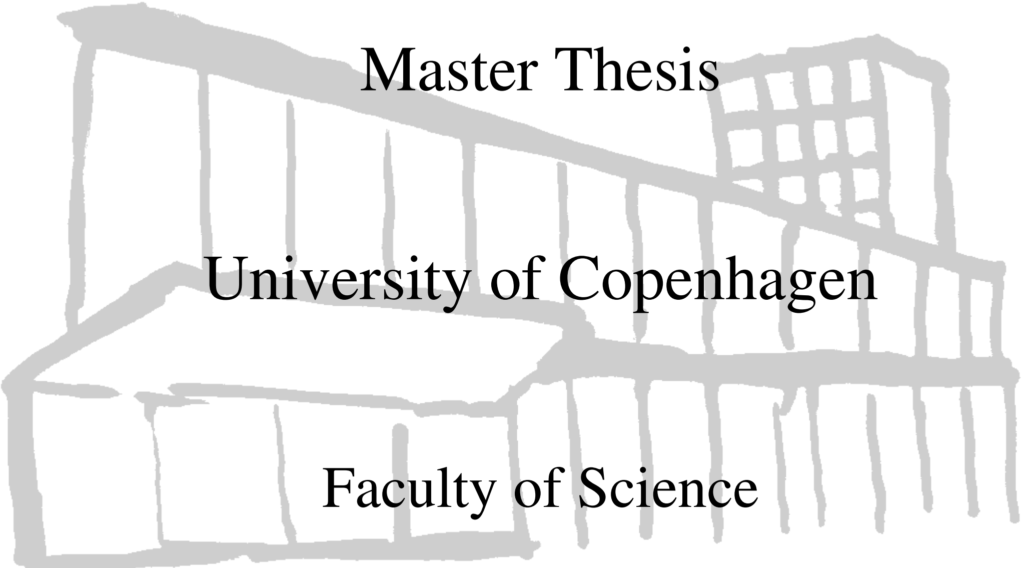
Liquid Crystalline Side Chain Polymers

Synthesis and characterisation

Erik Lund



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From outside the academic world, my mother Elinor gave her support in taking up the challenge to pass through a scientific education on an academically level in a mature age. She was looking forward to my graduation, unfortunately her weak health did not allow her to follow the last year of my work.

RESUME IN DANISH LANGUAGE.

Dette projekt har to dele; Første del er fokuseret på syntesen af to ny monomerer til anvendelse i funktionelle side kæde polymerer. Begge med funktionelle egenskaber som accepter enhed for hydrogen bindinger. De ønskede egenskaber søgtes tilvejebragt gennem terminale sidekæde grupper med nitrogen i heterocykliske aromatiske specier. I projektet blev anvend isonicotinsyre og stilbazol som terminale enheder. De to monomerer M1, 4-(6-acryloxyloxyhexyloxy) stilbazol og M2, 6-acryloyloxyhexyl-isonicotinat blev syntetiseret og efter følgende polymeriseret. Hydrogen bindings egenskaben blev efterprøvet ved hjælp af NMR, hvor de to nabo ^{1}H til nitrogen i aromaten har resonansfrekvensen $\delta = 8.5$ppm for nitrogen med et frit lone pair, når dette lone pair indgår i bland andet hydrogen bindinger ses et chemical shift i området fra 9 til 9,5 ppm. Ved henholdsvis protonisering og deprotonisering sås dette skift tydeligt i NMR spektrerne . 6-acryloyloxyhexyl-isonicotinat gav problemer på grund af en mørk rød farvning, dette blev tillagt oxidation af nitrogen, reduktion efter standart metoder gav ikke det ønskede resultat.

Den anden del af projektet var fokuseret på undersøgelse af mesofaser i polymer blandinger. Tre sidekæde polymer blev syntetiseret til formålet. Homopolymeren P3, cholesteryl-4- (6-acryloxyloxyhexyl oxy)-benzoat der har en smectic C* fase dannede grundlag, idet den ved copolymerisation med monomer M4, 4'-methoxyphenyl-(5-acryloyloxypentanoyloxy)-benzoat, der har en nematic fase, skulle overføre sine egenskaber til copolymeren, dette blev undersøgt dels ved DSC og dels ved mikroskopi med polariseret lys. Ved et blandingsforhold på M3/M4 i 30 til 70 mol % sås tydeligt tilsvarende egenskaber som ved homopolymer P3 der blev tolket som en smectic C* fase, der vil ved yderligere undersøgelser sikkert kunne findes en bedre ratio mellem specierne.

Ved at copolymerisere M3 og M5, 4- (6-acryloxyloxyhexyloxy)-benzoesyre blev det vist at M3 s egenskaber kunne forbedres så der fremkom helst skarpe fase transitioner, Dette blev også undersøgt ved hjælp af DSC og mikroskopi med polariseret lys, her viste DSC analysen at et optimum findes omkring et ratio M3/M5 90 til 10 mol % sammen med mikroskopien gav det anledning til at tolke mesofasen til at være, smectic C* fra 40^o til 140^{o}C.

Strukturerne af monomererne kan ses på plate II.

RESUME IN ENGLISH

This project has two parts. The first part was focused on the synthesis of two novel monomers for the use in functional side chain liquid crystal polymers. Both monomers should have the property to act as acceptor part in a hydrogen-bonding. Terminal side chain groups contain nitrogen in heterocyclic aromates established the wanted property. In this project was used isonicotinic acid and stilbazole as terminal moiety. The two monomers M1, 4-(6-acryloxyloxyhexyloxy) stilbazole and M2, 6-acryloyloxyhexyl-isonicotinate was synthesized and afterwards polymerised. The property to act as acceptor part in hydrogen bonding was tested on ^{1}H NMR because the resonance frequencies for the protons neighbour to the nitrogen with a free lone pair is 8.5ppm and the signal is shifted to approximately 9.0 to 9.5ppm when the lone pair is part in a bonding. This shift was easily monitorated by protonation and deprotonation the two compounds. The 6-acryloyloxyhexyl-isonicotinate was colorized, which was taken as a sign for oxidation; the colour was tried removed by reduction by standard methods, but without the wanted result.

The second part of this project was focused on the characterisation of the mesophases of polymer blends. Three side chain polymers was synthesised for this purpose. The homopolymer P3, cholesteryl-4- (6-acryloxyloxyhexyloxy)-benzoate which has a smectic C* phase gave the basic for the work. The M3 was copolymerised with the monomer M4, 4'-methoxyphenyl-(5-acryloyloxypentanoyloxy)-benzoat in different ratios to investigate if the M4 was able to adopt the properties from M3. For the ratio of M3/M4 in 30 to 70mol% it was clearly shown in DSC that the properties from M3 was adopted by the copolymer it has a smectic C* phase. For the optimising of the ratio between the two monomers further investigation is necessary.
For the copolymerising of M3 and M5, 4- (6-acryloxyloxyhexyloxy)-benzoic acid it was shown that the properties of M3 was improved by copolymerising it with monomer M5. The copolymer was investigated by DSC and an optimum was found for the ratio between the monomer M3/M5 in 90 to 10mol % this was also confirmed by microscopy investigation. A smectic C* phase was seen in the temperature interval from 40°C to 140°C.
The structure of the monomers can be seen on plate II.

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INTRODUCTION

During recent years significant interest of the scientific community has been paid to supramolecular structures with a wide spread area of applications reaching from spacecraft to microsurgery. Most people are familiar with strong polymer materials from car bumpers to bulletproof vests. It is less well known that some polymers can conduct electricity and emit light [20], these fact have open up for the use of semi conducting polymer in light-emitting diodes (LED technology) and as photovoltaic for use in detectors or solar-cells

Polymer compounds, which show mesophases, are among the subjects of major interest and research is striving towards finding new materials with useful optical and mechanical properties. For many of these new materials, side chain polymer serve as the fundamental structure, these polymers are often obtained from vinylic monomers. Moieties with mesogenic properties well know from of low molecular liquid crystal have been building into the side chain and so have chiral molecules. They have thereby given rise to new mesogenic and cholesteric materials with useful optical properties for devices such as displays and sensors. This way of working with liquid crystals has opened up for mixing of monomers and making copolymer with more stable mesophases or mesophases over a broader temperature range.

Polymers based on hydrogen bonding are of special interest, because they may respond to the action of external fields or charges of the chemical environment. These types of polymers can also be obtained from side chain polymers; in this case the hydrogen-bonding sites often are placed on the terminal end of the side chain. For the reason of the dualism this moiety can be, donating as well as accepting groups. Often are carboxylic acid and amino groups involved?

The same types of polymer systems involving other types of non-covalent bonding are in focus for research [21] and systems with metal complex bonding between a polymer backbone and metal atoms are described. Many of these non-covalent systems give rise to the idea that they can self organize in some kind of desired pattern. New molecular architecture as a product of a multi step hierarchy of self-assembling and even structures who can self-replicate has been realized [37].

All together this bring the side chain polymer system in front as a system that opens up a broad basis for the specific research work. Either it is used for a covalent incorporation of moieties with known properties or it serves as a structure in a self-assembling system to bring new chemical structures for benefit of human life.

THE EXPERIMENTEL WORK AND AIM OF THIS PROJECT.

This project has two parts. One part was concerned in synthesizing novel side chain polymers from monomer based on heterocyclic aromatic compound with hydrogen bonding site. It was decided to synthesize two monomer both having pyridine unit as the acceptor site for hydrogen bonding and an acrylate backbone. One based on isonicotinic acid where the spacer to the backbone should be build in with two ester groups to increase the solubility. This monomer gives rise to that idea that it can be used in copolymers to introduce new properties by hydrogen bonding moieties with known characteristics.
And a second monomer based on stilbazole connected to the spacer with an ether group. The stilbazole moiety is well known [46] in the polymer chemistry as a group added to polymer with a hydrogen-donating group. The stilbazole is also well known [47] in complex chemistry where it gives rise to cis trans isomerism. For that reason it is of great interest to investigate which new properties this monomer give rise to as mono-polymer and in blends of polymers

A second part was concerned with synthesizing and investigating the change in the mesophase behaviour of polymer mixtures. It was desired to synthesize three “side chain monomer” all having acrylate backbone. The one monomer should contain cholesterol M3 and thereby give rise to a chiral mesophase. The two other monomers were well known from the literature. One the M4 [36] is described having a nematic mesophase as mono polymer. It should be investigated by copolymerisation if the M4 monomer can adopt the characteristic from M3 by adding 15 to 30-mol % of M3.The mesophases if any should be characterized by differential scanning calorimetry DSC, and optical micrograph equipped with crossed polarizers. The other one the M5 [45] have a smectic mesophase as mono polymer and it should be investigated by adding 10 to 20 mol% in an copolymerisation with M3 if it can result in a sharper phase transition for the M3 polymer. The mesophases should be characterized with DSC and optical micrograph equipped with crossed polarizers.
The structures of the monomers can be seen on plate II.

POLYMER

Polymers are large molecule made up of repeating unit *monomers*. The word polymer is derived from Greek *poly,* meaning “many,” and *mer* meaning, “part.” Very often the acronym macromolecule is used instead of polymer. It means that to make a polymer we need monomers that are able to make bonding to each other (*polymerise*). This bonding will in most cases be covalent.

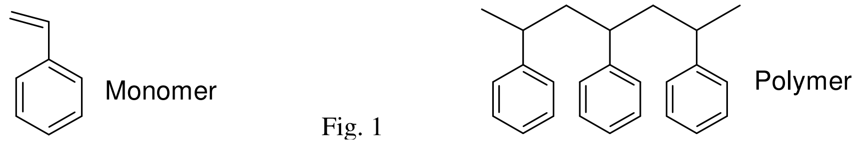
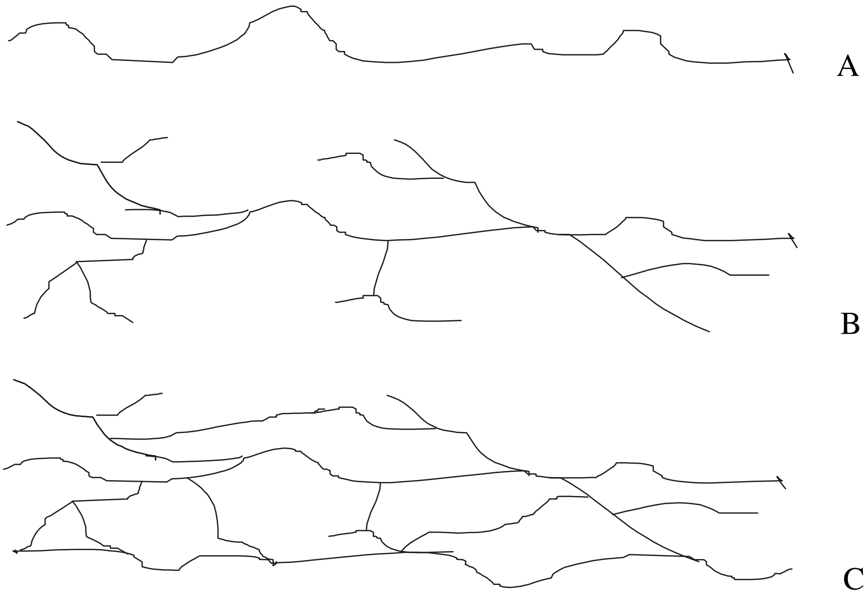


Fig. 1

If only a few molecules 10 to 30 polymerise the term oligomer is used for the product instead of polymer.
The repeating units can be of the same type, and then the product is a *homo polymer*. If two or more *base unit* are involved, the product is a copolymer. For getting a brief view of these types of polymer, it is easiest to look at them in an schematically way.

-M-M-M-M-M-M-M-M-	Homo polymer
-M-O-O-M-O-M-M-O-	Random copolymer
-M-O-M-O-M-O-M-O-	Alternating copolymer
-M-M-M-M-O-O-O-O	Block copolymer
-M-M-M-M-M-M-M- | -O-O-O-O-	Graft copolymer

Another way to describe polymer is to classify their shape as linear, branched and network fig.2



Polymer types: (A) linear, (B) Branched, and (C) Network

Fig.2

Some special polymer architectures have been named: (A) comb polymers, (B) star polymers, and (C) ladder polymer fig. 3

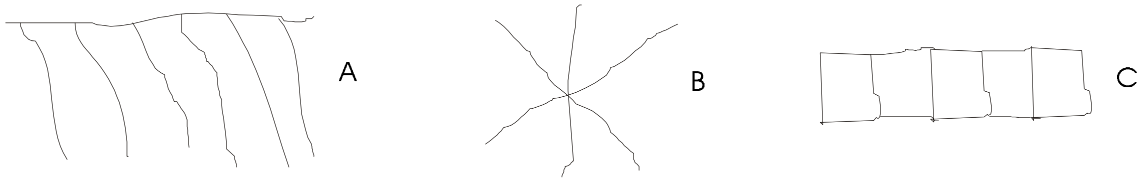


Fig. 3

There are numerous classifications for polymers, but most of the polymers fall in one of two main groups. The first group is the *thermosetting* polymer these are formed by network polymers; an example is vulcanisation of rubber. The original polymer is not containing many monomers but they are later linked together with each other in a network. This means that the polymer cannot melt or flow and heating will end in a degradation or decomposition. The second group of polymers is the *thermoplastic*; they differ from the thermosetting in that they do not cure (form networks) or set.

This group of polymers can melt and flow and since they do not cure or set they can be remelted and then rehardened by cooling.

Characterisation of a polymer often involves more complicated methods than normally used for low molecular weight compounds. The morphology of polymers, the way molecules shape and arrange in a solid tells us to distinguish between crystalline and amorphous materials. The ways they polymerise have influence on the physical behaviour. Vinyl monomers often under go head-to-tail polymerisation even head-to-head and tail-to-tail is represent fig. 4. For a head-to-tail vinyl polymer there is different stereo regularity, which influence the order in the polymer. The *isotactic* fig. 5 in which each chiral center has the same configuration and the *syndiotactic* fig. 6 where alternating chiral centers has the same configuration. If the chiral centers are randomly distributed it is called *atactic*.

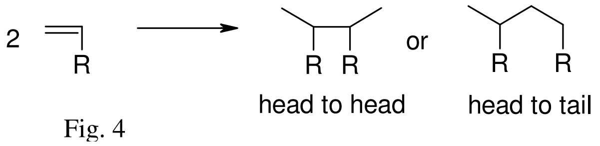


Fig. 4

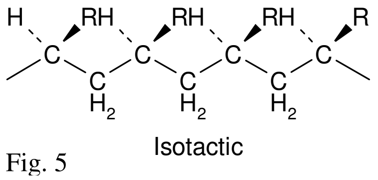


Fig. 5

Crystallinity is the presence of three-dimensional order on the level of atomic dimensions. In polymers, the range of order may be as small as about 2 nm in one (or more) crystallographic direction(s) and is usually below 50 nm in

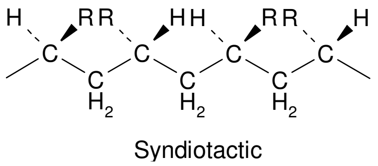


Fig. 6

at least one direction. Polymer crystals frequently do not display the perfection that is usual for low-molecular mass substances. Polymer crystals that can be manipulated individually are often called polymer single crystals.'[4]

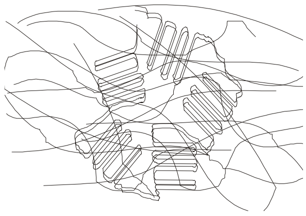


Fig. 7. Crystallinity

The crystalline polymer shows a high degree of order by folding the chain in a parallel and stacked structures fig. 7.

The amorphous phase is a glass like structure. The molecules are randomly arranged fig.8; it means that they have no single shape and that long-range order is absent. It is a structure with long and tangled chains, which twist and curve around one-another. In general the amorphous polymer change from a hard and brittle material at low temperature to a soft deformable materiel at high temperature, we use the term "glassy state" and "rubbery state". The change from glassy to rubbery state occurs over a narrow range of temperatures characterised as the glass *transition temperature* T_g. The nature of this transition has been under discussion. It is however clear that the specific heat, C_p, goes through a step as the glass transition is traversed. It has the typical signature of a second order phase transition. From the curve fig. 9 we see that the specific heat rises for a temperature over T_g. This is so because the chains is more mobile and have a higher flexibility to allow rotation about chemical bonds. T_g is a well-defined experimental quantity. But it should be taken into account that T_g can be manipulated by changing the structure of the polymer. Molecular weight as an example influence T_g, a low molecular weight is decreasing T_g and thereby the *degree of polymerisation* comes into play. The morphology of most polymers is semi-crystalline, so that it is a mixture of small amorphous and crystalline parts. This result in an interval melting point opposite to low molecular materials that have sharp melting points. In many polymers, the combination of crystalline and amorphous structures forms a material with desirable properties of strength and stiffness.

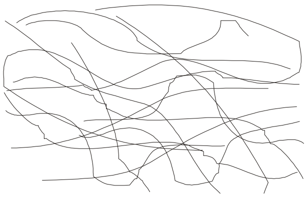


Fig. 8. Amorphous

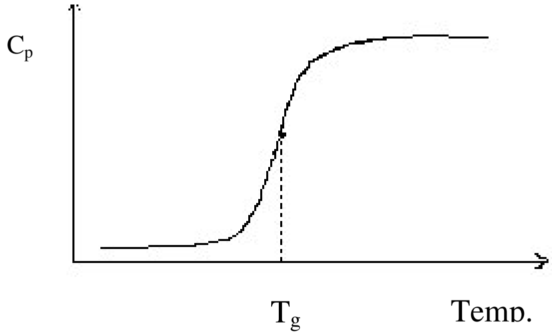


Fig. 9 typical amorphous polymer

The degree of polymerisation is a measure of how many units that stick together and thereby it gives us information on the chain length and molecular weight. In ordinary synthesis it is not possible to make a polymer with the same length for all molecules. They will always be a statistical mixture of length it is a polydisperse polymer. Monodisperse polymers are only produced in large scale in nature. But living polymer processes are known in synthesis [38], [39]. So the molecular weight is in general given as an average. There are several physical and chemical methods to determinate the molecular weight average and therefore also different ways to calculate it.

Here will be mentioned some of the commonly used molecular weight averages [13] [14] [15]. The number of a species is represented with *N* and its molecular mass by *M* and *w* is the weight.

Number Average:

$$M_n = \frac{\text{Total Weight}}{\text{Number of Molecules}} = \frac{\sum w_i}{\sum_i N_i} = \frac{\sum_i (N_i M_i)}{\sum_i N_i}$$

This emphasizes the presence of oligomers, because each species M_i contribute equally.

Weight Average:

$$M_w = \frac{\sum_i (w_i M_i)}{\sum_i w_i} = \frac{\sum_i (N_i M_i^2)}{\sum_i (N_i M_i)}$$

Every species is here contributing according to its weight w_i.

Viscosity Average:

$$M_\eta = \left[\sum_i w_i M_i^a\right]^{\frac{1}{a}} = \left[\frac{\sum_i \left(N_i M_i^{a+1}\right)}{\sum_i \left(N_i M_i\right)}\right]^{\frac{1}{a}} \qquad 0.5 \le a \le 1.0$$

The viscosity average can be derivate from the intrinsic viscosity $[\eta] = \frac{\sum_i w_i [\eta]_i}{\sum_i w_i}$. Using the Mark-Houwink-Sakurada relation $[\eta]=KM^a$ and substituting KM^a with the $[\eta]$. For solvent with a = 1, M_η becomes equal to M_w. For a monodisperse polymer the value for these mass averages is equal. But for a polydisperse polymer they will come out with different values where M_n is less than M_w and M_η often as a value between them. The ratio of M_w and M_n is called the dispersity d or the polydisperse index PD for the value PD=1 it is monodisperse.

$$PD = d = M_w / M_n \ge 1$$

There are a number of methods to characterise polymers, many are related to the development in spectroscopic equipment. One of those spectroscopic techniques that have provided much valuable information is the nuclear magnetic resonance NMR technique. It is possible to identify the structural units as well as the tacticity from a combination of chemical shift and spin-spin splitting from the ^1H proton spectrum. The ^{13}C spectrums can also indicating for which tacticity there is dominating the polymer.

Another tool is the infrared spectroscopy IR and the more recent Fourier transforms infrared FTIR. It is particular useful in studying polymer blends. Polymer blends that are immiscible show an IR spectrum that is the superposition of the two homopolymers spectra, for the miscible blend there is the superposition of three spectra those from the homopolymers and then an interaction spectrum from the chemical or physical interaction between the homopolymers.

For polymers containing chromophores ultraviolet (UV) visible spectroscopy can be used with advantage. Chromophores that undergoes $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ transition can be detected and quantified with UV-visible and because of high sensitivity it can also be used to identify and analysing foreign materials in the polymer [16] such as residual monomer, inhibitor and so on. If the polymer chain have chromophores in one or both ends UV-visible spectra also can serve as a tool to measure the number average molecular weight [17].

LIQUID CRYSTALS

In our everyday live we normally think of three states of matter: solid, liquid and gas. This however is not the whole story. There is a large class of organic molecules, which do not show a single transition from the solid to the liquid, but rather a series of transitions between the solid and the liquid phase.

The difference between these states of matter is the degree of order. The definition of a liquid crystal given by de Gennes and Prost [1] is an intermediate phase, which has, a liquid-like order in at least one direction, and possesses a degree of anisotropy, which is characteristic of some sort of order

The order parameter is directly related to the temperature and pressure of the surroundings. When we raise the temperature the energy content and thereby the vibrations are raised to. Finally when the transition temperature between the solid and the liquid phase is reached the long range positional order is broken. There are still attractive forces between the molecules, so there is still some short-range positional order. If we further raise the temperature until the next phase change.

The molecules enter the gas state and the molecules are no longer bound to each other.

The liquid crystal phases between solid and liquid state all exhibit high orientational order while the positional order is of lower magnitude.

Molecules that have shapes other than spherical, rod-like (prolate) or disk-like (oblate) may give rise to different liquid crystal phases. There are three types of order involved. The first one is the orientational order. The molecules do not all point in the same direction all the time. They merely tend to point more in one direction over time than in other directions. This direction is referred to as the director of the liquid crystal. The measurement of the order is then given by the order parameter.

$$\mathbf{S}=\langle 3/2 \cos^2\theta - 1/2 \rangle,$$

Where θ is the angle between the molecular symmetry axis and the director. Fig. 10. Because of averaging this function of θ, **S** has a value between -½ and 1. One for perfect alignment and zero for the isotropic (liquid) phase, this orientational order are highly dependent on the temperature.

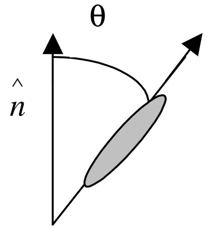


Fig. 10

The second type of order is positional order given by a density function, there in a simple case is given by the parameter

$$\boldsymbol{\rho}\ (z)=<\rho 0>(1+\psi\cos(2\ \pi z/d))$$

Where z is the coordinate parallel to the layer normal, the average density of the fluid is □, and d is the distance between layers and is the order parameter. When | |=0 there is no layering and the material is *nematic* but if |Ψ|>0 then some amount of sinusoidal layering exists and the material is *smectic.*

A third type of order is bond orientational order. A bond, in the present context, is not chemical bond but a line in space joining two adjacent molecules [2]. If the orientation of these bonds is preserved over a long range, the system possesses bond orientational order. It is found in phases called the hexatic smectics. Since the molecule best can pack in a hexagonal fashion, the six-fold symmetry of bond orientation give rise to a complex order parameter, ψ_{6}, witch have been used to account for this bond orientational order.

$$\psi_6 = \mathrm{Re}\ [I_6 \exp(6i\ \varphi)],$$

Where I_6 is a complex amplitude, Re means real part of, and φ is the azimuth angle with respect to the layer normal. Liquid crystallinity may be induced by the influence of solvents (*lyotropic systems)* or by purely thermal effects (*termotropic systems)*. Dissolving an amphiphilic mesogen forms the lyotropic mesophase in suitable solvents under appropriate condition with respect to concentration and temperature [3]. The lyotropic phase is out of the scope in this work and will not be paid further attention.

The termotropic mesophase is formed by heating a solid or by cooling an isotropic liquid, or by heating and cooling a thermodynamically stable mesophase. The mesogenics that are represented in this work are in the group of thermotropics therefore we will take a brief look at this group. Thermotropic liquid crystals usually contain rigid-rod chemical structure, rigidness of the long axis, the ratio between the diameter and the length should be about 3 to 8. The chemical structures have to show strong dipoles or substituents that have a high polarizabillity or both.

LIQUID CRYSTAL PHASES

The mesophases appear under thermal influence on the system and instead of a shift in the order from amorphous or crystalline state to the absent of order in the liquid phase, the order is broken down stepwise and bring the system through a number of measurable mesophases. Gradually as research move forward more phases have been recognised and here will just be mention some of the most common and well known see (Plate I.) For photo explanation see ‘Consequences of birefringence”

A liquid crystal behaves very much as an ordinary liquid in its isotropic phase where the molecules are randomly aligned and there is no long rage positional or orientational order. There may exist short-range order on the scale of angstrom although the isotropic phase behaves as normal fluid.

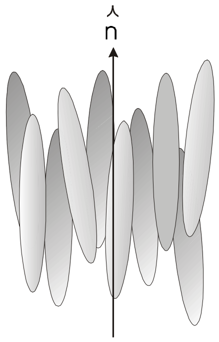


Fig. 11 Nematic

The nematic phase fig 11 (nematic come from Greek for thread-like, an observation done in microscope with polarized light) contain molecules that have a tendency to organize them self in parallel structures. The nematic phase can be generated from rod-like as well as discotic molecule structure. The transition from isotropic to nematic is found to be discontinuous and thereby of first order with a transitions enthalpy of approximately 0.5kJ mol^{-1} [8]. The orientational order is in average parallel to the **n** director present in the nematic phase, but positional order as well as bond order is absent fig x, y. When positional order is introduced to the nematic phases in one direction it leads to a smectic phase. The smectic phases can be subdivided into true liquid crystals and crystal smectics that are more ordered, and posse’s long-range positional order in tree dimension. The true liquid crystals are less ordered and have liquid properties. The simples phase is the smectic A phase (SmA) fig 12, it has two directions represented with the director and a layer normal. The transition from isotropic to SmA is discontinuous and of first order, but the transition from nematic phase to SmA show both continuous and discontinuous so it may be either first or second order transition. Often a broad nematic phase result in a second order N-SmA transition [18]. A phase very similar to SmA phase is the smectic C phase, SmC fig 13 it have a layered structure with no long range positional or bond order but it differ from the SmA phase because

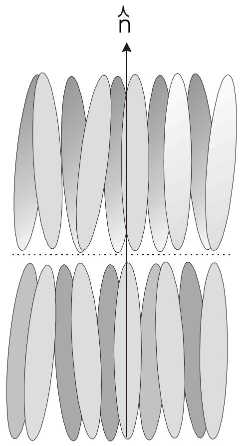


Fig. 12. Smectic A

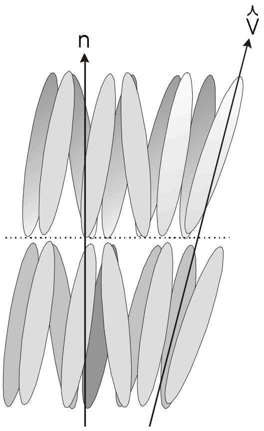


Fig. 13 Smectic C

the average molecule are tilted with respect to the layer normal i.e., **n** fig 13. The transition between the SmA and SmC phase is often second order, but first order is also reported. The layered and tilted structure means that it has an axial orientational order expressed by the orientational order parameter S that are very temperature dependent [19], and that it has short-range positional order in one direction just as SmA. An important property of the tilted phase is a different physical behaviour. One example is its biaxial optical properties.

Earlier some phases more ordered than the smectic A and C was called smectic, these is now referred as hexatic and crystal phases some times mentioned as soft crystals they have often long range positional order or bonding order in the plane. These are not true liquid crystal and they are taken in the table for the general view.

One special class of liquid crystals is, containing chiral centers in their molecules either the chirality's are in the mesogen or, it is introduced by adding a chiral molecule to the system. Molecules are said to be chiral when, their mirror image cannot coincide, a right hands mirror image is a left hand and they can never be brought to coincide.

The first discovered materiel exhibiting a mesophase was cholesteryl benzoate fig 14. It is a thermotropic liquid crystal that shows what is now known as the chiral nematic (N*) phase, the phase mentioned with an asterisk indicate that it contain chiral material, for the reason that the first observation was done on an ester of cholesterol it was and still are called the cholesteric phase.

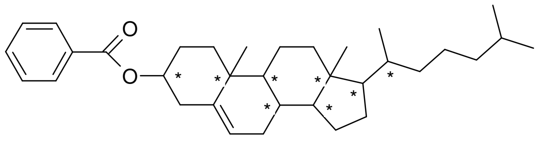


Fig. 14 Cholesteryl benzoate with 8 chiral centers
C 148 °C N* 178 °C I

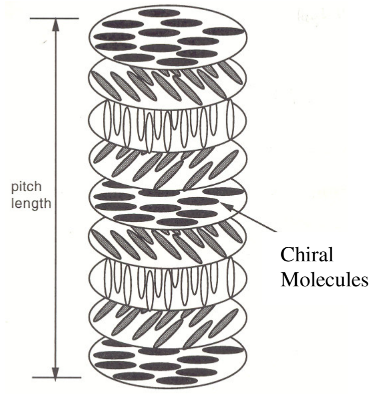


Fig. 15. The structure of chiral nematic phase. The views do not imply any type of layered structure

The structure of the chiral nematic phase is very similar to that of the ordinary nematic phase. It has an average parallel structure but the asymmetry, chirality, lead to a helical structure fig 15 in which the director **n** gradually rotate, say, around a z-axis. This gradual director change describe a helix witch has a specific temperature dependent pitch and for most system the pitch length increase with decreasing temperature [5].

