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SYNTHESIS OF HOMO- AND BLOCK COPOLYMER MULTI-ARMED METHACRYLIC STAR POLYMERS BY TRIISOBUTYLALUMINIUM/*tert*-BUTLYLLITHIUM INITIATION

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Abstract: Methacrylate star polymers were prepared using the "arm-first" strategy of star polymer formation by the addition of ethylene glycol dimethacrylate to living linear poly(methacrylate) arms synthesised by a trialkylaluminium/ alkyllithium initiating system. Control over star molar mass is discussed for poly(methyl methacrylate) armed star polymers as is the preparation of star polymers with block copolymer arms.

INTRODUCTION

The polymerisation of methacrylates to produce polymers of targetted geometry and topology is of continuing interest in both academia and industry (Ref. 1). Group Transfer Polymerisation (GTP) allows exceptional control to be established over macromolecular design (Ref. 2). Since this discovery several other polymerisation systems have been developed to achieve living polymerisation of the methacrylates (Refs. 3 - 8). We have been investigating an initiating system based on trialkylaluminium and *tert*-butyllithium which has been shown to give living polymerisation of methacrylates up to ambient temperatures in hydrocarbon solvents (Refs. 9 - 11). This system can be employed over a wide range of conditions and when the polymerisation is carried out at -10 °C in toluene with a 2:1 molar ratio of $^{i}Bu_3Al/^{t}BuLi$, polydispersities of less than 1.20 may be readily achieved. In this publication, we wish to demonstrate the use of this chemistry in the preparation of methacrylic star polymers.

We have previously reported the preparation of methacrylic star polymers by GTP (Ref. 12) utilising the "arm-first" method. We demonstrated a degree of control over these randomly branched species, showing the effect of living arm concentration, core dilution, and ratio of crosslinking monomer to living polymer on the number of arms and molar mass of the star polymer product. A number of other methods are available for the synthesis of star polymers,

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such as the attachment of living anionic arms to molecules susceptible to nuclephilic substitution. For example, $SiCl_4$ produces star polymers with 4 arms (Ref. 14). Although well defined, this "arm first" approach allows only a small number of arms to be incorporated onto each core. A way to produce star polymers with many arms is to allow a di- or multi-functional monomer to react with the monofunctional living polymers post propagation. Practically, this is straightforward to accomplish. For example, living poly(methyl methacrylate) (PMMA) was coupled with ethylene glycol dimethacrylate (EGDMA) to give poly(methyl methacrylate) star polymers with molar masses of approximately 300 000 g mol^{-1} (i.e. ~20 arms of $\bar{M}_n$ = 10 000 by GTP (Ref. 12).

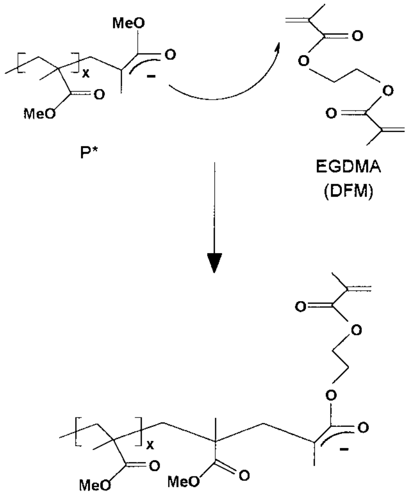

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Fig. 1. Reaction scheme for the formation of star polymer from preformed arms and difunctional monomer

This arm first / multifunctional monomer approach to star polymers with PMMA arms and an EGDMA core using GTP has also been reported by Burchard (Ref. 14) and using classical anionic polymerisation by Mays (Ref. 15). In order to investigate how the ratio of [living polymer] to [di-functional monomer], [P*]:[DFM], could influence the molar mass of the star polymer

Mays synthesised star polymers with arm molar masses of $\bar{M}_w$ = 10 000 and 40 000 and looked at [DFM]:[P*] ratios of 6:1, 3:1 and 1:1. This study showed that the number of arms per star increases with an increase in core size, but that fewer arms were present on star polymers with higher molar mass arms, $\bar{M}_w$ = 40 000. This was explained as shielding of the core by the longer arms, thus preventing intercore reactions. For star polymers with arm molar mass $\bar{M}_w$ = 10 000 Mays observed a gelling effect which made analysis difficult. When a 6:1 [DFM]:[P*] ratio was employed, the star polymers were impossible to analyse.

