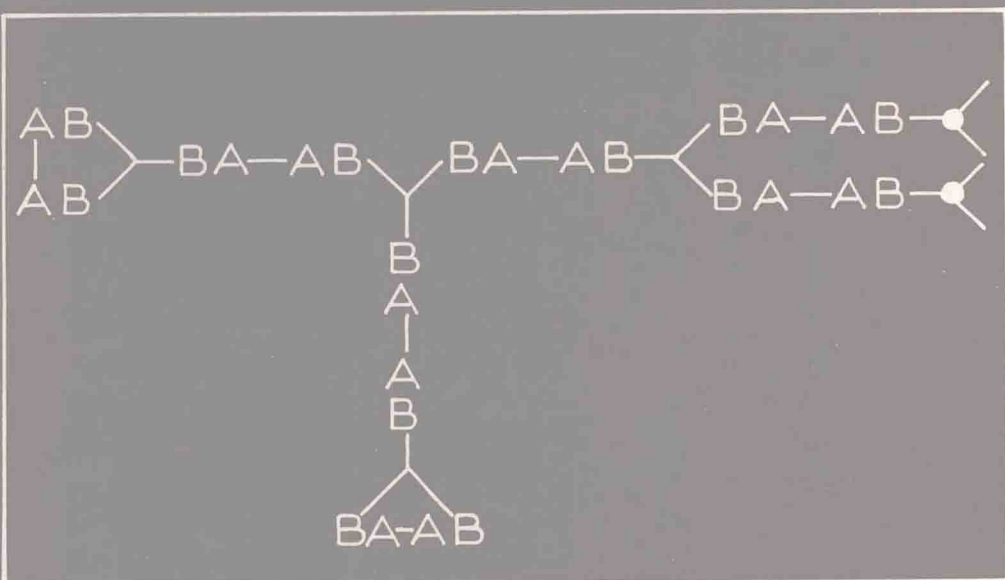


ADVANCES IN ELASTOMERS AND RUBBER ELASTICITY



Edited by Joginder Lal and James E. Mark

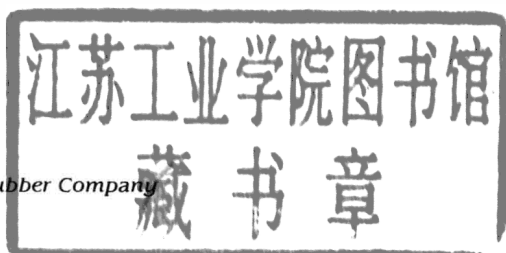
Advances in Elastomers and Rubber Elasticity

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PREFACE

The present book is a sequel to "Elastomers and Rubber Elasticity," edited by J.E. Mark and J. Lal and published by the American Chemical Society in 1982. It is also based on papers presented at an ACS Symposium, sponsored by the Division of Polymer Chemistry, Inc., in this case one held in Chicago in September of 1985. The keynote speaker was to have been Professor Paul J. Flory, and his untimely death just prior to the symposium was a tremendous loss to all of polymer science, in particular to those interested in elastomeric materials. It is to his memory that this book is dedicated.

There has been a great deal of progress in preparing and studying elastomers since the preceding symposium, which was in 1981. In the case of the synthesis and curing of elastomers, much of the background necessary to an appreciation of these advances is given in the first, introductory chapter. More specific subjects include the control of microstructure in the anionic polymerization of elastomers, polyurethane elastomers with monodisperse sequence length distributions, hysteresis and heat build-up in polyurethanes, polyurethane-polyurea copolymers, and new block copolymers with improved high-temperature properties, and methods for curing some of them. Also covered are the effects of microstructure on traction, fatigue resistance, and rolling resistance, curing of elastomers that are difficult to cure, polymer-bound antioxidants, and the chemical modification of elastomers (for example the hydrogenation of polydienes and the epoxidation of natural rubber).

