EFFECT OF VARIOUS ADDITIVES ON THE UV STABILITY OF POLYETHYLENE AND POLYPROPYLENE FILMS

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Submitted in partial fulfilment of the requirements for the degree Master of Engineering in the Faculty of Engineering, Built Environment and Information Technology, University of Pretoria, Pretoria

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2001 July

SYNOPSIS

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The service life of typical plastics is strongly influenced by the ultraviolet (UV) degradation caused by solar radiation. Additives can be used to control the UV stability of polymer products.

This study was initiated to address two problems. In some applications, such as greenhouse films, high UV stability is desirable. In others, for example shopping bags, rapid UV degradation could be desirable to reduce the visual impact of plastic litter. However in such instances it is also of interest to retain the recyclability of the base polymer.

In this study the effect of selected compounds on the UV stability of polyethylene and polypropylene films was investigated. Both UV stabilisers

and UV prodegradants were considered. The compounds included various metal complexes as well as substituted hindered amines.

With respect to the hindered amines, derivatives with higher molecular mass were prepared using esterification reactions. The objectives were two fold: first it is necessary to reduce the inherent volatility of the basic hindered amines (e.g., 2,2,6,6-tetramethyl-4-piperidinol [TAA-OL]) to avoid long-term loss from the polymer matrix. The second objective was to improve the compatibility of the very polar hindered amines with the non-polar polyolefin matrix. Alkyl esters and alkyl polyesters were chosen because of their relatively low polarity and their ease of synthesis.

The metal compounds and complexes investigated included metal stearates, metal 2,4 pentanediones and also nickel dimethyl glyoxime. Masterbatches containing the above additives were prepared by standard plastic compounding techniques. Films were blown on laboratory scale equipment. Accelerated weathering was done using a QUV weatherometer fitted with A 340 lamps using a dry cycle.

Films containing the commercial UV stabiliser Chimasorb 944 were used as reference. The progress of degradation was followed using infrared spectroscopy. The carbonyl index was taken as the absorbance at 1710 cm^{-1} relative to the absorbance at 729 cm^{-1} and used as measure of the degree of oxidative degradation in polyethylene. In polypropylene the corresponding absorbances were at 1710 cm^{-1} and 972 cm^{-1}. Chimasorb 944 outperformed all the UV stabilisers synthesised in this study. However, good UV stability was obtained for films that contained the copolymer of triacetone amino alcohol with caprolactone (TOTA), 1-stearoyloxy–2,2,6,6–tetramethylpiperidine (STETA) and nickel dimethyl glyoxime (Ni-dmg). Interestingly copper stearate also imparted a measure of UV stability to polyethylene film but not to polypropylene.

Most metal complexes were found to accelerate UV degradation. Ferric stearate and titanyl 2,4-pentanedione were found to be the most efficient prodegradants. Poly (1,2-dihydro-2,2,4-trimethyl quinoline) (OTMQ) is a hindered amine with a structure similar to that of 2,2,6,6-tetramethyl-4-piperidinol (TAA-OL). It is used as antioxidant in polyethylene and also in rubber applications. This study confirmed that OTMQ, despite its antioxidant nature, acts as a UV prodegradant in both polyethylene and polypropylene films. Derivatives of this compound could therefore have utility in applications where recyclability is important but where UV degradability is also of interest, e.g. plastic shopping bags.

Keywords: photodegradation, UV stability, polyethylene films, polypropylene films, additives, HALS, polyesters, transesterification, QUV weathering, FT-IR.

SINOPSIS

EFFEK VAN VERSKEIE BYMIDDELS OP DIE UV STABILITEIT VAN POLIETILEEN EN POLIPROPILEEN FILMS

deur

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Die diensleeftyd van tipiese plastieke word sterk deur ultraviolet (UV) degradasie, wat deur die son veroorsaak word, beïnvloed. Bymiddels kan gebruik word, om die UV stabiliteit van polimeer produkte te beheer.

Die studie was begin met die doel om twee probleme aan te spreek. In sekere toepassings soos in kweekhuisfilms, word hoë UV stabiliteit benodig. In ander gebruike, soos byvoorbeeld in inkopiesakke, kan vinnige UV degradasie wenslik wees om die visuele impak van afval

plastieksakke te verlaag. Dit is egter wenslik om die herwinbaarheid van die basis polimeer te behou.

Die effek van geselekteerde verbindings op die UV stabiliteit van poliëtileen en polipropileen films is tydens die studie ondersoek. Beide UV stabiliseerders en UV prodegradante is beskou. Die verbindings het verskeie metaalkomplekse, sowel as gesubstitueerde verhinderde amiene ingesluit.

In die geval van die verhinderde amiene is hoër molekulêre massa derivate deur middel van verestering berei. Die doel hiervan was tweevoudig. Dit is eerstens nodig om die inherente vlugtigheid van die basiese verhinderde amien (byvoorbeeld 2,2,6,6-tetrametiel-4-piperidinol [TAA-OL]) te verlaag, om die lang termyn verliese uit die polimeer matriks te voorkom. Tweedens moes die versoenbaarheid van die hoogs polêre verhinderde amien met die nie-polêre poliölefien matriks verhoog word. Alkiel esters en alkiel poliësters is weens hulle relatiewe lae polariteit en maklike sintese verkies.

Die metaalverbindings en metal komplekse wat ondersoek was het metaal stearate, metaal 2,4 pentaandioon en nikkel dimetielglioksiem ingesluit. Standaard plastiekvermenging en film-blaas prosedures met laboratoriumskaaltoerusting is gebruik om die films – met lae hoeveelhede van die bogenoemde bymiddels – voor te berei. 'n QUV verweringsmeter, toegerus met A 340 lampe, is gebruik om die versnelde verweringstoetse uit te voer, deur van die droë siklus gebruik te maak.

Films wat die kommersiële Chimasorb 944 UV stabiliseerder bevat, is as verwysing gebruik. Die proses van degradasie is deur middel van infrarooi (IR) spektroskopie gevolg. 'n Karbonielindeks is gedefinieer as die absorbansie by 1710 cm^{-1} relatief tot die absorbansie by 729 cm^{-1}. Dit was gebruik as maatstaf vir die oksiedatiewe degradasie van poliëtileen. In die geval van polipropileen was die ooreenstemmende absorbansies vir die

karbonielindeks 1710 cm^{-1} en 972 cm^{-1}. Chimasorb 944 was meer effektief as enige van die gesintetiseerde UV stabiliseerders. Goeie UV stabiliteit is nogtans verkry vir films wat bymiddels van kopolimere van triasetoon amino alkohol met kaprolaktoon (TOTA), 1-stearoïeloksie–2,2,6,6–tetrametielpiperidien (STETA) en nikkel dimetielglioksiem (Ni-dmg) bevat het. Interessant genoeg het koper stearaat ook 'n mate van UV stabiliteit aan poliëtileenfilm verleen, maar nie aan polipropileenfilm nie.

Daar is gevind dat meeste van die metaal kolmlekse UV degradasie versnel. Yster (III) stearaat en titaniel 2,4-pentaandioon is as die mees effektiewe prodegradante geïdentifiseer. Poli(1,2-dihidro-2,2,4-trimetielkinolin) (OTMQ) is 'n verhinderde amien met 'n struktuur soortgelyk aan die van 2,2,6,6-tetrametiel-4-piperidinol (TAA-OL). Dit word kommersieel as antioksidant in poliëtileen gebruik asook in rubbertoepassings. In die studie is bevestig dat OTMQ as 'n UV prodegradant optree in beide poliëtileen- en polipropileenfilms, ten spyte van sy antioksidasie eienskappe. Dit is dus moontlik dat derivate van die verbinding gebruik mag vind in toepassings waar herwinbaarheid, maar ook UV degradasie van belang is, soos byvoorbeeld plastiek inkopiesakke.

Sleutelwoorde: fotodegradasie, UV stabiliteit, poliëtileen films, Polipropileen films, bymiddels, HALS, poliësters, transverestering, QUV verwering, FT-IR.

ACKNOWLEDGEMENTS

I wish to thank gratefully:

- Prof. Dr. WW FOCKE, for identifying the project, valuable advice, guidance and supervision.

- The THRIP programme of the Department of Trade and Industry and the National Research Foundation as well as Xyris Technology for funding the project.

- BETTY EYENGA, for your unconditional support during the project.

- All friends, for your support and encouragement during the project.

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CHAPTER 1 - INTRODUCTION

Polymers play an essential role in everyday life. They have excellent properties that allow them to be used in many applications, such as electrical insulation, tyres, mouldings, films, fibres, and packaging for food. Each year, the demand for polymer increases. It is said that the market share of organic polymeric materials may exceed 50% of the total materials consumed in the 21st century [1].

Polyethylene (PE) and polypropylene (PP) are synthetic polymers with large annual sales volumes. The typical life cycle of PE and PP as synthetic polymers is [2]: synthesis, compounding, conversion and/or processing, usage, disposal or recovery and re-usage. Because of their relatively low cost, polyolefins (PE and PP) are widely used. However they are difficult to stabilise. Improvements in the exterior durability of polyethylene and polypropylene are desirable in external applications, e.g. green house film [3, 4, 5, 6]. Most polymers are susceptible to ultraviolet radiation in the 290-400 nm region. The absorption of this energy causes the chemical bonds in macromolecular chains to break. This in turn results in embrittlement, surface crazing, chalking, discoloration and loss of impact and tensile strength. The number and nature of light-absorbing groups in a polymeric system are important factors in photodegradation; in polymers that have no chromophores, impurities induce degradation [1-18].

Plastic shopping bags have become an integral part of the South African life-style. Most retailers supply them free of charge to their customers. Unfortunately, progress in film blowing and resin technology have made it possible to produce bags that are so thin that post-consumer recycling became impractical. Furthermore, the public is not yet sensitised with respect to environmental issues. Littering is therefore a major problem. The possible solution can be fast degradation under UV but good heat stability so that they can still be recycled.

Photodegradation can aid rapid disintegration of polymers into a powdery residue with a much-reduced visual impact [7, 11]. It is a strategy used in Israel for controlled mineralisation of mulch films used in agricultural applications. The problem with this approach is that it often precludes subsequent recycling. The photodegradants, once activated, also cause degradation during reprocessing.

On the other hand, outdoor use of polymeric materials often is practical only when 0.1-1% of UV stabilisers are added in order to postpone the inevitable effect of light (e.g. carbon black)[3]. These additives are believed to impart stability by absorbing UV radiation, by scavenging free radicals, by quenching excited states and free radical species, or by combinations of these processes. Over years, there have been many publications concerning the efficiency of particular UV stabilisers and prodegradants in term of their compatibility, solubility, volatility and diffusion in the polymer, UV absorption and UV screening [18 - 23].

The aim of this work is to study the efficiency of polyester-based polymeric UV stabilisers and metal-based prodegradants for polyethylene and polypropylene films under UV radiation. Both UV stabilisers and UV prodegradants were considered. The compounds investigated included various metal complexes as well as substituted hindered amines with available alcohol functionality. With respect to the hindered amines, derivatives with higher molecular mass were prepared using esterification and transesterification reactions to increase the effective molecular mass, to reduce the inherent volatility of the basic hindered amines and to improve the compatibility of very polar hindered amines with the non polar polyolefin matrix. Alkyl esters and alkyl polyesters were chosen because of their relatively low polarity and their ease of synthesis.

CHAPTER 2 - BACKGROUND INFORMATION

2.1 POLYOLEFINS STRUCTURE

2.1.1 POLYOLEFINS

Polymers are long chain macromolecules. Their properties depend on maintaining effective chain lengths. Mechanical properties are a function of morphology. Polyolefins are a subgroup of polymers that are obtained by polymerising α-olefins. They are commodity chemicals produced world wide on a large scale (> 40 × 10^6 ton/year)[24]. They are cheap to produce, non-toxic and have a wide range of properties. End uses include film packaging, containers, textile fabrics, woven bags, sandwich bags, pipes, car bumpers, etc. Their use in our everyday lives is predicted to grow. Polyolefins are replacing other polymers/plastics in current use. It was predicted that more than 70 % of all thermoplastics will be polyolefin based by the new millennium [24]. Plastics are usually coloured or printed to make them more appealing (e.g. shopping bags). Environmental issues relating to polymer disposal can be minimised by recycling and other procedures. This will reduce a serious negative feature related to their presence in society as "visual" pollution.

The polyolefins enterprise is directly related to the development of appropriate additives for conversion of the starting materials (the polyolefin) into the required plastic. One of the main reasons for using polyolefins as raw materials is their chemical inertness and resistance to a large number of packaged products or contact media [3, 20, 24].

Physical changes in a polyolefin formulation due to its environment have been recognised as a prime reason for polymer failure [2, 13,15]. Most polyolefins are semi-crystalline materials. Their behaviour can be traced to this multiphase structure. Polypropylene and polyethylene are the most important polyolefins because they are used more frequently than

others. Polyolefin types include polypropylene (PP) that can be made in isotactic, syndiotactic or atactic form, low-density polyethylene (LDPE) (a randomly branched structure), high-density polyethylene (HDPE) (primarily linear chains with few branches and high crystallinity), crosslinked low-density polyethylene (CLDPE), and linear low-density polyethylene (LLDPE) (longer chains with small branches). The variations in morphology due to these chain structure differences contribute to the wide range of physical properties in polyolefins and are a key to their extensive use [13,25].

Usually they have glass transition temperatures (Tg's) well below room temperature and, as a result, the amorphous regions are rubbery in nature. However the crystalline domains, which tend to be in the form of small platelets (lamellae), are nearly impermeable to small molecules due to the dense packing of the polymer chains. This mixture of rigid crystallites in a rubbery matrix gives the polyolefins their toughness [25].

Polyolefins have long passed the stage where they are regarded as a low-cost material that is useful for short-life applications only. Polyolefins (PP, HDPE, LDPE, CLDPE, and LLDPE) show a dramatic loss in strength when exposed to UV-radiation as experienced in outdoor weathering or exposure to sunlight. The degradation and stabilisation mechanisms are now fairly well understood [12]. By developing efficient stabilisers and sophisticated formulations, it has become possible to control their major disadvantages, namely degradation sensitivity during processing and poor long-term stability [3, 12].

2.1.2 POLYOLEFINS IN THE ENVIRONMENT

The polyolefins industry is permanently confronted with problems of quality and lifetime of its products. Initially, plastics came as a replacement for "traditional" materials; nowadays, they represent new materials with new properties. In order to meet the increasing

requirements, investigations of new synthesis and production technologies are needed [24].

UV degradation usually causes polymer embrittlement. They lose tensile properties and some polymers even become discoloured [7, 9, 15, 22, 26]. Because the useful lifetime of polymers depends on their retention of mechanical properties, it is important to counter the damage caused by UV light [12,17,26].

For this purpose, development is broadly supported by the use of effective additives. Stabilisers can frequently protect polyolefins, depending on what sorts of degradation reactions need to be interrupted. Therefore, the development of one of the most effective light stabiliser structures – Hindered Amine Light Stabilisers (HALS) – is directly linked to the expansion of polyolefin applications. In fact, in many applications, the stabilisation efficiency of this additive has still not been fully elucidated [16 - 20].

Polyolefins are displacing more expensive plastics from several applications. To compete, polyolefins require a significant improvement of performance such as durability, thermo-oxidative and light stability, colour, and gloss maintenance and impact resistance [24].

2.2 DEGRADATION OF POLYMERS

2.2.1 OVERVIEW OF POLYMER DEGRADATION

Degradation of polymers is a process that occurs with rupture of the main chain backbone or the side group bonds. The theory of polymer degradation is important in understanding polymer stability, durability, characterisation, synthesis, and recycling [12,13].

Polymeric materials have a high molecular weight which gives rise to their properties. Any foreign agent that gives rise to a change in this parameter can alter the properties significantly [12]. The types of degradation processes vary depending upon the environmental conditions in which the polymer is used, the manufacturing history as well as structure of the polymer. According to the literature, the types of degradation processes that polymers may undergo, are [8-10]:

I- **Chemical degradation**: this occurs in polymers that are attacked by chemical agents, corrosive chemicals or gases. The basic structural functionalities in the polymers cause chain scission and oxidation.

II- **Mechano-degradation**: this type of degradation happens to polymers by shearing forces, ultrasonic vibrations, repeated and rapid freezing of the solvent of a polymer solution, high-speed stirring. Chain scission may also occur here.

III- **Thermal degradation**: this occurs during processing or during use at elevated temperatures (heat) and may involve either oxidative or non-oxidative degradation.

IV- **Biodegradation**: this occurs to the polymers, which contain functional groups that are attacked by micro-organisms (enzymes, bacteria, and fungi).

V- **Radiative degradation**: in this case degradation is inititated by high energy radiation (e.g. gamma rays).

VI- **Photodegradation**: this happens to the polymers that are exposed to light. On exposure to sunlight, either the polymer itself or impurities in the polymer will absorb the radiation and induce reactions resulting in a loss of properties.

VII- **Hydrolytic degradation**: this occurs in polymers containing functional groups that are sensitive to the effects of water.

The thermal degradation and photodegradation degradation are the most important among these different types of degradation in the use of polymers [12].

The degradation can be caused by mechanical stress or thermal treatment oxidation, γ-radiation, oxidation, or by the addition of peroxides. Traces of impurities and contaminants and various structural irregularities are often responsible for causing or accentuating the degradation of polymer chains [8]. Therefore, polymers are liable to degrade when they are subjected to natural weathering conditions such as sunlight, moisture and rain [24, 27].

Depending on the chemical structure and the degradation condition, polymers have been observed to degrade by chain scission occurring randomly along the chain, or by an unzipping depolymerisation, or by a combination of these.

2.2.2 GENERAL TYPES OF POLYMER DEGRADATION PROCESSES

The degradation and/or oxidation reactions depend upon the structure of the polymer, the presence of oxygen and temperature.

There are two general types of polymer degradation processes, corresponding roughly to the two types of polymerisation, step-reaction and chain-reaction [8, 9]:

I- Random degradation is analogous to stepwise polymerisation. Here chain rupture or scission occurs at random points along the chain, leaving fragments, which are usually large, compared to monomer unit.

II- Chain depolymerisation involves the successive release of monomer units from a chain end in a depropagation or unzipping reaction, which is essentially the reverse of chain polymerisation.

These two types may occur separately or in combination, may be initiated thermally or by ultraviolet, oxygen, ozone, or other foreign agent, and may occur entirely at random or preferentially at chain ends or at other weak links in the chain.

It is possible to differentiate between the two processes in some cases by following the molecular weight of the residue as a function of the extent of reaction. When polymers degrade and oxidise one of the most important changes in structure is in molecular weight [12]. Molecular weight drops rapidly as random degradation proceeds but may remain constant in chain depolymerisation, as whole molecules are reduced to monomer, which escapes from the residual sample as a gas. Examination of the degradation products also differentiates between the two processes: the ultimate product of random degradation is likely to be a polydisperse mixture of fragments of low molecular weight, whereas chain depolymerisation yields large quantities of monomer [8, 9].

Since the degradation and oxidation of polymers causes chain scission, one of the most important factors controlling polymer stability is the stability of their primary valence bonds. Thus, the stronger the chemical bond, the more stable will be the polymer. In fact, this is generally true where the C-F bond is stronger than either –C-H or -C-C- bonds. In this regard PTFE $-(CF_2-CF_2)-$ is more stable than polyethylene $-(CH_2-CH_2)-$ and this is a well-known commercial fact [12].

2.2.3 DEGRADATION REACTIONS

The three general types of degradation reactions at high temperatures are [8, 12]:

1- Depolymerisation reactions where the polymer chain is

scissioned such that the products are similar in structure to that of the polymer but of a lower molecular weight.

2- Elimination reactions where degradation usually results in the formation of lower molecular weight fragments or molecules that are sometimes unrelated to that of the original polymer.

3- Substituent reactions where the main chain substituents undergo reactions such that the chemical nature of the repeat unit is changed although the chemical structure remains intact.

Most degradation reactions at high temperature are of free radical type. Scheme 2.1 shows the general types of free radical degradation reactions, where P_i represents unreactive polymer molecule, $P_i^{\bullet}$ represents a macro-radicals and the subscripts denote the number of monomer units in the polymer chain. Thus random initiation involves splitting of the polymer chain into unequal lengths to give two macro-radicals. Terminal initiation results in the loss of a single monomer radical fragment from the end of the polymer chain. Transfer in this case shows that one macro-radical can transfer its activity to another chain unit. Scission may occur randomly to give two more active radicals and termination may be due to the formation of two 'dead' polymer chains or the recombination of two macro-radicals giving a higher molecular weight fragment [9, 12].

Scheme 2.1

Random Initiation

$$P_x^{\bullet} \rightarrow P_j^{\bullet} + P_{x-j}^{\bullet}$$

Terminal Initiation

$$P_x \rightarrow P_{x-i}^{\bullet} + P^{\bullet}$$

Transfer

$$P_i^{\bullet} + P_x \rightarrow P_i + P_x^{\bullet}$$

Scission

$$P_x \rightarrow P_j^{\bullet} + P_{x-j}^{\bullet}$$

Termination

$$P_i^{\bullet} + P_j^{\bullet} \rightarrow P_i + P_j \text{ or } P_{i+j}$$

2.2.4 THERMAL OXIDATIVE REACTIONS OF POLYMERS

Molecular oxygen exists in its ground state as a triplet $^3O_2$. Oxygen has the ability to diffuse through the amorphous regions of the polyolefins. The crystalline regions are not accessible as they are too closely packed. In the solid state amorphous polymers are more susceptible to oxidation than crystalline polymers. This is illustrated for amorphous, semi-crystalline and single crystals of polypropylene in Figure 2.1.

The rate of diffusion of oxygen will be faster in the amorphous material which will oxidise faster followed by the moulded film and then the single crystals (act as a barrier to diffusion). In the presence of oxygen most polymers will undergo rapid chain scission reactions below their melting points [12]. In their study of the effect of structure on oxidation of polyolefins, Hanssen et al. observed that the greater the number of branches, the more easily the polymer is attacked by the oxygen. Consistent with this is the observation that the order of ease of oxidation is: PP > LDPE > HDPE [28]. However, bulky side groups that reduce the access of oxygen to the chain backbone modify this situation, implying that both the existence of and the accessibility to tertiary carbons are important in the oxidation reaction.

A typical mechanistic scheme for the oxidation of polymer systems is as follows:

- Molecular oxygen has a biradical nature, and reacts easily with other organic or polymer – free radicals ($P^\bullet$) giving polymer peroxy radicals ($POO^\bullet$):

$$P^\bullet + O_2 \rightarrow POO^\bullet \quad (1)$$

- The peroxy radical rapidly abstracts hydrogen from another polymer molecule (PH) to form a polymer hydroxyperoxide (POOH):

$$POO^{\bullet} + PH \rightarrow POOH + P^{\bullet} \quad (2)$$

- Alternatively two peroxy radicals may react with each other to produce polymer oxyradicals ($PO^{\bullet}$):

$$2\ POO^{\bullet} \rightarrow 2\ PO^{\bullet} + O_2 \quad (3)$$

- The polymer oxyradical can also be formed from the decomposition of polymer hydroperoxides (POOH):

$$POOH \rightarrow PO^{\bullet} + {}^{\bullet}OH \quad (4)$$

- Termination occurs by the following reactions:

$$\left.\begin{array}{l} POO^{\bullet} + POO^{\bullet} \\ PO^{\bullet} + POO^{\bullet} \\ PO^{\bullet} + PO^{\bullet} \end{array}\right\} \longrightarrow \text{Inactive products} \quad (5)$$

The inactive products include for example ether, ester and peroxide i.e

P — O — P, P — O — $\overset{\overset{O}{\|}}{C}$ — P, P — O — O — P. They contain either bridges or peroxide bridges depending on the reactions, which participate in the termination reaction.

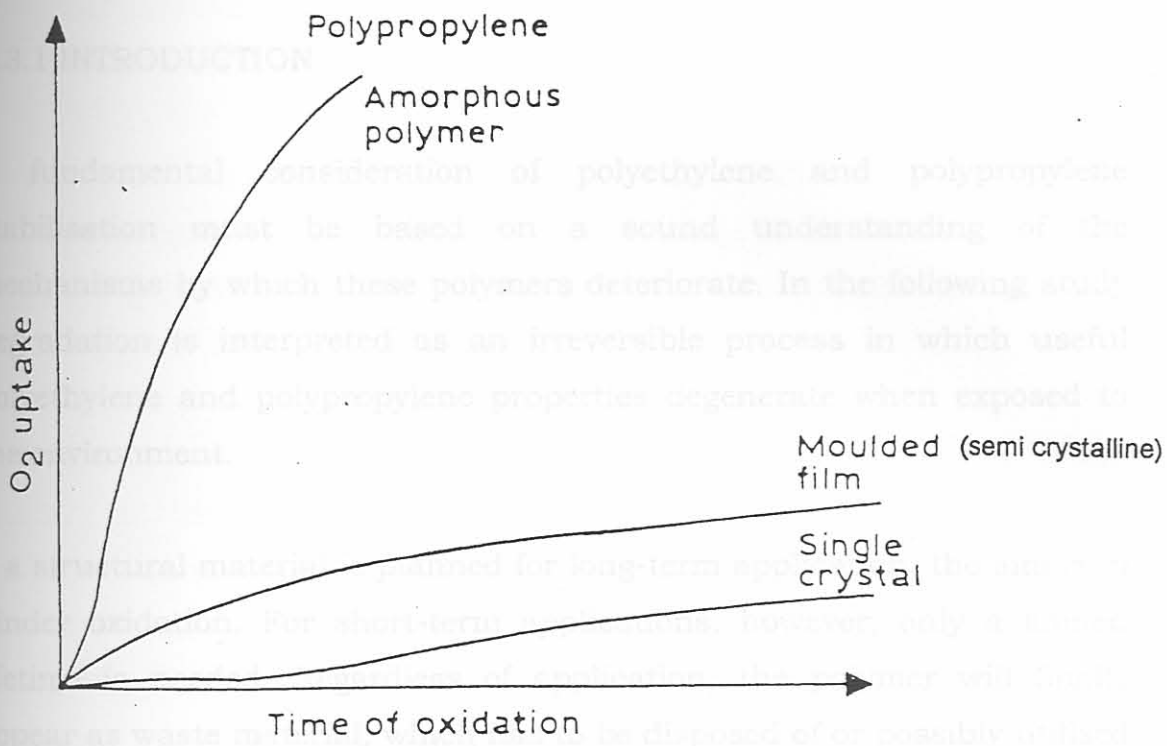


Figure 2.1. Thermal degradation rate of amorphous moulded and single crystals of polypropylene at 130°C measured by oxygen uptake (After Allen NS and Edge M, 1992).

Metal ions are invariably present in many polymer systems, especially the polyolefins, and they can accelerate (or i.e. catalyse) the decomposition of hydroperoxides as shown in scheme 2.2 producing alkoxy and peroxyradicals [12].

Scheme 2.2

$$POOH + M^{+} \rightarrow PO^{\bullet} + OH^{-} + M^{2+}$$

$$POOH + M^{2+} \rightarrow POO^{\bullet} + H^{+} + M^{+}$$

$$2\ POOH \rightarrow PO^{\bullet} + POO^{\bullet} + H_2O$$

2.3 DETAILED PHOTO-OXIDATION AND PHOTODEGRADATION MECHANISM FOR POLYETHYLENE AND POLYPROPYLENE

2.3.1 INTRODUCTION

A fundamental consideration of polyethylene and polypropylene stabilisation must be based on a sound understanding of the mechanisms by which these polymers deteriorate. In the following study degradation is interpreted as an irreversible process in which useful polyethylene and polypropylene properties degenerate when exposed to the environment.

If a structural material is planned for long-term application, the aim is to hinder oxidation. For short-term applications, however, only a limited lifetime is needed. Regardless of application, the polymer will finally appear as waste material, which has to be disposed of or possibly utilised for some other uses. A potential of the latter is controlled oxidation in which low molecular weight organic intermediates can be obtained. The first aim can be achieved by the use of a stabiliser-sensitiser system, while oxidising agents or initiators under special conditions can oxidise the waste materials. Whatever the practical aim is, the process to be controlled is the degradation reaction [2, 7, 11, 14, 22, 26].

2.3.2 LIGHT ABSORPTION PROCESSES

There are two types of photodegradation of polymers depending on the mode of light absorption, which itself is governed by the cut-off point for terrestrial sunlight, i.e. wavelengths > 290 nm [12].

(i) Direct photodegradation, when macro-molecules absorb light directly, and free radicals are formed after photo-excitation;

(ii) Sensitised photodegradation, when the degradation of macro-molecules is initiated by the free radicals which are formed from the photo-decomposition of low molecular weight photo-initiators (sensitisers).

Most polymers contain C-C, C-H, C-O, C-N and C-Cl bonds, and they do not absorb light with a wavelength longer than 190 nm. When polymers contain different types of chromophoric group, they can absorb light with wavelengths of 250 – 400 nm and higher [8, 9, 10].

A necessary condition for the dissociation of a particular bond into free radicals is the excitation of a molecule by the absorption of light of sufficient energy [10]. Pure polyolefins (PE and PP) do not absorb light in the wavelength region shorter than 200 nm. Thus generation of free radicals in them due exposure to light is only possible if impurity groups (carbonyl, peroxide, hydroperoxide groups, etc.) are present. The latter are formed in the polymer or entering into it in the course of synthesis, processing, usage. They may act as initiators or sensitisers when excited [12].

The formation of radical species in polyolefins also occurs under the action of ionising radiation, mechanical loads and other energetic factors, several types of macro-radicals (alkyl, allyl, polyene, peroxide, acyl, etc.) being formed in polyolefins of different chemical structures.

2.3.3 GENERAL FEATURES OF POLYETHYLENE AND POLYPROPYLENE OXIDATION: QUALITATIVE CHARACTERISATION OF PROCESS

The uptake of oxygen causes the formation of $RO_2^{\bullet}$ radicals in the chain. Some are transformed to end products and further $R^{\bullet}$ and $RO_2^{\bullet}$ radicals, while others abstract hydrogen from the CH_2 segments and are transformed into hydroperoxides. The latter are active intermediates,

which decompose at higher temperatures. After an additional series of elementary steps, the hydroperoxides cause additional changes in the polymer, namely [2]:

(i) Formation of oxidised structures in the chain,
(ii) Fragmentation of the polymer chain, and
(iii) Formation of low molecular weight products.

2.3.4 MECHANISM OF POLYETHYLENE AND POLYPROPYLENE OXIDATION

Most authors have been treated polyolefin oxidation in terms of the basic mechanism of Bolland and Gee [29, 30]. A version of it is given in Scheme 2.3. (a). It can be applied to describe oxidation at low and medium oxygen pressure when the rate of the process is determined by the reactions of hydrocarbon ($R^{\bullet}$) and peroxy ($RO_2^{\bullet}$) radicals.

