Three-Dimensional Coordination Polymers of Ruthenium(2+) with 1,4-Diisocyanobenzene Ligands and Their Catalytic Activity[†]

Rina Tannenbaum

Department of Chemical Engineering and Material Science, University of Minnesota, Minneapolis, Minnesota 55455

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Organometallic compounds have been playing an increasingly important role in a variety of technologically relevant fields such as catalytic processes and solid-state devices. Of special technological interest are organometallic materials which contain several metal sites, e.g., clusters. Multiple metal centers in a single complex may be achieved by utilizing multifunctional, nonchelating, rigid ligands such as aryldiisocyanides, which when coordinated to metal atoms, would act as bridges and would give rise to template polymerization. There are no studies to date concerning the coordination chemistry of the d^6 transition elements, e.g., Ru(II), Os(II), and Rh(III) with diisocyanide ligands. Since most of the complexes of these transition metals in these oxidation states exhibit octahedral geometry, template polymerization may be obtained, resulting in three-dimensional coordination polymers. In this paper we shall examine the polymerization process of Ru(II) with 1,4-diisocyanobenzene, the physical and spectral properties of the polymers formed, and their potential catalytic activity. Depending on the starting ruthenium carbonyl complex, it is possible to obtain two distinctly different materials, both in their structure and in their catalytic properties. The first compound, polymer **A**, has a three-dimensional structure with a tetragonal geometry, having Ru–Ru stacking interactions in the z direction, while the second compound, polymer **B**, has a cubic geometry, having all the Ru atoms separated by the 1,4-diisocyanobenzene ligands. Polymer **A** is the catalytically active compound, in spite of exhibiting an induction period, and its activity is enhanced by UV irradiation prior to the catalytic reaction, accompanied by the elimination of the induction period.

1. Introduction

Organometallic compounds have been found to play an increasingly important role in a variety of technologically relevant fields, such as catalytic processes and solid-state devices.[1] The interesting chemical and physical properties which characterize organometallic compounds are due to the nature of the metal atoms, the organic ligands and the bonding between the two moieties. In recent years, much attention has been focused on the catalytic properties of polynuclear organometallic species such as clusters.[2-4] These compounds have the ability to offer two or more sites of coordination since they provide the stabilization to release a place-holding ligand.[5] Of special technological interest are reactions catalyzed by several metal sites, in which case most homogeneous catalysts would be rather ineffective since most of them consist of only one metal site.[3,4] Multiple metal centers in a single complex may be achieved by utilizing multifunctional, nonchelating, rigid ligands which, when coordinated to metal atoms, would act as bridges and would give rise to template polymerization.[6,7] Therefore, if bidentate ligands are used, it may be possible to successfully prepare organometallic polymers having the typical empirical formula $[M(L\text{–}L)_x]_n$ (where $x = 1, 2, 3$, M = metal and L–L represents a rigid, nonchelating bifunctional bridging ligand), corresponding to the linear ($x = 1$), square-planar ($x = 2$), and octahedral ($x = 3$) coordination spheres of the metals present in the polymer.[7]

The choice of the proper ligands for these coordination polymers was based on the similarity between their coordination properties and those of carbon monoxide, due to the fact that the bonding mechanism in metal carbonyl complexes is well understood.[8] The isocyanide ligands chosen for the task have bonding properties quite analogous to carbon monoxide (in terms of their σ-donation and π^*-acceptor capabilities)[9-11] and moreover the RCNC–M bond may be approximated to be linear. The bonding versatility of the isocyanide group toward metallic centers covers both the transition as well as the main-group metals and is found in systems with valences ranging from −1 to +3. In this respect it is interesting to mention that the coordination chemistry of carbon monoxide is primarily confined to diamagnetic organometallic compounds of low-valent transition metals and hence lacking

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[†] Part of this work was performed in the Department of Materials Research, The Weizmann Insitute of Science, Rehovot 76100, Israel.

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the versatility found with isocyanide groups. Moreover, unlike carbon monoxide, isocyanide functionalities are part of larger organic molecules, whose size and shape may be varied in order to introduce steric constrictions in the bonding mechanism.

