

# Studies in switching the mechanism of polymerisation by single-site catalysts — from vinyl addition to metathesis

R. Manivannan<sup>a</sup>, G. Sundararajan<sup>a,\*</sup>, Walter Kaminsky<sup>b</sup>

<sup>a</sup> Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

<sup>b</sup> Institut für Technische und Makromolekulare Chemie, Universität Hamburg, Bundesstrasse 45, Hamburg 20146, Germany

## Abstract

Titanium/MAO-based catalyst systems were used to synthesise polycyclic olefins containing both vinyl and ring-opened units by converting the mechanism of polymerisation from vinyl addition (VA) to metathesis. The switch in mechanism was achieved by adding a reactivity transfer reagent like phenylacetylene (PA) during the course of VA polymerisation. The polymers synthesised contained nearly 30% ring-opened structures as indicated by their <sup>1</sup>H nuclear magnetic resonance (NMR). Kinetic studies indicated a change in mechanism of polymerisation after the addition of the reactivity transfer reagent. Arrhenius parameters calculated for both VA and metathesis polymerisation also suggested mechanism switching in the course of polymerisation. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Ti/MAO catalysts; Vinyl addition; Metathesis polymerisation; ROMP

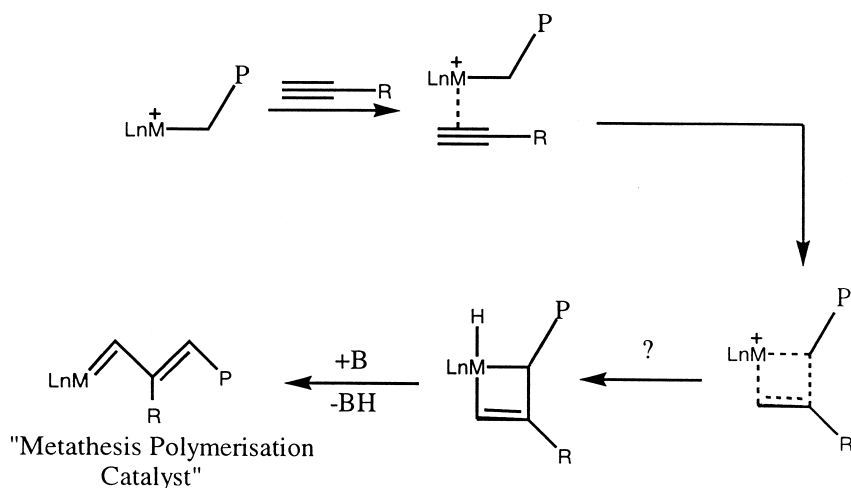
## 1. Introduction

Single-site catalysts based on metallocene–methylaluminoxane (MAO) system are in focus these days, both in academic and in industry, for ethylene and propylene polymerisation [1,2]. Recently, it has been noted that select *non*-metallocene complexes can also be effective for olefin polymerisation especially for the homo and copolymerisation of cyclic olefins like cyclopentene (CP) and norbornene (NBE), to give linear polymers *without* any ring opening [3,4].

Moreover, it is well known that cyclic olefins, in the presence of an olefin metathesis catalyst, undergo ring-opening-metathesis polymerisation (ROMP) to give polymers with special properties [5]. The later discovery, that Ziegler–Natta catalysts could sometimes bring about ROMP, has given rise to much discussion on the relationship between vinyl addition (VA) and ROMP [6–8]. In many cases, the same catalyst systems can induce VA of one olefin and ROMP of another [9,10]. This could be explained if an interconversion between the two propagating species occurs. For instance, Cooper provided evidence for the existence of an equilibrium between a metal methyl complex and a metal methylene hydride complex in a catalyst system for VA polymerisation [11]. If a cycloalkene can react separately with the two distinct species,

\* Corresponding author. Tel.: +91-44-445-8254; fax: +91-44-235-0509.

E-mail addresses: gsundar@acer.iitm.ernet.in (G. Sundararajan), kaminsky@chemie.uni-hamburg.de (W. Kaminsky).



Scheme 1. Suggested mechanism for the conversion of VA to metathesis.

then the polymerisation will result in polymers containing both vinyl-added and ring-opened units. Also, the catalyst systems that bring about VA or ROMP of cyclic olefin monomers are similar in structure. So with minor variations in reaction conditions, either of the two modes of polymerisations can be invoked [12]. Mechanistically also, similarities between polymerisation by VA and/or by metathesis exist. For example, the most commonly accepted Cossee–Arlman mechanism for Ziegler–Natta (or VA) polymerisation of olefin proposes an incipient metallacyclobutane intermediate [13]. In ROMP, the key intermediate also responsible for the propagation of the polymerisation is a metalla-

cyclobutane [14]. Besides, in metathesis polymerisation of alkynes, with a metal carbene catalyst, the propagating species is a metallacyclobutene. With these facts, we reasoned that a typical vinyl polymerisation could be converted to a metathesis polymerisation by interrupting the course of the reaction with a reactive transfer reagent like phenylacetylene (PA) (vide Scheme 1). In this paper, we report our results on the attempts made for switching the mechanism from VA to ROMP. The catalysts employed for this study were: (i) the titanium-based diolate catalyst **1** reported from our laboratory [15] and (ii) the well known constrained geometry complex **2** (Fig. 1). MAO was used as the cocatalyst<sup>1</sup>.

