

## Recent advances in the polymerisation of propylene\*

S SIVARAM

Research Centre, Indian Petrochemicals Corporation Limited, Vadodara 391 346, India

MS received 21 February 1983

**Abstract.** Since its discovery, the field of olefin polymerization using Ziegler-Natta catalysts has undergone rapid development both in terms of industrial catalysis as well as fundamental understanding of this polymerization process. This paper reviews some aspects of the recent developments with specific regard to propylene polymerizations.

**Keywords.** Polymerization; propylene; stereospecificity; regioselectivity

### 1. Introduction

Polymerization of ethylene to higher molecular weight polyethylene catalyzed by transition metal compounds was discovered by Ziegler and coworkers about 25 years ago. Subsequently, Natta extended this study to alpha olefins wherein he demonstrated the capability of these catalysts to synthesize sterically regular polymer chains (stereospecific polymerizations). His pioneering work uncovered a whole new field of polymer science with significant scientific and industrial potentialities. Polyolefins and polydienes manufactured using Ziegler-Natta catalysts, achieved rapid commercial maturity finding widespread applications as plastics, rubbers and fibers.

The field of Ziegler-Natta catalysts has been characterized since its discovery by two distinct features. One, it has had considerable commercial potential as a route to synthesise useful polymeric materials from relatively inexpensive chemical feedstocks such as ethylene, propylene, butadiene etc. Secondly, olefin polymerizations catalyzed by Ziegler-Natta catalysts provide an unique example of stereospecificity in organic non-enzymatic reactions. On both fronts, the field has witnessed rapid development in recent years. New developments in catalysts have considerably simplified polymer production processes; and the new understanding on the polymerization mechanism and the origin of stereospecificity has led to visions of even more significant discoveries in this area in years to come.

This paper reviews some recent developments in propylene polymerization processes and summarizes the present state of understanding of the mechanism of stereospecific polymerization. A wider coverage of the literature is available in a recent monograph (Boor 1979) and in a large number of reviews (Pino and Mulhaupt 1980; Sinn and Kaminsky 1980; Tait 1980).

### 2. Catalyst developments

The conventional Ziegler-Natta catalysts consists of a combination of transition metal halide or alkoxide or alkyl or aryl derivative with a main group element alkyl or

\* Presented at the Symposium on 'Polymer Science and Engineering during the Annual Meeting of the Academy, Nainital, October 1982

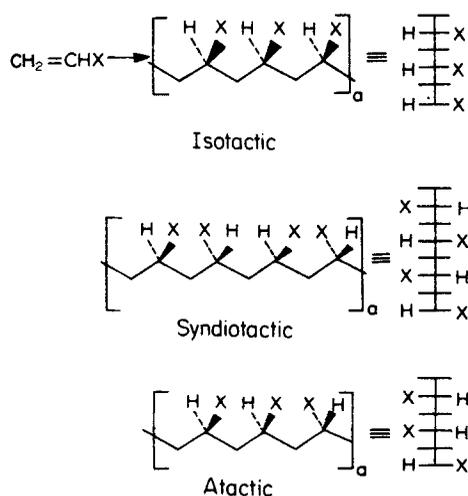
IPCL Communication No. 60

alkyl halide. Some typical catalyst combinations used for the polymerization of ethylene and propylene are shown in table 1. Unlike ethylene, which is achiral, propylene is prochiral and therefore upon polymerization gives polymers with two distinct configurations, namely isotactic and syndiotactic (scheme 1) depending on the position of the methyl group (Quirk 1981). A random distribution of the methyl group across the polymer chain is termed as atactic and is usually an undesirable product. The conventional Ziegler-Natta catalysts employed in industry produce about 1–5 kg polymer/g titanium and about 5–8% atactic polymer. It is therefore necessary to purify the polymer from metallic catalyst residues as well as from the less crystalline atactic polymer.