At high oxygen partial pressure the oxidation of the radicals is very fast compared to the other propagation steps (process 2b). In this case, the reactions of $RO_2^{\bullet}$ radicals are rate determining. This mechanism is suitable for describing the main features of kinetics in the oxidation of some polyolefins, but it does not give any information about the non-rate-determining elementary steps of the reaction.

If, however, the composition of the products formed in the oxidation is investigated, it is found that the reactions leading to the end products of the oxidation are just these non-rate-determining processes.

The detailed mechanisms of these processes and consequently the composition of the products depend on the chemical structure of the polymer [2, 9].

Scheme 2.3 Simplified mechanism scheme of polyolefin oxidation.
(f = radical efficiency factor.)

	(a) Low and medium O_2 pressure	(b) high O_2 pressure
(1)	Initiation	
(1.1)	$RH + O_2 + RH \rightarrow 2R^{\bullet} + H_2O_2$	$RH + O_2 + RH + 2O_2 \rightarrow 2RO_2^{\bullet} + 2H_2O$
(1.2)	$I + 2f' RH \rightarrow 2f' R^{\bullet}$ + products	$I + 2f' RH + 2f' O_2 \rightarrow 2f' RO_2^{\bullet}$ + products
(2)	Radical propagation	
	$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet}$	Very fast, non-rate-determining
(3)	Chain propagation	
(3.1)	$RO_2^{\bullet} + RH \rightarrow R^{\bullet} + RO_2H$	$RO_2^{\bullet} + RH + O_2 \rightarrow RO_2^{\bullet} + RO_2H$
(3.2)	$RO_2^{\bullet} + RH \rightarrow R^{\bullet}$ + products	$RO_2^{\bullet} + O_2 \rightarrow RO_2^{\bullet}$ + products
(4)	Degenerated branching	
	$RO_2H + 2fRH \rightarrow 2fR^{\bullet} + H_2O$ + other products	$RO_2H + 2fRH + 2fO_2 \rightarrow 2fRO_2^{\bullet} + H_2O$ + products
(5)	Termination	
(5.1)	$R^{\bullet} \rightarrow$ products	slow, rate is negligible
(5.2)	$RO_2^{\bullet} \rightarrow$ products	$RO_2^{\bullet} \rightarrow$ products
(5.3)	$R^{\bullet} + R^{\bullet} \rightarrow$ products	slow, rate is negligible
(5.4)	$R^{\bullet} + RO_2^{\bullet} \rightarrow$ products	slow, rate is negligible
(5.5)	$RO_2^{\bullet} + RO_2^{\bullet} \rightarrow$ products	$RO_2^{\bullet} + RO_2^{\bullet} \rightarrow$ products

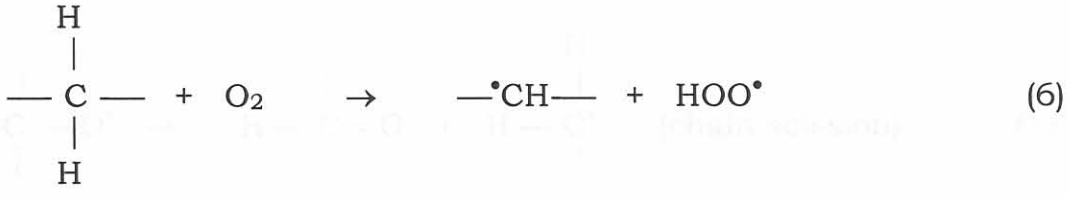
The majority of the oxidation product result from hydroperoxide decomposition processes [31]. In addition, a considerable proportion is formed in the transformation of peroxy radicals and a smaller fraction from radical termination processes. Most of the free radicals formed in hydroperoxide decomposition recombine within the molecular structure. About 80% of the end products resulting from PE-hydroperoxides and 90% of those from PP-hydroperoxides are formed in the structure processes. A smaller proportion, which is likely to be responsible for the broad spectrum of products, is formed by the reactions of radicals

escaping the cage and of active intermediate products formed from them [2, 7, 9, 28].

In the following scheme, we will survey the main processes leading to formation and decomposition of hydroperoxides and the structure of the active intermediate products in the cases of PE and PP. We will assume that the kinetic conditions of scheme 2.3 (b) are fulfilled, i.e. every macroradical formed is oxidised.

Polyethylene

Primary initiation



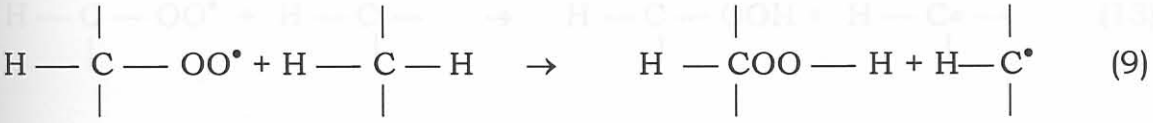
(6)

(7)

Radical oxidation

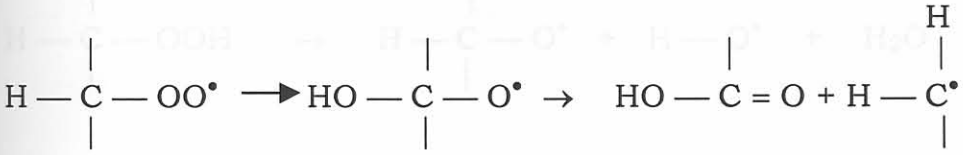
(8)

Polymer hydroperoxide formation



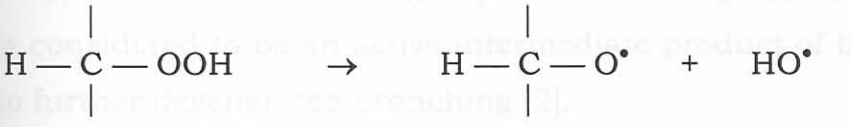
(9)

Peroxy radical transformation (formation of chain-end radicals and chain scission)



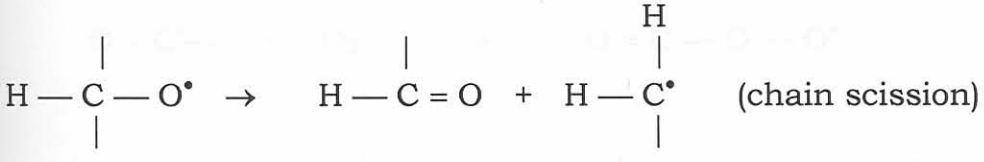
(9a)

Hydroperoxide decomposition



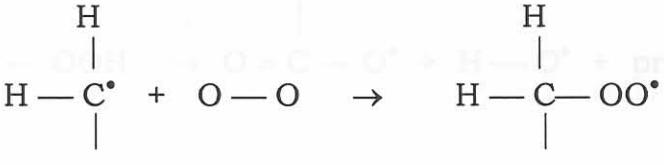
(10)

Transformation of alkoxy radical, formation of chain-end radicals

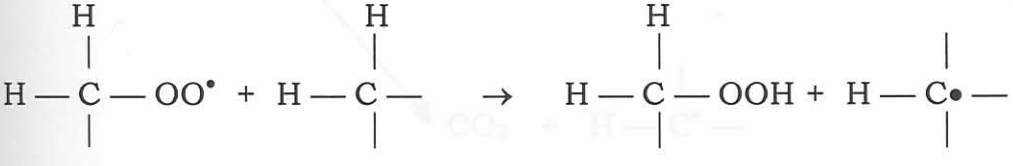


(chain scission) (11)

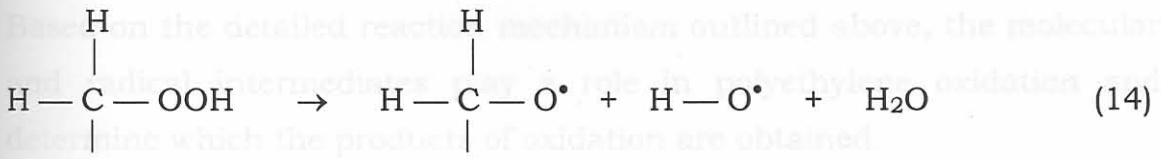
Formation of chain-end intermediate products



(12)



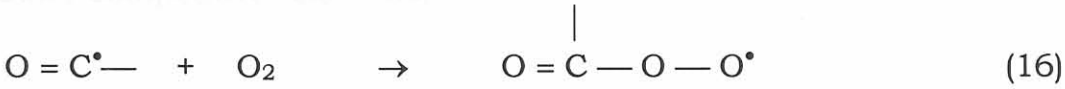
(13)



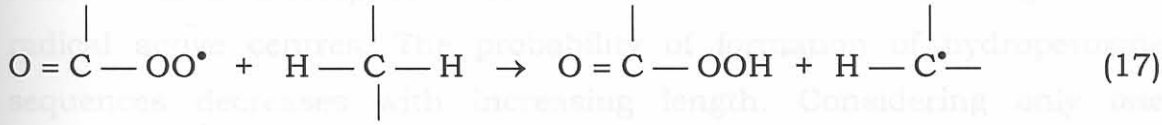
(14)

The reactions of H — C = O groups formed in process (11) can be regarded as secondary processes. However, both the formation and further oxidation of these groups are extremely fast. Therefore this group is considered to be an active intermediate product of the process, leading to further degenerated branching [2].

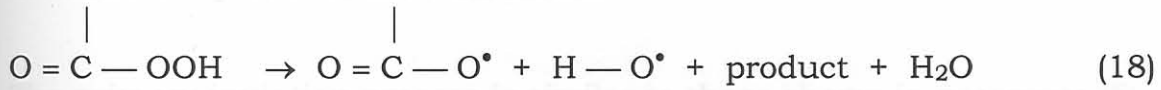
(15)



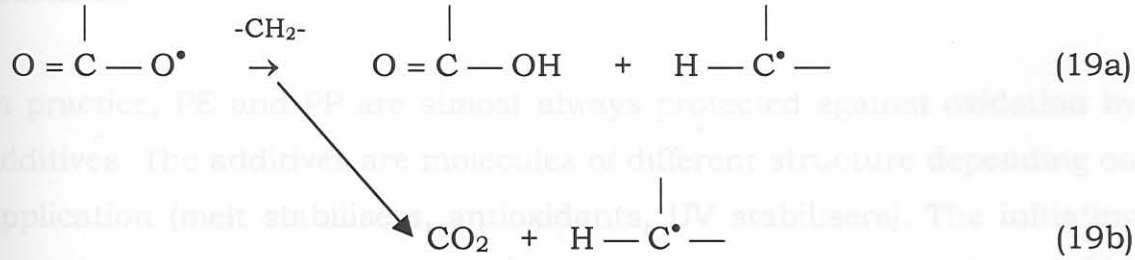
(16)



(17)



(18)



(19a)

(19b)

Based on the detailed reaction mechanism outlined above, the molecular and radical intermediates play a role in polyethylene oxidation and determine which the products of oxidation are obtained.

Polypropylene

In PP oxidation the number of propagating radicals and active intermediate products is higher than in PE oxidation. The polymer contains a very reactive tertiary hydrogen atom. The consequences of this fact for the degradation mechanism are the following [32]:

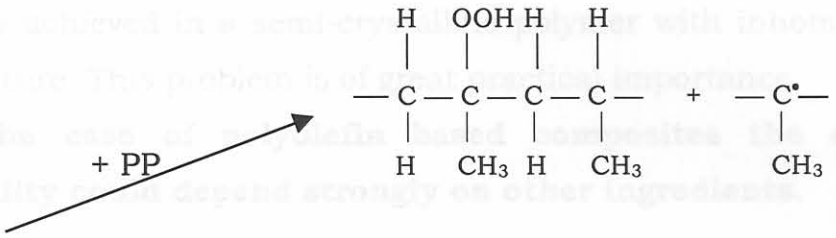
(1) High probability of intramolecular chain transfer,
(2) The oxidation rate of hydrocarbon radicals is in proportion to the rates of other competitive reactions.

As a result of intramolecular chain transfer, hydroperoxide sequences are formed which decompose to transitional structures containing several radical active centres. The probability of formation of hydroperoxide sequences decreases with increasing length. Considering only one intramolecular step, let's survey the reactions leading to active intermediate products of PP oxidation.

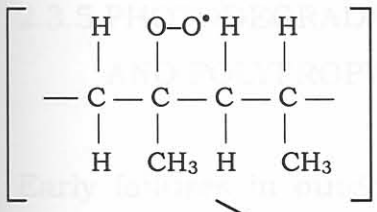
The primary initiation process is similar to those shown in processes (6) – (8). The peroxy radical formed may then part in several competitive reactions.

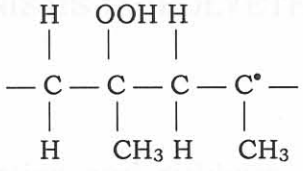
In practice, PE and PP are almost always protected against oxidation by additives. The additives are molecules of different structure depending on application (melt stabilisers, antioxidants, UV stabilisers). The initiating step of thermal oxidation cannot be avoided by the use of stabilisers. The primary process (1.1) always takes place and an $RO_2^{\bullet}$ radical is formed. One group of antioxidants hinders the chain reaction by substituting for the polymer in process (3.1) as an oxidation substrate. One of the

reaction products is, even in this case, a polymer hydroperoxide. This then may initiate a new oxidation chain, unless the system contains an antioxidant, which is also able to decompose peroxides to inactivate products in a molecular process.

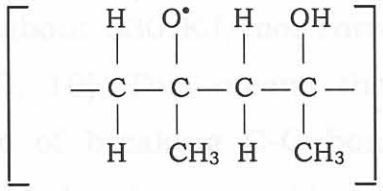


(20)

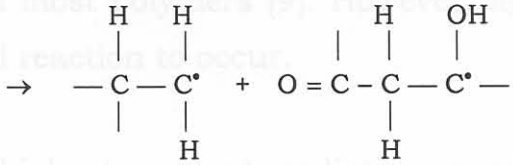




(21a)



(21b)



(21c)

Even in a system protected by an antioxidant, the following processes should be reckoned with:

(i) **The primary process of oxidation**; will occur and a slight structural change of the polymer is inevitable.

(ii) **Gradual stabiliser consumption in the primary process**; the protection is, therefore, transitional. The stabiliser system should

be chosen after a careful analysis of the demand and of the required lifetime.

(iii) **Unexpected local degradation due to the inhomogeneous distribution of the additives even in an optimally designed composition**. Homogeneous distribution, on the other hand, is not easily achieved in a semi-crystalline polymer with inhomogeneous structure. This problem is of great practical importance.

(iv) **In the case of polyolefin based composites the oxidative stability could depend strongly on other ingredients**.

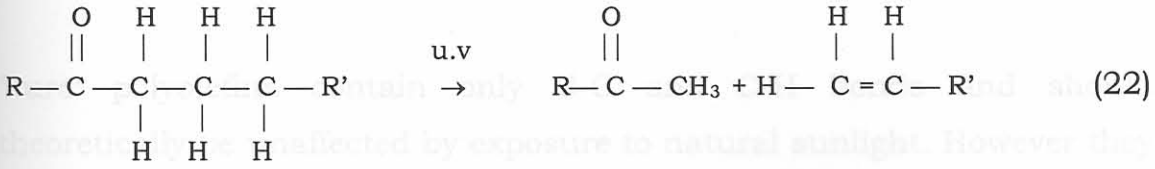
2.3.5 PHOTODEGRADATION MECHANISMS OF POLYETHYLENE AND POLYPROPYLENE

Early failures in outdoor uses of plastics and rubbers quickly revealed the severe effect of ultraviolet light on many polymers in the presence of oxygen. The C-C bond energy is about 330 KJ/mol corresponding to a photon wavelength of 360 nm [9, 10]. This means that light of this wavelength or shorter is capable of breaking C-C bonds in polymer molecules by which it is absorbed. It has been considered that quantum energies associated with light wavelengths 300 – 400 nm are sufficient to break the chemical bonds in most polymers [9]. However, light must be absorbed for a photochemical reaction to occur.

The shortest wavelength (highest energy) radiation present in the ultraviolet spectrum of the sun at ground level may be taken as 290 nm. Radiation of shorter wavelength is removed by molecular oxygen and ozone in the atmosphere [10].

The mechanisms of oxidative photodegradation are probably diverse, and it is only possible to indicate the kind of processes involved. In fact the direct breaking of single C-C and C-H bonds is relatively uncommon. The C=O bond absorbs more strongly and it appears that the following

reaction is important in initiating photo-oxidation in polymers containing CO groups.



Many engineering polymers including polyesters, polyurethanes and polyamides contain CO groups. In addition, CO groups are present as impurities in polyethylene and polypropylene, and also in other hydrocarbon polymers. The observation that radiation of wavelength longer than 340 nm does not produce photodegradation in polyethylene is one important piece of evidence for this [9]. Photo-oxidation leads generally to discoloration, surface cracking and deterioration of mechanical and electrical properties.

The term 'photodegradation' covers reactions carried out in the absence of oxygen and is often described as 'photolysis'. Photo-oxidation reactions, on the other hand, occur in the presence of air or oxygen. A third reaction arises when degradation or oxidation occurs under irradiation at an elevated temperature, but below the temperature necessary for purely thermal breakdown. This type of process is referred to as 'photothermal' degradation or oxidation [12,14].

Stability to sunlight exposure is one of the most important criteria in determining the practical application of all polymeric materials out of doors [12]. All unstabilised organic polymers are degraded upon exposure to terrestrial sunlight in the presence of oxygen [9,10]. However, the rates of photodegradation vary enormously with polymer structure, and range from a few months out-of-doors for polypropylene to, say, several years for poly(methyl methacrylate) and poly(tetrafluoroethylene) [12].

The basic mechanisms of photo-oxidation and photodegradation of commercial synthetic polymers are highly controversial and to a degree are not yet completely solved.

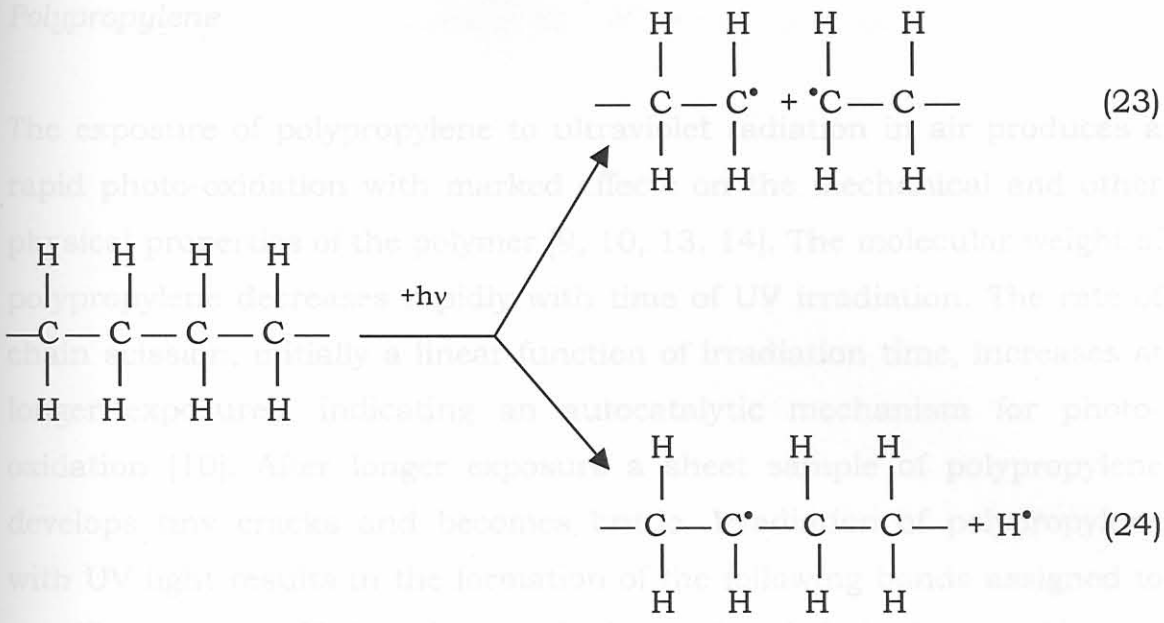
'Pure' polyolefins contain only C-C and C-H bonds and should theoretically be unaffected by exposure to natural sunlight. However they photo-oxidise through a number of impurity groups introduced during polymerization and/or processing. The main light-absorbing species are believed to be carbonyl groups, unsaturated carbonyl groups, hydroperoxides, unsaturated hydroperoxides, metallic impurities, aromatic compounds and oxygen-polymer charge-transfer complexes [8-10]. Much recent research indicates that carbonyl and hydroperoxide groups are the two most important species in the photo-oxidation of commercial polymers [2, 9].

Polyethylene

In the absence of oxygen, pure polyethylene is relatively stable material under ultraviolet radiation [10]. After long exposure to UV light of short wavelength (2537 Å) in a vacuum or in a nitrogen atmosphere, chain scission (23) and hydrogen abstraction (24) occur. Also crosslinking (25) and evolution of hydrogen (26) are observed.

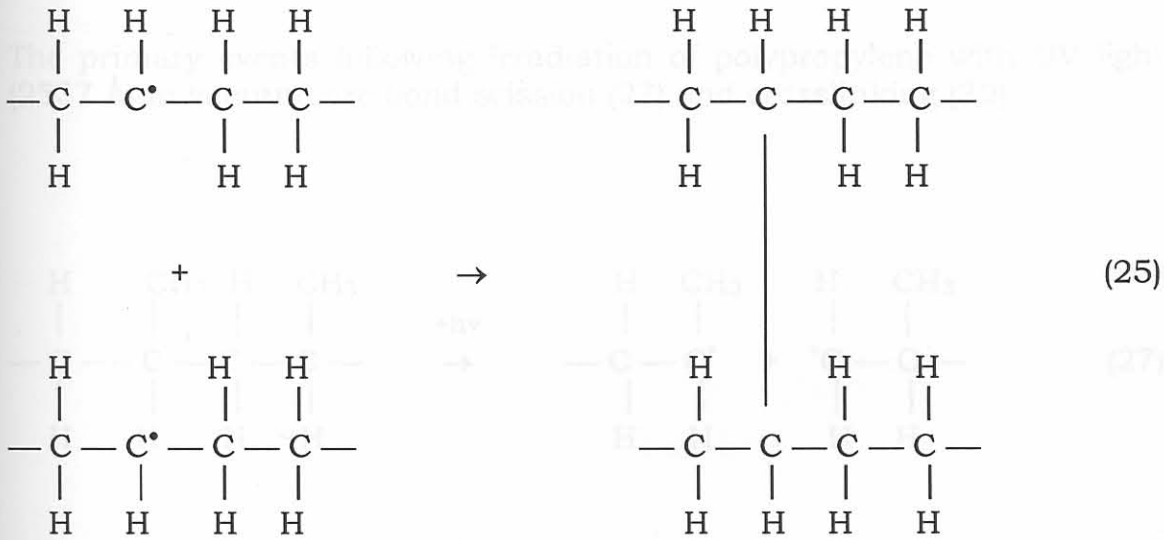
The mechanism of the degradation of polyethylene by UV light is complicated. At present this mechanism has not been satisfactorily established [8-10].

The photophysical processes affect the physical properties of polymers. It has been shown that the crosslinking of polyethylene chains is increased when the film thickness and the crystallinity decrease. The crosslinking promotes gel formation predominantly in the amorphous regions of the polymer [10].



(23)

(24)



(25)

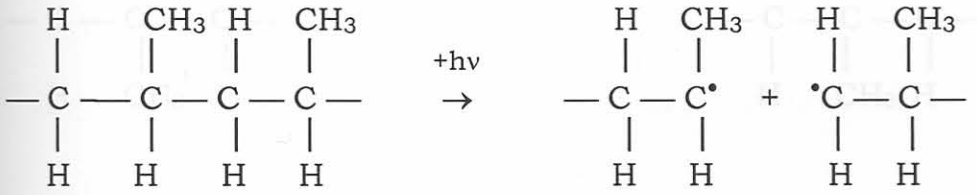
(26)

The weathering resistance of polyethylene of commercial grades has been related to the photo-oxidation reactions. They predominately occur close to the surface of the specimen [8] and are due to the presence of impurities or extraneous carbonyl groups [12, 22, 23].

Polypropylene

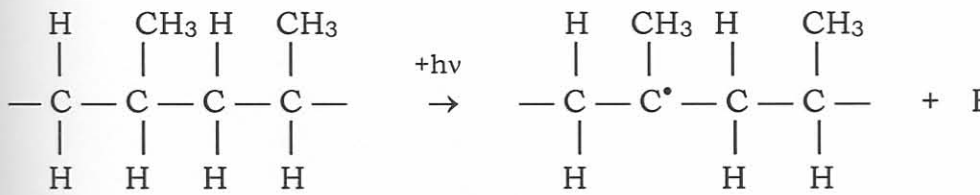
The exposure of polypropylene to ultraviolet radiation in air produces a rapid photo-oxidation with marked effects on the mechanical and other physical properties of the polymer [9, 10, 13, 14]. The molecular weight of polypropylene decreases rapidly with time of UV irradiation. The rate of chain scission, initially a linear function of irradiation time, increases at longer exposures, indicating an autocatalytic mechanism for photo-oxidation [10]. After longer exposure a sheet sample of polypropylene develops tiny cracks and becomes brittle. Irradiation of polypropylene with UV light results in the formation of the following bands assigned to specific groups: Hydroxyl and hydrogen-bonded hydroperoxides at 3400cm^{-1}, carbonyl at 1715-1720cm^{-1}, γ-lactone at 1728cm^{-1}, carboxylic acid at 1715cm^{-1}, and vinyl alkene at 1645cm^{-1} [10, 12, 13, 14].

The primary events following irradiation of polypropylene with UV light (2537 Å) in vacuum are bond scission (27) and crosslinking (30):



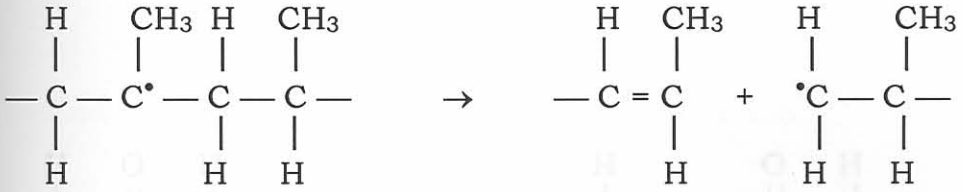
(27)

Another probable reaction is the dissociation of carbon – hydrogen bonds at the tertiary carbon:



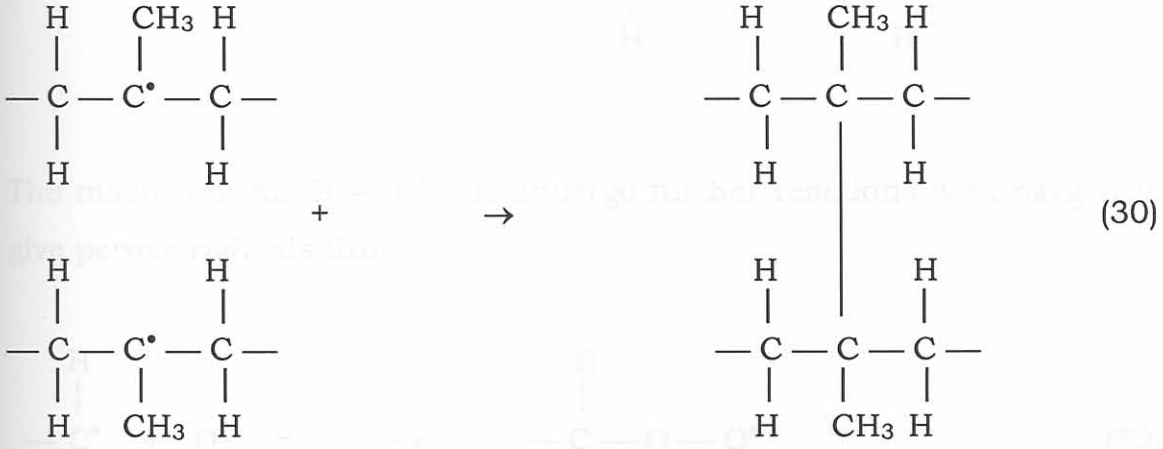
(28)

which may lead to chain scission by a disproportionation reaction:



(29)

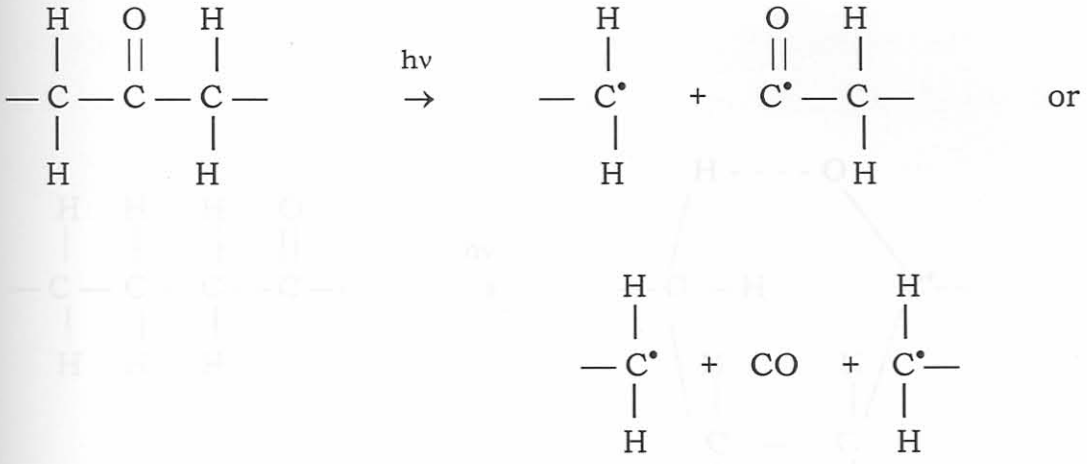
When two polypropylene radicals react by combination a crosslink is formed:



(30)

Two main primary photochemical processes are believed to be responsible for the carbonyl-initiated photo-oxidation of polyolefins [2]. Their nomenclature originates from the early pioneering work of Norrish on the photochemistry of liquid-phase aliphatic ketones [8-10].

Norrish type – I process: This leads to the formation of free radicals in which the excited singlet or triplet states of the carbonyl groups are precursors [10].

