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Well-defined graft copolymers via coupled living anionic and living ring opening metathesis polymerisation

W.J. Feast [a], V.C. Gibson [a,1], A.F. Johnson [b], E. Khosravi [a,*], M.A. Mohsin [b]

[a] *Interdisciplinary Research Centre in Polymer Science and Technology, Durham University, South Road, Durham, DH1 3LE, UK*
[b] *Interdisciplinary Research Centre in Polymer Science and Technology, Bradford University, Bradford, BD7 1DP, UK*

Abstract

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 and living ROMP of the macromonomers using well-defined Schrock molybdenum initiator to produce well-characterised graft copolymers is described. The scaling up of the ROMP of the macromonomers of different molecular weights revealed the presence of an experimental limit to the length of polynorbornene backbone chain and to the length of the polystyrene graft. It is found that as the length of polystyrene graft in the macromonomer is increased the length of polynorbornene backbone chain in the graft copolymer is decreased an observation ascribed due to steric hindrance. The ROMP of macromonomers of different molecular weight has been shown to be living allowing the synthesis of tapered and block copolymers.

Keywords: Copolymers; Anionic metathesis; Ring opening methatesis

1. Introduction

Recently we reported the first stage of a programme of work in which we explored the potential of combining the capabilities of living anionic and ring opening metathesis methods to prepare polymers with well defined structures and unusual topologies [1]. We reported 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 and the polymerisation of the macromonomers via living ring opening metathesis using a well-defined Schrock initiator to produce well defined graft copolymers, the process is outlined in Schemes 1 and 2, see below. Comb graft copolymers with polystyrene block number average degrees of polymerisation (DPs) of 4, 7 and 9 were successfully prepared exhibiting narrow molecular weight distributions. However, the ROMP of macromonomers with polystyrene block DPs of 14, 24 and 46 gave products which revealed two peaks in the GPC traces. The lower molecular weight peaks all had the same retention times as the macromonomers and were accompanied by a higher molecular

* Corresponding author.
[1] Present address: Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AY.

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weight peak due to polymer product. It appeared that as the length of the polystyrene blocks in the macromonomer was increased the metathesis reaction became sterically inhibited and eventually stopped. Qualitatively, the intensity of the residual macromonomer peak was found to be dependent on its molecular weight, the higher the molecular weight the bigger it was relative to the polymer peak at the time polymerisation stopped.

Recent work involving scaling up of the ROMP of macromonomers of different molecular weights revealed the presence of a limit to the length of the polymer backbone chain in addition to the limit to the length of the polystyrene graft observed previously. The work reported here describes an investigation carried out in an attempt to define the limits on both the length of polystyrene grafts and the length of polynorbornene backbone chain. It also reports further evidence of the living character of the ROMP of these macromonomers as revealed by the synthesis of tapered and block copolymers from the macromonomers and a fluorinated norbornadiene monomer.

