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RESEARCH ARTICLE

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Exploitation of rare earth catalysts in polymer syntheses

Abstract The studies over forty years on rare earth catalysts in polymer syntheses of diene, alkyne, alkylene oxide, thiirane, carbon dioxide copolymerization, lactide, caprolactone, cyclic carbonate and so forth in China have been reviewed.

Keywords polymer synthesis, rare earth catalyst, diene, alkyne, alkylene oxide

Polymer synthesis is the foundation of polymer science. The exploitation and development of new catalytic systems for polymer syntheses are the most important research projects for advancing polymer science. The discovery of Ziegler-Natta catalysts has opened a new era of polymer science and polymer industry. Due to their contributions, Dr. Ziegler (Germany) and Dr. Natta (Italy) were awarded Nobel Prize for Chemistry in 1963. Half century has passed since the discovery of Ziegler-Natta catalyst. The traditional Ziegler-Natta catalysts encompass literally thousands of different combinations of a Group I-III organometallic compound and a transition metal compound of Group IV-VIII. Abundant resources of rare earth ores (over half of whole world) in China has challenged our interest in investigation of using compounds of rare earth element (Group IIIB element) as new type of Ziegler-Natta catalysts. Early in the 1960's we scouted rare earth catalytic systems composed of rare earth chloride or rare earth diketonate with alkyl aluminum as heterogeneous or homogeneous butadiene polymerization catalysts for the first time [1, 2]. A new family of rare earth coordination catalysts with high activity and high stereospecificity in polymerizations of conjugated dienes has been successfully developed since then. Changchun Institute of Applied Chemistry, Chinese Academy of Sciences has investigated the polymerizations of various olefinic monomers using rare earth coordination catalysts since 1970 and has made very brilliant achievements and won 1982 National Natural Science Second Class Prize of China. Changchun Institute of Applied Chemistry collaborated closely with production departments. Rare earth polybutadiene rubber (PBd) and rare earth polyisoprene rubber (PIp) had been produced in pilot plants of Jinzhou Petroleum Company and Jilin Petroleum and Technology Research Institute respectively. The PBd and PIp synthesized by rare earth catalysts have been taken for tire mileage examination and results indicate their properties are comparable to those of foreign rubber brands. Later, groups in Russia, America, Italy, Japan, Germany, England and others also started research on polymerizations of dienes by rare earth catalysts. Companies in some countries have even built facilities to produce neodymium PBd such as Buna 22-24 in Bayer, Germany, BR40, BR60 in Enichem, Italy. They claimed that their properties are better than PBd obtained by Ni, Co, Ti and Li catalysts. Neodymium Pip-CKU-5 was produced in Russia and its properties are better than Ti-PIp approaching natural rubber.

In order to further explore the new applications of rare earth catalysts in polymer syntheses, Zhejiang University has exploited rare earth catalysts for *cis*- polymerization of acetylene at room temperature in 1981 [3,4], for phenyl acetylene and alkyl acetylene polymerizations in 1982 and 1983 [5] and preparing directly poly(phenyl acetylene) film [6]. Since 1985 we have been the first to carry out the studies of exploiting rare earth catalysts for ring-opening polymerizations of ethylene oxide, propylene oxide, epichlorohydrin, thiirane, chloromethyl thiirane [7–9], for ring-opening polymerizations of lactide, ε-caprolacton, and cyclic carbonate [10–12] and copolymerizations of CO_2-oxirane [13], oxirane-maleic anhydride [14], styrene-maleic anhydride, styrene-acrylate [15]; polymerization of acrylate [16] and oligomerizations of ethylene or octane [17] and so forth. It can be seen above that rare earth coordination polymerizations exploited firstly in China have greatly advanced in more than 20 years. The achievements not only

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have contributed to the development of Ziegler-Natta polymerization, but also have developed many new varieties of polymers with new structures and properties. Thus Zhejiang University has been awarded the Third Class National Natural Science Prize of China in 1993 and some ministry and provincial prizes.

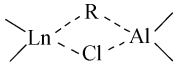
Recently considerable interests on polymerizations using organolanthanide compounds in both China and abroad and progresses has been made [18].

The major research achievements on exploration of rare earth catalysts in polymer syntheses obtained by Changchun Institute of Applied Chemistry, Chinese Academy of Sciences and Zhejiang University are briefly reviewed in this article.

