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Polymerization of 4-Vinyl-1-Cyclohexene Diepoxide by Rhenium Carbonyls Compounds

Ideisan I Abu-Abdoun*

Department of Chemistry, University of Sharjah, Sharjah, United Arab Emirates

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***Corresponding author:** Ideisan I Abu-Abdoun, Department of Chemistry, University of Sharjah, Sharjah, United Arab Emirates

Summary

The polymerization of 4-vinyl-1-cyclohexene diepoxide (4-VCHD) by rhenium carbonyl, Re(CO)5X (X = Br, Cl) and dirhenium decacarbonyls $Re_2(CO)_{10}$ has been carried out photochemically at 25°C, and thermally at 25 and 75°C witout cocatalysts. The effects of initiator structure, concentrations, and reaction temperature and time on the polymerization rate is reported here.

Keywords: 4-vinyl-1-cyclohexene diepoxide; Rhenium Carbonyl; Photoinitiated Polymeriation

Introduction

Diepoxy resins have found important commercial applications in UV radiation curing of surface coatings; a dhesives and in the plastic industry [1,2]. Photoinitiated cationic ring-opening polymerizations of cyclohexene oxide (CHO)1 (Figure 1) was conducted using dirhenium decacarbonyl [3] and rhenium carbonyl halides [4] without a cocatalyst. 4-vinyl-1-cyclohexene diepoxide 2 is used as a reactive diluent's for diepoxides and epoxy resins; this monomer is expected to form crosslinked polymers, if both epoxide groups are polymerized. Cationic photoolymerization of 4-VCHD by diphenyliodonium hexafluorophosphate was carried out and a mixture of crosslinked and benzene soluble polymers were obtained [5], cationic thermal polymerization by BF3. $O(C_2H_5)_2$ [6], and it has been reported that two epoxy rings can be opened for polymerization selectively by radiation, but not by chemical initiators.

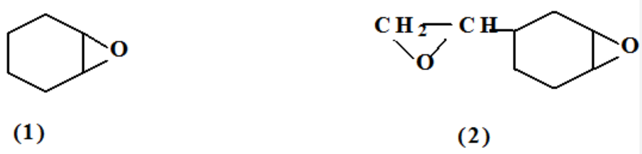

Figure 1: Structure of cyclohexene oxide (1) and 4-Viny-1-cylohexne diepoxide (2).

In this paper we report on the polymerization of 4-VCHD (Table 1) by rhenium carbonyl, $Re(CO)_5X$ (X = Br, Cl) and dirhenium decacarbonyls $Re_2(CO)_{10}$ photochemically and thermally without cocatalyst Table 2. Insoluble polymer was obtained in photo or thermal polymerization even at low conversion of monomer.

Table 1: Photopolymerization of 4-VCHD (bulk), initiator effect on the gel time. [initiator] = 2.50 x10^{-3}M.

Catalyst	Gel Time
$Re_2(CO)_{10}$	15 minutes
$Re(CO)_5Cl$	5 minutes
$Re(CO)_5Br$	15 minutes
$Re(CO)_5I$	14 hours

Experimental

Materials

4-vinyl-1-cyclohexene diepoxide (Fluka) was distilled over calcium hydride (CaH_2), and the middle fraction was collected. Solvent dichloromethane (Fluka) were dried over calcium hydride and distilled before use. Rhenium carbonyls were obtained from Pressure Chemical Company and used as received.

Instruments

Ultraviolet spectra were obtained on a Cary 2300 spectrophotometer. Infrared spectra were recorded on a Nicolet 50xB FT-IR spectrophotometer.

Polymerization

Photoinitiated polymerization was carried out in a 15mm diameter Pyrex tube using a tight syringe for monomer addition; a homogeneous solution was formed, the reaction tube was then closed with rubber septum, and irradiation was carried out using a merry-go-round photoreactor, Model RPR 100, which rotates continuously by a motor and is surrounded by 16 Hanovia 450 Watt, medium pressure mercury. The light source was equipped with 350 nm wavelength tubes. The samples were placed in the holder and irradiated for the required period.Thermal polymerization was conducted by placing the reaction tube in a water bath at the required temperature for the time indicated in dark. Isolated polymer was washed with dichloroethane, filtered, dried and weighed. The rate of polymerization was calculated gravimetrically as a function of reaction time [7].