To appreciate fully the nature of some recent developments in catalysts, it will be necessary to briefly summarize the present state of understanding of the mechanism of Ziegler-polymerization. Accumulated evidence now favours a mechanism in which polymer growth occurs on the transition metal part of the catalyst which first gets

**Table 1.** Olefin polymerization using Ziegler-Natta catalysts.

Olefins	Transition metal	Organometal	Physical state	Tacticity
Ethylene	TiCl <sub>4</sub> , Ti(OR) <sub>4</sub> VCl <sub>4</sub>	R <sub>3</sub> Al, R <sub>2</sub> AlCl	Partially hetero- geneous or homogeneous	—
Propylene	TiCl <sub>3</sub> , TiCl <sub>2</sub> , VCl <sub>2</sub> , CrCl <sub>3</sub>	R <sub>3</sub> Al, R <sub>2</sub> AlCl	Heterogeneous	Isotactic
	TiCl <sub>4</sub> , VCl <sub>4</sub> , VOCl <sub>3</sub>	R <sub>3</sub> Al, R <sub>2</sub> AlCl	Partially heterogeneous	Isotactic + Atactic
	VO(OR) <sub>3</sub>	R <sub>2</sub> AlCl	Homogeneous	Atactic
	VCl <sub>4</sub> , Anisole Cr(acac) <sub>3</sub>	R <sub>2</sub> AlCl	Homogeneous	Atactic (–30°C) Syndiotactic (–78°C)



**Scheme 1.** Configuration of isotactic, syndiotactic and atactic polypropylene.

alkylated by the alkyl aluminium compound. The active site is envisaged as a titanium centre with both an alkyl substituent and a chlorine vacancy located on the edges of the  $\text{TiCl}_3$  crystal. Growth occurs by complexation of propylene on the vacant site followed by insertion of the polymer chain at the transition metal-carbon bond (scheme 2). In a typical Ziegler catalyst consisting of  $\text{TiCl}_3\text{-Et}_2\text{AlCl}$ , the number of active sites is about  $1.5 \times 10^{-3}$  mole/mole titanium (Chumaevskii *et al* 1976). Although these are most likely instantaneous values, they do explain the low catalytic activity of Ziegler catalyst.

The active site described above could be located on the basal plane (A), edge (B) or corner (C) of the Ti crystal lattice (Boor 1963; Arlman and Cossee 1964; Carrick 1973). Microscopic examination of polymer growth suggests that the sites located on the basal planes are comparatively inert, being buried in a layer of chloride ion matrix (Rodriguez and van Looy 1966). Nevertheless, on sites A and B,  $\pi$ -complexation of the olefinic bond in propylene can occur only with its plane of symmetry perpendicular to the metal orbital and with the methyl group pointing away from the crystal surface and the ligands attached to it to minimize unfavourable interactions. Such restrictions is not operative at the corner sites (C) where the monomer can approach with equal ease either in the same manner as in A or B or in the flipped over position. On the basis of this model, site B will lead to isotactic placement whereas site C to atactic placement of the methyl group in polypropylene.

Based on this model it can be construed that increasing the dispersion of titanium on the surface could lead to improved catalytic activity. One approach to realize the objective was to support titanium halide on a high surface area support. Effective supports were identified as those which can form a continuous solid state structure with titanium halides. A variety of  $\text{Mg}^{+2}$  salts have been explored but  $\text{MgCl}_2$  has been particularly successful due to its crystalline similarity to  $\alpha$  or  $\nu$ - $\text{TiCl}_3$  (ionic radius of  $\text{Ti}^{+4}$  or  $\text{Ti}^{+3} = 0.68 \text{ \AA}$ ,  $\text{Mg}^{+2} = 0.65 \text{ \AA}$ ) and its ability to maximize the reactive sites by packing titanium at the edge of the carrier (Kashiwa 1981). X-ray evidence indicates that  $\text{Ti}^{+3}$  and  $\text{Ti}^{+4}$  can be effectively dispersed on  $\text{MgCl}_2$  lattice forming 'surface' mixed crystals (Galli *et al* 1981). Using such catalysts substantial increase in polymer yield per unit weight of catalyst has been achieved for polyethylene and polypropylene thereby eliminating the need to remove catalyst residues. A review of patent literature on such catalyst has been published (Sivaram 1977).

