



Photopolymerization of Epoxide and Vinyl Monomers by Metal Carbonyl Compounds

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***Corresponding Author:** Ideisan Ibrahim Abu-Abdoun, Department of Chemistry, University of Sharjah, Sharjah, United Arab Emirates.**Received:** July 26, 2019; **Published:** August 08, 2019**Abstract**

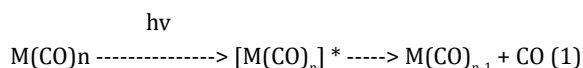
The polymerization of selected epoxide and vinyl monomers using metal carbonyl such rhenium, tungsten, chromium carbonyl compounds were studied photochemically with wavelength of 360 nm and, thermally in dichloromethane. Photoinitiation by these compounds was an effective method to initiate polymerization, thermal polymerization at 85°C leads to the formation of small amount of polymer in a long reaction time. Photosensitization by benzil, N-methylphenothiazine enhances the rate of cyclohexene oxide polymerization.

Keywords: Photopolymerization; Photosensitization; Metals Carbonyl; Vinyl and Epoxide Monomers**Introduction**

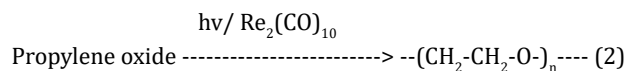
UV-curable coatings have found applications in the graphics arts, packaging, dental, medical and microelectronics industries [1,2]. Photoinitiated polymerization of epoxides has been carried out by different types of onium salts, such as diaryliodonium [3], triphenyl sulfonium [4], phenacyl phosphonium [5] and Arsonium salts [6].

Cobalt carbonyl such as $\text{Co}_2(\text{CO})_8$ has been used to catalyze the photopolymerization of epoxides in the presence of Si-H containing cocatalysts, and irradiation of $\text{Co}_2(\text{CO})_8$ in epoxides for long time results in the formation of trace amounts of polyepoxides [7,8].

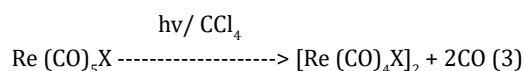
The primary photochemical process with a simple metal carbonyl is the dissociation with formation of a coordinatively unsaturated species as in equation (1) [9].



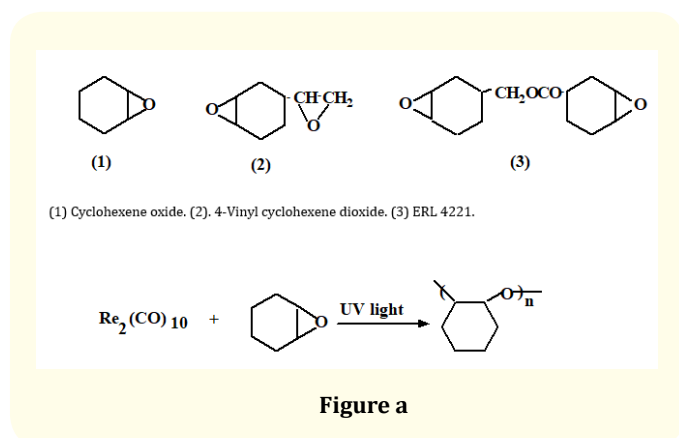
The chemistry of rhenium has been less extensively explored compared to other transition metals. Photopolymerization of propylene oxide using rhenium decacarbonyl as shown in equation (2).



Metal carbonyl halides such as $\text{Re}(\text{CO})_5\text{X}$ (X = Cl, Br, I) where the metal center is in an odd oxidation state are photo substitution labile, and will undergo atom transfer reactions under photolysis condition, as shown in equation (3), the quantum yields of these reactions are dependent on the X type and the ligand [9], these carbonyl compounds have been used as catalysts for olefin metathesis and cycloolefin polymerization in the presence of cocatalyst [10-12].



Light-curable coatings based on epoxides frequently include cyclohexene oxides (1), which we have used as a model monomer to examine the reactivity, structure and mechanism of polymerization reaction related to these systems, as multifunctional cycloaliphatic monomers such as 4-vinylcyclohexene dioxide (2) and 3,4-Epoxy-cyclohexylmethyl-3,4 epoxy cyclohexane carboxylate (ERL4221) (3) would be expected to form crosslinked polymers.



The photopolymerization of selected epoxides such as (1 and 2), and vinyl monomers such as N-vinylcarbazole and n-butylvinylether by rhenium carbonyl compounds will be examined, and preliminary results on the effects of catalysts and monomers structures, photosensitization, and studies on the living polymerization of (1) will be presented.

Materials and Methods

Materials: - Monomers and solvents (Flucka) were dried over calcium hydride and distilled before use. Rhenium carbonyl compounds were obtained from Pressure Chemical Company and used as received.

