

Syntheses and catalytic properties of alternating copolymers of poly[4-maleimidopyridyl(*p*-cymene)dichloro Ru(II)] with γ -methacryloxypropyl trimethoxysilane

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Abstract

A new monomer, 4-maleimidopyridyl(*p*-cymene)dichloro Ru(II), was synthesized by the reaction of maleic anhydride with *p*-dimethylaminopyridine(*p*-cymene)dichloro ruthenium(II). The homopolymer of maleimidopyridyl(*p*-cymene)dichloro Ru(II) and its copolymers with γ -methacryloxypropyl trimethoxysilane were prepared by radical polymerization with benzoyl peroxide as an initiator at 75 °C. The structures of the synthesized monomer and polymers were identified by Fourier transform infrared, ¹H NMR, and ¹³C NMR spectroscopies. Thermal behavior of the polymers were determined by differential thermal analysis, and thermogravimetric analysis, glass transition temperature was determined by differential scanning calorimeter.

Excellent selectivities were observed by using Ru(II) complex as the catalyst in hydrosilylation reactions. The heterogeneous Ru(II) catalyst can also be recycled and reused without significant loss of selectivity or activity. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ru(II) catalyst; Metal complex catalyst; Poly(4-maleimidopyridine); Polyimide; Hydrosilylation

1. Introduction

In recent years, major efforts have been directed toward the development of new catalytic systems that effectively combine the advantages of both heterogeneous and homogeneous catalysis [1–11]. Such catalyst would be easily recoverable and potentially recyclable while maintaining high catalytic efficiency. Though significant loss in catalytic activity or selectivity was observed in a polymer supported systems, majority of research has been focused on polymer supported catalysts [12].

Maleic anhydride has been utilized as a functional monomer in a wide range of applications including the surface functionalization of polyolefins and as reactive sites for the preparation of graft copolymers [13,14]. As a comonomer, it boasts two very useful characteristics, at first it can be copolymerized with electron donating comonomers to produce highly alternating copolymers at relatively high reaction rates. And a wide variety of chemistry can be performed at the anhydride functionality after or before copolymerization.

Recently, preparative and catalytic studies on cyclic diamino carbene and *N*-bound 2-imidazoline, and arene complexes of ruthenium(II) have been prepared due to their selective catalytic potential [15–18]. These complexes are effective catalysis for the intramolecular cyclization of (*Z*)-3-methylpent-2-en-4-yn-1-ol

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into 2,3-dimethyl furan [19]. Poly[1-vinylimidazole-Ru(II)] complexes were applied to photoinduced hydrogen generation in solution [20]. Polystyrene–divinylbenzene bound platinum complexes in hydrosilylation reaction of unsaturated hydrocarbons were studied [21]. Due to their stability under various conditions, current interest in pyridine based ligands has been growing [22–28]. The fact that lies behind this phenomenon is the basicity of the pyridine ligand.

This functionality promoted us to investigate maleic anhydride as a potential comonomer with γ -methacryloxypropyl trimethoxysilane (A-174) in the preparation of functional copolymers. This method involved modification of maleic anhydride with *p*-dimethylaminopyridine-*p*-cymenedichloro ruthenium(II), and its copolymerization with A-174. Apparently, this copolymerization system offered not only functional copolymers, but also space filling gel.

It is well known that an alternating copolymer can be easily obtained by the copolymerization of an electron rich monomer and an electron deficient monomer. Therefore, a controllable alternating copolymerization of *N*-substituted maleimide with A-174 was of concern. Excellent selectivities, favoring silylation of acetophenone using Ru(II) complex as the catalyst in the reactions were obtained. The heterogeneous Ru(II) catalyst can also be recycled and reused without significant loss of selectivity or activity.

