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Branched Polymers via Group Transfer Polymerization

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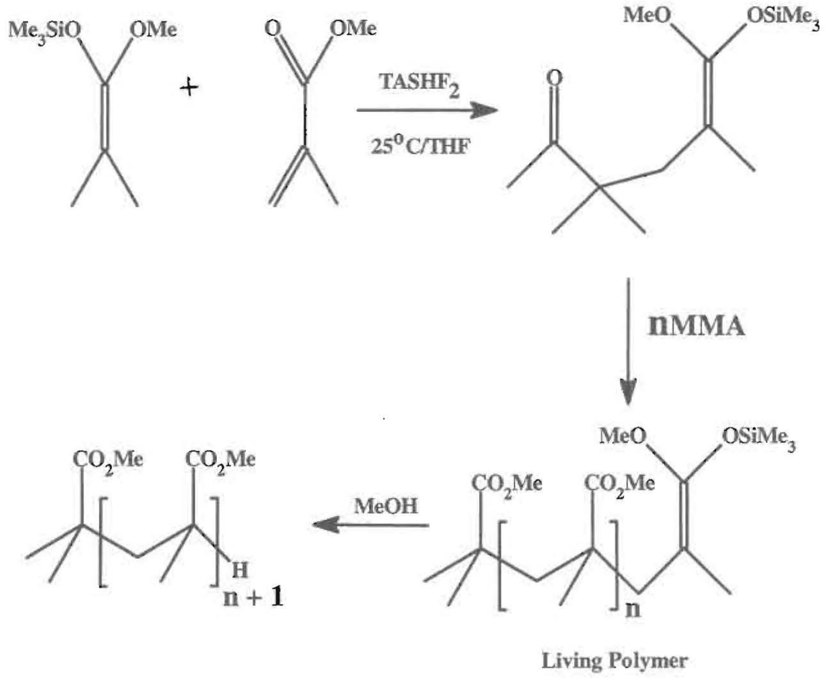
INTRODUCTION

Controlled synthesis of polymers of acrylic and methacrylic esters with predictable molecular weights, narrow molecular weight distributions, and well-defined molecular architecture is of fundamental and practical significance. For the controlled synthesis of acrylic polymers many excellent initiators have been reported, which include biphenyl sodium [1], *t*-BuMgBr coupled with $MgBr_2$ or R_3Al [2,3], metalloporphyrin of aluminum [4], (1,1-diphenylhexyl)lithium/LiCl [5], and organolanthanide [6] complexes. Among these, initiators based on ketene silyl acetals have proved to be among the most attractive methods for the synthesis of poly(alkyl methacrylate)s with controlled molecular structures.

Group transfer polymerization (GTP) is a technique for the polymerization of acrylic monomers discovered by the scientists at Dupont in 1983 [7–10]. The technique gives "living" polymers, remarkably free of termination or transfer reactions, at room temperatures or above. This is in distinct contrast to anionic polymerization of methacrylic monomers, which can be performed in a truly "living" manner only at low temperatures (much below 0°C). GTP works best for methacrylates and is considerably more complex as a process for acrylic monomers. In view of the "living" nature of GTP chain ends, a variety of well-defined methacrylate random, block, graft, and star-branched as well as functionally terminated polymers can be prepared.

GTP is an example of Michael addition polymerization involving the addition of a silyl ketene acetal to α,β-unsaturated carbonyl compounds. A typical polymerization scheme is illustrated in Scheme 1, using methyl methacrylate as the monomer and (1-methoxy-2-methyl-1-propenoxy) trimethyl silane (MTS) as the initiator in the presence of an anionic catalyst.

The original patent issued to Dupont describes several monomers for GTP [11]. However, methyl methacrylate (MMA) is the preferred monomer for most studies [12–16]. Typical examples of MMA polymerization using various anionic catalysts are shown in Table 1.



Scheme 1 GTP of MMA using MTS as initiator and $TASHF_2$ as catalyst.