Polymerization Procedures: The selected amount of monomer and catalyst were placed in a 15 mm diameter Pyrex tube which was closed with a rubber septum. Irradiation was carried out using a merry-go-round photoreactor, Model RPR 100, obtained from the Southern New England Company, which was surrounded by sixteen Honovia 450-Watt, medium pressure mercury lamps at a distance of 5 cm from the sample. The light source used with the system in this study gives 4.50 Watts of radiation with 90% in the range peaked at 350 nm. The obtained polymer was precipitated in methanol, filtered, dried and weighed, from the weight of the isolated polymer the % conversion was calculated.

Results and Discussion

Thermal polymerization of cyclohexene oxide (1) by $\text{Re}_2(\text{CO})_{10}$

Bulk polymerization of (1) by dirhenium decacarbonyls gave no polymer in the temperature range 25 – 70°C for 12 hours, monomer concentration was 9.85 M (bulk) and catalyst concentration was 1.91×10^{-3} M.

Figure 1 shows the results of thermal polymerization of (1) by $\text{Re}_2(\text{CO})_{10}$ in dichloromethane at 85°C, the catalyst concentration was 5.15×10^{-4} M, and the monomer concentration was 6.56 M.

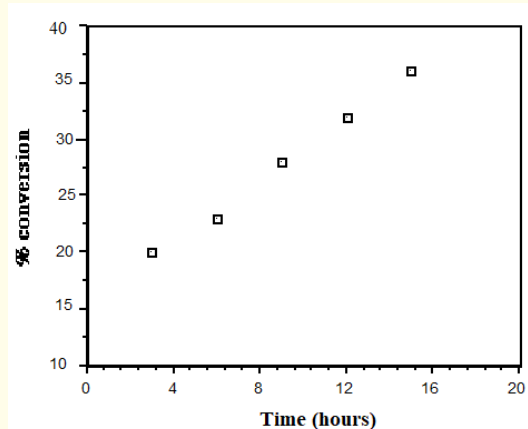


Figure 1: Thermal polymerization of cyclohexene oxide at 85°C

Photopolymerization of cyclohexene oxide (1) by $\text{Re}_2(\text{CO})_{10}$

The polymerization of (1) by $\text{Re}_2(\text{CO})_{10}$ in dichloromethane is shown in Figure 2, catalyst concentration was 5.15×10^{-4} M and monomer concentration was 6.56 M.

According to figure 2, rhenium carbonyls are very active photocatalyst, since the amount of polymer formed in figure 1 is about 13% in two hours, which is very small compared to photoinitiation process.

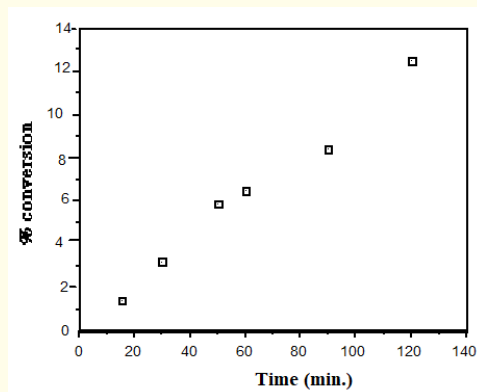


Figure 2: Photopolymerization of cyclohexene oxide by $\text{Re}_2(\text{CO})_{10}$

Table 1 shows the effect of the halide group (X) of $\text{Re}(\text{CO})_5\text{X}$ on the amount of polymer recovered, the catalyst reactivity in polymerization depends on the type of X, and under the reported conditions it fall in the sequence: $\text{Cl} > \text{Br} > \text{I}$.

Catalyst	% conversion
$\text{Re}(\text{CO})_5\text{Cl}$	10.0
$\text{Re}(\text{CO})_5\text{Br}$	5.2
$\text{Re}(\text{CO})_5\text{I}$	3.0
$\text{W}(\text{CO})_6$	2.0
$\text{Cr}(\text{CO})_6$	Viscous product

Table 1: Effect of catalyst structure on bulk photopolymerization of cyclohexene oxide. Conditions. $[\text{M}] = 9.85 \text{ M}$, $[\text{Cat.}] = 2.52 \times 10^{-3} \text{ M}$. Time was 3 minutes.

Studies on living polymerization of monomer (1) by $\text{Re}_2(\text{CO})_{10}$

Great progress in the field of living polymerization was made due to the discovery of various new initiators, since the initiator affects the relative rate of initiation to propagation and the potential for side reactions during chain growth [12,13].

It is expected that upon addition of a fresh feed of the monomer to the completely polymerized system, the second-stage polymerization ensures, resulting in further growth of all growing polymer molecules [14,15].