Delocalization of charge from the ArN=C—M bond region into the aromatic substituent system, as opposed to aliphatic systems, has been demonstrated by the infrared spectra,[9] where ν(CN) for aryl isocyanides is shifted in comparison to aliphatic isocyanides, and by relevant ^{13}C NMR.[12] On the basis of such evidence, it is reasonable to assume that aryl isocyanides would behave as better π-acceptors than alkyl isocyanides,[13] and therefore they are better suited to transmit electronic effects across the coordination oligomer.

The chemistry of the coordination properites of monoisocyanides has been extensively reviewed in the literature, but very limited attention has been paid so far to the study of polyisocyanide ligands. Among the research efforts in this latter area, Gray et al.[14] and Powell[15] deal with aliphatic diisocyanide ligands, while Efraty et al.[16,17] and Feinstein-Jaffe et al.[18,19] concentrate on aryl diisocyanide ligands. In both cases, when the ligands are coordinated to d^8 transition metals, e.g., Rh(I), Ir(I), Pd(II), and Pt(II),[16,18,20] the resulting complexes with two-dimensional geometries (x,y plane) are particularly suited for direct metal–metal interactions, in which planar or nearly planar monomeric units are stacked one above the other to form metal atom chains. These materials exhibit interesting UV and visible spectral features and also electrical conductivity properties, which are a direct result of the metal–metal stacking interactions.[16,18,20–22]

There are no studies to date concerning the coordination chemistry of the d^6 transition elements, e.g., Ru(II), Os(II), and Rh(III), with polyisocyanide ligands. Since most of the complexes of these transition metals in these oxidation states exhibit octahedral geometry, one may obtain template polymerization with aryldiisocyanide ligands, resulting in three-dimensional coordination polymers which will be unable to undergo metal–metal stacking interactions and hence their physical and spectral properties will be different than those observed with the d^8 group metals. It is the main purpose of this work to examine the polymerization process of Ru(II) with 1,4-diisocyanobenzene, the physical and spectral properties of the polymers formed, and their potential catalytic activity. Special attention will be devoted to the existence or absence of the metal–metal stacking interaction and its implication on the overall geometry of the new coordination polymers.

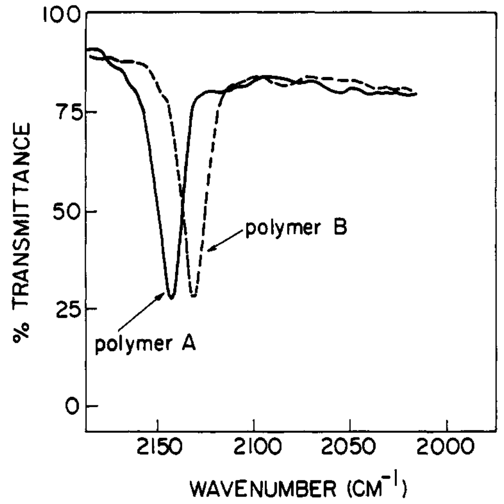

Figure 1. FTIR spectra of polymer **A** (solid line) and polymer **B** (dashed line) in the 2000–2200-cm^{-1} region, corresponding to the asymmetric ν(NC) absorption mode.

2. Results and Discussion

2.1. Chemical Characterization of the Ru(2+) Coordination Polymers. The geometry and stoichiometry of the ruthenium(2+) coordination polymers with 1,4-diisocyanobenzene (**P**) ligands depend to a large extent on the synthetic procedure by which these polymers were obtained. Specifically, there are distinct differences between the reaction of the above ligands with the "red solution" [$RuCl_2(CO)_2(EtOH)_2$] or with the "yellow solution" [$RuCl_2(CO)_3$ (ETOH)].[23] These ruthenium carbonyl solutions are the main chemical entry to most organometallic reactions of ruthenium and are generated by bubbling CO through an ethanol solution of $RuCl_3{\cdot}3H_2O$ for various periods at 80 °C (4 h for the "red solution" and 8 h for the "yellow solution"):[23]

$$RuCl_3{\cdot}3H_2O + CO(\text{in excess}) + EtOH(\text{in excess}) \rightarrow RuCl_2(CO)_2(EtOH)_2 \text{ ("red solution")}$$

$$RuCl_3{\cdot}3H_2O + CO(\text{in excess}) + EtOH(\text{in excess}) \rightarrow RuCl_2(CO)_3(EtOH) \text{ ("yellow solution")}$$