Table 1 Effect of Catalyst and Solvent on the Group Transfer Polymerization of Methyl Methacrylate Initiated by MTS

Sr. No.	*Catalyst*	*Solvent*	$M_n \times 10^{-3}$ *(theory)*	$M_n \times 10^{-3}$ *(GPC)*	M_w/M_n
1	TBAF, H_2O	THF	60.0	62.3	1.15
2	$TASHF_2$	THF	10.1	10.2	1.17
3	$ZnBr_2$	$ClCH_2CH_2Cl$	3.4	6.02	1.20
4	TBABOAc	THF	4.78	4.86	1.32
5	TBAB	THF	4.78	4.50	1.38
6	$(Ph_4P)_2HF_2$	THF	28.4	43.0	1.32

MTS, 1-methoxy-2-methyl-1-propenoxyl trimethyl silane; TBAF, tetra-*n*-butylammonium [fluoride]; $TASHF_2$, tris(dimethylamino)sulfonium [bifluoride]; TBABOAc, tetra-*n*-butylammonium biacetate; TBAB, tetra-*n*-butylammonium benzoate; $(Ph_4P)_2HF_2$, tetraphenylphosphonium bifluoride.

POLYMER SYNTHESIS THROUGH GTP

In view of the "living" nature of GTP, the method is amenable for the synthesis of well-defined random, block, graft, and star-branched polymers as well as macromonomers, end-functionalized polymers, and telechelics. Some examples of typical random and block copolymers prepared by GTP are shown in Tables 2 and 3. Macromonomers have been prepared by terminating "living" GTP chain ends with electrophilic reagents bearing a polymerizable group, namely, methacryloyl fluoride [17] or *p*-vinylbenzyl tosylate [18]. Alternatively, a silyl-protected hydroxy-containing initiator was used to synthesize a

Table 2 Random Copolymers Prepared by GTP (Initiator: MTS Catalyst: $TASHF_2$)

	Monomers					
Sr. No.	*A*	*B*	*C*	$M_n \times 10^{-3}$ *(theory)*	$M_n \times 10^{-3}$ *(GPC)*	M_w/M_n
1	MMA (35)	*n*-BMA(65)		20.21	22.21	1.11
2	MMA(58)	*n*-BMA(17)	GMA (25)	4.09	4.29	1.10
3	MMA	AMMA		4.81	16.99	1.10
4	1(75)	DMA (25)		80.6	127.0	1.06
5	1(78)	EMA(22)	2	100.0	142.0	1.27

n-BMA, *n*-butyl methacrylate; GMA, glycidyl methacrylate; AMMA, allyl methacrylate; DMA, decyl methacrylate; EMA, ethyl methacrylate;

Table 3 Block Copolymers Prepared by GTP

Sr. No.	Monomers A	Monomers B	Initiator	Type	$M_n \times 10^{-3}$ (theory)	$M_n \times 10^{-3}$	M_w/M_n
1	MMA(25)	2-EHMA (75)	MTS	A-B	—	41.50	1.30
2	MMA (90)	LMA (90)	MTS	A-B	7.14	6.65	1.06
3	LMA (10)	MMA (90)	MTS	A-B	7.12	6.54	1.14
4	*n*-BMA	MMA	SKA-OMC	A-B-A	—	7.2	1.21
5	*t*-BMA	MMA	SKA-OMC	A-B-A	4.5	4.3	1.34
6	MMA (10)	DMA (90)	MTS	A-B	135.0	185.0	1.18
7	*n*-BMA	TMS-HEMA	SKA-OMC	A-B-A	43.6	51.2	1.39
8	MMA	THPMA	MTS	A-B	8.6	7.73	1.08
9	MMA	DMAEM	MTS	A-B	9.44	8.69	1.07
10	MMA	2-EHA	MTS	A-B	12.2	18.2	2.09
11	MMA	tBA	MTS	A-B	10.9	15.9	1.91
12	MMA	BzMA	MTS	A-B	—	42.8	1.05
13	MMA	t-BMA	MTS	A-B	—	20.6	1.34
14	MMA	EA	MTS	A-B	9.5	11.1	2.33

2-EHMA, 2-ethylhexyl methacrylate; LMA, lauryl methacrylate; *n*-BMA, *n*-butyl methacrylate; *t*-BMA, *t*-butyl methacrylate; DMA, decyl methacrylate; TMS-HEMA, trimethylsilyloxyethyl methacrylate; THPMA, tetrahydropyranyl methacrylate; 2-EHA, 2-ethylhexyl acrylate; DMAEM, dimethylaminoethyl methacrylate; *t*-BA, *t*-butyl acrylate; BZMA, benzyl methacrylate; EA, ethyl acrylate; SKA-OMC, trimethyl silyl ketene acetal of octane—2-7-methylcarboxylate.

hydroxyl-containing poly(methyl methacrylate) [19,20]. When a GTP is initiated using a protected —OH or —CO_2H containing initiator and the "living" chain end is coupled using a bifunctional electrophile, telechelics can be synthesized. The best coupling agent for a GTP chain end appears to be terephthaloyl fluoride [7].

