Macromolecules **1986**, *19*, 1775–1777 **1775**

mentally in the thermal contraction of the c axis between PBA and PPTA could be attributed to the difference in ρv^2 or in the anisotropic intermolecular interaction and the chain conformation between the two crystals. The thermal expansion data presented in this paper, however, are not sufficient to estimate the magnitude of ρv^2. On the other hand, tensile property data (i.e., curves of ϵ vs. σ measured at various temperatures) will be available for the estimation of ρv^2, as understood from the presence of the external stress σ in the above equation. Detailed experimental results on the tensile property of these fibers will be reported later.[17]

Registry No. PBA (SRU), 24991-08-0; PBA (homopolymer), 25136-77-0; PPTA (SRU), 24938-64-5; PPTA (copolymer), 25035-37-4.

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Communications to the Editor

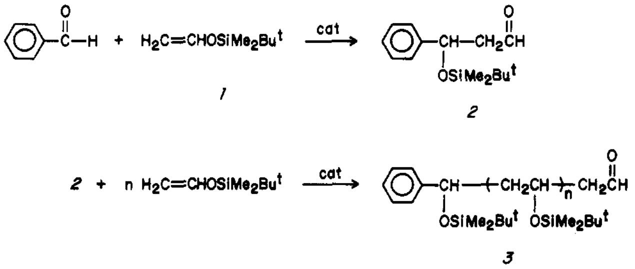
Sequential Silyl Aldol Condensation in Controlled Synthesis of Living Poly(vinyl alcohol) Precursors[†1]

Michael addition and aldol condensation constitute an important group of organic reactions available for carbon–carbon bond formation. We recently reported application of the former to controlled synthesis of acrylic polymers.[2] The method, termed group-transfer polymerization (GTP), give monodisperse living[3] methacrylate polymers of well-controlled molecular weight. In this communication we describe the first application of silyl aldol condensation to direct synthesis of living macromolecules whose structure and molecular weight are controlled by the initiator.

Aldehydes are known to react with silyl vinyl ethers to give silylated crossed-aldol products.[4] Since a new aldehyde group is formed in aldol condensation of silyl vinyl ethers, continued addition of the silyl vinyl ether should give a polymer. We find that addition of a several-fold excess of silyl vinyl ether 1[4c] to benzaldehyde as initiator gives a silylated vinyl alcohol polymer with a terminal aldehyde group (Scheme I). The molecular weight of the polymer as shown in Table I is controlled by the molar ratio of the silyl vinyl ether to the aldehyde initiator.

Unlike GTP of methyl methacrylate in which the *silyl group is transferred from the initiator to the monomer*, the polymerization of silyl vinyl ethers, hereafter referred to as *aldol-GTP*, involves *a transfer of the silyl group from monomer to initiator*. The products are stable, neutral living polymers whose hydrolytic stability depends on the bulkiness of the silyl group. In line with the well-known enhanced hydrolytic stability of *tert*-butyldimethylsilyl ethers compared to the corresponding trimethylsilyl ethers,[5] we find that the best control of molecular weight is obtained with *tert*-butyldimethylsilyl vinyl ethers over a wide temperature range (−80 to +70 °C).[6]

Scheme I



A catalyst is required for the process to occur. Although Lewis acids such as diisobutylaluminum chloride and titanium tetrachloride are effective (Table I, run nos. 9 and 10) as catalysts, the preferred catalysts are zinc halides (Table I, run nos. 1–7). Titanium tetrachloride gives low yields of polymer (<20%), presumably due to its depletion via exchange reactions which it is likely to undergo with silyl groups. Anionic catalysts, particularly fluoride sources such as tris(dimethylamino)sulfonium bifluoride (Table I, run no. 8), strongly coordinate not only to the incoming silyl vinyl ether but also to the backbone siloxy groups. This makes such species less efficient catalysts for the aldol-GTP than Lewis acids. Nonreactive chlorinated and nonpolar aromatic solvents are more compatible with Lewis acids than are polar solvents such as tetrahydrofuran and acetonitrile; hence, the former are preferred. In contrast to Lewis acid catalyzed GTP of methacrylates[7] in which catalyst levels of about 10–20 mol % *relative to monomer* are needed for complete monomer conversion, the aldol-GTP requires much less catalyst, usually ranging from 10^{-4} to 10^{-2} mol % *relative to the silyl vinyl ether (monomer)*.