The structure of the ruthenium complexes present in these solutions has a direct influence on the resulting polymeric complexes obtained with the diisocyanide ligands. Figure 1 shows the FTIR spectra of the polymeric complexes resulting from the reaction of the "red" solution (polymer **A**) and the "yellow" solution (polymer **B**) with 1,4-diisocyanobenzene. Polymer **A** exhibits one absorption at 2142 cm^{-1}, corresponding to an assymmetric ν(NC) mode (since both polymers belong to the D_{4h} point group, the highest normal vibration, the A_1 frequency, is infrared inactive, and the highest infrared active normal vibration is the B_2 frequency[24]), while polymer **B** exhibits a similar ν(NC) absorption band at 2129 cm^{-1}. The differences in the frequency of absorption between the two polymers may be attributed to fluctuations in the relative contributions of the σ-d donation and the d-π^* back-donation processes due to various degrees of substitution. This may be the first indication that the two polymers may have

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Table 1. Summary of the Elemental Analyses (% Ru, N, Cl, C, and O) of Polymer A (Swollen and Dry Networks) and of Polymer B (Swollen and Dry Networks)

polymer	Ru	N	Cl	C	O
A	23.1	12.8	15.9	43.5	2.1
dry **A**	23.4	13.2	16.6	44.6	0.2
B	17.8	14.5	12.5	50.3	2.3
dry **B**	18.3	15.1	13.2	51.4	0.3

Table 2. Experimental Stoichiometric Ratios of the Key Elements in the Swollen and Dry Networks of Polymer A and Polymer B

polymer	N/Cl	Ru/Cl	Ru/N	Ru/O
A	2.04	0.51	0.25	1.74
dry **A**	2.02	0.50	0.25	18.53
B	2.94	0.50	0.17	1.22
dry **B**	2.90	0.49	0.17	9.64

neither identical stoichiometries nor identical geometries. No additional absorption bands or shoulders which may suggest residual CO groups have been observed.

Table 1 summarizes the elemental analyses of the polymers obtained by the reaction of 1,4-diisocyanobenzene with both the "red" and "yellow" ruthenium carbonyl solutions. The presence of a small quantity of oxygen atoms in the complexes may be due either to terminal CO groups at the edges of the polymeric network or to the presence of water trapped within the network cavities. An indication that the latter assumption may be the correct one stems from the fact that when the polymeric complexes are rigorously dried for 7 days at 100 °C and at reduced pressure (0.1 Torr), the amount of oxygen decreases considerably and the ratio Ru:O corresponds to 18:1. The presence of oxygen and the discrepancies in the elemental analyses between the polymers **A** and **B** and the same polymers dried under rigorous conditions point to the possibility that this may be due to the ability of these polymers to swell in water, and hence, there are several water molecules associated with each polymer. The experimental ratios of N/Cl, Ru/Cl, and Ru/N, shown in Table 2, give a clear indication as to the chemical composition and stoichiometry of the resulting polymeric complexes. The ratio Ru/Cl for both polymers **A** and **B** is the same, at a value of about 0.5, which means that in both polymers there are 2 Cl atoms for every Ru atom in the chain. The N/Cl ratio, on the other hand, is 2.0 for polymer **A** and 2.9 for polymer **B**, indicating a greater extent of ligand substitution for polymer **B**. Finally, the ratio Ru/N for both polymers, clearly points to a higher content of the diisocyanide ligand for polymer **B**. The overall experimental ratios of Ru:Cl:N were calculated, and for polymer **A** it is 1:2:4, respectively, while for polymer **B** it is 1:2:6, respectively. This implies that in polymer **A** there are four diisocyanobenzene bridges coordinated to each Ru atom (each ligand is shared between two Ru atoms to form a bridge) and in polymer **B** there are six such ligands for every Ru atom. Therefore, the empirical formulas that can be offered for these polymers are as follows:

polymer **A**: $[\mathrm{Ru(1,4\text{-}diisocyanobenzene)}_{4/2}{}^{2+}(2\mathrm{Cl})^{2-}]_n$

polymer **B**: $[\mathrm{Ru(1,4\text{-}diisocyanobenzene)}_{6/2}{}^{2+}(2\mathrm{Cl})^{2-}]_n$

