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### Tandem Isomerization and Cationic Copolymerization of Allyl Ethers

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## TANDEM ISOMERIZATION AND CATIONIC COPOLYMERIZATION OF ALLYL ETHERS

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Key Words: Copolymerization; Allyl Ethers; Isomerization-polymerization of Allyl Ethers; Reactivity Ratios; Dicobalt Octacarbonyl; Diphenylsilane.

### ABSTRACT

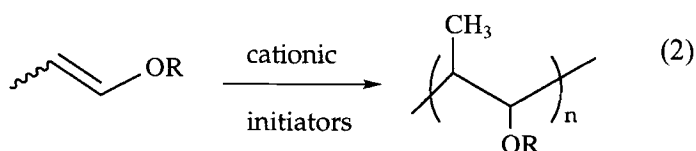
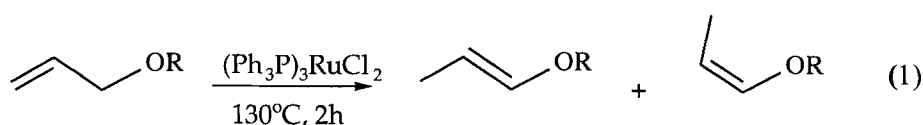
A new catalyst system comprising a combination of dicobalt octacarbonyl and a hydridosilane has been successfully employed for the tandem isomerization and cationic copolymerization of 1-allyloxy-2-phenoxyethane ( $M_1$ ) and 1-allyloxyoctane ( $M_2$ ). Reactivity ratios of  $r_1 = r_2 = 0.58 \pm 0.01$  were calculated for these monomers by both the Mayo-Lewis and the Fineman-Ross methods which are indicative of a statistical copolymerization. A GPC study of the copolymerization showed that only copolymers were obtained. This data further indicates that the isomerization of the individual monomers and their subsequent copolymerization proceed at very nearly identical rates. The copolymerization of allyl ether monomers presents an opportunity for designing novel polymers with tailored properties.

### INTRODUCTION

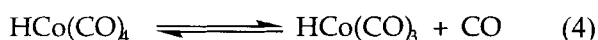
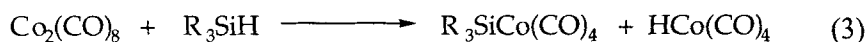
Recent investigations in this laboratory have focused on the development of novel catalyst systems for the polymerization of monomers, especially those obtained through simple, straightforward chemistry from readily available and

inexpensive starting materials. Allyl ethers are one such broad class of unsaturated compounds which can be prepared in high yields by the phase transfer catalyzed condensation of allyl halides with alcohols. [1] However, these compounds do not undergo efficient polymerization by free radical, anionic or cationic mechanisms.

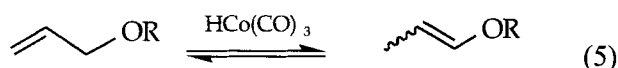
In all three cases, facile chain transfer to monomer occurs more rapidly than propagation, consequently, only low molecular weight, ill characterized oligomers are formed. One successful strategy for circumventing this problem has been described in a recent series of communications from this research group [2-6]. The methodology involves first, carrying out a transition metal catalyzed isomerization of an allyl ether to the corresponding 1-propenyl ether. Then, the 1-propenyl ether can be subjected to very efficient facile cationic polymerization in the presence of Lewis or Brønsted acids. Alternatively, they may be polymerized photochemically employing onium salt cationic photoinitiators. This strategy is outlined in Equation 1 and can be applied to a variety of other allylic compounds as for example; crotyl ethers and vinyl acetals.



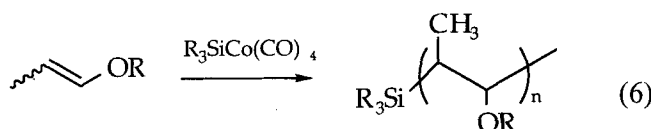
More recently, [7-10] we have described the development of a new catalyst system which for the first time permits the facile, efficient, tandem isomerization and cationic polymerization of allylic ethers to well characterized high polymers. Rapid exothermic polymerization results when allyl n-alkyl ethers are mixed with dicobalt octacarbonyl ( $\text{Co}_2(\text{CO})_8$ ) in presence of an organosilane bearing Si-H groups. Detailed mechanistic studies [8] have shown that the polymerization involves three important critical steps. The first step (Equation 3) involves the reaction of  $\text{Co}_2(\text{CO})_8$  with a hydrosilane,  $\text{R}_3\text{SiH}$ , to give two products  $\text{HCo}(\text{CO})_4$  and  $\text{R}_3\text{SiCo}(\text{CO})_4$ .  $\text{HCo}(\text{CO})_4$  can be thermally decomposed to give  $\text{HCo}(\text{CO})_3$  and CO (Equation 4) [11].



Allylic ethers undergo rapid isomerization (Equation 5) in the presence of  $\text{HCo}(\text{CO})_3$  at  $25^\circ\text{C}$  to give the corresponding 1-propenyl ether.



The ultimate step in this cascade of reactions is the facile, efficient polymerization of the alkyl 1-propenyl ether (Equation 6) mediated by  $\text{R}_3\text{SiCo}(\text{CO})_4$ . Due to the highly polarized character of the silicon-cobalt bond,  $\text{R}_3\text{SiCo}(\text{CO})_4$  interacts with nucleophilic monomers to undergo the formal transfer of a silyl cation,  $\text{R}_3\text{Si}^+$ , which initiates cationic polymerization.



It should be noted that Equations 4 and 5 are represented as equilibrium reactions. However, the cationic polymerization reaction is essentially an irreversible process which is strongly driven towards the formation of polymer by heat of polymerization of  $-14$  to  $-19$  kcal/mol [12]. Due to the exothermic nature of the polymerization step, all three reactions are driven strongly towards the right. In most cases, the polymerizations of allyl alkyl ethers occur at room temperature on addition of the above catalyst system.

Initial investigations [7, 8] were centered about studies of the polymerization of alkyl allyl ethers. More recently, we extended the range of monomers which can be polymerized to also include other typical allylic monomers such as cyclic allylic ethers, propargyl ethers, crotyl ethers and vinyl acetals [9]. In a recent communication, [10] we have described the results of other investigations

directed towards extending the scope of this novel tandem isomerization and cationic polymerization reaction to other transition metal carbonyl complexes and to the development of alternate cocatalysts.

To enhance the range of applicability of the polymers obtained by this unique, simple and inexpensive polymerization process and to further understand the structure-reactivity relationships, we decided to investigate the tandem isomerization and cationic copolymerization of combinations of allylic ether monomers. In this communication we describe the results of a study of the copolymerization of 1-allyloxyoctane (4-oxa-1-dodecene) with 1-allyloxydecane (4-oxa-1-tetradecene) and 1-allyloxyoctane with 1-allyloxy-2-phenoxyethane (7-phenyl-4,7-dioxahept-1-ene) using this new polymerization reaction.