Results and Discussion

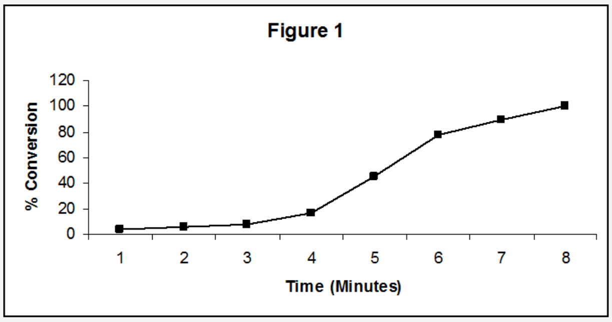

Figure 2: Photopolymerization of CHO 1 and 4VCHD 2 by $Re(CO)_5Cl$.

Polymerization of CHO monomer 1 proceeds through the opening of the epoxide ring to give soluble polymer poly (cyclohexene oxide), the product is long sequences of cyclohexane rings interlinked by oxygen atoms, Figure 3, however; the polymerization of the diepoxide monomer 2 was found to proceeds through the opening of both epoxide ring to give crosslinked polymer of poly (4-VCHD), as shown in Figure 4. Evidence for the structure of poly 4VCHD was obtained by studying the FTIR spectrum of the polymer obtained under different conditions. Typical epoxide bands characteristic of the monomer at 890, 850 and 913cm-^{1} are missing from the polymer spectra, and a new very powerful band at 1087 and 1157cm-^{1} associated with the ether linkage is present. The new band at 108 cm^{-1} is the strongest, and its position varies slightly with chemical structure of the polymer. The important characteristic in the polymerization reaction of 4-VCHD by rhenium carbonyls is the start of the polymerization of both of the epoxy rings at the early stages of polymerization, a crosslinked polymer was obtained at 2% conversion is an idication of reaction of both epoxides at the same time (Figure 4). Thermal polymerization of 4VCHD by dirhenium decacarbonyl and the rhenium pentacarbonyl halides is shown in (Table 2).

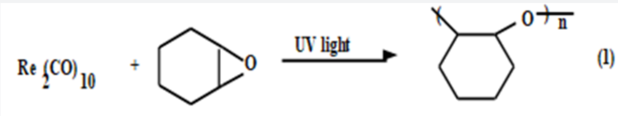

Figure 3: Polymerization of CHO 1.

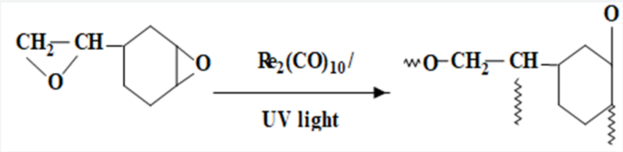

Figure 4: Polymerization of 4VCHD 2.

Table 2: Thermal polymerization of 4-VCHD (bulk), initiator effect on the gel time. [initiator] = 2.50 x10^{-3}M.

Initiator	Gel Time at 75°C	Gel Time at 25°C
	(Hours)	(hours)
$Re_2(CO)_{10}$	2 hours	72
$Re(CO)_5Cl$	10mins	72
$Re(CO)_5Br$	3mins	72
$Re(CO)_5I$	2mins	72

$Re(CO)_5Cl > Re(CO)5Br = Re_2(CO)_{10} >> Re(CO)_5I$

Thermal polymerization of monomer 2 by the rhenium carbonyl halides proceed very slowly at 25°C, and the gel time is 72 hours; and for polymerization at 75°C the gel time fall in the following sequence: $Re(CO)_5I > Re_2(CO)_{10} > Re(CO)_5Br > Re(CO)_5Cl$ (Table 2). This activity is in acrodance with the bond strength between the halide and the rhenium atom. Polymer obtained as a white powder, insoluble in all solvents.

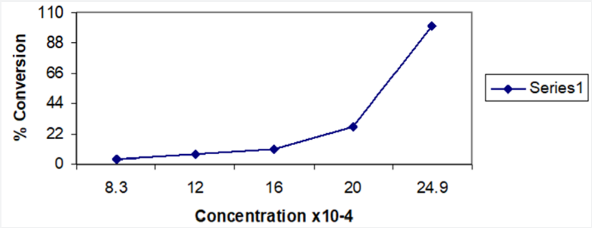

Figure 5: Bulk photopolymerization of monomer 2 by $Re(CO)_5Cl$, time = 5 minutes.