We have found that polymerization of (1) photoinitiated by rhenium carbonyl shows a long-lived after effect. When reaction mixture of cyclohexene oxide and dirhenium decacarbonyl was exposed to light of wavelength 350 nm for 5 minutes, then transfer to in the dark, polymerization reaction continued at room temperature for several hours after the light has been cut off.

Figure 3 shows the polymerization of monomer (1) by $\text{Re}_2(\text{CO})_{10}$ in dichloromethane, the monomer concentration was 4.92 M, and the catalyst concentration was $8.87 \times 10^{-4} \text{ M}$. Polymerization reaction progress in the dark slowly, and the amount of polymer isolated depends on the overall reaction time, this growth in the propagated chains is a characteristic of living polymerization reaction [16,17].

Table 2 shows the polymerization of selected epoxides and vinyl monomers by rhenium carbonyl chlorides. Based on the amount of polymer isolated, the rate of photopolymerization of these monomers depend on the monomer structure and reactivity and fall in the following sequence:

Cyclohexene diepoxide > p-methylstyrene > styrene > N-vinylcarbazole > cyclohexene oxide > n-butylvinylether > Epichlorhydrine.

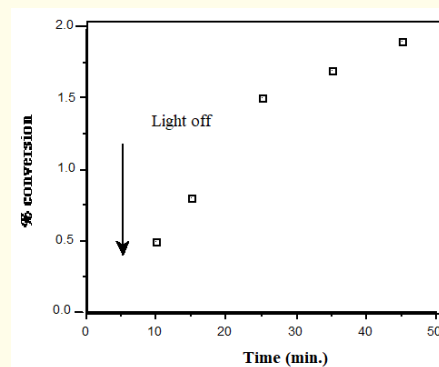


Figure 3: Living photopolymerization of cyclohexene oxide by $\text{Re}_2(\text{CO})_{10}$

Monomer	Time (mins)	% conversion
Cyclohexene oxide	5	62
4-Vinyl cyclohexene dioxide	5	100
N-Vinylcarbazole	5	84
Styrene	5	90
p-methylstyrene	5	95
n-Butylvinyl ether	30	Viscous liquid
Epichlorhydrine	60	Viscous liquid
4-vinylpyridine	60	Product

Table 2: Photopolymerization (bulk) by $\text{Re}(\text{CO})_5\text{Cl}$, $[\text{M}] = 9.85$, $[\text{cat.}] = 2.50 \times 10^{-3} \text{ M}$ Rayonet merry go round photoreactor with wavelength 350 nm tubes, time = 10 minutes.

Reaction mixture of cyclohexene oxide and $\text{Re}_2(\text{CO})_{10}$ containing quantitative amounts of the catalyst and a light absorbing compounds (photosensetizers), listed in Table 3 showed a retardation

effect in the presence of benzoin, however Benzil enhanced the rate of polymerization. This may be due to the difference in the sensitization mechanism and the photochemistry of these compounds, also the difference in the basicity of the excited state between these sensitizers and cyclohexene oxide.

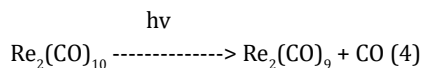
Sensitizer	% conversion
No additives	54.0
Benzil	65.0
Benzoin	17.2
Methyl phenothiazine	82

Table 3: Effect of additives on bulk polymerization of (1). Time = 30 minutes, [additive] = [catalyst] = 2.50×10^{-3} , [M] = 9.85 M.*

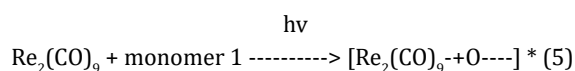
*photolysis source was Xenon ARC lamp, adjusted at 12 ampere constant current, and fixed at 60 cm distance from the reaction [4].

Suggested Mechanism for Epoxide Photopolymerization

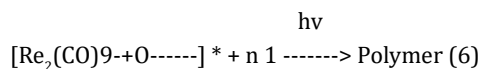
Using rhenium carbonyl compounds, polymer was formed from cyclohexene oxide which does not polymerize free radically, the proposed photoinitiation mechanism of epoxide can be presented in the equations (4 - 6) below:



where through coordination of the metal carbonyl with the epoxide followed by rapid addition of monomer molecules to the complex as follows: -



with subsequent propagation steps following conventional cationic polymerization mechanism for an epoxide,



Polymerization of other epoxides and vinyl derivatives of these monomers will also be examined.

Conclusions

Metals carbonyl compounds are effective photocatalysts for the polymerization of epoxide and vinyl monomers at 25°C. Thermal polymerization is very slow compared to photopolymerization according to recovered polymerization product. Addition of light absorbing compounds (photosensitizer) enhanced the rate of polymerization. Epoxide and vinyl monomers polymerized at different rate, depending on the polymerizable functional group.

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