

Development of heterogeneous catalyst by ionically bonding macrocyclic Zr–Zr complex to montmorillonite clay for depolymerization of polypropylene

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Abstract

The homonuclear macrocyclic Zr–Zr complex was synthesized by reacting 2,6-diformyl-4-methylphenol with 1,2-phenylenediamine and zirconium oxychloride. The heterogeneous complex catalyst was prepared by ionically bonding it on zirconium pillared montmorillonite. The heterogeneous complex catalyst was shown to be stable at the depolymerizing temperature of polypropylene and the reaction product was a waxy solid alone without forming liquid and gaseous material. The FTIR analysis of this solid was shown to have exactly the same IR of the polypropylene indicating that the depolymerization occurs predominately by first formation of polymer radicals by random scission of the polypropylene chain. The chain radical, thus generated, combines with the catalyst to give a radical cation complex and the movement of this along its chain by bond shift reaction produces low molecular waxy product. Experiments have shown that the molecular weight of this waxy product depends upon the reaction temperature as well as the residence time and all its physical properties (melting point and solubility) can be matched with those of the paraffin wax.

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Keywords: Heterogeneous catalyst; Depolymerization; Polypropylene; Wax; Zr–Zr complex clay catalyst

1. Introduction

Polyethylene (PE) and polypropylene (PP) are being used in a wide range of applications such as industrial, agricultural, automobile industries, packaging, etc. as they possess excellent mechanical and chemical properties. Since they are non-biodegradable and their incineration produces carcinogens (such as dioxins, furans and phosgene), there is a need to recycle the polymers. The process for recycling is currently based on pelletizing and moulding into low-grade plastics. The main disadvantage of this is that the recycled material possesses poor mechanical strength and color qualities and a low market value.

In view of the above, considerable amount of research is being done to convert it into more useful material like (monomer, fuels or valuable chemicals for petrochemistry). To achieve this, following different solutions have been considered [1]. In the first

approach, a catalytic cracking or hydrocracking of plastics is carried out to get gaseous, liquid hydrocarbons and solid residue. Most of the time these are used in combination, e.g. (a) catalytic degradation of plastic and obtain liquid stream for further degrading, (b) thermal cracking of plastics followed by catalytic upgrading and (c) catalytic cracking of plastics followed by hydrocracking. Catalytic degradation of PE over mesoporous silica (called KFS-16) has been studied at 430 °C [2]. The products of degradation were liquidous (which are condensable at room temperature), gaseous and solid residues (referring to both carbonaceous products as well as waxy components). The liquidous material have been analyzed and shown to be close to fuel oil.

Sakata et al. [3] have reported the use of acid catalyst silica–alumina (SA-1, SA-2), zeolite ZSM-5 and non-acidic mesoporous catalyst, silicates, mesoporous silica gel and mesoporous folded silica (FSH). The yield of individual product formed gas, liquid and solid residues have been determined and the boiling point distribution of the liquid product were compared with these obtained from thermal degradation. Some other

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catalysts for this purpose has that have been reported are BEA [3], ZSM-5 and MOR [4], lead sulfide [5] and ZSM-12 and ZSM-5 [6], mesoporous silica [7], β -zeolite [8], ultrastable Y zeolite [9]. Catalytic pyrolysis of HDPE was carried out to form C₃–C₅ hydrocarbon with high olefinic content [9], sapo-37 molecular sieve [10], nanosize ZSM-5 [11] solid acidic non-acidic catalyst [12], and activated carbon [13].

Literature also reports the production of high quality gasoline and kerosene from PE and PP waste [14] and for doing this nickel chloride is exchanged with Y zeolite to give Ni-REY catalyst which is used to catalytically crack polymer to heavy oil. Silica MCM-41 catalyst has been employed to crack PE and PP to produce isobutene and isobutane compound [15]. A carbenium ion mediated mechanism has been proposed for the cracking reaction and the product distribution compared with those obtained from thermal cracking. The studies reported up till now employed pure polymer and Ref. [16] reports the processing of municipal PE waste, Refs. [17–19] the decomposition of PVC mixed plastics, Ref. [20] the mixture of PP and polystyrene, and Ref. [21] the thermal degradation of mixture of PP with starched base materials and Ref. [22] catalytic degradation of polystyrene.