A similarly wide range of subjects is covered in the area of rubberlike elasticity. Primarily theoretical studies include the use of quantum statistical mechanical ideas in theories of entangled networks, calculations of molecular deformation tensors and molecular orientation, a memory-lattice theory of rubberlike elasticity, and strain-induced crystallization and its effects on the stress and other mechanical properties. More experimentally oriented topics include cross-linking reactions and the network imperfections they can introduce, model networks for estimating the possible importance of inter-chain entanglements, light scattering and small-angle neutron scattering in the study of network topology and chain extension, segmental orientation from fluorescence polarization, comparisons between stress-strain relationships for elastomeric networks and polymer melts, and the effects of chemical structure on the strength of elastomers (in tearing and abrasive wear).

The vitality and importance of the subject of elastomers and rubber elasticity are obvious from the above incomplete list of diverse topics, but also from the very wide organizational and geographical distribution of the authors. Various chapters in fact come from universities, industrial laboratories, and research institutes in the United States, Canada, England,

France, Germany, the Netherlands, Italy, Turkey, and Japan.

Finally, it is a pleasure to acknowledge that the symposium on which this book is based received financial support from the following organizations: ACS Division of Polymer Chemistry, Inc., Petroleum Research Fund, U.S. Army Research Office, American Hoechst Corporation, Dow Chemical, U.S.A., E.I. du Pont de Nemours & Company, Firestone Tire & Rubber Company, GenCorp, BFGoodrich Company, Goodyear Tire & Rubber Company, Hercules Incorporated, Monsanto Company, Nippon Zeon of American, Inc., Phillips Petroleum, Polysar Limited, Shell Development Company, and Uniroyal Chemical Division.

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INTRODUCTION TO SYNTHESIS OF ELASTOMERS*

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ABSTRACT

Polymerization and crosslinking reactions used for the synthesis of elastomers are reviewed. Step and chain polymerizations are characterized in terms of the reaction variables which must be controlled to obtain an elastomer. Radical and ionic chain polymerizations are discussed as well as the structural variations possible through copolymerization and stereoregularity

INTRODUCTION

Elastomers or rubbers are polymers which can undergo very large, reversible deformations at relatively low stresses. Only a polymer molecule can undergo large deformations since it can respond to stress without bond rupture by extension from a random coil to an extended chain molecule through bond rotation. Only an amorphous polymer with low glass transition temperature and low secondary forces has the required chain flexibility to meet these requirements. Crystalline polymers (e.g., polyethylene or isotactic polypropylene) or highly polar polymers (e.g., polyamides) do not have the necessary chain flexibility. Amorphous polymers with large bulky substituents (e.g., poly(methyl methacrylate) and polystyrene) are also too rigid to be elastomers. Elastomeric behavior is limited to those non-polar amorphous polymers with irregular structures (e.g., ethylene-propylene copolymers) and/or flexible chain units (e.g., polyisobutylene, polysiloxane, polysulfide,

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1,4-polyisoprene). Crosslinking of a polymer to form a network structure is an essential part of synthesizing an elastomeric product. The presence of a crosslinked network prevents polymer chains from irreversibly slipping past one another upon deformation. Either chemical or physical crosslinking can be used to produce the network structure. The various reactions for synthesizing polymers from monomers are discussed below together with a consideration of the processes used to achieve crosslinking.

POLYMERIZATION

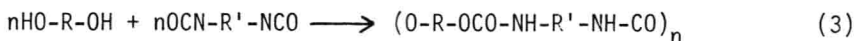
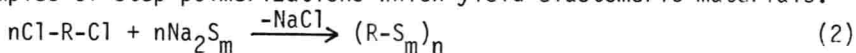
The prime consideration in any polymerization reaction is the control of polymer molecular weight (MW). A polymer requires a minimum molecular weight in order to possess sufficient physical strength to be useful. This minimum MW may be as low as a few thousand but is generally considerably higher. In any specific application, the desired MW is some compromise high MW which yields sufficient strength for the end-use application while retaining ease of processing the polymer into its final product shape. The need to control molecular weight places significant restrictions on any reaction used for polymer synthesis.