In polypropylene, such increase in catalyst activity is always accompanied by loss of stereospecificity. Subsequent developments showed that stereospecificities of supported catalysts can be enhanced in the same way as in  $\text{TiCl}_3$  catalyst, *viz* by the judicious choice and use of certain polar adjuvants termed electron donors. Although the precise role of electron donors on Ziegler-Natta catalyst is not yet clear (Caunt 1963; Langer 1977; Pino and Mulhaupt 1980), its desirable effects are well established and is used in commercial practice.

Use of supported catalyst along with an alkyl aluminum cocatalyst and an electron donor in propylene polymerization has led to high yields and high isotacticity index (Galli 1980; Cipriani and Trischman Jr 1981). Patent literature is replete with examples of polar organic compounds used as electron donors. The preferred donors appear to be aromatic carboxylic acid esters such as ethyl benzoate, methyl-*p*-toluate, ethyl-*p*-anisate etc. Commercial manufacturing process for polypropylene using catalysts described above is in operation.

Although industrial research in this area has been vigorous for the past ten years as evidenced by patent literature, significant scientific understanding on how these

catalysts function has begun appearing only recently. Physico-chemical studies on active  $\text{MgCl}_2$  support has led to the identification of factors responsible for activity and the structural changes undergone by the support during physical or chemical processes employed for activation of anhydrous  $\text{MgCl}_2$  (Keszler *et al* 1980; Simon and Grobler 1980; Yokoyama 1980; Keszler *et al* 1981; Yermakov 1981; Chien *et al* 1982). The reasons behind high activity of such catalysts has been explored by measuring the concentration of active sites as well as kinetic determination of propagation rate ( $k_p$ ) and conflicting views have been expressed on the origin of catalyst activity. One group of workers has attributed the high activity to an increase in the number of active sites (Galli *et al* 1981) whereas another group has reported negligible changes in the number of active sites but a hundred-fold increase in  $k_p$  indicating high atomic activity of titanium (Suzuki *et al* 1979; Keii 1982). An intriguing suggestion has been made that increase in catalyst activity for ethylene is a result of increase in active site concentration whereas for propylene it is due to increase in  $k_p$  (Yermakov 1981).

Despite the limited understanding, certain essential characteristics of these catalysts in propylene polymerization have emerged: (i) they are capable of polymerizing propylene with high yield/g of titanium and high stereospecificity; (ii) generally, the catalysts show high initial rates which decay rapidly with time. In this respect they are similar to homogeneous catalysts; (iii) they require the use of trialkylaluminum cocatalyst and show poorer performance with diethyl aluminum chloride (Duck *et al* 1979). This is in contrast to  $\text{TiCl}_3$  which shows optimum performance in conjunction with diethylaluminum chloride; (iv) unlike conventional catalysts, high Al:Ti ratio is employed with supported catalyst. Trialkyl aluminum is also partially complexed with an electron donor, preferably an aromatic ester. A typical catalyst composition would be Ti:Al:ED = 1:500:160; (v) stereospecificity can be controlled by adjusting the aluminum alkyl-to-electron donor ratio; and (vi) supported catalyst offer better control over polymer particle size distribution. Polyolefin catalysts capable of producing narrow particle size distribution polymers with well-defined particle shapes are under commercialization. Such processes will obviate the need to extrude and pelletize polymer powder resulting in further substantial energy savings.

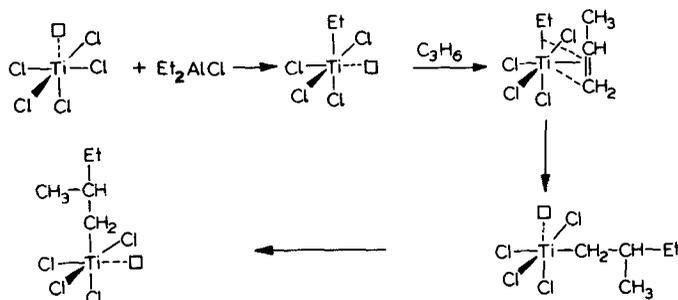
### 3. Origins of regio- and stereospecificity in olefin polymerizations

