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TANDEM TRANSITION METAL CATALYZED ISOMERIZATION AND CATIONIC POLYMERIZATION

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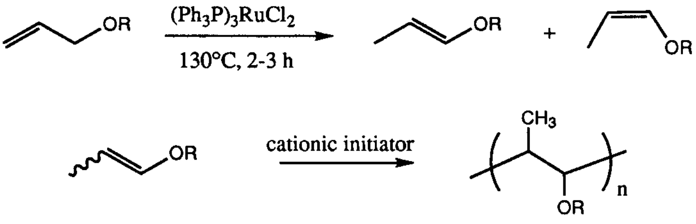
Abstract: A wide variety of mono-, di- and multifunctional allyl ethers and related compounds are readily polymerized using a newly discovered polymerization reaction which has been termed: a transition metal-catalyzed tandem isomerization and cationic polymerization. Employing dicobalt octacarbonyl in combination with organosilanes, the polymerization of these monomers takes place rapidly to give high molecular weight polymers.

INTRODUCTION

One of the long standing problems in polymer chemistry is the reluctance of allylic ethers to undergo efficient addition polymerization by free radical, cationic and anionic mechanisms. The failure of these monomers to give high molecular weight polymers is usually attributed to the propensity of these monomers to undergo rapid and facile degradative chain transfer reactions involving the allylic hydrogens and to the stability of the allylic free radicals, cations and anions which are formed (Ref. 1). The reluctance of allyl ethers to undergo polymerization is unfortunate, since these compounds are easily and inexpensively prepared in high yields by simple, straightforward nucleophilic displacement reactions of allylic halides with alkali metal alcoholates (Ref 2). In this laboratory, we have been seeking ways to circumvent this problem. One of the strategies we have employed is shown in Scheme 1.

Scheme 1



eq. 1

eq. 2

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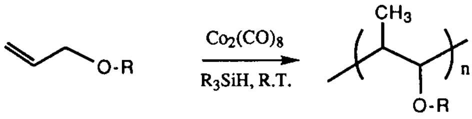
Although allyl ethers do not polymerize efficiently in the presence of cationic initiators, their isomers, the 1-propenyl ethers are exceptionally reactive in the presence of those same agents and high molecular weight polymers are obtained. We have found that allyl ethers can be rapidly and quantitatively converted to the corresponding 1-propenyl ethers in the presence of catalysts such as t-Bu-OK or $(Ph_3P)_3RuCl_2$ (Refs. 3-5). These methods could be employed for the preparation of a wide variety of mono- and multifunctional 1-propenyl ethers and further extended to the preparation of the analogous 1-butenyl ethers (Ref. 6). Cederstav and Novak (Ref. 7) have employed a similar approach for the isomerization and polymerization of acetaldehyde.

Further consideration of Scheme 1 led to the conclusion that if it were possible to carry out the isomerization of allyl ethers in the presence of a cationic initiator, the polymer should be obtained directly. Accordingly, we set about to devise a catalytic system which would confirm this hypothesis. The present paper describes the development of a novel transition metal catalyzed polymerization reaction which achieves the direct, facile, room temperature polymerization of allyl ethers as well as many other related compounds.

RESULTS AND DISCUSSION

Recently (Refs. 8, 9), it has been discovered that allyl ethers undergo smooth, exothermic polymerization at room temperature in the presence of dicobalt octacarbonyl and a silane containing a Si-H bond. ^1H NMR spectra clearly indicate that the polymers which are obtained have the general structures shown in equation 3.



eq. 3

Thus, the overall reaction can be characterized as taking place by a tandem or coupled process involving concurrent, isomerization of the allyl ether to the 1-propenyl ether and polymerization of this latter isomer.

Investigations of this new polymerization reaction have been conducted and we propose the mechanism as depicted in equations 4-7 of Scheme 2.

