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Polymerization of Butadiene Using Ziegler-Natta Catalysts—Recent Developments

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ABSTRACT

The products of Ziegler-Natta catalyzed reactions, including high density polyethylene, polypropylene, and other thermoplastics and elastomers, have become familiar to all. While an enormous volume of experimental work was completed during the 1950s and 1960s, it has only been during the 1970s that the multiplicity of mechanistic schemes developed have been subjected to scrutiny. The majority of these have been concerned with polymerization of ethylene and α-olefins and because they have been adequately reviewed recently, are discussed only briefly here. A similarly large volume of empirical experimental work has enabled commercial production of polybutadiene using stereoregular catalysts. However, the mechanisms involved are of recent development, largely due to the additional configurational complexity of products, the multicompound nature of the catalyst complex, and the susceptibility of the system to contamination. Advances which have been made during the last decade are highlighted, with particular emphasis on those modifications to catalyst or to polymer structure which are of practical importance. In Australia, all production of stereoregular (high cis) polybutadiene is achieved using an aluminum alkyl halide-cobalt salt based catalyst. The fundamental technology of this process is discussed with emphasis upon process control. In particular, the control of molecular weight, processing behavior, and reduction in cross-linked material are included in more recent developments. In a broader context, technological changes which have been stimulated by such diverse influences as the increased awareness of industrial hygiene, fluctuations in feedstock availability and cost, and the general acceptance of radial ply tires are discussed. Experimental activities currently in progress in Australia, together with challenges still remaining, are examined.

INTRODUCTION

The purpose of this review is to summarize the avenues being followed in the development of Ziegler-Natta catalyzed polymerization of olefins. The surge of activity which was maintained until the early 1970s has been thoroughly reviewed elsewhere, and so only the more salient details will be given here. The past decade has seen advances which are, in the main, refinements of existing systems, rather than novel discoveries, but the industrial significance of many of these evolutionary developments merits more detailed discussion.

The polymerization of butadiene using stereoselective catalysts has been exploited commercially for two decades, but because of the complexity of the catalyst system, much remains to be discovered. The developments of the last 10 years are reviewed, with some bias being applied to cobalt-based technology. This is done because there are adequate examples to illustrate the majority of advances being made, and because these catalysts are the most widely used for industrial production of high-cis polybutadiene. Changes which have arisen as a consequence of worldwide pressures (for example, the development of related polymers including high-impact polystyrenes, changes in occupational health standards, the shortage of suitable feedstocks during the 1974 "crisis," and the increasing demands for polymer with more stringently controlled molecular structure) have led chemical companies, in particular, to build heavily upon existing knowledge. The increasing demands placed upon the producer have produced highly refined process development, although much remains buried in patent literature or enshrined in proprietary files.

Major modifications will be highlighted, including some which have relevance to the Australian situation. Some of the challenges which the user of Ziegler-Natta catalysts will encounter during the 1980s will be mentioned.

GENERAL ASPECTS OF ZIEGLER-NATTA POLYMERIZATION OF OLEFINS

The pioneering studies of Ziegler [1] and Natta [2] during the early 1950s allowed, through the control of stereoregularity,

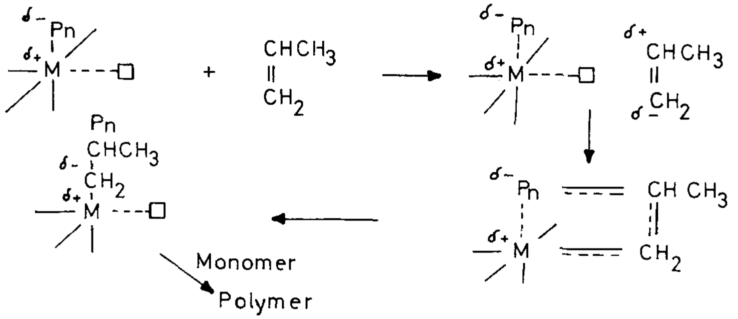

FIG. 1. Propagation with no prior coordination [8].

commercial exploitation, and major classes of thermoplastics (including high density polyethylene, isotactic and syndiotactic polypropylene) and elastomers (chiefly high cis polybutadiene) are now made in enormous volumes. The mechanism of the process by which a mixture of a metal salt and a metal alkyl, hydride, or alkyl halide can cause polymerization of vinyl monomers to high molecular weight, linear polymers has received continuing attention.