1 Diene polymerization catalyzed by rare earth catalysts

Great achievements of diene polymerizations by rare earth catalysts have been made in China. The studies including catalytic systems, influences of polymerization parameters, kinetic behavior, polymerization mechanism, polymerization process, polymer structure and property, rubber processing and anti-oxidizing and copolymerizations of diene have been carried out and have obtained great progress in Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, which had already been reported in collection [19], review [20–24] and book [25–27]. The investigations reveal that rare earth catalysts represent an unprecedented case other than Ti, Co, Ni, or Li etc. catalysts, where either butadiene, isoprene or mixtures of butadiene and isoprene can be polymerized to elastomers with high *cis*-1,4 content. The rare earth catalysts used for diene polymerization can be binary (two component) or ternary component catalytic systems. Two component catalytic systems generally are composed of complexes of rare earth chloride with electron donor and alkyl aluminum. There are many kinds of donor such as alcohol, tetrahydrofuran and neutral phosphonate (TBP, P_{350}), amine, dimethyl sulfoxide etc. Other types of two-component rare earth catalysts are composed of rare earth compound containing halogen and another group such as $Ln(OR)_nCl_{3-n}$ or $LnCpCl_2$ with alkyl aluminum. Ternary catalysts are composed of rare earth compound-halogen compound-alkyl aluminum. Alkyl aluminum halide (AlR_2X), alkyl halide, or silicon chloride are used as halogen compound. Rare earth compounds (Ln) having different ligands such as: rare earth carbonate, rare earth phosphonate (P_{204}, P_{507}, P_{229}), rare earth alkoxide, cyclopentadienyl rare earth and rare earth calixarene complex are used. To synthesize high *cis*-1,4 polydiene, the rare earth compound should have halogen group around rare earth ion; different halogen atoms lead to different catalytic activities. Chlorine is the cheapest and easy available element among halogen elements, which shows high catalytic activity. Thus chlorine-containing compound (Cl) has been used generally. Molar ratio of Cl/Ln affects catalytic activity and the phase of the catalytic system greatly. Most researches of diene polymerization use rare earth carbonate such as rare earth C_{5-9} carbonate, rare earth C_{9-11} carbonate [$Ln(vers)_3$] and rare earth naphthenate. Among these, rare earth naphthenate is often used due to it easy solubility in aliphatic hydrocarbon and preparation and higher activity under proper conditions. Rare earth phosphonates are used in another ternary system for their ligands. Acidic phosphonate: P_{507}, P_{204}, etc are common extractant for rare earth element separation. Rare earth phosphonate system shows higher activity at lower molar ratio of Al/Ln. The effect of alkyl aluminum is different in binary or ternary catalytic systems. The catalytic activities of various rare earth systems are quite different. Basically the catalytic activity sequence of various rare earth systems is as follows: Nd > Pr > Ce > Gd > Tb > Dy >La ~ Ho >Y > Er ~Sm > Tm > Yb > Lu ~Sc ~Eu. Recently we have found that ternary system: $La(naph)_3$–$Mg(n\text{-}Bu)_2$–THF is an effective catalyst for butadiene *trans*-1,4 polymerization. The conductivity of *trans*-polybutadiene doped with iodine has been investigated [28]. To find out if a supported catalytic system might raise its activity, Li et al. had carried out studies of diene polymerization by polymer–supported rare earth complex and had made some achievements [29].

In order to determine the reaction type of diene polymerization catalyzed by rare earth catalyst, Peng et al. quenched neodymium system catalyzed butadiene polymerization by $^{14}CH_3OH$ and CH_3OT respectively and found that polybutadiene obtained by CH_3OT quenching has 100 times more radioactivity than that by $^{14}CH_3OH$ quenching. Thus it had been presumed that the propagation of the polymerization active chain is conducted within M^+~C^-, the active species of rare earth catalyst is formed by alkylation and the diene polymerization proceeds via a coordination anionic mechanism [30]. The structure of active species of diene polymerization catalyzed by rare earth catalyst is another hot point. Some investigations have assumed that the active species might follow Al-Ln bimetallic structure:



Later crystallized Al-Ln bimetallic complex but not the single crystal had been separated from homogeneous system: $(CF_3COO)_2LnCl$. C_2H_5OH-$AlEt_3$ which showed the catalytic activity of Bd or Ip polymerization and prepared 94% *cis*-1,4 polydienes [31]. The active species single crystal appropriate for *x*-ray examination was cultivated from rare earth system: $Nd(O\text{-}i\text{-}Pr)_3$-$AlEt_2Cl$-$AlEt_3$ which is an important advance of active species structure [32]. The *x*-ray diffraction results indicate that the crystal belongs to triclinic system and is composed of multinuclear Nd–Al bimetallic complex dimer: $[Al_3Nd_6(\mu_2\text{-}Cl)_6(\mu_3\text{-}Cl)_6(\mu_2\text{-}Et)_9Et_5(O\text{-}i\text{-}Pr)]_2$ Nd atoms are connected by trichlorine or bichlorine bridges, while Nd atom and Al atom is joined by μ_2-Et bridge. The single crystal of bimetallic complex alone can catalyze *cis*-1,4-polymerization of butadiene and give polybutadiene the same microstructure as that prepared by ternary systems.

Diene polymerization with Ziegler-Natta catalysts generally carried out solution polymerization since was industrialized in 1960's. The advantages of solution polymerization are: polymerization heat produced in the reaction is easy to spread off; polymerization reaction proceeds steadily; the quality of the polymer can be controlled and it is easy to be realized in big continued production. However, solution polymerization has following shortcomings: it needs huge amount of solvent and many equipment, and great energy consumption are needed to purify, dry and recycle the solvent used. People want to achieve diene polymerization in bulk. Changchun Institute of Applied Chemistry, Chinese Academy of Sciences has studied the bulk polymerizations of Bd and Ip respectively. Jinzhou Petroleum Chemical Company has also studied the industrialization of Bd bulk polymerization catalyzed by rare earth catalyst [33]. The gas phase polymerization process raises the operation safety, decrease the cost of investment and manipulation due to not having to use a solvent, and no need for coagulation and separation processes Meantime it can decrease environmental pollution, avoid lower monomer conversion and improve the polymer quality caused by bulk polymerization. Gas phase polymerization process has already been used in industries of polyethylene and polypropylene showing great economic and environmental effect. We have been the first to study the gas phase polymerization of butadiene by rare earth catalyst under the financial support of Yanshan Petroleum Chemical Institute in 1997. We have successfully developed supported high active and high stereospecific rare earth catalysts containing aluminum alkyl as cocatalyst and chlorine organic chemical as activator for butadiene gas phase polymerization [34]. We have studied the kinetic model of gas phase polymerization of Bd catalyzed by supported rare earth coordination system and also established Monte Carlo simulation model and program to simulate gas phase polymerization of butadiene gas phase polymerization. Experimental results in the polymerization temperature range of 30℃ to 70℃ closely coincide the simulation results. The three elemental reactions of gas phase Bd polymerization: deactivation, initiation and chain transfer have been especially discussed in order to improve the gas phase polymerization technology [35].

