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The Dicobaltoctacarbonyl Catalyzed Polymerization of Allylic Ethers

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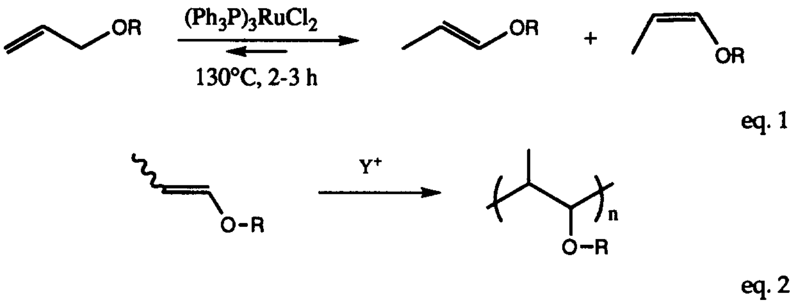
Abstract. Allylic ethers undergo spontaneous, exothermic polymerization in the presence catalytic amounts of dicobaltoctacarbonyl and silanes. Investigation of the mechanism of this new polymerization reaction indicates that the polymerization occurs by a multistep mechanism involving first, isomerization of the allylic ether to the corresponding 1-propenyl ether, then cationic polymerization of this latter species. It is proposed that two different cobalt-containing species are present which catalyze this tandem process.

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.[1] The failure of these monomers to give high polymers is usually attributed to the high propensity of these monomers to undergo rapid and facile chain transfer reactions involving the allylic hydrogens and to the stability of the allylic free radicals, cations and anions which are formed. This is unfortunate since allylic ethers are potentially attractive monomers which are readily prepared in nearly quantitative yields by simple etherification reactions either from allyl halides or allyl alcohol.[2,3] In this laboratory we have been seeking alternative means of polymerizing this interesting class of compounds.

One general approach which we have taken is depicted in Scheme 1.[4,5,6]

Scheme 1



Allylic ethers can be efficiently isomerized to the corresponding 1-propenyl ethers using ruthenium complexes as catalysts (equation 1). This reaction proceeds cleanly and nearly quantitatively at temperatures in excess of 130°C to afford a 40:60 mixture of *cis* and *trans* 1-propenyl ethers. 1-Propenyl ethers are a class of vinyl or enol ethers which undergo facile cationic polymerization (equation 2) in the presence of a wide variety of conventional cationic initiators (Y^+) such as Lewis and Brønsted acids.[3] Thus, although allylic ethers do not directly polymerize, they can be efficiently polymerized via the two-step process shown in Scheme 1.

Consideration of the thermodynamics of the above two reactions led to a new approach to the problem of the polymerization of allylic ethers. The isomerization reaction shown in equation 1 is driven towards the formation of the 1-propenyl ether product due to the resonance and inductive stabilization provided by the neighboring oxygen atom and the higher thermodynamic stability gained by the conversion of a terminal to an internal double bond. Calculations have given a ΔH value of -4 kcal/mol for this reaction.[7] The ΔH of the cationic polymerization of 1-propenyl ether monomers shown in equation 2 are of the order of -14 to -19 kcal/mol and are, therefore, highly exothermic.[3] The fact that both reactions have negative ΔH values suggested that if appropriate catalysts for both the isomerization and the cationic polymerization of the resulting 1-propenyl ether were present, both reactions would take place simultaneously. Moreover, the combined reactions would be strongly driven towards the formation of the products by the large ΔH of the polymerization step and consequently, only polymer would be isolated. An equivalent situation would also arise if the isomerization catalyst were also, fortuitously, a catalyst for the polymerization reaction. Based on this analysis, we undertook an investigation designed to determine whether such a dual or tandem process might be feasible.

RESULTS AND DISCUSSION

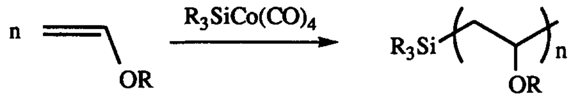
It should be pointed out that while cationic polymerizations of enol ethers are both exothermic and spontaneous, the ruthenium catalyzed isomerization reaction shown in equation 1 is exothermic but not spontaneous. Thus, in order to carry out a successful low temperature polymerization of an allyl ether, a more efficient catalyst than $(Ph_3P)_3RuCl_2$ for the isomerization of allyl ethers to 1-propenyl ethers must be found. Moreover, this catalyst must be compatible with the catalyst employed for the subsequent cationic polymerization reaction. The isomerization of a variety of terminal to internal olefins by $HCo(CO)_4$ has been reported to take place at room temperature.[8,9,10] Since $HCo(CO)_4$ is unstable at room temperature and rapidly loses CO, $HCo(CO)_3$ has been proposed as the active catalytic species in this reaction.[9,11]

