Studies on Conventional and Controlled Radical Polymerization Applied to Monomers From Renewable Resource: Polymerization of Cardanyl Acrylate

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By

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CERTIFICATE

This is to certify that the project work entitled **“Studies on Conventional and Controlled Radical Polymerization Applied to Monomers From Renewable Resource: Polymerization of Cardanyl Acrylate”** completed by **Mr. M.Jayakrishna** student of **Master of Engineering** (Polymer Technology), from Delhi College of Engineering, Delhi embodies the original work carried out by him under the joint super vision of Dr. D. Kumar, Assistant professor, Department of Applied chemistry, Delhi College of Engineering, Delhi and Dr. K.I. Suresh, Scientist(C), Organic Coatings and Polymer Division, Indian Institute of Chemical Technology (IICT), Hyderabad. His Work has been found excellent for the partial fulfillment of the requirement of the degree of M.E. This report has not been submitted in part or full in any other University/Institution for award of any degree or diploma.

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Dated: **(M.Jayakrishna)**

Dedicated

To my

Beloved

Parents

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1.1) Introduction.

The field of polymer material science has seen explosive growth since the pioneering work of Staudinger, Carothers, Mark, Flory, and others after the First World War. Initial advances focused on the development of new polymers from novel monomers, enabling unique physical and chemical properties based on individual atomic makeup. The utility of such novel polymers was determined based on their mechanical behavior, which is dependent upon degree of crystallinity, the degree of cross linking, and the value of the glass transition (T_g) and melt (T_m) temperatures, respectively [1]. Accordingly, a polymer was typically classified as a fiber, flexible plastic, rigid plastic, or elastomer [2,3] and this classification was taken as characteristic of the individual polymer. While variety of polymeric materials capable of being produced are limited only to one's imagination, recent advances have shied away from the relatively expensive design of new materials and towards the modification of existent macromolecules. Changing the method of polymer processing can readily alter mechanical properties. For example, perhaps best known for its widespread use as a foam insulator (coffee cups, food service packaging, etc), polystyrene was initially used as a component in synthetic elastomers during the second world war and has since also been used as a rigid plastic (CD jewel cases, plastic utensils, etc.). Simple variations on processing techniques enable polystyrene to take such vastly different forms.

Certain mechanical properties also vary with polymeric preparation methods. Carothers originally classified polymers as being condensation or addition polymers on the basis of preparation methods [4]. In 1956 Szwarc introduced a third classification that of ionic chain polymerization [5]. The major difference between all three routes is the time required for the growth of individual polymer chains and molecular weight distribution among these chains. Defining the molecular weight distribution, or polydispersity, as M_w / M_n (where M_w is the weight average molar mass and M_n is the number average molar mass), we can return to the polystyrene example from above. Being formed from a vinyl monomer, i.e. a substituted ethylene, polystyrene was first synthesized in an additive free radical chain growth fashion. In this manner, irreversible chain termination steps produce macromolecules of broad polydispersities and subsequently unpredictable behavior as the degree of polymerization greatly influences material properties [6]. Comparing this to Szwarc's preparation of polystyrene via an anionic route, which led to a polydispersity approaching unity, thus allowing more predictable macromolecular behavior at any degree of polymerization.

Szwarc defined his anionic route as being a "living" polymerization, characterized by polymer chains that grow linearly with time. Void of such chain breaking steps as chain transfer or termination, anionic chain ends remain alive in the sense that chain growth may be reinitiated by the addition of monomer. It is possible to synthesize block copolymers upon addition of a second type of monomer to a living anionic macromolecular chain. In this way, and unlike random or regular copolymers, the new polymer will retain many of the physical characteristics of the homo polymers that make up the block. In addition, varying monomer composition can lead to a variety of polymeric architectures ranging from linear to highly branched. Living polymerizations enable architectural and compositional control, thus permitting one to manipulate various properties.

In the following we discuss the advantages and disadvantages of free radical versus ionic polymerizations before introducing a recent marriage of the two techniques into a hybrid known as controlled/"living" free radical polymerization.

1.1.1) Conventional Free Radical Polymerizations:

Free radical polymerizations are of significant importance in the industrial sector for a variety of reasons. First, many monomers capable of undergoing chain reactions are available in large quantities from the petrochemical sector [7a]. In addition, free radical mechanisms are relatively well understood and extension of the concepts to new monomers is generally straightforward. A third advantage of free radical route is that the polymerization proceeds in a relatively facile manner: rigorous removal of moisture is generally unnecessary while polymerization can be carried out in either the bulk phase or in solution.

As chain reactions, free radical polymerizations proceed via four distinct processes:

i). Initiation. In this first step, a reactive site is formed, thereby “initiating” the polymerization.

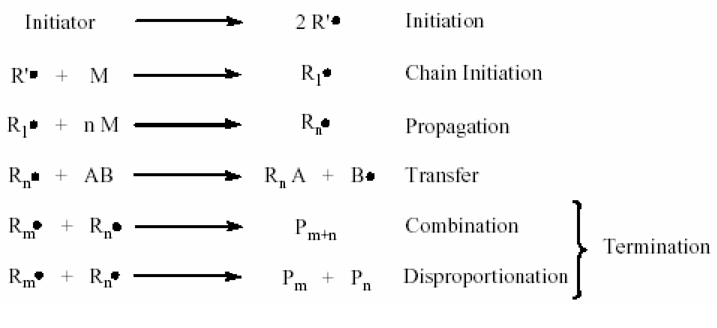
ii). Propagation. Once an initiator activates the polymerization, monomer molecules are added one by one to the active chain end in the propagation step. The reactive site is regenerated after each addition of monomer.

iii). Transfer: occurs when an active site is transferred to an independent molecule such as monomer, initiator, polymer, or solvent. This process results in both a terminated molecule (see step four) and a new active site that is capable of undergoing propagation.

iv). Termination. In this final step, eradication of active sites leads to “terminated,” or inert, macromolecules. Termination occurs via coupling reactions of two active centers (referred to as combination), or atomic transfer between active chains (termed disproportionation). The free radical chain process is demonstrated schematically below (Scheme 1): R• represents a free radical capable of initiating propagation; M denotes a molecule of monomer; R_m• and R_n• refer to propagating radical chains with degrees of polymerization of m and n, respectively; AB is a chain transfer agent; and $P_n + P_m$ represent terminated macromolecules.

Because chain transfer may occur for every radical at any and all degrees of polymerization, the influence of chain transfer on the average degree of polymerization and on polydispersity carries enormous consequences. Furthermore, propagation is a first order reaction while termination is second order. Thus, the proportion of termination to propagation increases substantially with increasing free radical concentrations. Chain transfer and termination are impossible to control in classical free radical processes, a major downfall when control over polymerization is desired.

Scheme 1. General Free Radical Polymerization Mechanism.



1.1.2) Conventional Living Polymerizations:

Living polymerizations are characterized by chain growth that matures linearly with time. Inherent in this definition are two characteristics of ionic co polymerizations that both liken and distinguish ionic routes from the aforementioned free radical route. In order to grow linearly with time, ionic polymerizations must proceed by a chain mechanism in which subsequent monomer molecules add to a single active site; furthermore, addition must occur without interruption throughout the life of the active site. Thus, the chain transfer mechanisms described above must be absent. A more exact definition has been established by IUPAC. As defined in Macromolecular Nomenclature living polymerizations may include slow initiation, reversible formation of species with various activities and lifetimes, reversible formation of inactive (dormant) species, and/or reversible transfer [8]. Living polymerizations must not include irreversible deactivation and irreversible transfer.

Classical living polymerizations occur by the formation of active ionic sites prior to any significant degree of polymerization. A well-suited initiator will completely and instantaneously dissociate into the initiating ions. Dependent on the solvent, Polymerization may then proceed via solvent pairs or free ions once a maximum number of chain centers are formed [7b]. Solvents of high dielectric constants favor free ions; solvents of low dielectric constants favor ionic pairs. Termination by coupling will not occur in ionic routes due to unfavorable electrostatic interactions between two like charges. Furthermore, chain transfer routes are not available to living polymerizations, provided the system is free of impurities. Polymerization will progress until all of the monomer is consumed or until a terminating agent of some sort is added.

On the flip side, ionic polymerizations are experimentally difficult to perform: a System free of moisture as well as oxygen, and void of impurities is needed. Moreover, there is not a general mechanism of polymerization on which to base one’s experiment: initiation may occur in some systems before complete dissociation of initiator. Knowledge of the initiating mechanism must be determined a priori to ensure a successful reaction. Despite the advantage of molecular control of living systems, the experimental rigor involved in ionic polymerization is often too costly for industrial use and free radical routes are preferred.

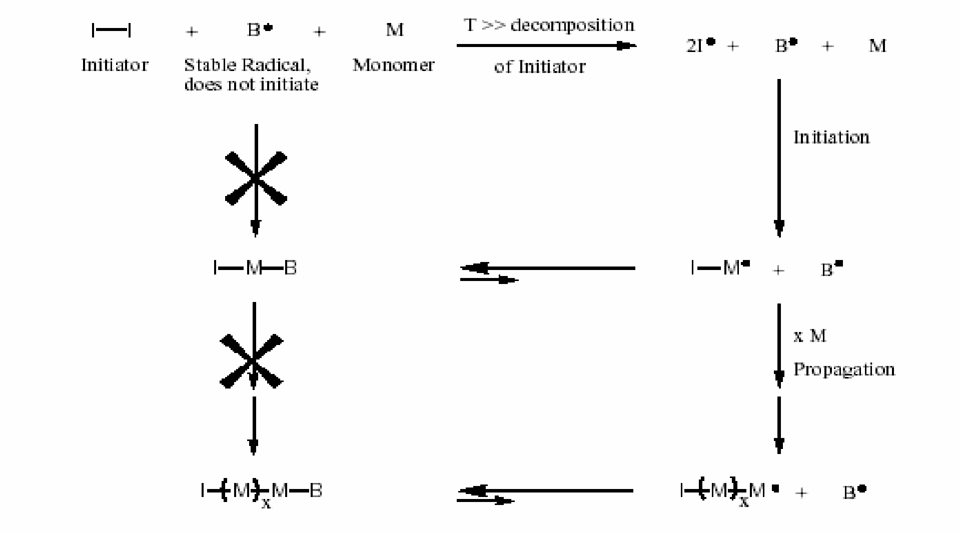
1.1.3) Controlled/“Living” Free Radical Polymerizations:

Conventional free radical polymerization techniques are inherently limited in their ability to synthesize resins with well-defined architectural and structural parameters. Free radical processes have been recently developed which allow for both control over molar masses and for complex architectures. Such processes combine both radical techniques with living supports, permitting reversible termination of propagating radicals. In particular, three controlled free radical polymerizations is briefly presented below and all are based upon early work involving the use of initiator-transfer-agent-terminators to control irreversible chain termination of classical free radical process.

In 1982, Otsu et al. extended the idea of living polymerizations to free radical systems in the use of initiator-transfer-agent-terminators, or iniferters [9]. Such initiators act both as primary radicals to initiate polymerization (R’•, Scheme 1) and as radical chain terminators (R_m• or R_n•, Scheme 1), consequently permitting a near linear increase of molar mass with time and percent conversion [10]. However, the similarities between living anionic systems and Otsu’s iniferter reaction end there. The iniferter mechanism yields radicals that can initiate new chains throughout the course of the reaction [11]. The iniferter systems also show significant loss of active end groups from the growing polymers [11b]. Consequently, these systems display relatively large polydispersities with a substantial amount of homopolymer being formed in conjunction with block Copolymer [11a].

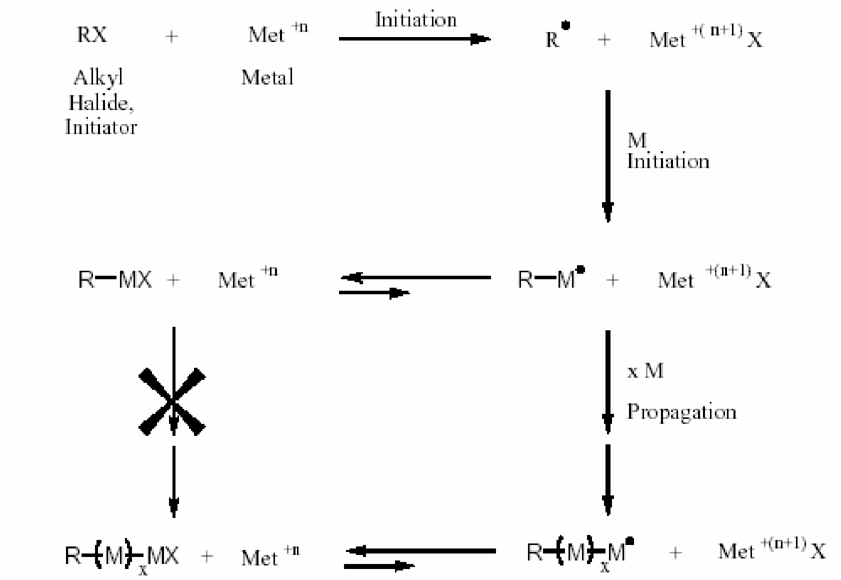
In 1986, Solomon, Rizzardo, and Cacioli synthesized methyl acrylate oligomers via reversible capping of the growing radical chain by a stable free radical [12]. Although they did not realize it at the time, perhaps because the extension of SFRP to polyacrylates has proven to be difficult [13], the reversible capping of growing chains defined the first mechanism of three general routes to controlled/”living” radical polymerization. The reversible homolytic cleavage of a dormant chain end to form a stable free radical as well as an active radical site was applied to the polymerization of styrene in 1993 [10], later to the polymerization of acrylates catalyzed by cobalt porphyrin alkyls [14], and more recently to a wide range of monomers via the preparation of monomer specific initiators. This route was coined “Stable Free Radical Polymerization” (SFRP) by its discoverers [16]. The general SFRP mechanism is shown in Scheme 2.

Scheme 2. SFRP Mechanism



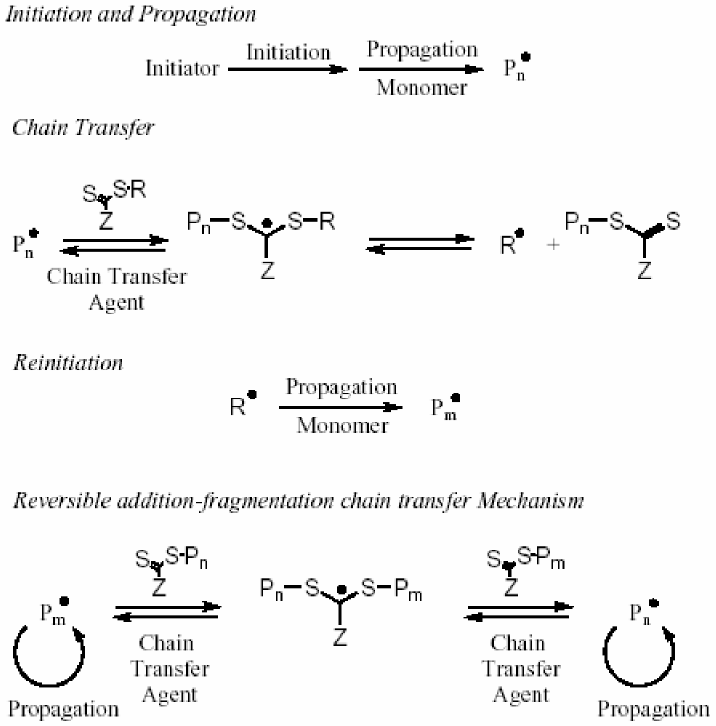
Matyjaszewski reported a second route (atom transfer radical polymerization ATRP) of control over radical polymerization by introducing a catalytic amount of a copper(I) coordination complex which reversibly abstracts a halide from the polymer chain end, thereby affording a switching mechanism between a dormant and an active, propagating state (Scheme 3) [17]. This will be discussed in detail later below.

Scheme 3: ATRP mechanism.



The third and most recent report of a controlled/"living" free radical polymerization has been reported by Haddleton and co-workers as well as Thang et al [18] is Reversible addition-fragmentation chain transfer (RAFT). RAFT is achieved by performing a free radical polymerization in the presence of dithiocompounds, which act as efficient reversible addition-fragmentation chain transfer agents (Scheme 4). Much like the first two routes, the rapid switching mechanism between dormant and active chain ends affords living polymerization character.

Scheme 4. RAFT Mechanism



Hyper-branched polymers with tunable branching density have been synthesized [21], and the grafting of polymers to various materials has been shown.

Each of the three new polymerization routes affords the chemist the opportunity to prepare a wide range of polymeric materials. Recent interest in the utilization of SFRP and ATRP towards the development of new materials has seen explosive growth: the homopolymerization of various monomers with well-defined parameters are well documented [19], block copolymers have been readily prepared by adding additional monomer to the reaction after the complete consumption of the starting material or by isolating and purifying the macromolecule prior its use as a macro initiator [20].