The helical structure has an ability to selectively reflect light of a wavelength equal to that of the pitch length if the light propagation direction is parallel to the helical axis. For light in the visible area it give rise to the phenomena that the colour of the reflected light change with the temperature if the pitch length is in the same area as the wavelength about 400 to 750 nanometre.

The chiral molecules also give rise to a series of chiral smectic phases and chiral crystal smectic phases. The most important of them are the SmC* phase it is similar to the SmC phase it have layered structure and the molecules is in average tilted to the layer normal. The chirality courses a slight and gradual change in the direction of the molecular tilt. The tilt direction is changed gradually from layer to layer and performs a helix fig x, y. There is no change in the tilt angel with respect to the layer normal. The pitch length is depending of the temperature, as the temperature rise the tilt angel become smaller and the pitch length increase so the effect of temperature is opposite of what normally is seen in the chiral nematic phase. One special characteristic for the SmC* phase is its capability to spontaneous polarisation (P_S) a property which is coupled to the tilt angel, in a bulk sample P_S is reduced to zero and thereby defined as an helielectric, but in a single layer the SmC* is ferroelectric. The helix can be unwound in a magnetic or electric field and a pyroelectric phase is then generated. For the reason of the reduced symmetry one given tilt direction leads to a ferroelectric ordering of the molecules witch means the molecules is packed with one particular direction of P_S event fig. 16. This reduced system and the spontaneous polarisation lead to the property that in an electric or magnetic field the molecules can be switched by a reversal of the polarity. The research had brought new pattern of the SmC* phase in focus so ferrielectric and antiferroelectric phases are well known fig. 17, these can all be switched in a magnetic or electric field. Specially the antiferroelectric phases has been paid much attention because of its capability to switch to ferroelectric phases in a field and afterwards switch bag to antiferroelectric phases when the field is removed, this property give it a great potential in display devices.

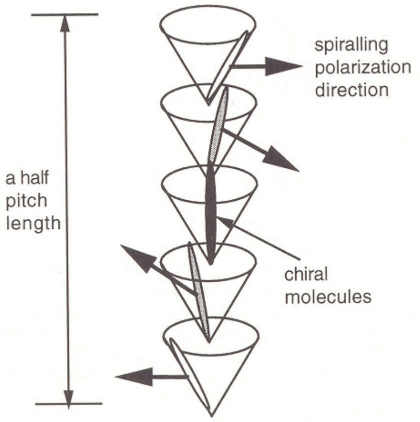


Fig. 16

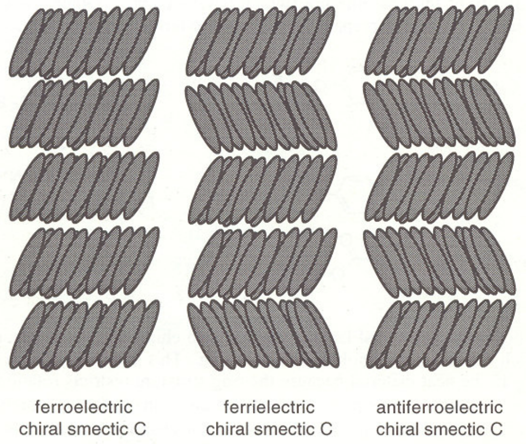


Fig. 17

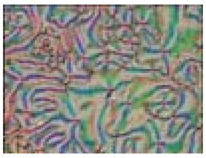
Plate I. Mesophases.

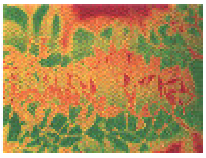
ORDER
decreasing

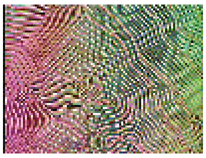
TEMPERATURE
increasing

Isotropic

N Nematic Cholesteric N*

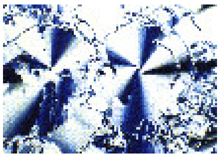






SmA Smectic A Smectic A* SmA*

SmC Smectic C **tilted** Smectic C* SmC*



Hexatic B

Hexatic I Hexatic F

tilted

Crystal B

Crystal J Crystal G

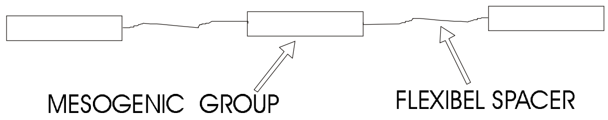
Crystal E

Crystal K **tilted** Crystal H

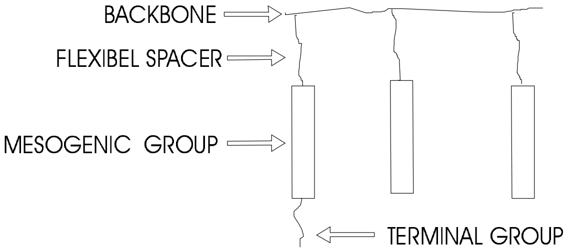
Crystalline Phase

THERMOTROPIC LIQUID CRYSTAL POLYMER

For many reasons it is practical to divide liquid crystal polymers LCP into two major groups, main chain liquid polymers MCLCP and side chain liquid crystal polymers SCLCP. Even then it should be mentioned that combinations of the two specific types exist, among other special constructed types of liquid crystal polymers. The structural units in main chain and side chain LCP is of the same type. In general they contain a rigid part, which is the mesogenics group. This is of the same types as mesogenics in low molecular mass compound.



Main chain liquid polymer



Side chain liquid polymer

In the MCLCP linking group, which tie this mesogenics together in long polymer chains. The linking groups can be flexible spacers. In the SCLCP the mesogenic groups is linked to the backbone with flexible spacers and the mesogenic can be mounted with a terminal group. The different groups in the system contribute each with their property to give the LCP its physical and mechanical characteristics; thereby it is possible to change these properties by adjustment on a single group in the synthesis. For the reason that MCLCP often have high clearing point 200 ^{0}C to 400 ^{0}C, they start decomposing before passing through the mesophases; it has been used to change the molecule architecture in order to reach more practical conditions for investigation. The most common way to reduce the mesophase temperature, is to introduce flexible spacers in the main chain in order to break up the rigidity, or to introduce lateral moieties on the mesogenic groups in order to decrease the symmetry and to avoid molecules packing into the crystalline state.

An example on a MCLCP with a flexible spacer containing six methylene (CH_2) units to lowering the mesophase transition temperatures is shown in fig 18. For the reason of the high clearing temperature and thereby unstable mesophase, many research resources has been directed to the field of SCLCP.

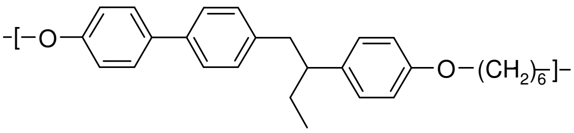


Fig. 18 MCLCP g 65^{0}C N 135^{0}C I

SIDE CHAIN LIQUID CRYSTAL POLYMER

The scope of this project includes the synthesis of known as well as novel side chain liquid crystal polymers SCLCP. For that reason it is relevant to take a closer look at this species. These polymers are often built up by structural monomers thereby exhibiting mesogenic behavior. It has been observed [6], [7] that if a monomeric unit shows a virtual or monotropic mesophase, the polymer obtained from these monomers will in general display either a monotropic or enantiotropic mesophase. If the monomeric unit exhibits an enantiotropic mesophase the resulting polymer should display an enantiotropic mesophase over a broader range of temperature. Another observation that has been done is that a polymer, which exhibits more than one virtual mesophase, has a tendency to show increasing number of mesophases with increasing molecular weights. This phenomenon is related to the thermodynamic, which gives a decrease in entropy when the degree of polymerization is increased.

When the mesogenic polymer system changes from MCLCP to SCLCP it could be expected that the influence of the polymer backbone no longer should influence the behavior of the mesogenics.

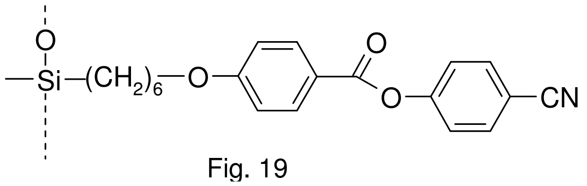


Fig. 19

Effect of <DP> on mesomorphic properties

<DP>	Transitions Temperatures (^oC)
40	g 2 S_A 128 1
55	g 9 S_A 128 1
84	g 13 S_A 128 1
107	g 14 S_A 145 1

However the spacer unit does not decouple the mesogenic completely so that the backbone does not influence the mesomorphic properties. In discussion of the backbones influences the flexibility of the back- bone is important. High flexibility increases the entropy and thereby decreases the T_g. This means that the mesomorphic temperature range increase. For that reason acrylates and methacrylates are very common in the synthesis of SCLCP. It is often difficult to rationalize the mesomorphic property with respect to the polymer backbone, it become clear when another non-structural factor regarding the backbone of significant impotents come into count, The average size of the backbone (<DP>) has influence on T_g. up to some limit increasing<DP> rise the T_g, when the <DP> reached around 100 the mesophase transitions temperature and T_g remain constant fig. 19. Among other conditions, which affect the mesophase, behavior should be mention two more. Firstly; the tacticity can be a determining factor to the flexibility of it own backbone, and therefore act on the phase transition behavior in the same way as the flexibility of the backbone. Isotactic conformation haves a tendency to show the lowest isotropizations temperature and atactic the highest.

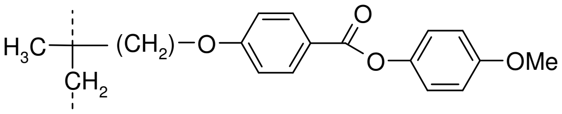


Fig. 20

Effect of spacer length on mesomorphic properties

Spacer length	Transitions Temperatures (°C)
0	S 255 l
2	g 120 N 152 l
6	C 119 S 136 l
11	g 54 S_C 87 S_A 142 l

Secondly, the polydispersity has some influence on the system but to a lesser extent.
The flexible spacers who serve to decouple the mesogenic moiety and the polymer backbone give rise to changing of the behavior of the SCLCP. The common types of spacers vary from simple methylene chain to alternating oxygen systems such as oxyethylene. For that reason it often difficult to find a pattern in the influence, but in general a polymer with a short spacer will exhibit only a nematic phase if any. With increasing spacer length the nematic phase is shifted to both a nematic and a smectic one and with very long spacers the nematic phase disappears and gives place for more smectic phases to display. An example is given in fig. 20 this should be taken as a general guideline only because different mesophases are connected to the transitions temperature witch can change dramatically by changing the terminal moiety, if –OMe is changed with –OEt the system will show a totally changed mesophase system. However increasing spacer length has a tendency to decrease the glass transition temperature. Another effect that the spacer gives rise to is the odd-even effect, when the spacer is still rather short it can be seen on the isotropizations temperature. The reason for this effect is related to the relative orientation between polymer backbone and the mesogenic part of the system. If the mesogenic part is perpendicular to the backbone the clearing point appears at a higher temperature then for analogous polymer with one more or one less unit in the spacer. The mesogenic units used in SCLCP are in general of the same type as those who is described for low molecular liquid crystals. Another form of SCLCP is a type where the side chain ends up in a site for non-covalent bonding, e.g. hydrogen bonding. One or more moieties with mesogenic properties can then be linked to the side chain polymer by self-assembling either before or after the polymerization. It also gives the possibility to derive advantage from using the polymer skeleton to many different SCLCP.

NON-COVALENT INTERACTION

Most polymer systems are constructed by covalent bonding, but also non-covalent interaction comes into play either as useful tool in constructing new polymers or as interactions, which should be avoided in the system. Ionic interaction, Van der Waals interactions, hydrogen bonds, hydrophobic interactions and metal coordination's bonding are among the best known non-covalent forces between atoms and molecules. In the development of polymers these give rise to molecular recognition and self-assembling the non-covalent interactions, the van der Waals forces, hydrogen bonds and metal coordination's bonding is the means to control the engineering.

The van der Waals attractions are electrical and thereby they can be both attractive and repulsive. The repulsive force are seen when two atoms or molecules come close enough to each other, then their electrons system repel each other, and so do their nuclei, these is often mention as the short range interaction.

The attractive forces come from three mechanisms. The first is the orientation effect it involve often permanent dipoles and give rise to rearrangement of molecules. It involves two possible components ion-dipole and dipol-dipol interaction in both cases the dipole response to the neighboring ion or dipole, which reduce the potential energy.

The second is the static induction effect; it appears from ions or permanent dipoles that may induce an additional dipole in another molecule, this other molecule may be a dipole itself or have a symmetrical electron distribution. Here it is the static electrically source dipole that make either a dipole-dipole or a dipole-non polar interaction.

The third one is the dynamic induction effect also called the dispersion effect it is present between all molecules and account for the symmetrical electrically neutral molecules or atoms, it shout be taken into account that the symmetrical distribution of electrons is an average over time.

These forces are often mentioning as long-range interactions. The half distance of the closest approach of two atoms or molecules that is not bonded is the van der Walls radii. Graphical the van der Waals interaction can be showed by the sum of attractive and repulsive forces as in fig 21.

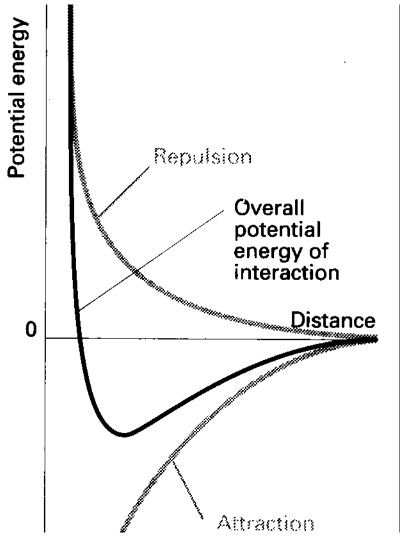


Fig.21
The general form of an inter-molecular potential energy curve

HYDROGEN BONDING

It is well known that hydrogen bonds are responsible for the structure and properties in biological macromolecules. This haves given rise to introduction the same effect in polymers where it gives access to many new application in the polymer world.

The hydrogen bond is a special case of the dipole-dipole interaction. They are stronger than other dipole-dipole interaction, and they occur as a donor acceptor system where a proton donor group interacts with a proton acceptor group. The donor part includes a hydrogen atom covalent by bound to an electronegative atom and an acceptor part, which also have to be highly electronegative. Often it is written as $A—H\cdots B$ where the dot line indicate the hydrogen bonding. The electronegative atoms in the system is in many cases O, N, and F but there is not a clear-cut whether an electronegative atom can participate in hydrogen bonding, so for recognizing hydrogen bonding in a system in liquid phase the attention should be on that Cl, Br and S can serve as acceptor part too. The most dramatically effect from the hydrogen bonding is the rise in boiling point. A compound that haves capacity for self-association haves a much higher boiling point than a homologous compound without this capacity, even when they have higher molecular weight Fig 22.

Boiling point °C 1. Atm.

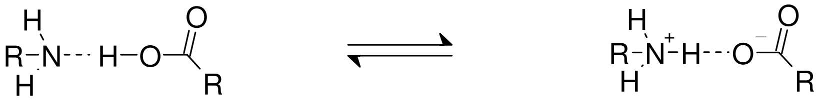
HF	20	H_2O	100	MeOH	60	NH_3	-33
HCl	- 85	H_2S	-61	MeSH	-78	PH_3	-87

Fig. 22

Hydrogen bonding also is lowering the vapor pressure as can be observed in a liquid two-component system where the derivation give a result lover than the predicted from Raoult's law. These effects may be due to hydrogen bonding. Many other phenomena depend more or less on these properties, mobility of the system decrease, which lead to increase in the coefficient of viscosity and decrease in diffusion coefficient.

Hydrogen bond is among the strong non-covalent forces, thermodynamically the enthalpies is in the range of 10- 40kJ mol^{-1} compared to covalent bonding with an enthalpies about 200kJ mol^{-1}. The length of these bonding is from 0.28nm up to 0.31nm where the covalent bond is about 0.15nm. For characterizing the hydrogen bonding both NMR and FTIR is used. In the proton NMR the hydrogen-bonded proton is indicating decreasing shielding. In the FTIR a band around 3100-2800cm-1, and a superimposed satellite band on the fundamental band monitor spectrometry the weak and moderate hydrogen bond. The strong hydrogen bond shows broad bands around 2800cm^{-1}, 2500cm^{-1} and 1800cm^{-1} and they will give broad torsions band around 1200cm^{-1} and 700cm^{-1}. In both cases the signal depend on the temperature [53], which do FTIR to an excellent way of investigating hydrogen bonds.

When proton donation is mention it leads to consideration of a connection to a Brønsted acid base pair. One can say that the strongest acid base pair form the strongest bonding and there is no sharp dividing into a proton transfer. It shortly can be explained as a system with two energy minima corresponding to two stable location of the proton. They are often referred as “salt bridges” shown in fig. 23.



Salt bridges fig. 23

The reason why hydrogen bonding is paid this overwhelming attention, because is for the reason that it has so many applications in the field of liquid crystals. For low molecular mass compound it has been showed [9] that by mixing two non-mesogenic moieties with donor and acceptor properties, the mixed phase after show mesogenic behavior. An example of very ordinary non mesogenic compound there by mixing 1:1 become a mesogenic and displaying a nematic phase from 153 ^{o}C to 163 ^{o}C is 4,4’-bipyridine and 4-methoxy benzoic acid. fig 24.

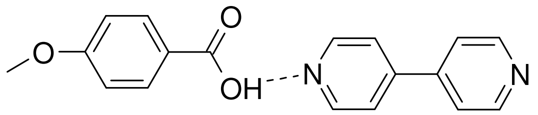


Fig. 24

It is also possible to build a new liquid crystal from a moiety showing mesogenic behavior by it self. T. Kato and coworkers has showed [10] that by mixing 4-butoxybenzoic acid, nematic from 147 ^{o}C to 160 ^{o}C and trans-4- [(4-etoxybenzoyl) oxy]-4’-stilbazole, nematic from 165 ^{o}C to 213 ^{o}C, in the ratio 1:1 displayed a smectic phase from 136 ^{o}C to 160 ^{o}C and a stable nematic phase up to 238 ^{o}C fig 25 So what we see in this case is that a single H bond is sufficient to preserve an extended mesogenic core, which result in an extended mesophase and even an additional phase. It have been reported [11] that hydrogen bonding between the pyridine ring and the carboxylic unit was preferred over the dimerisation between the carboxylic acid.

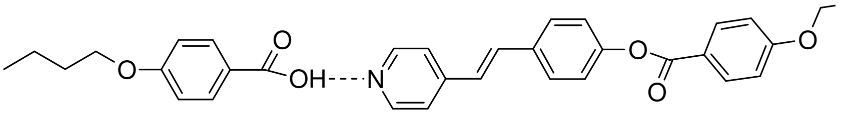
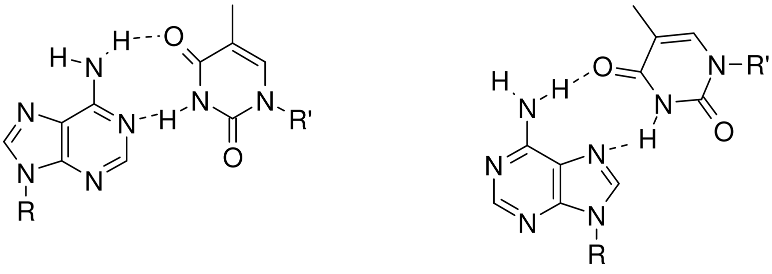


Fig. 25

SELF-ASSEMBLING

Hydrogen bonding is one of the major tools to design recognizing and self-assembling polymer nanostructured systems.

Nature is using self-assembling materials for nanoscale structures; the paring of nucleic bases in the DNA double helix is an example, which in addition shows some sort of recognizing. In the ordinary double helix the bases adenine and thymine pair in the Watson –Crick way, but sometimes it forms a triple-stranded helix the H-DNA, here it shows the Hoogsteen pairing fig. 26. These types of molecules are often termed Janus molecules, because they have a double-faced H-bonding recognizing unit. Man has taken up the challenge in designing polymer systems their taking advantage of using these intermolecular forces. SCLCP has been constructed [12]. In the simplest case the side chain has a site for making hydrogen bonding to one mesogenic moiety. Fig 27 is an example of an extended mesogenic, which has stabilized the nematic mesophase up to 252 °C.



Watson –Crick paring

Hoogsteen paring

Fig. 26

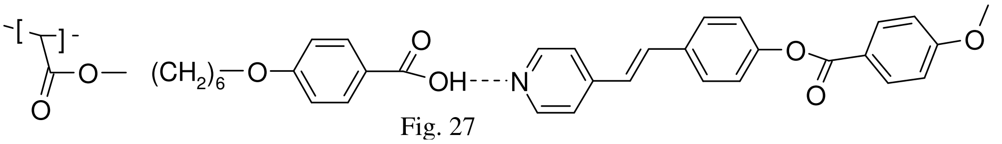


Fig. 27

A more sophisticated structures where SCLCP is used in combination with photo functional group changing between cis, trans configuration under influence of light is showed in fig. 28. Such applications have a great potential as memory storage and in non-linear optics.

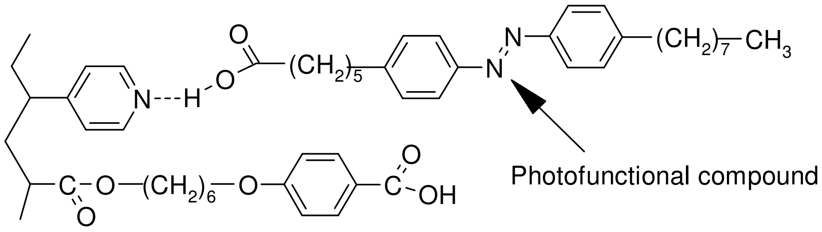


Fig. 28

Self-assembly of inorganic architectures has turned out very successful. In principle the formation of a complex from an organic ligand and a metal ion is an assembly process, so the emphasis here on its design of the ligand and the choice of the metal ion in order to produce the defined structures. Often these systems are reversible, so it is possible to make system that can assemble and after influence from the surrounding it can disassemble.

APPERATUS

In the next section the instruments used in the practical experimental work will be described. Some will be described briefly and others in more detail where it is support the understanding of the project. Some of the analysis was carried out on apparatus in other laboratories and other has been analysed in our own laboratory, which are reflected in the description of the instruments. The use of instruments fall in two parts, one part is used to characterize the organic compounds as a support for the synthesis work and for confirmation that the monomers were obtained. The other part is concerned about the investigation and characterising the polymers properties. There will obviously be some overlap and the single apparatus is then described under a heading where both aspects are treated together. A list of the used instruments are given beneath.

DSC:	PERKIN-ELMER DSC 7
Microscope:	NIKON OPTIPHOT with CCD. Camera ‘Euroline’CC V-931 connected to ordinary PC. The oven ‘Mettler Toledo FP82HT” with ‘Mettler Toledo FP90 central processor”
NMR:	“AM 250 Bruker” and ‘Unity 400 Varian”
Mass spectrometer:	Hewlett-Packard 59xx GC-MS instrument with electron ionisation
HPLC:	Knauer HPLC pump 64, Knauer Differential-Refractometer, columns: ‘Machery -Nagel Nucleosil 300-7 OH” and ‘Machery -Nagel Nucleosil 100-7 OH”

DIFFERTIAL SCANNING CALORIMETRIC

One of the working horses in the investigation and characterising of polymer material is the differential scanning calorimetric (DSC). The DSC is a thermal analysis method where the polymers are investigated for thermal transitions. The difference in heat flow to the sample and to the reference at the same temperature is recorded as a function of temperature. It means that the measured energy differential corresponds to the enthalpy or the specific heat for the polymer. The heat capacity is given as $C_P = \left(\frac{dH}{dT}\right)_P$

In a low molecular liquid crystal as well as in a liquid crystal polymer the phase transitions between the mesophases also are changes in enthalpy, which make the DSC an excellent method to characterize these materials.

The normal design in a DSC apparatus is two identical sample holders connected to a furnace, the sample is placed in an inert pan set in the one of the sample holders, and another equal empty pan is placed in the other sample holder, and used as a reference. So the DSC measures the difference in heat capacity. $\Delta C_P = C_P(\text{sample}) - C_P(\text{reference})$.

The heat flow control and the monitoring of the results are computerised. Both heating and cooling curves gives information so the melting point is shown on heating and crystallization on cooling. Figure 29 shows a typical DSC curve combining the heating and the cooling curve.

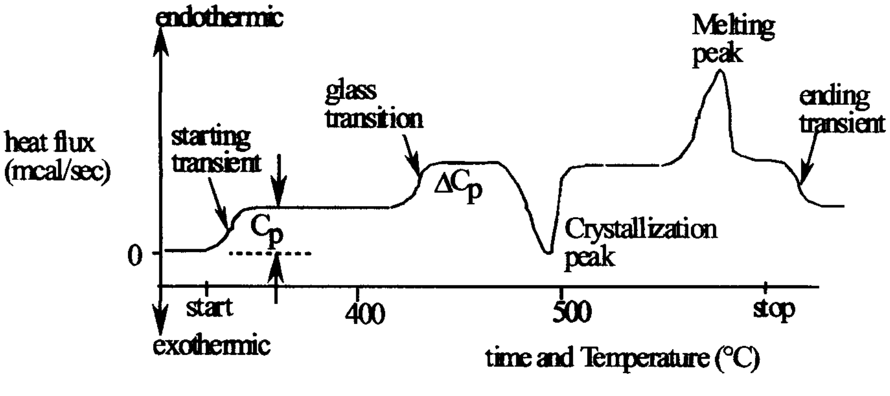


Fig. 29

It should be notice that whether the ordinate positive direction is endothermic depends on which sample holder is used for reference and which for the sample.

MICROSCOPY

Microscopy is a powerful tool in investigation of polymer and liquid crystals polymers. In combination with an oven it become possible to see the mesophases in an ordinary light microscope.

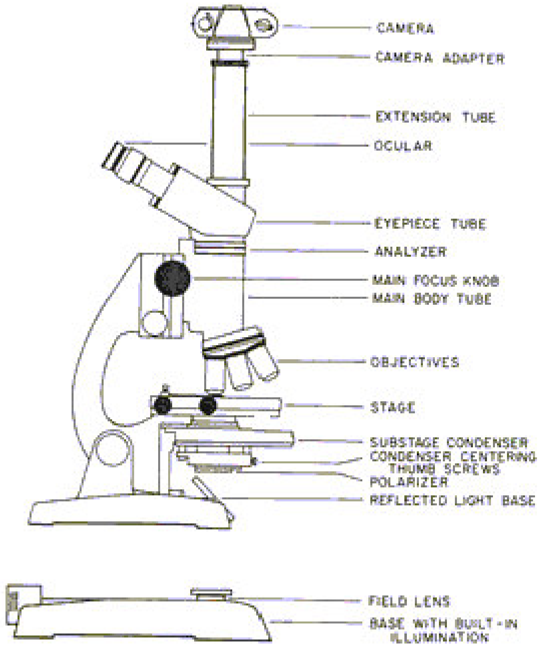


Fig. 30

With the light microscope the object is usually examined by transillumination. Is build up of both optical and mechanical parts. For the mechanical parts see fig 30. The optical components consist of tree system of lenses, condenser, objective and ocular. The condenser lens projects a cone of light on to the object to be observed, and the objective lens enlarge the object and project its image in the direction of the ocular lens which further amplifies the image and project it onto the viewers retina or some other system of monitoring. The total magnification is obtained by multiplying the magnifying power of the objective and ocular lenses. Two of the main characteristics are the resolution s, and the numerical aperture NA. The resolution is an expression expressing the smallest distance between two particles that can be distinguished from each other, Abbe's equation give the theoretical minimum separation s.

$s = \frac{0.61\lambda}{n\sin\theta}$. Where λ is the wavelength of light in air and n is the refractive index of the medium between the object and the objective, and θ is the extreme working angel fig 31. The quantity 'n sinθ ' depends on the working distance of the objective and is therefore characteristic of a particular objective and is called the numerical aperture.

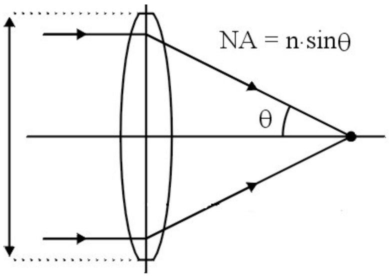


Fig. 31

When the microscope is used for studying birefringent materials such as a liquid crystal a polarizing microscope is used. It contain a rotating stage with 2 polarizing element: one located under the stage the polarizer and the other located above it, adjacent to the eyepiece on the analyser. The polarizer and the analyser are placed so that their main axes are perpendicular, thus preventing the appearance of light in the eyepiece.

When the stage contains an isotropic or amorphous object there is no light because, the object does not modify the incoming light beam. However when the object in the stage is a birefringent light appears with greater or lesser intensity in the microscope field, depending on the orientation of the analyser. The usual test is to rotate the object to find the points of maximum and minimum brightness. With the polarizing microscope it is therefore possible to distinguish between monorefringent and birefringent materiel, and when it is supplied with a computer controlled oven it also can show the different mesophases.

OBJECT GLASS

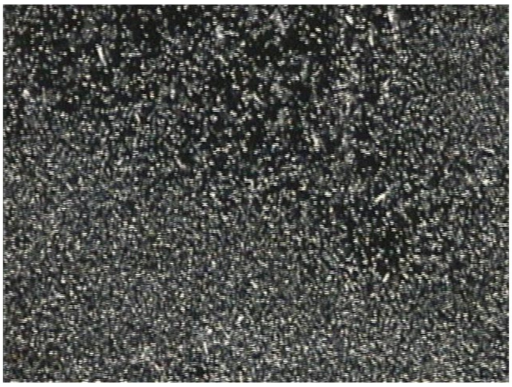
One of the problems in preparing liquid crystal polymers for microscopy is to get the sample orientated and amplifying the anisotropic property of the sample, so that the birefringence can be observed in the light microscope [52].

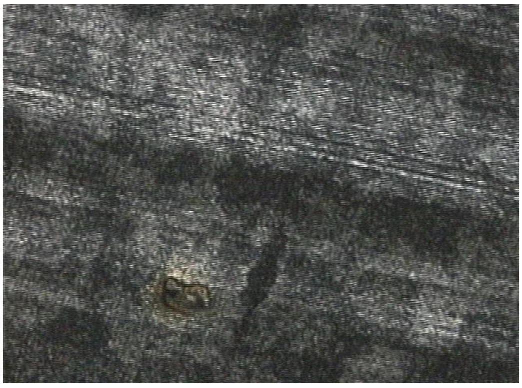
Many methods exist to give the object glass a uniformly oriented surface structure. One method that seems to work with has been set up and tested by M.Sc. Jeppe Madsen in our laboratory. The method is rather simple and consists of giving the object glass a polytetrafluoroethylene, PTFE (Teflon®) surface coating.