The arm first/crosslinking monomer addition to star polymers is a very versatile route for the preparation of poly(methacrylate) star polymers. In this present work we have explored the potential of the trialkylaluminium / *tert*-butyllithium initiators for the formation of star polymers from linear poly(methyl methacrylate) "arms" crosslinked with a core of ethylene glycol dimethacrylate, Fig. 1, and compared them with similar star polymers prepared by GTP (Refs. 12, 14) and classical anionic polymerisation techniques (Ref. 15). We have also investigated the effect of [DFM]:[P*] variations in star molar mass, and finally examined the preparation star polymers with block copolymer arms.

EXPERIMENTAL PART

General Methods and Materials

All reactions were carried out using standard Schlenk apparatus and syringe techniques for reagent transfer with all reaction vessels flame-dried under vacuum prior to use. Methyl methacrylate (MMA) was obtained from ICI Acrylics, Wilton U.K. (grade TA5) and purified by passing through a column of activated basic aluminium oxide and activated 4Å molecular sieves under a N_2 atmosphere. n-Butyl methacrylate (nBMA) and iso-butyl methacrylate (iBMA) were obtained from ICI Acrylics, Wilton, (grade TA5), *tert*-butyl methacrylate (tBMA) was obtained from TCI, trimethylsilylethyl methacrylate (TMSEMA) and ethylene glycol dimethacrylate (EGDMA) were obtained from Aldrich Chemical Co. Ltd. and purified by passing through a column of activated basic aluminium oxide. Purified monomers were stored under an atmosphere of nitrogen over 4Å and 13X molecular sieves. Triisobutylaluminium (1.0 M solution in toluene), was supplied by Aldrich Chemical Co. Ltd and used as received. *tert*-Butyllithium (Aldrich) was supplied as a 1.7 M solution in pentane and titrated against diphenylacetic acid in tetrahydrofuran before use. Toluene was dried over sodium and distilled immediately prior to use.

Typical Polymerisation Procedure

An aliquot of 30 mL of toluene was placed in a 100 mL flask equipped with a nitrogen inlet, to which triisobutylaluminium in toluene 1.12 mL (1.12×10^{-3} mol.) and *tert*-butyllithium 0.33 mL (5.6×10^{-4} mol.) were added prior to cooling to -12 °C. Several minutes were allowed to elapse to permit complete reaction/mixing of the two metal alkyls. MMA 3 mL (0.028 mol.)

was added rapidly, in a single addition, over a few seconds. Initially, the reaction produces a pronounced yellow coloration, which disappears when all the monomer is consumed. The reaction was allowed to proceed until the mixture had decolorised (approximately 15 minutes), a sample was taken and terminated by addition to 1-2 drops of methanol. SEC analysis of this sample, $\bar{M}_n$ = 11 500, Polydispersity Index (PDI) = 1.26, was assumed to give an accurate molar mass of the arms used in the synthesis of the corresponding star polymer.

An aliquot of 0.32 mL EGDMA (1.68 x 10^{-3} mol.) was added 5 minutes after decoloration. The reaction was removed from the ice bath and left stirring at ambient temperature for a further 18 hours prior to termination by addition of 1 mL methanol via syringe. The final product was recovered by precipitation into 300 mL of 60-80 petroleum ether. Removal of the low molar mass arms from star polymer was achieved by fractional precipitation. 1 g of product was dissolved in 50 mL of THF with stirring prior to 120 mL of methanol being added prior to being allowed to settle. The precipitate (star polymer product), was filtered from the cloudy solution containing linear PMMA arms. SEC-LALLS analysis of the precipitate revealed a product free from low molar mass linear polymer with a molar mass by light scattering of $\bar{M}_w$(LS) = 660 000. Tab. 1 lists all the reaction conditions for star polymers with homopolymer arms and Tab. 2 lists the reaction conditions for star polymers prepared with block copolymer arms.

Tab. 1. Summary of reaction conditions for star polymers with homopolymer arms.

	Composition of Crosslinking Aliquot*	
	EGDMA (mol.) x10^3	[EGDMA]:[P*][a]
A	1.64	5.0:1
B	1.64	5.4:1
C	1.64	6.7:1
D	1.64	6.9:1
E	1.64	7.6:1
F	4.99	16.4:1

* Initial reaction mixture 30 mL toluene, 1.12 mL ^{i}Bu$_3$Al, 0.33 mL ^{t}BuLi, 3 mL MMA.