The unique regio- and stereospecificity of Ziegler-Natta catalysts has attracted considerable attention since its discovery. Attempts have been made to clarify the nature of catalyst and cocatalyst interactions, structure of active site, polymerization mechanism, origin of stereospecificity and the mechanism of olefin activation under mild conditions. These include kinetics (Keii 1972), theoretical calculations on models of the catalytic centre (Cossee 1964; Armstrong *et al* 1972; Novaro *et al* 1978; Corradini *et al* 1979) reactions leading to catalytic species (Boor 1979), investigations of model reactions and analogs and structure and stereochemistry of synthesized polymers. Although every approach has contributed to our understanding, it is the last of those mentioned above which has provided some unequivocal answers to many of the outstanding problems in this area. The structure of the polymer is a sensitive yet permanent imprint of what happened during every stage of polymer growth. It is therefore natural that an ability to read the structure using tools such as proton NMR or  $^{13}\text{C}$ -NMR has led to valuable insight into the mechanism of polymerization.

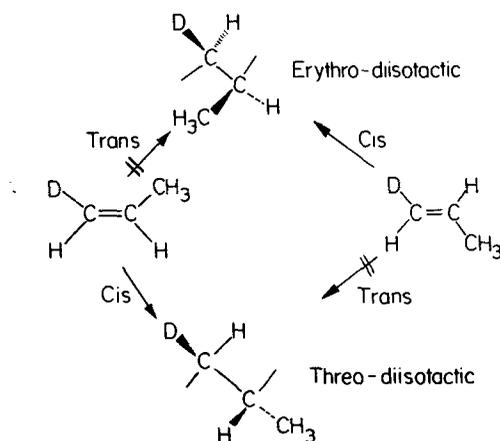
## 3.1 Regioselectivity

When ethylene polymerizes by an insertion reaction between a metal atom and the growing chain (scheme 2), only one product can form, since it is an olefin having  $D_{2h}$  symmetry. The situation is different with propylene ( $C_s$  symmetry). Depending upon whether (i) the primary or secondary carbon atom is linked to the metal atom (ii) the addition is 1,2 or 2,1 and (iii) which of the two prochiral faces of propylene participates in insertion, eight possible geometric structural variations can occur (Pino and Mulhaupt 1980). The type of insertion and its regularity will determine respectively the regiospecificity and stereospecificity of polymerization. It is now recognised that for isotactic polypropylene insertion proceeds with high regiospecificity (greater than 95% 1,2 addition). Studies of the structure of polymer produced from *cis* and *trans*-1-deuteriopropylene has also established that monomer insertion occurs through a *cis* addition to the double bond (scheme 3, Zambelli *et al* 1968).

Syndiotactic hydrocarbon polymers have been obtained only in polypropylene and 1,2-polybutadiene where the degree of regiospecificity is also less. It has been shown



**Scheme 2.** Monometallic mechanistic formalism for polymer chain growth on transition metal catalyst.



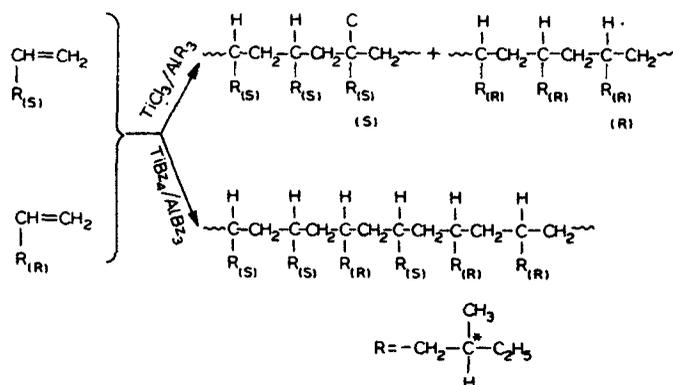
**Scheme 3.** Potential stereochemical structures from *cis*- and *trans* addition.

that with a soluble vanadium catalyst at low temperatures, a 2,1 insertion into a metal to secondary carbon bond predominates (Zambelli and Sacchi 1974). The generality of such addition is far from proven. The origin of regioselectivity in Ziegler-Natta catalysts has never been fully understood. Depending on the type of catalyst used, regioselectivity in the propylene polymerization can vary between 95–99% for 1,2 type and over 85% for 2,1 type. Neither can the catalyst be manipulated at the present time to produce a desired or variable combination of both 1,2 and 2,1 insertion.