First the object glass is put on a heating pad and a PTFE stick is set onto the object glass.

The temperature is set to about 225°C, the melting point for PTFE is 327°C, and the system is then given time to reach thermal equilibrium.

When the tip of the stick has acquired the temperature it is moved slowly over the object glass with a pressure of approximately 150 hPa. The object glass is afterwards cooled and ready for use. The coating is not visible for the eyes or in the polarizing microscope. The sample is then placed on the object glass and melted to flow out in a thin uniform layer ready for microscopy.





The left picture show polymer P1 at 22°C on an object glass without coating

Orientation of the polymer P1 at 22°C on the object glass coated with Teflon® right picture.

NUCLEAR MAGNETIC RESONANS SPECTROSCOPY. NMR.

One of the most powerful tools to determinate chemical structure is NMR it is based upon the measurement of absorption of electromagnetic radiation [22], [25]. It differs from other spectroscopic methods by involving the nuclei of the atoms in the absorptions process. The theoretically basis for NMR is the idea that certain atomic nuclei should have the property of spin and magnetic moment and when it is exposure to a magnetic field it will lead to a split in there level of energies. This effect is named after the physicist P. Zeeman (1865-1943) for his discovery of the magnetic splitting of spectral lines, the Zeeman effect, in 1896.

It is familiar that the electron is described by four quantum numbers [27] and that the fourth is the electron spin quantum number s, which can have the two values +½ or -½. Further the electron have a charge of $Z = -1$ and it is spinning on its axis it give rise to a magnetic moment. The proton is also a particle having a charge $Z = +1$ and it is spinning on its axis, it give rise to two differentiate nuclear spin states having the same energy with the nuclear spin quantum number m which can have the two values +½ or -½. We say such a nucleus having nuclear spin I of ½.

When those of nuclear spin different from zero are placed in a magnetic field they will separate in energy, it is this separation that is referred as the Zeeman effect. As indicated some nuclei is not measurable in NMR spectroscopy, it is those whit nuclear spin I =0.There are three rules to predict if a nuclei is detectable or not in NMR.

Nuclei with an even mass number and an even charge number have zero spin, ^{12}C, ^{16}O and ^{32}S. These cannot be detected in NMR.

Nuclei with an even mass number and an odd change will exhibit an integer value of I and be detectable.

Nuclei with an odd mass number will have I value which can be expressed as $n/2$ where n is an odd integer, ^{1}H, ^{13}C, ^{15}N and ^{17}O have $I = ½$ and they are detectible.

In this project NMR is used to confirm that the wanted product from the synthesis is obtained. This means that the spectra come from ^{1}H and ^{13}C.

Generally different hydrogen molecules in an organic molecule do not experience the same magnetic field they have different resonant frequency, this frequency known as chemical shift (δ) dependence on the chemistry in the molecule. Chemical shift is proportional to the magnetic field strength so it is measured as a ratio of frequencies, usually in parts per million (ppm.). The signal is referred in its distance from TMS tetramethylsilane, which is a common standard for an arbitrary point zero in NMR. Hydrogen bound to carbons attached to electron withdrawing groups tends to resonate at higher frequencies more downfield (to the left) from TMS. The nucleus is deshielded and feels a stronger magnetic field requiring more energy (higher frequency) to cause resonance. Other effects that influence the chemical shift is delocalised π electron systems in aromates and bond strain affect witch increased the chemical shift. : The peak intensity the area under peak of a ^{1}H NMR signal gives a measure of the number of equivalent atoms responsible for the signal. A two-^{1}H signal is twice as large as a one-^{1}H signal. The ^{1}H NMR spectra normally have signals from 14ppm for acidic protons to 0.6ppm for ^{1}H in methyl group in aliphatic chains.

For the ^{13}C NMR the signals come from 200ppm for carbon in carbonyl groups to 0ppm for the carbon in methyl groups. The peak intensities is not proportional to the number of carbons but the ^{13}C nuclei that do not bear protons can be recognized by their low intensity. For the reason that they have long relaxation times one must be careful to allow enough pulses or long enough intervals between pulses so that weak signals are not lost.

MASS SPECTROMETY.

Mass spectroscopy is a useful tool in structure determination of chemical compound and for that reason it is of great help in the synthesis work [22], [23], [24].

In the simplest instrument the mass spectrometer has three functions. First it has to produce ions from the molecule sample under investigation. Secondary it has to separate these ions according to their mass to charge ratio. And thirdly it has to give a measurement of the relative abundance of each ion.

The ionisation of the sample can be done by several different methods; often it is "hard" ionisation where the ionic products are produced by a beam of energetic electrons, approximately 70eV and a pressure in the neighbourhood of 10^{-3} Pa. This electron bombardment result in many ionic product from the sample, which are drawn-out by a small potential to the mass-analyser device.

The first step in the analyser is to get the ion beam into a velocity selector with crossed electrical E and magnetic B field, here will only ion with velocity v=E/B pass undeflected, according to Newton's second law. $\sum F = q(E + v \times B)$ Here the sum of the forces had to be 0 for constant velocity. $\sum F_y = 0$. $-qE + qvB = 0$ And $v = \frac{E}{B}$

The mass separation and mass analysing are obtained in a magnetic field B' where the ionic beam travels in circular arcs with the radius R that can be measured and used for calculate the mass *m*. $R = \frac{mv}{|q|B'}$ This measurement was first done on photographic plates but now there are several types of detectors available. The electron multiplier is often used in apparatus for routine experiments, here the incoming ions are detected and the signal amplified, the computerized instrument gives and output where the ionic fragments are given as m/z where z is the number of charges which for most cases is equal to one. And the intensity of the signals give the relative abundances.

The mass spectrometer can be directly coupled to a gas chromatograph GC/MS. It is very useful because it gives a total ion chromatogram telling how many species there are in the sample and the ratio between them. It means that impurities can be measured and where more than one single specie is formed in the synthesis, the ratio between them can be measured.

HIGH PERFORMANCE LIQUID CHROMATOGRAPHY. HPLC.

Chromatography is a group of methods that permits separation of closely related chemical compounds [24], [26]. In all chromatography the compound is dissolved in what is called the mobile phase, which may be a gas, liquid and even a supercritical fluid. The mobile phase is passed through an immiscible stationary phase, which is fixed, to a solid medium in a column or on a plate. The principle in chromatography is that each species in the sample exhibits a specific equilibrium between the mobile phase and the stationary phase.

$$A_{\text{mobile}} \rightleftharpoons A_{\text{stationary}}$$

The equilibrium constant, K, is termed the partition ratio or partition coefficient; defined as the molar concentration of specie in the stationary phase divided by the molar concentration of the specie in the mobile phase.

$$K = \frac{C_S}{C_M}$$

As a consequence the species will separate when the mobile phase parse though the stationary phase fig.32. Those species that have less affinity for the mobile phase will move faster than those who are ‘held” by the stationary phase.

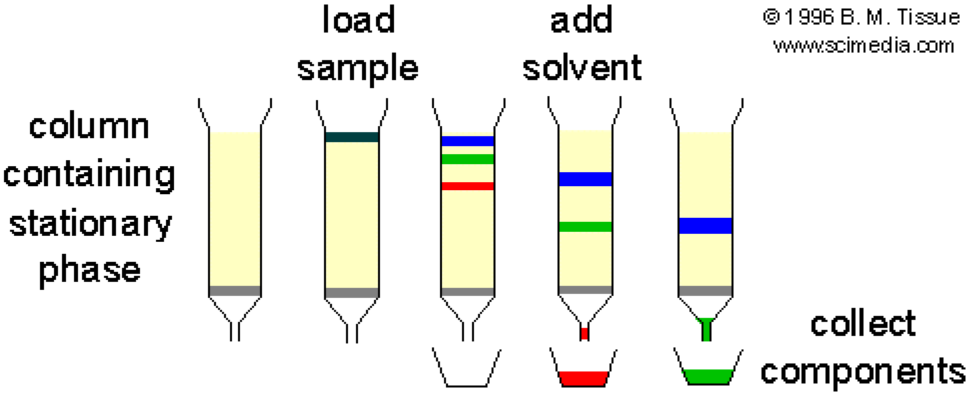


Fig. 32.

Schematic of a simple liquid chromatographic separation

This quantity is called the selectivity factor, α, which describes the separation of two species (A and B) on the column.

$$\alpha = \frac{K_A}{K_B} \geq 1$$

One way to increase the efficiency of the column is to decrease the particles size in the column; it required sophisticated equipment with high pressure, it is named high-performance liquid chromatography, HPLC. This system is build up with interchangeable solvent reservoir, which is able to give a constant flow though the column. It is equipped with a high-pressure pump, which can generate a pressure up to 6000 psi though the column and a particle size in 3 to 10 µm. The HPLC is fully computerized and different detectors can be connected. Often an UV absorbance or refractive-index-detector is used. One special feature is that the HPLC can be used for examination of the size of macromolecules. Size-exclusion chromatography or gel filtration chromatography is a method to separation of homologue molecular, where the column is packed with small silica or polymer particles containing a network of uniform pores into which the molecules and the solvent can diffuse. In the pores molecules are trapped from the flow of the mobile phase, the residence time in the pore depend of the molecule size.

Molecules larger than the pore size are excluded and have no retention, so they come out first. Molecules much smaller than the pore size are entrapped for the greatest time and thereby last to be eluted fig 33. Between these two extremes are molecules which average time in the pores depends of their diameter, from the retention it is possible to give an estimate of the molecule-size when the elution volumes of the sample is compared with the elution volumes for a series of standards.

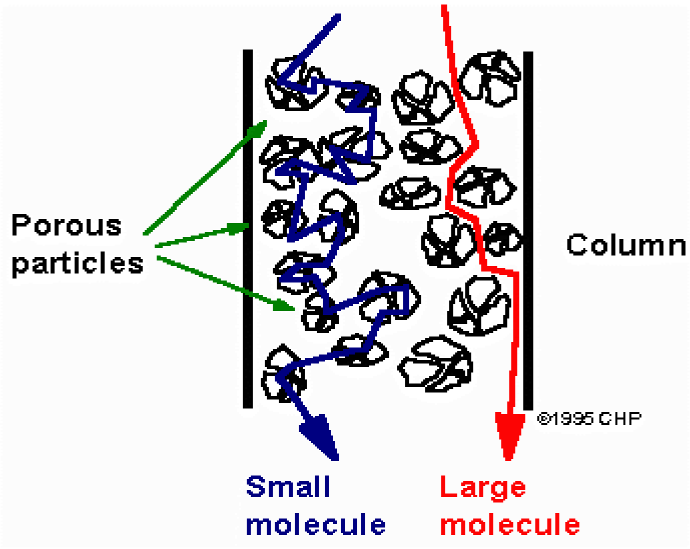


Fig 33
Schematic of a size-exclusion chromatography column.

BIREFRINGENCE

One of the most interesting phenomena's in liquid crystalline materials is the optical behaviour. When light is propagated though the material the optical property becomes visible.

Light is electromagnetic waves propagating with an electric and a magnetic field perpendicular to each other and perpendicular to the direction of propagation [54]. The fields oscillate as a function of time and the propagation direction. The distance it takes the fields to repeat themselves is called the wavelength, λ_0. The time it takes the field variation to repeat it self is called the period of the wave, T. Since the fields are moving one wavelength in one period the speed is given by λ_0/T, in vacuum it is an constant of nature and it is equal to $3*10^8$m/s. So the fundamental electromagnetic wave possesses electric and magnetic fields that oscillate sinusoidal in both space and time. Ordinary sources of electromagnetic waves send out fields having wave vectors in all direction, but it can be polarized so we have the electric field vector in the x-axis and its perpendicular magnetic field in the y-axis propagating in the direction of the z-axis. For the case where the x and the y corposants are rotating around the z-axis in the xy plane it is called circularly polarised and exist in a right circular and a left circular polarization.

An isotropic material such as a liquid and in amorphous material, the physical properties do not depend on the direction in the materials, it has a single index of refraction, and polarized light is propagating with one and same velocity in any direction in the material. When light enters materials, its wavelength and velocity decrease by a factor called the refractive index. In anisotropic and non-magnetically materials (which cover most of the liquid crystal systems) there are two different indices of refraction one index of refraction comes from light polarized along the director of the liquid crystal $n_{\parallel}$, and the other is for light polarized perpendicular to the director $n_{\perp}$. The refractive indexes in these liquid crystals are simply equal to the square root of the dielectric constant. The following relation can expressed the relationship between the refractive index n and the wavelength λ_0 and velocity of light v, in the liquid crystal. $v = \frac{c}{n}$ and

$\lambda = \frac{\lambda_0}{n}$ The wave vector in the system is given by the expression. $k = \frac{2\pi}{\lambda} = \frac{2n\pi}{\lambda_0} = nk_0$

Where k_0 is the wave vector in vacuum.

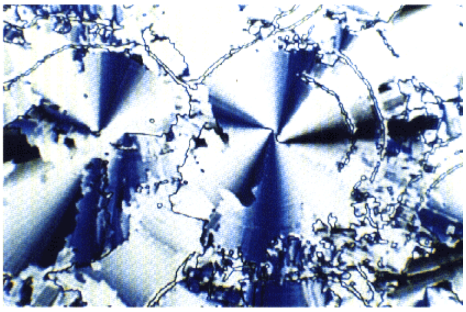
The difference between the two indices of refraction is $\Delta n = n_{\parallel} - n_{\perp}$ where $n_{\parallel} > n_{\perp}$ follow the tendency of the order parameter by decreasing with increasing temperature, and it is called the optical anisotropy or birefringence.

CONSEQUENCES OF THE BIREFRINGENCE

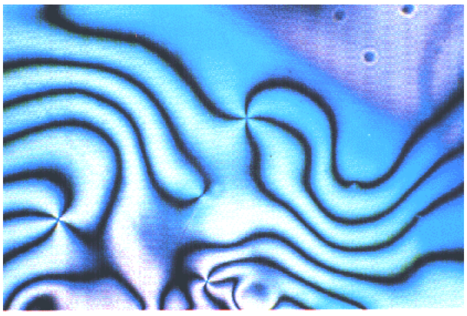
Liquid crystals have birefringent properties, which can be divided in two categories the uniaxial, and the biaxial. Nematic liquid crystal belong to the uniaxial group so they have one direction different from the other two and the index of light in the one direction is called the extraordinary index n_e witch correspond to $n_{\parallel}$ and the index for light for polarised perpendicular to this is called the ordinary index and correspond to $n_{\perp}$ for uniaxial systems $n_{\parallel} > n_{\perp}$ we said that they are positive uniaxial materials. In the biaxial system the birefringence normally is given as the difference between the indices with highest value and the lowest value. The birefringence in mesogenics result in that light polarised along different direction is travelling with different velocity though the sample of liquid crystal it means that light beams that enter the liquid crystal perpendicular to each other in phase grow out of phase when they propagate though the sample. This phenomena is known as the optical retardation an important parameter in working with different types of LC display, it can be measured and if the thickness of the sample is known it is a convenient way of measuring the birefringence [5], [8].

In the experimental work with liquid crystal the optical anisotropy give rise to the many patterns seen in a simple light microscope with polarizers. When the liquid crystal is placed in the microscope between two polarizer filters polarizing 90^o with respect to each other only light shifted by the liquid crystal will pass though the observers eyes. The different pattern of the texture seen appear as a consequence of the non-uniform orientation of the sample, it is orientated in domains with defects and not all wavelength are shifted the equally. The pattern of the texture gives a fingerprint of the mesophase some very characteristically texture are shown on fig 34.

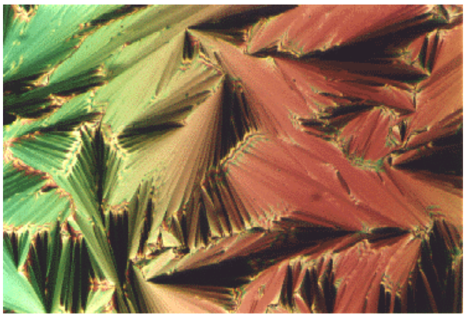
For a liquid crystal with one or more chiral groups in the molecule the birefringence is of a different character, compared to an ordinary liquid crystal. Thus show linearly birefringence the cholesteric liquid crystal show circular birefringence. It means that the cholesteric compound is not only birefringent for linearly polarised light but also for circular polarised light there can be divided into two component right and left circularly polarised light, which travel with different velocities. The difference in the refractive index for left and right polarised light, n_L and n_R defined the anisotropy for the system. The circular birefringence is highly wavelength dependent as a result light of different colours gets modified in different amounts. If a combination of left and right polarised light of equal amplitude is sent though the cholesteric compound it produces linearly polarised light with two equal components. If the linearly polarised light is sent though the cholesteric compound the component that matches the chirality best it will propagate with higher velocity than the other component when the two component again emerge it is linearly polarized, but the one component got ahead of the other so they are linearly polarised along a different angle. This phenomenon is called optical activity and is dependent of the thickness d of the sample and the rotation angle θ the magnitude is then given by $\frac{\theta}{d}$. If the light is right rotated for the viewer looking towards the light source the optical activity is positive, else it is negative.



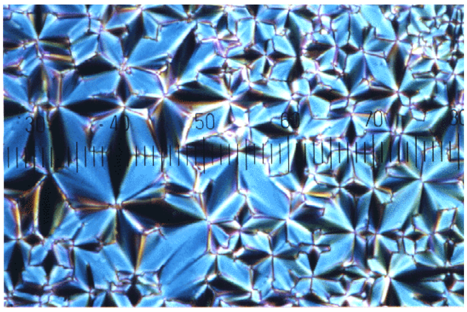
SMECTIC C*
The smectic layers create a fan or Schlierentextures, which only exhibit four-fold brushes.



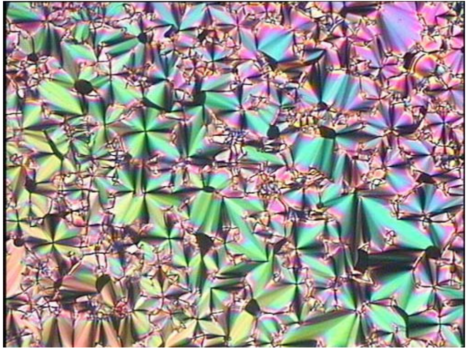
NEMATIC
Schlierentexture. Two- and four-fold brushes can be observed, leading into singularities.



SMECTIC A*
The fan-shaped texture is slightly striated, not as smooth in appearance as for the cholesteric phase.



CHOLESTERIC
Fan-like texture, which are the back of focal conic domains.



SMECTIC A
Smooth fan-like texture.

CRYSTALLINE PHASE
. Crystallization of a liquid crystal often nucleates in a spot and proceeds in a radial fashion, leading to spherulites.

Fig. 34

LIST OF CHEMICALS.

Acrylic acid (AA, Aldric 99%), acryloyl chloride(Aldrich 96%), azobisisobutyronitrile(AIBN, Acros), benzene(Lab-Scan HPLC), 5-bromopentanoic acid(Acros 97%), 2-butanone (Merck99%), calciumhydride(CaH_2, Merck), chloroform($CHCl_3$, Lab-Scan HPLC), 6-bromohexan-1-ol(produced in-house), cholesterol(Acros 95%), 1,3-dicyclohexylcarbodiimide(DCC, Aldrich 99%), diethylether(ether, Bie & Berntsen), 4-dimethylaminopyridine(DMAP, produced in-house), 1,4-dioxane(Acros 99%), ethyl-4-hydroxybenzoate(Acros 99%), hexamethylphosphoric triamide(HMPA, Fluka), 1,6-hexandiol (Fluka), hydrogenbromide 37% sol. (HBr, Bie & Berntsen) hydrogenchloride 35% (HCl, Bie & Berntsen), 4-hydroxybenzoic acid(Aldrich 99%), 4-hydroxyphenol(Fluka), magnesium sulfate anh. ($MgSO_4$, Bie &Berntsen), methylenchloride(CH_2Cl_2, Lab-Scan HPLC), 4-methyl-pyridin, 4-picolin(Aldrich), 1-methyl-2-pyrrolidinone(NMP, Lab-Scan HPLC), Molecular sieves(sieves, Merck 0,3 nm), potassium carbonate(K_2CO_3, Merck),potassium hydroxide(KOH, Riedel-de-Haën), potassium iodide(KI, Bie & Berntsen), sodium(Aldrich), sodiumhydroxide(NaOH, Riedel-de-Haën), sodium hydrogen carbonate($NaHCO_3$), Merck), tetrahydrofuran (THF, Lab-Scan HPLC), thionyl chloride(Riedel-de-Haën 98%), toluene (Aldrich 99%), triethylamine (Et_3N, Aldrich 99%). Trioctylmethylammoniumchloride, TCMAC, aliquat 336(Aldrich),

Acrylic acid was distilled once under reduced pressure and kept cold afterwards
Solvents were dried according to the text after two methods [51]:
THF was dried (refluxing under nitrogen) overnight over sodium with benzophenone added.
Distilled directly from the blue solution and used immediately.
Other solvents were dried over sieves and distilled before use.

PYRIDINE A HETEROCYCLIC AROMATE

The pyridine moiety is part in two of the monomer systems synthesised for a hydrogen-bonding site. For that reason the heterocyclic aromate is briefly described in the following.
Aromatic compounds are often described with benzene as model molecule, which exhibits the characteristic chemical and physical properties for aromates. In general these compound are described as containing a planar, cyclic, conjugated π bond system of ($4n + 2$) electrons, which say that system with 2, 6, and 10 π electrons are aromatic, system with $4n$ electrons are not aromatic. (So cyclopentadien is not an aromate but off course the anion with 6 π electrons are). The formation of an aromatic system is energetically very favourable. Aromaticity is not restricted to carbocyclic compounds and replacement of one or more carbon atom by an isoelectronic atom, result in a series of heterocyclic aromatic compound. One of the simplest compounds is pyridine here is only one CH group replaced with an isoelectronic nitrogen group fig.35. The aromaticity is retained because nitrogen can be trigonal and planar so there are still 6 π electrons and the orbital in the ring have not change in position or shape. The only difference is that nitrogen is trivalent and instead of a bonding to hydrogen it give us a lone pair. In the ^{1}H NMR spectrum the signal from the six protons of benzene resonate at δ 7.27 ppm. For the six protons in pyridine the signals resonate at δ 8.5ppm., δ 7.1ppm. and δ 7.5ppm. It is clear that this signal is downfield from the alkene region so even that the pyridine is not so symmetrical as benzene but it has the aromatic properties. The new feature is that there is a lone pair in and perpendicular to the plane of the ring, which can donate electrons to the formation of a hydrogen-bonding. If the double bonding CH=CH from the benzene is replaced with a nitrogen it is transformed into new heterocyclic aromate, the five-membered ring pyrrole. In one very significant way pyrrole differ from pyridine, to full fill the ($4n + 2$) rule it use the lone pair in the delocalised π electron system, it means that the electrons from the lone pair is put into a p-orbital fig 36, and that the N-H bonding is in the ring plane, the consequence is that opposite pyridine, pyrrole can not generate hydrogen bonding with its lone pair.

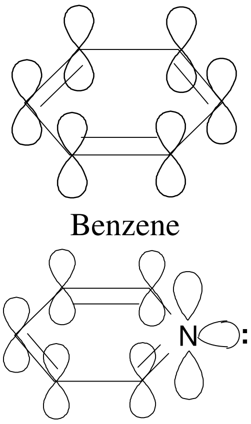


Fig. 35

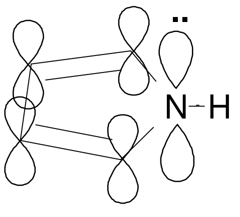
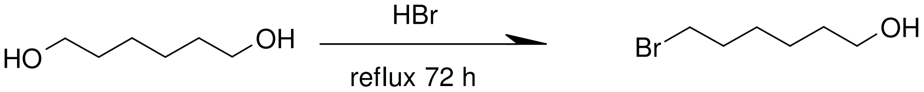


Fig. 36

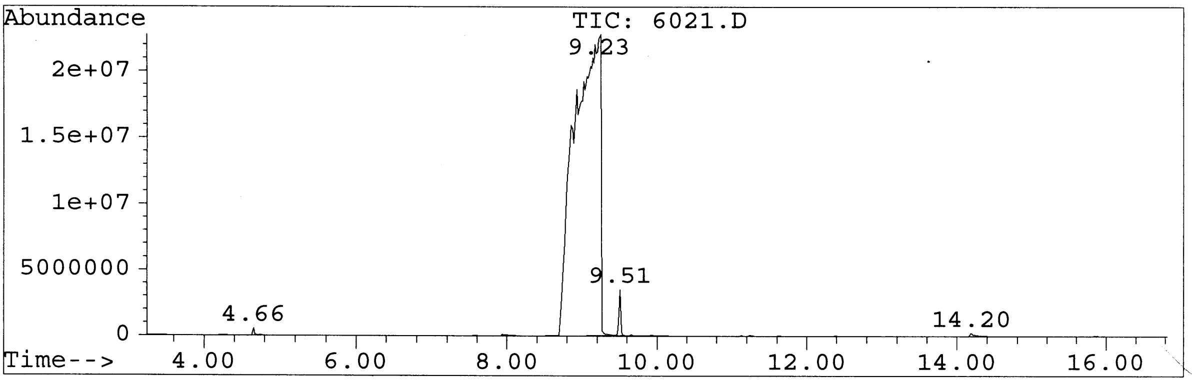
SYNTHESIS OF 6-BROMO-HEXAN-1-OL

In the work with synthesis of side chain polymers ω-halogen alcohol compounds are very often used as the reagent for the chain. For the preparation different classical strategies have been tried all of them based on a two phase system where HBr, H_2SO_4 and a α,ω diol was dissolved in a water phase and after reflux for a short period of 30 to 40 minutes the ω-bromo-alcohol was collected in a benzene or toluene phase. These methods were not very selective for the dibromide compound and it was inconvenient for large-scale synthesis. In 2000 it was reported, that experimental work [28] in synthesising ω-bromo-alcohol in different solvent and with or without a Dean-Stark trap for removing water have come up with the result that the synthesis should be carried out without Dean-Stark trap and that the best solvent was toluene.



A mixture of 0.2mol (24.37g) 1,6-hexandiol and 600 ml toluene was placed in a 1.5l three-necked round-bottom flask equipped with; magnetic stirring, a condenser and a dropping funnel. Carefully 0.24mol (27.33ml 48%) HBr (9M) was added drop wise to the stirred mixture, when all the HBr was added the mixture was heated at reflux for 72 hours. The reaction mixture was cooled to room temperature and transferred to a separatory funnel where the water and toluene phases separated. The water phase was removed and the organic phase was washed with 2 times 50ml 1M. NaOH and afterwards it was washed with H_2O until neutral reaction. The toluene was removed on a vacuum rotary evaporator (the toluene was reused later for the same synthesis) and a TLC analysis was made on the residue with diethylether as eluent, it showed three spots: very weak $R_f = 0,0$ diol, strong $R_f = 0,50$ mono bromo alcohol and $R_f = 0,98$ dibromide.

The light yellow liquid residue was diluted with 100ml. chloroform and dried with $MgSO_4$ to remove traces of water finely it was filtrated on a fluted filter, and the chloroform was removed on the vacuum rotary evaporator. The remaining clear liquid was send for GS-MS analysis.The analysis gave a total ion chromatogram fig 37 showing two significant signals one 98.6% for the mono bromo alcohol and second 1.0% for the dibromide, two small signals counting for total 0.4% is air. The mixture was set on a silica column and diethylether was used as eluent to isolate the 6-bromo-hexan-1-ol, similar as the TLC analysis. Yield was 29.7g 82% from 1,6-hexandiol.



```
 Retention Time          Area             Area %   Ratio %

Total Ion Chromatogram
   4.658               10961127             0.201      0.204
   9.234             5385614243            98.623    100.000
   9.511               54632094             1.000      1.014
  14.199                9595530             0.176      0.178
```

Total ion chromatogram fig. 37

In the paper [28] they give an account for the nonstatistical distribution between the dibromide and the bromo alcohol. It is proposed that the bromo alcohols are behaving like a surfactant making an aggregate such as reverse micelles, and thereby making it less reactive compared to the diol. I venture to, take the liberty of suggestion another mechanism fig 38.

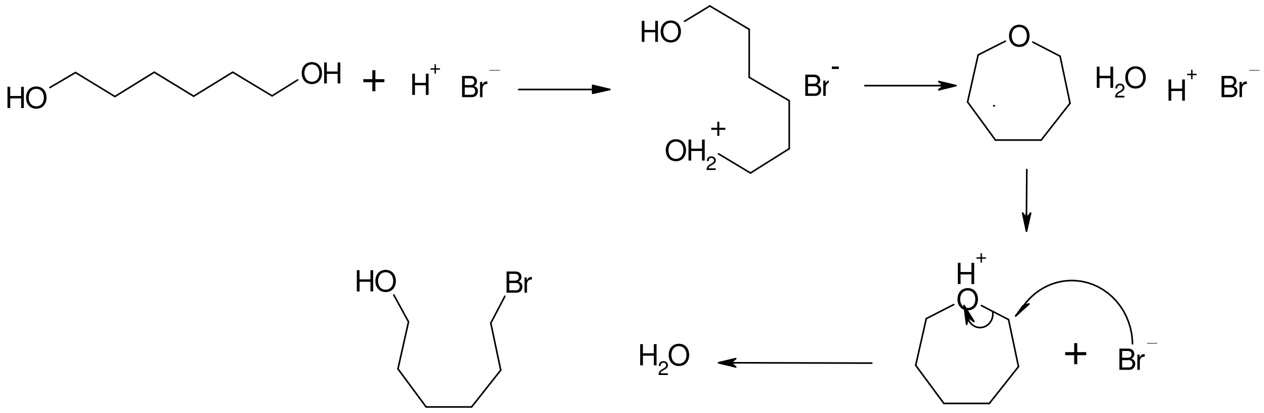
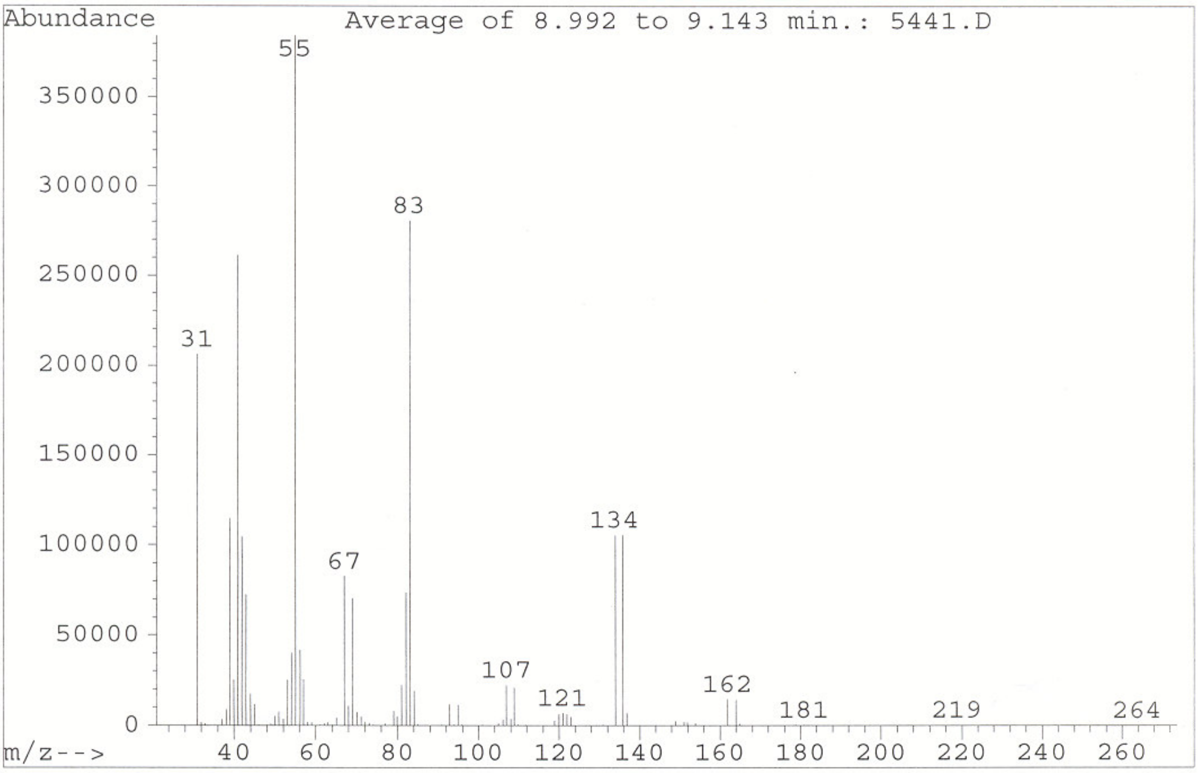


Fig 38

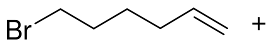
The 1,6-hexandiol will normally undergo an S_N2 reaction to substitute the hydroxy group with the bromide; in general the hydroxy group have a lower reactivity then bromide as leaving group. It counts for unreacted diol in the reversible process and it doesn't explain the preference for the bromo alcohol. In an S_N1 reaction the charge stabilisation on the carbocation will course rearrangement and give a mixture of bromo alcohols. But it is well known [29] [30] that oxepane can be synthesized from 1,6-hexanediol by refluxing under appropriate circumstances. Cyclic ethers are very unreactive but cleavages with strong acid often HI or HBr are known processes giving halo alcohols, synthesis of 6-bromo-hexane-1-ol from oxepane is rapid and well known [31] [32], and the reverse process only take places in strong basic condition [33]. So maybe the reaction first make the oxepane adduct fig x, y and afterwards the oxepane is cleaved to give the product. The condition for an S_N2 reaction is not very good because with water in the solvent the HBr is ionised and this can count for the low formation of the dibromide, the condition for S_N1 reaction is absent since it don't give even traces of rearrangement which is the normal indication for S_N1 reaction.