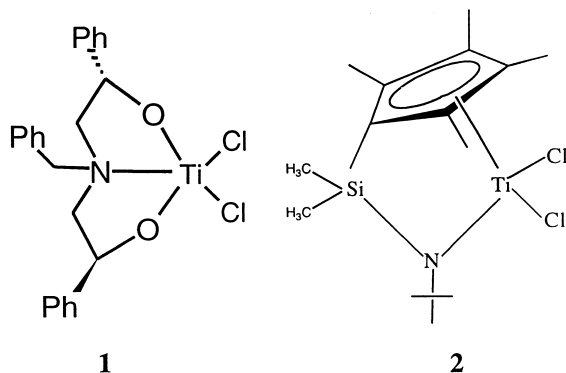


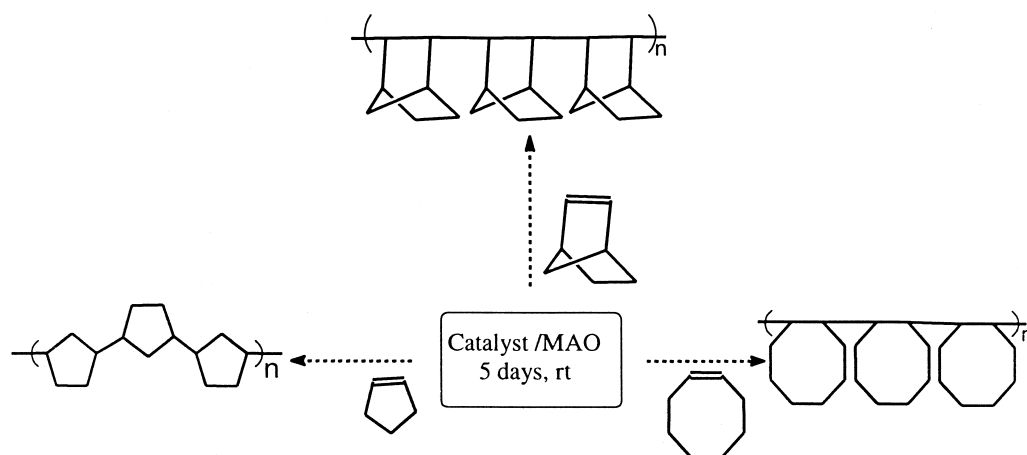
Fig. 1. Catalysts employed for polymerisation.

## 2. Experimental

### 2.1. General procedures

Catalyst preparation and polymerisations were carried out under dry and oxygen free argon

<sup>1</sup> Preliminary results have been communicated to *Macromol. Rapid Commun.* by the authors.



Scheme 2. Homopolymerisation of cyclic olefins.

atmosphere. Transfers were performed in argon-filled glove bag or by standard syringe techniques. Catalyst **1** was synthesised in our laboratory by reacting the diol derived from styrene oxide and benzylamine and  $\text{Ti}(\text{O}^i\text{Pr})_4$  [15]. MAO and catalyst **2** used were supplied by Witco, Germany. NBE, CP, cyclooctene (CO) and PA were bought from Merck–Schuchardt and were used as such.  $^1\text{H}$  nuclear magnetic resonance (NMR) (400 MHz) spectra were recorded using JEOL GSX400 high-resolution spectrometer in  $\text{CDCl}_3$  at  $45^\circ\text{C}$  or with 1,3,5-trichlorobenzene at  $100^\circ\text{C}$  with 10%  $\text{vol}^{-1}$  of benzene  $d_6$ . The monomer contents (for activity studies) were determined by Nucon 5700 Gas Chromatography using OV-17 stainless steel column of 3 m length maintained at  $90^\circ\text{C}$  using dodecane as internal standard.

## 2.2. Polymerisation procedure

Dry deaerated toluene (30 ml), the catalyst solution in toluene, (1 ml, 0.021 mmol) and MAO in toluene (2.1 ml, 4.2 mmol) were added by syringe to a clean, dry, argon-filled 100 ml round-bottomed flask equipped with a Teflon<sup>®</sup>-coated magnetic stirrer bar and a septum. The mixture was stirred for about 10 min and then NBE in toluene solution (10 ml, 0.04 mol) was added into the flask. The reaction mixture was

stirred for about a day, then PA in toluene (2 ml, 0.9 mmol) was added and stirring was continued under argon atmosphere. After some-time, the second monomer (5 ml, 0.03 mol) in toluene solution was added and stirred for another 2 days. The contents were then poured into 5% acidified methanol, filtered, washed and dried in vacuum. The second monomer used was NBE, CP or CO. The same procedure was adopted for homopolymerisation also except that the reaction mixture was stirred for 5 days after adding the required quantity of monomer.