Accordingly, $HCo(CO)_4$ was prepared and isolated at low temperatures by the method of Sternberg, Wender and Orchin[12] and subsequently employed for the isomerization of an allyl ether model compound. It was observed that allyl n-octyl ether undergoes facile isomerization at 25°C to give octyl 1-propenyl ether in the presence of $HCo(CO)_4$. It was also observed that a small amount (10%) of low molecular weight polymer was produced during the reaction. We propose that the polymer results from the strong acid (pK_a of 0.9[13]) $HCo(CO)_4$ induced cationic oligomerization of the 1-propenyl ether produced during the reaction. That $HCo(CO)_4$ can serve as an initiator for the cationic polymerization of 1-propenyl ether monomers was confirmed by independently carrying out the polymerization of n-octyl 1-propenyl ether in the presence of this strong acid. Again, a low yield of low molecular weight polymer was formed indicating that $HCo(CO)_4$ is a relatively inefficient cationic initiator.

In 1970 Chalk[14] showed that $HCo(CO)_4$ can be prepared via the reaction of $Co_2(CO)_8$ with Si-H containing compounds according to equation 3.

$$Co_2(CO)_8 + R_3SiH \longrightarrow R_3SiCo(CO)_4 + HCo(CO)_4 \quad \text{eq. 3}$$

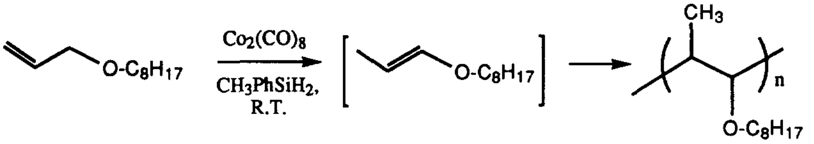
More recently, in this laboratory it was demonstrated that the other product of the reaction, $R_3SiCo(CO)_4$, is a potent cationogen capable of initiating the cationic polymerization of cyclic ethers as well as vinyl ethers (equation 4).[15]



eq. 4

As indicated in equation 4, trialkylsilyl moieties become bonded as end groups to the termini of the polymer chains. We proposed that polymerization in both cases takes place by the formal transfer of a trialkylsilyl cation (R_3Si^+) species. Such species have also been suggested as intermediates in the ring-opening reaction of epoxides in the presence of carbon monoxide and $Co_2(CO)_8$ to give esters.[16] In concert with these observations, Olah et al.[17] have very recently reported a novel method for the generation of trimethylsilyl cations and showed them capable of initiating a variety of vinyl and ring-opening cationic polymerizations. Although the $Co(CO)_4^-$ counterion has been described as a pseudohalide,[18] it appears to be of sufficiently low nucleophilic character to permit efficient propagation for both epoxides and vinyl ethers. High molecular weight polymers were obtained for the polymerization of both types of monomers.

Combining both the ability of $HCo(CO)_4$ to catalyze isomerization reactions together with the reactivity of $R_3SiCo(CO)_4$ as an initiator of cationic polymerization, we proposed that a system composed of $Co_2(CO)_8$ and a silane should function as a dual catalyst for the concurrent isomerization and cationic polymerization of allyl compounds. Accordingly, a series of experiments were conducted to verify this proposal which is described here. Allyl n-octyl ether was combined together with $Co_2(CO)_8$ and methylphenylsilane at room temperature. Methylphenylsilane was chosen for use in these initial studies simply because it is readily avaliable, reactive and easily handled. After a short (~45 second) induction period, spontaneous, exothermic polymerization ensued. This reaction is depicted in equation 5.