There are no direct measurements to determine the molecular weight of these polymers (or oligomers) merely due to the insolubility of these materials in conventional organic solvents. However, it is possible to make a qualitative assessment of the size of these polymers based on the Ru:O ratio. The presence of very small amounts of oxygen in the elemental analysis (even after the polymers were thoroughly dried) may be due to a small number of terminal CO groups which were not replaced by isocyanide ligands. As previously indicated, no CO absorption bands were observed in the infrared spectra of these materials. This suggests that the ratio between the fully reacted ruthenium sites (complete replacement of CO) and the only partially reacted ruthenium sites (partial replacement of CO) is very large. Since the 1,4-diisocyanobenzene groups are rigid, **nonchelating**, bidentate ligands, they are unlikely to terminally coordinate to the same metal (i.e., unlikely to occupy two coordination sites), and hence this type of substitution of CO groups cannot account for the extensive presence of fully reacted ruthenium sites. A quick and rough calculation over the unit cell of polymer **A**, as shown in Table 3 (approximate unit-cell dimensions (including D_{Ru} = 2.05 Å in the x and y directions): 13.50 × 13.50 × 3.25 Å) shows the complex $[\mathrm{Ru}^{2+}\mathrm{(1,4\text{-}diisocyanobenzene)}_{4/2}(2\mathrm{Cl})^{2-}]$ to have a concentration of $\sim 10^{-5}$ M in the unit cell. Assuming all 0.3% O comes from unsubstituted CO groups, then the concentration of CO in the unit cell will be $\sim 10^{-7}$ M, which will be very hard to detect with conventional infrared techniques. Therefore, it may be concluded that the template polymerization process described here, gives rise not merely to low molecular weight materials but mainly to cross-linked polymers.

Table 3. X-ray Powder Diffraction Analyses for Polymer A and Polymer B. Note the 001 Reflection Observed for Polymer A

polymer A		polymer B		Miller indices		
∠(deg)	d (Å)	∠(deg)	d (Å)	h	k	l
3.84	11.49	3.85	11.46	1	0	0
5.49	8.05	5.45	8.10	1	1	0
7.70	5.74	7.66	5.77	2	0	0
8.62	5.13	8.67	5.10	2	1	0
11.65	3.81	11.59	3.83	3	0	0
		15.54	2.87	4	0	0
13.71	3.25			0	0	1

2.2. Structural Characterization of the Ru(2+) Coordination Polymers. The geometry of polymer **A** is a square-planar geometry capable of undergoing metal–metal interactions to form stacked layers along the z axis (analogous to that found in similar complexes between Rh(I) and diisocyanobenzene ligands[16,18], while polymer **B** exibits octahedral geometry and hence the stacked configuration is not possible. X-ray powder diffraction data of polymer **A** and polymer **B** are shown in Table 3. The data for polymer **A** reveal a relatively strong 001 reflection corresponding to an intermetallic distance of 3.25 Å, consistent with structures resulting from the stacking of ruthenium-containing two- dimensional complexes, to form a three-dimensional network. No analogous reflection is observed for polymer **B**. For both polymers, the 100 reflection corresponds to 11.49 Å in polymer **A** and 11.46 Å in polymer **B**, which is actually the length of the diisocyanobenzene ligand. Hence, the Ru metallic centers are separated by the ligand (**P**) in the xy plane, and in polymer **B**, also along the z axis. The three-dimensional structure of the two polymers is described schematically in Figures 2 and 3. The structure in Figure 2 represents a tetragonal three-dimensional network with stacking Ru–Ru bonds in the z axis, while the structure