## EXPERIMENTAL

### Materials and Procedures

All organic reagents and solvents employed in this investigation were reagent quality and were used as received from the Aldrich Chemical Co. Tris(triphenylphosphine)ruthenium(II) dichloride was purchased from Alfa Research Chemicals.  $\text{Co}_2(\text{CO})_8$  was obtained from Strem Chemicals Inc. and used without purification. All operations involving  $\text{Co}_2(\text{CO})_8$  were carried out in an argon filled dry box. Diphenylsilane was purchased from the Silar Chemical Company and used without further purification. 1-Allyloxyoctane (**AO**), 1-allyloxydecane (**AD**) and 1-propenoxyoctane (**PO**) were prepared by known procedures [7, 8]. The photoinitiator, (4-n-decyloxyphenyl)phenyliodonium hexafluoroantimonate (**IOC-10**), was prepared as described previously [13].

Gel permeation chromatographic (GPC) analyses were carried out using a Hewlett Packard HP-1090M HPLC equipped with a refractive index detector and a  $\mu$ -styragel column (particle size 5  $\mu\text{m}$ , mixed 24-34  $\text{\AA}$  pores).  $\text{CHCl}_3$  was used as the eluent at a flow rate of 1.0 mL/min. Molecular weights were determined using poly(styrene) standards. GPC analyses were also carried out using a Hewlett Packard HP-1090M HPLC instrument containing a JASCO 880-PU precision pump equipped with a ultraviolet detector. Three poly(styrene) gel columns (Shodex K-802, K-803 and K-804) in series calibrated with polystyrene standards were used. Tetrahydrofuran was used as the eluent at a flow rate of 1.0 mL/min.

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  $\mu\text{m}$  film

thickness crosslinked methyl silicone gum column and a flame ionization detector. In this investigation, GC analysis was used to determine the percent conversions based on the change in concentration of the monomer during polymerization. In a typical run, 1 hour after the addition of the initiators, polymerization was terminated by the addition of a few drops of triethylamine and the semisolid polymer was dissolved in 2 mL of chloroform. To this solution was added 40 mL of ethanol to precipitate the polymer. The ethanolic top layer was removed by decantation and placed into a 50 mL volumetric flask and 1 mL of n-decane was added. The volumetric flask was topped up to 50 mL with ethanol. Approximately 0.1  $\mu\text{L}$  of this solution was injected into the GC with a microliter syringe. A reference solution consisting of 1 mL of decane, 1.0 g of the monomer and ethanol was also made up and approximately 0.1  $\mu\text{L}$  of this solution was also injected into the GC. A comparison of the integration of peak areas of the monomer to the internal standard of the reference with that of the run allowed the determination of the concentration of residual monomer after polymerization, and hence, the percent conversion.

Differential scanning calorimetry (DSC) was used for  $T_g$  determinations. Measurements were conducted on 50 mg samples of polymers using a Perkin-Elmer DSC-7 at a heating rate of 20°C/min.

$^1\text{H}$  NMR spectra were obtained using a Varian XL-200 spectrometer at room temperature in  $\text{CDCl}_3$  with tetramethylsilane (TMS) as an internal standard.

### Preparation of Allyl Ether and 1-Propenyl Ether Monomers

#### *Synthesis of 1-Allyloxy-2-phenoxyethane (APE)*

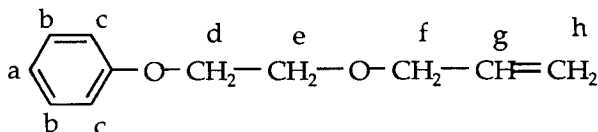
Into a 500 mL round bottom flask equipped with an overhead stirrer, thermometer and a nitrogen inlet were placed 69.35 g (0.50 mol) of distilled 2-phenoxyethanol, 90.73 g (0.75 mol) of allyl bromide, 150 mL of toluene and 28.0 g (0.7 mol) of NaOH. The reaction mixture was stirred at room temperature for 15 minutes. Then 1.0 g (0.003 mol) of tetra-n-butylammonium bromide was added and the reaction mixture slowly heated to reflux (65°C) and maintained at that temperature for 8 hours. The reaction mixture was cooled and filtered to remove the NaBr which precipitated during the reaction. The filtrate was poured into 500 mL of distilled water, the organic layers were separated and the aqueous layer extracted with fresh toluene. After combining the organic layers, they were washed with three 200 mL portions of distilled water and the organic phase was dried over anhydrous  $\text{Na}_2\text{SO}_4$ . Excess allyl bromide and toluene were removed using a rotary evaporator and the remaining oil subjected to vacuum distillation.

The volatile product amounted to 85.0 g (95% recovered yield). Fractional distillation gave pure **APE** with a boiling point of 70°C/1 mm Hg.

Elemental Analysis: Calcd. for C<sub>11</sub>H<sub>14</sub>O<sub>2</sub>: C, 73.71%; H, 8.44%.

Found: C, 73.41%; H, 8.42%.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm) 7.15-6.8 (H<sub>a,b</sub>, 3H); 7.5-7.2 (H<sub>c</sub>, 2H); 6.15-5.85 (H<sub>g</sub>, 1H); 5.5-5.1 (H<sub>h</sub>, 2H); 4.5-3.6 (H<sub>d,e,f</sub>, 6H).



### Synthesis of 1-Propenoxy-2-phenoxyethane (**PPE**)

To 25.0 g (0.14 mol) of **APE** in a 100 mL round bottom flask equipped with a magnetic stirrer, reflux condenser and a nitrogen inlet were added 0.008 g (0.0075 mmol) of tris(triphenylphosphine)ruthenium(II) dichloride. The reaction mixture was heated at 160°C for 45 minutes. After this time, the <sup>1</sup>H NMR showed that the bands assigned to allyl double bond δ (ppm) 6.15-5.85, CH=; 5.5-5.1, CH<sub>2</sub>=) had been completely replaced by new bands δ (ppm) 1.4-1.6, CH<sub>3</sub>-; 4.5-4.3, *cis* CH<sub>3</sub>-CH=; 4.9-4.7, *trans* CH<sub>3</sub>-CH=; 6.1-5.95, *cis* CH-O; 6.4-6.2, *trans* CH-O) assigned to the 1-propenyl ether groups. Pure 1-propenoxy-2-phenoxy-ethane (**PPE**) was isolated by vacuum distillation (bp 70°C/1 mm Hg) in 98% yield.