Literature sites zeolites as an important catalyst in reutilizing polymer waste. Modification of ZSM-5 zeolites has been carried out using desilication and incorporation of lanthanum under microwave radiation to give DeLaZSM-5 zeolites [23,24]. The modified catalyst gave the highest catalytic degradation rate, the liquid yield was slightly increased and the high catalytic activity was explained through increase of number and strength of weak acid sites on the catalyst. The kinetics aspects of thermal oxidative degradation have been studied using thermo gravimetric analysis [25]. This fundamental study has shown that the initiation step consists of forming polymer radicals which at the propagation step combines with oxygen molecule to give radicals and hydroperoxide radicals and both these species form carboxylic and polymer radicals during the chain degradation step. A similar mechanism for the oxidative degradation [26] in presence of a heterogeneous complex catalyst has been described for the depolymerizing of PE. In this, the polymer radicals formed by the random scission of PE combines with the catalyst to form a cation radical. Due to bond shift reaction of the cation radical portion gives rise to formation of oxidized wax of low molecular weight.

In this paper we show that a homonuclear complex catalyst serves an effective catalyst for depolymerizing of polypropylene. Unlike the catalysts described above, the product formed using this catalyst is only waxy solid with no gaseous and liquidous products formed. As a result of this, the reactor pressure does not rise beyond the vapor pressure of the waxy product at the reaction condition. Multimetallic complexes have been known from the early times and the focus of work reported in the literature has been their preparations and determination of their properties. Their application in catalysis has been limited in the view of the fact that these complexes breaks down at low temperatures (100–200 °C) where as we require above 200 °C for most of the commercial reactions (for depolymerization reaction, we require about 400 °C). It was argued that the metals within the

complex structure would interact with each other as well as the ligands and would lead to help in promoting the depolymerizing reaction with considerable efficiency. In this paper we show the complexes ionically bonded to a montmorillonite would be more stable thermally and can be used for depolymerizing reaction.

Macrocyclic complexes can be formed when a dialdehyde is reacted with diamines and some of the complexes utilized in the chemical reactions are presented in Table 1 [27–38]. In preparing various metal complexes, the size of the cavities for complexation are adjusted by selecting the ligands and the phenol group in the bridging ligand divides the over all cavity into two parts. The metal salts are complexes inside the ring either during the ring formation or after the ring is formed and there are very few examples of complexation with zirconium. Almost all reaction reported in the fifth column are biological which by its very nature require ambient conditions.

As stated above, the macrocyclic Zr–Zr complex is thermally unstable at high temperature. To overcome this problem, we have prepared Zr–Zr complex using 1,2-phenylene diamine and 2,6-diformyl-4-methyl phenol and ionically bonded it on zirconium pillared montmorillonite clay.

2. Experimental section

2.1. Preparation of macrocyclic Zr–Zr complex and characterization

The 2,6-diformyl-4-methylphenol needed for formation of cyclic complex is prepared following the procedure given in literature [39]. The NMR spectrum of the dialdehyde prepared by us shows singlets at 11.42 ppm (phenolic), 10.2 ppm (aldehydic), 7.74 ppm (aromatic) and 2.36 ppm (methyl) and matches with that given in Ref. [39]. The procedure for the preparation of the two-step reaction forming the cyclic complex with the zirconium is discussed below:

- *Step-I.* To 50 ml of *N,N*-dimethylformide, 2,6-diformyl-4-methylphenol (0.95 g, 0.012 mol) and 1,2-phenylenediamine (0.65 g, 0.006 mol) are added and this solution is maintained at 40 °C. Dissolving zirconium oxychloride (4.67 g, 0.014 mol) makes another solution in 20 ml methanol and both these solutions are mixed and stirred for 1 h and left for 24 h without stirring.
- *Step-II.* In this step solution of 1,2-phenyldiamine (0.336 g) in 30 ml methanol was prepared and added to the solution formed in Step-I solution. This solution was kept for 2 weeks and a precipitate collected slowly. The complex is removed by filtration; it is washed with diethyl ether and dried. The FTIR spectrum of the complex shows the C=N at 1512 cm⁻¹ corresponding to C=O group this way confirming the formation of the cyclic complex.

2.2. Preparation of the supported catalyst

The acid (using HCl) treated montmorillonite was procured from Ashapura Minechem Ltd., Mumbai, India and was first pillared using zirconium salt followed by the intercalation of

