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Recent Progress in the Preparation of Functional Methacrylate Polymers

F. P. Boettcher[a]
[a] Central Research and Development Department Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware

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Recent Progress in the Preparation of Functional Methacrylate Polymers

F. P. BOETTCHER

Central Research and Development Department*
Experimental Station
E. I. du Pont de Nemours and Company
Wilmington, Delaware 19898

ABSTRACT

Application of anionic polymerization and group transfer polymerization to the synthesis of methacrylate polymers with one or two functional endgroups and with functional groups in the side chain is described. Success in the preparation of end-functional polymers depends largely on the absence of chain transfer and chain termination reactions. The higher stability of living chains in group transfer polymerization at temperatures as high as 100°C makes it the preferred route to functional polymers.

In the last two decades, block and graft copolymers have found increasing use not only as elastomers but also as compatibilizers, adhesives and components of high performance finishes. As a result, there has been growing emphasis on new synthetic methods for the preparation of well characterized polymers with functional, i.e., reactive, endgroups which could serve as building blocks for copolymers of predetermined architecture. Condensation polymerization is

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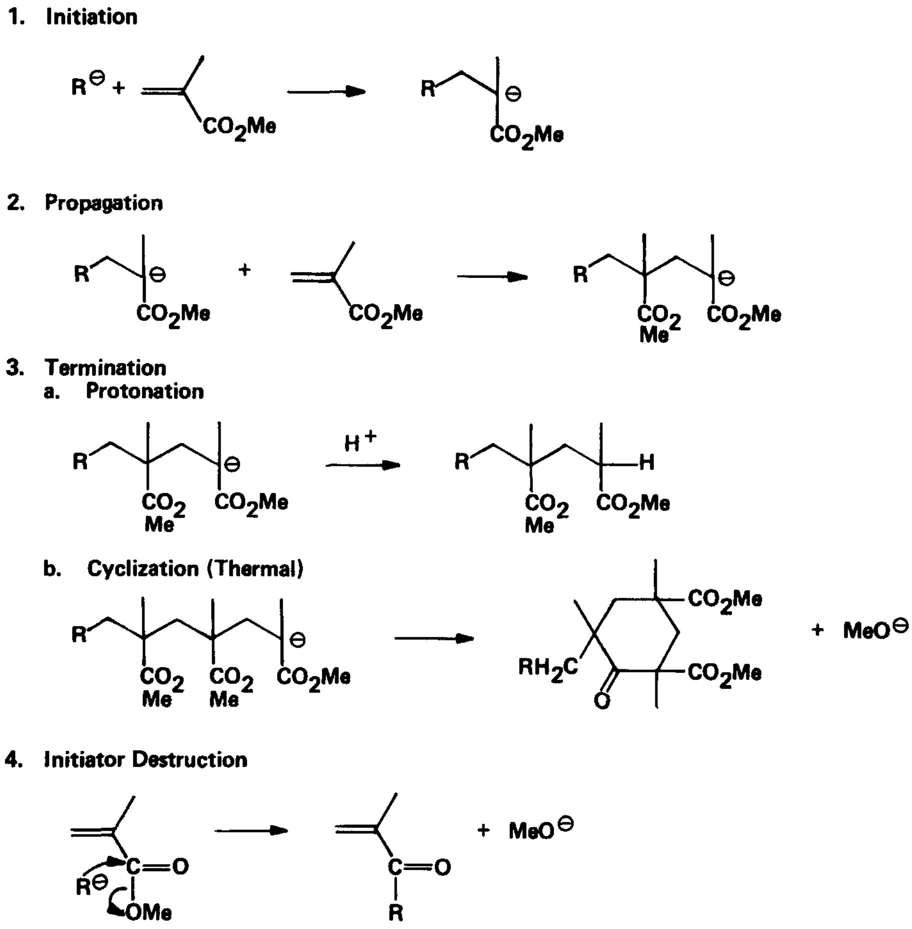
widely used for the preparation of functional blocks but has major disadvantages: for example, it leads to polymers of broad molecular weight distribution and hydrolytically unstable backbone linkages. Free radical polymerization is totally unsuited for this purpose because chain transfer and random termination reactions prevent control over the identity of either chain end. Living ionic polymerizations, on the other hand, are uniquely suited for the preparation of functional blocks. In the ideal case, chain transfer and unwanted termination reactions are absent and polymers with controlled molecular weight, dispersity of one and precisely defined endgroups are formed. Examples of ionic polymerizations with living character are the cationic polymerization of isobutylene [1] and N-substituted aziridines [2], and the anionic polymerization of styrene [3], butadiene [4], and methyl methacrylate [5]. While anionic polymerization of styrene and butadiene has been carried out commercially for some time, anionic polymerization of methacrylates is not yet practiced on a large scale, presumably because it is difficult to avoid side reactions even at very low temperatures.