Step Polymerization

Polymerizations are classified as either chain or step polymerizations. The two processes differ in the time required for the growth of large-sized (i.e., polymer) molecules compared to the time for achieving high conversions. Step polymerizations typically involve two different bifunctional reactants (referred to as monomers), each containing a different functional group X or Y. Polymer growth occurs through the formation of xy functional units by reaction of X and Y groups



The synthesis of polysulfides (Eq. 2) and polyurethanes (Eq. 3) are examples of step polymerizations which yield elastomeric materials.



The structural entity which repeats over and over again in the polymer, i.e., the structure within the parenthesis in Eq. 1 or 2 or 3, is referred to as the polymer repeat unit.

Step polymerization proceeds by the stepwise reaction between X and Y groups to form dimer, trimer, tetramer, pentamer, and so on until eventually polymer molecules are formed. As each larger-sized species is formed, it competes with the smaller-sized species for further reaction. Any two molecular species containing X and Y groups can react

with each other throughout the reaction. This results in a final polymer with a distribution of molecular weights. The average size of the molecules increases slowly with conversion since the reaction rate constants are typically not high (of the order of 0.001-0.1 L/mol-s).

The average degree of polymerization DP, defined as the average number of monomer units linked together per molecule in the reaction mixture, is dependent on the fractional conversion p and stoichiometric ratio r (the molar ratio of X and Y groups defined such that $r \leq 1$) according to the expression

$$DP = (1 + r)/(1 + r - 2rp) \quad (4)$$

Achieving high molecular weights ($DP \sim 50$, $MW \sim 5000$) requires both high conversions and near stoichiometric amounts of X and Y groups. Table 1 shows the dependence of DP on r and p as calculated from Eq. 4 for

Table 1. Variation of DP with p and r

p	r	DP
0.995	1.000	200
0.990	1.000	100
0.990	0.995	80.1
0.990	0.990	66.8
0.990	0.980	50.0
0.980	1.000	50.0
0.980	0.995	44.5
0.980	0.990	40.0
0.980	0.980	33.4
0.970	1.000	33.0
0.970	0.990	28.7
0.970	0.970	22.7
0.950	1.000	20.0
0.900	1.000	10.0

selected values of r and p. Polymer synthesis is much more difficult than carrying out the corresponding small molecule reaction. Conversions such as 90 and 95%, considered outstanding for small molecule reactions, are of little value for polymer synthesis since DP values of only 10 and 20, respectively, are produced even when $r = 1$. (Some exceptions to this generalization are described below in the section on Physical Crosslinking.) Minimal conversions of 98% are typically required in polymerizations. The need for such high conversions dictates that only a small fraction of all known chemical reactions be used in polymer synthesis. Few reactions can be carried to these conversions. Achieving conversions of 98% and higher requires reactions generally devoid of side reactions. Reversible reactions must be capable of being driven to high conversion by displacement of the equilibrium. Polymerization must be performed in media in which the polymer does not precipitate prior to reaching the desired MW.

Reasonable reaction rates are needed to achieve the synthesis in a reasonable time.

Step polymerizations proceed with second-order kinetics

$$1/[M] = 1/[M]_0 + kt \quad (5)$$

$$\text{or } DP = 1 + [M]_0 kt \quad (6)$$

where $[M]_0$ and $[M]$ are the concentrations of X(or Y) groups at times 0 and t, respectively. A characteristic of the second-order kinetics is that it takes progressively longer and longer reaction times to achieve each of the last few percent conversion. For example, it takes about as long to go from 96% conversion to 98% conversion as it takes to reach 96% conversion from 0% conversion.