Table 1
Bimetallic complex utilized in chemical reactions

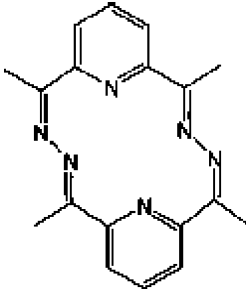
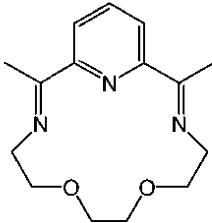
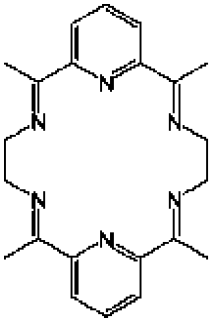
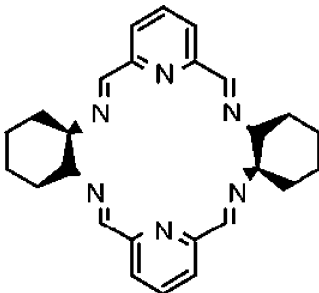
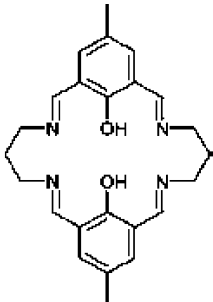
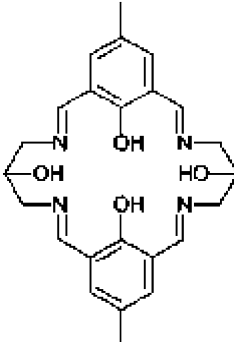
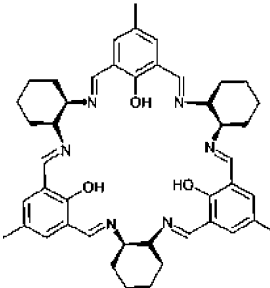
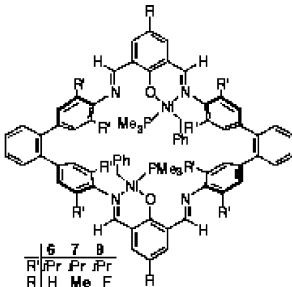
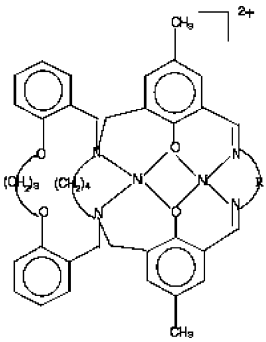
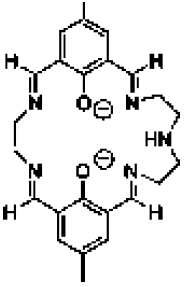
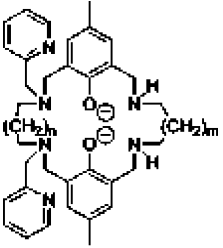
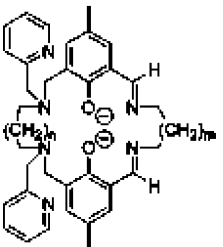
Names	Ligands	Structure	Metals	Usage	Reference
Tetradentate Schiff base complex	2,6-Diacetylpyridine + hydrazine		Scandium, zinc(II) and magnesium(II)	Site-specific DNA oxidation	[27]
Pentadentate Schiff base complex	2,6-Diacetylpyridine + 1,8-diamine-3,6-dioxaoctane		Yttrium(III), dysprosium(III), erbium(III), thulium(III) and lutetium(III)	Biological systems	[28]
Hexadentate Schiff base complex	2,6-Diacetylpyridine + ethylene diamine (or 0-phenylenediamine)		Lanthanum(III), cerium(III), praseodymium(III) and neodymium(III)	Synthetic nucleases catalysts for RNA transesterification	[29]
Chiral Schiff base macrocycles	2,6-Diformylpyridine + <i>R,R</i> - or <i>S,S</i> -1,2-diaminocyclohexane		Lanthanide(III)	Artificial catalysts for hydrolytic DNA cleavage	[30]

Table 1 (Continued)

Names	Ligands	Structure	Metals	Usage	Reference
Hexadentate macrocycles derived from 2,6-diformylphenols (Robsons ligand)	2,6-Diformylphenol + 1,3-propylenediamine		Cu(II), Cu(I), Ni(II), Zn(II), Fe(II), Fe(III), Pd(II) and Ru(III)	Metalloenzymes	[31]
Hexadentate macrocycles derived from 2,6-diformylphenols (Robsons ligand)	2,6-Diformyl-4-methylphenol + 1,3-diamino-2-hydroxypropane		La(III), Ce(III) and Eu(III) ions	Biomedical applications	[32]
Hexadentate macrocycles derived from 2,6-diformylphenols (Robsons ligand)	2,6-Diformylpyridine + 1,2-diaminocyclohexane		Zinc(II)	Biomedical applications	[33]
Macrocyclic complexes of tetraaminodiphenols	2,6-Diformyl-4-R-phenol (R = H, Me, F) + 4,4''-diamino-3,3'',5,5''-R'4-o-terphenyl (R' = <i>i</i> Pr, Et)		Nickel	Ethylene polymerization	[34]