A general picture has emerged for the polymerization of simple α-olefins; the reader is referred to a number of reviews [3-5]. Bimetallic models initially proposed by Natta [6], and modified by Boor [7, 8] have been refined to a propagation mechanism where "cis-four-center addition" (Fig. 1) is used [8].

Another significant advance, first formulated by Cossee [9] and later modified with Arlman [10-12] and Henrici-Olive [13], was based upon one vacant position of the octahedral configuration of the transition metal being the active site. The Cossee-Arlman mechanism, as summarized in Fig. 2, was developed in the mid-1960s and is still a model of wide acceptance, being selected as recently as 1977 [5].

The fundamental mechanism of Cossee, refined by minor adaptations, has been durable; a new mechanism of greater complexity has, however, been proposed [14]. The great advantage of this scheme (Fig. 3, as reported by Colquhoun et al. [15]) is that it provides a common mechanism for both olefin polymerization and metathesis. When the key elimination step of the α-hydrogen is slow, or if hydrogen can be removed from the metal center, metathesis is said to occur [15].

The advantages of using combinations of magnesium and aluminum alkyl based catalysts for the polymerization of simple olefins has only recently been discovered. When desolvated alkyl magnesium halides "activate" selected transition metal compounds and used in conjunction with aluminum alkyls, a hundredfold increase in

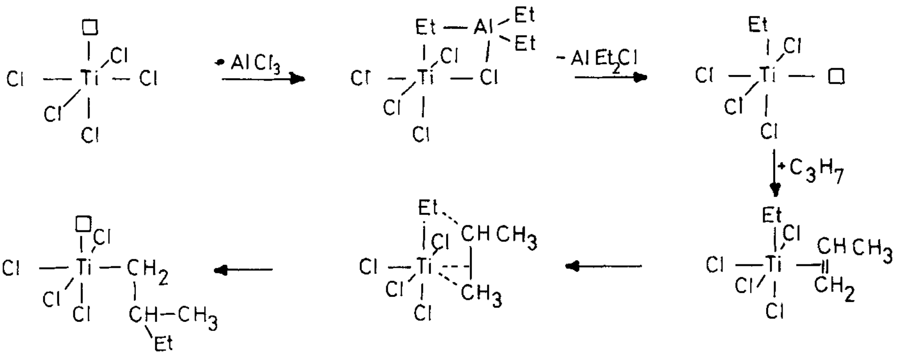

FIG. 2. The Cossee-Arlman mechanism: cis rearrangement.

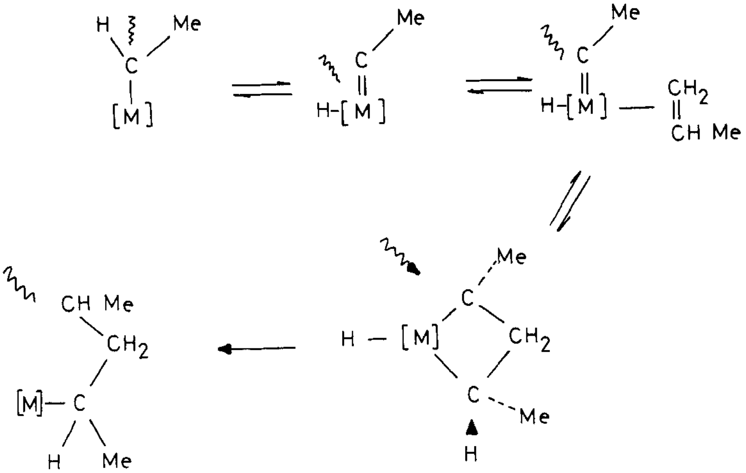

FIG. 3. Mechanism of Ivin, Rooney, et al. (from Ref. 15).