eq. 5

Similarly, a wide variety of other mono-, di- and multifunctional alkyl allyl ethers was observed to undergo facile exothermic polymerization in the presence of $Co_2(CO)_8$ and silanes. Table 1 gives some preliminary results using nine prototypical mono-, di- and multifunctional compounds. Monofunctional allyl ethers resulted in the formation of linear polymers while di- and multifunctional monomers gave crosslinked, insoluble networks. In all cases, polymerizations using the above catalyst system were spontaneous and exothermic at room temperature. The polymerizations are markedly inhibited by the presence of trialkylamines and other bases but not by typical free radical inhibitors. These results again strongly point to the cationic nature of the polymerization reactions. High molecular weight polymers as determined by GPC (using poly(styrene) standards) were obtained in these polymerizations for all the monofunctional alkyl allyl ethers. The low molecular weights obtained in the case of allyl benzyl ether appear to be the result of facile chain transfer due to abstraction of the highly labile benzylic hydrogens under the cationic conditions of this polymerization. Examination of the structures of the polymers produced in the polymerization of the monofunctional alkyl allyl ethers by ^{1}H- and ^{13}C-NMR and comparison with the polymers obtained by the cationic polymerization of the corresponding alkyl 1-propenyl ethers showed that they were identical. Further, the ^{1}H-NMR spectra of the polymers bear resonances in the aromatic region due to the presence of silane end groups. This data provides further evidence for the proposed mechanism shown in equation 5 involving concurrent isomerization and polymerization.

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.

Figure 1 shows the course of the polymerization of allyl n-decyl ether and 1,2-diallyloxyethane over 120 seconds as followed by monitoring the 1648 cm^{-1} band corresponding to the allylic double bonds using FT IR spectroscopy. The polymerizations are very rapid at room temperature and proceed to high conversions. The initial slopes of the polymerizations of the two monomers are identical. However, the polymerization of the monofunctional allyl ether proceeds to a higher ultimate conversion (96%). This is as expected since in the difunctional monomer, some unreacted allyl functional groups remain trapped within the rigid crosslinked resin matrix.

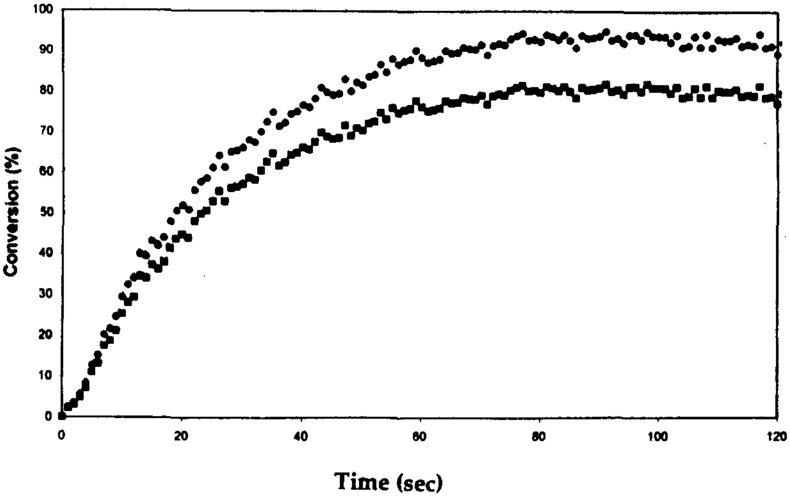


Figure 1. FTIR study of the rates of the bulk polymerizations of ●, allyl n-decyl ether and ■, 1,2-diallyloxyethane in the presence of 1.5 mol% $Co_2(CO)_8$ and 4 mol% methylphenylsilane.

All silanes bearing Si-H groups are active as cocatalysts for the polymerization of allylic ethers. This includes mono-, di-, and trialkyl and aryl substituted silanes. Shown in Table 2 is the effect of the structure of the silane on the polymerization of allyl n-decyl ether. High molecular weight polymers are formed in all cases, although the highest molecular weights are formed using either diaryl or arylalkyl silanes. As may also be noted in Table 2, germanes and stannanes which also bear respectively, Ge-H and Sn-H bonds also behave as cocatalysts in the polymerization of allylic ethers. Presumably, these compounds react in an analogous manner to silanes with $Co_2(CO)_8$ (equation 3) to generate the corresponding germanium-cobalt and tin-cobalt carbonyl complexes.

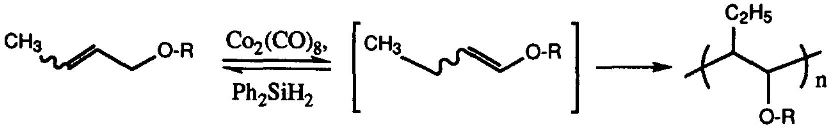
The $Co_2(CO)_8$ catalyzed tandem isomerization and polymerization reaction is a very general reaction and can be employed for the polymerization of a wide variety of structurally diverse allylic ethers and allylic ethers bearing a variety of different functional groups as well as monomers related to allylic ethers. Typical examples of the polymerizations of some of these monomers are included in Table 3.