Molecular weight control at the desired level is achieved by the simultaneous control of p and r. MW increases at any conversion as more nearly stoichiometric amounts of X and Y groups are used.

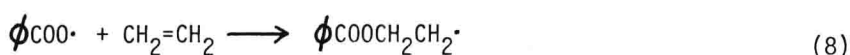
Stoichiometric imbalance lowers DP since at some point in the reaction all molecules in the polymerization system contain the same functional group, e.g., Y if Y groups are in excess, and further increase in molecular size does not occur since Y groups react only with X groups. The stoichiometric ratio must be precisely controlled since a difference of only a few tenths of a percent of excess of one reactant over the other yields a significant difference in DP. Control of r requires the use of high purity monomers. Reactant purity and stoichiometric balance is much more critical in step polymerization compared to a small molecule reaction. An impurity is generally carried along in the latter and ends up as a minor impurity in the final product. The same level of impurity in the polymerization can be disastrous -- yielding a lowered DP which makes the polymer unsuitable for a specified application, i.e., 0% yield of the desired product.

Chain Polymerization

Typical chain polymerizations are those of monomers containing the carbon-carbon double bond, e.g., ethylene, isobutylene, isoprene, styrene and acrylonitrile. Polymerization is initiated by radical, cationic, anionic or Ziegler-Natta (coordination) initiators. All monomers except 1-alkylethylenes, 1,1-dialkylethylenes and vinyl ethers undergo radical polymerization. Ionic chain polymerizations are much more selective than radical polymerizations. Cationic initiation is limited to monomers containing electron-donating substituents, e.g., alkoxy, 1,1-dialkyl, phenyl and vinyl. Anionic initiation is limited to monomers with electron-withdrawing substituents, e.g., CN, COOR, phenyl and vinyl. 1-Alkylethylenes such as propylene are polymerized only by

Ziegler-Natta initiators. 1,2-Disubstituted ethylenes are not polymerized by any initiators due to steric hindrance although they can be copolymerized.

Radical Chain Polymerization. Radical chain polymerization involves initiation, propagation and termination. Consider the polymerization of ethylene. The most widely used method of initiation is the thermal homolysis of an initiator such as benzoyl peroxide

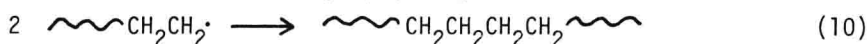


Other initiators such as alkyl peroxides and hydroperoxides and azo compounds allow the generation of initiator radicals over a wide range of temperatures (50-200 °C). Redox systems (e.g., Fe^{2+} or N,N-dimethylaniline with a peroxide) extend this temperature range down to 0 °C and lower. Ultraviolet radiation, usually in the presence of an initiator or photosensitizer, is useful for coatings, imaging and printed circuit board applications. Other techniques include ionizing radiation and electroinitiation.

Propagation of the radical center proceeds by the successive additions of large numbers of monomer molecules



Termination occurs when two propagating radicals combine



Disproportionation between propagating radicals also occurs but to a much lesser extent.

Propagation is favored over termination even though termination rate constants are larger than propagation rate constants (10^6 - 10^8 L/mol-s vs. 10^2 - 10^4 L/mol-s) because monomer concentrations are much larger than radical concentrations (0.1-10 M vs. 10^{-7} - 10^{-9} M). Many hundreds and even thousands of monomer molecules add to a propagating radical in times of 10^{-1} -10 s. The achievement of high MW does not require high conversions. High MW polymer is produced almost immediately after the start of reaction in a chain polymerization, in contrast to step polymerization, and continues throughout the complete conversion range.

The polymerization rate R_p and degree of polymerization are given by

$$R_p = k_p[M](R_i/2k_t)^{1/2} \quad (11)$$

$$\text{DP} = 2k_p[M]/(k_t R_i)^{1/2} \quad (12)$$

where R_i is the rate of initiation. Successful application of radical polymerization requires that the initiator and initiator concentration be chosen to give the appropriate initiation rate to achieve the desired

DP at the desired polymerization temperature. One must also realize that higher polymerization rates achieved by higher initiation rates come at the expense of lower polymer molecular weights.