In general, aromatic aldehydes react more cleanly as initiators than do aliphatic aldehydes (Table I, run nos. 4, 5, and 12). Besides aldehydes, electrophiles such as benzyl halides (Table I, run no. 6) and acetals (Table I, run no. 11) can be used as initiators. Use of either 1,4-bis(bromomethyl)benzene (Scheme II) or terephthalde-

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† Contribution No. 3852.

0024-9297/86/2219-1775$01.50/0

Table I
Polymerization of *tert*-Butyldimethylsilyl Vinyl Ether[a]

run no.	initiator (mmol)	catalyst (mmol)	solvent (mL)	temp, °C	conv, %	$\bar{M}_n$[b] (theory)	$\bar{M}_n$[c]	$\bar{M}_w$[c]	$\bar{M}_w/\bar{M}_n$[c]
1	PhCHO (1.88)	$ZnBr_2$ (0.26)	DCM (20)	30	100	4100	3610	4390	1.21
2	PhCHO (2.49)	$ZnCl_2$ (0.26)	DCM (20)	30	100	3120	2180	2800	1.28
3	*p*-$C_6H_4(CHO)_2$ (2.02)	$ZnBr_2$ (2.50)	DCM (20)	30	100	3840	4150	5130	1.24
4	Me_2CHCHO (2.40)	$ZnBr_2$ (0.20)	DCM (20)	30	70	3200	2900	2950	1.02
5	*trans*-retinal (0.62)	$ZnBr_2$ (0.20)	DCM (50)	30	100	12130	10400	15500	1.49
6	Ph_2CHCl (0.97)	$ZnBr_2$ (0.10)	DCM (20)	30	100	7900	6500	8000	1.23
7[d]	PhCHO (0.20)	$ZnBr_2$ (0.20)	DCM (50)	30	100	160000	78900	121000	1.51
8	PhCHO (2.45)	$TASHF_2$ (0.10)	THF (20)	−65	85	2650[e]	2400	3200	1.33
9	PhCHO (2.42)	*i*-Bu_2AlCl (0.25)	DCM (20)	30	95	3200	6640	11300	1.70
10	PhCHO (2.45)	$TiCl_4$ (0.25)	DCM (20)	30	10	300[e]	476	801	1.68
11	$PhCH(OMe)_2$ (1.81)	$ZnBr_2$ (0.26)	DCM (20)	30	100	4300	1490	3690	2.48
12	*trans*-PhCH=CHCHO (0.40)	$ZnBr_2$ (0.40)	DCM (20)	0	98	10130	7350	11000	1.50

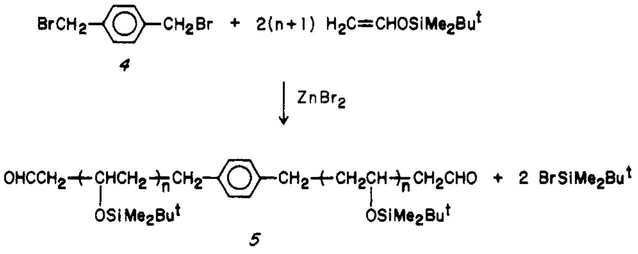
[a] Each run performed on 7.50 g of monomer. [b] Theoretical $\bar{M}_n$ = [(no. of moles of monomer)/(no. of moles initiator)] × (mol wt of monomer). [c] Determned by gel permeation chromatography. [d] Performed on 32.0 g of monomer. [e] Based upon isolated yield of polymer.

