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Synthesis of Reactive-Ended Acrylic Polymers by Group Transfer Polymerization: Initiation with Silyl Ketene Acetals

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ABSTRACT

Living methacrylate polymers are obtained at room temperature and above by initiation with ketene silyl acetals in the presence of a soluble bifluoride catalyst. During the polymerization, a trialkylsilyl group is transferred from the living chain end to incoming monomer. The new procedure has thus been named group transfer polymerization (GTP). Monodisperse polymers with predetermined molecular weights as high as 100,000 can be obtained by adjusting the monomer/initiator ratio. Telechelic poly(methyl methacrylate) with hydroxy or carboxy ends can be obtained by using an initiator containing a protected hydroxy or carboxy group and coupling the resulting living polymer.

INTRODUCTION

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 blocks with functional, i.e. reactive, end groups which could serve as building blocks for copolymers of predetermined architecture.

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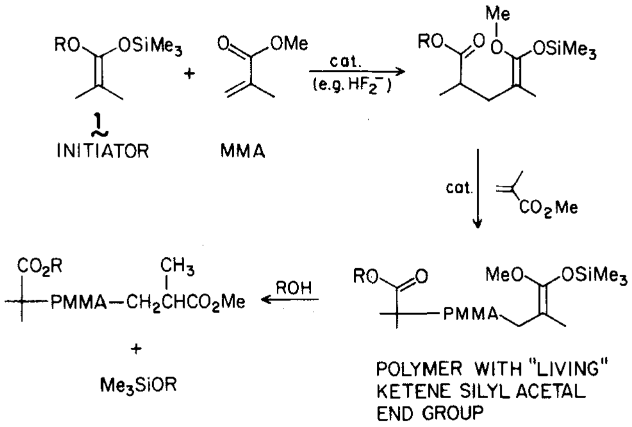
Condensation polymerization is widely used for the preparation of functional blocks but has major disadvantages: for example, it leads to polymers of broad molecular weight distribution and hydrolytically unstable backbone linkages. Free radical polymerization is totally unsuited for this purpose because the identity of either chain end cannot be rigorously controlled due to chain transfer and random termination reactions. Living ionic polymerizations, on the other hand, are uniquely suited for the preparation of functional blocks. In the ideal case in which chain transfer and unwanted termination reactions are absent, polymers with dispersity of one, controllable molecular weight and precisely defined end groups are formed. Good examples are the cationic polymerization of isobutylene [2] and 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 appears to be uneconomical because of the low temperatures required to maintain "living" conditions.

We have recently discovered a fundamentally new polymerization technique which gives living polymers of high stability and can be carried out at room temperature or above [6]. Thus far, the method works best for methacrylates but other monomers such as acrylates, acrylonitrile and maleimides can also be polymerized. We call this reaction, which is illustrated in Scheme I, group transfer polymerization (GTP), because it involves the repeated transfer of a trialkylsilyl group from the growing



SCHEME I

chain end to the incoming monomer. Polymerization is initiated by silyl ketene acetals, **1**, [7] but a catalyst, e.g. a soluble bifluoride, is also required for the reaction to proceed.

MATERIALS AND METHODS

All glassware and syringes were dried at 175°C for at least 24 hours before use. Reagents, solvents, and monomers were purified by normal procedures and handled under moisture-free atmospheres. Analytical HPLC was performed on a Du Pont 8800LC four solvent system with UV (Schoeffel, SF 770), and refractive index (Waters, R 401) detectors, and a Hewlett-Packard dual pen recorder (Model 7132N) connected in series. Average molecular weights and MWD of the polymers were obtained by GPC with a Waters' chromatographic system (Model 6000A), using commercial µ-styragel columns and Lucite® 40 acrylic standard.

Tris(dimethylamino)sulfonium Bifluoride

Although tetraalkylammonium bifluorides or even potassium bifluoride can be used as catalysts, we found tris(dimethylamino)sulfonium bifluoride (TAS HF_2) to give the best over-all results. Tris(dimethylamino)sulfonium bifluoride was prepared in quantitative yield by treatment of tris(dimethylamino)sulfonium difluorotrimethylsiliconate [8] (27.5 g, 0.10 mol) with water (1.0 ml, 0.055 mol) in acetonitrile (20 ml). Purification was achieved by crystallization from CH_3CN/THF (1/10, v/v). The product has the expected ^1H and ^{19}F NMR spectral properties, and the elemental analysis was within 0.3% of theory.

