# [Mo₂(MeCN)₈][BF₄]₄ and [Mo₂( μ-O₂CCH₃)₂(MeCN)₆][BF₄]₂ as catalysts for the cationic polymerization of cyclopentadiene and dicyclopentadiene

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## Abstract

The dimolybdenum(II,II) complex salts [Mo₂(MeCN)₈][BF₄]₄ and [Mo₂( μ-O₂CCH₃)₂(MeCN)₆][BF₄]₂ were found to be extremely efficient catalysts for the cationic polymerization of neat cyclopentadiene and also for solutions of the monomer in acetonitrile and in dichloromethane. The silica supported complexes [Mo₂(MeCN)₈][BF₄]₄–SiO₂ and [Mo₂( μ-O₂CCH₃)₂(MeCN)₆][BF₄]₂–SiO₂ only gave small polymer yields unless dichloromethane is used as a monomer solvent. Catalysts could be reused many times to polymerize successive batches of monomer. In most instances there was approximately equal amounts of the 1,2- and 1,4-structures present in the polymers. Solubility of the polycyclopentadiene product was dependent upon reaction conditions and on catalyst used, and with the [Mo₂( μ-O₂CCH₃)₂(MeCN)₆][BF₄]₂ catalyst in dichloromethane black conducting plastics could be precipitated. Soluble, ring-addition polydicyclopentadiene was formed in essentially quantitative yield when [Mo₂(MeCN)₈][BF₄]₄ and [Mo₂( μ-O₂CCH₃)₂(MeCN)₆][BF₄]₂ were reacted with neat dicyclopentadiene at 170°C.

*Keywords:* Dimolybdenum(II,II); Molybdenum; Polymerization; Cyclopentadiene; Dicyclopentadiene; Silica; Conducting

## 1. Introduction

Catalysts derived from complexes containing the quadruply bonded dimolybdenum(II,II) [Mo–Mo]⁴⁺ core
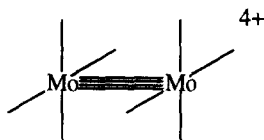


have been shown to be effective for a number of different organic transformations. In 1974 Whan and co-workers [1] used a dry-mix impregnation of the tetracarboxylates [Mo₂( μ-O₂CR)₄] (R = Me or CF₃) on silica and alumina as catalysts for propene metathesis. ESR [2,3] and EXAFS [3] studies of the [Mo₂( μ-O₂CCH₃)₄]–SiO₂ system revealed that at activation temperatures below 350°C the active catalytic species comprised an [Mo–Mo]⁵⁺ moiety, and that at 450°C cleavage of the Mo–Mo bond occurred with consequent loss in catalyst performance.

Candlin [4,5] prepared heterogeneous catalysts by impregnating Al₂O₃ and SiO₂ with solutions of the dimolybdenum(II,II) allyl complex [Mo₂(η³-C₃H₅)₄], and used them for the

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metathesis of hex-1-ene and also for the polymerization of ethylene. No suggestions were made with respect to the structure of the supported species, or as to whether or not the Mo–Mo quadruple bond was retained after supporting the complex. However, as the mononuclear molybdenum(IV) complex [Mo($\eta^3$-C$_3$H$_5$)$_4$] and its chromium, niobium, zirconium and tungsten analogues were also catalytically active for these reactions, it appears that it is the presence of the allyl groups rather than the dimolybdenum unit which is the source of the catalytic activity.

Iwasawa et al. [6,7] also supported [Mo$_2$($\eta^3$-C$_3$H$_5$)$_4$] on Al$_2$O$_3$ and SiO$_2$, and after reducing the supported complexes with H$_2$, followed by exposure to O$_2$, the resulting 'paired' oxo-bridged divalent molybdenum species acted as excellent catalysts for ethene hydrogenation at 200–293 K.

In the past we have demonstrated that in the presence of added EtAlCl$_2$ cocatalyst the neutral and tetraanionic quadruply bonded dimolybdenum(II,II) complexes [Mo$_2$($\mu$-O$_2$CCH$_3$)$_4$] and K$_4$[Mo$_2$Cl$_8$] catalyse the ring-opening metathesis polymerization (ROMP) of the strained bicyclic olefin 1-methylnorbornene at 20°C [8]. Furthermore, [Mo$_2$($\mu$-O$_2$CCF$_3$)$_4$] was found to polymerize the same monomer even in the absence of cocatalyst. In addition, the dianionic dimolybdenum(II,II) complex salt (Et$_4$N)$_2$[Mo$_2$($\mu$-O$_2$CCH$_3$)$_2$Br$_4$] [9] and the dicationic dimolybdenum(II,II) salts [Mo$_2$($\mu$-O$_2$CR)$_2$(MeCN)$_n$][BF$_4$]$_2$·$x$H$_2$O (R = CH$_3$, $n$ = 6; R = (CH$_3$)C=CH$_2$, $n$ = 4; $x$ = 0 or 1) [9] and [Mo$_2$($\mu$-(−)-ment)$_2$(MeCN)$_4$][BF$_4$]$_2$ ((−)-mentH = (−)-menthoxyacetic acid) [10], have been used in conjunction with EtAlCl$_2$ to polymerize norbornene.

More recently [11], we have anchored the salts [Mo$_2$(MeCN)$_8$][BF$_4$]$_4$ and [Mo$_2$($\mu$-O$_2$CR)$_2$(MeCN)$_6$][BF$_4$]$_2$ on silica to give materials represented as [Mo$_2$(MeCN)$_8$][BF$_4$]$_4$–SiO$_2$ and [Mo$_2$($\mu$-O$_2$CCH$_3$)$_2$(MeCN)$_6$][BF$_4$]$_2$–SiO$_2$, respectively. The binding of the Mo–Mo bonded complexes to SiO$_2$ was thought to occur at the