Table 2
Effect of Variation of the Structure of the Silane on the Polymerization of n-Decyl 1-Propenyl Ether*

Silane	Conversion (%)	M_w (g/mol)	M_n (g/mol)	M_w/M_n
n-Hexylsilane	66	18300	10000	1.8
Tri-n-hexylsilane	14	17000	12000	1.4
Triphenylsilane	52	23800	14500	1.6
Diphenylsilane	78	23000	13600	1.7
Methylphenylsilane	77	25700	15000	1.7
Triphenylgermane	50	630	590	-
Triphenylstannane	88	14000	7200	1.9
Tributylstannane	82	19300	14800	1.3

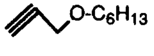
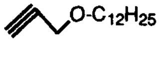
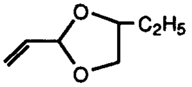
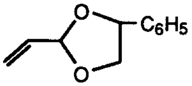
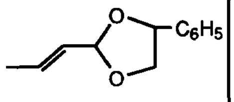
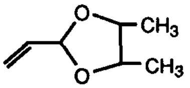
*2 mol% silane and 1 mol% $Co_2(CO)_8$ in n-decyl 1-propenyl ether, 25°C, 1h.

Crotyl ethers undergo facile polymerization in which the 1-butenyl ether is presumably the intermediate (equation 6).



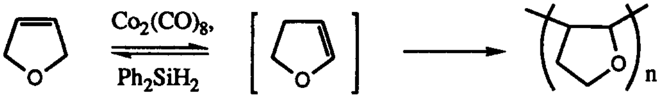
eq. 6

Table 3
Polymerization of Allylic Ether Monomers[a]

Monomer	Silane (4 mol%)	Temp. (°C)	Conv. (%)	M_w (g/mol)	M_n (g/mol)	M_w/M_n
	b	50	86	11500	8800	1.3
	b	50	78	4700	2300	2.05
	b	25	92	7900	6000	1.3
	b	25	87	2100	1750	1.2
	c	25	88	crosslinked gel		
	c	25	93	crosslinked gel		
	b	50	92	12800	8000	1.6
	b	50	83	69200	25200	2.7
	b	50	89	79500	29000	2.7
	b	50	77	11400	6300	1.8

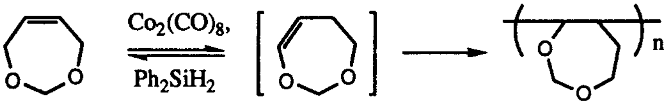
[a]1.5 mol% $Co_2(CO)_8$, reaction time 1 h. [b]diphenylsilane, [c]methylphenylsilane.

The cyclic allyl ether, 2,5-dihydrofuran undergoes smooth polymerization (equation 7) in the presence of $Co_2(CO)_8$ and diphenylsilane. That this reaction proceeds first by isomerization to the corresponding 2,3-dihydrofuran followed by cationic polymerization of this latter species was demonstrated by direct polymerization of 2,3-dihydrofuran under the same reaction conditions to give a polymer with an identical structure.



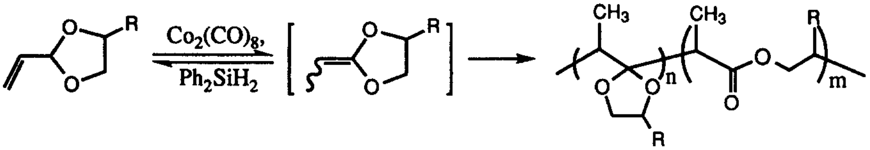
eq. 7

Similarly, the polymerization of the unsaturated cyclic acetal, 1,3-dioxep-5-ene, (equation 8) proceeds readily to give a polymer with the same structure as that obtained previously[19] by the polymerization of 1,3-dioxep-4-ene.



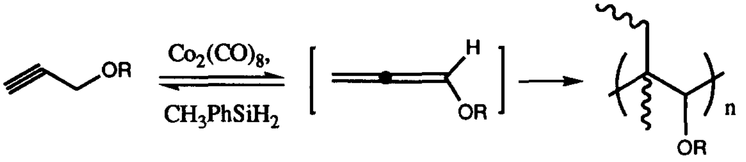
eq. 8

Vinyl acetals prepared by the condensation of acrolein with 1,2-diols undergo facile polymerization by both ring-opening and vinyl polymerization (equation 9). These polymerizations take place by prior isomerization first to the ketene acetal. Ketene acetals have been shown to be especially reactive under conditions of cationic polymerization.[20,21]