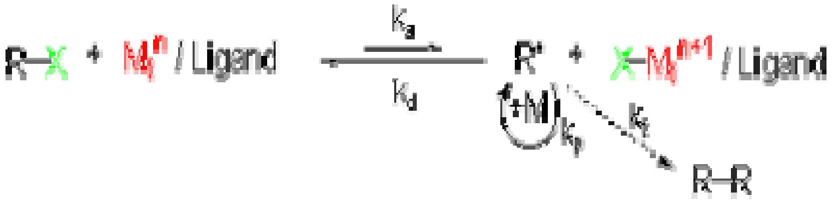
1.1.4) Atom transfer radical polymerization (ATRP):

Although many of the polymer types described have been prepared using other living polymerizations, researchers have been striving to develop a living radical polymerization for nearly 40 years. An alternative was sought because other types of living polymerizations are severely limited by many factors: only a small number of monomers can be used, the reactions are sensitive to moisture, and two or more monomers cannot be randomly co-polymerized. Radical polymerization, in contrast, can polymerize hundreds of monomers, can co-polymerize two or more monomers, and can be performed in water as emulsions or suspensions. Controlled/“living” radical polymerization promised to overcome these limitations and provide a method to maximize the potential of living polymerizations.

Despite the availability of several controlled radical polymerization systems reported by various groups, ATRP remains the most powerful, versatile, simple, and inexpensive. Only ATRP has been able to polymerize a wide range of monomers including various styrenes, acrylates, methacrylates as well as other monomers such as acrylonitrile, vinyl pyridine, and dienes. ATRP commonly uses simple alkyl halides as initiators and simple transition metals (iron, copper) as the catalysts. These catalysts can be used in very low amounts, whereas, other controlled polymerization systems require the use of expensive reagents in much higher concentrations.

The Matyjaszewski research group was the first to develop a controlled/“living” polymerization that used a simple, inexpensive polymerization system. It is capable of polymerizing a wide variety of monomers, is tolerant of trace impurities (water, oxygen, inhibitor), and is readily applicable to industrial processes. The system that was developed was termed Atom Transfer Radical Polymerization (ATRP). ATRP is a robust system that has generated much interest among polymer chemists in both industry and academia.

The control of the polymerization afforded by ATRP is a result of the formation of radicals that can grow, but are reversibly deactivated to form dormant species. Reactivation of the dormant species allows for the polymer chains to grow again, only to be deactivated later. Such a process results in a polymer chain that slowly, but steadily, grows and has a well-defined end group (for ATRP that end group is usually an alkyl halide).



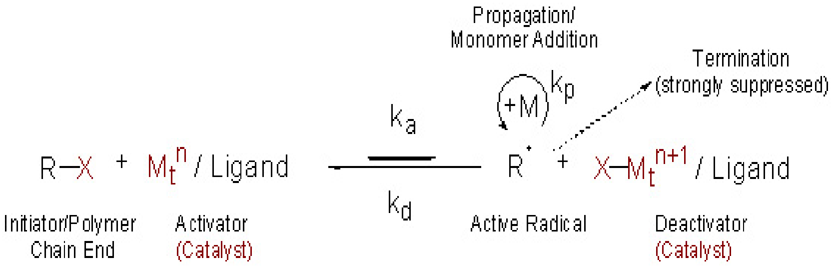
The initiator is generally a simple, commercially available, alkyl halide. The catalyst is a transition metal that is complexed by one or more ligands; the catalyst does not need to be used in a one-to-one ratio with the initiator but can be used in much smaller amounts. The deactivator can be formed in situ, or for better control, a small amount (relative to the catalyst) can be added. Additionally, the catalyst is tolerant of water and trace amounts of oxygen.

Procedures for Initiation of an ATRP Reaction:

Depending upon the type of initiation ATRP can be carried out as (a) Normal ATRP (b) Reverse ATRP (c) SR&NI ATRP (d) ATRP from surfaces and (e) Halogen Exchange.

Normal ATRP Initiation:

The procedure for "normal" initiation of an ATRP reaction employs a molecule, small molecule or macromolecule, with one or more radically transferable atoms or groups, normally a halide, that can undergo a one electron redox reaction with a transition metal catalyst [22-26].



The transition metal catalyst (M_t^n/L, where M_t^n is the transition metal in the lower

Oxidation state n complexed with an appropriate ligand L) reacts reversibly with the added initiator molecule and generates an oxidized transition metal halide complex ($X-M_t^{n+1}/L$) and a radical (R•). This radical propagates, adding monomer (M), and is rapidly deactivated by reaction with the oxidized transition metal halide complex to reform the initial transition metal catalyst and an oligomeric X-terminated chain (P_1-X).

This sequence can repeat itself, until desired consumption of the monomer is reached, resulting in the synthesis of polymers with predetermined molecular weights ($DP_n = \wedge[M]/[RX]_0$) and low polydispersities ($M_w/M_n < 1.5$).

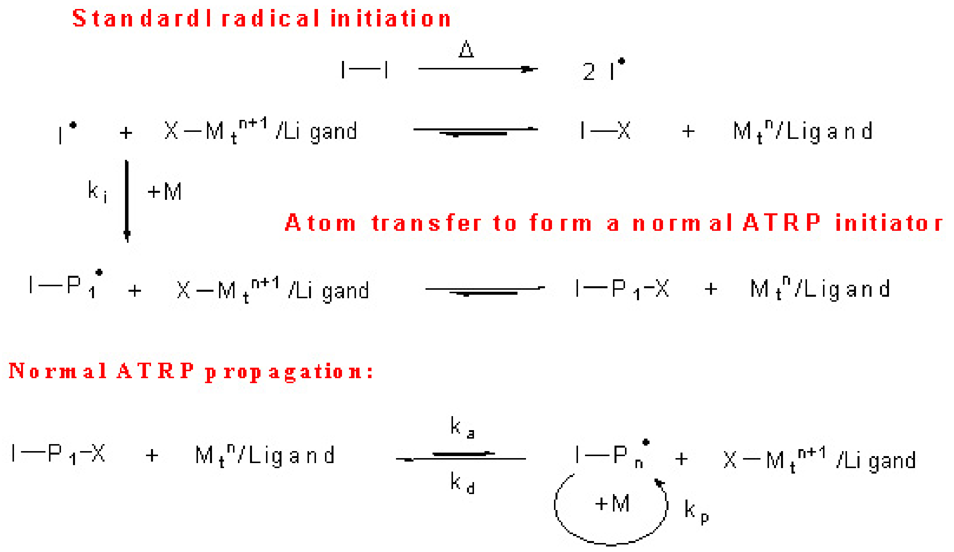
The advantage of normal ATRP initiation is that it provides great freedom on both the choice of initiator and catalyst complex. The most active catalyst can be selected providing low levels of transition metal in the final product. Care has to be taken to reduce the amount of dissolved oxygen in the system since that will oxidize the catalyst complex forming the redox conjugate, or persistent radical, and reduce the rate of reaction [28,29].

Note however the addition of a low level of the redox conjugate does provide control from the start of the polymerization, which increases the amount of added initiator incorporated into the final product, by reducing termination reactions between low molecular weight species [30,31].

Reverse ATRP:

In a reverse ATRP conventional radical initiators and transition metal complexes in the higher oxidation state (e.g. Cu (II) complex) are added to the reaction and the ATRP initiator (RX) and activator are generated *in situ.* [28-30] The initial system less air sensitive, therefore easy to handle, and the procedure is compatible with commercial processes.

The initiation step does not proceed by activation of an alkyl halide with a M_t^n/L catalyst, but rather by thermal decomposition of a conventional radical initiator, such as AIBN. Once radicals are generated, either they react immediately with the higher oxidation state transition-metal complex to form the reduced transition-metal species and a dormant species ($I\bullet + X\text{-}M_t^{n+1}/L$ forming I-X), or they react with monomer to form a propagating radical, $I\text{-}P_1\bullet$, which can then be deactivated by reaction with $X\text{-}M_t^{n+1}/L$ to form M_t^n/L and a dormant species ($I\text{-}P_1\text{-}X$).



In the subsequent step, the reduced transition-metal species, M_t^n/L, reacts with the newly formed halogenated-chains, as in a normal ATRP initiation/propagation process.

As noted above the advantages of reverse ATRP include starting with the more stable transition metal complex, (which is particularly useful for active catalyst complexes and in mini emulsion systems) preparation of a range of linear copolymers with good chain end functionality.

The disadvantage of reverse ATRP is that it limits the terminal functionality remaining on the initiator residue and the topology of the polymers that can be prepared. One can only prepare linear (co) polymers. Furthermore, the molecular weight of the final copolymer cannot be independently adjusted irrespective of the activity transition metal complex.

$[M]_0/[Cu(II)X_2\text{-ligand}]_0/[I]_0 = DPtarget/1/1$

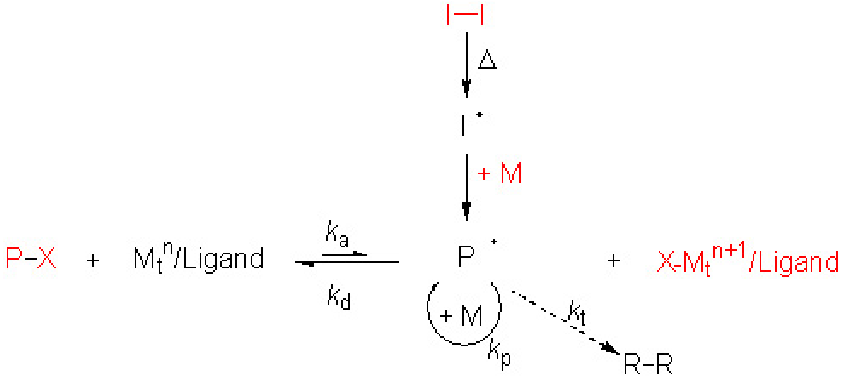
High amount of catalyst (Cu(II)-ligand) required ($[Cu(II)\text{-ligand}]_0/[I - I]_0 = 1 - 1.5$)

$$DP_{target} = \frac{\Delta[M]_0}{[I\bullet]_0} = \frac{\Delta[M]_0}{2 \times f_{I\text{-}I} \times [I\text{-}I]_0} \quad \text{and} \quad [I - I]_0 \sim [Cu^{II}/L]_0$$

Simultaneous Normal & Reverse ATRP (SR&NI):

In SR&NI a small amount of the activating catalyst complex is generated by decomposition of a standard free radical initiator, such as AIBN, while the majority of the polymer chains are initiated by an alkyl halide via a normal ATRP process.

The following schematic is a summary of the normal ATRP and reverse ATRP initiation mechanisms shown above showing how both initiation procedures are used in SR&NI. The reagents shown in red are added to the reaction. The first formed radicals undergo the reverse ATRP initiation reaction shown above but the bulk of the chains are initiated by a normal ATRP initiation mechanism.



The degree of polymerization is predominately controlled by the concentration of alkyl halide, as expressed in the following equation, where f is the initiation efficiency of the added free radical initiator.

$$DP = \frac{\Delta[M]}{[RX]_0 + (2 \times f \times [\mathrm{AIBN}]_0)}$$

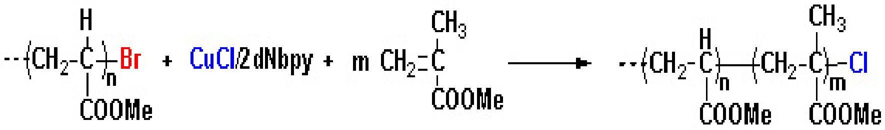
The SR&NI was initially developed using bulk polymerization [31]. Macro initiators were used to prepare block copolymers. However SR&NI was quickly adapted to mini emulsion systems where addition of the catalyst precursor as an oxidatively stable salt prior to sonification simplifies the procedure [32-35]. This results in a significant reduction in the amount of homopolymers present in the final product and allows the preparation of block, star and graft copolymers.

ATRP from Surfaces:

ATRP has been conducted from a range of surfaces including inorganic particles [36-40] and flat surfaces [41-43]. In bulk/solution copolymerization grafting from particle surfaces one should target a slow rate of reaction in order to minimize termination reactions and gel formation. A convenient tool for reduction in the rate is to add significant levels of the deactivator, or persistent radical, to the contact solution.

Halogen Exchange:

Halogen exchange is recommended for the preparation of block copolymers when one is moving from a macro initiator of lower activity, such as an acrylate, to a more active monomer such as a methacrylate or acrylonitrile [44-51].



The procedure works because the rate of activation of a bromine acrylate chain end by the copper chloride based catalyst complex is comparable to the activity of a chlorine terminated methacrylate chain end by cuprous bromide based complex.

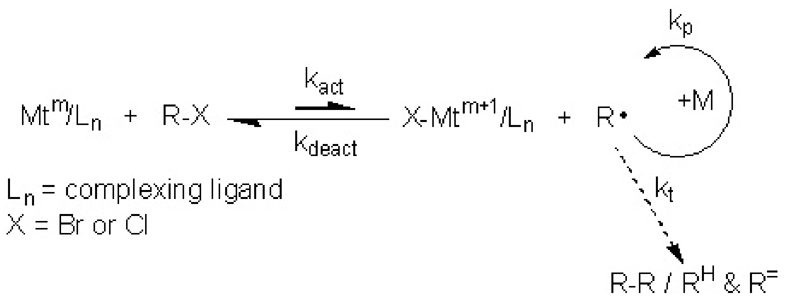
The R-Br bond is readily cleavable using a CuCl catalyst such that initiation (k_a,Br) is a fast process. However, since the C-Cl bond is stronger than the C-Br bond, after initiation most dormant chains have a terminal chlorine atom. These C-Cl bonds are activated more slowly, and thus the rate of propagation is decreased with respect to the rate of initiation, which effectively leads to increased initiation efficiency and preparation of a second block with narrower polydispersity

1.1.5) Kinetic studies in controlled/“living” radical polymerizations:

Knowledge of the dimension and impact of the kinetic parameters in controlled/"living" radical polymerization (CRP) is of major importance for the design of well-defined macromolecules. The rate of polymerization, molecular weight distribution and in case of copolymerization, the distribution of the co-monomers along a given polymer segment are a direct consequence of the kinetics. Therefore, understanding and measuring the kinetics parameters is important.

Nearly all the rules observed in conventional radical co-polymerizations apply to ATRP including chemo selectivity, regio selectivity and stereo selectivity of propagation, transfer and termination. There might be a caveat associated with diffusion rate phenomena, incompatibilities, chain length dependent termination and appearance of additional side reactions with ligand or complex but the general picture remains the same[52].

In the case of an ATRP reaction the equilibrium is strongly influenced by the choice of transition metal and complexing ligand(s).



Mt is a Transition metal with two stable oxidation states differing by 1 (n <-> n+1)

Mechanistically, ATRP is based on the inner sphere electron transfer process, which involves a reversible (pseudo) halogen transfer between a dormant species (R-X) and a transition metal complex (Mt^m/L_n) resulting in the formation of propagating radicals (R*) and the metal complex in the higher oxidation state (e.g. $X\text{-}Mt^{m+1}/L_n$). Radicals react reversibly with oxidized metal complexes, $X\text{-}Mt^{n+1}$/Ligand to reform the dormant species and the transition metal complex (Mt^m/L_n) in the lower oxidation state, the activator. This process occurs with a rate constant of activation, k_a, and deactivation k_{da}, respectively. Polymer chains grow by the addition of the free radicals to monomers in a manner similar to a conventional radical polymerization, with the rate constant of propagation, k_p. Termination reactions (k_t) also occur in ATRP, mainly through radical coupling and disproportionation; as shown above.

The following equation illustrates how the polydispersity index in ATRP in the absence of chain termination and transfer relates to the concentrations of initiator (RX) and deactivator (*D*), the rate constants of propagation (k_p) and deactivation (k_{da}), and the monomer conversion (*p*) [53].

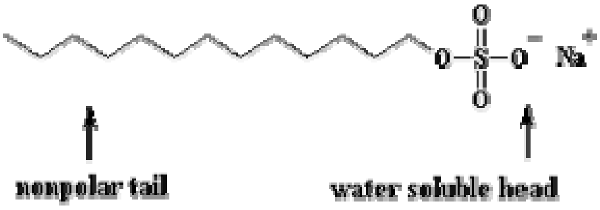
$$\frac{M_w}{M_n} = 1 + \left(\frac{([RX]_o - [RX]_t)k_p}{k_{da}[D]}\right)\left(\frac{2}{p} - 1\right)$$

Thus, for the same monomer, a catalyst that deactivates the growing chains faster will result in polymers with lower polydispersities (smaller k_p/k_{deact}). Alternatively, polydispersities decrease with an increasing concentration of deactivator, although at the cost of slower polymerization rates. For example, the addition of a small amount of Cu (II) halides in the copper-based ATRP lead to better controlled polymerizations with decreased polymerization rates.[54]

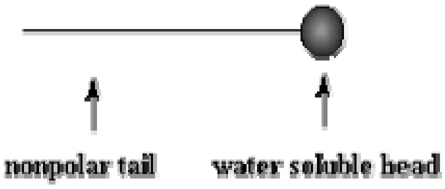
1.2) Emulsion polymerization:

The definition for emulsion is: "A stable colloidal suspension as milk, consisting of an immiscible liquid dispersed and held in another liquid by a substance called an emulsifier". In order to understand emulsion polymerization and emulsifiers, we've got to understand how soap works.