Table II
Comparison of Aldol-GTP and Cationic Polymerization[a]

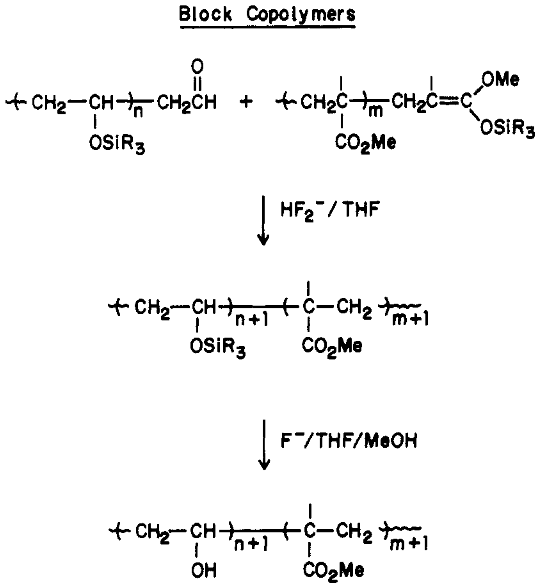
run no.	initiator (mmol)	catalyst (mmol)	temp, °C	conv, %	$\bar{M}_n$ (theory)	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
1		$ZnBr_2$ (0.25)	−60	59	9440[b]	7610	12000	1.58
2	PhCHO (2.46)	$ZnBr_2$ (0.25)	−60	100	1730[c]	2450	3080	1.25
3		$ZnBr_2$ (0.79)	−60	33	1675[b]	21600	38800	1.80
4	PhCHO (0.79)	$ZnBr_2$ (0.25)	−60	100	5100[c]	3930	5330	1.35
5		$ZnBr_2$ (2.50)	+25	3	1600[c]	7850	17400	2.22

[a] All runs performed in 1,2-dichloroethane (25 mL) on 4.0 g of *tert*-butyldimethylsilyl vinyl ether. [b] Based upon monomer consumed. [c] Based upon initial monomer and initiator concentrations.

Scheme II



Scheme III



hyde (Table I, run no. 3) enables polymer chain growth to occur in two directions.

Silyl ketene acetals react with aldehydes to give Reformatsky products.[4a,b] We have applied the reaction to the synthesis of unique block copolymers. For example, treatment of the aldehyde-terminated polymer ($\bar{M}_n$ = 1080, $\bar{M}_w$ = 1300) with living methacrylate polymer ($\bar{M}_n$ = 1080, $\bar{M}_w$ = 1390) made by GTP for 1 h in the presence of zinc bromide in dichloromethane gives a block copolymer ($\bar{M}_n$ = 1610, $\bar{M}_w$ = 1910) of silylated vinyl alcohol and methyl methacrylate in almost quantitative yields. Instead of $ZnBr_2$ in dichloromethane, one can also use tris(dimethylamino)sulfonium bifluoride in tetrahydrofuran as the catalyst/solvent system for the block copolymer preparation (Scheme III). Upon cleavage of the silyl groups with fluoride ion[5c] in the presence of methanol, a copolymer containing hydroxyl groups is obtained. *GTP processes, therefore, provide us with methodologies for making polymers of controlled structure, molecular weight, and degree of hydrophilicity.* These types of polymers are difficult to make by previously reported methods.[8] Additionally, terminal functional groups for use in postpolymerization reactions are readily introduced by either using an appropriately substituted aldehyde as initiator or capping the living end with a reagent containing the desired functional group. Thus, cinnamaldehyde (Table I, run no. 12) introduces a terminal olefin while *trans*-retinal (Table I, run no. 5) introduces terminal conjugated double bonds as potential cross-linking sites.

The aldol-GTP should be distinguished from the well-known cationic polymerization of silyl vinyl ethers that also gives silylated vinyl alcohol polymers.[8,9] The latter does not give a living polymer, lacks molecular weight control (Table II, run nos. 1 and 3), and does not give polymers at temperatures above 0 °C (Table II, run no. 5). Furthermore, neither block copolymers nor polymers containing terminal functional groups can be made via the cationic polymerization method. Higashimura and coworkers[10] recently reported a living HI/I_2-initiated cationic polymerization of alkyl vinyl ethers. The process, however, requires low temperatures and has not been shown to be applicable to polymerization of silyl vinyl ethers. The results of our comparative studies (Table II) clearly demonstrate that in aldol-GTP, the aldehyde controls the molecular weight (run nos. 2 and 4) while a cationic initiator such as $ZnBr_2$ alone does not (run nos. 1 and 3).