Mass spectrum for, 6-hexan-1-ol. [4286-55-9]



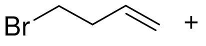
The spectrum does not show the molecular ion $M^{+\cdot}$ mass 180, but it clearly show the mono bromide pattern where bromides two isotopes mass 79 and mass 81 give rise to signals where the heavy bromide is 97.3% of the signal from specie containing the mass 79 isotope.

We see bromide signals in mass 162 and mass 164.

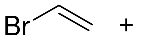


Mass 162 and 164

The same fragmentations patterns come up with mass 134/136 and mass 106/108

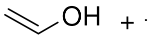


Mass 134 and 136



Mass 106 and 108

Mass 31 is a significant signal for alcohols, and gives evidence for the hydroxy group



Mass 31

Secondary fragmentations give rise to a series of signals significant to alkenes. This pattern is often seen when an alkane chain is part of the specie.

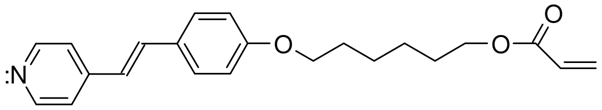
	C_3H_5+	C_4H_7+	C_5H_9+	C_6H_{11}+
Mass	41	55	69	83

The GS-MS analyses give a significant evidence that the synthesised compound is 6-bromo-hexan-1-ol.

PLATE II

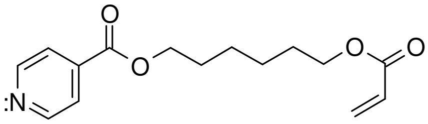
MONOMERS

M1



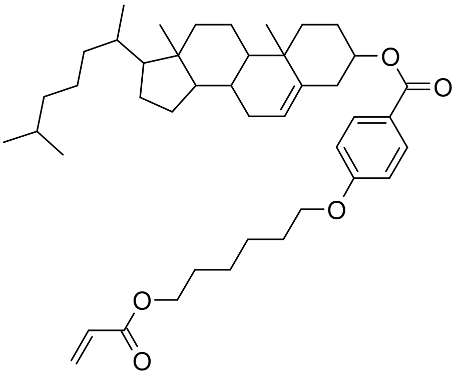
4-(6-ACRYLOXYLOXYHEXYLOXY)STILBAZOLE

M2



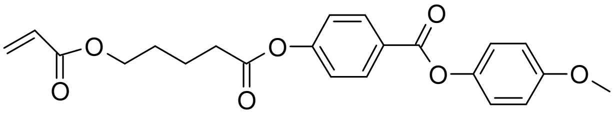
6-ACRYLOYLOXYHEXYL-ISONICOTINATE

M3



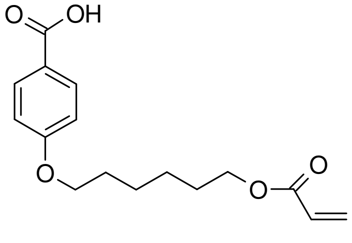
choleteryl-4-(6-acryloyloxyhexyloxy)benzoate

M4



4' -methoxyphenyl-(5-acryloyloxypentanoyloxy)-benzoate

M5



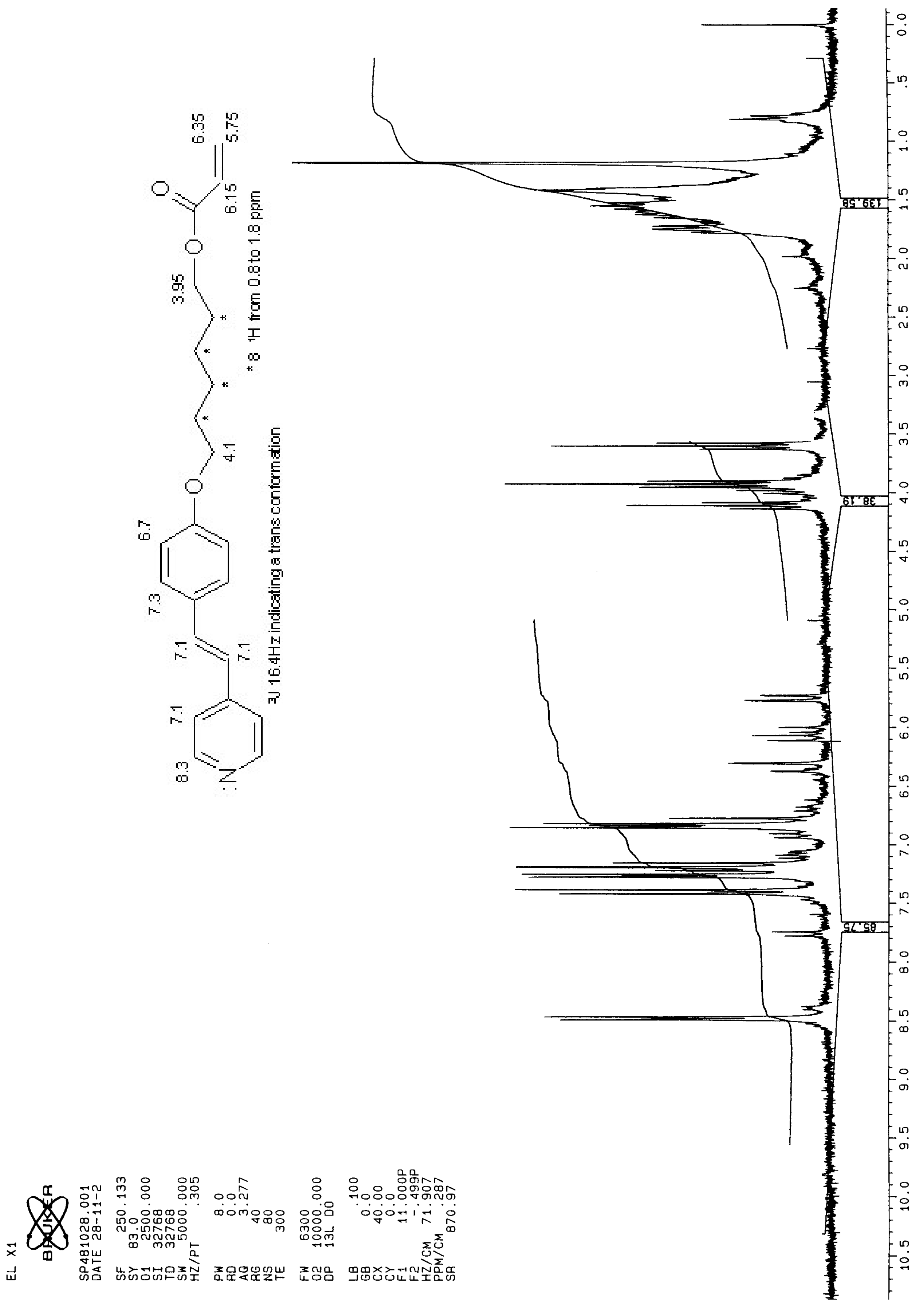
4-(6-acryloyloxyhexyloxy)-benzoic acid

SYNTHESIS OF4-(6-ACRYLOXYLOXYHEXYLOXY)STILBAZOLE.

For the synthesis of *hydroxystilbazole*, 0.10mol (12.2g) 4-hydroxy-benzaldehyd, 0.12mol (11.2g) 4-methyl-pyridine (picolin) and 0.10mol (10.3g) acetic anhydride was placed in a 150ml three necked round-bottom flask equipped with a condenser, magnetic stirring and a thermometer. The stirred mixture was refluxed at 145^0C after half an hour it become dark brown, the refluxing was continued for 12 hour while the condensations reaction took place. After 12-hours the mixture was allowed to cool to approximately 50^0C before the flask was set up for simple distillation to remove the excess picolin, a clear liquid was distillate at 110^0C to 115^0C. The sticky product was washed on a Büchner funnel with 4-time 150 ml demineralised water, and afterwards recrystallized 2-time from dry ethanol it gave a pale yellow powder with a melting point 276^0C to 277^0C, the yield was 0.084mol (16.56g) 83.95%.

The synthesis of *4-(6-bromo-hexyloxy) stilbazole* was carried out at room temperature in a 100ml three-necked round-bottom flask equipped with a dropping funnel and magnetic stirring. 7.35mmol (1,45g) hydroxystilbazole and 14.7mmol (2.09g) K_2CO_2 was placed in the flask and dissolved in 25 ml DMF, the mixture become dark brown, afterward 7.35mmol (1.33g) 6-bromo-hexan-1-ol was added slowly and under stirring from the dropping funnel. The mixture was stirred for 24 hour. After 24 hour the mixture has dark reddish brown colour it was filtrated on a fluted filter and the DMF was removed on vacuum rotary evaporator at 77^0C and 33 mbar. The dark red residue was solid at room temperature. It was dissolved in chloroform and set on a separatory funnel where it was washed with 3 time 200ml aqueous 5% NaOH. The water phase become orange and the chloroform phase dark blue / black. The chloroform phase was taken to an Erlenmeyer flask and dried with $MgSO_4$ for 12 hour. Afterwards the solution was filtrated on fluted paper and the chloroform was removed by evaporation, there was made a TLC analysis on the crude yellow/brown compound it show that there was some impurity, so the compound was set on a chromatography column and eluted with methylene-chloride and methanol 10:1.
The final product weight where 0.73g yellow powder with a melting point 137^0C-139^0C. The yield 33% seem very low so the synthesis was repeated under other conditions, the temperature was set up to 60^0C but it did not change the yield significant. In the paper [55] there gave the idea to this synthesis step they use an aliphatic chain without a terminal alcohol group and report a yield 80% before the final purification.
The synthesis of *4-(6-acryloxyloxyhexyloxy) stilbazole* was carried out in a 150ml three-neck flask equipped with condenser, dropping funnel, magnetic stirring and a thermometer.

0.002mol (0.6g) 4-(6-bromo-hexyloxy) stilbazole and 0.002mol (0.2g) tri-ethylamine was dissolved in 75ml dioxane and placed in the flask under stirring. From the dropping funnel was slowly added 0.002mol (0.18g) Acroleylchloride and the temperature was raised to 60^0C for four hour. Afterwards the dioxane was removed on vacuum evaporator and the residue was dissolved in chloroform a transfer to separatory funnel and washed with 4-time 100ml water. The chloroform phase was dried with $MgSO_4$ for 12 hour and then filtrated on a fluted paper, the chloroform was removed by evaporation and the yellow product sent to NMR analysis.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BRUKER
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DATE 28-11-2
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SI 32768
TD 32768
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HZ/PT .305
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RG 40
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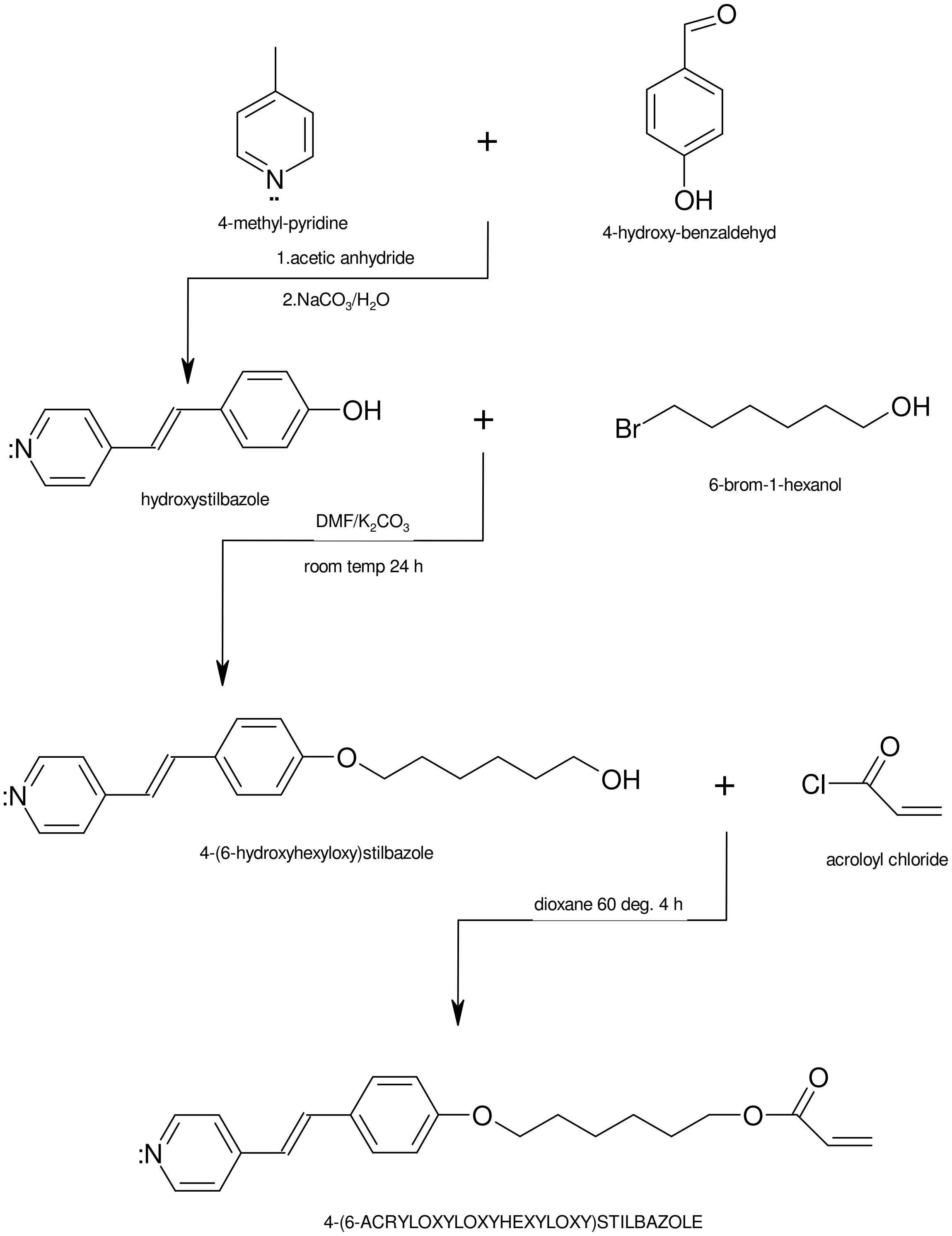
TE 300
FW 6300
O2 10000.000
DP 13L DO
LB .100
GB 0.0
CX 40.00
CY 0.0
F1 11.000P
F2 -.499P
HZ/CM 71.907
PPM/CM .287
SR 870.97
8.3
7.1
7.1
7.1
7.3
6.7
4.1
3.95
6.15
6.35
5.75
³J 16.4Hz indicating a trans conformation
* 8 ¹H from 0.8 to 1.8 ppm
85.75
38.19
139.58
PPM
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
.5
0.0

PLATE III

4-(6-ACRYLOXYLOXYHEXYLOXY)STILBAZOLE



SYNTHESIS OF 6-ACRYLOYLOXYHEXYL-ISONICOTINATE

The preparation of isonicotinic acid was done by aromatic side chain oxidation [34]. In a 500ml Erlenmeyer flask with magnetic stirring 0.4mol (63,21g) potassium permanganate $KMnO_4$ was dissolved in 300ml of water, 4ml of 10% NaOH was added. Slowly and under stirring 0.1mol (9.31g) 4-methyl-pyridine was added, this process is exothermic and the temperature should not be allowed to come over 45^0C. The suspension was set for stirring in 2 hour at 45^0C. The suspension had now the brown colour from the manganese dioxide MnO_2 and the temperature was raised to the suspension was gently boiling, afterwards it was cooled to room temperature and 1.0g sodium bisulphite added to react with unreacted $KMnO_4$. The suspension was filtrated on a Büchner funnel with sand (Celite) the manganese dioxide was washed with 50ml of water and the water phase was reduced to approximately 150ml and acidified with concentrated HCl to pH 1 to 2 and then an additional 5ml of HCl. The mixture was cooled and the white isonicotinic acid precipitate it was collected in fluted paper and dried in a vacuum oven 80^0C over night. The product was sent to NMR analysis yield 11.99g or 97.3%.

The next step to reach an adduct there is able to react with acroloyl species was carried out after two different methods, one in dry THF and second as a phase transfer reaction. The first pathway was over isonicotinoyl chloride hydrochloride.

The syntheses of *6-bromohexyl-isonicotinate* were carried out in a 100ml three-necked round-bottom flask equipped with a condenser, thermometer, dropping funnel and magnetic stirring, were placed 0.03mol (3.69g) of isonicotinic acid and 5 drops of DMF. Carefully under stirring 0.09mol (3.69g) of thionylchloride was added from the dropping funnel and a gas evolution started to take place and the temperature raised to about 36°C. After one hour all the isonicotinic acid was all in solution. The excess of thionylchloride was removed on vacuum rotary evaporator and 50ml diethyl ether was stirred into the residue and white crystal participated. The product was filtered on a Büchner funnel and washed with diethyl ether afterwards it was dried in vacuum at 40 °C. Yield 5.18 g 96% isonicotinoyl chloride hydrochloride. The melting point was measured with out further purification to 159 °c -160°C

The ester formation was carried out in a 100ml three-necked round bottom flask equipped with condenser, thermometer and magnetic stirring. In 40ml of THF was dissolved 0.026mol (4.61g) isonicotinoyl chloride hydrochloride and 0.025mol (4.53g) 6-bromo-hexan-1-ol. To the stirred suspension was carefully and over 10 minutes added 0.052mol (5.33g) triethyl amine to cancel the HCl coming from the ester formation in the same way the hydrochloride at the nitrogen is removed, the suspension becomes white. The mixture was set for refluxed at 80°C in 24 hour.

After the 24-hour there was a white participate, triethyl-ammonium-chloride, it was removed by filtration on a Büchner funnel and washed with THF, the liquor was set on vacuum rotary evaporator to remove THF. To the residue was added 20 ml of chloroform and it was set on a separatory funnel and washed with 4-time 30ml water. The chloroform phase was dried with MgSO4 in 6 hour and then filtrated on fluted paper afterwards the chloroform was removed by evaporation. The clear liquid product was send for NMR analysis. Yield 3.51g 63% from 6-bromo-hexan-1-ol.

^{1}H-NMR (400 MHz; DMSO) 8δ: 8.79(m; 2 H), δ 7.82(m; 2 H), δ4.3(t; 2 H), δ 3.62(t; 2 H) δ1.72(m; 4 H), δ1.42(m; 4 H).

The last step is to introduce the acroloyl moiety into the molecule; it was done with *potassium acroloylate*, which was synthesized by placing a solution of 0.5mol (36.3g) acrylic acid in 250ml dry ethanol in a 500ml three-necked flask equipped with thermometer, magnetic stirring, dropping funnel and an ice bathe. The solution was cooled to a temperature between 0°C and 5°C. In another portion of 200ml dry ethanol was dissolved 0.5mol (28,1g) KOH this was placed in the dropping funnel and added slowly and under stirring while the temperature was kept below 5°C. Afterwards the mixture was poured into a large volume cool diethylether and the salt precipitated and was filtrated on fluted paper. The filtration was troublesome it look like the salt dissolve in its own crystal water. The crystal was washed with diethylether and dried under vacuum at room temperature over night. Yield 21.6g. 39.1% from acrylic acid.

The synthesis of *6-acroloyloxyhexyl-isonicotinate* was carried out in 100ml Erlenmeyer flask

0.0013mol (3,0g) 6-bromohexyl-isonicotinate was mixed with 4 equivalents 0.005mol (0.6g) potassium acroloylate in 50ml of HMPA, a few grain hydroquinon was added to avoid polymerization. The mixture was stirred for 48 hour at 60°C and the colour was changing to dark red / brownish. The mixture was set on a separatory funnel and 100ml of acetone was added, it was washed with 4-time 20ml of water, the acetone phase was dried with $MgSO_4$ and filtrated on a fluted paper, the acetone was removed on a rotary vacuum evaporator. The remaining reddish high viscose liquid was send to NMR analysis. Yield 0.08g 23%.

6-acroloyloxyhexyl-isonicotinate

^{1}H-NMR (400 Mhz. DMSO) δ: 8.8 (M. 2H). δ: 7.8 (M. 2H). δ: 6.3 (M. 1H). δ: 6.15 (M. IH). δ: 5.9 (M. 1H). δ: 4.3 (M. 2H). δ: 4.1 (M. 2H). δ: 1.6 (M. 4H) δ: 1.4 (M. 4H).

^{13}C-NMR (60 Mhz. DMSO) δ: 165.54, 164.69, 150.80, 137.03, 131.28, 128.43, 122.52, 65.42, 64.02, 28.04, 27.96, 25.21 and 25.11.

The second pathway went though *potassium isonicotinate*; it was carried out in solid-liquid phase transfer catalysis conditions PTC without adding solvent [35] with a tetraalkylammonium halide as catalyst. The preparation of potassium isonicotinate was carried out in a 250ml one-neck round-bottom flask; 0.1mol (12.3g) isonicotinic acid was dissolved in an aqueous solution of 0.1mol (5.61g) potassium hydroxide KOH. Water was added to all the acid was dissolved. Afterwards the flask was set directly on the vacuum rotary evaporator and the water was removed and the salt was grounded into a fine powder and used without further purification.

The synthesis of 6-hydroxyhexyl-isonicotinate was done in a beaker glass, 0.02mol (3.22g) potassium isonicotinate and 0.02mol (3.61g) 6-bromo-hexan-1-ol was mixed together and 0.002mol (0.81g) of trioctylmethylammoniumchloride, TCMAC, (aliquat336) was stirred into the suspension, and the stirring was continued for 15 minutes. The beaker was closed with watch glass and set in an oven for 30 hour at 60°C. The mixture was cooled to room temperature and a to phase system has been formed a light brown solid phase and a brown liquid phase, it was diluted with 10ml of diethylether and filtrated on a fluted paper and the solid residue was washed with 2-time10ml of diethylether, the diethylether was evaporated and clear liquid with a stick of yellow was reminding. The crude product was analysed by TCL, with diethylether as eluent it showed one product with R_f 0.23. From the NMR analyse it was concluded that it was 6-hydroxyhexyl-isonicotinate. Yield 78% 3.48g

The synthesis of *6-acroloyloxyhexyl-isonicotinate* was carried out in 250ml three-necked flask equipped with magnetic stirring, condenser and a dropping funnel. 0.015mol(3.35g) 6-hydroxyhexyl-isonicotinate and 0.016mol (1.60g) tri-ethylamine was dissolved in 125ml 1,4-dioxane from the dropping funnel drop vice was added 0.016mol (1.45g) acroloyl chloride dissolved in 25ml 1,4-dioxane. The temperature was set to 60° and the mixture was stirred for 3 hour, the colour become dark red. The 1,4- dioxane was removed under vacuum and the residue was dissolved in 100ml of chloroform a transferred to a separator funnel and washed with 6-time 25ml water. The chloroform phase was dried with $MgSO_4$ and filtrated on a fluted paper and afterwards the chloroform was removed by evaporation. The product had a dark red colour and it was suspected that it come from oxidation of the pyridine moiety, so it was tried to reduce it with PCl_3 the colour was still remaining. The product was sending for NMR analysis and gave spectre similar to those mentions above. The yield was 2.95g 71% from 6-hydroxyhexyl-isonicotinate.

^{1}H

6-acroloyloxyhexyl-isonicotinate

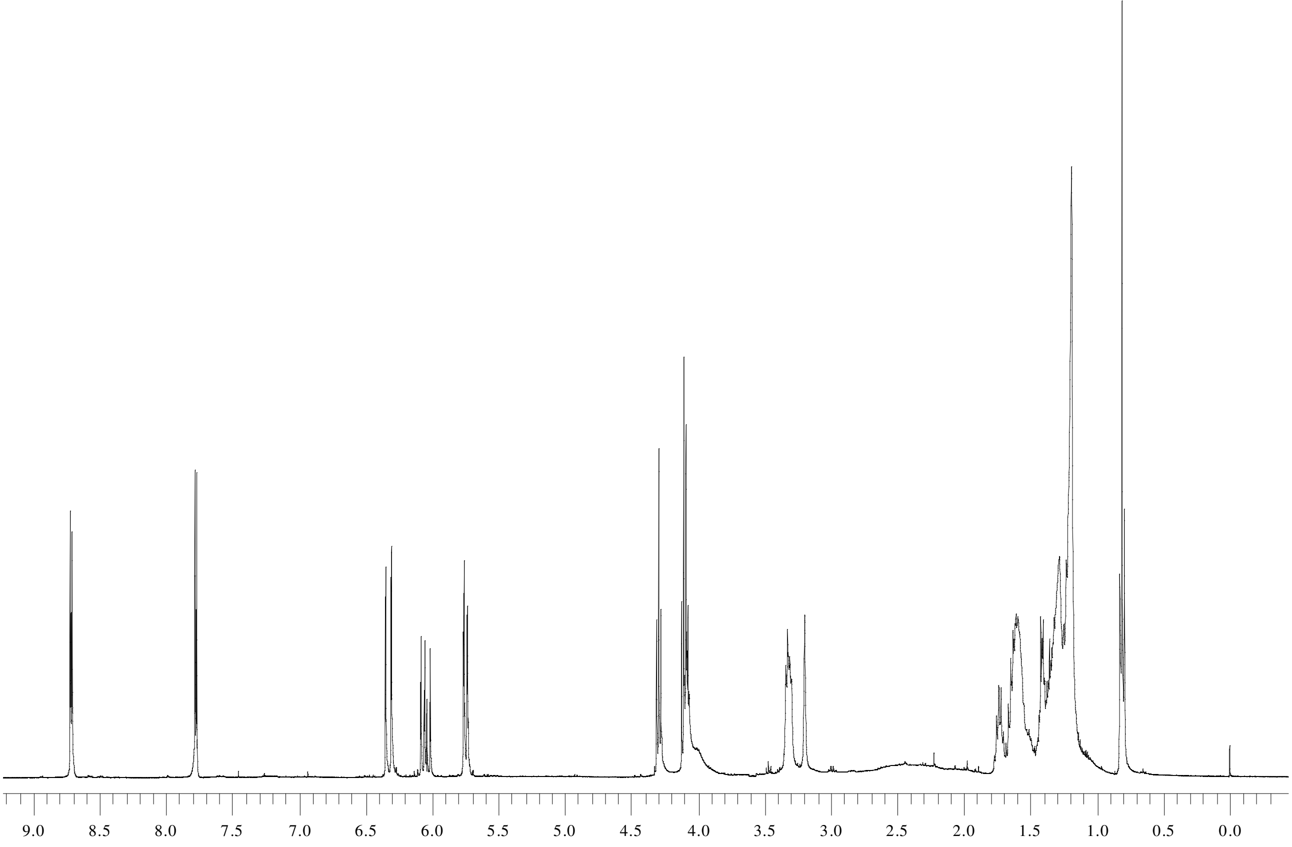
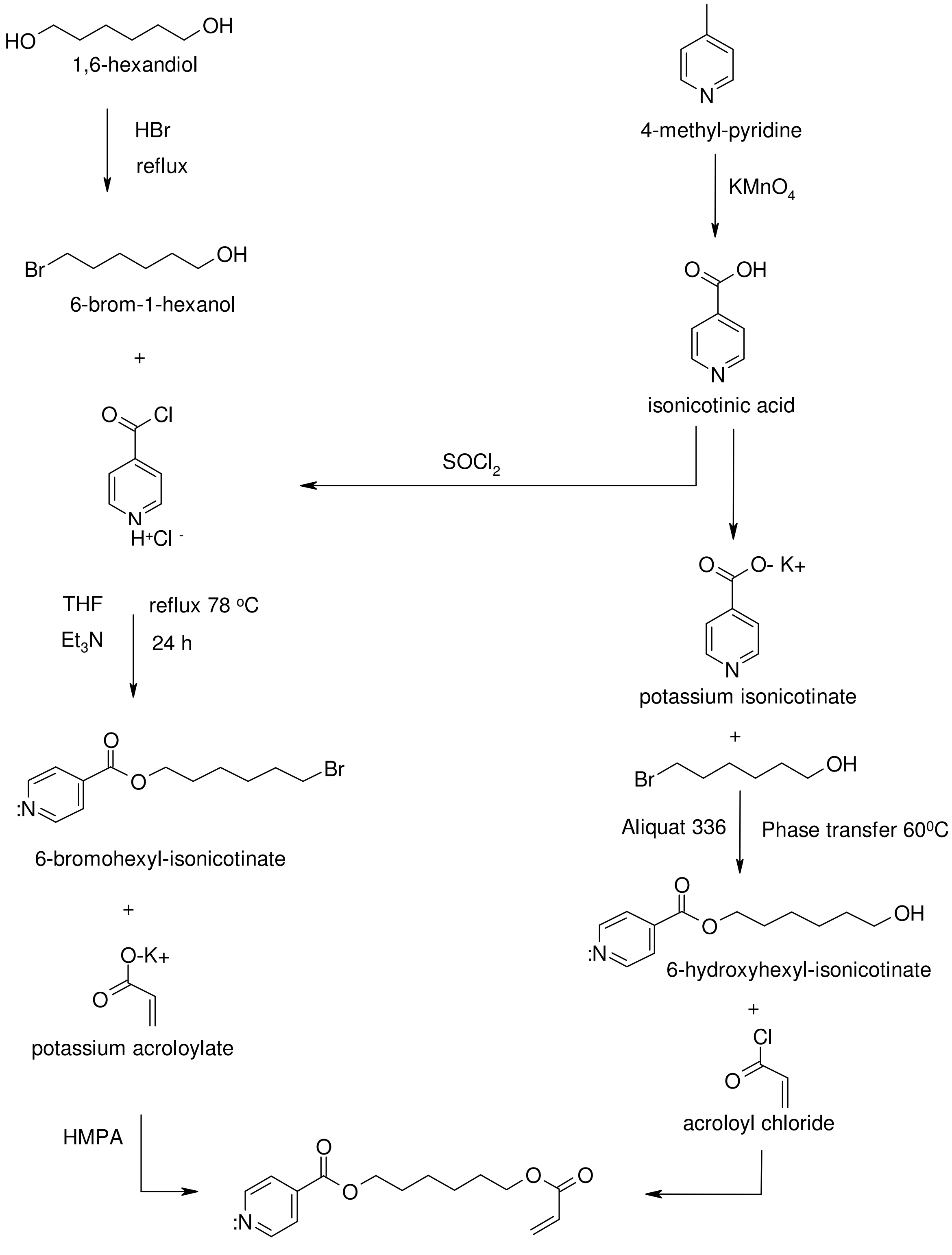


PLATE IV

SYNTHESIS OF 6-ACRYLOYLOXYHEXYL-ISONICOTINATE



6-ACRYLOYLOXYHEXYL-ISONICOTINATE

SYNTHESIS OF CHOLESTERYL 4-(6-ACRYLOYLOXYHEXYLOXY) BENZOATE

The synthesis of cholesteryl 4-(6-acryloyloxyheeyloxy) benzoate was carried out after a convergent strategy where the two ester groups were introduced in separate molecules, table xy, and afterwards linked together with an ether group, a synthesis step which normally can be done under condition that will not affect the ester groups.

