Synthesis, Characterization, and Properties Evaluation of New Degradable Materials

Dissertation

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Vom Fachbereich Chemie, Philipps-Universität Marburg als

Dissertation angenomen am:

Erstgutachter: PD Dr. Seema Agarwal

Zweitgutachter: Prof. Dr. Andreas Greiner

Tag der Disputation am: 10. 08. 2010

To my Mummy and Papa

Contents

1. Aim and Introduction

The Aim of this work is to synthesize new degradable materials, based on vinyl monomers, which can be used for various applications.

Further, to characterize the obtained materials, evaluate the physical properties (including molecular weight, glass transition temperature, mechanical properties, etc.) and to correlate the structure-property relationship, is an indispensable part of this research work.

This thesis consists of two main parts. Firstly, synthesis of polycaprolactone based new materials : poly(vinyl acetate-co-cyclic ketene acetals) or poly(VAc-co-esters) showing a combination of hydrolytic degradability, biocompatibility and low softening temperature is shown. Polymerization has been carried out between vinyl acetate and 2-methylene-1,3-dioxepane and initiated using a free-radical initiator. The materials thus formed, have been proposed to be used as degradable materials for chewing gums or other gum applications.

The second part deals with yet another combination to produce degradable and eco-friendly materials using a naturally originating monomer: α-methylene-γ-butyrolactone (Tulipalin A). Here, poly(α-methylene-γ-butyrolactone-co-cyclic ketene acetals) or poly(MBL-co-esters) are synthesized to produce thermally stable, solvent resistant, degradable materials having very high glass transition temperature. Such materials, having a biobase, have been proposed to be used as eco-plastics for various applications including packaging. With this aim, copolymerization of MBL has been carried out with cyclic ketene acetal, 2-methylene-1,3-dioxepane, providing degradable polycaprolactone units. An attempt to find out the mechanism of polymerization is also mentioned.

2. Motivation

Issues surrounding waste management has been the "key" inspiration for this work. It motivates to come up with new materials which would reduce environmental pressures and carbon footprints.

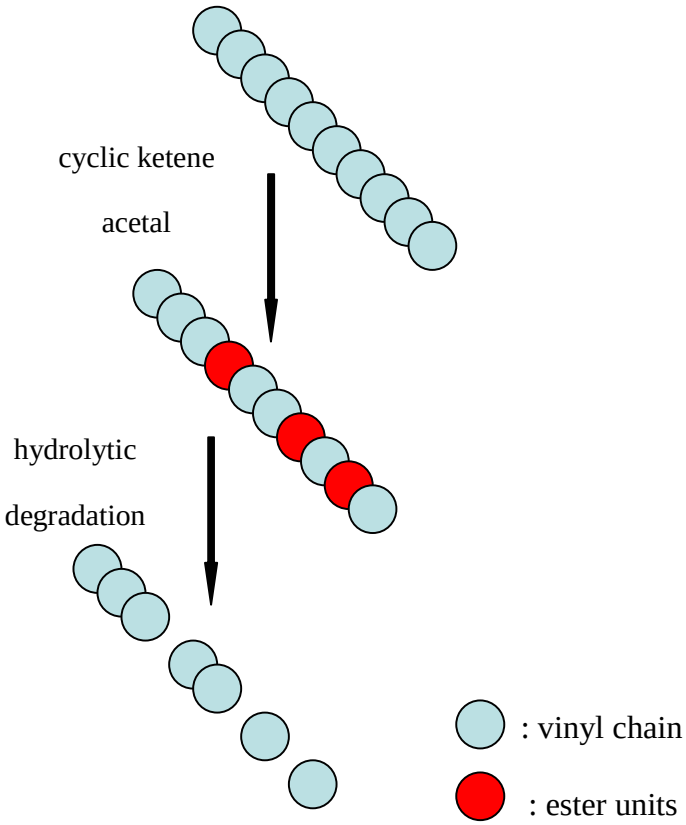
Degradable materials are those materials which can be completely degraded in landfills by various means, leaving behind no toxic, visible or distinguishable residues. Hence an effort has been done to contribute some degradable materials for the benefit of mankind.

Also, the omnipresent use of petroleum based plastics, and their persistence in the environment, and their fossil fuel derivation further motivates to combine degradability with bio-origin, in the later part of this research work, wherein some alternatives to traditional materials have been found out.

3. Concept

The highly stable carbon-carbon linkages in vinyl polymers, provides stability and resistance towards degradation, be it by chemical, mechanical, enzymatic, or by any other means. However, desired degradability can be introduced in such polymers by incorporating heteroatomic functional groups like ester, carbonate, anhydride, acetal, amide, phosphazene or hydroxyl esters in the polymeric backbone.

The present work deals with incorporation of ester linkages using cyclic ketene acetals via radical polymerization, into vinyl polymers. Henceforth, it can be considered as a combination of ring-opening polymerization and 1,2-vinyl addition polymerization methods.



Scheme 3.1: Pictorial representation of concept of this research work

4. Background

4.1 Polymer degradation

What is Polymer degradation? Is it useful? These are some of the questions which need to be answered before we go into further details of the thesis. The deterioration in polymer properties, accompanied by reduction in molecular weight is what we call polymer degradation. It is a both, desirable and undesirable phenomena. While in some cases, polymer degradation is prevented or delayed as far as possible, in others like waste management programs, polymer molecular weights are deliberately lowered. One such benefit of polymer degradation is applied in spacecrafts, wherein a polymeric material is used as a "heat shield". In cases of increased temperature, the heat shield protects the metal and craft by itself taking the intense heat and getting charred/degraded.[1]

Degradation could be randomly at any point of the polymer chain, leading to a drastic change in molecular weight, or could be along the chain ends (depolymerization) whereby liberating the monomers. The various possible ways of inducing degradability:

A. Thermal degradation[2]

B. Mechanical degradation[3]

C. Degradation by ultrasonic waves[4]

D. Photodegradation[5]

E. Degradation by high-energy radiation[6]

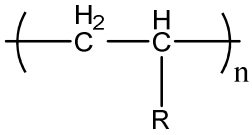
F. Oxidative degradation[7]

G. Biodegradation[8]

H. Hydrolytic degradation[9]

4.2 Degradable Vinylic Polymers

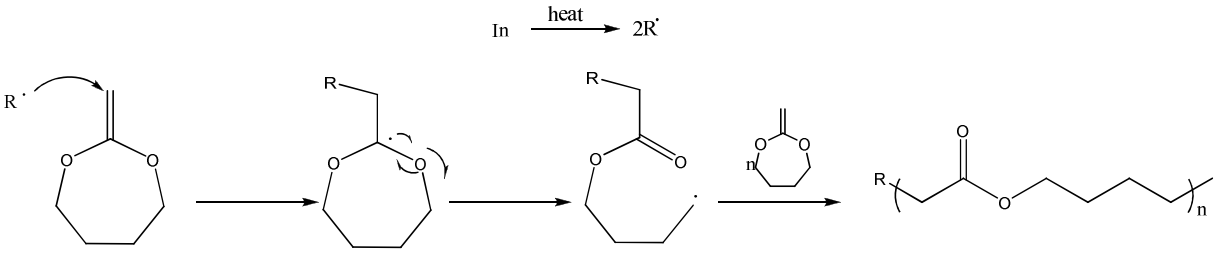
Vinyl polymers/polyolefins are generally represented as:



where, 'R' could be hydrogen, alkyl, aryl, halogen, ester, ether or any other functionality. Vinyl polymers are a group of industrial polymers that serve important purposes in plastic industry, paints, adhesives, cosmetics, and even for biomedical applications like, in medicine and pharmacy. Depending on the requirements, the polymer properties can be easily modified. Due to such vast range of applications, the significance of bio(degradable) materials is reinforced. Many groups, including our group, the Agarwal group[9-17], are active in this field for synthesizing such useful and degradable materials.

4.3 Radical ring-opening polymerization (RROP) of cyclic ketene acetals

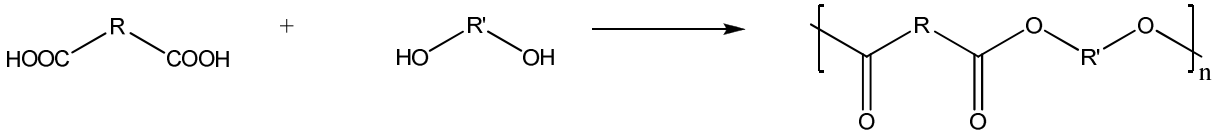
Radical ring-opening polymerization of cyclic ketene acetals incorporate ester linkages onto the very stable C-C backbone, thereby integrating degradability in them. Considering the example of 2-methylene-1,3-dioxepane (MDO), ring opening in presence of radical initiator takes place as given in Scheme 4.3.1.



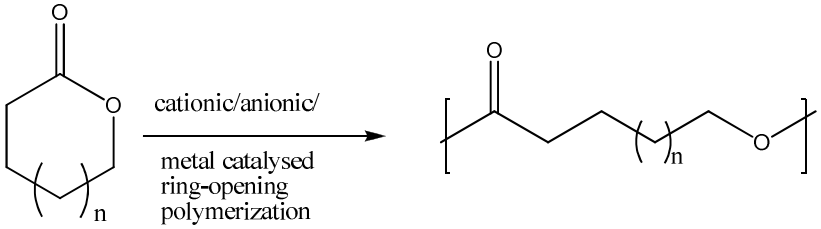
Scheme 4.3.1: Ring-opening polymerization of MDO in presence of radical initiator

Other methods to synthesize polyesters include:

1. Condensation polymerization of dicarboxylic acids with dialcohols[18,19]



2. Ring-opening polymerization of cyclic esters[105,106]



The benefits of using radical ring-opening polymerization of cyclic ketene acetals are that firstly, it is the only method which incorporates ester linkages at random positions in the main polymer chain. And secondly, it is accompanied by low volume shrinkage. During the ring-opening polymerization of cyclic monomers, one ring is opened in each monomeric unit, and thus one bond is broken for each new bond formed thereby showing low volume shrinkages.[20]

Apart from this, conventional condensation method has its own limitations:

A. Perfect stoichiometry of the reactants should be maintained

B. High temperature is the prerequisite condition for melt condensation

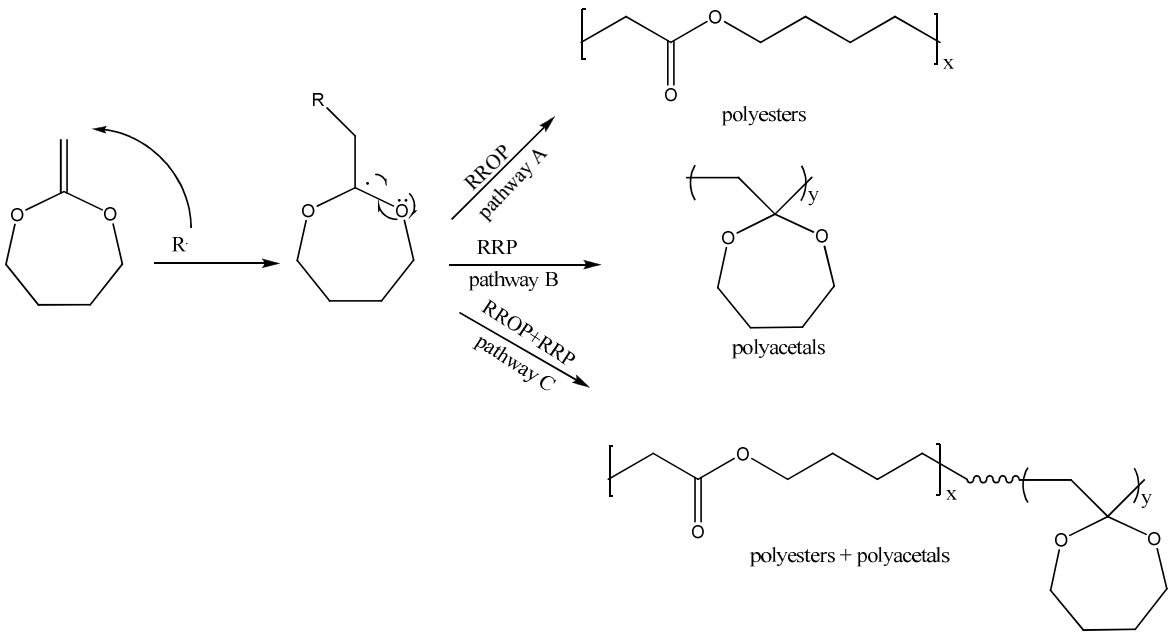
C. High conversion is difficult to achieve

D. Control over the chain length is not possible

E. High molecular weight polymers cannot be formed because of the possibilities of reversibility of the condensation reaction and cyclization reaction.

4.4 Polymerization routes of cyclic ketene acetals via Radical polymerization

The free radical polymerization of cyclic ketene acetals with vinyl monomers is a combination of ring-opening polymerization of the acetals and 1,2-vinyl addition of the vinylic monomers. The various polymerization routes of cyclic ketene acetals was first studied by Bailey and coworkers in 1979[21]. All the possibilities of radical addition at the double bond are presented as given in the Scheme 4.4.1, taking the example of 2-methylene-1,3-dioxepane:



Scheme 4.4.1: Possible pathways for radical polymerization of cyclic ketene acetals

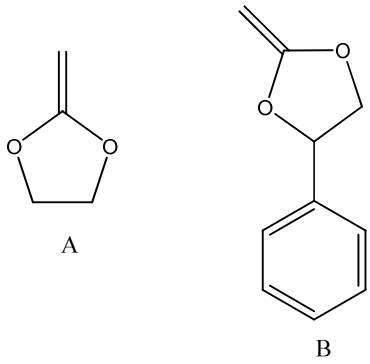
As shown, CKAs can undergo radical ring opening polymerization (RROP) to form polyesters, or the ring can remain intact and undergo 1,2-vinyl addition polymerization, via ring-retaining polymerization (RRP) to yield polyacetals, or it can be a mixed mechanism, by combining the two possibilities to form both type of products.

4.5 Factors influencing RROP over ring-retaining polymerization (RRP)

Of the above given possibilities, which route would be followed by cyclic ketene acetals in a particular reaction depends upon:

1. Substituents on the ring
2. Ring-size of CKA
3. Temperature of reaction
4. Monomer concentration

Effect of substituents can be understood by taking the example of 2-methylene-1,3-dioxalane (A) and 2-methylene-4-phenyl-1,3-dioxalane (B). Structures are given in Scheme 4.5.1.

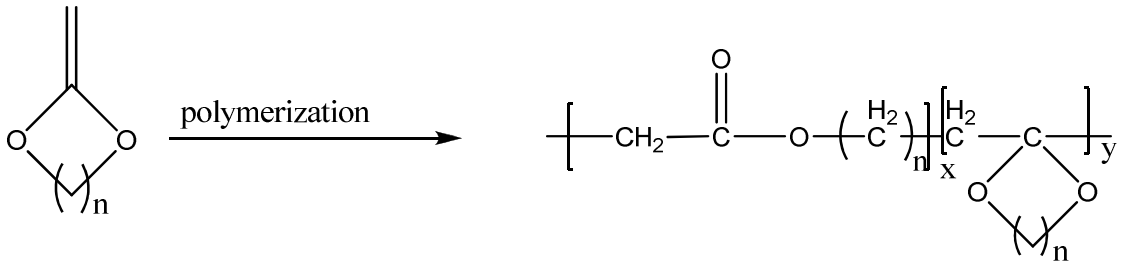


A B

Scheme 4.5.1: Structures of (A): 2-methylene-1,3-dioxalane; (B): 2-methylene-4-phenyl-1,3-dioxalane

Monomer B undergoes quantitative and regioselective RROP from 60-150°C to give polyesters, whereas monomer A undergoes ROP depending on temperature[22]. This variation is attributed to the fact that in monomer B, the stabilizing substituent, phenyl group ($-C_6H_5$) leads to the formation of a stable benzyl radical, whereas monomer A results only in a primary radical.

Size of the ring also plays an important role in deciding the mechanism of reaction followed by CKAs. Considering 5,6, and 7 membered non-substituted CKAs, this effect was studied by Bailey et al. in 1982[23], wherein the following scheme 4.5.2 was presented:



n=2, x=0.83, y=0.17
n=3, x=0.85, y=0.15
n=4, x=1.00, y=0.00

Scheme 4.5.2: The effect of ring size on radical ring-opening polymerization

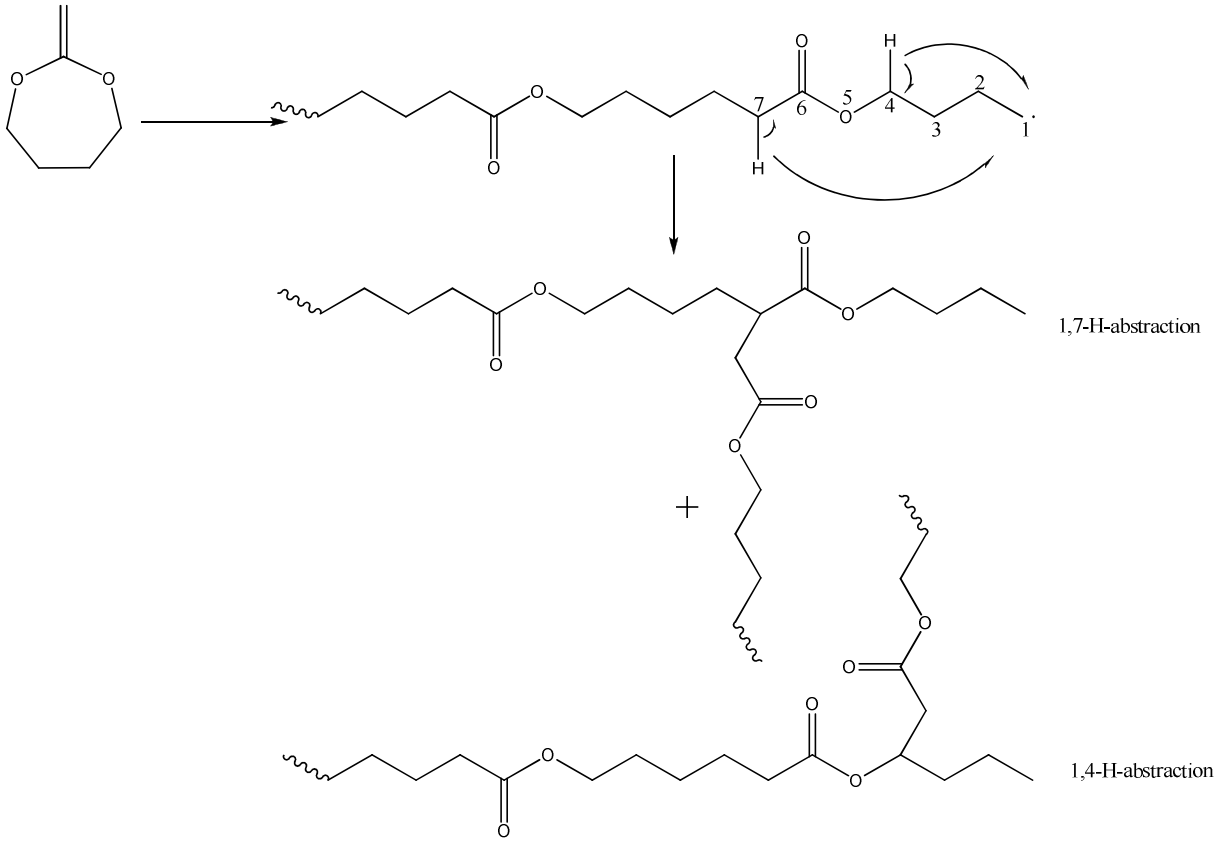
The basis of this observation lies in the fact that the steric hindrance in 7-membered ring radical is more as compared to 5- or 6- membered rings. Hence favoring the reaction to proceed via ring-opening mechanism. Also, the relief of ring strain in 7-membered ring as compared to the others promotes the ring to open.

Temperature also plays a crucial role in choosing RROP or RRP. High temperature favors the formation of polyesters while low temperature yields polyacetals preferably, in most of the cases. 2-methylene-1,3-dioxalane undergoes 50% RROP at 60°C and 83% at 125°C[23].

Apart from this, ring-opening increased with decrease in the concentration of monomer.

4.6 Back biting reactions

In 1997, Jin and Gonsalves reported complete details of polymerization mechanism of ring-opening polymerization of MDO[24]. The very reactive primary growing radical could be easily converted into a more stable species via 1,4- and 1,7-hydrogen abstraction reactions, forming short chain branches (Refer Scheme 4.6.1).

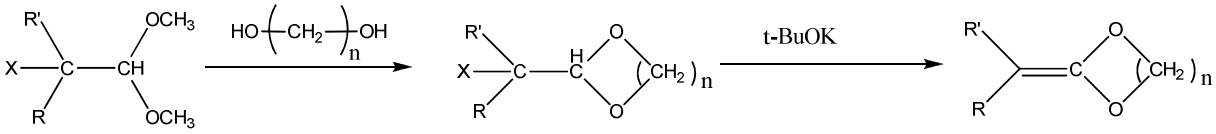


Scheme 4.6.1: Back biting reaction during polymerization of MDO

At 50°C, in 72 h, polymerization of MDO using AIBN was found to yield 20% of branched poly(caprolactone) structures. Due to these chain transfer reactions, the polymer obtained was amorphous, and not crystalline, and of much reduced molecular weight than expected.

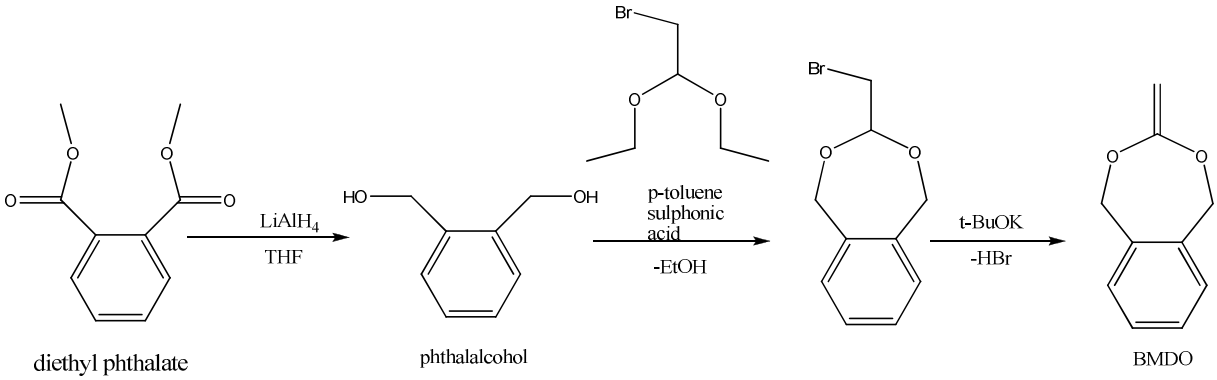
4.7 Synthesis of cyclic ketene acetals

Preparation of a variety of cyclic ketene acetals emerged from the Laboratory of Mc Elvain and Curry in 1940s[25]. They proposed a method of deriving CKAs from ethylene and trimethylene glycols, which is still followed with slight modifications. The 5- and 6-membered CKAs, were obtained by the dehydrohalogenation of the corresponding halogenated cyclic acetals (B). The latter compounds, with the exception of the chloral cyclic acetals, were prepared by an alcohol exchange between the glycol and the methyl (or ethyl) acetals (A) (Scheme 4.7.1).



Scheme 4.7.1: Synthetic procedure for cyclic ketene acetals

5,6-benzo-2-methylene-1,3-dioxepane was synthesized via similar three-step synthetic route according to Scheme 4.7.2[26]. Here, the glycol, phthalalcohol was first derived from Diethyl phthalate using $LiAlH_4$ as the reducing agent.



Scheme 4.7.2: Synthetic procedure for 5,6-benzo-2-methylene-1,3-dioxepane (BMDO)

The most striking property of CKAs is their tendency to undergo spontaneous polymerization. Therefore, it is extremely difficult to obtain pure CKAs after synthesis. Polymerization occurs during their isolation. The purer the acetal, the more readily it gets polymerized, giving a voluminous white precipitate, along with the main product.

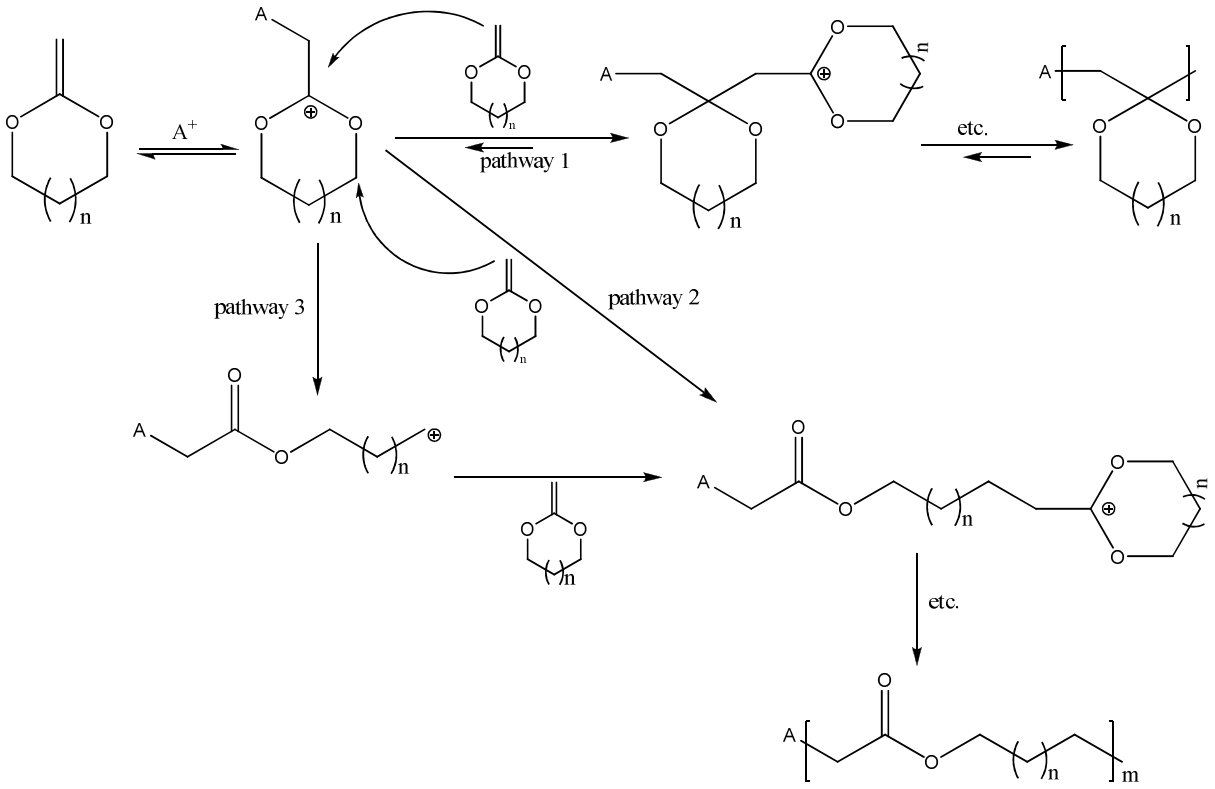
4.8 Cationic Polymerization of cyclic ketene acetals

The very first cationic ring opening polymerization was studied in 1962[27], wherein cyclic iminocarbonates were polymerized using various catalysts including BF_3, $SnCl_4$, $ZnCl_2$, H_2SO_4, etc. to give ring opened structures. Further, the technique was then extended to compounds which possessed the structural possibility of ring opening polymerization: cyclic ketene acetals

and iminooxazolidines. The presence of two strongly electron releasing alkoxy substituents on the double bond makes CKAs prone to be attacked by electrophilic agents. Schildknecht[28] and McElvain et al.[25,29,30] reported cationic polymerization of typical Lewis acid initiators like BF_3 etherate and weak protonic acids. But since such polymerizations led to unstable polymers which undergo immediate degradation, hence Pittman et al.[31] studied cationic polymerizations of CKAs like MDO using heterogenous H_2SO_4 supported on activated carbon black which gave both ring retained as well as ring-opened structures.

Apart from this, cationic photopolymerization of CKAs has also been investigated by Crivello and co-workers.[32]

Similar to radical polymerizations, cationic polymerizations can proceed through both 1,2-vinyl additions or ring-opening polymerizations, or even a combination of them (Scheme 4.8.1).[33] Depending on similar factors like: steric hindrance, stability of reaction intermediate and ring-size affect the chances of ring opening versus ring retaining. Apart from this, type of acid-initiator also affected ratio between ring-opening and ring-retaining polymerization. Stronger acids give less ring-opening.[34]



Scheme 4.8.1: Three possible pathways for cationic polymerization of cyclic ketene acetals

In pathway 1, the propagating ring (dioxonium cation) is attached at sp^2 hybrid carbon by exo-methylene carbon of other monomer and a new ring-dioxonium is formed.

In pathway 2, the activated sp^3 alkoxyl carbon is attacked by nucleophilic methylene carbon of the other monomer, thereby inducing ring-opening polymerization via an S_N2 reaction. This thus forms a new propagating cation containing a penultimate ester linkage, ultimately producing polyesters.

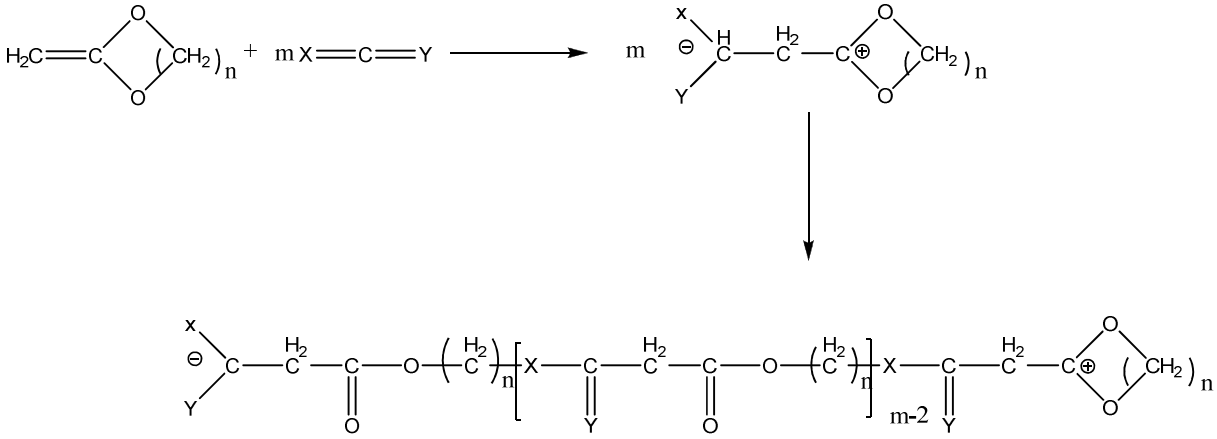
Pathway 3 proceeds by isomerization taking place in the propagating cation via $S_N1$opening of the ring and thereby forming ester linkage and primary cation. The new cation, then adds to another monomer giving ring-dioxonium cation. The formation of this primary cation is unfavorable due to its high energy which finally leads to polyesters.

The energy of activation is less for 1,2-vinyl addition polymerization and the products obtained are thermally stable as compared to ring-opening polymerization, but still at higher temperature, ring-opening polymerization is preferred over ring-retaining. This is attributed to the Ceiling temperature effect. At higher temperatures, rate of 1,2-depropagation reaction increases much

faster than the forward 1,2-propagation reaction.[33] Hence, ring-opening increasingly competes with ring-retaining.

4.9 Zwitter ionic polymerization of cyclic ketene acetals

The double bond of CKAs have strong anionoide character because of electron donating property of the two conjugated oxygen atoms. Henceforth, such compounds tend to polymerize in presence of protic or electron-withdrawing substrates like PhNCO,[35] heterocumulenes (Scheme 4.9.1) like CS_2[36] (N,O-acetals), cyanoallene[37], via a zwitter ionic tetramethylene intermediate or a biradical tetramethylene intermediate.



Scheme 4.9.1: Copolymerization route of cyclic ketene acetals with heterocumulenes (e.g. CS_2) through macrozwitterion mechanism[41]

Hall and Padias[38] reported zwitter ionic specie can initiate cationic or anionic homopolymerization, whereas biradical specie is responsible for alternating copolymers in such charge-transfer polymerizations. Earlier[39,40], number of spontaneous polymerizations of nucleophilic and electrophilic vinyl monomers have also been found to undergo only cycloadditions in reactions of cyclic ketene acetals with elctrophilic monomers. Further, Endo and co-workers made more contributions by investigating the mechanism of reaction taking place between CKA (2-methylene-4-phenyl-1,3-dioxolane) and electrophilic monomers like methyl α-cyanoacrylate, acrylonitrile, and methylmethacrylate[41,42] and found out through

solvent effect and by reactions using some additives like epichlorohydrin, radical trapping agents, etc., that the path followed in their system was Zwitter ionic.

4.10 Need for polymers originating from bio-resources

The wide range of properties of polymers allow them to find extensive importance in the society. Through macromolecular engineering, the properties can be modified and tailored in order to achieve a polymer of the desired property. Today a vast number of polymers used in paints, plastics, rubbers, detergents, cosmetics, medicines, etc. originate from fossil fuels.

Due to the awareness among humans about the rapid depletion of fossil fuels, research is diverting towards the usage of renewable sources, before the Earth gets completely exhausted of all its energy reserves. Apart from this, fossil fuels generate a large amount of energy on being burnt (combustion), but the problem is they emit huge concentrations of green house gases, like carbon dioxide, to the atmosphere. There is a need to control the steady increase of such gases to decrease the rapid increase in global warming and the ocean acidification.

4.11 Renewable and non-renewable resources

Renewable energy resources are “never-exhausting” natural sources such as Solar energy, wind, ocean thermal energy, tidal and wave energy, geothermal and hydro energy, etc. Their supply is unlimited and can be used again and again without the fear of getting depleted ever.

In contrast, non-renewable resources are naturally occurring sources that cannot be regenerated or replenished very easily and very soon. Once exhausted, they will take hundreds and thousands of years to be reformed. Or in other words, their consumption rate is far more than their regeneration rate. Some examples of non-renewable energy sources are fossil fuels such as coal, petroleum and natural gas.

4.12 α-methylene-γ-butyrolactone and recent developments

The main aim of this Thesis was to synthesize new degradable materials. Henceforth, the need for “Degradable polymers” has been combined in the second part of the thesis, with that of “polymers originating from renewable resources”. Degradable plastics could be bioplastics (or organic plastics) whose components are derived from renewable biomass sources, such as vegetable oil, corn, starch, etc.[43-45], or could be ″fossil fuel plastics″ (i.e. derived from petroleum) with some additive. Use of bioplastics not only takes care of the ″environmental concerns″ by decreasing the amount of green house emissions, when degraded, but also takes care of the ″finite petroleum resources problems”[46] by decreasing the dependency on such non-renewable fossil fuel resources.