surface OH groups upon removal of labile CH$_3$CN ligands from the complexes. Although there was no direct physical evidence as to the exact structure of the silica-bound molybdenum complexes it is possible that either the Mo–Mo bond is retained on the silica surface (as observed for [Mo$_2$($\mu$-O$_2$CCH$_3$)$_4$]–SiO$_2$ [3]) or that it ruptures to give mononuclear species (as reported for [Mo$_2$($\eta^3$-C$_3$H$_5$)$_4$]–SiO$_2$ [6,7]). The supported and unsupported complexes were each tested as heterogeneous catalysts for norbornene polymerization. In the absence of EtAlCl$_2$ cocatalyst [Mo$_2$(MeCN)$_8$][BF$_4$]$_4$–SiO$_2$ was the only species to polymerize norbornene, and at 90°C and a reaction time of 48 h the polymerization was essentially quantitative. [Mo$_2$(MeCN)$_8$][BF$_4$]$_4$, [Mo$_2$($\mu$-O$_2$CCH$_3$)$_2$(MeCN)$_6$][BF$_4$]$_2$ and [Mo$_2$($\mu$-O$_2$CCH$_3$)$_2$(MeCN)$_6$][BF$_4$]$_2$–SiO$_2$ were found to be completely inactive without EtAlCl$_2$, even at elevated temperatures. In the presence of EtAlCl$_2$ [Mo$_2$(MeCN)$_8$][BF$_4$]$_4$–SiO$_2$ was the only material which failed to polymerize norbornene at 20°C. It was thought that the lability of the MeCN ligands [12,13] attached to the supported and unsupported complexes was a contributory factor in these polymerizations.

Preliminary experiments conducted in our laboratory on the room temperature homogeneous addition polymerization of cyclopentadiene in acetonitrile solution have shown that the dicationic salts [Mo$_2$($\mu$-O$_2$CR)$_2$(MeCN)$_n$][BF$_4$]$_2$·$x$H$_2$O (R = CH$_3$, $n$ = 6; R = HC=CH$_2$, $n$ = 4; R = (CH$_3$)C=CH$_2$, $n$ = 4; $x$ = 0–2) are good catalysts for this reaction [9]. We have now conducted a detailed study of the homogeneous and heterogeneous polymerization of cyclopentadiene using the four catalyst systems [Mo$_2$(MeCN)$_8$][BF$_4$]$_4$, [Mo$_2$($\mu$-O$_2$CCH$_3$)$_2$(MeCN)$_6$][BF$_4$]$_2$, [Mo$_2$(MeCN)$_8$] [BF$_4$]$_4$–SiO$_2$ and [Mo$_2$($\mu$-O$_2$CCH$_3$)$_2$(MeCN)$_6$][BF$_4$]$_2$–SiO$_2$, and the results of this work are presented herein. The use of [Mo$_2$(MeCN)$_8$][BF$_4$]$_4$ and [Mo$_2$($\mu$-O$_2$CCH$_3$)$_2$(MeCN)$_6$][BF$_4$]$_2$ for the polymerization of dicyclopentadiene is also outlined.

## 2. Experimental

Acetonitrile and dichloromethane were each dried by refluxing over $P_2O_5$ and then distilled. Cyclopentadiene was distilled from dicyclopentadiene and collected in an ice-cooled receiver. This cyclopentadiene was stored for a maximum of three days at $-25°C$ prior to use. Dicyclopentadiene was obtained by leaving freshly distilled cyclopentadiene to stand for 3 weeks at 20°C (composition confirmed by $^1H$ NMR spectroscopy). Literature methods were used to prepare $[Mo_2(MeCN)_8][BF_4]_4$ [11,14], $[Mo_2(\mu-O_2CCH_3)_2(MeCN)_6][BF_4]_2$ [12], $[Mo_2(MeCN)_8][BF_4]_4–SiO_2$ [11] and $[Mo_2(\mu-O_2CCH_3)_2(MeCN)_6][BF_4]_2–SiO_2$ [11].

### 2.1. Instrumentation

$^1H$ NMR spectra of the polymers, as solutions in $CDCl_3$ and with TMS as internal standard, were run on a Bruker AC 80 spectrometer. Conductance measurements were obtained using a Wayne Kerr Autobalance Universal Bridge B641 instrument, and the polymer samples were cut into strips ca. 1 cm long and the diameter was measured with Vernier calipers.

### 2.2. Polymerization reactions

Ace pressure tubes, purchased from Aldrich, were used for the polymerization reactions and all operations were conducted under $N_2$. To the tube was added the appropriate mass of unsupported or silica-supported catalyst, the solvent (if used) and the monomer (cyclopentadiene and/or dicyclopentadiene), in that order. The tube was sealed and then agitated on a mechanical shaker for experiments carried out at room temperature. For experiments conducted at higher temperatures the tube was immersed in an oil bath and the contents agitated using a magnetic stirrer. After the required reaction time had elapsed ethanol (20 cm³) was added to the mixture to quench the reaction and also to dissolve the catalyst (the ethanol causes the catalyst to decompose). The precipitated polymer was redissolved in dichloromethane (50 cm³) and slowly dripped into ethanol (200 cm³) containing HCl (2 cm³). The ethanol/HCl mixture was decanted off and the remaining polymer was washed with three portions of ethanol and then dried in vacuo.

For silica-supported catalysts the polymer/catalyst mixture was washed with three portions of dichloromethane (30 cm³), left to settle, and the supernatant then decanted off. The combined supernatants were added to acidified ethanol and the polymer was worked up as before. When a catalyst was being reused it was washed with dichloromethane to dissolve the polymer. The polymer solution was decanted off the catalyst, and the polymer then reprecipitated as before. The catalyst was then dried in vacuo for a short time before addition of the next batch of monomer.

## 3. Results and discussion

Cyclopentadiene and dicyclopentadiene provide olefinic sites in terpolymers with ethylene and propylene, and are also employed in blends with other olefins and diolefins which are then polymerised to hydrocarbon resins. These copolymers have many commercial applications e.g. tackifier resins, hot-melt and pressure-sensitive adhesives [15]. In 1985 Hercules established a production unit using dicyclopentadiene in a metathesis reaction injection moulding (RIM) process [16]. The thermoset polymer, which has a high modulus and impact strength, is sold under the name Metton. Heating dicyclopentadiene alone at ca. 200°C yields oligomers up to the pentamers [17].

In 1926 Staudinger and Bruson introduced inorganic halides, such as $SnCl_4$, $AlBr_3$ and $TiCl_4$, to initiate the cationic polymerization of cyclopentadiene [18]. Wassermann [19–21] reported the formation of deeply coloured conjugated polycyclopentadiene possessing electrical conductance properties when trichloroacetic acid

was used as catalyst. Ziegler-type catalysts, like $(^iBu)_3Al$ mixed with $TiCl_4$, have also been used for the homogeneous polymerization of cyclopentadiene [22]. In addition, the radiation induced stereospecific and asymmetric inclusion polymerization of cyclopentadiene has been carried out in crystal canals of thiourea [23,24] and deoxycholic acid [25], respectively.