activity over conventional catalysts is claimed [16, 17], reducing the problem of catalyst residues [18]. The high activity of these organomagnesium reduced catalysts is considered a result of the high concentration rather than abnormally high vigor of individual catalyst sites [19]. This is consistent with very small catalyst particles of little regularity [18]. Both Duck [16] and Haward [18] use partly solvated systems, in contrast with most of the patent literature.

Although the pyrophoric nature and normally short "half-life" of most Ziegler-Natta catalysts have delayed attempts to observe directly the catalyst and growing polymer structure, procedures have been recently developed which enable polymerization mechanisms to be linked with nascent polymer morphology [20, 21]. By determining in situ levels of Ti^{4+} and $\alpha TiCl_3$ and observing the size of "growing globules," an estimate of growing sites per "polymerization locus" is ultimately made. However, because of the inherent complexity and variety of Ziegler-Natta catalysts, structural determinations have not allowed a unitary model to evolve [5].

DEVELOPMENT OF REACTION MODELS

The relative paucity of literature describing process control and model development for Ziegler-Natta systems has been overcome with a text by Schildknecht and Skeist [22] and a series of articles by Bohm [23]. Applied articles (for example, where the temperature dependence of stereospecificity in heterogeneous propylene polymerization is discussed [24]) are also becoming more common so that commercially significant technology is being exposed.

In the chapter "Ziegler-Type Polymerizations" [22], a wide variety of processes is revealed, including polyethylene production using the Hoechst and Solvay methods, as well as gas-phase production of high density polyethylene (the Union Carbide process). While polypropylene and certain elastomers and copolymers (including EPDM) are discussed, the production of high cis polybutadiene is omitted.

"Second generation Ziegler-Natta polyolefin processes" (essentially high activity, supported catalysts) are reviewed by Sivaram [25]. Although of immense commercial importance, they have yet to be employed for butadiene polymerization and so no attempt to give a superficial resume is made here.

ZIEGLER-NATTA POLYMERIZATION OF CONJUGATED DIENES

Production of high cis polybutadiene in 1978 was reported [26] to be approximately 750,000 tonnes per annum, and the corresponding figure for cis 1,4-polyisoprene (synthetic natural rubber) about 500,000 tonnes. It is obvious that these two materials are of considerable commercial significance. Because a large percentage of the total output is destined for automobile tire use, the influence of polymerization conditions upon molecular weight properties and processing behavior is now receiving increased attention.

Since the landmark reports by Gippin [27, 28] and Bawn [29] in the early 1960s, a continuous stream of activity has been maintained but results have largely been restricted to the patent literature. Further, two major computer abstracting services provide total

TABLE 1. Number of Citations for Total Ziegler-Natta Polymerization Citations versus Those for Butadiene Polymerization Only

Abstracting service	Total Z-N polymerization citations	Z-N polymerization of butadiene
RAPRA (1974-November 79)	172	10
American Chemical Society (CA Condens, 1969-1980)	393	10

citations for Ziegler-Natta polymerization which greatly outnumber those primarily concerned with butadiene polymerization only (Table 1).

As another indicator of the small amount of information publicly available, the paper by Richards [30] reviewing newer developments in butadiene polymerization contained little material relating to Ziegler-Natta polymerization studies. There is, however, a recent trend toward releasing information of a more technical nature (for example, a kinetic study of butadiene polymerization using a titanium-based catalyst, with polymers prepared in a batch reactor under a variety of conditions being characterized [31]).