Polymers from renewable resources fall into three major categories[47]:

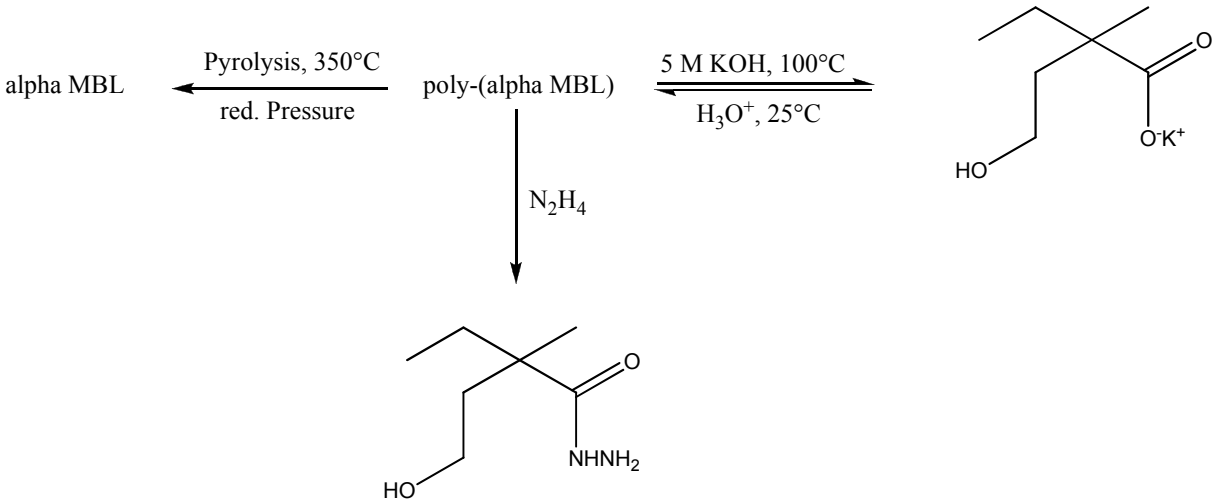
(a). Natural polymers (e.g. proteins, starch, cellulose)

(b). Synthetic polymers from naturally originated monomers (e.g. poly lactic acid)

(c). polymers from microbial fermentation (e.g. polyhydroxybutyrate)

Polymers obtained from Category (b), described above, has been of great importance recently [48,49]. To exemplify, compounds belonging to the class of sesquiterpene lactone family have been isolated from various plants.[50-53] α-methylene-γ- butyrolactone (MBL), also known as Tulipalin A, is found to be present in common tulips. By virtue of its exo-methylene double bond, it can be used as a naturally originated monomer in order to synthesize biopolymers. The very first free radical polymerization of such compounds was reported in a patent by Mc Graw in 1953.[54] Prior to which more attention was given by medicinal chemists for biomedical applications due to their cytotoxicity and tumor inhibitory properties.[55] Having a natural source origin inculcates biocompatibility, biodegradability, eco-friendly and renewable characteristics in these compounds.

Monomers of exocyclic methylene butyrolactone category that have already been polymerized include α-methylene-γ-butyrolactone (α-MBL), β-methyl-α-methylene-γ-butyrolactone (γ-MBL or MMBL)[56,57] and γ-methyl- α-methylene-γ-butyrolactone (MeMBL).[58, 59] Polymerization of α-MBL using radical initiator AIBN has been carried out many times.[60-62] Apart from this, also known is the photopolymerization of this monomer with methoxystyrene[63] and the group transfer polymerization using tris-(dimethylamino) sulfonium difluoride as catalyst.[64] Akkapeddi[60] presented some aspects of both free radical as well as anionic polymerization characteristics of α-MBL. He determined the stereochemical configuration of the homopolymers produced and discussed various other significant properties like alkaline hydrolysis at 100°C, pyrolysis beyond 360°C under reduced pressure, and the effect of hydrazinolysis (Refer Scheme 4.12.1).



Scheme 4.12.1: Alkaline hydrolysis at 100°C, Pyrolysis beyond 360°C under reduced pressure, and the effect of hydrazinolysis of α-MBL.[60]

Controlled radical polymerization of α-MBL to obtain predetermined molecular weight and narrow polydispersity has been achieved by Matyjaszewski and Mosnacek[65] wherein, CuBr/2,2'-bipyridine (bpy) catalyst complex and Bromopropionitrile (BPN) initiator was used to synthesize homopolymers of MBL. Also, they obtained well defined diblock and triblock copolymers by chain extension of various macroinitiators, for example, PMMA and P(n-BA) with α-MBL, using CuBr/N,N,N',N",N"-pentamethyldiethylenetriamine (PMDETA) as catalyst.

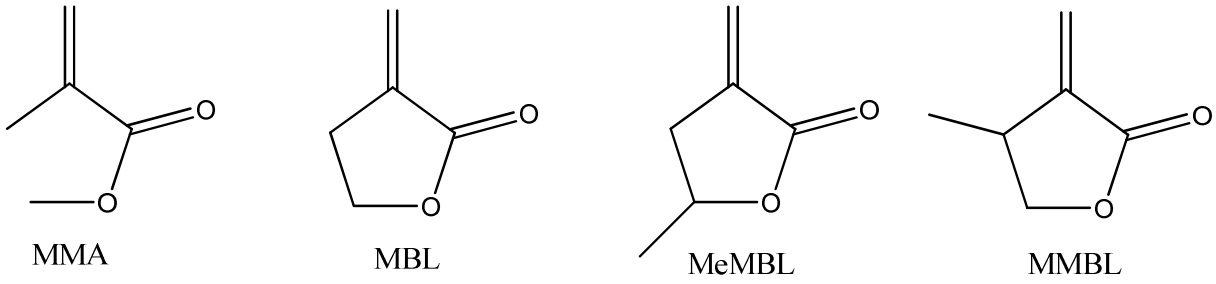
Later, some hybrid materials of poly(ethylene oxide) methyl ether methacrylate (PEOMA) and α-MBL were produced by Kubo et al.[66] via radical polymerization. The ionic conductivities and thermal properties of solid polymer electrolytes were investigated. It was found that the solid polymer electrolyte using P (PEOMA) had higher ionic conductivity and larger temperature dependence of ionic conductivity than those of the solid polymer electrolyte using homopolymer of MBL. Furthermore, physical mixture or blends were formed with graft copolymers comprising of α-MBL with thermoplastic matrix resins in order to improve the mechanical properties of the resins.[67]

Recently, transparent copolymers having unsaturated polyester networks were synthesized wherein for the first time α-MBL could be ring opened using a catalytic system, i.e., Bismuth (III) trifluoro methane sulphonate.[68] Resulting unsaturated polyesters were crosslinked with methacrylates to obtain transparent bicomponent networks which showed shape memory effect. The crystallization of polycaprolactone mainly gives rise to the shape memory effect of the networks. The normal crystallization temperature of 55°C got influenced by the incorporation of α-MBL units in the polyester backbone. The more the amount of α-MBL sequences, lower the melting point of the copolyester becomes.

Not only this, but the homopolymers of α-MBL have been reported to have good durability and high refractive index (1.540).[69] Poly(α-MBL) obtained by free radical polymerization was found to be atactic and amorphous having a T_g of as high as 195°C, whereas PMBL obtained from anionic polymerization was found to be isotactic, but still amorphous.[60]

4.13 Resemblance and differences of MBL and MMA

Monomers belonging to methylene butyrolactone category are structurally similar to MMA, and hence polymerize in a similar fashion (Scheme 4.13.1).



Scheme 4.13.1: Structure similarity between MMA and methylene butyrolactone monomers

Considering the example of monomer, MBL, similar to MMA, can undergo anionic as well as radical polymerization because the propagating specie: carbanion or free radical is stabilized by adjacent carbonyl group.[60]

Also stated by Akkapeddi is the fact that the polymers resulting from MBL resemble PMMA in mechanical properties, optical clarity and thermal stability. The polymers were found to be stable upto 320°C, above which they got depolymerized to give back the monomers via "unzipping mechanism of thermal degradation". The optical clarity and brilliance is much more for poly (α-methylene lactones) than that of polystyrene, henceforth, can be applied for optical fibres, moldings or organic glasses.[70-72]

But, reactivity of MBL in radical polymerization has been reported to be higher even than that of MMA. This has been attributed to three main reasons.[57,73] Firstly, due to the planar structure of MBL, it exhibits less steric effects and the exocyclic double bond is more accessible and secondly, planarity favors delocalization of chain radical's spin density and hence results in maximum resonance stabilization. These conditions favour the interaction between growing radical and the approaching monomer in the transition state for propagation. Thirdly, the exocyclic double bond is at a higher energy level as compared to the vinylic group of MMA. This is attributed to the ring strain, and relief of this strain provides additional driving force for the polymerization of MBL. The overall rate constant (k) for bulk polymerization of MBL using radical initiator, AIBN, at 55°C was calculated to be 190 by Akkapeddi[60] using the following equation:

Initial rate (% conversion h^{-1}) $= k\,[AIBN]^{1/2}$

This value was comparable with the rate constant for bulk polymerization of MMA at 60°C.[74] Due to the polar cyclic structure, α-methylene butyrolactones possess very low volatility, no odour and higher boiling points as compared to that of MMA. Apart from this, the side groups of PMMA have better freedom of rotation as compared with the highly structurally rigid lactone ring which is perpendicular to the plane of the polymer backbone. Such rigidity results in a better solvent resistance (common organic solvents) and a higher T_g for PMBL (195°C) compared to that of atactic PMMA (105°C).[75] Such properties have found applications for these polymers as thermoplastic toughners, heat resistant resins and dental resins.[73,76-78]

5. Results and Discussion

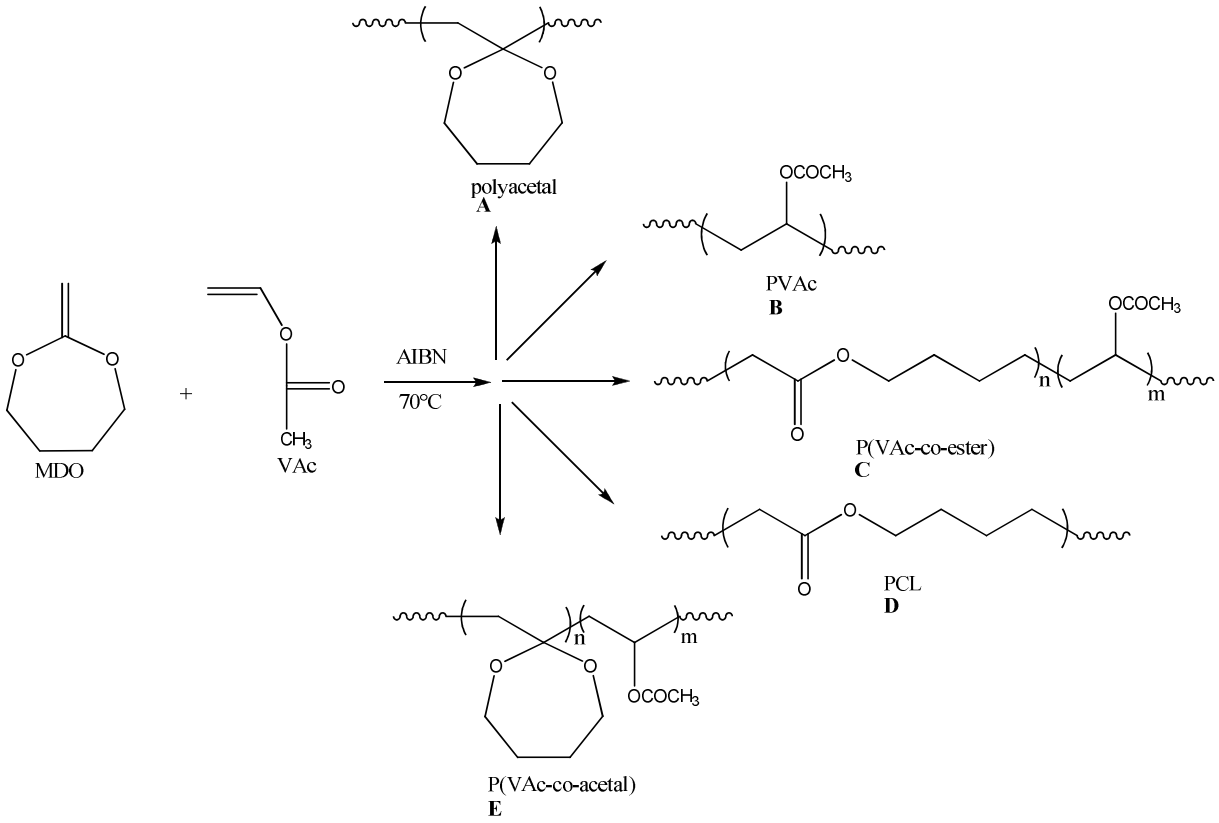
5.1 Degradable gummy materials

5.1.1 Synthesis of Poly(vinyl acetate-co-cyclic ketene acetals) or Poly(vinyl acetate-co-esters)

S. Agarwal, **R. Kumar**, T. Kissel, R. Reul, *Polym. J.* **2009,** 41(8), 650.

Poly(vinyl acetate) is yet another important and interesting vinyl polymer which is used for various applications, including as a base for chewing gums,[80] but due to its stable C-C backbone, degradation under environmental conditions is very slow and is not counted in the category of degradable polymers. The degradation mechanism firstly leads to hydrolysis to poly(vinyl alcohol) and then further degradation takes place. On the other hand, polycaprolactone (PCL) is a very well known biodegradable polymer. Bringing hydrolysable and biodegradable PCL structure onto the PVAc backbone could lead to, in general, hydrolysable and biodegradable environmentally friendly gums and adhesives for short duration applications. Bringing PCL structure randomly onto PVAc backbone by conventional routes of either condensation polymerization or ring-opening polymerization of cyclic esters for the formation of esters is not possible. Therefore, here an attempt has been made to provide a CL and VAc based degradable material by radical ring-opening copolymerization of MDO with VAc, and the material has been proposed to be used as adhesives or chewing gum base.

The various possible products of copolymerization of MDO with VAc are given in Scheme 5.1.1. MDO being a cyclic ketene acetal, could react via ring-opening polymerization to give polycaprolactone type units (**B**, **C** or **D**), or via ring-retaining polymerization to give polyacetals (**A** or **E**). Also, the reaction could lead to formation of copolymers (**C** or **E**) or simply homopolymers (**A**, **B** or **D**) as given in Scheme 5.1.1.



Scheme 5.1.1: Various possible polymerization products of reaction between vinyl acetate (VAc) and 2-methylene-1,3-dioxepane (MDO).

All the copolymerization reactions of MDO and VAc were carried out under conventional free radical polymerization reaction conditions. AIBN was used as an initiator at 70^{o}C.

The detailed studies regarding the copolymerization behavior and properties evaluation of MDO and VAc are required in order to recommend the new materials for different applications including degradable gums. The various copolymers of MDO with VAc were made by changing the molar ratio of the two monomers in the initial feed (Table 5.1.1). In ^{13}C NMR spectra of all the copolymers made in this work, no peak between 100 - 110 ppm is seen thereby showing the complete ring-opening reaction forming ester linkages.[11] Henceforth, formation of structures **A** and **E** of scheme 5.1.1 is clearly ruled out.

Table 5.1.1: Copolymerization of 2-methylene-1,3-dioxepane (MDO) and Vinyl acetate (VAc) by bulk polymerization method, at 70°C, using AIBN initiator and varying monomer feeds (reaction time = 4h).

Run	*Feed composition (molar ratio) MDO : VAc*	*Yield %*	*Copolymer composition[a] (molar ratio) MDO : VAc*	*T_g [b] (°C)*	*$[\eta]$[c]*	*T_i (°C)*
1[d]	8 : 92	80	5 : 95	38	1.5575	290
2	19 : 81	77	18 : 82	17	1.2041	300
3	29 : 71	73	25 : 75	5	0.9831	285
4	52 : 48	48	47 : 53	-22	0.5618	280
5	76 : 24	64	73 : 27	-44	0.3360	280

[a]obtained from ^{1}H NMR [b]T_g is the glass transition temperature, [c]$[\eta]$ is the intrinsic viscosity calculated at 25°C using Viscosimetry method using DMF as the solvent, [d]Reaction time = 4h.

5.1.2 Structure characterization

The structural characterization of the homopolymers and copolymers was done in $CDCl_3$ using various NMR spectroscopic techniques. A representative ^{1}H NMR of copolymers is shown in Figure 5.1.1 (entry 3, table 5.1.1)

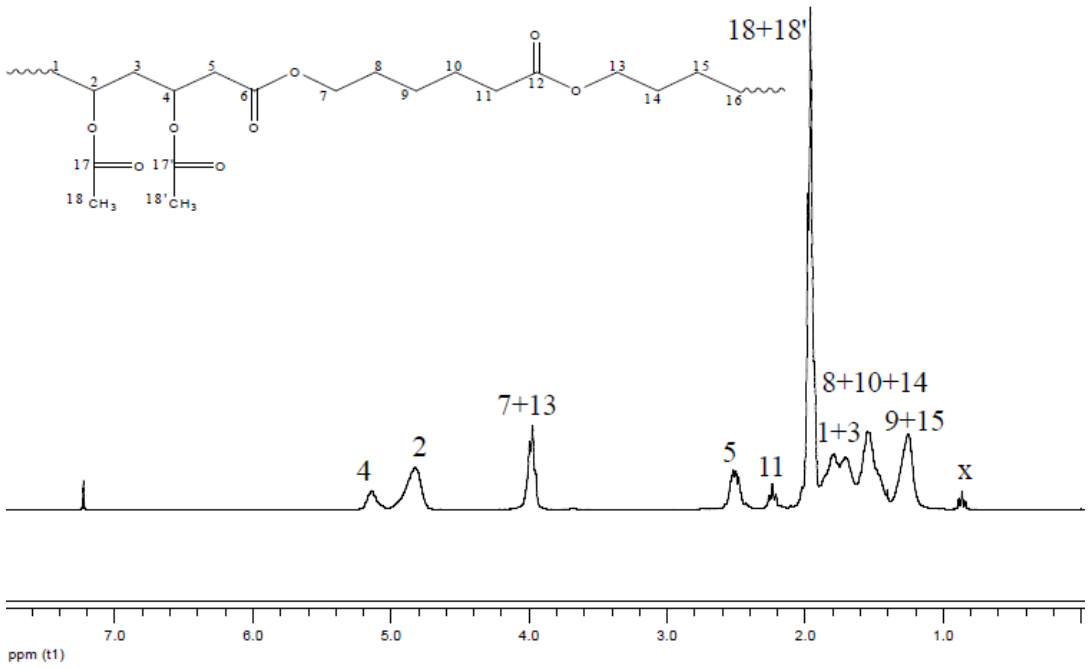
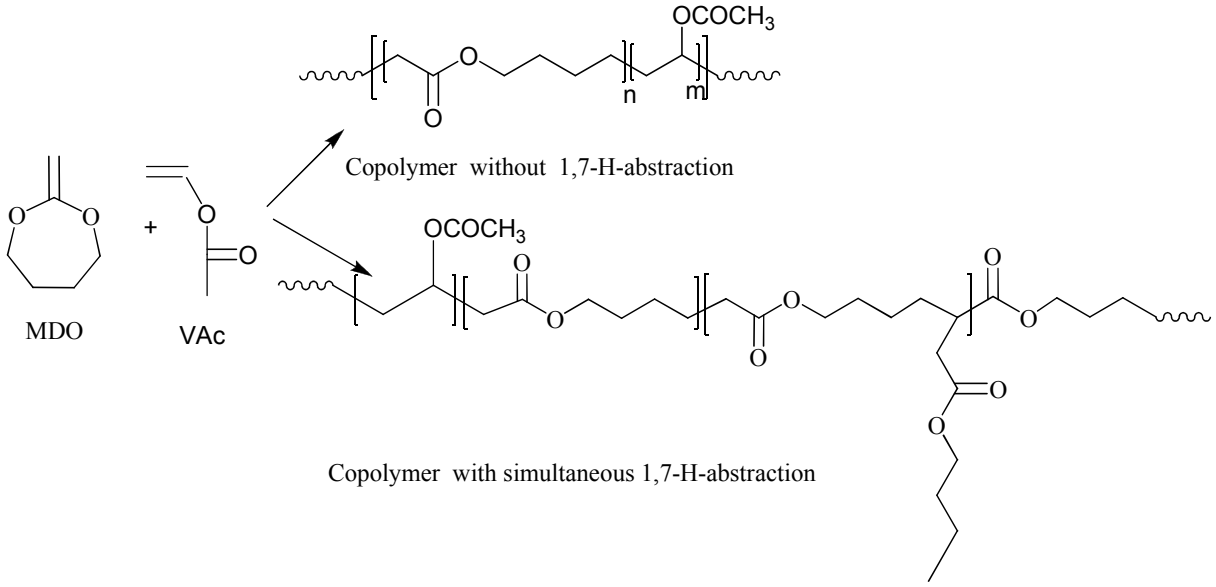


Figure 5.1.1: ^{1}H NMR spectrum of poly(VAc-co-MDO) (entry 3, Table 5.1.1) in $CDCl_3$ as solvent.

The characteristic signals of both VAc and MDO were seen in the polymers. And, by the occurrence of only one glass transition temperature in all the samples, the formation of homopolymers of VAc and MDO (structures **B** and **D** of scheme 5.1.1) can be ruled out, leaving the copolymer structure **C** (scheme 5.1.1) to be the most plausible one. The $-CH_2C(O)OC\underline{H}_2-$ protons of MDO were seen between 4.0 - 4.1 ppm. Other aliphatic protons of MDO ($-C\underline{H}_2C(O)OCH_2CH_2CH_2CH_2-$, $-CH_2C(O)OCH_2C\underline{H}_2CH_2CH_2-$ and $-CH_2C(O)OCH_2CH_2C\underline{H}_2CH_2-$ were obtained at 2.2, 1.5 and 1.3 ppm, respectively, in accordance with reference[10]. ^{1}H NMR also showed a small peak at 0.85 ppm (marked X). The origin of this extra peak during homopolymerization of MDO[10] comes mainly from the 1,7-H abstraction reactions (scheme 5.1.2) leading to some branches having $-CH_3$ groups as branch ends.



Scheme 5.1.2: Copolymerization of 2-methylene-1,3-dioxepane (MDO) and vinylacetate (VAc) using azobisisobutyronitrile (AIBN) as radical initiator at 70^{o}C.

In the present work, although 1,7-H abstraction reactions are also seen during copolymerization leading to branched structures in very small amounts but the quantitative estimation of branches could not be estimated with any accuracy because of very low intensity.

–C<u>H</u>OC(O)CH_3 protons from VAc units were observed as two peaks centered on 4.8 and 5.1 ppm. Methyl protons of VAc were obtained around 2.0 ppm and other aliphatic protons (-C<u>H</u>$_2$CHOC(O)CH_3)-) were observed between 1.7 - 1.8 ppm. The splitting of –C<u>H</u>OC(O)CH_3 peak of VAc units between 4.8 and 5.1 ppm and the presence of an additional peak at 2.6 ppm showed the presence of different configurational and conformational sequencing of the two comonomeric units (MDO and VAc) onto the polymer backbone.

The copolymer composition (Table 5.1.1) was determined by using the peak intensities at 4.8 - 5.1 ppm of VAc (I_{VAc} (–C<u>H</u>OC(O)CH_3)) and 4.0 - 4.1 ppm of MDO I_{MDO} (–CH_2C(O)OC<u>H</u>$_2$-) in ^{1}H NMR. The molar ratio of VAc : MDO in the copolymer for high conversions (till about 80%) was always found to be almost same as that of the feed (Table 5.1.1). A negligibly small variation of copolymer composition from feed composition could be due to the inherent experimental error in integrations of NMR spectra which could not be avoided. The different

copolymers could be made in high yields having increasing amount of MDO units just by changing the molar ratio of the two comonomers in the initial feed (Figure 5.1.2).

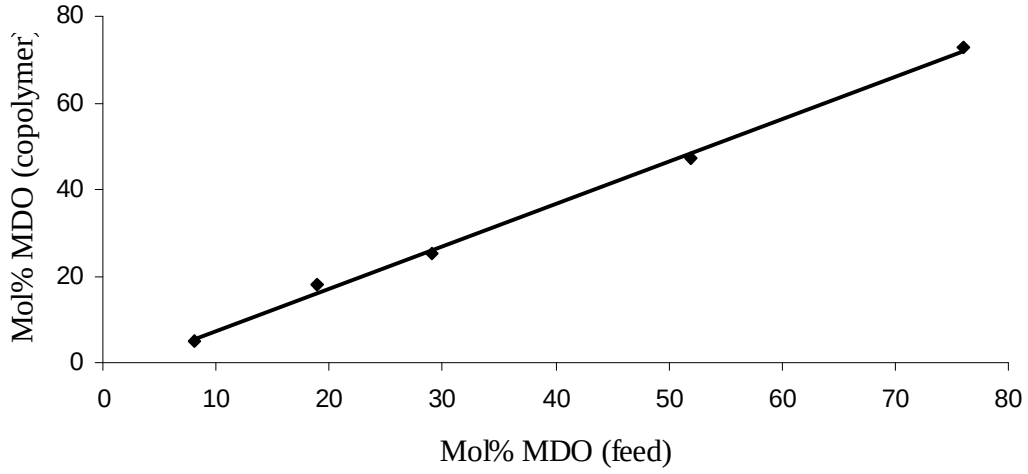


Figure 5.1.2: Mol-% of MDO in the feed versus mol-% of MDO in the copolymer (details of reactions given in Table 5.1.1).

The intrinsic viscosity as measured in DMF (according to method given in section 6.2.4) which is an indirect measure of molecular weight decreased with increasing amount of the MDO units in the polymer chain under similar reaction conditions. But, in general very high intrinsic viscosity polymers could be made (Table 5.1.1). Efforts to determine molecular weights by gel permeation chromatography (GPC) were not successful because of interaction of materials with GPC columns. Therefore, intrinsic viscosities are reported in the Table 5.1.1. There was a decrease in the intrinsic viscosity on increasing the amount of MDO in the copolymers. The values were between 0.33 - 1.55 dL/g depending upon the ratio of VAc and MDO in the copolymers. For homo polycaprolactone (PCL), the intrinsic viscosity of 0.33 dL/g corresponds to M_n (number average molecular weight) of about 14000[87] and for homo poly(vinyl acetate) the intrinsic viscosity of 0.33 dL/g corresponds to molecular weight of about 75000 according to the literature.[88] This gives a hint of having relatively high molecular weight copolymers in this study.

5.1.3 Reactivity ratios and polymerization parameters of monomers

For reactivity ratio determinations a separate batch of copolymerizations were carried out and the reactions were stopped at low conversions (15 - 20%) and copolymer composition which is required for the calculation of reactivity ratios was determined by using the peak intensities at 4.8 - 5.1 ppm of VAc (I_{VAc} (–C<u>H</u>OC(O)CH_3)) and 4.0 - 4.1 ppm of MDO I_{MDO} (–CH_2C(O)OC<u>H_2</u>-) in ^{1}H NMR. Table 5.1.2 presents the details.

Table 5.1.2: Calculation of various parameters for reactivity ratio determination by Kelen Tüdos method

Run.	*Feed composition* VAc : MDO	*Copolymer composition* VAc : MDO	$x^{a)}$	$Y^{b)}$	$F^{c)}$	$G^{d)}$	$\eta^{e)}$	$\xi^{f)}$
1	50 : 50	65 : 35	1	0.55	1.83	-0.83	-0.29	0.64
2	92 : 8	96 : 4	0.09	0.05	0.16	-1.71	-1.45	0.14
3	72 : 28	77 : 23	0.39	0.31	0.51	-0.90	-0.59	0.33
4	82 : 18	88 : 12	0.22	0.14	0.35	-1.40	-1.02	0.26
5	24 : 76	39 : 61	3.21	1.6	6.44	-1.20	0.16	0.86

[a)] x = Feed molar ratio: MDO/VAc; [b)] y = copolymer molar ratio: MDO/VAc; [c)] $F = x^2/y$; [d)] $G = x(y-1)/y$; $\alpha = \sqrt{(F_{max} F_{min})}$; [e)] $\eta = G/ \alpha+F$; [f)] $\xi = F/ \alpha+F$.

Reactivity ratios for MDO and VAc are determined using Kelen-Tüdos method[83] and was determined to be r_{VAc} = 1.56 and r_{MDO} = 0.47 (Figure 5.1.3).

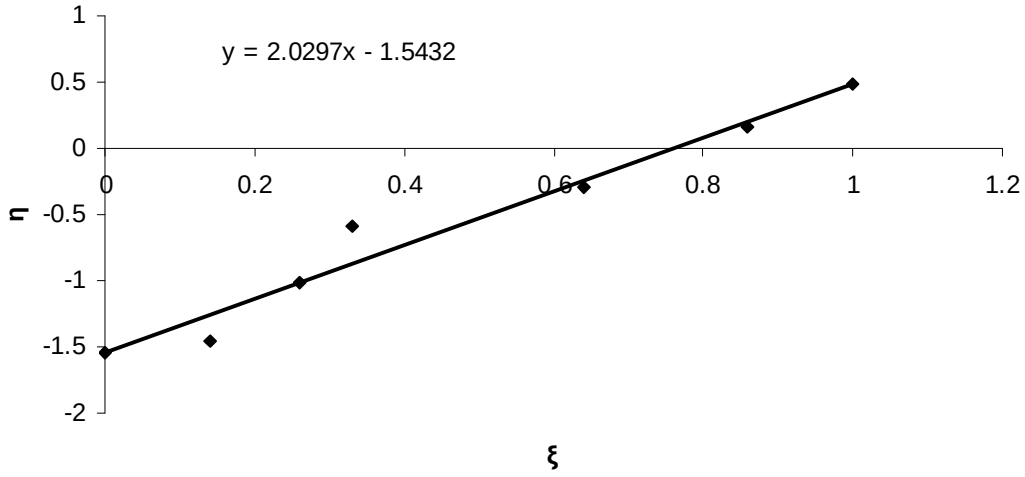


Figure 5.1.3: Kelen - Tüdos plot for VAc - MDO copolymers; copolymer composition was determined from ^{1}H NMR for low conversions (15 - 20 %).

The reactivity parameters give a hint about the copolymer microstructure as statistical comonomer sequences along the polymer chains. The copolymer composition is decided by the amount of the monomers in the feed. The reactivity ratio data available in the literature for MDO during its copolymerization with other vinyl monomers showed very high reactivity of the vinyl monomers as compared to the cyclic ketene acetals, for example, Bailey et al showed r_{MDO} = 0.021; r_{St} = 22.6[23]. On contrary to it, Davis et al. have reported a complete absence of copolymerization and their experimental data indicated the homopolymerization of styrene, with the MDO merely acting as a diluents.[84] Davis et al. have reported copolymerization parameters for copolymerization of MDO with MMA at 40^{o}C as r_{MDO} = 0.057 and r_{MMA} = 34.12 thereby showing the low tendency of cyclic ketene acetals to copolymerize with vinyl monomers.[85] In this work, a very good copolymerizability of MDO with VAc which is due to the similarity in monomer structures in terms of nucleophilic double bond and stability of growing radicals, is shown.

Q (monomer reactivity) and e (monomer polarity) values for MDO using a well known Alfrey-Price equation were calculated.[86] The Q (0.026) and e (-0.88) values for vinyl acetate were taken from the literature. The Q and e values for MDO were calculated to be 0.010 and -0.3363, respectively. Very similar Q values of VAc and MDO explains good copolymerizability of the two monomers.

5.1.4 Structure-property relationship

Before the materials could be utilized for any application, the basic studies in terms of copolymerizability and properties evaluation is required. Therefore, studies have been carried out to have the basic understanding of the copolymerization process between MDO and VAc. The microstructure of the resulting materials is a key factor in deciding the end-use properties as degradable material.

Further careful examination of the ^{1}H NMR spectrum helped in analysing the microstructure of the copolymers. With increase in the amount of MDO in the copolymers the peaks at 5.2 and 2.6 ppm increased and also a new peak at 2.2 ppm appeared (Figure 5.1.4).

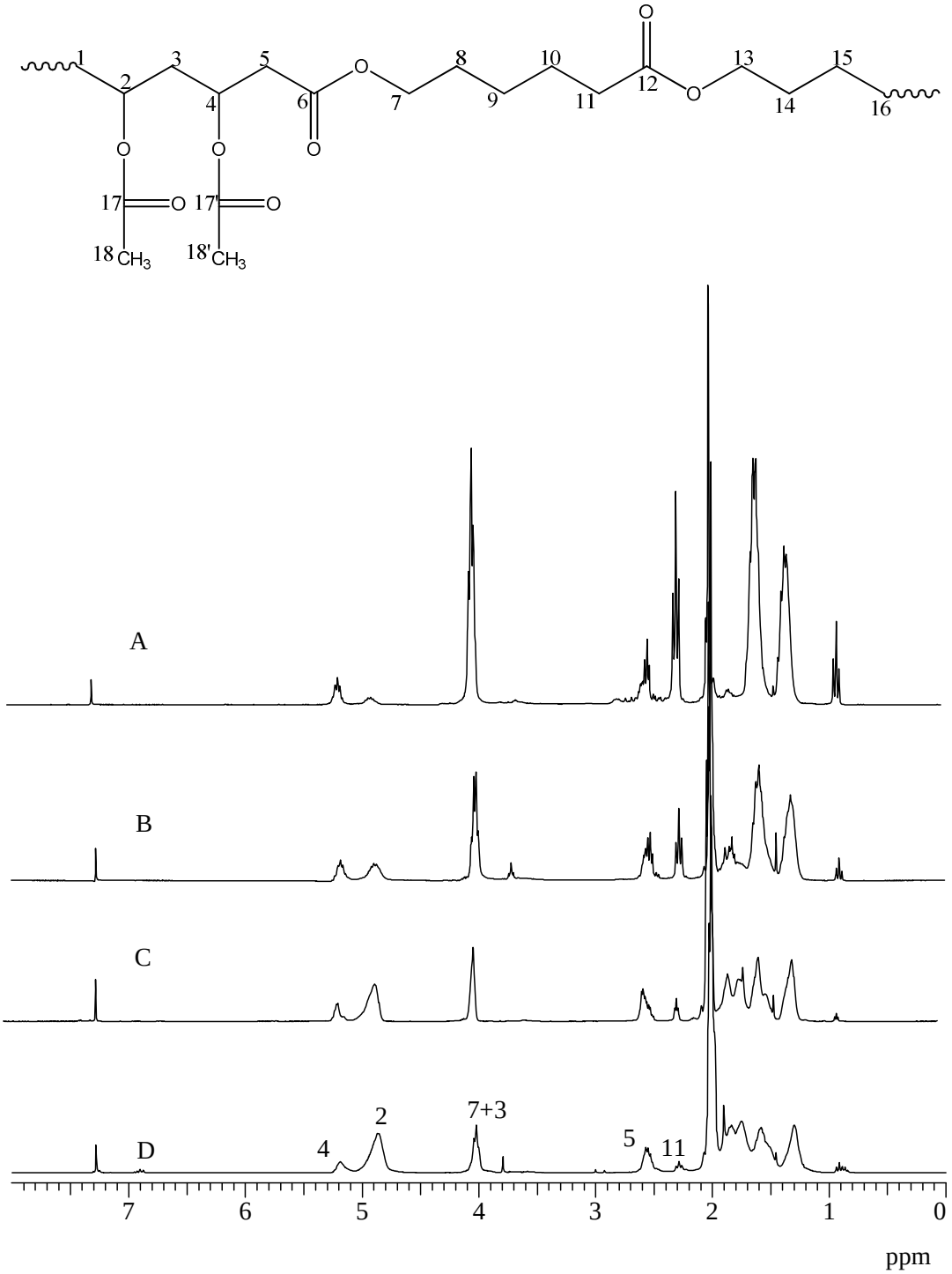


Figure 5.1.4: ^{1}H NMR spectra of copolymers (in $CDCl_3$), with copolymer composition, MDO : VAc (in mole percent): A) 73 : 27 (Entry 5 Table 5.1.1); B) 47 : 53 (Entry 4 Table 5.1.1); C) 25 : 75 (Entry 3 Table 5.1.1); D) 18 : 82 (Entry 2 Table 5.1.1).