Anionic polymerization of methacrylate esters with, e.g., fluorenyllithium or naphthalene sodium, is truly living if monomer and solvent meet stringent purity criteria and the temperature is maintained at -75°C. (Scheme I) Termination can occur by protonation or by thermally induced cyclization of the growing end as shown by Goode and co-workers [6]. Initiator destruction by reaction with the ester group is another possible side reaction, but this affects only molecular weight and not molecular weight distribution or chain functionality.

The most convenient and dependable initiator, in recent work of Du Pont scientists [7, 8], was 1,1-diphenylhexyllithium (DPHL), probably first used by Wiles and Bywater [9]. It is obtained in quantitative yield by addition of n-butyllithium to 1,1-diphenylethylene at room temperature. The preferred solvent is tetrahydrofuran. After cooling to -78°C, monomer addition is started; solution color changes from deep red to yellow when the first mole of monomer has been added.

Initiators with a masked functionality were used to make monofunctional polymers and difunctional, i.e., telechelic, polymers [7, 8]. The acetal obtained from 3-chloropropanol and ethyl vinyl ether was reacted with lithium and then with 1,1-diphenylethylene to prepare an initiator with a masked hydroxyl group (Scheme II). Polymerization of methyl methacrylate with this initiator gave, after hydrolysis, monohydroxy polymer. Molecular weights were as high as 50,000 and could be controlled by changing initiator concentration; dispersity was below 1.2. Coupling of the living polymer with, e.g., α,ω-dibromo-p-xylene, led to the corresponding dihydroxy polymers; polyfunctional coupling agents gave star polymers (Scheme III).

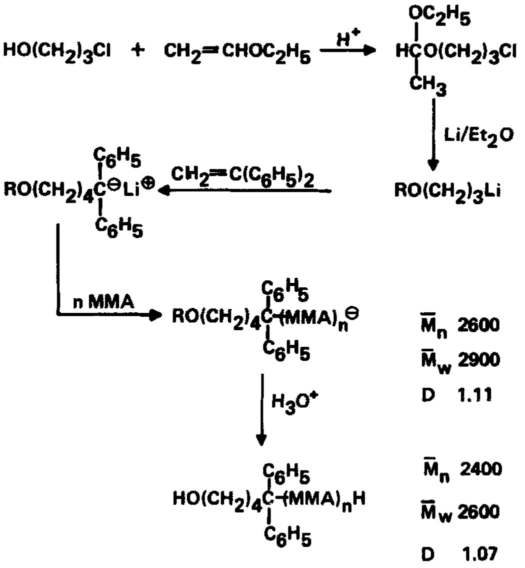
High performance liquid chromatography (HPLC) was extremely helpful in the characterization of functional polymethacrylates. Andrews and Vatvars [10] in our laboratories found that low molecular weight acetal-ended and hydroxy-ended polymers are cleanly separated