STAR-BRANCHED METHACRYLATE POLYMERS

The term "star" polymers denotes a polymer with branches emanating from a common source or core. The first star polymers were synthesized by coupling living polymer chain ends with polyfunctional molecules (e.g., polystyryl lithium with $SiCl_4$) [21,22]. Multiarm star polymers were synthesized by reacting a "living" chain end [e.g., poly(butadienyl) lithium] with divinylbenzene.

In general, star polymers can be synthesized by two different approaches, known as "arm-first" and "core-first" methods [23]. The "arm-first" method consists of either terminating the "living" chain end by plurifunctional electrophiles or reinitiation using bis unsaturated monomers. In the "core-first" method, a plurifunctional initiator core is first synthesized by reaction of an initiator with a bis-unsaturated monomer (e.g., reaction of *n*-BuLi with divinylbenzne). The plurifunctional initiator core is used to initiate further polymerization. The synthetic advantages and drawbacks of the two methods are summarized in Table 4.

Table 4 Synthesis of Branched Polymers

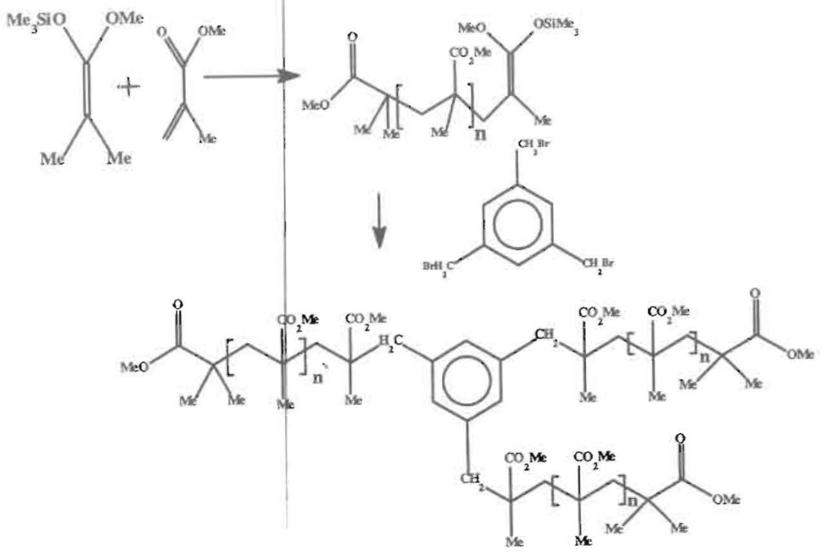
Technique	*Approach*	*Remarks*
Arm-first	Termination by plurifunctional electrophiles	• Functionality determined by electrophilic reagent • Knowledge of precise concentration of chain ends required
	Reinitiation using bisunsaturated monomers	• Functionality cannot be chosen at will • Suitable for $F_n = 5–15$
	—	• Arm-first techniques cannot be used for branch functionalization at outer end
Core-first	Multifunctional initiation from a core of bisunsaturated polymer	• Functionality cannot be chosen at will • Suitable for $F_n = 20–1000$ • Branch ends can be functionalized

Both approaches have been used for the synthesis of star-branched (meth)acrylate polymers using classical "living" anionic polymerization. 1,3,5-bromomethyl benzene has been used for the termination of living anionic chain ends of methacrylate polymers [24]. The low reactivity of enolate chain ends, derived from MMA, especially, at low temperatures makes the nucleophilic substitution reactions somewhat less efficient, leading to less than quantitative coupling. On the contrary, greater success has been obtained with the sterically less hindered enolate derived from *t*-butylacrylate as monomer. Living cores from the reaction of lithium naphthalene with divinylbenzenes were prepared. The lithium chain ends were end-capped with diphenyl ethylene and were used to polymerize *t*-butyl acrylate in the presence of LiCl [25]. A star-branched poly(*t*-butyl acrylate) could be obtained with an average functionality (number of arms per molecule) 22–130. The polymer had broad/multimodal molecular weight distribution. Similarly, a 3-arm star poly(*t*-butylacrylate) was prepared by terminating the living chain end of poly (*t*-butylacrylate) with 1,3,5-triformyl benzene at –80°C in tetrahydrofuran (THF) [26].