Elemental Analysis: Calcd. for C<sub>11</sub>H<sub>14</sub>O<sub>2</sub>: C, 73.71%; H, 8.44%. Found: C, 73.60%; H, 8.3%.

### Fourier Transform Real Time Infrared (FT-RTIR) Measurements

Polymerizations of the 1-propenoxyalkanes were monitored using FT real-time infrared spectroscopy (FT-RTIR). A Midac M-1300 FTIR spectrometer equipped with a liquid nitrogen cooled MCT detector was used. The instrument was fitted with a UVEXS Model SCU-110 mercury arc lamp which carried light through a flexible fiber optic wand. The end of this wand was placed at a distance of 5 cm and directed at an incident angle of 45° onto the sample window. The UV light intensity was measured with the aid of a International Light Co. Control-Cure Radiometer at the sample window and was found to be 800 mJ/cm<sup>2</sup> min.

Photopolymerizations were carried out at room temperature in bulk 1-propenyl ether monomers containing 1 mol% IOC-10 as the photoinitiator. The monomer/photoinitiator solutions were coated onto a 0.1 mil polypropylene film,

covered with another polypropylene film, and then mounted on a 5 cm X 5 cm slide frame. Infrared spectra were collected at a rate of 60 spectra per second using a LabCalc, data acquisition program obtained from the Galactic Corp. and were processed using GRAMS-386 software from the same company. During irradiation, the decrease of the absorbance due to the 1-propenyl ether double bond centered at  $1667\text{ cm}^{-1}$  was monitored. In each case, triplicate experiments were performed to verify reproducibility.

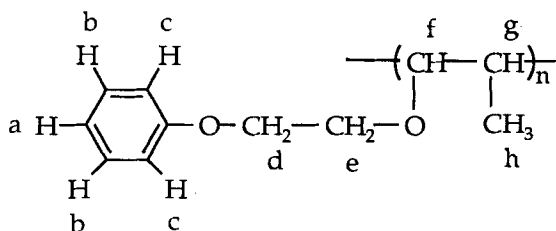
### Tandem Isomerization and Polymerization of Allyl Ethers

The following are typical procedures which were used for the tandem isomerization and homopolymerization and copolymerization of the allyl ethers shown in Tables 1, 2 and 3. All transfers of  $\text{Co}_2(\text{CO})_8$  were carried out under argon in a dry box.

#### Homopolymerization of 1-Allyloxy-2-phenoxyethane (APE)

In a small vial, 38 mg ( $1.12 \times 10^{-4}$  mol) of  $\text{Co}_2(\text{CO})_8$  was dissolved in a mixture of 1.0 g (0.0056 mol) of APE. The vial was sealed with a rubber septum and then 41  $\mu\text{L}$  ( $2.28 \times 10^{-4}$  mol) of diphenylsilane was injected using a microliter syringe at room temperature. Very rapid, exothermic polymerization took place after a few seconds induction period. After 1 hour, the polymerization was terminated using triethylamine and the polymer was dissolved in chloroform. GC analysis of the chloroform solution for APE with n-decane as a internal standard showed that conversion of the monomers was 90%. The polymer was precipitated into ethanol. The polymer was dissolved and precipitated three more times and then dried *in vacuo* at  $50^\circ\text{C}$  for 24 hours before submission for  $^1\text{H}$  NMR spectroscopy.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.00-6.7 ( $\text{H}_{\text{a,b}}$ , 3H); 7.4-7.1 ( $\text{H}_{\text{c}}$ , 2H); 4.25-2.9 ( $\text{H}_{\text{d,e,f}}$ , 5H); 2.5-1.5 ( $\text{H}_{\text{g}}$ , 1H); 1.4-0.4 ( $\text{H}_{\text{h}}$ , 3H).



GPC of this polymer using a RI detector gave a  $M_n = 7970$  g/mol,  $M_w = 16630$  g/mol with a dispersity of 2.08. When a UV detector was used a  $M_n = 8100$  g/mol,  $M_w = 16800$  g/mol with a polydispersity index of 2.12 was obtained.



TABLE 1. Copolymerization of 1-Allyloxyoctane and 1-Allyloxydecane

1-Allyloxy-octane (g)	1-Allyloxy-decane (g)	Co <sub>2</sub> (CO) <sub>8</sub> 1 (g)	Ph <sub>2</sub> SiH <sub>2</sub> 2 (g)	Conversion AO (%)	Conversion AD (%)	M <sub>w</sub>	M <sub>n</sub>	MWD
1	0	0.040	0.043	88	-	14800	7470	1.98
0.8	0.2	0.033	0.035	87	91	15230	8680	1.75
0.6	0.4	0.037	0.040	89	88	18345	9150	2.00
0.4	0.6	0.036	0.039	82	84	19940	10250	1.90
0.2	0.8	0.035	0.037	87	86	22240	11290	1.95
0	1	0.034	0.037	-	89	24570	12250	2.00

1/2 mol% Co<sub>2</sub>(CO)<sub>8</sub>; 2/4 mol% Ph<sub>2</sub>SiH<sub>2</sub> with respect to monomers, 25°C, 1 hour.

TABLE 2. Copolymerization of 1-Allyloxy-2-phenoxyethane ( $M_1$ ) and 1-Allyloxyoctane ( $M_2$ ).

Exp. no.	1-Allyloxy-2-phenoxyethane ( $M_1$ ) (g)	1-Allyloxyoctane ( $M_2$ ) (g)	$\text{Co}_2(\text{CO})_8$ (g)	$\text{Ph}_2\text{SiH}_2$ (g)	Conversion of $M_1$ (%)	Conversion of $M_2$ (%)	$nM_1$ in feed	$nM_2$ in feed	$NM_1$ in copolymer
1	1	0	0.038	0.041	90	-	1	1	1
2	0.8	0.2	0.038	0.041	82	87	0.792	0.782	0.736
3	0.6	0.4	0.039	0.041	78	90	0.588	0.553	0.551
4	0.5	0.5	0.039	0.041	85	90	0.488	0.473	0.439
5	0.4	0.6	0.039	0.042	86	84	0.389	0.394	0.412
6	0.2	0.8	0.039	0.042	88	72	0.193	0.225	0.257
7	0	1	0.040	0.043	-	88	0	0	0

$^{12}\text{C}$  1 mol%  $\text{Co}_2(\text{CO})_8$ ; 24 mol%  $\text{Ph}_2\text{SiH}_2$  with respect to monomers, 25°C, 1 hour.

