

Preparation of ester terminated poly(alkyl vinyl ether) oligomers and block copolymers using a combination of living cationic and group transfer polymerization

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Summary

This paper reports the synthesis and characterization of new, functionalized poly(alkyl vinyl ether) oligomers, and block copolymers containing poly(alkyl vinyl ether) and poly(methyl methacrylate). Using the HI/ZnI₂ initiating system in nonpolar solvents (hexane, toluene) at -15 °C, both monofunctional and difunctional poly(alkyl vinyl ether) oligomers of predicted molecular weights precisely terminated with ester end groups have been prepared. Novel diblock copolymers comprised of poly(methyl methacrylate) and poly(alkyl vinyl ether) have also been synthesized using a combination of living cationic and living group transfer polymerization (GTP) techniques.

Introduction

End-functionalized, or telechelic, polymers are indispensable building blocks for multiphase polymeric materials. Hence, there has been a growing interest in new synthetic methods for the preparation of these polymers. Among possible methods for preparation of the telechelics, living polymerization is the simplest and the most effective and versatile. The growing chain ends of living polymers are highly reactive and can therefore be used for the synthesis of telechelics, block copolymers and other functionalized polymers.

Quasi-living and living cationic polymerization of alkyl vinyl ethers has been well established by Kennedy, Sawamoto & Higashimura [1-12].

This study focuses on (i) the synthesis of monofunctional poly(alkyl vinyl ether) oligomers of predicted molecular weights with ester end groups using the HI/ZnI₂ initiating system, and (ii) extension of the termination reaction used for those oligomers to the synthesis of novel diblock copolymers comprised of poly(butyl vinyl ether) and poly(methyl methacrylate) using a combination of living cationic and living group transfer polymerization (GTP) [13] techniques.

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Experimental

Materials.

Commercial n-butyl vinyl ether (BVE) (Aldrich, 98%) was washed with 10% aqueous sodium hydroxide solution, then with water, dried overnight with potassium hydroxide pellets, then distilled from calcium hydride. Gaseous methyl vinyl ether (MVE) was dried by passing it through a tube containing calcium hydride. It was subsequently condensed into the reaction flask at $-15\text{ }^{\circ}\text{C}$. Anhydrous hydrogen iodide (in hexane solution) was obtained from a 57% aqueous solution (Aldrich) by dehydration with phosphorus pentoxide [14]. Zinc iodide (Aldrich, purity $>99.99\%$) was used as received without further purification. It was dried under vacuum at room temperature in the absence of light for at least 24 hours before use. Toluene, hexane, diethyl ether, and THF were purified according to known literature procedures [15]. Dimethyl(trimethylsilyl)methyl ketene acetal (Aldrich) was purified by fractional vacuum distillation ($40\text{ }^{\circ}\text{C}$, 15 mm Hg). The purity of the collected fractions was determined by ^1H NMR (Bruker, 270 MHz instrument). Tetrabutylammonium benzoate was prepared from tetrabutylammonium hydroxide and benzoic acid as previously described [16]. The catalyst composition was verified by elemental analysis. Methyl methacrylate (MMA) (Rohm and Haas) was vacuum distilled from calcium hydride and stored under a nitrogen atmosphere at $-20\text{ }^{\circ}\text{C}$. An aliquot of the calcium hydride purified MMA was titrated with a 25 wt% triethylaluminum (TEA) solution in hexane (Ethyl Corporation) to remove residual alcohol and distilled under vacuum from the complex [17].

General Synthetic Procedures.

All polymerizations were carried out under a dry nitrogen atmosphere. Monofunctional poly(alkyl vinyl ethers) were prepared by adding, successively, a hexane solution of HI (in hexane) and ZnI_2 (in diethyl ether) to a monomer (butyl vinyl ether or methyl vinyl ether) solution in hexane or toluene at $-15\text{ }^{\circ}\text{C}$. The reaction was terminated with dimethyl(trimethylsilyl)methyl ketene acetal in the presence of tetrabutylammonium benzoate to afford ester terminated poly(alkyl vinyl ethers). Number average molecular weights of these ester terminated polymers were determined by vapor phase osmometry (VPO) in toluene.