Poly(methyl methacrylate)

In a typical procedure, MMA (360 mmol) is slowly added to a solution of 1-methoxy-1-trimethylsiloxy-2-methyl-1-propene,[7] (8.5 mmol), and tris(dimethylamino)sulfonium bifluoride (0.01 mmol) in tetrahydrofuran (20 ml) at room temperature with exclusion of moisture. When the exothermic reaction is complete, methanol (3 ml) is added, and the solution is evaporated to give a quantitative yield of poly(methyl methacrylate), Mn 4300, Mw 5300, (Theory, 4343) dispersity (D) = $\frac{M_w}{M_n}$ = 1.24, as determined by GPC.

Telechelic Poly(methyl methacrylate)

To a 3-necked flask, fitted with an argon inlet, a stirrer and thermocouple well were added with stirring THF (20 ml), initiator 9 (2.60 g, 9.40 mmol), and tris(dimethylamino)sulfonium bifluoride (0.05 ml of 0.1M in CH_3CN). Then methyl methacrylate (20 g, 200 mmol) was added via a syringe pump at 1.0 ml/min. After the exothermic reaction had subsided, the mixture was treated as follows (Methods A, B, C):

Method A. Coupling with $Br_2/TiCl_4$

A 15 ml aliquot of the mixture was transferred with a syringe into a 25 ml, 3-necked flask under argon. The solvent was evaporated at 25°C/0.1 mm Hg. Then dry dichloromethane (20 ml) was added, and the resulting solution cooled to 0°C. A mixture of Br_2 (0.32 g) and $TiCl_4$ (0.39 ml) in 10 ml CH_2Cl_2 was added and the mixture stirred for one hour. It was poured into 100 ml 1M HCl and extracted with 200 ml CH_2Cl_2. Evaporation of solvent, followed by precipitation from hexane gave 7.45 g of polymer. GPC: Mn, 3600; Mw, 4400. HPLC and ^1H NMR confirmed the structure to be α,ω-dihydroxypoly(methyl methacrylate).

Method B. Coupling with 1,4-bis(bromomethyl)benzene

A second 15-ml aliquot was treated (in a set-up similar to that in A) with 1,4-bis(bromomethyl)benzene (0.48 g in 10 ml THF) at 0°C over 20 minutes. Then tris(dimethylamino)sulfonium difluorotrimethylsiliconate [10] (1.1 g) was added. The mixture was stirred for 1.5 hours, allowed to warm up to 25°C, and then quenched with methanol (10 ml). The reaction mixture was refluxed for 1 hour, cooled, and then evaporated to dryness *in vacuo*. The residue was dissolved in 20 ml acetone and added dropwise to 1 ℓ hexane. Filtration gave 7.30 g of α,ω-dihydroxypoly(methyl methacrylate). GPC: Mn, 3400; Mw, 4200.

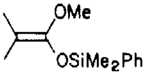
Method C. Reaction with Benzyl Bromide (Control)

The rest of the original reaction mixture was cooled to 0°C and treated with benzyl bromide (0.70 g). Work-up, as described in Method B, gave 7.25 g of α-hydroxy-ω-benzylpoly(methyl methacrylate). GPC: Mn, 1800; Mw, 2300.

MECHANISM STUDIES

Our mechanistic studies on GTP of methyl methacrylate with tris(dimethylamino)sulfonium (TAS) bifluoride and TAS difluorotrimethylsiliconate as catalysts show that a fluorosilane is not produced in a reversible, dissociative step. As evidence, polymerization of MMA with phenyldimethylsilyl initiator 2 in the presence of an equimolar quantity of tolyldimethylsilyl fluoride with TAS bifluoride catalyst (25°-50°C, 0.75 h) provided phenyldimethylsilyl oligomer 3 (n = ca. 14) which contained less than 5% of the corresponding tolyldimethylsilyl derivative. Exchange studies under polymerization conditions also show there is no silyl group exchange taking place between different polymer chains.

We propose an intramolecular transfer mechanism in which the silyl group is transferred directly from the living end of the polymer to the carboxyl oxygen of the monomer via hypervalent silicon intermediates 4 and 5 (Scheme II).



