Journal of Advances in Science and Technology
Vol. III, Issue No. V, May-2012, ISSN 2230-9659

A Comparative Study on Polymerization Techniques of ALKYL Acrylates

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Abstract – A series of C_4-C_{12} alkyl acrylates and methacrylates was polymerized with starch by irradiating starch-monomer mixtures with ^{60}CO. Homopolymers were extracted with cyclohexane. The amounts of insoluble versus soluble synthetic polymer in polymerizations run with alkyl acrylates varied less with the chain length of the alkyl substituent than in the polymerizations run with alkyl methacrylates: and the poly(alkyl acrylate) contents of cyclohexane-insoluble fractions were all in the 38-45% range. Synthetic polymer contents of the products from butyl, hexyl, and decyl methacrylates were also close to this range. In a series of polymerizations run with hexyl acrylate and hexyl methacrylate, lower irradiation doses led to more cyclohexane-soluble polymer and less synthetic polymer in the starch-containing fractions. Enzymatic digestion of starch-containing polymers gave synthetic polymer fractions that were largely insoluble in cyclohexane. Crosslinking is, therefore, probably taking place during these polymerizations; however, we could not eliminate the possibility that reduced solubility was caused by small amounts of residual carbohydrate in these polymer fractions.

Here we present the polymerization of n-butyl acrylate (BA), ethyl acrylate (EA) and methyl acrylate (MA) in tri-component microemulsions, using a cationic surfactant such as dodecyl trimetyl ammonium bromide in water, as a function of temperature, initiator type and, monomer and initiator concentration. The final latexes are transparent and blue color, with particle size ranging between 20 and 60 nm determined by quasielastic light scattering (QLD) and SEC molar masses of the order of 10^6 g/mol. Reaction times are short and reaction rates are high with final conversions between 70 and 98% depending on the monomer and the reaction conditions.

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INTRODUCTION

Although the literature contains reports on graft polymerizations of methyl methacrylate,l methyl acrylate, ethyl acrylate, and butyl acrylate onto starch, free-radical graft polymerizations of higher alkyl acrylates and methacrylates have not been described. Our interest in these materials comes from their potential use as absorbents for oils and other hydrocarbons. In this report, we will describe first the polymerization of several C_4 to C_{12} acrylate and methacrylate esters with starch using both ^{60}CO and ceric ammonium nitrate initiation and then the evaluation of the resulting polymers as absorbents for isooctane.

The polymerization of isoprene can afford polymers with various regio- and/or stereoregularities such as isotactic or syndiotactic polyisoprene via 1,2 or 3,4 addition, and cis- or trans-1,4 polyisoprene via 1,4 addition. The structures of polyisoprene strongly influence the properties of the resulting material. For example, the properties of cis-1,4 polyisoprene is very similar to those of natural rubber, while the properties of trans-1,4 polyisoprene is very close to those of gutta-percha. The development of highly efficient and highly regio- and stereoselective catalysts plays a key role in the field of metal-catalyzed polymerization of conjugate dienes. Titanium and rare-earth metal catalysts can afford cis-1,4 and trans-1,4 polybutadienes and polyisoprenes with up to 98% selectivity.

In addition, some late transition-metal catalytic systems were successfully applied in olefins, butadiene, and isoprene polymerization. Late transition-metal catalysts have lower Lewis acid characteristics and may possess high tolerance towards functional groups and polar additives. Special attention was paid to low-cost and earthabundant iron- and cobalt-based catalysts with well-defined molecular structures that could be easily prepared.

Recently, Dai et al. showed that an aryl-substituted iminopyridine Co(II) catalyst exhibited high catalytic activity and cis-1,4-selectivity for 1,3-butadiene polymerization. Raynaud et al. reported that the combination of the iminopyridine Fe(II) complexes, alkylaluminum, and dealkylating reagent $[Ph_3C][B(C_6F_5)_4]$ can polymerize isoprene with high stereoselectivity. The octyl-substituted imines favor trans-1,4 insertion, whereas supermesityl-substituted imines favor cis-1,4 insertion.