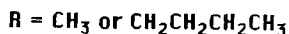
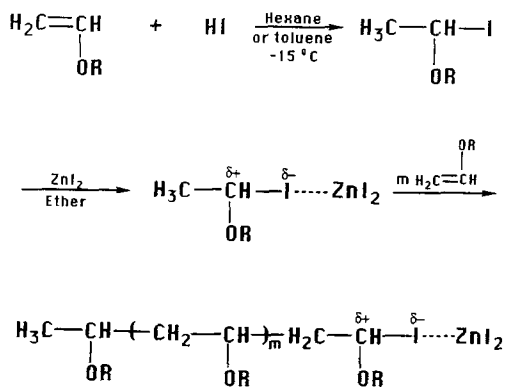
The polymerization of MMA was carried out in toluene. The mode of addition of reagents begins with the charge of the GTP initiator, a silyl ketene acetal, followed by the addition of an aliquot of the tetrabutylammonium benzoate (TBAB) solution in THF. The initiator and catalyst were allowed to complex for 30 minutes at room temperature, then MMA was added dropwise via syringe over a period of 20

minutes . After the exotherm had subsided, the reaction was allowed to stir at room temperature for an additional hour. This living PMMA can be used to terminate the solutions of living cations described above to afford diblock copolymers comprised of poly(butyl vinyl ether) and poly(methyl methacrylate) segments. Characterization of the poly(butyl vinyl ether)-b-poly(methyl methacrylate) was done using ^1H and ^{13}C NMR, and gel permeation chromatography.

Results & Discussion

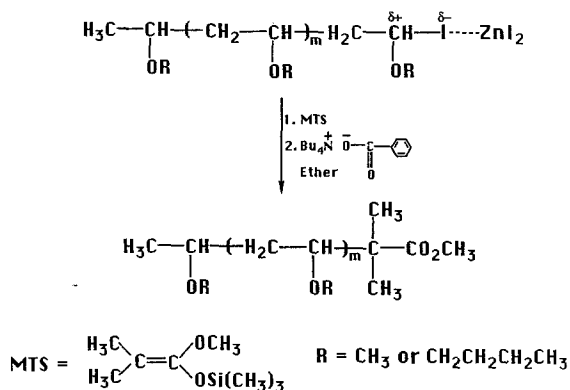
Synthesis and characterization of ester terminated poly(alkyl vinyl ethers)

HI/ZnI_2 initiated living polymerization of alkyl vinyl ethers (butyl vinyl ether or methyl vinyl ether) were carried out at -15°C in nonpolar solvents such as hexane or toluene as shown in Scheme 1. The living nature of such polymerizations has been well established by Higashimura and Sawamoto [8]. It would be anticipated that reaction rate would be dependent on both the concentration of Lewis acid as well as the concentration of the initiator as was previously established for the HI/I_2 initiated polymerization [18]. For this particular study however, the molar ratio of HI to ZnI_2 was held constant at 25:1. Reaction progress was monitored by observing the disappearance of the vinylic protons from the monomers in the ^1H NMR.



Scheme 1. Living polymerization of alkyl vinyl ethers mediated by HI/ZnI_2 .

Monofunctional ester terminated poly(alkyl vinyl ether) oligomers were prepared by terminating the living cations shown in Scheme 1 with dimethyl(trimethylsilyl)methyl ketene acetal in the presence of tetrabutylammonium benzoate (Scheme 2).



Scheme 2. Synthesis of ester terminated poly(alkyl vinyl ethers).

This carbon-carbon bond forming termination reaction has a distinct advantage over introducing an amino or alkoxy group to the chain end of the living polymers, since the latter reactions would introduce hydrolytically unstable aminal and acetal end groups respectively. The number average molecular weights ($\langle \text{Mn} \rangle$) of the ester terminated poly(alkyl vinyl ether) oligomers shown in Scheme 2 were determined by vapor phase osmometry (Table 1).