The unit ring contained in polycyclopentadiene can have the following 1,4- and/or 1,2-structures when side reactions such as branching and double-bond migration (isomerization) are excluded.



1,4-polymer        1,2-polymer
(cis and trans)    (cis and trans)
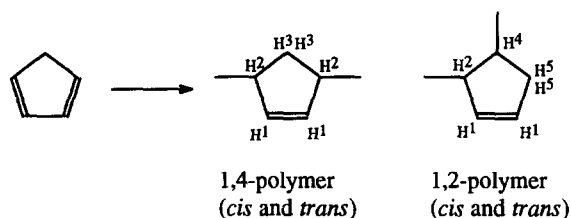
The $^1H$ NMR spectrum of chloroform-soluble polycyclopentadiene [26,27] contains a fairly sharp peak (D) at $\delta = 5.6$ ppm (olefinic protons $H^1$), and three broad and partially overlapped peaks (A, B and C) ranging from $\delta = 1.5$–3.0 ppm (methine and methylene protons $H^2$–$H^5$). Comparison of the polymer spectrum with those of model compounds suggests that peak A is probably due to $\beta$-methylene protons $(H^3)$ in the 1,4-structure. Peaks B and C appear to be due to $\alpha$-methylene $(H^5)$ and $\alpha$-, $\beta$-methine protons $(H^2$ and $H^4)$ and are unable to be assigned separately. Thus, the content of the 1,2-structure in the polymer can be calculated from the relative peak areas as follows:

$$1,2\text{-structure}\,(\%) = \frac{\{(B + C) - A\}}{\{A + (B + C)\}} \times 100$$

The error in the calculated content of the 1,2-structure (%), arising from overlapping peaks, is likely to be a few percent. The aliphatic:olefinic proton ratio (a/o) is simply calculated as (A + B + C)/D and should be equal to 2 for a polymer containing only 1,4- and/or 1,2-units in the

chain. This value can change if the polymer undergoes cross-linking, or if double-bond migration occurs to give isomerized units of the type shown below.
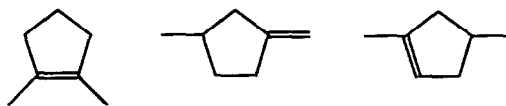


In order to facilitate the interpretation of the present experimental results for the polymerization of cyclopentadiene some studies were also conducted on the polymerization of dicyclopentadiene. Dicyclopentadiene polymerizes in the presence of $MoCl_5$, $ReCl_5$ and $WCl_6$ to give the ring-opened polyalkenamer (a) [28], whilst with Ziegler–Natta catalysts a mixture of (a) and the ring-addition polymer (b) are obtained [29].
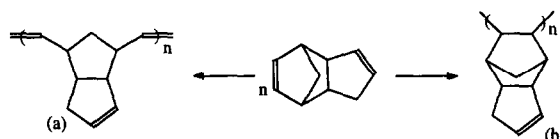


The aliphatic:olefinic proton ratio for polymer (a) should be 2, whilst for (b) it should have a value of 5.

The air-sensitive catalysts used in the present work, $[Mo_2(MeCN)_8][BF_4]_4$, $[Mo_2(\mu\text{-}O_2CCH_3)_2(MeCN)_6][BF_4]_2$, $[Mo_2(MeCN)_8][BF_4]_4$–$SiO_2$ and $[Mo_2(\mu\text{-}O_2CCH_3)_2(MeCN)_6][BF_4]_2$–$SiO_2$, were prepared as previously described, and all polymerization reactions were conducted under nitrogen. The polycyclopentadiene samples formed as light brown or cream powders and these were, in general, very soluble in chlorinated solvents. The microstructures of the polymers were investigated using NMR spectroscopy, and the aliphatic:olefinic proton ratios were found to be in the region 2.0–2.5 and with 1,2-structures in the range of 30–50%. The polymers tended to lose solubility fairly rapidly, and this was

Table 1
Comparison of the different catalyst systems for the polymerization of cyclopentadiene [a]

| Catalyst system | $[Mo_2(MeCN)_8][BF_4]_4$ | | | $[Mo_2(\mu-O_2CCH_3)_2(MeCN)_6][BF_4]_2$ | | |
|---|---|---|---|---|---|---|
| | Yield (%) | a/o | 1,2-content (%) | Yield (%) | a/o | 1,2-content (%) |
| no solvent | 36 | 2.2 | 47 | 76 | 2.4 | 41 |
| MeCN | 53 | 2.5 | 26 | 72 | 2.0 | 45 |
| $CH_2Cl_2$ | 76 | 2.3 | 42 | 141 [b] | – | – |
| $SiO_2$-supported (no solvent) | 9 | – | – | 5 | – | – |
| $SiO_2$-supported ($CH_2Cl_2$) | 22 | 2.1 | 48 | 23 | 3.0 | 65 |

[a] Unsupported catalyst (0.1 g); supported catalyst (1.0 g – this is equivalent to ca. 0.05 g of unsupported catalyst); cyclopentadiene (3 g); solvent (where used, 5 cm$^3$); temperature 20°C; reaction time 16 h.
[b] Hard, insoluble black plastic (this reaction will be discussed in detail later).

accompanied by a darkening in colour, an increase in the aliphatic:olefinic ratio and a corresponding decrease in the 1,2-structural content. It has previously been reported [4,30,31] that cyclopentadiene polymers absorb oxygen from the air to form inter- and intra-molecular oxygen bridged (C–O–O–C and C–O–C) cross-linked products having significantly increased molecular weight and decreased solubility.

Polymerizations were carried out in either neat cyclopentadiene, or a solution of the monomer in acetonitrile or dichloromethane. All four catalysts were insoluble in neat cyclopentadiene and thus these were heterogeneous systems. In addition, the polycyclopentadiene product forms as a gel in the neat monomer. When acetonitrile was used as solvent both the monomer and the unsupported salts $[Mo_2(MeCN)_8][BF_4]_4$ and $[Mo_2(\mu-O_2CCH_3)_2(MeCN)_6][BF_4]_2$ were soluble, and thus these could be described as homogeneous

reactions. The supported complexes $[Mo_2(MeCN)_8][BF_4]_4$–$SiO_2$ and $[Mo_2(\mu-O_2CCH_3)_2(MeCN)_6][BF_4]_2$–$SiO_2$ were insoluble in acetonitrile and were thus heterogeneous systems. The polycyclopentadiene products were also insoluble in acetonitrile. All four catalysts were insoluble in dichloromethane, again giving rise to heterogeneous systems. With one exception, all of the freshly formed polycyclopentadiene products were completely soluble in dichloromethane.