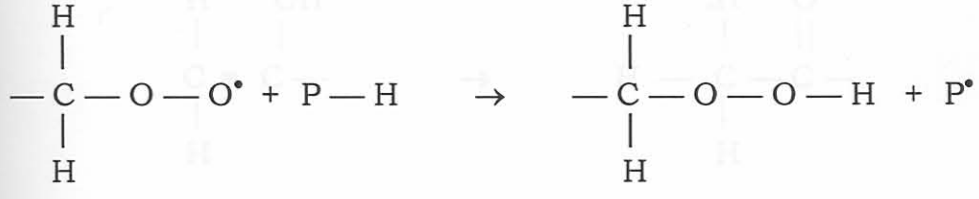


(31)

The macroradicals H — C•— H undergo further reactions with oxygen to give peroxy radicals thus

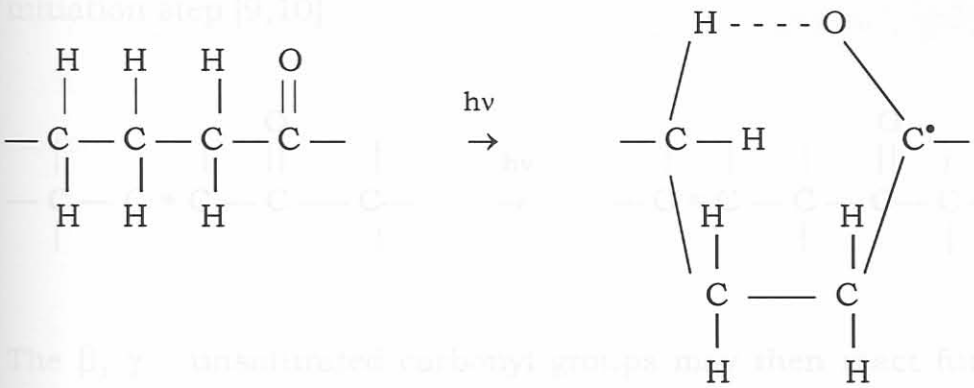
(32)

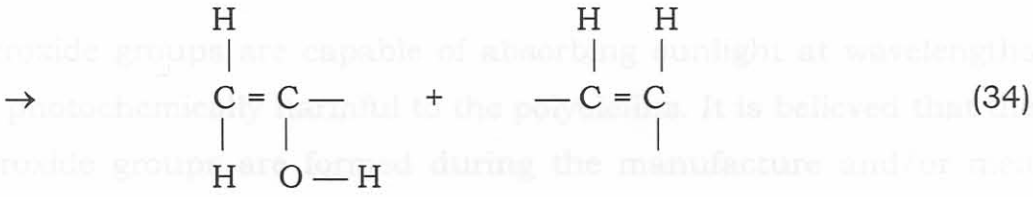
The peroxy radicals may then abstract hydrogen atoms from the polymer substrate, P-H, to form hydroperoxide groups thus



(33)

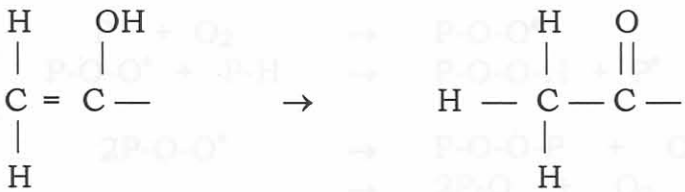
Norrish – type II process: This only occurs when the ketone possesses at least one hydrogen atom on a γ-carbon with respect to the carbonyl group. The reaction occurs via a six-membered cyclic intermediate involving intramolecular hydrogen-atom abstraction and produces one olefinic and one enolic group in the polymer [8-12].





(34)

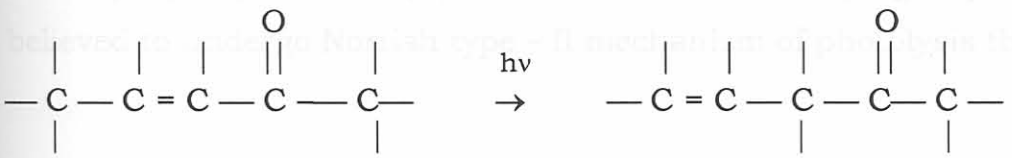
The enolic group then rearranges to give a ketone group thus



(35)

Although the Norrish type-II process does not directly produce free radicals, it is nevertheless considered to be the most important primary reaction at ambient temperatures in the mechanism of the oxidative photodegradation of polyethylene containing carbonyl groups randomly distributed along the hydrocarbon chain [9].

On photo-oxidation, the luminescent α, β - unsaturated carbonyl groups are converted into β, γ - unsaturated carbonyl groups via the following initiation step [9,10]



(36)

The β, γ - unsaturated carbonyl groups may then react further via the Norrish type – I and II processes to give aliphatic carbonyl products, e.g. carboxylic acids and esters.

Hydroperoxide groups are capable of absorbing sunlight at wavelengths that are photochemically harmful to the polyolefins. It is believed that the hydroperoxide groups are formed during the manufacture and/or melt processing of the polyolefin by the Bolland – Gee auto-oxidation mechanism thus [29, 30]:

Initiation

$$PH \xrightarrow{\Delta} P^{\bullet} + H^{\bullet} \quad (37)$$

Propagation

$$P^{\bullet} + O_2 \rightarrow P\text{-}O\text{-}O^{\bullet} \quad (38)$$

$$P\text{-}O\text{-}O^{\bullet} + P\text{-}H \rightarrow P\text{-}O\text{-}O\text{-}H + P^{\bullet} \quad (39)$$

Termination

$$2P\text{-}O\text{-}O^{\bullet} \rightarrow P\text{-}O\text{-}O\text{-}P + O_2$$

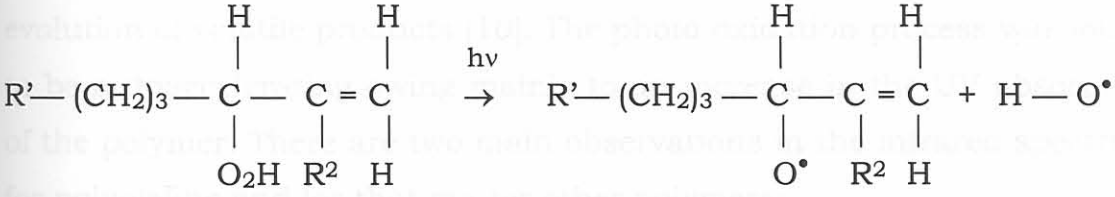
$$\rightarrow 2P\text{-}O + O_2 \quad (40)$$

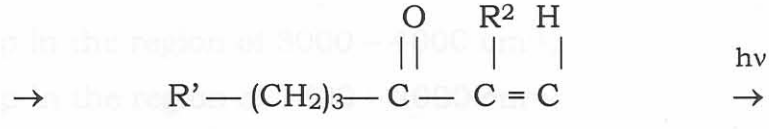
On exposure to light, the hydroperoxides dissociate in the excited state to give alkoxy and hydroxyl radicals thus

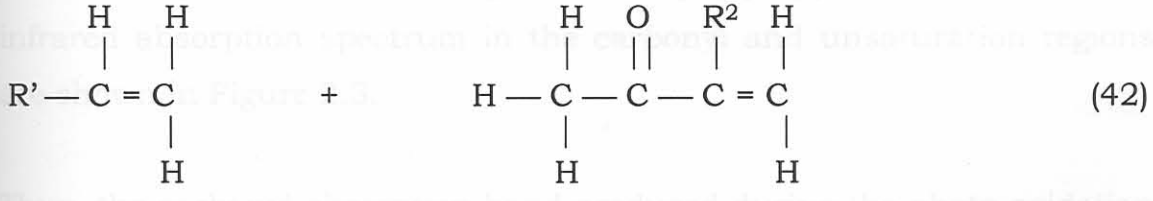
$$P-O-O-H \xrightarrow{h\nu} P-O^{\bullet} + H-O^{\bullet} \qquad (41)$$

The radicals $PO^{\bullet}$ and $HO^{\bullet}$ can then start the free – radical chain process.

On irradiation these groups are photolysed initially to α, β - unsaturated carbonyl groups. The α, β - unsaturated carbonyl groups are then believed to undergo Norrish type – II mechanism of photolysis thus







(42)

2.3.6 EFFECTS OF ULTRAVIOLET IRRADIATION

Photo-oxidation of polyolefins results in marked changes in both the physical and mechanical properties of the polymers. It leads to chain scission and a consequent reduction in the molecular weight of the

polymer [9]. Further exposure results in an increase in the rate of degradation, indicating that an autocatalytic mechanism is dominant. Accompanying chain scission is a significant increase in the degree of crosslinking [13, 14]. This increase in crosslinking also causes a corresponding initial increase in the percent elongation at break. Continued irradiation, however, eventually results in a marked decrease of the elongation at break.

There is considerable chain restructuring during the irradiation of polyolefins [9, 10]. Photo-oxidation of polyolefins also results in a marked deterioration in the electrical resistivity of the polymer [13].

Exposure of polyolefins to ultraviolet light in air leads to the uptake of oxygen, formation of carbonyl, hydroxyl, and vinyl groups and the evolution of volatile products [10]. The photo-oxidation process was found to be autoaccelerating owing mainly to an increase in the UV absorption of the polymer. There are two main observations in the infrared spectrum for polyolefins and for that matter other polymers:

O – H build up in the region of 3000 – 4000 cm^{-1},
C = O build up in the region of 1500 – 2000 cm^{-1}.

These changes are shown in Figure 2.2 for polypropylene. Changes in the infrared absorption spectrum in the carbonyl and unsaturation regions are shown in Figure 2.3.

Thus, the carbonyl absorption band produced during the photo-oxidation of polyolefins is very broad and consists of various types of carbonylic product [8,12].

Attenuated total reflectance spectroscopy which analyses the surface layers of the polymer indicates that photo-oxidation occurs at the surface layers where oxygen has access and it is believed that the carbonyl group

formation decreases with increasing effective depth of light penetration on both sides of the film [12].

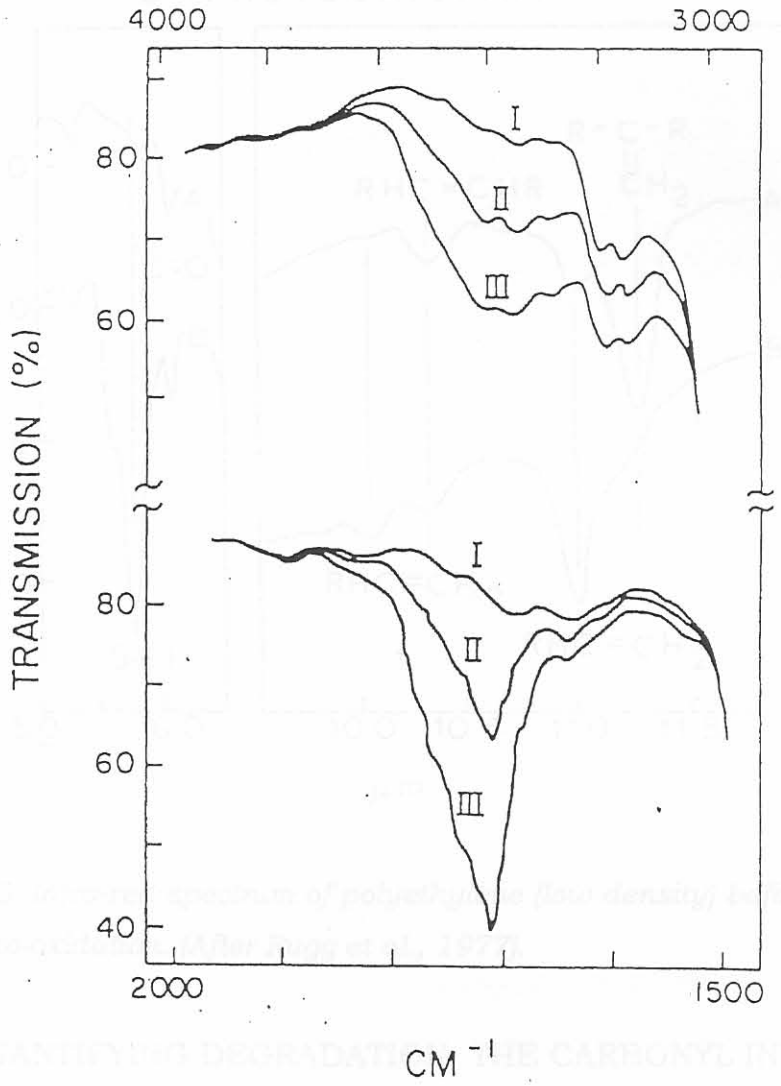


Figure 2.2. Formation of photo-oxidation products in polypropylene film monitored by infrared after irradiation for: I, 0h, II, 6h, III, 110h. (After Wiles, 1973).

As seen from the figure, the carbonyl absorption band is very broad extending from 1650 to 1850 cm^{-1} and is resolvable into six overlapping peaks. The main broad hydroxyl band at 3400 cm^{-1} contains a small band at 3340 cm^{-1} which has been attributed to the formation of hydrogen – bonded hydroperoxides produced by oxidation of the tertiary C – H bonds [8-10].

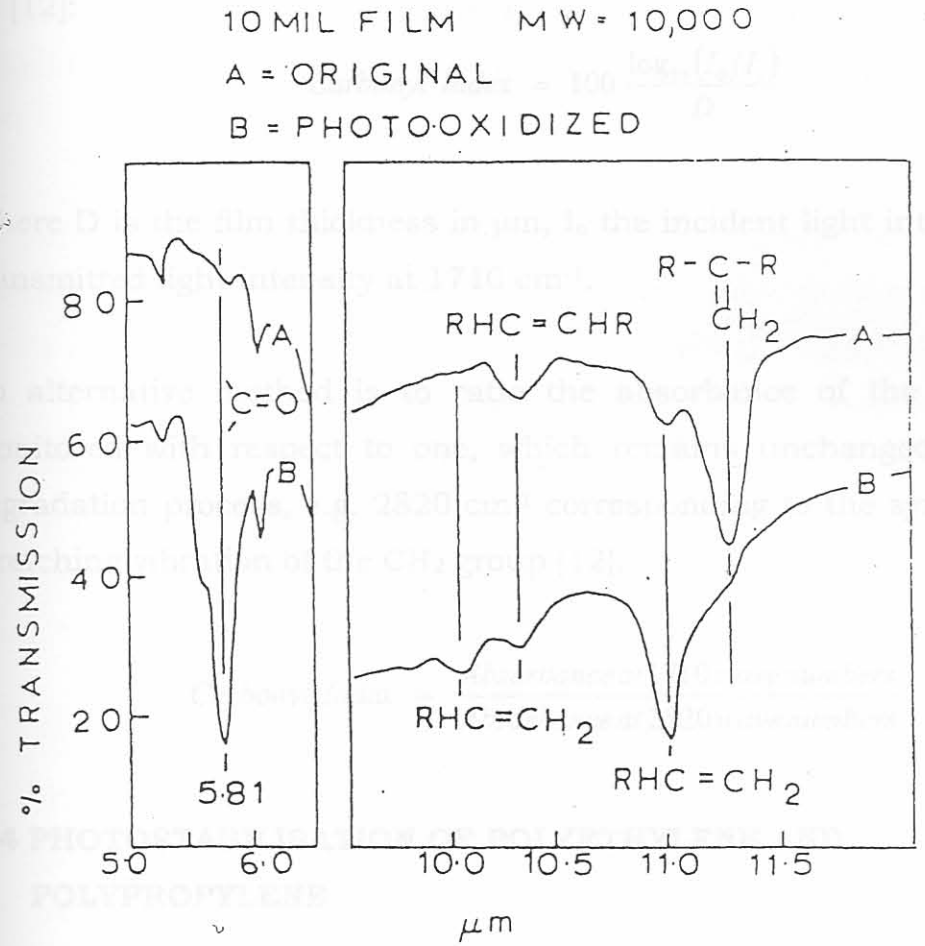


Figure 2.3. Infra-red spectrum of polyethylene (low density) before irradiation and after photo-oxidation. (After Rugg et al., 1977).

2.3.7 QUANTIFYING DEGRADATION: THE CARBONYL INDEX

Carbonyl groups are formed during the oxidation of polymers. These include ketones, aldehydes, acids, esters systems and cyclic esters (e.g. lactones) [8-12]. Therefore, the pure polyolefin contains no carbonyl groups. The concentration of carbonyl groups in the material will give an indication of the degree of degradation that has occurred. This is measured by IR spectroscopy.

In most oxidised polymers, carbonyl absorption lies in the range 1780 – 1640 cm^{-1} [8 – 12]. It is conventional to use the Carbonyl Index as a

measure of the degree of oxidation that has taken place. It can be defined as [12]:

$$Carbonyl\ Index\ =\ 100\ \frac{\log_{10}(I_0/I_t)}{D}$$

Where D is the film thickness in μm, I_o the incident light intensity, I_t the transmitted light intensity at 1710 cm^{-1}.

An alternative method is to ratio the absorbance of the band to be monitored with respect to one, which remains unchanged during the degradation process, e.g. 2820 cm^{-1} corresponding to the symmetric C-H stretching vibration of the CH_2 group [12].

$$Carbonyl\ Index\ =\ \frac{Absorbance\ at\ 1710\ wave\ numbers}{Absorbance\ at\ 2820\ wave\ numbers}$$

2.4 PHOTOSTABILISATION OF POLYETHYLENE AND POLYPROPYLENE

2.4.1 MECHANISM OF PHOTOSTABILISATION

Oxidation of polyolefins, in the absence of any additives, results in rapid chain scission, crosslinking and formation of oxygen – containing functional groups in the polymer [10, 12].

The photostabilisation of light – sensitive polymers involves the retardation or elimination of the various photophysical and photochemical processes that occur during photo-oxidation and may be achieved in many ways, depending on the type of stabiliser and the type of mechanism that is operative in the polymer [1-7].

The compounds, which are used to retard or arrest these processes, have traditionally been referred to as 'stabilisers' in plastic technology and

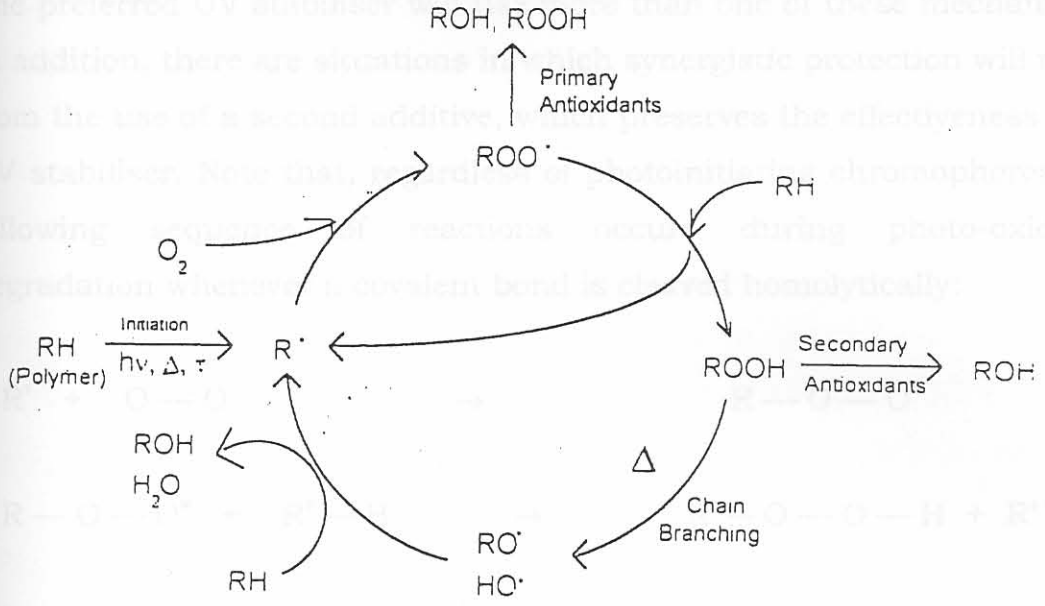
'antioxidants' in rubber technology [35-38]. The commercially available UV stabilisers range from extremely good to poor in protecting polyolefins against sunlight and have largely been developed by empirical routes [38].

In many cases antioxidant and light stabiliser degradation products can reduce the final stability of the polymer. The development of UV stabilisers and their mode of action have received widespread interest in the field of research over the years. Four different classes of stabilising systems have been developed and it is now believed that the mechanisms operating during stabilisation are more complex and more diverse. However, all stabilisers are believed to owe their mode of action to some or all of the following mechanisms [10, 12]:

(i)- ultraviolet screening;
(ii)- ultraviolet absorption;
(iii)- excited state deactivation; and
(iv)- free radical scavenging and/or hydroperoxide decomposition.

Of these, it is generally believed that (iii) and (iv) are the most effective mechanisms.

The mechanisms involved in photostabilisation are directly dependent on those involved in photo-oxidation and these, in turn, depend on the polymer structure and other variables, such as manufacturing operations, processing conditions, and so forth [8]. Most or, indeed, all stabilisers are believed to be multifunctional in their mode of operation in inhibiting photo-oxidation of a polymer. Many factors have to be taken into consideration such as light and heat stability of the stabiliser at its compatibility with the polymer [12]. A schematic representation of stabilisation is shown in Scheme 2.4.



Scheme 2.4. Inhibition of the oxidation mechanism by Antioxidants

We can describe the photo-oxidation of hydrocarbon polymers with the following sequence: absorption of photons by chromophores, resulting in electronic excitation of the chromophores. The breaking of some bonds by a fraction of the excitation energy to produce free radicals; subsequent reaction(s) of the radicals, frequently with atmospheric oxygen, in chain processes. A large number of secondary reactions may occur.

The Scheme 2.4 indicates the potentially useful functions of additives that impart UV stabilisation:

- absorbers to reduce the number of photons absorbed by chromophores,
- compounds which can deactivate excited species, such as $R^{\bullet}$ and O_2, normally in some collisional process,
- compounds which can catalyse the decomposition of peroxides before these groups absorb photons,
- compounds, which can react with free radicals and thus interrupt degradation chain processes.

The preferred UV stabiliser will use more than one of these mechanisms. In addition, there are situations in which synergistic protection will result from the use of a second additive, which preserves the effectiveness of an UV stabiliser. Note that, regardless of photoinitiating chromophores, the following sequence of reactions occurs during photo-oxidative degradation whenever a covalent bond is cleaved homolytically:

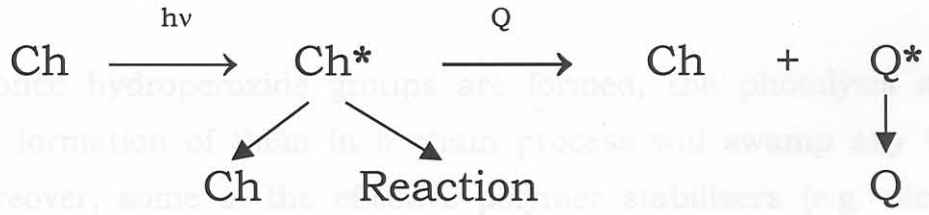
$$R^{\bullet} + O-O \rightarrow R-O-O^{\bullet}$$

$$R-O-O^{\bullet} + R'-H \rightarrow R-O-O-H + R'^{\bullet}$$

Since polymeric hydroperoxides absorb in the near ultraviolet, this group will usually be a significant chromophore. Thus, photodegradation should be reduced if stabilising additives can interrupt radical chain reactions. Finally, although initiating chromophores vary from one polymer to the next, Scheme 2.4 indicates that UV stabilisation can be approached in the same general way for all hydrocarbon polymers.

2.4.2 PHOTOSTABILISATION BY EXCITED-STATE QUENCHING

Following absorption of a photon, a chromophore (Ch) may revert to the ground state by some photophysical processes; it may react; or it can be made to transfer its excess electronic energy to a quenching additive (Q):



If the rate of energy transfer to quencher can compete with reaction by Ch* and if Q* can dissipate the excess energy harmlessly, then the

system is stabilised. Energy transfer can occur efficiently only if the energy level of the quencher is below that of the chromophore [8].

One of the more common chromophores in macromolecular systems is the carbonyl group. Not only is it present in the repeat units of many systems (polyesters, polyamides, polyalkyl or aryl vinyl ketones, ethylene, etc), it is also present as a low-level impurity in many "non-absorbing" polymers, frequently as a consequence of thermal oxidation. Absorbers in " non- absorbing" polymers such as PP, PE, PS, PVC, etc. are [9, 10]:

- Peroxides and hydroperoxides
- Carbonyls
- C = C
- Catalyst residues
- O_2 – Hydrocarbon change transfer complexes

Polymeric carbonyl groups absorb UV radiation and an electronically excited C = O will cause bond-breaking breaking reactions when it undergoes a Norrish – type process [8-10]. In principle, a quenching additive should impart photostability to a wide variety of polymer types. During the light deterioration of polymeric materials, singlet molecular oxygen can be formed by the interaction of atmospheric oxygen with electronically excited chromophores. If this occurs, the singlet oxygen $^1O_2$ will interact with the carbon – carbon unsaturated present in many polymers to form hydroperoxide groups by the "ene" mechanism [12].

Note that once hydroperoxide groups are formed, the photolysis and subsequent formation of them in a chain process will swamp any $^1O_2$ effects. Moreover, some of the effective polymer stabilisers (e.g. nickel chelates, amines) will, among other things, quench singlet oxygen.

There is good evidence that hydroperoxides, formed in polymers through inadvertent thermal oxidation during processing, are significant

chromophores in the photodegradation of polyolefins [39], polyvinyl chloride [1], polystyrene [40], and possibly polyamide [41].
Further more, formation and photolysis of hydroperoxides are important in the photodegradation of at least one strongly absorbing polymer, poly(ethylene terephtalene) [42].

It is obvious from Scheme 2.4 that hydroperoxides will be significant in the photo-oxidation of any hydrocarbon polymer, owing to the sequence:

$$R^{\bullet} + O-O \rightarrow R-O-O^{\bullet} \xrightarrow{R'H} R^{\bullet} + R-O-O-H$$

$$\xrightarrow{h\nu} R-O^{\bullet} + H-O^{\bullet}$$

Effective photostabilisation must cope with this chain reaction in one of the following ways. One can not quench an electronically excited hydroperoxide (after it has absorbed a photon) because the first excited state is dissociative. There are additives, however, which can catalyse the decomposition of hydroperoxides and thus reduce the rate of photoinitiation, at least for "non-absorbing" polymers.

A truly universal feature of the deterioration of all hydrocarbon polymers is the homolytic cleavage of covalent bonds (Scheme 2.4). Inevitably there will be a profusion of radicals (including alkyl, peroxyl, alkoxyl, hydroxyl) regardless of the photoinitiating species; and one or more of these reactive radicals will be involved in a kinetic chain – carrying sequence that perpetuates photodegradation. Free radical scavenging is important in the UV stabilisation of polymer [40] and it can lower the rate of photo-oxidation by irradiating hydroperoxidised polymer film into which scavenging additives have been diffused [22].

Efforts have been made to identify the mechanism(s) by which hindered amines derived from piperidine provide such effective UV stabilisation for

a number of polymers [43, 44]. It is generally agreed that the starting structure of the additive is altered during UV exposure [45]:

$$=N-H \xrightarrow[O_2]{\text{Radicals}} =N-O^{\bullet} \xrightarrow{R^{\bullet}} =N-O-R$$

A low level ($\cong 10^{-4}$ M) of nitroxide (nitroxyl) radical persists until brittle failure of the irradiated polymer film occurs.

The = N — O — R entity reacts with peroxyl radicals to interrupt the degradative chain – reaction sequence and to regenerate nitroxide radicals:

$$=N-O-R + R-O-O^{\bullet} \rightarrow =N-O^{\bullet} + R-O-O-R$$

It may be that this reaction is quite efficient because of the relatively long half -life of peroxy radicals.

2.5 FUNCTIONAL ADDITIVES FOR POLYMERS

2.5.1 INTRODUCTION

Functional additives are chemical agents that are added at relatively low dosage levels to a system in order to achieve a desired effect. As polymers find new applications, they face increasingly stringent requirements regarding their service life, durability, and many other properties. A variety of approaches are taken to meet these requirements. One approach is to modify the chemistry of the macromolecules from which polymers are made (e.g., by using new monomers or copolymerisation). Current developments in the area of polymer blends also offer a great deal of scope for innovation. Another important way of improving the properties of plastics is to employ additives. These agents have made a

decisive contribution to the widespread use of polymers and promise to be useful tools for solving future problems.

Polymer additives can be classified into three main groups [4, 18, 19, 36, 37, 38, 45]:

(i)- **Additives that stabilise polymers against degradation and aging processing during use**. Degradation usually involves chain cleavage of the macromolecules and can proceed through the addition of energy (e.g., shear forces, heat, UV light) or chemical attack (e.g., oxidation, hydrolysis). These additives are called antioxidants, light stabilisers, or heat stabilisers.

(ii)- **Additives that facilitate or control processing** (e.g., lubricants, mold-release agents, or blowing agents).

(iii)- **Additives that impart new, desirable qualities to polymers**, such as resistance to burning, transparency or color, improved mechanical or electrical properties, dimensional stability, and degradability. Such additives include flame retardant, fillers, dyes, pigments, antistatic agents, nucleating agents, optical brighteners, impact modifiers, and plasticisers. The concentration of additives varies greatly, ranging from a few parts per million for some stabilisers to more than 50 % for certain flame retardants or fillers.

Although additives can be added to the monomer prior to polymerisation, they are usually introduced immediately after polymerisation, blended, and extruded to form granular (pelletised) products and compounds. Polymers generally contain many additives. Preblended additive systems and combination masterbatches are commercially available; they contain optimal proportions of additives that are mutually compatible or have a synergistic action.

2.5.2 PHYSICAL PROPERTIES OF ADDITIVES

Polymer additives are primarily responsible for enhancing the properties and performance of commodity polymers. Loss and migration of additives are a major concern because of adverse effects on polymer performance and durability [37].

The secondary bonding forces present in polymers, e.g. Van der Waals and dipole – dipole forces, are identical to those present in small molecules. In polymers, however, all the types of electrostatic forces can be present and acting between different parts of the same molecule. The strength of these bonds increases with increasing polarity. Van der Waals forces are the weakest type of intermolecular bonds found in polymers. Linear, non-polar polymers, such as polyethylene, that have only Van der Waals attractions between the chains, must have relatively high molecular weights. It should not be too surprising that many commercial polymers contain polar functional groups that provide stronger dipole-dipole interactions between the chains. Ester groups are common pendant substituents. Polar ester linkages are also incorporated in many polymer chains [25, 37, 54].

An efficient additive should be soluble in the polymer to be stabilised. The efficient stabiliser should be able to diffuse easily throughout the polymer matrix. However, the diffusion rate should be optimal i.e. providing a sufficient mobility of the stabiliser while keeping the physical losses low [54]. Solubility of the stabiliser in the polymer will determine how many additives can exist in the matrix at equilibrium. The solubility depends on both the interactions between the small molecule and the polymer and on the physical states of the polymer and additive. Linear polymers are only soluble in solvents that have the solubility parameters very close to their own (like dissolves like) [25].

The criteria for effective additives depend not only on intrinsic additive activity, but also on the parameters that affect permanence, the most important of which are solubility and the ability of the additive to stay in the polymer (low volatility). In general, additives are less soluble in macromolecules than in lower molecular weight analogues. At concentrations greater than their equilibrium concentration additives may diffuse to the surface of the polymer, where they may deposit on the surface (blooming) and be subsequently lost [37].