The synthesis of *acrylic acid 6-bromo-hexyl ester* was carried out in a 500ml two-necked round bottom flask placed on an ice bath, equipped with a dropping funnel and magnetic stirring.

In 200ml of dichloromethane was dissolved 0.05mol (9.06g) of 6-brom-1-hexanol and 0.125mol (12.65g) triethylamine, the mixture was stirred cooled to temperature between $0^{o}C$ and $5^{o}C$.

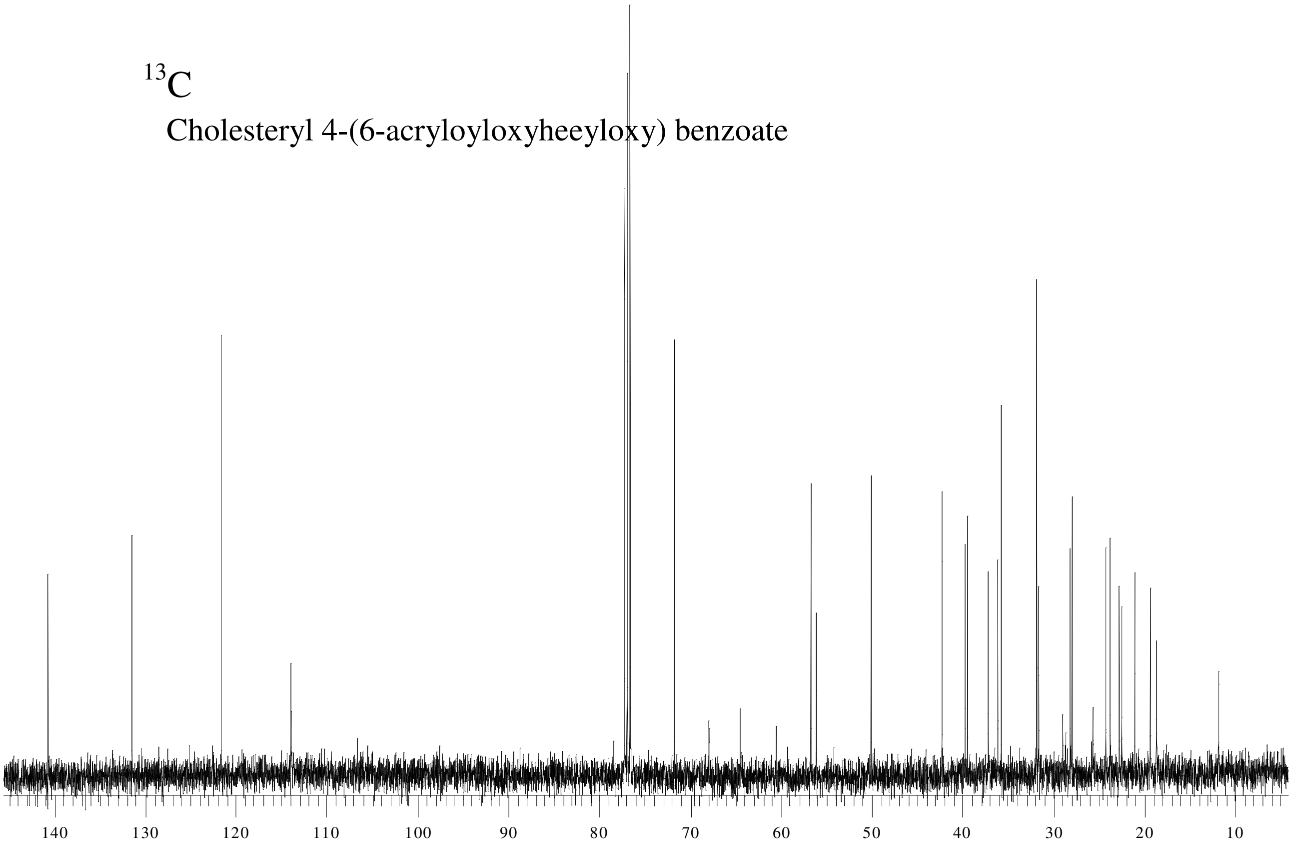
From the dropping funnel was drop wise added 0.125mol (12.65g) of acroloylchloride dissolved in 100ml of dichloromethane together with 0.2g hydroquinon to avoid polymerisation. The mixture was stirred for 12 hours and the temperature was allowed to rise to room temperature. Afterwards the yellow liquor was filtrated on a fluted paper and the dichloromethane was removed on the vacuum rotary evaporator, the residue was dissolved in chloroform and set on a separatory funnel and washed with 3-time 100ml of water and finally with 100ml 0.1M K_2CO_3 which resulted in a quick phase separation with a clear chloroform phase and an opaque water phase. The chloroform phase was dried with $MgSO_4$ and filtrated on a Büchner filter and the chloroform was removed by evaporation and the clear liquid acrylic acid 6-bromo-hexyl ester was added a few grain hydroquinon and stored I a freezer. Yield 58% or 6.81g.

A tree-necked round bottom flask equipped with nitrogen flow, dropping funnel and magnetic stirring was used for the synthesis of *cholesteryl-4-hydroxy-benzoate*. 0.05mol (6.91g) of 4-hydroxy-benzoic acid and 0.05mol (19.34g) of cholesterol was dissolved in 200ml anhydrous tetrahydrofuran THF and 10 mol % from the acid of DMAP is added as catalyst. From the dropping funnel was slowly added 0.125mol (25.76g) of DCC dissolved in100ml of anhydrous THF to take up the water from the ester formation. After 24 hours of stirring at room temperature a sample was taken out for TLC analysis, which shows that most, of the initial compounds has reacted and formed one single product. The eluent was ethyl acetate and petrolether in ratio 1:1. The THF was removed on rotary vacuum evaporator and the residue was redissolved in chloroform and set on a separatory funnel and washed with 4-time 50ml of water. The chloroform phase was dried with $MgSO_4$ and then filtrated on Büchner funnel. The chloroform was evaporated and the product dried in exicator over silica. Yield 67% or 16.98g.

The synthesis of *cholesteryl 4-(6-acryloyloxyheeyloxy) benzoate* was carried out as a classical Williamsons ether synthesis.

A solution of 0.02mol (4.70g) acrylic acid 6-bromo-hexyl ester was dissolved in 100 ml of anhydrous THF it was added drop wise from a dropping funnel to a suspension of 0.025mol (14.00g) of potassium hydroxide, 0.02mol (3.32g) of KI and 0.02mol (10.14g) of cholesteryl-4-hydroxy-benzoate in 200 ml of anhydrous THF placed in a 500 ml round-bottomed flask with magnetic stirring, the stirring was continued for 4 hour at room temperature under nitrogen atmosphere. Afterwards the THF vas removed on vacuum rotary evaporator and the residue was taken into 150ml of chloroform and set on a separatory funnel and washed with 5-time 50ml of water. The chloroform phase was dried with $MgSO_4$ for 6 hour and then filtrated on a fluted paper the chloroform was evaporated. The purification of the crude product was done on a silica column eluted with a mixture of ethyl acetate and petrolether in ratio 1:1 the product was still greasy so I was recrystallized to time from methanol, witch gave a fine white voluminous powder. The product was sending for NMR analysis. Yield 62% or 8.19g.

The synthesis of cholesteryl 4-(6-acryloyloxyheeyloxy) benzoate has also been done from 4-(6-acroloxyhexyloxy) benzoic acid[1] where the cholesterol moiety was introduced by an esterfication procedure similar to that used for the synthesis of cholesteryl-4-hydroxy-benzoate. This second pathway did not give any significant chance in purification work or in yield.



^1H δ 5.23ppm characteristically signal in the polymer blends.

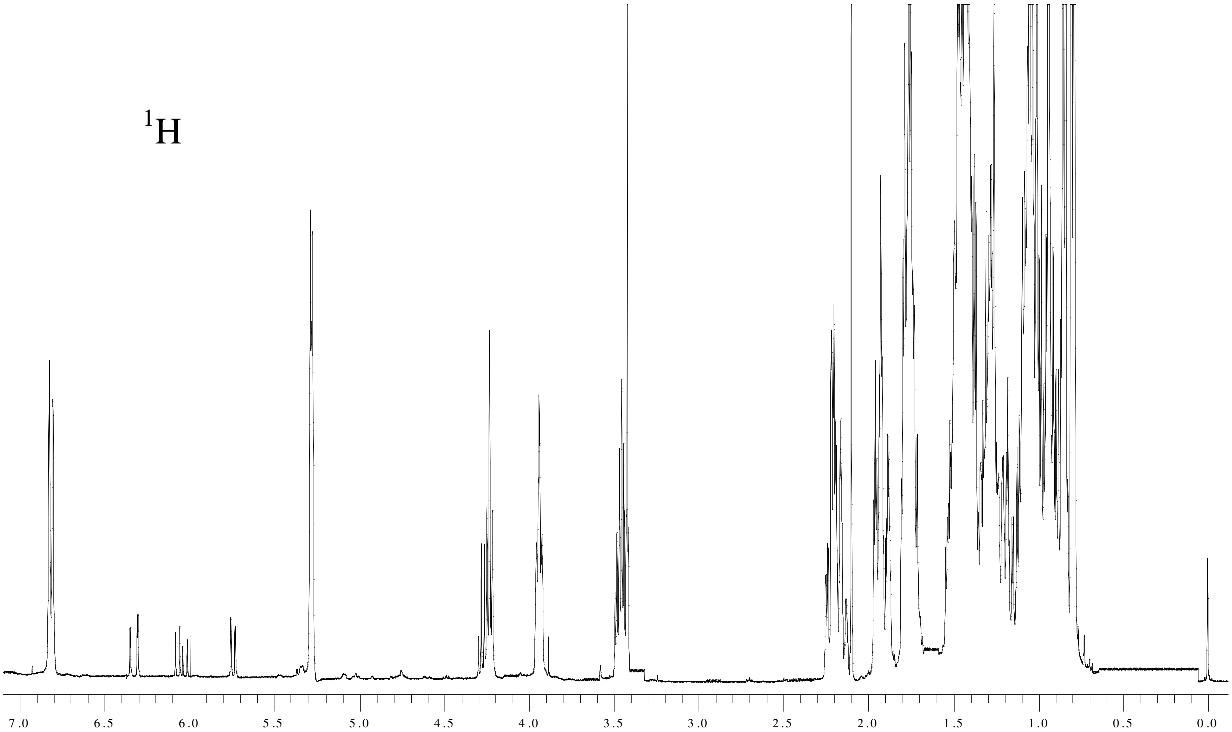
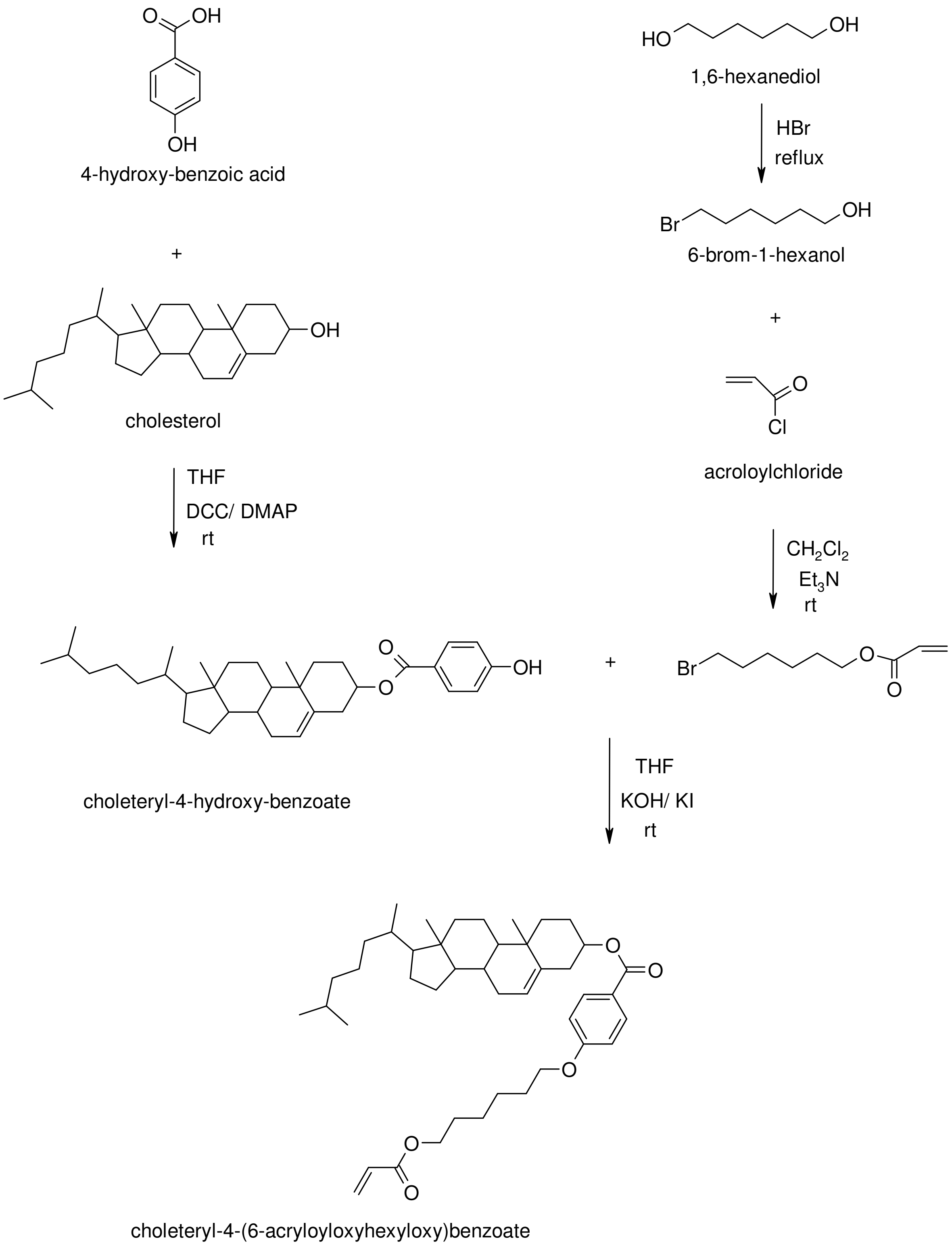


PLATE V

SYNTHESIS OF CHOLESTERYL-4-(6-ACRYLOYLOXYHEXYLOXY) BENZOATE



SYNTHESIS OF 4'-METHOXYPHENYL-(5-ACRYLOYLOXYPENTANOYLOXY)-BENZOATE

The first step, the synthesis of *4'-methoxyphenyl-4-hydroxybenzoate* is described in the literature [40]. The synthesis was modified to avoid the use of benzene. For the reason that I have good experience in using DDC/DMPA in THF it was tried first. It turned out to give almost no product and when the temperature was set up from room temperature to 60 degrees it result in large molecules, oligomers or polymers.

In the second attempt, the synthesis was carried out in toluene instead of benzene as described in the literature. The use of toluene gave a lover yield but a clean product with some discoloration. In a 250 mL round-bottomed flask, equipped with a magnetic stirring and a Dean and Stark apparatus with a stopcock at the lower end carrying a reflux condenser, was placed 0.10 mol (13.81g) 4-hydroxybenzoic acid, 0.1mol (12.4g) 4-methoxyphenol in 75 mL of dry toluene. 10 mL of dry toluene was placed in the trap. To the stirring mixture was added 0.4 g of concentrated sulfuric acid or 3 per cent of the alcohol by weight. The mixture was headed to reflux under nitrogen atmosphere. The process was monitories by measuring the formation of water after 36 hour no visible amount of water was collected in the trap and the process was stopped. After cooling to room temperature there was a solid precipitate, the mixture was filtrated on a fluted filter paper, and the toluene phase was then removed on a vacuum rotary evaporator the reminiscence and the solid precipitant was put together and dissolved in diethylether and set on a separatory funnel. The diethylether phase was washed with 3 times 20 mL of water and afterwards with 3 times 10 mL saturated sodium bicarbonate. The organic phase was dried over $MgSO_4$ and filtrated on a fluted paper and finally the solvent was removed by evaporation. The product was recrystallized from hexane and then dried in oven for 24 hour at 100^{o}C, the melting point was 191^{o}C–193^{o}C (Litt.:192-194°C) It was sent for ^{1}H NMR(DMSO-d6): and the spectrum was similar to that in [40]. Yield was 11,8g or 48.3%.

The second step, the synthesis of *4'-methoxyphenyl-4-(5-bromopentanoyloxy)-benzoate* is another esterfication in the molecule for that reason the reaction was carried out under mild condition to avoid hydrolysis or trans-esterfication on the existing ester functionality. One mild and direct method for esterfication between carboxylic acid and alcohol is to use the dehydrating agent

N. N'-dicyclohexylcarbodiimide (DCC) together with a catalytic amount of 4-dimethylamino-pyridine (DMAP) [41], [42], [43].

Before use the equipment was dried in oven overnight as well as the solvent methylene chloride was dried over molecule sieves.

In a 250 mL three necked round bottomed flask fitted with a tube for inlet and outlet of nitrogen, dropping funnel and magnetic stirring was placed 0.02 mol (3.62 g) 5-bromopentanoic acid and 0.020 mol (4.89 g) 4'-methoxyphenyl-4-hydroxybenzoate dissolved in 70 mL of dry methylene chloride. To this was added slowly from the dropping funnel under stirring a solution of 0,03mol(6.18g) DCC and 0.003mol (0.37g) DMAP in 100 mL of dry methylene chloride. The reaction mixture was then stirred for two days at room temperature under nitrogen atmosphere. After the two days, a white precipitate has appeared it was filtered off and washed with methylene chloride. The two organic methylene chloride phases where set on a separatory funnel and washed with 3 times 30 mL of water, 3 times30 mL 0.5 M NaOH and finally with 2 times 30 mL of water.

The methylene chloride phase was dried over $MgSO_4$ and afterwards filtrated on a fluted paper and the methylene chloride was removed by evaporation under removed pressure and the product was dried in oven overnight. The melting point was 70.5°C – 71.5°C that was the same as obtained earlier in the laboratory and taken as indication for the right product.

Yield 7.39g or 90.73 per cent.

The third and last step is the introduction of the acrylate group. Using a potassium salt of the acroloyl acid in a dipolar aprotic solvent HMPA did it. It is a S_{N2} mechanism and it is reported to give a good yield [44]. Several attempts in our laboratory on different species gave 23 to 40 per cent.

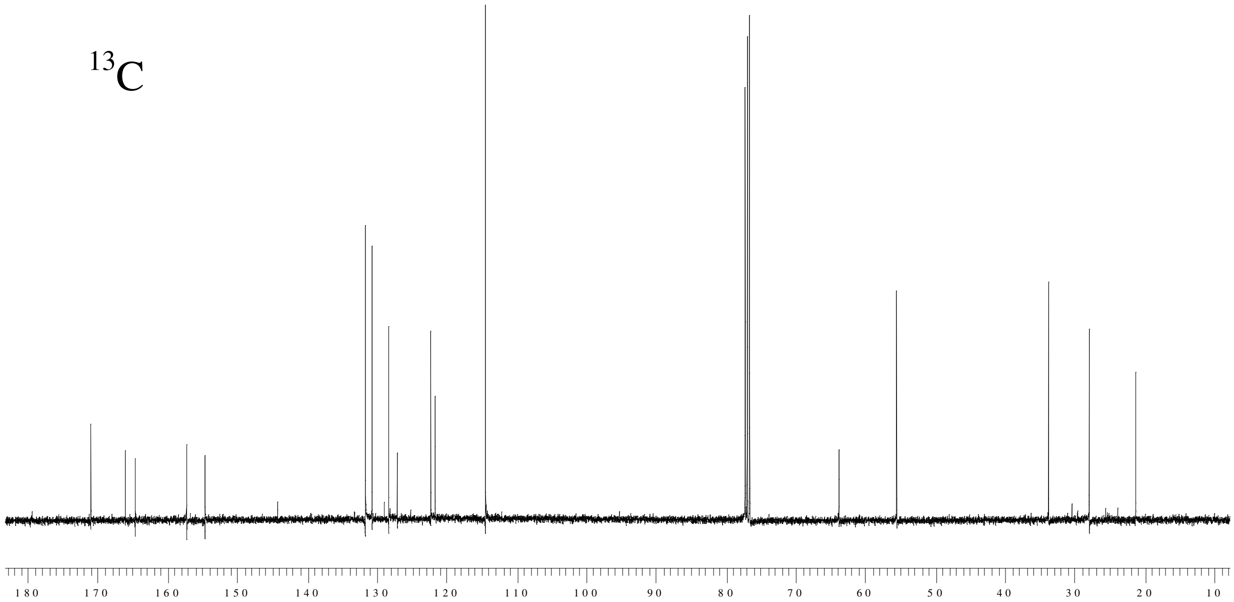
The synthesis of *4'-methoxyphenyl-(5-acryloyloxypentanoyloxy)-benzoate* was carried out in a 100mL Erlenmeyer flask. 0,01 mol (4.07g) 4'-methoxyphenyl-(5-bromopentanoyloxy)-benzoate were mixed with 2 equivalents 0.02mol (2.21g) potassium acroloylate in 50ml of HMPA and a few grain hydroquinon was added to avoid polymerization. The mixture was stirred for 48 hour at 30°C

The process was monitored by TCL (ethylacetate and toluene 1:4) and after 48 hour it did not change. The mixture was set on a separatory funnel and 150 mL of chloroform was added. It was washed with 4 time 50mL of water, which remove the carcinogen HMPA. The separation become troublesome so finally it was washed with 2 times 50 mL of brine. The chloroform phase was dried with $MgSO_4$ and filtrated on a fluted paper the chloroform was removed on a vacuum rotary evaporator. The product was greasy so it was taken into 100 mL of petrolether where it participated.

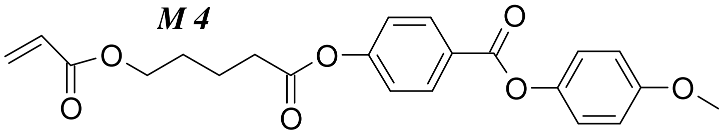
The product was filtrated of and dried finally it was purified on a column with ethylacetate and toluene 1:4 as eluent and dried in exicator overnight and sent for NMR analysis. The melting point: 66°C-67°C Yield 38 per cent or 1.56g.

1H-NMR(CDCl3): δ 1.85-1.89(4H, m); 2.66(2H); 3.82(3H); 4.23(2H); 5.85(1H); 6.22(1H); 6.4(1H); 6.94(2H); 7.1(2H); 7,23(2H); 8,22(2H) ppm

13C-NMR: d 21,3; 27,9; 33,7; 55,5(C-spacer); 63,8(CH3O-); 114,4; 121,6; 122,3; 131,6 (Ar-C-H);
127,0(Ar-C-O); 128,3; 130,7(CH=CH2); 131,6(Ar-C-H); 144,2(Ar-C-O); 155,6(Ar-C-O); 157,2(Ar-C-O); 164,6(C=O); 166,0(C=O); 171,0(C=O) ppm


^{13}C
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

M 4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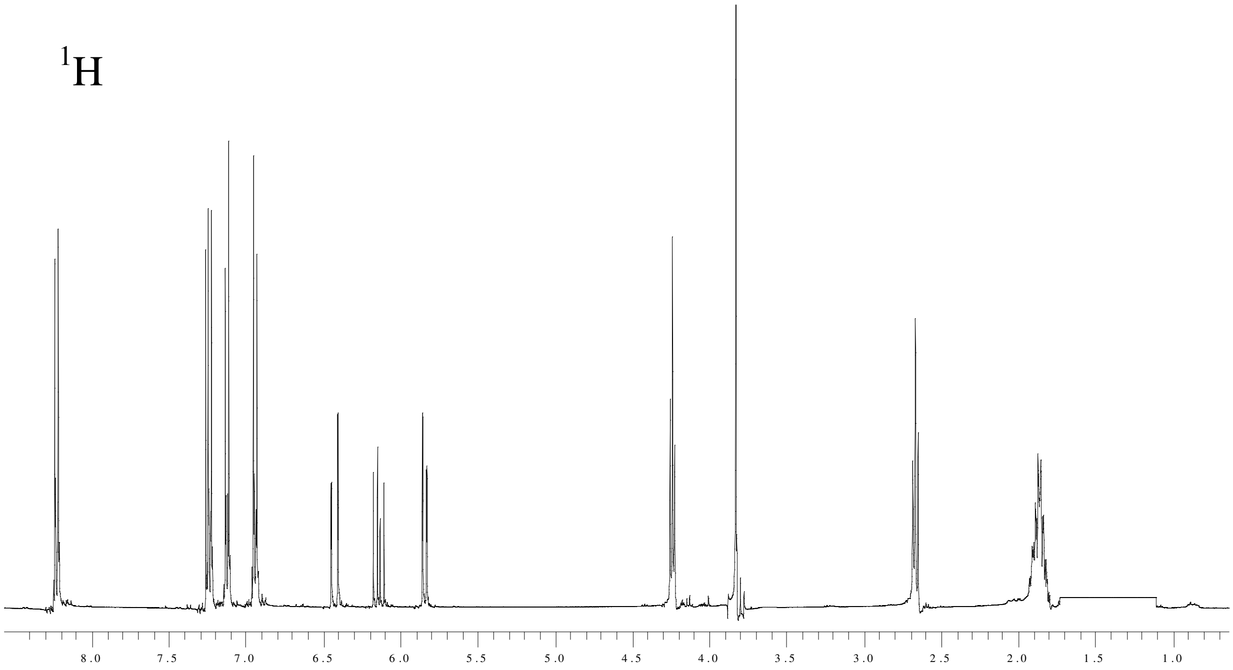
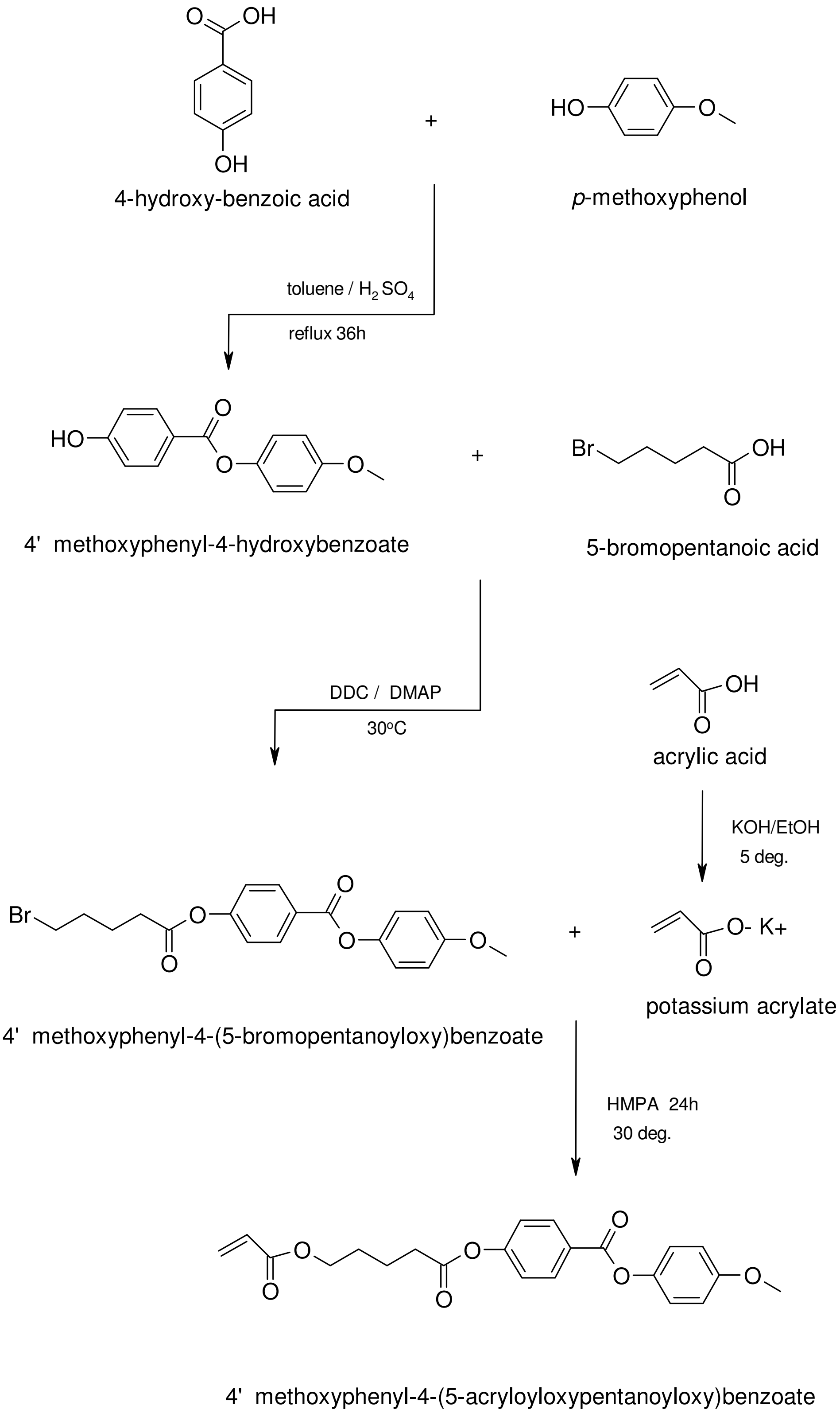