The authors suggested that higher electron density at the iron center may increase the trans-1,4 selectivity. However, this accidental discovery and studies of only these two catalysts make it difficult draw any rational conclusions.

Inspired by these works, we became very interested in the influence of iminopyridine ligand substituents on the selectivity of isoprene polymerization. In this work, various alkyl- and arylsubstituted iminopyridine Fe(II) and Co(II) complexes were synthesized and employed in isoprene polymerization when activated using an alkylaluminum (methylaluminoxane (MAO) or $AlEtCl_2$). The effects of the imine moiety on the catalytic activity, molecular weight, and, particularly, the regio- and stereoselectivity were

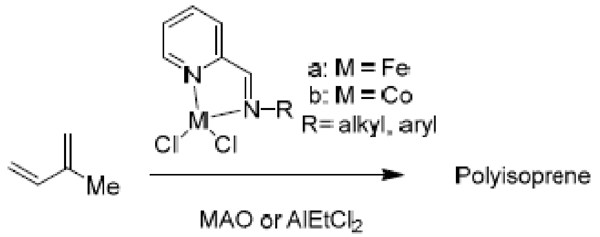

Figure 1. Alkyl- and aryl-substituted iminopyridine Fe(II) and Co(II) complexes for isoprene polymerization.

MICROEMULSION POLYMERIZATION OF ALKYL ACRYLATES

Microemulsion polymerization was born as an alternative process for the production of polymeric latexes with unique particle size, molar masses and structure. Synthesis of stable latexes with particle size ranging from 10 a 35 nm has been possible through this process where a fast polymerization affords high molar mass polymers. Stoffer and Bone (1980) first reported microemulsion polymerization in 1980. Most microemulsion polymerization reported in the 80's, were carried out in four and five component systems. The first three component microemulsion polymerization (water, surfactant and monomer) was reported by Pérez-Luna et al. in 1990. Since then microemulsion polymerization of different monomers in three component systems have been reported , where the influence of different parameters on the polymerization kinetics and on the obtained latexes have been studied. Some of the parameters are: 1) Initial monomer concentration in the system, polymerization rate and conversion increase with initial monomer concentration due to the higher number and size of the drops being formed in the microemulsion.

Gan et al. (1994) and Pérez-Luna et al. (1992) report similar behavior of the polymerization reaction rates for styrene in three and four components, 2) Temperature, reaction rates are higher when temperature is raised due to a quick increase in the initiator decomposition rate. Final conversion increases as the mobility of the macromolecules increases with temperature. Guo et al. (1992) and Rodríguez-Guadarrama (1993) report activation energy values for microemulsion polymerization of methyl methacrylate and, 3) The initiator and the surfactant, the rate of polymerization and the rate of conversion increase with initiator concentration. To understand the influence of the type of initiator and surfactant the structure of them has to be considered. Guo et al. (1992) studied the polymerization of styrene in SDS and pentanol and reported higher reaction and conversion rates; with an initiator soluble in the aqueous phase KPS, than those obtained in the oil phase AMBN. Gan et al. (1994) study styrene polymerizations with SDS or CTAB using different initiators. They observed a higher reaction rate with SDS than with CTAB. Similar results were observed for other systems attributed to the "electrostatic charge effect" and to a chain transfer reaction between the bromide ion of the surfactant and the KPS free radical , 4) electrolyte addition, this effect depends on factors such as structure and concentration of the electrolyte; addition of the electrolyte greatly alters one phase region of these systems decreasing the solubility between water and surfactants.

Full et al.(1996), studied the addition of KBr on KPS initiated styrene microemulsion polymerization in microemulsion with dodecyl trimetyl ammonium bromide, finding that reaction rate decreases, as well as particle size and molar masses as salt concentration increases.