## 2.3. Kinetics of polymerisation

The activities of the catalysts were determined by monitoring the concentration of NBE at the start of the reaction and at regular intervals of time. This was done by withdrawing 1

Table 1  
Homopolymerisation of cyclic olefins

Number	Polymer	Yield %	
		Catalyst <b>1</b>	Catalyst <b>2</b>
1	PolyNBE	26	21
2	PolyCP	21	–
3	PolyCO	20	23

Reaction volume = 50 ml; solvent = toluene; catalyst = 0.021 mmol; MAO = 4.2 mmol; monomer = 0.05 mol; temperature =  $30^\circ\text{C}$ .

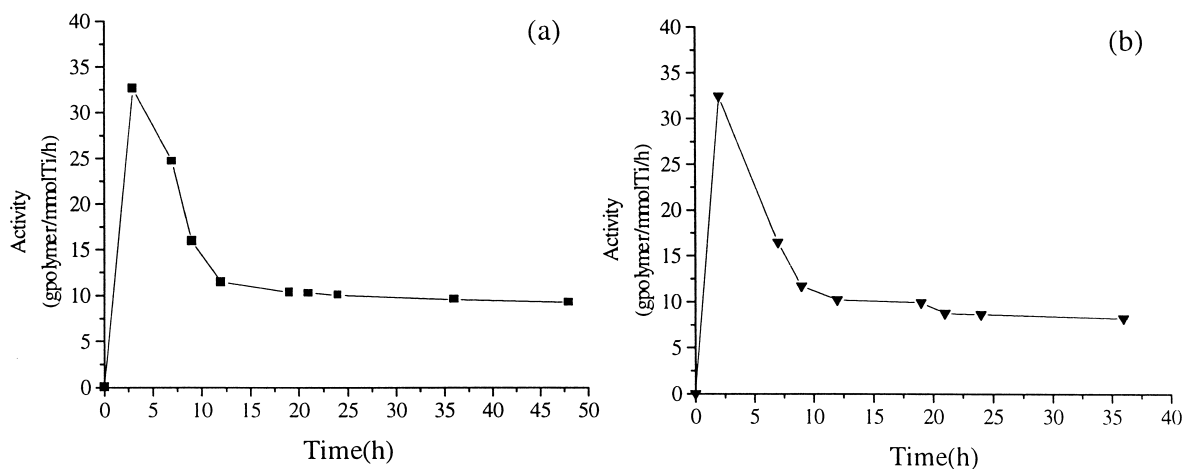
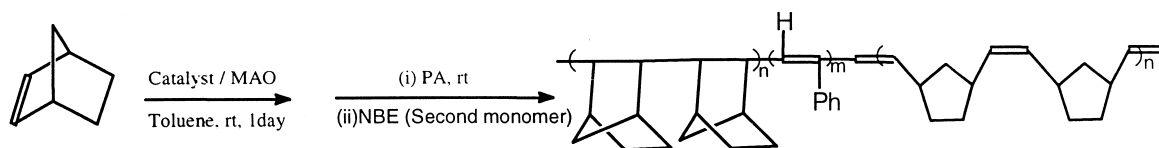


Fig. 2. Time-dependent activity for the homopolymerisation of NBE: (a) catalyst **1**, (b) catalyst **2**.



Scheme 3. Proposed structure for the product obtained by switching the mechanism from vinyl addition to ROMP.

ml aliquots, quenched with 4 ml of 5% acidic methanol and the amount of unreacted NBE in the solution was determined by gas chromatography.

### 3. Results and discussion

#### 3.1. Homopolymerisation of cyclic olefins

Catalysts **1** and **2** along with MAO were used for the polymerisation of cyclic olefins like

NBE, CP and CO (Scheme 2). Upon addition of MAO to catalyst **1**, the solution turned pale yellow in colour (with **2**, the solution turned to a dark orange). To this, the appropriate monomers were added and were stirred for 5 days. The results of the reactions are given in Table 1. The polymers were obtained in low but tangible yields as white fine powder. They had poor solubility in common organic solvents that precluded molecular weight determination by GPC. The  $^1\text{H}$  NMR spectrum of the polyNBE had broad signals in the region 1.0–2.3 ppm

Table 2  
Experimental details for converting the mechanism of polymerisation from VA to ROMP<sup>a</sup>

Number	First monomer	Second monomer	% Yield (% ring-opened units)	
			Catalyst <b>1</b>	Catalyst <b>2</b>
1	NBE	NBE	23 (37 <sup>b</sup> )	21 (39 <sup>b</sup> )
2	NBE	CP	21 ( <sup>c</sup> )	20 ( <sup>c</sup> )
3	NBE	CO	17 (32 <sup>b</sup> )	21 (30 <sup>b</sup> )

<sup>a</sup>Reaction volume = 50 ml; catalyst = 0.021 mmol; MAO = 4.2 mmol; NBE = 0.042 mol; PA = 0.9 mmol; second monomer = 0.03 mol; temperature = 30°C.

<sup>b</sup>Calculated from  $^1\text{H}$  NMR.

<sup>c</sup>Excess NBE underwent ring opening but not CP.