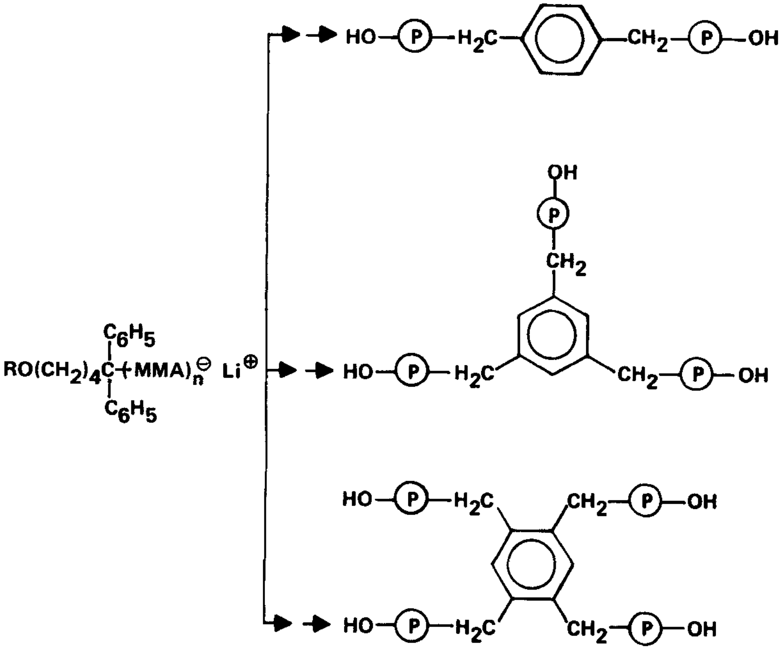
SCHEME I. Anionic polymerization.

(Fig. 1) on silica gel columns with ethyl acetate as eluent. Similarly, mono- and dihydroxy-poly(methyl methacrylate) can be separated from each other (Fig. 2). This permits purity analysis and kinetic studies. Further, the HPLC method provides direct proof of the presence of one or two hydroxyl groups per polymer chain. The classical titration method only gives an average hydroxyl value.

Functional ends were also introduced by capping the growing anion with suitable electrophiles [7, 8]. Scheme IV shows examples for vinyl, allyl, ester, ketone, and lactone endgroups. The styryl-terminated methacrylate block was extended by free radical polymerization



SCHEME II. Functional initiators.



SCHEME III. Coupling with poly(bromomethyl)benzenes.

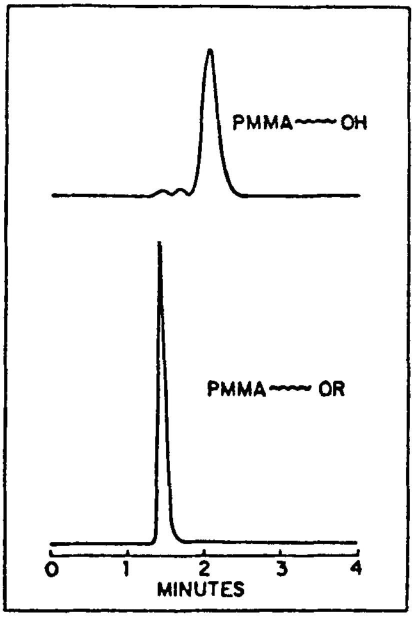


FIG. 1. HPLC of acetal- and hydroxy-ended PMMA on a 250 × 3.2 mm silica gel (5-μm particles, 6-nm pores) column with ethyl acetate eluent at 1.0 mL/min; UV detector at 254 nm [10].