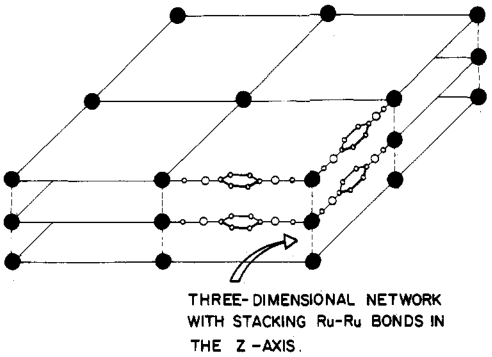


Figure 2. Three-dimensional tetragonal network structure of polymer **A** exhibiting stacking Ru–Ru bonds along the *z* axis (●, Ru; ○, N; ∘, C).

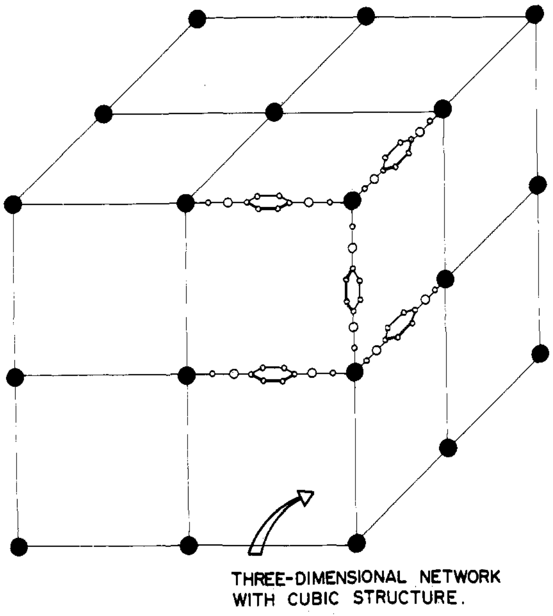


Figure 3. Three-dimensional cubic network structure of polymer **B** (●, Ru; ○, N; ∘, C).

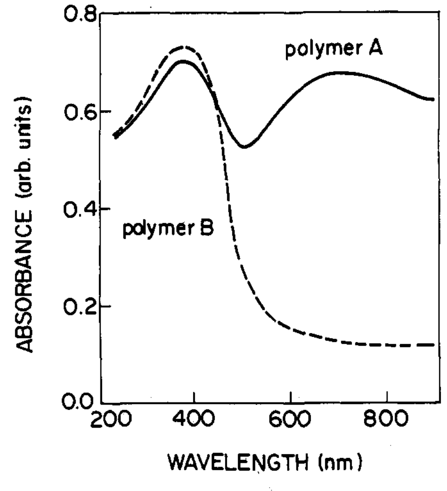
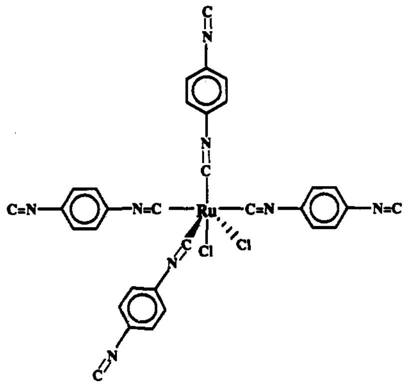


Figure 4. UV–vis (200–800-nm range) diffuse reflectance spectra of polymer **A** (solid line) and polymer **B** (dashed line).

in Figure 3 represents a cubic three-dimensional network.