Macrobicyclic complexes	5-Methylsalicyl aldehyde + 3,4:10,11-dibenzo-1,13[<i>N,N'</i> -bis{(3-formyl-2-hydroxy-5-methyl)benzyl}diaz]-5,9-dioxocycloheptadecane		Nickel(II)	Hydrolysis of 4-nitrophenyl phosphate	[35]
Heteronuclear bimetallic macrocyclic complexes	2,6-bis(Iminomethyl)-4-methylphenolate + $-(CH_2)_m$ NH(CH ₂) _m – (<i>m</i> = 2,3)		Cu, Mn; Cu, Fe; Cu, Co; Cu, Pb; DiCu	Supramolecular chemistry	[36]
Homonuclear bimetallic macrocyclic complexes	Dialdehyde + diamine	 <i>n</i> = 0, 1; <i>m</i> = 0, 1	DiCo, DiZn and DiFe	Bimetallic reactivity	[37]
Heteronuclear bimetallic macrocyclic complexes	Dialdehyde + diamine	 <i>n</i> = 0, 1; <i>m</i> = 0, 1	DiCo, DiNi, DiMn, Cu–Zn and Co–Mn	Bimetallic reactivity	[38]

The selectivity of ligands depends upon the size of the cavity needs for the complexing metal.

the complex. In the first step, the clay (20 g) is subjected to swelling by adding water (1 l) to the clay and stirring it for 5 h and the mixture was finally centrifuged and dried. In the next step, the clay is treated with NaCl solution (1 M) and was aged for 24 h. The clay was separated, dried and then refluxed with freshly prepared zirconium oxychloride (0.1 M) solution for 24 h at 100 °C to obtain zirconium pillared montmorillonite. The final step is the intercalation of the complex in the clay layers. The clay from the previous step is refluxed with the complex solution (dissolved in acetonitrile) for 24 h at 80 °C. The catalyst thus obtained is separated, washed with acetone and dried.

2.3. Degradation of polypropylene

Experiments were conducted in a high-pressure batch reactor made of stainless steel (reactor volume of 980 cm³) with a heating furnace. The reactor consists of a pressure indicator and there is provision of gas purging. The reactor is heated to desired temperature and a temperature controller was used to regulate temperature with a thermocouple inserted into the reactor.

Polypropylene having molecular weight of 44.00×10^3 was obtained from a local market and the degradation of PP was performed in a batch reactor with catalyst prepared by ionically bonding the macrocyclic zirconium complex to montmorillonite clay (abbreviated as clay-ZrZrC₆H₄). In this study we have systematically varied the reaction time (1–8 h) and temperature (300–400 °C) in the presence of nitrogen.

3. Results and discussion

The complex exists as ZrZrL(OCl₂) where L is the ligand CH₂C₆H₂OCHN(C₆H₄) and the –OCl₂ group is present from the starting zirconium oxychloride which is the metal salt used for the complex making. The theoretical values of the C, H and N calculated from the structure of the complex are 28.987%, 6.404% and 6.795%, respectively, and are close to the experimental values of 21.1%, 6.885%, 7.466%, respectively. The match is very close and confirms the complex formation. The FTIR spectrum of the complex catalyst shows NH group at 3337 cm⁻¹, OH at 3466 cm⁻¹ and C=N at 1512 cm⁻¹ which are present in the structure of the complex. We have attempted to prepare a single crystal of the complex to obtain its structure by X-ray diffraction analysis. We used the evaporation technique (employing methanol and dimethyl formamides solvents), solvent–non-solvent diffusion techniques (using methanol and *n*-hexane) and vapour diffusion technique (using methanol and diethyl ether) and single crystal could not be prepared due to low solubility of the complex.

The surface area of the catalyst at various stages of the catalyst formation and depolymerization reaction has been measured on a Coulter SA 2100 instrument and is analyzed by the BET method. The surface area of the montmorillonite clay was found to be 331.12 m² g⁻¹ and after pillaring with zirconium ions, the surface area decreased to 115.63 m² g⁻¹. On loading the complex, the surface area of the clay was further reduced to 101.65 m² g⁻¹ and the surface area of the catalyst further decreases after 10 h reaction of depolymerization to 75 m² g⁻¹