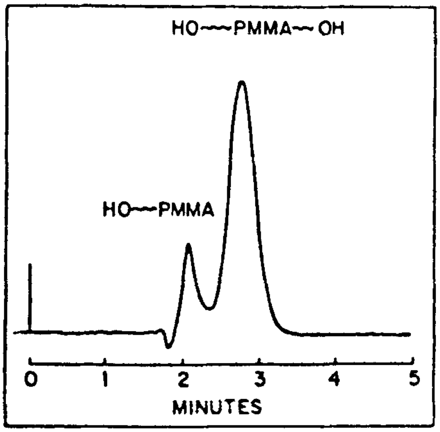
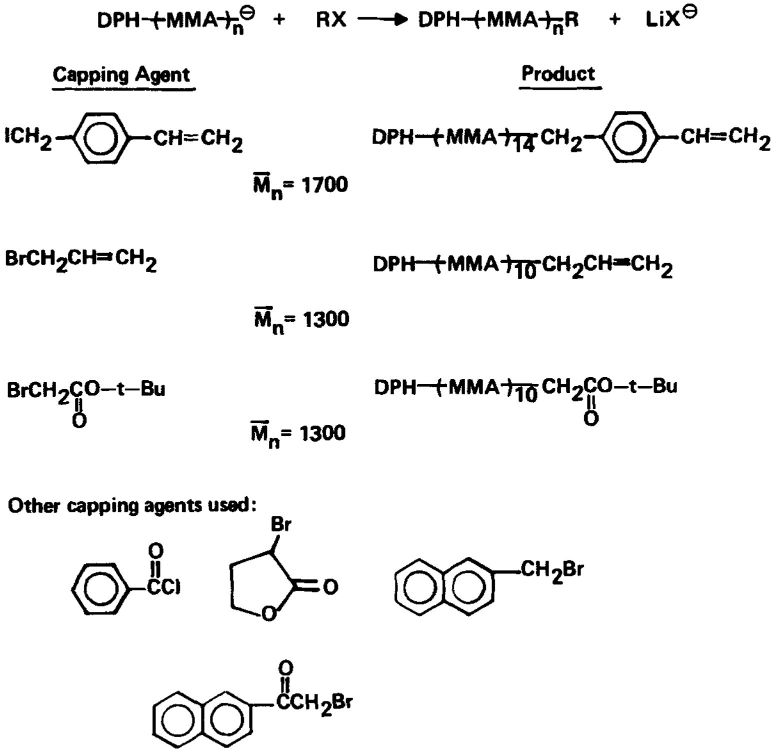


FIG. 2. HPLC separation of mono- and dihydroxy PMMA prepared by anionic initiation [10].

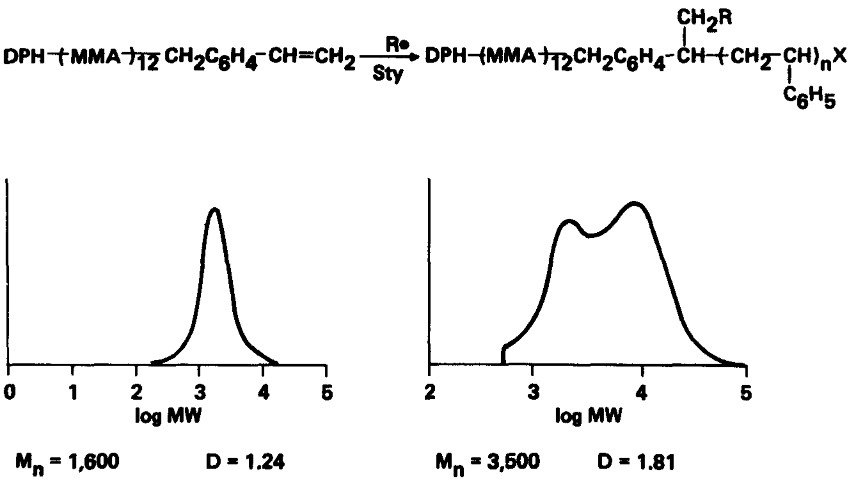


SCHEME IV. Capping reactions of the PMMA anion.

with styrene, leading to a block copolymer with doubled molecular weight (Scheme V).