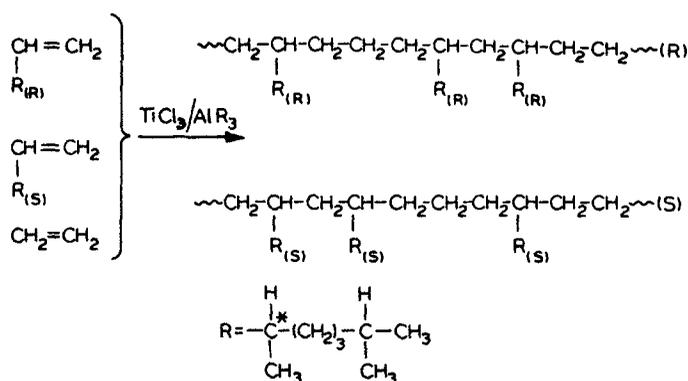
### 3.2 Stereospecificity and stereoselectivity

The unique feature of the Ziegler-Natta catalysts lies in their ability to regulate the stereochemistry of insertion of every successive propylene molecule. This is related to the ability of the active centre on the catalyst to favour complexation of one prochiral face of propylene over the other for which the active centre should itself be chiral. Experimental evidence shows that the metal atom bound to a solid surface possesses centres of chirality. Catalysts of the type  $TiCl_3/AlR_3$  are able to distinguish between the *R* and *S* isomer of a racemic  $\alpha$ -olefin, resulting in stereoselective polymerizations (scheme 4, Pino *et al* 1975). Copolymerization of ethylene with a racemic  $\alpha$  olefin also leads to stereoselective polymerization although the asymmetric carbon atom is in position  $\delta$  to the metal centre (scheme 5, Ciardelli *et al* 1974). Further evidence that the stereoregulating factor does not lie in the penultimate asymmetric carbon atom, but actually on the metal centre comes from an analysis of the defect structures in polypropylene (Wolfgruber *et al* 1974). The various possible defect structures in polypropylene are shown in scheme 6 using the *m* and *r* notation (Frisch *et al* 1966). The fact that pentads of the type *mrmm* have never been found but *mrmm* occurs indicates that even if occasional configurational inversion occurs, it is not perpetuated, as would be the case if the penultimate asymmetric carbon atom were to control the stereochemistry of the incoming propylene molecule.

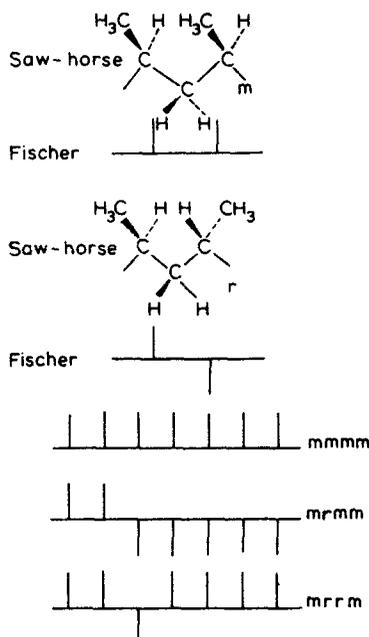
The precise factors which enables the catalytic centre to exercise such sharp selection is not known. An energy difference exists between transition states leading to an isotactic dyad or to a syndiotactic dyad which could be attributed to steric and



**Scheme 4.** Stereoselective polymerization of racemic 4-methyl-1-hexene using insoluble catalyst  $TiCl_3/AlR_3$ .



**Scheme 5.** Stereoselective co-polymerization of racemic 3,7-dimethyl-1-octene with ethylene.



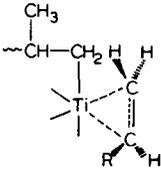
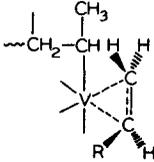
**Schem 6.** Representative pentad structures in polypropylene depicted using the m(meso) and r(racemic) relation for diastereo isomeric dyads according to Frisch *et al* 1966.

electrostatic interaction of the ligand-monomer type originally proposed for isotactic regulation on  $\text{TiCl}_3$  surfaces (Boor 1963; Arlman and Cossee 1964; Carrick 1973).