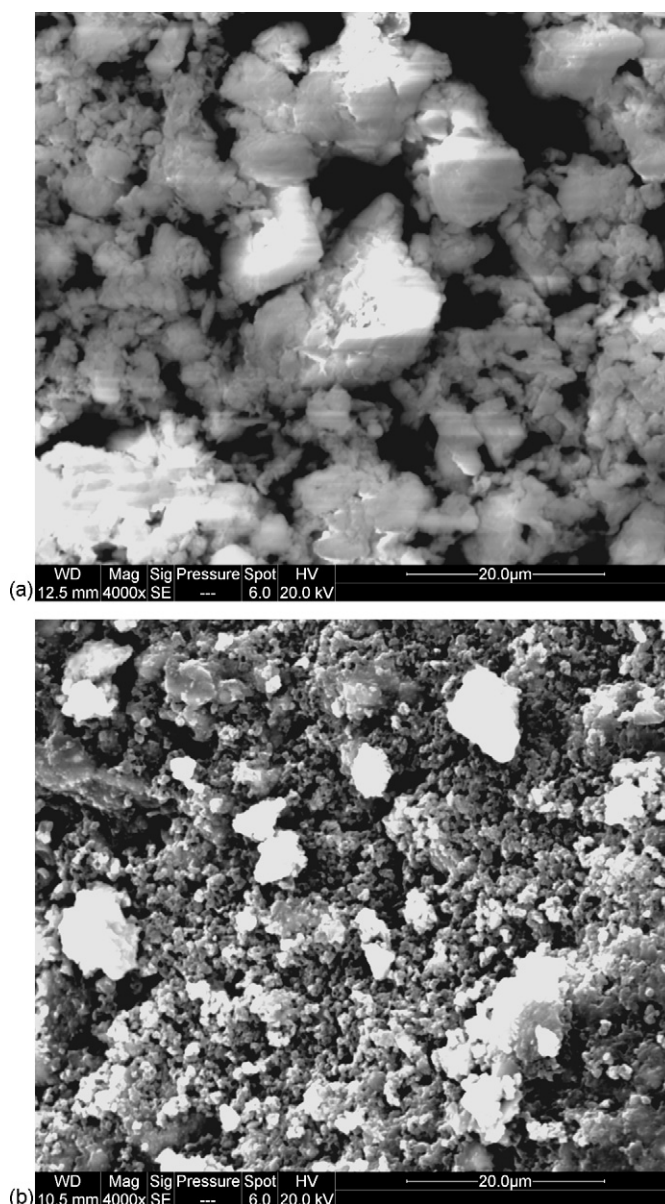


Fig. 1. Micrograph of the catalyst using SEM at 4000× magnification: (a) fresh catalyst and (b) used catalyst.

possibly due to the blocking of pores by the reaction products but does not change any further (tested up to 100 h of reaction). We have also studied the surface morphology of the catalyst before and after the depolymerization reaction using scanning electron microscopy (SEM). The micrographs of the surface of the catalyst are shown in Fig. 1 and these figures confirm that there is very little carbon deposition on the surface. In order to determine the acid sites, the catalyst was treated with ammonia and the FTIR of the catalyst before and after the treatment were taken. The two spectra are given in Fig. 2 and the acid sites have been suitably marked.

Thermal degradation of polyethylene (PE) and polypropylene (PP) have been studied extensively in the past and the overall degradation has been observed to occur individually or by any combination of the following modes [40–42]:

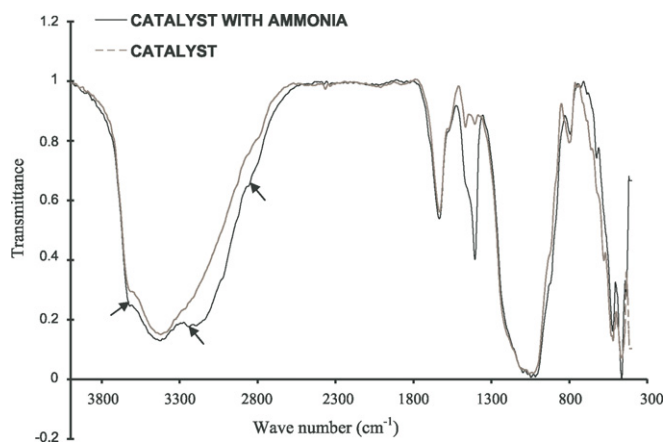


Fig. 2. FTIR of the catalyst before and after saturation with ammonia. The peaks marked with an arrow are the additional peaks due to ammonia adsorption.

- Elimination of low molecular weight compound (such as HCl in PVC).
- Unzipping of monomers (as in PMMA).
- Cyclization (as in polyacrylonitrile).
- Random scission of polymer chains.
- Formation of specific molecular weight compounds.

The mode (b) is a specific situation of mode (e) in that, only monomer is formed in this step. The study on thermal degradation of PE and PP have shown that both these degrade as if it is a solid state reaction with dominant random scission mechanism even though in thermal depolymerization, species such as ethylene, styrene, $C_8H_8-C_3H_3O$, $C_8H_8-(C_3H_6O)_2$, etc. have been identified.