^{1}H
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

PLATE VI

4' METHOXYPHENYL-4-(5-ACRYLOYLOXYPENTANOYLOXY)BENZOATE

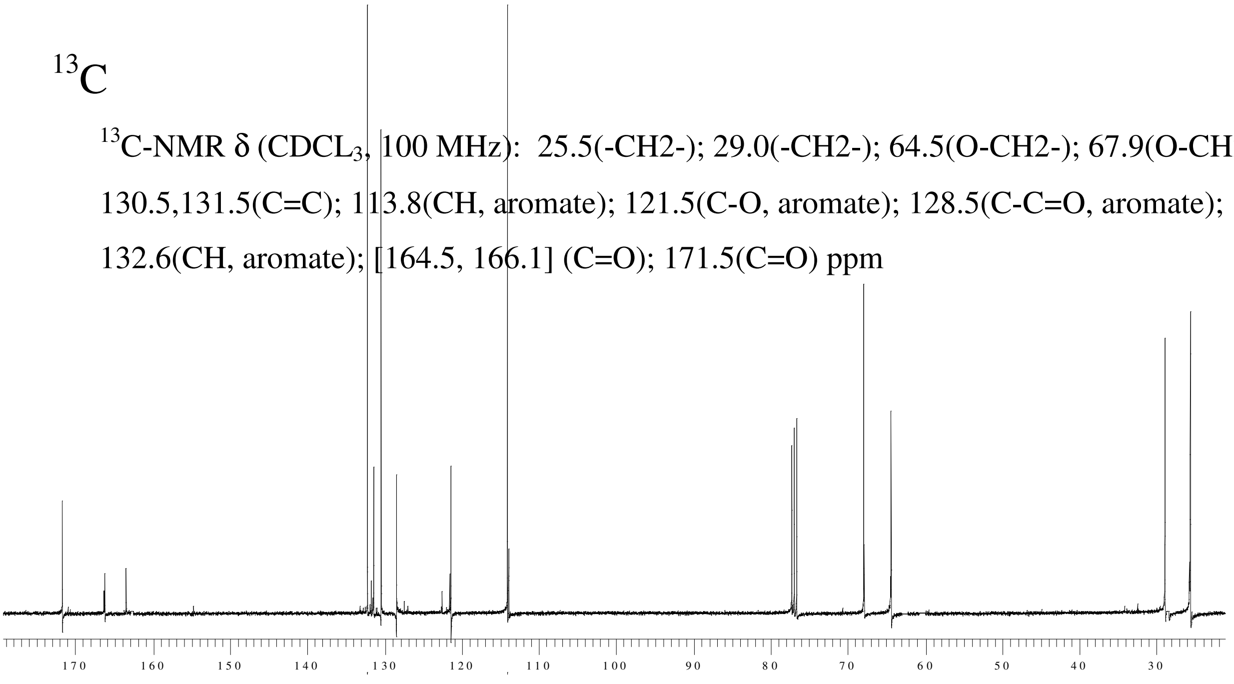


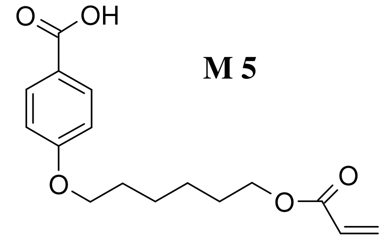
SYNTHESIS OF 4-(6-ACRYLOYLOXYHEXYLOXY) BENZOIC ACID

The synthesis of *4-(6-hydroxyhexyloxy)-benzoic acid* was carried out from *p*-hydroxybenzoic acid [56] as well as from the ester ethyl-4-hydroxybenzoate [57]. The synthesis with the acid was troublesome and gave a mixture of compound so the ester was preferred for the first etherification step. In 400mL of 2-butanon was dissolved 0.3mol (49.85g) of ethyl-4-hydroxybenzoate 0,30 mol (16.83 g) of KOH, 0,3mol (49,80g) of KI and 0,30 mol (54.32g) of 6-bromohexan-1-ol it was placed in a 1L three necked round bottom flask equipped with condenser and magnetic stirring and set for reflux 65°C in 10 hour. Afterwards the dioxan was removed on vacuum rotary evaporator and the residue was taken back to the flask and 500mL 0,5 M KOH was added and the reflux was continued for another 5 hour to hydrolysis the ester. After 5 h the mixture was cooled and acidified with HCl by slowly adding 4M HCl. When acidifying a white compound begin to precipitate. The mixture was stored overnight in the refrigerator for further precipitating. The precipitate was filtered on a Büchner funnel and dried. The compound was send to NMR analysis and it was concluded it was the expected product. Yield 58.62g or 82%. Melting point 128^{0}C-130^{0}C. It was used without further purification.
In the synthesis of *4-(6-acryloyloxyhexyloxy)-benzoic acid* the introduction of the vinyl moiety by acryloyl chloride was done at shifted temperature and time. At room temperature and a reaction time at12 hours the yield was significant lower than it was, when the temperature was shifted to 60^{0}C and it was allowed to react in only 2 hours. In a two-necked round bottom flask equipped with a dropping funnel, condenser and magnetic stirring was placed 350mL of 1,4-dioxane, 0.20mol (47.66g) 4-(6-hydroxyhexyloxy)-4-benzoic acid, and 0,22 mol (22,2 g) of triethylamine it was stirred and cooled to 5°C on ice bath. 0.22mol (19.91g) acryloyl chloride was dissolved in 150mL of 1,4-dioxane and slowly added from the dropping funnel. The solution was heated to 60°C for 2 hours under nitrogen atmosphere. The 1,4-dioxane was removed on vacuum rotary evaporator and the residue was dissolved in chloroform and set on a separatory funnel and washed with 4-time 50mL of water, the chloroform phase was dried with $MgSO_4$ and filtrated on a fluted paper, the chloroform was removed by evaporation, the residue a white powder was purified on a silica column the eluent was a mixture of ethyl acetate and methylenchloride in the ratio 1:4. It was necessary recrystallized ones from dry ethanol. The yield was33.9g 58 % from 4-(6-hydroxyhexyloxy)-4-benzoic acid and the melting point was 91°C-92°C. The final product was sent for NMR analysis.

^{13}C

^{13}C-NMR δ ($CDCL_3$, 100 MHz): 25.5(-CH2-); 29.0(-CH2-); 64.5(O-CH2-); 67.9(O-CH2); 130.5,131.5(C=C); 113.8(CH, aromate); 121.5(C-O, aromate); 128.5(C-C=O, aromate); 132.6(CH, aromate); [164.5, 166.1] (C=O); 171.5(C=O) ppm





M 5

^1H

^1H-NMR: δ($CDCl_3$, 400 MHz) 1.3-1.5(4H); 1.8(4H); 4.0(2H); 4.1(2H); 5.8(1H); 6.1(1H); 6.4(1H); 6.9(2H, aromate); 8.0(2H aromate) ppm

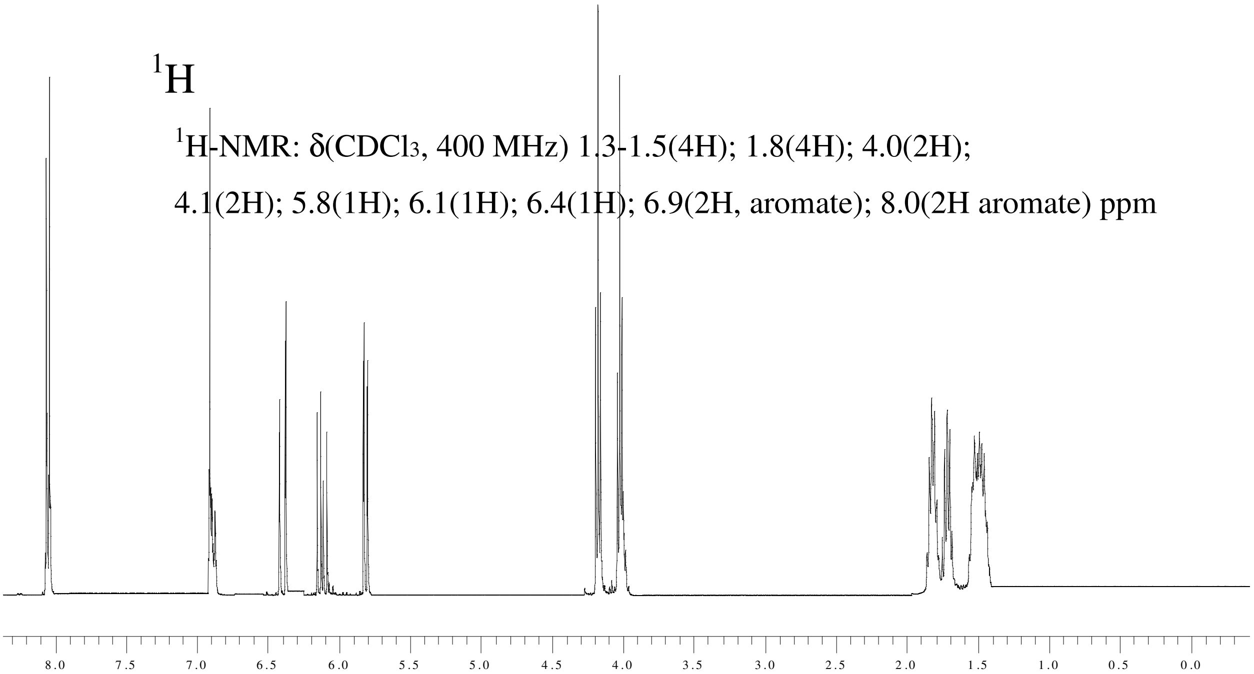
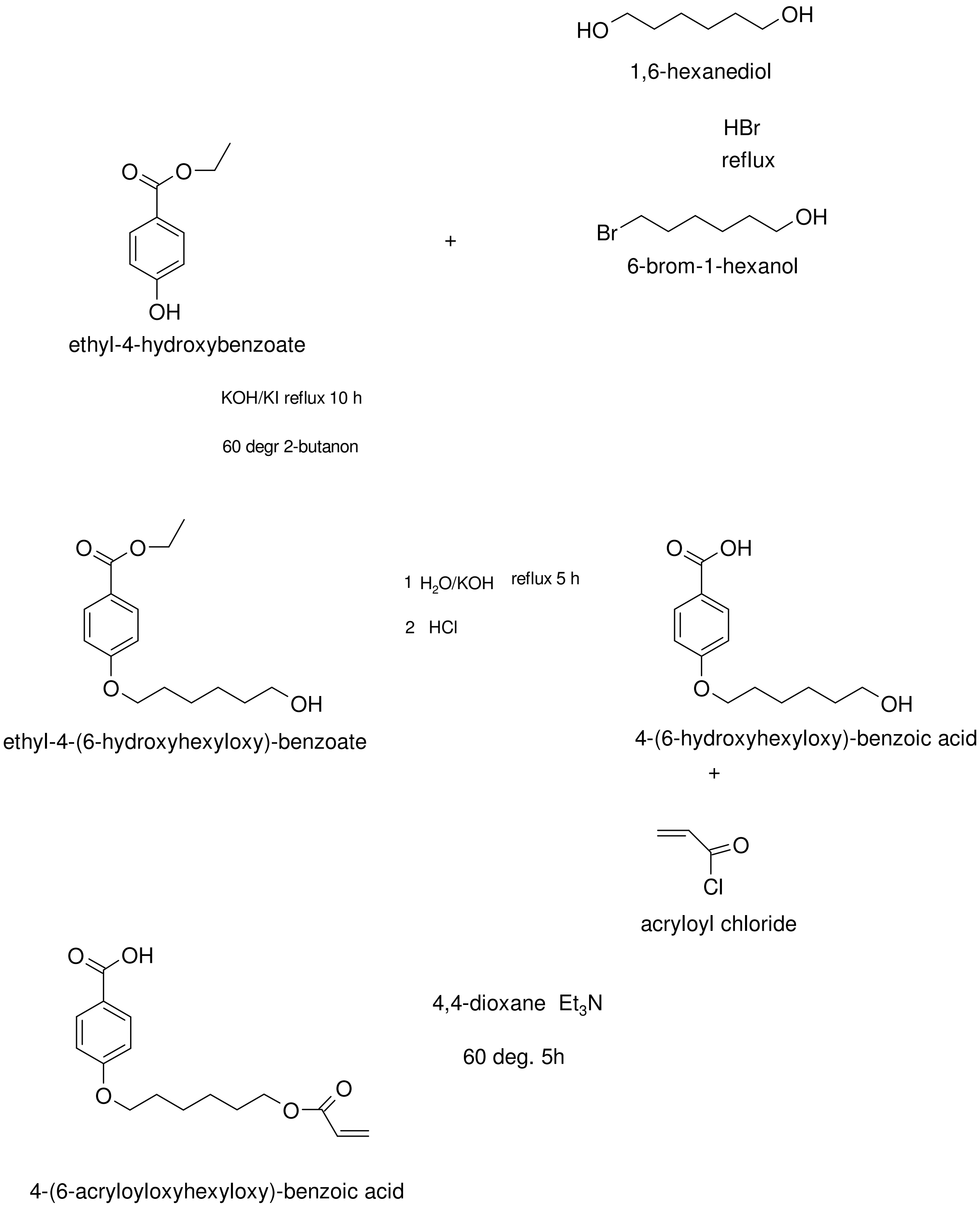


PLATE VII

SYNTHESIS OF 4-(6-ACRYLOYLOXYHEXYLOXY)-BENZOIC ACID



POLYMERISATION.

There are many methods for transforming the monomer units into polymer substance, every method has its advantages and disadvantages [48]. There is also different way to classify the type of polymerisation even they some time are used in combination with each other.

In this project is used solution polymerisation executed as a radical polymerisation.

In the solution polymerising system the monomer units are dissolved in appropriate solvent with initiating agent. The initiating agent may be soluble in the solvent or exist as a suspension.

The advantage for this method is the easy way to control the polymerization temperature. Because of the good heat transfer the system have constant temperature and the solvent dilutes monomers react less intense so auto-acceleration as well as viscosity build-up can be avoid. The main disadvantages to the solution polymerisation are the separation of polymer and solvent and the purification. The degree of polymerization and the rate of polymerization are proportional to the monomer concentration this result in low molecular weight. If the solvent acts as a chain transfer agent it will also decrease the degree of polymerization.

The solution polymerising system open up for different method to initiate the polymerisation, in this case radical polymerisation was chosen.

Radical polymerisation has three general steps: Initiation, propagation and termination.

The initiation happens in two steps: In the first step the radical specie has to be produced by decomposing of peroxide or azo compounds. The second step is the addition of the radical to the monomer to give a new radical.

$$Initiator \xrightarrow{\mathrm{k_d}} R\cdot$$

$$R\cdot \xrightarrow{\mathrm{k_i}} M_1\cdot$$

In the propagation step a radical monomer or polymer adds to another monomer to form a new radical.

$$M_i\cdot + M \xrightarrow{\mathrm{k_p}} M\cdot_{i+1}$$

In copolymerisation with two monomers as in this project the mechanism are analogue to that in homopolymerisation, but the reactivity of the monomers towards other monomers can vary.

Two monomers M_a and M_b can undergo either self-propagation $M_a\cdot$ reacting with M_a and $M_b\cdot$ reacting with M_b or cross-propagation where $M_a\cdot$ reacting with M_b and $M_b\cdot$ reacting with M_a. This results I four different reactions each with its own rate constant.

$$M_a \cdot + M_a \xrightarrow{k_{aa}} M_a \cdot$$

$$M_a \cdot + M_b \xrightarrow{k_{ab}} M_b \cdot$$

$$M_b \cdot + M_a \xrightarrow{k_{ba}} M_a \cdot$$

$$M_b \cdot + M_b \xrightarrow{k_{bb}} M_b \cdot$$

The two principal ways that terminations occur in radical polymerisation are radical coupling or disproportionation.

$$M_l \cdot + M_m \cdot \xrightarrow{k_{tc}} M_{l+m} \qquad \text{Coupling}$$

$$M_l \cdot + M_m \cdot \xrightarrow{k_{td}} M_l + M_m \quad \text{Disproportionation}$$

The solvents used in solution polymerisation are required not to react chemically with the initiator and it should have a low transfer constant to provide sufficiently high degree of polymerisation. In this project tetrahydrofuran THF has been chosen as solvent, from what mention above it cut be criticised because THF quince the radicals from the initiator 2,2'-azobisisobutyronitril AIBN and THF can polymerise it self, but free radical initiation occur with difficulty and is complicated by competing hydrogen abstraction reaction. THF has one advantage it is its capability to dissolve a wide spectrum of polymers: Polyvinyl acetate (PVA), poly vinyl butyral (PVB), poly vinyl chloride (PVC) and polymethyl methacrylate PMMA.
The Hansen solubility parameters [49] for THF are for the dispersion component 8.2, polar component 2.8 and hydrogen-bonding component 3.9 it place THF in the Teas diagram where the "window" for many polymers is. THF is mixable wit h lower alcohols and water, which give the opportunity to make mixed solvent with the right conditions for a specific system. The fraction to be mixed can easily found by calculating, for the reason that the Hansen parameters are additive by volume fraction. In this project participation under the polymerisation should be avoid and for ensuring that all monomers and copolymers was soluble under the polymerisations process THF was chosen as solvent together with AIBN as initiator. The quenching can be compensated by adding more AIBN which has a half live time in toluene varying from 70 days at 30°C to 4 min. at the melting point at 105°C.

SYNTHESIS OF POLYMERS.

With the exception of monomer M1 the 4-(6-acryloyloxyhexyloxy) stilbazole, all the polymers was synthesized by solution free radical polymerisation using 2,2'-azobisisobutyronitril AIBN as initiator in tetrahydrofuran THF. The polymerisation process was very sensitive towards small impurities in the solvent as well as in the initiator. These impurities come from inhibitor added to the THF and decomposing product in the AIBN. The polymers come up with collared products and for that reason both the THF and the AIBN was carefully purificated.
The THF is a cyclic ether there if it is allowed to stand for some time in contact with air and exposed to light can form peroxides [50]. For the reason that the last step in the purification and drying the THF is fractional distillation the peroxides had to be removed else it can become concentrated and give undesirable reaction in the residue in the distillation. The peroxide was removed by shaking one litre of THF with 10-20ml of a concentrated solution of an iron (II) salt prepared by dissolving 60g of iron (II) sulphate in a mixture of 6ml concentrated sulphuric acid and 110 ml of water. The THF was the dried initially over calcium sulphate or solid potassium hydroxide before refluxing it with sodium under nitrogen atmosphere a few grain of benzophenone was added it com up with a beautiful blue colour from the sodium ketyl radical which is formed when no water or oxygen are present in the THF. The THF was distillated of just before use.
The AIBN was recrystallized in small quantities from methanol [51] and dried at room temperature in vacuum over P_2O_5 in the dark just before use.

The polymerisation was carried out in THF for 48 hours at 60°C with 2% of AIBN by weight as initiator, the half live for AIBN in toluene at 60°C is approximately 20 hours. For all homopolymer as well as copolymer the total sample weight was 0.2g. The procedure was the same for all samples and for that reason it only descripted ones with monomer M3 as an example. For the monomer M1 was used methanol instead of THF and 4% of AIBN

In a reaction tube with stopcock on side arm equipped with septum was dissolved 0.2g of monomer M3 in 15mL of THF and 0.004g AIBN was added. A syringe needles was pierced though the septum and nitrogen was bobbled though the mixture for some minutes to remove oxygen, the stopcock was closed and the needles removed. The reaction tube was placed in an oil-bath at 60°C for 48 hour. The attention was paid to the building up pressure in the tube, first from heating to the 60°C, second from de decomposing AIBN, which can give maximum 0.7mL of N_2 gas. Quick opening and closing the stopcock after 6 hours and then again after 12 hours reduced the pressure. After 48 hours the mixture was cooled to room temperature before opening the tube and placed in the hut where the THF was allowed to evaporate. The residue was a white powder; it was washed with a little absolute ethanol to remove un-polymerised material. Afterwards the product was dried over night in a vacuum oven at 50°C. To control if the monomers was polymerised the product was sent to NMR analysis if the double bonding from the acrylic group is absent it can be taken as a first sign for that the polymerisation have taken place. An analysis was also done on the HPLC apparatus, it was set up for size exclusion chromatography, the apparatus was not calibrated to give an exact value for the size, but by comparing with sample of monomers and mixtures of monomers similar to the compositions in the polymers it show very different retention times. The entire polymer come up with one broad signal where the single monomer gave one sharp signal and the mixtures of the monomers gave to signals close in retentions time. The broadness in the signal from the polymers gives an impression of the dispersity of the polymers. If the polymers not were washed with absolute methanol, as mention before, the signals become very broad, so this procedure narrowed the polydispersity. Afterwards the polymers were examined on DSC an in microscope.

The homo polymers was all polymerised from 0.2 g of the monomer M1, M2, M3, M4 and M5 And the copolymers was mixed after the scheme 1

Monomer	Ratio	M3	M4	M5	Total
	mol %	gram	gram	gram	gram
M3-M4	15-85	0.0453	0.1547		0.2
M3-M4	30-70	0.0836	0.1168		0.2
M3-M5	90-10	0.1906		0.0094	0.2
M3-M5	80-20	0.1801		0.0199	0.2

The numbers for the weight are given with the precision of the balance
Scheme 1

RESULTS AND CONCLUSION

The aim of this project was focused on two parts. The first, synthesis of two novel polymers with hydrogen bonding site, and the second, synthesizing three monomers and investigate their copolymers in different ratios.

Two novel side chain polymers from monomer based on heterocyclic aromatic compound with hydrogen bonding site have been synthesized.

Synthesizing the M1 monomer 4-(6-acryloxyloxyhexyloxy) stilbazole have been troublesome, the ether connection between the hydroxystilbazole and the 6-bromohexan-1-ol have come out in an unsatisfactory yield this need further investigation either with protection of the alcohol or changing the solvent. The capability to form hydrogen bonding has been shown from ^{1}H NMR where the neighbour protons to nitrogen have chemical shift at 8.5ppm. in pyridine when the nitrogen is bonded to hydrogen the chemical shift is approximately 9.3ppm. The DSC analysis gave for the monomer an exothermic melting peak at 157^0C and when cooling a sharp endothermic peak of crystallisation appeared at 136^oC. The polymer shows a different behaviour in the DSC analysis, an exothermic small glass transition peak at 49^0C was seen and the heat capacity change significant and when cooling a small endothermic peak appeared at 38^oC.

Synthesizing the M2 monomer 6-acryloyloxyhexyl-isonicotinate come in a good yield when the phase transfer catalyse was used for connecting the spacer to the isonicotinic acid. The last step in the synthesis the introduction of the acroloyl moiety unfortunately colorizes the product, the interpretation of this colour was an oxidation on the nitrogen therefore a reduction with PCl_3 was tried but with out success. The last synthesis step should be repeated under total oxygen free conditions or if this not remove the colour, further investigation to find the reason to the colorizing is necessary. The capability to form hydrogen bonding was shown in the same way as mention above. The monomer was a viscose liquid and it was not examined by DSC analysis. The polymer did not give any significant signal in the DSC analysis from 10^0C to 200^0C but show behaviour as an amorphous compound.

Synthesizing the three monomers M3, M4 and M5 were less painless only it should be notified that the purification on silica column with benefit could be accompanied of recrystallization. The

monomer M5 4-(6-acryloxyloxyhexyloxy)-benzoic acid is very sensitive to moister from the air, which should be taken into account when the monomer is examined by DSC analysis.
First the homopolymers was analysed by DSC and microscope with cross polarizer.

The homopolymer P3 from, cholesteryl-4- (6-acryloxyloxyhexyloxy)-benzoate show a smectic C* phase in the temperature range from 31^{o}C to 143^{0}C picture from the microscope also indicate a smectic C* phase. Results in album 1 page 77.

The homopolymer P4 from, 4'-methoxyphenyl-(5-acryloyloxypentanoyloxy)-benzoate shows a phase transition between nematic and isotropic phase 55^{o}C the lover limit for the nematic phase was not observed. Results in album 2 and 3, page 79.

The homopolymer P5 from, 4- (6-acryloxyloxyhexyloxy)-benzoic acid shows from the DSC curve a smectic mesophase in the range between 86^{o}C and 103^{o}C. The transition between smectic and isotropic phase at 103^{o}C was difficult to monitored and appeared only just after drying the polymer in exicator. Results in album 4 page 83.

The two monomers M3 and M4 was mixed in two ratios and polymerised.
With the monomers M3/M4 in ratio 15 to 85 in mol% the DSC curve show a glass transition at 40^{o}C. Picture from the microscope show a crystalline phase at 22^{o}C and an isotropic phase above 58^{o}C. Results in album 5 page 85.
When M3/M4 system was mixed in ratio 30 to 70 in mol% the DSC analysis shows a curve, which have similar characteristics as for the homopolymer P3. The copolymer have a glass transition at 33^{o}C and a smectic C* phase to 130^{o}C. The pictures from the microscope indicate a smectic C* phase even the pictures are not representative for the phase. Results in album 6 page 87.
The system has adopted the properties from the P3 by only using 30 % of M3 in the polymer. But further investigation is necessary to find the optimum for the system.

The two monomers M3 and M5 was mixed in two ratios and polymerised.
With the monomers M3/M5 in ratio 80 to 20 in mol% the DSC curve shows a curve, which have similar characteristics as for the homopolymer P3 but with a sharper profile, it shows a glass

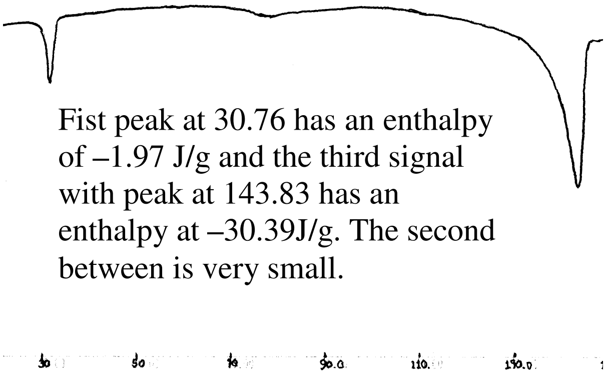
transition at 32^{o}C and a smectic C* to isotropic phase transition at 145^{o}C. The pictures from the microscope taken in the temperature interval from 30^{o}C to 138^{0}C shows Schlieren brushes and focal fan texture as good indication for the smectic C* phase. Results in album 7 page 89.

When M3/M5 system was mixed in ratio 90 to 100 in mol% the DSC analysis shows a curve, which have very similar characteristics as for the homopolymer P3. In this ratio it is clear that by adding the monomer M5 a system with very sharp transitions point has appeared with a glass transition at 31.5 ^{o}C and a smectic C* to isotropic phase transition at 144.5^{o}C. The cooling curve show a very sharp transition from isotropic to smectic C* at 122.4^{0}C. The pictures from the microscope confirm the smectic C* phase with typical Schlieren brushes and focal fan texture. Results in album 8 page 91.

It has been shown that by adding a small amount of a monomer with structural similarity to chiral main monomer a polymer with sharp and distinct mesophase properties can be created.

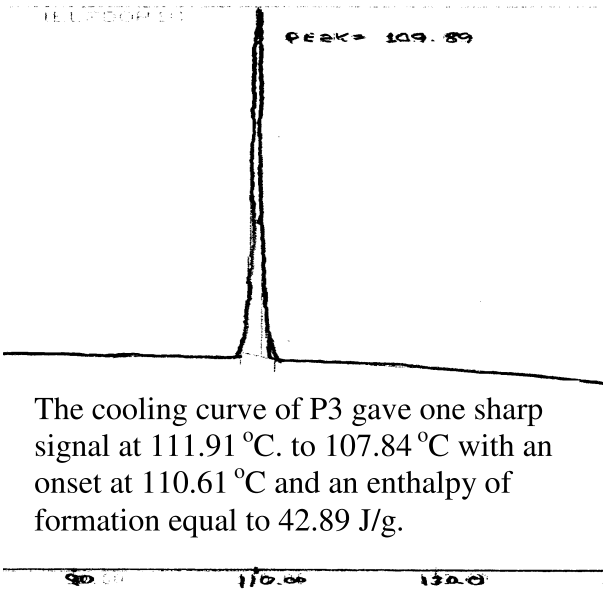
ALBUM 1

Polymer P3 show three signals. The monomer M3 show the signals more diffuse and these are not with taken.



Fist peak at 30.76 has an enthalpy of –1.97 J/g and the third signal with peak at 143.83 has an enthalpy at –30.39J/g. The second between is very small.

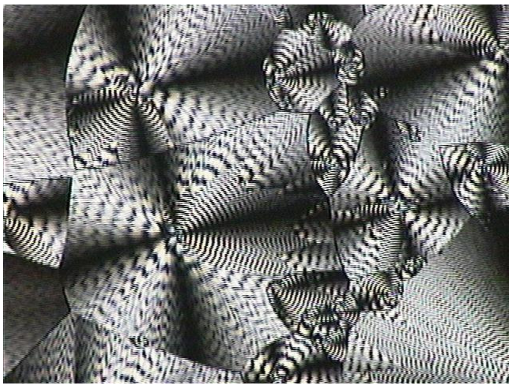
The last peak is large indicating that we come from some smectic phase C* to isotropic phase. The small first peak says that is not a dramatically chance in enthalpy. Can be a crystalline to smectic C* transition.



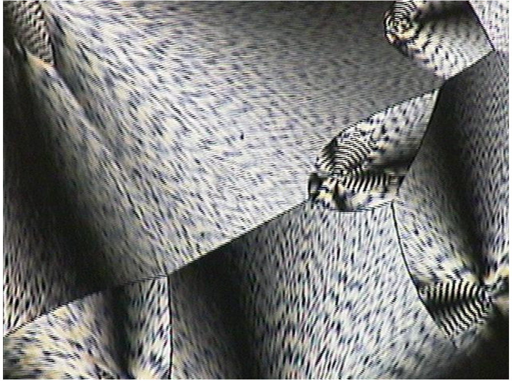
The cooling curve of P3 gave one sharp signal at 111.91 °C. to 107.84 °C with an onset at 110.61 °C and an enthalpy of formation equal to 42.89 J/g.

The picture in the top of the right side shows the P3 on 20 °C the pattern did not change in a significant way until the isotropic phase was reach. The three pictures down under were taken of the monomer at 55 °C, 65 °C and in the bottom120°C where it is clear that the pattern had start to disappear. The texture indicate a smectic C* phase.