Similar results were obtained when NaBr was used as electrolyte in styrene microemulsion polymerization and, 5) alcohol addition, alcohols drastically modify the one phase region of water-oil-surfactant, as shown by Gan et al. (1994) and Puig et al.(1994). Gan et al. (1994), reported higher molar masses for more amphifilic surfactants. Puig et al.(1994), report that reaction rate, conversion degree and molar mass decrease with alcohol content. They also found influence of the cosurfactant.

In this work we present the polymerization of n-butyl acrylate (BA), ethyl acrylate (EA) and methyl acrylate (MA) in tricomponent microemulsions, using a cationic surfactant such as dodecyl trimetyl ammonium bromide in water as a function of temperature, monomer and initiator concentration and initiator type. Particle size and molar mass of the final latexes are of the order of 20 and 60 nm and 106 g/mol, respectively. High reaction rates and conversions above 70% were found in all cases. Final latexes were transparent and slightly blue.

LIVING RADICAL POLYMERIZATION

Free radical polymerization is one of the most widely employed polymerization techniques. This technique is applied to prepare latexes to be used in paints, high molecular weight poly (methyl methacrylate) for safety glass (Plexiglas), or foamed poly (styrene) to be applied in coffee cups. Some advantages of radical polymerizations, with respect to other techniques, are the relative insensitivity to impurities, the moderate reaction temperatures and the multiple polymerization processes available, e.g., bulk, solution, precipitation or emulsion polymerization. Some disadvantages related to the mechanism of free radical polymerization is the poor control of the molecular weight and the molecular weight distribution, and the difficulty (or even impossibility) of preparing well-defined copolymers or polymers with a predetermined functionality.

To overcome these disadvantages new techniques were developed based on either reversible deactivation of polymer radicals or a degenerative transfer process, called ‘living’ or controlled radical polymerizations (CRP). It will be worthwhile to discuss the significance of the living radical polymerization process because of which it was selected for the present investigation. Controlled radical polymerizations, like atom transfer radical polymerizations (ATRP), reversible addition-fragmentation chain transfer polymerization (RAFT), and nitroxide-mediated polymerizations (NMP) represent key strategies for the preparation of polymers with narrow molecular weight distributions. To understand the living radical polymerization, firstly it is important to outline the significant of polymers.

Significance of Polymers: Polymer constitutes an important material for meeting demand in specialized fields. In the present civilization, there is hardly any sphere of human life where polymers are not being used in one form or other. The human life would have been quite miserable without their applications. In fact, polymer forms the backbone of modern society. The idea is often expressed that we live in 'a plastic age'. Synthetic polymers form the largest and most diverse class of biomaterials. We are familiar with range from the plastic bags and bottles used daily to the Kevlar and Mylar used to protect astronauts while they are in space.

Polymers are large molecules built up by covalent linking of a large number of much smaller molecules. The term is derives from the Greek words: polys meaning many and meros meaning parts. A polymer may consist of hundreds, thousands, tens of thousands or more monomer molecules. Hence, its molecular weight is very large, giving it interesting and useful mechanical and chemical properties. The volume of synthetic polymers produced worldwide is greater than the volume of steel. Polymer industry is a multi-billion dollar business, and still growing at a rate faster than most other industries. In the last decades, polymers have not only used as industrial bulk materials but also attracted great attention in high technology fields, e.g. nanotechnology, optics and biomaterials. Therefore, the synthesis of tailor–made macromolecules with desired molecular design and understanding of the quantitative structure-property relationships (QSPR) have become main focus area for synthetic chemists. On the behalf of considerable demand of specialty requirements for specialty polymeric materials has arisen an increasing tendency to design “intelligent polymers” i.e. specialty polymers, which extend the scope of polymeric materials.

