THE SYNTHESIS OF BRANCHED POLY(METHYL METHACRYLATE)

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On the occasion of Professor Wichterle's 80th birthday, we wish to pay tribute to his magnificent example as scientist and gentleman. Without people like him, the Czech Republic would not be a free country today, neither would it have its reputation for research and development, particularly in the field of polymer science.

The synthesis of branched poly(methyl methacrylate) is described. The method used is based on an anionic technique with initiation by enolate ions. Details of product characterization are included.

The development of graft polymers has largely taken place as a consequence of industrial research on surface modification of polymers and, as a result, a vast number of early reports on graft polymerization are to be found in the form of patents[1]: Most of the literature deals with graft reactions on natural polymers and fibers, such as rubber, cotton, cellulose, etc. Radiation techniques have provided a popular route to graft polymers but, as with any method based on free radicals, the products are always contaminated with homopolymers.

Apart from being difficult to prepare, pure graft polymers are also not easy to characterize, for thorough characterization should provide information on molecular weights and polydispersities for both the backbone and the grafts, together with the number of grafts per molecule, and the manner of distribution of the grafted segments along the backbone chain. Characterization of graft polymers to such an extent still remains a challenge, nevertheless considerable progress has been made in the last two decades concerning the preparation of polymers with controlled architecture of this and other types.

The term "branched polymers" refers to graft polymers in which the backbone and grafts comprise the same chemical species. Not surprisingly, synthetic routes for producing branched polymers are essentially the same as those employed in graft poly-

merization. These routes are generally classified as being based on: grafting *onto*; grafting *from*; or the incorporation of *macromonomers*. Before describing the synthetic methods available for the production of branched polymers, a distinction should be made between two particular types. These are star-shaped polymers, in which three or more branches spread radially from a common centre (the synthesis and properties of which have been reviewed elsewhere[2]) and comb-shaped polymers which contain side chains attached to each monomeric unit; a review of the structure and properties of comb polymers has been published[3]. This latter definition is somewhat arbitrary and, may be confusing as, because of their structural similarity, it is common to refer to graft polymers as comb-shaped.

In grafting *onto* a backbone growing polymer chains are made to interact with a preformed backbone containing reactive sites, usually at irregular intervals. The grafting can take place by different mechanisms, such as a transfer reaction, if the polymerization proceeds via free radicals, or by mutual neutralization, if the chain end and the reactive sites on the backbone have opposite polarities.

Thus, graft polymers result when poly(methyl methacrylate) (PMMA) is added to anionically-initiated polystyrene, though restricted accessibility causes only a small fraction of the available ester groups to react[4]. Similarly, a backbone can be prepared by free-radical copolymerization of styrene with about ten mole per cent methyl methacrylate (MMA), and the ester functions of this copolymer used as electrophile deactivators for anionically-initiated polystyrene[5]. Both the examples mentioned result to some extent in the formation of homopolymer, which must be separated by fractionation. As a route to prepare graft polymers, there is a serious disadvantage in using ester functions as electrophilic deactivators, because grafts and backbone remain linked by carbonyl groups; these are sensitive to photochemical oxidation, which leads to chain scission and degradation.

In grafting *from* a backbone, reactive groups appended along a polymer chain are activated, so that in the presence of monomer they are able to initiate polymerization, and produce grafts from the backbone. Again, initiation can take place either by free-radical or ionic species. The reactive groups are introduced in the backbone usually by copolymerization with a suitable monomer, by chemical reactions on a preformed polymer, or both. It is generally expected that the reactive groups will be evenly distributed along the polymer chain, but this depends on the reactivity ratios of the comonomers.

Macromonomers are oligomers or polymers that carry a polymerizable group at one end, and which can be used as preformed branches in the preparation of graft polymers. A typical example of this type of molecule is polystyrene containing a methacryloyl group at one end, prepared from living polystyrene anions[6]. Radical polymerization can also be used to prepare macromonomers, but control of chain-end functionality and average chain-length and its distribution is best afforded by living systems. The advent

of macromonomers represented a step towards the preparation of true graft polymers. When a macromonomer is copolymerized with, say, MMA in a reaction initiated by enolate ions derived from 1-methoxy-2-methyl-1-trimethylsilyloxypropene (MTS)[7], the expected graft polymer is obtained with very little homopolymer formation[8]. The use of macromonomers in the preparation of graft polymers with PMMA branches is relatively recent. Because macromonomers are prepared preferably by living polymerization, their application to MMA often demands the synthesis of special initiators.