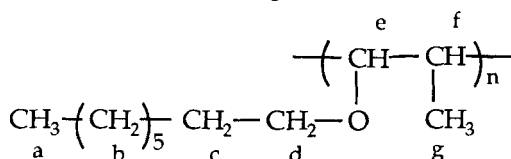
TABLE 3. GPC Molecular Weight Data for Copolymers of 1-Allyloxy-2-phenoxyethane and 1-Allyloxyoctane

Exp. No.	RI Detector			UV Detector		
	$M_w$	$M_n$	MWD	$M_w$	$M_n$	MWD
1	16630	7970	2.08	16800	8100	2.07
2	15090	7250	2.07	15350	7490	2.04
3	14340	6760	2.12	14530	6980	2.08
4	15750	7300	2.15	15970	7500	2.12
5	18930	9330	2.02	19230	9600	2.00
6	15530	7750	2.00	15740	7950	1.97
7	14800	7470	2.00	-	-	-

*Homopolymerization of 1-Allyloxyoctane (AO)*

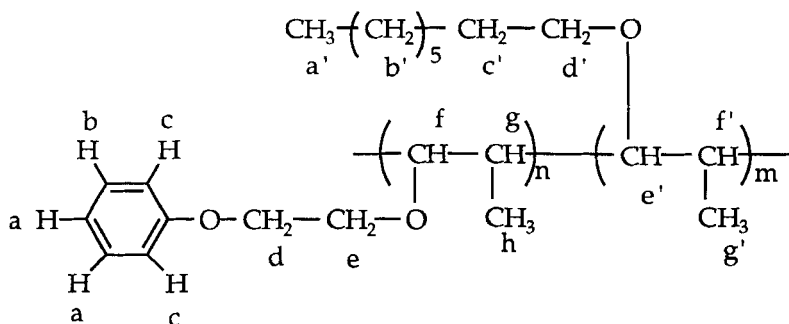
The tandem isomerization and homopolymerization of **AO** was conducted as described above. There was obtained an 88% conversion which by analysis by GPC using a RI detector gave a  $M_n = 7470$  g/mol,  $M_w = 14800$  g/mol with a dispersity of 2.00. There was no response in the GPC when a UV detector was used.

$^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 3.9-3.0 ( $\text{H}_{\text{d,e}}$ , 3H); 2.0-1.8 ( $\text{H}_{\text{f}}$ , 1H); 1.7-1.4 ( $\text{H}_{\text{c}}$ , 2H); 21.4-1 ( $\text{H}_{\text{b}}$ , 10H); 1.0-0.6 ( $\text{H}_{\text{a,g}}$ , 6H).

*Copolymerization of 1-Allyloxyoctane and 1-Allyloxy-2-phenoxyethane*

In a small vial, 39 mg ( $1.14 \times 10^{-4}$  mol) of  $\text{Co}_2(\text{CO})_8$  was dissolved in a mixture of 0.5 g (0.0029 mol) of **AO** and 0.5 g (0.0028 mol) of **APE**. The vial was sealed with a rubber septum and then 41  $\mu\text{L}$  ( $2.28 \times 10^{-4}$  mol) of diphenylsilane was injected using a microliter syringe at room temperature. Very rapid, exothermic polymerization took place after a few seconds induction period. After 1 hour, the polymerization was terminated using a few drops of triethylamine and the polymer was dissolved in chloroform. GC analysis of the chloroform solution for residual **AO** and **APE** with *n*-decane as a internal standard showed that conversion of the two monomers were 85% and 90% respectively. The reaction mixture was poured into ethanol and the polymer recovered by filtration. This process was repeated three more times and the polymer was dried in vacuo at 50°C for 24 hours before submission for  $^1\text{H NMR}$  analysis.

$^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.00-6.7 ( $\text{H}_{\text{a,b}}$ , 3H); 7.4-7.1 ( $\text{H}_{\text{c}}$ , 2H); 4.25-2.9 ( $\text{H}_{\text{d,e,f,d',e'}}$ , 8H); 2.3-1.7 ( $\text{H}_{\text{g,f}}$ , 2H); 1.65-1.4 ( $\text{H}_{\text{c'}}$ , 2H); 1.4-1.1 ( $\text{H}_{\text{b',10H}}$ ); 1.1-0.5 ( $\text{H}_{\text{a',g',h}}$ , 9H).



GPC of the copolymer using a RI detector gave a  $M_n = 7300$  g/mol,  $M_w = 15750$  g/mol with a dispersity of 2.15. When a UV detector was used a  $M_n = 7500$  g/mol,  $M_w = 15970$  g/mol with a polydispersity index of 2.12 was obtained.

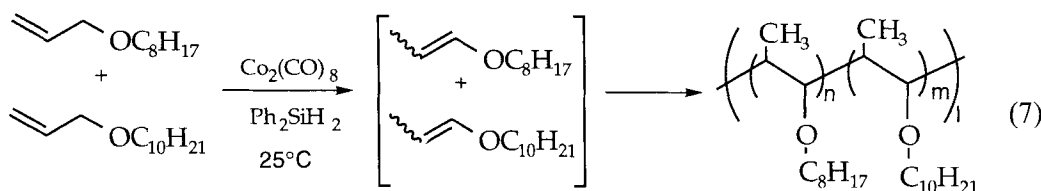
## RESULTS AND DISCUSSION

### General Considerations

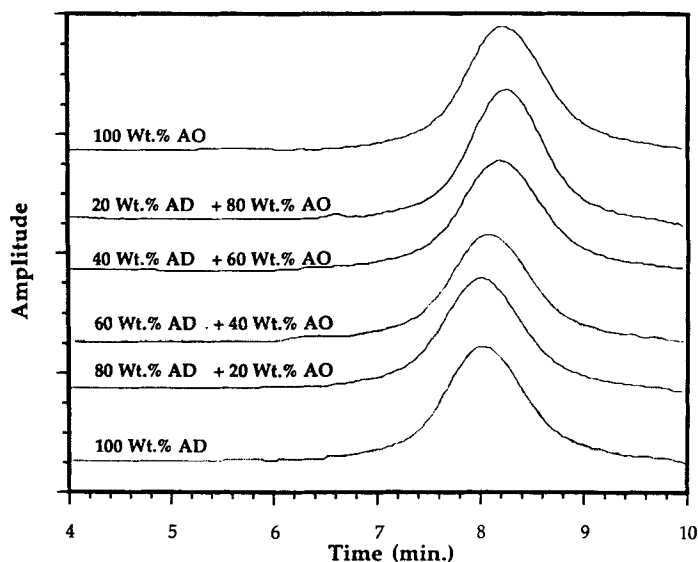
The complex, three-step mechanism of the tandem isomerization and cationic polymerization of allyl ethers makes it difficult to predict the outcome of copolymerization reactions. For successful copolymerization to occur, the two allyl ethers must undergo isomerization at similar rates. Further, the resulting 1-propenyl ethers must have similar reactivities in the subsequent cationic polymerization.

