxylate) macromonomers were subjected to ROMP using the Schrock molybdenum initiators, Mo(N-2,6-i-$Pr_2C_6H_3$)($OCMe_3$)$_2$(CHR), where R is CMe_3 or CMe_2Ph, and the living polymerization reactions were terminated with benzaldehyde to give the final product graft copolymer. The reaction scheme is outlined in *Figure 2*.

The ^{1}H n.m.r. spectrum of the living polymerization reaction mixture (*Figure 3*) shows two broad unresolved signals at 11.44 and 11.62 ppm, characteristic of the hydrogens of the propagating alkylidenes. These signals could be due to *head* or *tail* insertion of the macromonomer to the active site (*a* and *b* in *Figure 4*) leading to *head–tail*, *tail–tail* or *head–head* placements of repeat units in the polymer chain. The broad unresolved nature of these n.m.r. signals could be due to the complexity of the slightly differing environments of the nuclei. Furthermore, another signal was observed at 11.31 ppm, characteristic of the hydrogen of the initiator alkylidene, indicating that propagation is faster than initiation. On further addition of macromonomer to the polymerizing mixture, the intensity of this peak gradually diminishes.

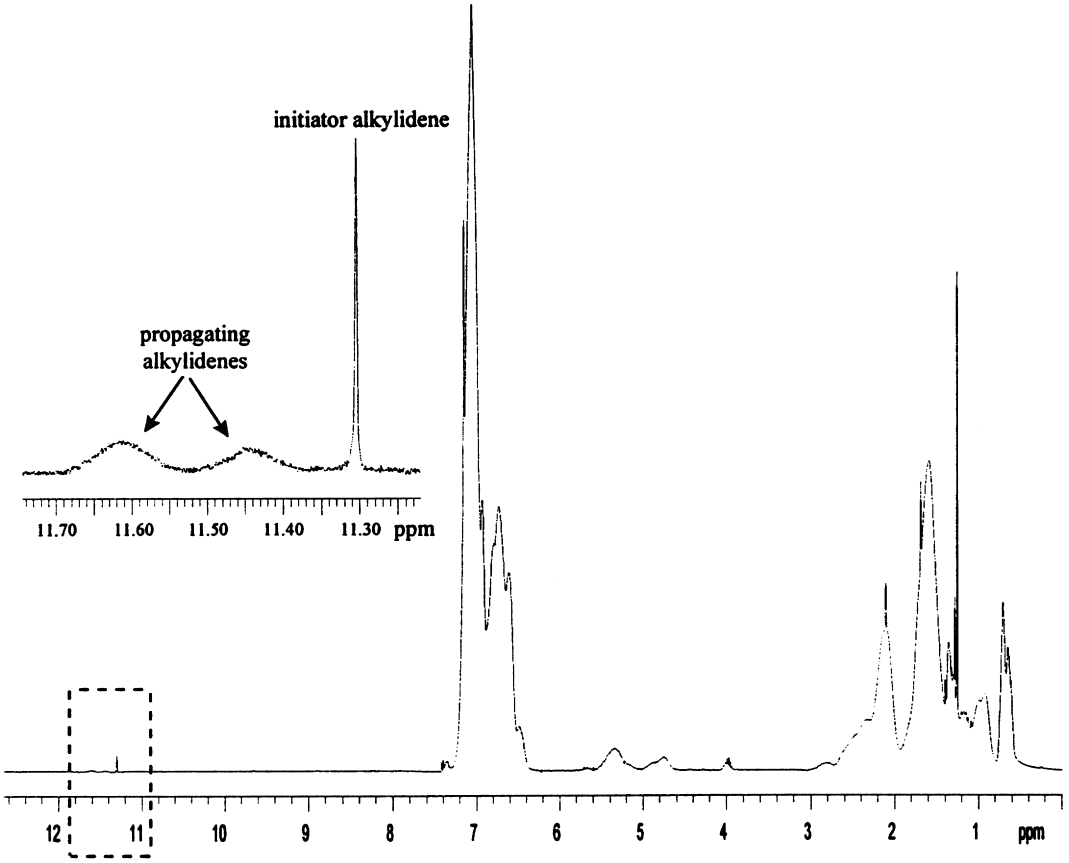

Figure 3 A typical ^{1}H n.m.r. spectrum of an n.m.r. scale ROMP after adding 10 equivalents of macromonomer ($\overline{Mn} = 1460$)