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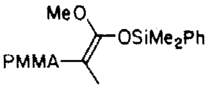

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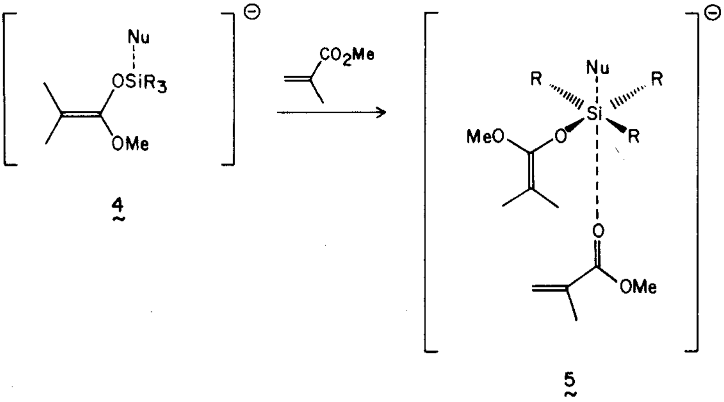
RESULTS AND DISCUSSION

Polymerization of methyl methacrylate is rapid and exothermic in the temperature range from -100° to +110°C, giving a quantitative yield of polymer. Because initiators and living polymer ends are very water-sensitive, equipment and reagents must be scrupulously dry. Monomer to initiator ratio determines the molecular



SCHEME II

weight which may be varied over a wide range. Only trace amounts of catalyst are required. Since the reaction is very fast and the heat of polymerization high, addition of monomer over a period of time is often advantageous. The living silyl-terminated polymer can be isolated by solvent removal and can be chain-extended by addition of more monomer. There is no loss in activity even after storing at room temperature for several days. Quenching with a proton source gives the silicon-free polymer. The molecular weight shows narrow dispersity, typically $\bar{M}w/\bar{M}n = 1.1$ to 1.4. The degree of polymerization is controlled by the ratio of the monomer to the initiator. Nearly monodisperse poly(methyl methacrylate) with a molecular weight as high as 100,000 can be obtained by using highly purified solvents and reagents. For most of our research, however, we have aimed for polymer with molecular weights of 5000 to 10,000. In this range the sensitivity to impurities is greatly reduced.

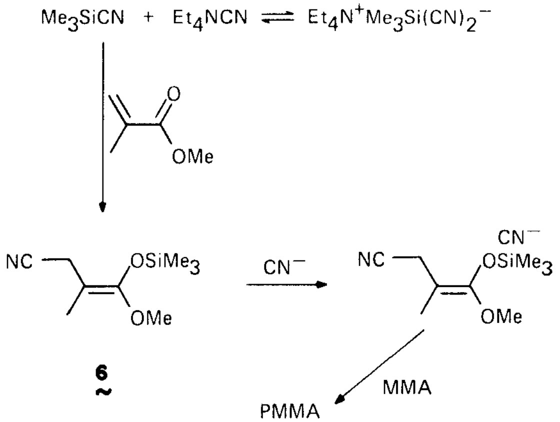
The silyl ketene acetal initiators are conveniently synthesized by treatment of lithium enolates of esters with trialkyl-

SCHEME III

silylchloride [7]. Several other initiators are listed in Scheme III.

When trimethylsilyl cyanide (TMSCN) is used as initiator and tetraethyl ammonium cyanide as catalyst, there is an induction period during which polymerization proceeds very slowly and the TMSCN is consumed at about one-half the rate at which methacrylate is reacting (NMR). When the trimethylsilyl cyanide is depleted, the polymerization rate suddenly increases to the normal rate. We postulate that the cyanide ion (from the catalyst) is complexing more strongly with trimethylsilyl cyanide than with silated enolate, and polymerization takes place only when all of the TMSCN has been converted to adduct 6, freeing cyanide to catalyze the reaction with monomer (Scheme IV).

As mentioned earlier, a catalyst is required for the polymerization to proceed and, surprisingly, one of the most generally useful catalysts is bifluoride ion. Although fluorides have been widely used for the catalysis of nucleophilic reactions of organosilanes [9], this is the first report of the general utility of bifluoride ion in the catalysis of such reactions. (Proton sources quench reactions of silyl enolates and ketene