Soap molecules suffer from a multiple personality disorder, but their dual personalities are always apparent. A soap, or surfactant as it is referred to in emulsion polymerizations, has two ends of different solubility. One end, termed the tail, is a long hydrocarbon that is soluble in nonpolar, organic compounds. The other, the head, is often a sodium or potassium salt, which is water soluble. The water soluble salt can be the salt of a carboxylic acid or sulfonic acid. The technical term for the chemical display of "dual personalities" is *amphipathic*.

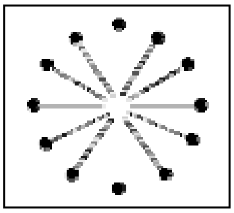


Sodium Lauryl Sulfate

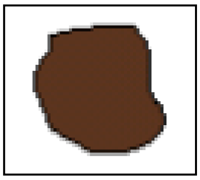


Lazy chemist's representation of Sodium Lauryl Sulfate

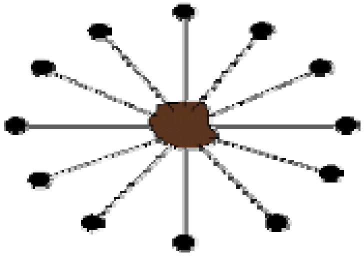
One soap molecule isn't much good to you. But when you get a whole bunch of 'em together, neat stuff starts to happen. At a certain concentration in water, soap molecules congregate and form micelles. Scientists have an apt (if not original) name for this called the critical micelle concentration, or CMC for short. They're really doin' the hokey pokey, tails inward as shown in scheme



Any dirt, grease, or grime that you happen to have on your hands is most likely organic and looks like this:



When you wash your hands with soapy water the hokey pokey party really gets goin’. The jubilant dirt particle jumps right in the middle where it's pretty happy. It doesn't want to get out so it stays dissolved in the organic tails of the micelle.



Now the dirt is dissolved in the micelle, and the micelle is dissolved in water, and...Voila! With copious amounts of water, you can wash everything down the drain.

In an emulsion polymerization, the soap, or surfactant, is dissolved in water until the critical micelle concentration (CMC) is reached. The interior of the micelle provides the site necessary for polymerization. A monomer (like styrene or methyl methacrylate) and a water soluble free radical initiator are added and the whole batch is shaken or stirred .Emulsion polymerizations are always performed free radically. Anionic and cationic chain ends would be rapidly quenched by the water. The product of an emulsion polymerization is called a latex.

Once everything is thrown in the pot, the monomer can be found in three different places. First, it can be in large monomer droplets floating around aimlessly in the water. Second, some of the monomer may be dissolved in the water, but this is unlikely. Remember, organic monomers like styrene and methyl methacrylate are hydrophobic. Lastly, the monomer may be found in micelles, which is exactly where we want it. The immiscible liquid is the hydrophobic monomer, the mother liquor is water, and the emulsifier is soap.

Initiation and Polymerization:

Initiation takes place when an initiator fragment migrates into a micelle and reacts with a monomer molecule. Water soluble initiators, such as peroxides and per sulfates, are commonly used (This also prevents polymerization in the big monomer droplets). Once polymerization starts, the micelle is referred to as a particle. Polymer particles can grow to extremely high molecular weights, especially if the initiator concentration is low. That makes the radical concentration and the rate of termination low as well. Sometimes a chain transfer agent is added to the mix to keep the molecular weight from getting too high.

Propagation:

Monomer migrates from the large monomer droplets to the micelles to sustain polymerization. On average, there is one radical per micelle. Because of this, there isn't much competition for monomer between the growing chains in the particles, so they grow to nearly identical molecular weights and the polydispersity is very close to one. Practically all the monomer is consumed in emulsion polymerizations, meaning the latex can be used without purification. This is important for paints and coatings. Just add some color to the latex, pour it into a can, and it's ready to use.

Here's the neat aspect of emulsion polymerization: each micelle can be considered as a mini bulk polymerization. Unlike traditional bulk polymerizations there is no unreacted monomer leftover, and no thermal "hot spots" form. In bulk polymerizations (no solvent, just monomer and initiator), thermal hot spots cause degradation and discoloration and chain transfer broadens the molecular weight distribution. An increase in temperature sometimes cause the rate of polymerization to increase explosively. The water here acts as a heat sink for all those mini reactors and keeps them from blowing up.

Molecular Weight:

Now this is cool too: The rate of polymerization is the same as the rate of disappearance of monomer. Monomer disappears faster when there are more particles. In order to have more particles there must be more micelles. If the soap sud concentration is increased, this ought to give us more micelles. Now suppose the concentration of initiator is left the same. This will give us more particles and less radicals. What this means is the number of radicals per micelle drops below one. In other words, the rate of termination will be low since there are less radicals. So the end result is this: *decreasing the initiator concentration increases molecular weight and rate of polymerization!* This is completely opposite from bulk and solution polymerization. To increase the rate of polymerization for those you have to heat the reaction or increase the initiator concentration, both of which increase the rate of termination and lower the molecular weight.

Advantages of emulsion polymerization:

The continuous water phase is an excellent conductor of heat and allows the heat to be removed from the systems, allowing many reaction methods to increase their rate.

Since polymer molecules are contained with in the particles, viscosity remains close to that of water and is not dependent on molecular weight.

Final product can be used as is and does not generally need to be altered or processed. Most emulsion polymerizations use a free-radical polymerization method. Emulsion polymerization can be carried out as a batch reaction, but in many cases is performed as a starve-fed reaction to insure a good distribution of monomers into the polymer backbone chain.

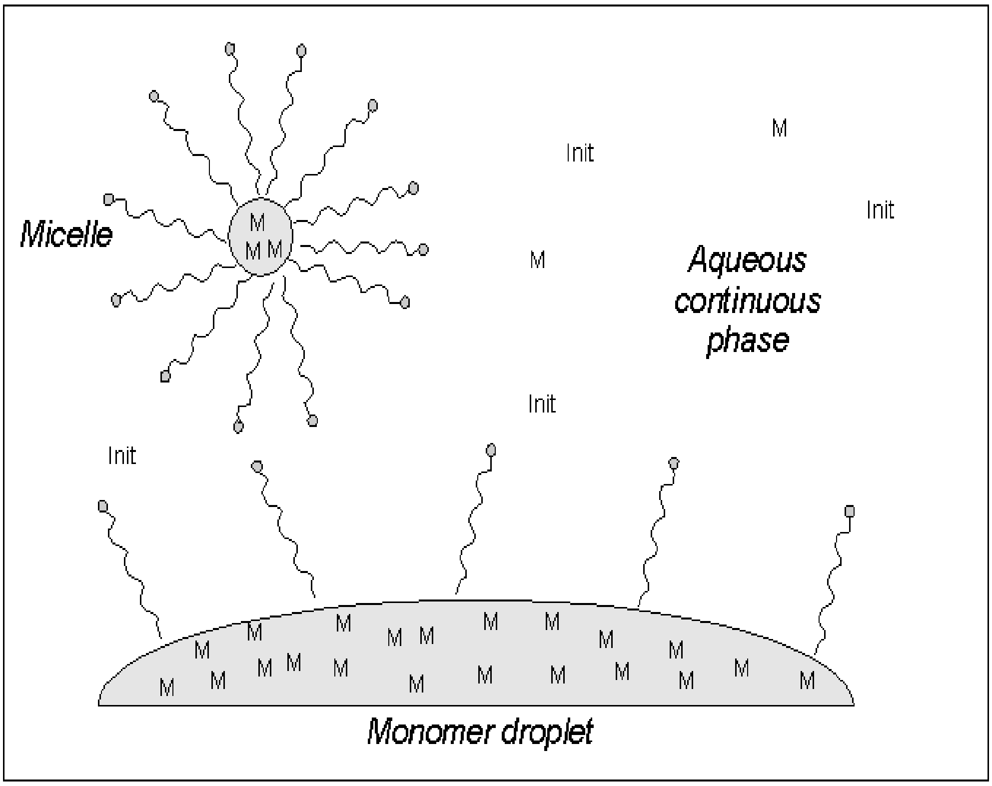
Mechanism of Emulsion Polymerization:

The mechanism is actually very complicated and continues to be studied to this day. The reaction actually takes place in several stages, but, to a first approximation, the following description suffices:

The surfactant molecules surround small amounts of monomer molecules, creating *micelles*. However, the usual recipe contains much more monomer than can be accommodated in micelles, so there are also large droplets of monomer that are stabilized by small amounts of surfactant. Depending on the monomer, there may also be a small amount of monomer dissolved in the water.

Initiator forms free radicals *in the water*, where they may find a few monomers to react with. In any case, the radicals diffuse into the micelles, where they find lots of monomer but *no other growing chains to cause termination* (at least, for a while). The growing chain is then protected from termination until a second radical diffuses into the micelle. This is why the MW can be so high in emulsion polymerization without slowing the rate of conversion.

No polymerization seems to occur in the large monomer droplets. Why? The explanation lies in simple statistics. Compared to the droplets, there are a large number of micelles, with much higher surface area (estimated 1000 times more). It is simply more likely for a radical to diffuse into a micelle than a droplet.



1.3) Monomers from Renewable Resources: Cardanol

India is the largest producer, processor, and exporter of cashews (Anacardium occidentale Linn.) in the world. Cashew cultivation now covers a total area of 700 kha of land, producing over 400 kt of raw cashew nuts. Cashew nut shell liquid (CNSL) is an agricultural byproduct abundantly available in the country. It occurs as a reddish brown viscous fluid in the soft honeycomb structure of the shell of cashew nut. Many researchers investigated its extraction [55-58], chemistry, and composition[59-68] .The cashew nut shell liquid contains four major components, namely, cardanol, cardol, anacardicacid, and 2-methylcardol, whose structures are given in Figure 1.1. Double vacuum distillation of CNSL yields pure cardanol [58,69,70], the yield being 50%. Cardanol the main constituent of distilled CNSL holds considerable promise as a source of unsaturated hydrocarbon phenol, an excellent monomer for polymer production. It has been found that cardanol and its polymers have interesting structural features for chemical modification and polymerization into speciality polymers. Cashew nut shell liquid and cardanol are in use in the manufacture of special phenolic resins for coatings, for lamination, and as friction materials [61-73]. Recently there has been an increasing interest in the development of polymers on cardanol extracted from cashew nut shell liquid (CNSL), which is a mixture of natural alkyl phenols with c15 at the Meta position. It has been especially consider as an excellent monomer with an advantageous long chain substituent for thermo setting polymer production, and has been used in a variety of applications. We can see the structure of cardanol in Figure 1.2., Cardanyl acrylate or3-penta decenyl phenyl acrylate obtained by base catalysed reaction of cardanol and acryloyl chloride, has received considerable attention due to the presence of the acrylic group and the un saturation in the long alkyl side chain (c15), We can see the structure of cardanyl acrylate in Figure 1.3., This potential vinyl monomer provides improved flexibility for many products of the vinyl polymerization reactions.

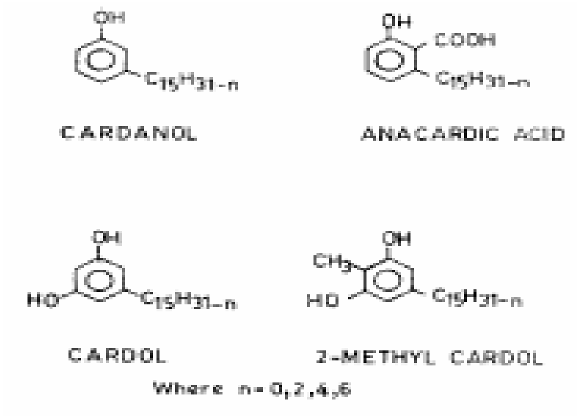
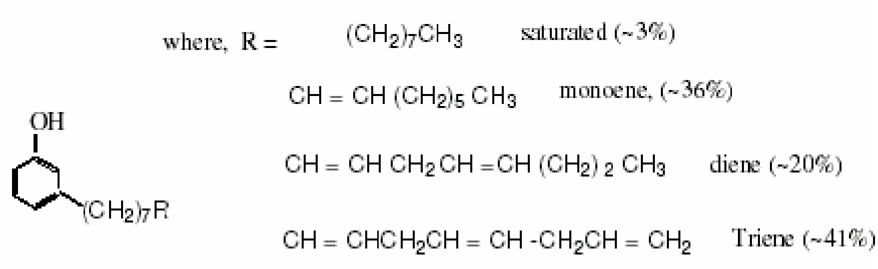


Figure. 1.1 Structures of cardanol, cardol, 2-methylcardol, and anacardic acid.



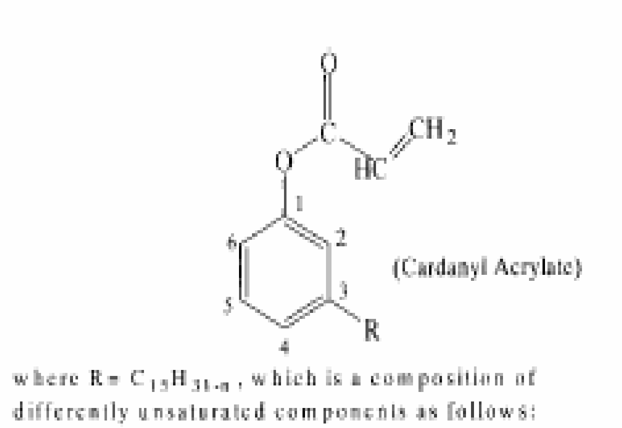
where, R = $(CH_2)_7CH_3$ saturated (~3%)

$CH = CH\ (CH_2)_5\ CH_3$ monoene, (~36%)

$CH = CH\ CH_2CH = CH\ (CH_2)_2\ CH_3$ diene (~20%)

$CH = CHCH_2CH = CH\ \text{-}CH_2CH = CH_2$ Triene (~41%)

Figure1.2 Structure of cardanol



where R = $C_{15}H_{31\text{-}n}$, which is a composition of differently unsaturated components as follows:

Figure.1.3 Structure of cardanyl acrylate (CA).

1.4) Scope of the Present work:

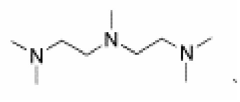
Sustainability, industrial ecology, eco-efficiency, and green chemistry are guiding the development of the next generation of materials, products, and processes. In recent years, the synthesis of polymers from renewable resources has received considerable attention of research workers through out the world because of the escalating price of petrochemicals and high rate of depletion of the natural fossil resources. This necessitates a look at the renewable natural resources that can serve as alternative feed stocks for monomers in the polymer industry. Cardanyl acrylate or 3-pentadecenyl phenyl acrylate, obtained by the base catalyzed reaction of cardanol and acryloyl chloride, [18] has also received the attention of researchers world wide as a possible substitute in flexible thermo set polymer production. These products are light colored in comparison to cardanol based products. The gelation, free radical polymerization kinetics and cross linking mechanism has been studied in detail, recently implying that it could be valuable raw material to reckon with for the production of high performance materials. The objective of the present work was to study the synthesis of cardanyl acrylate and its controlled radical polymerization. The resulting materials will be useful in the formulation of adhesives, inks and coatings. In the first part the preparation of cardanyl acrylate from cardanol and acryloyl chloride is reported. It has been characterized by spectroscopic techniques. In the second part application of ATRP technique to the preparation of crosslinkable poly cardanyl acrylate and methyl methacrylate-cardanyl acrylate co polymers is studied. Our aim was the synthesis of a soluble polymer that can afterward be crosslinked on demand. Also preliminary work on preparation of copolymer emulsions with styrene, MMA and cardanyl acrylate is also reported. The prepared emulsions were characterized for its solid content.

Chapter-2.

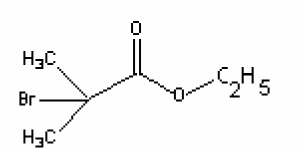
2.1) Experimental

2.1.1) Materials: Cardanol, obtained from M/s. Mercury Engineering, Hyderabad, was purified by vacuum distillation[74]and the fraction distilling at 220-230ºC at 0-3 mm Hg was collected. Acryloyl chloride was prepared from acrylic acid and benzoyl chloride under basic conditions [76,80]. MMA, butyl acrylate were freed from inhibiters by extraction with diluted alkali solution and then used.

The ligand pentamethyl diethylene triamine (PMDETA), catalyst, Cuprous bromide (CuBr) and initiator ethyl-2-bromoisobutyrate were procured from Aldrich and used as such. Styrene, Hydroquinone, Potasiumpersulphate, toluene, diethyl ether, SDS are some other chemicals which are used.