Thermal degradation of PE are known to occur at high temperature than PP because of its higher bond dissociation energy (341.1 kJ/mol) than that for PP (334.4 kJ/mol). We have carried out the thermal depolymerization of PE and in 8 h of reaction time, we obtain 12.5% solid, 63.5% liquid and 25% gas while for PP we obtained 5% solid, 65% liquid and 30% of gases. The

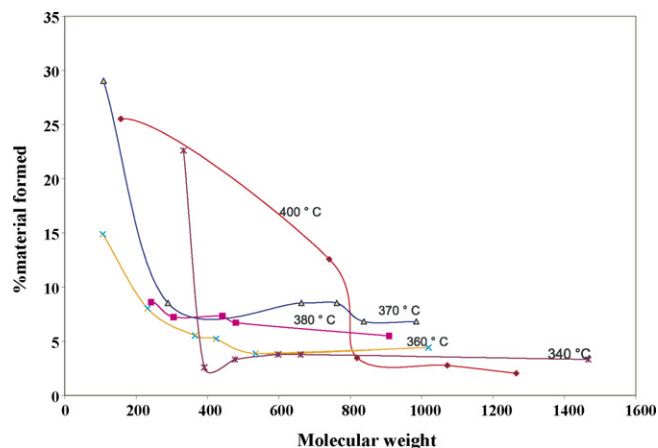


Fig. 4. Molecular weight distribution of the wax product after 8 h of depolymerization reaction.

liquids for PE had C_7-C_{20} alkanes only while that for PP had C_4-C_{18} alkanes and these distributions are little affected by the reaction temperature [26].

The depolymerization of PP in this work has been done by charging 100 g of PP and 1 g of the complex catalyst developed in this work in a batch reactor. As the low molecular weight depolymerizing products are formed, the reactor pressure increased corresponding to its pressure and on cooling the reactor to the room temperature; the pressure reverts to the original reactor pressure. This clearly indicates the formation of only waxy solid products. We present the FTIR of the solid product in Fig. 3, which is seen to be that of typical polypropylene. This means that the reaction by mode (a) to mode (c) must not have occurred because of which the waxy product is the only low molecular weight polypropylene formed by step (e).

We have carried out the depolymerization for 8 h batch time for different temperature and from the FAB analysis of the product, the molecular weight distribution is determined and reported in Fig. 4. With the increase in reaction temperature, the distribu-

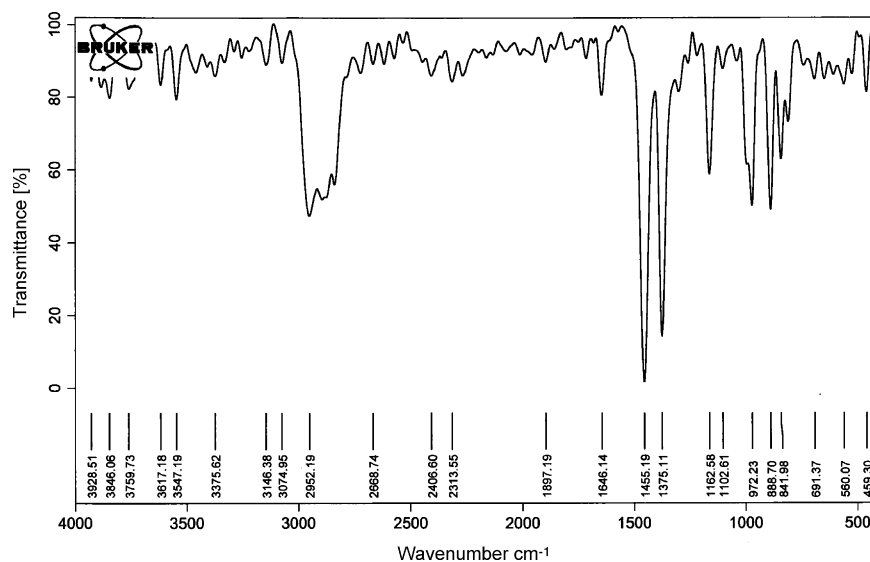


Fig. 3. The FTIR of the product polypropylene wax formed after 8 h of depolymerization reaction in presence of the catalyst.

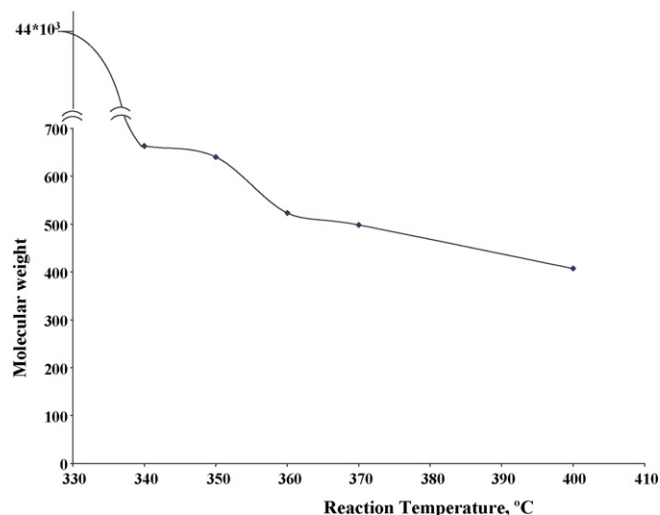


Fig. 5. Effect of reaction temperature on the number average molecular weight after 8 h of depolymerization reaction.

tion tends to become more flat. The number average molecular weight of the wax formed can be calculated and is plotted in Fig. 5 for different reaction temperature and it is observed that the average molecular weight falls with increasing temperature. In Fig. 6 the melting point of the PE wax has been plotted as a function of reaction. At 320 °C, there is no depolymerization of PP and the melting point of 165 °C corresponds to that of original PP.