The majority of accessible material remains within a small number of texts. The first review of significance, by Cooper and Vaughan [32], summarizes anionic and coordination catalysis studies conducted during the 1960s (when diene polymer manufacture increased from zero to 250,000 tons). The influence of allotropic form and halogen identity in titanium halide-based catalysts upon cis content of polymer and the broader effects of catalyst composition upon yield and molecular weight were known [33]. The use of vanadium and chromium-based catalysts to give unusual high trans 1,4 [34] or 1,2 vinyl polymers [35] was also recognized, but nickel and cobalt catalysts of economic significance are emphasized. Of particular significance in Cooper and Vaughan's review are the extensive tables linking catalyst makeup with polymer structure and a survey of polymerization mechanism.

Studies in which trans-1,3-pentadiene was polymerized in the presence of $CoCl_2/AlEt_2Cl$, but where cis-1,3-pentadiene was not, suggest that two point coordination is required. The reaction scheme which provides for attack at either C1 or C4 positions is shown in Fig. 4 (from Ref. 36).

The next substantial review was provided by Ledwith and Sherrington [4], in which they point out that catalysts commonly used to yield polymers of high steric purity are heterogeneous, so that factors including metal type, complexing agents, and many others will affect catalysis. For cobalt-based systems it was considered difficult to draw analogies with single component catalysis of mono-olefins

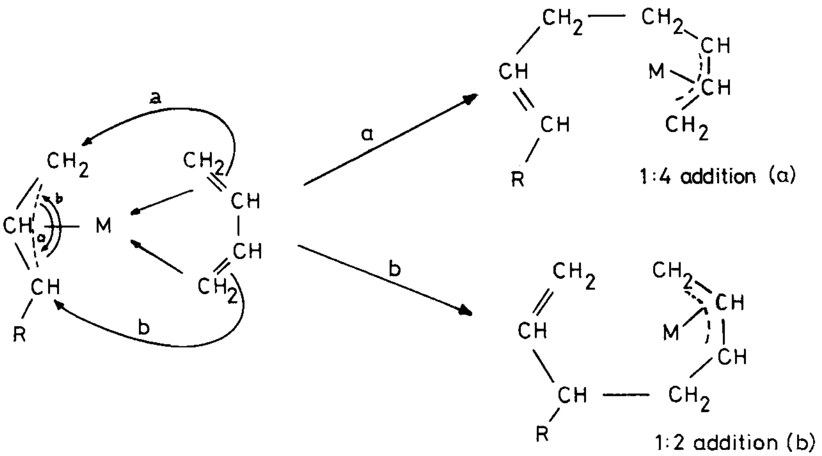

FIG. 4. C1, C4 binding at active site to give 1,4 or 1,2 addition [36].

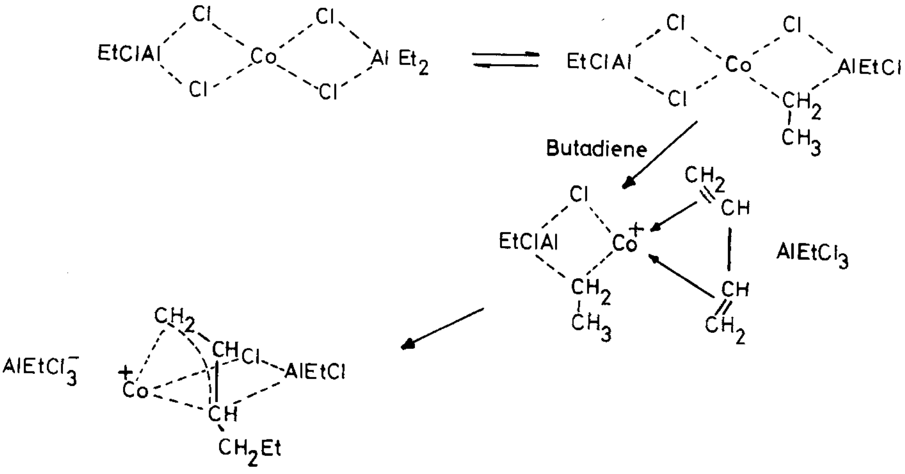

FIG. 5. Catalyst structure for $CoCl_2/Al_2Cl_3Et_3$.