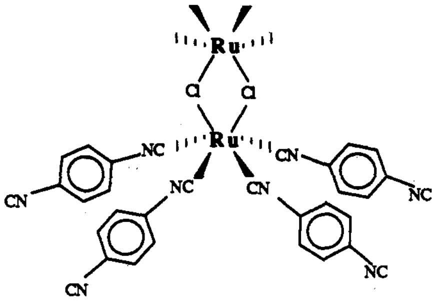
The existence of the intermetallic bonds found in polymer **A** is further demonstrated by the diffuse reflectance spectra shown in Figure 4. Both polymers have a common broad absorption at 370 nm, while polymer **A** has an additional very broad absorption with its center at 620 nm. The high-energy absorptions in the spectra may be assigned to a transition of the type $^1A_{1g} \rightarrow {}^1A_{2u}$,[25] assuming a D_{4h} symmetry point group for both polymers. The low-energy absorptions consist of several transitions between the upper region of the bonding (HOMO) and the lower region the antibonding orbitals (LUMO) and are greatly influenced by the presence of intermetallic interactions, because these interactions reduce the energy of transition between the two molecular orbital levels. Therefore, polymer **B**, which lacks the capability of forming these interactions, has no absorption in this region, similar to a material such as TiO_2, which is a known photosemiconductor.

There are other possible interpretations of the results presented so far, which might suggest a different structure for polymer **A**. One possibility is the formation of *cis*-dichloro complexes, in which for each Ru atom there are 4/2 (1,4-diisocyanobenzene) ligands and 2 chloro ligands coordinated in a cis position:[26]



This structure implies that there should be *two* ν(NC) absorption bands in the infrared spectrum, but an examination of Figure 1, shows clearly that there is only *one* ν(NC) band. Also, far-infrared studies on these compounds *did not* exhibit any ν(Ru–Cl) band which would be consistent with a direct bonding of the chloride ions to the metallic center. Moreover, this structure does not explain the 001 reflection, and consequently the 3.25-Å spacing observed with X-ray analysis.

Another structure which might be consistent with this latter result is a diruthenium complex with bridged chloro ligands:[26]



In this case, the bridging chloro ligands create a proximity between the two Ru atoms which may give rise to a 001 reflection and an intermetallic distance of 3.25 Å.

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This structure is also consistent with the presence of only *one* ν(NC) absorption band in the infrared. The only inconsistency is the absence of ν(Ru–Cl) in the far-infrared region. Therefore, it seems that the layered structure of polymer **A**, with the proposed Ru–Ru intermetallic stacking interactions, is the one that most fits the structural data. However, this structure does not eliminate the possibility that the chloro ligands would intercalate between two Ru atoms of adjacent layers to form "quasi" bridges, without actually forming a covalent bond with the metal atoms.

The differences in the structures of polymers **A** and **B** undoubtedly stem from the differences in the structure of the starting ruthenium compounds. In both cases, the 1,4-diisocyanobenzene (**P**) ligands enter the coordination sphere of the metal, and as a first step substitute the CO groups, followed by the elimination of the coordinated EtOH groups. Since the polymerization reaction is carried out in ethanol, the rate of the elimination of the EtOH groups is most likely slower than the metal–metal interactions, and therefore, the latter occur prior to the total elimination of the EtOH groups and their substitution with the bridging ligands. It is important to remember that the dissociation reaction of the EtOH groups is reversible, and since EtOH is present in excess, the equilibrium is pushed toward the associative direction. Therefore, the "leaving quality" of the EtOH groups is reduced by a kinetic effect, rather than being a "true" thermodynamic property. This mechanism promotes the formation of metal–metal interactions in the oligomer generated by the ruthenium complex containing only two CO groups (the "red" solution), while at the same time it prevents this process in the oligomer generated by the ruthenium complex containing three CO groups (the "yellow" solution). In this latter case, there are two equatorial and one axial CO's, and once they are substituted by the **P** groups, the stage is set for a three-dimensional network without the capability of undergoing metal–metal interactions.

2.3. Catalytic Properties of the Ru(2+) Coordination Polymers. Further support for the proposed structure of polymer **A** can be obtained from the study of the catalytic properties of polymers **A** and **B**. The presence of the columnar interlayer Ru–Ru interactions in polymer **A** is further evidenced by the behavior of this material as a catalyst. The possibility of separation of the layers in polymer **A** (by breaking the Ru–Ru interactions) will create the capability of undergoing oxidative–addition reactions and hence act as a heterogeneous catalyst. Conversely, the octagonal geometry of polymer **B** and its three-dimensional rigid structure, render it incapable of undergoing such interlayer separation and therefore prevent any meaningful catalytic activity.