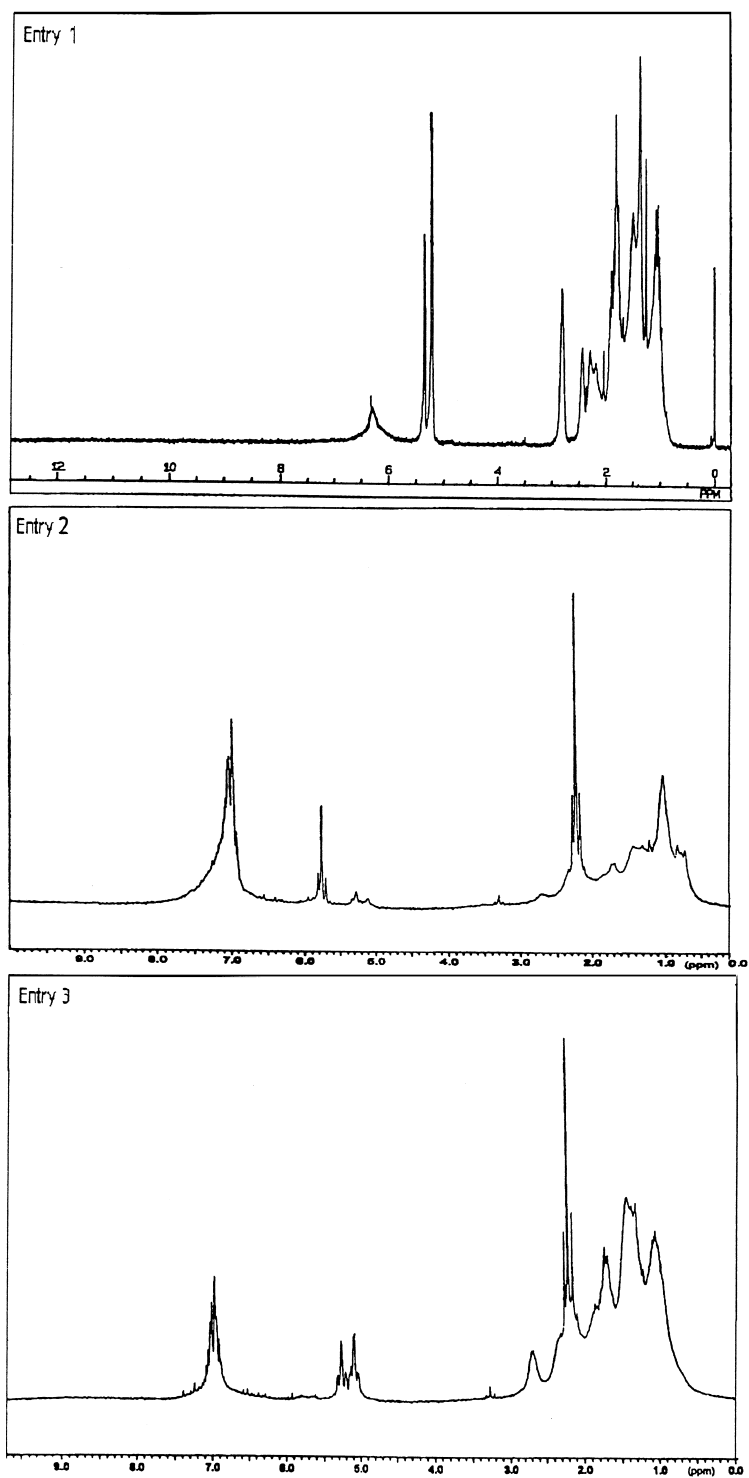


Fig. 3.  $^1\text{H}$  NMR of polymers in Table 2 obtained using **1**.