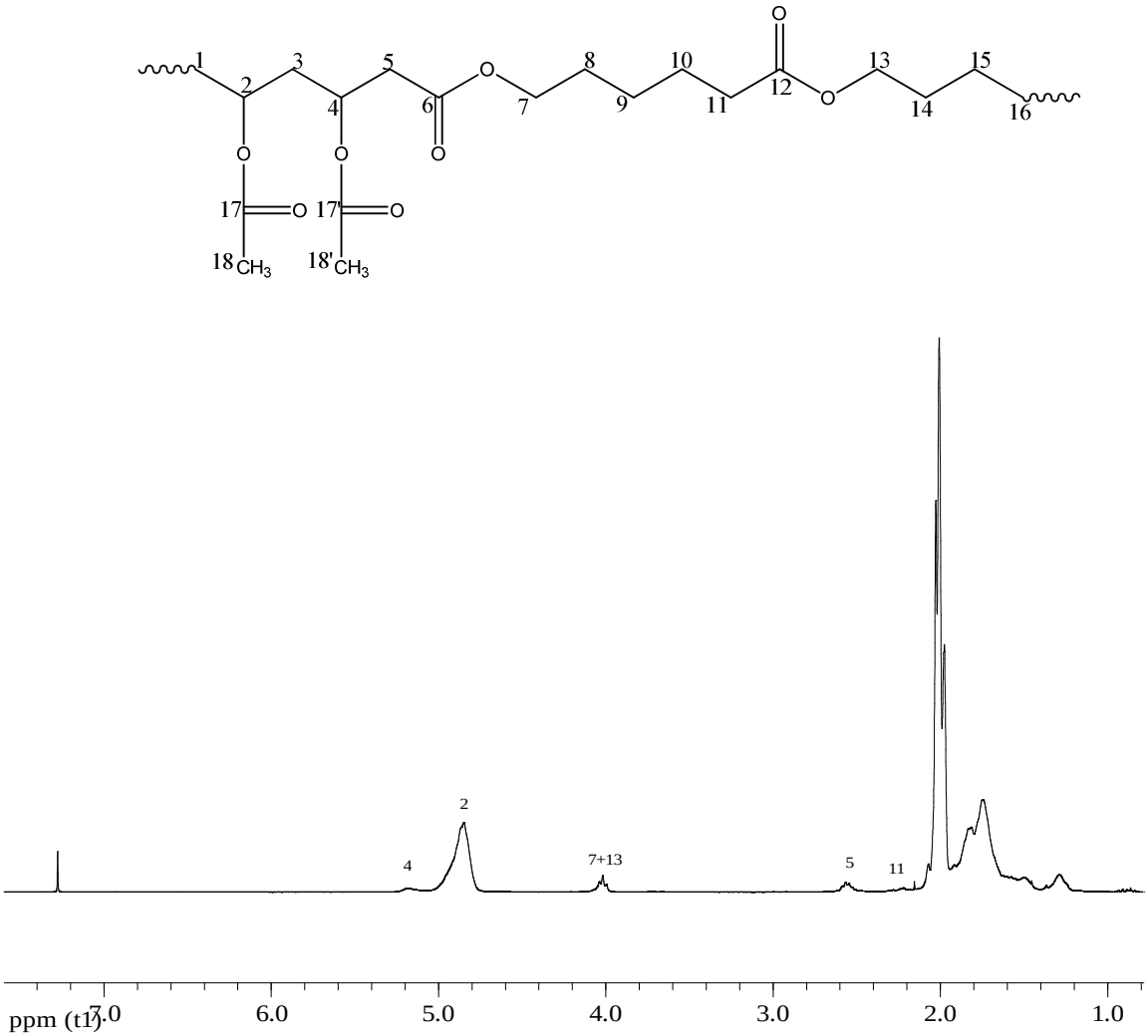


Figure 5.1.5: ^{1}H NMR spectra of copolymer with copolymer composition, MDO : VAc (in mole percent): 5 : 95 (Entry 1, Table 5.1.1): hardly any peak 11 is visible.

The new peak appearing at 2.2 ppm is assigned to the (-C<u>H</u>$_2$C(O)OCH$_2$CH$_2$CH$_2$CH$_2$- protons of MDO-MDO diad with reference to our previous work on homopolymerization of MDO[10]. The other two prominent peaks that increased with an increase in the amount of MDO in the copolymers could be due to the -C<u>H</u>OC(O)CH$_3$ VAc protons linked to MDO (<u>VAc</u>-MDO) (5.2 ppm) and -C<u>H</u>$_2$C (O)OCH$_2$CH$_2$CH$_2$CH$_2$- protons of MDO linked to VAc (VAc-<u>MDO</u> diads sequences) (2.6 ppm) in the copolymers. This shows with increase in the amount of MDO in the copolymers the diads of the types both VAc-MDO and MDO-MDO increases showing more

randomisation of the copolymer structure. In fact, at very low concentrations of MDO in the copolymers i.e. 5 : 95 molar ratio, hardly any diads of the type MDO-MDO were seen. The MDO units were present in this particular copolymer as isolated units mainly in the form of VAc-MDO diads. Since microstructure of the polymers could influence the final properties of materials, efforts were made to further confirm it using 2D NMR techniques like HMQC (heteronuclear multiple quantum correlation) and HMBC (heteronuclear multiple bond correlation).

2D HMQC was used to provide unambiguous ^{13}C NMR peak assignments and 2D HMBC was used to prove chemical links between VAc and MDO units. Also, HMBC helped in confirming the correct peak assignments to the ^{1}H NMR. The representative 2D HMQC NMR spectrum is shown in figure 5.1.6 with the cross peaks used for assigning the ^{13}C NMR spectrum.

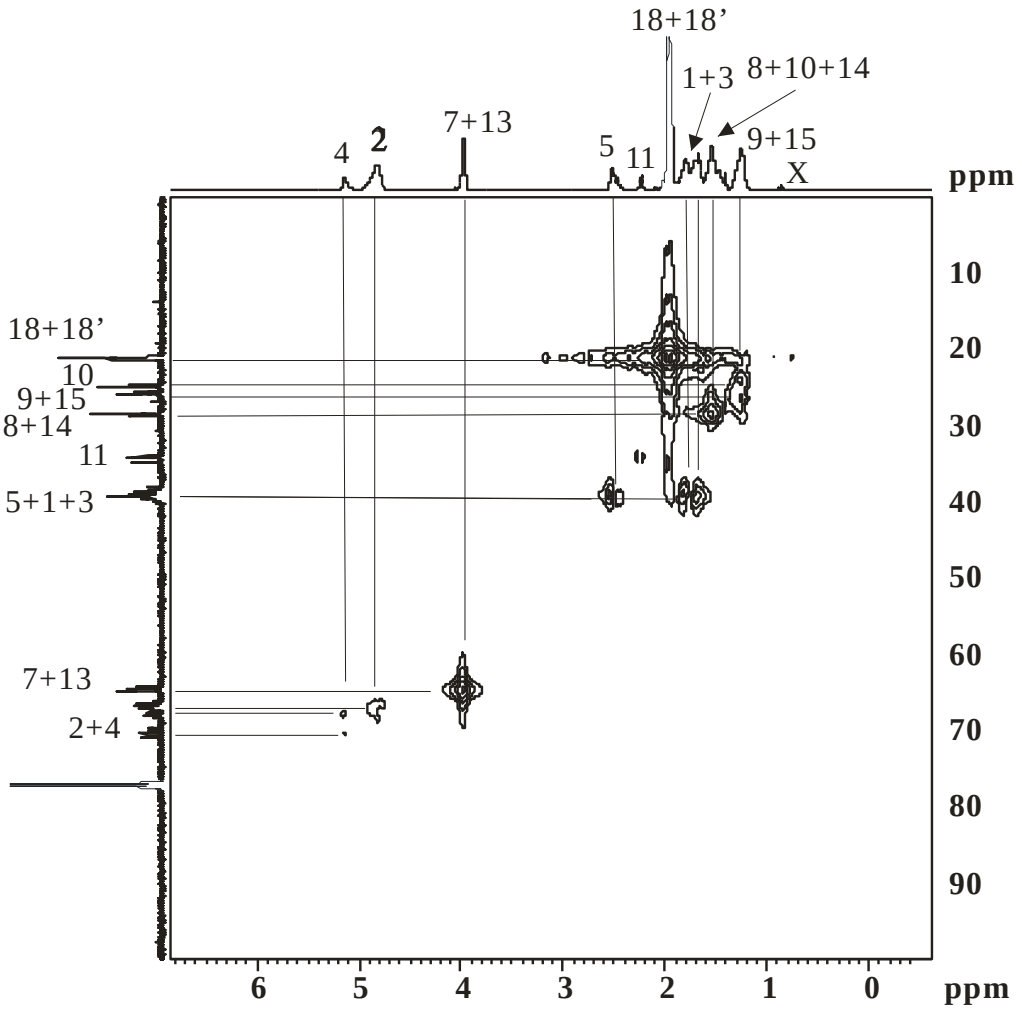


Figure 5.1.6: A part of 2D HMQC (heteronuclear multiple quantum correlation) NMR spectrum (entry 3 table 5.1.1) (^{1}H NMR 0 - 7 ppm ; ^{13}C NMR 0 - 100 ppm) in $CDCl_3$ as solvent.

The representative 2D HMBC NMR spectrum is shown in figure 5.1.7.

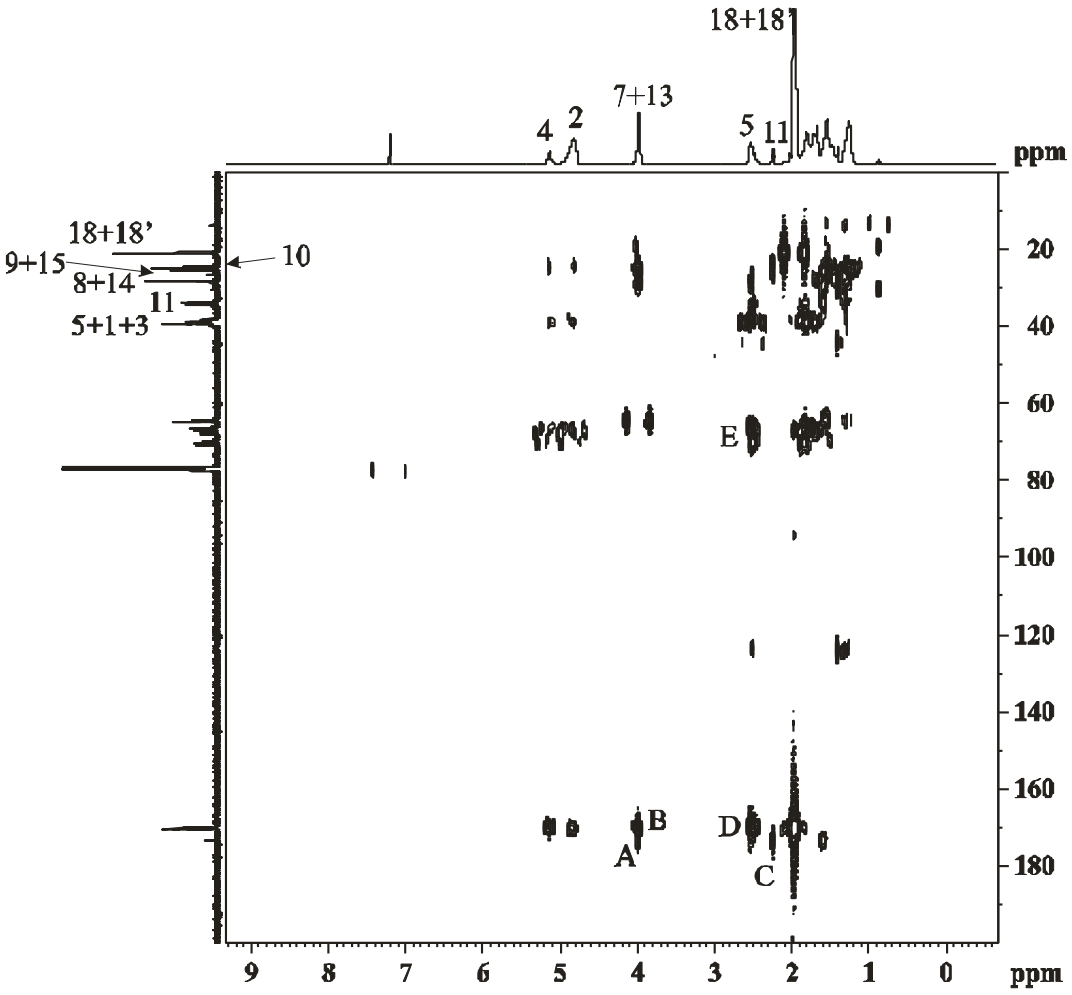


Figure 5.1.7: 2D HMBC (heteronuclear multiple bond correlation) NMR spectrum (entry 3 table 5.1.1) (^{1}H NMR 0 - 10 ppm ; ^{13}C NMR 0 - 200 ppm) in $CDCl_3$ as solvent.

The proposed peak from MDO-MDO diad at 2.2 ppm in ^{1}H NMR (Figure 5.1.7) from the protons (-C$\underline{H}_2$C(O)OCH$_2$CH$_2$CH$_2$CH$_2$-) showed only one correlation in the ester carbonyl carbon region with ^{13}C NMR peak at 173.4 ppm (cross peak A). This shows the peak in ^{1}H NMR spectrum at 2.2 ppm is correctly assigned as it should show only one ^{1}H NMR-^{13}C NMR cross-correlation through one bond in HMBC with carbonyl carbon 12. The protons 5 of MDO at 2.6 ppm (-C$\underline{H}_2$C(O)OCH$_2$CH$_2$CH$_2$CH$_2$-) from linking MDO unit (VAc - MDO diad) did not show any correlation with carbonyl carbon 12, instead it showed strong correlations in the peak region 170 - 171 ppm (cross peaks D) (carbonyl carbon 6 and carbonyl carbons of neighboring VAc). Also, protons 5 showed broad and strong 1 and 3 bond correlations (cross peak E) with the

carbons 2 and 4 of VAc units and therefore, is correctly assigned. The increased amount of MDO - MDO diads on increasing the amount of MDO in the feed i.e. from going from entry 1 to entry 5 of table 5.1.1 could also be clearly seen from the carbonyl carbon region of ^{13}C NMR spectra. The ^{13}C NMR spectra of copolymers having low mole % of MDO in the copolymers (5 - 18 mol%) hardly show any carbonyl peak at 173.4 ppm arising from homo MDO - MDO diads (Figure 5.1.8).

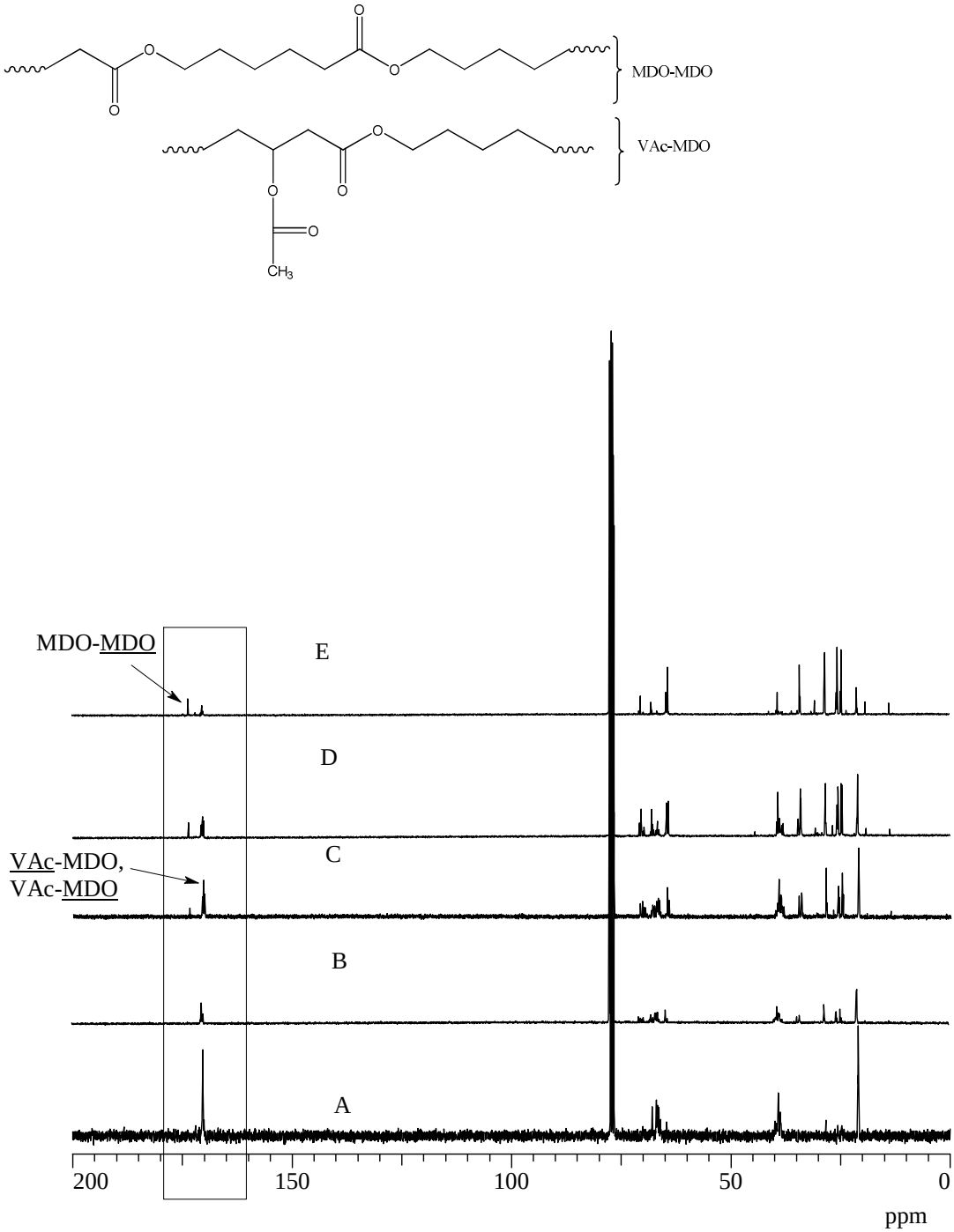


Figure 5.1.8: ^{13}C NMR spectra (in $CDCl_3$) of different copolymers with copolymer composition, MDO : VAc (mole percent): A) 5 : 95 (Entry 1 Table 5.1.1); B) 18 : 82 (Entry 2 Table 5.1.1); C) 25 : 75 (Entry 3 Table 5.1.1); D) 47 : 53 (Entry 4 Table 5.1.1) E) 73 : 27 (Entry 5 Table 5.1.1); Clearly shows the appearance of MDO - MDO diads with increasing amount of MDO in feed.

5.1.5 Influence of time on copolymer microstructure

Copolymerization reaction was followed at different intervals of time and change in microstructure of the copolymers is studied with time. For a sample with initial feed molar ratio of MDO : VAc 1 : 1, copolymer composition was determined at different time intervals using ^{1}H NMR technique and is given in Table 5.1.3. It can be seen from the data (Table 5.1.3) that rate of consumption of VAc was more at the start. This also gives a hint that at the start there were more VAc-VAc type of sequences followed by the more randomisation and more VAc-MDO diads. After about one hour of polymerization, the yield increased but the copolymer composition remained almost same.

Table 5.1.3: Copolymerization of 2-methylene-1,3-dioxepane (MDO) and vinyl acetate (VAc) [MDO : VAc 50 : 50 (molar ratio)] at 70°C, using AIBN initiator for different time intervals by bulk polymerization [monomer : initiator = 100 : 1 (molar ratio)].

Run	*Time*	*Yield %*	*Copolymer composition (molar ratio) MDO : VAc*
1	30 min	33	37 : 63
2	1 h	42	50 : 50
3	2 h	48	43 : 57
4	4 h	52	47 : 53
5	70 h	74	47 : 53

5.1.6 Thermal analysis of P(VAc-co-esters)

Effect of the incorporation of MDO ester units onto the PVAc hydrocarbon chain is also investigated on the thermal stability and glass transition temperature. The degradation of polycaprolactone generally takes place in one step (figure 5.1.11), while the degradation of PVAc prepared by the radical polymerization generally takes place in two steps (figure 5.1.11).[88] The acetate group elimination takes place at lower temperature between 300 and 330^{o}C followed by breakdown of polymeric backbone at higher temperature (between 360 – 450^{o}C). Addition of MDO units on the PVAc backbone did not affect the thermal stability of PVAc and the copolymers also showed two step degradations with T_i (initial degradation temperature) in the range of 300^{o}C - 280^{o}C.

A comparison of TGA curves of PCL, P(VAc-co-ester) (Entry 3, Table 5.1.1) and PVAc is shown below in figure 5.1.11.

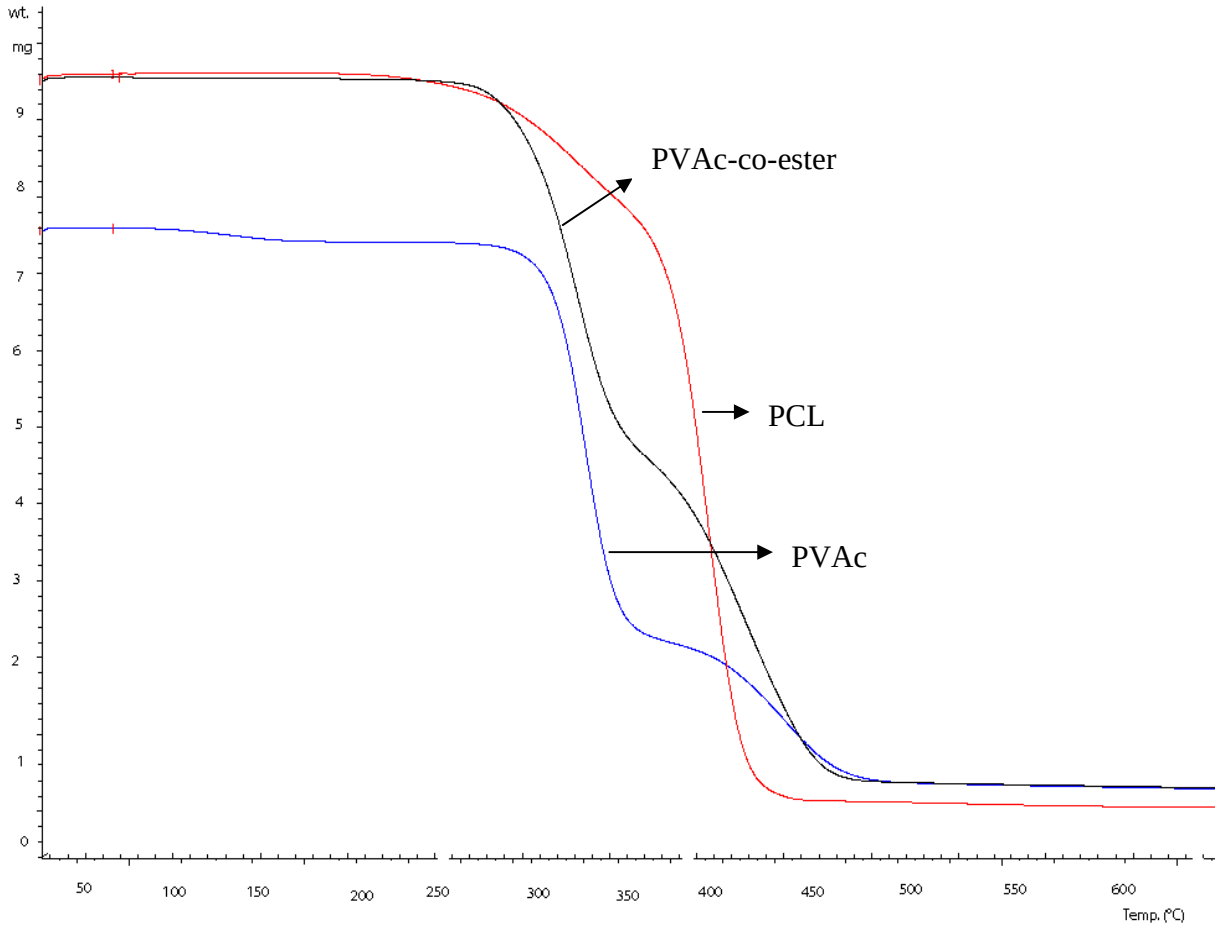


Figure 5.1.11: A comparison of TGA curves of commercial PCL, copolymer with composition MDO : VAc = 25 : 75 (Entry 3, Table 5.1.1) and PVAc.

For DSC measurements the samples were heated in the first heating cycle from –60^{o}C till 200^{o}C at a heating rate of 10^{o}C / min. The samples were cooled again to –60^{o}C with a cooling rate of 10^{o}C / min and again heated in the second heating cycle till 200^{o}C. The glass transition temperatures are (noted in the Table 5.1.1) from the second heating cycle. Single glass transition temperature was observed for the copolymers (poly(VAc-co-ester)s. There is a decrease in the glass transition temperature on increasing the amount of MDO onto the PVAc backbone (Table 5.1.1). Different copolymers with a wide range of glass transition temperatures from 38^{o}C to -44^{o}C were obtained. Figure 5.1.12 gives a comparison of DSC curves of copolymer samples with varying copolymer composition.

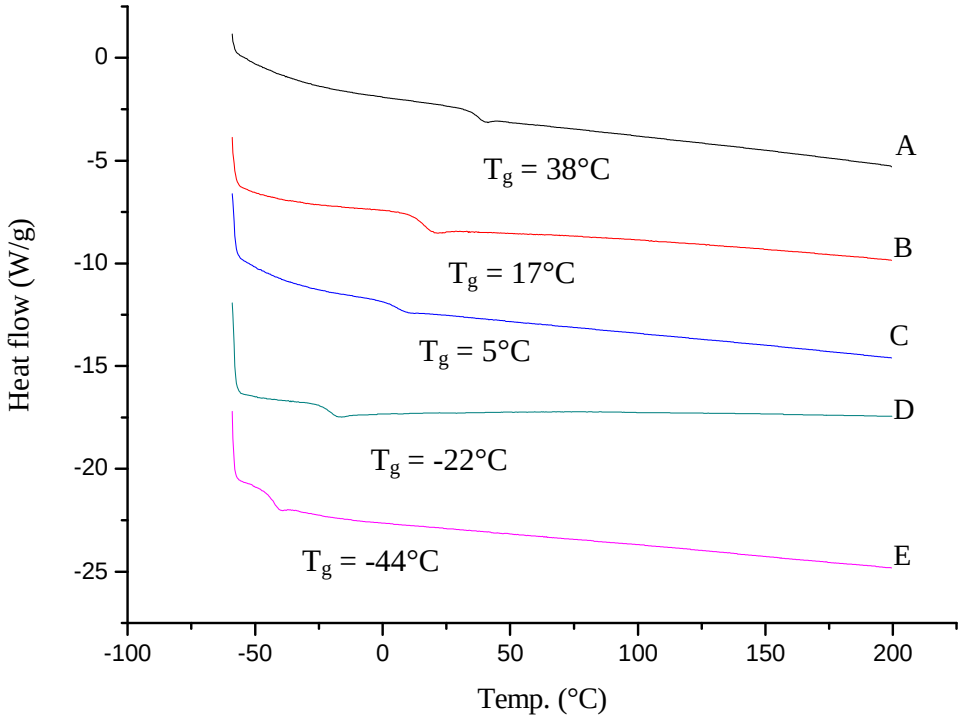


Figure 5.1.12: Comparison of DSC curves of different copolymers with copolymer composition, MDO : VAc (mole percent): A) 5 : 95 (Entry 1 Table 5.1.1); B) 18 : 82 (Entry 2 Table 5.1.1); C) 25 : 75 (Entry 3 Table 5.1.1); D) 47 : 53 (Entry 4 Table 5.1.1) E) 73 : 27 (Entry 5 Table 5.1.1).

5.1.7 Hydrolytic Degradability

Since the incorporation of ester linkages are expected to introduce degradability and was one of the aims of this work, the studies on hydrolytic degradation of the MDO-PVAc copolymer samples were carried out in KOH (5 wt% in methanol). After 20 hrs of hydrolysis, the polymer was completely soluble in the hydrolysis medium. The degraded material was extracted with chloroform, dried over sodium sulphate and after evaporation and drying the left over waxy/oily material was subjected to NMR analysis.

Figure 5.1.13 (a and b) show a comparison of ^{13}C NMR spectra, before hydrolysis and after hydrolysis. The disappearance of acetate peak at 170 - 173 ppm and the appearance of carboxyl peak at 177 ppm clearly indicated that the hydrolysis took place.

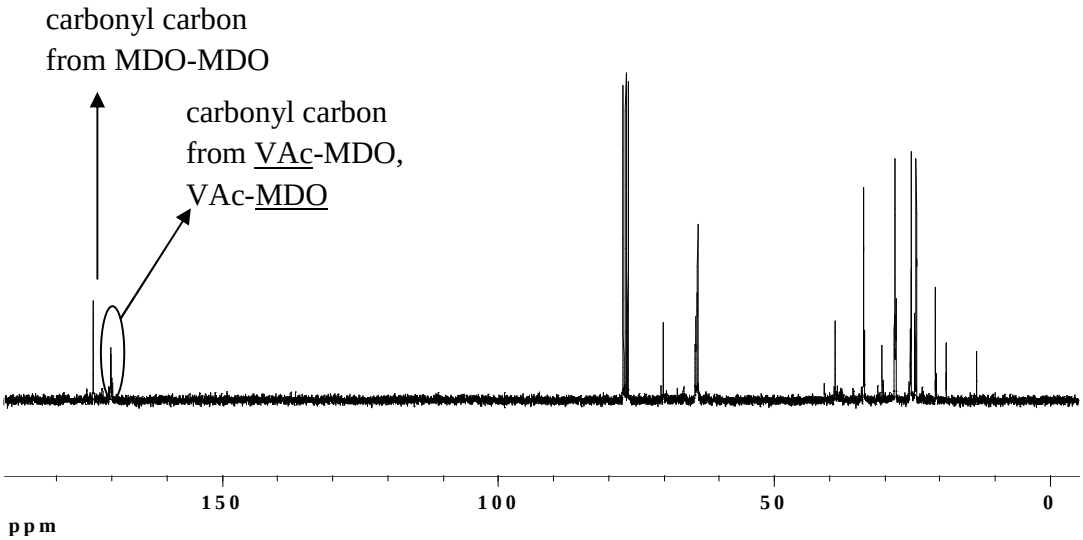


Figure 5.1.13 (a): ^{13}C NMR spectra, before hydrolysis (entry 5, Table 5.1.1)

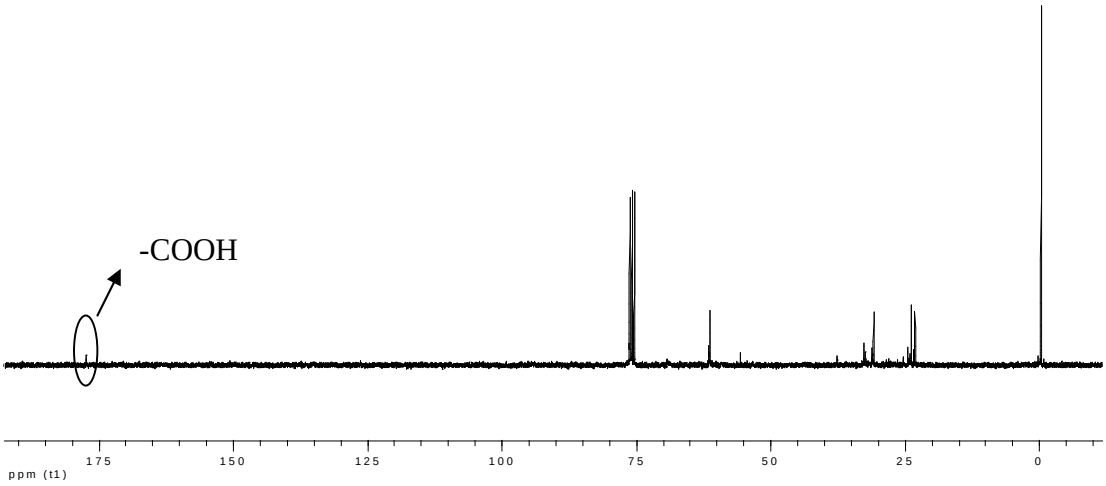
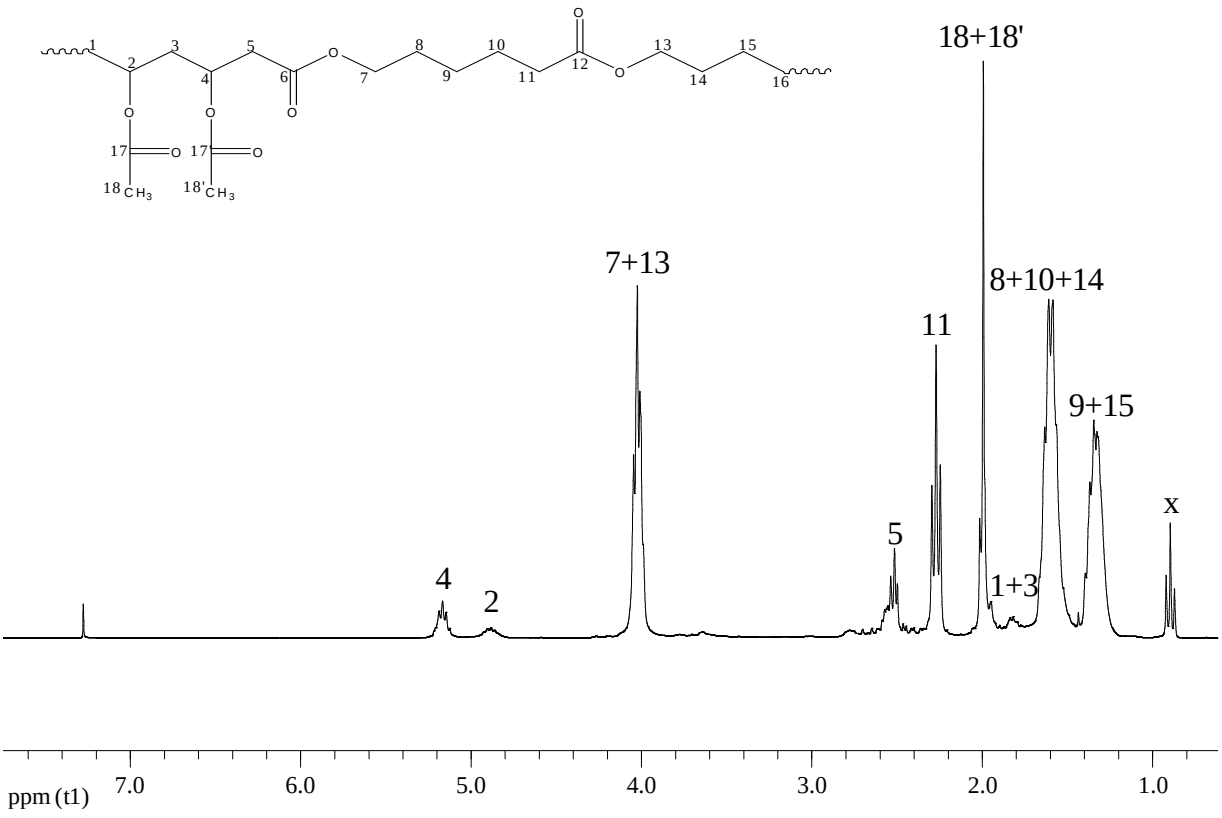
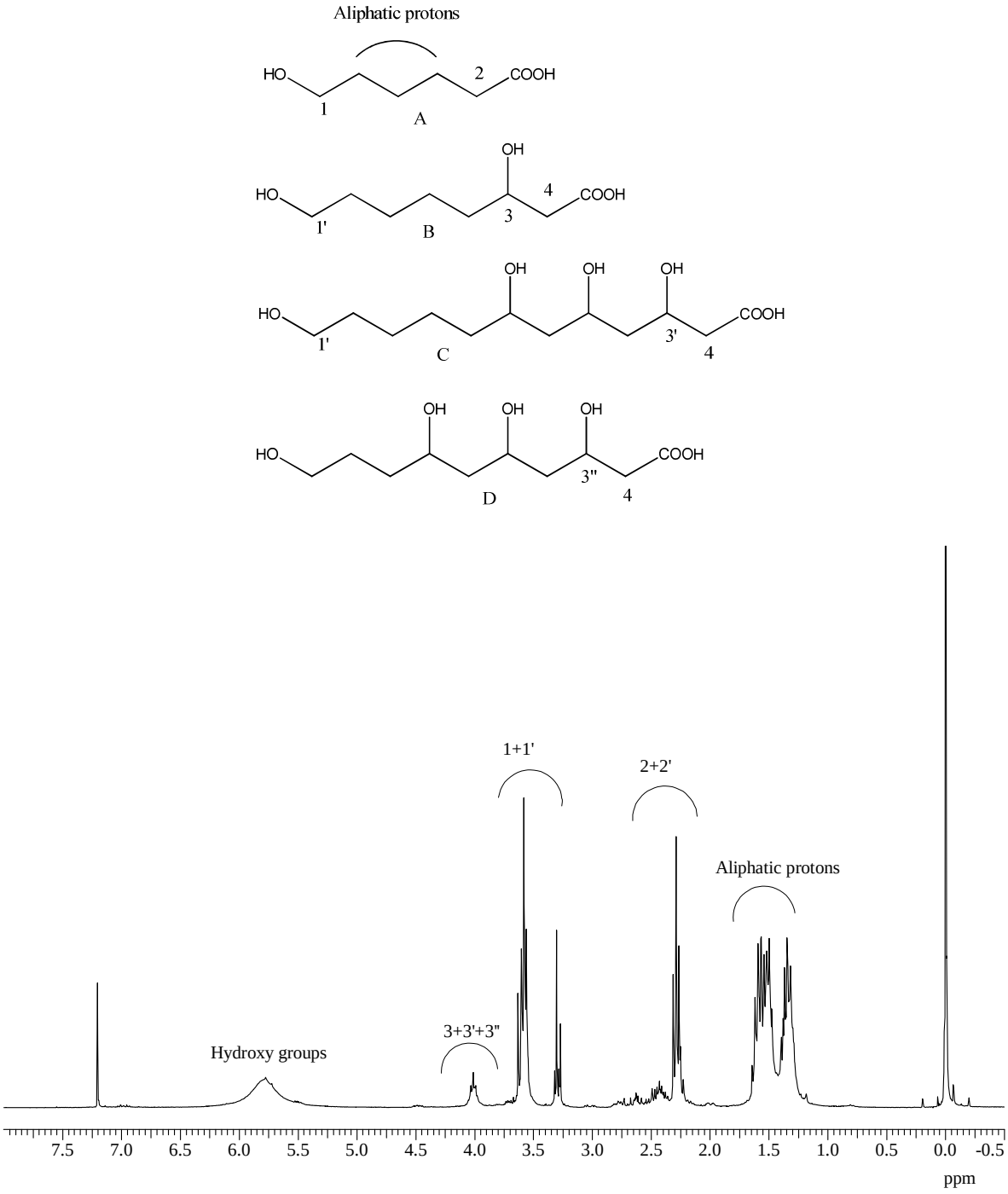


Figure 5.1.13 (b): ^{13}C NMR spectra, after hydrolysis (entry 5, Table 5.1.1)

^{1}H NMR was further used to identify the hydrolysed products (Figure 5.1.14 gives a comparison of entry 5, Table 5.1.1, a) before hydrolysis, and b) after hydrolysis).