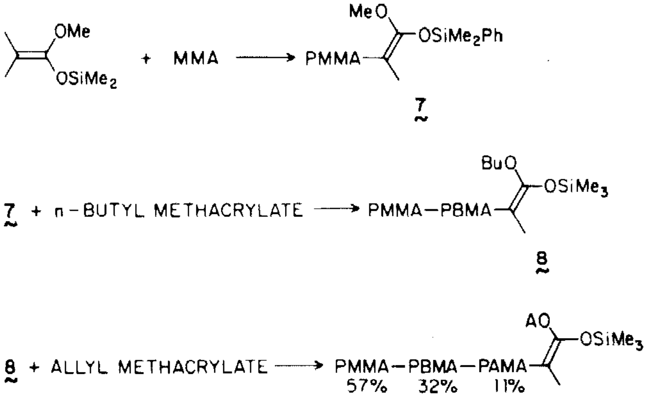
SCHEME IV

silyl acetals. One can, therefore, speculate that bifluoride is not a good proton source since the hydrogen is tightly bound between the two fluorine atoms.) Other anions which catalyze GTP are fluoride, difluorotrimethylsiliconate [8], cyanide, and azide. Lewis acids such as zinc halide, alkylaluminum chlorides and alkylaluminum oxides also catalyze GTP. Tetrahydrofuran, toluene and acetonitrile are typical solvents for nucleophile catalyzed GTP and toluene and halocarbons for Lewis acid catalyzed polymerization. Nucleophilic catalysts are used at ∼1% of the initiator concentration, Lewis acid catalysts at ∼10%.

Poly(methyl methacrylate) prepared by GTP with nucleophilic catalysts at ambient temperature characteristically contains approximately equal numbers of syndiotactic and heterotactic sequences. Polymer prepared using nucleophilic catalysts at -78°C or Lewis acid catalysts is predominantly syndiotactic. The tacticity is independent of solvent polarity, contrary to the anionic polymerization of methyl methacrylate with lithium alkyls in which the polymer tacticity is not dependent on temperature but depends on solvent. Thus, non-polar solvents give highly isotactic polymer and polar solvents syndiotactic polymer [10].

The ketene silyl acetal end group is stable and may be used for further reactions or for preparing block polymers by changing monomer feed. The size of each block can be accurately controlled. Scheme V illustrates formation of a triblock polymer from methyl methacrylate, n-butyl methacrylate and allyl methacrylate.

Scheme V also illustrates the point that methacrylates bearing free radical sensitive groups can be introduced into the polymer chains by group transfer polymerization. A polymer with 11% allyl methacrylate would be gelled if prepared by free radical initiation. Polymers with thermally sensitive functionality such



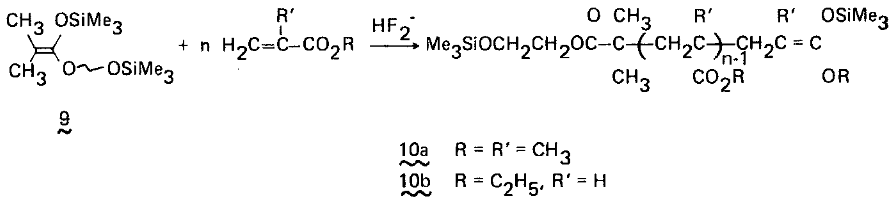
Mn 3800 Mw 4060 (THEORY 4060)
Tg = −19°, +38°, and +108°C

SCHEME V

as glycidyl groups can also be prepared, but polymerization temperatures must be maintained at 0°C or lower. When mixtures of various methacrylate monomers are used, random copolymers result.

End functionalized polyacrylics can be obtained by employing properly designed initiators. The corresponding living polymers can be coupled readily to telechelic polymers. Thus, use of (**9**) (Scheme VI) as initiator for polymerization of methyl methacrylate or ethyl acrylate gave polymers with protected terminal functional groups. The existence of **10a** or **10b** in solution was demonstrated by reaction with a proton source (e.g., methanol) or with a suitable alkylating agent (e.g., benzyl bromide) [11] in the presence of stoichiometric amounts of fluoride ion, to give **11** or **12** (Scheme VII). Deprotection of **11** and **12** with Bu_4NF gave the corresponding polymers with 100% hydroxyl groups in one terminal position. The functionalized polymers were readily distinguished from the non-functionalized species by high performance liquid chromatography (HPLC) [12]. Gel permeation chromatography (GPC) analyses showed that the polymers were monodisperse ($\bar{M}w/\bar{M}n$ = 1.0-1.3), a characteristic.feature of GTP.