GTP, on the other hand, offers good potential for the synthesis of star-and comb-branched polymers. The GTP chain ends are "living" even at temperatures as high as 70°C and, thus, are capable of participating efficiently in branching reactions. Both the "arm-first" and "core-first" approaches have been reported for the synthesis of multiarm star-branched acrylic polymers. However, very few details of experimental conditions and polymer characterization have been reported for star-branched polymers synthesized using the "arm-first" approach.

Treatment of a "living" GTP chain end with 1,3,5-tris(bromomethyl) benzene has been reported to yield a three-arm star poly(methyl methacrylate) (PMMA) [27] ((Scheme 2). However, no experimental methods were reported. Recently, a critical reexamination of this reaction revealed that the termination reaction is less than quantitative. Using MTS as initiator and tetra-*n*-butylammonium bibenzoate (TBABB) as catalyst, the PMMA obtained was found to be a mixture of linear and three-arm star-branched copolymers [28]. This is attributed to the fact that the reaction of the —CH_2Br group with the GTP chain end occurs in a stepwise manner and with every substitution, the reactivity of the remaining CH_2Br group is reduced, leading to less than quantitative conversion to three-arm star polymers. A three-arm heteroarm star-branched polymer via the combined anionic–GTP has been reported (Scheme 3) [29]. However, no details on experimental methods or polymer characterization are described.

Another variant of the "arm-first" method involves preparing the living polymer chain using GTP (polymer A), followed by reacting the living chain end with a multifunctional linking agent, having at least two polymerizable groups (monomer B). This produces a star polymer having arms of polymerized monomer A attached to a crosslinked core of polymerized monomer B. The active group transfer sites in the core can be deactivated by reaction with a proton source. The multifunctional linking agent is typically ethylene glycol dimethacrylate. However, other multifunctional unsaturated monomers such as tetraethyleneglycol dimethacrylate, trimethylol propane trimethacrylate, and 1,4-butylene dimethacrylate can be used.

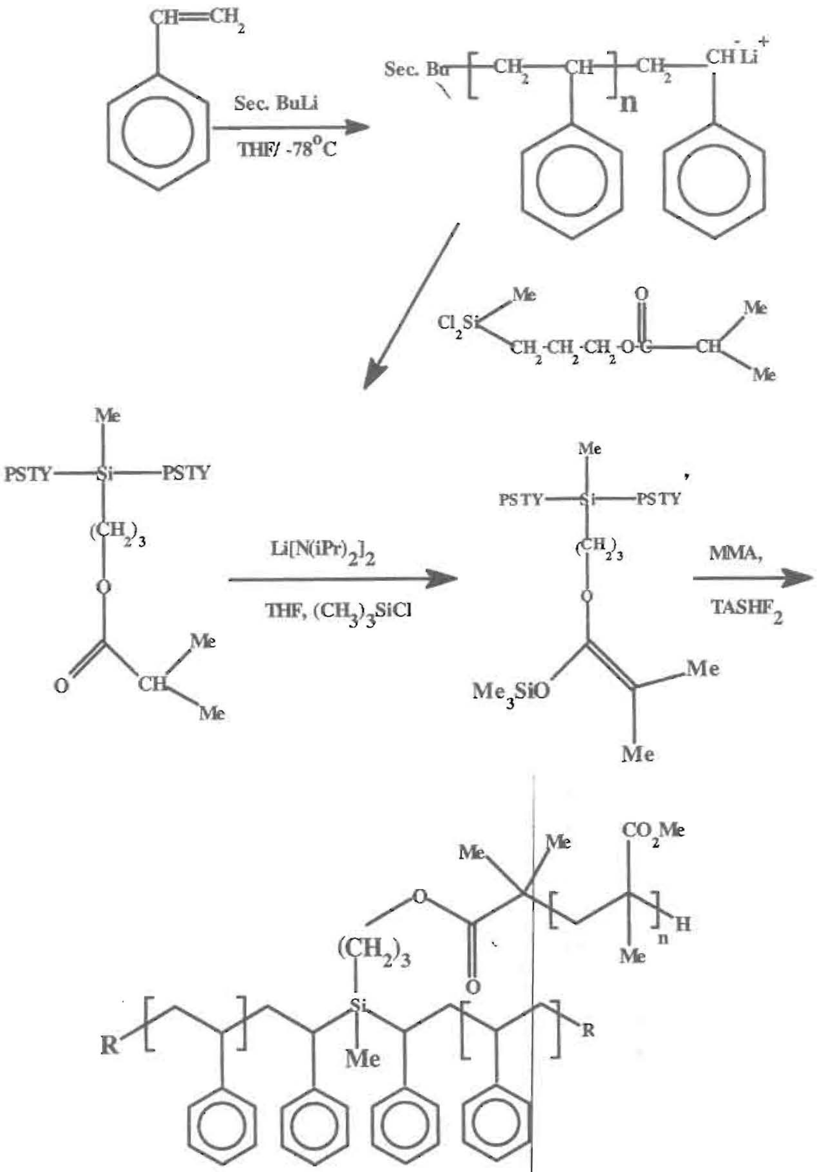


Scheme 2 Three-arm PMMA star.