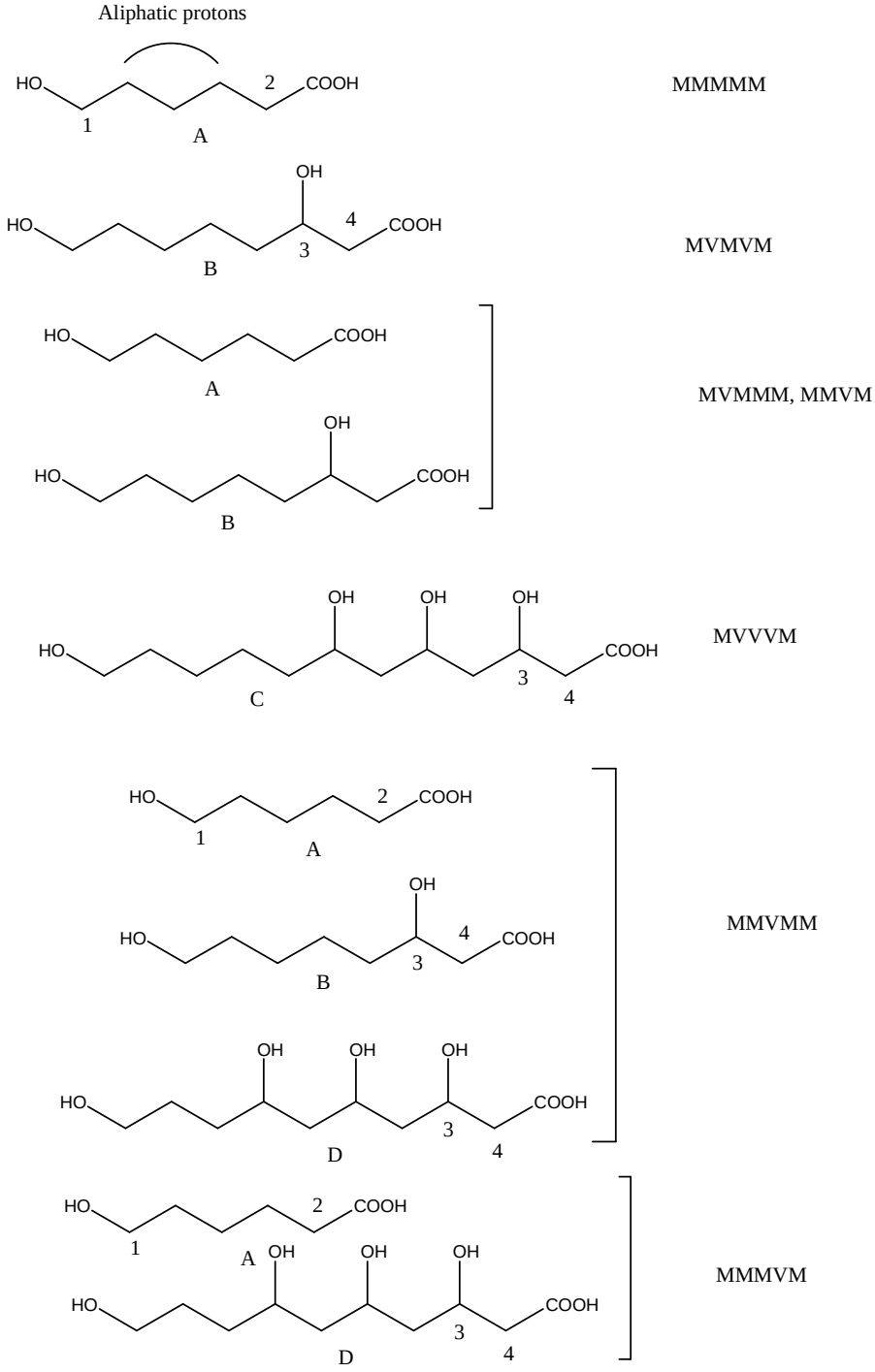
a) before hydrolysis



b) after hydrolysis

Figure 5.1.14: ^{1}H NMR spectrum in $CDCl_3$ of poly(VAc-co-ester) (entry 5 Table 5.1.1) a) before hydrolysis; b) after hydrolysis

Since the polymer degradation would be by hydrolysis of the ester linkages of PCL units, all degradation products i.e. oligomers / small organic molecules with hydroxyl and acid functional groups would be formed. The probable hydrolysis products from the linear copolymer structure are shown in scheme 5.1.4.



Scheme 5.1.4: Probable hydrolysis products of poly(VAc-co-MDO) with random distribution of ester linkages with pentads of the type: (M-M-M-M-M), (M-V-M-V-M), (M-V-M-M-M), (M-V-V-V-M), (M-M-V-M-M), (M-M-V-V-M), (M-V-V-M-M), (M-M-M-V-M); where M: MDO and V: VAc, respectively; **A**, **B**, **C**, **D** : Distinguished hydrolysis products from all pentads given above having molecular weights 132, 176, 264, 220, respectively.

As mentioned above, the branches due to 1,7-H abstractions reactions were negligibly small, the hydrolysis products formed from such structures are not considered. Besides oligomeric hydroxyl and acid functionalised poly(vinyl alcohol) units due to VAc-VAc-VAc-VAc-VAc type of units and 6-hydroxy pentanoic acid (structure A) from MDO-MDO-MDO-MDO-MDO units, other structures as shown in scheme 5.1.4 are also possible from hetero structures. From all these degradation products mainly overlapping signals in the region for protons 1(HO-C$\underline{H}_2$-), 2(-C$\underline{H}_2$-COOH), 3 (-C$\underline{H}$(OH)-), 4 (-CH(OH)C$\underline{H}_2$COOH) and aliphatic protons are expected (Scheme 5.1.4) in ^{1}H NMR. There was a clear change in the NMR peak positions (Figure 5.1.14) of the hydrolysed product as compared to the original NMR of the copolymer). The very strong and characteristic peaks of VAc units i.e. –OC$\underline{H}_3$ protons and –C$\underline{H}$(OCOCH$_3$)- in the unhydrolysed copolymer at 1.996 ppm and between 4.8-5.2 ppm respectively (Figure 5.1.1) disappeared after hydrolysis and a new and very broad peak appeared between 5.3 – 6.2 ppm from chain end –OH and –CH(OH) groups appeared . The –COOH protons could not be seen in ^{1}H NMR which could be due to the fast relaxation but ^{13}C NMR showed the presence of this group, as a peak at 177 ppm was observed. Also, the hydrolysis of ester linkages led to the formation of small moieties as shown in the scheme 5.1.4 with –OH and –COOH functional groups. This changed the peak position of –CH$_2$C(O)OCH$_2$CH$_2$CH$_2$- and –CH$_2$C(O)OCH$_2$CH$_2$CH$_2$- protons of PCL units in the unhydrolysed copolymer from 4 ppm to the new characteristic peaks of 1, 2, 3, 4 and aliphatic protons (Scheme 5.1.4) at 3.3 - 3.6 ppm, 2.3 ppm, 4.1 ppm and between 1.2 - 1.7 ppm (Figure 5.1.14). Although, in this study it was not possible to identify each degradation product quantitatively but the NMR clearly showed the hydrolytic degradability tendency of the new materials .

Hydrolysed sample (poly(VAc-co-ester) (entry 5 table 5.1.1)) was analysed by LCMS in negative ion mode to get further insight into the hydrolysis products (figure 5.1.15).

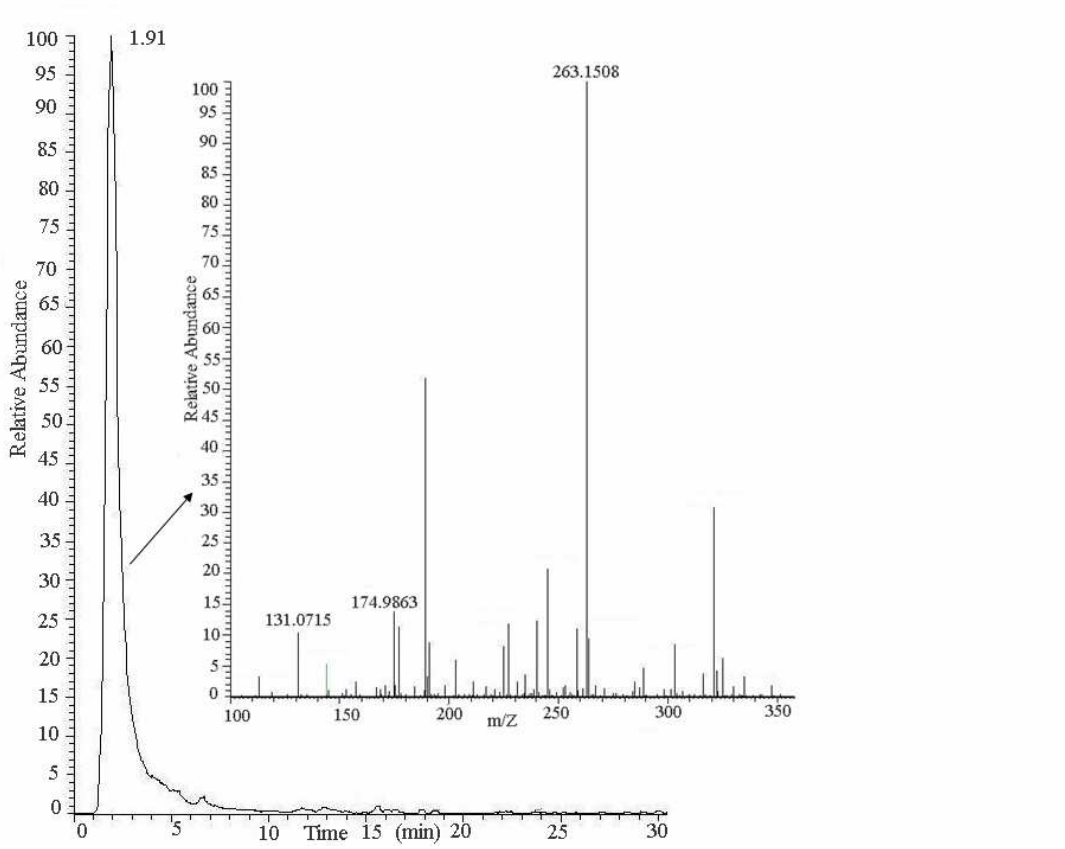


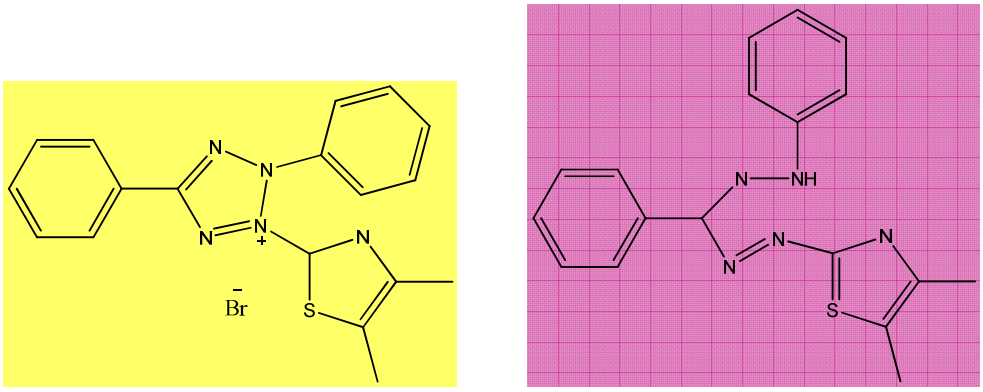
Figure 5.1.15: LCMS data for hydrolysed product of poly(VAC-co-ester) (entry 5 table 5.1.1) when measured in negative ion mode; **A**, **B**, **C** in Scheme 5.1.4 are confirmed at molecular ion peaks 131.0715, 174.9863, and 263.1508, respectively.

The compounds showed no retention in the column and all relevant masses were detected directly in the breakthrough. Three hydrolysed components could be confirmed viz.a.viz. $C_6H_{11}O_3$, $C_8H_{14}O_4$, $C_{12}H_{22}O_6$, having molecular weights 131, 175, 263, respectively (Structures **A**, **B**, **C** in Scheme 5.1.4). However, by ESI-MS, it is not possible to assign the positions of the OH groups. Absence of the fourth expected component, i.e., $C_{10}H_{18}O_5$, (Scheme 5.1.4; structure **D**) could not be seen and proved that (M-M-V-V-M) or (M-V-V-M-M) type of pentad were less probable. This result is again in accordance to our NMR results for microstructure analysis, which states that MDO prefers VAc as its comonomer rather than MDO.

5.1.8 Cell Viability Studies of hydrolysed polymer sample

(This work was done in cooperation with Research group of Prof. Dr. Thomas H. Kissel, Department of Pharmaceutics, Philipps Universität)

This work was carried out in the Research group of Prof. Dr. Thomas H. Kissel, by a former co-worker Dr. Regina Reul. It is always good to know the toxicity of materials before using for various applications such as adhesives or chewing gums. With this aim, the study was done by a calorimetric assay, based on tetrazolium salt MTT (3-(4,5-dimethylthiazole-2-yl)-2,5-diphenyl tetrazolium bromide).[91] The principle behind is that it measures the activity of enzymes that reduce the yellow coloured MTT to purple coloured Formazan in the mitochondria. Toxic materials result in cell toxicity and hence mitochondrial dysfunction. Figure 5.1.16 shows the structures of MTT and Formazan, respectively.



a) MTT b) Formazan

Figure 5.1.16: Structure of: a) MTT(3-(4,5-dimethylthiazole-2-yl)-2,5-diphenyl tetrazolium bromide); b) Purple Formazan

More the amount of Formazan generated, more is the number of active cells, hence lesser is the toxicity of the material under consideration.

Hydrolyzed materials (entry 3 table 5.1.1) were also tested for cytotoxicity studies in L929 cells and compared with that of known and accepted non-toxic materials like poly(ethyleneimine) (figure 5.1.17).

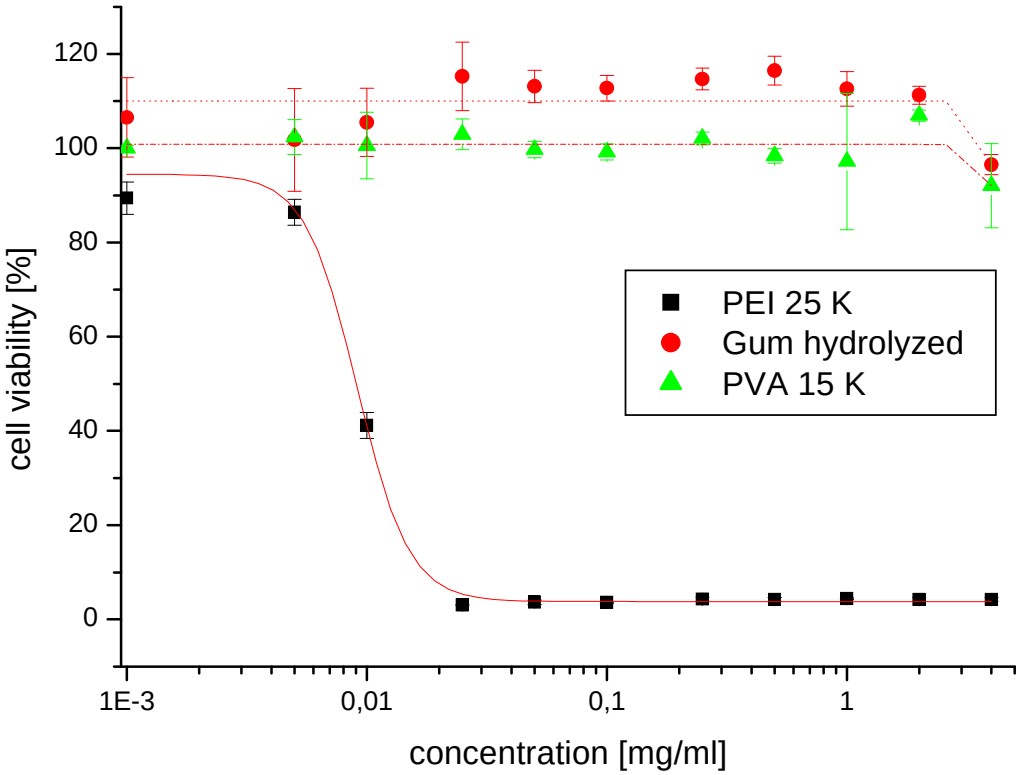


Figure 5.1.17: Cell viability studies for poly(VAC-co-ester) (entry 3 table 5.1.1).

The hydrolysed products were non toxic and showed a cell viability > 95%. Therefore, no IC_{50} (half maximal inhibitory concentration) value could be calculated. PVA was also used as a comparison as PVA is also one of the hydrolysis products. PVA also displayed no cytotoxicity and no IC_{50} value could be calculated. PEI 25 K was used as positive control and showed the typical sigmoidal curve and an IC_{50} value of 0.0091 mg/mL.

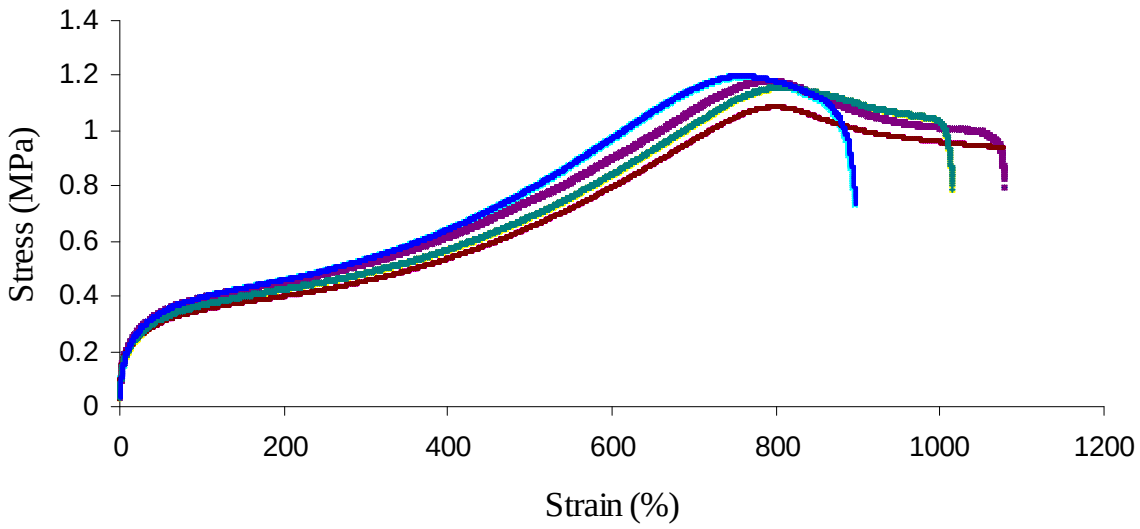
5.1.9 Mechanical Tests

An attempt has also been made to evaluate the mechanical properties of resulting materials, because it is always important to know how strong the materials are and how much stress can they withstand. The new materials having higher ratios of ester linkages i.e ≥ 29 mole% of MDO units in the copolymer had very low glass transition temperatures and, therefore, could not be

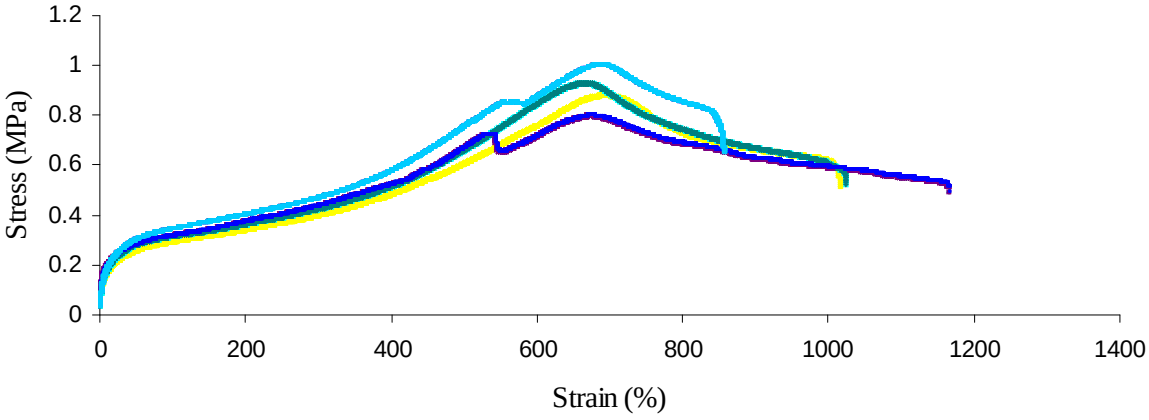
obtained in the film forms for mechanical testing. Mechanical properties of copolymers having low molar ratios of MDO i.e. 5 and 18 mole% have been compared with the homo PVAc (Table 5.1.4). Stress-strain curves of Runs 1, 2 and 3 of Table 5.1.4 are shown in Figure 5.1.18 (a-c).

Table 5.1.4: Mechanical properties of poly(VAc-co-ester)s

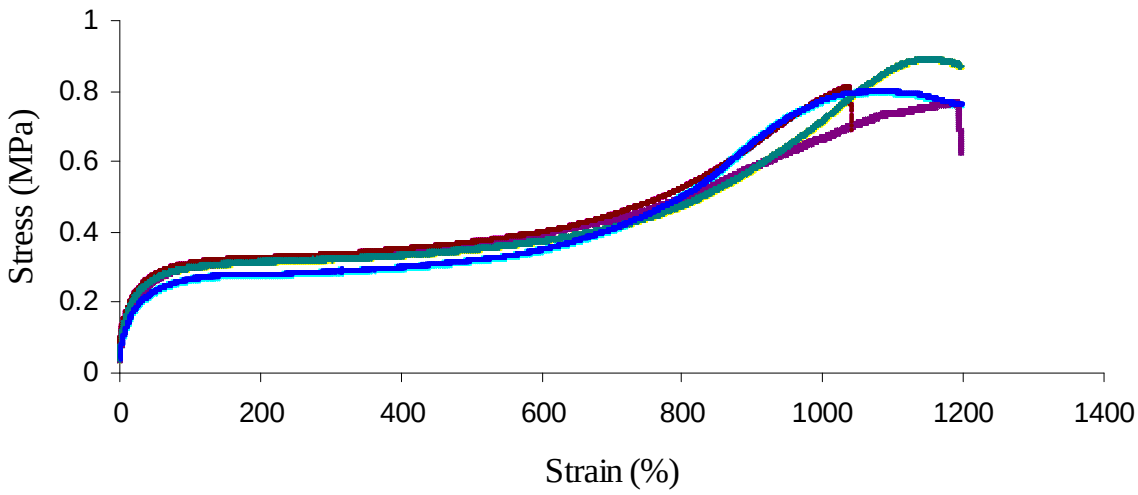
Run	*Copolymer composition MDO : VAc*	*$E_{modulus}$ (stress/strain (GPa))*	*Maximum stress σ_M (MPa)*	*Stress at break σ_B (MPa)*	*Elongation or Strain at break %*
1	0 : 100	0.0065	1.15	0.77	1007
2	5 : 95	0.0051	0.91	0.52	1093
3	18 : 82	0.0029	0.82	0.67	1285


1.4
1.2
1
0.8
0.6
0.4
0.2
0
Stress (MPa)
0
200
400
600
800
1000
1200
Strain (%)

a)


1.2
1
0.8
0.6
0.4
0.2
0
Stress (MPa)
0
200
400
600
800
1000
1200
1400
Strain (%)

b)



c)

Figure 5.1.18: Stress-strain curves of copolymer samples with copolymer composition, MDO : VAc a) 100 : 0 (entry 1, Table 5.1.4); b) 5 : 95 (entry 2, Table 5.1.4); 18 : 82 (entry 3, Table 5.1.4)

The introduction of low mole% of MDO led to significant decrease in modulus and increase in elongation of the polymers which are required for a gum material.

5.1.10 Applications

Due to the characteristic properties of PVAc, it is known to be used for numerous other applications, apart from chewing gums. Some of the recent inventions include : adhesives [92,93], coatings with good ink absorption and surface strength[94], or coatings to build decorative finishing of walls, slopes, ceilings[95], or even as fire retardants[96]. Our materials (P(VAc-co-esters)) when used for these applications, would provide an added advantage of degradability.

5.1.11 Conclusions

The ester units having PCL structure were successfully introduced onto PVAc backbone by ring-opening polymerization of MDO and VAc to make PCL based degradable materials. 1D and 2D

NMR studies gave an insight into the polymer microstructure and shown to have random distribution of ester linkages onto the PVAc backbone. It was possible to control the properties of new materials such as glass transition temperature, viscosity, mechanical properties etc. by controlling the amount of MDO in the copolymers. The polymers were shown to be hydrolytically degradable due to the presence of ester linkage in the backbone and showed large elongations as compared to pure PVAc. The PCL based new materials poly(VAc-co-PCL) showing a combination of hydrolytic degradability and low glass transition temperatures, could be suggested as degradable substitute for chewing gums or other gum applications.

Tulip

Tulipalin A-co-esters

Eco-friendly plastic

5.2 Synthesis of bio-based eco-friendly plastic

R. Kumar, S. Agarwal, "Synthesis of Bio-Based Eco-friendly plastic using polymerization of cyclic ketene acetals with Tulipalin A", *in preparation.*

Poly(α-methylene-γ-butyrolactone) (PMBL), a homopolymer having a bioresource origin, is a very useful polymer due to its interesting properties like: biodegradability, durability, solvent resistance, mechanical strength, and optical clarity. It has a very high glass transition temperature of 195°C. Figure 5.2.1 shows a representative picture of a PMBL film (M_n = 4.3 x 10^4) formed by solvent casting method, by dissolving in DMF.

Figure 5.2.1: A representative picture of a PMBL film (M_n = 4.3 x 10^4) formed by solvent casting method, taking DMF as the solvent.

The monomer, α-methylene-γ-butyrolactone (MBL), is found in common tulips and henceforth is also known as Tulipalin A. The use of MBL, being a naturally-originated monomer, decreases the dependence on finite petroleum resources. But, the need of performance and processability cannot be overlooked for incorporating degradability and renewability, there is a need for a better alternative than merely using a homopolymer of MBL, which has a very high glass transition temperature of 195°C.

In this work, α-MBL is copolymerized with monomers of the cyclic ketene acetal category. Such a combination is expected to have properties similar to PMMA, with an added advantage of being degradable and hence eco-friendly.

5.2.1 Introduction and Requirements

Due to the numerous applications of plastics, like, in packaging industry, in manufacturing of machine spare parts, household products, laboratory equipments, toys, etc., the use of plastics by mankind is rising endlessly day by day. Figure 5.2.2 shows an analysis of world's plastics production for the year 2008, done by Plastics Europe Market Research Group (PEMRG). Europe produced 60 million tonnes and was found out to be a major region contributing about 25% of the global total.[101]

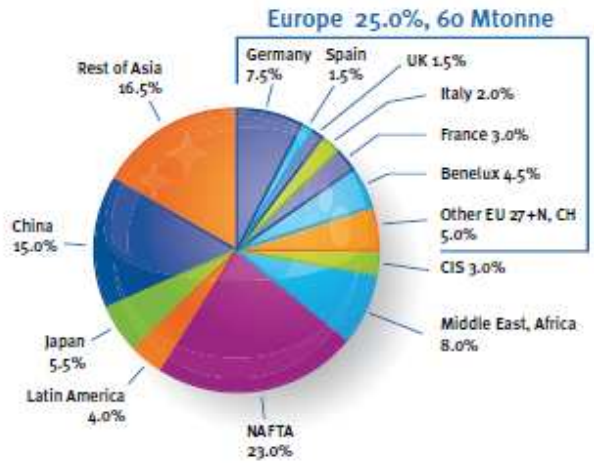


Figure 5.2.2 Worlds plastic production in the year 2008, in various countries and region (source: Plastics Europe Market Research Group-PEMRG).[101]

Being cheap, light weight, strong and easily processable, plastics are a choice of raw materials for most of the industries including packaging, building and construction, automotive and transportation, inks and coatings. Some of the basic properties of plastics include transparency, elasticity, flexibility, electrical and heat resistance, thermal stability, solubility, chemical resistance, etc. Depending upon the end-use requirements, through macromolecular engineering, it is possible to fabricate a material of choice. Likewise, based upon the aim of this project for synthesizing a degradable material, which would not only originate from a natural source, but would have properties similar to PMMA, it was required to use a monomer with similar properties to that of MMA. For this purpose, α-MBL was the chosen monomer, and was copolymerized with various cyclic ketene acetals, to find the best possible combination.

5.2.2 Copolymerization of BMDO and MBL using radical polymerization

Firstly, copolymerization was carried out with 5,6-benzo-2-methylene-1,3-dioxepane (BMDO) and MBL at 120°C, using di-tertiary butylperoxide (dtbp) as initiator, in dimethylformamide (DMF).

BMDO is reported to be extremely sensitive to moisture, hence proper care was taken to carry out reactions in air-free and inert atmosphere. Efforts were also done to study the influence of atmosphere (at 22°C) and water on BMDO under room temperature. It was found to be easily protonated to generate stable cyclic dioxonium ions. These cations are ambident reagents which undergo nucleophilic attack at three possible locations[97].

Figure 5.2.1 shows a representative ^{1}H NMR of BMDO, taken in $CDCl_3$. All possible efforts were taken to avoid any exposure to atmosphere, henceforth the NMR was also measured by sealing the NMR tube under inert gas (Argon). But still, few extra peaks appeared in the spectra. The peak integrations are in agreement with the peak assignments.

