

THE POLYMERIZATION OF 1,2-EPOXIDES CATALYZED BY THE CONDENSATION PRODUCTS OF METAL-CONTAINING COMPOUNDS WITH ALKYLPHOSPHATES. T. Nakata, Research Laboratories, Osaka Soda Co., Ltd. 9 Otakasu-cho, Amagasaki City, Hyogo Pref. 660, Japan

It was found that the condensation product of certain metal-containing compounds with an alkylphosphate exerts remarkable catalytic activity in the polymerization reaction of 1,2-epoxides yielding high molecular weight polymers.

Some Friedel-Crafts type metal halide catalysts or organotin compounds easily condense, releasing alkyl halide or olefins mainly, with an alkylphosphate on heating. The condensation products are reasonably assumed to be poly-metal- or poly-organotin- poly-alkylphosphates.

The condensates from organotins exhibited higher catalytic activities compared with the other catalysts prepared similarly from various metal compounds, for the polymerization of ethylene oxide and its monosubstituted derivatives, such as propylene oxide, glycidyl ethers and epichlorohydrin.

The catalysts prepared from organotins showed interesting properties for the polymerization reaction. Their activities and acidities seemed to depend on the degree of condensation. They seemed to exert high steric regulation in the polymerization reaction and gave the highest crystalline polymers of epichlorohydrin among the polymers by the other catalysts we prepared.

STEREOCHEMICAL ASPECTS OF THE CATIONIC POLYMERIZATION OF CHIRAL ALKYL VINYL ETHERS. Emo Chiellini, Roberto Solaro, and Francesco Masi, Istituto di Chimica Organica Industriale, Università di Pisa, 56100 Pisa, Italy

Studies on the polymerization of chiral monomers have been useful in helping to understand details of the stereospecific polymerization of several types of vinyl monomers. Among these alkyl vinyl ethers constitutes a class of compounds that due to their high tendency to be cationically polymerized under either homogeneous or heterogeneous conditions, is particularly attractive with respect to a possible semi-quantitative evaluation of the parameters affecting the stereochemistry of well-defined polymerization processes.

In fact, depending upon monomer structure, catalyst types and reaction conditions, alkyl vinyl ethers are able to give both stereoregular and atactic macromolecules. In the present topic, attention will be paid to the analysis of the stereochemical aspects inherent to the polymerization of racemic and optically active alkyl vinyl ethers carried out in the presence of heterogeneous "coordinated cationic catalysts" based on aluminum alkyls (or alcoholates) and sulphuric acid as introduced by E. Vandenberg in early 60's.

From the comparison of the intrinsic catalytic activity and stereospecificity of the mentioned two-component catalysts with that of diisobutylaluminum (or diisopropylaluminum) sulphate, taken as suitable limit models of the catalytic sites present in the former systems, it is possible to get a direct confirmation of the coordinated cationic nature of the heterogeneous multicomponent catalysts.

STEREOCHEMICAL ASPECTS OF THE POLYMERIZATION ON CIS AND TRANS THIIRANES USING CHIRAL INITIATORS. N. Spassky, A. Momtaz, and P. Sigwalt, Laboratory of Macromolecular Chemistry, University of Paris VI, 4, Place Jussieu, 75230 Paris Cedex, France

In the polymerization of resolvable heterocyclic monomers such as mono-substituted thiiranes by means of chiral initiators the enantiomeric choice follows homo-chiral relationships. Optically active polymers with predominance of one enantiomer are produced and the unreacted monomer is enriched in the opposite enantiomer. For a given initiator, the kinetics of resolution varies with the nature of the monomer. Disubstituted monomers with two vicinal asymmetric centers have a particular behavior. Trans-dimethyl thiirane, a resolvable monomer, when polymerized with a chiral initiator, leads to an optically inactive polymer, due to complete inversion of the asymmetric carbon atoms at ring opening as shown previously by Vandenberg. The unreacted monomer is optically active, but the resolution kinetics is very different from that of other thiiranes. Cis-dimethyl thiirane, a meso, unresolvable compound, leads on polymerization with chiral initiators to optically active polymers. This is an enantiogenic process comparable to asymmetric synthesis. The stereochemistry of this reaction is in agreement with homo-chiral rules developed for resolvable monomers. This shows that the initiator is able to recognize in the heterocycle an asymmetric carbon atom of a given configuration and to direct a regioselective ring-opening on one of the sides of the ring.

COORDINATION POLYMERIZATION. E. J. Vandenberg, Hercules Research Center, Lancaster Pike & Hercules Road, Wilmington, Delaware 19899.