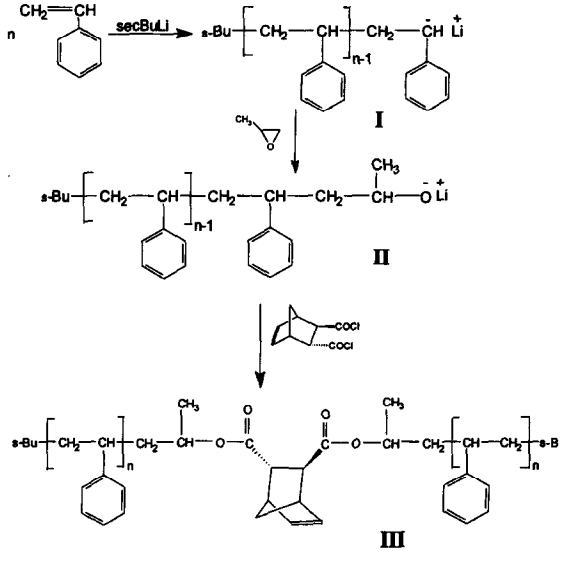
2. Experimental

2.1. General

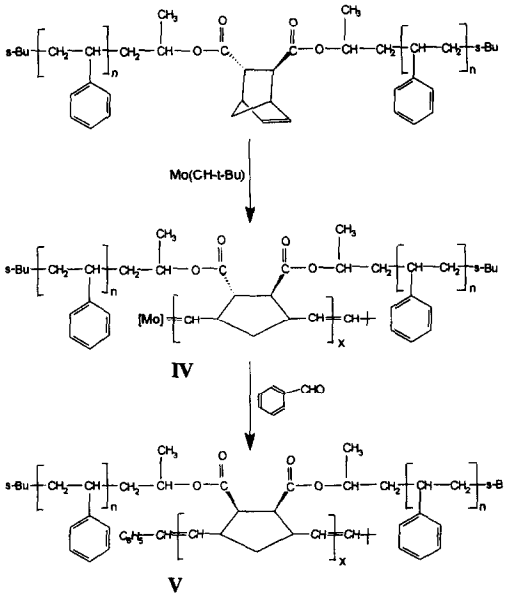
All manipulations of air and or moisture sensitive materials were performed on a conventional vacuum/inert atmosphere (nitrogen) line using standard Schlenk and cannular techniques, or in an inert atmosphere (nitrogen) filled glove box. NMR spectra were recorded using a Varian VXR400S (^{1}H @ 399.95 MHz and ^{13}C @ 100.58 MHz). Chemical shifts are reported in parts per million with respect to the internal reference tetramethylsilane. GPC traces were recorded for solutions in chloroform using a Waters 590 HPLC pump, a Waters R401 RI detector and three PLgel 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 μm filter to remove particulates before injection. The columns were calibrated using polystyrene standards (Polymer Laboratories Ltd.) ranging from 162 to 2.31×10^6 $g\,mol^{-1}$. Infrared spectra were recorded on a Perkin Elmer 1720-X series FTIR.

2.2. Reagents

Deuterated solvents were stirred over the appropriate drying agent and vacuum distilled immediately prior to use. Polymerisation solvents (drying agent in parenthesis) were dried by prolonged reflux over the appropriate drying agent, freshly distilled and degassed before use: benzene (calcium hydride), benzene-d_6 (phosphorous pentoxide), toluene (sodium metal), 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 vacuum transferred from calcium hydride immediately prior to use. Bicyclo[2.2.1]hept-5-ene-2,3-*trans*-dicarbonyl chloride (Aldrich Chemical Co. Ltd.) was fractionally distilled under reduced pressure (74°C, 0.05 mm Hg) and dried over molecular sieves.



Scheme 1. Schematic route for the synthesis of macromonomers.



Scheme 2. Schematic route for the synthesis of graft copolymers.

Propylene oxide (Aldrich Chemical Co. Ltd.) was stirred over calcium hydride overnight and distilled under reduced pressure prior to use.

2.3. Initiators

Sec-Butyllithium (Aldrich) was used as supplied. The ROMP initiators, Mo(=N-2,6-i-Pr_2-C_6H_3)(=CHR)(OR′)$_2$ [R=CMe_2Ph,R′=Me_3C], were prepared following the published methods [2].

2.4. Synthesis of macromonomers

The macromonomers were prepared using the published route [1]. The synthesis is outlined in Scheme 1.

2.5. ROMP of the macromonomers

Polymerisations were studied by NMR prior to attempting syntheses on a larger scale. In a typical NMR scale polymerisation 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 polymerisation 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 ten-fold excess). The volume of the mixture was reduced by about 70% by vacuum transfer of solvent and the resulting solution was added dropwise to ten 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 72 h.

2.6. Block copolymerisation

In a typical NMR reaction macromonomer (10–20 equivalents) in benzene-d_6 (1000 μl) was added to a stirring solution of the well defined initiator, Mo(CH–t–Bu)(NAr)(O–t–Bu)$_2$, (10–20 mg) in benzene-d_6 (400 μl). Upon the completion of the polymerisation of macromonomer bis(trifluoromethyl)norbornadiene monomer (20–40 equivalents) in the same solvent (200 μl) was added. The reactions were terminated by the addition of benzaldehyde (ten-fold excess) after the total consumption of the comonomer. The recovery procedure used for the copolymers was similar to that used for the graft copolymers.

3. Results and discussion

A series of macromonomers with different polystyrene block lengths were prepared and characterised. The characterisation of these macromonomers has been discussed in detail previously [1].

The scaling up of the ROMP of the macromonomers of different molecular weights,

Table 1
Summary of GPC analysis of ROMP of macromonomers with different polystyrene graft length

Molecular weight of macromonomer (Mn)	DP Polystyrene graft	Macromonomer/ initiator molar ratio	No. of peaks in GPC
1200	6	10	1
		26	1
		30	2
1600	8	10	1
		13	1
		15	1
		20	1
		25	2
2100	10	7	1
		16	1
		20	2
2800	14	9	1
		10	2
		12	2
5000	25	5	2
		11	2

i.e., different polystyrene graft lengths, revealed the presence of a limit on the attainable length of the polynorbornene backbone chain in the graft copolymer in addition to the limit on the length of polystyrene graft in the macromonomer observed previously. The ROMP reactions of the macromonomers were therefore investigated in detail for different molecular weight macromonomers to determine the limits on the length of polynorbornene backbone chain in the graft copolymer.