The melting point and solubility of the wax formed (partially soluble in acetone and totally soluble in cyclohexane) mostly govern the physical properties of ordinary paraffin wax. In Figs. 7 and 8, we present the solubility of the PP wax in these solvents. We find that cyclohexane dissolves it completely when it is depolymerized at 400 °C, while it is partially soluble in acetone. It is thus seen that the physical properties of the PP wax can be matched with those of paraffin wax simply by manipulating the reactor temperature and the reaction time. Next we found that the PP wax thus formed was totally miscible with the

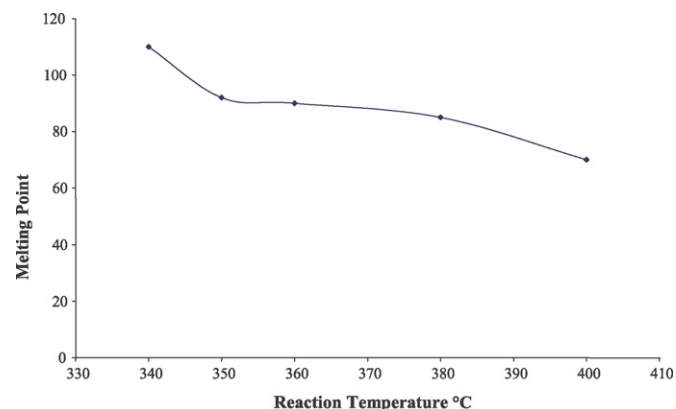


Fig. 6. Reaction temperature vs. melting point after 8 h of depolymerization reaction. The melting point of pure PP is 165 °C which is not shown in the figure.

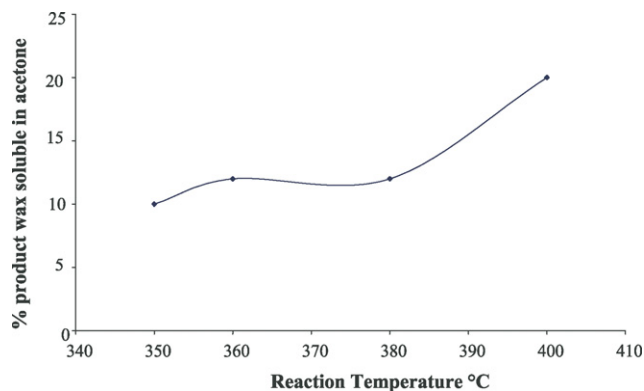


Fig. 7. Reaction temperature vs. % product wax soluble in acetone after 8 h of depolymerization reaction.

paraffin wax formed by depolymerizing polyethylene (HDPE) wax formed similarly.

The oxidative degradation of polypropylene has been a subject of extensive study and it has been agreed that the initiation step consists of random scission of polymer chains due to heat. The polymer radicals thus formed combine with oxygen to give hydroperoxide radicals or hydroperoxides, which give chain branching as well as chain scission. The mechanism for depolymerization of PP in presence of nitrogen is given in Table 2 and is similar in which reaction 1 produces polymer radicals through random chain scission of neutral chain. These radicals form a complex with the catalyst in reaction 2 of this table. Since the catalyst is acidic in nature, it can abstract an electron from P_m , the ligand gains an electron and the polymer radical becomes a cation radical at its chain end. Such cation radical can easily undergo a bond shift reaction in which the cation radical can move to any intermediate position on the chain as shown in Eq. (3) of Table 2. The complex formed in reaction 3 of Table 2 forms the wax through the depropagation reaction (reaction 4) and can undergo termination reactions 5 and 6. This can occur through combination as well as disproportionation as shown in Table 2.