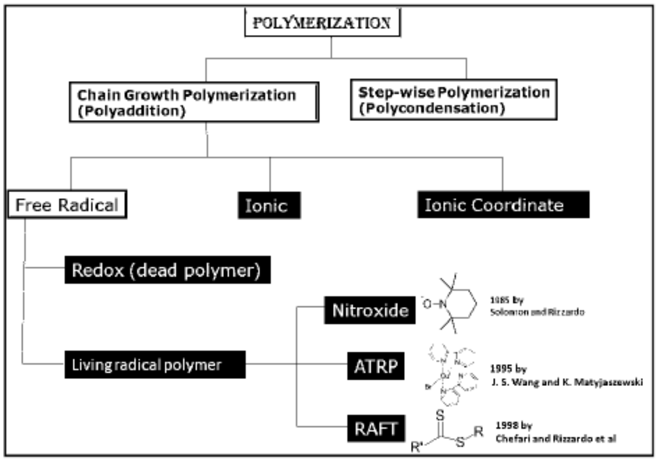

Figure 2 Route of the Polymerization.

Background -Polymerization of vinyl monomers [Fig. 2] shown earlier is of enormous industrial importance. These vinyl polymers are mostly thermoplastics and used in the wide variety of applications. Many vinyl monomers polymerized by free radical, ionic and ionic coordinate polymerization mechanism.

For several reasons, radical polymerization has significant advantages over ionic and coordination polymerizations. The reaction conditions are usually not as demanding, they exhibit a tolerance of trace impurities, and it is possible to polymerize a variety of monomers by radical polymerization. Because of these characteristics, it is possible to prepare high molecular weight polymers without removing the stabilizers present in commercial monomers, in the presence of trace amounts of oxygen. In solvents, they have not been rigorously dried, or even in aqueous media. Today free radical polymerization accounts for a large portion of mass-produced polymers.

Free radical polymerization: Free radical polymerization (FRP) is a type of chain growth polymerization, along with anionic, cationic and coordination polymerization. Free radical polymerization is one of the processes of polymer formation in which polymer grows by successive addition of the monomer units. It takes place via the breaking of a double bond of the monomer unit, converting it into an active propagating radical. Despite its many benefits and wide spread use, the fast chain growth and the presence of the rapid irreversible termination impose some limitation with respect to the degree of control that can be asserted over polymer molecular weight distribution and polymer structure. Furthermore, producing block copolymers, and polymers with complex structure via FRP is impractical.

In order to grow long chains in radical polymerization, the termination rate must be much slower than propagation rate. Since termination is a 2nd order reaction w. r. t. radical concentration while propagation rate is 1st order, the rate of termination becomes slower than that of propagation at very low radical concentrations. Consequently, the radical concentration must be in the range of ppm or even ppb. Because the average life of a propagating chain is < 1s, which constitutes >1000s acts of propagation with a frequency ~1 ms, the life of a propagating chain is too short for any synthetic manipulation, end functionalization, or addition of a second monomer to make a block copolymer.

APPLICATIONS OF LIVING RADICAL POLYMERIZATION

Applications discussed in the literature for materials prepared through living radical polymerization range from replacement of existing products in existing markets to novel material concepts, creating new applications such as some very novel approaches to drug delivery through the synthesis of well-defined diblock copolymers by ATRP. The block copolymers with a short hydrophobic block (5 < DPn < 9) were explored in detail for the development of new colloidal carriers for the delivery of electro statically charged compounds (e.g., DNA), through the formation of polyion complex micelles. A similar approach has been taken in electronics manufacture where the selforganizing ability of materials prepared by living radical polymerization is being exploited.

Some existing markets targeted by materials prepared by living radical polymerization process [Fig. 3] are: Adhesives; Sealants; Emulsifiers; Polymer blend compatibilizers; Coatings; Toners; Dispersants; Lubricants; Curable sealing compositions; Elastomeric materials, Drug delivery, Cosmetics, Materials comprising specific bulk physical properties.

The above references have focused on applications identified by corporate research, in patents and patent applications. Academic workers are also disclosing some new applications. Although this has been but a brief review of novel materials prepared using controlled radical polymerizations, one can easily see that, regardless of the type of controlled radical polymerization employed, these methodologies open the door to a wide range of novel polymers with unique properties.