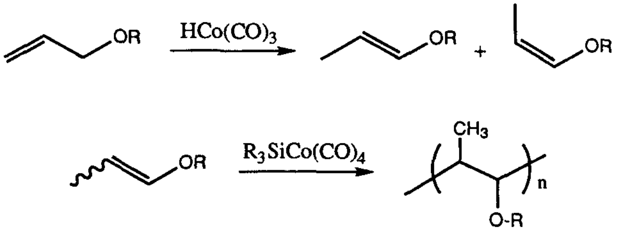
Scheme 2

$$Co_2(CO)_8 + R_3SiH \longrightarrow R_3SiCo(CO)_4 + HCo(CO)_4$$

eq. 4

$$HCo(CO)_4 \longrightarrow HCo(CO)_3 + CO$$

eq. 5



eq. 6

eq. 7

In the first step (eq. 4), dicobalt octacarbonyl ($Co_2(CO)_8$) reacts with a Si-H containing compound to generate two species: $HCo(CO)_4$ and $R_3SiCo(CO)_4$ (Ref. 10). Under the reaction conditions, $HCo(CO)_4$ (eq. 5) undergoes loss of carbon monoxide to generate $HCo(CO)_3$ (Ref. 11). Thereafter (eq. 6), $HCo(CO)_3$ catalyzes the isomerization of the allyl ether to a mixture of *cis* and *trans* 1-propenyl ethers (Ref. 12). In the last step (eq. 7), $R_3SiCo(CO)_4$ initiates the cationic polymerization of the enol ether. Considerable literature precedent and experimental evidence for each step of the above mechanism has been gathered. During this investigation, $HCo(CO)_4$ and $R_3SiCo(CO)_4$ were independently prepared and successfully employed for the respective isomerization of allyl ethers and for the polymerization of 1-propenyl ethers. In certain cases, traces of 1-propenyl ethers can be detected by gas chromatography and by NMR in the reaction mixtures during polymerization confirming that the polymerization involves these isomeric compounds as intermediates.

Typically, the polymerization of an allyl ether proceeds exothermically at room temperature after a short (~45 second) induction period. The polymerization is inhibited by Lewis bases but not by free radical inhibitors. These results are strongly suggestive of a cationic mechanism. Carbon monoxide is liberated during the polymerization. The highest molecular weight polymers are obtained at $Co_2(CO)_8$ and silane concentrations of 0.5-1.0 mol%. A wide variety of silanes may be employed for the polymerization and these include mono-, di and trisubstituted silanes. The only requirement is that the silane bear a Si-H bond. Similarly, stannanes and germanes containing Sn-H and Ge-H bonds may be employed in place of the silane. A preliminary survey of the use of various transition metal complexes in this polymerization revealed that all the Group VIII metal carbonyl complexes were active while those metal carbonyl complexes outside this group were not. Of the Group VIII metal carbonyl complexes, $Co_2(CO)_8$ was the most active and catalyzed the reaction at room temperature, while the others did so at elevated temperatures.

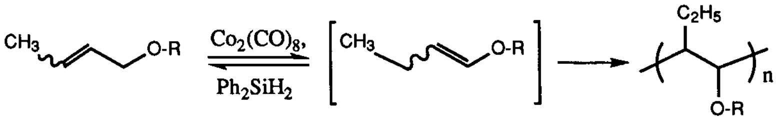
The same catalyst system is capable of mediating the polymerization other types of monomers which polymerize by a cationic mechanism including; vinyl ethers, 1-propenyl ethers and the ring-opening polymerization of epoxides (Refs. 13, 14). Simple allyl ethers bearing a variety of nonbasic functional groups undergo smooth isomerization and polymerization in the presence of this new catalyst system. Similarly, oligomers with allyl ether end groups also polymerize smoothly. Di- and multifunctional allylic ethers polymerize readily to give crosslinked, insoluble matrices. It has also been observed that mixtures of different allyl ethers can be polymerized to give copolymers with a random placement of repeating units. The ^1H NMR spectra indicate the resulting polymers bear silicon-containing endgroups which are derived from the silane. The results of the homopolymerizations of several typical mono- and multifunctional allyl ethers are given in Table 1.