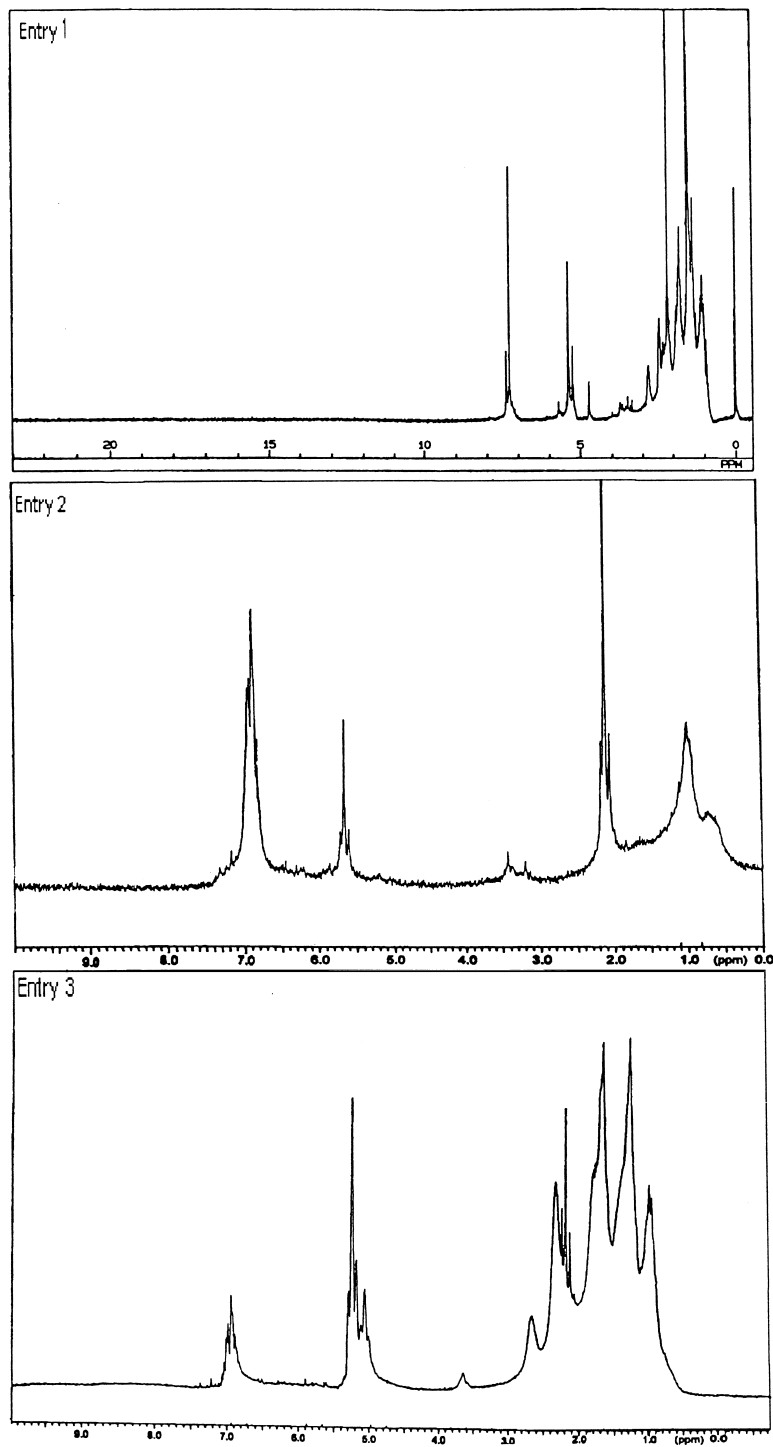


Fig. 4.  $^1\text{H}$  NMR of polymers in Table 2 obtained using 2.

which showed that only VA has occurred without any ROMP side reactions. The time-dependent activity of both the catalysts for the homopolymerisation of NBE was evaluated. It was found that the catalyst activity reached its maximum in 2 h after which, it reached a constant value at the end of 20 h (Fig. 2). The activity of catalyst **1** was found to be 10 g polymer mmol Ti<sup>-1</sup> h<sup>-1</sup> and **2** had an activity of 8 g polymer mmol Ti<sup>-1</sup> h<sup>-1</sup>.

### 3.2. Switching the mechanism of polymerisation from VA to metathesis

The polyNBE so obtained showed no ring-opened units by NMR. This encouraged us to test our hypothesis for switching the mechanism of polymerisation from VA to ROMP by addition of a reactivity transfer agent like PA. The expected outcome of such experiment is shown below (Scheme 3) and the yield of the polymers obtained is given in Table 2. The polymers obtained were pale yellow amorphous powders and were highly insoluble in common organic solvents, but could be analysed by <sup>1</sup>H NMR using 1,3,5-trichlorobenzene with 10% v/v of C<sub>6</sub>D<sub>6</sub> at 100°C. For polymers obtained after the addition of PA, signals were seen in the alkyl region as well as in the olefinic regions (Fig. 3 and 4). The ratio of integration of the peaks in the alkyl regions and the olefinic regions in the <sup>1</sup>H NMR spectra of polymer was used to calculate the percentage of ring-opened structures (Table 2). From the NMR of the polymer obtained with CP as second monomer (entry 2, Table 2) we could infer that apart from CP, some of the NBE present in the reaction mixture had also undergone ring-opening. This might be due to the lesser strain in the CP molecule compared to that of NBE, making NBE more reactive towards ROMP.

In the above experiment, PA was added after 24 h of VA of NBE and the ring-opened units were found to be 37%. In order to see whether the composition of the ring-opened units could

be increased if PA were added earlier, PA was added after 6 and 12 h of initiating VA polymerisation. It was seen from the <sup>1</sup>H NMR of the concerned product polymer that there was a substantial increase in the relative amount of ring-opened units. These polymers were also pale yellow in colour and had poor solubility. Since addition of PA brought about a change in the mechanism, we wanted to check whether ROMP could be brought about if the polymerisation were initiated by PA, i.e. adding the alkyne to the catalyst/MAO unit *prior* to the addition of the cyclic olefin. Here, the polymerisation was induced in the same way as described earlier by adding 20 equivalents of PA. After 2 h, NBE was added and the mixture was stirred for 3 days at room temperature. The <sup>1</sup>H NMR of the polymers so obtained indicated 79% of the ring-opened units for the catalyst **1**, whereas the catalyst **2** gave 84% ring-opened units (see Fig. 5, 0 h of PA addition)

### 3.3. Kinetics of mechanism switching process

The kinetic studies on the homopolymerisation of NBE by both catalysts **1** and **2**, upon monitoring of the change in concentration of the monomer, gave linear plots with rate constants of  $1.5 \times 10^{-2}$  and  $1.76 \times 10^{-2}$  h<sup>-1</sup>, respec-