A comparison of the different catalyst systems for the polymerization of cyclopentadiene under specific reaction time and temperature conditions is shown in Table 1. Compared to the $SiO_2$-supported salts the unsupported salts were more efficient catalysts for the polymerization of both neat monomer and a solution of monomer in dichloromethane. Whereas the two $SiO_2$-supported salts produced similar amounts of polymer the unsupported salt $[Mo_2(\mu-$

Table 2
Polymerization of neat cyclopentadiene as a function of time using $[Mo_2(MeCN)_8][BF_4]_4$ and $[Mo_2(\mu-O_2CCH_3)_2(MeCN)_6][BF_4]_2$ catalysts [a]

| Reaction time (h) | $[Mo_2(MeCN)_8][BF_4]_4$ | | | $[Mo_2(\mu-O_2CCH_3)_2(MeCN)_6][BF_4]_2$ | | |
|---|---|---|---|---|---|---|
| | Yield (%) | a/o | 1,2-content (%) | Yield (%) | a/o | 1,2-content (%) |
| 0.25 | – | – | – | 2 | 2.0 | 20 |
| 2 | 9 | 2.7 | 48 | 26 | 2.3 | 43 |
| 16 | 36 | 2.2 | 47 | 76 | 2.4 | 41 |
| 48 | 36 | 3.8 | 22 | 76 | 3.0 | 43 |
| 120 | 42 | 2.4 | 57 | 65 | 2.5 | 43 |

[a] Catalyst (0.1 g); neat cyclopentadiene (3 g); temperature 20°C.

$O_2CCH_3)_2(MeCN)_6][BF_4]_2$ gave consistently higher polymer yields than $[Mo_2(MeCN)_8][BF_4]_4$ under the specified reaction conditions.

The effect of reaction time on the room temperature heterogeneous polymerization of neat cyclopentadiene using the unsupported salts is summarised in Table 2. Addition of neat monomer to the catalyst salt causes an immediate exothermic reaction (typically, a temperature rise of ca. 7°C for 3 g of monomer). For both catalysts increasing the reaction time beyond 16 h does not produce any significant increase in polymer yield. At this time the competing dimerization reaction probably limits the amount of free cyclopentadiene available for polymerization. Furthermore, the increase in viscosity of the reaction mixture is likely to inhibit the diffusion of fresh monomer to the propagation site.

In a study of the effect of the monomer (neat):catalyst molar ratio in the $[Mo_2(MeCN)_8][BF_4]_4$ catalysed reaction (Table 3) it was found that an increase in this ratio had very little effect on the yield of polycyclopentadiene (g/g of catalyst), indicating that here again an increase in viscosity was limiting the diffusion of cyclopentadiene to the propagation site. Tazuma [32] reported that the amount of tungsten halide catalyst employed to effect the polymerization of cyclopentadiene in a hydrocarbon solvent could vary considerably, and he found that an efficient and rapid reaction occurred when the concentration varied from about $5 \times 10^{-4}$ to about $20 \times 10^{-4}$ moles of catalyst per mole of monomer.

Table 3
Polymerization of neat cyclopentadiene as a function of monomer:$[Mo_2(MeCN)_8][BF_4]_4$ molar ratio [a]

| Monomer:catalyst ratio | Yield | | a/o | 1,2-content (%) |
|---|---|---|---|---|
| | % | g/g catalyst | | |
| 390:1 | 36 | 11 | 2.2 | 47 |
| 790:1 | 11 | 6 | 2.3 | 50 |
| 1580:1 | 6 | 10 | 2.4 | 40 |

[a] Neat cyclopentadiene (3 g); temperature 20°C; reaction time 16 h.

Table 4
Reuse of the $[Mo_2(MeCN)_8][BF_4]_4$ catalyst for the polymerization of neat cyclopentadiene [a,b]

| Run No. | Yield (%) | a/o | 1,2-content (%) |
|---|---|---|---|
| 1 | 36 | 3.8 | 22 |
| 2 | 45 | 3.0 | 15 |
| 3 | 71 | 2.5 | 31 |
| 4 | 62 | – | – |
| 5 | 38 | 2.2 | 46 |
| 6 | 37 | 2.1 | 44 |
| 7 | 42 | 2.2 | 44 |
| 8 | 40 | 2.5 | 47 |
| 9 | 45 | 2.1 | 45 |
| 10 | 9 | – | – |

[a] Catalyst (0.1 g); neat cyclopentadiene (3 g batches); temperature 20°C; reaction time 48 h.
[b] Catalyst ended up as a brown–yellow brittle plastic material (weight = 0.24 g).

The ability of a single sample of the $[Mo_2(MeCN)_8][BF_4]_4$ catalyst to polymerize successive 3 g batches of neat cyclopentadiene was also investigated (Table 4). The catalyst was washed thoroughly with $CH_2Cl_2$ after each polymerization run in order to dissolve any precipitated polycyclopentadiene. During the first few runs the blue catalyst powder appeared to aggregate into clumps in the liquid monomer. Upon further reuse of the catalyst it was noted that there was a progressive build up of $CH_2Cl_2$-insoluble polymer on the catalyst surface which appeared to have the effect of causing a greater dispersal of the catalyst in the monomer. This increased dispersion may account for the observed increase in polymer yield for runs three and four. On progressive reuse the catalyst morphology itself changed from a blue powder to a hard insoluble brown plastic material. In this latter form the catalyst (which was insoluble in $CH_2Cl_2$) was easier to separate from polymer and residual monomer. Although the catalyst material at this stage bore no physical resemblance to the original $[Mo_2(MeCN)_8][BF_4]_4$ powder it remained quite active. After nine runs (ca. total 27 g) of monomer there was still a significant quantity of polymer being produced, but on subsequent runs the activity of the catalyst decreased markedly.