EXPERIMENTAL

Monomers

2-(Isobutyryloxy)ethyl Methacrylate (IBEM)

To a solution of 2-hydroxyethyl methacrylate (13.0 g, 0.1 mol) in dry benzene (50 ml), pyridine (8.0 ml, 0.1 mol) was added under stirring and the mixture was cooled to 0 °C. Isobutyryl chloride (11.6 g, 0.11 mol; 10% excess) was added through the droppping funnel at a slow rate, so that the temperature was kept as low as possible. A white solid started to precipitate immediately. After addition was complete, the mixture was kept stirring at 0 °C for 3 h. Benzene (30 ml) was then introduced to the reaction mixture in order to facilitate filtration of the pyridine hydrochloride by-product. The solution was collected and the solvent removed on a rotatory evaporator. The pale yellow oil which remained was distilled at reduced pressure to give a colourless liquid. Yield 18.7 g (90%), b.p. 64 –65 °C/40 Pa. ^{1}H NMR spectrum ($CDCl_3$; δ/ppm): 6.13 s, 1 H; 5.60 m, 1 H; 4.35 m, 4 H; 2.70 m, 1 H; 1.95 s, 3 H; 1.18 d, 6 H. ^{13}C NMR spectrum ($CDCl_3$; δ/ppm): 176.73 ($COCHMe_2$), 166.97 ($OCO(CH_2)_2$), 135.87 (=CMeCO), 125.84 (CH_2=CMe), 62.32 ($OCOCH_2CH_2$), 61.77 ($CH_2CH_2OCOCHMe_2$), 33.79 ($CHMe_2$), 18.78 (CH_2=CMe), 18.12 ($CHMe_2$). IR spectrum (NaCl disc, neat; ν_{max}/cm^{-1}): 1 724 (C=O); 1 637 (C=C).

Diethyl Methacryloylmalonate (DEMM)

In a 250 ml three-necked flask equipped with a dropping funnel, a reflux condenser attached to a $CaCl_2$ drying tube, and a magnetic bar were placed magnesium turnings (2.5 g, 0.1 mol), absolute ethanol (3 ml), CCl_4 (0.1 ml), and 4 ml of a mixture of diethyl malonate (16 ml, 0.2 mol) in EtOH (8 ml). The reaction started shortly afterwards, and the mixture was cooled in an ice-bath before the remaining diethyl malonate solution was added slowly. A white crystalline cake was formed and, when reaction seemed to have stopped, ether (30 ml, Na dried) was added slowly and, after a gentle heating had been provided (30 °C), the reaction set in again. When the Mg had completely disappeared, EtOH and ether were distilled off, first at atmospheric pressure and then at reduced pressure. Dry benzene (60 ml) was added to the white crystalline solid, which was subsequently removed by distillation at atmospheric pressure and then reduce pressure. The residue was diluted in ether (50 ml) and transferred to a dropping funnel, to be used in the next step.

In a 250 ml three-necked flask equipped with a thermometer, a Suba seal, a magnetic bar, and a dropping funnel containing the ethoxymagnesium salt solution, were placed dry benzene (30 ml) and methacryloyl chloride (12 ml, 0.12 mol). This solution was cooled down to –10 °C, followed by the slow addition of the malonate derivative solution through the dropping funnel, during which time the solution turned pale yellow. As the malonate derivative solution was added, the reaction mixture divided into two phases. Addition was controlled, so that the temperature was kept under 0 °C;

manual stirring was necessary, since the lower phase was extremely viscous. After addition was complete, the mixture was allowed to stand overnight and come to room temperature. It assumed a strong yellow colour and the lower phase solidified as a button in the bottom of the flask. The flask was cooled in an ice-bath, and two portions of 5 ml concentrated H_2SO_4 in ice-water were added to the mixture, the reaction mass being slowly dissolved. The aqueous phase was washed with 20 ml ether, and the extract together with the organic phase was neutralized with a concentrated $NaHCO_3$ solution, and washed once with distilled water. The ether solution was treated with anhydrous Na_2SO_4 for drying during half a day. Na_2SO_4 was removed by filtration and solvents were eliminated at water-pump pressure from a water bath held at about 50 °C. The remaining yellowish liquid was distilled under vacuum, resulting in a colourless product. Yield 10.08 g (22%, based on diethyl malonate). ^{1}H NMR spectrum ($CDCl_3$; δ/ppm): 5.92 s, 1 H; 5.88 s, 1 H; 4.20 q, 4 H; 1.90 s, 3 H; 1.25 t, 6 H. ^{13}C NMR spectrum ($CDCl_3$; δ/ppm): 190.9 (CH_2=CMeCO), 165.2 (EtCOO), 144.0 (CH_2=CMe), 126.9 (CH_2=CMe), 62.3 (OCH_2CH_3), 60.9 (CH), 17.5 (CH_2=CMe), 14.0 (CH_2CH_3).