Furthermore, at 25 °C and in the absence of aldehyde (Table II, run no. 5), only about 3% of the polymer was isolated. This is in agreement with Murahashi's early observation[8a] that cationic polymerization of silyl vinyl ethers gives little or no polymer at temperatures higher than 0 °C.

The general concept underlying GTP processes is that the initiator reacts with the monomer in such a fashion that the reactive functional group originally present in the initiator is regenerated. Similar to the previously reported GTP, the aldol-GTP has several advantages over the previously known methods (e.g., cationic polymerization): operability over a broad temperature range, complete monomer conversion, facile introduction of functional groups, living polymer formation, very good molecular weight control, and facile block copolymer synthesis. The process permits control of the hydrophilic characters of polymers by introducing PVA blocks of varying sizes. The results of aldol-GTP reported here demonstrate another instance where organic synthetic methods can be applied to the controlled synthesis of living polymers. The important distinction is that most organic bond-forming reactions *are not* efficient or quantitative enough to be used in the formation of high polymers, let alone *living high polymers*.

Registry No. 1, 66031-93-4; 1 (homopolymer), 100547-15-7; PhCHO, 100-52-7; $ZnBr_2$, 7699-45-8; $ZnCl_2$, 7646-85-7; p-$C_6H_4(CHO)_2$, 623-27-8; Me_2CHCHO, 78-84-2; Ph_2CHCl, 41376-15-2; i-Bu_2AlCl, 1779-25-5; $TiCl_4$, 7550-45-0; $PhCH(OMe)_2$, 1125-88-8; (*E*)-PhCH=CHCHO, 14371-10-9; $TASHF_2$, 85248-37-9; *trans*-retinal, 116-31-4.

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(6) Typical procedure: A three-necked 50-mL flask, fitted with a stirrer, argon inlet, and a thermocouple, was charged with zinc chloride (anhydrous, 0.035 g, 0.26 mmol) dichloromethane (20 mL), and benzaldehyde (0.25 mL, 2.46 mmol). Then *tert*-butyldimethylsilyl vinyl ether (7.41 g, 46.81 mmol) was added via a syringe pump at 0.5 mL/min. The ensuing reaction was accompanied by a temperature rise to 35.4 °C from 26.0 °C. The mixture was stirred for 3 h and evaporated. The residue (7.70 g, 100%) was dissolved in dichloromethane (10 mL) and added to methanol (1 L) to precipitate the polymer. The white precipitate was collected by filtration and dried at 60 °C (0.1 mmHg) to give 7.50 g (98%) of white powdery material. Molecular weight was determined by gel permeation chromatography (GPC) (PMMA Lucite standard) to be $\bar{M}_n = 2180$, $\bar{M}_w = 2800$, $\bar{M}_w/\bar{M}_n = 1.28$, $\bar{M}_n$(calcd) = 3112. ^{1}H NMR ($CDCl_3$), δ 9.82 (CHO, triplet, 1 H), 7.20 (C_6H_5, singlet 5 H), 5.45 (ArCH, triplet, 1 H), 3.87 (HCOSi, broad, 16 H), 1.58 (CH_2, broad, 34 H), 0.88 ($SiC(CH_3)_3$, singlet, 144 H), 0.08 ($Si(CH_3)_2$, singlet, 96 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ −3.7 ($Si(CH_3)_2$), 18.1 (quaternary carbon of *tert*-butyl group), 26.2 (*tert*-butyl methyl carbon), 46.8 (chain methine carbon), 72.4 (terminal methine carbon), 126.3 (orthoaromatic carbon), 127.0 (para-aromatic carbon), 128.1 (meta-aromatic carbon), 202.1 (terminal aldehyde carbon).

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Received December 17, 1985