Table 5
Polymerization of neat cyclopentadiene as a function of temperature using $[Mo_2(MeCN)_8][BF_4]_4$ and $[Mo_2(\mu\text{-}O_2CCH_3)_2(MeCN)_6][BF_4]_2$ catalysts [a]

| Reaction temperature (°C) | $[Mo_2(MeCN)_8][BF_4]_4$ | | | $[Mo_2(\mu\text{-}O_2CCH_3)_2(MeCN)_6][BF_4]_2$ | | |
|---|---|---|---|---|---|---|
| | Yield (%) | a/o | 1,2-content (%) | Yield (%) | a/o | 1,2-content (%) |
| − 25 | 0.2 | – | – | 1 | – | – |
| 20 | 36 | 2.2 | 47 | 76 | 2.4 | 41 |
| 60 | 30 | 2.5 | 56 | 49 | 3.4 | 35 |
| 90 | – | – | – | 42 | 3.4 | 31 |
| 100 | 20 | 2.5 | 53 | – | – | – |
| 170 | 97 [b] | 7.4 | – | 98 [b] | 4.8 | – |

[a] Catalyst (0.1 g); neat cyclopentadiene (3 g); reaction time (16 h).
[b] Polydicyclopentadiene.

The effect of reaction temperature on the polymerization of cyclopentadiene solutions in hydrocarbon solvents has been well documented. High yields of insoluble or partially soluble polymers have been obtained at − 60 to − 90°C using cationic catalysts such as $TiCl_4$, $SnCl_4$ and $EtAlCl_2$ [33,34]. Interestingly, Blatz [35] discovered that the polymerization in toluene by $TiCl_4$ (cationic catalyst) and by $TiCl_4/Al(CH_2CH(CH_3)CH_3)_3$ (Ziegler-type catalyst) gave opposite temperature dependence. At − 78°C polymer yield was highest and decreased as temperature increased with $TiCl_4$ alone. With $TiCl_4/Al(CH_2CH(CH_3)CH_3)_3$ the yield increased as the temperature was raised from − 70°C to 0°C. Tazuma [32] found that the temperature used in the polymerization was not critical, and may be varied from the freezing point of the liquid system up to 150°C.

In the present experiments on neat cyclopentadiene using $[Mo_2(MeCN)_8][BF_4]_4$ and $[Mo_2(\mu\text{-}O_2CCH_3)_2(MeCN)_6][BF_4]_2$ catalysts little or no polymer is formed at − 25°C (Table 5). Raising the temperature to 20°C causes a substantial increase in polymer yield. However, further elevation of the temperature (ca. 100°C) results in a marked decrease in polymer production, and this is attributed to the competing dimerization reaction which effectively lowers the concentration of available free monomer (at 25°C, and in the absence of a catalyst, the dimerization rate of cyclopentadiene is 3.5 mol%/h. [15]). Reactions catalysed by

$[Mo_2(MeCN)_8][BF_4]_4$ gave polymers with consistently higher 1,2-content than those produced using $[Mo_2(\mu\text{-}O_2CCH_3)_2(MeCN)_6][BF_4]_2$. At 170°C the polymer yield is essentially quantitative, and the high aliphatic:olefinic proton ratios calculated from the NMR spectra signifies that with each of the two catalysts it is ring-addition polydicyclopentadiene and not polycyclopentadiene that is formed at this temperature.

In order to substantiate the arguments concerning the formation of polydicyclopentadiene two series of experiments involving dicyclopentadiene were conducted. The effect of reaction temperature on the polymerization of neat dicyclopentadiene using $[Mo_2(MeCN)_8][BF_4]_4$ was studied (Table 6). No significant yield of polydicyclopentadiene was obtained below 120°C. However, at 170°C production of soluble polymer was essentially quantitative. At this temperature $[Mo_2(\mu\text{-}O_2CCH_3)_2(MeCN)_6][BF_4]_2$ also gave a high yield of polymer (92%; a/o = 5.8).

Table 6
Polymerization of neat dicyclopentadiene as a function of temperature using $[Mo_2(MeCN)_8][BF_4]_4$ [a]

| Reaction temperature (°C) | Yield (%) | a/o |
|---|---|---|
| 20 | 0 | – |
| 50 | 4 | – |
| 90 | 12 | 7.1 |
| 120 | 17 | 7.0 |
| 170 | 101 | 5.6 |

[a] Catalyst (0.1 g); neat dicyclopentadiene (3 g); reaction time (16 h).

Table 7
Polymerization of cyclopentadiene in the presence of added dicyclopentadiene [a]

| Catalyst system | $[Mo_2(MeCN)_8][BF_4]_4$ | | |
|---|---|---|---|
| | Yield (%) | a/o | 1,2-content (%) |
| no solvent | 46 | 2.3 | 51 |
| MeCN | 83 | 2.3 | 45 |
| $CH_2Cl_2$ | 78 | 2.2 | 50 |

[a] Catalyst (0.1 g); cyclopentadiene (3 g) plus dicyclopentadiene (0.75 g); solvent (where used, 5 cm$^3$); temperature 20°C; reaction time 16 h.

The high a/o values indicate that it is ring-addition rather than ring-opened polydicyclopentadiene that is formed in these reactions. Values of a/o > 5 may be due to the further addition polymerization of some of the cyclopentene rings remaining in the polymer [29]. When cyclopentadiene is heated to 170°C in the absence of a dimolybdenum catalyst the normal Diels–Alder cycloaddition products (a mixture of trimer, tetramer etc. [15,17]) formed.

The inability of $[Mo_2(MeCN)_8][BF_4]_4$ to induce formation of ring-opened polydicyclopentadiene is not totally surprising in view of the fact that this salt has previously been shown to be a poor catalyst for the ring-opening polymerization of the related strained bicyclic monomer norbornene [11].

Using the $[Mo_2(MeCN)_8][BF_4]_4$ catalyst a study of the room temperature polymerization of cyclopentadiene in the presence of added dicyclopentadiene was carried out on neat monomer mixtures and also on solutions of the monomer mixtures in acetonitrile and in dichloromethane (Table 7). The results of this study were compared to those obtained using neat cyclopentadiene and solutions of the pure monomer in the same two solvents (Table 1). No polydicyclopentadiene formed in these reactions. Furthermore, the addition of dicyclopentadiene to the cyclopentadiene appears to enhance the yield of polycyclopentadiene, and this effect is particularly marked when the reaction is conducted in acetonitrile. It has previously been reported that the presence of dicyclopentadiene in the monomer feed substantially reduces the molecular weight of the polycyclopentadiene [33].