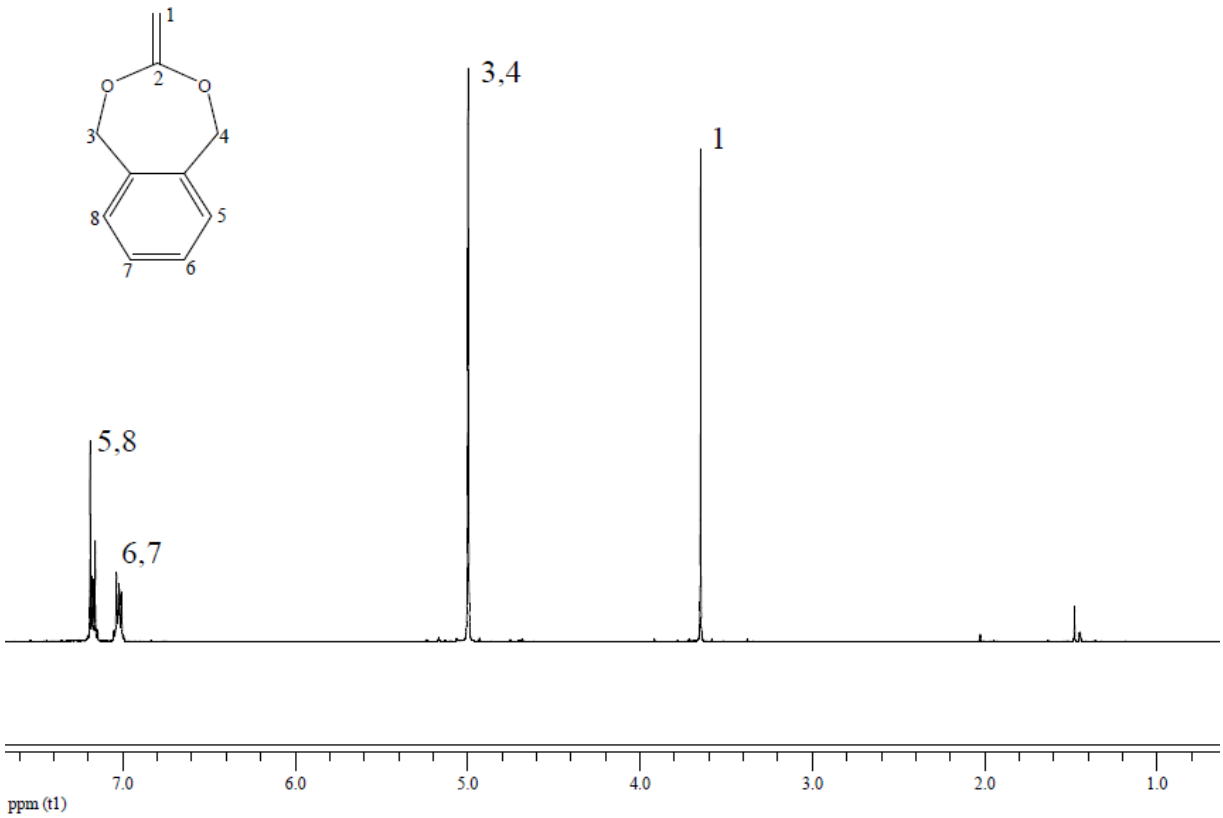
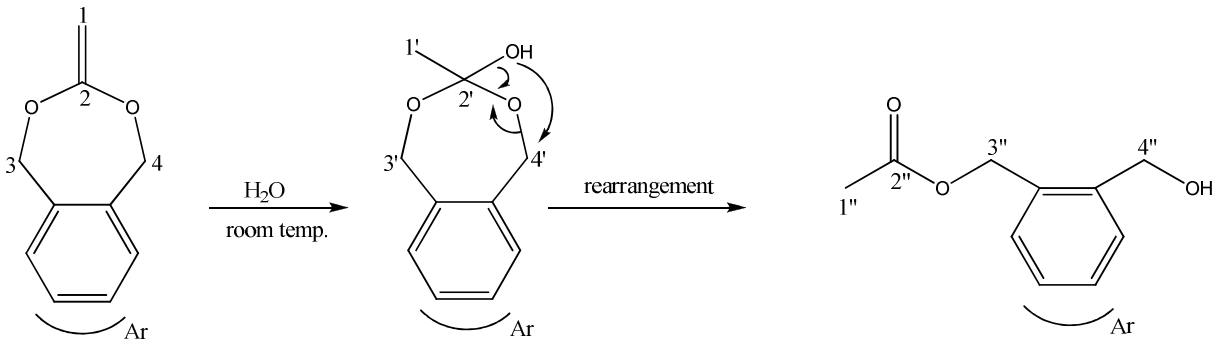


Figure 5.2.1: A representative ^{1}H NMR of 2-methylene-1,3-dioxepane (BMDO), taken in $CDCl_3$.

The two adjacent O-atoms impart nucleophilicity to the double bond, by making it highly electron rich and hence prone to protonation by acidic groups and even water. Previously, it has also been shown in our group, that electrophilic addition by acidic vinylic monomer, methyl acrylic acid (MAA) took place on the nucleophilic double bond of BMDO thereby yielding a new monomer which could further be polymerized via radical polymerization [15]. On a similar basis, effect of moisture was studied, wherein, BMDO was exposed to the atmosphere and after definite intervals of time, it was analysed under ^{1}H NMR to see the structure changes.

The possible reaction taking place is given in Scheme 5.2.1. Firstly, protonation of the double bond occurred due to the moisture present in atmosphere (at 22°C), which gave a structure 3-methyl-1,5-dihydrobenzo-[e][1,3]dioxepin-3-ol (structure B) wherein the cyclic ring was intact. Further, this cyclic structure underwent structural rearrangement to give a product : 2-(hydroxymethyl)benzyl acetate (structure C).



(A) **(B)** **(C)**

Scheme 5.2.1: Reaction of 5,6-benzo-2-methylene-1,3-dioxepane with moisture in air at room temperature (22°C).

This reaction Scheme was confirmed by the presence of characteristic peaks of both B and C, marked as 1' and 1", respectively. ^{1}H NMR measurements were done after every hour. Figure 5.2.2 shows a comparison of ^{1}H NMR spectra of BMDO depicting structural changes due to the formation of B and C, after 10 min, 2 h and 4 h of exposure to atmosphere.

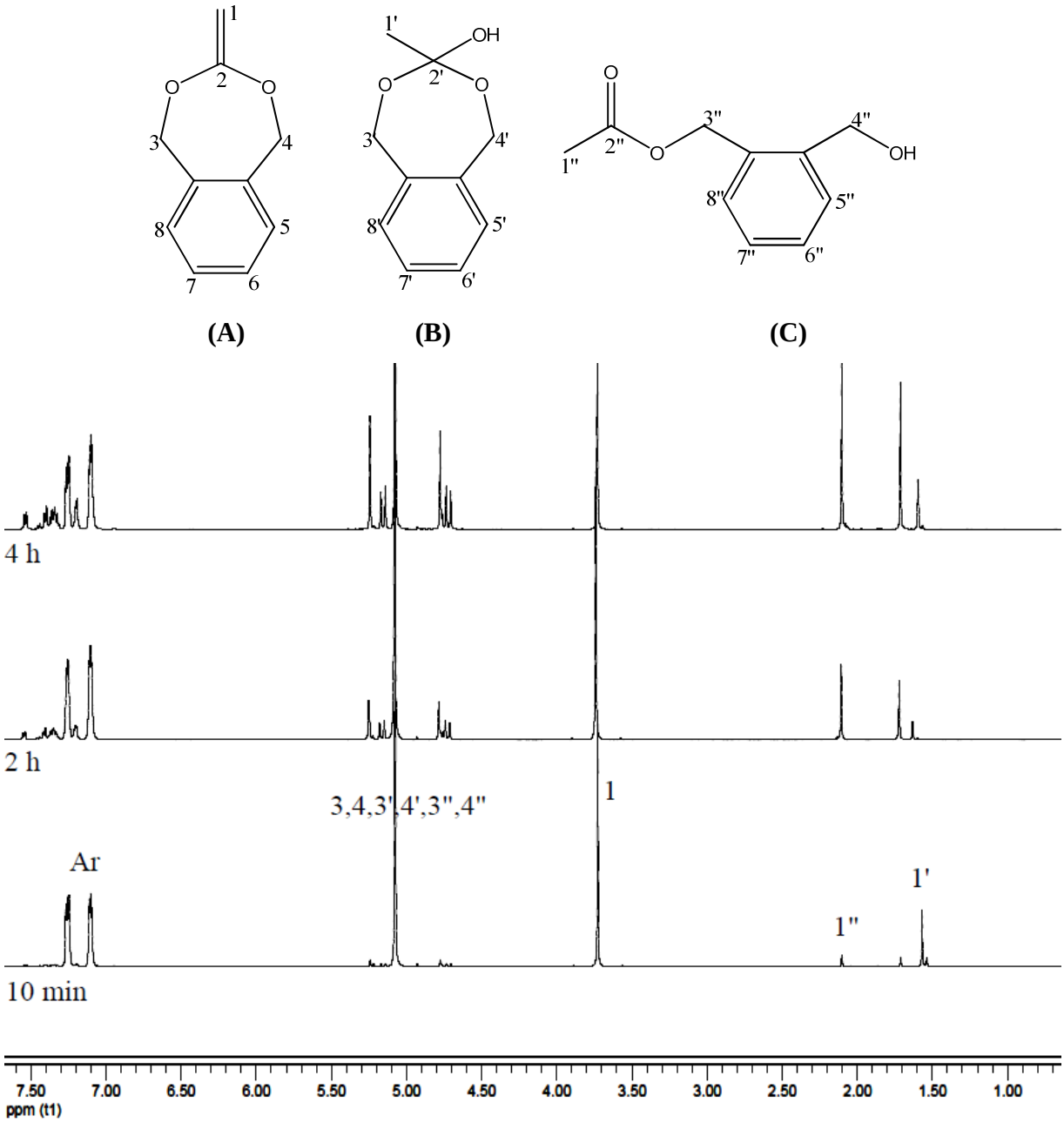


Figure 5.2.2: A comparison of ^{1}H NMR spectra of BMDO depicting structural changes after 10 min, 2h and 4h of exposure to atmosphere.

By integrating the characteristic peaks of BMDO, structure B and C, i.e., peaks due to protons 1, 1' and 1", the molar ratio was calculated. Details are given in Table 5.2.1.

Table 5.2.1: Variation in molar ratio of BMDO, structure B, and structure C, when exposed to atmosphere at room temperature (22°C), with respect to time

Run	*Time*	*Mole percent*		
		BMDO	*Structure B*	*Structure C*
1	10 min	77	18	5
2	1 h	73	17	10
3	2 h	72	14	14
4	3 h	59	21	20
5	4 h	48	48	24

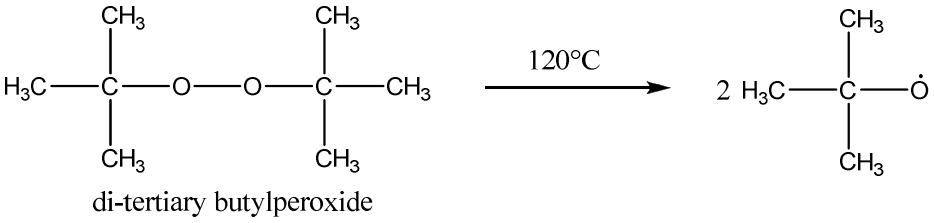
It was found that in 4h, about 48% of BMDO was left and the rest was converted to structure B and C. Similarly, study was done by deliberately mixing water in BMDO at room temperature (Table 5.2.2).

Table 5.2.2: Variation in molar ratio of BMDO, structure B, and structure C, in water, with respect to time

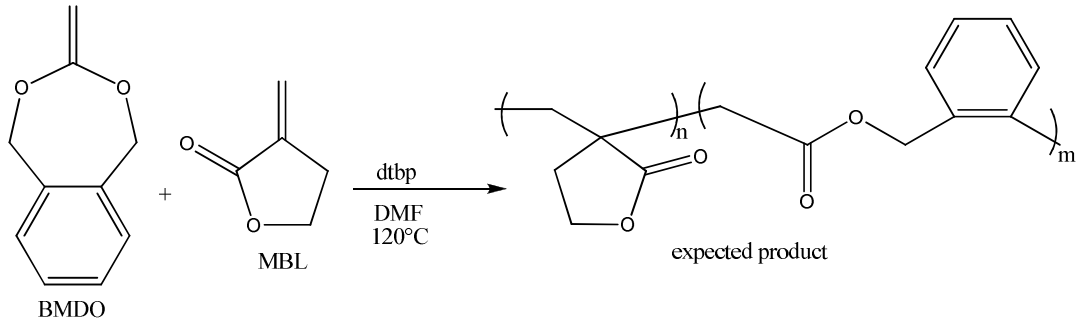
Run	*Time*	*Mole percent*		
		BMDO	*Structure B*	*Structure C*
1	1 h	92	7	1
2	5 h	89	7	4
3	10 h	86	7	7
4	14 h	84	8	8
5	15 h	83	7	10

Therefore, it was observed, that at room temperature, on mixing BMDO with a small amount of water, 83% of it was left after 15h.

After the studies of influence of air and water on BMDO, in order to achieve the target, some preliminary tests were done with this system (BMDO and MBL reaction system). Schemes 5.2.1 and 5.2.2 show the reactions taking place in the reaction system



Scheme 5.2.1 Thermal dissociation of di-tertiary butylperoxide (dtbp) at 120°C



Scheme: 5.2.2 Expected polymerization of 5,6-benzo-2-methylene-1,3-dioxepane (BMDO) with α-methylene-γ-butyrolactone using dtbp

Polymerization of both monomers was successful due to the occurrence of characteristic peaks in ^{1}H NMR, of both the polymerized monomers, in the obtained product. The peak from -$CH_2COOC\underline{H}_2$- protons of BMDO at 5.0 ppm and peak from –$CH_2(C)C(O)OC\underline{H}_2CH_2(C)$- protons of MBL at 4.3 ppm were integrated to find out the copolymer composition. The results with different feed ratios of the monomers can be found in Table 5.2.1.

Table 5.2.1: Copolymerization of 5,6-benzo-2-methylene-1,3-dioxepane (BMDO) and α-methylene-γ-butyrolactone (MBL) in DMF, at 120°C, using dtbp initiator and varying monomer feeds (reaction time = 24 h).

Run	*Feed composition (molar ratio) MBL : BMDO*	*Yield*[a] *(%)*	*Copolymer composition*[b] *(molar ratio) MBL : BMDO*	T_g[c] *(°C)*	M_n[d]	*PDI*
1	10 : 90	11	24 : 76	33	6.1×10^3	1.8
2	20 : 80	31	47 : 53	73	7.2×10^3	1.8
3	50 : 50	72	67 : 33	104	1.1×10^4	1.9
4	80 : 20	81	84 : 16	143	1.4×10^4	2.0
5	90 : 10	66	92 : 08	163	1.7×10^4	2.2
6	100 : 0	82	100 : 0	195	4.3×10^4	2.6

[a]calculated by Gravimetry; [b]calculated by ^{1}H NMR; [c]T_g is the glass transition temperature, determined by DSC; [d]determined by GPC using DMF as eluent, and PMMA as calibrating standard.

Conversion of the polymerization reaction was directly proportional to the feed of MBL. Also, the amount of MBL present in the copolymer was always higher than the amount of BMDO, because of the high reactivity of MBL with respect to BMDO. Still a copolymer with maximum of 76% BMDO was synthesized by using 90% of BMDO in the reaction mixture, but it gave a very low yield of 11% (Table 5.2.1, Run 1). It was also possible to reduce the glass transition temperature from 195°C of PMBL to 33°C (Table 5.2.1, Run 1), due to the incorporation of ester linkages in the polymeric chain. This method can therefore be used to increase the processability of PMBL. With changing the copolymer composition, the thermal stability did not change to a large extent, and the initial degradation temperature (T_i) remained almost the same (320 -

330°C). Also, all the samples were amorphous, which is indicated by the absence of any melting peak in DSC curve. GPC showed uni-modal broad curves.

5.2.3 Modification

There was a need for modification in this system due to the following problems:

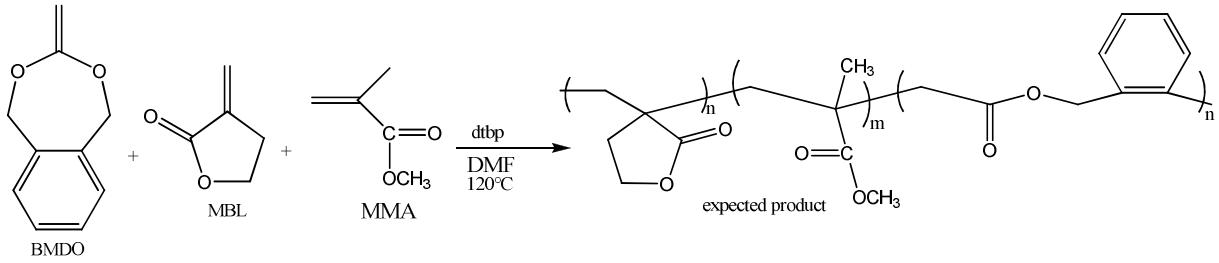
a) With higher ester incorporation (76%), the conversion (11%) and molecular weight (6.1 x 10^3) were low.

b) Because of the low molecular weights (6.1 x 10^3-1.7 x 10^4) obtained, materials were not film formable and hence were bad-processable.

Due to the above stated problems, a new concept was followed, wherein terpolymerization was carried out between BMDO, MBL and MMA.

5.2.4 Terpolymerization of BMDO, MBL, MMA using radical polymerization

The most critical problem in the MBL - BMDO system was the low molecular weight of the obtained polymers. So, an attempt was made to increase it, by adding an additional monomer (MMA) to the system. This monomer was not only expected to increase the molecular weight, but also to improve the mechanical properties.



Scheme 5.2.3: Expected terpolymerization of BMDO with α-MBL and MMA

Here again, polymers were prepared by using constant MMA feed and by varying the amount of the other two (MBL : MMA : BMDO = x : 50 : y). From ^{1}H NMR, it was confirmed that polymerization of all three monomers was taking place. While the characteristic peaks of BMDO

and MBL were clearly distinct, no distinct peak could be observed for MMA (Figure 6.4.3). It overlapped with the peak due to water present in DMSO-d_6 (around 2.9 - 3.0 ppm) and with the peaks due to MBL in 0.3 - 1.8 ppm range, as shown in the representative ^{1}H NMR (Figure 5.2.3).

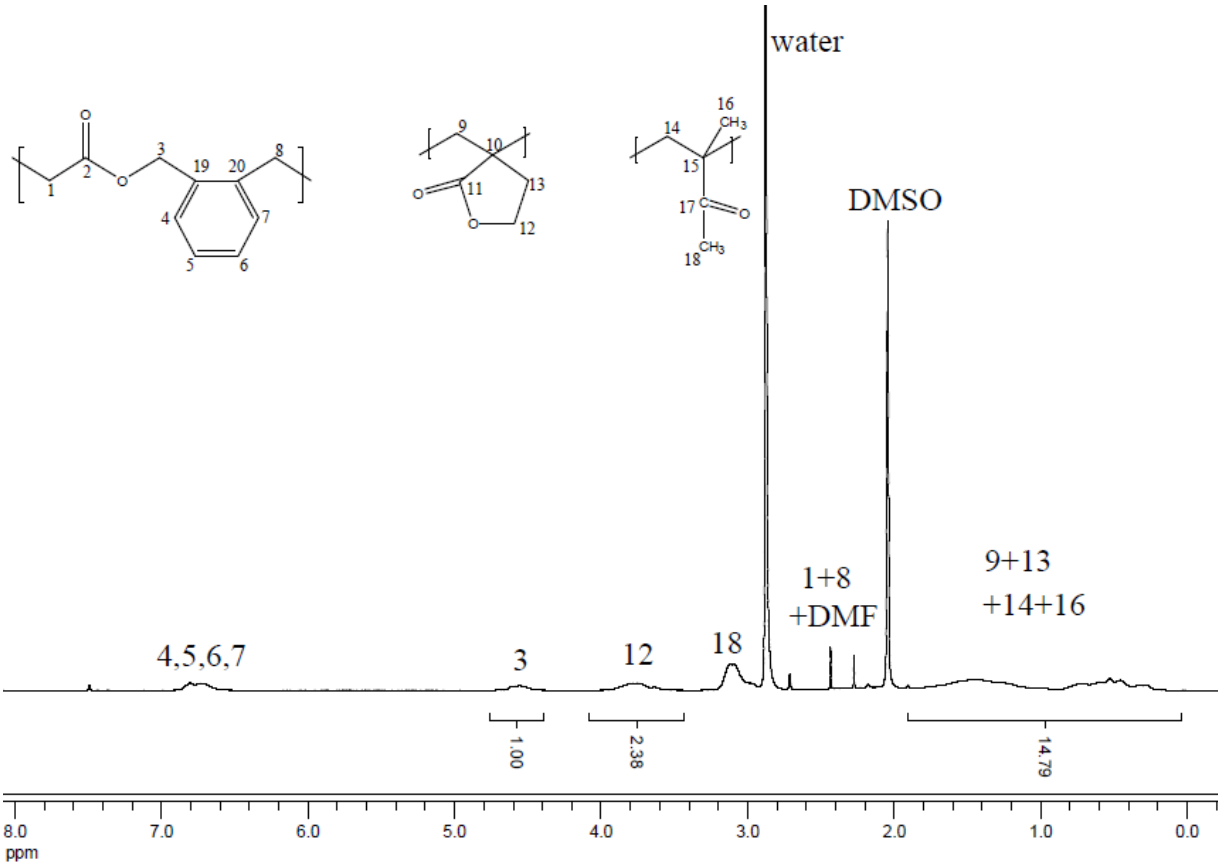


Figure 5.2.3: A representative ^{1}H NMR of Run 2 of Table 5.2.2

Therefore, the copolymer composition was found out indirectly by integrating the region 0.3 - 1.8 ppm and by subtracting the contribution from MBL to get the integrals of the MMA protons, 3.6 - 3.8 ppm to get the integrals of MBL and 4.6 ppm to obtain the integrals of BMDO protons.

A short summary of the observations is tabulated in Table 5.2.2 below.

Table 5.2.2: Terpolymerization of 5,6-benzo-2-methylene-1,3-dioxepane (BMDO), α-methylene-γ-butyrolactone (α-MBL), and methyl methacrylate (MMA) in DMF, at 120°C, using dtbp initiator and varying monomer feeds (reaction time = 24h).

Run	*Monomer feed*	*Yield*	M_n	*Copolymer composition*	T_g
	MMA : MBL : BMDO	*(%)*		*MMA : MBL : BMDO*	*(°C)*
1	50 : 40 : 10	95	4.6×10^4	38 : 51 : 11	$T_{g1} = 70$
					$T_{g2} = 141$
2	50 : 25 : 25	83	3.1×10^4	54 : 32 : 14	$T_{g1} = 64$
					$T_{g2} = 109$
3	50 : 20 : 30	82	2.4×10^4	59 : 25 : 16	$T_{g1} = 49$
					$T_{g2} = 102$
4	50 : 10 : 40	82	2.1×10^4	70 : 10 : 20	$T_{g1} = 50$

Terpolymers with high yield were formed, with moderate molecular weights (in the range of 10^4). But still the incorporation of ester units was not as desired. Also, the appearance of two glass transition temperatures indicated the presence of two different type of species present in the system. But, before going into much detail of the microstructure, it was important to test the processability. For this, efforts were done to prepare films of Runs 1 and 2 of Table 5.2.2 by using compression moulding machine (processing temperature was 250°C). But, the films could not be formed.

Since out of all the common solvents, the materials were found to be soluble only in DMF and DMSO, the next step was to test the ability of materials to be film-formable via solvent casting. For this, Runs 1 and 2 (Table 5.2.2) were dissolved in minimum amount of DMF, and a solution having honey-like consistency was made. It was then poured on a glass petri dish, and the

solvent was allowed to evaporate slowly, under constant heat by bulbs (Apparatus is shown in section 6.3.1).

The films were formed, but were turbid and extremely brittle and were therefore impossible to be handled.

5.2.5 Modification

No doubt that adding MMA to the original reaction system, increased the molecular weight to a large extent (from a maximum of 1.7 x 10^4 obtained in the first system to a maximum of 4.6 x 10^4 in the second system), but still there were some problems which had to be overcome:

a) Limited ester incorporation, and hence poor solubility (only in DMF and DMSO)

b) Extremely brittle materials

Further, the cyclic ketene acetal BMDO was substituted with another monomer of this category i.e. 2-methylene-1,3-dioxepane (MDO). Such a replacement would also lead to an added advantage of biodegradability, since polycaprolactone formed from ring-opening polymerization of MDO is reported to be biodegradable since long.[102]

5.2.6 Spontaneous Copolymerization of MDO and MBL

The copolymerization of a cyclic ketene acetal, MDO, with the naturally occurring monomer vis-à-vis α-methylene-γ-butyrolactone (MBL), was carried out with the same aim of obtaining a degradable polymer with high glass transition temperature. Surprisingly, the two monomers reacted even in the absence of any radical initiator at 70°C and above, to form high molecular weight materials.

In this work, for the very first time, a mixed type of reaction mechanism initiated by charge transfer between electrophilic butyrolactone moiety and nucleophilic cyclic ketene acetal moiety, following radical and zwitter ionic mechanism is presented.

5.2.6.1 Influence of temperature on spontaneous copolymerization between MDO and MBL

During the copolymerization studies, surprisingly, the two monomers reacted even in the absence of any radical initiator at 70°C and above. For a 50 : 50 monomer feed ratio (α-MBL : MDO) without any initiator, no reaction took place when heated upto 60°C, whereas white powders of very high molecular weights (M_n = 2.6 x 10^5 and 7.9 x 10^4 for spontaneous polymerizations at 70 and 120°C, respectively) were obtained at higher temperatures like 70°C and 120°C. Figure 5.2.4 shows comparison of GPC elugrams of the two samples. Details are summarized in Table 5.2.3.

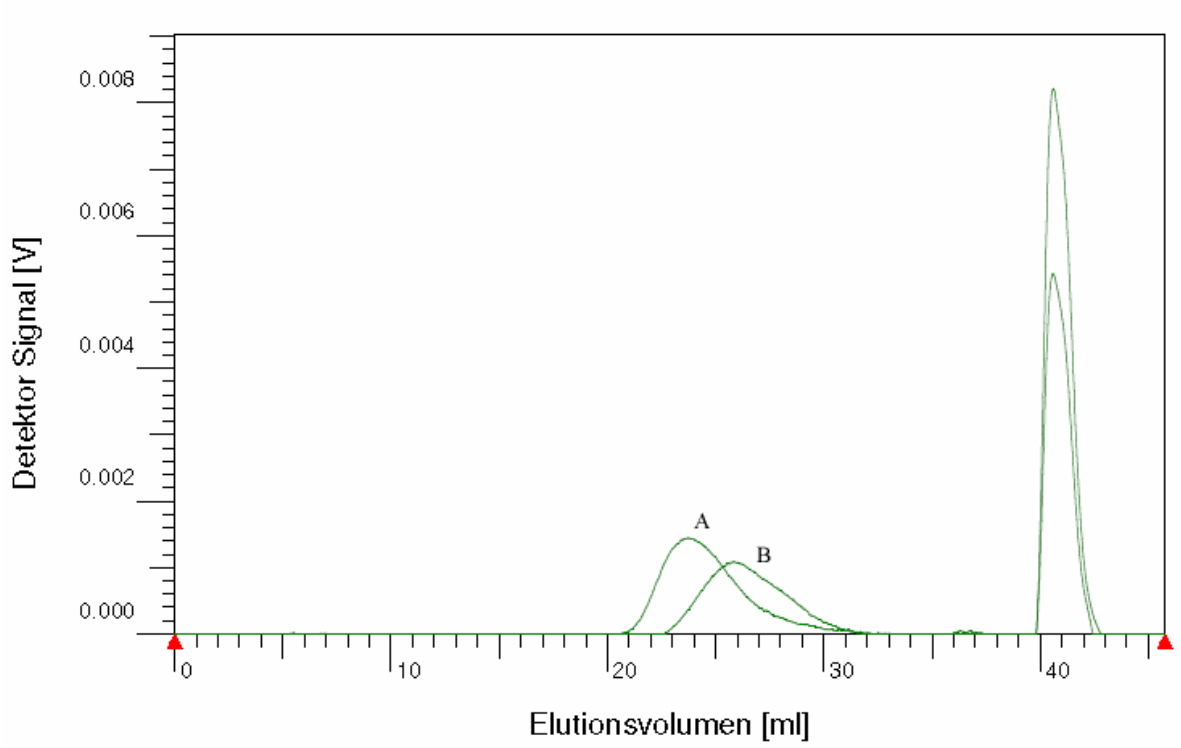


Figure 5.2.4: GPC traces of MBL-MDO polymers differentiating elugrams of two samples (A: Table 5.2.3, Run 5; B: Table 5.2.3, Run 4).

Table 5.2.3: Spontaneous copolymerization of 2-methylene-1,3-dioxepane (MDO) and α-methylene-γ-butyrolactone (MBL) at varying temperatures, in bulk, without any initiator and using monomer feed 50 : 50 (reaction time = 24 h).

Run	*Temp. (°C)*	*Yield (%)*	*Copolymer composition* *MBL : MDO*	T_g [a] *(°C)*	M_n	*PDI*	*Ring retained MDO %*
1	Room temperature	Nil					
2	50	Nil					
3	60	Nil					
4	70	43	75 : 25	T_{g1} = 145 T_{g2} = 189	2.6 x 10^5	2.4	53
5	120	52	71 : 29	T_g = 118	7.9 x 10^4	2.8	28

[a] In DSC, heating and cooling cycles were performed in the range -120°C to 180°C at 20°C/min rate. T_g were noted from second heating cycles.

Some blank experiments (homopolzmerizations) were carried out at 70 and 120°C to rule out the possibility of thermal self polymerization of the monomers. For the blank reaction, the viscosity of the reaction systems remained apparently unchanged even after 24h, and on adding it to methanol (the precipitating solvent), no product was obtained. The polymers obtained at 70°C and 120°C were analyzed by NMR spectroscopy.

5.2.6.2 Structure Characterization

A representative ^{1}H NMR is given in Figure 5.2.5 (Table 5.2.3, Run 4 and 5), wherein the spectra obtained from Run 4 (70°C) and Run 5 (120°C) are compared.

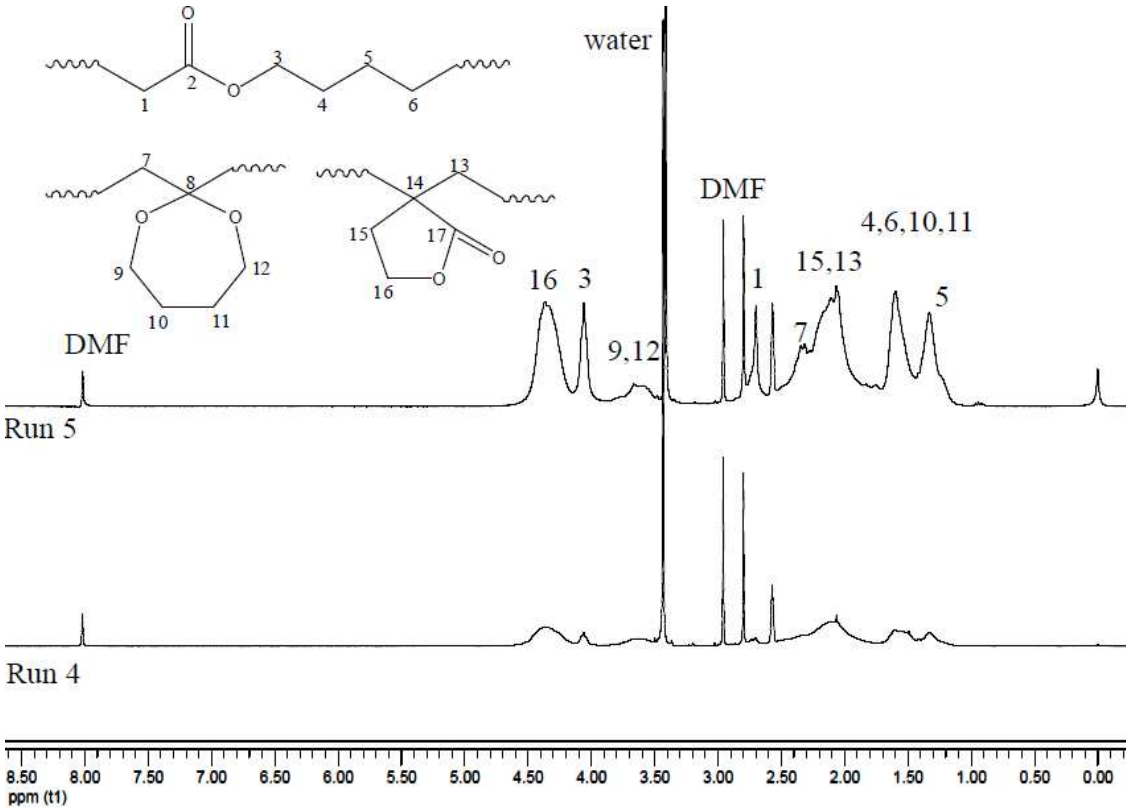


Figure 5.2.5: ^{1}H NMR Spectrum of poly(MBL-co-MDO) (Table 5.2.3, Run 4 and 5), in DMSO-d_6 as solvent, at 70°C.

The NMR was taken in DMSO-d_6 at 70°C to get a better resolution of the peaks. The presence of characteristic peaks of MDO and α-MBL in all the samples were seen in the NMRs. Protons –CH_2(C)C(O)OC$\underline{H}_2$$CH_2$(C)- of MBL were observed at 4.3 ppm, while –C$\underline{H}_2$(C)C(O)OCH_2CH_2(C)- and -CH_2(C)C(O)OCH_2C$\underline{H}_2$(C)- were found in the region 1.9 ppm - 2.2 ppm. Protons –C$\underline{H}_2$C(O)OCH_2- and –CH_2-C(O)OC$\underline{H}_2$- of ring opened MDO appeared at 2.6 ppm and 4.0 ppm, respectively, while protons –CH_2C(O)OCH_2CH_2C$\underline{H}_2$$CH_2$- of ring opened MDO were found in the region 1.1 ppm - 1.3 ppm. The peaks due to –CH_2C(O)OCH_2C$\underline{H}_2$$CH_2C\underline{H}_2$- of the acyclic MDO and peaks due to –CH_2(C)OCH_2C$\underline{H}_2$C$\underline{H}_2$$CH_2$O(C)- of the cyclic MDO overlapped in the region 1.3 ppm - 1.6 ppm. Finally, the peaks of –C$\underline{H}_2$(C)O$CH_2CH_2CH_2CH_2$O(C)- and –CH_2(C)OC$\underline{H}_2$$CH_2CH_2C\underline{H}_2$O(C)- protons of the ring-retained MDO were seen at 2.3 ppm and 3.5 ppm - 3.6 ppm. The ^{13}C NMR also showed the presence of ring retained structure (quaternary carbon –CH_2(C)O$CH_2CH_2CH_2CH_2$O(C)-) by the presence of peak at 102 ppm.[11] A representative ^{13}C NMR is given in Figure 5.2.6 (Table 5.2.3, Run 4).