Backbones

Poly{methyl methacrylate-stat-[2-(isobutyryloxy)ethyl methacrylate]}

By radical polymerization. The desired amount of MMA and freshly distilled IBEM were charged to a three-necked round-bottomed flask, equipped with a condenser, an N_2 inlet, a magnetic bar and a Suba seal, and containing dry tetrahydrofuran (THF). The mixture was stirred under N_2 for a few minutes prior to addition of a small amount of azobisisobutyronitrile (AIBN) dissolved in dry THF, and the flask containing the reaction mixture was placed in a thermostat at 60 °C. It was left stirring for some time (usually 4 h) and subsequently poured into an excess of MeOH, to precipitate the polymer. The solid recovered was purified by twice dissolving in THF and precipitating from MeOH. The polymer was finally dried under vacuum. Polymerization times of just about 60 min were maintained for the reactivity ratio experiments, in order to keep conversions down, and the concentration of AIBN was kept constant throughout the monomer feed ratio.

By group-transfer polymerization (GTP). The desired amounts of MMA, freshly distilled IBEM and THF were placed in a three-necked flask and the initiator MTS was added, followed by a solution of the catalyst tris(dimethylamino)sulfonium bifluoride ($TASHF_2$) in acetonitrile. The mixture was left stirring for several days at room temperature, and a few drops of MeOH were added to terminate the polymerization; thereafter it was poured into an excess of petroleum ether to precipitate the polymer. The white polymer was purified by twice dissolving in THF and precipitating from petroleum ether, and drying under vacuum. In a variation of the above procedure, a mixture of MMA and IBEM kept under N_2 was added, via a double-tipped needle (cannula), to a solution of MTS and $TASHF_2$ in THF. After addition was complete, the mixture was left stirring at room temperature for several days, followed by work-up as described in the previous paragraph.

Benzoylation of Poly{[methyl methacrylate-stat-[2-(isobutyryloxy)ethyl methacrylate]}

First, a solution of lithium diisopropylamide (LDA) in THF was prepared by treating the appropriate amount of diisopropylamine with 1.55 M BuLi in hexane at 0 °C. A 100 ml three-necked flask equipped with a thermocouple was charged with 0.1 M LDA solution (20 ml) in THF, and cooled to −75 °C. Then a solution of backbone (1.2 g, 0.002 mol IBEM units) in THF (50 ml) was added via cannula, and the mixture was left stirring for a period of 15 min., after which benzoyl chloride (0.5 ml, 0.004 mol) was added from a syringe. Reaction was allowed to proceed for one hour, before warming up to room temperature, and the LiCl precipitate was removed by filtration. The backbone,

now having benzoyl groups attached to its IBEM units, was recovered by precipitating from MeOH. It was purified by twice dissolving in THF, precipitating in MeOH, and drying under vacuum.

Poly(methyl methacrylate-stat-diethyl methacryloylmalonate)

A 50 ml dry ampoule was charged with MMA (2.8 g, 0.028 mol), DEMM (3.35 g, 0.014 mol) and AIBN (0.05 g). The mixture was degassed by a sequence of freeze-thaw cycles, and the ampoule was sealed, before being placed in a thermostat at 70 °C. After four hours, the ampoule was removed from the thermostat, opened, and the viscous product diluted with dichloromethane and poured into MeOH. The polymer that precipitated was purified by twice dissolving in CH_2Cl_2, precipitating into MeOH and drying under vacuum. Yield: 1.82 g (30%). ^{1}H NMR spectrum: 9% DEMM units.