When solutions of $[Mo_2(MeCN)_8][BF_4]_4$ and $[Mo_2(\mu\text{-}O_2CCH_3)_2(MeCN)_6][BF_4]_2$ in acetonitrile are used as homogeneous catalysts for the polymerization of cyclopentadiene an almost quantitative yield of polymer is obtained after 48 h (Table 8). Formation of dicyclopentadiene is expected to be significantly less in an acetonitrile solution of cyclopentadiene than in the case where the neat monomer is present. As the polycyclopentadiene product precipitates from the acetonitrile solution during formation there is then no appreciable viscosity increase of the solution, and hence no restrictions on the diffusion of fresh monomer to the propagation site. Interestingly, polymer yields obtained from neat cyclopentadiene and its solution in acetonitrile were essentially the same using $[Mo_2(\mu\text{-}O_2CCH_3)_2(MeCN)_6][BF_4]_2$, whereas with the $[Mo_2(MeCN)_8][BF_4]_4$ catalyst the yields were much superior when the monomer was dissolved in acetonitrile.

Table 8
Polymerization of cyclopentadiene in acetonitrile as a function of time using $[Mo_2(MeCN)_8][BF_4]_4$ and $[Mo_2(\mu\text{-}O_2CCH_3)_2 (MeCN)_6][BF_4]_2$ catalysts [a]

| Reaction time (h) | $[Mo_2(MeCN)_8][BF_4]_4$ | | | $[Mo_2(\mu\text{-}O_2CCH_3)_2(MeCN)_6][BF_4]_2$ | | |
|---|---|---|---|---|---|---|
| | Yield (%) | a/o | 1,2-content (%) | Yield (%) | a/o | 1,2-content (%) |
| 2 | 10 | 2.3 | 45 | 15 | 2.4 | 16 |
| 16 | 53 | 2.5 | 26 | 72 | 2.0 | 45 |
| 48 | 96 | 2.0 | 47 | 90 | 2.2 | 35 |
| 120 | 91 | 2.2 | 46 | 88 | 2.3 | 32 |

[a] Catalyst (0.1 g); cyclopentadiene (3 g); acetonitrile (5 cm$^3$); temperature 20°C.

Table 9

Polymerization of acetonitrile solutions of cyclopentadiene as a function of monomer:catalyst molar ratio [a]

| Monomer:catalyst ratio | $[Mo_2(MeCN)_8][BF_4]_4$ | | | | $[Mo_2(\mu\text{-}O_2CCH_3)_2(MeCN)_6][BF_4]_2$ | | | |
|---|---|---|---|---|---|---|---|---|
| | Yield | | a/o | 1,2-content (%) | Yield | | a/o | 1,2-content (%) |
| | % | g/g catalyst | | | % | g/g catalyst | | |
| 350:1 | 53 | 16 | 2.5 | 26 | 72 | 22 | 2.0 | 45 |
| 700:1 | 93 | 56 | 2.5 | 25 | – | – | – | – |
| 1400:1 | 66 | 79 | 3.5 | 21 | 61 | 74 | 3.4 | – |
| 3500:1 | – | – | – | – | 55 | 165 | 2.7 | – |
| 5000:1 | 6 | 22 | – | – | – | – | – | – |
| 10000:1 | – | – | – | – | 29 | 285 | 2.1 | 35 |

[a] Cyclopentadiene (3 g); acetonitrile (5 cm³); temperature 20°C; reaction time 16 h.

The chloroform solubility of the polymers formed in acetonitrile is in marked contrast to that previously reported by us [9] for the polymerization of cyclopentadiene in acetonitrile using the dicationic salts $[Mo_2(\mu\text{-}O_2CR)_2(MeCN)_n][BF_4]_2 \cdot xH_2O$ (R = $CH_3$, $n$ = 6; R = HC=$CH_2$, $n$ = 4; R = $(CH_3)C$=$CH_2$, $n$ = 4; $x$ = 0–2). The chloroform insolubility of the latter polymers is almost certainly attributable to the cross-linking that occurred during the somewhat longer time interval between polymer preparation and solubility testing.

In contrast to the results obtained using neat cyclopentadiene it was found that with acetonitrile as solvent an increase in the monomer:catalyst molar ratio generally gave an increase in polymer yield (g/g of catalyst, Table 9). However, as indicated in Table 10 reuse of the $[Mo_2(MeCN)_8][BF_4]_4$ catalyst was limited to three successive batches of cyclopentadiene in acetonitrile solution.

A series of experiments were carried out on the polymerization of cyclopentadiene in which dichloromethane was used as the reaction solvent (Table 1). With $[Mo_2(MeCN)_8][BF_4]_4$ as catalyst it was found that both the polymer yield and the physical properties of the polymer were very dependent upon the monomer:catalyst molar ratio (Table 11). As this ratio was increased there was generally a corresponding increase in the polymer yield (g/g of catalyst). Interestingly, as the monomer:catalyst ratio was increased there was a marked tendency for the

polymers to become insoluble upon reprecipitation from ethanol. This insolubility problem can be overcome to some extent if precautions are taken to ensure that dilute (rather than concentrated) solutions of the polymers in dichloromethane are added slowly to the precipitating solvent ethanol. Similarly, Honeychuck and coworkers [36] reported that the tungsten complex $(Me_3P)(CO)_3(NO)W$–$FSbF_5$ polymerized cyclopentadiene in diethyl ether to give a white chloroform-soluble polymer, whereas a light brown brittle and insoluble polymer formed in dichloromethane solution.

A single 0.1 g sample of $[Mo_2(MeCN)_8][BF_4]_4$ could be used to polymerize up to eight batches of cyclopentadiene in dichloromethane, and after this the activity of the catalyst diminished significantly (Table 12). As happened in the case of neat cyclopentadiene there was again a gradual build up of an insoluble plastic material around the catalyst upon successive reuse.

As in the cases of neat cyclopentadiene and

Table 10

Reuse of the $[Mo_2(MeCN)_8][BF_4]_4$ catalyst for the polymerization of acetonitrile solutions of cyclopentadiene [a,b]

| Run No. | Yield (%) | a/o | 1,2-content (%) |
|---|---|---|---|
| 1 | 72 | 2.8 | 50 |
| 2 | 95 | 2.6 | 39 |
| 3 | 69 | 3.4 | 39 |
| 4 | 0 | – | – |

[a] Catalyst (0.1 g); cyclopentadiene (3 g batches); acetonitrile (10 cm³); temperature 20°C; reaction time 48 h.