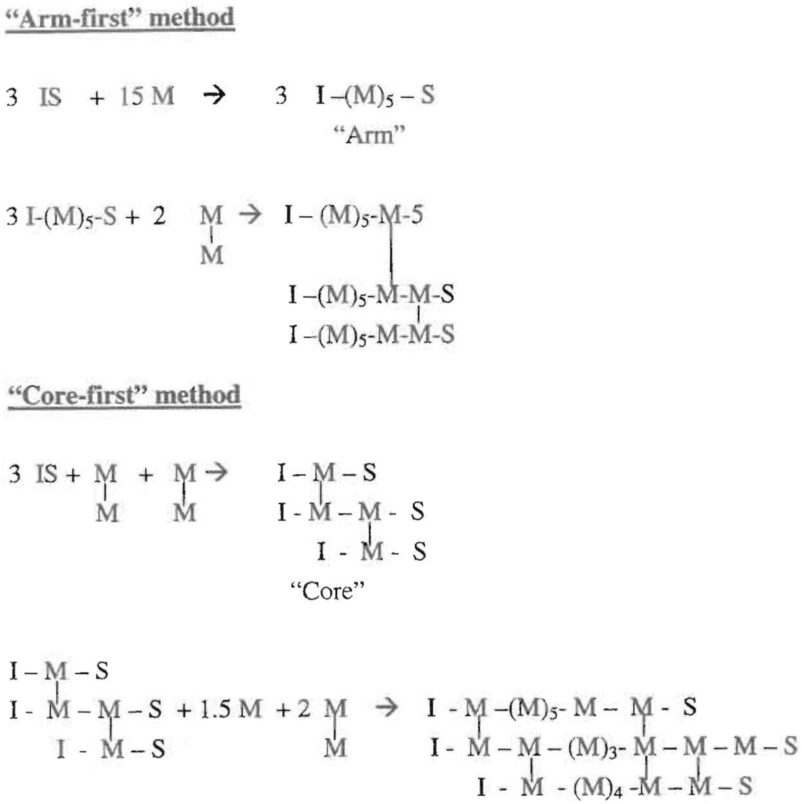
Similarly, one can prepare a "living" core by the reaction of GTP initiator with a multifunctional linking agent (monomer B) having at least two polymerizable groups. The resulting living core is then contacted with a monomer (A) to produce a star polymer having arms of polymerized monomer "A" attached to a crosslinked core of polymerized monomer "B."

These two methods for the synthesis of star-branched polymers are illustrated schematically in Scheme 4. In the formalism shown, each method produces a star of three arms, wherein each arm is made up of five monomer molecules. Thus, the number of arms can be expressed by the relationship:

$$\frac{1}{\frac{[IS]}{[M\text{–}M]}-1}+1$$



Scheme 3 Three-arm hetero star of poly(methyl methacrylate) and poly(styrene).



Scheme 4 Star formation using "arm-first" and "core-first" approach.

where [IS] is the moles of initiator and [M–M] = moles of difunctional monomer.

The size of the arms can be varied by changing the ratio of [M]/[IS]. Long arms are obtained when the [M]/[IS] ratio is large. The number of arms can be varied by changing the ratio of [IS]/[M–M]. If the ratio of [IS]/[M–M] is slightly higher than 1 (say 1.05), then the resulting star will have 21 arms:

$$\left[\frac{1}{(1.05/1.00) - 1} + 1\right]$$

If the ratio of [IS]/[M–M] is equal to or less than 1.00, the preceding equation cannot be used to calculate the number of arms. In such a case, a crosslinked core having a very large number of arms will result. These are called giant stars.