eq. 9

Related to the allylic ethers described above are propargyl ethers. As may be noted in Table 3, $Co_2(CO)_8$ in the presence of methylphenylsilane, catalyzes the rapid polymerization propargyl ethers to give insoluble, crosslinked polymers. Recently, Crivello, et al.[22] synthesized a variety of monofunctional allene ethers and reported that they undergo facile onium salt photoinitiated cationic polymerization. These polymers were also crosslinked indicating that both double bonds of the allene functional group participated in the polymerization. Similar results were reported by Endo and his coworkers,[23,24,25] under both free radical and cationic conditions. In contrast, the polymerization of propargyl ethers was not found to take place under any cationic or free radical conditions employed. With these considerations in mind, we suggest that the polymerization of propargyl ethers proceeds as shown in equation 10 via first, the formation of the isomeric allene ether.



eq. 10

CONCLUSIONS

A novel 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 critical 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 $HCo(CO)_4$ 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.

ACKNOWLEDGMENT

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EXPERIMENTAL SECTION

General

All organic reagents employed in this investigation were reagent quality and were used as purchased from the Aldrich Chemical Co unless otherwise noted. Dicobalt octacarbonyl ($Co_2(CO)_8$) was obtained from Strem Chemicals, Inc. and used without purification. All operations involving $Co_2(CO)_8$ were carried out under argon in a dry box. The silanes used in this work were obtained from Hüls America. Allyl ethers[4], propargyl ethers,[19] and vinyl acetals[20] were prepared via previously published synthetic procedures.

Gel permeation chromatographic (GPC) analyses were carried out using a Hewlett Packard HP-1090M HPLC equipped with a refractive index detector and a µ-styragel column (particle size 5 µm, mixed 24-34 Å pores). $CHCl_3$ was used as the eluent at a flow rate of 1.0 mL/min. All molecular weights are reported relative to polystyrene standards. Gas chromatographic (GC) analyses were performed on a Hewlett Packard HP-5840A gas chromatograph equipped with a 15 m x 0.53 mm x 1.5 µm film thickness crosslinked methyl silicone gum column and a flame ionization detector. ^1H and ^{13}C NMR spectra were obtained using Varian XL-200 and XL-500 spectrometers respectively, at room temperature in $CDCl_3$. All chemical shifts are reported relative to tetramethylsilane as an internal standard. Polymerization reactions were monitored using a Midac Series M Fourier Transform Infrared Spectrometer equipped with a liquid nitrogen cooled MCD detector.

$Co_2(CO)_8$ Catalyzed Polymerizations

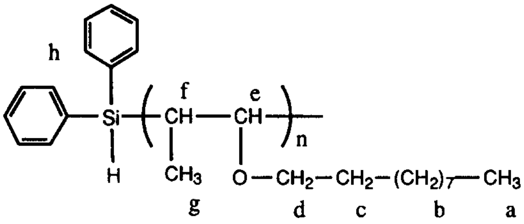
The following procedures are typical of the polymerization reactions employed in this investigation. Polymerizations were conducted in an atmosphere of ambient air unless otherwise indicated. Temperature control was maintained through the use of an oil bath.

Polymerization of Allyl n-decyl Ether

Into a small vial, 17 mg (5.0×10^{-5} mol) of $Co_2(CO)_8$ was dissolved in 1.0 g (0.005 mol) of allyl n-decyl ether. The vial was sealed with a rubber septum and then 19 mL (1.02×10^{-4}

mol) of diphenylsilane was injected through the septum. Very rapid, exothermic polymerization took place after a few seconds induction period. After 1 h, the polymerization was terminated by the injection of a small amount of triethylamine and the polymer was dissolved in chloroform. GC analysis of the chloroform solution for residual allyl n-decyl ether with n-decane as a internal standard gave a conversion to polymer of 92%. GC analysis of reaction mixture also showed the presence of traces of n-decyl 1-propenyl ether. The presence of traces of n-decyl 1-propenyl ether was also confirmed by ^1H NMR. Similar behavior was seen in the polymerizations of other allyl ethers. The polymer was precipitated into methanol, filtered and dried. The process was repeated three more times to remove traces of monomer and catalyst residues and the polymer was dried in vacuo at 50°C before submission for ^1H NMR analysis. GPC analysis of the polymer gave a M_n = 14000 g/mol, M_w = 23000 g/mol with a dispersity of 1.6.