2.5.3 ULTRAVIOLET STABLE ANTIOXIDANTS

Antioxidants prevent or retard the auto-oxidation of polymers and minimise associated damage (e.g., discoloration, reduction in gloss, cracking, and embrittlement); i.e., they stabilise the physical properties of polymers. Oxidation reactions generally proceed via different mechanisms that depend on the structure of the polymer. Catalyst residues and contaminants often catalyse them. They are also accelerated by the addition of thermal or mechanical energy during polymer production and processing.

Three forms of stabilisation are used: prestabilisation, stabilisation during processing and long-term stabilisation. Most antioxidants are themselves oxidised and consumed in performing their function, so that the oxidation behaviour of the additive in a given polymer is crucial for its effectiveness. A number of other requirements apply to antioxidants [12]:

I- They must be thermally stable and non-volatile at processing temperatures.
II- They must be soluble in polymers and no chalking should occur at service temperatures.
III- They must not have an intrinsic colour, and their oxidation products must have minimal colour.
IV- Any acidic hydrolysis products must not corrode machinery.

V- They must resist extraction.

VI- They must be odourless and tasteless.

VII- They must not create toxicity problems.

Antioxidants act by interrupting the degradation process (See Scheme 2.4). They trap the free radicals (primary antioxidants) formed in the polymer, reduce hydroperoxides to alcohols (secondary antioxidants) and deactivate trace metals by complexation (metal deactivators). A commonly encountered classification is:

- **Primary antioxidants (HA) typically are hydrogen donors**. They function by a chain breaking mechanism by terminating the propagation reaction. However, they also permit the chain initiating hydroperoxide to be regenerated. They are generally consumed in the stabilisation process.

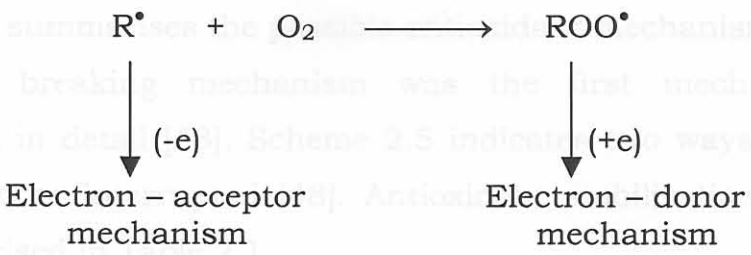
- **Secondary antioxidant (D) decompose hydroperoxides to non-radical products**. As these are the root cause of oxidative degradation, they represent an ideal case. They often operate by a catalytic mechanism.

In summary, the two basic mechanisms can be represented as following:

Primary: $ROO^{\bullet} + AH \rightarrow ROOH + A^{\bullet}$

Secondary: $ROOH + D \rightarrow$ non radical products

Ultraviolet stable antioxidants operate by inhibiting the propagation processes in the oxidative chain. Scott [47] has classified antioxidants into two types, namely kinetic chain breaking (radical scavengers) and initiation preventive (hydroperoxide decomposers). The first type embraces the aromatic amines and the phenols, and the second includes the transition metal complexes.



Scheme 2.5. Chain – breaking mechanism

Table 2.1. Antioxidant stabilisation mechanisms.

STABILISER TYPE	MECHANISM	EXAMPLES
Radical scavengers	Convert active free radicals into non – reactive ones	Sterically hindered phenolics aromatic amines
Peroxide decomposers	Remove hydroperoxides as potential sources of oxidation initiators	Divalent Sulphur compounds (Sulphides/thioethers) Trivalent phosphorus compounds (phosphites, phophonites)
HALS	Trap alkyl and peroxy radicals	Hindered amines
Synergism	Combination of primary and secondary antioxidants often provide improved stabilisation	- Phenols plus Sulphides - Phenols plus Phosphites
Antagonism	Under certain circumstances, combination of antioxidants may also result in decreased stabilisation.	-HALS and Thioethers

Scheme 2.4 summarises the possible antioxidant mechanism routes. The chain breaking mechanism was the first mechanism to be investigated in detail [48]. Scheme 2.5 indicates two ways in which the chain might be interrupted [48]. Antioxidant stabilisation mechanisms are summarised in Table 2.1.

2.5.4 LIGHT STABILISERS

Synthetic and natural polymers vary in their sensitivity to environmental influences. Ultraviolet radiation in sunlight plays a critical role because it has sufficient energy to break chemical bonds. The cleavage sites react with atmospheric oxygen and accelerate degradation (free – radical chain reactions). Many polymers therefore suffer yellowing, surface cracking, embrittlement, reduction of gloss, or chalking after a short time in outdoor service, and ultimately disintegrate. Light stabilisers are used to maximise protection against photodegradation [19, 49].

Ultraviolet radiation is subdivided into UV – A (λ = 320 – 400 nm), UV – B (λ = 280 – 320 nm), and UV – C (λ < 280 nm). Only UV – A and UV – B reaches the Earth's surface in sunlight, and UV – B is largely responsible for the degradation of polymers. Polymers are generally fairly stable in the long – wavelength UV – A (350 – 400 nm). Most polymers are sensitive to wavelengths of 290 – 320 nm.

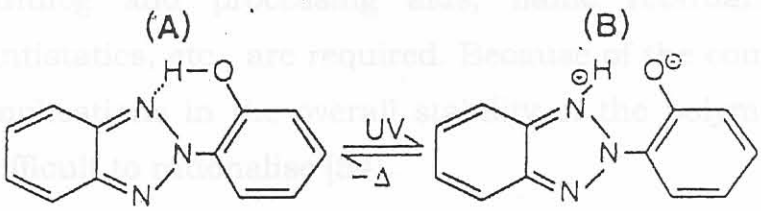
Two methods are used to protect polymers against photodegradation: (1) incorporation of light stabilisers in the bulk polymer, and (2) coating with a light - stable or light – stabilised material that is largely opaque to the dangerous UV range.

Light stabilisers must have light absorption; must resist extraction with water, hydrolysis, and thermal volatilisation; and they must be stable toward UV radiation. Ideally, a light stabiliser should not be consumed while carrying out its function; it should operate in a closed cycle so that

it still exists in active form even after a long period of weathering or use [50]. Other requirements include solubility in the polymer, stability under processing conditions, compatibility with other additives, and colourlessness.

Light stabilisers can more than double the service life of a polymer. Modern systems extend service life by a factor of 10 – 20 in many polymers, thus permitting their outdoor use [27, 45].

The first thrust of light stabiliser development was the inhibition of the photoinitiation processes. Thus additives were incorporated into the polymers that absorb UV light energy or quench the photo – excited states of the chromophores. The excited state quenchers return excited states of the chromophores on the polymer chains to their ground state by means of an energy transfer process. The UV absorber instead competes with the chromophores for the damaging UV radiation. In the ideal case the UV radiation is preferentially absorbed by UV absorber and then dissipated harmlessly as heat. UV absorbers do not themselves rapidly degrade because through a process known as tautomerism, they convert UV energy into harmless heat energy (Scheme 2.6).



Scheme 2.6. Tautomerism of a typical UV absorber [49]

Both tautomeric forms A and B have the same atoms and the same molecular weight; they only differ in the way the electronic bonding is arranged. Moreover, they are in equilibrium. The absorption of UV energy

by molecule A results in the formation of the molecule B, which through the dissipation of heat energy, reverts to the original form, molecule A. This process can be repeated many times.

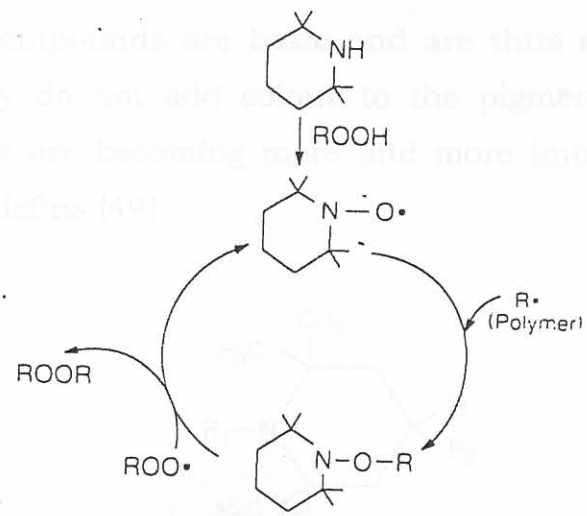
For UV absorbers to effectively screen a polymer, an exact matching of the absorption maximum of the UV absorber with those wavelengths at which the polymer concerned is most photosensitive is a prime consideration. But other requirements such as heat stability, volatility, effect of colour and synergistic effects with other additives must also be taken into account.

Hindered Amine Light Stabilisers (HALS) represents an important class of inhibitors of the photo-oxidation of polymers that are especially efficient in polyolefins [43, 51-54]. During the last 20 – 25 years many authors have published papers on their mechanism of action, the interaction with other stabilisers (phenolic antioxidants, phosphites, thioethers, etc.) and their mechanism of action is not yet fully elucidated [12]. In most of the applications HALS are used jointly with other stabilisers in order to achieve the best stability performances of the final manufactures through all the manufacturing steps. Processing stabilisers such as phenolic antioxidants and phosphites are necessary, together with long-term antioxidants such as thioethers. In some other case additives like, for example, antifog and processing aids, flame retardant, dyes and pigments, antistatics, etc., are required. Because of the complexity of the system, complications in the overall stability of the polymer often arise which are difficult to rationalise [54].

The high efficiency of HALS in some polymers is commonly ascribed to a fortunate combination of several factors [18, 49, 51, 52]:
(i)- first, as polar additives they tend to concentrate in oxidised regions of hydrocarbon polymers where initiation of the photo-oxidation is most likely to occur as a consequence of the photolysis of hydroperoxides and/or ketones;

(ii)- secondly, HALS are oxidised there to stable nitroxy radicals acting as scavengers of alkyl radicals. Formation of N – alkyloxy compounds thus competes with propagation of the oxidative process;
(iii)- last but a key aspect is that the nitroxy radicals can be regenerated from the N – alkyloxy compounds as these react with peroxy radicals. The high efficiency of nitroxy radicals, even at very low steady state concentration, is thus also associated with a new catalytic type of termination involving alkyl and peroxy radicals.

UV stabilisers have been developed which function by radical scavenging and hydroperoxide decomposition mechanisms. In this case the UV stabiliser undergoes chemical reactions with the products of photo – induced polymer degradation. In some cases the UV stabiliser is gradually consumed during this process, in other cases it has been postulated that UV stabiliser forms an active group which interacts with polymer radicals in a cyclic manner decomposing the polymer radical while at the same time regenerating itself. This mechanism has been put forward to explain the effectiveness of Hindered Amine – type (HALS) Stabilisers (Scheme 2.7).



Scheme 2.7. The regenerative mechanism of Hindered Amine – type stabilisers (HALS) [49]

HALS are able to affect in many ways the chemical and physical factors controlling the polymer stability. In 1986 Allen [55] summarised the possible modes of action of HALS as following:

I- Chain breaking donor/acceptor redox mechanism through the nitroxyl/substituted hydroxylamine intermediates.

II- Decomposition of hydroperoxides by the amine during processing.

III- Inhibition of photo - reaction of α, β - unsaturated carbonyl groups in polyolefins.

IV- Reduction in quantum yield of hydroperoxides photolysis.

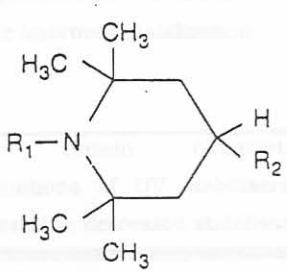
V- Singlet – oxygen quenching (only in polydienes).

VI- Complexation with hydroperoxides/oxygen.

VII- Complexation with transition metal ions.

Each one the above listed actions has been demonstrated to be part of the reaction mechanism of HALS and may contribute, in a complementary fashion, to the overall stabilisation process although the relative relevance can be strongly different for different substrates.

The Hindered Amine Light Stabilisers, which have the characteristic tetramethyl piperidine structure (Scheme 2.8) are the newest type of UV stabiliser and have been proved effective in many applications[56, 57, 58]. HALS compounds are basic and are thus acid sensitive. However, because they do not add colour to the pigment system and are very effective they are becoming more and more important especially in the area of polyolefins [49].



Scheme 2.8. Characteristic structure of HALS compounds [49]

On the other hand, even though HALS compounds undoubtedly represent a major advance in UV stabiliser technology their basicity and reactivity with some additives will limit their usefulness in some applications.

Furthermore synergistic and antagonistic effects with other stabilisers may result in different reaction pathways being activated with suppression of some chemical species or generation of others and drastic changes in the overall results. UV stabilisation mechanism is summarised in Table 2.2.

Table 2.2. UV stabilisation mechanisms

STABILISER TYPE	MECHANISM	EXAMPLES
Ultraviolet Screener	Prevents UV light from reaching the polymer substrate	Reflective or opaque pigments or coatings, carbon black, Zinc Oxide, Titanium dioxide
Ultraviolet Absorber	Filters UV light by absorbing it and dissipating it as heat. Not effective in thin films and fibers	2-hydroxy-benzophenones and 2-hydroxyphenyl-benzotriazoles
Energy Quencher	Deactivate excited states by absorbing energy from excited polymer region and dissipating it as heat	Nickel complexes
Hydroperoxide decomposer	Decomposes hydroperoxides, which can lead to chain splitting and free radical formation, into less harmful species	Transition metal complexes particularly those containing sulphur e.g. metal dithiocarbamates
Radical Scavenger	Scavenges free radicals in a regenerating cycle	Aromatic amines and phenols, hindered amines (HALS) and benzoate esters
Synergism	Combinations of UV stabilisers often provide improved stabilisation	-Nickel quencher plus Absorber -HALS plus benzoate esters -Dithiocarbamates with 2-hydroxyphenones
Antagonism	Under certain circumstances, combinations of UV stabilisers may also result in decreased stabilisation	HALS plus nickel quencher

2.5.5 SYNERGISM AND ANTAGONISM

Synergism occurs when the stabilising effect of a combination of additives in the polymer is greater than the sum of their separate effects [18, 57, 59, 60]. The opposite behaviour is termed antagonism [8-10]. Figure 2.4 shows a typical diagrammatic representation of the synergism and antagonism effects [12].

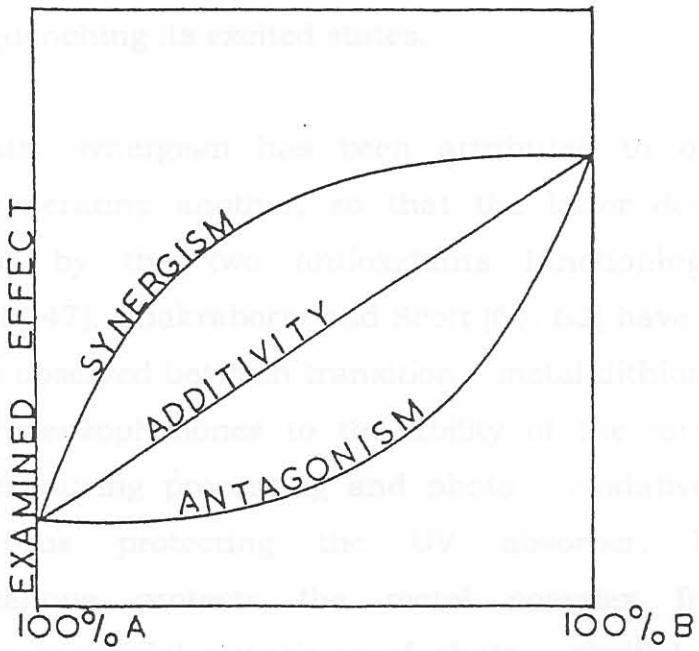


Figure 2.4. Synergism and antagonism effects (After Allen NS and Mc Kellar JF, 1979).

In commercial systems, it may be that, although synergism occurs, one additive may be sufficiently less expensive than the other(s) for more to be used to achieve the required stability and still give the lowest overall cost. Many light stabilisers and antioxidants give synergism. There are two complementary effects here [12]:

1- absorber prevents the antioxidant from photolysis;
2- antioxidant inhibits/destroys POOH which can (via PO· and OH·) attack the absorber.

There are many examples of synergism between ultraviolet stabilisers and antioxidants. This is presumably due to the stabiliser protecting the antioxidant during irradiation so that it may scavenge free radicals or decompose hydroperoxides while the stabiliser also performs its normal function. The light stabiliser may protect the antioxidant by either screening or quenching its excited states.

In antioxidants, synergism has been attributed to one antioxidant effectively regenerating another, so that the latter does not become consumed, or by the two antioxidants functioning by different mechanisms [8, 47]. Chakraborty and Scott [61, 62] have thus attributed the synergism observed between transition – metal dithiocarbamates and the 2 – hydrobenzophenones to the ability of the former to destroy hydroperoxides during processing and photo – oxidative conditions in polyolefins, thus protecting the UV absorber. In turn, the hydrobenzophenone protects the metal complex from photolytic destruction by sacrificial quenching of photo – excited species formed from the metal complex during photo-oxidation.

Synergism is more easily understood when it occurs with two additives which operate by different mechanisms. Thus, powerful antioxidant effects have been observed with chain – breaking antioxidants and peroxide decomposers [63]. In addition to synergism combination of antioxidants, antagonism effects have also been observed [64, 65]. The hindered piperidines show a complex behaviour in combination with other additives [8, 63]. A recent wide ranging survey of phenolic antioxidants and hindered piperidine compounds and their interactions during thermal and photochemical oxidation in both polypropylene and high-density polyethylene has been carried out. During thermal oxidation

(oven ageing) the interactions are seen to be synergistic in most cases, whereas on photo-oxidation the majority of the effects are seen to be antagonistic. For high-density polyethylene the effects were also highly synergistic during oven ageing whereas during photo-oxidation the effects were found to be variable, both synergism and antagonism being operative. In many cases the stability of the phenolic antioxidant itself was the determining factor in controlling performance. Synergism thermally and photochemically is probably associated with the fact that the generated nitroxyl and hydroxylamine products from the parent amine are scavenging macroalkyl and macroperoxy radicals and protecting the phenolic antioxidant [12].

2.5.6 FACTORS CONTROLLING THE CHOICE OF STABILISER

If any significant protection is to be derived from an ultraviolet stabiliser then the following factors must be considered [8-12]:

(1)- the stabiliser must be compatible with the polymer: many stabilisers may exude from the polymer during fabrication, storage or irradiation. One effective method of overcoming this problem is to substitute a long aliphatic hydrocarbon chain (alkyl chain) in the stabiliser molecule.
Other ways include – grafting onto polymer chains,
- polymeric stabilisers,
- copolymerisable stabilisers.

(2)- The stabiliser must, of course, be stable to light: despite the high inherent ultraviolet stability of many light stabilisers, their concentrations nevertheless do fall steady during irradiation. Many stabilisers are photolysed early in the degradation process and the products are often better light stabilisers [12].

(3)- The stabiliser must be stable to high temperature processing conditions for sufficiently long periods of time.

(4)- The stabiliser must not react chemically with the polymer.

Other important factors, which have to be considered when choosing a stabiliser, are:

(5)- Low toxicity

(6)- Colour. A coloured stabiliser may often be undesirable.

(7)- cost. Lowest consistent with stabiliser performance.

2.6 PHOTODEGRADABLE POLYMERS

2.6.1 INTRODUCTION

In the early 1960s and 1970s it was realised that sensitised photodegradation could be an effective method of combating environmental pollution by plastic litter [24]. There was awareness that discarded plastics materials posed a potential threat to the environment not only on the land but also the sea. Since then, numerous patents have been filed claiming the use of systems that will accelerate the photodegradation of various plastics and this has led to the new concept of photodegradable plastics [7, 11, 45].

Photodegradable plastics are used for applications where materials are used out-of–doors for a limited time only and it is not economically desirable to collect the residual materials after use. Examples are agricultural cordage and films, packaging films and drinking cups. Although recycling has been considered, it needs to be more effectively implemented. For most thermoplastics recycling results in the formation of inferior products that often end up as fuel. In this respect many of the bulk thermoplastics that end up as waste products are made photo – and/or biodegradable [45].

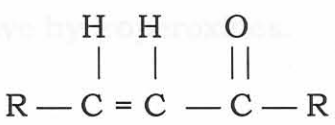
Many unstabilised plastics such as polypropylene are themselves light sensitive, if ultraviolet deterioration by sunlight exposure is desirable then it is important to be able to control and, indeed, monitor this effect. At present there are two ways of achieving this aim: one is the use of

specially prepared photosensitive plastics, and the other, appropriate selection of photoactive additives which are incorporated in the commercial plastic during processing. Presently, many plastic articles such as plastic carrier bags are made to be photodegradable by law, e.g. Italy [12].

2.6.2 PHOTOSENSITIVE PLASTICS

One effective method of preparing photosensitive plastics is to copolymerise the monomer with variable amounts of carbon monoxide or a vinyl ketone monomer. The plastics will degrade when exposed to outdoor sunlight of wavelengths > 300 nm but will remain intact if kept indoors which transmits light above 330 nm. This is because the ketonic groups introduced into the plastics do not absorb light of wavelengths greater than about 330nm. On exposure out-of-doors, where the light also contains radiation in the region 290 – 330 nm, the same ketonic groups are photoactive and can initiate degradation of the polymer by Norrish type – II process [8, 12]. Control of photodegradation is achieved by varying the concentration of carbon monoxide gas or ketone monomer during polymerisation.

Sensitised photodegradation is believed to occur predominantly by the Norrish type – I and II processes involving the 'in-chain' ketone groups [10]. The general structure of a vinyl ketone monomer is:



2.6.3 PHOTOACTIVE ADDITIVES

A wide range of derivatives of aromatic aldehydes, ketones and quinones effectively sensitise the photodegradation of polymer [8] and carbonyl compounds were amongst the first such types of structures.

These compounds sensitise through a primary photochemical process of hydrogen atom abstraction from the polymer involving the photo-excited triplet-state of the carbonyl group. A macroradical is formed that initiates the oxidative chain process. The sensitising efficiency of these molecules may be controlled through altering either their concentration or more effectively the nature of the substituents. Variables in the concentrations of these molecules will produce polymers with different life expectancies [8-12].

Apart from the carbonyl – based prodegradants, certain types of transition metal complexes and salts have also been found to be effective as photosensitisers in polymers [8, 11, 12, 64, 65, 66].

It is interesting to note that only the transition metal salts are photosensitisers. Among different transition–metal complexes, iron complexes are particularly favoured because of their low cost and low toxic [12]. Ferric stearate is believed to sensitise by first absorbing light [11], then undergoing electron transfer to give a carboxylic acid free radical. This species then dissociates to give an alkyl radical, which initiates polymer degradation, and carbon dioxide, the former being attached by oxygen to give hydroperoxides.

$$Fe^{3+}(O^{-}{}_2CR)_3 \xrightarrow{h\nu} Fe^{2+}(O^{-}{}_2CR)_2 + {}^{\bullet}O_2CR \rightarrow CO_2 + R^{\bullet}$$

With regard to the factors controlling the rate of photo-oxidation of polymers, the behavior of transition – metal acetylacetonates and

dithiocarbamates have been of considerable interest. The photosensitising efficiency of transition – metal acetylacetonates in polyethylene, for instance, decreases in the order Co(III) > Fe(III) > Zn(II) > Ni(II) [12]. The Cobalt(III) complex is very powerful photosensitiser whereas the Nickel(II) complex is a mild photostabiliser. In contrast to the acetylacetonates, the transition – metal dithiocarbamates exhibit a completely different pattern of behaviour. In polyethylene for example, while the Nickel, Zinc and Cobalt complexes are more stable towards ultraviolet light and indeed act as mild light stabilisers, the Iron and Copper complexes are much less stable and act as effective sensitisers [8-12].

One major difference between the two types of complexes is that the acetylacetonates are all much less oxidatively stable and are destroyed rapidly during the processing procedure. Further, the acetylacetonates exhibit no antioxidant activity and this can lead to thermal breakdown of the polymer.

2.7 WEATHERING OF POLYMERS

2.7.1 INTRODUCTION

The increased outdoor use of polymers has created a need for a better understanding of effect of the environment on polymeric materials. The environmental factors have significant detrimental effects on appearance and properties. The severity of damage depends largely on factors such as the nature of the environment, geographic location, type of polymeric material, and duration of exposure [63, 67, 68, 69]. The effect can be anywhere from a mere loss of colour or a slight crazing and cracking to a complete breakdown of the polymer structure. Any attempt to design polymer parts without a clear understanding of the degradation mechanisms induced by the environment would result in a premature

failure of the product. The major environmental factors that seriously affect polymers are:

1- Solar radiations – UV, IR, X – rays.
2- Microorganisms, bacteria, fungus, mould.
3- High humidity.
4- Ozone, oxygen.
5- Water: vapour, liquid, or solid.
6- Thermal energy.
7- Pollution: industrial chemicals.

The combined effect of the factors mentioned above may be much more severe than the effect of any single factor, and degradation processes are accelerated many times. Many test results do not include these synergistic effects that almost always exist in real – life situation.

2.7.2 AGEING AND WEATHERING OF POLYMERS

No material is immutably stable. The outdoor weathering of polymers is dependent on many atmospheric factors include light intensity, ambient temperature, humidity and wetness, all of which are in turn subject to seasonal, yearly and location variations [22].

The processes of metallic corrosion have their counterparts in the science of polymers. Even the mildest of human environments may be extremely aggressive to a synthetic material. To compensate for this, the resistance to what are ordinarily regarded as highly corrosive, substances may be excellent. Each application and each material must be considered carefully and objectively. Almost all polymers age at a significant rate unless steps are taken to stabilise them. In some cases the rate of deterioration of commercial formulations may set surprisingly short limits on the excepted lifetime.

Loss of appearance frequently occurs long before the component becomes functionally unserviceable. Quite reasonably the designer and the consumer seek reliable information on durability from materials suppliers. Polymer scientists and technologists have studied intensively the problems of predicting weathering performance [67-72].

The natural environment is enormously varied. Weathering is the result of exposure of polymers to conditions under which thermal oxidation and photo-oxidation may proceed simultaneously; and in addition the effects of water, abrasion and atmospheric pollution need to be evaluated. Microclimates may vary even over small distances, and features of the component such as its surface – to – volume ratio and the aspect of its surfaces may strongly influence weathering.

It is of course impossible to obtain information on long – term weathering performance quickly. Many possible methods of accelerated testing have been advocated. Testing machines range from crude devices (in which, for example, test samples are simply exposed to high intensity visible/ultraviolet radiation) to elaborate environment simulators. Inevitably, however, the process of photodegradation are somewhat distorted by the intensification of the environmental conditions, the greater the acceleration the less the reliability [15, 22]. Despite this, accelerated test methods are widely employed and for limited extrapolations may be useful.

The degradation rate of polymers depends markedly on the intensity and energy distribution of the solar spectrum in the ultraviolet region, both of which vary with the season [22].

2.7.3 ACCELERATED WEATHERING TESTS

Most data on the ageing of polymers are acquired through accelerated tests and actual outdoor exposure. The latter being a time – consuming method, accelerated tests are often used to expedite screening the samples with various combinations of additive levels and ratios. A variety

of light sources are used to simulate the natural sunlight. The artificial light sources include carbon arc lamps, xenon arc lamps, fluorescent sun lamps, and mercury lamps. These light sources, except fluorescent, generate a much higher intensity light than natural sunlight. Quite often, a condensation apparatus is used to simulate the deterioration caused by sunlight and water as rain or dew [21, 22, 71, 72].

There are three major accelerated weathering tests:

1- Exposure to carbon arc lamps.
2- Exposure to xenon arc lamps.
3- Exposure to fluorescent UV lamps.

2.7.4 PHOTODEGRADATION TESTS

When new materials are developed it is often important to determine how durable they will be when exposed to the weather. Will they chalk, haze, craze or peel? Or will they retain a reasonable percentage of original appearance and physical properties. Today, it is not important to wait a year or two for outdoor exposure tests to show whether the latest "improved" formulation is really an improvement. In these times, there is the need of weatherability data in a matter of weeks, not years [10].

Three crucial concepts provide the key to successful accelerated weathering in the laboratory [73]:

1- It is not necessary to simulate the full spectrum of sunlight in order to simulate the UV effects of sunlight. In fact, the best approach is to reproduce just the lowest part of the UV region, i.e. the UV – B range.
2- The most stringent way to simulate the effect of humidity is to use hot condensation. Not water immersion, high humidity, spray or fog but condensation, and condensation at elevated temperature at that.

3- The effects of UV and condensation are further enhanced by elevating the test temperature.

The Q.U.V accelerated weathering tester has been designed to meet the requirements of the above concepts.

2.7.5 ASSESSMENT OF WEATHERING

Prediction of the weathering performance or service life of a polymer formulation may also be very dependent on the technique used to measure the rate of degradation [9, 10]. Therefore, the criterion used to assess weathering performance will depend heavily on the end – use of the polymer formulation.

CHAPTER 3 - EXPERIMENTAL TECHNIQUES

3.1 INTRODUCTION

The general transesterification reaction between two esters is defined as follows:

$$RCO_2R'' + R'CO_2R''' \Leftrightarrow R'CO_2R'' + RCO_2R'''$$

Transesterification is a generic term applied to a collection of intermolecular reactions and includes alcoholysis, acidolysis, and ester interchange. In the presence of an organic acid, polyester may undergo acidolysis, reducing the molecular mass. In the special case of alcoholysis the reaction is between an ester and an alcohol:

$$RCO_2R'' + R'''OH \Leftrightarrow R''OH + RCO_2R'''$$

The alcoholysis reaction is an exchange of the alcohol of the ester with another alcohol to form a new ester.

Transesterification reactions take place readily between polyesters such as polymethacrylate and polycarbonate, polyethylene terephthalate (PET) and polycarbonate and polymethacrylate with polyethylene terephthalate (PET) [67]. The analogous reaction in polyamides is termed transamidation. Since reaction time influences the transesterification reaction [74], the method used for processing also has an influence on the transesterification.

3.2 MATERIALS

Table 3.1 lists the materials used as additives in this study. Unstabilised samples of low-density polyethylene (LDPE) and polypropylene homopolymer were obtained from Polifin. Commercially stabiliser

additives were masterbatched (10% actives level by mass) into MFI polyethylene resin on a laboratory extruder. For the other additives, high speed mixing was used to incorporate them into the polymer resin in powder form.

The first four compounds listed in Table 3.1 are hindered amine stabilisers with available alcohol functionality. They are too volatile to use as light stabilisers. Esterification and transesterification reactions were therefore employed to increase their effective molecular mass.