A comparison beteen the bulk photopolymerization of CHO 1 and 4VCHD 2 under the same conditions using $Re(CO)_5Cl$ (2.50x10^{-3}M), shows the required time for complete polymerization (100% conversion) of CHO 1 is 10 minutes and for 4VCHD 2 is 5 minutes, this indicates that the reactivity of monomer 2 almost is twice as that of monomr 1, and both epoxide rings react and opened at the same time.

Effect of initiator concentration

The effect of $Re(CO)_5Cl$ concentration on 4VCHD photopolymerization in the range (1.80 x10^{-3} to 3.69 x10^{-3}M) for fxied time of 5 minutes and without solvent is shown in Figure 5, this indicates an increase in the rate of polymerization as the initiator concentration increases, polymer obtained as crystalline solid which is insoluble in aromatic and halogenated hydrocarbon solvents.

Poly4-VCHD characterization

The polymer structure was identified by FTIR spectroscopy. The FT-IR spectrum of poly (4-VCHD) prepared photochemically and thermally by $Re(CO)_5Cl$ and $Re_2(CO)_{10}$. Poly (4-VCHD) prepared photochemically by by $Re_2(CO)_{10}$ shows the OH group at 3400, aliphatic (CH_2, CH) at 2960, 2850, and 1920, 1720 (CO) and 1655, 1470 (six member ring in polymer), 1440, 1050, 1087 and 913cm^{-1} for the C-O-C stretching frequency [8,9]. These assignment suggest that the catalyst is attached to the poly (4-VCHD).

Proposed polymerization mechanism

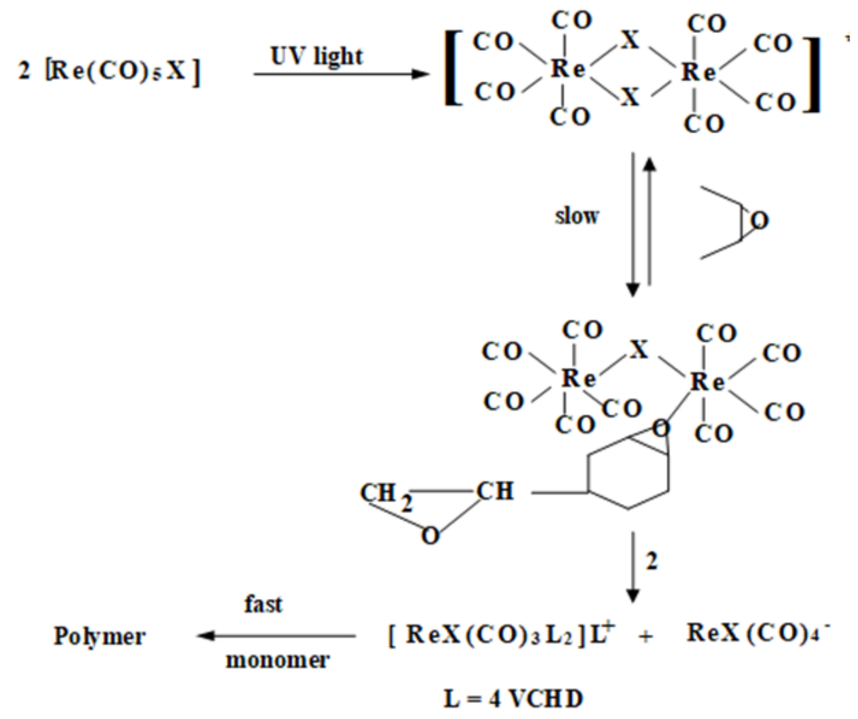

Figure 6: Proposed mechanism of 4-vinyl-1-cyclohexene diepoxide polymerization.

The photodisproportionation of the complex (Re $(CO)_5Cl$ is shown in (Figure 6), L represent a coordinating monomer. The dimerization of the photoexited $Re(CO)_5X$ is bridged through the halogen (X), the bridges is broken by the monomer (4-VCHD), further addition of the monomer to the complex induce the initial propagation reaction. For photoinitiation of the polymerization of 4-VCHD by $Re_2(CO)_{10}$ compounds, we suggested the same mechanism as reported for photopolymerization of cyclohexene oxide [8], the growth of the two epoxide functional groups will leads to crosslinked polymer(Figure 6).

Conclusions

Rhenium carbonyls are effective photoinitiator for the polymerization of (4-VCHD) without cocatalyst, in absence of UV light long reaction time is required. Polymerization by Rhenium carbonyls shows that both epoxide ring were opened. The rate of polymerization depends on the structure of the rhenium carbonyl. Insoluble polymer was obtained in photo or thermal polymerization even at low conversion of monomer.

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