When the alkylation reaction was carried out with 1,4-bis(bromomethyl)benzene, the intermediate **10a** gave, after



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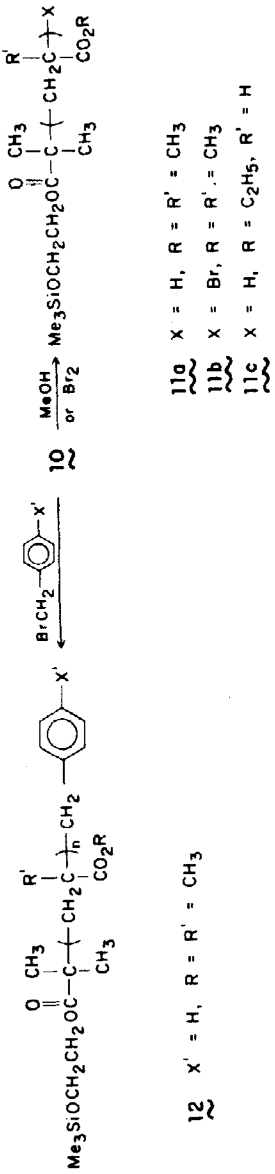
10a $R = R' = CH_3$

10b $R = C_2H_5, R' = H$

SCHEME VI



12 $X' = H$, $R = R' = CH_3$

11a $X = H$, $R = R' = CH_3$

11b $X = Br$, $R = R' = CH_3$

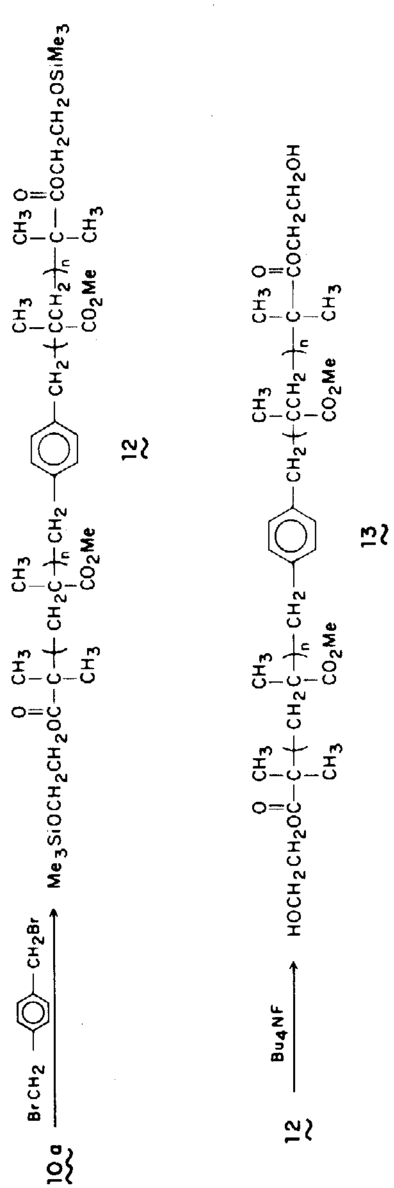
11c $X = H$, $R = C_2H_5$, $R' = H$

SCHEME VII

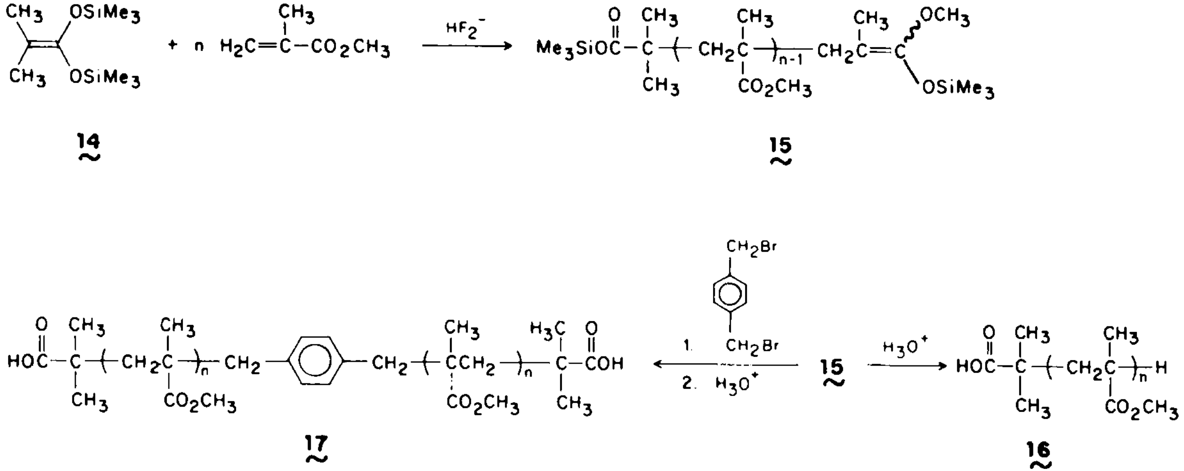
deprotection, monodisperse α,ω-dihydroxypoly(methyl methacrylate), **13**, in a quantitative yield (Scheme VIII). This coupling reaction was best carried out in the presence of one equivalent fluoride ion. The extent of coupling was determined by GPC, HPLC,[12] and hydroxyl group analyses.