The copolymerization of butadiene and isoprene catalyzed with rare earth coordination catalysts had been carried out at the same time in 1970's in Changchun Institute of Applied Chemistry. The distinguishing feature of Bd and Ip copolymerization is that copolymer has high *cis*-1,4 content above 96% of both butadiene monomer and isoprene monomer which could not be obtained by any other catalytic systems. The copolymerization of Bd and Ip with $LnCl_3$-ROH-AlR_3 catalytic system had been studied systematically The equation of copolymerization rate and the reactivity ratio of Bd and Ip were established; $r_{Bd}>1$, $r_{Ip}<1$, $r_{Bd}\cdot r_{Ip}\approx 1$ [36]. Ji Xianzhong et al. studied the polymerization of Bd with $NdCl_3$*i*PrOH-$AlEt_3$-Heptane system at −70℃ and −30℃ and have found that the polymerization had no deactivation of active species i.e. no termination, number average molecular weight of PBd increased linearly with polymerization time and polymerization conversion indicating the polymer chain produced by each Nd atom is not related with the polymerization time and conversion. Thus they concluded that the Bd polymerization at −70℃ is an idea living coordination polymerization and at −30℃ is an approaching living polymerization and they had prepared the block copolymer of Bd and Ip under the conditions [37]. The copolymerization of diene and styrene has attracted interest in the end of 1980's. $(CF_3COO)_3Nd$-$Al(C_8H_{17})_3$-$(CH_3)_2$ $CHCH_2Br$ and $Nd(Oct)_3$-Al(*i*-Bu)$_3$- $CHCl_3$ catalytic systems had been used for the copolymerization of butadiene and styrene [38]. Recently we have carried out the random copolymerization of styrene with butadiene or isoprene and have found that $Nd(naph)_3$-Al(*i*-Bu)$_3$-Al(*i*-Bu)$_2$Cl, $Nd(ver)_3$-Al(*i*-Bu)$_3$-$CHCl_3$ and $Nd(P_{507})_3$-Mg(*n*-Bu)$_2$-$CHCl_3$ systems are effective catalytic systems for the copolymerization of butadiene with styrene preparing the copolymer with higher styrene content and molecular weight. The monomer reactivity ratios of Bd and styrene under the conditions tested were determined [39]. We have found that $Nd(ver)_3$- Al(*i*-Bu)$_3$-$CHCl_3$ system is an effective catalytic system for the homopolymerization of isoprene, styrene or their copolymerization. Copolymer containing 40 mol% styrene and isoprene unit of *cis*-1,4 content above 85% were prepared by $Nd(acac)_3$-Mg(*n*-Bu)$_2$-$CHCl_3$ system, with which the monomer reactivity ratios of isoprene and styrene under typical conditions $r_{Ip}=5.4$, $r_{St}=0.38$ were found. $NdCl_3$·HMPA-Al(*i*-Bu)$_3$ system also is an effective catalytic system for the copolymerization of styrene with isoprene [40]. We also found that block copolymers of isoprene with epichlorohydrin, isoprene with butyl methacrylate, isoprene with methyl methacrylate, isoprene with 1,2-cyclo hexane-oxide and isoprene with acrylnitrile could be prepared by ternary rare earth catalytic system: $Nd(P_{204})_3$-Al(*i*-Bu)$_3$-$BrCH_2CH_2Br$ using sequencial addition mode of the monomers. $Nd(naph)_3$-$AlEt_3$ system could prepare alternating copolymer of isoprene with maleic anhydride [41].

2 Alkyne polymerization catalyzed by rare earth catalysts [42]

The Nobel Prize for Chemistry in 2000 was awarded to Professor Heeger of University of California, Santa Barbara (USA), Professor MacDiarmid of University of Pensylvania (USA) and Professor Shirakawa of Tsukuba University of Japan for their outstanding contributions on researches in the chemistry, structure, property, physics and applications of semi-conductive and metallic organic polymers since the middle of 1970s. Polyacetylene after doping with electron donor or electron acceptor becomes P type or N type semi conductor or even metal, thus it is called synthetic metal. Polyacetylene (PA) has *cis* and *trans* isomers. Both isomers can be doped and the doped isomers' conductivities rise to the level of metallic conductivity. The doping effect of the *cis* PA is 4-5 order greater than that of the *trans* one and the *cis* PA is more elastic, flexible and easy to process. There-

fore efforts have been made to synthesize high *cis* polyacetylene. The commonly used catalyst is $Ti(OC_4H_9)_4$-$Al(C_2H_5)_3$ at −78℃ preparing ~95% *cis* polyacetylene film. In 1981 we were the first to use the rare earth coordination catalysts for preparing high *cis* content, high thermal stability and antioxidation polyacetylene film at room temperature. Thus a new variety of polyacetylene–rare earth polyacetylene has been obtained and an effective novel family of catalysts for preparing high *cis* polyacetylene has been developed. The detailed polymerization regularity of acetylene by all sixteen rare earth elements: Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu naphthenate, phophonate and isopropoxide combined with trialkyl aluminum had been investigated. The scandium system shows fair activity in acetylene polymerization, although its activity in diene polymerization is small [3, 43]. The catalytic activity sequence of rare earth naphthenate for acetylene polymerization at 30°C is as follows: Y, Ce > Nd, Yb > Pr, La > Lu, Gd > Tm, Er > Ho, Yb, Eu > Sm > Dy > Sc. The catalytic activity sequence of rare earth phophonate is: Nd > Gd >La >Y ~ Er >Lu >Sc which may be related to the radii of the rare earth ions and hardness of ionic hard soft acid. In order to get more insight into the polymerization reaction of acetylene, a kinetic study with $Nd(P_{204})_3$-$Al(C_2H_5)_3$-P_{204} catalytic system was carried out. The experimental results indicated that the polymerization rate of acetylene is proportional to the pressure of acetylene and the concentration of the catalyst. A bimolecular deactivation anionic coordination mechanism was postulated [44]. The density, paramagnetism, crystallinity, antioxidizing stability, FTIR spectra of *cis* and *trans* polyacetylene and their thermal isomerization kinetics and mechanism, electronic micrograph, chemical doping effect and ionic junction have been examined. The electrical chemistry behavior of the electrode and property of the rare earth polyacetylene battery were studied [45].