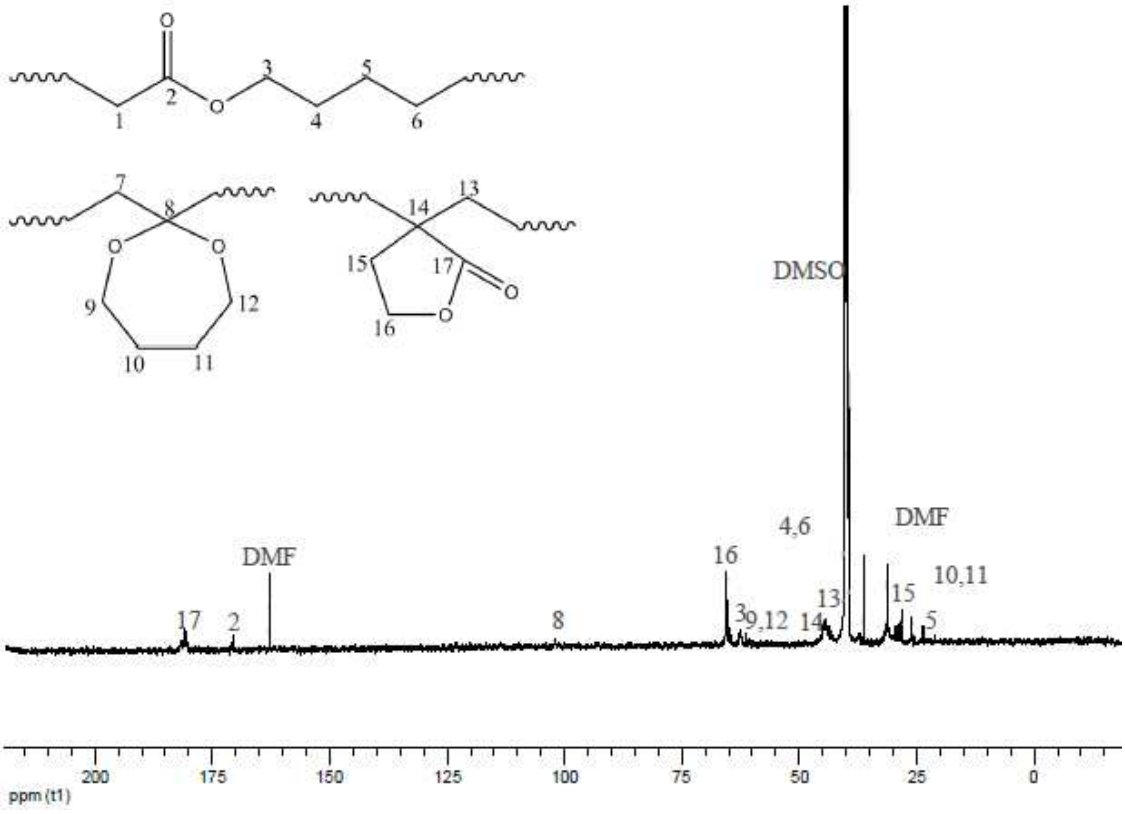


Figure 5.2.6. ^{13}C NMR spectra in DMSO-d_6 (Table 5.2.3, Run 4).

2D NMR (HMQC) was used to provide definite ^{13}C NMR peak assignments (Figure 5.2.7, Table 5.2.3, Run 4).

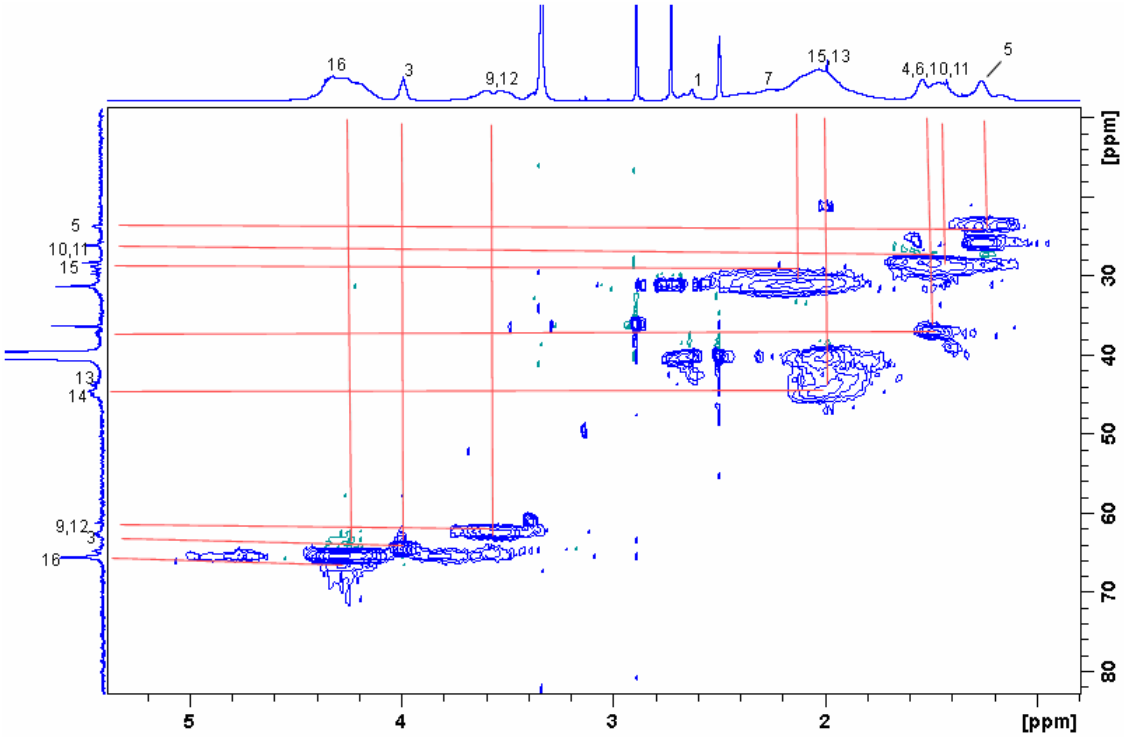
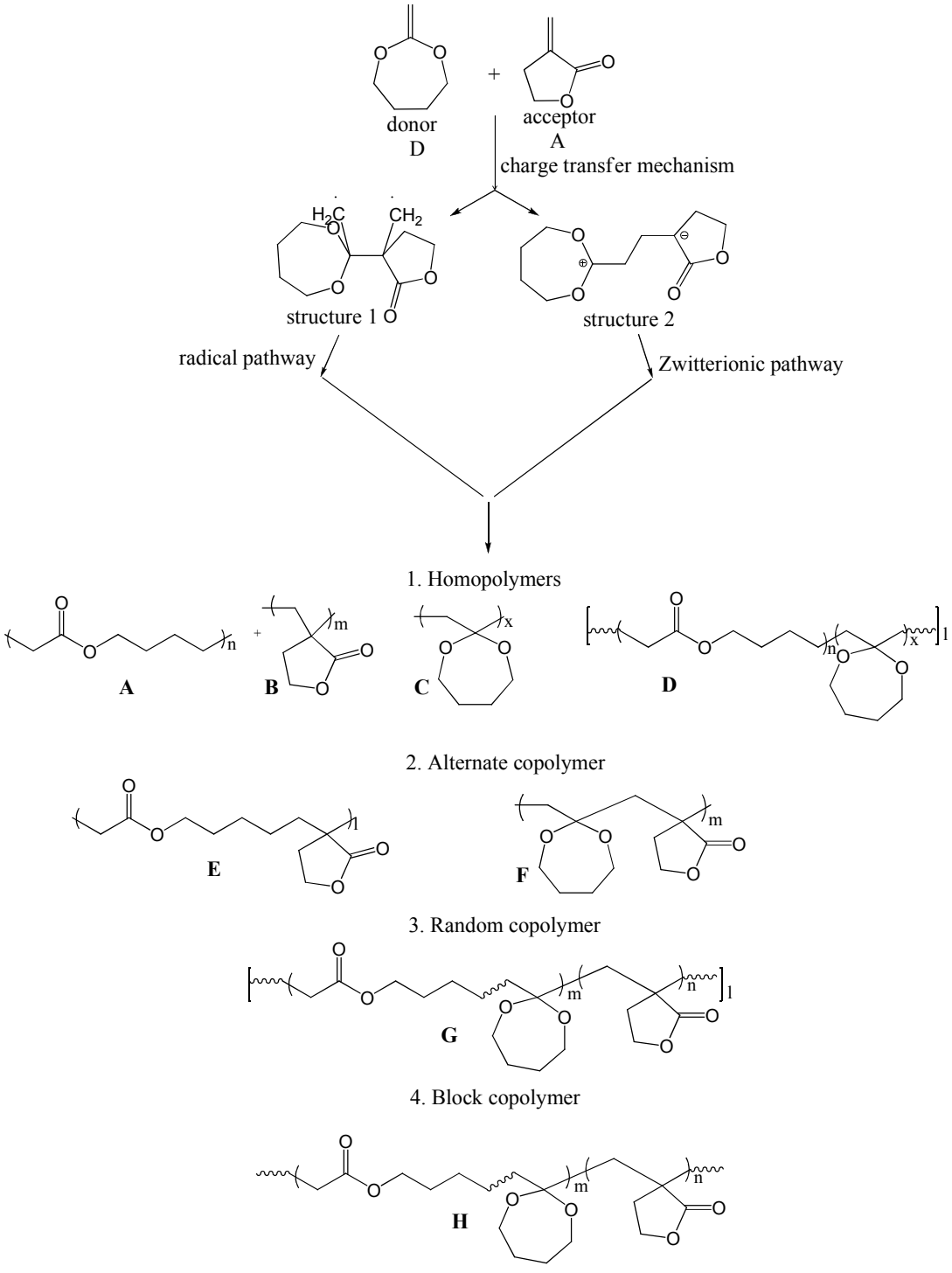


Figure 5.2.7. A part of 2D HMQC (heteronuclear multiple quantum correlation) NMR spectrum (Table 5.2.3, Run 4), in DMSO-d_6 solvent.

The copolymer composition and the ratio of ring-open and ring-retained structures was calculated using ^{1}H NMR. The –CH_2-C(O)O$C\underline{H}_2$- protons of ring-opened MDO at 4.0 ppm, the –CH_2(C)C(O)O$C\underline{H}_2CH_2$(C)- protons of MBL at 4.3 ppm, and –CH_2(C)O$C\underline{H}_2CH_2CH_2C\underline{H}_2$O(C)- protons of ring retained MDO around 3.5 ppm - 3.6 ppm were considered as characteristic peaks and their integrals were compared to calculate the copolymer composition. A small error in calculation of copolymer composition is acceptable due to the inherent experimental error in integration. With increase in temperature, the copolymer conversion did not vary much (from 43% to 52%) (Table 5.2.3, Runs 4 and 5) and the copolymers contained more MBL units with the ratio of MBL : MDO around 75 : 25. Further from Table 5.2.3, another point to be considered is that the percentage of ring retained cyclic ketene acetal structures decreased with increase in temperature. Such variation encouraged me to explore the mechanism and microstructure of the formed polymers at these temperatures.

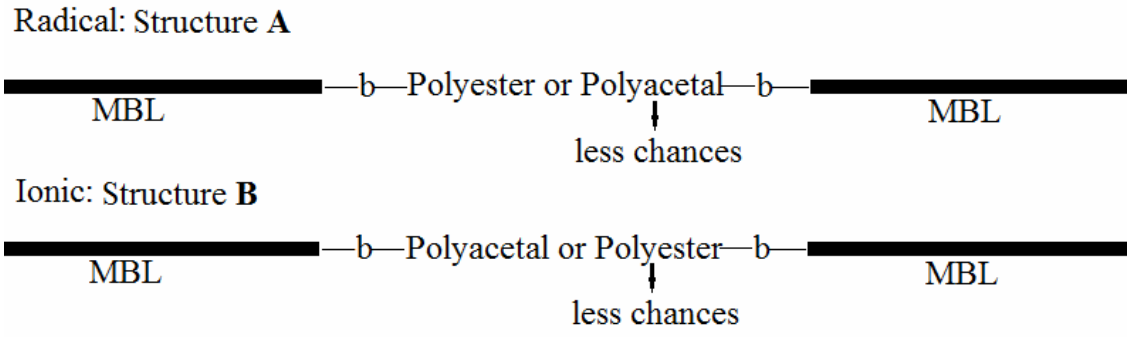
5.2.6.3 Mechanistic study of spontaneous copolymerization between MDO and MBL

As already stated, there was no thermal polymerization of the two monomers MDO and MBL observed, charge transfer polymerization seems to occur in the reaction system under consideration. Our system has nucleophilic double bond of MDO and electrophilic double bond of MBL. The charge transfer would lead to the formation of intermediates i.e. diradical or di-ion (Scheme 5.2.4, structure 1 and 2).



Scheme 5.2.4. Expected copolymerization routes of MBL and MDO at 70°C and 120°C, via charge transfer mechanism.

The further polymerization, via radical pathway or zwitterionic pathway could lead to various possibilities due to the combination of MBL, ring-opened MDO and ring-retained MDO, as mentioned in Scheme 5.2.4, to yield homopolymers (**A**-**D**: Scheme 5.2.4), or alternate (**E**, **F**), random (**G**) or block (**H**) copolymers. Although, radical polymerization of MDO is known to give complete (100%) ring-opening polymerization (ROP)[23] with vinyl monomers like methyl methacrylate (MMA), vinyl acetate (VAc), etc., but still it is not adequate to rule out the formation of ring-retained structures of MDO here due to the extremely high reactivity of its comonomer[60] in comparison to it. Due to the highly reactive MBL, chances are there, though less, that MDO would not get enough time to give quantitative ring-opening polymerization. Further, MBL is known to get polymerized via anionic polymerization[60] and MDO by cationic polymerization[98,99] to give both ring-opening (to give polyesters) and ring-retaining (to give polyacetals) polymerization, though ring-retaining is the more preferred one. The possibilities of formation of homopolymers can be ruled out easily because the glass transition temperature of the obtained polymers matches with neither of the homopolymers (**A**-**D**: Scheme 5.2.4)[60,102]. Further, a polycombination of either of the two intermediates (Structure 1 and 2, Scheme 5.2.4) would lead to the formation of an alternate copolymer with copolymer composition 50 : 50. Therefore, the copolymer composition of 75 : 25 (MBL : MDO) for our system rules out the formation of alternate copolymer structures (**E** or **F**: Scheme 5.2.4). The other possibilities as shown in the Scheme are the formation of either random or block copolymer of MBL and MDO (with the possibility of both ring-opened and ring-retained structures). The present system led to a blocky-random structure by the combination of radical and ionic mechanism (Scheme 5.2.5), wherein the sizes of blocks varied depending upon reaction conditions.



Scheme 5.2.5. Blocky-random structures via radical (leading to structure **A**) and ionic mechanism (leading to structure **B**)

At 70°C, two glass transition temperatures were seen. This confirms the presence of two types of species, where T_g ~ 189°C could be due to the blocky-random structure (close to the T_g of homoMBL ~ 195°C) giving a rigid structure containing mostly cyclic units (**B**: Scheme 5.2.5), and T_g ~ 145°C could be due to blocky-random structure obtained by radical mechanism, wherein ester linkages in the polymer backbone includes flexibility and the segments become mobile, thus leading to decrease in glass transition temperature. The sharp carbonyl peak of MDO in ^{13}C NMR (Figure 5.2.6) at 171 ppm suggests the presence of single MDO units between blocks of MBL, whereas the splitting in carbonyl peak of MBL at 181 ppm suggest the presence of different type of MBL units in the copolymer (i.e. linking and non-linking MBLs giving MBL-MDO, MBL-MBL and MDO-MBL types of diads).

2D NMR (HMBC) was used to find out the exact microstructure of the copolymer. From the 2D NMR (HMBC), (Figure 5.2.8, Table 5.2.3, Run 4), it can be seen that at point A, the carbonyl carbon of MBL in ^{13}C NMR at 181 ppm correlates with the –C$\underline{H}_2$C(O)OCH$_2$CH$_2$CH$_2$CH$_2$- protons of the caprolactone units formed via its ring opening in the ^{1}H NMR at 2.6 ppm. Another correlation that links the two monomers can be seen in the figure, at position B. This shows the correlation of carbonyl carbon of caprolactone unit in ^{13}C NMR at 171 ppm with that of –C$\underline{H}_2$(C)C(O)OCH$_2$CH$_2$(C)- protons of MBL in ^{1}H NMR around 2 ppm. Hence it can be very well concluded that MBL correlates with the caprolactone unit formed from ring opening polymerization of MDO confirming the formation of a copolymer of MBL with MDO with ring-opened structures. No correlation of quaternary carbon of ring-retained MDO structure at 102 ppm could be seen with either MBL or with ring-opened MDO unit, or even with itself. This is attributed to the very weak

signal at 102 ppm, and hence due to sensitivity of resolution, the correlation was not distinctly visible.

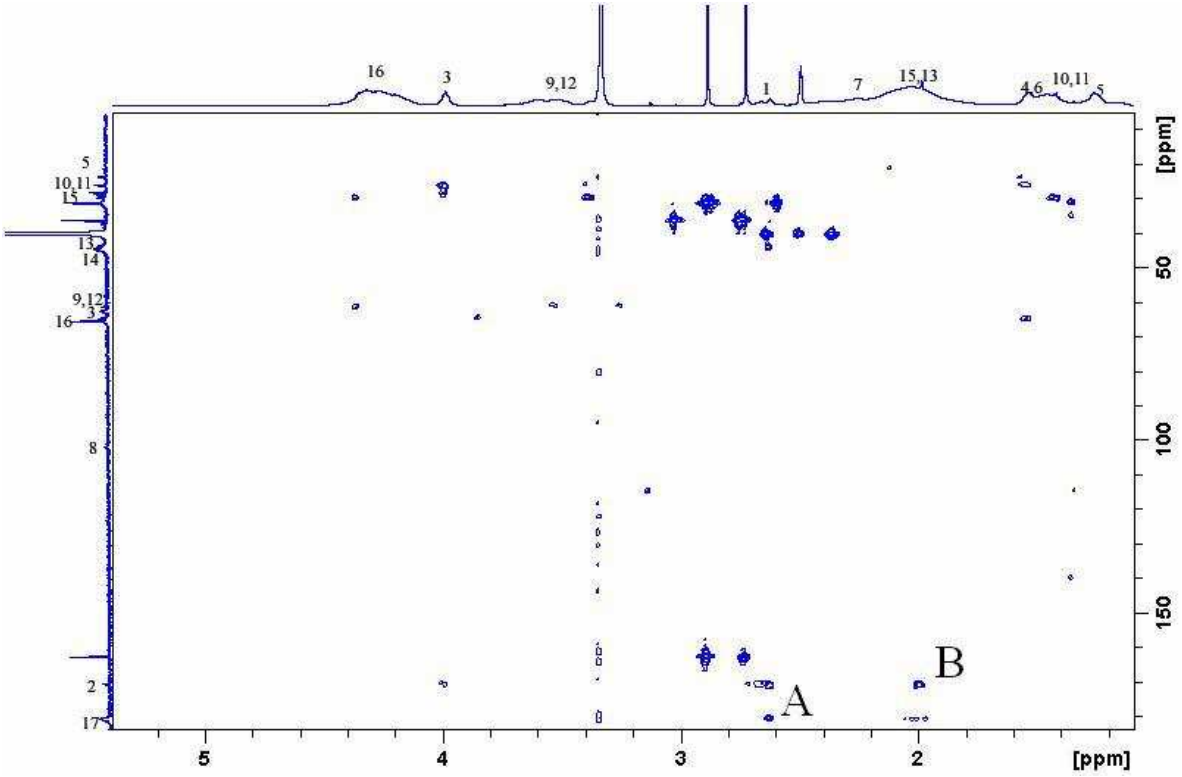


Figure 5.2.8. A part of HMBC (heteronuclear multiple bond correlation) NMR spectrum (Table 5.2.3, Run 4), in DMSO-d_6 solvent.

When spontaneous reaction without any initiator was carried out at higher temperature of 120°C, one T_g disappeared. Figure 5.2.9 shows the comparison of DSC plots of Runs 4 and 5 of Table 5.2.8 at 70°C and 120°C, respectively.

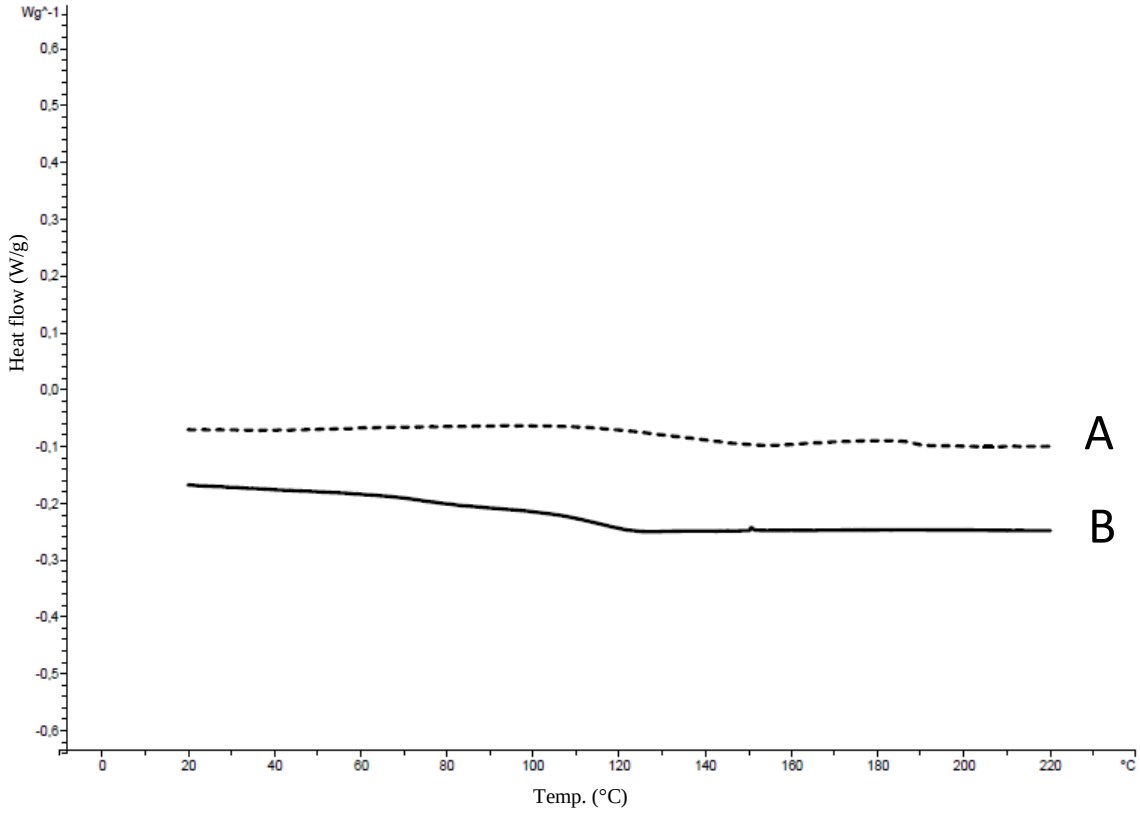


Figure 5.2.9. DSC plots: Curve A (Table 5.2.3, Run 4), Curve B (Table 5.2.3, Run 5).

The disappearance of the higher T_{g2} and the much more lowering of T_{g1} indicated the preference of reaction to proceed via radical pathway with much more incorporation of polyester units, than at 70°C. This was also confirmed by copolymer composition (calculated by ^{1}H NMR) which gave 53% of ring retained structures of MDO at 70°C, while 28% at 120°C (Table 5.2.3, Runs 4 and 5). Also, much lower molecular weight (7.9×10^{4}) at 120°C than at 70°C (2.6×10^{5}) point towards radical mechanism. The blocky random structure became more random with increase in temperature, which was clearly observed by comparing the carbonyl peaks of both reactions (Table 5.2.3, Runs 4 and 5) in ^{13}C NMR (Figure 5.2.10).

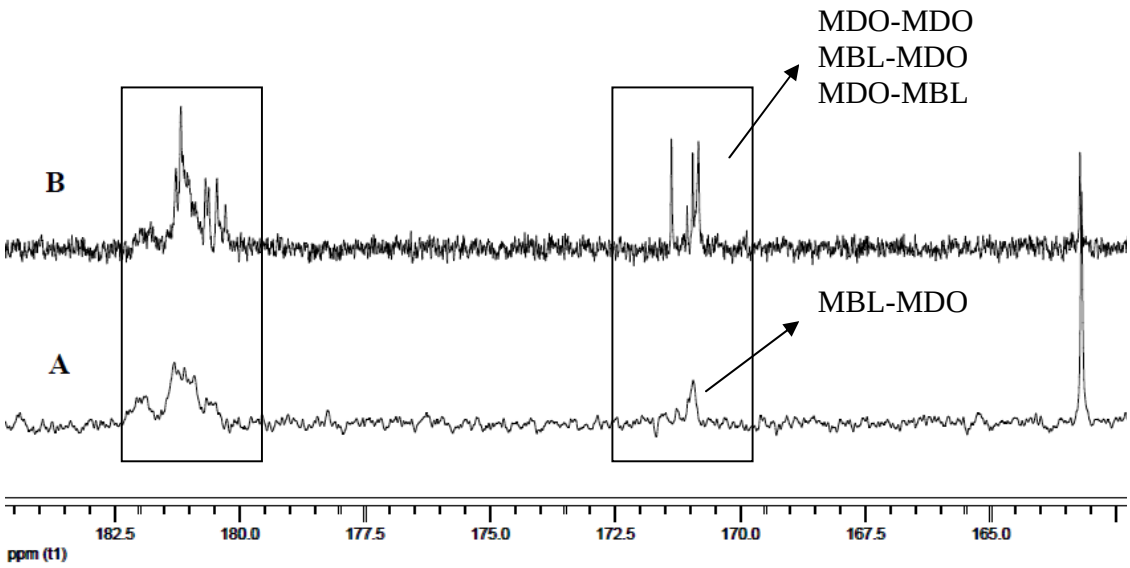


Figure 5.2.10. Comparison of a part of ^{13}C NMR (160 - 185 ppm) : A: Run 4, Table 5.2.3; B: Run 5, Table 5.2.3.

At 70°C, as already stated, the structure seemed to contain big blocks of MBL, having small unit of MDO in between, which corresponded to a single peak at 171 ppm (A: Figure 5.2.10), while more and more MDO units start to join together at 120°C, forming bigger blocks in between that of MBL blocks, which is evident from B:Figure 5.2.10, wherein several peaks can be seen between 171-171.5 ppm. Likewise, the increase in number of splitting in carbonyl peak of MBL at 181 ppm with increase in temperature further confirm the fact.

5.2.6.4 Evidence to prove mixed-mechanism following both Radical and Zwitter ionic pathway

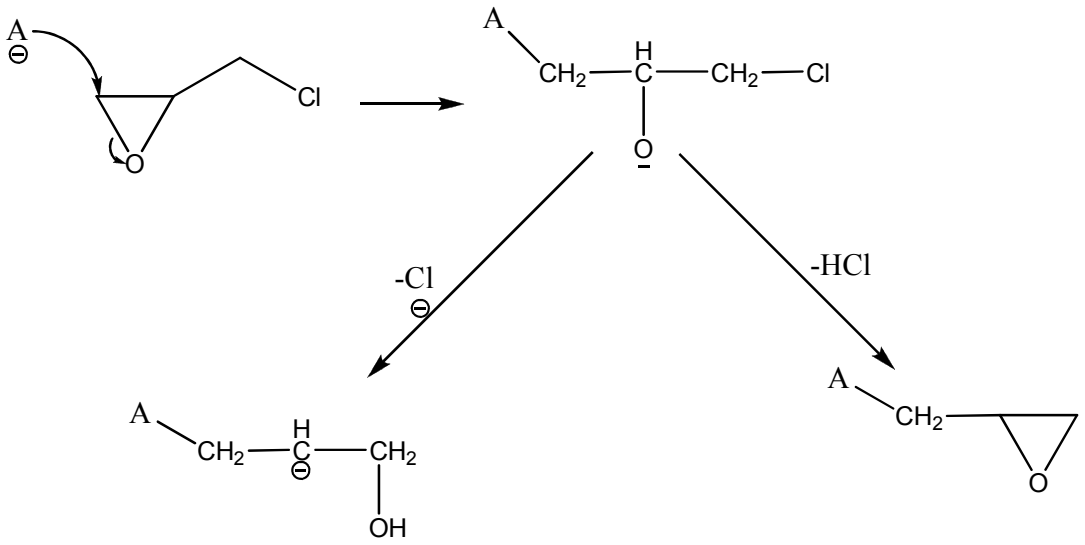
In order to prove that both pathways (radical and ionic) were running parallel, some experiments were done with 50:50 monomer feed (MBL:MDO) in presence of a pinch of hydroquinone (9.2 mg) which is a radical trapping agent, and in presence of dtbp/AIBN (1 mol-%), which are radical initiators. These reactions were done at both temperatures (Details can be seen in Table 5.2.4).

Table 5.2.4: Comparison of copolymerization reaction of 2-methylene-1,3-dioxepane (MDO) and α-methylene-γ-butyrolactone (α-MBL) at 70 and 120°C in presence of inhibitor or initiator (monomer feed: MBL : MDO = 50 : 50; reaction time = 24 h) .

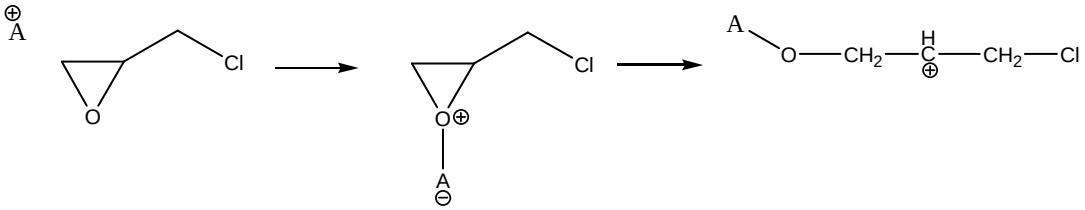
Run	*Temp. (°C)*	*Inhibitor/ Initiator*	*Yield (%)*	*Copolymer composition* *MBL : MDO*	M_n	T_g *(°C)*	*MDO (% ring retained)*
1	70	Hydroquinone	71	66 : 34	2.6×10^5	168	44
2	120	Hydroquinone	60	74 : 26	8.1×10^4	107	27
3	70	AIBN	87	75 : 25	8.0×10^4	136	35
4	120	dtbp	72	66 : 34	4.0×10^4	112	10

If the reaction pathway would have been only via radicals, then no polymer should have been obtained in presence of radical trapping agent, hydroquinone. But actually, the reaction did take place, and that too with a higher conversion and increased molecular weight (Comparing Runs 4 and 5 of Table 5.2.3 with Runs 1 and 2 of Table 5.2.4, respectively). This happened, because hydroquinone trapped all the radicals of the system, thereby forcing the reaction to now proceed via ionic mechanism. Likewise, considering reactions in presence and absence of initiators (Runs 4 and 5 of Table 5.2.3 with Runs 3 and 4 of Table 5.2.4, respectively), it can be seen that the conversion increased drastically due to the presence of radical initiators, whereas the molecular weight decreased drastically. This also correlates with the above stated fact because now the radical initiator favored the radical polymerization over ionic polymerization. The highest molecular weight obtained in case of HQ-reaction and the lowest obtained in case of initiator-reaction further confirmed the same.

Furthermore, epicholorohydrin (ECH), does not polymerize under radical chain mechanism, but only polymerizes under ionic mechanism. Its reaction in presence of charged species is expected to be as given in Scheme 5.2.6[41].



Whereas in presence of a cation, it polymerizes as:



Scheme 5.2.6: Expected copolymerization route of Epichlorohydrin in presence of ions.

If the reaction system under consideration, underwent ionic mechanism also, it was important to analyze and prove that it followed any of the above given pathway, in presence of epichlorohydrin, and therefore, there should be incorporation of extra molecules in the polymeric

chain. To prove this, two sets of reactions were carried out under similar reaction conditions, using 1 : 1 : 1 monomer feed of MBL : MDO : ECH. Refer Table 5.2.5 for details.

Table 5.2.5: Copolymerization reaction of 2-methylene-1,3-dioxepane (MDO) and α-methylene-γ-butyrolactone (α-MBL) at 70 and 120°C in presence of epichlorohydrin (ECH) (monomer feed: MBL : MDO : ECH = 1 : 1 : 1; reaction time = 24 h) .

Run	***Temp.***	***Elemental analysis (%)***			***Yield***	***Mn***
	(°C)	**C**	**H**	**Cl**	***%***	
1	70	60.6	6.0	0.6	10	2.6×10^5
2	120	60.2	7.2	0.42	36	4.2×10^4

With elemental analysis result, it was clearly seen that epichlorohydrin got incorporated in the polymer chain, thereby confirming the occurrence of ionic mechanism in addition to radical mechanism.

5.2.6.5 Kinetic study of spontaneous copolymerization between MBL and MDO

Kinetics was studied at both reaction temperatures vis-à-vis. 70°C and 120°C, taking two different reaction systems (monomer feed MBL : MDO = 20 : 80 at 70°C, and monomer feed MBL : MDO = 50 : 50 at 120°C), and following the polymerization at different intervals of time. Details are listed in Tables 5.2.6 (a) and 5.2.6 (b).

Table 5.2.6 (a): Copolymerization of 2-methylene-1,3-dioxepane (MDO) and α-methylene-γ-butyrolactone (MBL) (feed ratio MBL : MDO = 20 : 80) at 70°C for different time intervals, by bulk polymerization

Run	*Time (h)*	*Yield (%)*	*Copolymer composition MBL : MDO*	*MDO (% ring retained)*
1	5	Nil		
2	6	19	66 : 34	50
3	20	25	66 : 34	45
4	24	21	62 : 38	37

Table 5.2.6 (b): Copolymerization of 2-methylene-1,3-dioxepane (MDO) and α-methylene-γ-butyrolactone (MBL) (feed ratio MBL : MDO = 50 : 50) at 120°C for different time intervals, by bulk polymerization.

Run	*Time (h)*	*Yield %*	*Copolymer composition MBL : MDO*	*Mn*	*PDI*	*MDO(% ring retained)*
1	5	36	78 : 22	9.2×10^4	3.1	49
2	6	42	74 : 26	8.5×10^4	3.0	29
3	20	52	74 : 26	7.4×10^4	3.8	29
4	24	52	71 : 29	7.9×10^4	2.8	28

From the above given data, it was known that polymerization did not initiate until 5 hours, at 70°C, whereas at higher temperature, (120°C) 36% of the reaction was over in this much time. There was

neither much change in copolymer composition nor a remarkable drift in copolymer conversion of both the systems with increase in reaction time. But, the amount of ring opening in MDO increased drastically as the time progressed. At 120ºC, in 24 hours, 52% of reaction was complete. From the tables, it is clear that initially almost half of the MDO molecules underwent ring retaining, while half of them underwent ring-opening. But, as the reaction time increased (at both the temperatures), more and more MDO was able to proceed via ring-opening polymerization to form polyesters.

5.2.6.6 Influence of varying monomer feed on copolymerization of MDO with MBL

To apply the new materials for various applications, it was very important to get a better understanding of the reaction system. Efforts were therefore done to go more into the depth of it. Various polymers were synthesized with diverse combination of monomer feed (at both temperatures: 70°C and 120°C) and gradation in physical properties were observed carefully. Details can be seen from Table 5.2.7(a) and 5.2.7(b).

Table 5.2.7(a): Spontaneous copolymerization of MDO and α-MBL at 70°C without any solvent or initiator and varying monomer feeds (reaction time = 24 h).