PMDETA



Ethyl-2-bromoisobutyrate

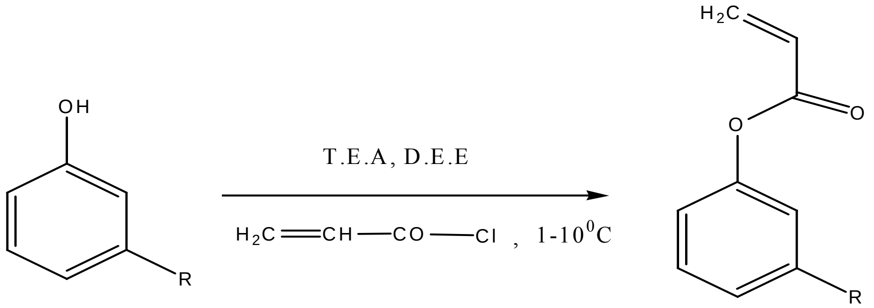
2.1.2) Recovery of Caradnol:

Cardanol was obtained from cashew nut shell liquid by direct double vacuum distillation (5–10 mmHg) in the temperature range 180–240°C. Initially, CNSL was heated to about 170–180°C and kept for 2 h under vacuum so that anacardic acid was converted into cardanol. As soon as the evolution of CO_2 stopped, the mother liquor was further heated under vacuum and the temperature was raised to 230–240°C. About 65% of the liquid distilled over as a light yellow oil, which was collected leaving behind a black viscous solid resinous mass in the flask. On analysis it was found that cardanol has a refractive index of 1.509 and Brookfield viscosity of 950–520 cp at 30°C. The methylformamide (DMF) as the solvent. The pH of cardanol was measured to be 6.5, which agrees with that of pure cardanol [69].

2.1.3) Preparation of Cardanyl acrylate:

Cardanyl acrylate was prepared by two methods.

First method: In first method cardanyl acrylate was prepared according to reaction scheme 2.1.3.1. The synthesis was carried out as below.



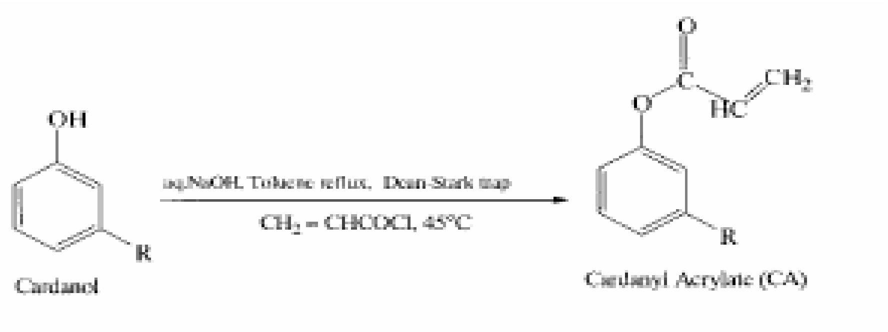
Scheme2.1.3.1. Preparation of cardanyl acrylate

In a typical experiment a double-necked kettle fitted with condenser and an additional funnel, containing 15grams of phenol, 5grams of T.E.A, and 10ml of D.E.E. The cattle kept on ice tub to maintain the temperature between 0-10ºc. the tub was placed on the magnetic stirrer. Above solution was stirred for 15 minutes to obtain good mixed solution. 4.4 grams of acryloyl chloride was added to the vessel through the additional funnel by drop wise, while stirring the solution.

The reaction was allowed to proceed for 5-6 hours at 1-10°c temperature. There after reaction was allowed to proceed for 16 hours at room temperature. Then the product was washed with water and extracted with D.E.E. the extract was dried over anhydrous sodium sulphate and evaporated at reduced pressure. The residue was purified by preparative TLC. Yield was 67%.

Second method:

In second method cardanyl acrylate (CA) was synthesized according to reaction scheme 2.1.3.2. The synthesis was carried out as below.



Scheme2.1.3.2. Preparation of cardanyl acrylate

In a typical experiment a double-necked kettle fitted with stirrer and a water condenser, containing 30 grams of cardanol, 10ml of toluene. The kettle was kept in a heating mantel, and the temperature was maintained at 50°c. 5ml of NaOH solution was added to the vessel while stirring the above solution with a Teflon blade stirrer at 230 rpm. The reaction was allowed for 30 minutes. Then water was removed from above mixture by using agiotropic mixture separation method.

Condenser was replaced by additional funnel. cardanyl acrylate was added to the above reaction mixture through additional funnel while stirring it. The temperature was kept at 40°c. The reaction was allowed to proceed for 24 hours. After, the reaction mixture was washed with water to remove un reacted acryloyl chloride and extracted with toluene. The extract was dried over anhydrous sodium sulfate and evaporated at reduced pressure. The residue was purified by preparative TLC. Yield was 73%.

2.1.4) Preliminary Experiments:

Preparation of co-polymers by using emulsion polymerization method:

2.1.4.1. Preparation of styrene-butyl acrylate copolymer emulsions:

In a typical reaction, triple necked reaction kettle fitted with a stirrer, nitrogen in let, and a nitrogen out let, containing 50ml of water with 0.13 grams 0f SDS. The kettle was kept in thermostatic oil bath, and the temperature was maintained at $80+1^0$c. Now 5 grams of styrene was thoroughly flushed with nitrogen and was added to the vessel, while stirring the aqueous solution with Teflon blade stirrer at 320 rpm. 10 minutes later $K_2S_2O_8$ solution was added to above solution.

When the reaction mixture was turned white (after 5-10 minutes) then 5 grams of butyl acrylate was added by using additional funnel. The polymerization was allowed to proceed for 24 hours. After that the emulsion mixture was taken out and tested for solid content value. Theoretically the emulsion mixture should contain 17.1% of solids. But it contains 16.3% of solids

2.1.4.2. Preparation of Cardanyl acrylate, Styrene copolymer emulsions:

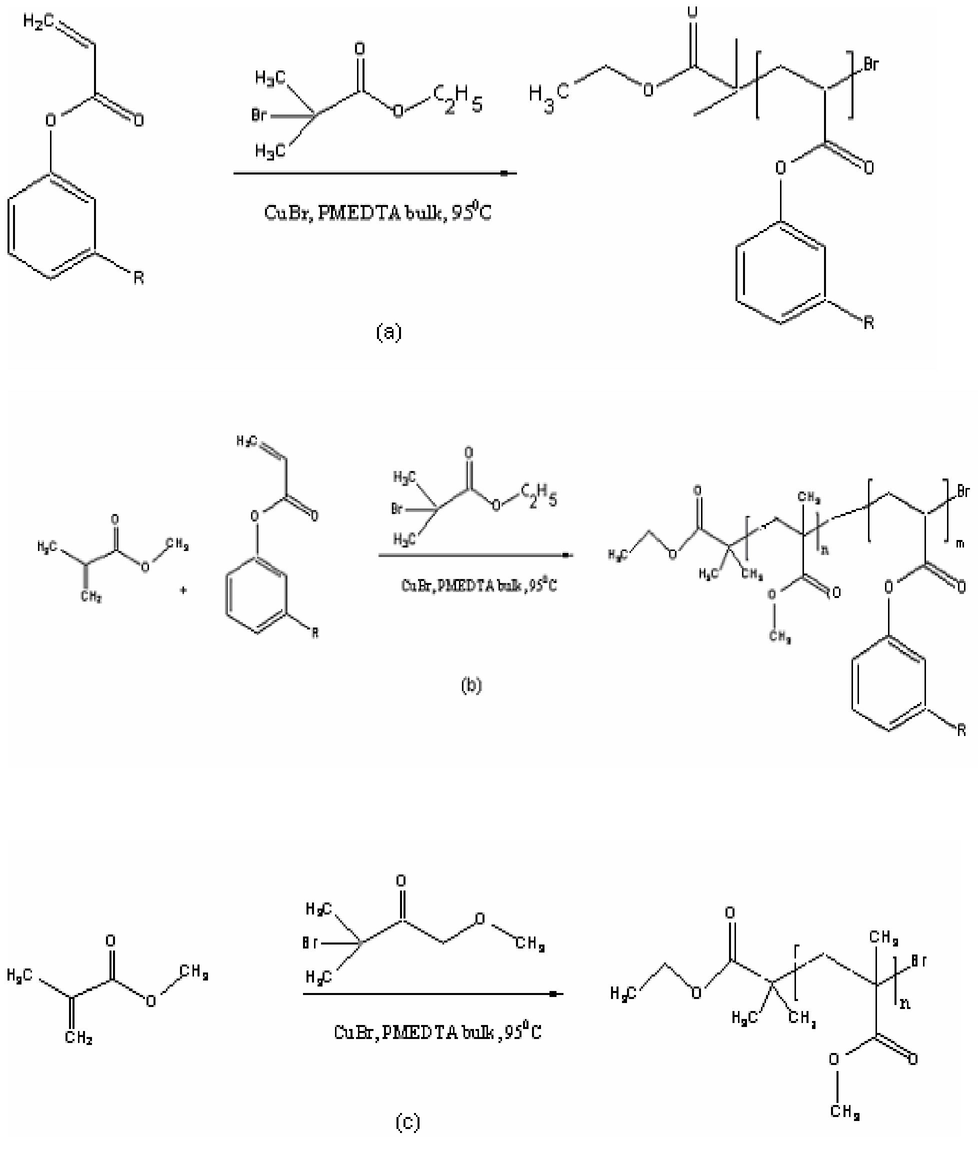
In a representative experiment, triple necked reaction kettle fitted with a stirrer, nitrogen in let, and a nitrogen out let, containing 50ml of water, 0.13 grams of SDS. The kettle was kept in a thermostatic oil bath and heated up to 40^0c. 20 minutes later 5grams of cardanyl acrylate, 5grams of styrene were added to the above solution while stirring it. Temperature was maintained at60°c. The above mixture was allowed to mixed well for 20 minuets, there after 100 m.g $K_2S_2O_8$ Was added to solution. This time temperature was 80°c. Now the temperature was standardized to 80+2°c. The polymerization was allowed to proceed for 24 hours. Emulsion mixture was taken out from mantel and tested for solid content.
Theoretically prepared emulsion should contain 17.1%. But it contains 16.3% only.

2.1.4.3. Preparation of butyl acrylate and cardanyl acrylate copolymer emulsion:

In a representative experiment, triple necked reaction kettle was fixed with stirrer, nitrogen in let, and nitrogen out let, containing 50 ml of water with 0.13 grams of SDS. The kettle was kept on thermostatic oil both, and temperature was maintained at 80+2°c. 8.98 grams of butyl acrylate was thoroughly flushed with nitrogen gas and was added to the vessel while stirring the aqueous solution with Teflon blade stirrer at 300 rpm. 5mininutes later $K_2S_2O_8$ was added to the above solution. Polymerization was started with in 3-5 minutes. This we can find out by observing color of solution becoming milk white. The polymerization was allowed to proceed for 24 hours. 1.8 grams of cardanyl acrylate was added to the above solution reaction mixture, and allowed to 24 hours more to complete reaction. Finally prepared emulsion was taken out from oil bath and tested it for solid content. Theoretically prepared emulsion should contain 21.56 %. But it contains 11.81% only.

2.1.5) Preparation of Polymers by using ATRP Method:

All polymerizations were performed under ATRP conditions. In a typical copolymerization experiment (28mg, 0.193 mmol), PMDETA (81μl, 0.387 mmol) and monomers methyl methacrylate [3.1119 g, 31.12 mmol] and cardanyl acrylate [1.086g, 3.03 mmol] were added to a 2 neck flask, purged with N_2, magnetically stirred until homogenous. The initiator (58 μl, 0.391 mmol) is injected and polymerization was run for 5 hours at 95 °C in an oil bath. DOWEX 50 (Fluka) ion exchanger was added to deactivate the catalyst at the end of the polymerization time, diluted with THF and precipitated in to methanol-water [75:25] mixture for recovery of the polymer. Conversions were determined gravimetrically. Synthesis of polymers were carried out as showed in scheme 2.1.5



Scheme 2.1.5. (a) Preparation method of cadanyl acylate polymer, (b) preparation method of MMA and cardanyl acrylate copolymer, (c) preparation method of MMA polymer

2.2) Characterization Techniques:

The characterization of the cardanol, cardanol acrylate and copolymers were done by spectroscopic and other techniques. IR spectra (was recorded on a Nicolet Machine). The NMR spectra (was recorded in $CDCl_3$ on a Bruker 300MHz machine). Mass spectra (was recorded on Vin Micromass machine model 70-70H from U.K). CHN analysis (was carried out on a Vario EL analyzer). Electronic absorption spectra (UV spectra) were recorded with ocean optics fiber(400**) spectrometry SD 1000 using 1cm quartz cell in different solvents.

(a) **Gel Permeation Chromatography (GPC)**: Molecular weight and MWD of the samples were determined by Gel Permeation Chromatograph (GPC) equipped with UV, RI detectors and styragel columns, (102–105 A°). PMMA standards (Polymer Laboratories) were used for the calibration. THF was used as an eluent at 1 ml/min flow rate at room temperature.

(b) **Dynamic Mechanical Thermal Analysis:** The curing behaviour of polycardanyl acrylate was studied on DMTA (model: Rheometric IV machine) in dual cantilever mode. The viscous resin is applied to E-glass fabric of dimensions 10 mm width, 28 mm length and a thickness of 0.1mm and the test was done at a heating rate of 3°C /minute to monitor the variation of E', E'' and tan delta.

(c) **Thermo gravimetric Analysis:** To assess the thermal stability the polymer samples were analyzed on a Mettler Toledo thermo gravimetric analyzer at a heating rate of 10 °C/min in N_2 atmosphere.

Chapter-3.

3.Results and discussions.

3.1. Characterization of Cardanol:

Cardanol as recovered from cashew nut shell liquid was characterized by elemental analysis (CHN analyzer) (table 3.1), IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopy techniques. The IR spectrum of cardanol (Figure 3.1) showed clear and sharp absorption peaks in the region 3900–850 cm^{-1}. The stretching vibrations at 3375–3000 cm^{-1} were due to the phenolic hydroxyl groups. The sharp absorption bands in the region 2925–2854 cm^{-1} are characteristic of C—H stretching vibrations, and those between 3000 and 3100 cm^{-1} for C—H groups. The latter may be present in an olefinic or an aromatic structure, but the appearance of the strong band at 1589 cm^{-1}, the aromatic ring ''breathing'' vibration, shows that it must be the second of the two possibilities. Aromatic ring (C=C) stretching vibrations occurred in the region 1620–1430 cm^{-1}. Cardanol peaks appeared at 1456, 1486, and 1589 cm^{-1}. The appearance of peaks at 943 and 873 cm^{-1} confirmed that cardanol is a meta-substituted phenol.

^{1}H-NMR spectroscopy of cardanol (Figure 3.2) reveals the presence of multiplets corresponding to the aromatic protons in the range of δ 6.59–7.26 ppm (4H). The olefinic protons (-CH=CH-) appeared as a multiplet in the range of 5.30–5.36 ppm (2H). The peak at 5.00 ppm belongs to (-CH=CH$_2$), and (CH=CH-$\underline{CH_2}$-CH=CH-) showing peak at 2.8 ppm. The signal at 2.51–2.58 ppm could be attributed to the —CH$_2$—Ar triplet (2H), and that at 2.0 ppm (4H, m) was assigned to the (—$\underline{CH_2}$—CH=CH—) component of the cardanol.signal at 1.8 ppm corresponding to (-$\underline{CH_2}$-CH$_2$-Ar). These assignments were confirmed by decoupling experiments. The groups (—CH$_2$—) $_n$ appeared as a singlet of sharp intensity at 1.32 ppm (16H), and the terminal —CH$_3$ group in the side chain gave a triplet centered at 0.89 ppm (3H). So after double vacuum distillation (5–10 mmHg) cardanol obtained was basically a monoene meta-substituted phenol; i.e., the empirical formula of cardanol is $C_{21}H_{29}O$. The other component of CNSL double distillation was a highly viscous dark plastic mass remaining as a residue in the flask. The ^{13}C-NMR study of cardanol also supported the aforesaid viewpoint. The ^{13}C-NMR (proton decoupled) spectra (Figure 3.3) was recorded in CDCl$_3$. The various signals (proton decoupled) could be assigned with the help of DEPT-90 and DEPT-135 spectra. It showed the presence of quaternary methane carbon (CH), methylene (CH_2), and CH_3, consistent with the structure. So it has been confirmed that double vacuum distillation of cardanol yields only a monoene meta-substituted phenol. The results agree with those of previous workers.

Further the mass spectra of cardanol (Figure 3.4) give the molecular ion peak, and other fragment ions.