Polymer molecular weight is often lower than that described by Eq. 12 because of chain transfer (radical displacement) reactions of the type



where XA may be monomer, initiator, solvent or any other substance present in the reaction system. Chain transfer decreases the polymer DP by prematurely terminating growth of the propagating radical although the polymerization rate is usually not affected since $\text{A}\cdot$ is sufficiently reactive to reinitiate polymerization. Control of the polymer MW requires that one control the identities of the components of the reaction system to avoid chain transfer reactions which would decrease MW below the desired level. On the other hand, the deliberate addition of a strong chain transfer agent allows one to decrease MW to the desired level when the MW in a polymerization system is too high.

Radical polymerizations are performed in bulk, solution, suspension and emulsion. The reaction characteristics of emulsion polymerization are different than those of the other techniques. Radicals produced in an aqueous phase diffuse into colloidal particles (micelles) where propagation takes place with an alternating on-off mechanism. Immediate termination occurs whenever a radical enters a micelle containing a propagating radical since the micelle size is such that the presence of two radicals corresponds to an exceptionally high molar radical concentration. Successive radicals entering a micelle alternately terminate and re-initiate polymerization. The rate and degree of polymerization are given by

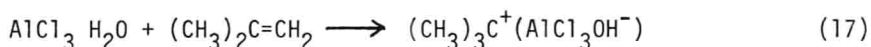
$$R_p = Nk_p[M]/2 \quad (14)$$

$$\text{DP} = Nk_p[M]/R_i \quad (15)$$

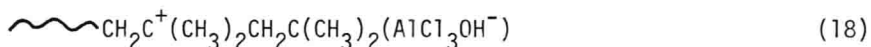
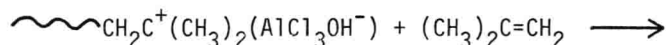
where N is the steady-state concentration of micelles. Emulsion polymerization has the unique feature that both R_p and DP can be increased by increasing N . For radical polymerizations in bulk, solution and suspension, increasing R_p by altering a reaction variable such as R_i or temperature almost always decreases DP. Emulsion polymerization is especially useful for low reactivity monomers such as 1,3-dienes. Bulk, solution and suspension polymerization typically yield low rates and low molecular weights. High R_p and DP are achieved in emulsion polymerization by using high concentrations of micelles.

Ionic Chain Polymerization. Ionic chain polymerizations take place at relatively low or moderate temperatures and in solvating media so that the ionic centers propagate to polymeric size prior to termination. Only solvents of low or moderate polarity, e.g., alkanes, chlorinated hydrocarbons, toluene, nitrobenzene and tetrahydrofuran, are employed. Highly polar solvents such as alcohols or ketones cannot be used since they inactivate ionic initiators and propagating centers by reaction or strong complexation.

Lewis acids such as AlCl_3 or BF_3 together with small concentrations of water or other proton source are most often used to initiate cationic chain polymerization. The two components of the initiating system form an initiator-coinitiator complex which donates a proton to monomer



Propagation proceeds by successive additions of monomer molecules to the carbenium ion center



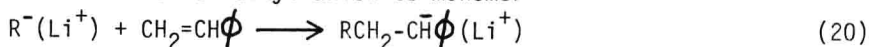
Protonic acids such as hydrochloric and sulfuric acids are far less suitable as initiators. Their conjugate bases, being strong nucleophiles, react rapidly with the carbenium ion center and prevent propagation. The advantage of the Lewis acid system is the low nucleophilicity of the anion (AlCl_3OH^- in the example above).