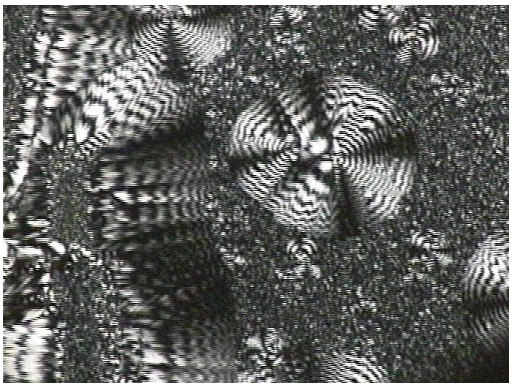
50 x magnification



50 x magnification

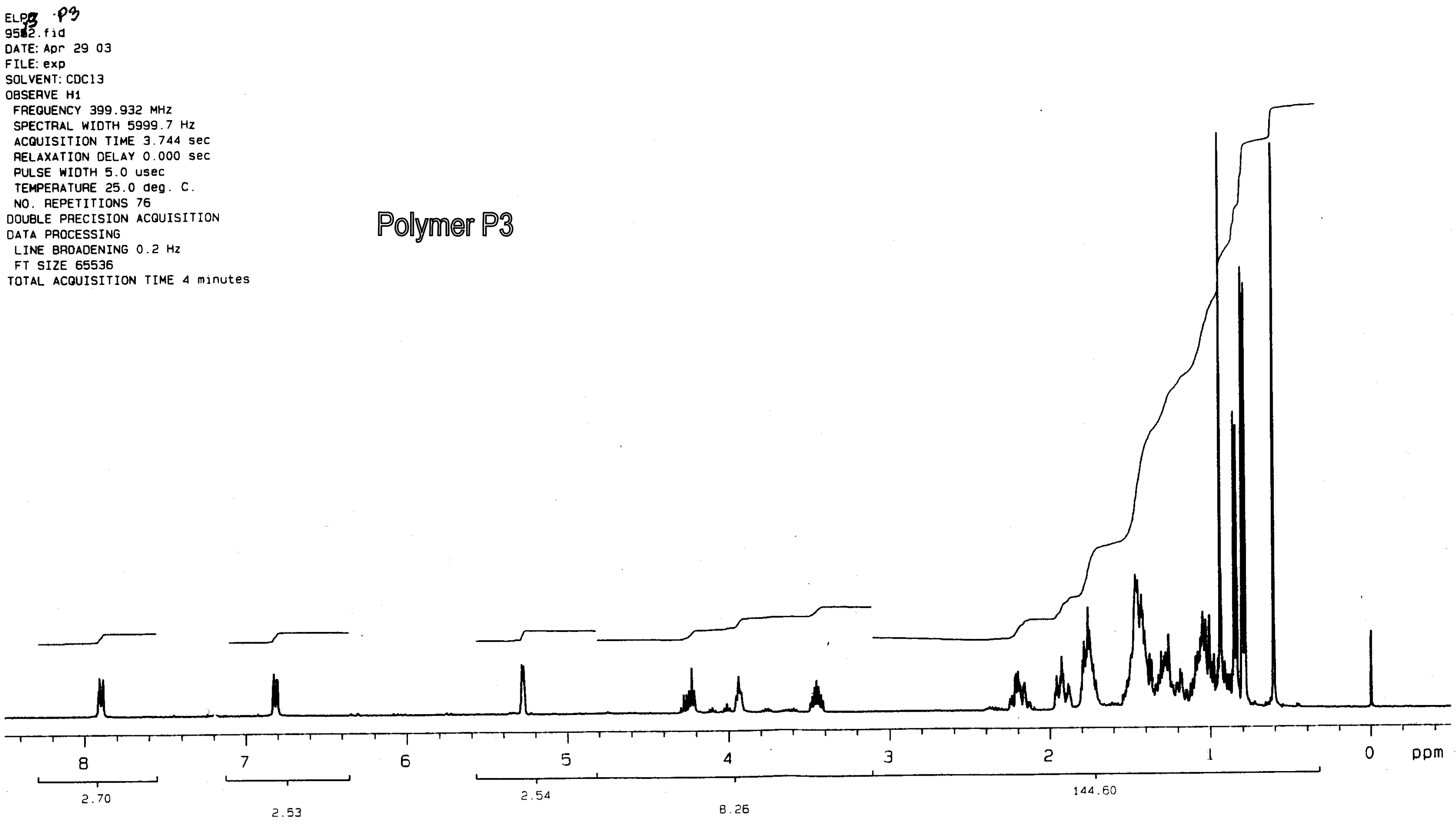


50 x magnification



50 x magnification

Polymer P3



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ELP3 ·P3
95[illegible]2.fid
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FILE: exp
SOLVENT: CDC13
OBSERVE H1
 FREQUENCY 399.932 MHz
 SPECTRAL WIDTH 5999.7 Hz
 ACQUISITION TIME 3.744 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 5.0 usec
 TEMPERATURE 25.0 deg. C.
 NO. REPETITIONS 76
DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 0.2 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 4 minutes
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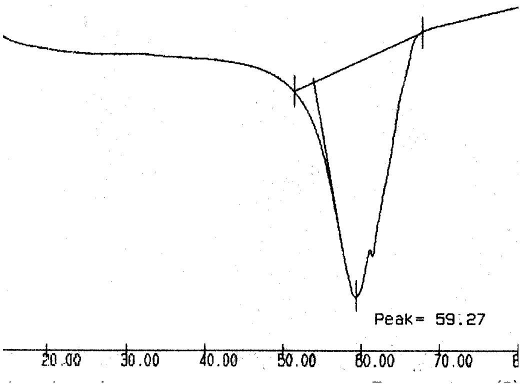
ALBUM 2

Monomer M4 with a broad transition point

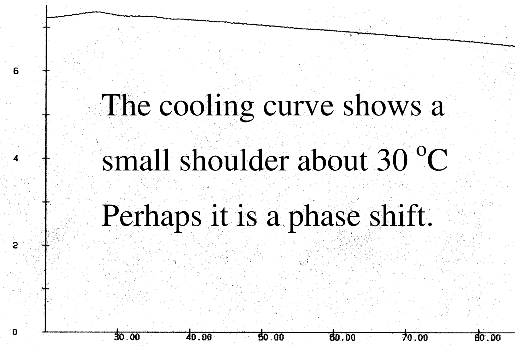


Peak from 51.23°C to 67.73°C

Onset = 53.86 °C J/g = -61.65

It looks like a nematic to isotropic transition or a melting point $\Delta_m H$ 24.54kJ/mol

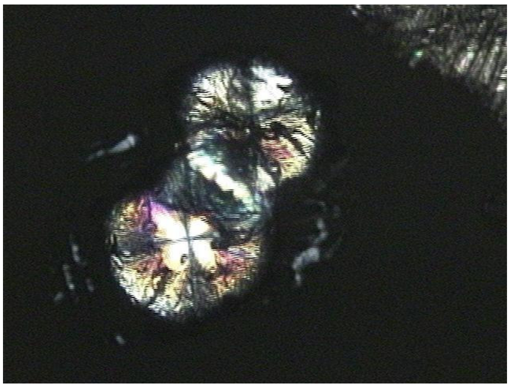
Indicating that M4 is nematic or crystalline.



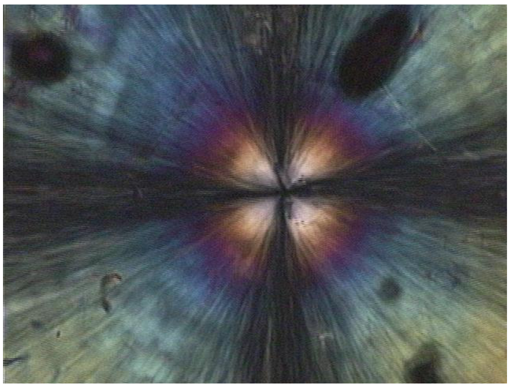
The cooling curve shows a small shoulder about 30 °C Perhaps it is a phase shift.

On the right side the first three pictures from top show the monomer M4 at temperature around 40 °C. Schlieren brushes indicate nematic phase. The last picture in bottom is taken after M4 has been melted and a short time of annealing at 25 °C if there is a separate phase it can be crystalline.

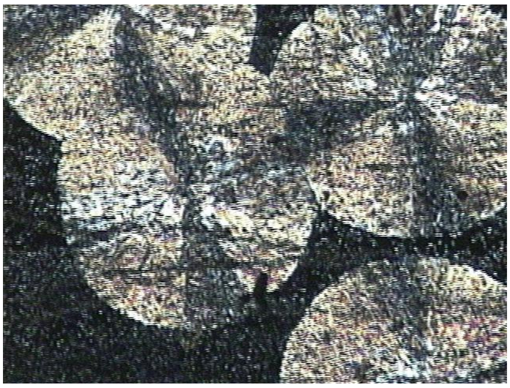
If M4 is not only crystalline there are indication for it is crystalline until 30 °C and then nematic to about 53 °C where it become isotropic.



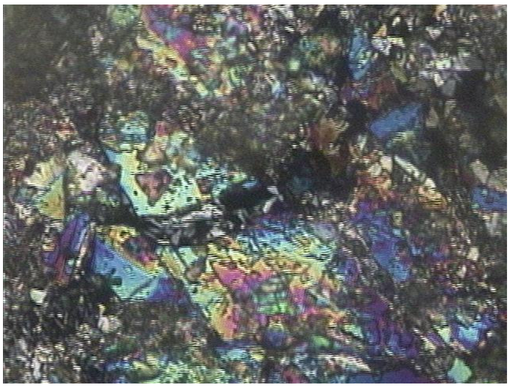
50 x magnification



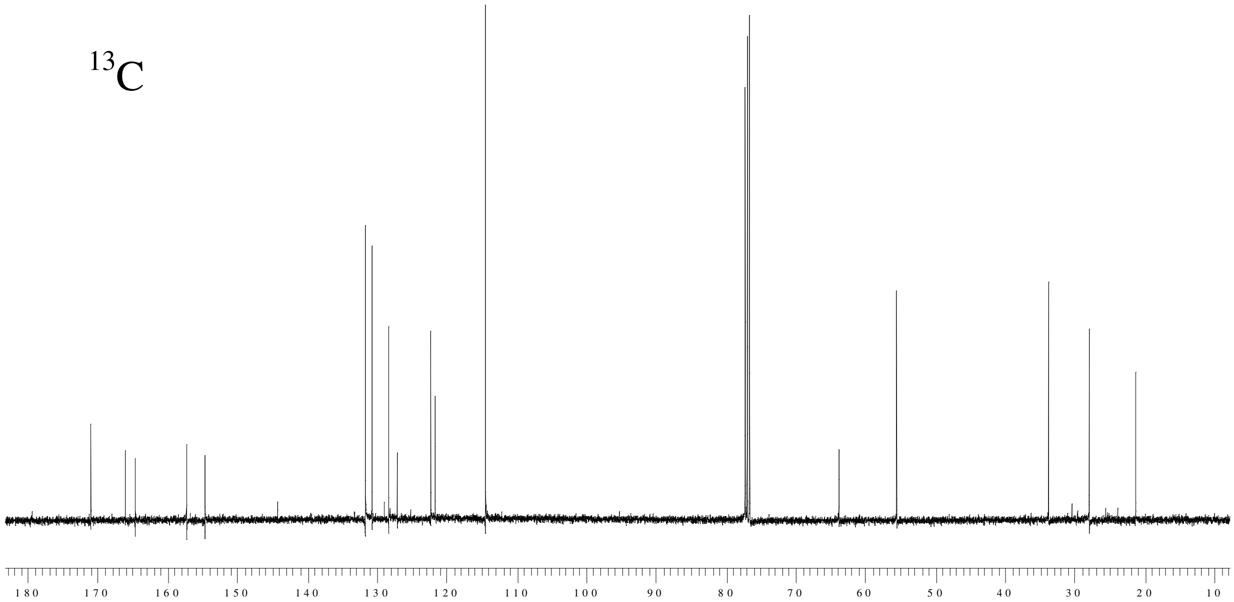
200 x magnification



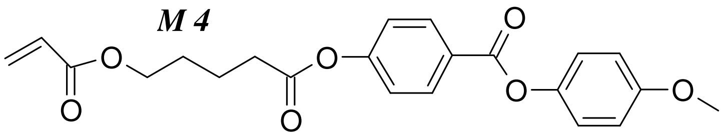
50 x magnification



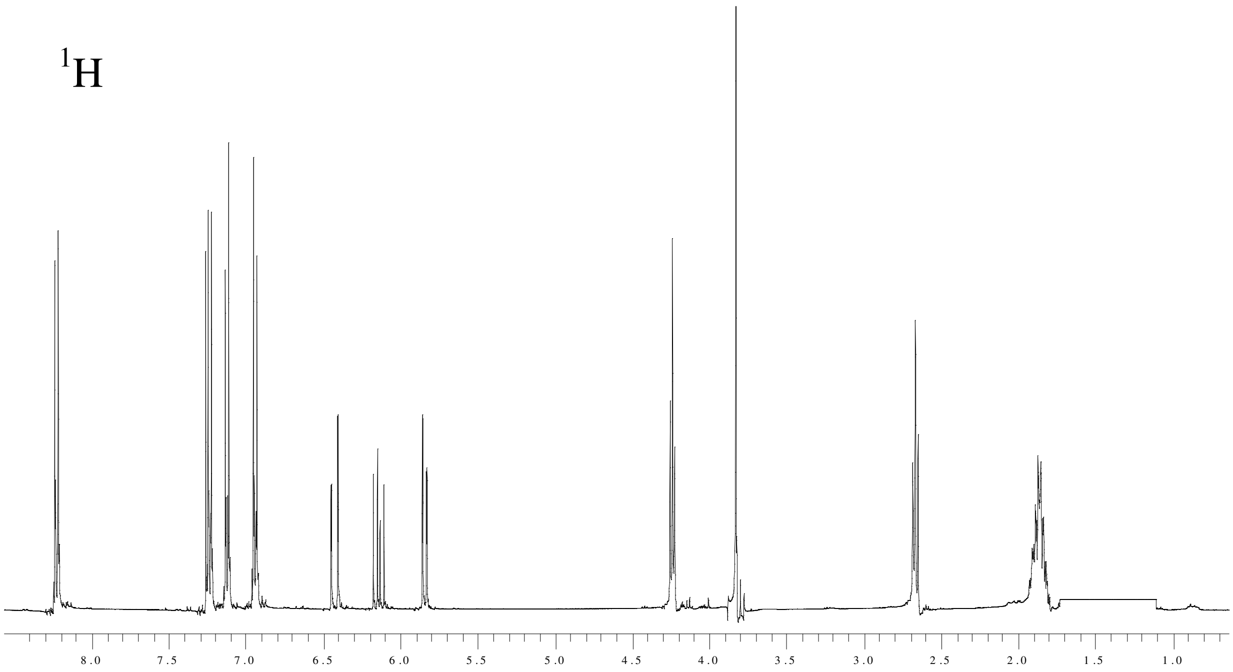
50 x magnification



^{13}C
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

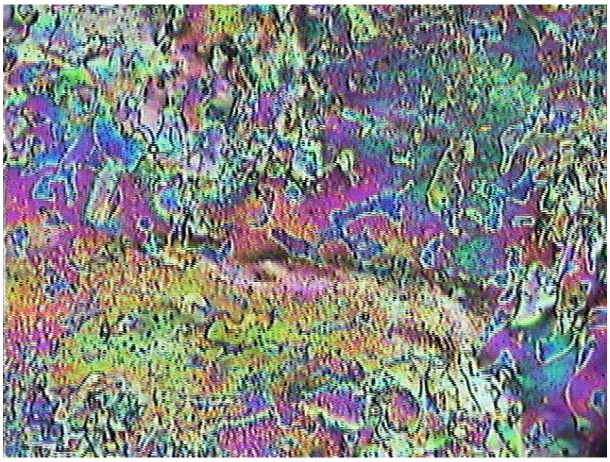


M 4

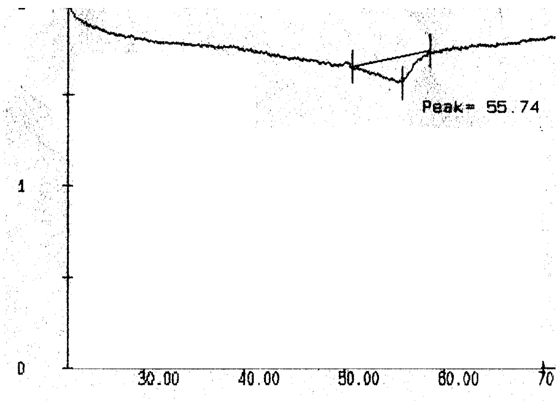


^{1}H
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

ALBUM 3

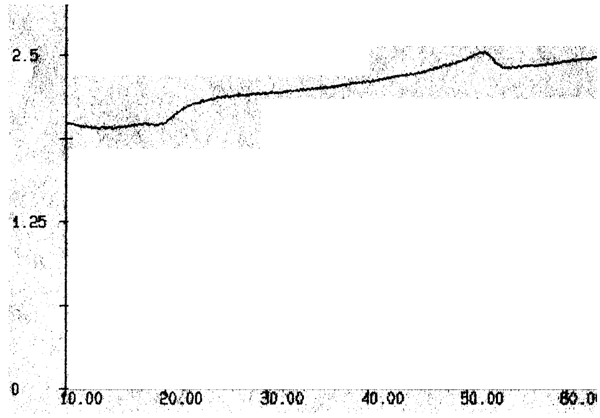

50 x magnification

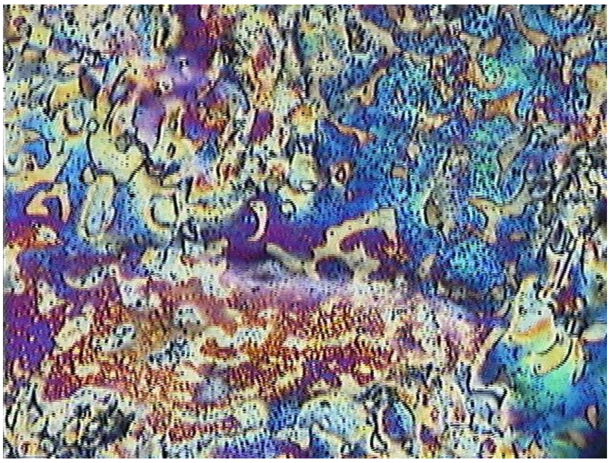
Polymer P4 show a small broad peak, from a phase transition different from melting.



Peak from 49.48 °C to 58.79 °C.

Onset 50.47°C. J/g = - 0.48 which indicate a nematic isotropic phase transition.




50 x magnification

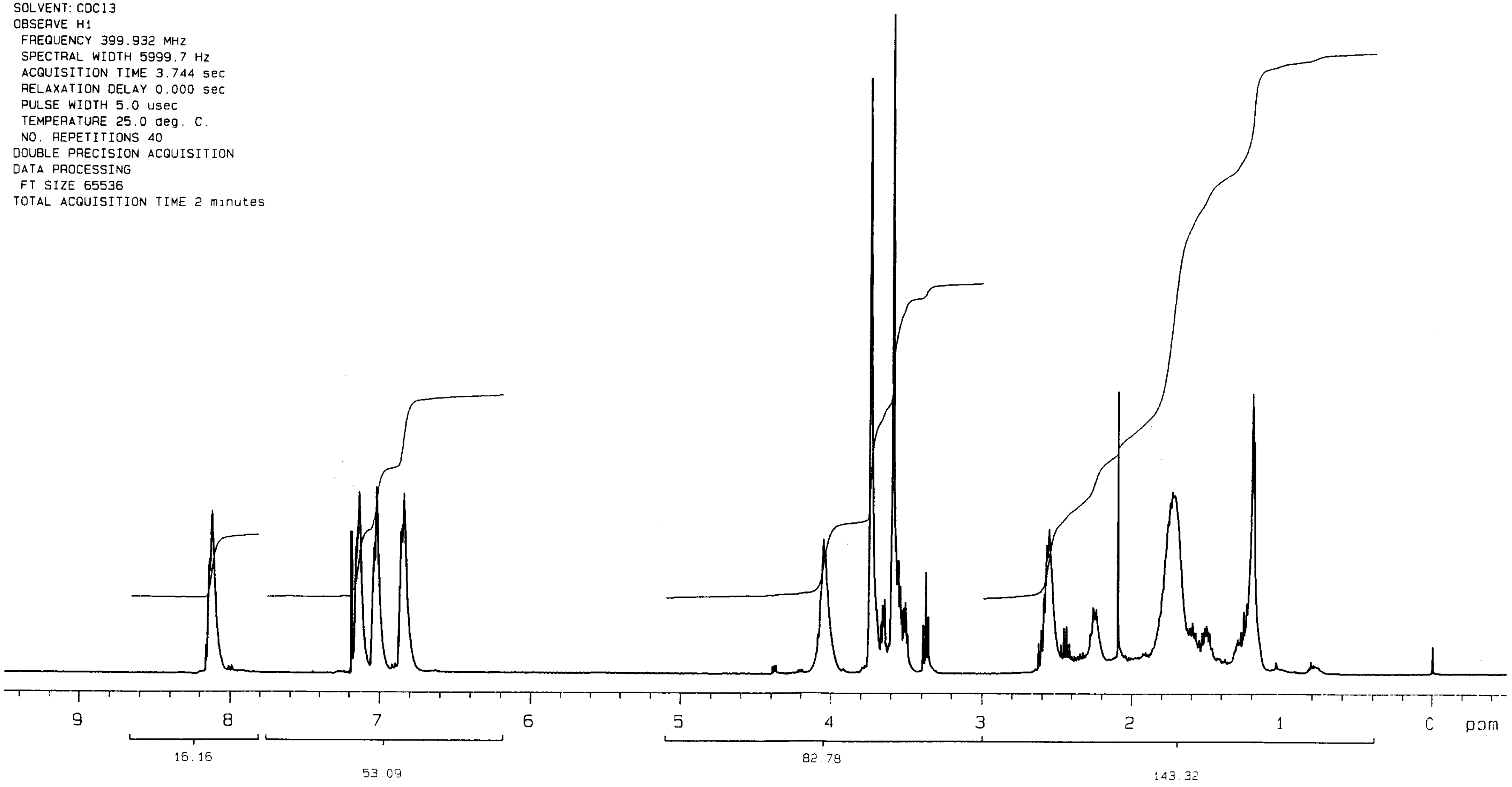
The cooling curve shows two signals 19 °C and 52 °C.
It indicate a phase shift from isotropic to nematic at 52 °C and

The two pictures on the right side is take after the sample has been brought to the isotropic phase and afterwards allowed to anneal at 2 hour at 50 °C. Both indicate nematic phase.

Phase transition has been reported at a higher temperature [36].

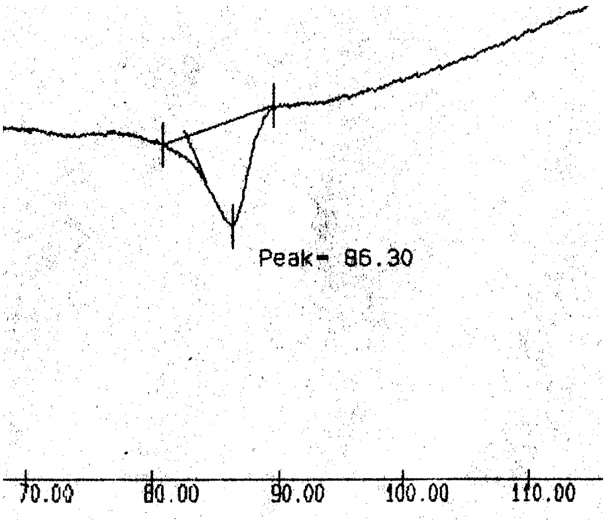
Polymer P4

ELP4
9440.fid
DATE: Apr 28 03
FILE: exp
SOLVENT: CDCl3
OBSERVE H1
FREQUENCY 399.932 MHz
SPECTRAL WIDTH 5999.7 Hz
ACQUISITION TIME 3.744 sec
RELAXATION DELAY 0.000 sec
PULSE WIDTH 5.0 usec
TEMPERATURE 25.0 deg. C.
NO. REPETITIONS 40
DOUBLE PRECISION ACQUISITION
DATA PROCESSING
FT SIZE 65536
TOTAL ACQUISITION TIME 2 minutes



ALBUM 4

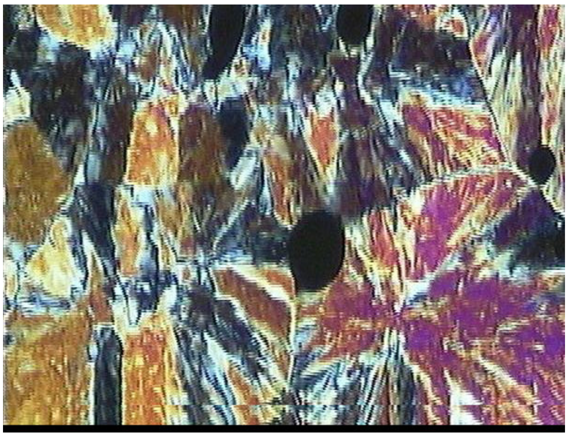
DSC of the polymer P5 is giving one clear signal at 86 °C and one very weak at 103 °C. The cooling curve does not give any signal but is a smooth curve.



The peak at 86.30 shows an enthalpy of -1.82J/g. It is 0.5kJ/mol monomer, indicating some transition to a smectic phase.

The polymer as well as the monomer is extremely sensitive to moisture in the air and the weak signal at 103°C was only seen when the polymer was taken directly from the exicator to the DCS apparatus. It shout also be notice that the acidic part of the molecule have a tendency to dimerism and braking the weak hydrogen bonds could give rise to the diffuse picture in enthalpy change.

The two pictures on the right side show in top the polymer P5 at 22 °C and down under are the P5 shown at 60 °C. They look crystalline. For higher temperature the picture that appears was quit dark.

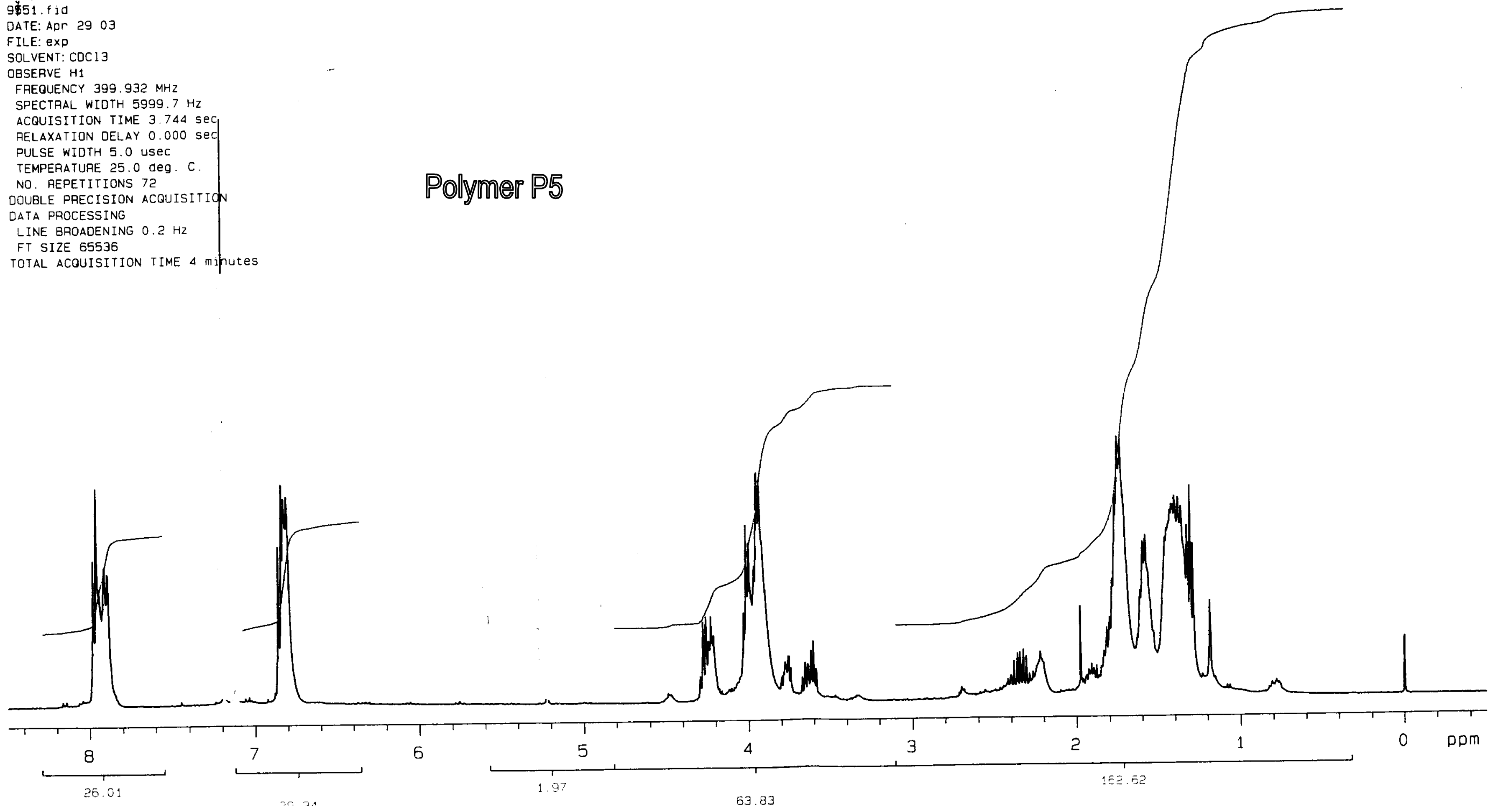


50 x magnification

50 x magnification

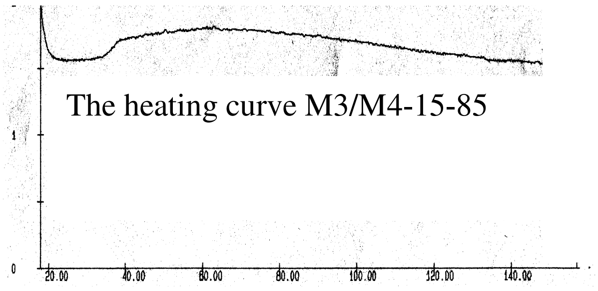
```
ELP5
9551.fid
DATE: Apr 29 03
FILE: exp
SOLVENT: CDCl3
OBSERVE H1
 FREQUENCY 399.932 MHz
 SPECTRAL WIDTH 5999.7 Hz
 ACQUISITION TIME 3.744 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 5.0 usec
 TEMPERATURE 25.0 deg. C.
 NO. REPETITIONS 72
DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 0.2 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 4 minutes
```

Polymer P5



ALBUM 5

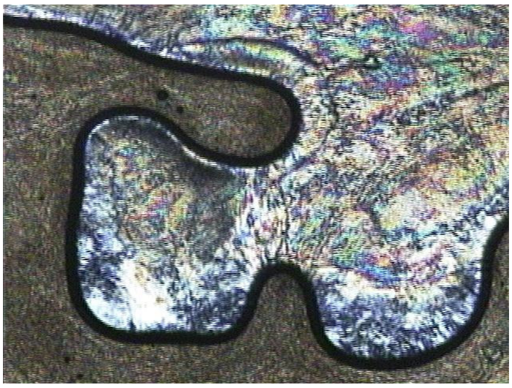
Copolymer M3/M4-15-85 is a mixture of 15mol% of the chiral M3 and 85mol% of M4 polymerised in THF it did not show a DSC curve with any significant signals. The cooling curve was smooth from 140^{0}C to 20^{0}C. The material behaves amorphous when it goes from solid to liquid phase.