Run	*Feed composition*	*Yield %*	*Copolymer composition*	T_g *(°C)*	M_n	*PDI*	*MDO (% Ring retained)*
	MBL : MDO		*MBL : MDO*				
1	90 : 10	21	96 : 4	T_{g1} = 192 T_{g2} = 156	3.6 x 10^5	2.9	75
2	50 : 50	43	75 : 25	T_g = 189 T_g = 145	2.9 x 10^5	2.3	53
3	20 : 80	21	62 : 38	T_g = 100	1.9 x 10^5	2.4	37
4	10 : 90	5.4	63 : 37	T_g = 96	1.9 x 10^5	2.2	41

Table 5.2.7(b): Spontaneous copolymerization of 2-methylene-1,3-dioxepane (MDO) and α-methylene-γ-butyrolactone (α-MBL) at 120°C without any solvent or initiator and varying monomer feeds (reaction time = 24 h).

Run	*Feed composition*	*Yield (%)*	*Copolymer composition*	T_g *(°C)*	M_n	*PDI*	*MDO (% Ring retained)*
	MBL : MDO		*MBL : MDO*				
1	90 : 10	39	91 : 9	150	2.6×10^5 bimodal	2.4	37
2	50 : 50	52	71 : 29	118	7.9×10^4	2.8	28
3	20 : 80	31	61 : 39	80	5.6×10^4	3.4	14
4	10 : 90	14	52 : 48	50	4.8×10^4	3.3	9

All reactions at 70°C, formed materials with the molecular weights of the order 10^5, whereas, the reactions at 120°C gave molecular weights in the range of 10^4. This discrepancy (as already discussed) was because at 70°C, ionic mechanism was more predominant, while at higher temperature, radical mechanism was. Also due to the same reason, at 70°C, the percentage of ring-retained structures was very high in comparison to that of ring-opened structures. At both temperatures, conversion followed the same trend, being maximum for the reaction in which 1 : 1 moles of both reacting species were used. As already stated, disregard whether ionic or radical mechanism is predominant, reaction got initiated via formation of zwitter ion, and hence faster the formation of this reaction intermediate, faster would be the propagation rate which thereby would lead to higher reaction yield. The appearance of two glass transition temperatures at 70°C, for higher feed of MBL in Table 5.2.7(a) (Runs 1 and 2) and bimodal curve distribution in GPC for Run 1, Table 5.2.5(b) again depicts that the reaction proceeded via radical and ionic pathway with equal probability initially, which then drifted towards radical mechanism with increase in MDO feed.

Considering reactions at 120°C, when more amount of MBL was fed into the reaction mixture, more amount of it was present in the copolymer. This led to a higher molecular weight and a higher softening temperature of 150°C (Table 5.2.7(b), Run 1). With increase in incorporation of MDO units into the long polymer chain, it was possible to lower the glass transition temperature to as low as 50°C. The ester linkages in the polymer backbone included flexibility and the segments became mobile, which led to a decrease in glass transition temperature. At 120°C, by varying the monomeric feed, it was possible to synthesize materials with about 50:50 copolymer composition, with about 91% of MDO forming polyesters in the polymeric backbone, but with a very less conversion of only 14%. Hence there was a need to find a alternative.

5.2.6.7 Copolymerization of MDO and MBL using radical initiator (dtbp) at 120°C

For the aim of this project, in order to achieve degradability and processability, more polyester incorporation was a prerequisite. Keeping this in mind. a series of six more reactions were then performed in presence of radical initiator, dtbp, so as to obtain the best possible material, which could serve as a eco-friendly plastic (Table 5.2.8 presents details).

Table 5.2.8: Copolymerization of 2-methylene-1,3-dioxepane (MDO) and α-methylene-γ-butyrolactone (MBL) using varying monomer feed at 120°C for 24h, using dtbp initiator, by bulk polymerization.

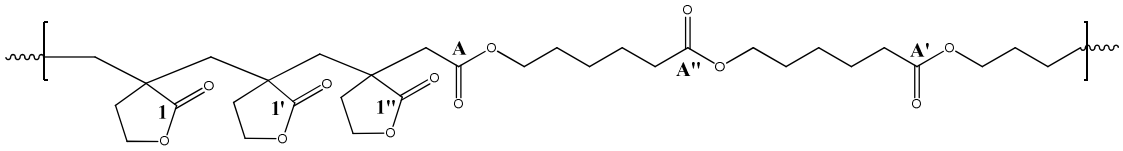
Run	*Feed composition*	*Yield (%)*	*Copolymer composition*	T_g *(°C)*	M_n	*PDI*	*% Ring Retained*
	MBL : MDO		*MBL : MDO*				
1	90 : 10	97	93 : 7	$T_g = 163$	2.2×10^4	8.7	20
2	80 : 20	93	86 : 14	$T_g = 125$	2.7×10^4	4.8	19
3	50 : 50	72	66 : 34	$T_g = 112$	4.0×10^4	3.7	10
4	30 : 70	60	53 : 47	$T_g = 96$ $T_m = 37$	7.0×10^4	3.8	11
5	20 : 80	58	39 : 61	$T_{g1} = -53$ $T_{g2} = 67$	4.4×10^4	3.8	5
6	10 : 90	36	38 : 62	$T_g = -52$ $T_m = 42$	5.4×10^4	3.5	5

The idea was to obtain a polymer which could be used as an eco-friendly plastic material.

Here again, the yield decreased with decrease in MBL feed. Samples with large amount of caprolactone units could be incorporated in the polymer (as large as 60%), and the molecular weights were also in a very good range. With dtbp initiator, the reaction was pushed towards ring opening (as already discussed) and hence, very less zwitter ionic mechanism was followed which led to less amount of ring retained structure.

Microstructure variations (and hence mechanistic variation) due to varying monomer feed was nicely seen by comparing the ^{13}C NMR spectra (Figure 5.2.11) of polymer samples obtained in

Table 5.2.8. Neglecting the ring retained structure of MDO, the most plausible blocky random structure of polymers obtained by synthesizing in presence of radical initiator would be as given in Scheme 5.2.7.



Scheme 5.2.7: Blocky random structure of copolymers obtained by carrying out synthesis in presence of radical initiator.

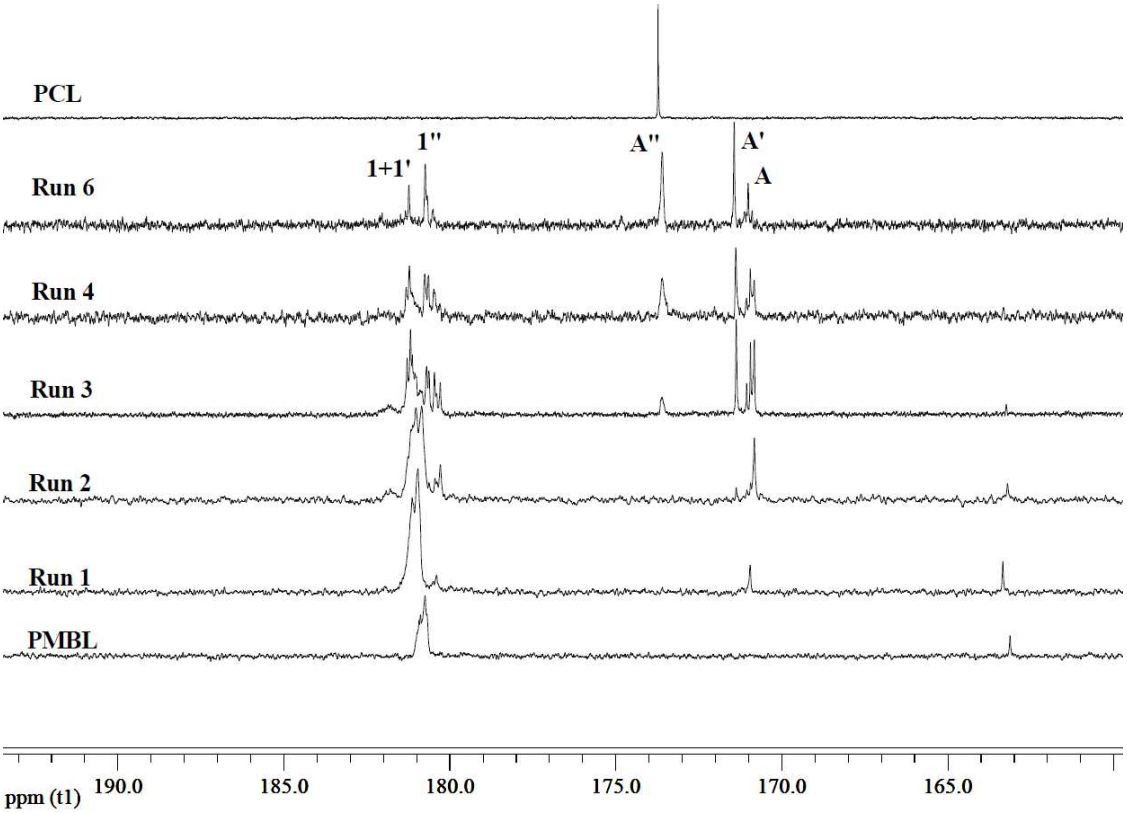


Figure 5.2.11: Comparison of ^{13}C NMR spectra of Table 5 (Runs 1, 2, 3, 4, 6) with ^{13}C NMR spectra of homopolymers PMBL and PCL. Clearly shows the appearance of MDO-MDO diads and triads with increasing amount of MDO in feed.

The new peak appearing and marked as **A'** is due to the carbonyl carbons of MDO-MDO diad sequence which is hardly visible when monomer feed (MBL : MDO) is 90 : 10, and the new

peak appearing at 173.0 ppm with reference to our previous work[9] is assigned to the carbonyl carbons of the MDO-MDO-MDO triad type of sequences which appears only with monomer feed of MDO more than 20%. This peak also matched with the carbonyl peak of commercial polycaprolactone as shown in the figure. The other two prominent difference observed by increasing MDO monomer feed was in the linking carbonyl group of MBL linked to MDO (MBL-MDO) (180 ppm, marked as **1"** in figure 5.2.11) and the carbonyl groups of MBL which are linked to another unit of itself (181 ppm, marked as **1+1"** in the figure). The splitting in the peaks increases showing more randomisation of the copolymer structure.

Also, observing down the table, (Table 5.2.8; Runs 4, 5, 6) the copolymers start gaining the commercial polycaprolactone characteristics, which has a melting point of 60°C and a glass transition temperature of -60°C.[102] The melting peaks were observed in first as well as second heating cycles of DSC, which meant that there was no change in crystallinity upon heating. Crystallinity of Runs 4 and 6 of Table 5.2.8 were compared by integrating the melting peaks obtained in DSC curves for both the samples. Run 4 was found to be more crystalline (which absorbed 10.88 mJ of energy during endothermic phase transition from solid to liquid) as compared to Run 6 (which absorbed 101.16 mJ energy during phase transition). Samples with more amount of MBL (Table 5.2.8; Runs 1 and 2) gave very nice white pearl-shaped polymers. A representative picture of Run 2 is given in Figure 5.2.12.

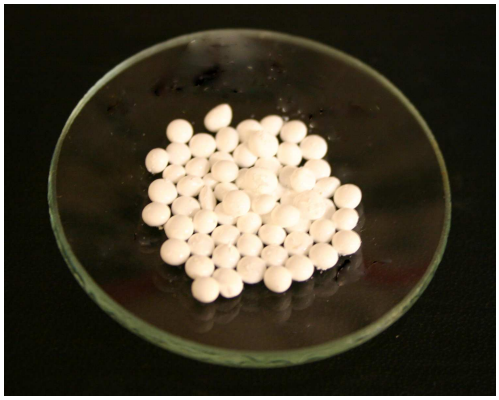
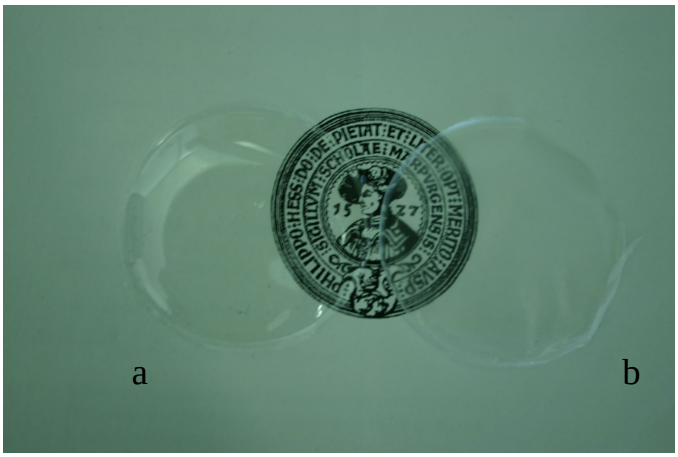


Figure 5.2.12: A representative diagram of a copolymer of MBL-co-MDO (Table 5.2.8, Run 2).

5.2.6.8 Transparency studies by UV-Vis spectroscopy

Films of Runs 1 and 2 (Table 5.2.8) could not be formed because the samples were hardly soluble in any solvent. These samples dissolved only in DMF or DMSO, which have a high boiling point and are hard to evaporate. Whereas, the samples with higher amount of ester links (Runs 3-6) were soluble in chloroform too. Here again, Runs 5 and 6, being extremely soft materials, were not film formable. These samples were too sticky and could not be handled easily.

Finally, films of Runs 3 and 4 were formed by solvent casting using chloroform as the solvent (Figure 5.2.13). A 7 x 10^{-3} mm thick film of Run 3 was found to show less than 20% transmittance to visible light while a 6.5 x 10^{-2} mm thick film of Run 4 was found to show less than 30% transmittance. Compared to this, a 1.2 x 10^{-1} mm thick film of PMMA formed in chloroform, was found to be 90% transparent to visible light, while a 6.2 x 10^{-2} mm thick film of polycaprolactone (M_n = 8.0 x 10^4) was found to show less than 30% transmittance (due to semi-crystalline characteristics).



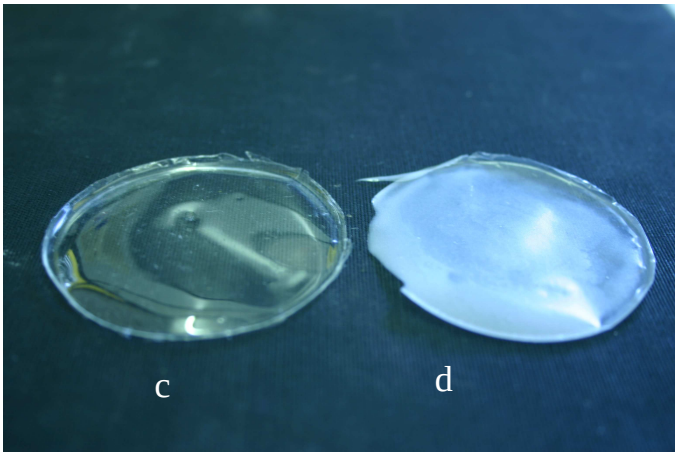
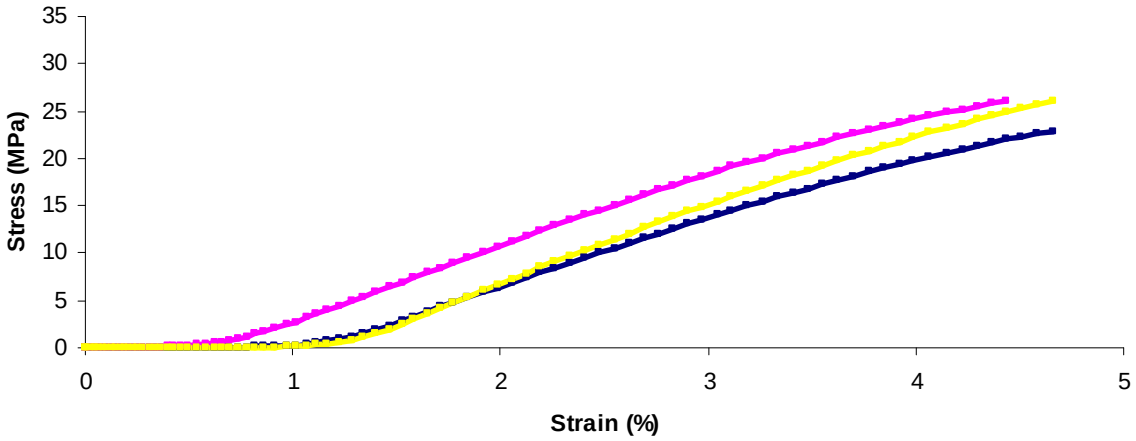


Figure 5.2.13. Films of polymer samples formed by solvent casting, using $CHCl_3$ as solvent (a: PMMA, 1.2 x 10^{-1} mm thick, 90% transparent; b: PCL, 6.2 x 10^{-2} mm thick, less than 30% transmittance; c: PMMA film kept on dark surface for better photography; d: PCL film kept on dark surface for better photography; e: Table 5.2.8, Run 3, 7 x 10^{-3} mm thick, showed less than 20% transmittance (crystalline characteristics); f: Table 5.2.8, Run 4, 6.5 x 10^{-2} mm thick, showed less than 30% transmittance (crystalline characteristics).

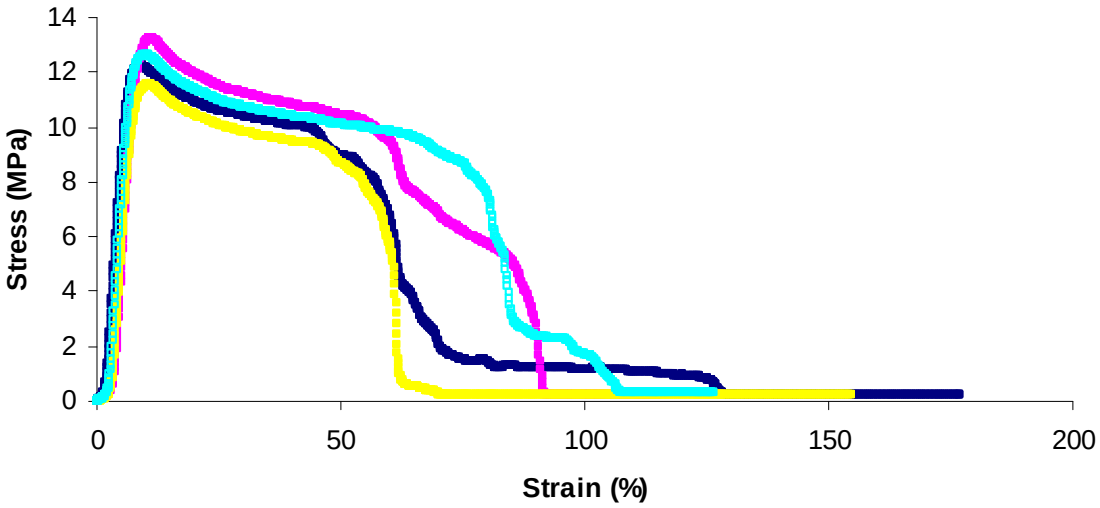
5.2.6.9 Study of mechanical properties

An attempt has also been made to evaluate the mechanical properties of the above formed films. The polymer sample having more amount of ester linkages, i.e., 47% MDO in the copolymer was found to be elastic, where as that with lower amount of ester, i.e., 34% MDO in the

copolymer was brittle. Figure 5.2.15 shows a plot of stress-strain curves of Runs 3 and 4 of Table 5.2.8.



a)



b)

Figure 5.2.15: a) Plots of stress-strain curves of Run 3; b) Run 4 of Table 5.2.8.

Details can be seen in Table 5.2.9. Introduction of esters led to a decrease in $E_{modulus}$, and an increase in elasticity.

Table 5.2.9: Mechanical properties of poly(MBL-co-esters)

Run	*Copolymer composition MBL : MDO*	*$E_{modulas}$ (stress/strain) (GPa)*	*Maximum Force (F_{max}) (N)*	*Maximum stress (σ_{max}) (MPa)*	*Elongation at F_{max} (%)*
1[a)]	66 : 34	0.00655	18.5	26.15	5
2[b)]	53 : 47	0.00569	21.6	12.43	9.9

[a)] Run 3, Table 5.2.8; [b)] Run 4; Table 5.2.8

Compared to this, the modulus of elasticity for commercial PMMA ($10^5 < M_w < 2 \times 10^5$) is reported to be 3.3 GPa and elongation at break to be 4%.[103] The synthesized materials, therefore, may not be as strong as PMMA, but were therefore, tougher than it.

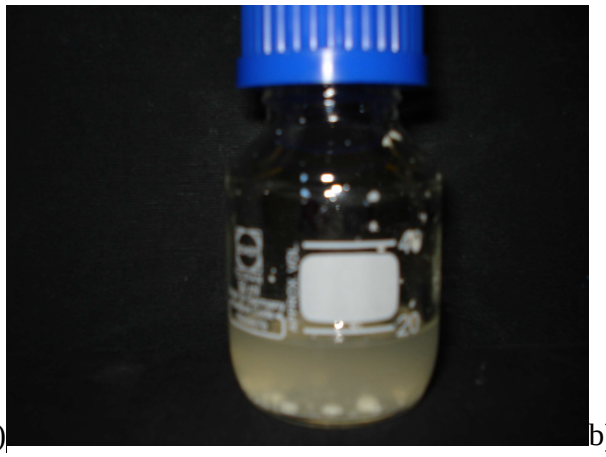
5.2.6.10 Thermal studies

The thermal stability for all samples was measured by thermogravimetric analysis (TGA), and the samples were found to be very stable until 320°C. One-step degradation was observed until about 340°C.

All samples were only soluble in DMF and DMSO, and hence were found to have solvent resistance properties. The synthesized polymers were expected to be degradable due to the degradable polyester linkages incorporated in the C-C chain, and also due to the degradable property of MBL.

5.2.6.11 Study of Hydrolytic degradation behavior of Polymer by base hydrolysis

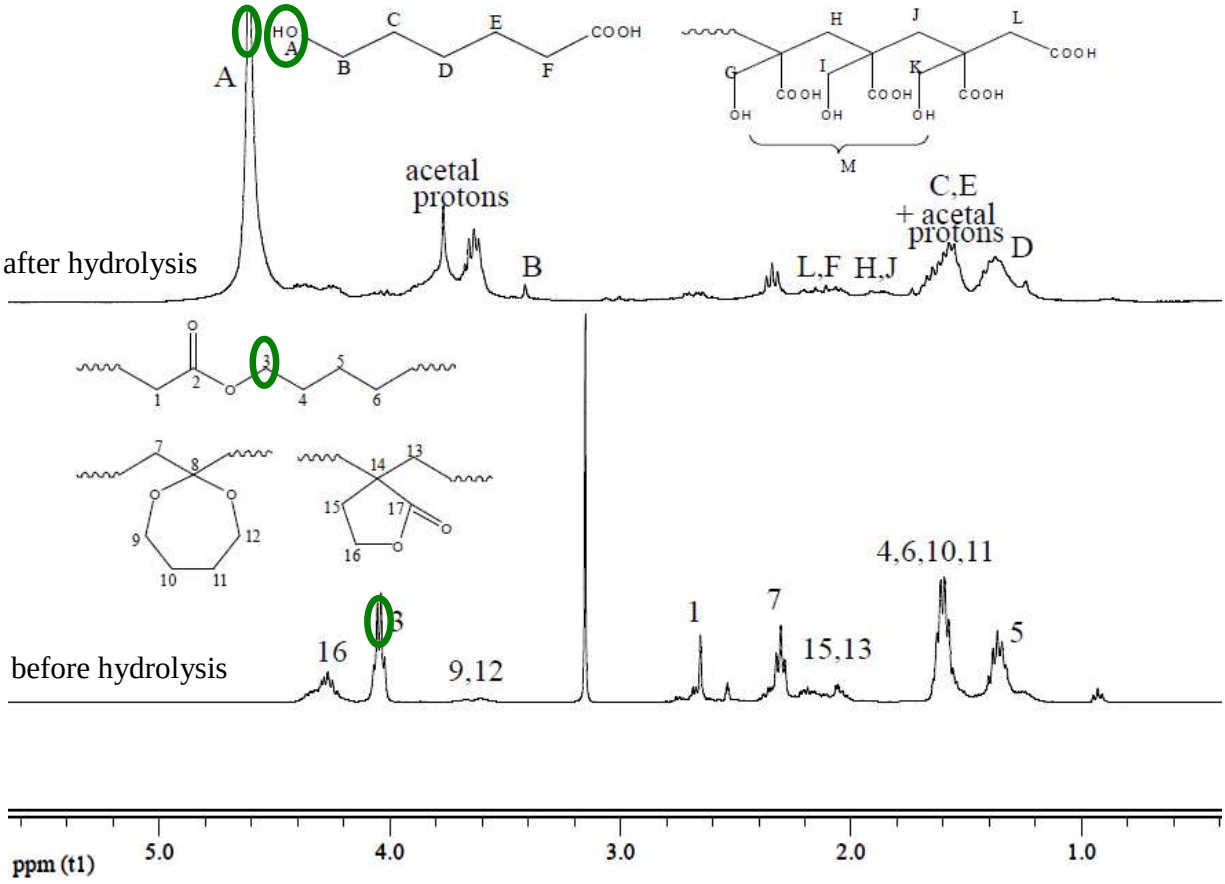
Finally, the main aim of obtaining a degradable plastic was to be analyzed. This was checked by base hydrolysis (5% wt. NaOH in methanol) of copolymer samples, overnight at room temperature. Two samples were kept for stirring overnight under basic medium (Table 5.2.8, Run 1 and 6). After hydrolysis, the polymeric material having 62% of ester groups, Run 6, was completely soluble in hydrolysis medium, whereas Run 1, having 7% of ester groups was found to be turbid (Figure 5.2.16 shows the difference).

a)


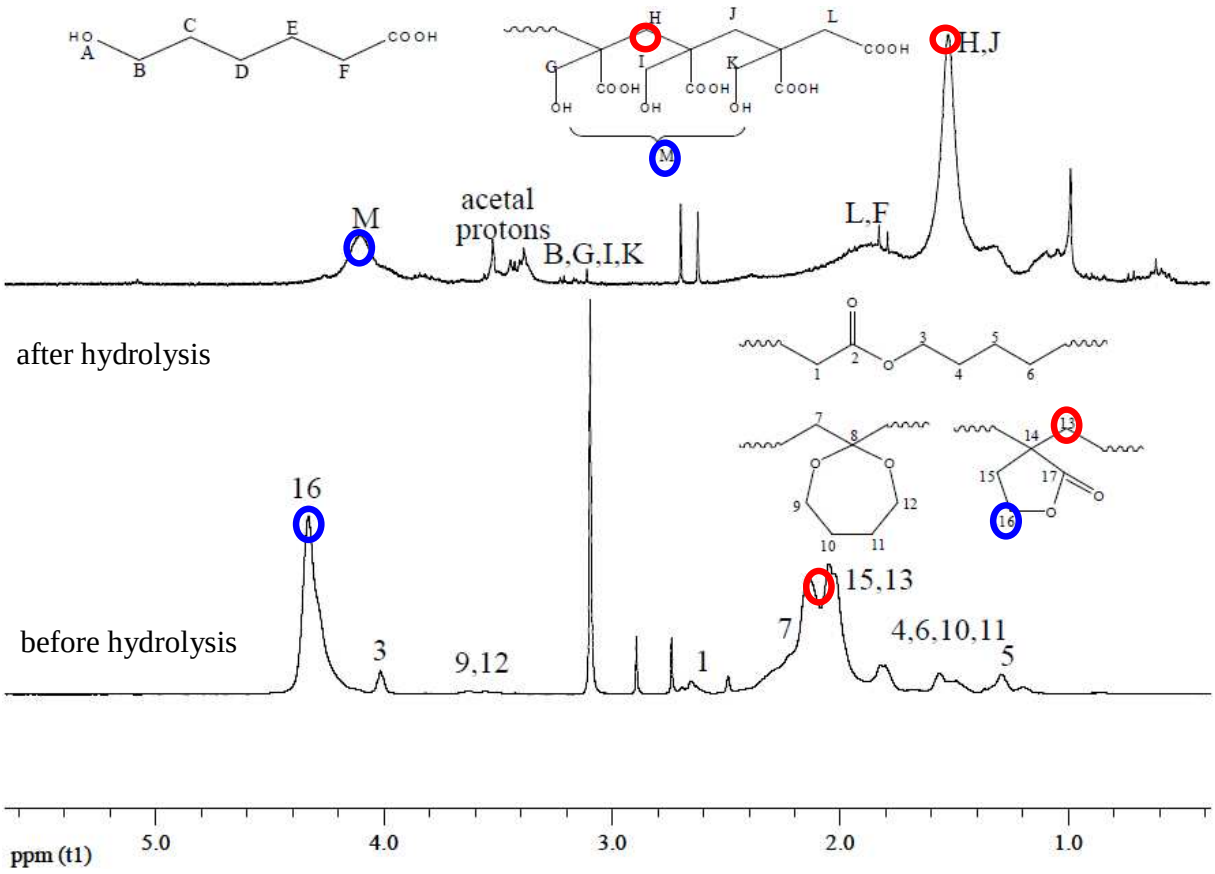
b)

Figure 5.2.16: a) Hydrolysis of Run 6, Table 5.2.8; b) Hydrolysis of Run 1, Table 5.2.8

The hydrolyzed products were then extracted using chloroform, dried over sodium sulphate and after evaporation and drying, the left over sticky material were subjected to ^{1}H NMR (Figure 5.2.17). The sample containing 62% of MDO (Run 6) gave more amount of hydrolyzed product obtained from polycaprolactone, than that from polyMBL, while the sample containing 93% of MBL (Run 1) gave hydrolyzed products from both. Various hydroxy acids obtained from the hydrolysis of the block copolymers are given in Figure 5.2.17, with their NMR peak assignments and are compared with the ^{1}H NMR spectrum of the respective non-hydrolyzed samples. Molecular weight of the hydrolyzed material could not be taken because the material was not soluble in DMF.



a) the shift in peaks marked (in green) before hydrolysis and after hydrolysis, gave a clear indication of hydrolysis taking place



b) the shift in peaks marked (in blue and red) before hydrolysis and after hydrolysis, gave a clear indication of hydrolysis taking place

Figure 5.2.17: Comparison of ^{1}H NMR spectrum of non-hydrolyzed polymer with hydrolyzed product for a) Run 6, Table 5.2.8 and b) Run 1, Table 5.2.8 (NMR for hydrolysed product was taken using $CDCl_3$ as solvent).

5.3 Conclusion

Out of the three systems, vis-à-vis MBL-BMDO system, MBL-BMDO-MMA system and MBL-MDO system, the most suitable was the MBL-MDO system. Degradable and eco-friendly materials of high molecular weight and high glass transition temperature were synthesized by spontaneous polymerization between MBL and MDO, without the usage of initiator, as well as by radical polymerization with radical initiator. Two parallel reaction mechanisms initiated by charge transfer, i.e. zwitterionic and biradical mechanism were running in the system, which

could be easily controlled to get the desired microstructure. The microstructure of the obtained polymers consisted of blocks of polyMBL and poly MDO, wherein MDO polymerized both via ring-opening and ring-retaining polymerization. Due to the thermal stability, solvent resistance, suitable mechanical properties, degradability, and natural source origin, the synthesized materials can be used in many applications.

6. Experimental

6.1 Materials

Material	Source
2-methylene-1,3-dioxepane (MDO)	Polysciences Inc., used as received
5,6-benzo-2-methylene-1,3-dioxepane (BMDO)	Synthesized in the laboratory according to previously reported method
Azobisisobutyronitrile (AIBN)	Recrystallized from Methanol
$CDCl_3$	Roth, used as received
Chloroform	BASF, distilled before use
d-DMSO	Roth, used as received
Diethyl ether	BASF, distilled before use
Dimethylformamide (DMF)	BASF, distilled before use
Di-tertiary-butyl-peroxide (dtbp)	Aldrich, used as received
Methanol	BASF, distilled before use
Methylmethacrylate (MMA)	BASF, distilled before use
n-hexane	BASF, distilled before use
Sodium hydroxide	Grüssing GmbH, used as received
Sodium sulphate (anhydrous)	Chemical shop, Philipps Universität
Tetrahydrofuran (THF)	BASF, distilled before use
Vinyl acetate (VAc)	Acros organics, distilled before use
α-methylene-γ-butyrolactone (MBL)	Aldrich, used as received

6.2 Instrumentation and characterization techniques

6.2.1 Nuclear magnetic resonance spectroscopy

1D and 2D NMR measurements were done in the NMR Department at the Philipps Universität Marburg. ^{1}H (400.13 MHz) and ^{13}C (100.21 MHz)-NMR spectra were recorded on a Bruker DRX-400 spectrometer using Tetramethylsilane (TMS) as an internal standard. ^{1}H-^{13}C NMR correlation experiments were performed on a Bruker DRX-500 spectrometer, with a 5 mm

multinuclear gradient probe and using gs-HMQC (heteronuclear multiple quantum correlation) and gs-HMBC (heteronuclear multiple bond correlation) pulse sequences. The HMQC experiment was optimized for coupling of 8 Hz, with decoupling during acquisition. 2D NMR data were acquired with 2048 points in t_2, and the number of increments for t_1 was 256. Four and Eight scans were used for HMQC and HMBC experiments respectively, and 4 dummy scans were used for both the experiments. A relaxation delay of 1s was used for all 1D experiments and 2s for all 2D experiments. Typical experiment time was about 1.5 and 3.0 h for HMQC and HMBC, respectively.

6.2.2 Thermogravimetric analysis (TGA)

Thermal gravimetric analysis was done by using Mettler thermal analyzers having 851 thermogravimetric modules. Thermal stability was determined by recording TGA traces in nitrogen atmosphere (flow rate = 50 mL min^{-1}). A heating rate of 10°C min^{-1} and a sample size of 10 ± 1 mg was used in each experiment.

6.2.3 Differential scanning calorimetry (DSC)

Mettler Thermal Analyser having 821 DSC module was used for thermal analysis of the polymers. DSC scans were recorded in nitrogen atmosphere (flow rate = 80 ml min^{-1}) at a heating rate of 10°C min^{-1}. A heating rate of 10°C min^{-1} and a sample size of 10 ± 1 mg was used in each experiment for DSC.

6.2.4 Viscosimetry

Viscometric studies were done by dissolving the co-polymers in DMF. All the measurements were done at a constant temperature of 25±1°C using Ubbelohde viscosimeter.

A representative picture of the viscosimeter is given in Figure 6.2.1

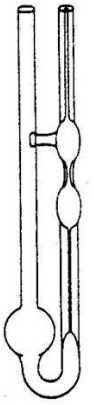


Figure 6.2.1: A representative diagram of Ubbelohde viscosimeter.

Viscosity, also called internal friction, is the resistance of a liquid to flow. The viscosity of polymer solutions (η) are considerably higher than that of the pure solvent (η_0).

Relative viscosity, η_{rel}:

$$\eta_{rel} = \frac{\eta}{\eta_0} \qquad \textbf{(1)}$$

Specific viscosity, η_{sp}:

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta} = \frac{\eta}{\eta_0} - 1 = \eta_{rel} - 1 \qquad \textbf{(2)}$$

Reduced specific viscosity, or intrinsic viscosity, or viscosity number, or Staudinger index $[\eta]$:

$$[\eta] = \lim_{C \to 0} \frac{\eta_{sp}}{C} \qquad \textbf{(3)}$$

where, "C" is the concentration of solution

By Mark-Houwink equation:

$$\lim_{C \to 0} \frac{\eta_{sp}}{C} = [\eta] = K \cdot M^{a} \qquad \textbf{(4)}$$

where,

K is a constant,

M is the molecular weight

exponent "a" is the conformation of macromolecules, which contains information about the shape of molecules.