^1H NMR ($CDCl_3$): δ(ppm) 0.7-1 (H_a, 3H); 1.1-1.4 (H_b+H_g, 17H); 1.4-1.7 (H_c, 2H); 1.7-2.0 (H_f, 1H); 3.1-3.8 (H_d+H_e, 3H); 7.3-7.8 (H_h).

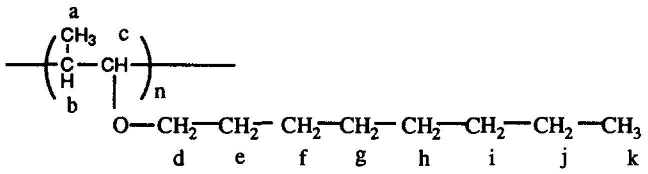


Solution Polymerization of Allyl n-Octyl Ether

Allyl n-octyl ether 1.0 g (0.0058 mol) was mixed with 2.00 mL of dry toluene in a small vial and the vial was sealed with a rubber septum. To this solution was added 32 μL (2.32 x 10^{-4} mol) of dry methylphenylsilane and 30 mg (8.77 x 10^{-5}mol) of $Co_2(CO)_8$. Polymerization took place after a brief induction period indicated by a rapid rise in the temperature of the reaction mixture. The polymerization was terminated using a few drops of triethylamine after 1 h. GC analysis for residual allyl n-octyl ether with n-decane as an internal standard showed that conversion was 80%. The polymer was isolated by addition of methanol to the reaction mixture. GPC chromatography of the polymer gave a M_n = 14000 g/mol, M_w = 26200 g/mol with a dispersity of 1.87.

^{1}H NMR ($CDCl_3$): δ(ppm) 0.6-1 (H_a, 3H); 1-1.4 (H_f+H_g+H_h+H_i+H_j+H_k, 13H); 1.4-1.6 (H_e, 2H); 1.7-2 (H_b, 1H); 3-3.8 (H_c+H_d, 3H).

^{13}C NMR ($CDCl_3$): δ(ppm) 79.1-84.0 (C_c), 65.4-68.2 (C_d), 37.4-41.5 (C_b), 32.0 (C_i), 30.7 (C_e), 29.8 (C_g), 29.4 (C_h), 26.5(C_f), 22.8 (C_j), 14.1(C_k), 13.8-9.9 (C_a).

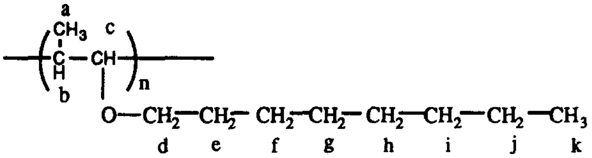


$HCo(CO)_4$ Catalyzed Isomerization and Polymerization of Allyl n-Octyl Ether

The procedure by Sternberg, Wender and Orchin[12], was used for the preparation of hydridocobalttetracarbonyl ($HCo(CO)_4$). Into a trap were weighed 2 g (0.0117mol%) of allyl n-octyl ether and the trap immersed into liquid nitrogen. $HCo(CO)_4$ 0.04 g (2 mol% based on the allyl ether monomer) was condensed into the trap which was allowed to slowly warm to 0°C. The reaction vessel was transferred to ice bath and then allowed to come to room temperature over the course of 10 h Thereafter, the reaction mixture was added to 200 mL of n-hexane resulting in the precipitation of a liquid polymer. After the n-hexane was decanted from the polymer, it was dissolved in chloroform and reprecipitated once more into n-hexane. The resulting polymer was dried in vacuo at 50°C before submission for ^{1}H NMR spectroscopy.

The yield of the polymer was 0.2 g (10%). Gel permeation chromatography of the polymer gave a M_n = 2600 g/mol, M_w = 6310 g/mol with a dispersity of 2.36.

^{1}H NMR ($CDCl_3$): δ(ppm) 0.6-1 (H_a, 3H); 1-1.4 (H_f+H_g+H_h+H_i+H_j+H_k, 13H); 1.4-1.6 (H_e, 2H); 1.7-2 (H_b, 1H); 3-3.8 (H_c+H_d, 3H).