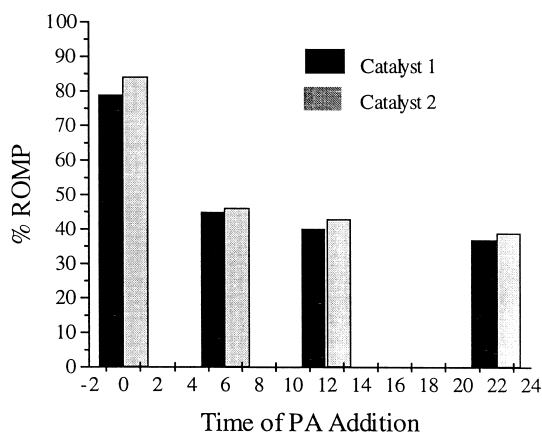


Fig. 5. Plot of percent ROMP vs. time of PA addition.

tively (Fig. 6a and b). When we brought about a change in mechanism of polymerisation from VA to ROMP by adding PA in the middle of

the reaction, we found that in case of catalyst **1**, the rate constant increased from  $1.4 \times 10^{-2}$  (VA) to  $5.8 \times 10^{-2} \text{ h}^{-1}$  (ROMP) after the addi-

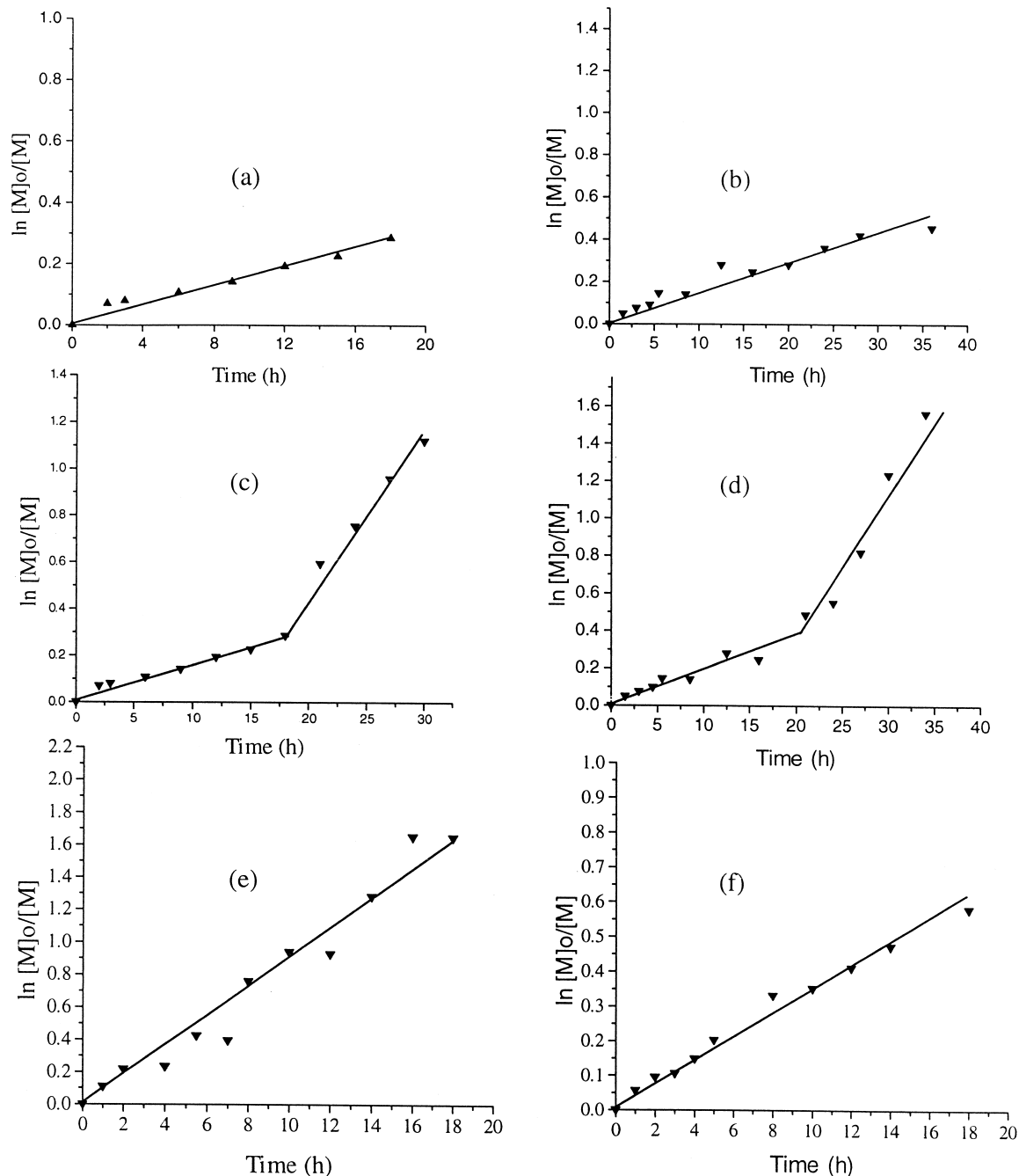


Fig. 6. Plots of  $\ln [M]_0/[M]$  vs. time. (i) Homopolymerisation of NBE using (a) catalyst **1**, (b) catalyst **2**, (ii) conversion of VA to ROMP using (c) catalyst **1**, (d) catalyst **2**, (iii) PA-initiated NBE polymerisation using (e) catalyst **1**, (f) catalyst **2**.