The results of a preliminary study of the catalytic properties of polymer **A** in the hydrogenation reaction of 1-hexene are shown in Table 4. The polymer seems to be an efficient but a nonselective catalyst with a turnover ratio of 1:100 within the experimental setup used. The hydrogenation reaction is accompanied by the isomerization reaction, with the *trans* 2-hexene as the leading isomer, which in turn is hydrogenated as well after all the initial 1-hexene has been used up.

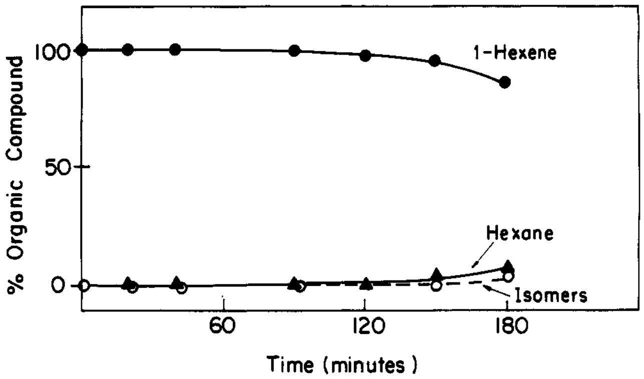

Figure 5. Induction period for the hydrogenation reaction of 1-hexene with polymer **A** as the catalyst (●, 1-hexene; ▲, hexane; ○, Isomers).

Table 4. Results of the Preliminary Study of the Catalytic Properties of Polymer A in the Hydrogenation Reaction of 1-Hexene

			isomerization	
t (h)	hexane (%)	1-Hexene (%)	trans (%)	cis (%)
0	0	100	0	0
3	8	85	4	3
6	17	70	9	4
20	47	10	32	11
22	56	7	26	11
25	64	6	19	11
27	73	3	15	9
44	85	0	8	7
47	85	0	8	7

A closer examination of the initial period of the catalytic reaction, shown in Figure 5, depicts an induction period during which no reaction takes place. The regular mechanism offered in the literature for these types of hydrogenation reactions does not explain the presence of such an induction period, unless the polymer **A** in its original structure is not the actual catalyst.[27,28] A possible explanation for this phenomenon is that the two-dimensional layers of polymer **A**, which are held together by the Ru–Ru interaction, are undergoing separation due to the intercalation of the organic compound, resulting in the partial breakage of these bonds, and the formation of electron-deficient ruthenium sites. These ruthenium sites in turn are capable of coordinating the 1-hexene molecule and perform the catalytic reaction. A schematic description of this mechanism is shown in Figure 6. Irradiation of the reaction mixture with 350-nm UV light prior to and during the reaction drastically reduces the induction period. This indicates that the energy of irradiation is sufficient to break the Ru–Ru stacking bonds, thus creating electron-deficient Ru sites prior to the addition of the olefin. As expected, polymer **B** did not exhibit any noteworthy catalytic activity. An in-depth study on the detailed catalytic properties of these polymers with respect to different catalytic processes is underway and will be published a later date.

3. Experimental Part

Synthesis of the Starting Ru Complexes. $RuCl_3{\cdot}3H_2O$ (1 g, Alfa Chemicals, Ventron Division) was placed in a three-neck, 100-mL round-bottom flask and dissolved in 30 mL ethanol. The solution was flushed with Ar and heated to 78 °C, and when

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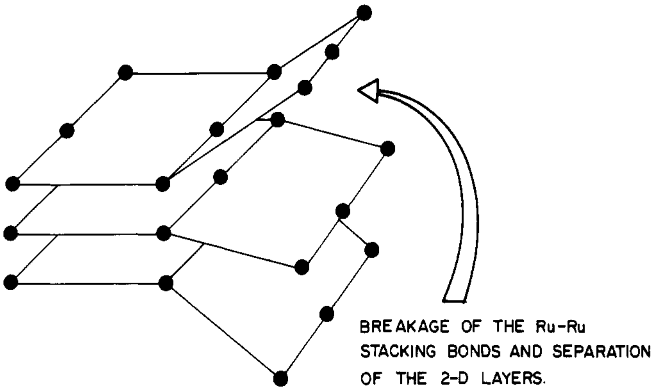