### Copolymerization of 1-Allyloxyoctane and 1-Allyloxydecane

Initial copolymerization experiments were conducted using 1-allyloxyoctane (AO) and 1-allyloxydecane (AD), since the tandem isomerization and cationic homopolymerization of these two individual monomers had been well studied in our previous investigations. [7-10] The experimental conditions and the results of copolymerization experiments with different molar ratios of these two monomers are given in Table 1. Copolymerizations were conducted at 25°C using 2 mol% of  $\text{Co}_2(\text{CO})_8$  as the catalyst and 4 mol% of diphenylsilane as the cocatalyst. Like their respective homopolymerizations, the copolymerizations took place spontaneously and exothermically after a brief (~45 s) induction period. The copolymerization reaction is depicted in Equation 7.



The presence of monomodal GPC curves (Figure 1) strongly suggested the formation of a copolymer, but the evidence was not conclusive. Further, the general increase in the molecular weights with a corresponding increase of amount

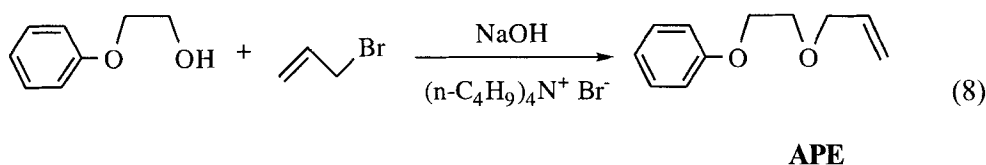


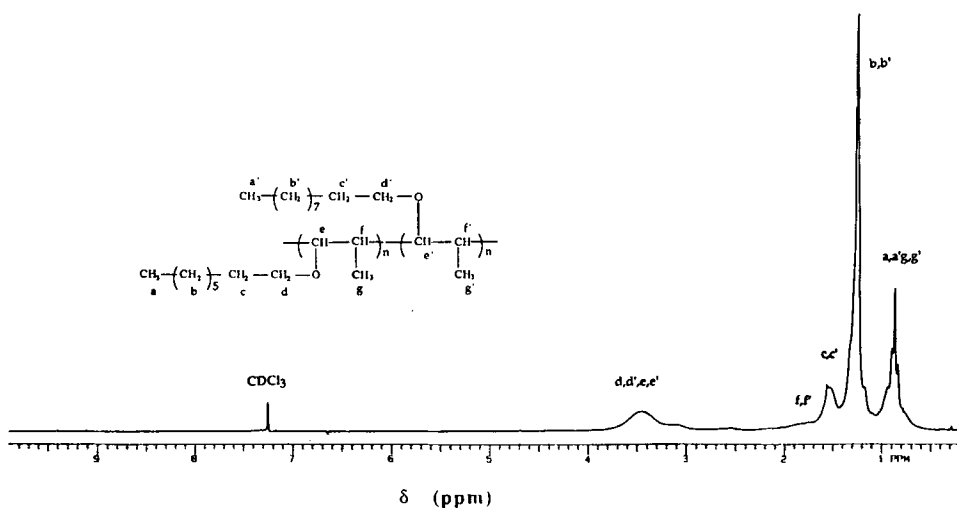
**Figure 1.** GPC curves for copolymerization of 1-allyloxyoctane and 1-allyloxydecane.

of the higher molecular weight monomer, **AD**, in the feed was indicative of copolymerization rather than homopolymerization. No definitive direct information regarding the incorporation of both monomers into a copolymer could be obtained by  $^1\text{H}$  NMR (Figure 2) since the spectrum of the polymer which was obtained exhibited overlapping peaks. This difficulty arises due to the fact that the structures of the two comonomers are very closely related. For this reason, a new monomer having characteristic UV and  $^1\text{H}$  NMR absorption characteristics was required. A monomer which fulfils these criteria is 1-allyloxy-2-phenoxyethane (**APE**).

#### Synthesis and Homopolymerization of 1-Allyloxy-2-phenoxyethane

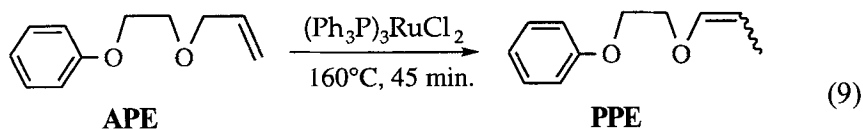
**APE** was synthesized in high yields and high purity using the phase transfer catalyzed Williamson ether synthesis as shown in Equation 8.





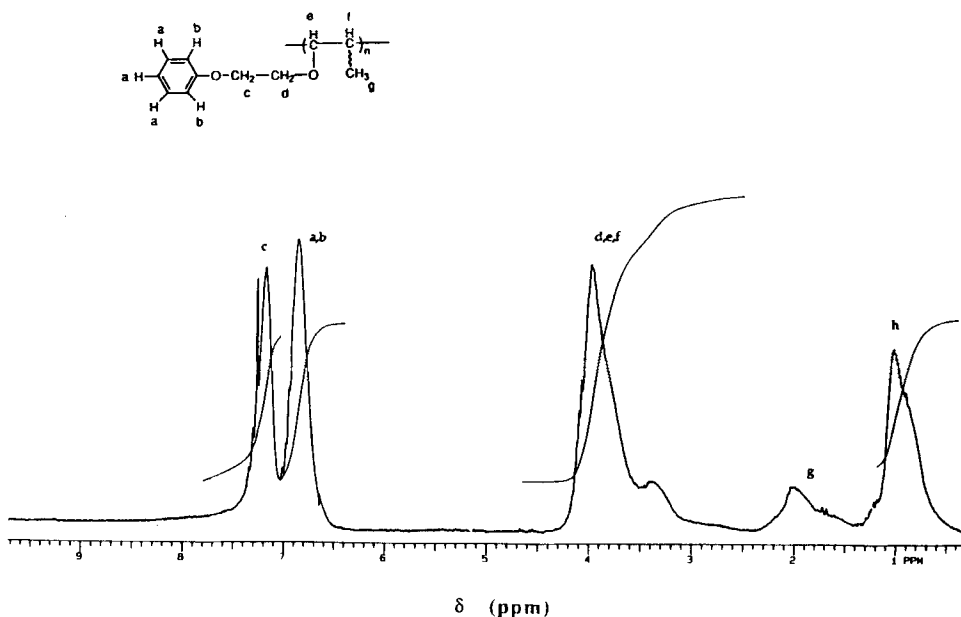
**Figure 2.**  $^1\text{H}$  NMR of the copolymer derived from 1-allyloxydecane (0.4 g) and 1-allyloxyoctane (0.6 g) in  $\text{CDCl}_3$ .