Although investigated to a lesser degree; it appears that syndiotactic propagation by homogeneous catalyst ( $\text{VCl}_4/\text{Et}_2\text{AlCl}$ ) can be attributed to the chirality of the secondary carbon atom attached to the metal (Zambelli *et al* 1978; Zambelli and Allegra 1980).

The distinguishing features of isotactic and syndiotactic propagation of propylene are summarized in table 2.

Table 2. Essential features of isotactic and syndiotactic polymerization.

	Propagation	
	Isotactic	Syndiotactic
Addition to double bond	Cis	Cis
Monomer insertion	1,2	2,1
Chiral centre of steric control	Transition metal	Penultimate asymmetric secondary carbon atom
		

#### 4. Prognosis

The area of Ziegler polymerization continues to be as exciting as it was when it was first discovered some 25 years ago. Advances based on empirical concepts have changed the nature of industrial process, resulting in energy-efficient, effluent-free production processes. Simultaneously, a better understanding of how these catalysts function has been gained as a result of which further significant developments in this area can be expected. Some of these are tailored catalysts that will enable control of regio- and stereospecificity as well as molecular weight distribution and catalysts capable of polymerizing propylene with high yield and high stereospecificities at temperatures higher than presently used (greater than 80°C) resulting in better utilization of enthalpy of polymerization which is otherwise wasted, reduced residence time, better polymer morphologies and if the temperature is sufficiently high, energy savings in powder melting prior to extrusion.

Our understanding of how active centres perform stereospecific polymerization can also be expected. Insufficient attention has so far been paid to the following approaches: (i) direct examination of catalysts with high concentration of active sites using newer tools of surface analysis; (ii) study of discrete isolable organometallic complexes capable of undergoing insertion reaction with olefins, either in solution or anchored to surfaces permitting observation of polymer chain growth. The recently reported tantalum neopentylidene hydride diiodide complex capable of polymerizing ethylene without an alkylaluminum cocatalyst offers a rare glimpse of the potentialities of this approach (Turner and Schrock 1982). Also, all isospecific propylene polymerization catalysts are heterogeneous. Although at one time zirconium tetrabenzyl was thought of as a homogeneous catalyst capable of polymerizing propylene to isotactic polypropylene (Giannini *et al* 1970), later results have failed to confirm this hypothesis (Soga *et al* 1977). Yet, the present understanding of the origin of stereospecificity does not preclude the existence of a chiral homogeneous catalyst capable of producing isotactic polypropylene. A key to the progress in this area is a systematic study of the chemistry of soluble titanium complexes with varying ligand environments, capable of inducing or conserving a chiral environment around the metal atom yet possessing the necessary electronic structure required for chain growth.