[a] from $\bar{M}_n$(arm)

Tab. 2 : Summary of reaction conditions for star polymers with copolymer arms

	Addition 1*				Addition 2		Addition 3	
	monomer 1	moles (x 10^3)	^{i}Bu$_3$Al /mol. (x 10^3)	^{t}BuLi /mol. (x 10^4)	monomer 2	moles (x 10^3)	EGDMA /mol. (x10^3)	[DFM]:[P*]
G	nBMA	0.0314	2.512	12.56	MMA	0.0314	5.23	7.5
H	MMA	0.0467	1.87	9.35	iBMA	0.0467	5.30	17.5
I	TMSEMA	0.0046	1.83	9.15	MMA	0.0458	2.75	6.2

* Initial reaction mixture containing 30 mL toluene.

Analysis

SEC-LALLS: Size exclusion chromatography was carried out using THF as an eluent at 1 mL min^{-1} with toluene (0.2 wt.%) as flow marker in each sample. Two Polymer Laboratories PLgel 5 μm Mixed-C columns (300 mm x 7.5 mm) and a PLgel 5 μm guard column (50 mm x 7.5 mm) were employed and calibrated with Polymer Laboratories PMMA standards from 1 100 to 1 577 000. All chromatograms were analysed using Polymer Laboratories Calibre gel-permeation chromatography/SEC software. The low-angle (5°) light scattering was detected with a PL LALS low-angle light scattering detector. Conversion of light scattering intensity to molar mass was performed by Polymer Laboratories Calibre LALS software.

RESULTS AND DISCUSSION

A series of PMMA star polymers were synthesised with arms of different $\bar{M}_n$ by addition of exactly the same amount of EGDMA whilst keeping other conditions identical. The SEC analysis is summarised in Tab. 3. Fig. 2 shows the SEC trace of the arm and star polymer, after purification, from reaction A. The number of arms per star (f) was calculated by two different methods (1) by dividing the absolute $\bar{M}_w$ of the star from LALLS-SEC by the weight average molar mass ($\bar{M}_w$) of the arm and (2) by the number average molar mass ($\bar{M}_n$) of the arm (for comparison). There is some disagreement in the literature as the most appropriate way

Tab. 3. SEC and SEC-LALLS data for star polymers A-F

	$\bar{M}_n$ (arm) #	$\bar{M}_w$ (arm) #	PDI (arm) #	$\bar{M}_w$ (star) *	$f(\bar{M}_n)^{a)}$ $(f_c(\bar{M}_n))^{c)}$	$f(\bar{M}_w)^{b)}$ $(f_c(\bar{M}_w))^{d)}$	PDI (star)$^{e)}$
A	8 500	11 000	1.26	600 000	71	56	2.10
B	9 200	11 000	1.23	640 000	69	56	1.95
C	11 000	14 000	1.26	660 000	57	45	1.30
D	12 000	15 000	1.27	580 000	49	39	1.70
E	13 000	16 000	1.27	650 000	50	40	1.35
F	9 200	12 000	1.27	6 000 000	657	518	2.24

from SEC with Differential Refractive Index detection (SEC-DRI), * from SEC-LALLS
a) $f(\bar{M}_n) = \bar{M}_w(\text{star}) / \bar{M}_n(\text{arm})$; b) $f(\bar{M}_w) = \bar{M}_w(\text{star}) / \bar{M}_w(\text{arm})$; c) $f_c(\bar{M}_n) = \bar{M}_w(\text{star}) \times \text{wt.fraction(arm)} / \bar{M}_n(\text{arm})$; d) $f_c(\bar{M}_w) = \bar{M}_w(\text{star}) \times \text{wt.fraction(arm)} / \bar{M}_w(\text{arm})$
e) PDI (star) = $\bar{M}_w$(LALLS-DRI) / $\bar{M}_n$(LALLS-DRI)

of obtaining f (Ref. 14,16-18). We have chosen the method used by Mays (Ref. 15) and ourselves (Ref. 12) so as to allow a direct comparison with Mays' results from classical anionic polymerisation, and our previous results for star polymers prepared by GTP. These calculations neglect any contribution made by the core to the overall molar mass of the star polymer. Our observations, which are in agreement with those of Burchard (Ref. 14), show the weight percent of the core, by NMR spectroscopy, to be <5%. For samples in which additional crosslinking monomer was used, f is also calculated by the method used by Higashimura (Ref. 16), where $f_c = \overline{M}_w$(star) x weight fraction(arm)/ Molar mass(arm), to allow for some representation of the core and provide a comparative value for f.