Sample code	Nitrogen%	Carbon%	Sulphur%	Hydrogen%	O_2%
Cardanyl acrylate Ex.	NA	80.8	NA	10.15	9.04
Cardanyl acrylate theory	NA	80.8	NA	10.18	8.97

Table 3.1. Elemental analysis. NA=not applicable

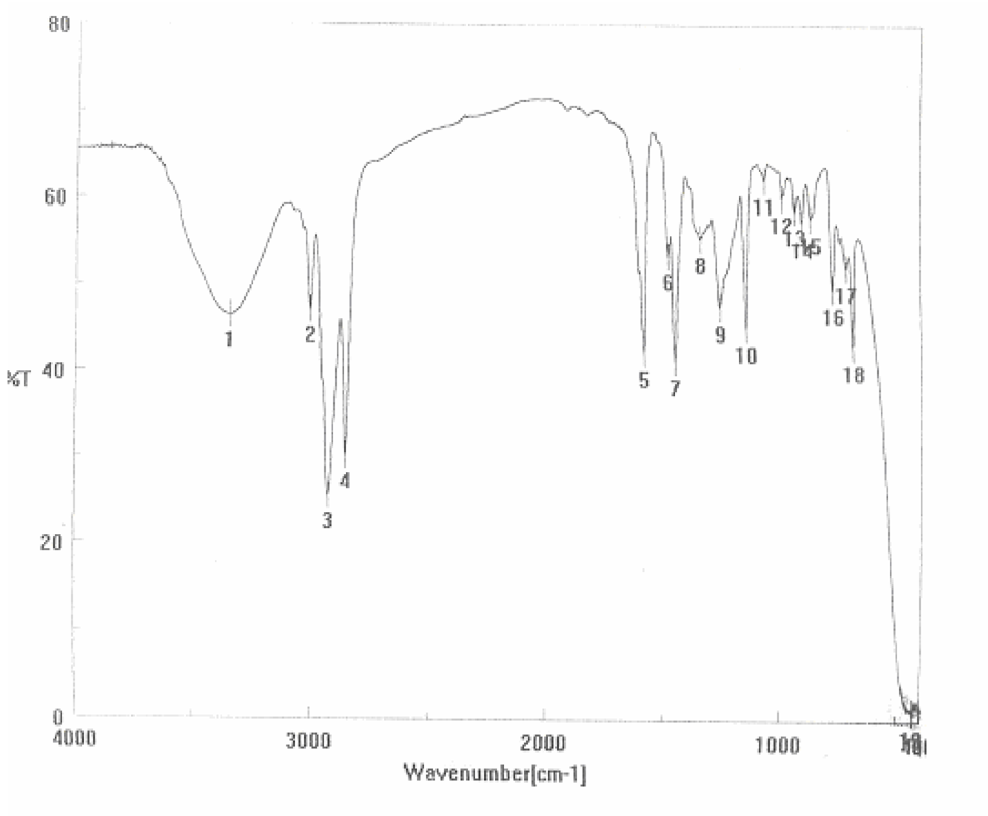


Figure 3.1. IR spectrum of cardanol

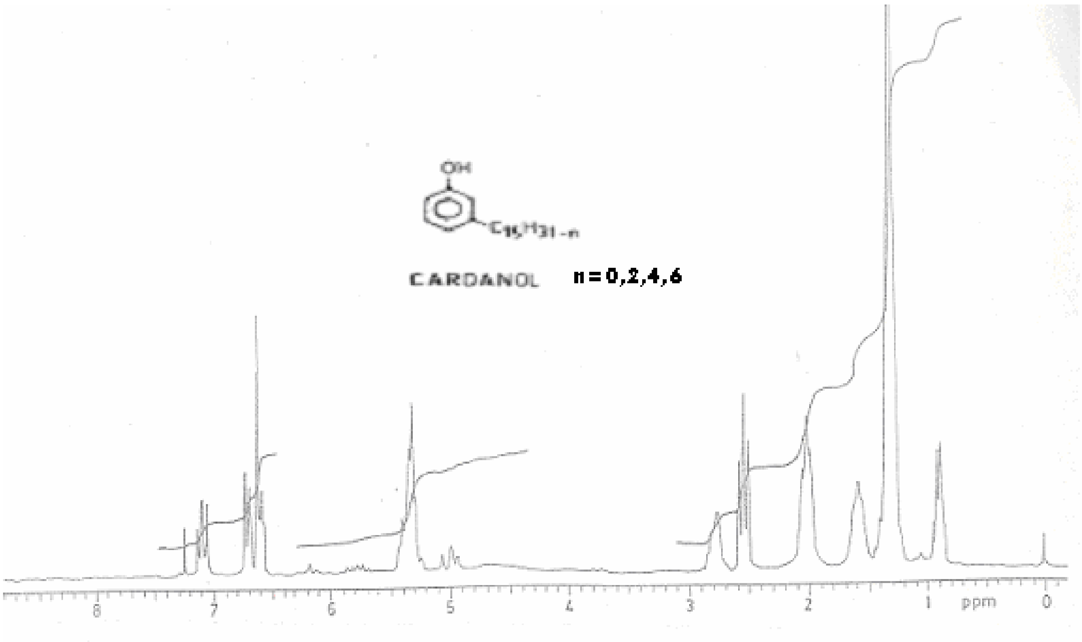


Figure 3.2. ^{1}H-NMR spectra of cardanol

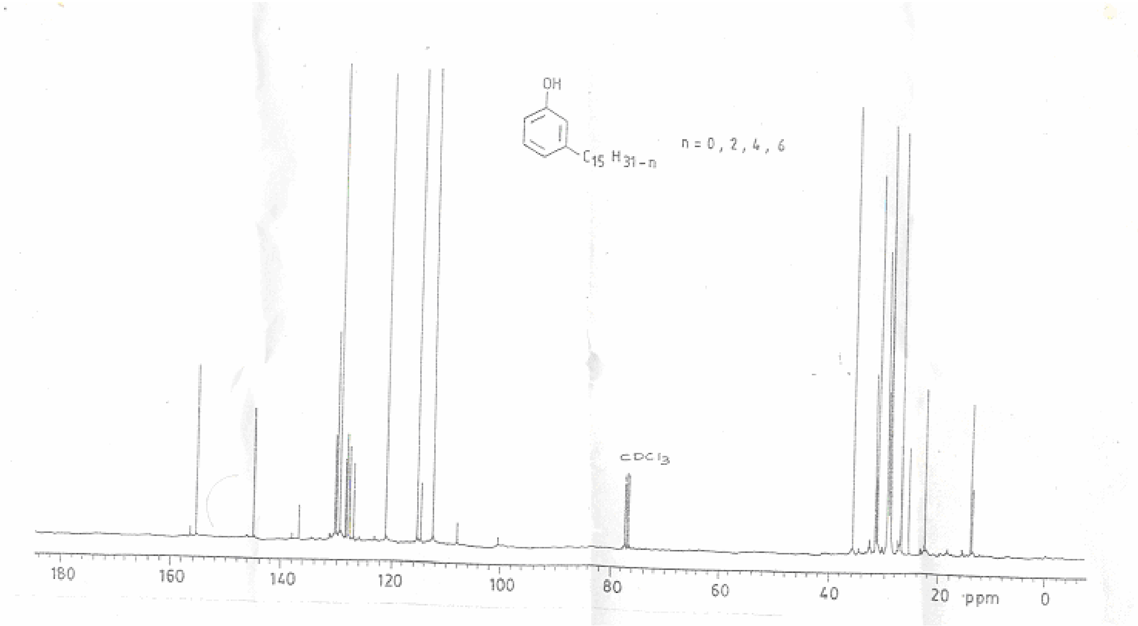


Figure 3.3. ^{13}C-NMR spectra of cardanol

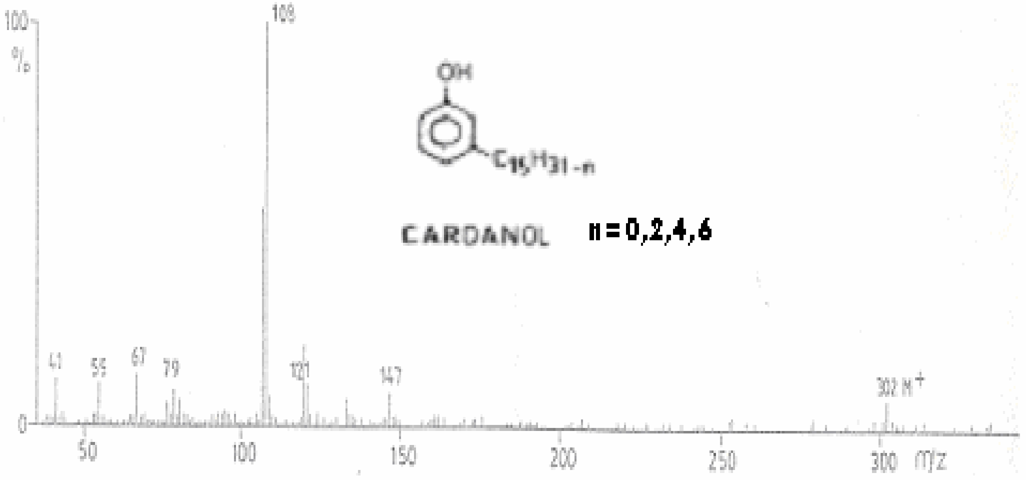


Figure 3.4 Mass spectra of cardanol

3.2. Synthesis and Characterization of Cardanyl acrylate:

The IR spectrum of cardanyl acrylate (Figure 3.5) monomer and polymer showed the characteristic carbonyl stretching frequency of ester group at 1747cm^{-1} the C-H stretching vibrations of –$(CH_2)_2$-- groups present in the side chain of the cardanyl acrylate were obtained at 2925 and 2855 cm^{-1}. The double bond of acrylic moiety was observed at 1658cm^{-1},and in the cardanyl acrylate polymer, the peak at 1658cm^{-1} was not observed, due to the conversion of acrylic C=C to C-C.

In the ^{1}H-NMR of cardanyl acrylate (Figure 3.6) monomer the peaks were assigned for different protons (δ, ppm): 0.8 (t, CH_3), 1.2-1.4 (m, CH_2), 1.65 (nr, –CH_2-CH_2-Ar), 2.0 (nr, -CH_2-CH=CH-), 2.6 (nr, -CH_2-AR), 2.8 (nr, -CH=CH-CH_2-CH-=CH-) 5.0-5.5 (t, CH_2=CH-, -CH=CH-), 6.0-6.6 (m, =CH_2, m, -CH=), 6.8-7.3 (m, aromatic). In the NMR spectra of cardnyl acrylate polymer (Figure 3.8) the peak at δ = 6.0-6.6 (acrylic) is not present due to polymerization through acrylate moiety and the peak at δ = 5.2-5.5 for the double bonds in the side chain of the monomer remains intact after the polymerization reaction, which also support the IR data. Further the mass spectra of cardanyl acrylate (Figure 3.7) give the molecular ion peak, and other fragment ions.