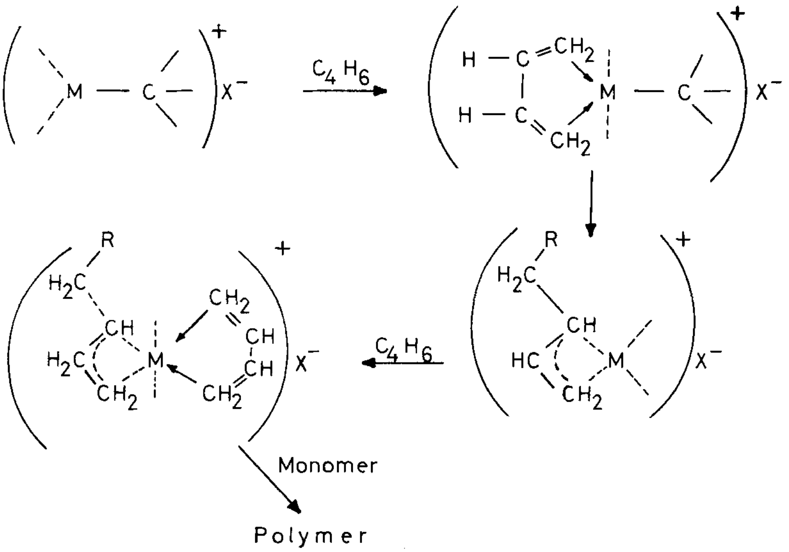

FIG. 6. Mechanism proposed by Ledwith and Sherrington [4].

because of the intricacy of the catalyst complex. The structure of the catalyst was that given by Cooper [37] and is shown in Fig. 5.

In this case the aluminum alkyl acts primarily as a reducing agent. However, for the $CoX_2/AlEt_2Cl$ system a co-catalyst such as water, oxygen, or methanol is required, and generally it is believed that the aluminum compound is converted to a stronger Lewis acid. The consensus in 1973 was that the active center has an alkylated transition metal ion with a polarized metal-carbon bond, similar to most other Ziegler-Natta systems. A mechanism proposed by Ledwith and Sherrington is shown in Fig. 6; cobalt can occur in a variety of coordination states and any of a number of geometries can be suitable. In solvents of low dielectric constants, it is proposed that the catalyst complexes will either act as ion pairs or as independent solvated entities. The proponents do not specify whether the growing chain is bound by a π or σ linkage but suspect that continuous $\sigma \leftrightarrow \pi$ isomerism is possible.

The third and most recent of the major review texts is that edited by Saltman [5]. The distinction of this volume is that the more commercial aspects of polymer processing and properties are included together with polymerization technology; a unique format. A variety of reaction mechanisms are provided for the titanium-catalyzed polymerization reaction (including the Cossee and Arlman and the Rodriguez and Van Looy schemes), but of particular interest here are

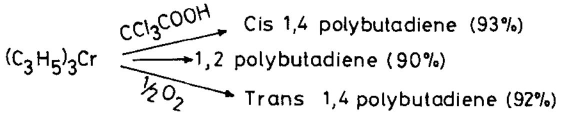

FIG. 7. Influence of ligand upon polymer structure (from Ref. 5).

the recent developments in diolefin polymerization. Changes in ligand bound into the coordination sphere is a major controller of polymer sterochemistry, as is shown for the chromium allylic system of Fig. 7.

Changes in transition metal, counterion, and ligands will affect both the structure of the polymer and the kinetics of polymerization. An interesting development is where the distribution of the two isomeric units can be changed by solvent selection without affecting the total composition of the polymer. For example, an equibinary mixture of cis and trans 1,4 units can be changed from random distribution (in benzene) to alternate (in dichloromethane) [38].