Polymer	$\langle \text{Mn} \rangle$ Theoretical	$\langle \text{Mn} \rangle$ Observed
p(BVE)	1000	1150
p(BVE)	5000	5100
P(BVE)	10000	10700
p(BVE)	20000	19600
p(MVE)	500	600

BVE = butyl vinyl ether

MVE = methyl vinyl ether

Table 1. $\langle \text{Mn} \rangle$ of ester terminated poly(alkyl vinyl ethers) as determined by VPO.

As can be seen from Table 1, there is a good correlation between the observed $\langle \text{Mn} \rangle$ and the molecular weight regulated by the monomer to initiator feed ratio (theoretical $\langle \text{Mn} \rangle$). It should be noted that this molecular weight data further confirms the living polymerization process. This was deemed important since the preparation of precisely functionalized oligomers is dependent on this concept.

The end group structure of these poly(alkyl vinyl ethers) was determined by the spectroscopic methods FTIR, ^1H and ^{13}C NMR. FTIR of the poly(butyl vinyl ether) having

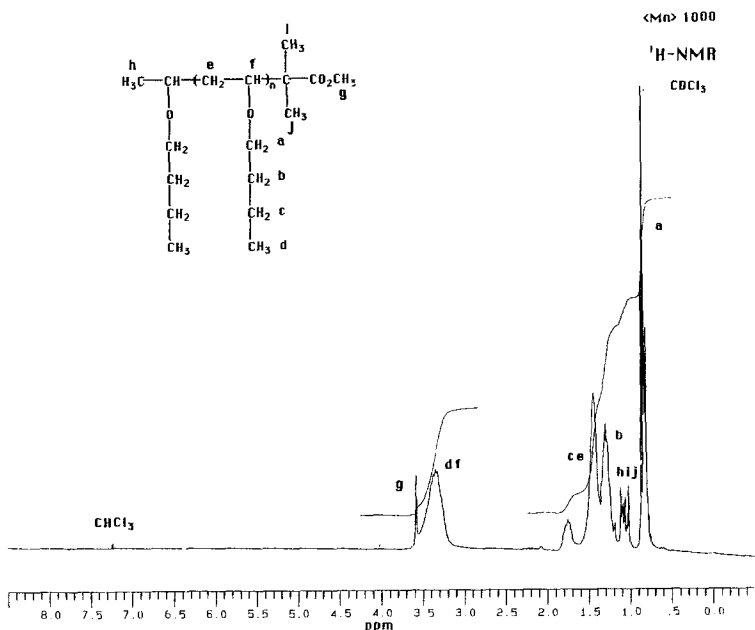


Figure 1. ¹H NMR of poly(butyl vinyl ether) having theoretical <Mn> = 1000.

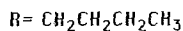
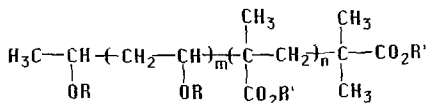
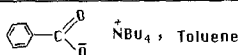
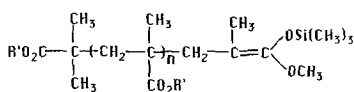
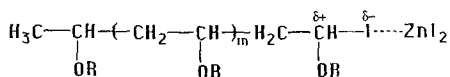
theoretical <Mn> = 1000 indicates a strong ester carbonyl stretch at 1740 cm⁻¹. This observation was confirmed by ¹³C NMR, which clearly shows the presence of the carbonyl carbon at 176 ppm in CDCl₃. The ¹H NMR spectrum of this polymer is shown in Figure 1. All key absorptions of both the methoxy group on the head of the polymer and the methyl group on the tail of the polymer are seen. Moreover, the intensity ratio of these end groups was very close to the theoretical value of (1:1), confirming that each chain had exactly one monofunctional methyl endgroup and one ester endgroup.