2. Experimental

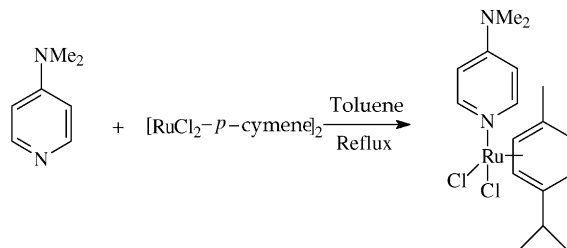
Maleic anhydride (Aldrich Co.), dimethylaminoaniline (Fluka Co.), A-174 (Wacker Chemie) and all other chemicals were reagent grade and were used without further purification. All solvents were purified by conventional methods and freshly used. $[\text{RuCl}_2(p\text{-cymene})]_2$ was synthesized according to the published procedure [28]. All manipulations were performed under argon atmosphere using standard Schlenk techniques. ^1H NMR and ^{13}C NMR spectra were recorded using a Bruker AC300P FT spectrometer operating at 300.13 MHz (^1H), 75.47 MHz (^{13}C). FT-IR spectra were recorded on a Mattson 100 spectrophotometer. The thermal behavior was examined by DSC system 60, DTA system 50, and TGA

system 50 (Shimadzu Inc.) $10^\circ\text{C}/\text{min}$ under an air atmosphere. Purity of the substrates and analysis of the products were determined on a Hewlett-Packard 5890A gas chromatograph (GC) using a capillary column (50 m, 0.20 mm i.d. 0.50 μm film thickness) packed with 10% SE-30 and a flame ionization detector. Elemental analyses were performed by Tübitak Microlab.

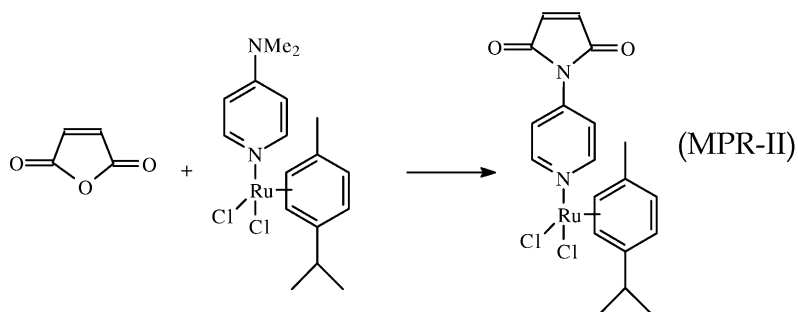
2.1. Synthesis of *p*-dimethylaminopyridine (*p*-cymene) dichloro ruthenium(II)

The general condition for the preparation of the *p*-dimethylaminopyridine(*p*-cymene)dichloro ruthenium(II) was as follows. Dimethylaminopyridine (3.30 mmol), the required $[\text{RuCl}_2(p\text{-cymene})]_2$ (1.00 g, 1.65 mmol) and toluene (15 ml) were heated under reflux for 4 h. Upon cooling to room temperature orange crystals were deposited. They were filtered off, washed with hexane (3×10 ml) and crystallized in $\text{CH}_2\text{Cl}_2/\text{hexane}$. ^1H NMR and ^{13}C NMR in $\text{DMSO-}d_6$ data are given in Scheme 1. Anal. calc. for $\text{C}_{17}\text{H}_{24}\text{N}_2\text{Cl}_2\text{Ru}$: C: 47.60; H: 5.60; N: 6.54; found: C: 47.46; H: 5.56; N: 6.34.