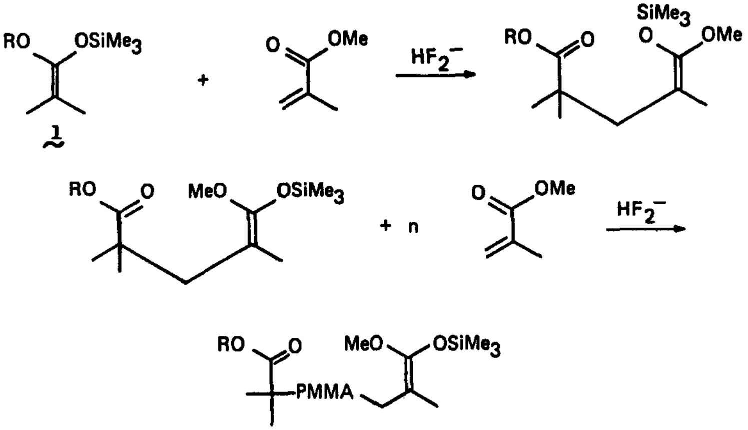
Finally, anionic polymerization can be used to prepare methacrylates with functional groups in the side chain. Thus, allyl methacrylate, which rapidly forms a crosslinked polymer with free radical initiation, gives linear polymers of narrow molecular weight distribution by the anionic method [8, 11]. Application to the previously unknown 1,3- and 1,4-dienyl methacrylates led to polymers that are excellent raw materials for air-drying finishes [8, 11]. Another side-chain functionalized monomer, i.e., glycidyl methacrylate (GMA), was polymerized [8] by switching from 1,1-diphenylhexyllithium (DPHL) as initiator to the less nucleophilic reaction product of DPHL and methyl methacrylate.

The marked instability of the growing end in anionic polymerizations of methacrylates, requiring work at very low temperatures, is a major deficiency which limits practical applications of this process. A fundamentally new polymerization technique was recently discovered by Webster and co-workers at Du Pont; it gives living polymers of high


$$\mathrm{DPH{-}(MMA)_{12}CH_2C_6H_4{-}CH{=}CH_2 \xrightarrow[Sty]{R\bullet} DPH{-}(MMA)_{12}CH_2C_6H_4{-}\underset{}{\overset{CH_2R}{CH}}{-}(CH_2{-}\underset{C_6H_5}{CH})_nX}$$

SCHEME V. PMMA block copolymers.

stability and can be carried out at room temperature or above [12]. This reaction, illustrated in Scheme VI for a methacrylate, is called group transfer polymerization because it involves the repeated transfer of a trialkylsilyl group from the growing chain end (or, at first, from the initiator) to the incoming monomer. Polymerization is initiated by silyl ketene acetals 1 [13], but a catalyst, e.g., a soluble bifluoride, is also required for the reaction to proceed.

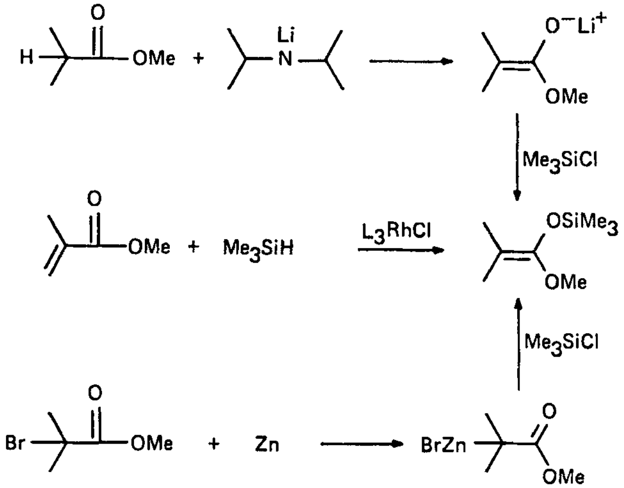


SCHEME VI. Group transfer polymerization.