A new, broad-based method of polymerization, commonly referred to as "Coordination Polymerization" was first recognized about 25 years ago as the probable mechanism of the newly-discovered Ziegler, transition metal-based, low pressure ethylene polymerization catalyst. Rapidly this system was found to apply to other olefins, diolefins, epoxides, and vinyl ethers. The author's involvement in this area from the inception will be reviewed, including some unpublished aspects of his work as well as his extension of the area to cyclic ethers with non-transition metals such as Al and Mg. Some of the commercial aspects of this work will be discussed. The limited knowledge of the mechanism aspects of this unusual polymerization will be reviewed and suggestions made for future investigations. Some of the author's recent unpublished work in the epoxide area will be presented, including the first preparation and description of the properties of high molecular weight polyglycidol, an unusual water-soluble polymer.

STEREOSELECTIVE AND STEREOELECTIVE POLYMERIZATION OF RACEMIC α -OLEFINS WITH SUPPORTED TITANIUM CATALYSTS. P. Pino, G. Pochi, R. Mulhaupt, O. Piccolo, U. Giannini, and A. Oschwald, Swiss Federal Institute of Technology, Zurich, Switzerland

Racemic olefins such as 4-methyl-1-hexene and 3,7-dimethyl-1-octene have been polymerized using a $MgCl_2$ supported titanium catalyst in the presence of $Al(C_2H_5)_3$ or

$Al(iC_4H_9)_3$ and Lewis bases. The stereoselectivity was higher than that observed using conventional catalysts. In the presence of (-)-menthylisolate as Lewis base, the polymerization of both racemic 4-methyl-1-hexene and racemic 3,7-dimethyl-1-octene becomes stereoselective.

Surprisingly, in the case of 4-methyl-1-hexene, the stereoregular fractions show an optical activity with opposite sign compared to low stereoregular fractions which have the same linear regular structure. The asymmetric carbon atoms of the lateral chains of the prevailing type of monomeric units in the fractions with low stereoregularity, have the same absolute configuration as the prevailing antipode in the non-polymerized monomer. Similar, but even more complicated phenomena have been observed in the case of 3,7-dimethyloctene polymerization. The results have been interpreted as being due to the existence in the catalyst of chiral, and non-chiral active centers having largely different geometry.

1,4 POLYBUTADIENE (1.4.) BLOCK COPOLYMERS FROM "LIVING" COORDINATION CATALYSTS. Ph. Teyssie, P. Hadjiandreou, M. Julemont, Laboratory of Macromolecular Chemistry and Organic Catalysis, University of Liege, Sart-Tilman, 4000 Liege, Belgium

Under specific kinetic conditions by $(\eta^3 \text{ allyl-X-nickel})$ complexes are able to promote a regioselective (99% 1.4) and perfectly "living" polymerization of butadiene (as evidenced by the $M_n = [BD]/[Ni]$ experimental relationship, and polymerization resumption experiments).

That unique behavior has been applied to the synthesis of interesting new polymeric structures:

- 1) a distereoblock poly(cis 1.4-b-trans 1.4) butadiene of high molecular weight, both sequences of which are able to crystallize independently;
- 2) a diblock poly(cis 1.4 butadiene-b-styrene), which upon hydrogenation yields a poly(ethylene H.D.-b-styrene), a very interesting emulgator for stabilizing polystyrene HD polyethylene blends;
- 3) a multistereoblock poly(cis 1.4-b-trans 1.4)_n butadiene, obtained by "coding" the previously described equibinary 1.4 polymerization of butadiene, and representing the first example of a thermoplastic elastomer (m.p. 137°C) prepared in one step from one single monomer.

SUPPORTED CATALYSTS FOR POLYPROPYLENE: ALUMINUM ALKYL-ESTER CHEMISTRY

by
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Introduction

The reactions of aluminum alkyl cocatalysts with the ethyl benzoate (EB) component of $MgCl_2$ supported $TiCl_4$ catalysts have a strong influence on both activity and stereospecificity. NMR investigations show that AlR_3 alkylates ethyl benzoate by the following reaction: $\theta CO_2Et + 3 AlR_3 \rightarrow \frac{1}{2} (R_2AlOEt)_2 + R_2Al \cdot R_2AlOCR_2\theta$. The rate of ethyl benzoate consumption decreases with lower $Al/\theta CO_2Et$ ratios. Atmospheric pressure polymerization studies reveal that the interaction of ethyl benzoate with the catalyst is responsible for achieving high isotacticity as measured by heptane insolubles (% HI). The aluminum alkoxide products from the alkylation reaction increase HI indirectly by complexing $AlEt_3$, lowering the free $[AlEt_3]$ and the $AlEt_3/\theta CO_2Et$ ratio. However, lower free $[AlEt_3]$ also reduces polymerization rate. The introduction of steric bulk into the aluminum alkyl component minimizes the ester alkylation reaction while maintaining catalyst activity. Two types of cocatalysts have been found which give significantly better catalyst performance than the $AlEt_3$ cocatalyst: (1) sterically hindered trialkyl aluminum cocatalysts, such as *s*-Bu₂AlEt and *t*-Bu₂AlEt and (2) certain aluminum dialkyl and diaryl amides such as Et₂Al-2,2,6,6-tetramethylpiperidine and Et₂AlN θ .