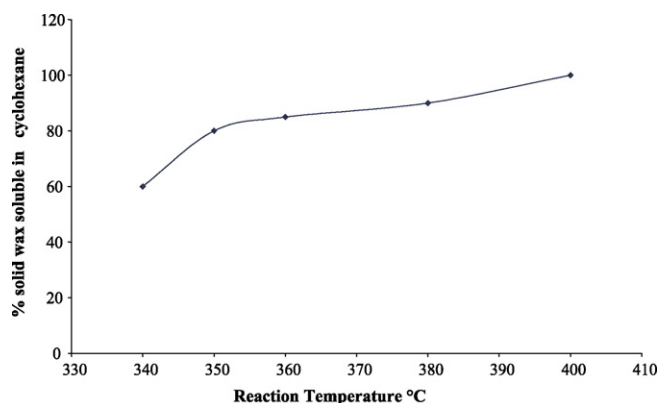
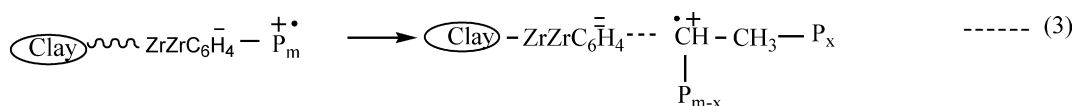
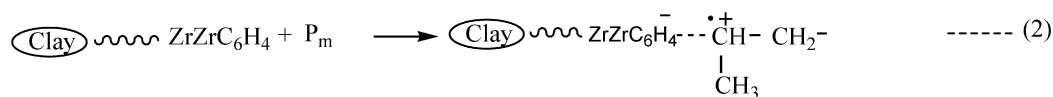
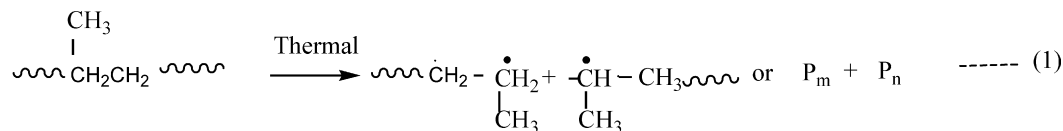
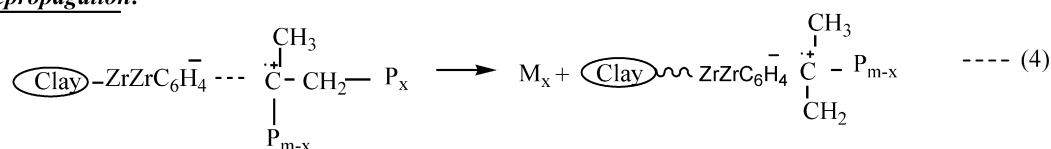
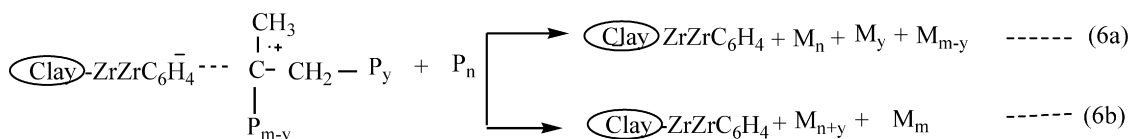
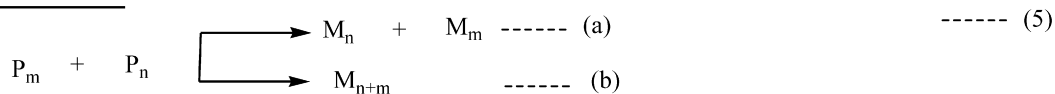


Fig. 8. Reaction temperature vs. % product wax dissolving in cyclohexane after 8 h of depolymerization reaction.

Table 2

Mechanism of depolymerization of polypropylene

Initiation:**Depropagation:****Termination:**

(6)

4. Conclusions

Polymers like polyethylene and polypropylene are common commercial materials and are non-biodegradable. Normal trend of treating their waste is to degrade these at high temperature which produces gases, liquid and solid waxy products. There is a great effort in the literature to use the liquid product either as fuel oil or recover some useful chemicals out of this liquid by further processing it. In this paper we report a heterogeneous Zr–Zr macrocyclic complex catalyst which degrades PP forming only waxy product without any liquid or gaseous materials.

Experiments with depolymerization of PP in presence of our complex catalyst have shown that the molecular weight of the solid product (as determined by the FAB analysis) depends only upon the reaction temperature and the time of reaction. Since there is no gaseous or liquid (at the room temperature) product, the pressure of the reactor is the same as the vapor pressure of the product wax at the reactor temperature which is small. Lastly, the waxy product is completely miscible with commercially available paraffin wax and its physical properties (melting point and

solubility) can be made identical to those of the latter by properly choosing the reactor residence time and the depolymerizing temperature.

The FTIR of the waxy product was found to be exactly the same as that of polypropylene which implies that during the depolymerization, there is no elimination of low molecular weight compounds, cyclization or monomer unzipping. The predominant mechanism of degradation should be random scission of polymer chains giving polymer radicals. These polymer radicals would then form cation radical complex with our catalyst. Such complexes can easily undergo a bond shift reaction in which the cation radical can move to anywhere on the chain. Low molecular weight waxy product can be formed by elimination of P_x (or P_y) which would constitute the major catalytic depolymerization step of polypropylene.

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