The reaction mechanisms have not developed beyond those given in Ledwith [4]; this is not surprising in the light of "the enormous amount of sometimes contradictory experimental data pertaining to the same polymerization process" and the conclusion that "many reaction mechanisms find it difficult to explain cis-trans isomerism" [5].

The diversity of dienic monomers which can be polymerized using coordination catalysts is detailed by Cooper [39]. While much of the chapter deals (not surprisingly) with butadiene, other derivatives from isoprene, 1,3-pentadiene, and other conjugated and nonconjugated dienes are discussed. Commercial catalysts for cis butadiene polymerization are based on cobalt, titanium, and nickel, with recent interest being also directed to cerium and uranium. trans 1,4 Polybutadiene can be made from vanadium, titanium, nickel, cobalt, and rhodium; modified cobalt, titanium, and vanadium catalyst may also produce syndiotactic 1,2 polybutadiene. The isotactic polymer is comparatively difficult to prepare; surprisingly, molecular weight is low and independent of the level of chromium catalyst employed [40].

Cooper's chapter also contains a useful flowsheet showing production of high cis 1,4 polybutadiene based on aluminum-cobalt based system. More specific manufacturing detail is usually less accessible, being restricted to individual proprietary technology reports, the patent literature, or commissioned reviews (for example, The Stanford Report [41]).

Within the limits of this brief review, it is not possible to do justice to a number of other proceedings and symposia [42-44] concerned with Ziegler-Natta polymerization of butadiene. Instead, the reader is advised to refer to them directly for full detail; interesting developments have been selected from them and are discussed below.

AREAS OF RECENT ACTIVITY IN POLYBUTADIENE TECHNOLOGY

Development of High-cis Polybutadiene using Uranium-Based Catalyst

Polybutadienes can be prepared with varying stereoregularity by using differing transition elements (for example, see Ref. 45). The production of ultrahigh cis ($>99\%$) polybutadiene using uranium-based catalysts was reported in 1974 [46] using allylic complexes; these polymers are of broad molecular weight ($M_W/M_N \approx 6$) and have excellent processing characteristics. High efficiency catalysts prepared from uranium alkoxides together with a Lewis acid (for example, $AlEtCl_2$ or $TiCl_4$ [47]) have also been used; the cis content decreases slightly as molecular weight increases, although $>98.5\%$ is usually achieved. Polymer structure is unaffected by changes in the halide of the uranium allyl salt (this contrasts with the trend shown for many other catalysts [48]). Catalyst aging for several hours is required for high yields [45].

Preparation of Syndiotactic Polybutadiene with 1,2 Microstructure

Interest in medium-vinyl polybutadienes (which can have many of the mechanical and thermal characteristics of styrene-butadiene elastomer and which had been prepared using cobalt-based catalysts since 1964 [49]) intensified during the styrene shortage experienced in the mid-1970s [50]. When mixed dialkyl and trialkyl aluminum salts are used in molar ratios (with respect to cobalt) of from 0.3 up to 600, syndiotactic 1,2 polybutadienes are prepared. While this technology was commercially exploited overseas, the Australian response was to reduce the styrene level in cold-polymerized emulsion SBR from 23.5 to 20.0%.

A Firestone patent [51] claimed that the prior art method of preparing polymer was unsatisfactory because of low yields and poor polymer properties. This patent gives numerous examples of catalyst component compositions; a typical 28 oz bottle mixture contains "27.2 g of butadiene, 21 g propylene, 223.8 g toluene and cobalt bis (acetylacetonate), tetramethyl ethylene diamine, $SOCl_2$ and triisobutyl aluminum are added to give 3.68 millimoles of Co compound per 100 g of monomer, a TMEDA/Co ratio of 1/1, a S/Co ratio of 1/1 and an Al/Co ratio of 30/1." High yields of a high melting, white powder, with 92% 1,2 content, are obtained.