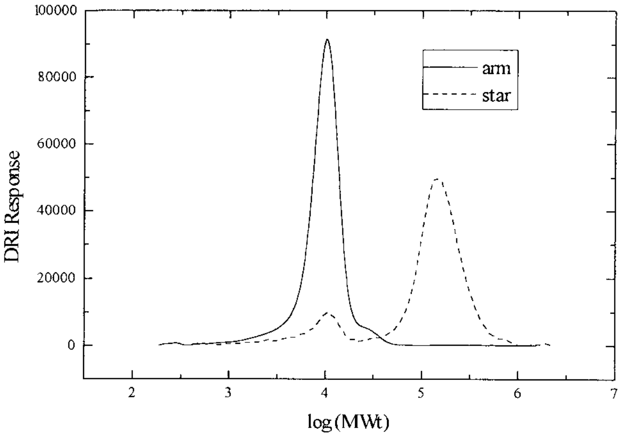

Fig. 2. SEC traces for arm and star polymers from reaction A

Star polymers were prepared by addition of the same amount of difunctional monomer (DFM) to living PMMA arm, in an approximately 6:1 ratio, Tab. 3, so as to allow a comparison with previous results for stars from GTP. The [DFM]:[P*] ratio for star polymers A-E actually varies between 5.0(**A**) and 7.6(**E**) as calculated using [P*] from the $\overline{M}_n$ of the arms. It is interesting to note that the lower ratios of [DFM]:[P*], star polymers **A** and **B**, with lower arm $\overline{M}_n$'s have higher values for f, which conflicts with observations by Mays (Ref. 15) , Higashimura (Ref. 16) and Burchard (Ref. 14) who observed an increase in f with higher [DFM]:[P*] ratios. Both Higashimura and Burchard also report a decrease in f for higher arm lengths, it is noted that these studies covered a much greater variation in arm length. Our previously reported results from GTP differ from this, in that *f* was found to be constant and star molar mass is directly proportional to arm length.

By comparing star polymers A-E to results obtained by GTP and those reported by Mays, the most significant aspect is the differences in star molar mass. Using arm lengths of $\overline{M}_w$ = 10 000 and [DFM]:[P*] of 6:1, Mays star product by classical anionic polymerisation was an uncharacterisable gel, whereas the star polymers from GTP prepared with the same molar concentration of monomer (10% v/v) formed star polymers of approximately half the molar mass than those reported here. Fig. 3 illustrates the difference in molar mass from star polymers prepared by GTP and Li/Al initiated polymerisation.

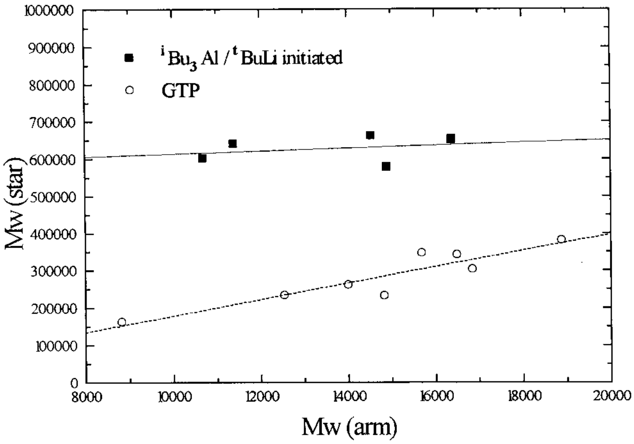

Fig. 3. Plot of the variation $\overline{M}_w$(star) vs $\overline{M}_w$(arm) for $^iBu_3Al/^tBuLi$ initiated star polymers A-E (■) compared with star polymers prepared by GTP (○) (Ref. 12).

The molar mass of star polymers from Li/Al alkyl initiation are approximately twice that from GTP. A possible explanation for this observation is that after P* and EGDMA have reacted to form **1**, (Fig. 1), subsequent reaction can be with either **1**, EGDMA or P*. The living chains have an electronic repulsion between the chain ends, such that the living polymer will react preferentially with a new difunctional monomer rather than polymers containing pendant functionality. As the concentration of P* increases the solvation is reduced, the electronic repulsion of the living ends increases and higher molar mass star polymers are formed (an increase in *f*), the pendant functionality is now further away from the living chain end thus reducing the electronic repulsion effects. Changing solvents from THF to toluene reduces solvation of the propagating end resulting in the production of higher molar mass star polymers. In contrast to $^{i}Bu_3Al/^{t}BuLi$ initiation, GTP does not involve a discrete ion-pair and does not show the same effects.