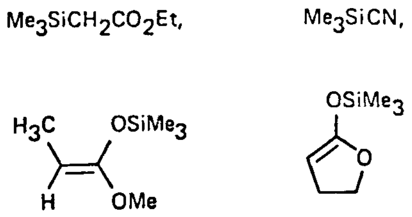
Group transfer polymerization of methyl methacrylate is rapid and exothermic in the temperature range from -100 to +110°C. Addition of monomer over a period of time is often advantageous. Cooling can be affected by letting the reaction mixture warm up to the boiling point of the solvent. Tetrahydrofuran and toluene are examples of solvents which can be used. Because initiators and living polymer ends are very water sensitive in the presence of catalyst, equipment and reagents must be scrupulously dry. Monomer to initiator ratio determines the molecular weight which may be varied over a wide range. Only trace amounts of catalyst are required. The living silyl-terminated polymer is formed in quantitative yield and can be isolated by solvent removal. It can be chain-extended by addition of more monomer and there is no loss in activity even after storing at room temperature for several days. Quenching with a proton source gives the silicon-free methacrylate polymer.

The silyl ketene acetal initiators are conveniently synthesized by treatment of lithium enolates of esters with trialkylsilyl chloride [13]. Alternatively, reaction of ω-bromoesters with zinc and trialkylsilyl chloride [14] or of vinyl esters with trialkylsilyl hydride in the presence of rhodium catalysts [15] can be used to prepare silyl ketene acetals (Scheme VII). Several other initiators are listed in Scheme VIII. There is an induction period with trimethylsilyl cyanide, indicating that the true initiator is formed in the reaction mixture.

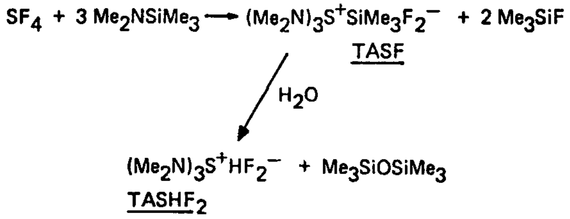
Certain nucleophiles are one class of catalysts which can be used [12]; especially effective is bifluoride. In order to achieve solubility in organic solvents, the counterion must be properly selected. The tris(dimethylamino)sulfonium (TAS) cation [16] is very suitable but



SCHEME VII. Initiator synthesis.



SCHEME VIII. Some other initiators.

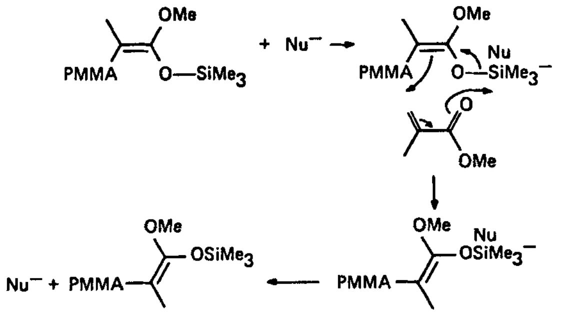


SCHEME IX. Synthesis of $TASHF_2$.

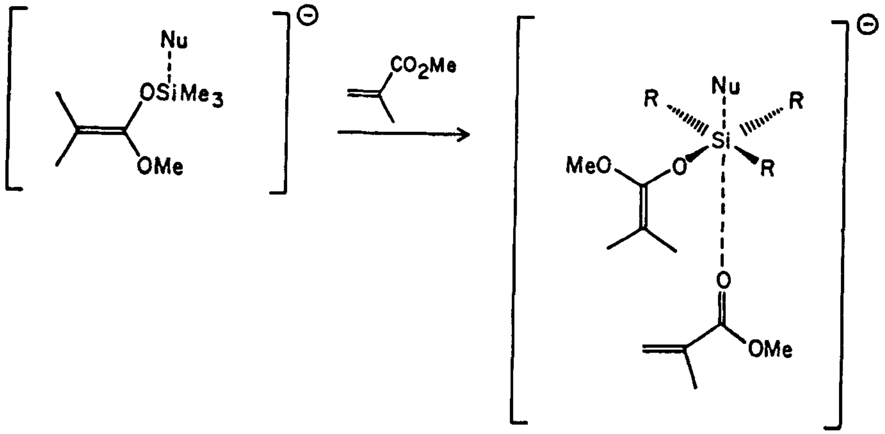
tetralkylammonium salts can also be used. Scheme IX shows the preparation of TAS-bifluoride ($TASHF_2$). Other anions which catalyze group transfer polymerization are fluoride, difluorotrimethyl siliconate [16], cyanide and azide. These catalysts are used at about 1% of the initiator concentration and in solvents such as tetrahydrofuran, toluene and acetonitrile. Lewis acids such as zinc halides, alkylaluminum chlorides, and alkylaluminum oxides are also catalysts. They are used at about 10% monomer concentration and in halocarbon solvents.