Another approach to introduce high vinyl groups into the polymer is to utilize anionic polymerization in the presence of Lewis acids. By using ethyl lithium and any of a variety of solvents, 1,2-1,4 polybutadienes with from 7 to 92% vinyl content have been produced [52], under adiabatic conditions, in a Chemische Werke Huls pilot plant. Long chain branching is encouraged by using temperatures over 80° C. Broad molecular weight polymers are obtained by pulsating the alkyl addition because the reaction time may be as low as 3 min.

Sequence Distribution of Polybutadienes

The sequence of polybutadienes is of obvious usefulness both in determining the mechanism of polymerization as well as in correlating polymer structure with mechanical and processing behavior. The final aim of using both infrared and NMR techniques is to determine the conformation and sequence of each moiety along a polymer chain. Ultimately, both the stereochemistry and composition of each unit needs to be identified. To determine the cis, trans, and vinyl content of polybutadiene, infrared alone is often adequate [53, 54], but to determine the additivity of extinction coefficients, NMR spectra of deuterated diene derivatives is required [55].

While the amounts of the various structural subunits have been able to be determined accurately for some time [56], recent studies have been directed toward providing information on the distribution of units. The ^{13}C NMR spectra of 1,4 polybutadienes have now been analyzed so that the olefinic ^{13}C chemical shift assignments for all triads are known [57]. The technique has come under criticism, however, because of the difficulties in identifying cis-trans unit linkages and the 1,2 unit distribution [58, 59]. Polymers having significant 1,2 vinyl structure, prepared by lithium alkyl-initiated catalysis, were analyzed with a higher resolution 300 MHz ^{1}H NMR spectrometer, and it was found that the triad sequences fit a random distribution [58].

The mechanism of stereospecific polymerization of cis,cis-1,4-dideutero-1,3-butadiene to trans-1,4 or cis-1,4 polymers has been deduced mainly by infrared analysis of both polymers and low molecular weight fragments produced by degradative oxidation [60]. A scheme for the formation of threo stereoregular polymers via insertion through a cis-addition is proposed. More recently, high resolution proton NMR and ^{13}C NMR techniques have been combined to analyze deuterated polybutadienes, and the results for diad and triad sequence distributions were compared with those obtained by infrared methods [61].

NMR analysis of stereoregular homopolymers [62] and copolymers [63] has recently been reported by Harwood. In the first article, bond opening modes have been examined using deuterated monomers, while in the latter it was shown that equibinary mixtures of 1,4 cis and 1,4 trans butadienes were of random distribution and were predominantly joined "head to tail." Similarly, equibinary 1,2/cis 1,4 and 1,2/trans 1,4 polybutadienes were mainly of random structure.

Determination of Molecular Weight and Branching Characteristics

The importance of molecular architecture in polybutadienes was recognized as early as 1961 when 11 high cis-polymers and five emulsion polymers were analyzed by established techniques [64].

The importance of molecular weight distribution upon processing behavior has been continually emphasized, but only the advent of rapid methods, principally gel permeation chromatography (GPC), has made a strong impact upon routine quality control [65]. Rapid on-line GPC's are now used as process control instruments, with impressive separation achievable in minutes [66] and polystyrene has been analyzed in 90 s [67].

The significance of molecular weight distribution upon processing behavior of both emulsion SBR [68] and SBR made by both solution and emulsion processes [69] has been established. In the latter work quite marked differences in processing behavior are largely a consequence of polydispersity. Increases in molecular weight of high cis-polybutadiene account for longer black incorporation times in BR and SBR/BR blends, although oil appears to improve dramatically the behavior of high BR-loaded compounds [70].

Until recently, attempts to determine chain branching were complex and only partially successful [64]. However, using an on-line viscometer and assuming a Zimm-Stockmeyer branching model (where trifunctional branch points/molecule are determined as a function of intrinsic viscosity), it is possible to gauge long-chain branching frequency across the GPC chromatogram [67].