Similarly, α,ω-dicarboxypoly(methyl methacrylate) was prepared by initiating the polymerization with 1,1'-bis(trimethylsiloxy)-2-methylpropene-1 (**14**) [13] and hydrolyzing the end group of the resulting polymer (Scheme IX). In all coupling reactions, a control sample was removed before addition of the coupling agent. Comparison of the control with the coupled product enables one to determine the extent of coupling. Thus, the monofunctionalized polymer **16** (control) had Mn = 2100, Mw = 2700, while the α,ω-difunctionalized coupled product **17** had Mn = 4200 and Mw = 5600, indicating quantitative coupling.

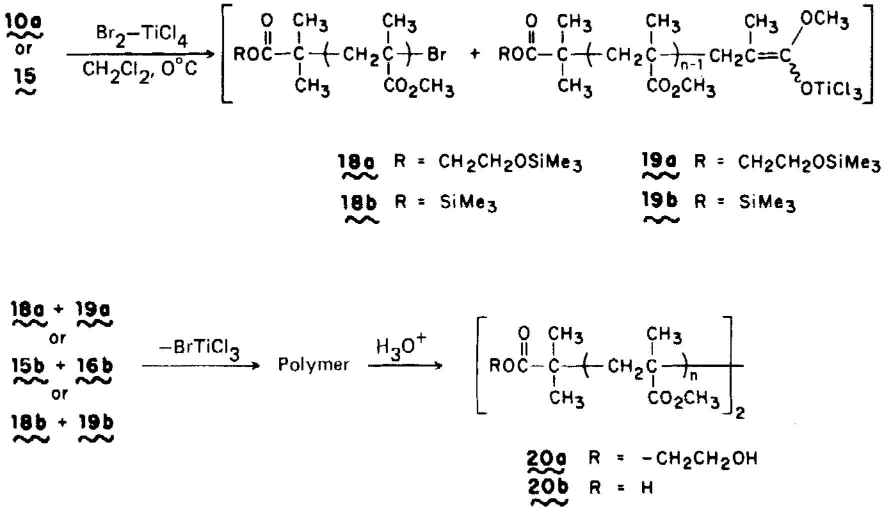
Reaction of silyl enol ethers with tertiary alkyl halides in the presence of $TiCl_4$ is well documented.[14] Likewise, direct coupling of silyl ketene acetals with $TiCl_4$ is known.[15] In our preparation of telechelic polymers containing a central head-to-head linkage, we have modified the above reactions by employing a mixture of Br_2 and $TiCl_4$ as the coupling agent. Thus, when living polymers **10a** and **15** were reacted, independently, with a mixture of Br_2-$TiCl_4$ (Scheme X) in dichloromethane between 0° and 25°C, **20a** and **20b**, respectively, were obtained in quantitative yields.


10a
BrCH2–C6H4–CH2Br
Me3SiOCH2CH2OC(O)C(CH3)(CH3)–(CH2C(CH3)(CO2Me))n–CH2–C6H4–CH2–(C(CH3)(CO2Me)CH2)n–C(CH3)(CH3)C(O)OCH2CH2OSiMe3
12
12
Bu4NF
HOCH2CH2OC(O)C(CH3)(CH3)–(CH2C(CH3)(CO2Me))n–CH2–C6H4–CH2–(C(CH3)(CO2Me)CH2)n–C(CH3)(CH3)C(O)OCH2CH2OH
13

SCHEME VIII



SCHEME IX



SCHEME X

SUMMARY

Group transfer polymerization of α,ω-unsaturated esters offers the following advantages: operability over a broad temperature range, wide choice of solvents, excellent molecular weight control, compatibility with a variety of pendent functional groups, ability to functionalize the polymer ends, and ability to prepare block and random copolymers. No other method for polymerization of these monomers gives the synthetic latitude available by GTP.

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B. C. Anderson, T. Fukunaga and B. E. Smart also contributed substantially.

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