To evaluate whether **APE** is a suitable candidate as a comonomer in tandem isomerization and cationic polymerizations, it was necessary to conduct a brief study to determine if this monomer can be first isomerized to the corresponding 1-propenoxy-2-phenoxyethane (**PPE**). It was also necessary to determine whether this latter compound undergoes cationic polymerization. Accordingly, **PPE** was prepared by the trisphenylphosphine-ruthenium(II) chloride catalyzed isomerization of **APE**<sup>1</sup> as shown in Equation 9.



A mixture of *cis* and *trans* **PPE**s were obtained in a ratio of approximately 45:55. Similarly, **AO** can be isomerized in quantitative yield to a mixture of *cis* and *trans* 1-propenoxyoctanes (**PO**).

**PPE** undergoes facile cationic photopolymerization in the presence of 1 mol% of (4-*n*-decyloxyphenyl)phenyliodonium hexafluoroantimonate (IOC-10) as a photoinitiator. The polymer obtained on irradiation was dissolved in chloroform and precipitated into ethanol to give a white powder. The low molecular weight

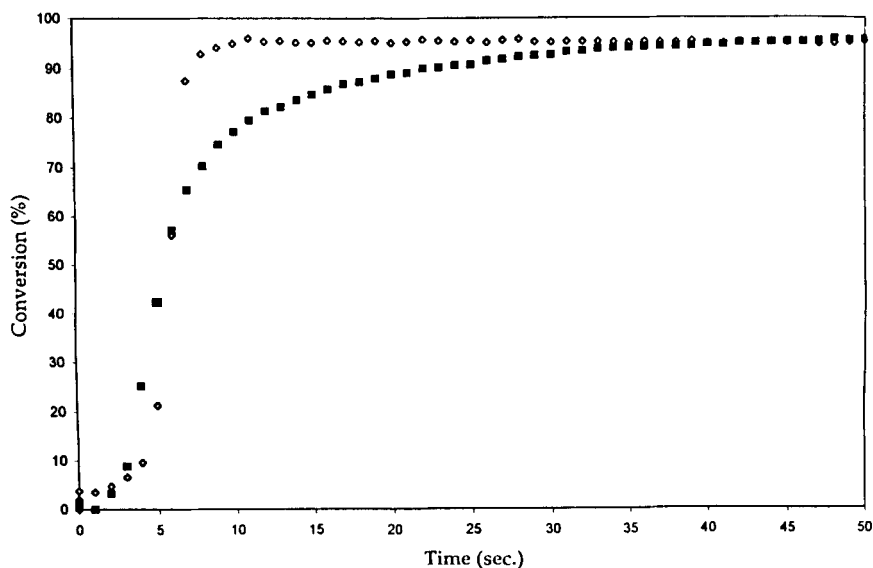


**Figure 3.**  $^1\text{H}$  NMR in  $\text{CDCl}_3$  of the polymer derived from 1-propenoxy-2-phenoxyethane.

(GPC- RI detector,  $M_w = 13600$ ;  $M_n = 7900$ ) polymer could be cast from chloroform as a clear, brittle film. The polymer is UV active and GPC analysis using a UV detector gives comparable molecular weight results. The  $^1\text{H}$  NMR spectrum of this polymer is shown in Figure 3 and the chemical shifts are recorded in the experimental portion of this paper. The NMR data is in accord with the expected structure. Most importantly, the spectrum contains prominent absorptions in the downfield aromatic region of the spectrum which were used for computing the molecular composition of the copolymers in later copolymerization experiments.

Fourier transform real-time infrared spectroscopy (FT-RTIR) was used to determine the rate of disappearance of the 1-propenyl ether functional groups in both **PO** and **PPE** during their photoinitiated cationic homopolymerizations. This method involves monitoring the decrease of distinctive infrared bands during simultaneous UV irradiation. The IR spectra of 1-propenyl ether monomers have characteristic absorptions due to carbon-carbon double bond stretching centered at  $1667\text{ cm}^{-1}$  and this band was monitored during FT-RTIR studies. In Figure 4 are





**Figure 4.** RTIR Study of the rates of photoinitiated cationic bulk polymerization of ■, 1-propenoxy-2-phenoxyethane and ◇, 1-propenoxyoctane in the presence of 1 mol% IOC-10.

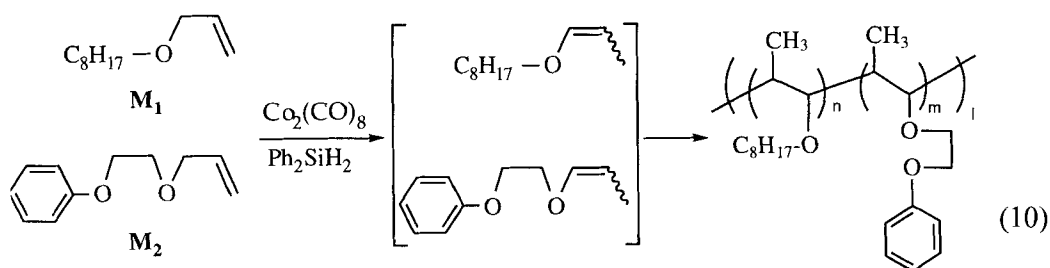
shown conversion versus time plots for **PO** and **PPE**. The very short induction periods seen in the polymerizations of both of these monomers is indicative of their high purity. The initial slopes of both curves are almost identical indicating that the rates of polymerization of these monomers and hence, their reactivities are essentially the same. After about 70% conversion, the slopes of the two curves diverge. At this point, the polymerization of **PPE** shows a considerable decrease in rate. The homopolymer derived from **PO** is a liquid while that from **PPE** has a glass transition temperature ( $T_g$ ) of 55°C. As the polymerization of **PPE** proceeds, the  $T_g$  of the polymer being formed increases until it rises above the ambient temperature. At that point, a phase change occurs as the polymer is transformed from a liquid to a glassy solid. At the same time, the mobility of both the growing chain ends and the monomer are decreased within the glassy polymer and polymerization slows. In contrast, since the polymerization of **PO** does not involve a phase change, the rate does not exhibit this dramatic deceleration effect. The homopolymerizations of both of these monomers proceed to high conversions (~90%) in approximately 50 s.

**APE** undergoes facile tandem isomerization and cationic homopolymerization. In the presence of  $\text{Co}_2(\text{CO})_8$  and diphenylsilane as catalyst and cocatalyst respectively, polymerization proceeded rapidly to give a polymer ( $M_w = 16600$  g/mol) which had a  $^1\text{H}$  NMR spectrum identical to that obtained from the cationic photopolymerization of **PPE**.

With this preliminary data in hand, it was decided to proceed forward with the copolymerization studies of these two monomers. The results of these investigations are described below.