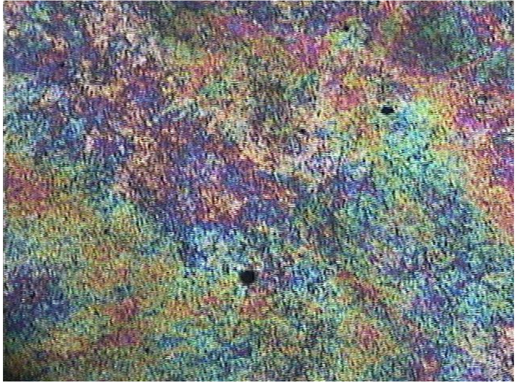
The heating curve M3/M4-15-85

The pictures on the right side from top show the polymer blend at 22^{0}C it could be a crystalline phase, the second picture is taken at 38^{0}C the polarised light is shifted but the picture do not indicate a specific phase.

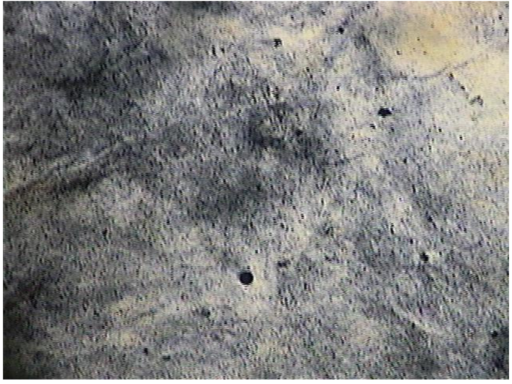
The last two pictures are taken at 46^{0}C and 58^{0}C and show the transition to isotropic phase. The pictures compared with the DSC curve indicate a glass transition T_g in the temperature interval from 20^{0}C to 40^{0}C.



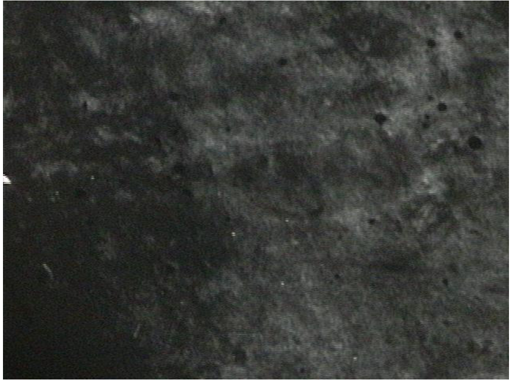
50 x magnification



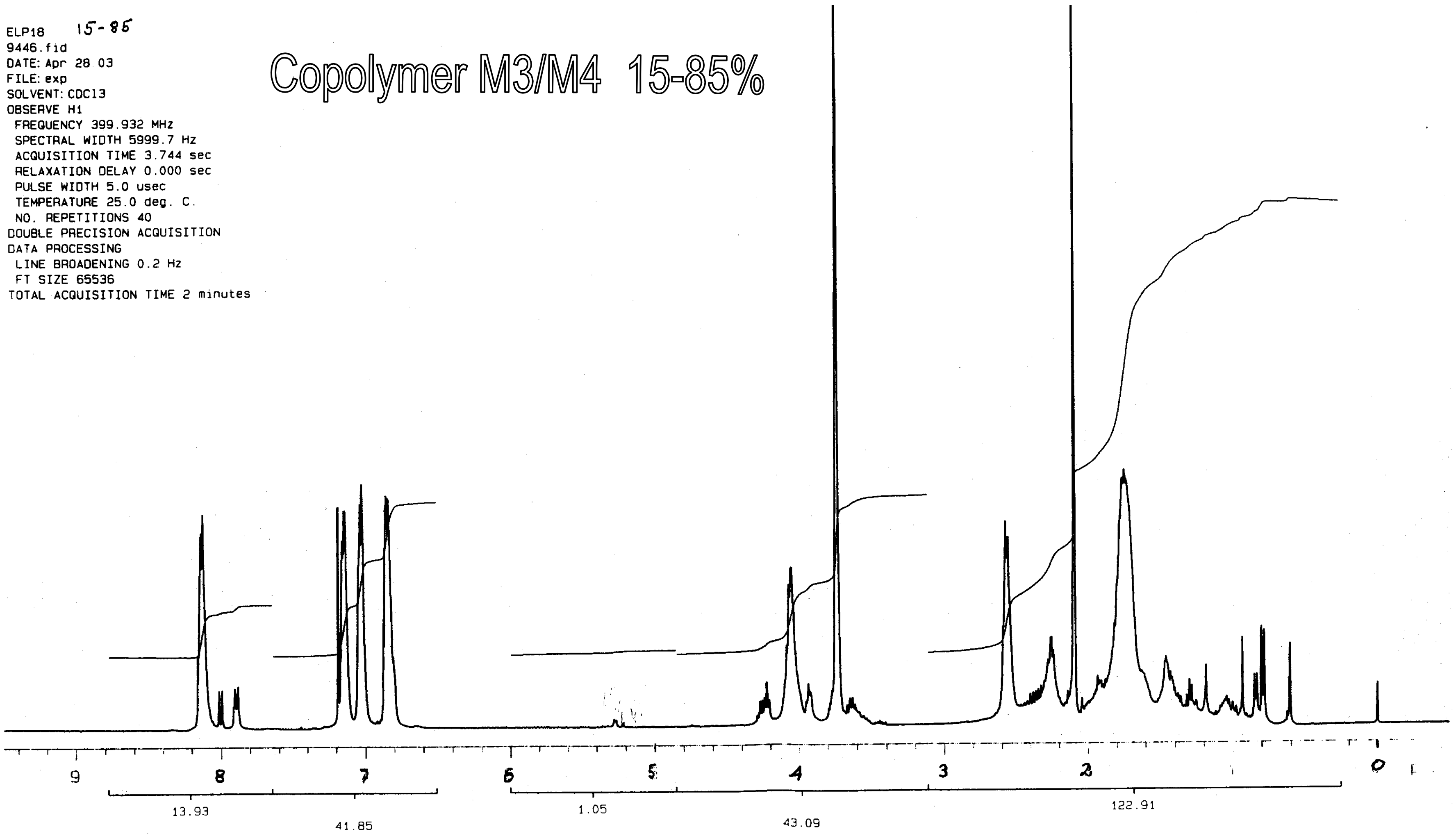
50 x magnification



50 x magnification



50 x magnification

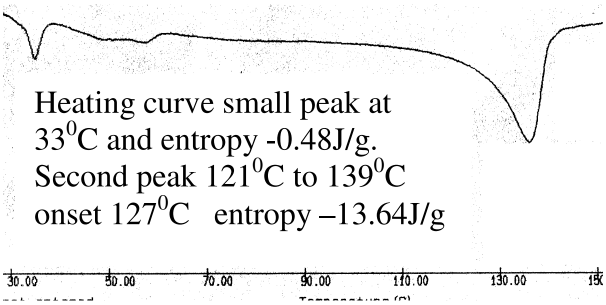


ELP18 15-85
9446.fid
DATE: Apr 28 03
FILE: exp
SOLVENT: CDCl3
OBSERVE H1
 FREQUENCY 399.932 MHz
 SPECTRAL WIDTH 5999.7 Hz
 ACQUISITION TIME 3.744 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 5.0 usec
 TEMPERATURE 25.0 deg. C.
 NO. REPETITIONS 40
DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 0.2 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 2 minutes

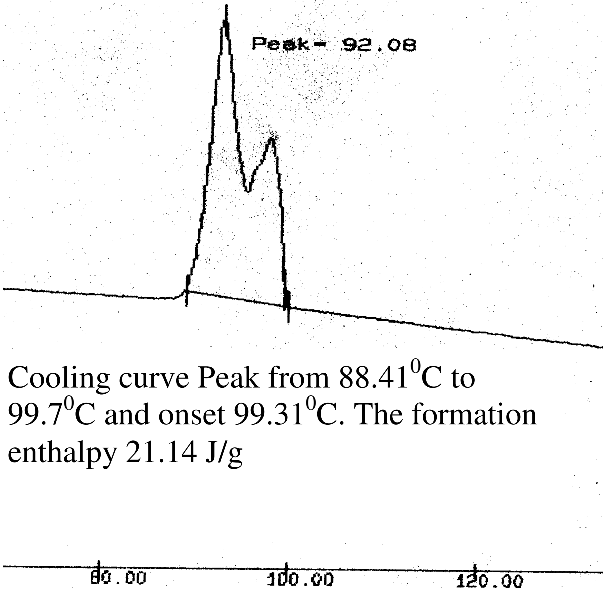
Copolymer M3/M4 15-85%

ALBUM 6

Copolymer M3/M4-30-70 is a mixture of 30mol% of the chiral M3 and 70mol% of M4 polymerised in THF it show a DSC curve with two significant signals in the heating curve and one signal in the cooling curve. Both curves had characteristics similar to what is seen in the curves for the P3.

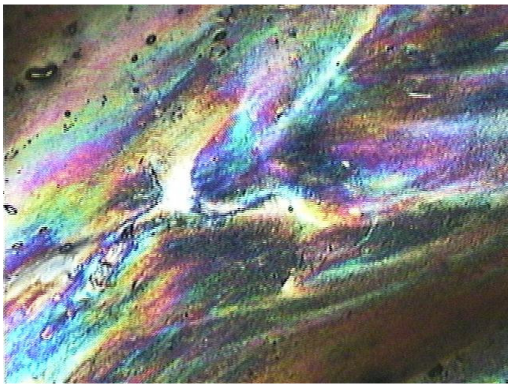


Heating curve small peak at 33^0C and entropy -0.48J/g.
Second peak 121^0C to 139^0C
onset 127^0C   entropy –13.64J/g



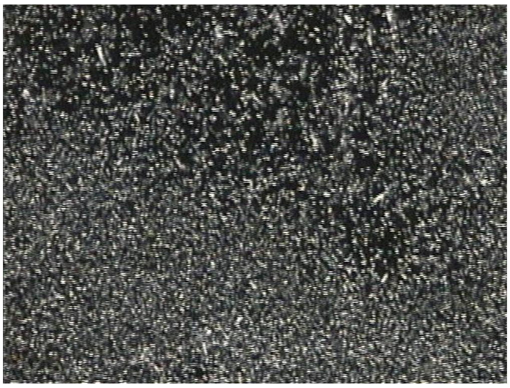
Cooling curve Peak from 88.41^0C to 99.7^0C and onset 99.31^0C. The formation enthalpy 21.14 J/g

The pictures were taken with different temperatures from above at 20^0C, 37^0C, 60^0C and 85^0C they do not give ideas to which phase there appears. From the heating curve we first have a small transition it could be into a smectic C* and from the shoulder at 55^0C we went into a nematic phase.

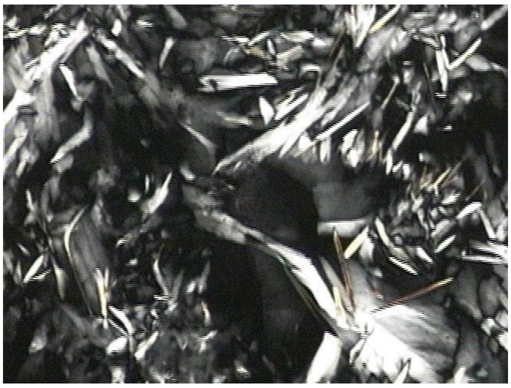


50 x magnification

50 x magnification



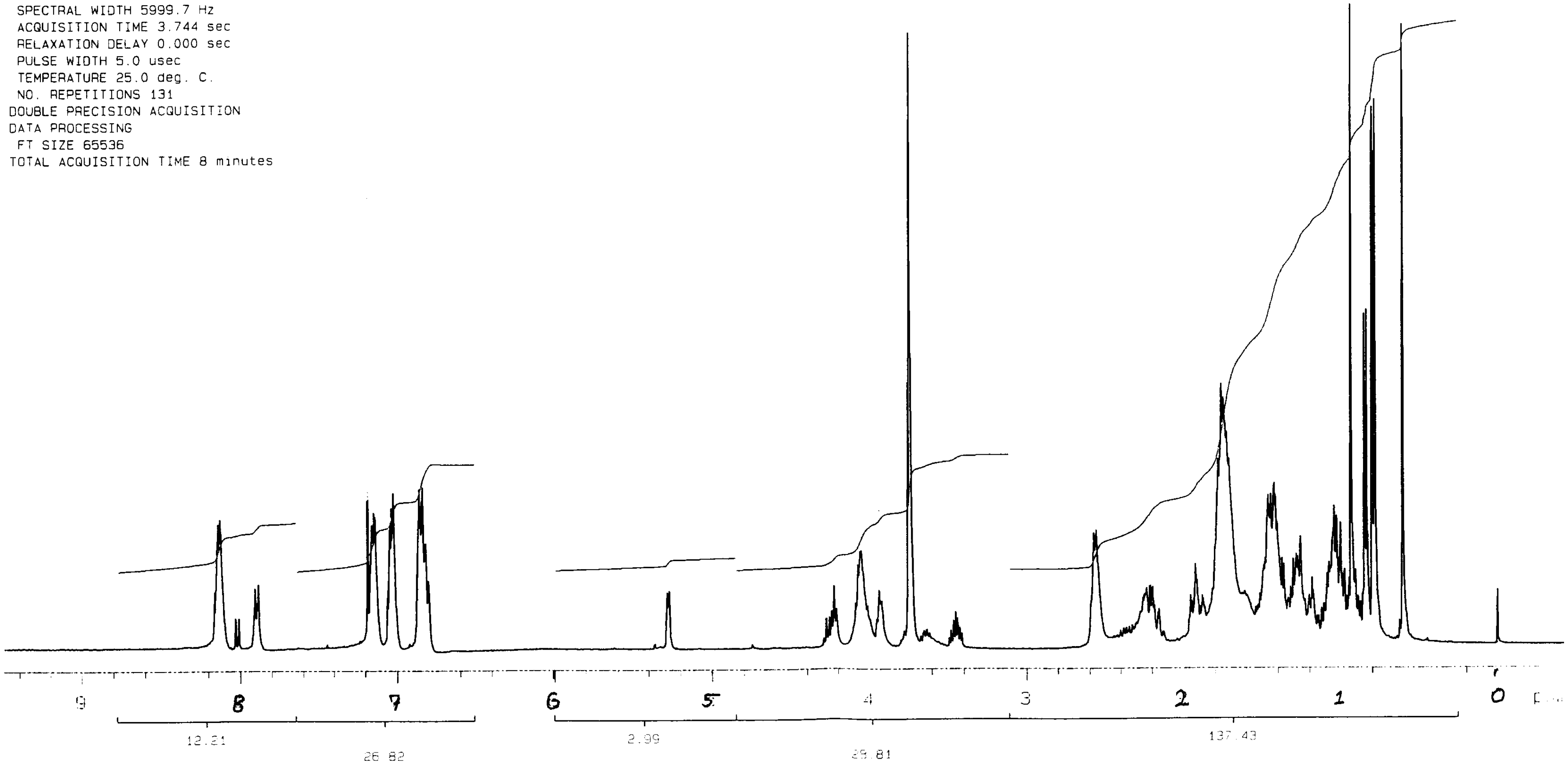
50 x magnification



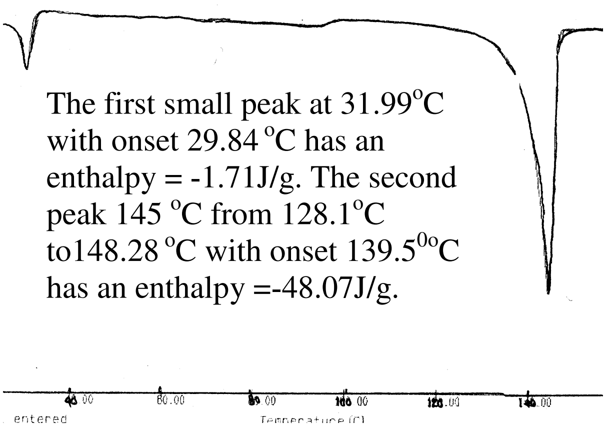
50 x magnification

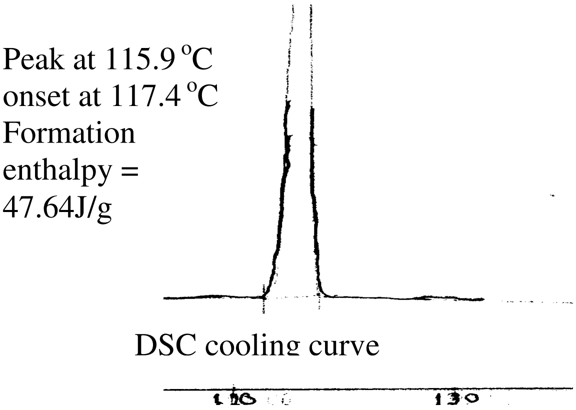
ELP37 30-70
9445.fid
DATE: Apr 28 03
FILE: exp
SOLVENT: CDCl3
OBSERVE H1
FREQUENCY 399.932 MHz
SPECTRAL WIDTH 5999.7 Hz
ACQUISITION TIME 3.744 sec
RELAXATION DELAY 0.000 sec
PULSE WIDTH 5.0 usec
TEMPERATURE 25.0 deg. C.
NO. REPETITIONS 131
DOUBLE PRECISION ACQUISITION
DATA PROCESSING
FT SIZE 65536
TOTAL ACQUISITION TIME 8 minutes

Copolymer M3/M4 30-70%



Copolymer M3/M5-80-20 is a mixture of 80mol% of the chiral M3 and 20mol% of acid M5 polymerised in THF it show a DSC curve with two significant signals in the heating curve and one sharp signal in the cooling curve. Both curves had characteristics similar to what is seen in the curves for the P3 but more sharp in the signal.


The first small peak at 31.99°C with onset 29.84 °C has an enthalpy = -1.71J/g. The second peak 145 °C from 128.1°C to148.28 °C with onset 139.5°°C has an enthalpy =-48.07J/g.

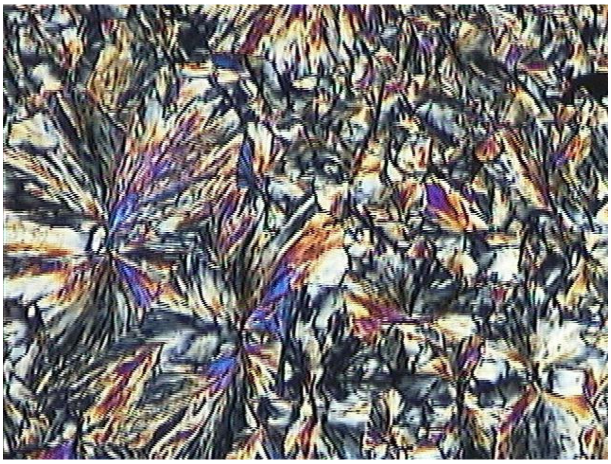

Peak at 115.9 °C
onset at 117.4 °C
Formation
enthalpy =
47.64J/g

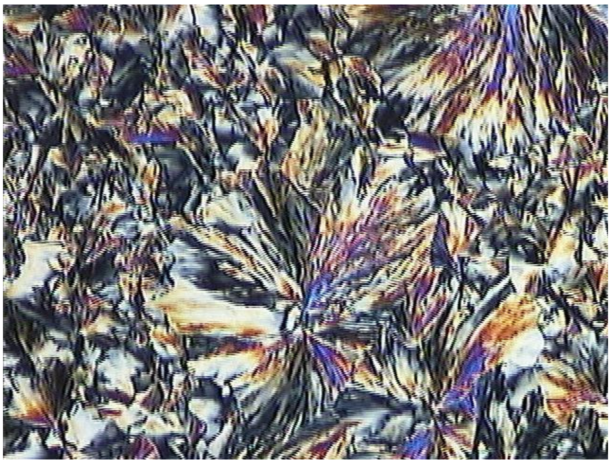
DSC cooling curve

The three pictures is from top exposed at 30 °C, 40 °C and 138°C Schlieren brushes and focal fan texture are seen.

The DSC curve and the picture with focal pattern and Schlieren texture indicate smectic C* phase.

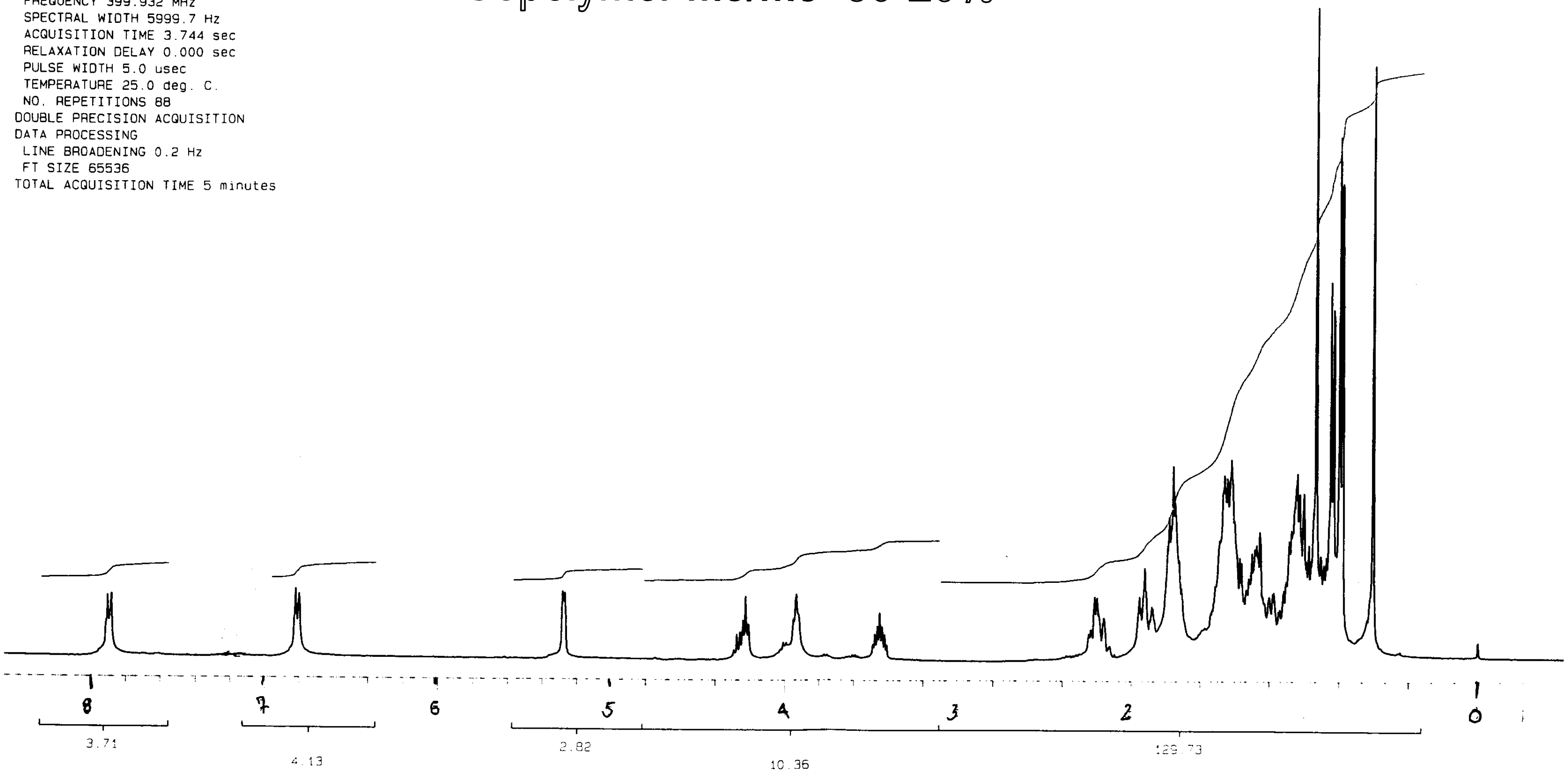

50 x magnification


50 x magnification


50 x magnification

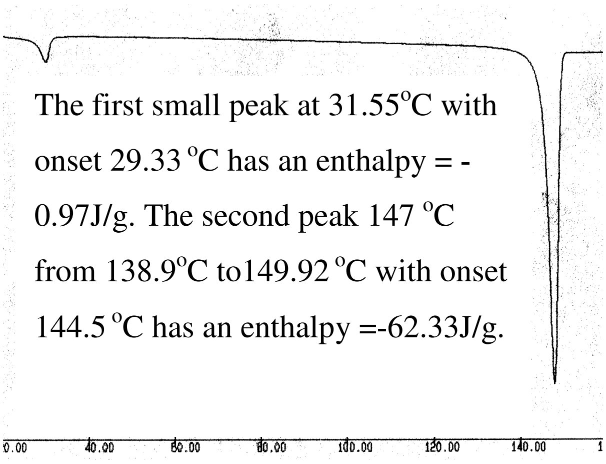
ELP82 80-20
9453.fid
DATE: Apr 29 03
FILE: exp
SOLVENT: CDCl3
OBSERVE H1
 FREQUENCY 399.932 MHz
 SPECTRAL WIDTH 5999.7 Hz
 ACQUISITION TIME 3.744 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 5.0 usec
 TEMPERATURE 25.0 deg. C.
 NO. REPETITIONS 88
DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 0.2 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 5 minutes

Copolymer M3/M5 80-20%

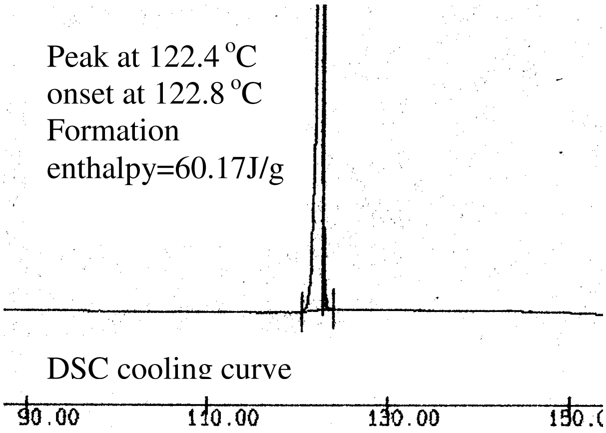


ALBUM 8

Copolymer M3/M5-90-10 is a mixture of 90mol% of the chiral M3 and 10mol% of acid M5 polymerised in THF it show a DSC curve with two significant signals in the heating curve and one sharp signal in the cooling curve. Both curves had characteristics similar to what is seen in the curves for the P3 but more sharp in the signal.



The first small peak at 31.55°C with onset 29.33 °C has an enthalpy = -0.97J/g. The second peak 147 °C from 138.9°C to149.92 °C with onset 144.5 °C has an enthalpy =-62.33J/g.



Peak at 122.4 °C
onset at 122.8 °C
Formation
enthalpy=60.17J/g

DSC cooling curve

The pictures were very similar in the interval from 40°C to 140 °C. On the right side from top the picture is taken at 90°C and 137°C. The picture in the bottom was taken after the polymer was in isotropic phase here it had annealed for 30 minutes at 122°C.
The DSC and the picture with focal pattern indicate smectic C*.

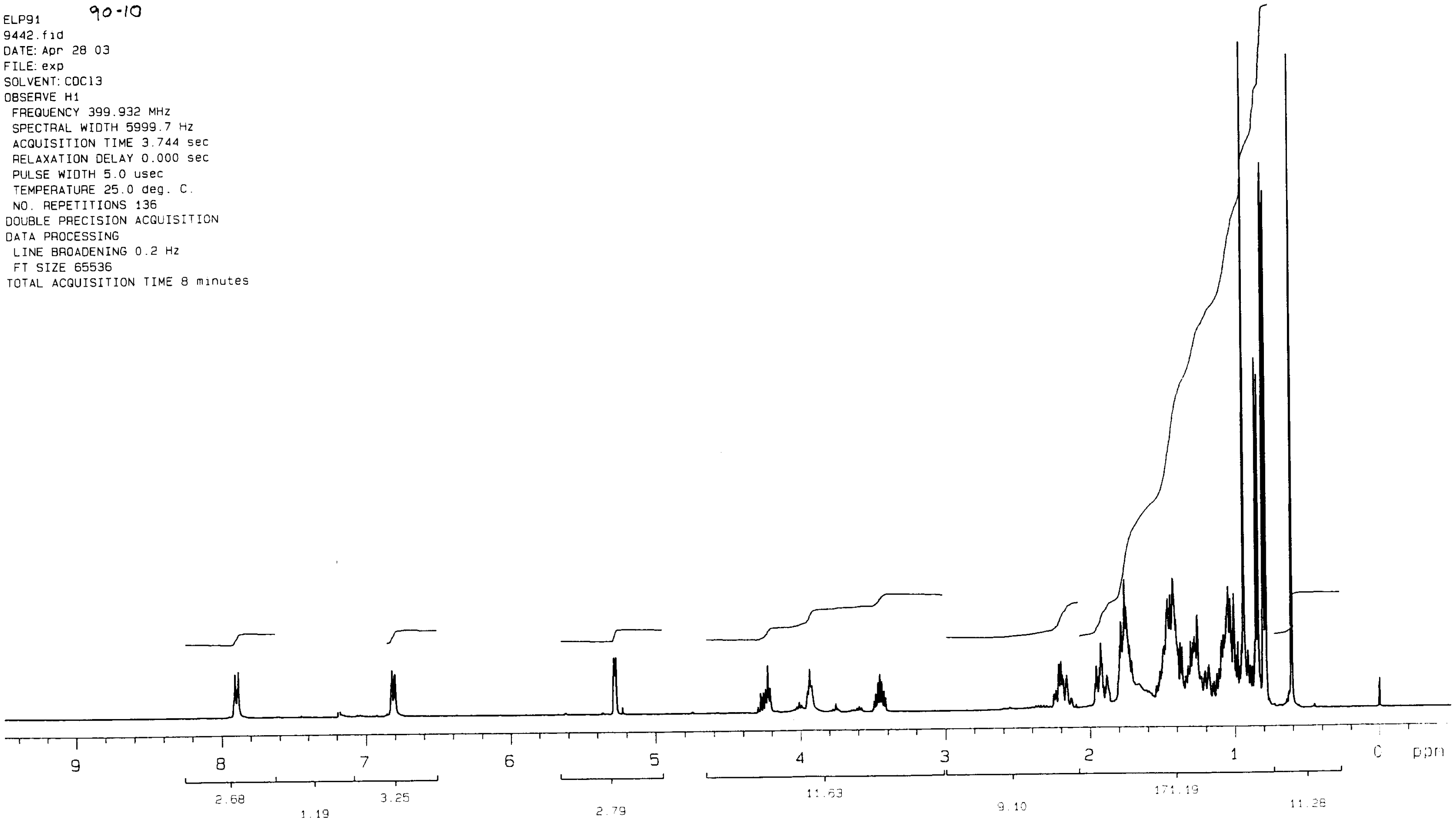
50 x magnification

50 x magnification

50 x magnification

Copolymer M3/M5 90-10%

```
ELP91        90-10
9442.fid
DATE: Apr 28 03
FILE: exp
SOLVENT: CDCl3
OBSERVE H1
 FREQUENCY 399.932 MHz
 SPECTRAL WIDTH 5999.7 Hz
 ACQUISITION TIME 3.744 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 5.0 usec
 TEMPERATURE 25.0 deg. C.
 NO. REPETITIONS 136
DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 0.2 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 8 minutes
```



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