According to Ligner and Malik [54] the key requirements for an effective UV stabiliser are (1) high solubility, (2) minimal diffusion and (3) high homogeneity in the distribution of the additive. The HALS radicals, **TA**, **TOL**, **MA** and **DIOL**, are highly polar whereas polyethylene and polypropylene are highly non-polar. In an attempt to satisfy requirement (1), we invoke the principle of "like dissolves like". We used polyesters and stearic acid as co-reactants. The long alkyl chain of stearic acid (≡ **STE**) is similar in structure to polyethylene and should improve solubility in both polyethylene and polypropylene. Esters feature relatively low polarity as is attested by the corresponding low polarity of ester-based solvents. In order to satisfy the low mobility requirement (2), we tried to synthesize oligomers with reasonably high molecular masses of the order of 2000 Daltons. Requirement (3) should be satisfied, provided requirements (1) and (2) are met, and if good dispersion of additive is ensured during processing.

In order to simplify synthesis we opted to react the additives into high molecular mass polyesters such as polycaprolactone (grade 767 ex Union Carbide ≡ **TO**) and polybutylene succinate (grade Bionolle # 1001 ≡ **BU**).

Table 3.1 Compounds used as additives

Abbreviations	*Name of additives*	*CAS No.*	*Suppliers**
TA	2,2,6,6-Tetramethyl-4-piperidinol (TAA-OL)	[2403-88-5]	1
TOL	4-Hydroxy-2,2,6,6-Tetramethyl –Piperidin-1-Ethanol (N-HE-TAA-OL)		1
MA	1,2,2,6,6-Pentamethyl-Piperidin-4-0L (N-METHYL-TAA-OL)		1
DIOL	2,2-(2,2,6,6-Tetramethyl-4-piperidinyl)imino)bis (Ethanol)		1
Fe Acac	Iron (III) 2,4-pentanedione	[14024-18-1]	2
Ti Acac	Titanyl 2,4-pentanedione	[14024-64-7]	3
Zir Acac	Zirconium (IV) 2,4-pentane dione	[17501-44-9]	3
Mg Acac	Magnesium 2,4-pentanedione	[68488-07-9]	2
Va Acac	Vanadyl 2,4-pentanedione	[3153-26-2]	2
Cu Acac	Copper (II) 2,4-pentanedione	[13395-16-9]	3
Ca Acac	Calcium 2,4-pentanedione	[19372-44-2]	2
Al Acac	Aluminum 2,4-pentanedione	[13963-57-0]	2
Fe-Stea	Iron (III) Stearate	[2980-59-8]	-
Phetln	Phenolphtalein	[77-09-8]	3
Ni-Dmg	Nickel dimethyl glyoxime	[13478-93-8]	-
OTMQ	Poly (1,2 – dihydro – 2,2,4 – trimethylquinoline)	[26780-96-1]	-
Anox 20	Tetrakis methylene (3.5-di-t-butyl-4-hydroxy hydrocinnamate) methane		-

* 1. Creanova; 2. Aldrich; 3. Merck- Schuchardt

3.3 SYNTHESIS OF UV STABILISERS

The reactor consisted of a three neck round-bottomed flask, having a capacity of one litter, fitted with a condenser. The three openings allowed the insertion of a thermometer, connection with a reflux condenser and the collection of solvent. In order to form a homogeneous solution between UV stabilisers and the polymers, an appropriate solvent was added. The following solvents were used: Toluene, acetone and chloroform. Tetrabutylorthotitanate [$(C_{16}H_{36}O_4)Ti$] obtained from Merck-Schuchardt was used as catalyst. All the chemicals used in the experiments were of analytical grade.

3.3.1 HALS BASED ON OLIGOMERIC POLYESTERS.

The polymers and the UV stabilisers were dissolved in an appropriate solvent and the mixture was heated at reflux for several hours. After the reaction was deemed complete the mixture was removed from the reactor. The solvent was then removed from the product using roto-evaporation. The final product was finally washed with distilled water and dried at room temperature.

3.3.1.1 SYNTHESIS OF STETA

We have used the transesterification reaction of secondary alcohol with aliphatic carboxylic acids to prepare 4 - stearoyloxy- 2,2,6,6 – tetramethylpiperidine (STETA).

The overall reaction can be written as:

$$\mathbf{C_{18}H_{36}O_2 + C_9H_{19}NO \Rightarrow C_{27}H_{53}O_2N + H_2O} \quad [1]$$

Mm (g/mol)	284.48	157.24	423.72	18
Mass used (g)	45.3	25		
Mass expected (g)			67.43	

Stearic acid dissolved readily in toluene at room temperature, but TAA-OL was dissolved in toluene only at high temperature (80°C). The mixture of 45.3 g (0.159 mol) of stearic acid, 25 g (0.159 mol) of TAA-OL and 150.14 g of toluene as solvent was heated at reflux (105 °C) for 28h30'. In order to accelerate the reaction, tetrabutylorthotitanate (1%) was used as catalyst. Toluene was removed using roto-evaporation. The residue was poured into 750 ml of acetone and filtered. The acetone was evaporated and the residue was dissolved in 170 g of hexane and extracted three times with distilled water to remove catalyst residues. The hexane solution was dried by anhydrous sodium sulphate. By cooling the hexane solution, a white powder was obtained as the final product (yield 87.3 %). The theoretical elemental analysis for $C_{27}H_{53}O_2N$ was C:N = 23.2, while it was found to be C:N = 20.7.

3.3.1.2. SYNTHESIS OF TOTOL

The transesterification reaction between N-hydroxyethyl triacetone amino alcohol with caprolactone can be expressed by the following equation:

$$\mathbf{C_{11}H_{23}NO_2 + 5\ C_6H_{10}O_2 \Rightarrow C_{41}H_{63}O_7N + 5\ H_2O} \qquad [2]$$

Mm (g/mol)	201.3	114.13	681.95	18
Mass used (g)	12.3	35		
Mass expected (g)			41.78	

From preliminary work it was found that N-hydroxyethyl triacetone amino alcohol did not dissolve in toluene but it dissolved in acetone. On the other hand, caprolactone did not dissolve in acetone but it dissolved in toluene. Since toluene and acetone were miscible, N-hydroxyethyl triacetone amino alcohol and caprolactone were dissolved respectively in acetone (300 g) and toluene (300 g), and the two solutions were mixed later. The solution (caprolactone and Toluene) was put in a tumbler mixer

for 24 hours to allow the caprolactone to be completely dissolved in toluene. On the other hand, N-hydroxyethyl triacetone amino alcohol was dissolved in acetone after stirring for thirty minutes at room temperature. The mixture was then heated up to the boiling point of the solution (65 °C) for 24h 18'. The vapour was recycled after condensation during the experiment. Tetrabutylortotitanate (1%) was used as catalyst. The final product was separated from the solvent by using the roto-evaporator and yielded 82.3% of a gelatinous product after cooling to room temperature. The theoretical elemental analysis for $C_{41}H_{63}O_7N$ was C:N = 35.2; the following value was found C:N = 33.5.

3.3.1.3 SYNTHESIS OF TOTA

The transesterification reaction between triacetone amino alcohol with caprolactone can be expressed by the following equation:

$$\mathbf{C_9H_{19}NO + 5\ C_6H_{10}O_2 \Rightarrow C_{39}H_{59}O_6N + 5\ H_2O} \qquad [3]$$

Mm (g/mol)	157.24	114.13	637.89	18
Mass used (g)	8.3	35		
Mass expected (g)			37.95	

Toluene (300 g) was used to dissolve the two reactants and the mixture was heated up to 105 °C for 23h 40'. The same procedure as described previously was used to obtain the final product. The residue was separated from the solvent by using the roto-evaporator and yielded 81.7% of a gelatinous product after cooling at room temperature.

Tetrabutylorthotitanate (1%) was used as catalyst. The residue formed a viscous solution with the solvent, which did not allow a good separation. The theoretical elemental analysis for $C_{39}H_{59}O_6N$ was C:N = 33.5; that found was C:N = 35.0.

3.3.1.4 SYNTHESIS OF BUTA

The transesterification reaction between triacetone amino alcohol with polybutylene succinate can be expressed by the following equation:

$$\mathbf{C_9H_{19}NO + 5\ C_8H_{12}O_4 \Rightarrow C_{49}H_{69}O_{16}N + 5\ H_2O} \quad [4]$$

Mm (g/mol)	157.24	172.17	928.09	18
Mass used (g)	9.13	50		
Mass expected (g)			53.9	

600 g of Chloroform was used to dissolve the two reactants. Tetrabutylorthotitanate (1%) was used as catalyst. The mixture was refluxed at 58 °C for 20h 45'. The reaction mixture was rotor-evaporated and yielded 81.6% of a white powder. The theoretical elemental analysis for $C_{49}H_{69}O_{16}N$ gave C:N = 42.0; while it was found to be C:N = 44.3.

3.3.1.5 SYNTHESIS OF BUTOL

The transesterification reaction between N-Hydroxyethyl triacetone amino alcohol with polybutylene succinate can be expressed by the following equation:

$$\mathbf{C_{11}H_{23}NO_2 + 5\ C_8H_{12}O_4 \Rightarrow C_{51}H_{73}O_{17}N + 5\ H_2O} \quad [5]$$

Mm (g/mol)	201.3	172.17	972.15	18
Mass used (g)	11.7	50		
Mass expected (g)			56.47	

600 g of Chloroform was used to dissolve the two reactants and tetrabutylorthotitanate (1%) was used as catalyst. The mixture was heated up to 58 °C for 20h 15'. The final product was separated from the solvent by using the roto-evaporator and yielded 88.7% of a white

powder. The theoretical elemental analysis for $C_{51}H_{73}O_{17}N$ was C:N = 43.8; the following value was found C:N = 38.5.

3.3.1.6 SYNTHESIS OF BUMA

The transesterification reaction between N-methyl triacetone amino alcohol with polybutylene succinate can be expressed by the following equation:

$$\mathbf{C_{10}H_{21}NO + 5\ C_8H_{12}O_4 \Rightarrow C_{50}H_{71}O_{16}N + 5\ H_2O} \quad [6]$$

Mm (g/mol)	171.28	172.17	942.13	18
Mass used (g)	10	50.3		
Mass expected (g)			55.04	

456.5 g of Chloroform was used to dissolve the two reactants and tetrabutylorthotitanate (1%) was used as catalyst. The mixture was heated up to 58 °C for 27h 10'. The final product was separated from the solvent by using the roto-evaporator and yielded 87.6% of a white powder. The theoretical elemental analysis for $C_{50}H_{71}O_{16}N$ was C:N = 42.9; while it was found to be C:N = 37.2.

3.3.1.7 SYNTHESIS OF BUDIOL

The transesterification reaction between 2,2-(2,2,6,6-Tetramethyl-4 Piperidinyl) imino) bis (Ethanol) with Polybutylene succinate can be expressed by the following equation:

$$\mathbf{C_{13}H_{28}N_2O_2 + 5\ C_8H_{12}O_4 \Rightarrow C_{53}H_{78}O_{17}N_2 + 5\ H_2O} \quad [7]$$

Mm (g/mol)	244.38	172.17	1015.23	18
Mass used (g)	15	52.5		
Mass expected (g)			62	

360.3 g of Chloroform was used to dissolve the two reactants and tetrabutylorthotitanate (1%) was used as catalyst. The mixture was heated up to 59 °C for 28h 20'. The final product was separated from the solvent by using the roto-evaporator and yielded 93.4% of a white powder. The theoretical elemental analysis for $C_{53}H_{78}O_{17}N_2$ was C:N = 22.7; the value found was C:N = 19.5.

3.3.1.8 SYNTHESIS OF STEMA

The transesterification reaction between N-Methyl triacetone amino alcohol (N-METHYL-TAA-OL) with stearic acid can be expressed by:

$$\mathbf{C_{10}H_{21}NO + C_{18}H_{36}O_2 \Rightarrow C_{28}H_{55}O_2N + H_2O} \qquad [8]$$

Mm (g/mol)	171.28	284.48	437.76	18
Mass used (g)	27.2	45.2		
Mass expected (g)			69.54	

350 g of Chloroform was used to dissolve the two reactants and tetrabutylorthotitanate (1%) was used as catalyst. The mixture was heated up to 60 °C for 25h 50'. The final product was separated from the solvent by using the rotor-evaporator and yielded 90.5% of a white powder. The theoretical elemental analysis for $C_{28}H_{55}O_2N$ was C:N = 24.0; while it was found to be C:N = 22.7.

3.3.1.9 SYNTHESIS OF STEDIOL

The transesterification reaction between 2,2-(2,2,6,6- tetramethyl 4-piperidinyl) imino) bis (ethanol) with stearic acid can be expressed by :

$$C_{13}H_{28}N_2O_2 + 2\ C_{18}H_{36}O_2 \Rightarrow C_{49}H_{96}O_4N_2 + 2\ H_2O \quad [9]$$

Mm (g/mol)	244.38	284.48	777.34	18
Mass used (g)	24.4	56.9		
Mass expected (g)			77.7	

330 g of Chloroform was used to dissolve the two reactants and tetrabutylorthotitanate (1%) was used as catalyst. The mixture was heated at 60 °C for 28h35'. The final product was separated from the solvent by using the rotor-evaporator and yielded 88.3% of a white powder. The theoretical elemental analysis for $C_{49}H_{96}O_4N_2$ was C:N = 21.0; the following value was found to be C:N = 22.6.

3.3.2 METAL COMPLEXES

Ferric stearate was prepared as follows. Potassium hydroxide (0.165 mol) was dissolved in 1 litre of distilled water. A total of 46.94 g (0.165 mol) stearic acid was added in small portions while stirring. The next quantity was only added upon complete dissolution of the previous quantity. To this solution was added a total of 26.94 g (0.055 mol) ferric sulphate pentahydrate. The resultant precipitate was recovered by filtration. The filter cake was washed with copious quantities of distilled water to remove the soluble potassium sulphate. The product was dried for 24 hours at 60°C in a convection oven. The yield was 48.6 g (96.7%).

Nickel dimethyl glyoxime was prepared as follows. 20.92 g of sodium salt (0.06877 mol) was used. 20% excess of sodium salt (25.11 g) was dissolved in 1 litter of water. 20 g of nickel salt was completely dissolved in water also. The sodium salt was added upon complete dissolution of the nickel salt solution. The solution forms a pink precipitate immediately that was recovered by filtration. The filter cake was washed with an excess of distilled water and latter with hexane. The product was dried for 21 days in a dessicator. The yield was 93.5%.

3.4 ANTI-OXIDANT PROPERTIES

The oxidation induction temperature (OIT) was used to determine the effect of the additives on the thermal stability of the polymers. OIT's were obtained by Differential Scanning Calorimetry (DSC) on a Perkin Elmer DSC 7 at a scan rate of 2°C/min in a stream of air or at a scan rate of 10°C/min in oxygen flowing at 20 ml/min.

The effect of some additives on the process stability of the polymers was also evaluated using the method of repeated extrusion. The experimental procedures and conditions were as follows.

POLYPROPYLENE. Grade 1100K unstabilised homopolymer powder, ex Polifin, with a nominal MFI of 3.5 g/10 min @ 230°C/2.16 kg, was used. Test mixtures were prepared by dry blending the polypropylene powder with the required amount of stabilisers in a coffee grinder. The standard recipe was 0.2% calcium stearate together with 0.1% antioxidant blend. These mixtures were then extruded directly.

POLYETHYLENE. Since oxidative degradation initially leads to an increase in melt viscosity, it was decided to use LDPE grade WNG 14 ex Polifin. The initial melt flow index of this resin was 7.0 g/10 min @ 190° C/2.16 kg. In this case 0.1% stabiliser blend was incorporated via the 10% masterbatches. No calcium stearate was used with the polyethylene.

3.5 CHARACTERISATION OF ADDITIVES

3.5.1 THERMAL ANALYSIS (DSC/TGA)

The spectra of all products are attached as Appendix A. A Perkin Elmer DSC 7 instrument was used to collect calorimetric data. Sample masses of approximately 10±1 mg were weighed into aluminium pans. Air was

used as a dynamic atmosphere with a flow rate of approximately 20 ml/min.

A Netzsch STA 409 simultaneous TG/DSC instrument was used to collect thermogravimetric and calorimetric data. Sample masses of approximately 10±1 mg were weighed into aluminium pans. Air was used as a dynamic atmosphere with a flow rate of approximately 20 ml/min.

3.5.2 SPECTROSCOPIC CHARACTERISATION (UV)

IR spectra were obtained using pressed KBr pellets. The spectra of all the products are attached as Appendix B. Mid-infrared absorption spectra were recorded of the additives in a Bruker® 113V FTIR spectrometer. The sample chamber of the instrument was evacuated during the recordings to minimise any effects caused by water vapour and carbon dioxide. The resolution was 2 cm^{-1} and 32 scans were signal-averaged in each interferogram.

3.5.3 ELEMENTAL ANALYSIS

Elemental analysis of UV stabilisers for C and N were performed by the Agricultural Research Council.

3.6 CHARACTERISATION OF FILM

Films were obtained by using a laboratory film blower. High speed mixing was used to incorporate additives (different dosage level was used) into the polymer resin in powder form. 0.05% of Anox 20 was added to all additives synthesized.

The additives TOTOL and TOTA were gelatinous products. To incorporate them into the polymer resin, they were first dissolved in chloroform. This solution was poured into polymer resin for good mixing. The resultant

mixture was then dried for 14 days in room temperature to remove chloroform.

3.6.1 UV TEST

In order to evaluate the performance of metal 2,4-pentanedione complexes, anti-oxidants and ferric stearate compounded in polyethylene and polypropylene films in UV, UV-VIS purge trials were performed. A single layer of each film mounted at right angles to the light path in calibrate UV-VIS spectrophotometer [Spectronic genesys 5 (Beack = 4.00 and O = 0.006)] and scanned from 700 to 400 nm.

3.6.2 ACCELERATED UV AGEING

Low-density polyethylene (MFI 2,0) and polypropylene film samples (MFI 1,8) were blown on a laboratory film blower. The ca. 40 µm thick films samples were weathered in a QUV fitted with A340 UV lamps for up to 2900 hours. A dry cycle was used with the temperature set at 45°C.

Mid-infrared absorption spectra were recorded of the samples mounted on plastic squares to fit into the sample holder of a Bruker® 113V FTIR spectrometer. The sample chamber of the instrument was evacuated during the recordings to minimise any effects caused by water vapour and carbon dioxide. The resolution was 2 cm^{-1} and 32 scans were signal-averaged in each interferogram.

The recorded spectra were baseline corrected. The Carbonyl Index [12] used here was defined as the ratio of the intensities of the C=O band at 1710 cm^{-1} to the C-H rocking band at 729 cm^{-1} for polyethylene films and the band at 972 cm^{-1} for polypropylene films. The latter peaks remained unchanged during the degradation process. In our study the C-H stretch vibration band at 2820 cm^{-1} could not be used as the film thickness of the samples was sufficient to cause the intensity of this band to be so

high that it was cut off, i.e. it was saturated. A specific fixed Carbonyl Index value may be used to define a failure criterion for use in photo-stabilisation studies of polymers. A value of CI = 0.1 in this study.

CHAPTER 4 - RESULTS AND DISCUSSION

4.1 COMPLETE ANALYSIS OF ADDITIVES

Elemental analysis values found the UV stabilisers are given in Table 4.1.

Table 4.1 Elemental analyses: Mass ratios of C:N found for UV stabilisers

UV stabilisers	***C:N*** Experimental	**C:N** Theoretical
STETA	**20.7**	**23.2**
TOTOL	**33.5**	**35.2**
TOTA	**35.0**	**33.5**
BUTA	**44.3**	**42.0**
BUTOL	**38.5**	**43.8**
BUMA	**37.2**	**42.9**
BUDIOL	**19.5**	**22.7**
STEMA	**22.7**	**24.0**
STEDIOL	**22.6**	**21.0**

The DSC/TGA traces are presented as Appendix C lists DSC data for reagents and products. The DSC curves show that some of the reaction products e.g. BUTOL feature more than one melting endotherm. This implies that the reaction was not complete or that more than one product was formed. The TGA data shows that most additives started to volatilise below 200 °C. This is accompanied by exothermic peaks. It implies that the volatilisation is associated with an oxidative reaction or with the air atmosphere. However, OTMQ was stable up to about 400 °C. This is attributed to its antioxidant activity.

Figure 4.1 shows typical UV spectra for nickel dimethyl glyoxime in PE film (0.5%) and PP film (1%) and for Iron (III) 2.4-pentanedione in PP film (0.5%). Table 4.3 lists the characteristics of UV spectra of these additives. The nickel dimethyl glyoxime additive provides greater UV absorbance

over a broad wavelength range. Actually the UV absorbance of nickel dimethyl glyoxime is superior to other additives.

Table 4.3 Characteristics of UV spectra.

Additives	Peak, **nm**	Absorbance
Nickel dimethyl glyoxime (0,5%) in PE	560 421	0.42 0.33
Nickel dimethyl glyoxime (1%) in PP	418 538	0.50 0.52
Iron (III) 2,4-pentanedione (0.5%) in PP	424	0.49

4.2 OXIDATION INDUCTION TEMPERATURE (OIT)

Measured OIT's for the polypropylene and polyethylene samples are given in Table 4.4 for oxygen. These results suggest that OTMQ, in combination with calcium stearate is an excellent antioxidant combination for polypropylene. OIT measurements are presented as Appendix D.

Table 4.4 Effect of various additives on the OIT of LDPE and PP films.

Measured oxidation induction temperature at a scan of 10°C/min in oxygen flowing at 20ml/min. Additive (0.5% unless stated otherwise)	LDPE (XJF 46/60) OIT, [°C]	PP (1102H) OIT, [°C]
None	217	177
OTMQ (concentration in PE (0.4%)	255	202
Nickel dimethyl glyoxime	230	179
Phenolphthalein	199	-
Aluminium 2,4-pentanedione	189	175
Iron (III) stearate	164	164
Copper 2,4-pentanedione	177	154

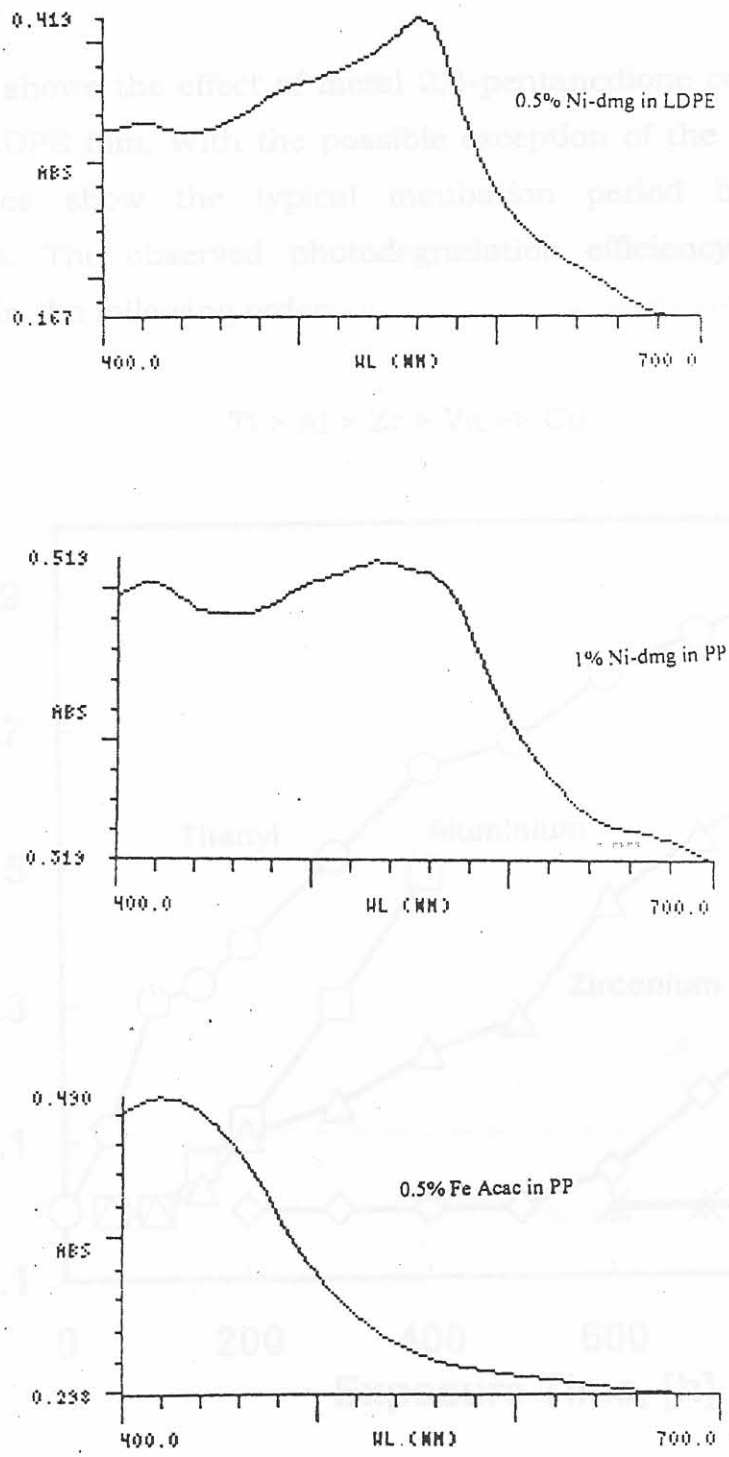


Figure 4.1 UV spectra of Nickel dimethyl glyoxime in PE and PP films and Iron (III) 2,4-pentanedione in PP film.

4.3 ACCELERATED WEATHERING

Figure 4.2 shows the effect of metal 2,4-pentanedione complexes on UV ageing of LDPE film. With the possible exception of the titanyl complex, all additives show the typical incubation period before oxidation commences. The observed photodegradation efficiency of the metals decreased in the following order:

Ti > Al > Zr > Va >> Cu

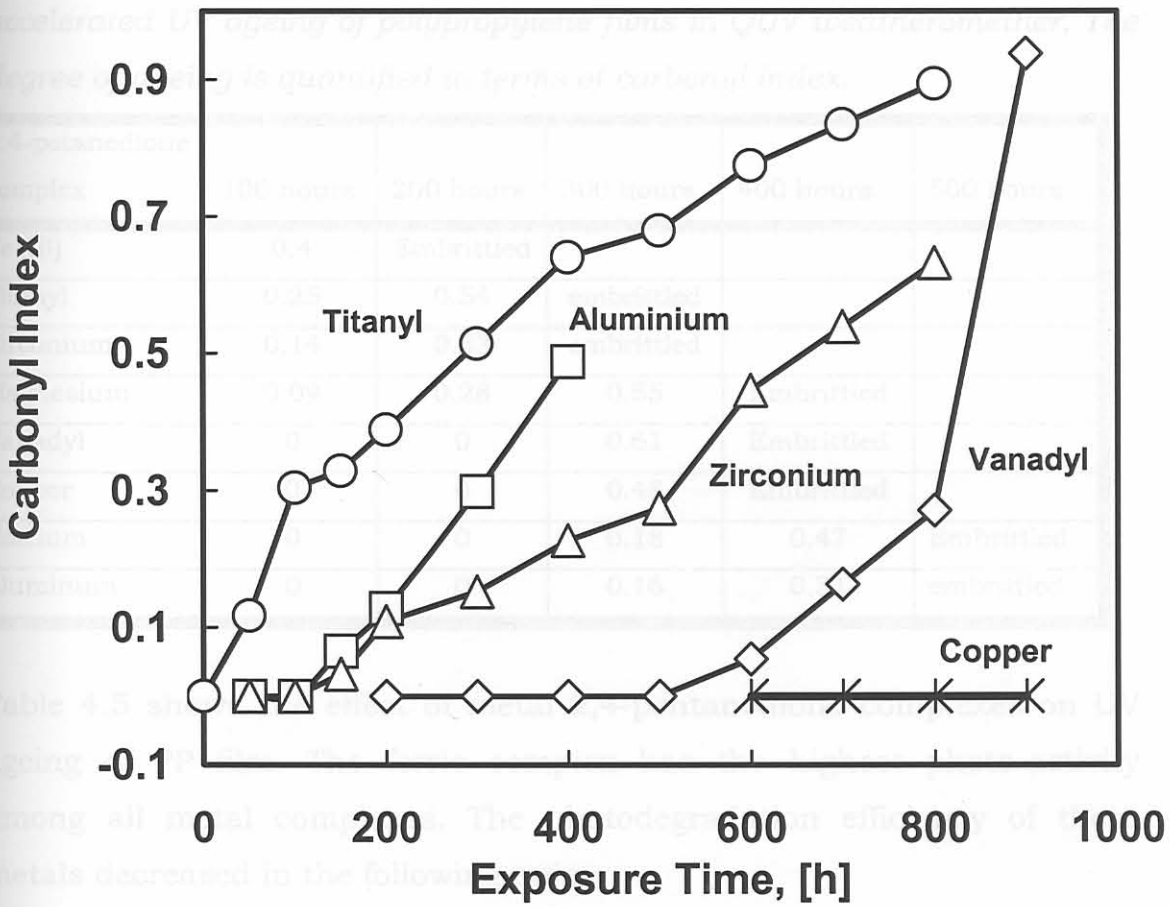


Figure 4.2 Effect of selected metal 2,4-pentanedione complexes on the UV degradation of LDPE film. Additives dosage level was 0.5%. Films were weathered in a QUV tester fitted with A340 lamps using a dry cycle (temperature: 45°C).

The high photo activity of the aluminium complex is encouraging, as it reportedly does not appreciably affect oxidative degradation in polyolefins [11]. Copper, a well-known and potent thermo-oxidation promoter actually acts as an UV stabiliser in polyethylene. Osawa *et al.* [11] previously noted similar behaviour. They studied the effect of metal stearates on the degradation of polyethylene and polypropylene. The photo-stabilising activity of copper stearate was attributed to an UV absorption mechanism [11, 66].

Table 4.5 Effect of metal 2,4-pentanedione complexes (0.5%) on the accelerated UV ageing of polypropylene films in QUV weatheromether. The degree of ageing is quantified in terms of carbonyl index.

2.4-petanedione complex	100 hours	200 hours	300 hours	400 hours	500 hours
Fe (III)	0.4	Embrittled			
Titanyl	0.25	0.54	embrittled		
Zirconium	0.14	0.33	embrittled		
Magnesium	0.09	0.28	0.55	Embrittled	
Vanadyl	0	0	0.61	Embrittled	
Copper	0	0	0.48	Embrittled	
Calcium	0	0	0.18	0.47	Embrittled
Aluminum	0	0	0.16	0.31	embrittled

Table 4.5 shows the effect of metal 2,4-pentanedione complexes on UV ageing of PP film. The ferric complex has the highest photo-activity among all metal complexes. The photodegradation efficiency of these metals decreased in the following order:

$$Fe > Ti > Zr > Mg > Va > Cu > Ca > Al$$

The vanadyl and copper complexes showed a distinct induction time followed by rapid oxidative degradation. Interestingly, even the calcium

and magnesium complexes showed photoactivity. It is suspected that for these complexes it derives from the carbonyl functionality of the organic residue rather than from the activity of the metal.