The polymerization of phenyl acetylene was first catalyzed by rare earth coordination catalysts composed of Y, Sc, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm ,Yb and Lu naphthenate and trialkyl aluminum in 1983 [5]. The poly(phenyl acetylene) film was formed directly during the polymerization with rare earth coordination catalyst in mixture of hexane and toluene at room temperature and the structure and property of which were studied in 1987 [6]. The effects of catalyst preparation mode, molar ratio of Al/Ln, polymerization temperature, various rare earth systems and the kinetics had been studied. Experimental data show that the polymerization has typical chain polymerization reaction features: slow initiation, quick propagation and automatic deactivation. The polymerization rate is first order with respect to both monomer concentration and active species concentration. The catalytic activity sequence of various rare earth systems is as follows: Gd > Lu > Nd ~ Ce > Ho > Sm > Dy > Eu > Er > Pr >> La > Y~Tm >Yb. Ferric compound cooperated lanthanide compound for film polymerization of phenyl acetylene have also been studied. Rare earth poly(phenyl acetylene) has high *cis* structure. The photosensitivity of rare earth poly(phenyl acetylene) can be enhanced significantly by the radiation of ^{60}Co γ-ray or electronic beam or using sensitizer, thus it might be used as photosensitive material [46].

Rare earth coordination catalysts composed of rare earth naphthenate, trialkyl aluminum and ethanol were first used as catalysts for the polymerizations of 1-hexyne, 1-pentyne, 3-methyl-1-pentyne, 4-methyl-1-pentyne and 3-methyl-1-butyne in 1982. Scandium and neodymium systems show high activity for these polymerizations, which would promote the catalytic study of scandium compound [5].

3 Ring-opening polymerization of alkylene oxide catalyzed by rare earth catalysts

Poly(alkylene oxide)s are a family of versatile polymer. In 1985 we found for the first time that ternary rare earth systems consisting of rare earth compound, alkyl aluminum and water are new efficient catalysts for the polymerization of ethylene oxide, propylene oxide and epichlohydrin showing high catalytic activity and high polymerization rate and giving high yield high molecular weight polymers[7]. Polyethylene oxide with over 80% yield and molecular weight of 50×10^4–300×10^4 can be prepared by the rare earth coordination catalysts. The effects of molar ratio of catalyst components, catalyst concentration, polymerization temperature on the ethylene oxide ring opening polymeri-zation catalyzed by $Nd(P_{204})_3$-Al(*i*-Bu)$_3$-H_2O and $Y(P_{204})_3$-Al(*i*-Bu)$_3$-H_2O had been studied, which indicated that the polymerizations are first order with respect to both monomer and catalyst concentrations, having apparent activity energy of 33.8 kJ·mol^{-1}. The rare earth poly(ethylene oxide) (PEO) obtained has crystallinity of 60%–70% [47].

The above mentioned ternary rare earth coordination catalytic systems are also good catalysts for preparing high molecular weight poly(propylene oxide) (PPO). A small amount of water is necessary for the catalyst. The yield and molecular weight of PPO are higher at molar ratio of H_2O/Al=0.5–0.7. Methanol, ethanol, isopropanol and acetylacetone have been used to substitute water as third component, but they are not as good as water. The catalytic system composed of rare earth acetylacetonate and hydrolyzed alkyl aluminum [$(Al(C_2H_5)_3\cdot1/2H_2O$] has the highest catalytic activity. Only 2 hours polymerization give high yield and high viscosity average molecular weight over 3×10^6 and high stereospecific PPO [48]. The dilatory study of kinetics of PO polymerization with $Nd(P_{204})_3$-Al(*i*-Bu)$_3$-H_2O catalyst indicated that polymerization rate is first order with respect to monomer concentration and catalyst concentration and the overall activity energy of the ring-opening polymerization amounts to 61.3 kJ·mol^{-1}. The formation of the active species of this system had been studied by UV, IR, and ^{31}P-NMR and the results revealed that no valence state change occurred; alkyl group exchange occurred between $Nd(P_{204})_3$ and Al(*i*-Bu)$_3$ and an rare earth ternary active species: Nd-O-Al formed upon the addition of small amount of

water [49]. We also studied the propylene oxide polymerization with chitosan–supported rare earth catalysts which is a high active and high stereospecific catalyst giving high molecular weight of 2×10^6 PPO. Kinetic studies show that the polymerization rate is first order with respect to monomer and catalyst concentration and the apparent activity energy is 37.1 kJ·mol^{-1} [50]. Neodymium calyx[4]arene derivative complex-Al(*i*-Bu)$_3$-H_2O is a good yield and stereospecific catalyst for the polymerization of propylene oxide [51].

Ln(acac)$_3$-Al(*i*-Bu)$_3$-H_2O systems can catalyze the polymerization of epichlohydrin (ECH) showing fast polymerization rate and producing molecular weight of 1×10^6 polyepichlohydrin containing 10%–20% crystallinity which is good for use as rubber-like material [52]. The effects of Al/Nd molar ratio, H_2O/Al molar ratio, solvent sort and polymerization temperature on the polymerization was studied. The polymerization rate of ECH polymerization is first order with respect to monomer and catalyst concentration by measuring monomer concentration in the reaction with ^{1}H-NMR. The dilatory study of the kinetics of ECH polymerization catalyzed by Nd(P_{204})$_3$-Al(*i*-Bu)$_3$-H_2O indicated that the polymerization rate is same first order with respect to both monomer and catalyst concentration having overall activity energy of 48.9 kJ·mol^{-1}. A mechanism of quick initiation, bideactivation of active species and chain transfer to alkyl aluminum has been proposed [49, 52]. Nd(O-*i*-Pr)$_3$-Al(*i*-Bu)$_3$ catalytic system can polymerize ECH at −22℃ producing molecular weight of 10×10^4–30×10^4 PECH. Low crystallinity and molecular weight of 2.82×10^6 PECH can also be prepared by catalytic system composed of chitosan supported neodymium complex, triisobutyl aluminum and methyl benzoate [53].