### Copolymerization of 1-Allyloxy-2-phenoxyethane with 1-Allyloxyoctane

Copolymerization studies of the tandem isomerization and cationic polymerization of **APE** ( $M_1$ ) and **AO** ( $M_2$ ) were carried out (Equation 10) and the results are presented in Tables 2 and 3. In these studies, 2 mol% of  $\text{Co}_2(\text{CO})_8$  and 4 mol% of diphenylsilane relative to the monomers were used in all cases based on the previous optimization studies of their respective homopolymerizations [7]. As with the homopolymerizations, all the copolymerizations were preceded by a brief (~45 s) induction period during which  $\text{Co}_2(\text{CO})_8$  and diphenylsilane react and the concentrations of the corresponding 1-propenyl ether intermediates are built up. This is followed by rapid and exothermic polymerization.



The conversions of the individual comonomers to polymers were calculated by measuring the amount of residual monomer remaining in the reaction mixture after polymerization by gas chromatography. In all cases, the conversions were high (72-90%). The weight average molecular weights varied between 14530 and 16800 g/mol with quite narrow polydispersity indices (~2.00). However, it should be stated that the narrow polydispersity indices may be artifacts due to unintentional fractionation of the copolymers due to the precipitation and workup procedures. No attempts were made to optimize the molecular weights of the copolymers. Molecular weights measured by GPC using RI and UV detectors are comparable (Table 3). Since the RI detector is diagnostic for the presence of both monomers in the copolymer while the UV detector is responsive

to only **APE** repeating units, one can conclude on the basis of these results that the polymers are compositionally homogeneous across the full range of their molecular weight distributions. Moreover, the GPC curves were monomodal in all cases. This strongly suggests that the polymers obtained are copolymers rather than a simple mixture of homopolymers.

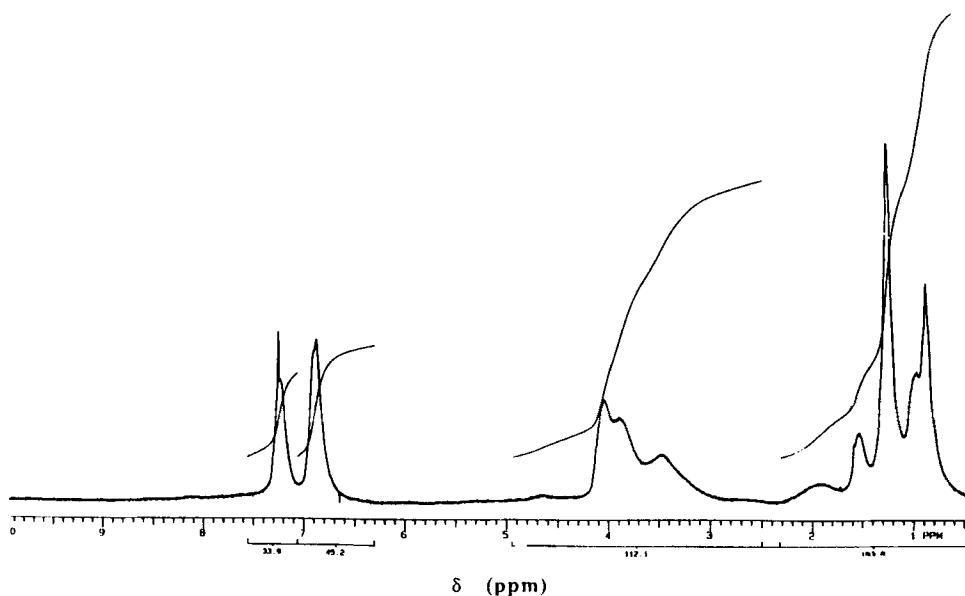
The polymer obtained from the homopolymerization of **APE** is an amorphous colorless solid ( $T_g = 55^\circ\text{C}$ ) at room temperature, whereas the homopolymer of **AO** and copolymers with less than 20 wt% of **APE** are liquids. Thus, as expected, the  $T_g$  of the copolymers is lowered by increasing the amount of the monomer giving the lower  $T_g$  homopolymer, i.e. **AO**. The homopolymer from **APE** can be cast from chloroform as a clear, transparent, brittle film. Similarly, the copolymer formed from an 80/20 wt% feed mixture of **APE** and **AO**, can be cast as a clear transparent, but flexible film ( $T_g = 38^\circ\text{C}$ ). The apparent lack of phase separation in all the cases also seems to support the hypothesis that copolymers are indeed formed. In contrast, films cast from chloroform of a 50/50 wt% mixture of the two homopolymers exhibit obvious phase separation. Thermal and mechanical characterization of the solid copolymers are underway.

### Determination of the Reactivity Ratios

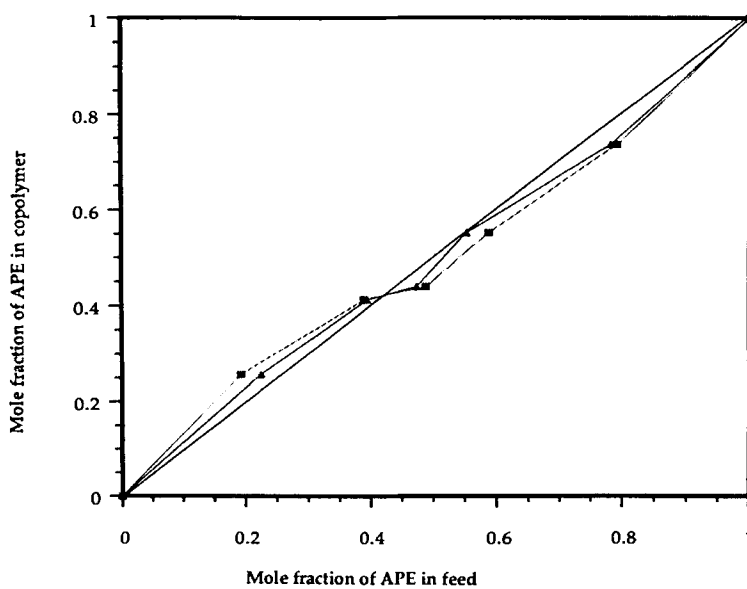
Given in Table 2 are the values of the mole fractions of **APE** in the feed,  $nM_1$ , the mole fraction of **APE** in the feed assuming 100% conversion,  $nM_1'$ , and the mole fraction of **APE** incorporated in the copolymer,  $NM_1$ .  $NM_1$  was determined by integration of appropriate bands in the  $^1\text{H}$  NMR spectra of the copolymer. The  $^1\text{H}$  NMR of a copolymer with the composition shown in entry 3 in Table 2 is given in Figure 5 and a model calculation for this case is presented. [14]

In Figure 6 are plotted the composition of **APE** in the feed,  $nM_1$  versus the composition of **APE** incorporated in the copolymer,  $NM_1$ . A second plot using  $nM_1'$  calculated assuming 100% conversion of the monomers is also included in this figure. The data points for both curves are close to the theoretical bold line drawn for a completely statistical copolymerization. Statistical copolymerization occurs when the composition of monomers in the feed is the same as the composition of monomers in the copolymer. The values of  $nM_1'$  are slightly closer to the theoretical line as expected.