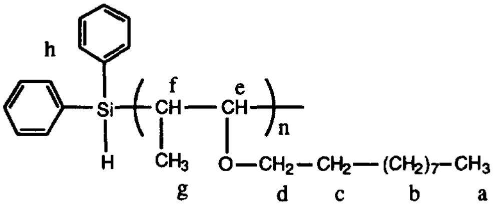


The hexane extracts were combined and the solvent was removed on a rotary evaporator. The ^1H NMR of the residue shows in addition to bands associated with the starting allyl ether monomer, new peaks at 4.3-4.9 and between 6.1-6.3 ppm. These bands are are identical to those present in the spectrum of n-octyl 1-propenyl ether. Integration of the peaks at 3.9 (allyl CH=) and the peaks at 4.3-4.4 ppm (1-propenyl CH=) showed that there was 9% n-octyl 1-propenyl ether present in the extract.

Polymerization Of n-Decyl 1-Propenyl Ether With Tetracarbonyl-(diphenyhydridosilyl)cobalt(I)

In a small vial fitted with a rubber septum, 31 mg (8.76×10^{-5} mol) of tetracarbonyl(diphenyhydridosilyl)cobalt(I)[14] was dissolved in 1.0 g (0.005 mol) of n-decyl 1-propenyl ether. Very rapid, exothermic polymerization took place after a few seconds induction period. After 1 h, the polymerization was terminated with triethylamine and the polymer was dissolved in chloroform. GC analysis for residual n-decyl 1-propenyl ether gave a conversion of 80%. The polymer precipitated into methanol, the methanol decanted and the polymer redissolved in chloroform. This process was repeated three more times and the purified polymer dried in vacuo at 50°C before ^1H NMR analysis. GPC analysis of the polymer gave a M_n = 30100 g/mol, M_w = 49500 g/mol with a dispersity of 1.6.

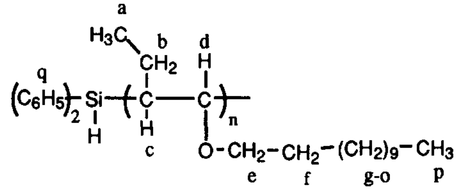
^1H NMR ($CDCl_3$): δ(ppm) 0.7-1 (H_a, 3H); 1.1-1.4 (H_b+H_g, 17H); 1.4-1.7 (H_c, 2H); 1.7-2.1 (H_f, 1H); 3.2-3.8 (H_d+H_e, 3H); 7.3-7.8 (H_h).



Polymerization of 2-Butenyl 1-Dodecyl Ether

In a small vial fitted with a rubber serum cap, 21 mg (6.25×10^{-5} mol) of $Co_2(CO)_8$ was dissolved in 1.0 g (0.0041 mol) of 2-butenyl 1-dodecyl ether and then 30 µL (1.64×10^{-4} mol) of diphenylsilane was injected using a syringe at 50°C. Very rapid, exothermic polymerization took place after a few seconds induction period. After 1 h, the polymerization was terminated by the addition of a few drops of triethylamine and the semisolid polymer was dissolved in chloroform. GC analysis for residual 2-butenyl 1-dodecyl ether with n-decane as a internal standard showed that conversion of monomer to polymer was 86%. The chloroform solution of the polymer was poured into methanol to precipitate the polymer. The polymer was collected by vacuum filtration and redissolved and reprecipitated two more times to free the polymer of residual monomer and catalyst residues. GPC of the resulting dried polymer dried in vacuo at 50°C gave a M_n = 8800 g/mol, M_w = 11500 g/mol with a dispersity of 1.3.

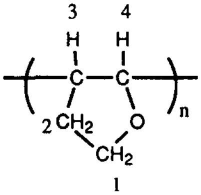
^1H NMR ($CDCl_3$): δ(ppm) 0.8-1.1 (H_a+H_b, 5H); 1.1-1.5 ($H_{g\text{-}o}$+ H_p, 21H); 1.5-2.1 (H_f+H_c, 3H); 3.3-3.9 (H_d+H_e, 3H); 7.4-7.7 (H_q).



$Co_2(CO)_8$ Initiated Polymerization of 2,5-Dihydrofuran

2,5-Dihydrofuran was purified by fractional distillation at atmospheric pressure. Into a small vial, 72 mg (2.13×10^{-4} mol) of $Co_2(CO)_8$ was dissolved in 1.0 g (0.0142 mol) of 2,5-dihydrofuran and then 106 µL (5.68×10^{-4} mol) of diphenylsilane was injected by syringe at room temperature. Very rapid, exothermic polymerization took place after a few seconds induction period. After 1 h, the polymerization was terminated by the addition of triethylamine and the semisolid polymer was dissolved in chloroform. GC analysis for residual 2,5-dihydrofuran with n-decane as a internal standard showed that the conversion to polymer was 92%. The polymer was dissolved in chloroform and precipitated into n-hexane, recovered by filtration and dried in a vacuum oven. GPC of the polymer gave a M_w = 7900 g/mol, M_n = 6000 g/mol with a dispersity of 1.3.