The results shown in Table 1 indicate that the ROMP of macromonomers with different polystyrene graft lengths go to completion only up to a certain molar ratio of macromonomer to initiator and 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 GPC. 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. For example for the ROMP of the macromonomer with polystyrene graft length of DP 8, the metathesis reactions for molar ratio of macromonomer to initiator of up to 20 go to completion and only one peak is seen in the GPC whereas for molar ratio of macromonomer to initiator of 25 two peaks appear in the GPC, see Fig. 1. For the ROMP of macromonomer with polystyrene graft length of 25 the limit on the length of polynorbornene backbone chain turns out to be less than 5 macromonomer repeat units (see Table 1). These limits are independent of the duration of the reaction and the chain ends remain living and active (see below).

These results suggest that the graft copolymer backbone chain grows up to a certain length beyond which the metathesis polymerisation reaction becomes sterically hindered and eventually stops. It is evident from the results in Table 1 that at the point where propagation ceases there is a correlation between the length of polynorbornene backbone chain in the graft copolymer and polystyrene graft length in the macromonomer. As the length of polystyrene graft in the macromonomer is increased the length of polynorbornene backbone chain in the

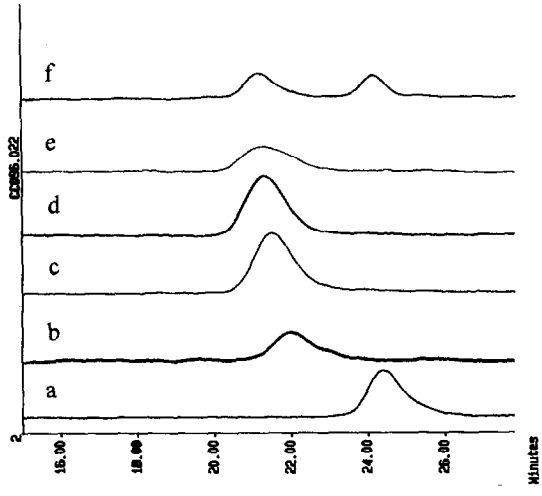


Fig. 1. Illustrative GPC traces for (a) macromonomer, (b) molar ratio of macromonomer to initiator 10, (c) molar ratio of macromonomer to initiator 13, (d) molar ratio of macromonomer to initiator 15, (e) molar ratio of macromonomer to initiator 20, (f) molar ratio of macromonomer to initiator 25.

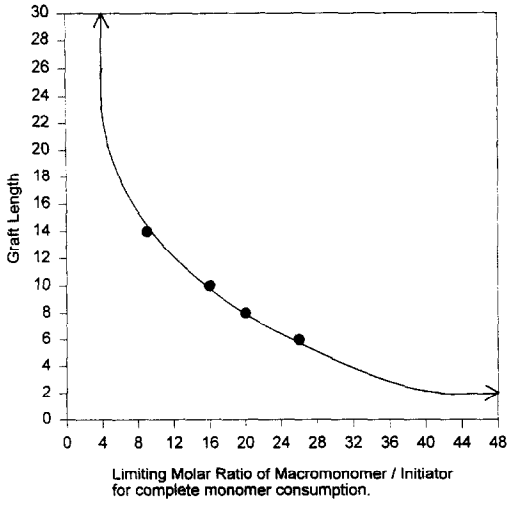


Fig. 2. Relationship between the length of polystyrene graft in the macromonomer and limiting molar ratio of macromonomer to initiator which results in complete monomer consumption.

graft copolymer is decreased. Fig. 2 shows the relationship between the length of polystyrene graft in the macromonomer and limiting molar ratio of macromonomer to initiator which results in complete monomer consumption. Although the plotted points appear to indicate a linear relationship, we know that the limit of polymerisability of macromonomers with polystyrene grafts of DP > 25 is less than DP ≈ 5 and can therefore assume that the curve will tend to the direction shown; similarly, when there is no graft the molecular weight attainable in the polymerisation of norbornene is unrestricted as indicated in the bottom right hand corner of Fig. 2.