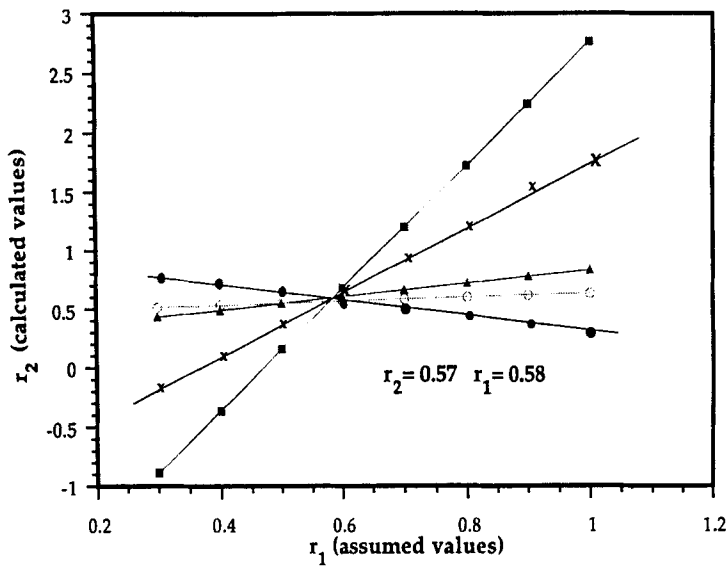
Both Mayo-Lewis [15] and Fineman-Ross [16] methods were used to calculate the reactivity ratios,  $r_1$  and  $r_2$ , for these two monomers. Figure 7 shows a Mayo-Lewis plot for the tandem isomerization and cationic copolymerization of



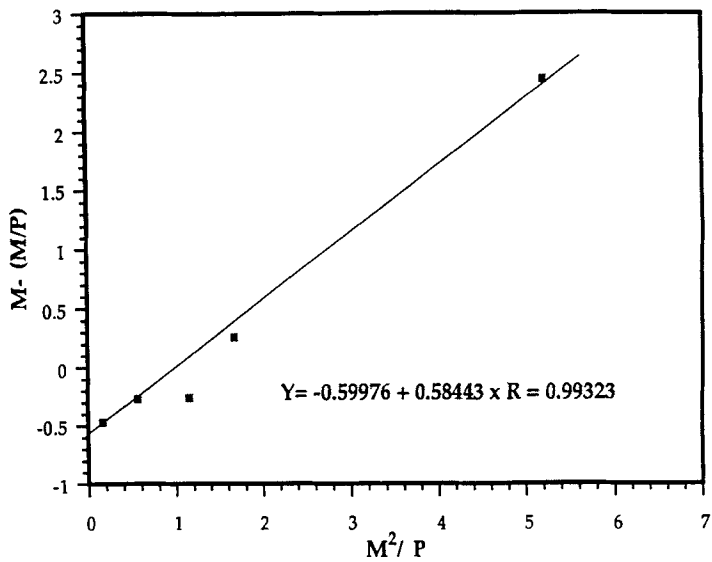
**Figure 5.**  $^1\text{H}$  NMR in  $\text{CDCl}_3$  of the polymer derived from copolymerization of 0.6 g 1-allyloxy-2-phenoxyethane and 0.4 g 1-allyloxyoctane (Entry 3, Table 2).



**Figure 6.** Study of copolymerization behavior of 1-allyloxy-2-phenoxyethane with 1-allyloxyoctane ■, in the feed; ▲, in the feed assuming 100% conversion.



**Figure 7.** Mayo-Lewis plot for copolymerization of 1-allyloxy-2-phenoxyethane with 1-allyloxyoctane.



**Figure 8.** Fineman-Ross plot for copolymerization of 1-allyloxy-2-phenoxyethane and 1-allyloxyoctane.

the monomers with four out of the five lines intersecting at a single point. The calculated reactivity ratio values of  $r_1 = 0.58$  and  $r_2 = 0.57$  were obtained. Figure 8 depicts the Fineman-Ross plots for this same copolymerization. The points were fit using a standard linear regression routine. The slope gave a  $r_1$  value of 0.58 and the intercept a  $r_2$  value of 0.59, for **APE** and **AO** respectively. The values obtained by both methods are comparable. Use of the Kelen-Tüdös method [17] a recent modification (1976) of the Fineman-Ross method, also gives similar values for  $r_1$  and  $r_2$ . The identical values of  $r_1$  and  $r_2$  indicate that both the propagating cations generated during polymerization have the same preference for the other monomer. They also suggest that the prior isomerizations of the allyl ether starting materials to the corresponding 1-propenyl ethers take place at essentially the same rates.

## CONCLUSIONS

A study of the tandem isomerization and cationic copolymerization of **APE** ( $M_1$ ) and **AO** ( $M_2$ ) was carried out. Efficient copolymerization occurred and the results of GPC studies indicated formation of a random copolymer. Reactivity ratios of  $r_1 = r_2 = 0.58 \pm 0.01$  were calculated for this set of monomers. Copolymerization of allyl ethers using the  $\text{Co}_2(\text{CO})_8/\text{R}_3\text{SiH}$  catalyst system is a suitable method for obtaining copolymers with a range of potential interesting properties.

## ACKNOWLEDGEMENTS

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- [14] Model calculation of the mole fraction of APE incorporated in copolymer, NM<sub>1</sub> (Experiment 3, Tables 2 and 3) from <sup>1</sup>H NMR spectrum (Figure 5).  
 Mole fraction of phenoxy ethyl 2-allyl ether in feed, nM<sub>1</sub> = 0.59  
 Integrated area of region d 7.0-6.3 ppm = 45.2 units = 3 aromatic protons (H<sub>a,b</sub>) of APE i.e. 1H of APE = 15.1 units.  
 Integrated area of region d 2.7-4.9 ppm = 112.1 units = 5 protons adjacent to oxygen (H<sub>d,e,f</sub>) of APE and 3 protons adjacent to oxygen (H<sub>d',e'</sub>) of AO.  
 Thus, 112.1 units = 5 x 15.1 + 3H protons of AO.  
 3H protons of AO = 36.8 units or 1 proton AO = 12.3 units.  
 NM<sub>1</sub> APE incorporated in the copolymer = 15.067/(15.067+12.25) = 0.55.
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