Branched Polymers

Poly[(methyl methacrylate)-graft-(methyl methacrylate)]

By group-transfer polymerization. To LDA solution a calculated amount of backbone dissolved in THF was added; equimolar amounts of LDA and IBEM should be present. Subsequently, a small excess of chlorotrimethylsilane (CTMS) was added, and the mixture was stirred for 30 min at 0 °C and 1 h at room temperature. The white precipitate of LiCl was removed by filtration under nitrogen, with solvents and excess reagents being pumped off afterwards. The activated backbone was dissolved in freshly distilled THF, and the required amount of $TASHF_2$ solution was added. The mixture was stirred under N_2 for some time before monomer was added dropwise, and the reaction was left to proceed for several hours, prior to addition of a few drops of MeOH. The solution was poured into an excess of MeOH to precipitate the polymer, which was purified by redissolving in THF and reprecipitating from MeOH, and dried under vacuum.

By anionic polymerization. For this polymerization, we have employed the same procedure described above, except that no treatment with CTMS was used, and the backbone activated with LDA was cooled to −75 °C before monomer was added dropwise. Polymerization was terminated with MeOH, and the polymer was isolated and purified by the usual work-up.

Other Polymers

Poly(methyl methacrylate) by Anionic Polymerization

In order to check if LDA was able to initiate the polymerization of MMA and to demonstrate the importance of using the proper amount of LDA to avoid homopolymer formation during the grafting process, a reaction between these two compounds was carried out. A 100 ml three-necked flask equipped with a thermocouple, a nitrogen inlet, a Suba seal and a magnetic bar, was charged with 0.14 M LDA solution (20 ml) in THF, and cooled to −75 °C by means of dry ice-acetone slush. Then MMA (5.6 g, 0.056 mol) was added via cannula, at such a rate that the temperature did not increase beyond −72 °C. When addition was complete, the reaction was left stirring for about two hours, before a few drops of MeOH were added to terminate the polymerization. The solution was poured into an excess of petroleum ether, the polymer being recovered by filtration and dried under vacuum. Yield: 4.85 g (87%).

RESULTS AND DISCUSSION

Preparation of Backbones

We set out to prepare branched polymers of methyl methacrylate using the "grafting from" approach, and the first step towards this aim was to produce a backbone composed principally of MMA but including a chosen small amount of 2-(isobutyryloxy)ethyl methacrylate (IBEM) units. The monomer IBEM was synthesized by an esterification reaction between 2-hydroxyethyl methacrylate and isobutyryl chloride, and the method of Ainsworth et al.[9] was used to convert the IBEM units of the polymer into a silyl ketene acetal, from which the initiation of the polymerization of MMA was attempted by successive treatments with lithium diisopropylamide and chlorotrimethylsilane.

Poly(MMA-*stat*-IBEM) backbones were prepared by radical polymerization initiated with AIBN at 60 °C, and the resulting copolymers were analysed by NMR spectroscopy, in order to calculate their molar compositions. The contents of MMA and IBEM were estimated from the integrals of the broad singlet at δ 3.60 ppm, characteristic of the methoxy group, and of the doublet at δ 1.20 ppm from the isobutyryloxy group; the IBEM content was further checked by reference of the integrals of the signals at 4.2 – 4.0 ppm, characteristic of the $-OCH_2CH_2O-$ unit. In Table I, the monomer feed and copolymer composition are shown for a series of experiments covering a wide range of monomer feed compositions. In order to determine the reactivity ratios, the conversions of these experiments were kept at a low value around 7%, and the results were treated according to the Kelen–Tüdös procedure[10]. It is necessary to assign a value[10] to α, an arbitrary constant often put equal to $(F_M F_m)^{1/2}$, F_M and F_m being the maximum and minimum values of F obtained in the series of experiments (cf. Table I). Thus, using $\alpha = 1.95$, the experimental data could be represented by a straight line (Fig. 1), from which the reactivity ratios were found to be $r_{MMA} = 0.96$ and $r_{IBEM} = 0.64$. The IBEM