We found that Nd(P_{204})$_3$-Al(*i*-Bu)$_3$-H_2O also could catalyze the random and block copolymerization of ethylene oxide and propylene oxide. Their reactivity ratios are: r_1(EO)=1.60±0.04, r_2(PO)=0.45±0.02 [54]. The ionic conductivity of EO–PO copolymer containing 27% PO unit complexed with sodium thiocyanate (NaSCN) has been determined to be 5×10^{-5} S·cm^{-1} at 30 ℃ [54]. The ring-opening polymerization of styrene oxide with rare earth calyx[6] arene complex-Al(*i*-Bu)$_3$-P_{204} system were also studied. The influences of molar ratio of catalyst components, solvent sort and polymerization temperature on the polymerization and the structure of the polymer also been investigated [55].

4 Ring-opening polymerization of thiirane catalyzed by rare earth catalysts

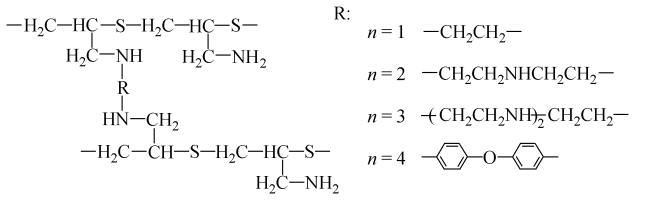
Poly(propylene sulfide) (PPS) has good oil resistance, heat resistance and mechanical properties and can be used in rubber and plastics. We have discovered for the first time that rare earth coordination catalysts are good catalysts for the ring-opening polymerization of propylene sulfide [8]. Rare earth catalytic systems containing La, Pr, Nd and Yb can catalyze the polymerization of propylene sulfide [PS] quickly at lower temperature giving higher yield of molecular weight over 2×10^6 poly(propylene sulfide). The catalytic activity sequence of various rare earth systems under the tested conditions were as follows: Yb ~ La > Pr > Nd > Eu > Lu > Gd > Dy > Ho > Er. The effect of various ligands on the catalytic activity and molecular weight of the polymer is small, but rare earth acetylacetonate system gives higher results. The influences of catalyst composition, catalyst aging time and polymerization time on the polymerization of propylene sulfide catalyzed by Nd(P_{204})$_3$-Al(*i*-Bu)$_3$-H_2O were studied. The PS polymerization rate is first order with respect to both monomer concentration and catalyst concentration, and the apparent activity energy is 61.4 kJ·mol^{-1}. The structure of PPS was studied by ^{13}C-NMR, X-ray diffraction, GPC and DSC, which revealed that the monomer ring was opening in *β*-direction and over 60% isotacticity PPS was obtained indicating again the high stereospecificity of rare earth coordination catalyst [8].

Chloromethyl thiirane (CMT) has useful chloromethyl group good for preparing functional polymer, but it is not easy for ring-opening polymerization. It had been reported only a few cationic initiator can catalyze the polymerization of CMT giving small amount of low molecular weight polymer for long duration polymerization such as BF_3·Et_2O at −78℃ for several days. We found that the rare earth coordination catalytic systems composed of rare earth complex and triisobutyl aluminum could catalyze the polymerization of CMT preparing white soft solid polymer with rather high yield, and small influence between various ligands and rare earth elements [9]. The effects of polymerization parameters such as catalyst concentration, catalyst composition, polymerization temperature and polymerization time in Nd(P_{204})$_3$-Al(*i*-Bu)$_3$ system on polymerization had been studied and the kinetic study revealed that the polymerization rate is first order with respect to both monomer and catalyst concentration and the apparent activity energy is 28.4 kJ·mol^{-1}. Substituting $Al_2Et_3Cl_3$ for Al(*i*-Bu)$_3$, higher molecular weight PCMT could be obtained. Our further study showed that rare earth solid superacids: SO_4^{2-}/TiO_2/Ln^{3+} are the best catalysts for CMT polymerization giving rather high yield and highest molecular weight (viscosity average molecular weight of 40×10^3) PCMT. Chloromethyl thiirane polymerization proceeds via cationic mechanism and its active species is a chelating bidentate Bronsted acid [56]. We also found that rare earth coordination catalysts composed of rare earth acetylacetonate or rare earth naphthenate and triisobutyl aluminum are good catalysts for the copolymerization of chloromethyl thiirane with epichlorohydrin preparing alternating-like copolymer which has never been reported in literature. The characteristics of the copolymerization with above neodymium catalytic systems had been examined. The highest catalytic activity of Nd(acac)$_3$-Al(*i*-Bu)$_3$ reached over 10000 g copolymer/mol Nd and the monomer reactivity ratios are r_{CMT} 0.022 and r_{ECH} 0.097. Y(P_{204})$_3$-Al(*i*-Bu)$_3$-H_2O system is a good catalyst for the copolymerization of CMT and propylene oxide, its catalytic activity was 6000 g copolymer/mol Y showing the

monomer reactivity ratios as r_{CMT}=0.014, r_{PO}=1.37 [57].

Based on the high reactive chloromethyl group in the side chain of poly CMT and copolymer of CMT and ECH, twelve novel functional chelating resins had been prepared by the reactions of the crosslinked prepolymer obtained with small amount of diethylene triamine, with sodium thiosulfate, sodium azide, 2-amino thiazole, 4-amino antipyrine, potassium ethyl ortho sulfonate and potassium thiocyanate and so forth. These resins have higher adsorption and fair selectivity of noble metal ions of Au(III), Pt(IX), Pd(II) and Ag^+ [58].

We also synthesized primary amine resin (CAn) containing polythioether back bone as shown in following:



(1)

Other 19 resins were prepared by CAn resins reacted with carbon disulfide to prepare CDTC resins; with dialdehyde compounds to prepare Shiff base type CSH resins and precrosslinked polythiirane reacted with sodium thiocyanate or azide. Their adsorption ability of noble ions were determined. CA resins have exceptional adsorption for Au(III) and Ag^+ and CDTC resin has exceptional adsorption for Ag^+. The results indicate that these resins might be useful in separation of noble metal ions from non-noble ones [59].