^1H NMR (CDCl_3 , δ , ppm) 8.35 and 6.35 [q, 4H, $J = 1.3$ Hz, 4-(CH_3) $_2\text{N-C}_5\text{H}_4\text{N}$]; 2.95 [s, 6H, 4-(CH_3) $_2\text{N-C}_5\text{H}_4\text{N}$]; 5.13 and 5.31 [d, 4H, $J = 6.0$ Hz, (CH_3) $_2\text{CHC}_6\text{H}_4(\text{CH}_3)$ -*p*]; 2.90 [sept, 1H, $J = 7.0$ Hz, (CH_3) $_2\text{CHC}_6\text{H}_4(\text{CH}_3)$ -*p*]; 2.02 [s, 3H, (CH_3) $_2\text{CHC}_6\text{H}_4(\text{CH}_3)$ -*p*]; 1.22 [d, 6H, $J = 7.0$ Hz, (CH_3) $_2\text{CHC}_6\text{H}_4(\text{CH}_3)$ -*p*]; ^{13}C NMR (CDCl_3 , δ , ppm) 154.7; 153.6; 107.8 [4-(CH_3) $_2\text{N-C}_5\text{H}_4\text{N}$]; 103.1, 97.2, 83.2, 82.2 [(CH_3) $_2\text{CHC}_6\text{H}_4(\text{CH}_3)$ -*p*]; 39.7 [4-(CH_3) $_2\text{N-C}_5\text{H}_4\text{N}$]; 31.0 [(CH_3) $_2\text{CHC}_6\text{H}_4(\text{CH}_3)$ -*p*]; 22.7 [(CH_3) $_2\text{CHC}_6\text{H}_4(\text{CH}_3)$ -*p*]; 18.8 [(CH_3) $_2\text{CHC}_6\text{H}_4(\text{CH}_3)$ -*p*].



Scheme 1. Synthesis of *p*-dimethylaminopyridine(*p*-cymene)dichloro ruthenium(II).

Scheme 2. 4-Maleimidopyridyl(*p*-cymene)dichloro ruthenium(II) synthesis.

2.2. 4-Maleimidopyridyl(*p*-cymene)dichloro ruthenium(II) synthesis

4-Maleimidopyridyl(*p*-cymene)dichloro ruthenium(II) (MPR-II) was prepared from maleic anhydride and 4-dimethylaminopyridine(*p*-cymene)dichloro ruthenium(II). The 4-dimethylaminopyridine(*p*-cymene)dichloro ruthenium(II) (5.50 mmol) and the required quantity of the maleic anhydride (5.50 mmol) and toluene (25 ml) were heated to 30 °C for 3 h. Then the mixture was heated under reflux for 18 h. The residual solvent was removed and the solid was recovered, washed with hexane and crystallized from toluene; mp 227–229 °C. And the yield was 76%. ¹H NMR and ¹³C NMR in DMSO-*d*₆ data are given in Scheme 2. Anal. calc. for C₁₉H₂₀N₂O₂Cl₂Ru: C: 47.50; H: 4.17; N: 5.83; found: C: 47.39; H: 4.09; N: 5.57.

¹H NMR (CDCl₃, δ, ppm) 7.90 [s, 2H, CH=CH]; 8.44 and 7.44 [q, 4H, *J* = 1.4 Hz, 4-(CH₃)₂N-C₅H₄N]; 5.18 and 5.36 [d, 4H, *J* = 6.0 Hz, (CH₃)₂CHC₆H₄(CH₃)-*p*]; 2.92 [sept, 1H, *J* = 7.0 Hz, (CH₃)₂CHC₆H₄(CH₃)-*p*]; 2.01 [s, 3H, (CH₃)₂CHC₆H₄(CH₃)-*p*]; 1.21 [d, 6H, *J* = 7.0 Hz, (CH₃)₂CHC₆H₄(CH₃)-*p*]; ¹³C NMR (CDCl₃, δ, ppm) 155.2; 154.8; 108.3 [4-(CH₃)₂N-C₅H₄N]; 138.2 (CH=CH); 103.7, 97.5, 84.0, 82.8 [(CH₃)₂CHC₆H₄(CH₃)-*p*]; 31.2 [(CH₃)₂CHC₆H₄(CH₃)-*p*]; 22.9 [(CH₃)₂CHC₆H₄(CH₃)-*p*]; 18.9 [(CH₃)₂CHC₆H₄(CH₃)-*p*].

2.3. Homopolymerization of MPR-II

MPR-II (0.40 g, 1.5 mmol) and benzoylperoxide (0.12 mmol) as an initiator were dissolved in 10 ml

of toluene. The solution was poured into dry Schlenk tube and degassed twice by being purged with argon. The tube was closed and heated in an oil bath with stirring at 75 °C. The obtained polymer solution was slowly poured into 100 ml diethyl ether to precipitate the polymer. The precipitated polymer was collected by filtration and washed several times with an excess of hexane. The product was dried until the weight loss became essentially constant, 75% yield.