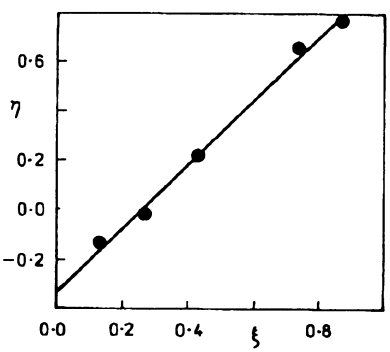

FIG. 1
Kelen–Tüdös plot[10] for the radical copolymerization of MMA and IBEM

radical, in particular, shows a preference for reaction with the partner monomer rather than with its own parent, possibly due to steric effects. These values of reactivity ratios indicate that the IBEM units will be distributed fairly evenly along the polymer chain. Several backbones were prepared by radical polymerization using different amounts of IBEM in the monomer feed, their molecular weights being estimated by size-exclusion chromatography (SEC), as shown in Table II for a few examples. Conversions were kept between 30 and 60% to avoid too broad a distribution of molecular weights. Because both monomers have the same elemental composition, elemental analysis could not be used to estimate the IBEM content in the copolymers. It could, however, be used to evaluate the purity of the backbones, and all of them indicated carbon and hydrogen contents close to the expected values, within experimental error.

As IBEM is a methacrylate, and therefore subject to initiation of polymerization by silyl ketene acetals, some backbones were prepared by copolymerization of MMA and IBEM initiated by MTS. Polymerizations were carried out at room temperature with tris(dimethylamino)sulfonium bifluoride as catalyst. Backbones prepared in this way were also characterized by SEC, and the IBEM contents were calculated from NMR integrals. Copolymerization of MMA and IBEM initiated by MTS was very slow by comparison with the homopolymerization of MMA under identical conditions. After the initiator and catalyst had been added to a solution of the monomers, it took at least two days before any polymerization was apparent, and no variation in temperature was observed; this is in sharp contrast to the homopolymerization of MMA, which is fast and exothermic. It is very difficult to keep the necessary conditions for living polymerization in such circumstances, and this was reflected by the surprisingly high polydis-

TABLE I
Radical copolymerization of methyl methacrylate (MMA) and 2-(isobutyryloxy)ethyl methacrylate (IBEM)

Experiment No.	Mole ratio MMA/IBEM		$G = x(y - 1)/y$	$F = x^2/y$
	x^a	y^b		
1	12.89	12.33	11.85	13.48
2	5.67	6.14	4.74	5.23
3	1.66	1.87	0.77	1.48
4	0.82	0.94	−0.06	0.72
5	0.40	0.58	−0.29	0.28

[a] In monomer feed; [b] in the copolymer.

persity encountered, indicating that termination occurred to some extent during polymerization.

Grafting by Group-Transfer Polymerization

Following our usual synthetic route[11], poly(MMA-*stat*-IBEM) backbones were treated with lithium diisopropylamide (LDA) and chlorotrimethylsilane (CTMS); subsequently, selected amounts of MMA and $TASHF_2$ were added to the activated backbone to grow PMMA branches from the silyl ketene acetal units. As an example, MMA was reacted this way to 20% conversion, grafting from the backbone B4 (Table II), which contains 18 wt.% of IBEM units. The SEC estimates of molecular weights are shown in Table II. The shift of the peak towards a higher value of molecular weight, however moderate, is better visualized when the SEC traces of both the backbone and branched polymers are overlayed (Fig. 2). One would not expect a substantial increase in molecular weight or variation in the polydispersity index, due to the low conversion achieved; yet it seems that a greater number of short branches rather than a few long ones were formed, as the width of the peaks did not change dramatically.

Since the molecular weights were calculated from elution volumes by using SEC calibration obtained from polystyrene standards, the results in Table II and Figs 2 and 3, especially those assumed for branched structures, have only indicative value because the relation between molecular weight and hydrodynamic volume is not valid any more.

Although the grafting of B4 (Table II) established the feasibility of preparing branched polymers following the proposed route, the results obtained from most of the attempts were rather disappointing. Despite the fact that homopolymer formation was thought to be unlikely to happen, due to the nature of the polymerization mechanism employed, a shoulder in the SEC trace of many branched polymers indicated the

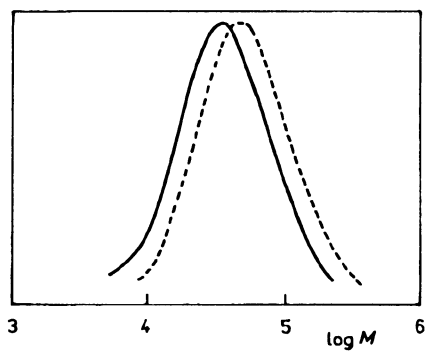

FIG. 2
SEC traces of backbone B4 (——), and corresponding branched polymer, initiated by silyl ketene acetal and prepared by group-transfer polymerization (– – –)

presence of low-molecular-weight polymer. In addition, molecular weights determined by light scattering (LS), for samples which were expected to be branched, were actually lower than for the backbones from which they originated, or seemed to be virtually unchanged. This also supports the view that a homopolymer unattached to the backbones was formed.