5 Ring-opening copolymerization of carbon dioxide and alkylene oxide catalyzed by rare earth catalysts

Chemical fixation of carbon dioxide is a very attractive subject in views of resource utilization and environmental protection. As a kind of catalytic fixation of carbon dioxide, copolymerization of carbon dioxide with various epoxides has been investigated extensively in recent years. The effective catalysts reported so far for the copolymerization consisting of diethyl zinc and compounds having active hydrogen, such as water, di or trihydric phenol. The yield and molecular weight of the copolymer are still to be improved. We have found for the first time that rare earth coordination catalysts composed of rare earth phosphonate, triisobutyl aluminum and glycerin are novel effective catalysts for the copolymerization of carbon dioxide with propylene oxide. The catalytic system of $Y(P_{204})_3$-Al(*i*-Bu)$_3$-glycerin shows the highest catalytic activity. The copolymer obtained has high molecular weight of 47×10^4 and high thermal stability showing thermal decomposition temperature over 300℃. The influences of third component sort, solvent sort, catalyst composition, polymerization temperature and polymerization time of $Y(P_{204})_3$ system on the copolymerization had been studied [13a]. Based on this study some other work reported later [60].

The data in literature showed that the copolymerizing activity of epoxide ($H_2C(O)CH-X$) with carbon dioxide has following reactivity order of (-X) group: $ClCH_2-$< $C_6H_5CH_2-$ < C_6H_5-< $ROCH_2-$ (R=butyl or phenyl) <CH_3-. This sequence means that propylene oxide has the highest activity, while epichlorohydrin shows the lowest activity and no catalyst for the copolymerization of carbon dioxide with epichlor ohydrin has been reported until now. We have found that rare earth catalysts composed of $Ln(P_{204})_3$ and Al(*i*-Bu)$_3$ are effective catalysts for the copolymerization of carbon dioxide and epichlorohydrin preparing copolymer of 30% ECH unit with high yield and high molecular weight and high decomposition temperature of 320°C [13b]. $Lu(P_{204})_3$-Al(*i*-Bu)$_3$ catalyst gives the highest yield and molecular weight copolymer. The influences of solvent sort, catalyst concentration, polymerization temperature and third component on the copolymerization catalyzed by $Y(P_{204})_3$-Al(*i*-Bu)$_3$ system and $Nd(P_{204})_3$-Al(*i*-Bu)$_3$ system had been investigated and the results indicated that no third component and 1,4-dioxane as solvent are the better. Ternary copolymer of epichlorohydrin, maleic anhydride and carbon dioxide also had been prepared by $Y(P_{204})_3$-Al(*i*-Bu)$_3$ [13d].

6 Ring-opening polymerization of lactide, caprolactone and cyclic carbonate catalyzed by rare earth catalysts

Aliphatic polyesters (polylactide, polycaprolactone) and poly(cyclocarbonate) have attracted growing interest for their excellent properties of biodegradability, biocompatibility and low toxicity use as biocontrollable release medium, surgical suture and so forth. Thus the ring-opening polymerizations of lactide, caprolactone and cyclic carbonate become hot subjects in polymer synthesis.

6.1 Ring-opening polymerization of lactide

We have found that rare earth coordination catalysts composed of rare earth compound, trialkyl aluminum and water are a new family catalysts for the ring-opening polymerization of lactide which could prepare stable and controllable molecular weight polylactide with narrow molecular weight distribution (M_w/M_n=1.5) under mild conditions [10]. We have also found that rare earth (La, Nd, Dy and Y) isopropoxide single component could polymerize D,L-lactide (DLLA) in toluene preparing higher molecular weight (M_n=4×10^4) PLA. The polymerization reaction is first order with respect to both monomer concentration and catalyst concentration and has apparent activity energy of 67.7 kJ·mol^{-1} [61].

Recently we have found three new efficient single component initiators: rare earth tris(4-tertbutyl phenolate com-

plex [Ln(OTBP)$_3$] rare earth tris(2,6-dimethyl- phenolate) complex [Ln(ODMP)$_3$] and rare earth tris (2,4,6-trimethyl phenolate) complex [Ln(OTMP)$_3$] for the polymerization or copolymerization of DLLA and L-lactide (LLA). The catalytic activity sequence of DLLA polymerization by [Ln(ODMP)$_3$] is La >Nd > Sm >Gd >Er >Y. The appropriate conditions for DLLA polymerization in toluene catalyzed by [Ln(ODMP)$_3$] are as follows: [DLLA]=2.0 mol/L, [DLLA]/[La]=1000 molar ratio, 100℃, 45 min. The kinetics study of [La(ODMP)$_3$] system showed that polymerization reaction is first order with respect to both monomer concentration and catalyst concentration and has apparent activity energy of 69.6 kJ·mol^{-1} [61]. The analysis of the end group of the polymer verified that the polymerization proceeds via 'coordination insertion' mechanism. The influences of rare earth element, monomer concentration, molar ratio of monomer and catalyst, polymerization temperature and polymerization time on the polymerization of L-lactide (LLA) by single component [Ln(ODMP)$_3$] had been investigated. Experimental results revealed that [La(ODMP)$_3$] is an effective catalyst for LLA polymerization. The molecular weight and molecular weight distribution could be controlled by reaction conditions. The favorable conditions for polymerization of LLA in toluene are [LLA]/[La]=1000 molar ratio, 80℃, 40 min and PLLA with 97% yield, viscosity average molecular weight of 5.2×10^4 and MWD of 1.54 were obtained. [La(ODMP)$_3$] also can catalyze the block copolymerization of L-lactide with ε-caprolacton, but the monomer addition mode affect greatly. Block copolymer could only be prepared by sequencial addition of monomer that is ε-caprolacton added and polymerized first then lactide follows. PLLA homopolymer obtained by anyother monomer addition modes. The preferable conditions for the block copolymerization are toluene as solvent, [CL]=1.0 mol/L, [LLA]=1.0 mol/L, [CL+LLA]/[La]=200 molar ratio, first ε-caprolactone polymerized at 60℃ for 0.5 hours then L-lactide added and polymerized at 80℃ for 2 hours. The structure of the block copolymer characterized by IR and ^{13}C-NMR and the copolymer has two crystal melting endothermic peaks at 55.8℃ and 155.4℃ [61].