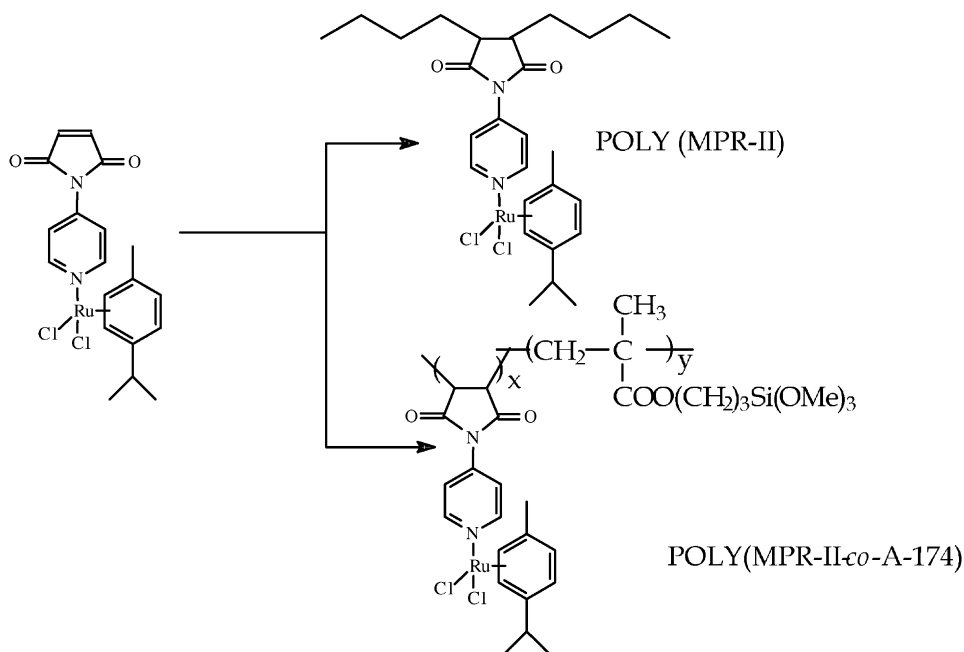
2.4. Copolymerization of MPR-II with A-174

A solution of MPR-II (1.5 mmol), A-174 (1.5 mmol), and radical initiator benzoyl peroxide in 15 ml THF was added to a dry polymerization tube and degassed with argon. The preparation procedure of poly(MPR-II-*co*-A-174) was the same as homopolymerization of MPR-II except for the monomer pairs. The copolymerization conversions of MPR-II with A-174 was found to be 92% (Scheme 3).

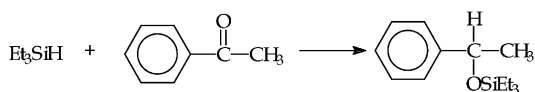
2.5. General procedure for the hydrosilylation reaction

The hydrosilylation reaction are shown in Scheme 4. In a typical run, 0.1 g of complex catalyst, 0.065 mol hydrosilylation reagent and 0.05 mol of unsaturated compound were located in a three necked flask (50 ml) equipped with a mechanical stirrer, reflux condenser and thermometer.

The conversion of hydrosilylation based on the acetophenone was determined on GC packed with 10% SE-30 on 101 support. To identify the product structure, the reaction medium was distilled first at



Scheme 3. Homopolymerization of MPR-II and its copolymerization with A-174.



Scheme 4. Catalytic reaction.

atmospheric pressure and then reduced pressure was applied to separate the hydrosilylated products from the residual reactants and the by products.

3. Results and discussion

The structures of synthesized monomer and polymers were confirmed by FT-IR, ^1H NMR in $\text{DMSO-}d_6$ spectroscopies. The FT-IR spectrum of poly(MPR-II) indicated characteristics absorption peaks at 1725 and 1705 cm^{-1} ($\text{C}=\text{O}$ stretching) with the disappearance of vinyl absorption at 1655 cm^{-1} that had appeared in the MPR-II monomer. The ^1H NMR spectrum of poly(MPR-II) showed methine protons of the polymer backbone at 1.2 ppm, and the disappearance of the vinyl absorption peak at 7.2 ppm, which was ascribed in the MPR-II monomer.