tion of PA (Fig. 6c). For **2**, the rate constants increased from  $1.65 \times 10^{-2}$  to  $8.96 \times 10^{-2} \text{ h}^{-1}$  (Fig. 6d). As expected, the initial rate constants for the vinyl polymerisation in the switching process matched well with the homopolymerisation values. For the polymerisation of NBE initiated by PA, the rate constants for catalysts **1** and **2** were  $6.4 \times 10^{-2}$  and  $9.1 \times 10^{-2} \text{ h}^{-1}$ , respectively. These values also correlated well with the rate constants obtained after addition of PA in the conversion process (Fig. 6e and f). The change in kinetic profile was the same even if the PA addition was done after 6 and 12 h. (Fig. 7) The rate constants were found to be

linearly dependent on the concentration of the catalyst following a pseudo-first-order law as expected and also suggested that the concentration of the active centres remained constant.

### 3.4. Arrhenius parameters for VA and ROMP

The kinetic profile shown for the switchover in mechanism was also found to be similar for a range of temperatures allowing us to determine the activation parameters for this reaction (Fig. 8). Thus, the Arrhenius parameters for both VA and ROMP using both the catalysts with NBE

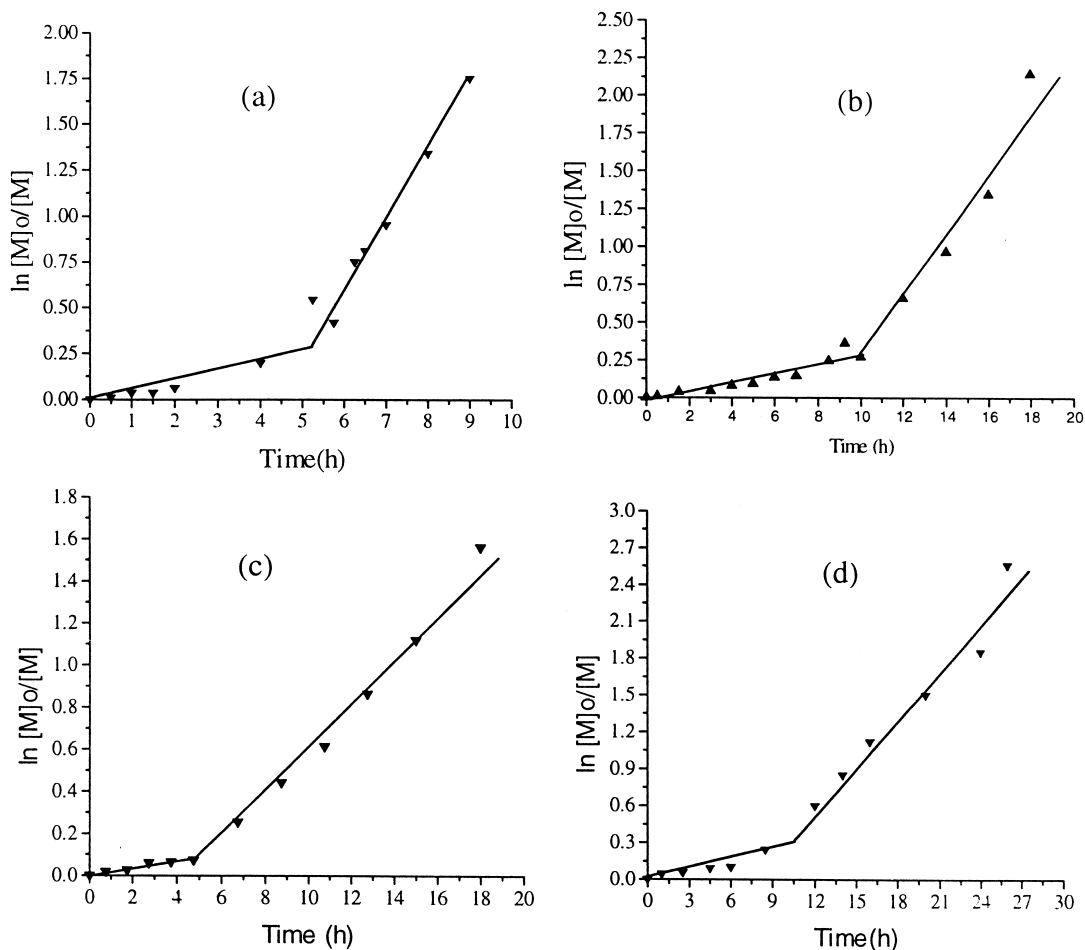


Fig. 7. Kinetic plots for switching the mechanism of polymerisation at different time intervals of PA addition (i) using catalyst **1** (a) after 6 h (b), after 12 h, (ii) using catalyst **2** (c) after 6 h, (d) after 12 h.