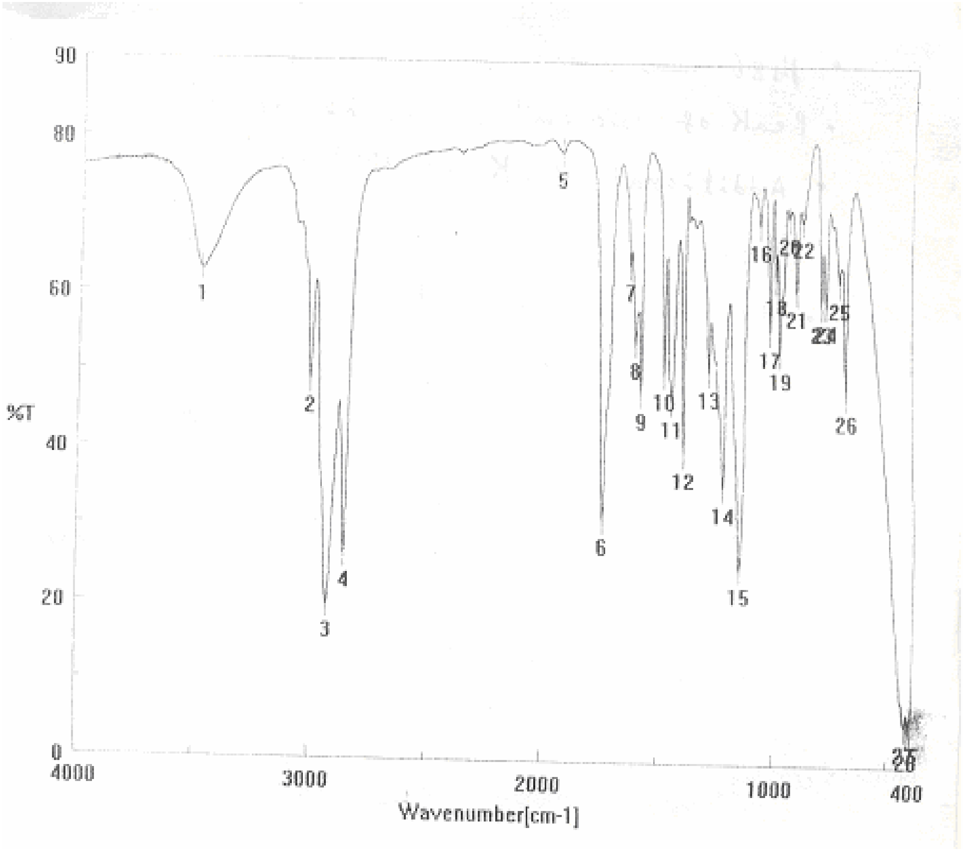


Figure 3.5. IR spectrum of cardanyl acrylate

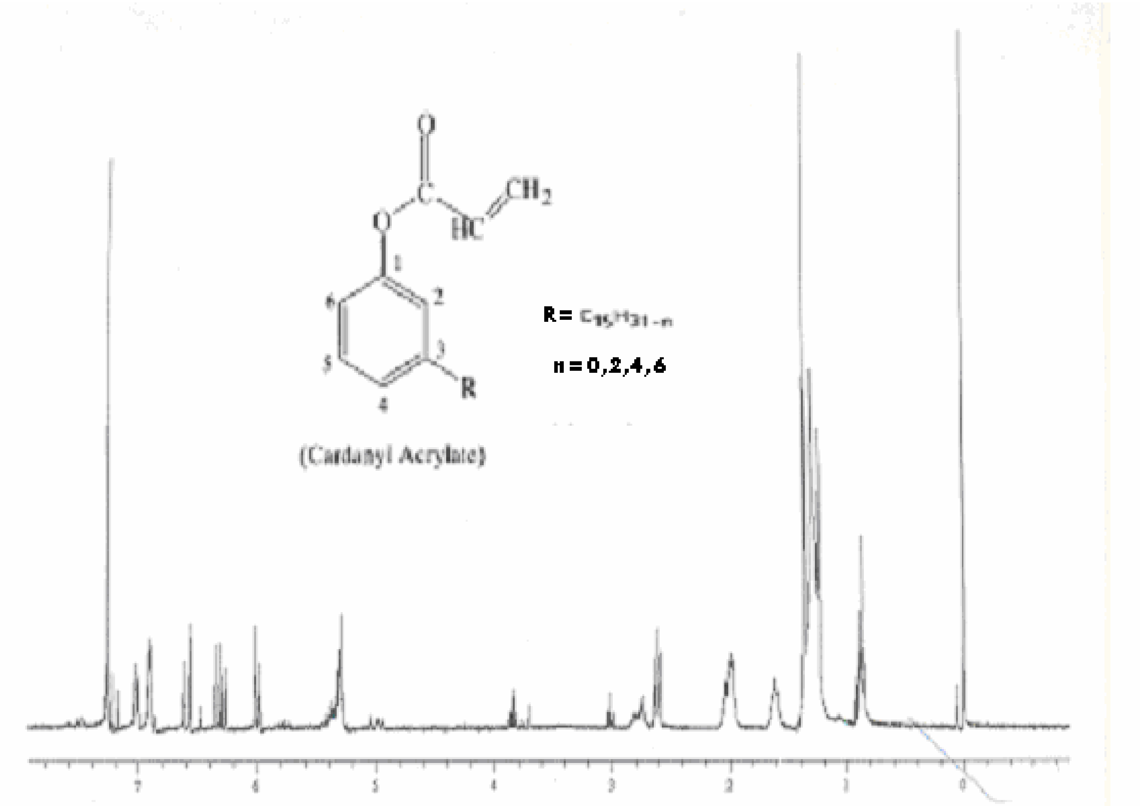


Figure 3.6. ^{1}H-NMR Spetrum of cardanyl acrylate

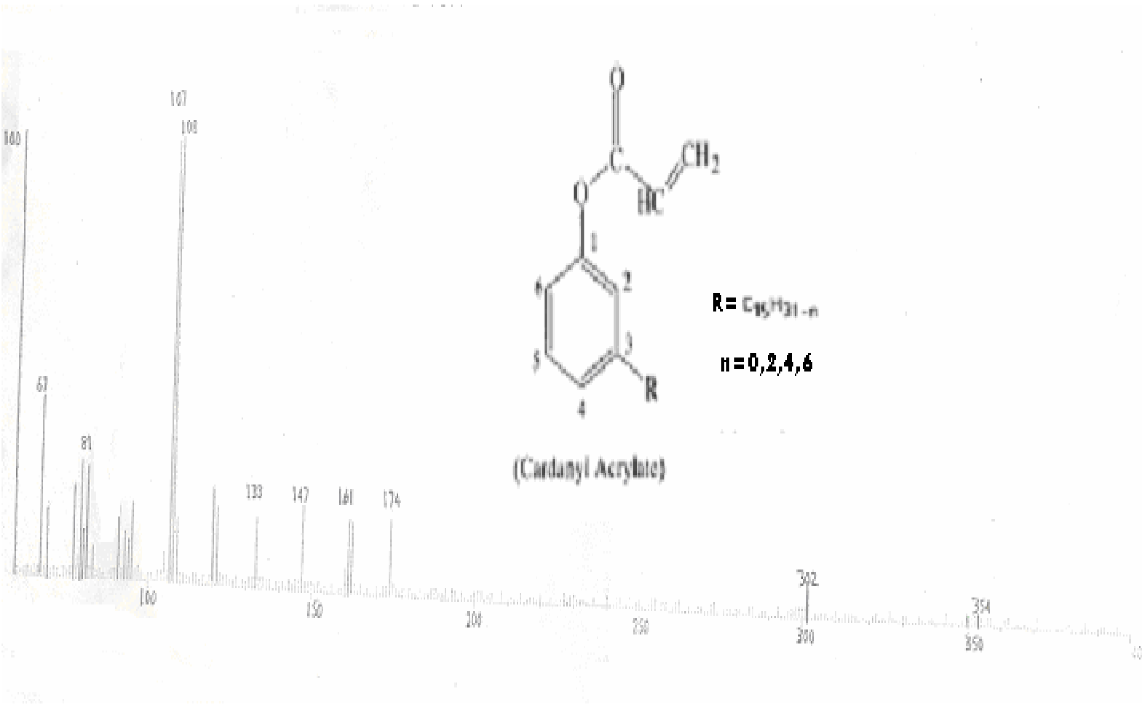
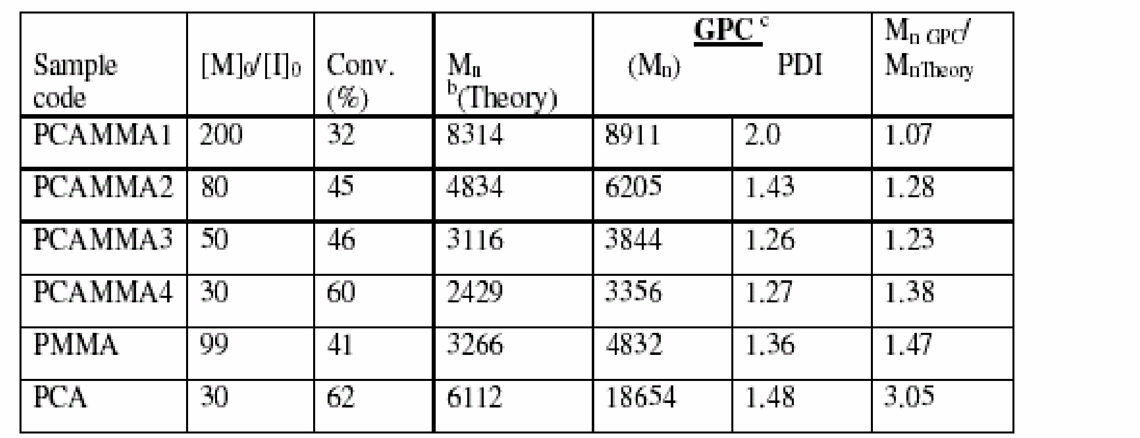


Figure 3.7 Mass spectra of cardanyl acrylate

3.3. Synthesis & Characterization of Homopolymers and Copolymers of Cardanyl acrylate:

The synthesis of polycardanyl acrylate and methyl methacrylate-cardanyl acrylate copolymers were carried out by Atom Transfer radical Polymerization in bulk at 95°C. First, cardanyl acrylate was prepared from cardanol and acryloyl chloride and the spectral data confirmed its structure which was in agreement with earlier reports by other workers[76, 80]. Free radical polymerization of cardanyl acrylate by conventional methods would normally lead to the preparation of cross-linked materials. Copolymerization with methyl methacrylate (MMA) using AIBN or benzoyl peroxide by suspension technique lead to formation of crosslinked beads as reported by George et al[77]. Applying ATRP technique to any monomer requires to optimise the concentration of catalyst–ligand system. In this regard, ATRP of acrylates has been one of the most widely studied. Triamine ligands such as pentamethyl diethylene triamine (PMDETA) was successfully used for ATRP of several acrylates by Matyjaszewski and coworkers [82,83]. When PMDETA was used as ligand, it was observed that the solubility of the catalyst complex is low at low ligand concentration at room temperature. However, the reaction mixture was homogenous at 95 °C. Further decrease in the ratio of ligand with respect to initiator resulted in an insufficient complexation leading to a partial precipitation of CuBr. So in the present work the ratio of CuBr to ligand was kept at 1:2. All polymerizations were conducted under the same conditions. Ethyl-2-bromo isobutyrate, CuBr, PMDETA catalyst-cocatalyst system initiated the polymerization in bulk at 95°C. The polymers were isolated by dissolving in THF and purified by precipitation to methanol water mixture. The reaction conditions and other characteristics of the homopolymers and copolymers are summarized in Table 3.2

Table 3.2. Conditions and results for the ATRP of cardanyl acrylate and its copolymers at varying initiator ratio[a].



Sample code	$[M]_0/[I]_0$	Conv. (%)	M_n [b](Theory)	GPC[c] (M_n)	PDI	$M_{n\,GPC}/M_{n\,Theory}$
PCAMMA1	200	32	8314	8911	2.0	1.07
PCAMMA2	80	45	4834	6205	1.43	1.28
PCAMMA3	50	46	3116	3844	1.26	1.23
PCAMMA4	30	60	2429	3356	1.27	1.38
PMMA	99	41	3266	4832	1.36	1.47
PCA	30	62	6112	18654	1.48	3.05

[a]reaction conditions: 95°C, bulk, 5 hours.[PMDETA]:[CuBr]:[M] =2:1:100. [b]$[M]_o/[I]_o$ × conversion × repeat unit molecular weight (g/mol). [c]The mol.wt.was calculated from GPC. Measurements were done in THF at flow rateof 1ml/min.

The copolymers were prepared at a constant feed composition of 90 mol% methyl methacrylate and 10 mol% cardanyl acrylate. The initiator dependence for constant monomer feed composition in the copolymerization is visible from Table 3.2. As expected with increasing initiator concentration, lower molecular weight was obtained. But the polydispersity was found to decrease with increasing initiator concentration. The polymerization rate was low and low conversion achieved at lower initiator concentration [PCAMMA-1] in comparison to entry 4 at high initiator concentration. In other words, variation of the ratio $[M]_0/[I]_0$ provided two inferences. The maximum conversion is higher, the lower the ratio is (entry 4, cf. Table 3.2). High concentration of initiator leads to a higher apparent rate coefficient than low initiator concentration and hence higher rates. As evident from Table 3.3.1, in the case of MMA-cardanyl acrylate copolymers better control in terms of both molecular weight and polydispersities were achieved at low $[M]_0/[I]_0$ values. This is in agreement with the general observations that full control of living radical polymerizations are observed at lower ratio of monomer to initiator as the equilibrium concentration of dormant species to active species are better maintained

[84]. Similar to our work Reghunadh etal [85], who have studied the effect of ligand concentration and type in the polymerization of lauryl methacrylate, have observed a narrow molecular weight distribution at lower ligand concentration and broad molecular weight distribution at high ligand concentration. At higher ligand concentration higher rates were observed and a slower rate in the presence of lower concentration of ligand. It was suggested that the polymerization is uncontrolled at higher concentration of ligand due to a fast equilibrium dynamics between the propagating chain ends and the catalyst, and at higher concentration of the ligand, due to inefficient co-ordination with the catalyst. Here in the present study since the catalyst/ligand concentration is constant, it is clear that the initiator influences the polydispersity and molecular weight as expected.

These results can be rationalized on assuming that in ATRP polymerization Kinetics, the rate of polymerization is directly proportional to the rate constant for Propagation and any factor enhancing this will improve k_p [86,87] and initiation is a complex process involving catalyst /ligand and initiator. So change in ligand or /initiator concentration can be anticipated to produce the same effective, a decrease or increase of the rate. The polymerization rate of pure cardanyl acrylate was found to be high as indicated by the higher conversion [62% for entry 6 cf. Table 3.2] in comparison to PMMA [entry 4 (60%)], despite the polymerization conditions being nearly the same. In general, the polymers were completely soluble in standard organic solvents like THF and chloroform and were obtained as pale yellow powders upon precipitation from THF into methanol-water mixture (75:25) and drying under vacuum at 50 °C for 24 hours. Pure polycardanyl acrylate (PCA) was obtained as a viscous resin. Comparing the ^{1}H-NMR spectra of PCA (Figure 7.8) and the copolymers with that of cardanol suggest peaks due to unsaturation in side chain of cardanol [δ4.9-5.4 ppm] are present in the copolymer also. Figure 3.9 shows typical ^{1}H-NMR spectrum of a copolymer. [see Ref.1b and 19 for a detailed assignment of the peaks due to the alkyl side chain of cardanol, the peaks marked as ‘f,g,h,I,j’ are due to proton in the side chain of cardanol]. The copolymer composition determined from ^{1}HNMR (Comparison of $-OCH_3$ and phenyl group signals at 3.6 ppm and 6.7-7.2 ppm respectively) suggest it to be identical to the feed composition, i.e., of 90 mole% MMA (93 mol% from ^{1}H-NMR) and 10 mol% cardanyl acrylate (7 mol% from. ^{1}HNMR). The broadening of the NMR peak could be attributed to the monomer sequence distribution, in addition to atacticity, in the random copolymer[85].

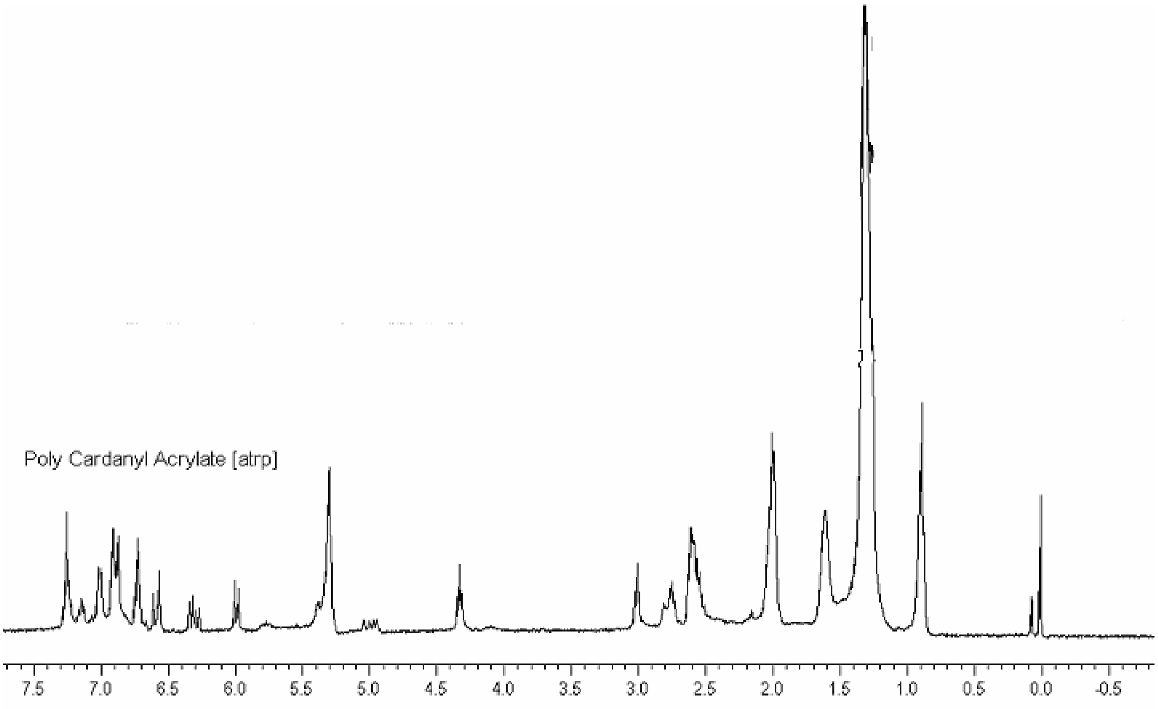


Figure 3.8. ^{1}H-NMR spectra of cardanyl acrylate polymer

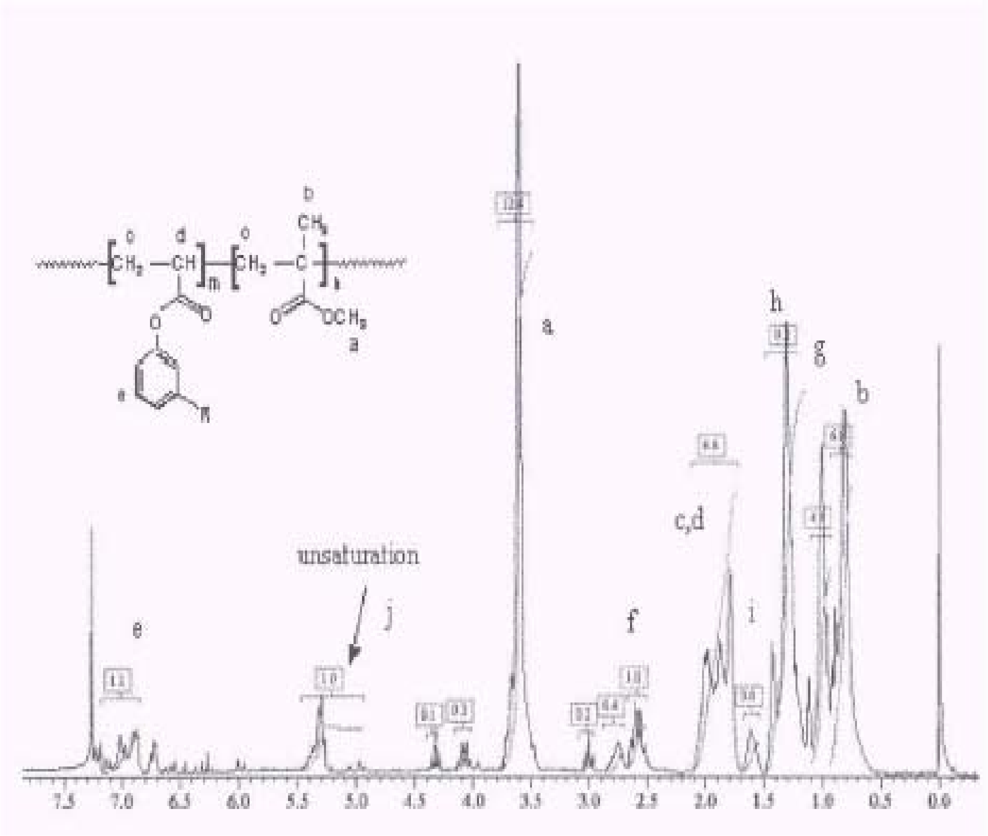


Figure 3.9: Typical ^{1}H-NMR spectrum of methyl methacrylate-cardanyl acrylate copolymer [PCAMMA-4] prepared by ATRP, with a feed composition of 90:10.

A look at the molecular weight data [cf. Tabel 3.2] show that the copolymers were relatively well defined with moderate conversion. The copolymers had molecular weight values in the range [M_n= 8300-2400 g/mole] and polydispersity index (PDI) was in the range 1.27-2.00. The molecular weight of pure poly cardanyl acrylate obtained from GPC was found to be higher than the theoretically calculated values. The larger discrepancy in molecular weights from GPC could be due to a large hydrodynamic volume of cardanyl acrylate resulting from the alkyl chain at m-position as compared with PMMA standards used for GPC calibration [85]. To evaluate the control of the polymerization reactions, the ratio $Mn,_{GPC}/Mn,_{Theory}$ was calculated (cf.Table 3.2.) A constant value of $Mn,_{GPC}/Mn,_{Theory}$ (~1-1.5) was obtained indicating a controlled polymerization for all co polymerizations, but higher values for the cardanyl acrylate homopolymerization, nearly 3.(cf.Table 3.2, entries 6). This suggests that the reactions were better controlled at low initiator concentration and the control was better in copolymerizations (in cases the values are less than 2) than in the homopolymerization. However the poydispersity of the copolymers showed increase with decreasing initiator concentration as observed in the APTRP of acrylates by a Wilkinson's catalyst [88]. This could be due to the fact that at lower rate of polymerization (R_p) due to a slow increase of viscosity termination and recombination reactions become more prominent and affects polydispersity.

Reactivity ratios of two monomers in a copolymerization are normally expected to be very similar for free radical and controlled radical polymerization. However as recently reported by Haddleton[89] significant differences of the monomer activity ratios can be found between free radical polymerization and ATRP in special cases are attributed to the complex formation between monomer and catalyst which is formed in the case of fictionalized monomers containing donor atoms such as N or O. In the present work the monomer catalyst complex was pale green colored in the case of MMA but when cardanyl acrylate was also present, the colour was light brown probably due to the differing complexation. However, as the composition determined from ^{1}H-NMR nearly matches that of feed composition it is anticipated that their reactivities are nearly the same.