The FT-IR spectrum of poly(MPR-II-co-A-174) obtained by the radical polymerization of MPR-II and A-174 indicated absorption peaks at 1776, 1724 cm^{-1} ($\nu\text{C}=\text{O}$ stretching of imide), and 1092 cm^{-1} ($\text{Si}-\text{O}-\text{C}$, bending), 402 cm^{-1} ($\text{Si}-\text{O}-\text{C}$ *asym* stretching) (Fig. 1).

Copolymerization was carried out by using four different mole fraction of A-174 in the initial feed. The extent of reaction was estimated gravimetrically by weighing the copolymer formed. The results are summarized in Table 1. The silicon estimation was made to determine copolymer compositions. For a given monomer feed, the copolymer composition was almost constant irrespective of percent conversion in the steady state of copolymerization.

The exothermic transitions were observed in differential thermal analysis (DTA). In most of the copolymer samples, the exotherm was above 540°C . The complete weight loss occurred above 540°C evidenced by TGA. The residual weight loss above this temperature dependent on the initial silicon content of the polymers. No significant change in thermal behavior of poly(MPR-II) was observed by incorporation

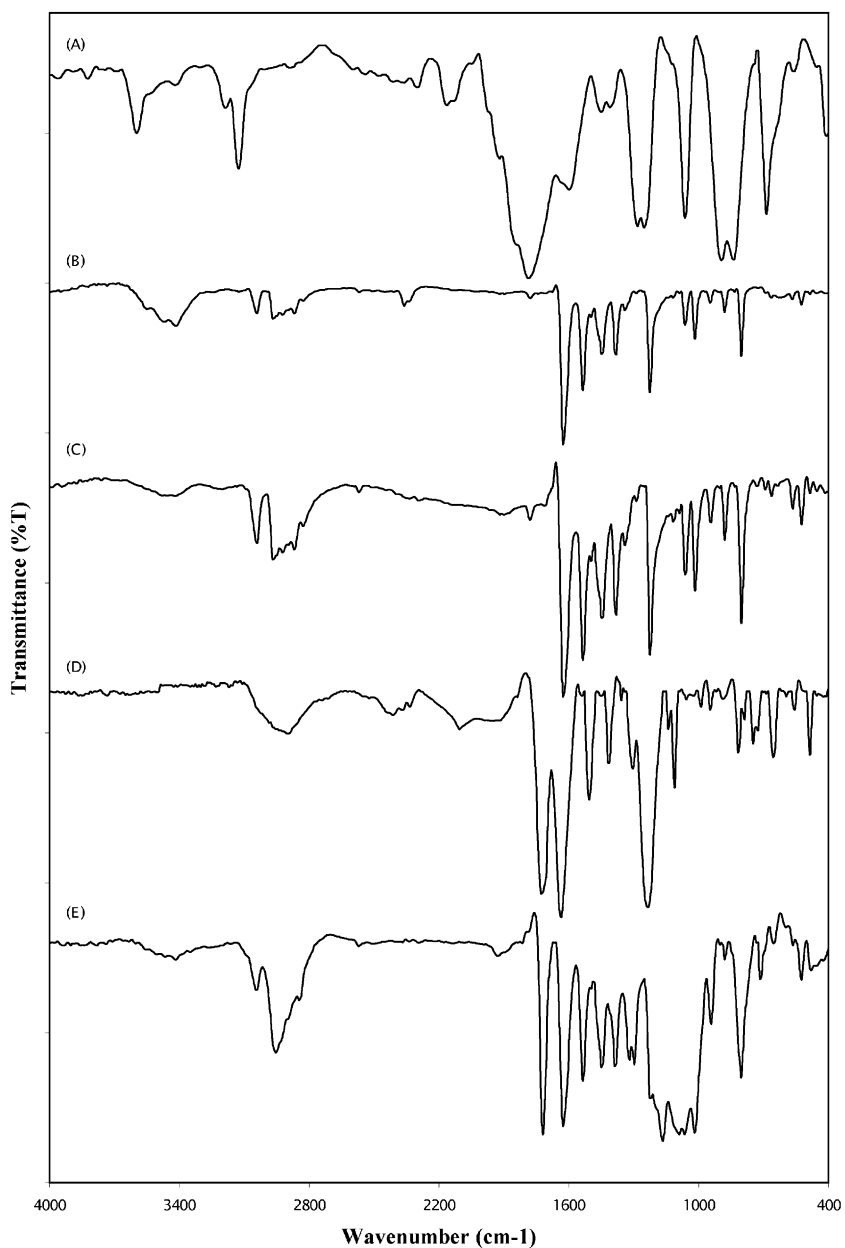


Fig. 1. FT-IR spectra of maleic anhydride (A), poly(MPR-II) (E), 5M4 (D), *p*-dimethylaminopyridine(*p*-cymene)dichloro ruthenium(II) (C), MPR-II (B).

