Novel Alternating Copolymers of Controlled Sequence. Regiochemical Control in Aldol Group Transfer Polymerization of Substituted (Butadienyloxy)trialkylsilanes

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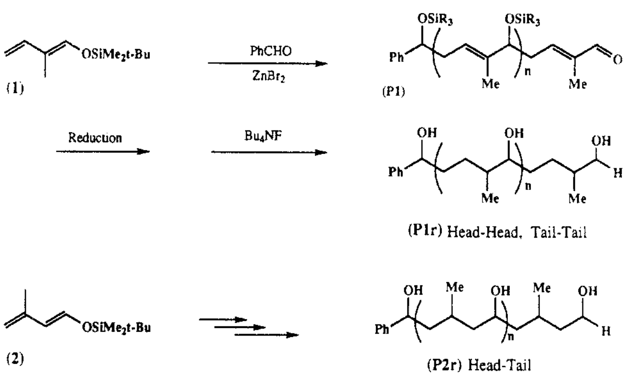
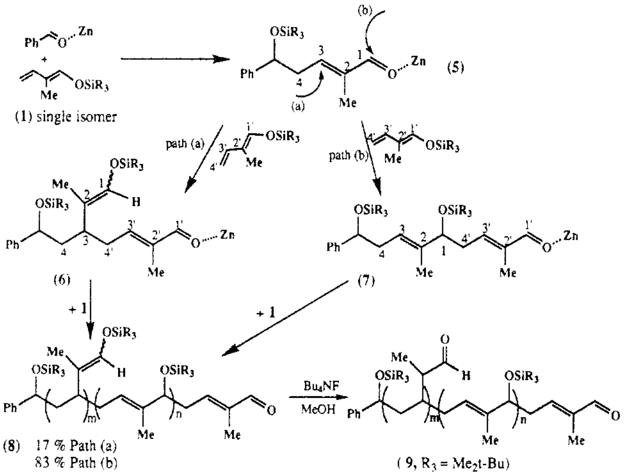
The trend in macromolecular chemistry is toward precise structure control and this is best done using "living" polymerization methods. Aldol group transfer polymerization (aldol-GTP) is a "living" polymerization method that gives control over polymer characteristics.[1-6] As part of our continuing effort to understand the mechanisms of GTP processes and prepare materials of controlled sequence, we synthesized (by modification of literature procedures[7,8]) and polymerized the substituted silyl dienolates ((2-methylbutadienyl)oxy)*tert*-butyldimethylsilane (1) and ((3-methylbutadienyl)oxy)*tert*-butyldimethylsilane (2) by aldol-GTP (Scheme 1). The reduced polymer **P1r** is a propylene–vinyl alcohol copolymer with head–head, tail–tail linkages while the corresponding polymer **P2r** is the same copolymer but with head–tail linkages. Thus, by appropriate placement of substituents, polymers of controlled sequence that cannot be made easily by existing methods should now be obtainable using aldol-GTP. The issues we chose to address in this Communication are (1) the effect of monomer substitution on molecular weight control and distribution, livingness of the chains, and chain length and (2) the regiochemistry of the reaction. We report herein the results of our studies.

The reaction conditions and polymerization results summarized in Table 1 reveal the following: (i) Polymers of very high molecular weight (up to 110 000) which hitherto have not been observed in aldol-GTP were obtained in almost quantitative yields with very good molecular weight control. (ii) Reactions carried out in the absence of benzaldehyde to determine the extent of purely *$ZnBr_2$-initiated cationic* polymerization gave polymers of uncontrolled and extremely high molecular weight (Table 1, runs 5 and 9). (iii) Monomer **2** appeared to react faster than **1** (runs 1–4 vs runs 9–12). Additionally, the molecular weight increased linearly with conversion within experimental error (Supplementary Material). These results and the observation that molecular weights were controlled with complete conversion of monomer reflect the "living" character of the reaction. The results further showed that the aldehyde indeed controlled the molecular weight and upon reaction regenerated a new aldehyde functional group (^{1}H NMR revealed the presence of the initiator fragments, the aldehyde and phenyl groups; Supplementary Material). These and the observation that the molecular weight was uncontrolled in the absence of the aldehyde initiator indicate that the purely *$ZnBr_2$-initiated cationic* polymerization does not seriously compete with the *$ZnBr_2$-catalyzed, aldehyde-initiated* aldol-GTP.