Table 5 Synthesis of Star-Shaped Poly (methyl methacrylate)s by "Arm-First" Method: Some Examples

Initiator	*1-Trimethylsiloxy-1-isobutoxy-2-methylpropene*			*(1-Methoxy-2-methyl 1-propenoxy) trimethyl silane (MTS)*	
Conditions	*1*	*2*	*3*	*4*	*5*
[I], mol	0.07	0.006	0.006	0.00123	0.00028
[MMA], mol	8.5	0.64	1.19	0.056	0.028
[EGDMA], mol	0.27	0.022	0.015	0.00319	0.00168
[I]/[EGDMA]	0.26	0.27	0.40	0.40	0.25
Catalyst	TBA HF_2	TBA HF_2	TBA HF_2	TBABB	TBAmCB
Solvent, g	1200 (glyme)	91 (glyme)	184 (glyme)	THF,25	THF,25
M_w (arm)	18,100	16,600	27,900	6,720	8,827
M_w/M_n (arm)	1.52	—	—	1.20	1.35
M_w (star)	$2.7.00 \times 10^5$	6.3×10^5	4.3×10^5	7.6×10^5	1.998×10^5
N_{arms}	149	38	15	113	23
M_w/M_n (star)	—	—	—	1.80	1.42
Reference	30	30	30	31	32

$TBAHF_2$, tetrabutyl ammonium hydrogen difluoride; TBABB, tetrabutyl ammonium bibenzoate; TBAmCB, tetrabutyl ammonium-*m*-chlorobenzoate.

Some typical examples of synthesis of giant stars are shown in Table 5 [30]. In Examples 4 of Table 5 [31], by varying the reaction conditions, star-branched PMMAs with varying arm lengths of average degree of polymerization between 15 and 150 could be prepared. The number of arms is also dependent on the molecular weight of precursor polymer at constant core-to-arm ratio. In our study, the lag time between completion of arm formation and addition of EGDMA was kept at 2 min to minimize free-arm formation due to premature termination. The polydispersity of the star is broader than the arm. The high polydispersities of the star-branched polymers are not caused by differences in the arm length of the stars but are a result of variation in the number of arms per microgel, that is, the polydispersity of the microgel.

In all the reactions, the addition sequence was as follows. Initially, the desired quantities of solvent, initiator, and catalyst were mixed at room temperature. The desired quantity of MMA was added over a period of 40 min followed by addition of ethylene glycol dimethacrylate over a period of 15 min. The reaction was quenched 30 minutes later. The reaction was accompanied by a significant exotherm.

The synthesis of star-branched polymers was performed with different catalyst concentrations (1.0 and 0.5 mol % based on initiator concentration). When 0.5 mol % of catalyst was used, the star polymer showed a trimodal distribution of molecular weights. However, at 1.0 mol % catalyst a star polymer free of linear arm polymer contamination was obtained.

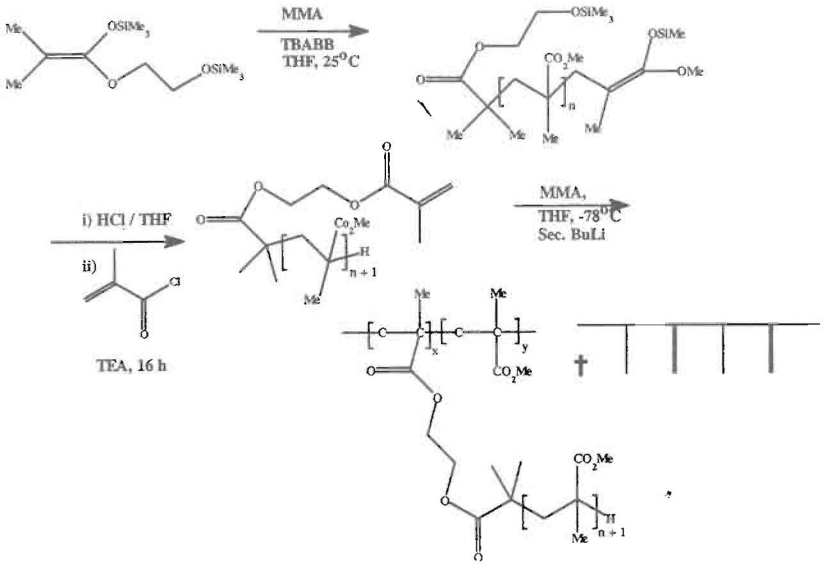
The conditions used for the synthesis of star polymerization of methyl methacrylate has been extended to lauryl methacrylate (LMA). However, the linear living poly(LMA) chain end did not undergo star polymerization with EGDMA. However, when a second dose of catalyst was introduced after the complete homopolymerization of LMA, prior to addition of EGDMA, star formation was found to occur. Poly(LMA) stars with a polydispersity of 1.9 and possessing up to ten arms could be prepared [31].