of low mole fraction of A-174 in the backbone. DSC curves of the polymers showed the glass transition temperature (T_g) around 234–251 °C for poly(MPR-II) (Fig. 2).

Metal complexes able to catalyze hydrosilylation reaction of organic substrate under mild conditions are very attractive for many process. We have observed that Ru(II) complexes of 4-maleimidopyridyl

Table 1
Copolymerization of MPR-II and A-174

Sample designation	M ₁ (A-174 in feed)	M ₁ ^a (A-174 in copolymer)	Reaction time (min)	Conversion (%)
3M1	0.3	0.28	60	11.3
3M2	0.3	0.29	75	25.2
5M3	0.5	0.46	60	12.2
5M4	0.5	0.44	80	19.0
7M5	0.7	0.59	60	17.2
7M6	0.7	0.65	90	28.4
9M7	0.9	0.72	60	11.3
9M8	0.9	0.77	110	29.7

^a Mole fraction of A-174 in copolymers were determined by Si estimation (1:1 HNO₃:H₂SO₄ was added and charred 200 °C, the heated 800 °C for 3 h).

(*p*-cymene) can be used as effective catalysts for hydrosilylation reaction of acetophenone.

The catalytic activity of the ruthenium complexed poly(MPR-II), and poly(MPR-II-co-A-174) were

investigated with regard to hydrosilylation reaction and the results are summarized in Table 2. The catalytic activity is significantly less at room temperature when copolymer was used as catalyst. After