Scheme 1



Scheme 2



The possible reaction pathways for the polymerization of **1** are shown in Scheme 2. There are two possible reaction pathways available to the 1:1 adduct **5**: conjugate addition of **1** (nucleophile) to the 3-position of **5** to give **6** (path a) or 1,2-nucleophilic carbonyl addition (path b) to give **7**. ^{1}H NMR, ^{13}C NMR, and IR spectroscopies confirmed that both occur. However, the relative NMR peak areas showed that **8** contained only 17% pendent silyl enolate. Thus, nucleophilic 1,2-carbonyl addition is the *predominant pathway* as suggested in our earlier work involving the corresponding unsubstituted (butadienyloxy)trialkylsilanes.[2,3] Further confirmation was obtained by selective desilylation (Bu_4NF) of polymer **8** to give **9** (400 MHz ^{1}H NMR spectrum, Supplementary Material). The presence of approximately 17% branched material may account for the deviation from ideal "living" behavior manifested in the broader than expected molecular weight distribution and nonzero intercept in the molecular weight versus conversion plot. Regarding regioselectivity in the dienolate monomer itself, our earlier studies showed that the polymers contained no vinyl group.[3] This was taken to indicate that attack occurs at the 4-position and not the 2-position of the silyl dienolate monomer. In the present studies, we again did not observe any product corresponding to reaction at the 2-position of the monomer. Hirabayashi[5] and co-workers observed pendent silyl enolate in the aldol-GTP polymer of unsubstituted (butadienyloxy)trimethylsilane. They attributed this to *3,4-addition* but provided no unequivocal evidence. We are not aware of any example in the literature that suggests that silyl dienolates react at their 3,4-positions as isoprene does. Their observation is, however, readily explained by our results depicted in Scheme 2.

We obtained further evidence for our explanations by carrying out model reactions under conditions where pure intermediates could be isolated. Thus, three major products **5**–**7** were isolated from the model reaction involving a benzaldehyde:**1** ratio of 1:2 using column chromatography on silica gel and characterized by COSY and NOESY. Product **7** was obtained free of any other species while **6** was obtained in 70% purity with the only contaminant being **7**. The overall mole ratio of **7**:**6** was

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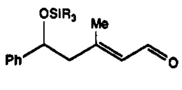
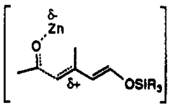
Table 1. Polymerization Conditions and Results (Control Runs in Italics)

run no.	mon (mmol)	PhCHO (mmol)	$ZnBr_2$ (mmol)	time (h)	% yield	M_n(calcd.) × 10^{-3}	$\bar{M}_n$(GPC) × 10^{-3}	$\bar{M}_w/\bar{M}_n$ (GPC)
1	**1** (8.44)	0.150	0.11	6.5	99	11.1	14.1	1.12
2	**1** (8.44)	0.075	0.09	6.0	99	22.3	21.0	1.39
3	**1** (8.44)	0.025	0.07	48.0	92	66.8	67.0	1.51
4	**1** (8.44)	0.013	0.04	60.0	90	128.6	109.0	1.44
5	*1 (4.22)*	*none*	*0.07*	*16.0*	*86*	—	*169.0*	*1.72*
6	**2** (2.11)	0.025	0.04	1.0	95	16.7	18.8	1.25
7	**2** (4.22)	0.025	0.04	1.3	95	33.4	26.5	1.55
8	**2** (4.22)	0.013	0.04	1.3	94	64.3	62.6	1.58
9	*2 (2.11)*	*none*	*0.12*	*0.5*	*95*	—	*450.0*	*1.63*

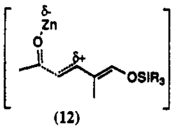
Chart 1



(10)



(11)



(12)

determined by ^{1}H NMR and confirmed by gas chromatographic analyses to be 84:16. These results indicate that the principal pathways in the reaction are as shown in Scheme 2 and rule out the possibility that the aldehyde is acting purely as a "livingness enhancer" by interacting reversibly with growing carbenium species to give a living-like cationic polymerization. For that to happen a small concentration of a very reactive species (carbenium ion) must be in dynamic equilibrium with a large concentration of very unreactive species (aldehyde). However, the model reaction and the polymerization results show that the aldehyde is a reactant whose relative molar amount controls the molecular weight of the polymer. Examples in the literature involving the use of nucleophiles such as esters, sulfides, aldehydes, ethers, and amines as livingness enhancers in cationic polymerizations suggest that the nucleophile be unreactive under the reaction conditions.[9]