Figure 6. Schematic description of the proposed mechanism for the formation of electron-deficient ruthenium sites in polymer A during the catalytic hydrogenation reaction (●, Ru).

reflux started, the Ar inlet neck of the flask was replaced by a CO bubbler. Samples of 0.5 mL each were removed with a syringe through another neck which was equipped with a rubber stopper. When the solution became either wine red or lemon yellow (depending which complex we were interested in), the heating was stopped, the CO bubbler was replaced with N_2 or Ar, and the soltuion was allowed to reach room temperature.[23,29]

Synthesis of Polymers A and B. The 1,4-diisocyanobenzene ligand was prepared by treating a boiling suspension of the corresponding bis(formylamino)benzene, $C_6H_4(NHCHO)_2$, in a dichloromethane–triethylamine mixture, with diphosgene (best prepared by the photochlorination of methyl chloroformate) as the dehydrating agent, dissolved in dichloromethane. The detailed synthetic procedure is described elsewhere.[30] The polymerization reaction was carried out in the same flask described in the previous section, at room temperature. A 4-fold excess (2.0 g) of 1,4-diisocyanobenzene was dissolved in 30 mL of ethanol and placed in a dropping funnel attached to one of the necks. The solution containing the ligand was then introduced dropwise into the main reaction flask at a rate of 3–5 mL/min, and the reaction was let to equilibrate for about an hour. The reaction mixture was then carefully filtered, and the remaining precipitate was dried in vacuum (0.1 Torr) at 100 °C for 7–8 days to eliminate traces of H_2O. The blue (resulting from the "red solution") and the off-white (resulting from the "yellow solution") precipitate were stored in the dark in small vials and under Ar atmosphere.

Characterization of Polymers A and B. (1) Microanalyses were performed in the Department of Materials Science and Engineering at the University of Florida, as well as by the Microanalytical Laboratories at the Hebrew University in Jerusalem and the Weizmann Institute of Science in Rehovot. (2) Infrared spectra, taken in KBr pellets or Nujol mull, were recorded on a Nicolet Model MX-1 FTIR spectrophotometer with a 2-cm^{-1} resolution. Far-IR experiments were performed on an IBM-IR-90 FTIR spectrophotometer. (3) Diffuse reflectance spectra (UV–vis) were measured on a Cary-15 spectrophotometer. (4) Trace metal analyses were performed using a Varian-Techtron Model 1000 atomic absorption spectrophotometer. (4) X-ray powder diffraction data were collected on a Philips diffractometer using Cu Kα radiation.

Heterogeneous Catalytic Experiments. The typical hydrogenation experiment was performed in a 100-mL glass autoclave, equipped with a small sidearm permitting the removal of samples during reaction. Polymer A (40 mg) was suspended in 10 mL of methanol and 1 mL of 1-hexene. The autoclave was pressurized to 2 atm of H_2, and the reaction was conducted at room temperature, ~25 °C. Samples of 0.1 mL were removed initially every 30 min for the first 2 h and thereafter every 3 h and were analyzed by gas chromatography.

4. Conclusions

The three-dimensional structures of these polymers and especially the Ru–Ru metal stacking interactions observed in polymer A lend themselves to a variety of physical and chemical properties of an applied nature. Due to the combination between extended conjugated π ligands and the d orbitals of the transition metal, it is expected that these polymers will exhibit electrical conductivity properties. The presence of the columnar interlayer Ru–Ru interactions in polymer A may suggest two different conductivities: one in the xy plane and the other in the z axis, compatible with the metal–metal stacking direction. In addition, the possibility of separation of the layers in polymer A (by breaking the Ru–Ru interactions), and the intercalation of small organic molecules, will render the polymer capable of undergoing oxidative–addition reactions and hence act as a heterogeneous catalyst. A detailed study of the conductivity and catalytic properties of these polymers is currently underway and will be published separately.

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