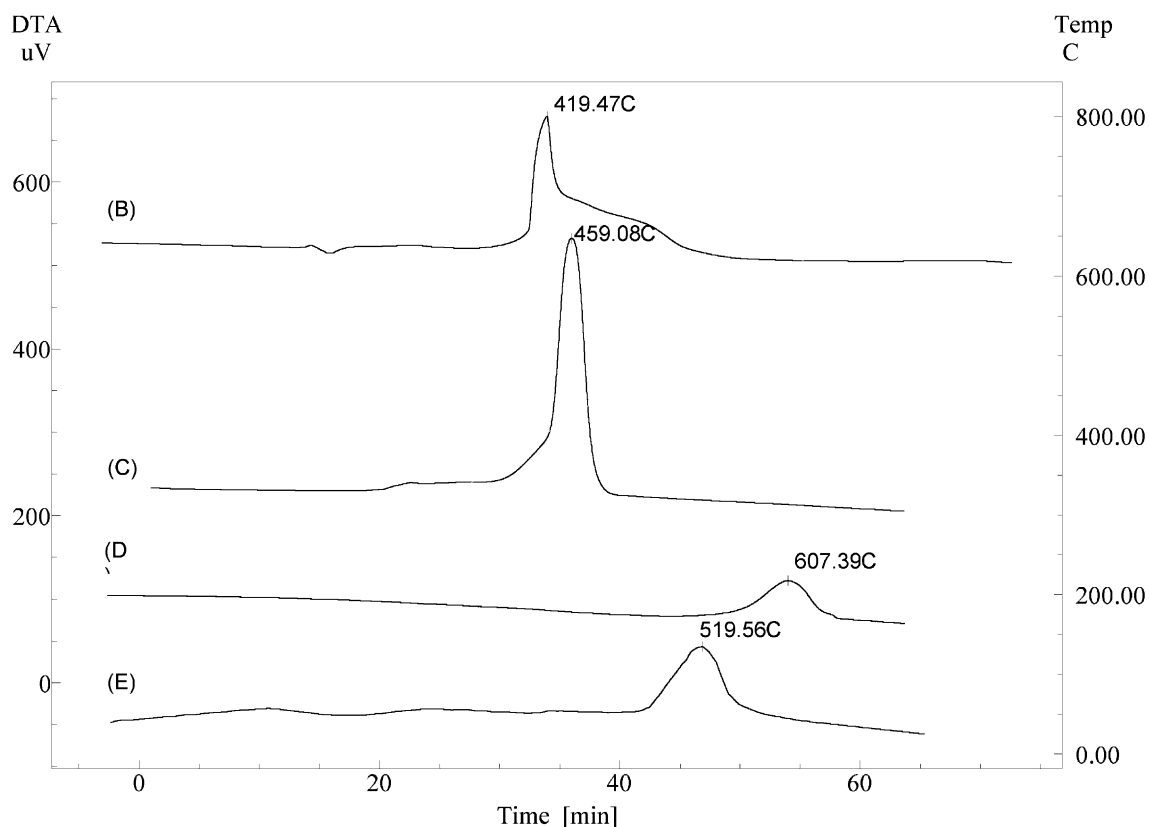


Fig. 2. DTA thermogram of poly(MPR-II) (E), 5M4 (D), *p*-dimethylaminopyridine(*p*-cymene)dichloro ruthenium(II) (C), MPR-II (B).

Table 2
The hydrosilylation of acetophenone with various 5M4 catalyst^a

Run	Regeneration ^b	Temperature (°C)	Conversion (%) ^c
1	0	70	95
2	1	55	93
3	2	90	92
4	3	65	91
5	4	75	87
6	5	70	87
7	6	70	86
8	6	90	85

^a A 0.1 g of catalyst, 0.05 mmol of acetophenone, 0.065 mmol of hydrosilylation agent, 10 ml of CH₂Cl₂, 22 h.

^b Determined by GC.

^c Catalyst was recovered by microporus filtration, washed with distilled hexane, and reused six times without significant loss of activity.

the hydrosilylation reaction, the product solution is colorless suggesting that no leaching of ruthenium metal took place. Turnover number results for the hydrosilylation of styrene with catalysts are presented in Table 3. Turnover number results for the hydrosilylation of styrene with various catalysts are given in Table 3. At room temperature, the turnover numbers for MPR-II, 3M1, 5M3, 7M5 and 9M7 are generally of the order of 20–60 mmol of substrate to mmol of Ru/h, while the other catalysts gave relatively higher turnover numbers.

Table 3
Turnover numbers of the hydrosilylation of acetophenone with various catalysts^a

Catalyst	Temperature (°C)	Time (h)	Conversion (%)	Turnover (h ⁻¹)
MPR-II	70	22	95	18
Poly(MPR-II)	70	18	93	102
3M1	25	2	29	14
3M2	70	4	88	87
5M3	25	8	48	45
5M4	70	27	98	180
7M5	25	68	54	55
7M6	70	27	88	110
9M7	25	68	28	64
9M8	70	27	86	102

^a A 0.1 g of catalyst, 0.05 mmol of acetophenone, 0.065 mmol of hydrosilylation agent, 10 ml of CH₂Cl₂, 22 h; determined by GC.

4. Conclusion

Ru(II) complex containing polymers were prepared and used to catalyze hydrosilylation of acetophenone compound with a good reusability. The polymer and copolymers were structurally elucidated. In comparison with the other polymer supported catalysts used for hydrosilylation higher activity and reusage have been observed for a compound tested by this catalyst. Thermal stability of the copolymer and polymer was found to be very high indicating that this support could be used at elevated temperatures, and no filling is necessary since the silane group can easily be linked to the net work by sol–gel process in different morphological state.

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