Table 1
Tandem Isomerization and Polymerization Of Various Allyl n-Alkyl Ethers*

Monomer	Conversion (%)	M_w (g/mol)	M_n (g/mol)	M_w/M_n
Allyl n-octyl ether	60	37000	24000	1.5
Allyl n-decyl ether	68	34700	18000	1.9
Allyl n-dodecyl ether	65	24300	14800	1.6
Allyl benzyl ether	62	840	760	1.1
1,2-Diallyloxyethane	80	Crosslinked Network		-
1.4-Diallyloxybutane	72	Crosslinked Network		-
1,6-Diallyloxyhexane	70	Crosslinked Network		-
1,2,3-Triallyloxy propane	54	Crosslinked Network		-
Pentaerythritol tetraallyl ether	59	Crosslinked Network		-

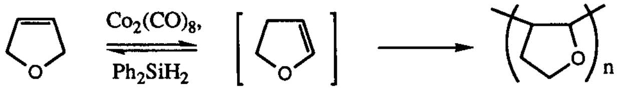
*[($Co_2(CO)_8$] = 1 x 10^{-5} mol, [n-hexyl silane] = 8.4 x 10^{-4} mol/g monomer, 25°C, 1 h.

Cobalt-catalyzed tandem isomerization and cationic polymerizations are quite general and can be applied to a wide variety of different allylic and related monomers. For example, the polymerization of crotyl ethers (2-butenyl ethers) proceeds smoothly to give high molecular weight polymers as shown in equation 8.

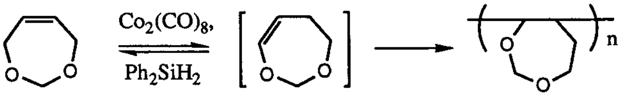


eq. 8

The polymerization of cyclic allylic ethers such as 2,5-dihydrofuran (eq. 9) and 1,3-dioxep-4-ene (eq. 10) take place readily by concurrent isomerization and polymerization in the presence of $Co_2(CO)_8$ and diphenylsilane. In all cases, the



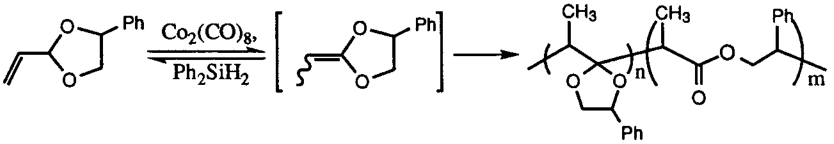
eq. 9



eq. 10

structure of the final polymer as determined by ^{1}H NMR is indicative of first an isomerization of the initial allylic ethers to the enolic isomers, shown in parentheses, and then cationic polymerization of these latter species.

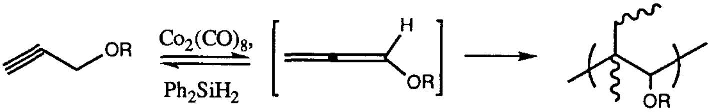
Similarly as depicted in equation 11, 2-vinyl-1,3-dioxolanes first undergo isomerization to the corresponding ketene acetals and then the polymerization of these latter compounds takes place.



eq. 11

${}^1H$ NMR spectroscopy reveals that both vinyl and ring-opening polymerization have occurred. This polymerization reaction is applicable to a wide variety of vinyl acetals bearing different substituents on the 1,3-dioxolane ring. The starting vinyl acetals are readily obtained from the condensation of acrolein with 1,2-diols.

Lastly, propargyl ethers are acetylenic analogs of allylic ethers. These monomers undergo very facile polymerization in the presence of $Co_2(CO)_8$ and a silane to give crosslinked, insoluble polymers (eq. 12). The polymerization of these compounds is proposed to take place by first isomerization of the propargyl ether to an allenic ether. Cationic polymerization of the allenic ether by the silyl-cobalt species takes place with reaction at both double bonds of the allene group.



eq. 12

CONCLUSIONS

A novel transition metal catalyzed polymerization reaction has been discovered in which a wide variety of allylic ethers and related compounds undergo facile polymerization to give high molecular weight polymers. The mechanism of the reaction is complex and involves a sequence of steps. In the presence of $Co_2(CO)_8$ and a Si-H containing silane, isomerization of the allylic ether first proceeds to give the corresponding vinyl or enol ether. This reaction is catalyzed by $HCo(CO)_3$ generated by reaction of $Co_2(CO)_8$ with the silane. Thereafter, cationic polymerization of the enol ether proceeds initiated by a silyl-cobalt species also produced in the reaction of $Co_2(CO)_8$ with the silane. Allylic ethers are readily prepared, inexpensive monomers. Consequently, these novel polymerizations have many potentially interesting applications. The use of these novel polymerization initiators to prepare comb, graft and star polymers is currently being investigated.

ACKNOWLEDGMENT

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