Basing on these observations a few comparative comments, on the behaviour of cardanyl acrylate in ATRP could be made in comparison to conventional radical polymerization. The probability of a radical attack at the side chain unsaturation is much lower in ATRP than in conventional free radical polymerization. The concentration of active radicals is several orders of magnitude lower in ATRP [86], The attack of an active free radical at a pendent double bond (on the alkyl chain) would generate a reactive radical that in free radical polymerization bears the potential of cross linking upon reaction with another molecule [77,78,79]. By reaction with a growing radical, the different unsaturated C_{15} alkyl chain in cardanyl acrylate, in most cases, form allyl radical, which are hardly capable of chain propagation[79]. Also, in ATRP, the reactive acrylic species is converted to a dead species by reaction with Cu(II) complex. In other words termination or transfer reactions in ATRP are irreversible. Hence it is thought that of co polymerization of the more reactive acrylate function leaving the side chain unsaturation intact.

3.4 Thermal and Dynamic Mechanical Behaviour.

With the objective of ensuring NMR group assignment and the reactivity of pendent double bond, dynamic mechanical analysis of pure polycardanyl acrylate was carried out on a dynamic mechanical thermal analyzer (DMTA). Also the cure characterization is of prime interest in technological coating developments. In this regard supported DMTA was shown to be an easy, powerful and very sensitive technique to assess the thermal properties of a coating [90,91].

The cure curve, as shown in Figure 3.10, show that the storage modulus increases slowly on heating, except that at about 90°C a slight decrease of modulus observed due to glass transition of polycardanyl acrylate. The tan δ curve also exhibit a shoulder, at about 110°C, probably due to this phenomenon. This value is close to the T_g value reported by Ikeda et al [74] in oxidatively polymerized CNSL. Thereafter the modulus increases continuously until the sample decomposition starts around 335°C and shows a decrease in modulus. Additionally thermal curing was also carried out with benzoyl peroxide (4 wt%) at 100°C for 4 hours. The solubility of the product was checked and insolubility in THF is attributed to the network formation. Thermo gravimetric analysis of the copolymer samples revealed that the incorporation of 10 mol% cardanyl acrylate as a comonomer improved the thermal stability by ~35 °C. The derivative TGA plots show peaks at 390°C for pure PMMA but for the copolymer PCAMMA-4 the peak temperature is around 425°C. The weight loss trend also shows a similar behaviour, when the temperatures for 50% decomposition are compared.

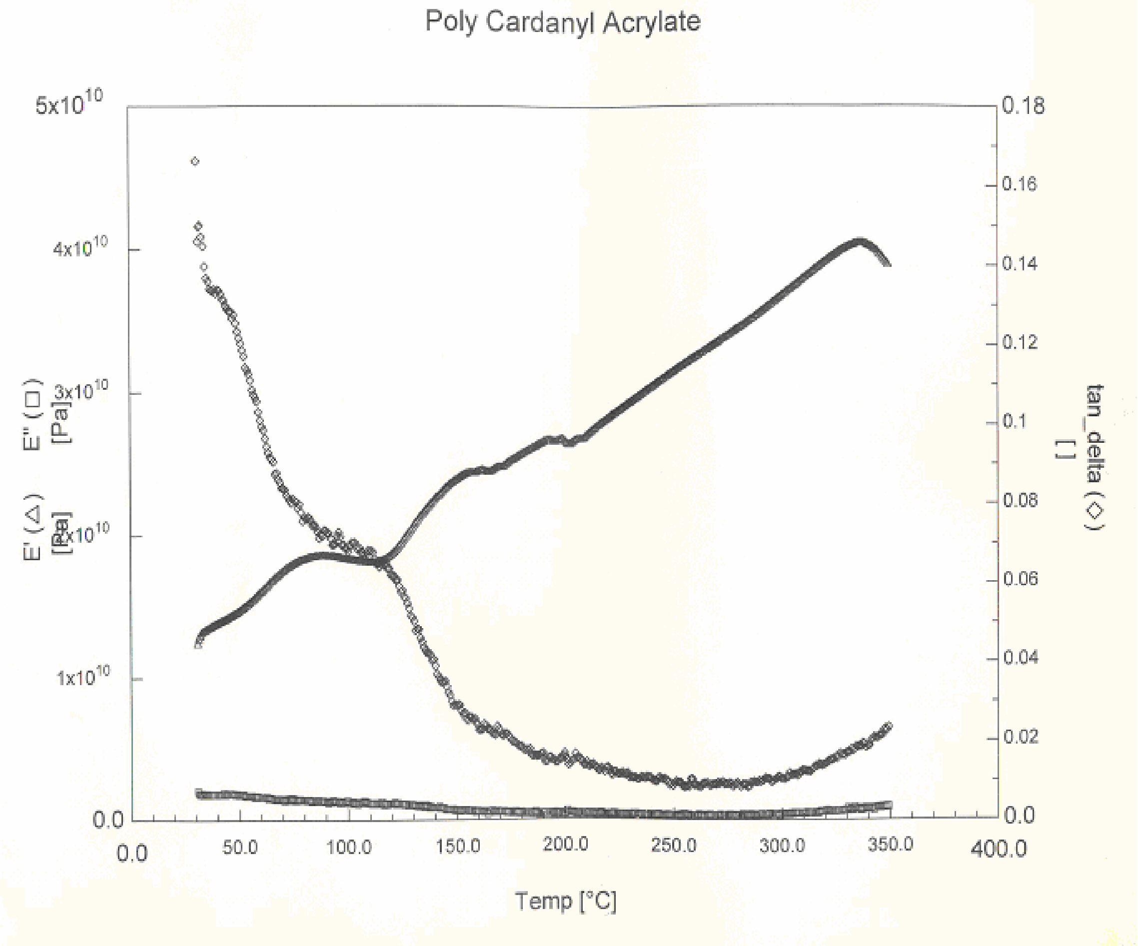
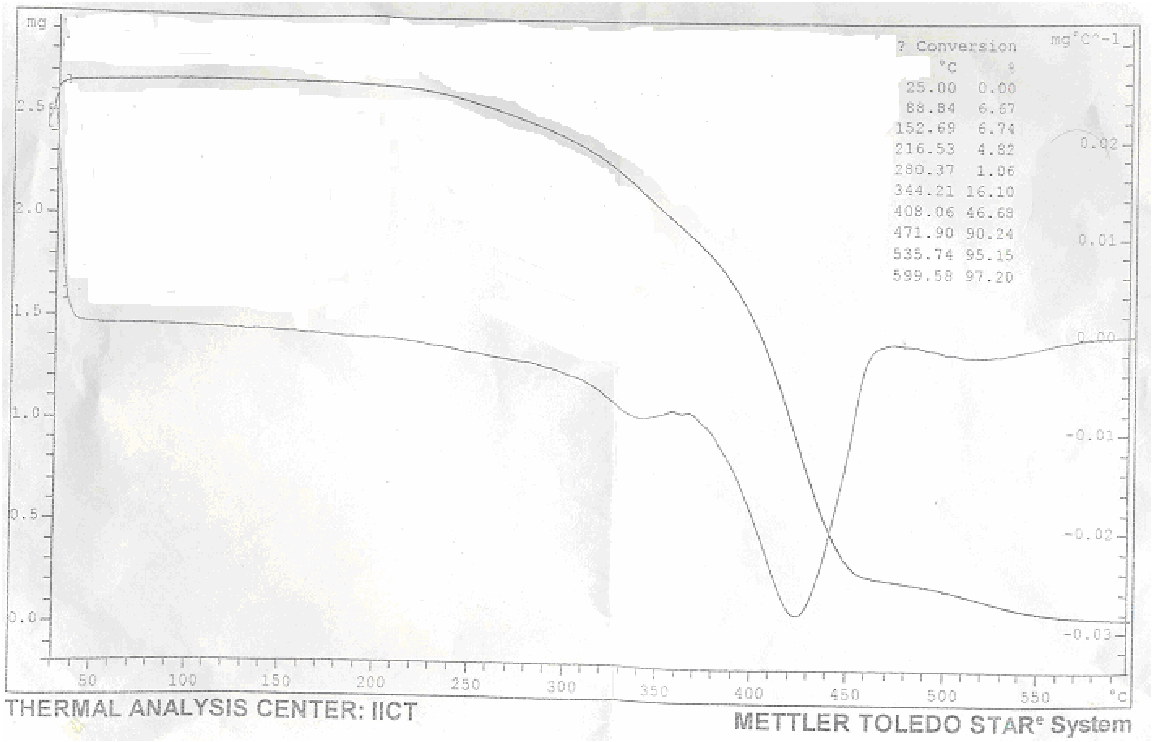


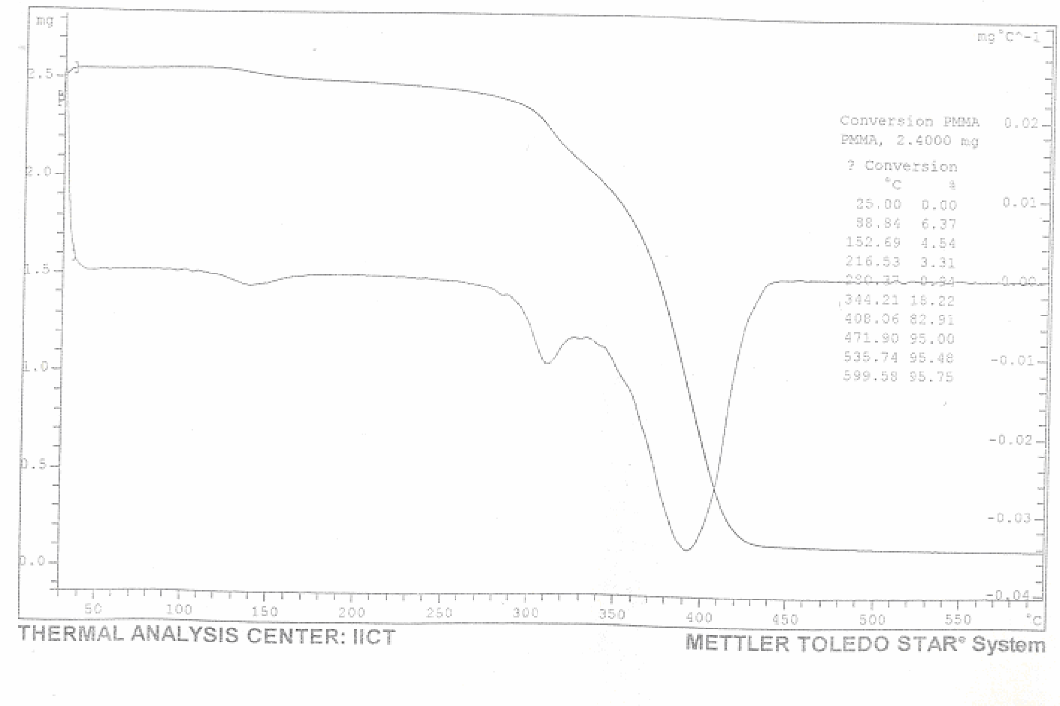
Figure 3.10 Typical DMTA cure curve of polycardanyl acrylate catalysed by benzoyl peroxide (4 wt%) at a heating rate of 3°C/min in dual cantilever mode.



? Conversion

°C	%
25.00	0.00
88.84	6.67
152.69	6.74
216.53	4.82
280.37	1.06
344.21	16.10
408.06	46.68
471.90	90.24
535.74	95.15
599.58	97.20

(a)



(b)

Figure 3.11: TG/DTGA curves of (a) PMMA and (b) MMA-Cardanyl acrylate (PCA-4) copolymer synthesized by ATRP (N_2 atmosphere) at a heating rate of (10°C/min).

3.5 UV-VIS Characterization of Monomer and Copolymers:

The absorption characteristic of organic molecules in the UV region depends upon the electronic transition that can occur and the effect of the atomic environment on the transitions. Increased molecular structure complexity in NMR,IR and mass spectra, but this is not necessarily true for UV spectra. The UV-Vis. Spectroscopy has shown to use full in the charecterisation of copolymer by Suphie [92] et.al. and absorption structure relation ship study of some dyes [93] earlier.

Molecular absorption in the Ultra violet (UV) and visible region of the spectrum is dependent on the electronic structure of the molecule, absorption of energy is quantized, resulting in the elevation of electron from orbitals in the ground state to higher energy orbitals in an excited state .for many electronic structures, the absorption does not occur in the readily accessible portion of the UV region. In practice, UV spectrometry is normally limited to conjugated systems.

There is, however, an advantage to the selectivity of UV absorption. Characteristic groups may be recognized in molecules of widely varying complexities a large portion of a relatively complex molecule may be transparent in the UV so that we may obtain a spectrum similar to that of a much similar molecule.

The π-π^* transitions (K bands) of conjugated di or polyene systems can be distinguished from those of enone systems by observing the effect of changing solvent polarity. The π-π^* transition of diene or polyene systems are essentially unresponsive to solvent polarity; the hydrocarbon double bonds are non polar. The corresponding absorption of enones, however, under go a bathochromic shift, frequently accompanied by increasing intensity, as polarity of the solvent is increased. The red shift presumably results from a reduction in energy level of the excited state state accompaining dipole-dipole interaction and hydrogen bonding.

B band (benzenoid bands) are characteristic of the spectrum of aromatic or hetiroatomic molecules. benzene shows a broad absorption band, containing multiple peaks or fine structure, in the near-UV region between 230 and 270nm (ε of most intense peak λ255nm).the fine structure arraises from vibrationel sub levels affecting the electronic transition. When chromophoric group is attached to an aromatic ring the B bands are observed at longer wave lengths than the more intense π-π^* trasitions. The characteristic fine structure of the B band may be absent in spectra of substituted aromatics. The fine structure is often destroyed by the use of polar solvent.

In this work we studied the electronic spectrums of the cardanyl acrylate (monomer), cardanyl acrylate-methylmethacrylate copolymer, and polymethyl methacrylate in two solvents methanol, chloroform. Based on the principals described above the following obsorption were made in comparing the spectrum of cardanyl acrylate monomer,CA-MMA copolymer and pure PMMA polymer. The results are presented in table 3.3.

The π-π* transition (K bands) of enone in cardanyl acrylate (monomer) gave absorption peaks at 217nm in $CHCl_3$ and at 236 in MeOH. The π-π* transition B band (benzenoid band) of aromatic ring of cardanyl acrylate appear at 253nm in $CHCl_3$ and at 271 in MeOH.

The n-π* transition of carbonyl group in copolymer gave absorption peak at below 190nm in $CHCl_3$ and at 214nm in MeOH. π-π* transition of aromatic ring in copolymer gave absorption at 261nm in $CHCl_3$ and at 270nm in MeOH. Here in copolymer there is no enone group that's reason it absorbs the peak in higher energy range compared to the monomer. Absorption in this region is absent for pure PMMA.

Compounds	R band (n-π*)	K band (π-π*)	B band (π-π*)	solvent
	λ_{max} nm	λ_{max} nm	λ_{max} nm	
Monomer	-----	217	253,270	$CHCl_3$
Copolymer	below 190	-------	256,261	$CHCl_3$
. PMMA	below 190	--------	---------	$CHCl_3$
Monomer	---------	236	271	MeOH
Copolymer	214	---------	270	MeOH
PMMA	206	--------	---------	MeOH

Table 3.3. Absorption spectra results

The n-π* transition of carbonyl group in PMMA absorbs peak below 190nm in $CHCl_3$, but in MeOH it gave peak at 206nm. It is because of solvent effect when solvent polarity is increase the absorption peak of carbonyl group gives at higher wavelength region. Thus the UV-Vis studies also point the formation of a copolymer from cardanyl acrylate and methylmethacrylate.

3.6. Synthesis and Characterization of Cardanyl acrylate Emulsions:

For the preparation of cardanyl acrylate copolymer emulsions first the emulsion polymerization procedure is standardized by preparing a standard emulsion of styrene and butyl acrylate. In this case stable emulsions with solid content of 16% was prepared by at 1:1 composition of styrene and butyl acrylate. Almost 95% conversion was achieved.

Later styrene and cardanyl acrylate was polymerized in emulsion using the same procedure except that butyl acrylate was replaced by cardanyl acrylate. The reaction temperature was the same 80^0C. The cardanyl acrylate was added after styrene polymerization initiated. Here also we achieved 95% conversion. And the solid content was 18%. To be of practical use high solid contents are required.

Similarly cardanyl acrylate and butyl acrylate emulsion was also prepared. First butyl acrylate emulsion was prepared by polymerizing for 24 hours and then cardanyl acrylate was added. All the polymerizations were conducted under N_2 atmosphere. However in this case only 55% conversion could be achieved. The reason for the lower conversion is not clear, even though the copolymer analysis by H-NMR showed peaks due to both the monomers. One reason for the decreased coagulum may be due to the high coagulum formed in the polymerization. However further studies are required to get high solid stable emulsions.

4. Summary and Conclusions:

To summarize, in this thesis work a vinyl monomer, cardanyl acrylate (CA) was synthesized from cardanol.

The reaction conditions for the preparation of cardanyl acrylate have been standardized. The method using alkali catalyzed reaction of cardanol and acryloyl chloride was found to give a better yield.

The procedure for the purification of cardanyl acrylate by column chromatography is standardized. Separation on silica gel column (mesh size finer than 200 micron) using toluene as the eluent was found to give better separation and quantitative yield. The column separation can be followed by thin layer chromatography.