Current experimental evidence, including results of labeling experiments, argues against a dissociative mechanism in which an ester enolate anion is the propagating species [17]. The most reasonable mechanism involves associative, intramolecular silyl transfer facilitated by coordination of the nucleophilic catalyst with the silicon (Scheme X). It is conceivable that the hexacoordinate silicon species 2 is involved as in intermediate (Scheme XI).

Group transfer polymerization is the most convenient route for the preparation of monofunctional and telechelic methacrylate polymers as shown in Scheme XII for hydroxy-ended polymers [18]. The capped hydroxy-functional initiator 3 only reacts at the enol ether silicon. Many electrophiles can be used as coupling agents for the preparation of telechelic polymers. Direct coupling of two silyl ketene acetal ends by Br_2-$TiCl_4$ gives polymers with a central head-to-head linkage. Using disilyl ketene acetals, carboxy-terminated polymers were pre-



SCHEME X. Associative, intramolecular silyl transfer mechanism.



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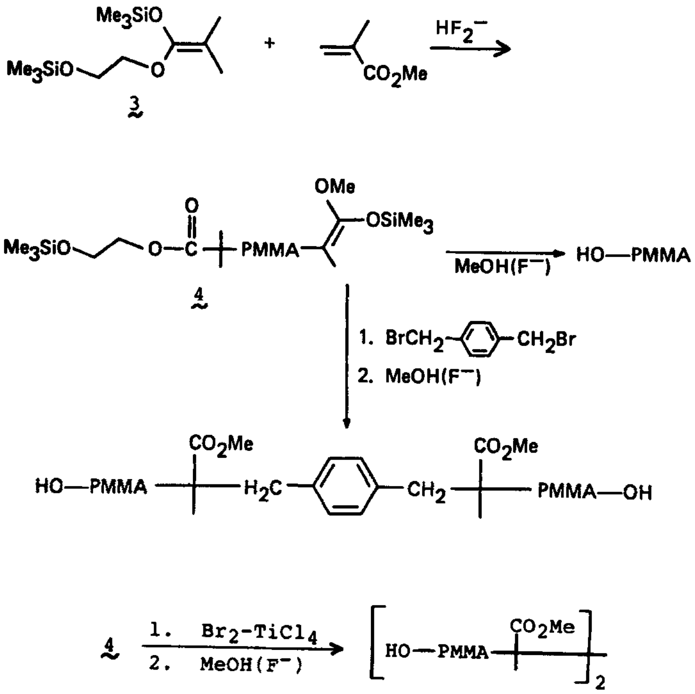
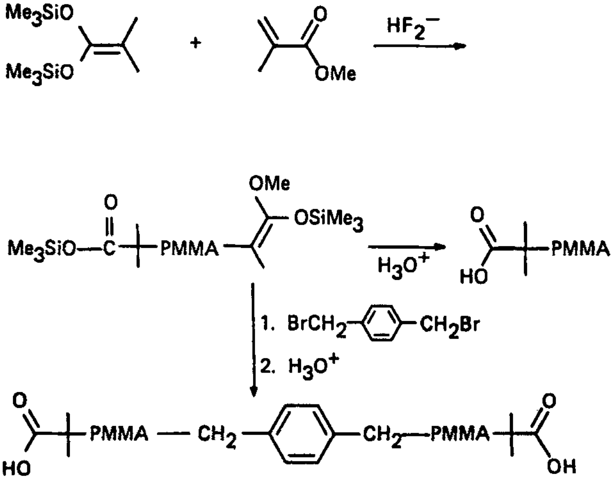
SCHEME XI. Hexacoordinate silicon intermediate.