In Figures 4.3 and 4.4 the photo-activity of molecules with potential anti-oxidant properties are compared with that of ferric stearate in LDPE and polypropylene. While ferric stearate is much more efficient, it is clear that OTMQ does show promising photo-degradation properties. Figure 4.5 shows the effect of dosage level of the anti-oxidant, OTMQ, on the time to reach a Carbonyl Index of 0,2 for polyethylene film. By comparison, films containing ferric stearate reached this level at irradiation times less than 150 hours.

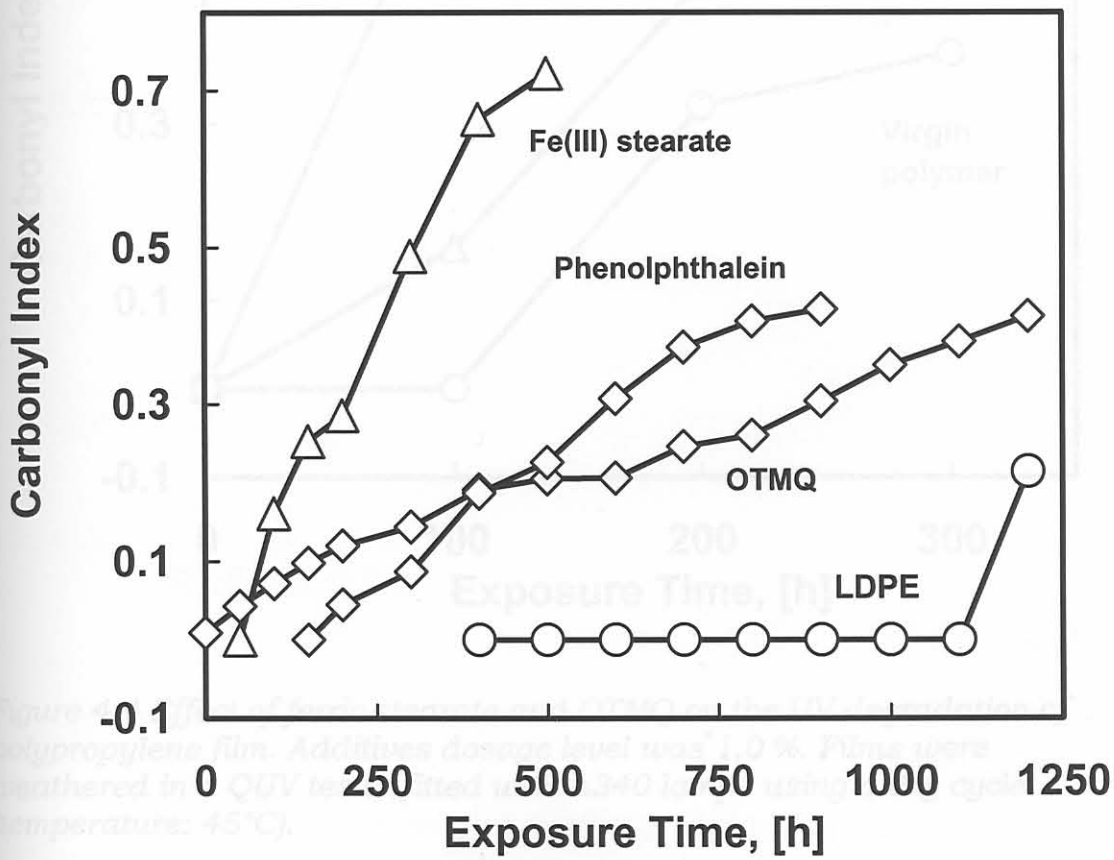


Figure 4.3 Effect of ferric stearate and OTMQ on the UV degradation of polyethylene film. Additives dosage level was 0,5%. Films were weathered in a QUV tester fitted with A340 lamps using a dry cycle (temperature: 45°C).

The influence of polyester-based UV stabilisers and nickel dimethyl glyoxime on the light stability of polyethylene (LDPE) and polypropylene (PP) films has been examined and compared to the corresponding activity of chimasorb 944 compound.

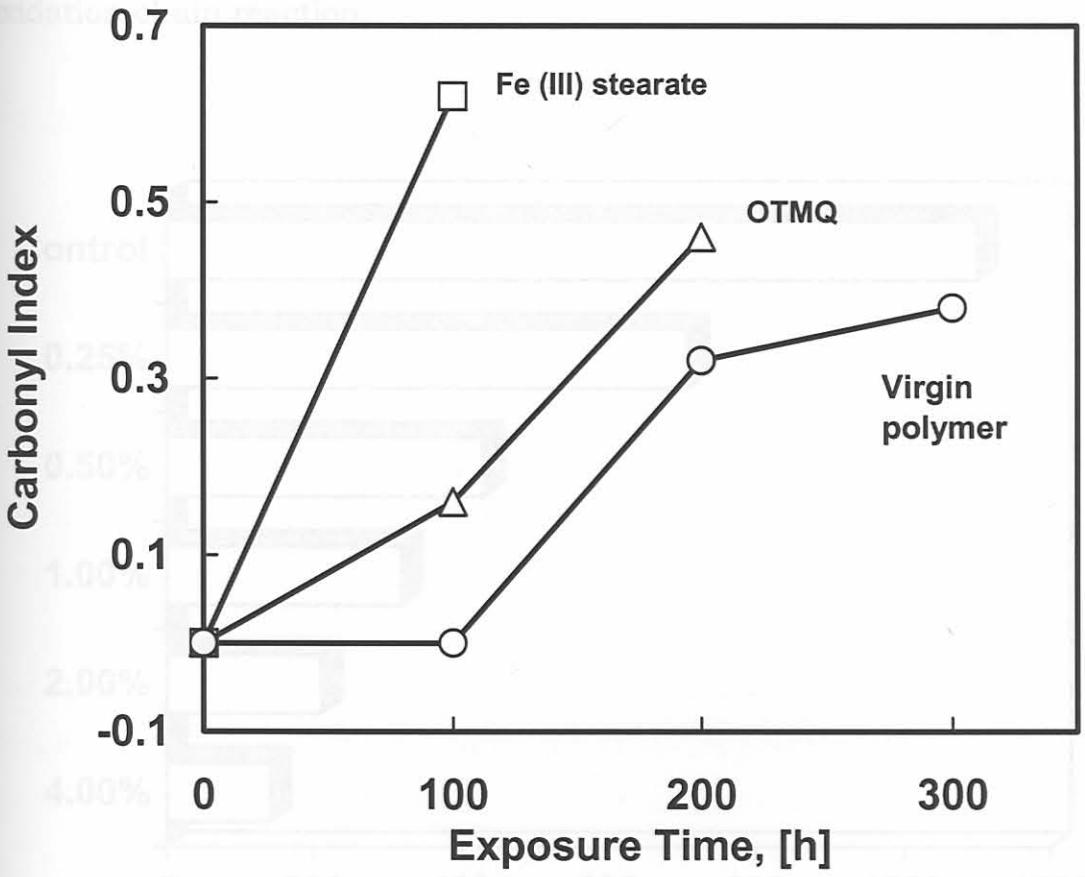


Figure 4.4 Effect of ferric stearate and OTMQ on the UV degradation of polypropylene film. Additives dosage level was 1,0 %. Films were weathered in a QUV tester fitted with A340 lamps using a dry cycle (temperature: 45°C).

The oxidation rates have been determined by measuring the rate of carbonyl growth in the films through FT-IR analysis and the respective absorption peak maxima. Embrittlement values for the films are normally taken at 0.1 carbonyl units as a comparison of stabilities. The weathering of polyethylene (LDPE) and polypropylene (PP) leads to the production of several oxidation products. Most of these can be truly characterised and quantified with FT-IR. Several mechanisms have been proposed to explain chemical changes during UV exposure of polyethylene (LDPE) and polypropylene (PP) in which hydroperoxy radicals play a major role in the oxidation chain reaction.

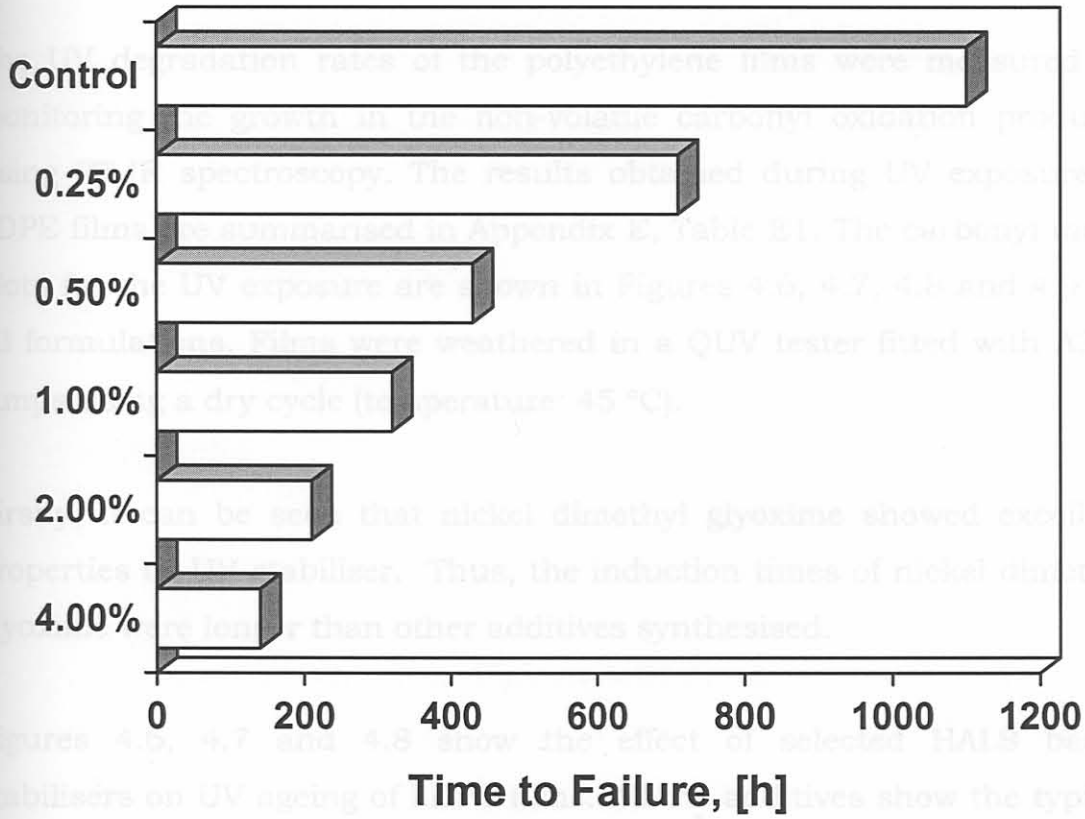


Figure 4.5 QUV photo degradation of LDPE film: Effect of the OTMQ dosage level on the time to reach a Carbonyl Index of 0,2 in polyethylene film.

It is generally accepted that hydroperoxides are the key compounds in the mechanism of photo-oxidation of polyethylene (LDPE) and polypropylene (PP). Their production is generally followed by their photochemical decomposition. Under UV exposure, the quantum yield of hydroperoxide decomposition may lead to several photo-products such as carboxylic acid, alcohol, ketone, etc...[22].

The oxidation rates of the polyethylene (LDPE) and polypropylene (PP) were measured by monitoring the growth in the non-volatile carbonyl oxidation products using FT-IR spectroscopy.

POLYETHYLENE

The UV degradation rates of the polyethylene films were measured by monitoring the growth in the non-volatile carbonyl oxidation products using FT-IR spectroscopy. The results obtained during UV exposure of LDPE films are summarised in Appendix E, Table E1. The carbonyl index plots for the UV exposure are shown in Figures 4.6, 4.7, 4.8 and 4.9 for all formulations. Films were weathered in a QUV tester fitted with A340 lamps using a dry cycle (temperature: 45 °C).

Firstly, it can be seen that nickel dimethyl glyoxime showed excellent properties as UV stabilizer. Thus, the induction times of nickel dimethyl glyoxime were longer than other additives synthesised.

Figures 4.6, 4.7 and 4.8 show the effect of selected HALS based stabilisers on UV ageing of LDPE films. All the additives show the typical induction time before oxidation commences. The observed UV stability efficiency of UV stabilisers synthesised decreased in the following order:

STEMA > BUMA > BUTA > STEDIOL > BUTOL > STETA > TOTOL > TOTA.

It is important to remark at this stage that additives STETA, TOTOL and TOTA show promising UV stabilisers properties. The oxygen scavenging activity of STETA, TOTOL and TOTA is good and this behavior can help to enhance the UV stability of the films by preventing the growth of hydroperoxides. Simultaneously, this would also protect the HALS functionality.

It is very likely that certain intramolecular interactions between the moieties of the molecule can be taking place. Anox 20 is very effective as antioxidant and this behavior combined with the ability of hindered piperidines to react with oxygen and alkyl radicals result in synergism.
On the other hand, the phenomenon of synergism was not observed in the mixture of other additives (STEMA, BUMA, BUTA, STEDIOL and BUTOL) and Anox 20. Furthermore, the induction time was decreasing and the carbonyl induction was very high.

Figure 4.9 shows the effect of nickel dimethyl glyoxime on the UV degradation of LDPE films. The result is encouraging and it can be seen that this additive presents excellent properties as UV stabiliser.

POLYPROPYLENE

The results observed when the PP films were subjected to UV exposure are summarised in Appendix E, Table E2. The carbonyl index plots for the UV exposure are shown in Figures 4.10, 4.11, 4.12 and 4.13. Films were weathered in a QUV tester fitted with A340 lamps using a dry cycle (temperature: 45 °C). It is clear that polypropylene is more susceptible to degradation than polyethylene. As before, all graphs show a typical induction time before oxidation starts.

The UV stability efficiency of the synthesized additives in polypropylene films increased in the following order:

BUDIOL<BUTA<BUMA<STEMA<BUTOL<TOTOL<STEDIOL<TOTA<STETA

STETA showed the highest UV stabilisation activity of the additives synthesised. Chmela and Hrdlovic [18] previously noted similar behavior. Additive TOTA showed only a moderate activity as an ultraviolet stabiliser for PP films.

Figure 4.13 shows the effect of nickel dimethyl glyoxime alone and together with Anox 20 on the UV degradation of PP films. Films were weathered in a QUV tester fitted with A340 lamps using a dry cycle (temperature: 45 °C).

The result is very encouraging. Addition of Anox 20 marginally improved the performance of the nickel dimethyl glyoxime.

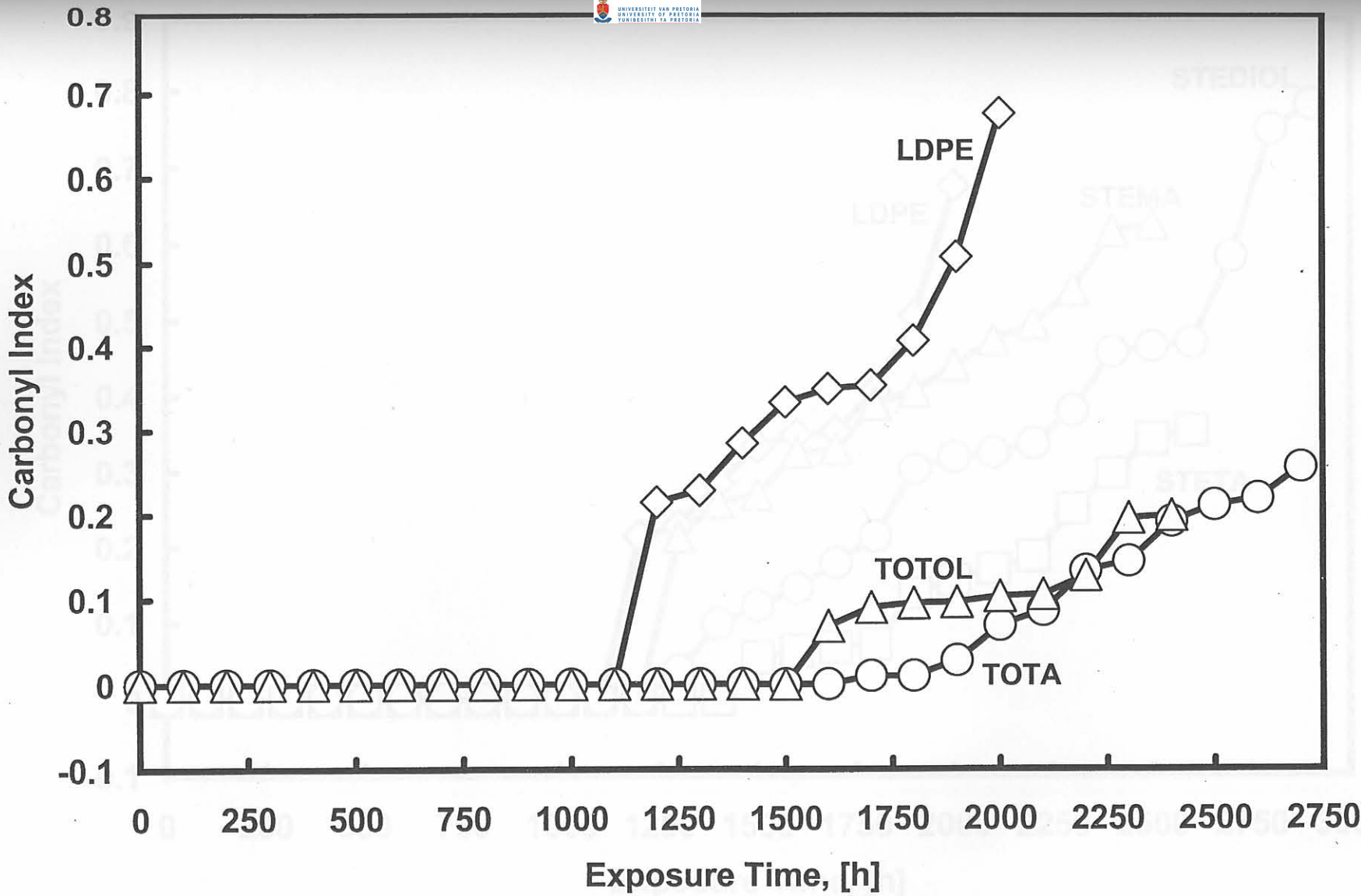


Figure 4.6 Effect of selected synthesised UV stabilisers (TOTOL and TOTA) on the UV degradation of LDPE film. Additives dosage level was 0.5%. Films were weathered in a QUV tester fitted with A340 lamps using a dry cycle (temperature: 45°C)

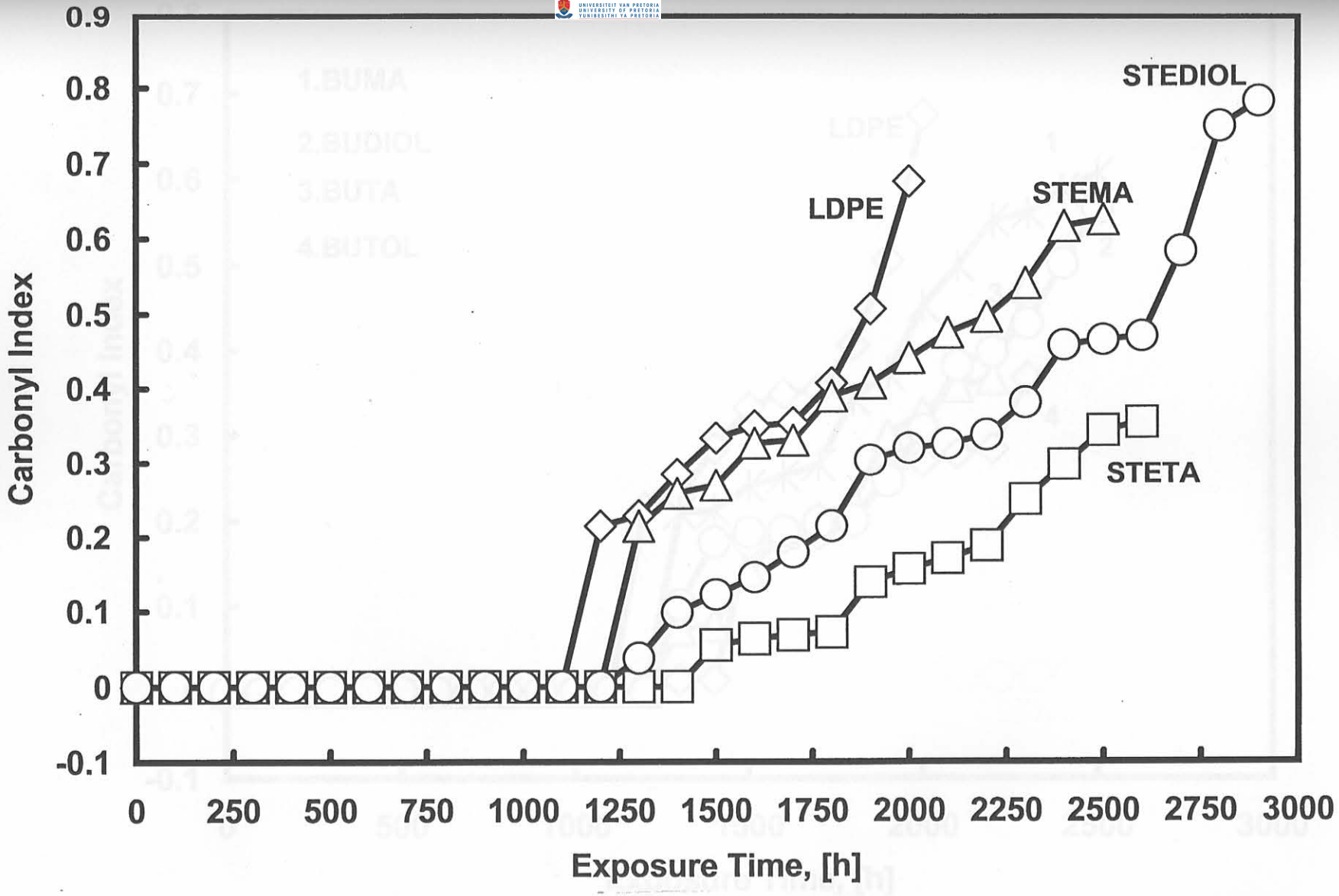


Figure 4.7 Effect of selected synthesised UV stabilisers (STEMA, STEDIOL, STETA) on the UV degradation of LDPE film. Additives dosage level was 0.5%. Films were weathered in a QUV tester fitted with A340 lamps using a dry cycle (temperature: 45°C)

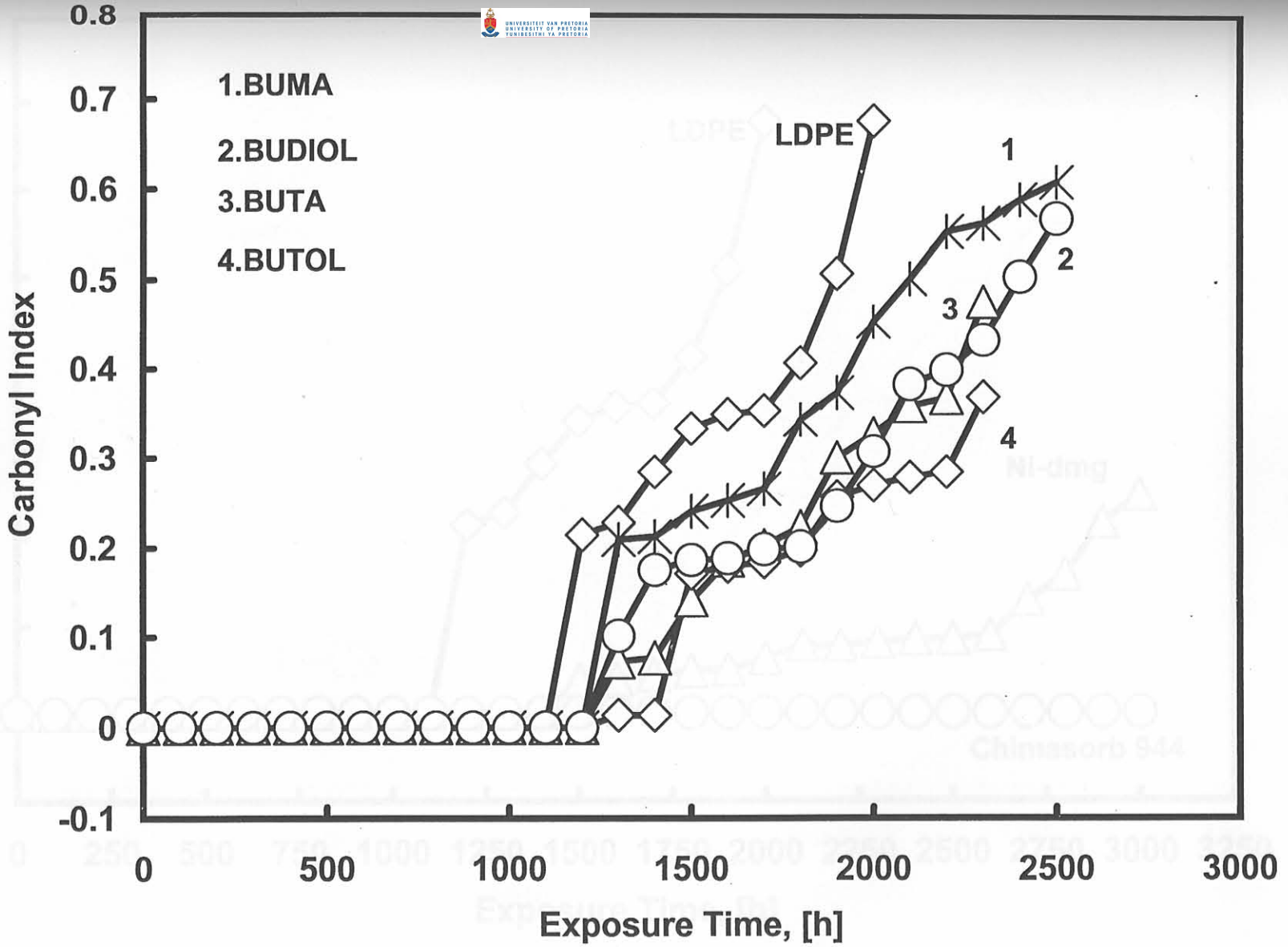


Figure 4.8 Effect of selected synthesised UV stabilisers (BUMA, BUDIOL, BUTA, BUTOL) on the UV degradation of LDPE film. Additives dosage level was 0.5%. Films were weathered in a QUV tester fitted with A340 lamps using a dry cycle

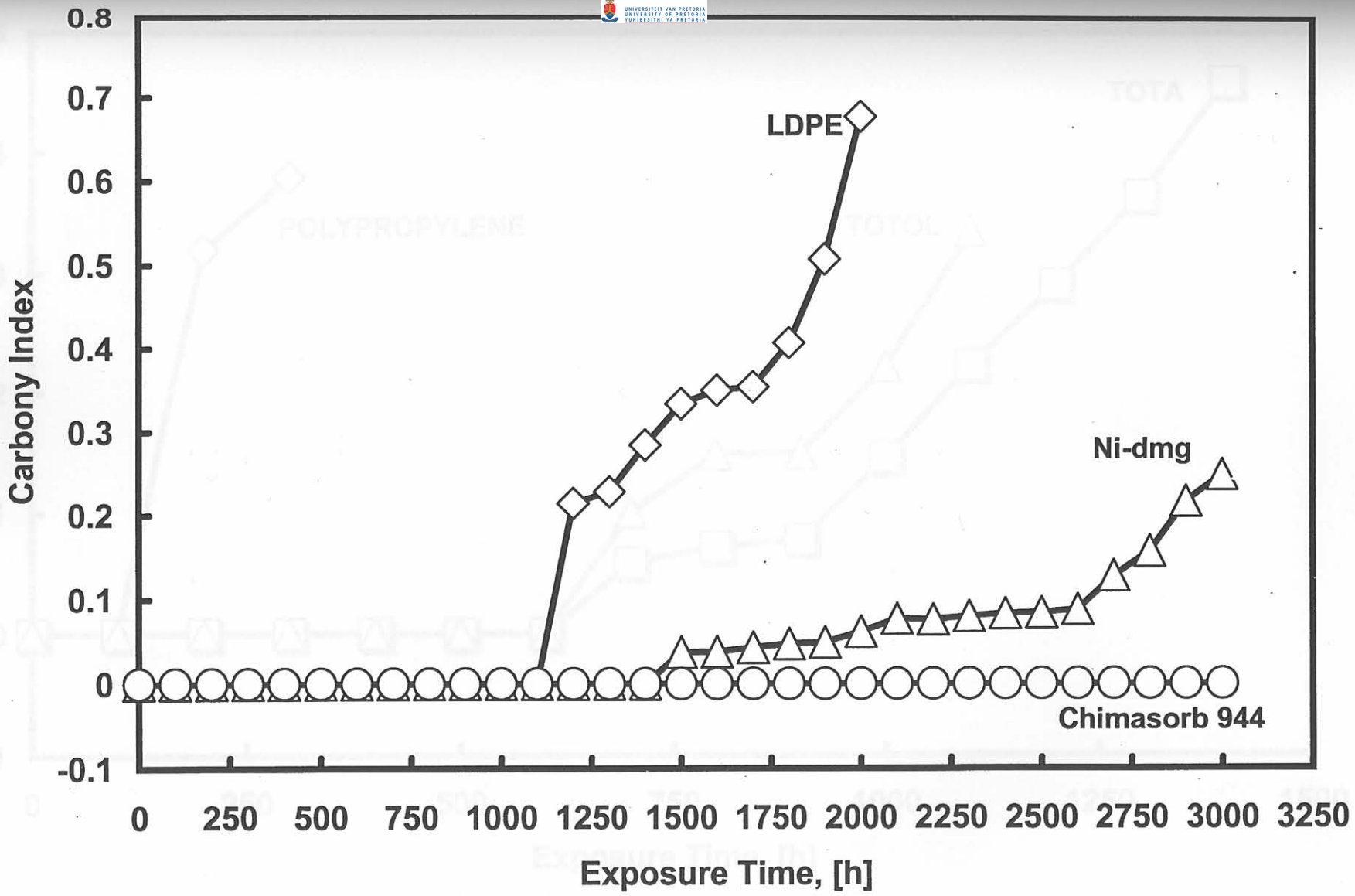


Figure 4.9 Effect of synthesised additive (Ni-dmg) and Chimasorb 944 on the UV degradation of LDPE film. Additives dosage level was 0.5%. Films were weathered in a QUV tester fitted with A340 lamps using a dry cycle (temperature: 45°C)

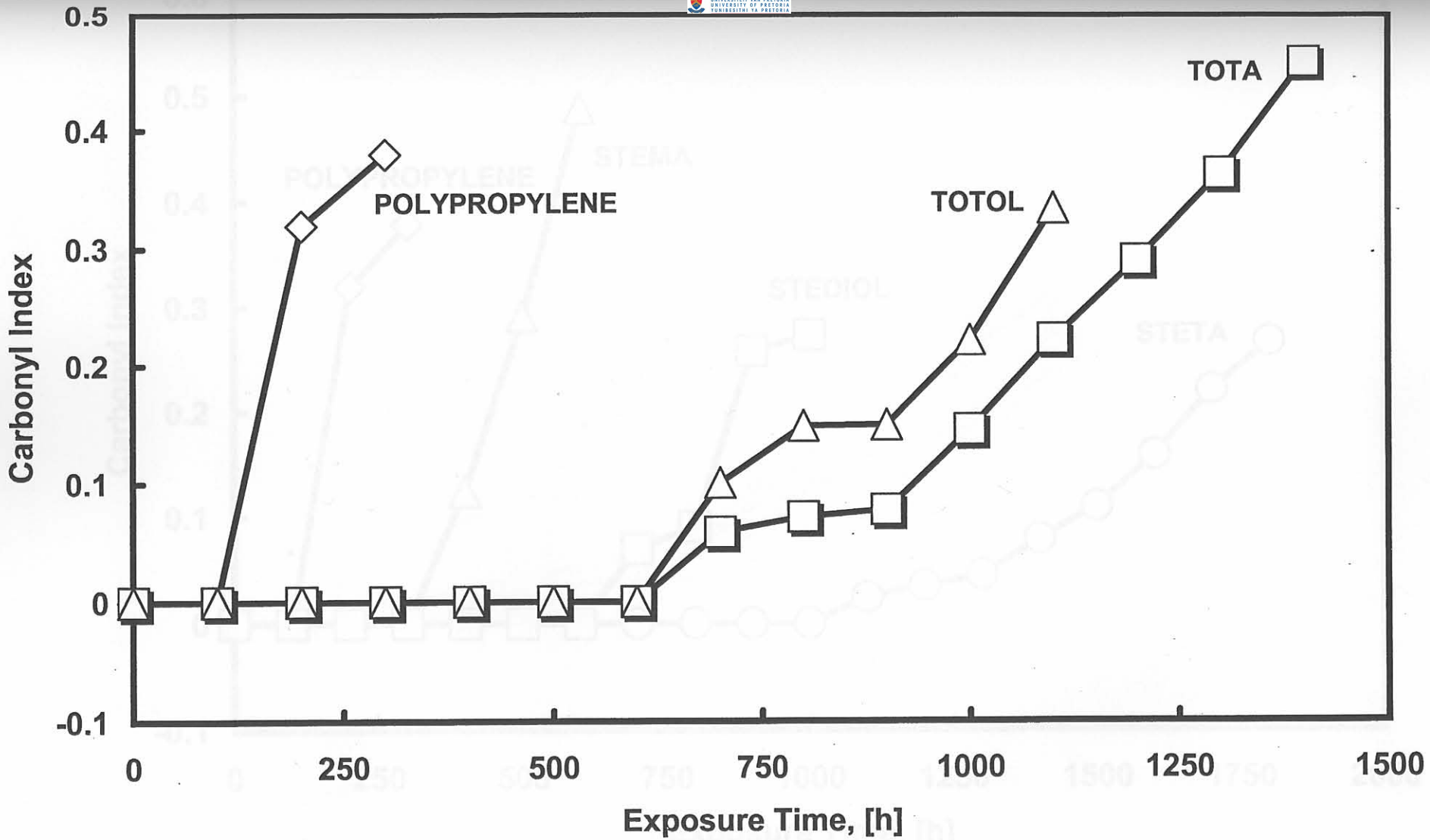


Figure 4.10 Effect of selected synthesised UV stabilisers (TOTOL and TOTA) on the UV degradation of polypropylene film. Additives dosage level was 1%. Films were weathered in a QUV tester fitted with A340 lamps using a dry cycle (temperature: 45°C).