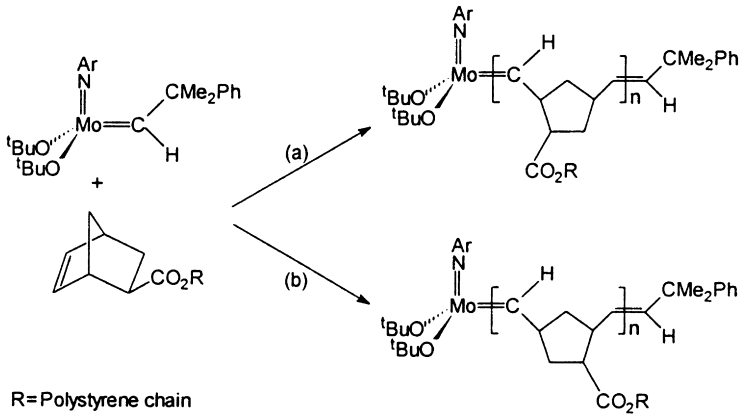

Figure 4 *Head* (a) and *tail* (b) insertion of macromonomers at the active site in living ROMP

The polymer microstructure is represented diagrammatically in *Figure 5*. Since *exo*-5-norbornene-2-carbonyl chloride was used for end capping living polystyrene homopolymer to synthesize the macromonomer, the polystyrene chain in the macromonomer and in the graft copolymer have the same '*exo*' configuration. Considerable microstructural variety is possible in these systems owing to the possibility of *head–tail* additions, *cis* and *trans* vinylene units and *meso* or *racemic* dyads. Unfortunately, the ^{1}H and ^{13}C n.m.r. spectra were very complex with many overlapping multiplets or broad unresolved peaks and it was not possible to interpret them in terms of microstructural detail, as is often possible for polymers produced by ROMP[13]. However, these multiplicities together with the broad unresolved peaks for the propagating alkylidene signals are consistent only with an irregular microstructure. The *head* and *tail* inserted propagating alkylidene signals are not equal in intensity so the microstructure is not totally random.

The g.p.c. results for all the graft copolymers prepared are tabulated (*Table 2*), and indicate a narrow polydispersity for all samples. These g.p.c. data yielded no useful quantitative information since the numerical values for molecular weight are calculated with reference to calibration with linear polystyrene standards, and the hydrodynamic volume-to-molecular weight relationship for these comb–graft copolymers is, as yet, unknown.

However, the g.p.c. results reveal that for the ROMP of macromonomers with a molecular weight of 1550 ($\overline{DP} = 13$), macromonomer is completely consumed at a monomer-to-initiator molar ratio of 200. Similarly, for the

Table 2 G.p.c. analysis and d.s.c. and t.g.a. results

Run	Macromonomer				Graft copolymer				
	$\overline{Mn}$	PDI	$\overline{DP}$ of PS	[M]/[I] ratio[a]	$\overline{Mn}$	PDI	No. of peaks	D.s.c. T_g/°C	T.g.a. T_d/°C[b]
1	1550	1.05	13	8	13 650	1.07	1		
2				10	15 100	1.20	1	79.67	389
3				40	38 000	1.10	1	82.04	380
4				50	60 400	1.13	1	79.59	379
5				60	73 000	1.16	1	80.05	380
6				120	101 600	1.28	1		
7				200	277 200	1.51	1	84.17	388
8	2250	1.05	20	30	36 300	1.07	1	89.26	392
9				40	44 800	1.06	1	89.63	395
10				40	48 200	1.13	1		
11				50	60 600	1.10	1	87.87	399
12	3500	1.04	32	10	23 900	1.06	1		
13				10	23 100	1.09	1	94.54	—
14				20	37 000	1.07	1	95.10	408
15				30	47 500	1.08	1	95.25	407
16				50	76 400	1.16	1		
17				50	74 300	1.16	1	93.55	405
18				100	130 800	1.13	1	93.77	402
19	4900	1.08	46	100	271 500	1.31	1	91.97	407
20	10 200	1.13	96	15	100 000	1.09	1	101.13	414
21				20	107 700	1.12	1	101.91	417
22				30	178 600	2.01	2	101.06	410
23	13 200	1.08	127	5	63 200	1.13	1	100.17	409
24				10	82 700	1.11	1	100.00	420
25				15	117 600	1.11	2	99.57	412