Haddleton and Crossman have recently reported a more detailed study of methacrylic multiarm star copolymers by GTP [32]. Example 5 in Table 5 is taken from this work. It was shown that the molecular weight of randomly branched PMMA armed star polymers was controlled by (1) the concentration of living arm (P*) in solution prior to addition of EGDMA, (2) the ratio of P* to EGDMA, and (3) dilution of the star polymer core. The molecular weight of star increases linearly with the M_w arm. Increasing monomer-to-solvent ratio (increasing P*) leads to increase in the number of arms per star.

During the synthesis of star polymers, addition of certain silyl esters has been reported to improve conversion and reduce the wt % of unattached arms [33]. These silyl esters, whose pK_a value is equal to or lower than the pK_a value of the catalyst used in the polymerization are believed to enhance the livingness of the chain end. The beneficial use of such "livingness-enhancing agent" in the synthesis of well-defined block copolymers by GTP has been recently reported [34]. The beneficial action of the 'livingness enhancer" is proposed to be the result of the formation of a complex between the silyl ester and the carboxylate anion that ensures maintenance of a low concentration of the "active" species in equilibrium with the "dormant" species (Scheme 5).

The addition of livingness enhancer is reported to improve the efficiency of the star-forming reaction. Addition of trimethyl silyl-3-chlorobenzoate (TMSCB) catalyst results in a 99.7% and 99.0% conversion of EGDMA and MMA. Similarly, when TMSCB was added to a polymerization using tetra-*n*-butylammonium acetate as catalyst, the conversions of MMA and EGDMA were 98.5% and 98% respectively. Furthermore, the wt % of unattached arms was only 21. In the absence of TMSCB, large quantities unattached arms (obtained via premature termination) of living ends were obtained.

A detailed study of the methacrylate star synthesis by GTP has been presented by Simms [35]. The purpose of the study was to define experimental conditions to minimize termination process of the living chain ends and to ensure that the maximum level of living arms could be carried into the core-



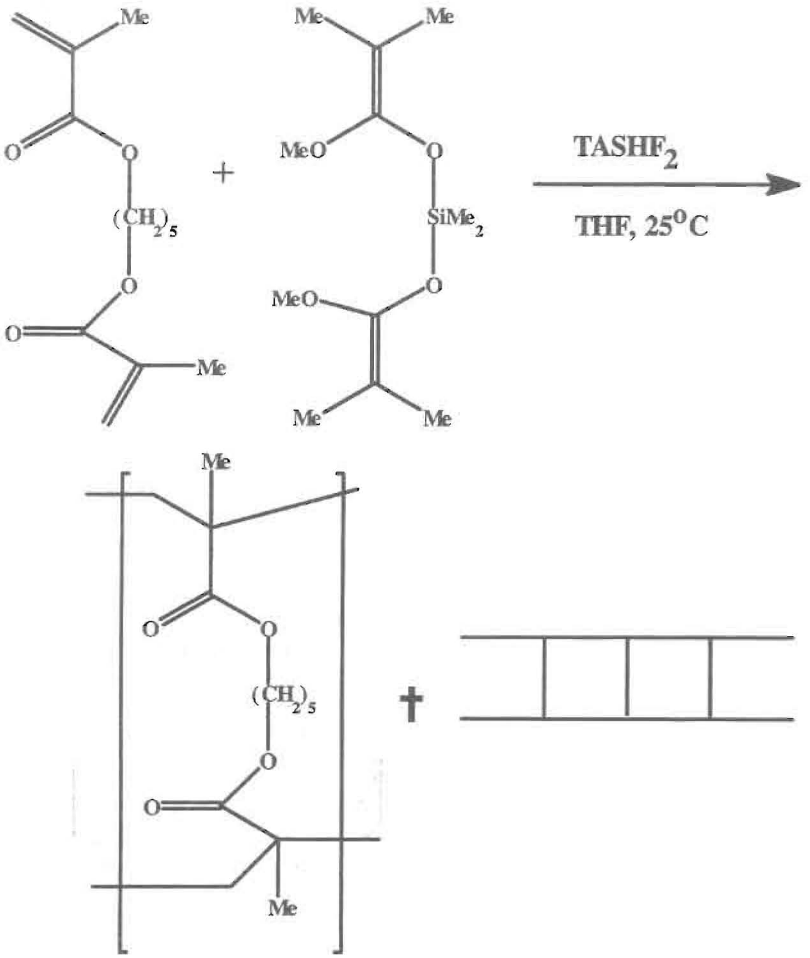
Scheme 7 Comb-shaped poly(methyl methacrylate).

units [40]. Star formation was established by chemically cleaving the arm from the core and determining the M_n of the cleared arm. It was found that the ratio of M_n of star (calculated) to arm (found) was about 4. However, since the gel permeation chromatography (GPC) data on the star polymer was based on an RI detector using linear PMMA as the standard, the determination of exact number of arms based on experimentally found M_n of star was not reliable.