The same synthetic pathway has been applied successfully to the grafting of MMA from a backbone of styrene and IBEM[11]. A similar approach has also been used to graft MMA from crosslinked polystyrene, containing some amount of chloromethyl groups, which could be converted to silyl ketene acetal[12], and minute amount of PMMA homopolymer was reported to be formed. The basic difference between our polymer system and those just mentioned was the presence of MMA, rather than styrene, in the backbone. The presence of a large quantity of methyl methacrylate residues may have interfered with the conversion of IBEM units into silyl ketene acetal groups in ways we did not anticipate and for which we have not found a convincing explanation.

TABLE II
Characteristics of MMA-IBEM backbones and derived graft MMA polymers

Copolymer	IBEM content mole %	Method of preparation backbone/ grafts	$M_w \cdot 10^{-4}$		$M_n \cdot 10^{-4}$	M_w/M_n
			SEC	LS	SEC	SEC
B2	3.5	RP	–	–	4.2	1.7
B3	6.5	RP	–	–	2.9	1.7
B4	10	RP	–	–	2.2	2.1
B4 grafted	–	RP/GTP	6.4	–	2.8	2.2
B8	23	RP	8.2	8	4.6	1.8
B8 grafted	–	RP/A	1 900	464	110	1.7
B10	26	RP	9.1	–	5.4	1.6
B11	–	GTP	11.8	18	5.8	2.0
B11 grafted	–	GTP/A	–	58	–	13.8
	–	GTP/A	–	81	–	3.6
	–	GTP/A	–	280	–	6.4
B12	–	GTP	23.3	18	12.5	1.9
B12 grafted	–	GTP/A	–	297	–	9.4
B15	–	GTP	22.0	27	10.5	2.1
B15 grafted	–	GTP/A	–	472	–	10.2

Method of preparation: RP radical polymerization, GTP group-transfer polymerization, A anionic polymerization

Grafting by Anionic Polymerization

A somewhat different approach towards the synthesis of branched polymers was investigated, initiating the grafting reaction with enolate anions formed by treating the backbone with the lithium base but without the subsequent treatment with CTMS. Since the step involving silylation of the lithium enolate was omitted, and monomer was added to the backbones treated with LDA, there was no need of added catalyst, and this was an attractive feature of this approach. As a general procedure, a calculated amount of backbone dissolved in tetrahydrofuran (THF) was treated with LDA solution at 0 °C, IBEM units and LDA being present in stoichiometric quantities.

In branching reaction, gel formation was observed in many experiments. This can clearly be associated with the initiator concentration; thus, the initiator concentration should be lower than 10^{-2} mol l^{-1} to prevent gel formation but it was found that, when the initiator concentration is as low as 10^{-3} mol l^{-1}, no reaction was observed, even if LDA was kept in contact with the backbone for extended periods of time. Gel formation is most likely to result from intermolecular reactions involving the attack of the propagating branches on the ester groups of another backbone chain. Reaction between two propagating chains can also be envisaged, as well as the corresponding intramolecular process. These reactions are related to the backbiting condensation observed in the homopolymerization of MMA[13].

A simple experiment was carried out to demonstrate whether the IBEM units were being activated. A backbone containing 32.8 wt.% IBEM units was treated with LDA at 0 °C in THF and, instead of adding MMA, the Li enolates were quenched with an excess of benzoyl chloride. The NMR spectrum of the capped backbone shows the presence of aromatic protons and, at the same time, indicates a sharp decrease of intensity for the doublet at δ 1.20 ppm, corresponding to the isobutyryloxy group from