Table 11
Polymerization of dichloromethane solutions of cyclopentadiene as a function of monomer:[Mo$_2$(MeCN)$_8$][BF$_4$]$_4$ molar ratio [a]

| Monomer:catalyst ratio | Yield | | a/o | 1,2-content (%) | Polymer description |
|---|---|---|---|---|---|
| | % | g/g catalyst | | | |
| 390:1 | 76 | 23 | 2.3 | 42 | light brown powder |
| 2600:1 | 34 | 68 | 3.5 | 7 | white fibrous powder |
| 13000:1 | 103 | 1025 | – | – | hard brown rubber [b] |
| 26000:1 | 79 | 1580 | – | – | hard brown rubber [b] |
| 26000:1 | 43 | 861 | 2.8 | 44 | light brown powder [c] |
| 65000:1 | 38 | 1875 | 2.2 | 44 | light brown powder [c] |

[a] Cyclopentadiene (1 g); dichloromethane (1 cm$^3$); temperature 20°C; reaction time 16 h.
[b] Polymer was initially totally soluble in dichloromethane upon formation, but became insoluble when reprecipitated in ethanol.
[c] Polymer was initially totally soluble in dichloromethane upon formation, and remained soluble when reprecipitated by slowly adding it as a dilute dichloromethane solution into ethanol.

solutions of cyclopentadiene in acetonitrile the diacetate complex [Mo$_2$($\mu$-O$_2$CCH$_3$)$_2$(MeCN)$_6$][BF$_4$]$_2$ was a more active catalyst than [Mo$_2$(MeCN)$_8$][BF$_4$]$_4$ for the polymerization of dichloromethane solutions of the monomer (Table 13). At low cyclopentadiene:[Mo$_2$($\mu$-O$_2$CCH$_3$)$_2$(MeCN)$_6$][BF$_4$]$_2$ molar ratios an insoluble black plastic is formed unless relatively dilute solutions of the monomer are used. Even when the reaction time is decreased to 1 h the polymer formed is inherently insoluble. In many of the reactions detailed in Table 13 the yield of insoluble polymer was significantly greater than 100%, and it is thought that in these cases there is solvent encapsulation by the plastic product. It is interesting to note that

Table 12
Reuse of the [Mo$_2$(MeCN)$_8$][BF$_4$]$_4$ catalyst for the polymerization of dichloromethane solutions of cyclopentadiene [a,b]

| Run No. | Yield (%) | a/o | 1,2-content (%) |
|---|---|---|---|
| 1 | 99 | 2.9 | 26 |
| 2 | 98 | 2.8 | 27 |
| 3 | 92 | 2.2 | 37 |
| 4 | 47 | – | – |
| 5 | 56 | 2.3 | 44 |
| 6 | 60 | 2.3 | 46 |
| 7 | 96 | 2.5 | 34 |
| 8 | 34 | 2.2 | 46 |
| 9 | 10 | 2.2 | 43 |
| 10 | 7 | 2.1 | 43 |

[a] Catalyst (0.1 g); cyclopentadiene (3 g batches); dichloromethane (10 cm$^3$); temperature 20°C; reaction time 48 h.

there was no weight loss by the latter polymers upon storage for 9 months.

The insoluble black plastics mentioned above are believed to contain long sequences of conjugated double bonds in the polymer chain [20,21,35]. The resistivity of one of these solid black plastics was found to be 8 × 10$^5$ ohm cm, and this value was very similar to that reported by Blatz [35] for bromodehydropolycyclopentadiene polymers (ca. 10$^6$ ohm cm), thus placing the materials in the semiconducting range. In addition, Blatz found the electron spin density of his polymers to be 10$^{18}$ spins g$^{-1}$, indicating an abundance of free radicals. These free radicals were unquestionably stabilized by extended sequences of conjugation.

Only small amounts of polymer were obtained when neat cyclopentadiene was polymerized using the silica-supported catalysts when [Mo$_2$(MeCN)$_8$][BF$_4$]$_4$–SiO$_2$ and [Mo$_2$($\mu$-O$_2$CCH$_3$)$_2$(MeCN)$_6$][BF$_4$]$_2$–SiO$_2$ (Table 1). However, when dichloromethane was employed as a monomer solvent the polymer yield increased significantly, presumably because the use of a solvent helps maintain a relatively low viscosity for the reaction mixture thus allowing fresh monomer to diffuse readily to the propagation site.

One of the main advantages of using supported catalysts is their ease of removal from the reaction mixture after completion of the polymerization. Results obtained for studies into the reuse of [Mo$_2$($\mu$-

Table 13
Polymerization of dichloromethane solutions of cyclopentadiene as a function of monomer:[Mo$_2$( $\mu$-O$_2$CCH$_3$)$_2$(MeCN)$_6$][BF$_4$]$_2$ molar ratio and solvent volume [a]

| Monomer:catalyst ratio | Solvent volume (cm$^3$) | Reaction time (h) | Yield (%) | Polymer description |
|---|---|---|---|---|
| 330:1 | 5 | 16 | 141 | insoluble black plastic |
| 330:1 | 10 | 16 | 120 | insoluble black plastic [b] |
| 330:1 | 20 | 16 | 115 | insoluble black plastic |
| 330:1 | 50 | 16 | 98 | light yellow powder [c] |
| 330:1 | 10 | 1 | 119 | brown rubbery solid [c] |
| 1300:1 | 10 | 16 | 75 [d] | (i) brown rubbery solid (65%), a/o = 2.4, 1,2-content = 41%; (ii) brown rubbery solid (10%) [c] |
| 1300:1 | 20 | 16 | 116 | insoluble brown plastic |
| 1300:1 | 50 | 16 | 78 | brown powder, a/o = 2.3, 1,2-content = 52% |

[a] Temperature 20°C.
[b] Resistivity measurements carried out on this sample.
[c] Polymer was initially totally soluble in dichloromethane upon formation, but became insoluble when reprecipitated in ethanol.
[d] Two products formed.

O$_2$CCH$_3$)$_2$(MeCN)$_6$][BF$_4$]$_2$–SiO$_2$ for the polymerization of successive batches of cyclopentadiene in dichloromethane solution are shown in Table 14. Although only soluble polymer was obtained in these reactions there was a gradual decrease in product yield with each reuse of the catalyst. This deterioration in catalyst performance may, in part, be due to the air and moisture sensitivity of the molybdenum complex which causes problems during handling.