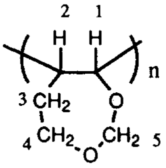
^{1}H NMR ($CDCl_3$): δ(ppm) 3.3-3.4 (H_1+H_4, 3H); 2.1-2.2 (H_3, threo); 2.25-2.35 (H_3, erythro); 1.9-1.95 (H_2).



Polymerization of 1,3-Dioxep-5-ene

In a small vial, 51 mg (1.5 x 10^{-4} mol) of $Co_2(CO)_8$ was dissolved in 1.0 g (0.010 mol) of 1,3-dioxep-5-ene and then 74 μL (4 x 10^{-4} mol) of diphenylsilane was added at 25°C. Rapid, exothermic polymerization took place after a few seconds induction period. After 1 h, the polymerization was terminated by the addition of triethylamine and chloroform was added to reaction mixture to dissolve the polymer. GC analysis for residual 1,3-dioxep-5-ene with n-decane as a internal standard showed that conversion was 87%. The polymer was precipitated into methanol. Then the polymer was dissolved in chloroform and reprecipitated into methanol. This process was repeated three more times and the polymer was dried in vacuo before submission for GPC analysis. GPC of the polymer gave a M_w=2100 g/mol and M_n=1750 g/mol with a dispersity of 1.2.

^{1}H NMR ($CDCl_3$): δ(ppm) 1.0-2.0 (H_3, 2H); 2.0-2.6.0 (H_2, 1H); 3.0-4.0 ($H_{4,5}$, 4H); 4.2-5.0 (H_1, 1H); 9.3-9.6 (aldehyde protons).



Polymerization of n-Hexyl Propargyl Ether

$Co_2(CO)_8$ (36 mg, 1.05×10^{-4} mol) was dissolved in 1.0 g (0.007 mol) of n-hexyl propargyl ether. To this solution 39 µL (2.84×10^{-4} mol) of methylphenylsilane was added and reaction mixture was vigorously stirred. Rapid polymerization took place accompanied by gas evolution and the formation of a foamed solid polymer. The resulting crosslinked polymer was insoluble in chloroform as well as other solvents. The polymer was broken up and extracted with 20 mL of ethanol. GC analysis of the ethanolic solution solution for residual n-hexyl propargyl ether with n-decane as a internal standard showed that conversion was 88%.

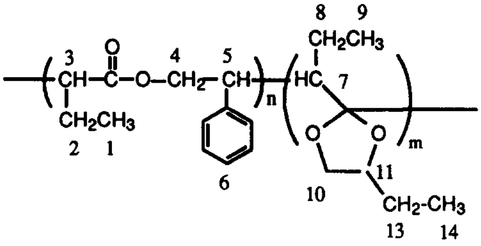
Polymerization of 2-Vinyl-4-ethyl-1,3-dioxolane

To, 40 mg (1.17×10^{-4}mol) of $Co_2(CO)_8$ dissolved in 1.0 g (0.0078 mol) of 2-vinyl-4-ethyl-1,3-dioxolane was added 58 µL (3.12×10^{-4} mol) of diphenylsilane at 50°C. Very rapid, exothermic polymerization took place after a few seconds induction period. After 1 h, the polymerization was terminated by the addition of a small amount of triethylamine and the semisolid polymer was dissolved in chloroform. GC analysis for residual 2-vinyl-4-ethyl-1,3-dioxolane with n-decane as a internal standard gave a conversion of 92%. The polymer was precipitated into methanol and recovered by vacuum filtration. GPC analysis of the polymer gave a M_n = 8000 g/mol, M_w = 12800 g/mol with a dispersity of 1.6.

Polymerization of 2-Propylidene-4-ethyl-1,3-dioxolane

2-Propylidene-4-ethyl-1,3-dioxolane was polymerized as described above to give a 94% conversion of polymer which by GPC gave a M_n = 6450 g/mol, M_w = 8550 g/mol with a dispersity of 1.3.

^{1}H NMR ($CDCl_3$): δ(ppm) 0.8-1.1 (H_1+H_7+H_9+H_{14}); 1.1-2.2 (H_2+H_6+H_8+H_{13}); 2.1-2.9 (H_3+H_{10}); 3.1-4.6 (H_4+H_5+H_{10}+H_{12} 4.6-5.4 (H_{11}).



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