Ring opening metathesis polymerisation of cyclic olefins using Schrock initiator has been shown to be living allowing the synthesis of block copolymers by the sequential addition of monomers [3]. The advantage of these systems is that the complete course of the copolymerisation reactions can be followed by ^{1}H-NMR. When the first monomer is polymerised characteristic propagating alkylidene resonances are seen in the ^{1}H-NMR spectrum of the reaction mixture at a monomer specific chemical shift. The addition of a comonomer, after the complete polymerisation of the first monomer, results in appearance of a new propagating alkylidene signal typical of the second monomer [4]. The ^{1}H-NMR spectrum of polymerising macromonomer initiated by molybdenum Schrock initiator shows a broad unresolved signal at 11.50 ppm characteristic of the propagating alkylidene of the polynorbornene backbone chain, see Fig. 3 (upper spectrum) which shows only the downfield alkylidene region for simplicity, the complex set of overlapping resonances due to polystyrene and polynorbornene occur at higher field. The broad unresolved nature of the alkylidene signal is consistent with either low molecular mobility at the chain end and/or a multiplicity of slightly differing environments for the nuclei representative of nominally similar structural features in an essentially atactic material. When bis(trifluoromethyl)norbornadiene, BTFMND, monomer is

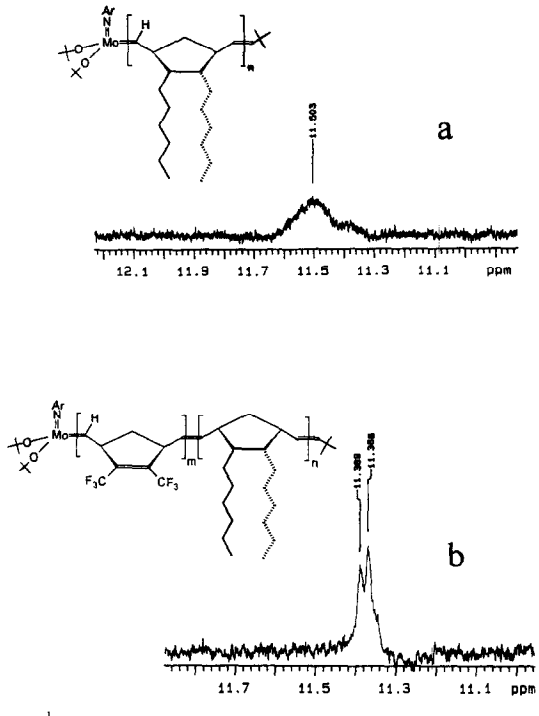


Fig. 3. ^{1}H-NMR spectra in the alkylidene proton region for (a) the living homopolymerisation of macromonomer and (b) the living copolymerisation after the addition of bis(trifluoromethyl)norbornadiene comonomer.

added to the metathesis polymerisation reaction mixtures, which are shown to have gone to completion by GPC analysis, a new propagating alkylidene signal appears at 11.38 ppm which is characteristic of poly BTFMND [5], Fig. 3 (lower spectrum). This is consistent with the formation of block copolymer and a further demonstration of the living character of these metathesis polymerisations. The block copolymers obtained exhibit single mode molecular weight distribution and narrow polydispersity in GPC. The addition of the fluorinated monomer to the reaction mixture that is shown to exhibit two peaks in the GPC, due to living macromonomer polymer plus unreacted macromonomer, leads to the disappearance of the low molecular weight macromonomer peak. It appears that the incorporation of the fluorinated monomer in the chain eliminates the steric hindrance effects and hence the unreacted macromonomer in the mixture participates in further polymerisation resulting in the formation of tapered block copolymers. This unambiguously demonstrates that the metathesis polymerization reaction for molar ratio of macromonomer to initiator bigger than the limits indicated in Table 1 stops as a consequence of steric hindrance and not as a result of the deactivation of the initiator. The polymerisation mixtures are still living and when a less sterically hindered monomer is added the polymerisation reaction continues.

4. Conclusions

The results of the work presented here demonstrate that well-defined ring opening polymerisable macromonomers of different molecular weight can be obtained via reaction of propylene oxide capped living polystyrene with bicyclo[2.2.1]hept-5-ene-2,3-*trans*-dicarbonyl chloride and the formation of graft copolymers via ROMP of norbornene-2,3-*trans*-polystyrylcarboxylate macromonomers. The ROMP of these macromonomers with different molecular weights indicates the existence of a limit to the length of polystyrene graft and to the length of polynorbornene backbone chain attainable in these polymerisations. There appears to be a correlation between the length of polynorbornene backbone chain in the graft copolymer and polystyrene graft length (or the molecular weight) of the macromonomer. As the length of polystyrene graft in the macromonomer is increased the length of polynorbornene backbone chain in the graft copolymer is decreased. The results also unambiguously demonstrate that the metathesis polymerisation reaction at high molar ratio of macromonomer to initiator cease to propagate as a consequence of steric hindrance and that the chain ends remain living can be used to produce tapered or block copolymers from less sterically demanding monomers.

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