The most important termination for many polymerizations is chain transfer to monomer in which a proton along with the counter-anion AlCl_3OH^- is expelled from the propagating center with the formation of terminal unsaturation in the polymer



Chain transfer of the propagating carbenium ion to a negative fragment from the counter-ion (e.g., transfer of OH^- or Cl^- from AlCl_3OH^-) or solvent or some other component (e.g., water) of the reaction system are also important.

Anionic chain polymerization can be initiated by metal alkoxides, aryls and alkyls and electron-transfer from sodium naphthalene. Alkylolithiums are among the most useful, being employed commercially in the polymerization of 1,3-butadiene, isoprene, and styrene. Initiation involves addition of alkyl anion to monomer

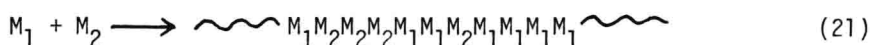


The anionic chain polymerizations of polar monomers, such as methyl methacrylate, methyl vinyl ketone and acrylonitrile, often yield complex polymer structures due to nucleophilic reactions of the carbonyl and nitrile groups.

For many anionic polymerizations of nonpolar monomers such as styrene, isoprene and 1,3-butadiene, there are no effective termination reactions if moisture, oxygen and carbon dioxide are absent. Propagation proceeds with complete consumption of monomer and the propagating anionic centers remain intact as long as one employs solvents such as benzene, n-hexane and tetrahydrofuran which are inactive in transferring a proton to the propagating anion. These polymerizations, referred to as living polymerizations, are terminated when desired by the deliberate addition of a proton source such as water or alcohol.

Both cationic and anionic chain polymerization are very sensitive to changes in the reaction medium due to changes in the nature of the propagating centers. In the low to moderate polarity solvents used, two types of propagating species coexist -- the free ion and ion-pair. The ion-pair consists of the propagating center and its tightly held counter-ion. The free ion consists of the propagating center separated from the counter-ion by solvent. The ion-pair and free ion propagate concurrently and in equilibrium with each other. The ion-pair is the more plentiful species but the free ion is much more reactive, often by as much as three orders of magnitude. Changing the reaction solvent to a more polar solvent (e.g., from n-hexane to THF) results in large increases in both rate and degree of polymerization by increasing the concentration of free ion. The identity of the counter-ion also affects polymerization. Less tightly-held counter-ions yield more reactive ion-pairs.

Copolymerization. Chain copolymerization, the polymerization of a mixture of two monomers, yields a copolymer with two different repeat units distributed along the polymer chain



Copolymerization has practical utility for changing the properties of a homopolymer in a desired direction. A number of commercially-important elastomers are copolymers. Butyl rubber is a copolymer of isobutylene with 1-2% isoprene. The isoprene units in the copolymer allow it to be crosslinked. Although polystyrene is far too rigid to be elastomeric, styrene-1,3-butadiene copolymers (SBR) are useful as elastomers. Polyethylene is a semi-crystalline plastic while ethylene-propylene copolymers and terpolymers of ethylene, propylene and a diene (e.g.,

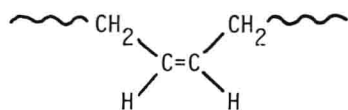
hexa-1,4-diene, dicyclopentadiene, 2-ethylidenenorborn-5-ene) are elastomers (EPR and EPDM rubbers). Nitrile or NBR rubber is a copolymer of acrylonitrile and 1,3-butadiene. Vinylidene fluoride-chlorotrifluoroethylene, olefin-acrylic ester copolymers and 1,3-butadiene-styrene-vinyl pyridine terpolymer are examples of specialty elastomers.

The properties of a copolymer are dependent on the identities of the monomers and their relative proportions within the copolymer chain. The copolymer composition is determined by the feed composition and the relative reactivities of the monomers undergoing copolymerization. The latter is determined by the competition among four propagation reactions. There are two types of propagating centers -- those ending in M_1 and those ending in M_2 -- and each type of propagating center can react with either of two monomers, M_1 or M_2 . The copolymer composition is usually different from the comonomer feed composition, the difference depending on the interplay of the four propagation reactions.