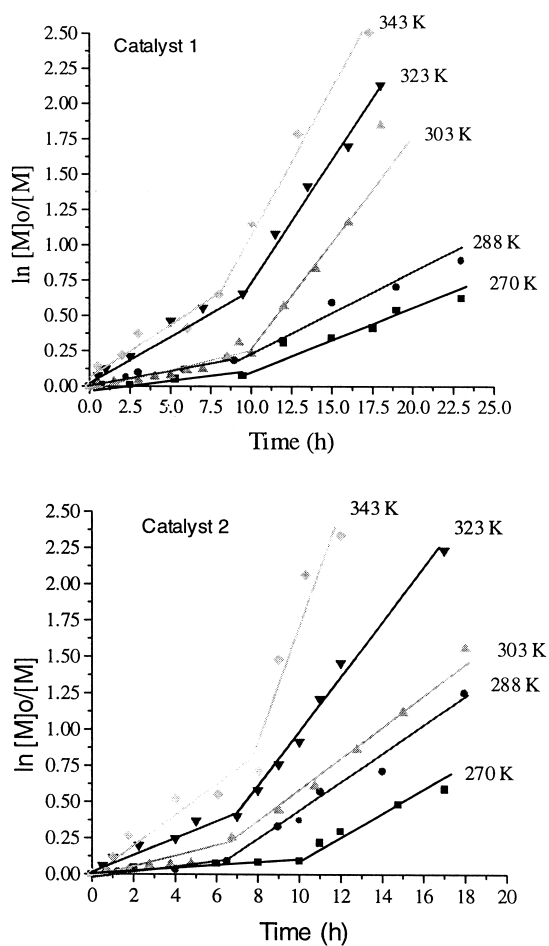


Fig. 8. Kinetic profile for the conversion at different temperatures.

as monomers were calculated and shown in Table 3. The Arrhenius parameters obtained for both the catalysts also indicate a similarity in the catalyst behaviour and support the suggested

Table 3  
Arrhenius parameters<sup>a</sup> for VA and ROMP

Number	Mode of polymerisation	Catalyst 1		Catalyst 2	
		ln A	$E_a$ (kJ mol <sup>-1</sup> )	ln A	$E_a$ (kJ mol <sup>-1</sup> )
1	Vinyl addition	10.4	15.2	10.5	16.1
2	ROMP	9.8	11.3	9.6	9.6

<sup>a</sup>The activation parameters relate to pseudo-first-order rate constants and also to the assumption that the concentration of the active centres does not change with temperature (refer to text).

change in mechanism during the course of polymerisation by addition of PA.

#### 4. Conclusion

Polymers containing both the vinyl and the ring-opened structure were synthesised by switching the mechanism of polymerisation from VA to ROMP by adding a suitable reactivity transfer reagent in the middle of the polymerisation. This was supported by kinetic data and the corresponding activation parameters. Further attempts to characterise these polymers are in progress.

#### Acknowledgements

One of the authors (G.S.) thanks BMBF Germany for the collaborative research work. We thank Witco, Germany, for supplying MAO and catalyst 2 as gift samples and RSIC, IIT Madras for high-resolution NMR.

#### References

- [1] W. Kaminsky, J. Chem. Soc., Dalton Trans. (1998) 1413.
- [2] A. Montagna, A.H. Dekmezian, R.M. Brukhart, CHEMTECH (1997) 26, December.
- [3] W. Kaminsky, R. Spiechel, Makromol. Chem. 190 (1989) 515.
- [4] G.J.P. Britovsek, V.C. Gibson, D.F. Wass, Angew. Chem., Int. Ed. Engl. 38 (1999) 428.

- [5] K.J. Ivin, J.C. Mol, *Olefin Metathesis and Metathesis Polymerisation*, Academic Press, London, 1997.
- [6] G. Dall'Asta, *J. Polym. Sci., Part A-1* 6 (1968) 2397.
- [7] A.A. Olsthoon, C. Boelhouwer, *J. Catal.* 44 (1976) 207.
- [8] D.T. Lavery, J.J. Rooney, *J. Chem. Soc., Faraday Trans. 1* 79 (1983) 869.
- [9] P.R. Hein, *J. Polym. Sci., Polym. Chem. Ed.* 11 (1973) 163.
- [10] G. Natta, G. Dall'Asta, G. Mazzanti, *Angew. Chem., Int. Ed. Engl.* 3 (1960) 723.
- [11] N.J. Cooper, M.L.H. Green, *J. Chem. Soc., Chem. Commun.* (1974) 209.
- [12] I. Tritto, M.C. Sacchi, R.H. Grubbs, *J. Mol. Catal.* 82 (1993) 103.
- [13] E.J. Arlman, P. Cossee, *J. Catal.* 3 (1964) 99.
- [14] L.R. Gilliom, R.H. Grubbs, *J. Am. Chem. Soc.* 108 (1986) 733.
- [15] G. Manickam, G. Sundararajan, *Ind. J. Chem., Sect. B* 35 B (1996) 1006.