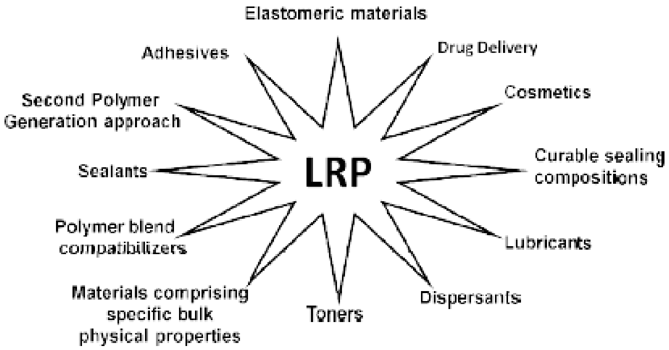

Figure 3 Applications of Living radical polymerization.

Indeed control over polymer sequence distributions continuously expanding and recently multi-block heteropolymer chains with upto 100 blocks in an ordered sequence and controllable block lengths have been reported. CRP is among the most rapidly developing areas of chemistry, with the number of publications approximately doubling each year.

ANIONIC POLYMERIZATION OF ALKYL METHACRYLATES

The anionic polymerization of alkyl methacrylates has been intensively studied in recent years. Several new strategies have been developed to circumvent the problem of termination and aggregation of "living" species. One possibility is the use of various ligands in conjunction with classical anionic initiators. σ-Ligands, such as crown ethers, cryptands, and tertiary amines; μ-ligands, such as alkali metal alkoxides, halides, and perchlorates, as well as aluminum alkyls, and σ,μ-ligands, such as alkoxyalkoxides, aminoalkoxides, and silanolates, have been used with much success. Another possibility' is exchange of the counter-ion. Many non-metallie cations, such as tetra-w-butylammonium, tetraphenylpliosphomi W, and tetrakis[tri(dimethylamino) phosphor any lidenamino] phosphonium, can be used as the counter-ion in anionic polymerizations of alkyl methacrylates.

Organocuprates are widely used in synthetic organic chemistry because of their ability to induce very high regioselectivity in conjugate addition reactions to various or, α,β -unsaturated esters and ketones. Their use as initiators in polymerizations of the analogous vinylic monomers is thus of interest.

Lithium organocuprates are among the most widely investigated organocuprates and have been used to initiate the anionic polymerization of methyl methacrylate (MMA). However, lithium organocuprates have several shortcomings, such as poor thermal stability and low reactivity, broad molecular weight distribution (MWD) of the resulting polymer, low initiator efficiency and preparation difficulties, when used as initiators for the anionic polymerization of alkyl methacrylates. Herein, we descnbe the use of a lithium heterocuprate, nBuCu(NCy$_2$)Li (1), for the anionic polymerization of alkyl methacrylate. The results have shown that 1 serves as an efficient initiator for the synthesis of poly(alkvl methacrylate) at -10°C.

CONCLUSION

Monomer solubility has a very strong effect on conversion and reaction rate, as it plays a very important role in the initiation step of microemulsion polymerizations. Polymerization rate increases as monomer water solubility decreases, independent of other factors such as temperature, monomer initial concentration, and initiator type and concentration. As monomer water solubility becomes higher, monomer to polymer conversion graphs change from the typical monomer to polymer conversion curves for microemulsion polymerizations to a typical solution polymerization curve. Final conversion and reaction rates do not show an initial monomer concentration effect, which only becomes slightly apparent at concentrations smaller than 1%. Final conversion and reaction rates as a function of temperature, type and initiator concentration change as observed in other systems.

In conclusion, a series of iminopyridine Fe(II) and Co(II) complexes bearing various alkyl and aryl substituents was prepared. The aim is to systematically investigate the influence of alkyl and aryl substituents on the isoprene polymerization. Activated by MAO, the Fe(II) complexes exhibited moderate cis-1,4 selectivity, generating high molecular weight polyisoprenes. A cuprate reagent with non-transferable groups (nBuCu(Cy2N)Li) has been used to initiate the anionic polymerization of alkyl methacrylates. The experiments were performed under simplified conditions at −10°C.

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