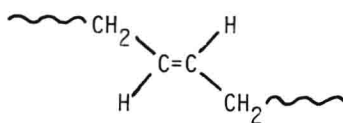
Structural and Stereo-Isomerism. Stereo-isomerism is possible in the polymerization of a monosubstituted alkene such as propylene. Every other carbon in the polymer chain is a chiral center and the substituent on each chiral center can have either of two configurations. Two ordered or stereoregular polymers are possible -- isotactic and syndiotactic -- where the substituent groups on successive chiral carbons have the same or opposite configurations, respectively. The unordered or atactic structure has a random distribution of equal numbers of the two configurations.

Both structural and stereo-isomerism are possible in the polymerization of conjugated dienes such as 1,3-butadiene. Polymerization can proceed by 1,2- and 1,4-reaction. Isotactic, syndiotactic and atactic polymers are possible for 1,2-polymerization analogous to the situation for a monosubstituted alkene.

1,4-Polymerization yields products in which the repeat units can be either cis(I) or trans (II)



I



II

The polymer produced in a polymerization is highly dependent on the specific choice of reaction conditions (initiator, solvent, counter-ion and temperature). 1,4-Polymerization dominates over 1,2-polymerization and trans-1,4-polymerization over cis-1,4-polymerization for radical polymerization of conjugated dienes. These preferences are stronger at

lower reaction temperatures. Higher temperatures yield more random placement of successive monomer units in the polymer chain. Cationic polymerizations proceed similarly but are not generally useful (except for Butyl rubber) because the products are usually low MW and extensively cyclized. 1,2-Polymerization is favored over 1,4-polymerization in anionic polymerizations in polar solvents (where the counter-ion is weakly coordinated with the propagating center). The Symposium paper by Bywater and Worsfold describes the large increase in the extent of 1,2-polymerization achieved upon the addition of a polar material to the reaction system.

The trends noted above are not exceptionally strong. Dramatically different results are observed for anionic polymerizations under conditions wherein there is strong coordination among the propagating center, counter-ion and monomer. Strong coordination results in very greatly increased preferences -- some in the same direction as for polymerization under non-coordination conditions and some in the opposite directions. The most remarkable results are obtained with the Ziegler-Natta catalysts obtained by combining a Group I-III metal derivative (e.g., AlR_3 , AlR_2Cl , MgR_2) with a transition metal derivative (e.g., TiCl_3 , TiCl_4 , VCl_3). Polymerizations initiated by these catalysts yield polymers with high degrees of structural purity. Judicious choice of the components of the catalyst system allow one to synthesize either the cis-1,4-polymer or the trans-1,4-polymer or the 1,2-polymer each in high purity (>95% pure). For example, trans-1,4-polybutadiene is obtained using $\text{TiCl}_4/\text{AlR}_3$ or Co chelates/ AlR_3 , and 1,2-polybutadiene using $\text{Ti}(\text{OR})_4/\text{AlR}_3$ or $\text{V}(\text{acetylacetonate})_3/\text{AlR}_3$. The identity of the counter-ion determines the specific coordination among counter-ion, propagating center, and monomer which in turn determines how successive monomer molecules are allowed to enter the polymer chain in these coordination polymerizations.

The ability to synthesize each of the isomeric polymers in high purity is important since the different polymers have different properties. For example, cis-1,4-polyisoprene is an excellent elastomer over a large temperature range due to its very low degree of crystallinity and low glass transition and melting temperatures. About two billion pounds are used annually in the United State for such typical applications as tires, coated fabrics, molded objects, adhesives and rubber bands. Trans-1,4-polyisoprene is a much harder and less rubbery elastomer since it crystallizes to an appreciable extent and has higher glass transition and melting temperatures. Small amounts