COMB- AND LADDER-SHAPED POLYMERS

Comb-shaped polymers are derived from polymerizing or copolymerizing macromonomers. Macromonomers can be synthesized by a variety of synthetic techniques. Asami and co-workers prepared a methacrylate-terminated polystyrene by anionic polymerization. The macromonomer was then polymerized using GTP [41] to yield an oligomer with a polystyrene backbone and PMMA grafts. McGrath and co-workers prepared a poly(dimethyl siloxane) macromonomer end-capped with a methacrylate group. This macromonomer was polymerized by GTP to yield a comb-shaped polymer with PDMS branches [19].

Witkowski and Bandermann used GTP initiator bearing a styryl group to make PMMA macromonomer with a styryl head group. This was later copolymerized with styrene using free radical initiators [42].



Scheme 8 Ladder-shaped poly(methyl methacrylate).

McGrath and co-workers synthesized a novel all-PMMA comb polymer by a combination of GTP and anionic polymerization (Scheme 7) [19]. The resulting comb had a M_n = 2,48,600, with an average of 14 grafted PMMA chains per molecule. The grafted PMMA chain had a M_n = 6300 and M_w/M_n =

1.11. Additional examples of comb-grafted polymers via GTP have been reported by Heitz and Webster [43], Hertler et al. [44], and Jenkins et al. [45]. A ladder-type polymer can be prepared from GTP using a bis-methacrylate monomer and a difunctional initiator using dilute solutions [46]. If a monofunctional initiator is used, crosslinked polymer is obtained. The ladder polymer had a $M_n = 5100$ and a $M_w/M_n = 1.89$ and was free of gel (Scheme 8). The number of spacer atoms between methacrylate functions is critical for successful synthesis, the optimum being 4 to 7.

CONCLUSIONS

GTP, by virtue of its many desirable features, offers a versatile method for the synthesis of star-branched and comb-branched polymers of (meth)acrylic monomers. (The mechanism and kinetics have been examined by different authors [13] and the living character of the polymerization has been established.) The fact that GTP can tolerate many diverse type of functional groups implies that synthesis of functional stars will be possible. The largest success to date has been with the synthesis of multi-arm stars using an "arm-first" approach and using a difunctional acrylic monomer as the core-forming monomer. Very limited reports are available on the synthesis of well-defined stars with precise numbers of arms. This is due to two factors. First, access to plurifunctional GTP initiators is synthetically difficult. Second, enolates derived from GTP chain ends are unreactive in nucleophilic substitution reactions for the synthesis of star polymers using an "arm-first" approach and terminating the living end using multifunctional electrophilic reagents. Precisely those conditions that make GTP chain ends living, namely, a solvent of low polarity, a weak nucleophilic catalyst, and a high concentration of "dormant" species, renders such nucleophilic displacement difficult and less than quantitative. Additional studies are warranted in this area since GTP appears to be the synthetic method of promise for producing well-defined star-branched polymers of methyl methacrylate.

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Star-Shaped Polymers via Living Cationic Polymerization

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Star-shaped polymers steadily grow into a field of high potentiality by virtue of the unique properties they exhibit both in solution and in bulk. Nanoscale-ordered materials, low-viscosity paints, and thickeners are examples of technological applications that include star polymers. However, the synthesis of well-defined star polymers having a known number of arms with a precise molecular weight and narrow polydispersity is a challenge to the macromolecular engineer. Particularly, it was a major challenge to synthesize stars via cationic polymerizations per se until the discovery of living polymerization of isobutylene and vinyl ethers during the early 1980s. To date, three major synthesis techniques have been described and used for the synthesis of stars: (1) the use of multifunctional linking agents, (2) sequential copolymerization/linking with a divinyl monomer, and (3) use of multifunctional initiators. The use of multifunctional linking agents has been proven effective by anionic techniques for the preparation of a variety of star polymers with a varying number of arms. The detailed description of stars via anionic polymerization is given in other chapters. This chapter mainly focuses on the star polymers via cationic polymerization involving vinyl ethers and isobutylene monomers.