Initiation of the homogeneous and heterogeneous polymerization reactions is thought to involve the association of a cyclopentadiene molecule with the bimetallic [Mo–Mo]$^{4+}$ catalyst centre to give species (a) shown in Scheme 1. In the homogeneous reactions access to the bimetallic centres can be achieved by displace-

ment of one or more of the labile MeCN ligands, whilst with the heterogeneous catalysts it may be that some surface [Mo–Mo] sites may be exposed for attack by nucleophilic cyclopentadiene molecules. The cyclopentadiene molecule may bond to either one or both (i.e. bridging) molybdenum atoms of the bimetallic core to give the carbocation (b), which may
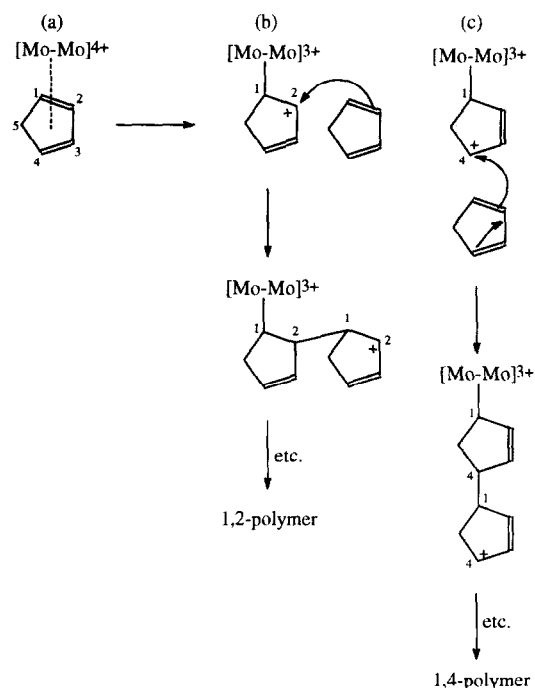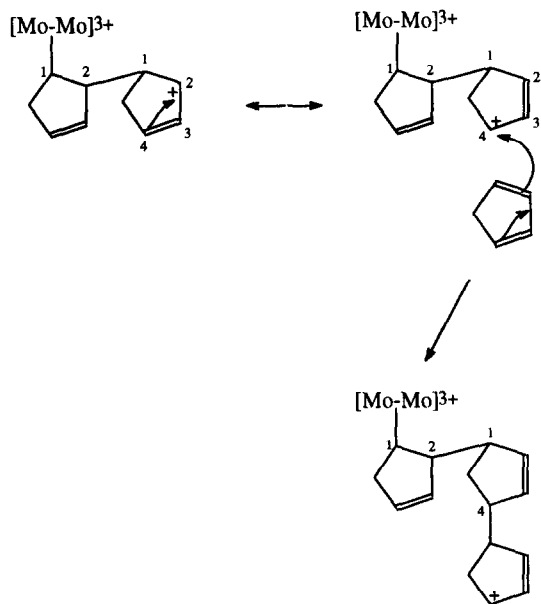
Table 14
Reuse of the [Mo$_2$( $\mu$-O$_2$CCH$_3$)$_2$(MeCN)$_6$][BF$_4$]$_2$–SiO$_2$ catalyst for the polymerization of dichloromethane solutions of cyclopentadiene [a]

| Run No. | Yield (%) | a/o | 1,2-content (%) |
|---|---|---|---|
| 1 | 23 | 2.4 | 48 |
| 2 | 12 | 3.6 | 14 |
| 3 | 6 | – | – |
| 4 | 6 | 2.3 | 43 |
| 5 | 6 | 2.2 | 45 |
| 6 | 4 | 2.5 | 44 |

[a] Catalyst (1.0 g); cyclopentadiene (3 g batches); dichloromethane (10 cm$^3$ each batch); temperature 20°C; reaction time 48 h.



Scheme 1.

Scheme 2.

isomerize to (c). Addition of cyclopentadiene molecules to (b) and (c) will produce separate 1,2- and 1,4-polycyclopentadiene chains, respectively. A single polymer chain containing a mixture of 1,2- and 1,4-units can form if there is isomerization of either (b) or (c) during the polymerization (Scheme 2). At present it is uncertain whether or not the present products are mixtures of separate 1,2- and 1,4-polymers, or if each polymer chain comprises a mixture of 1,2- and 1,4-units.

In conclusion, the effect of supporting the dimolybdenum salts on silica is to severely diminish their catalytic activity, suggesting that substantial structural and electronic changes occur upon binding the salts to the support material [6,7,11]. Unsupported and supported catalysts all give enhanced polymer yields when the polymerization reactions are carried out on solutions of cpd when compared to reactions conducted with neat monomer. The presence of the solvent ensures the following beneficial effects: (i) the tendency of the cyclopentadiene to form dicyclopentadiene is reduced, (ii) viscosity increases are minimised, thus permitting the relatively unrestricted diffusion of fresh monomer

to the propagation site. Catalysts can be reused many times to polymerize successive batches of monomer. When a monomer solvent is used with the $[Mo_2(MeCN)_8][BF_4]_4$ and $[Mo_2(\mu\text{-}O_2CCH_3)_2(MeCN)_6][BF_4]_2$ catalysts, large yields of polycyclopentadiene can be obtained at high monomer:catalyst molar ratios. Solubility of the polycyclopentadiene product is dependent upon reaction conditions and on catalyst used, and with the $[Mo_2(\mu\text{-}O_2CCH_3)_2(MeCN)_6][BF_4]_2$ catalyst in dichloromethane black conducting plastics are precipitated. Soluble, ring-addition polydicyclopentadiene is formed in essentially quantitative yield when $[Mo_2(MeCN)_8][BF_4]_4$ and $[Mo_2(\mu\text{-}O_2CCH_3)_2(MeCN)_6][BF_4]_2$ are reacted with neat dicyclopentadiene at 170°C. Although $[Mo_2(MeCN)_8][BF_4]_4$ was generally found to be a less active catalyst than $[Mo_2(\mu\text{-}O_2CCH_3)_2(MeCN)_6][BF_4]_2$ there was little difference between the microstructures of the polycyclopentadiene products obtained from each system. In most instances there was approximately equal amounts of the 1,2- and 1,4-structures present in the polymers, and in any cases where there was a marked deviation from a 50% 1,2-content there was no obvious trend. Furthermore, there was no significant difference in the 1,2-content of samples obtained from the heterogeneous systems (neat cyclopentadiene, cyclopentadiene in dichloromethane solution and reactions where silica supported catalysts were used) compared to samples formed in the homogeneous reactions (cyclopentadiene in acetonitrile solution).

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