We repeated our studies with monomer **2**. In this case we observed only a trace (<2% by ^{1}H NMR) of the product expected to form by path a. This suggests that **2** reacted almost exclusively by path b. Thus, by placing the substituent in the 3-position instead of the 2-position the undesirable conjugate addition of the monomer to the α,β-unsaturated aldehyde was significantly suppressed. This change in regiochemistry may be attributed to steric hindrance at the 3-position of **10** (Chart 1). The observed relative reactivities of **2** and **1** may be explained by the relative stabilities of the possible transition states (Chart 1). Assuming that the rate-determining step is the C–C bond formation, reaction of **2** will involve a tertiary allylic incipient carbenium ion (**11**) while that of **1** will involve a secondary allylic incipient carbenium ion (**12**) which should be less stable than **11**. Hence, **2** may be expected to react faster than **1**. Additionally, consideration of steric factors suggests the same trend since reaction of **5** at its C═O is expected to be more sensitive to steric hindrance than the corresponding reaction of **10**.

In conclusion, we have shown that aldol-GTP of **1** and **2** is a "living" system giving well-defined polymers of controlled high molecular weight, molecular weight distribution, and sequence. We have further shown that 2-substituted dienolate reacts both by 1,2-carbonyl addition (83%) and 1,4-conjugate addition (17%) with an α,β-unsaturated aldehyde, but the corresponding 3-substituted monomer reacts almost exclusively by 1,2-addition to the carbonyl carbon. This regiochemical result is attributed to steric hindrance at the 3-position. We further found that the 3-substituted monomer reacts faster than the 2-substituted one for steric reasons and possibly due to the formation of a more stable allylic carbenium ion-like transition state. Further mechanistic studies and reductions of the polyenes to propylene–vinyl alcohol copolymers are in progress.

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Supplementary Material Available: Listings of ^{1}H NMR spectra with complete peak assignments for polymers of monomers **1** and **2**, polymer **9**, and products **6** and **7** isolated from the model reaction involving a **1**:benzaldehyde ratio of 2:1, and molecular weight vs conversion plot for the polymerization of **1** (7 pages). Ordering information is available on any current masthead page.

References and Notes

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(8) ((2-Methylbutadienyl)oxy)*tert*-butyldimethylsilane (**1**) and ((3-methylbutadienyl)oxy)*tert*-butyldimethylsilane (**2**) were synthesized by modifications of the literature procedure.[7] For example, toluene was used as solvent instead of benzene, a half equivalent of zinc chloride was used rather than the catalytic amount, and the reaction was carried out at reflux temperature. Both monomers were purified by distillation from sodium. **1**: 76% yield (single isomer). Bp: 43.5 °C/0.34 mmHg. ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.4 (s, 1H); 6.3 (dd, J = 10.5, 17.1 Hz, 1H); 4.96 (d, J = 17.1 Hz, 1H); 4.8 (dd, J = 10.5, 1.3 Hz, 1H); 1.7 (d, J = 1.3 Hz, 3H); 0.9 (s, 9H); 0.15 (s, 6H). HRMS (EI): obsd 198.143967, calcd 198.143994. **2**: 51% yield (E:Z ratio = 8:1 by GC). Bp: 40–41 °C/0.45 mmHg. ^{1}H NMR (200 MHz, $CDCl_3$): E-isomer: δ 6.50 (d, J = 12.1 Hz, 1H); 5.80 (d, J = 12.1 Hz, 1H); 4.56 (s, 1H); 4.72 (s, 1H); 1.78 (s, 3H); 0.91 (s, 9H); 0.15 (s, 6H). Z-isomer: δ 6.14 (d, J = 6.1 Hz, 1H); 4.95 (2 singlets, 2H); 4.90 (d, J = 6.1 Hz, 1H); 2.00 (s, 3H); 0.91 (s, 9H); 0.15 (s, 6H). HRMS (EI): obsd 198.143967, calcd 198.143994.

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