An important consideration in preparing star polymers by this methodology is the speed of addition of the difunctional monomer, [P*] decreasing with time due to termination reactions. We have found that if the EGDMA is added 30-60 minutes after decolouration only approximately 5 % of the arms are converted to stars (compared to ~90% using the standard conditions). This also has an effect on the crosslinking process by increasing [DFM]:[P*]. For example, a star polymer synthesised from arms of $\bar{M}_n$ = 11 000, $\bar{M}_w$ = 13400 and left for 45 minutes after the discolouration of the reaction mixture prior to EGDMA addition had $\bar{M}_w$ (LS) = 1 100 000, equivalent to $f(\bar{M}_n)$ = 100, $f(\bar{M}_w)$ = 81. Star polymer **F**, Tab. 3, illustrates the effect of increasing the [DFM]:[P*] ratio to 16.4:1 (approximately 3 times that of star polymers **A-E**). This produces a very high molar mass star polymer (10 x greater than **A-E**) $\bar{M}_w$(LS) = 6 000 000, f_c = 383. This effect is again much greater than for the equivalent GTP reaction, where an arm length of $\bar{M}_w$ = 17 000 with [DFM]:[P*] = 16.2:1, produced a star polymer of molar mass $\bar{M}_w$(LS) = 660 000, f_c = 31, only twice the molar mass as obtained with [DFM]:[P*] = 6:1.

Stars with block copolymer arms were synthesised, **G-I** Tab. 4. Considerably higher molar masses were obtained suggesting complications arising from termination reactions. For example, star polymers **B** and **G** both have similar arm molar mass and [DFM]:[P*] ratios, but much different values for $f(\bar{M}_w)$, with **G** approaching the value for f_c obtained for **F** (high [DFM]:[P*]), implying a highly efficient crosslinking reaction for this nBMA/MMA block copolymer arm.

The polydispersities of star polymers **A-I**, Tabs. 3, 4, show no discernible trend, and this seems to be due to the variation in the number of arms per star and not of the variation in arm length. This and other factors effecting star polymer polydispersity have been discussed by Burchard (Ref. 14). However, it is noted that a contributing factor to this will be that the values for $\bar{M}_w$(LALLS-DRI) and $\bar{M}_n$(LALLS-DRI) are taken from SEC with the calibration curve determined by combining the signals from the DRI and LALLS detectors, and hence contains error associated with all of the complications which arise from multidetector size exclusion chromatography (Ref. 19).

Tab. 4: SEC and SEC-LALLS data for star polymers G-J

	Monomer 1	$\bar{M}_n$ (1) #	Monomer 2	$\bar{M}_w$ (arm) #	PDI (arm) #	$\bar{M}_w$ (star) *	$f(\bar{M}_w)$ b	PDI (star)^c
G	nBMA	5 600	MMA	11 000	1.28	3 600 000	313	1.20
H	MMA	11 000	iBMA	42 000	1.35	1 800 000	43	1.32
I	TMSEMA	1 800	MMA	21 000	1.87	2 400 000	114	2.09

from SEC-DRI,* from SEC-LALLS,ϕ from MMA : tBMA ratio in NMR spectrum of the fractionated star polymer: a) $f(\bar{M}_n) = \bar{M}_w(\text{star}) / \bar{M}_n(\text{arm})$, b) $f(\bar{M}_w) = \bar{M}_w(\text{star}) / \bar{M}_w(\text{arm})$, c) PDI (star) = $\bar{M}_w$(LALLS-DRI) / $\bar{M}_n$(LALLS-DRI)

CONCLUSION

In this paper we have demonstrated that the ^{i}Bu$_3$Al/^{t}BuLi initiating system can be an efficient tool for the anionic synthesis of methacrylate star polymers at ambient temperatures, and that a degree of control may be imposed over star polymer molar mass when it is composed of homopolymer PMMA arms. Attempts to produce star polymers with block copolymer arms, although successful, produced slightly surprising results and imply that the molar mass of the star polymer may not simply be extrapolated from homopolymer armed star polymers with arms of similar molar mass.

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