[La(OTBP)$_3$], [Gd(OTBP)$_3$], and [Nd(OTBP)$_3$] are effective single component catalysts for the ring-opening polymerization of DLLA. [La(OTBP)$_3$] has the highest activity among the catalyst tested. The favorable conditions of which are as follows: [DLLA]=1.0 mol/L, [DLLA]/[La]=1000 molar ratio, toluene as solvent, 90℃, 50 min and PDLLA of number average molecular weight of 5.3×10^4 prepared. The DLLA polymerization rate is first order with respect to both DLLA concentration and catalyst concentration and its apparent activity energy is 81.7 kJ·mol^{-1}. [Ln(OTBP)$_3$] (Ln = La, Gd, Nd, Y) also could catalyze the ring-opening polymerization of LLA to prepare 100% pure photoactive poly(L-lactide). The catalytic activity sequence of various rare earth systems is La >Gd > Nd > Y > Er. The preferable conditions for LLA polymerization by [La(OTBP)$_3$] are [LLA]=1.5 mol/L; [LLA]/[La]=1000 molar ratio, toluene, 70℃, 110 min. The LLa polymerization reaction is first order with respect to both monomer and catalyst concentration. and has apparent activity energy of 79.2 kJ·mol^{-1}. Both polymerizations of LLA and DLLA by [La(OTBP)$_3$] proceed *via* coordination-insertion and acy-oxygen bond opening of LA [62].

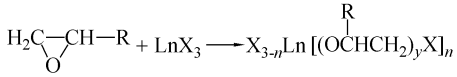
6.2 Ring-opening polymerization of ε-caprolactone

We found for the first time that rare earth phosphonate or rare earth naphthenate or rare earth acetylacetonate combined with trialkyl aluminum are highly active catalysts for the ring-opening polymerization of ε-caprolactone (CL). Among which rare earth acetylacetonate system showed higher catalytic activity and prepared higher molecular weight PCL [11a]. The polymerization reaction rate of CL by Nd(acac)$_3$·3H$_2$O-AlEt$_3$ system is first order to monomer concentration, 1/2 order to catalyst concentration and has apparent activity energy of 59.4 kJ·mol^{-1}. The polymerization mechanism studied by IR, UV-Vis, NMR etc. showed it is a coordination-insertion process that is CL coordinated on Nd-Al bimetallic complex, then opened its acyl-oxygen bond.

We also found that rare earth alkoxides in carbon tetrachloride are highly active catalytic systems for CL polymerization and PCL with viscosity average molecular weight of 15×10^4 can be prepared [63].

Further study has shown that single component rare earth halides, the easily available raw material of organolanthanide, are also effective catalysts for CL polymerization, such as all rare earth chloride or neodymium bromide or iodide can catalyze the CL polymerization at 100℃ giving molecular weight of 5×10^4 telechelic PCL. The catalytic activity of rare earth halide can be greatly enhanced by adding a small amount of epoxides [11b, 11c]. The kind and amount of epoxide affect the CL bulk polymerization. Rare earth chloride-propylene oxide system has high catalytic activity for the CL bulk polymerization. The catalytic activities of $NdBr_3$, NdI_3 are higher than $NdCl_3$ system, and the catalytic efficiency increases with the increase of polymerization temperature. PCL with viscosity average molecular weight of 28×10^4 can be obtained at 30℃ with an efficiency of 440 kg/mol $NdCl_3$, while at 60℃ molecular weight of 40×10^4 PCL with an efficiency of 1000 kg/mol $NdCl_3$ is obtained. Heavy rare earth chloride can react with epoxide in toluene and produce homogeneous solution, which can catalyze the solution polymerization of CL, but light rare earth chloride such as La, Pr, Nd cannot react with epoxide in toluene, and cannot catalyze the CL solution polymerization. It was found that light rare earth chloride and epoxide can dissolve in γ-butyl lactone forming homogeneous solution that can polymerize CL in toluene at 60℃ giving PCL of molecular weight of 40×10^4 [11d]. The study on the CL polymerization mechanism showed that rare earth alkoxide formed from the reaction between rare earth halide and epoxide as shown in

the following:



$$H_2C\!-\!CH\!-\!R + LnX_3 \longrightarrow X_{3-n}Ln[(OCHCH_2)_yX]_n \quad (2)$$

X＝Cl, Br, I; R＝H, CH_3, CH_2Cl, $CH_2OCH_2CH{=}CH_2$

which initiate the polymerization via a 'coordination-insertion' mechanism with acyl-oxygen bond cleavage of CL.

Living polymerization is one of the most important subjects in polymer synthesis for polymer structure and molecular weight and so forth can be controlled by living polymerization. Based on the finding of some living polymerization characters of CL polymerization catalyzed by rare earth alkoxide, our further study has shown that isopropoxy rare earth diethyl acetylacetonate [$(EA)_2$LnO-*i*-Pr] or neodymium isopropoxide with donor adduct (1,10-phenanthroline, 2,2-bipyridyl, 18 crown ether) are excellent catalysts for the living polymerization of CL obtaining narrow molecular weight distribution PCL and block copolymers of CL with trimethylene carbonate (TMC) or Block copolymer of CL with lactide [11d,11e].

Random copolymer of CL and TMC having narrow molecular weight distribution can be prepared by small amount of rare earth isopropoxide in high yield. Rare earth chloride–propylene oxide system also is an efficient catalyst for preparing CL-LA random copolymer. The reactivity ratios of CL and LA are r_C =0.37; r_{LA}=10.8 [64].

Recently we have found that tris(2,6-di-tert-butyl-4-methyl phenolate) rare earth complex [$Ln(OAr)_3$] is highly active single component catalyst for CL polymerization. Weight average molecular weight of 21×10^4 and MWD of 2.37 poly caprolactone can be obtained by [$La(OAr)_3$] at following conditions: [CL]/[La] = 3000 molar ratio, toluene, 30, 90 min [65].