- *a = 1/2* $\Rightarrow$ flexible polymer chain in "ideal" solvent
- *0.5 < a < 0.8* $\Rightarrow$ flexible polymer chain in "good" solvent (excluded volume limit)
- a > *0.8* $\Rightarrow$ "stiff" chain

6.2.5 Zwick Roell-tensile tests

Mechanical properties of the copolymer samples were measured by Zwick Roell-tensile testing machine. Thin films were prepared by dissolving the samples in THF or chloroform (as stated). Films were cut out in the shape of a rectangle having width of 10 mm and the grip to grip separation was kept to be 10 mm. Pre-load was set to 0.01 N and test speed was 50 mm min^{-1}.

6.2.6 Liquid chromatography mass spectroscopy (LCMS)

Hydrolyzed sample was analyzed with a 125/2 Nucleodur C18ec column (Macherey-Nagel, Germany) utilizing a Agilent 1100 series HPLC-system (Hewlett Packard, Germany), which was directly coupled with a LTQ-FT mass spectrometer (Thermo, Germany) through an ESI interface and with a linear gradient from 0-30% acetonitrile in water within 30 minutes. Masses were measured in negative ion mode and parent ion peaks were detected. The capillary temperature was 280°C and the injection volume was 25 µL.

6.2.7 Gel permeation chromatography (GPC)

The molecular weights of P(MBL-co-ester)s were measured by GPC at 25°C. Sample concentration was 1 g L^{-1}. The apparatus consists of a Gynkotek HPLC pump, a Agilent Autosampler 1200, linear columns (PSS, polystyrene) consisting of a pre-column 10 µ, 8 x 50 mm, a column 10 Å, 8 x 300 mm and two columns 3000 Å, 8 x 300 mm. As detector, a RI detector of Knauer Company was used. As calibration, linear PMMA with a narrow mass distribution and molecular weight between 500 and 1,000,000 was used. Toluene was used as an internal standard. The elugram was evaluated with PSS WinGPC Unity program.

6.2.8 Film preparation (Compression moulding machine)

Compression moulding machine of the company Schwabenthan was used for film formation. Water was used as the cooling medium. The processing temperature was chosen to be 250°C.

6.2.9 UV-Vis spectroscopy

All UV-Vis spectra were taken up with the help of a spectrometer of the type Lambda 9 of the company Perkin Elmer, which was operated by the software Lambda SPX. For the measurement, two quartz cuvettes (Perkin Elmer) were used with 2 mL capacity. The spectra were evaluated and analyzed by the software Lambda SPX.

6.2.10 Elemental analysis

Elemental Analysis was done in the Central analytical Department of Philipps Universität Marburg. The elements carbon, hydrogen and chlorine were analysed two times, using 25 mg of sample and then the average of the two values were taken.

6.3 Methods

6.3.1 Film preparation (solvent casting)

Films were prepared by dissolving polymer samples in minimum amount of suitable solvent (THF or chloroform or DMF, as stated), to make a highly consistent solution (consistency was similar to that of honey). The solutions were uniformly put on a petri dish using a glass pipette and were covered with aluminium foil having holes on top of it, to let the solvent evaporate slowly. In case of DMF solvent, the evaporation process was activated by the heat of bulbs, as shown in the figure of apparatus used. (Figure 63.1)

Figure 6.3.1: Apparatus used to dry DMF solvent during film formation by solvent casting method

Finally, the films were dried under reduced pressure for many days, until TGA showed no traces of extra solvent.

6.3.2 Hydrolytic Degradability Test

200 mg of the copolymer samples were stirred in 20 mL of KOH in Methanol (5 wt.-%) for 20 h. The extra base was neutralized by 10 mL of 10% HCl. The solution was extracted with chloroform, dried over sodium sulfate, and the material left after evaporation of the solvent was further characterized.

6.3.3 Cell viability studies/ Cytotoxicity studies: MTT Assay

(This work was done in the Research group of Prof. Dr. Thomas H. Kissel, Department of Pharmaceutics, Philipps Universität)

Cell viability studies of hydrolysed products were also carried out using the MTT assay as described previously.[100] Briefly, L929 cells were seeded into 96-well microtiter plates (NunclonTM, Nunc, Germany) at a density of 8000 cells/well. After 24 h, the culture medium was replaced with serial dilutions of polymer or hydrolyzed polymer stock solutions in antibiotic-free DMEM with FCS (n = 11, concentrations 0.001-4 mg mL^{-1}). After an incubation period of 24 h, 200 µL of DMEM and 20 µL MTT (Sigma, Deisenhofen, Germany) (2 mg mL^{-1} in PBS) were added. After an incubation time of 4 h, unreacted dye was removed by aspiration and the purple formazan product was dissolved in 200 mL/well dimethylsulfoxide (Merck, Darmstadt, Germany) and quantified by a plate reader (Titertek Plus MS 212, ICN, Germany) at wavelengths of 570 and 690 nm.

The relative cell viability [%] related to control wells containing cell culture medium without polymer was calculated by absorbance test/absorbance control × 100. Poly(ethylene imine) 25 kDa (BASF, Germany), a water-soluble polycationic polymer used in gene delivery and known to induce a cytotoxic response in cells, was used as a positive control. The IC_{50} was calculated as polymer concentration which inhibits growth of 50% of cells relative to non treated control cells. Data are presented as a mean of four measurements. IC_{50} was calculated using the Boltzman sigmoidal function from Microcal Origin® v 7.0 (OriginLab, Northampton, USA).

6.3.4 To study the influence of air on BMDO

In order to study the effect of air on BMDO, ^{1}H NMR was used as the analytical technique. ^{1}H NMR of pure BMDO was taken under inert atmosphere of argon, by sealing the tube using bunsen burner. 100 mg of BMDO was kept on a petri dish and was then exposed to the atmosphere. ^{1}H NMR measurements were taken after definite intervals of time.

6.3.5 To study the influence of water on BMDO

To study the effect of water on BMDO, 67.8 mg (0.4 mmol) of BMDO was mixed with 455 µL (25 mmol) of water under inert atmosphere. The ^{1}H NMR was measured every hour for 16 regular times.

6.3.6 Synthesis and Polymerization Techniques

6.3.6.1 Homo- and Copolymerization of MDO and VAc using radical initiator

Co-polymerizations were carried out under Argon in pre-dried Schlenk tubes using free radical initiator, AIBN, at 70°C. In a typical bulk polymerization reaction (entry 3, Table 5.1.1), 0.5750 g (6.6 mmol) of VAc and 0.3028g (2.6 mmol) of MDO, followed by 1 mol-% (0.01 mg) of initiator (AIBN) were added and kept for polymerization in an pre-heated oil bath at 70°C for 4 h. The reaction was then quenched by immediately taking out the tube from oil bath and immersing into liquid nitrogen. Post-polymerization, THF was used as the dissolving medium, while n-hexane was the precipitating medium. The reaction mixture was dissolved in 15 ml THF and precipitated in 250 mL of n-hexane. The polymer was obtained as white powder and was dried in vacuum at 40°C for 15 h. For purification, the sample was re-dissolved in THF and re-precipitated in n-hexane. The reaction conversion was estimated by Gravimetry, i.e., by taking the mass of the polymer as compared to the mass of the initial monomers used and was found to be 73%.

^{1}H NMR (400 MHz, $CDCl_3$):

δ/ppm = 4.8-5.1(s, 1H, –C<u>H</u>OC(O)CH_3 from VAc), 2.0 (s, 3H, –CHOC(O)C<u>H</u>$_3$ from VAc), 1.7-1.8(d, 2H, -C<u>H</u>$_2$CHOC(O)CH_3 from VAc), 4.0-4.1 (t, 2H, CH_2C(O)OC<u>H</u>$_2$- from MDO), 2.2 (t,

2H, -C<u>H</u>$_2$C(O)OCH$_2$CH$_2$CH$_2$CH$_2$-from MDO), 1.5(m, 2H, -CH$_2$C(O)OCH$_2$C<u>H</u>$_2$CH$_2$CH$_2$- from MDO) and 1.3(m, 2H, -CH$_2$C (O)OCH$_2$CH$_2$C<u>H</u>$_2$CH$_2$- from MDO).

6.3.6.2 Homo- and copolymerization of BMDO and MBL using radical initiator

Co-polymerizations were carried out under Argon in pre-dried Schlenk tubes using free radical initiator, dtbp, at 120°C. In a typical solution polymerization reaction (using 1 mL of dry DMF) (entry 1, Table 5.3.1), 1.1861 g (7.3 mmol) of BMDO and 70.2 μL (0.8 mmol) of MBL, followed by 1 mol-% (14.6 μL) of initiator (dtbp) were added and kept for polymerization in an pre-heated oil bath at 120°C for 24 h. The reaction was then quenched by immediately taking out the tube from oil bath and immersing into liquid nitrogen. Post-polymerization, DMF was used as the dissolving medium, while methanol was the precipitating medium. The reaction mixture was dissolved in 10 mL DMF and precipitated in 250 mL of methanol. The polymer was obtained as white powder and was dried in vacuum at 60°C for 48 h. For purification, the sample was re-dissolved in DMF and re-precipitated in methanol. The reaction conversion was estimated by gravimetry, i.e. by taking the mass of the polymer as compared to the mass of the initial monomers used and was found to be 11%.

6.3.6.3 Terpolymerization of BMDO, MBL and MMA using radical initiator

Co-polymerizations were carried out under Argon in pre-dried Schlenk tubes using free radical initiator, dtbp, at 120°C. In a typical solution polymerization reaction (using 1 mL of dry DMF) (entry 2, Table 5.3.2), 0.3264 g (2 mmol) of BMDO, 175 μL (2 mmol) of MBL, and 426 μL (4 mmol) of MMA followed by 1 mol-% (14.6 μL) of initiator (dtbp) were added and kept for polymerization in an preheated oil bath at 120°C for 24 h. The reaction was then quenched by immediately taking out the tube from oil bath and immersing into liquid nitrogen. Post-polymerization, DMF was used as the dissolving medium, while methanol was the precipitating medium. The reaction mixture was dissolved in 10 mL DMF and precipitated in 250 ml of methanol. The polymer was obtained as white powder and was dried in vacuum at 60°C for 48 h. For purification, the sample was re-dissolved in DMF and re-precipitated in methanol. The reaction conversion was estimated by Gravimetry, i.e., by taking the mass of the polymer as compared to the mass of the initial monomers used and was found to be 83%.

^{1}H NMR (400 MHz, $CDCl_3$):

δ/ppm = 0.2 -1.8 (2H, -C<u>H</u>$_2$(C)- from MBL), (2H, -(C)-C<u>H</u>$_2$-CH$_2$- from MBL), (2H, -C<u>H</u>$_2$-(C)- from MMA), (3H, -C<u>H</u>$_3$- from MMA), 3.1 (s, 3H, -COC<u>H</u>$_3$- from MMA), 3.7 (d, -CH$_2$-C<u>H</u>$_2$-O- from MBL), 4.5 (s, -C(O)OC<u>H</u>$_2$- from BMDO).

6.3.6.4 Spontaneous copolymerization of MDO and MBL

All co-polymerizations were carried out under Argon in pre-dried, schlenk tubes without any initiator, at 70°C for 24 h (if not stated otherwise). In a typical bulk copolymerization reaction (Table 5.3.3, Run 4), 270 µL (3.09 mmol) of α-MBL and 350 µL (3.09 mmol) of MDO were added and kept for polymerization at 70°C in a pre-heated oil bath for 24 h. The reaction was then quenched by immediately taking out the tube from oil bath and immersing into liquid nitrogen. After polymerization, 2 mL of DMF was used to dilute the viscous material thus obtained, while 250 mL methanol was used to precipitate it out from the mixture of unreacted monomers. The polymer was obtained as a white powder and was dried in vacuum at 65°C for a week under reduced pressure. For purification, the sample was re-dissolved in DMF and re-precipitated in methanol. The reaction conversion was estimated by Gravimetry, i.e by taking the mass of the polymer as compared to the mass of the initial monomers used and was found out to be 43%.

^{1}H NMR (400 MHz, $CDCl_3$):

δ/ppm = 4.3(2H, –CH$_2$(C)C(O)OC<u>H</u>$_2$CH$_2$(C)- from MBL), 1.9 - 2.2(2H, –C<u>H</u>$_2$(C)C(O)OCH$_2$CH$_2$(C)-) and (2H, -CH$_2$(C)C(O)OCH$_2$C<u>H</u>$_2$(C)- from MBL), 2.6 (2H, –C<u>H</u>$_2$C(O)OCH$_2$-), 4.0(2H, –CH$_2$-C(O)OC<u>H</u>$_2$- from ring opened MDO), 1.1 - 1.3 (2H, –CH$_2$C(O)OCH$_2$CH$_2$C<u>H</u>$_2$CH$_2$- from ring opened MDO), 1.3 - 1.6 (4H, –CH$_2$C(O)OCH$_2$C<u>H</u>$_2$CH$_2$C<u>H</u>$_2$- from acyclic MDO) and (4H, –CH$_2$(C)OCH$_2$C<u>H</u>$_2$C<u>H</u>$_2$CH$_2$O(C)-), 2.3 (2H, –C<u>H</u>$_2$(C)OCH$_2$CH$_2$CH$_2$CH$_2$O(C)- from acyclic MDO), 3.5 - 3.6 (4H, –CH$_2$(C)OC<u>H</u>$_2$CH$_2$CH$_2$C<u>H</u>$_2$O(C)-from acyclic MDO.

6.3.6.5 Homo and copolymerization of MDO and MBL using radical initiator

All co-polymerizations were carried out under Argon in pre-dried Schlenk tubes with dtbp initiator, at 120°C for 24 h. In a typical bulk copolymerization reaction (Table 5.3.6, Run 1), 975 µL (11.124 mmol) of α-MBL and 139.4 µL (1.236 mmol) of MDO, and 22.7 µL of dtbp initiator (1mol-%) were added and kept for polymerization at 120°C in a preheated oil bath for 24 h. The reaction was then quenched by immediately taking out the tube from oil bath and immersing into liquid nitrogen. After polymerization, 2 mL of DMF was used to dilute the viscous material thus obtained, while 250 mL methanol was used to precipitate it out from the mixture of unreacted monomers. The polymer was obtained as a white powder and was dried in vacuum at 65°C for a week under reduced pressure. For purification, the sample was re-dissolved in DMF and re-precipitated in methanol. The reaction conversion was estimated by Gravimetry, i.e, by taking the mass of the polymer as compared to the mass of the initial monomers used and was found out to be 97%.

^{1}H NMR (400 MHz, $CDCl_3$):

δ/ppm = 4.3(2H, $–CH_2(C)C(O)OC\underline{H}_2CH_2(C)$- from MBL), 1.9 - 2.2(2H, $–C\underline{H}_2(C)C(O)OCH_2CH_2(C)$-) and (2H, $-CH_2(C)C(O)OCH_2C\underline{H}_2(C)$- from MBL), 2.6 (2H, $–C\underline{H}_2C(O)OCH_2$-), 4.0(2H, $–CH_2$-$C(O)OC\underline{H}_2$- from ring opened MDO), 1.1 - 1.3 (2H, $–CH_2C(O)OCH_2CH_2C\underline{H}_2CH_2$- from ring opened MDO), 1.3 - 1.6 (4H, $–CH_2C(O)OCH_2C\underline{H}_2CH_2C\underline{H}_2$- from acyclic MDO) and (4H, $–CH_2(C)OCH_2C\underline{H}_2C\underline{H}_2CH_2O(C)$-), 2.3 (2H, $–C\underline{H}_2(C)OCH_2CH_2CH_2CH_2O(C)$- from acyclic MDO), 3.5 - 3.6 (4H, $–CH_2(C)OC\underline{H}_2CH_2CH_2C\underline{H}_2O(C)$-from acyclic MDO.

7. Zusammenfassung

7.1 In English

New degradable materials having extremely low (-44°C) and extremely high (163°C) glass transition temperature were synthesized by radical chemistry, using various combinations of vinyl acetate (VAc) and α-methylene-γ-butyrolactone (α-MBL) (present in common tulips) monomers with a cyclic ketene acetal, 2-methylene-1,3-dioxepane (MDO). Degradability was catered in polymer chains by ring opening polymerization of the cyclic ketene acetal.

Firstly, synthesis of P(VAc-co-esters) was carried out with an aim to make degradable materials based on MDO and VAc units using radical chemistry. Radical ring-opening copolymerization of 2-methylene-1,3-dioxepane with vinyl acetate in presence of AIBN initiator at 70^{o}C was carried out to achieve the aim. Complete ring opening of MDO was observed during copolymerization which introduced degradable PCL repeat units onto the C-C backbone of poly(vinyl acetate). Microstructure analysis of the copolymers was done using different 1D and 2D NMR techniques. Reactivity ratios were found out by Kelen Tüdos method and were r_{VAc} = 1.53 and r_{MDO} = 0.47 leading to statistical introduction of ester linkages onto the polymer backbone. The materials showed varied glass transition temperatures (from 37 to -44^{o}C) depending upon the amount of ester linkages and very high elongations. Compared to 6.5 x 10^{-3} GPa modulus and 1007% elongation at break of PVAc, a P(VAc-co-ester) with 5% ester incorporation gave 5.1 x 10^{-3} GPa modulus and 1093% elongation, while 18% ester incorporation led to 2.9 x 10^{-3} GPa modulus and 1285% elongation. The hydrolysis products were also tested for cytotoxicity studies in L929 cells and compared with that of known and accepted non-toxic materials like poly(ethyleneimine). The hydrolysed products were non toxic and showed a cell viability > 95%. Keeping in view the combined properties like degradability, non-toxicity and low glass transition temperatures, the resulting materials could therefore be proposed for different applications like degradable gums, coatings etc.

Additionally, a successful effort of synthesizing degradable materials, which could be used for various applications, was carried out. Due to the high softening temperatures (as high as 163°C),

these materials were proposed to be used as thermoplastics that would not only be eco-friendly due to their ability to be easily degraded to harmless substances, but would also be useful due to their origin from a plant source. Polymerization of cyclic ketene acetal MDO with a naturally occurring monomer vis-à-vis α-MBL, was carried out to achieve the target. Surprisingly, the two monomers reacted even in absence of any radical initiator at 70°C and above. Complete ring-opening of MDO did not take place, and some ring-retained structures were also present. On investigation, the reaction under consideration was found out to be initiated via charge transfer between nucleophilic double bond of MDO and electrophilic double bond of MBL, and was thereafter proceeded by a mixed mechanism of radical and ionic. The microstructure of the obtained polymers was blocky-random, wherein blocks of MBL and polyester or polyacetal of unequal sizes was obtained. Radical mechanism yielded mostly blocks of MBL and polyesters, whereas ionic mechanism yielded mostly blocks of MBL and polyacetals. It was possible to monitor the mechanism and hence the microstructure of the materials by varying reaction conditions like temperature, monomer feed, and time. Due to the addition of radical initiator, reaction was allowed to undergo mostly via radical mechanism, thereby yielding P(MBL-co-esters).

PMBL being itself degradable due to ester group present in it, not only enhances its degradability due to the incorporation of ester linkages of cyclic ketene acetal units, but also enhances its processability by increasing the softness and thereby decreasing the glass transition temperature from 195°C to as low as -52°C. The copolymer having 47% of MDO units was found to give 9.9% elongation at F_{max} and was also found to be elastic, while the sample that constituted 34% MDO gave 5% elongation at F_{max} and was found to be brittle. The synthesized materials were also tested for base hydrolysis (5% wt. NaOH in methanol) overnight, and were found to be degradable.

Degradable, eco-friendly, natural source originated, materials were finally synthesized.which could be used for various applications

7.2 In German

Es wurden neue, abbaubare Materialien mit extrem niedrigen (-44°C) sowie sehr hohen (163°C) Glasübergangstemperaturen mittels radikalischer Polymerisationstechniken synthetisiert. Dazu wurden unterschiedlichste Monomerkombinationen von Vinylacetat (VAc) und α-Methylen-γ-butyrolacton (α-MBL) (in der gemeinen Tulpe enthalten) mit dem zyklischen Ketenacetal 2-Methylen-1,3-dioxepan (MDO) eingesetzt. Abbaubarkeit der Polymerketten wurde durch ringöffnende Polymerisation des zyklischen Ketenacetals erreicht.

Abbaubare P(VAc-co-Ester) Polymere (auf Basis von MDO und Vinylacetat) wurden durch radikalische ringöffnende Copolymerisation von 2-Methylen-1,3-dioxepane mit Vinylacetat in Gegenwart von AIBN als Initiator bei 70°C hergestellt. Die Mikrostruktur der erhaltenen Copolymere wurde NMR-spektroskopisch (1D und 2D Techniken) aufgeklärt. Die so nachgewiesene vollständige Ringöffnung von MDO führte zum Einbau von hydrolysierbaren Estergruppen in das C-C-Rückgrat von Poly(vinylacetat). Die nach Kelen und Tüdos bestimmten Reaktivitätsparameter r_{VAc} = 1.53 und r_{MDO} = 0.47 sprechen für eine statistische Anordnung der Estergruppen im Polymerrückgrat. Die erhaltenen Materialien zeigten Glasübergangstemperaturen zwischen 37 und -44°C in Abhängigkeit des Ester-Anteils und eine sehr hohe Bruchdehnung. Während reines PVAc einen E-Modul von 6.5 x 10^{-3} GPa und eine Bruchdehnung von 1007% hat, konnte für P(VAc-co-Ester) mit einem Esteranteil von 5% ein E-Modul von 5.1 x 10^{-3} GPa sowie eine Bruchdehnung von 1093% und bei 18% Esteranteil ein E-Modul von 2.9 x 10^{-3} GPa bei einer Bruchdehnung von 1285% ermittelt werden. Die Hydrolyseprodukte wurden auf Zytotoxizität (L929 Zelllinie) getestet und mit der von als nicht-toxisch geltenden Materialien wie Poly(ethylenimin) verglichen. Die Hydrolyseprodukte waren nicht-toxisch, die Zell-Viabilität lag bei > 95%. Eigenschaften wie Abbaubarkeit in Verbindung mit nicht toxischen Abbauprodukten und niedrige Glasübergangstemperaturen machen einen Einsatz der Materialien als abbaubare Kaugummis, Beschichtungen usw. möglich.

Zusätzlich wurden abbaubare Materialien für unterschiedlichste Einsatzbereiche synthetisiert. Aufgrund der hohen Erweichungstemperaturen (bis zu 163°C) könnten diese Polymere als umweltfreundliche thermoplastische Materialien Anwendung finden, die leicht zu unbedenklichen Produkten abgebaut werden können und auf einer pflanzlichen Quelle basieren.

Polymerisationen des zyklischen Ketenacetals MDO mit dem natürlich vorkommenden Monomer α-MBL wurden durchgeführt um dieses Ziel zu erreichen. Überraschender Weise reagierten die beiden Monomere in Abwesenheit eines Radikalstarters bei Temperaturen von 70°C und darüber. Eine vollständige Ringöffnung von MDO fand nicht statt - einige zyklische Strukturen blieben erhalten. Ein Untersuchung des Reaktionsmechanismus zeigte, dass die Polymerisation durch Ladungstransfer von der nukleophilen MDO Doppelbindung auf die elektrophile MBL Doppelbindung initiiert wurde und das anschließende Kettenwachstum auf einem gemischt ionisch-radikalischen Mechanismus beruht. Eine statistische Abfolge von unterschiedlich großen Blöcken aus MBL und Polyester oder Polyacetal wurde durch Analyse der Mikrostruktur der erhaltenen Polymere bestimmt. Der radikalische Mechanismus führte hauptsächlich zu MBL- und Polyester- Blöcken, wohingegen der ionische Mechanismus hauptsächlich zu MBL- und Polyacetal-Blöcken führte. Es war möglich den Mechanismus und damit auch die Polymermikrostruktur der Materialien durch Variation der Reaktionsbedingungen wie Temperatur, Monomerzusammensetzung und Zeit zu beobachten. Durch den Zusatz eines Radikalstarters erfolgte das Kettenwachstum hauptsächlich radikalisch und führte zu Polymeren P(MBL-co-Ester).

Das bioabbaubare PMBL wird durch die Estergruppen, die der ringöffnende Einbau des zyklischen Ketenacetals beisteuert, nicht nur noch besser abbaubar, sondern lässt sich auf Grund der höheren Weichheit der Copolymere (Reduzierung der Glasübergangstemperatur von 195°C auf Temperaturen bis -52°C) auch besser verarbeiten. Das Copolymer mit einem MDO Anteil von 47% zeigte ein elastisches Verhalten bei einer Bruchdehnung von 9.9% während das Material mit 34% MDO spröde war und eine Bruchdehnung von 5% aufwies. Die Abbaubarkeit konnte durch basische Hydrolyse (5 Gew.-% NaOH in Methanol) der synthetisierten Materialien über Nacht gezeigt werden.

Schließlich wurden, abbaubare, umweltfreundliche und auf natürlichen Rohstoffen basierende Materialien synthetisiert, die viele nutzliche Anwendungen haben.

8. Appendix

8.1 List of Symbols and Abbreviations

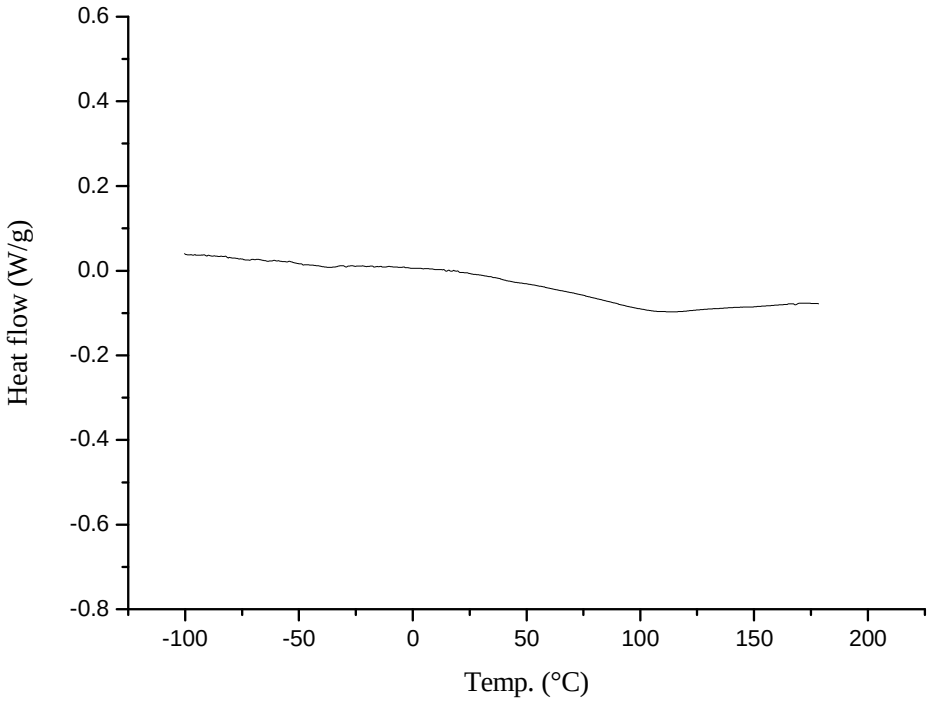
[η]	Intrinsic viscosity
AIBN	Azobisisobutyronitrile
BMDO	5,6-benzo-2-methylene-1,3-dioxepane
$CDCl_3$	deuterated chloroform
CH_3OH	Methanol
$CHCl_3$	Chloroform
CKA	cyclic ketene acetal
DMSO-d_6	deuterated dimethyl sulfoxide
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
DSC	differential scanning calorimetry
dtbp	di-tertiary butyl peroxide
ECH	Epichlorohydrin
GPC	gel permeation chromatography
H_2SO_4	sulfuric acid
HCl	hydrochloric acid
HMBC	heteronuclear multiple bond coherence

HMQC	heteronuclear multiple quantum coherence
HQ	Hydroquinone
LCMS	liquid chromatography mass spectroscopy
MBL	α-methylene-γ-butyrolactone
MDO	2-methylene-1,3-dioxepane
MMA	methyl methacrylate
mol-%	mole percentage
MTT	3-(4,5-dimethylthiazole-2-yl)-2,5-diphenyl tetrazolium bromide
M_n	number average molecular weight
M_w	weight average molecular weight
Na_2SO_4	sodium sulfate
NaOH	sodium hydroxide
NMR	nuclear magnetic resonance
PCL	poly(caprolactone)
PDI	polydispersity index
PMBL	poly(α-methylene-γ-butyrolactone)
PMMA	poly(methylmethacrylate)
PVAc	poly(vinyl acetate)
r	reactivity ratio
T_g	glass transition temperature

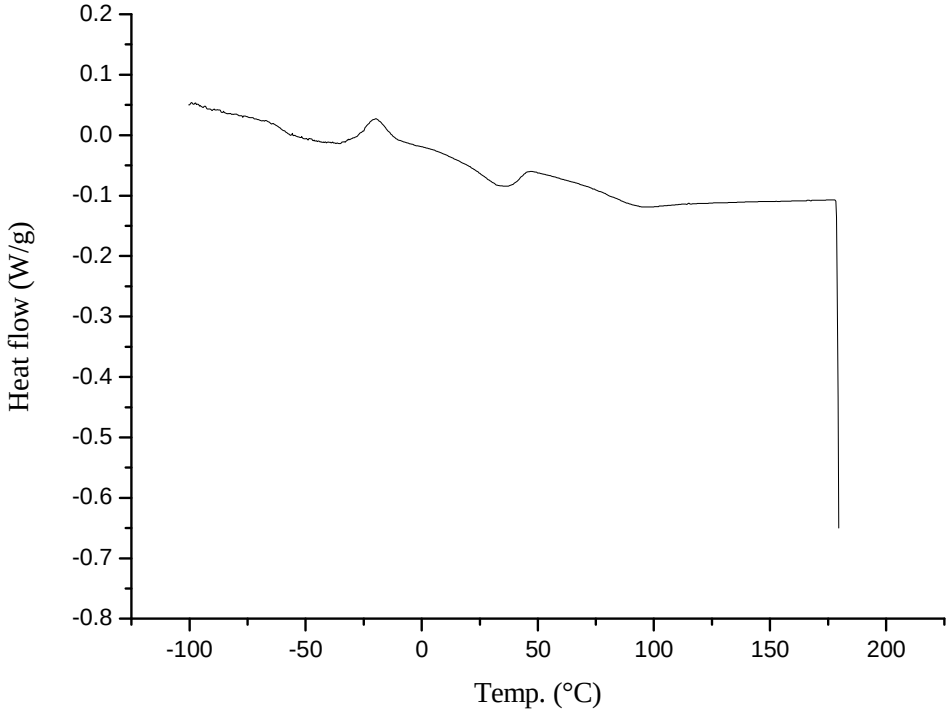
TGA	thermo gravimetric analysis
THF	Tetrahydrofuran
UV-Vis	ultra violet-visible spectroscopy
VAc	vinyl acetate
η_{sp}	specific viscosity

8.2 DSC curves

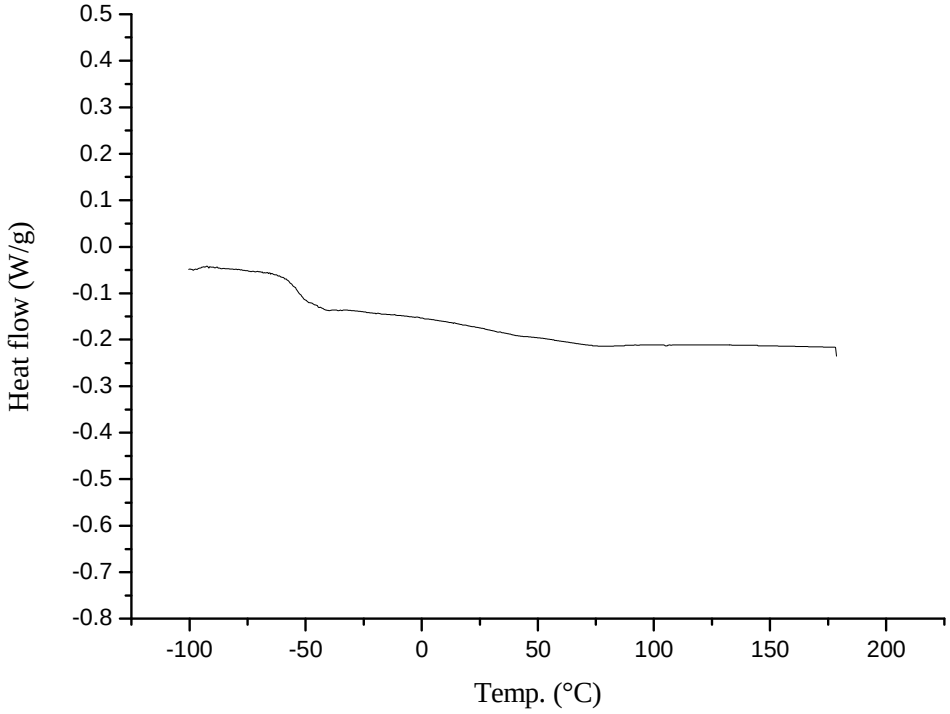
Some relevant DSC Curves:



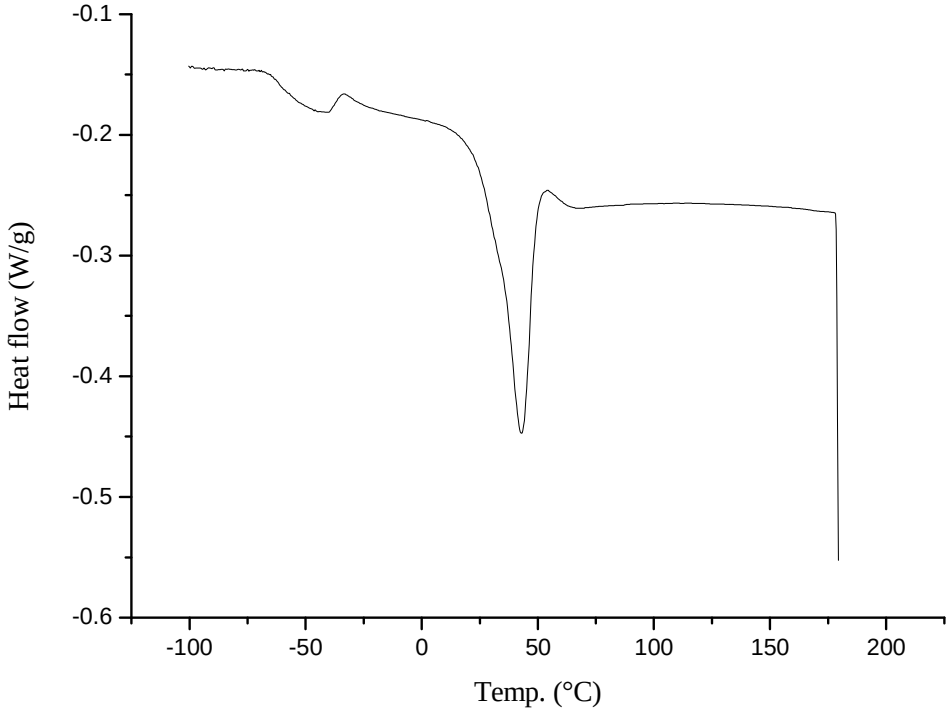
Run 3, Table 5.3.8



Run 4, Table 5.3.8



Run 5, Table 5.3.8



Run 6, Table 5.3.8

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