[a]Macromonomer-to-initiator molar ratio
[b]For 2% weight loss

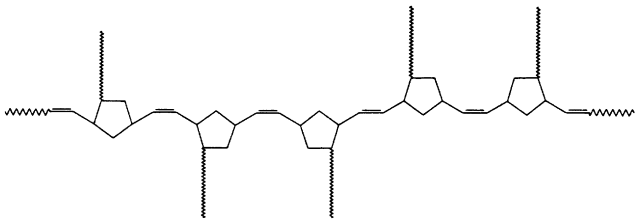

Figure 5 Diagrammatic representation of the polymer microstructure

ROMP of macromonomers with molecular weights of 3500 and 4900 ($\overline{DP}$s of 32 and 46, respectively), complete consumption of macromonomer is achieved even at a monomer-to-initiator molar ratio of 100. In these cases only one peak is observed in the g.p.c. traces due to the product graft copolymer. The broadening of molecular weight distribution for the monomer-to-initiator molar ratios of 120 and 200 (runs 6, 7 and 19) could be due to reduced mixing efficiency at the higher macromonomer-to-initiator molar ratios. On the other hand, the fact that the rate of propagation is faster than initiation for these systems could also have contributed to this broadening effect. When the macromonomer molecular weight is 10 200 or 13 200 ($\overline{DP}$s of 96 and 127, respectively), complete polymerization is obtained at monomer-to-initiator molar ratios of only up to 20 and 10, respectively. Beyond these ratios the ROMP reaction stops before complete consumption of macromonomers and two peaks are observed in the g.p.c. traces. The lower molecular weight peaks have the same retention time as the macromonomer; the high molecular weight peaks are due to the product graft copolymer.

It should be noted that in the case of the disubstituted norbornene macromonomer with 14 styrene units in each graft ($\overline{DP} = 14$), the complete polymerization of the macromonomer is achieved only at molar ratios of monomer to initiator up to 9, and when the molar ratio of monomer to initiator is 10 or greater the polymerization stops before complete consumption of macromonomers[1,2]. Moreover, for the disubstituted norbornene macromonomer with 25 styrene units in each graft, the ROMP reaction stops after only one or two macromonomers have been inserted at the active site[2].

The results clearly suggest that, in contrast to two polystyrene grafts on the same norbornene unit, with one polystyrene graft on the norbornene unit graft copolymers with relatively long backbone and side chains can be prepared, probably as a consequence of lowered steric hindrance. As observed by ^{1}H n.m.r. (*Figure 3*) the macromonomer currently under discussion can add *head* or *tail* to the propagating chain end which reduces the steric hindrance at the growing chain end and allows the synthesis of high molecular weight graft copolymers.

The d.s.c. and t.g.a. results for graft copolymers are also listed in *Table 2*. In all cases, only one T_g was observed for these graft copolymers. This indicates that the polynorbornene and polystyrene segments do not undergo phase segregation. The T_g of these graft copolymers shows that there is an overall increase in T_g on going from graft copolymers containing short polystyrene chains to longer polystyrene chains. The T_g of polynorbornene is 35°C and that of polystyrene is 100°C, thus the T_g process observed is primarily associated with polystyrene grafts in these systems. A similar trend was observed in relation to thermal decomposition temperatures, using 2% weight loss as an arbitrary criterion for degradation. As the polystyrene graft length increases, the thermal decomposition temperature also increases.

CONCLUSIONS

The results described here indicate that well-defined graft copolymers can be prepared by living ROMP of well-characterized *exo*-5-norbornene-2-(polystyrylcarboxylate) macromonomers, synthesized by living anionic polymerization. The ^{1}H n.m.r. spectrum of the living ROMP

reaction mixture indicates that for this system the rate of propagation is faster than the rate of initiation. G.p.c. analysis indicates that the graft copolymers obtained in this work have both longer polynorbornene backbones and polystyrene grafts than was possible for the disubstituted macromonomers investigated previously. This is most probably because steric hindrance at the growing chain end during the ROMP step is significantly reduced. This hypothesis is supported by the fact that ^{1}H n.m.r. spectrum of the living ROMP reaction mixture shows two propagating alkylidene signals due to *head* or *tail* insertion of macromonomer to the active site probably indicating *head–tail*, *tail–tail* or *head–head* placements of repeat units in the polymer chain and a highly disordered microstructure, a view consistent with the complex ^{1}H and ^{13}C n.m.r. spectra recorded. D.s.c. analysis of these graft copolymers indicate that polynorbornene and polystyrene segments do not undergo phase segregation.

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