Tris(4-tert-butyl-phenolate)rare earth complex, tris(2,6-di-methyl phenolate) rare earth complex, tris(2,4,6-trimethyl phenolate) rare earth complex are all effective single component catalysts for the ring-opening polymerization of CL. The electronic effect and steric effect of samarium phenolate complexes on the catalytic activity of CL polymerization have been studied [66].

6.3 Ring-opening polymerization of cyclic carbonate

Poly(trimethylene carbonate) is an attractive biode-gradable material. We have found rare earth halides single component are effective catalysts for the ring-opening polymerization of trimethylene carbonate (TMC). Light or heavy rare earth chloride, neodymium bromide or iodide all can catalyze TMC bulk polymerization quickly with small amount of catalyst ([TMC]/[Ln]=3000 molar ratio) at 80℃. The reason why the catalytic activity of TMC polymerization is higher than that of CL polymerization has been studied and shown that the difference arises from different polymerization mechanisms of TMC and CL with rare earth halides. The polymerization of TMC by rare earth halide proceeds via a cationic mechanism [67].

Rare earth halide single component also can catalyze the copolymerization of TMC and D, L-LA and the catalytic activity sequence of various rare earth chlorides is as follows: $LaCl_3 > YCl_3$, $PrCl_3 > NdCl_3 >> DyCl_3$. The effects of polymerization temperature and time on the polymerization had been studied and the reactivity ratios of TMC and D, L-LA had been found to be r_{TMC}=0.19, r_{LA}=15.4 [68].

We have found firstly that calix[8]arene neodymium chloride [C[8]NdCl] single component is an effective catalyst for the ring-opening polymerization of TMC. The favorable conditions of which are: [TMC]/[catalyst] = 2000 molar ratio, 0℃, bulk polymerization, 5 h producing PTMC of viscosity average molecular weight of 6×10^4 with 70% yield [69].

Tris(2,6-di-tert-butyl-4-methyl phenolate) lanthan- ium [$La(OAr)_3$] single component is also an effective catalyst for the ring-opening polymerization of TMC. PTMC with 94% yield, weight average molecular weight of $1.6\times10^4$and MWD of 2.45 can be obtained under following conditions: [TMC]/[La]=1000 molar ratio, 15°C, 30 min [65b].

We have found for the first time that tris(2, 6-di-tert-butyl-4-methyl phenolate) rare earth complex [$Ln(OAr)_3$] are highly active catalysts for the ring-opening polymerization of 2,2-dimethyl trime-thylene carbonate (DTC) and random copolymeri-zation of DTC and TMC or DTC and CL [12a, 65a]. The preparation of [$Ln(OAr)_3$] is easy, and low cost and it is stable, low toxicity and easy to be stored.

The reason for different catalytic activities of various light or heavy rare earth systems and molecular weights of the polymer may be related to their different electronic structures and coordination abilities. A rare earth atom has larger atomic radius, DTC unit is easier to insert into more space of the three phenol groups and the rare earth system shows higher polymerization activity. The study of the polymerization mechanism reveals that the polymeri-zation proceeds according to a coordination-insertion mechanism. First, DTC coordinates on rare earth metal, then the addition of the double bond of the monomer occurs and acyl-oxygen bond breaks inserting into the Ln-O bond for propagation [12e].

The reactivity ratios of DTC and CL in the copolymerization catalyzed by [$Ln(OAr)_3$] are: r_{CL}=0.2, r_{DTC}=13.4. In order to get more insight into the chain structure of the DTC and CL copolymer by ring-opening polymerization, we used Monte Carlo simulation to study the multi-dispersive copolymerization system. Based on the experimental data of molecular weight and its dispersion of the copolymer via GPC measurement, a Monte Carlo algorithm for multi-dispersive copolymerization system has been established. The program simulates the insertion of every monomer unit and records the structure and microscopical sequence of every chain in various lengths and has been applied successfully for the copolymerization of DTC and CL. The simulation coincides with the experimental results and provides microscopical data of triad fractions, lengths of homopolymer segments etc. which are difficult to obtaine by experiments

[70].

Calixarenes are cyclic oligomers obtained from the condensation of formaldehyde with *p*-alkyl (4-tert-butyl) phenol which have been used as special ligands in guest-host chemistry, coordination chemistry and analytical chemistry etc. Recently we have synthesized rare earth (Nd, Y) *p*-tert-butyl calix[*n*]arene (*n*=4, 6, 8) complexes from rare earth isopropoxide in toluene. The complexes were characterized having following structures: $[C_4(OH)O_3CH_3$-$C_6H_5]Ln$, $[C_6(OH)_2O_4{\cdot}CH_3C_6H_5]Ln$ and $[C_8(OH)_2O_6$-$CH_3C_6H_5]Ln_2$.

We firstly studied the ring-opening polymerization of 2,2-dimethyl trimethylene carbonate (DTC) with these rare earth complexes alone. PDTC with weight average molecular weight of 5700, 69.1% yield and polydispersity index of 1.11 could be prepared by using $[C_6(OH)_2O_4{\cdot}CH_3C_6H_5]Nd$ as single component catalyst under 80℃ 6 hour in toluene. The structure of the PolyDTC obtained had been studied by GPC, NMR and DSC etc. reveals no polyether segment, no rare earth or calixarene in the polymer chain. The DTC polymerization could carry out in low polarity solvent such as toluene and trichloromethane, but could not proceed in strong polarity solvent as nitrobenzene and without carbon dioxide elimination. The experimental results illustrate that DTC ring is opened via acyl-oxygen bond cleavage and the polymerization proceeds *via* a 'coordination-insertion' mechanism[12]. Very recently the copolymerization of DTC and TMC has been studied by using single component rare earth calixarene complexes.

7 Conclusions

The exploitation of rare earth catalysts in polymer syntheses more widely and deeply would certainly further promote the development of polymer science and catalytic chemistry and so forth.

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