pared in an analogous manner (Scheme XIII). Again, only one of the trimethylsilyl groups in the initiator participates in polymerization, leaving the other as part of a capped carboxy group. HPLC further proved its value as a powerful tool for purity analysis of these polymers, demonstrating that telechelic polymers with a high degree of bifunctionality were obtained by group transfer polymerization (Fig. 3). Spiking dihydroxy-PMMA with varying amounts of monofunctional polymer helped to show that the small impurity in the dihydroxy polymer was not monohydroxy-PMMA.



SCHEME XII. Hydroxy-ended polymers.



SCHEME XIII. Carboxy-ended polymers.

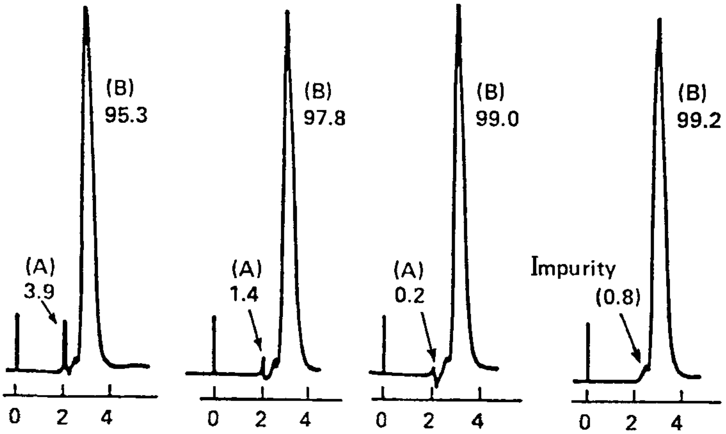
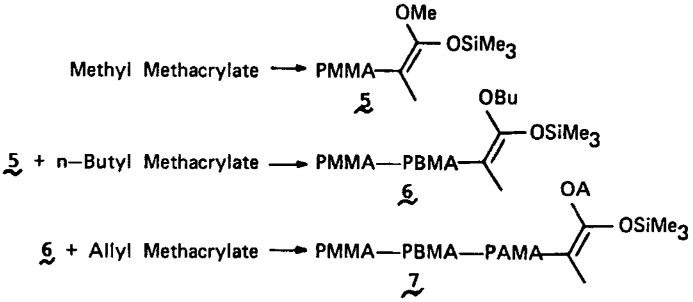


FIG. 3. HPLC analyses of mixture of monohydroxy (A) and α,ω-dihydroxy (B) PMMA. Values are relative percentages. Lichrosorb Si 60, 3.2 × 250 mm, ethyl acetate as eluent.



M_n = 3800 M_w 4060 (Theory 4060)

T_g = −19°, +38° and +108°C

SCHEME XIV. Block polymers.

The outstanding stability of silyl-terminated methacrylates facilitates preparation of multiblock copolymers. In the example of Scheme XIV, addition of methyl methacrylate is followed, after complete polymerization, by addition of n-butyl methacrylate which, in turn, is followed by allyl methacrylate. Excellent molecular weight control is maintained to the end of the polymerization, opening the way to the design of carefully tailored polymers and the subsequent determination of structure/property correlations. This example also shows that group transfer polymerization is not affected by unsaturation in the side chain: the soluble block copolymer **7** contained 11 mol% allyl methacrylate, enough to lead to severe gelation in a free radical polymerization. Similarly, many silicon-masked functional groups can also be present, either as end groups or in the pendent groups.

In summary, group transfer polymerization, because of the high stability and selective reactivity of the propagating end, offers substantial practical advantages over anionic polymerization as a method for the synthesis of functional methacrylates. Similar results can be obtained with acrylates, and work on the use of other monomers is underway.

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