## References

- Arلمان E J and Cossee P 1964 *J. Catal.* **3** 99
- Armstrong D R, Perkins P G and Stewart J J P 1972 *J. Chem. Soc. Dalton. Trans.* **1** 1972
- Boor J 1963 *J. Polym. Sci.* **C1** 237
- Boor J 1970 *Ind. Eng. Chem. Prod. Res. Dev.* **9** 437
- Boor J 1979 *Ziegler-Natta catalysts and polymerizations* (New York: Academic Press)
- Burfield D R and Tait P J T 1974 *Polymer* **15** 87
- Carrick W L 1973 *Adv. Polym. Sci.* **12** 65
- Caunt A D 1963 *J. Polym. Sci.* **C4** 49
- Chien J C W, Wu J C and Kuo C I 1982 *J. Polym. Sci. Polym. Chem. Educ.* **20** 2019, 2461
- Chumaevskii N B, Zakharov V A, Buktov G D, Kuzhetzova G I and Yermakov Y I 1976 *Makromol. Chem.* **177** 747
- Ciardelli F, Locatelli P, Marchetti M and Zambelli A 1974 *Makromol. Chem.* **175** 923
- Cipriani C and Trischman C A Jr 1981 *J. Appl. Polym. Sci. Appl. Polym. Symp.* **36** 101
- Corradini P, Barone V, Fiusco R and Guerra G 1979 *Eur. Polym. J.* **15** 1133
- Cossee P 1964 *J. Catal.* **399**
- Duck E W, Grant D and Kronfli E 1979 *Eur. Polym. J.* **15** 625
- Frisch H L, Mallovs C L and Bovey F A 1966 *J. Chem. Phys.* **45** 1505
- Galli P 1980 *IUPAC Int. Symp. Macromolecules* (Florence) p. 63
- Galli P, Luciani L and Cechin G 1981 *Die Angew Makromol Chem.* **94** 63
- Giannini U, Zucchini U and Albizzati E 1970 *J. Polym. Sci. Polym. Lett. Educ.* **8** 405
- Kashiwa N 1981 *Polymer J.* **12** 603
- Keii T 1972 *Kinetics of Ziegler-Natta polymerization* (London: Chapman Hall)
- Keii T, Suzuki E, Tamura M, Murata M and Doi Y 1982 *Makromol. Chem.* **183** 2285
- Keszler B, Bodor G and Simon A 1980 *Polymer* **21** 1037
- Keszler B, Grobler A, Takaes E and Simon A 1981 *Polymer* **22** 818
- Langer A W 1977 *Ann. NY Acad. Sci.* **295** 110
- Novaro O, Blaisten-Barojas E, Clementi E, Giunchi G, Ruiz-Vizcaya M E 1978 *J. Chem. Phys.* **68** 2337
- Pino P and Mulhaupt R 1980 *Angew. Chem. Int. Ed. English* **19** 857
- Pino P, Oschwald A, Ciardelli F, Carlini C and Chiellini E 1975 *Coordination polymerization* (ed.) J C Chien (New York: Academic Press) p. 25
- Quirk R P 1981 *J. Chem. Educ.* **58** 540
- Rodriguez L A M and Van Looy H M 1966 *J. Polym. Sci.* **A1** 1951, 1971
- Simon A and Grobler A 1980 *J. Polym. Sci. Polym. Chem. Ed.* **18** 3111
- Sinn H and Kaminsky W 1980 *Adv. Organometallic. Chem.* **18** 99
- Sivaram S 1977 *Ind. Eng. Chem. Prod. Res. Dev.* **16** 121
- Soga K, Takanoy Gos and Keii T 1967 *J. Polym. Sci.* **5** 2815
- Soga K, Izumi K, Ikeda S and Keii T 1977 *Makromol. Chem.* **178** 337
- Suzuki C, Tamura M, Doi Y and Keii T 1979 *Makromol. Chem.* **180** 2235
- Tait P J T 1980 *Macromolecular chemistry* (Specialist)
- Turner H W and Schrock R R 1982 *J. Am. Chem. Soc.* **104** 2331
- Periodical Report (London: Royal Society of Chemistry)<sup>3</sup>
- Wolfsgruber C, Zannoni G, Rigamonti E and Zambelli A 1974 *Makromol. Chem.* **176** 2766
- Yermakov Y I 1981 *IUPAC Symp. on structural order in Polymers* **37**
- Yokoyama M 1980 *Proc 2nd Japan-Korea Symp. Polym. Sci. and Technol.* **78**
- Zambelli A, Giongo M and Natta G 1968 *Makromol. Chem.* **112** 183
- Zambelli A and Sacchi C 1974 *Makromol. Chem.* **175** 2213
- Zambelli A, Bajo G and Rigamonti E 1978 *Makromol. Chem.* **179** 1249
- Zambelli A and Allegra G 1980 *Macromolecules* **13** 42