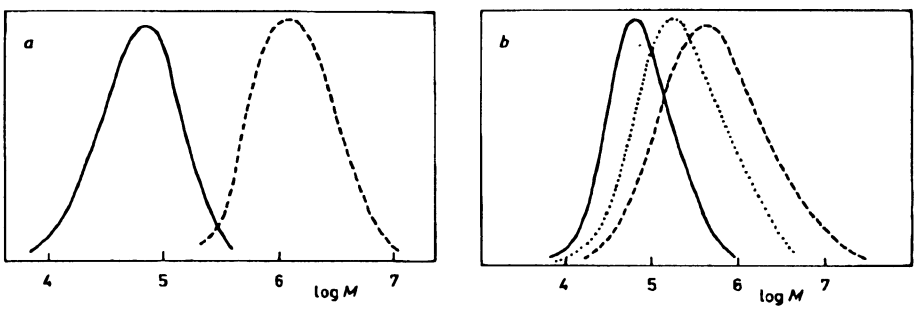

FIG. 3

SEC traces of two types of backbone and their corresponding branched polymers, initiated by lithium enolate and prepared by anionic mechanism. *a* backbone B8 (——), branched polymer (– – –); *b* backbone B11 (——), branched polymers (– – –, · · · ·)

IBEM. Rather than suggesting that the coupling reaction was not efficient, the presence of unchanged IBEM units in the capped backbone is probably an indication that the amount of LDA used was not enough to activate all the sites available. Since the IBEM content was calculated from the integral of the doublet at δ 1.20 ppm, situated amidst many other signals, it may have been underestimated. In spite of that, we did not attempt to use an excess of LDA to bring about complete activation of the backbone, for this would inevitably lead to homopolymer formation, defeating the objective of preparing true branched polymers.

Backbones and their derivative branched polymers were characterized by SEC and LS in order to establish the pure graft nature of the products. Although the SEC traces were unimodal, there was a systematic broadening of the peaks, caused by grafting process. This indicates that a wide range of branch lengths or numbers of grafts per backbone must exist in the grafted material. SEC traces of backbone and derived branched polymers are shown in Fig. 3 for two different types of backbone. The increase in hydrodynamic volume distribution on grafting, and consequently in the average molecular size, can clearly be inferred, and there is no evidence for contamination by ungrafted parent backbone.

The absolute molecular weights determined by light scattering for pairs of backbone and branched polymers are summarized in Table II. LS determinations, together with the results obtained by SEC analyses, support our view that true graft polymers can be prepared by enolate initiation.

Recently, acrylates and methacrylates have been shown to polymerize by a living mechanism at room temperature, when certain metal-free carbanion salts are used as initiators[14]. These initiators are prepared, for instance, by deprotonation of a diethyl malonate derivative with tetrabutylammonium hydroxide, and the ammonium methanide formed initiates the polymerization. Tetrabutylammonium salts of diethyl malonate derivatives have been used as initiators for the polymerizations of methyl acrylate and acrylonitrile[15,16]. In our attempt to prepare branched polymers of MMA using a similar initiating system, we synthesised the monomer diethyl methacryloylmalonate (DEMM), and prepared a backbone by radical copolymerization of DEMM and MMA, containing 9 mole % of DEMM. The monomer DEMM was synthesised by treating the ethoxymagnesium salt of diethyl malonate with methacryloyl chloride[17]. It is reasonable to suppose that a copolymer of DEMM and MMA could be treated with $Bu_4N^+OH^-$ in order to create initiation sites for the polymerization of MMA or other monomers, and form branched or graft polymers; we hope to test this method in the near future.

CONCLUSIONS

We have prepared backbones by the copolymerization of MMA and IBEM, and our initial intention was to convert the isobutyryloxy groups of these backbones into silyl

enolates, which could subsequently be used to grow branches of MMA. Although this approach has been used successfully to prepare graft polymers of MMA on a backbone of polystyrene[11], problems were encountered using the backbones based on MMA. Nevertheless, the isobutyryloxy groups could be converted to lithium enolates, and these were able to initiate the polymerization of MMA to produce branched polymers.

In our approach, we preferred to obtain a backbone with reactive groups along the chain as a first step, and then carry out the chemical transformations to obtain the polymeric silyl ketene acetal, rather than prepare the corresponding monomer containing the silyl ketene acetal and then copolymerize it with MMA. In doing so, we expected to avoid unnecessary manipulations of the sensitive silyl ketene acetal; since we were unable to prepare the branched polymers as initially intended, this second option could be attempted in future work. Thus, IBEM could be converted into a silyl ketene acetal, and radical copolymerization with MMA should then result in the polymeric silyl ketene acetal; a further portion of MMA together with a suitable catalyst would be expected to form the branched polymer. We note that graft polymers on a backbone of polystyrene have been prepared by a similar synthetic route[18].

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