ABSTRACT. Sequential silyl aldol condensation involving aldehydes and silyl vinyl ethers gives monodisperse poly(silyl vinyl ether) whose molecular weight (Rₙ 1000–160,000) is controlled by the aldehyde initiator. The new process, termed aldol-group transfer polymerization (aldol-GTP) involves a silyl group transfer from monomer to the carbonyl oxygen of either the initiator or the living polymer, leading to generation of a new terminal aldehyde functional group. The reaction is catalyzed by Lewis acids and can be initiated by other electrophiles, e.g., alkyl halides and acetals. The living polymers are stable, neutral materials whose hydrolytic stability depends on the bulkiness of the silyl group. In general, aromatic aldehydes tend to react more cleanly as initiators than do aliphatic aldehydes. Unlike the GTP of methyl methacrylate in which the silyl group is transferred from the initiator to the monomer, aldol-GTP involves a transfer of silyl group from monomer to initiator. Some of the advantages of aldol-GTP over existing methods such as cationic polymerization include operability over a broad temperature range, complete monomer conversion, living polymer formation, very good molecular weight control, and facile block copolymer synthesis. It permits control of hydrophilicity of block copolymers.

I. INTRODUCTION

We recently reported application of Michael addition to controlled synthesis of acrylic polymers. The method, named group transfer polymerization (GTP), involves addition of silyl ketene acetals (as Michael donors) to α,β-unsaturated carbonyl and nitrile compounds (as Michael acceptors) in the presence of a suitable catalyst (Scheme 1).

Scheme 1. Group Transfer Polymerization

GTP gives monodisperse living methacrylate polymers of well-controlled molecular weights. Another reaction that has been critical in making carbon–carbon bonds is aldol condensation. However, it has been exploited in preparation of polymers. In our earlier communication, we described the first application of aldol condensation to direct synthesis of living polymers whose structure and molecular weight are well-controlled. To accomplish this, we took advantage of the fact that aldehydes react with silyl vinyl ethers to give silylated cross-aldol products containing a new terminal aldehyde group. Thus, addition of excess silyl vinyl ether to benzaldehyde as initiator gives a silylated vinyl alcohol polymer (Scheme 2). This method was named "aldol-GTP".

Scheme 2. Aldol-GTP

\[
\begin{align*}
\text{O} & \quad \text{C–H} + \text{H}_2\text{C}–\text{CHO} & \text{cat} \quad \rightarrow \quad \text{O} \\
\text{2} & \quad \text{CH}–\text{CH}_2\text{CH} & \\
\text{1} & \quad \text{OSiMe}_2\text{Bu}^t & \\
\text{2} + n \text{H}_2\text{C}–\text{CHO} & \text{cat} \quad \rightarrow \quad \text{O} \\
\text{3} & \quad \text{CH}–(\text{CH}_2\text{CH})_n\text{CH}_2\text{CH} & \\
\text{O} & \quad \text{SiMe}_2\text{Bu}^t & \\
\text{OSiMe}_2\text{Bu}^t & \quad \text{OSiMe}_2\text{Bu}^t & 
\end{align*}
\]

2. RESULTS AND DISCUSSION

In GTP of methacrylates (Scheme 1), the silyl group is transferred from the initiator to the monomer, thereby regenerating the silyl ketene acetal functionality. In contrast, aldol-GTP involves a transfer of silyl group backwards from monomer to initiator. The aldehyde functionality is regenerated. The adduct is stable, and upon further addition of monomer, reacts with the excess silyl vinyl ether to give a stable polymer.

2.1 Solvents and Catalysts

The catalysts that are operative include Lewis acids such as di(isobutyl)aluminum chloride, titanium tetrachloride, tin tetrachloride, boron trifluoride, zinc bromide, zinc iodide and zinc chloride. The preferred catalysts are the zinc halides. The results are summarized in Table I. Whereas TiCl₄ gives low yields, the zinc halides tend to give quantitative yields of polymers of narrow molecular weight distribution. Anion catalysts, such as tris(dimethylamino)sulfonium bifluoride, tetrabutylammonium bifluoride and tetrabutylammonium acetate give less satisfactory results. These anions strongly coordinate to the backbone siloxy groups. This makes