Influence of Polybutadiene Microstructure upon Processing Behavior

Processing behavior of polymers with the same chemical composition is affected by molecular weight distribution, stereoregularity, linearity, and sequence distribution within the chain. No studies where each of these parameters has been varied independently have been reported. However, the difference between the processing behavior and cold flow properties of low dispersity ($\rho > 1.5$) medium cis polybutadiene and that of medium polydisperse cobalt catalyzed, high cis BR ($\rho \approx 2.4$) is well recognized [71]. Tokita and Pliskin [72] have shown that emulsion SBR's and solution SBR and BR of broad molecular weight distribution have suitable mixing and milling behavior but narrow MWD solution SBR and BR do not.

The change in rheological and other processing properties as the molecular structure of polybutadienes is changed has recently been reported by Eisele [73]. However, not only is there a discontinuous selection of cis contents (being 38%, then 92% and greater), but interpretation of results is ambiguous because the polydispersity of the polymer samples also increases with cis content.

AUSTRALIAN DEVELOPMENTS IN ZIEGLER-NATTA POLYMERIZATION OF BUTADIENE

Effect of Catalyst Composition and Preparation upon Molecular Weight Characteristics of Polymer

The components used commercially are cobalt octoate, diethyl aluminum chloride, and water; control of each concentration, as well as constancy of mixing and ageing, is required for consistent molecular weight development. As the reaction kinetics show first-order dependence upon both cobalt and butadiene concentration, these two factors are significant. In addition, the level of moisture is critical for both yield and molecular weight control [41, 74]. The yield and molecular weight are both affected by cobalt compound level and temperature, but these variables have little effect upon cis content. Changes in molecular weight distribution are monitored by GPC. The ultimate aim is to ensure high uniformity of polymer, with the optimum microstructure for good mechanical and processing behavior. Tighter quality control has been necessary because radial ply tires, now of wide acceptance, demand highly uniform polymers with predictable processing behavior.

Effect of Catalyst Preparation upon Gel Content and Solution Properties

Studies relating catalyst makeup, aging conditions, and physical structure with cross-linked material in polybutadiene have been conducted to enable polymer suitable for high impact polystyrene applications to be produced. Patent information indicates that the degree of homogeneity of the catalyst is an important factor in reducing gel [75], and the branched structure enables rapid dissolution and low solution viscosities to be achieved. Studies directed at achieving similar objectives are being pursued in Australia [74].

Solvent Substitution

The use of benzene as the principal solvent has been questioned as a result of recommendations from the Occupational Safety and

Health Administration that maximum exposure levels be 1 ppm [76]. Investigation of suitable replacements, including toluene and cyclohexane, is in progress [77] to show how polymerization conditions and polymer physical properties will be affected.

CONCLUSIONS AND OUTLOOK

John Boor, Jr., in 1974 stated [78]

> . . . Yet the worker, while he cannot ignore the past work, cannot allow himself to be overwhelmed by the large volume of patents and journal papers and feel that nothing significant can be done.

At the time of writing there exists no scheme which can explain and predict the molecular architecture of a polybutadiene for all polymerization conditions. From an industrial viewpoint, this may not be a prerequisite for successful modification of existing polymer production; however, the development of "tailor-made" polymers from first principles is certainly difficult to accomplish.

It is concluded that many mechanisms persist which attempt to explain butadiene polymerization kinetics, but few have successfully incorporated the physical nature of the active center.

The adaptation of more rapid methods of polybutadiene characterization (particularly GPC) has had a profound effect upon both research and development. However, it appears that length and distribution of side branches must be known if a complete "structure-property" analysis is to be undertaken and a convenient method for this is still lacking.

Within Australia, it is expected that the main thrust will be toward the commercial implementation and exploitation of existing technology as well as participation in the worldwide trends toward increasing catalyst efficiencies and minimizing environmental hazards.

Further attention is also expected to be directed toward producing polymers with physical and processing properties more ideally suited to the elastomer processor.

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