Atom transfer radical polymerization of cardanyl acrylate and its copolymer with MMA, characterization and curing study is reported. The unsaturation in the side chain of cardanyl acrylate is unaffected during polymerization as revealed by ^{1}H NMR and curing reactions, which can later take part in thermal or photochemical curing reactions. The molecular weight and polydispersity was found to be close to the theoretical value and depends on the $[M]_0/[I]_0$ ratio. The formation of copolymer is also studied by the application of UV-Vis spectroscopy.

TGA studies show an increased thermal stability of copolymer in comparison to pure PMMA. The fact that these polymers can be solution processed and crosslinked later by thermal or other means underlines the potential of such polymers in the design of low energy coatings, crosslinkable adhesives and inks with better gloss and adhesion properties.

Dynamic Mechanical Thermal analysis shows that the copolymer undergoes crosslinking as indicated by an increase in modulus with temperature.

Preliminary experiments on preparation of emulsions show that cardanyl acrylate is not completely incorporated in to the copolymer. But the bulk polymerization studies using ATRP showed the formation of a crosslinkable copolymer. This is reflected in the solid contents lower than the theoretical value. The reason for this is not clear presently, and has to be studied in detail.

Preliminary experiments show that stable emulsions could be prepared using cardanyl acrylate. But higher solid content needs to be achieved to be useful for practical applications

Currently efforts are under way to synthesize prepolymers of varying cardanyl acrylate content, comonomer type and formulate UV curable inks based on them. The method also offers the possibility to prepare block copolymers.

Based on the results obtained in this work one manuscript has been communicated to Journal of Polymer science Part A; Polymer Chemistry.

REFERENCES

1. Odian, G. *Principles of Polymerization*. John Wiley & Sons: New York, 1981, 2nd Ed., 33.
2. Nielsen, L. E. *Mechanical Properties of Polymers and Composites*. Marcel Dicker: New York, 1974, chapter 5.
3. Billmeyer, F. W., Jr. *Textbook of Polymer Science*. Wiley-Interscience: New York, 1971, chapters 5-7.
4. Carothers, W. H. *J. Am. Chem. Soc.* 1929, *51*, 2548.
5. a. Szwarc, M. *Nature* 1956, *176*, 1168. b) Szwarc, M. *Pure Appl. Chem.* 1966, *12*, 127. c) Bywater, S. *Prog. Polym. Sci.* 1994, *19*, 287. c) Quirk, R.; Zhuo, Q.; Jang, S. H.; Lee, Y.; Gilda, L. *ACS Symp. Ser.* 1998, 2, *696*.
6. Such termination routes include disproportionation and coupling. Typical free radical chain polymerizations show polydispersities in the range 2-5, while theoretical calculations show that the limiting polydispersity is 1.5.
7. a) Allcock, H. R.; Lampe, F. W. *Contemporary Polymer Chemistry*. Prentice Hall: New Jersey, 1990, 2nd Ed., chapter 3. b) Chapter 13.
8. Matyjaszewski, K.; Muller, A. H. E. *Macromolecular Nomenclature Note No. 12*. The Nomenclature Committee of the ACS Division of Polymer Chemistry.
9. a) Otsu, T.; Yoshida, M. *Makromol. Chem., Rapid Commun.* 1982, *3*, 127. b) Otsu, T.; Yoshida, M. Tazaki, T. *Makromol. Chem., Rapid Commun.* 1982, 3, 133.
10. Georges, M. K.; Veregin, R. P. N.; Kzamaier, P. M.; Hamer, G. K. *Macromolecules* 1995, *28*, 4391.
11. a) Turner, S. R.; Blevins, R. W. *Poly. Prepr. Am. Chem. Soc. Div. Polym. Chem.* 1988, *29*, 6. b) Lambrinos, P.; Tardi, M.; Poulton, A.; Sigwalt, P. *Eur. Polym. J.* 1990, *26*, 1125. 32.
12. a) Solomon, D. H.; Rizzardo, E.; Cacioli, P. U.S. Patent 4,581,429, 1986. b) Rizzardo, E. *Chem. Aust.* 1987, 32.
13. Listigovers, N. A.; Georges, M. K.; Odell, P. G.; Keoshkerian, B. *Macromolecules* 1996, *29*, 8992.
14. a) Harwood, H. J. Arvanitopoulos, L. D.; Greuel, M. P. *Poly. Prepr. Am. Chem. Soc. Div. Polym. Chem.* 1994, *35*, 549. b) Wayland, B. B.; Pszmik, G.;. Mukerjee, S. L.; Fryd, M. *J. Am. Chem. Soc.* 1994, *116*, 7943

15. a) Benoit, D.; Grimaldi, S.; Finet, J. P.; Tordo, P.; Fontanille, M.; Gnanou, Y. Polym. Prepr. 1997, 38, 729. b) Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker; C. J. *J. Am. Chem. Soc.* 1999, *121*, 3904.
16. a) Georges, M. K.; Veregin, R. P. N.; Hamer, G. K.; Kazmaier, P. M. *Macromol. Symp.* 1994, *88*, 89. b) Georges, M. K. *Can. Chem. News* 2000, *52*, 24. c) Otsu, T. *J. Polym. Sci., Part A: Polym. Chem.* 2000, *38*, 2121. d) Fukuda, T.; Goto, A.; Ohno, K. *Macromol. Rapid Commun.* 2000, *21*, 151.
17. a) Mardare, D.; Matyjaszewski, K. *Macromolecules* 1994, *27*, 645. Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* 1995, *117*, 5614. b) Queffelec, J.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* 2000, *33*, 8629. c) *Controlled/Living Radical Polymerization. Progress in ATRP, NMP, and RAFT: ACS Symp. Ser., 2000; 768.* Matyjaszewski, K., Ed. American Chemical Society, Washington D.C., 2000.
18. a) Haddleton, D. M.; Topping, C.; Hastings, J. J.; Suddaby, K. G. *Macromolecules* 1996, *29*, 481. b) Chong, Y. K.; Le, T. P. T.; Moad, G.; Rizzardo, E.; Thang, S. *Macromolecules* 1999, *32*, 2071. c) Rizzardo, E.; Chiefari, J.; Mayadunne, R. T. A.; Moad, G.; Thang, S. H. *ACS Symp. Ser.* 2000, 768, 278.
19. For example, see a) Keoshkerian, B.; Georges, M.; Quinlan, M.; Veregin, R.; Goodbrand, B. *Macromolecules* 1998, *31*, 7559. b) Keul, H.; Achten, D.; Hocker, H. *Polym. Prepr.* (Am. Chem. Soc., Div. Polym. Chem.) 1999, *40*(2), 368. c) Shen, Y. Q.; Zhu S. P.; Zeng F. Q.; Pelton, R. *Macromolecules* 2000, *33*, 5399. D) Pan, C. Y.; Lou, X. D. *Macromol. Chem. Phys.* 2000, *201*, 1115.
20. For example, see a) Kanagasabapathy, S.; Benicewicz, B. C. *Polym. Prepr.* (Am. Chem. Soc., Div. Polym. Chem.) 1999, *40*(2), 1080. b) Shen Y. Q.; Zhu, S.P.: Zeng, F.Q.; Pelton, R. *Macromol. Chem. Phys.* 2000, *201*, 1387.
21. Gaynor, S. C.; Edelman, S. Z.; Matyjaszewski, K. *Macromolecules* 1996, *29*, 1079.
22. Wang, J.-S.; Matyjaszewski, K. J. Am. Chem. Soc. 1995, 117, 5614-5615.
23. Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. Macromolecules 1995,28,1721-1723.
24. Percec, V.; Barboiu, B. Macromolecules 1995, 28, 7970-7972.

25. Granel, C.; Dubois, P.; Jerome, R.; Teyssie, P. Macromolecules 1996, 29, 8576.
26. Patten, T. E.; Matyjaszewski, K. Adv. Mater. 1998, 10, 901-915.
27. Matyjaszewski, K.; Wang, J.-S. In PCT Int. Appl.; (Carnegie Mellon University,USA).WO9630421,1996,p129pp.
28. Matyjaszewski, K. et. al. In PCT Int. Appl.; (Carnegie Mellon University, . USA). WO 9718247, 1997, p 182 pp.
29. Fischer, H. J. Polym. Sci., Part A: Polym. Chem. 1999, 37, 1885-1901.
30. Gillies, M. B.; Matyjaszewski, K.; Norrby, P.-O.; Pintauer, T.; Poli, R.; Richard,P.9718247,1997,p182pp. Macromolecules 2003, 36, 8551-8559.
31. Krzysztof Matyjaszewski, Shuhui Qin, Jamie R. Boyce, David Shirvanyants and Sergei S. Sheiko, Macromolecules 2003, 36, 1843.
32. Wang, J.-S.; Matyjaszewski, K. *Macromolecules* 1995, *28*, 7572-7573.
33. Xia, J.; Matyjaszewski, K. *Macromolecules* 1997, *30*, 7692-7696.
34. Moineau, G.; Dubois, P.; Jerome, R.; Senninger, T.; Teyssie, P. *Macromolecules* 1998, *31*, 545-547.
35. Gromada, J.; Matyjaszewski, K. Macromolecules 2001, 34, 7664-7671.
36. Pyun, J.; Matyjaszewski, K.; Kowalewski, T.; Savin, D.; Patterson, G.; Kickelbick, G.; Huesing, N. J. Am. Chem. Soc. 2001, 123, 9445-9446.
37. Savin, D. A.; Pyun, J.; Patterson, G. D.; Kowalewski, T.; Matyjaszewski, K. Journal of Polymer Science, Part B: Polymer Physics 2002, 40, 2667-2676.
38. Pyun, J.; Jia, S.; Kowalewski, T.; Patterson, G. D.; Matyjaszewski, K. Macromolecules 2003, 36, 5094-5104.
39. Matyjaszewski, K.; Pyun, J. In PCT Int. Appl.; (Carnegie Mellon University, USA). WO 0228912, 2002, p 77 pp.
40. Liu, T.; Jia, S.; Kowalewski, T.; Matyjaszewski, K.; Casado-Portilla, R.; Belmont, J.Langmuir 2003, 19, 6342-6345
41. Jones, D. M.; Brown, A. A.; Huck, W. T. S. Langmuir 2002, 18, 1265-1269.
42. Von Werne, T. A.; Germack, D. S.; Hagberg, E. C.; Sheares, V. V.; Hawker, C. J.; Carter, K. R. Journal of the American Chemical Society 2003, 125, 3831- 3838.
43. Pyun, J.; Kowalewski, T.; Matyjaszewski, K. Macromolecular Rapid Communications 2003, 24, 1043-1059.
44. Shipp, D. A.; Wang J.-L.; Matyjaszewski, K. Macromolecules 1998, 31,

8005- 8008.

45. Matyjaszewski, K.; Shipp, D. A.; McMurtry, G. P.; Gaynor, S. G.; Pakula, T. J. Polym. Sci., Part A: Polym. Chem. 2000, 38, 2023-2031.
46. Hong, S. C.; Pakula, T.; Matyjaszewski, K. Macromolecular Chemistry and Physics 2001, 202, 3392-3402.
47. Matyjaszewski, K. et. al. In PCT Int. Appl.; (Carnegie Mellon University, USA). WO 0056795, 2000, p 200 pp.
48. Jousset, S.; Qiu, J.; Matyjaszewski, K.; Granel, C. Macromolecules 2001, 34, 6641-6648
49. Tsarevsky, N. V.; Sarbu, T.; Goebelt, B.; Matyjaszewski, K. Macromolecules 2002, 35,6142-6148.
50. Tang, C.; Kowalewski, T.; Matyjaszewski, K. Macromolecules 2003, 36, 1465- 1473.
51. Ramakrishnan, A.; Dhamodharan, R. Macromolecules 2003, 36, 1039-1046.
52. Krzysztof Matyjaszewski, *Macromol. Symp.*182, 209-224 (2002)
53. K. Matyjaszewski, *Macromol. Symp* 1996, *111*, 47.
54. K. Matyjaszewski, M. Wei, J. Xia, S. G. Gaynor, *Macromol. Chem. Phys.* 1998, *199*, 2289.
55. M. K. Nair, E. V. V. Bhaskara Rao, K. K. N. Mambiar,and M. C. Mambiar, *Cashew (AnacardiumOccidentale L.),* Monograph on plantation crops-I,Central Plantation Crops Research Institute, Kasaragod, Kerala, 1979.
56. K. V. George, *Improvement of quantity of CNSL obtained by expelling from Oil Both roasted shells,* Third Annual Symposium on Plantation Crops-Placrosym III, Kerala, 1980.
57. R. J. Wilson, *The market for cashew kernels and cashewnut shell liquid,* Report No. G91, Tropical Products Institute, London, 1975.
58. H. P. Tyman, R. A. Johnson, M. Muir, and R. Rokhgar, *J. Am. Oil Chem. Soc.* 66, 553 (1989).
59. D. Wasserman and C. R. Dawson, *Ind. Eng. Chem.,*38, 396 (1945).
60. J. S. Aggarwal, *Paint Manuf.,* 31, 28 (1972).
61. J. H. P. Tyman, D. Wilczynski, and M. A. Kashani, *J. Am. Oil. Chem. Soc.,* 55, 663, (1978).
62. J. H. Tyman, *Anal. Chem.,* 48, 30 (1976).
63. H. A. Lloyd, C. Denny, and G. Krishna, *J. Liq.Chromatogr.,* 3, 1497 (1980).

64. J. H. Tyman, *J. Chem. Soc., Perkin Trans,* 1, 1639 (1973).
65. H. P. Tyman, *J. Chromatogr.,* 111, 277 (1975).
66. H. P. Tyman, *J. Chromatogr.,* 111, 285 (1975).
67. J. H. Tyman and L. S. Kiong, *Lipids,* 13, 525 (1978).
68. J. H. P. Tyman, V. Tychopoulos, and P. Chain, *J. Chromatogr.,* 303, 137 1984.
69. B. G. K. Murty, M. C. Menon, J. S. Aggarwal, and S. H. Zaheer, *Paint Manuf.,* 31, 47, (1961)
70. A. Durrani, G. L. Davis, S. K. Sood, and H. P. Tyman, *J. Chem. Technol. Biotechnol.,* 32, 681, (1982).
71. J. H. P. Tyman, *Chem. Soc. Rev.,* 8, 499 (1979).
72. A. R. R. Menon, C. K. S. Pillai, J. D. Sudha, and A. G. Mathew, *J. Sci. Ind. Rev.,* 44, 324 (1985).
73. P. H. Gedam and P. S. Sampathkumaran, *Prog. Org. Coatings,* 14, 115 1986.
74. Mele, G.;Sole, R. D.;Vasapollo, G.;Lopez, E.G.; Palmisano, L. Mazzetto, S.E.; Attanasi, O.A. ;Fillippone, P.Green Chem 2004,6,604.
75. Bhunia, H. P.; Basak, A.; Chaki, T. K.; Nando, G.B. Eur Polym J 2000,36,1157.
76. John, G.; Pillai, C.K.S. Makromol Chem Rapid Commun 1992,13, 255.
77. John, G.; Shali, K.T.; Pillai, C.K.S. J Appl Polym Sci 1994,53,1415.
78. Nguyen, L.H.; Koerner,H.; Lederer, K. J Appl Polym Sci 2002,85,2034.
79. Nguyen, L.H.; Koerner, H.; Lederer, K. J Appl Polym Sci 2003,89, 2385.
80. John, G.;Pillai, C.K.S. J Polym.Sci Part A: Polym Chem 1993,31,1069.
81. Nayak, S.S.; Das, S.K.; Lenka, S. Reac & Funct Polym 1999,40,249.
82. Xia, J.; Gaynor, S.G.; Matyjaszewski, K. Macromolecules 1998,31,5958.
83. Xia, J.;Matyjaszewski, K. Macromolecules 1997, 30, 7697.
84. Goto, A.; Fukuda, T. Prog Polym Sci 2004,29,329.
85. Reghunadh, V.; Bhaskaran, D.; Sivaram, S. Polymer 2004,45,3149.
86. Matyjaszewski, K.; Paton, J. J Am Chem Soc 1997,119,674.
87. Schipp, D.A.; Matyjaszewski, K. Macromolecules 2000,33,1553.
88. Moineau, G.; Granel,C.; Dubois;;Jerome, R.; Teyssie, Ph. Macromolecules 1998, 31, 542.

89. Lad, J.; Harrison, S.; Mantovani, G.; Haddleton, Dalton Transactions 2003,21, 44175.

90. Campbell, D.; White, J.R. Polymer Characterization: Physical Techniques, Chapman & Hall, London, 1989,page 319.

91. Carlier, V.; Sclavons, M.; Legras, R. Polymer 2001,42,5327.

92. Sophie.V.; K.Tauer, M.Antometti, R.P.Kriiger, W.Bremser Polymer 43, 2002, 7231-7241.

93. H.A.Shindy and A I M Icoraiem Proc. Of ind . Acad .sci . (chem. Sci) vol . 114, (2) 2002, 125-136.