²⁹Si NMR Studies to monitor side products in the termination step

In order to further understand the reaction between the living cation with the trimethylsilyl ketene acetal, ²⁹Si NMR was used to monitor the products in the termination step. To obtain this information, the preparation of an ester terminated poly(butyl vinyl ether) having a theoretical <Mn> = 1000 was performed in an NMR tube using deuterated toluene as the solvent. Following termination of the polymer, two silicon species were seen at 7.09 and 15.10 ppm with respect to TMS (tetramethylsilane). The chemical shifts of these silicon species match well with the chemical shift of trimethylsilyl iodide (7.10 ppm with respect to TMS) and a trimethylsilyl benzoate-zinc iodide complex (15.14 ppm with respect to TMS).

Synthesis and characterization of novel poly(butyl vinyl ether)-*b*-poly(methyl methacrylate) copolymers

Since the ketene silyl acetal structure is also the end group in the group transfer polymerization of methacrylate monomers, we were interested in investigating the feasibility of terminating the living cations with living PMMA prepared by group transfer polymerization (Scheme 3). In order to achieve this, the solution of the living cation of poly(butyl vinyl ether) in toluene at $-15\text{ }^{\circ}\text{C}$ was quenched with a solution of living PMMA prepared by group transfer polymerization in the same solvent.



Scheme 3. Synthesis of novel poly(butyl vinyl ether)-*b*-poly(methyl methacrylate) copolymers.

The formation of the diblock copolymer shown in Scheme 3 was established by ^1H NMR, ^{13}C NMR, and gel permeation chromatography (Figure 2).

Solvent: Chloroform

Temp.: 30°C

Column: Permugel

Detector: RI

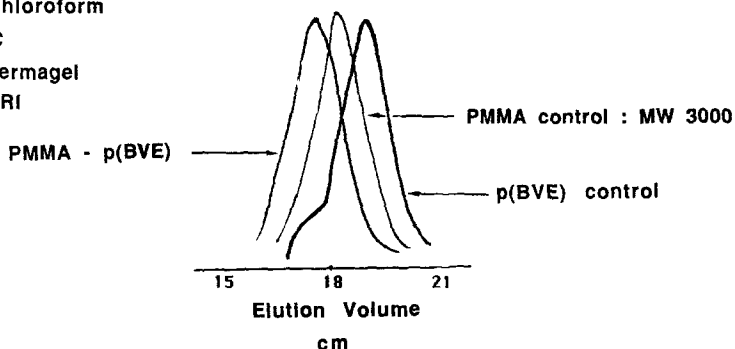


Figure 2. GPC analysis of the homopolymers and the diblock copolymer.

Both ^1H and ^{13}C NMR clearly show the presence of both poly(butyl vinyl ether) and poly(methyl methacrylate) species corresponding to the theoretical compositions. Gel permeation chromatographic analyses of both blocks separately and of the diblock clearly show the progression of the copolymer to higher molecular weight (Figure 6). It is noteworthy that polar coordinating solvents such as THF must be excluded from this polymer coupling reaction. In the presence of the lewis acid (ZnI_2), THF can undergo a ring opening reaction. Moreover, in polar coordinating solvents, the poly(alkyl vinyl ether) cations would be more solvated, thus making them more reactive and susceptible to termination reactions such as elimination. If the rate of this termination reaction is faster than the coupling reaction with living PMMA, little or no block copolymer would be formed.

Conclusions & Future Work

Thus far, we have been successful in preparing new ester terminated poly(alkyl vinyl ethers) using living cationic polymerization methods. These may be useful for incorporation into polyester engineering thermoplastics as soft segments via transesterification. Moreover, a novel copolymer containing poly(methyl methacrylate) and poly(butyl vinyl ether) has been prepared by terminating living poly(butyl vinyl ether) with living poly(methyl methacrylate). For this copolymerization, living poly(methyl methacrylate) was prepared using group transfer polymerization techniques. Future work will focus on studying the morphology, thermal and mechanical properties of these block copolymers.

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