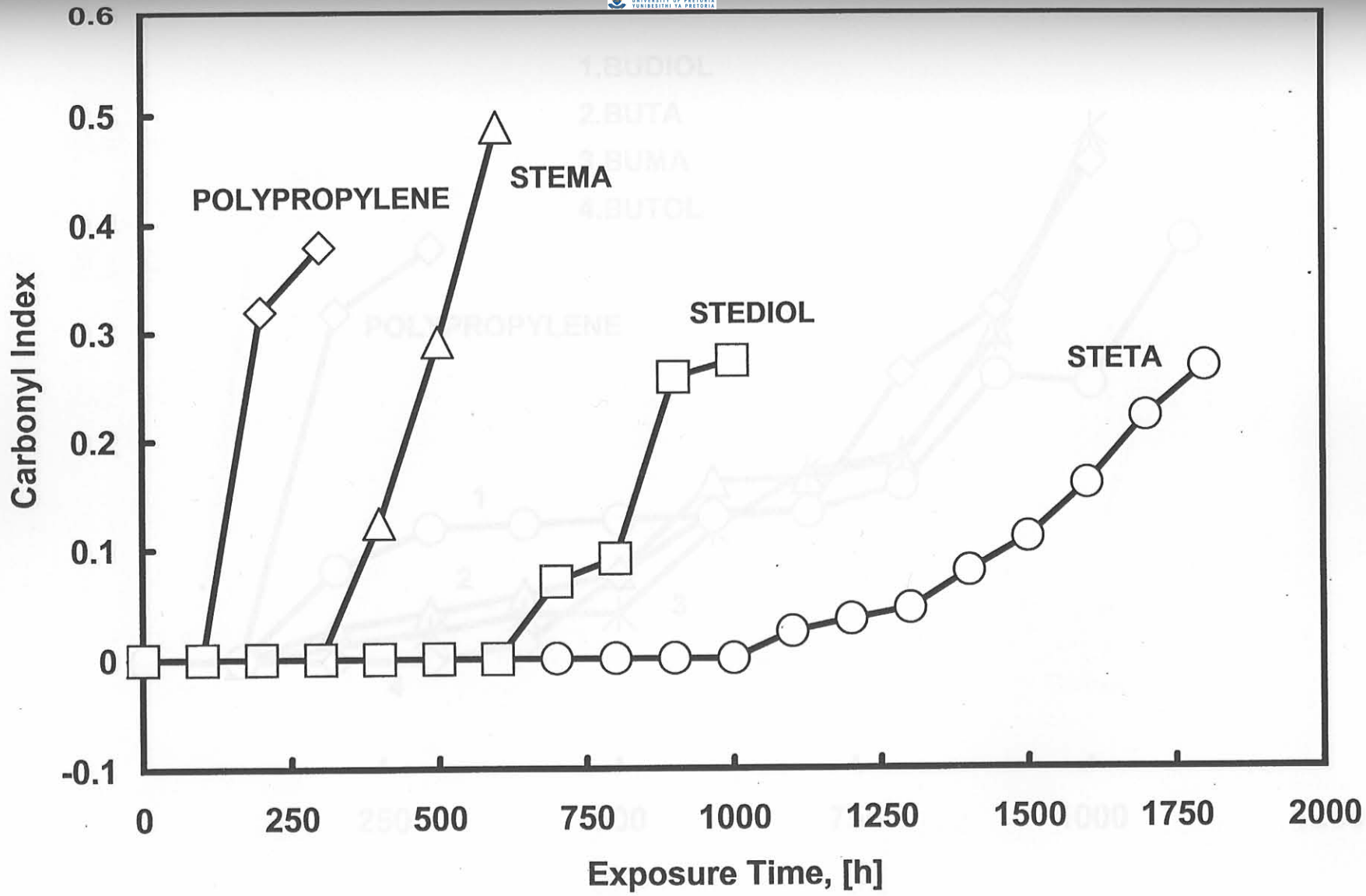


Figure 4.11 Effect of selected synthesised UV stabilisers (STEMA, STEDIOL, STETA) on the UV degradation of polypropylene film. Additives dosage level was 1%. Films were weathered in a QUV tester fitted with A340 lamps using a dry cycle (temperature: 45°C).

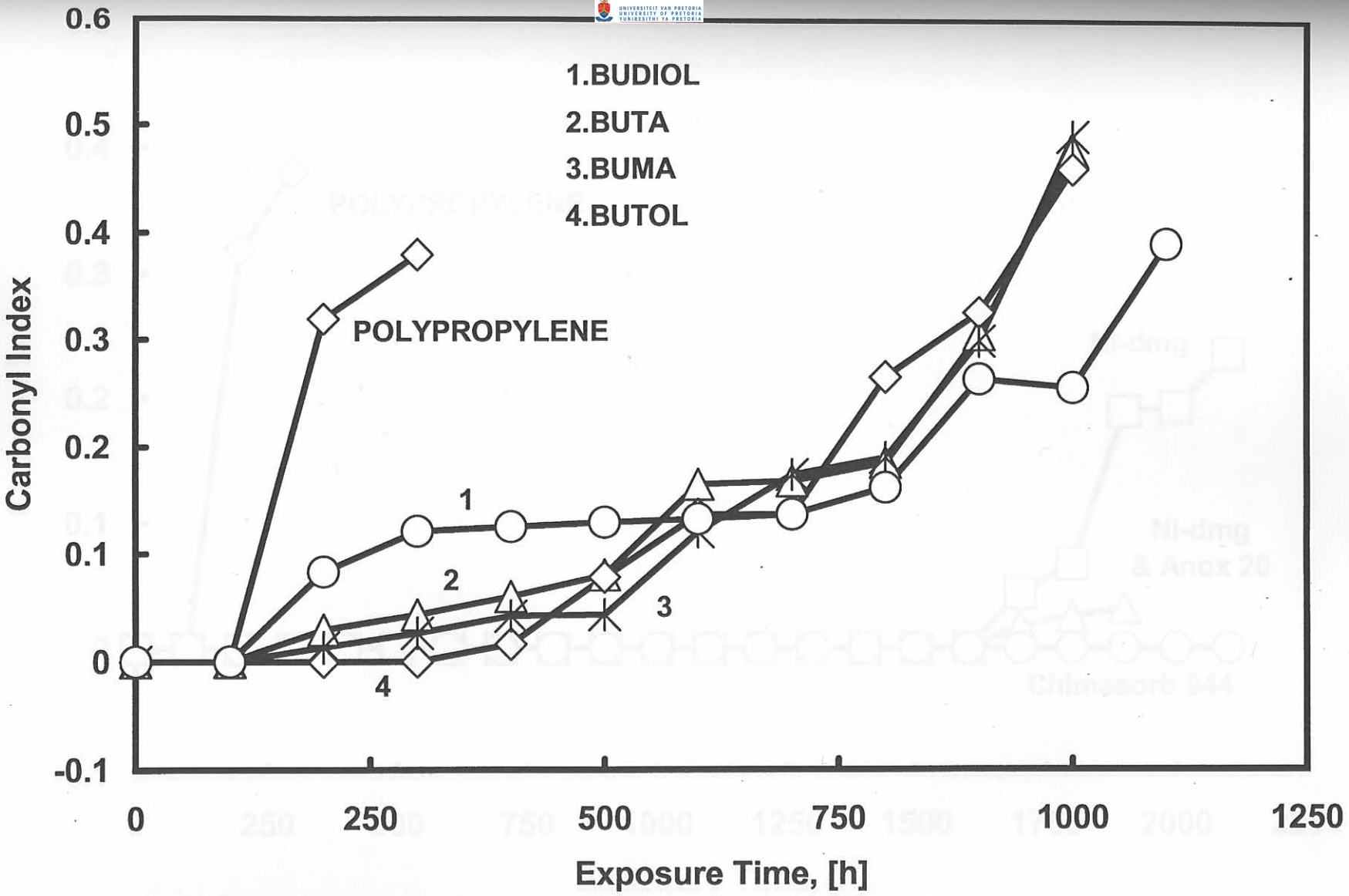


Figure 4.12 Effect of selected synthesised UV stabilisers (BUDIOL, BUTA, BUMA, BUTIOL) on the UV degradation of polypropylene film. Additives dosage level was 1%. Films were weathered in a QUV tester fitted with A340 lamps using a dry cycle (temperature: 45°C).

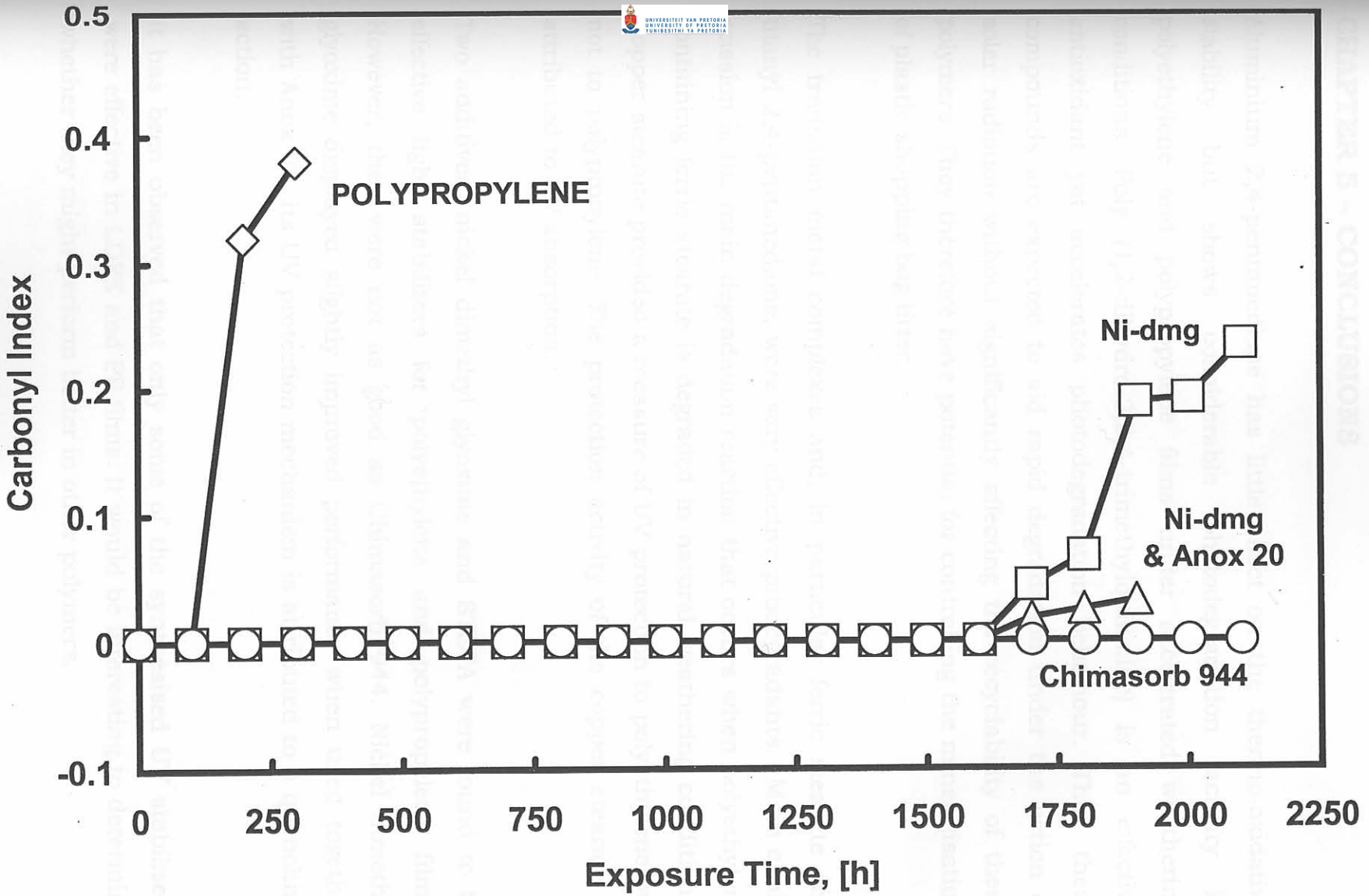


Figure 4.13 Effects of additives Ni-dmg, Ni-dmg mixed with Anox 20 and Chimasorb 944 on the UV degradation of polypropylene film. Additives dosage level were: 1% for Ni-dmg, 1% Ni-dmg mixed with 0.05% of Anox 20, and 0.5% for Chimasorb 944 as reference. Films were weathered in a QUV tester fitted with A340 lamps using a dry cycle (temperature: 45°C).

CHAPTER 5 – CONCLUSIONS

Aluminium 2,4-pentanedione has little effect on the thermo-oxidative stability but shows considerable photodegradation activity in polyethylene and polypropylene films under accelerated weathering conditions. Poly (1,2-dihydro-2,2,4-trimethylquinoline) is an effective antioxidant yet accelerates photodegradation behaviour. Thus these compounds are expected to aid rapid degradation under the action of solar radiation without significantly affecting the recyclability of these polymers. They therefore have potential for controlling the mineralisation of plastic shopping bag litter.

The transition metal complexes and, in particular ferric stearate and titanyl 2,4-pentanedione, were very effective prodegradants. Main chain scission is the main degradation reaction that occurs when polyethylene containing ferric stearate is degraded in natural weathering conditions. Copper stearate provided a measure of UV protection to polyethylene but not to polypropylene. The protection activity of the copper stearate is attributed to UV absorption.

Two additives: nickel dimethyl glyoxime and STETA were found to be effective light stabilizers for polyethylene and polypropylene films. However, they were not as good as Chimasorb 944. Nickel dimethyl glyoxime displayed slightly improved performance when used together with Anox 20. Its UV protection mechanism is attributed to a quenching action.

It has been observed that only some of the synthesised UV stabilisers were effective in LDPE and PP films. It would be interesting to determine whether they might perform better in other polymers.

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APPENDICES

APPENDIX A: DSC spectra for reagents and additives synthesised

APPENDIX B: UV spectra for additives synthesised

APPENDIX C: DSC/TGA traces for additives synthesised

APPENDIX D: DSC OIT scans

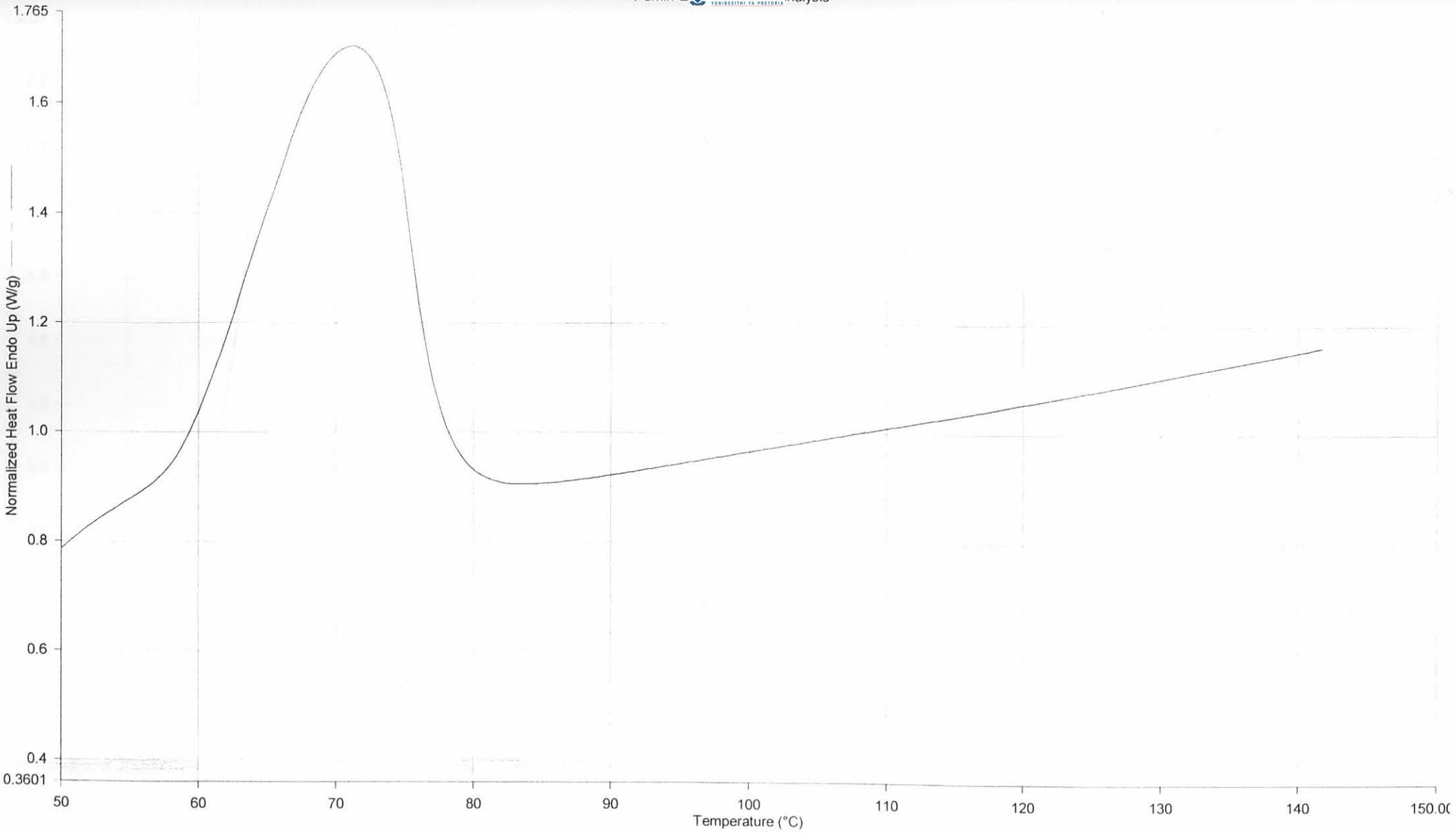
APPENDIX E: Table E1: Measured Carbonyl Indices for weathered LDPE film samples

Table E2: Measured Carbonyl Indices for weathered Polypropylene film samples

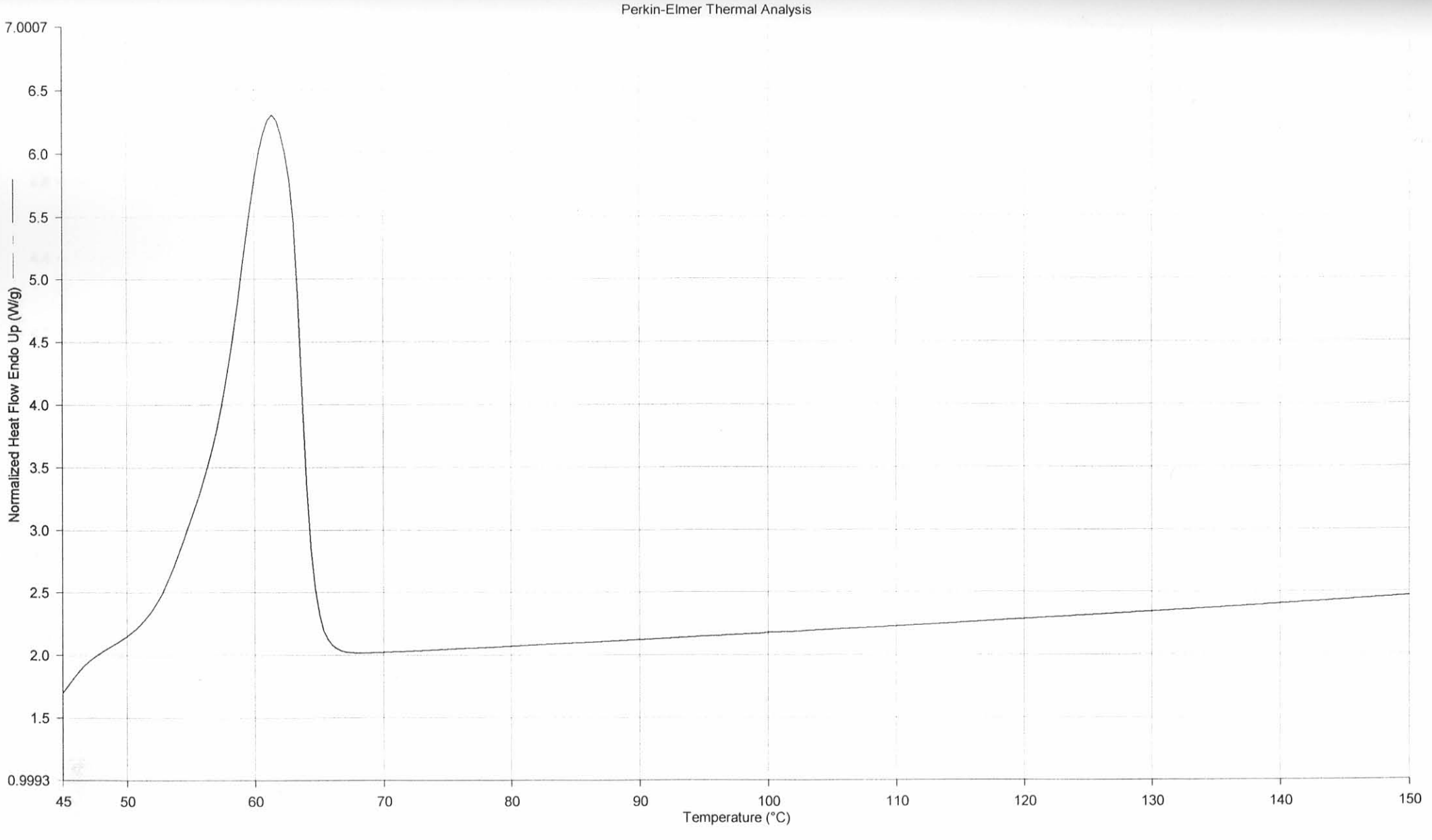
APPENDIX A

DSC spectra for reagents and additives synthesised

Figure	Reagents and additive
A1	Melting scan for polycaprolactone (Tone 767 ex Union Carbide)
A2	Melting scan for stearic acid (Aldrich)
A3	Melting scan for polybutylene succinate (grade Bionolle#1001)
A4	Melting scan for TAA-OL (Creanova)
A5	Melting scan for N-HE-TAA-OL (Creanova)
A6	Melting scan for N-METYL-TAA-OL (Creanova)
A7	Melting scan for Imino-bis ethanol (Creanova)
A8	Melting scan for TOTOL
A9	Melting scan for STETA
A10	Melting scan for STEMA
A11	Melting scan for STEDIOL
A12	Melting scan for BUTA
A13	Melting scan for BUTOL
A14	Melting scan for BUMA
A15	Melting scan for BUDIOL
A16	Melting scan for OTMQ

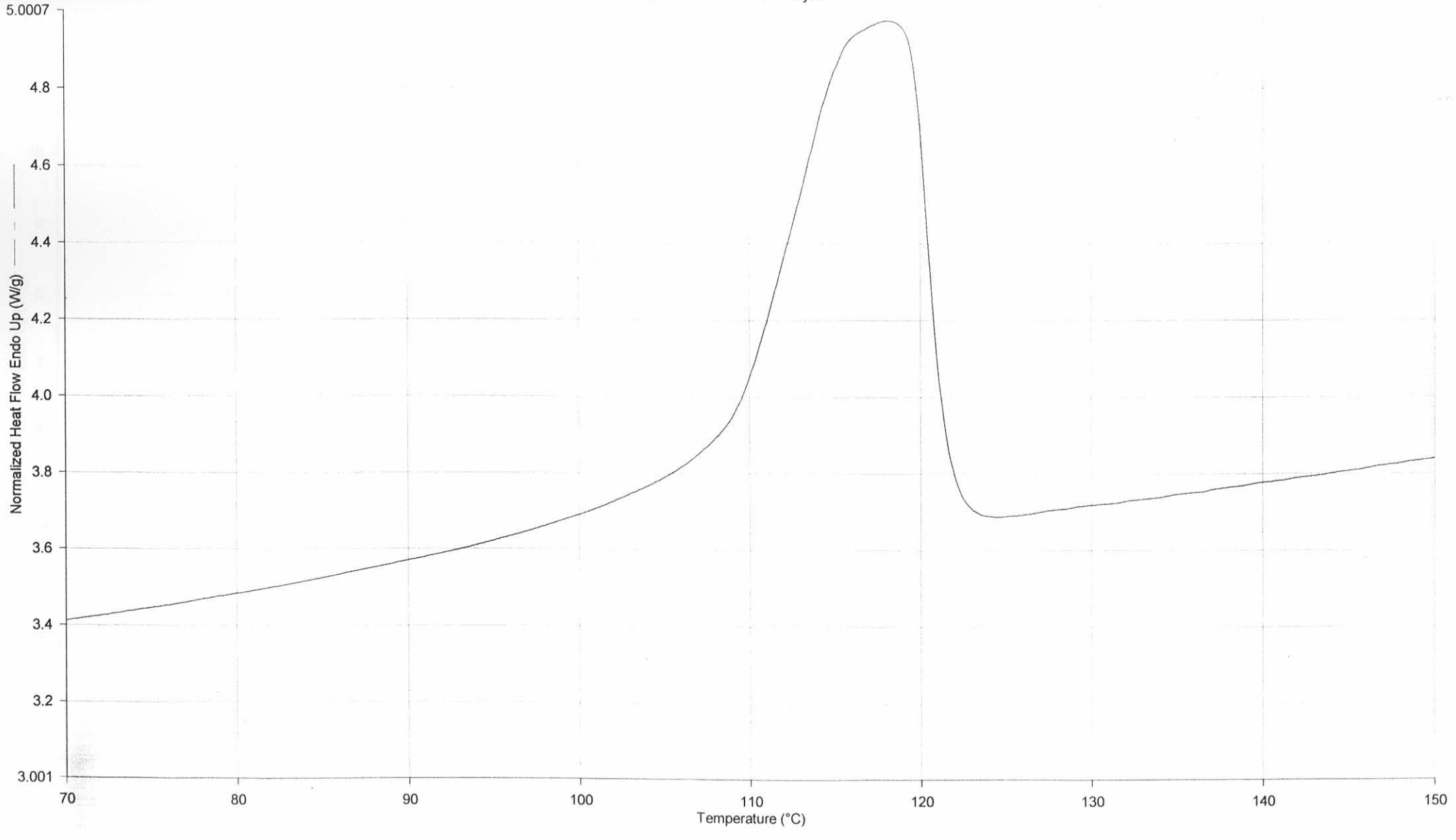

1.765
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.3601
Normalized Heat Flow Endo Up (W/g)
50
60
70
80
90
100
110
120
130
140
150.0(
Temperature (°C)

Sample Weight: 20.150 mg
Comment:



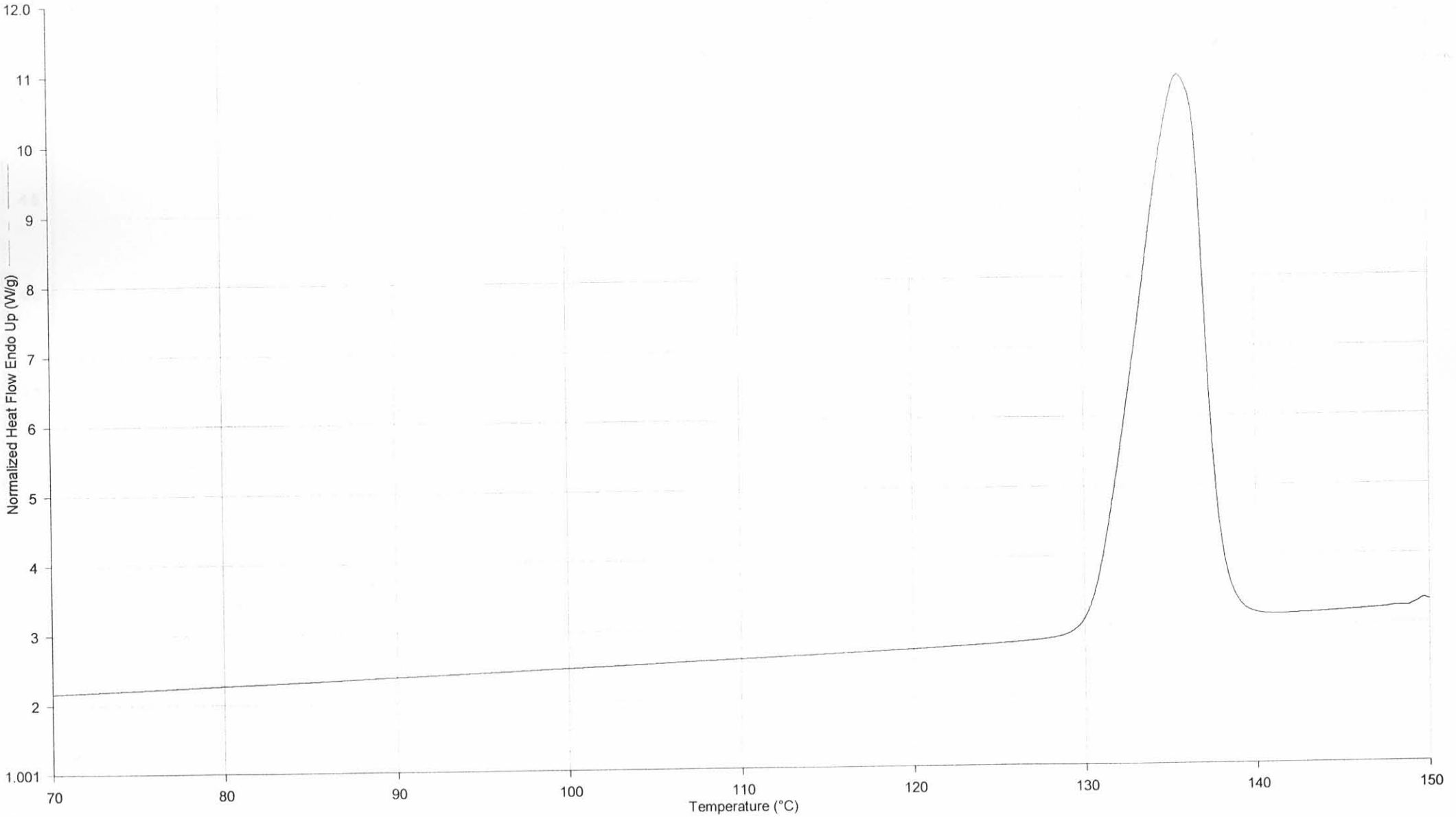
Sample Weight: 13.780 mg
Comment: Samples for Walter

Perkin-Elmer Thermal Analysis



Sample ID: [illegible]
Sample Weight: 13.170 mg
Comment: Samples for Walter

Perkin-Elmer Thermal Analysis



9/20/00 1:23:45 PM

Sample Weight: 13.680 mg
Comment: Samples for Walter

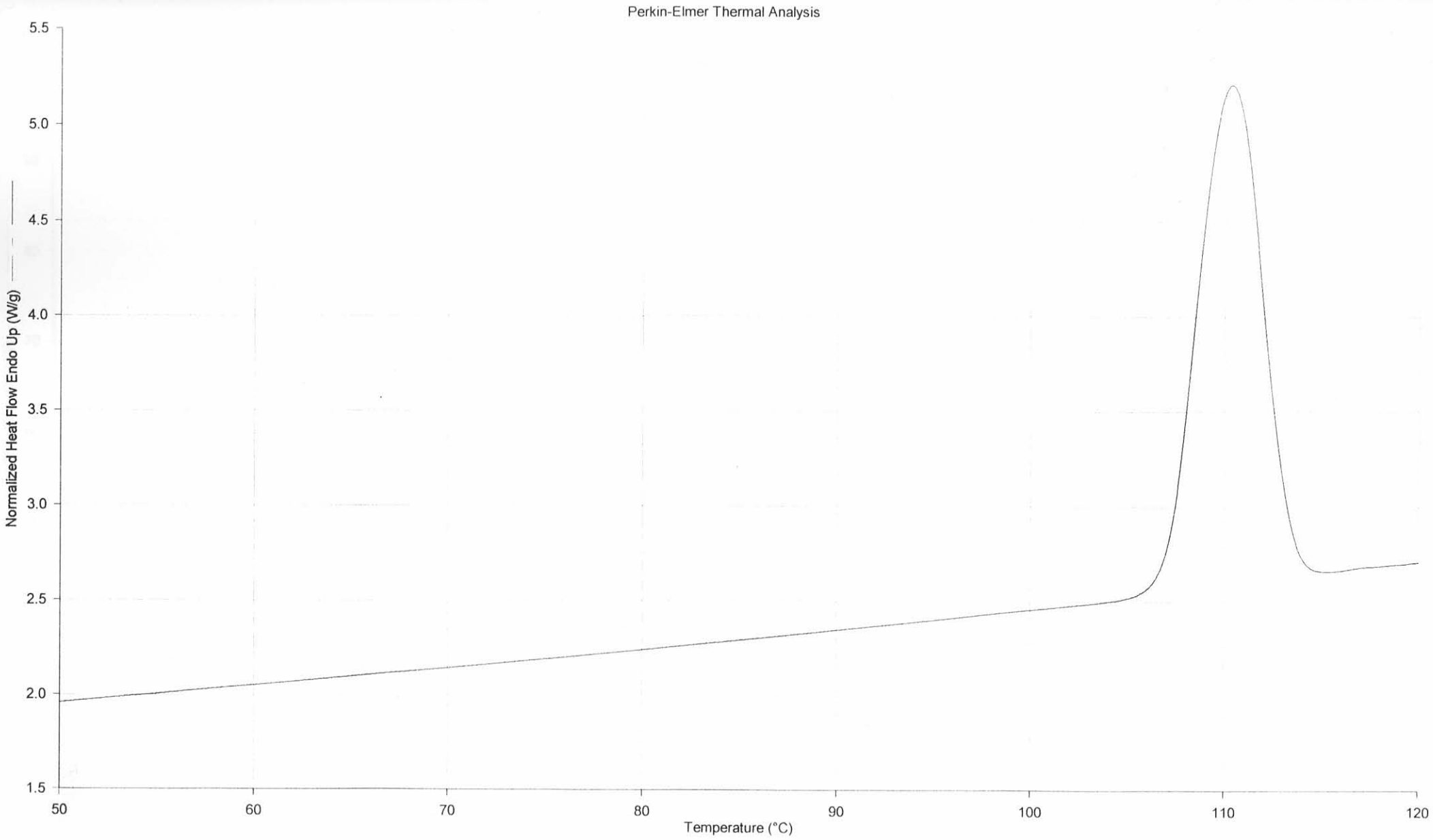
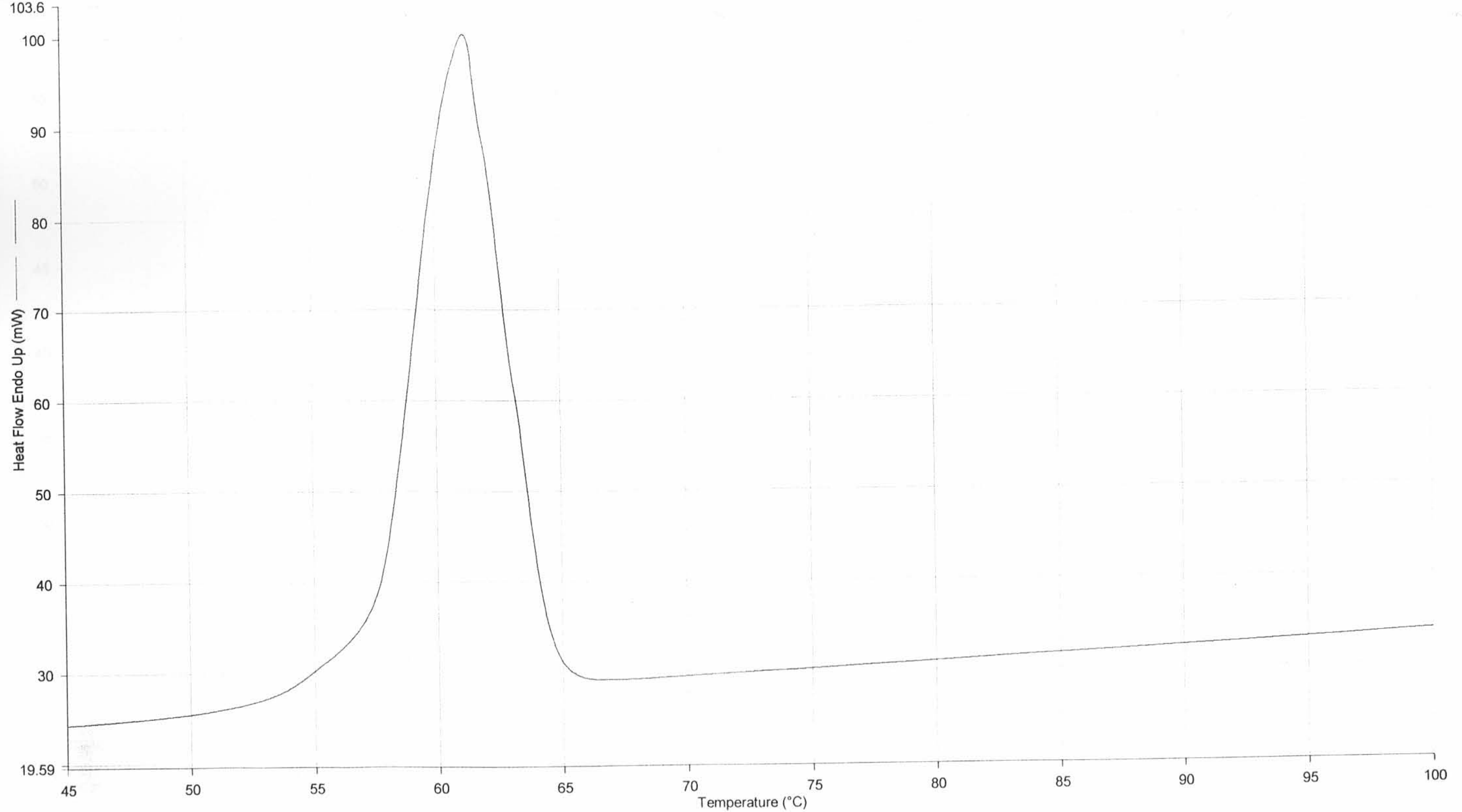


Figure A5 Melting scan for 4-Hydroxy-2,2,6,6-Tetramethyl piperidin-1-Ethanol

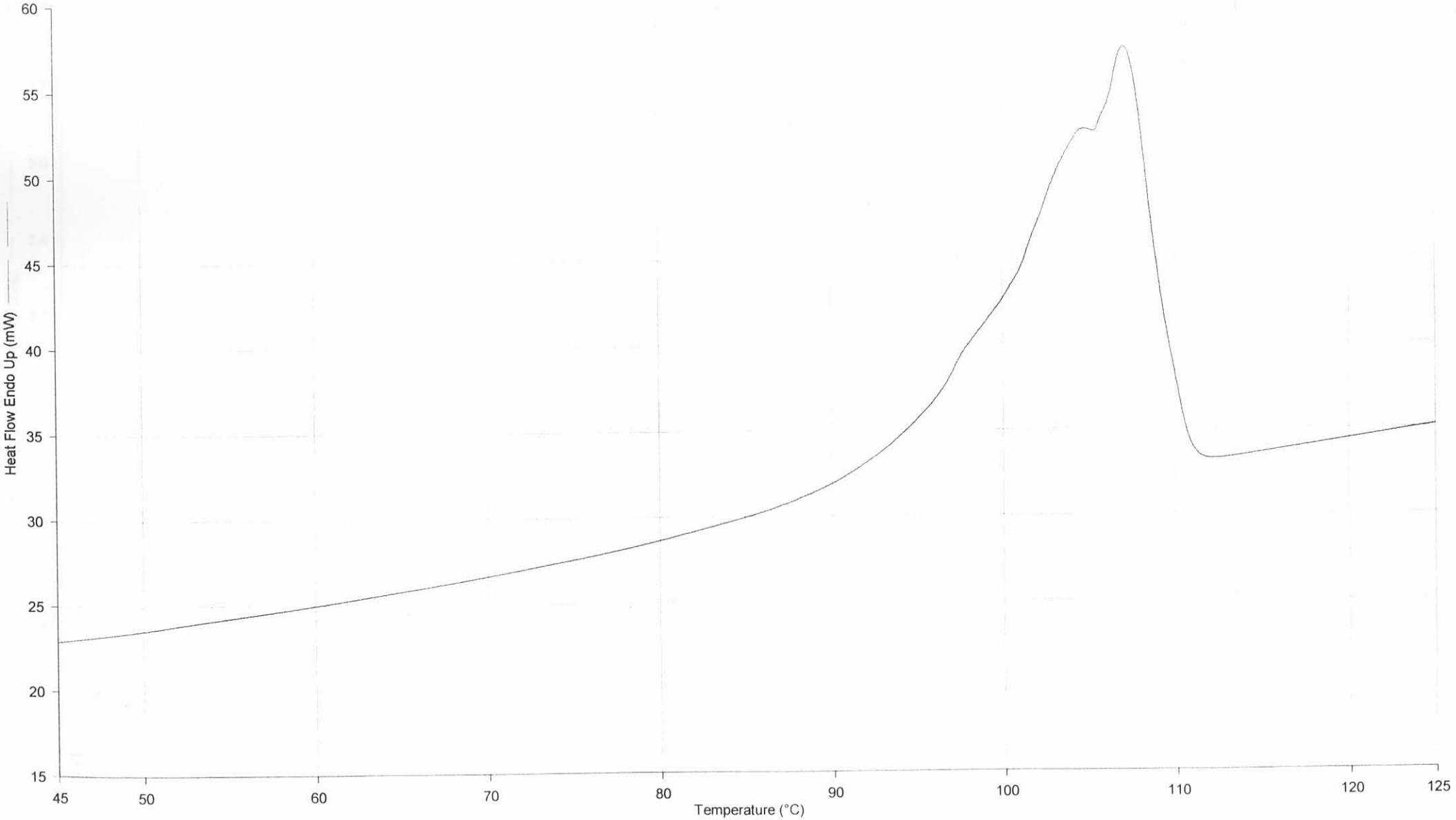
Sample Weight: 14.350 mg
Comment: Samples for Walter

Perkin-Elmer Thermal Analysis



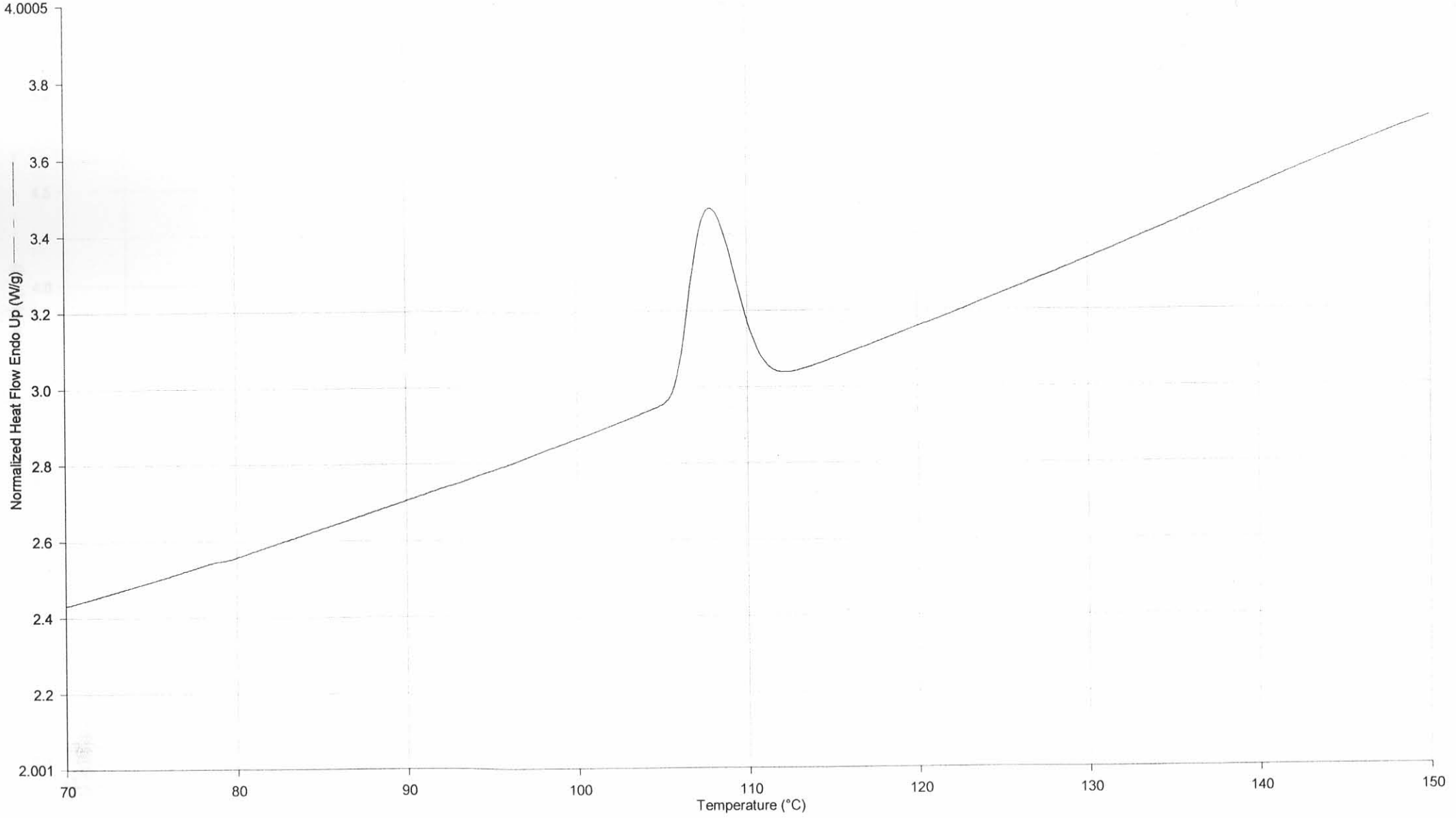
Sample ID: imino_bis_ethanol
Sample Weight: 11.490 mg
Comment: Samples for Walter

Perkin-Elmer Thermal Analysis



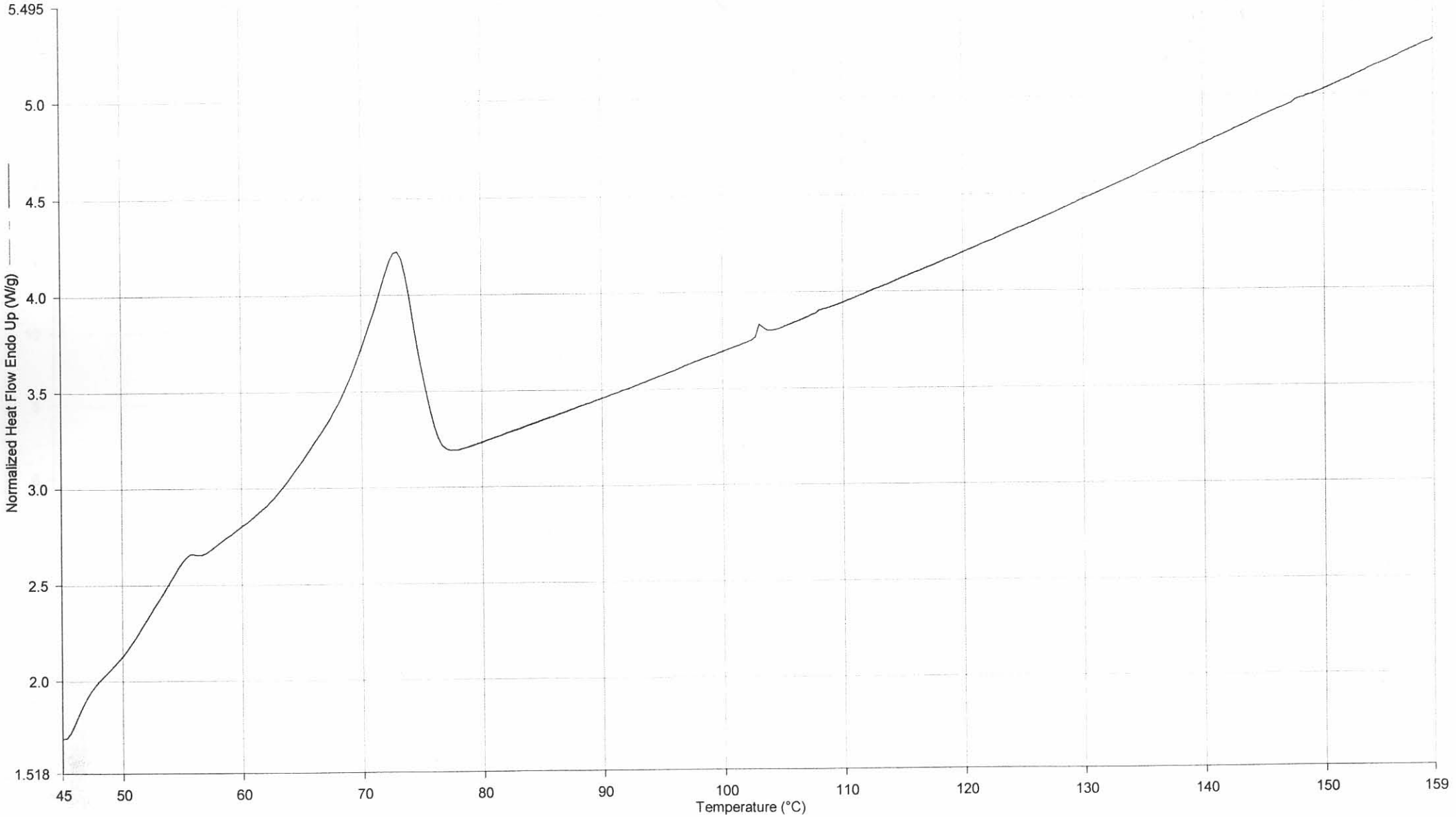
Sample ID: total
Sample Weight: 12.980 mg
Comment: Samples for Walter

Perkin-Elmer Thermal Analysis



Sample Weight: 9.600 mg
Comment:

Perkin-Elmer Thermal Analysis



9/15/00 4:18:37 PM

Sample Weight: 11.150 mg
Comment:

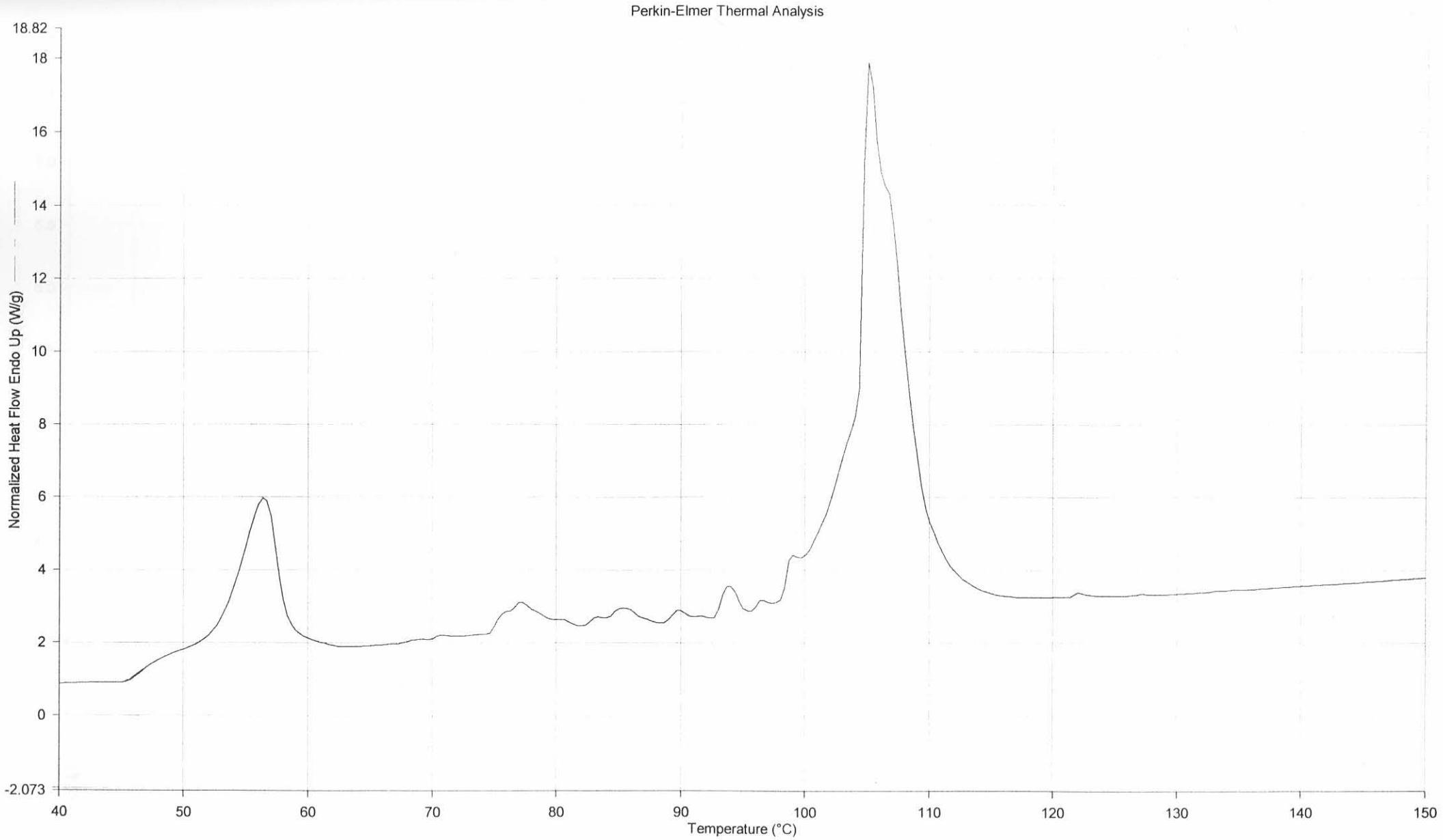
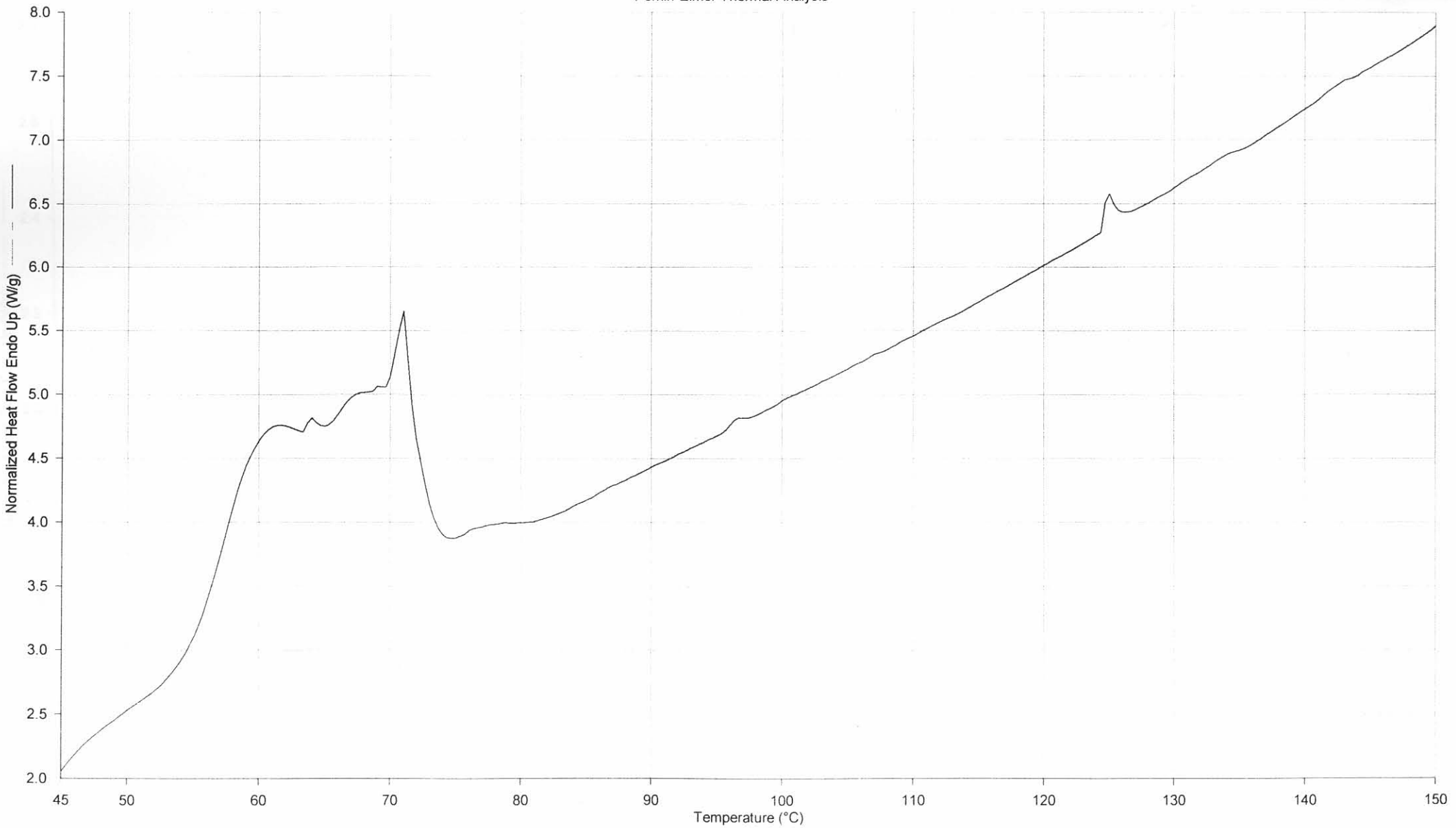
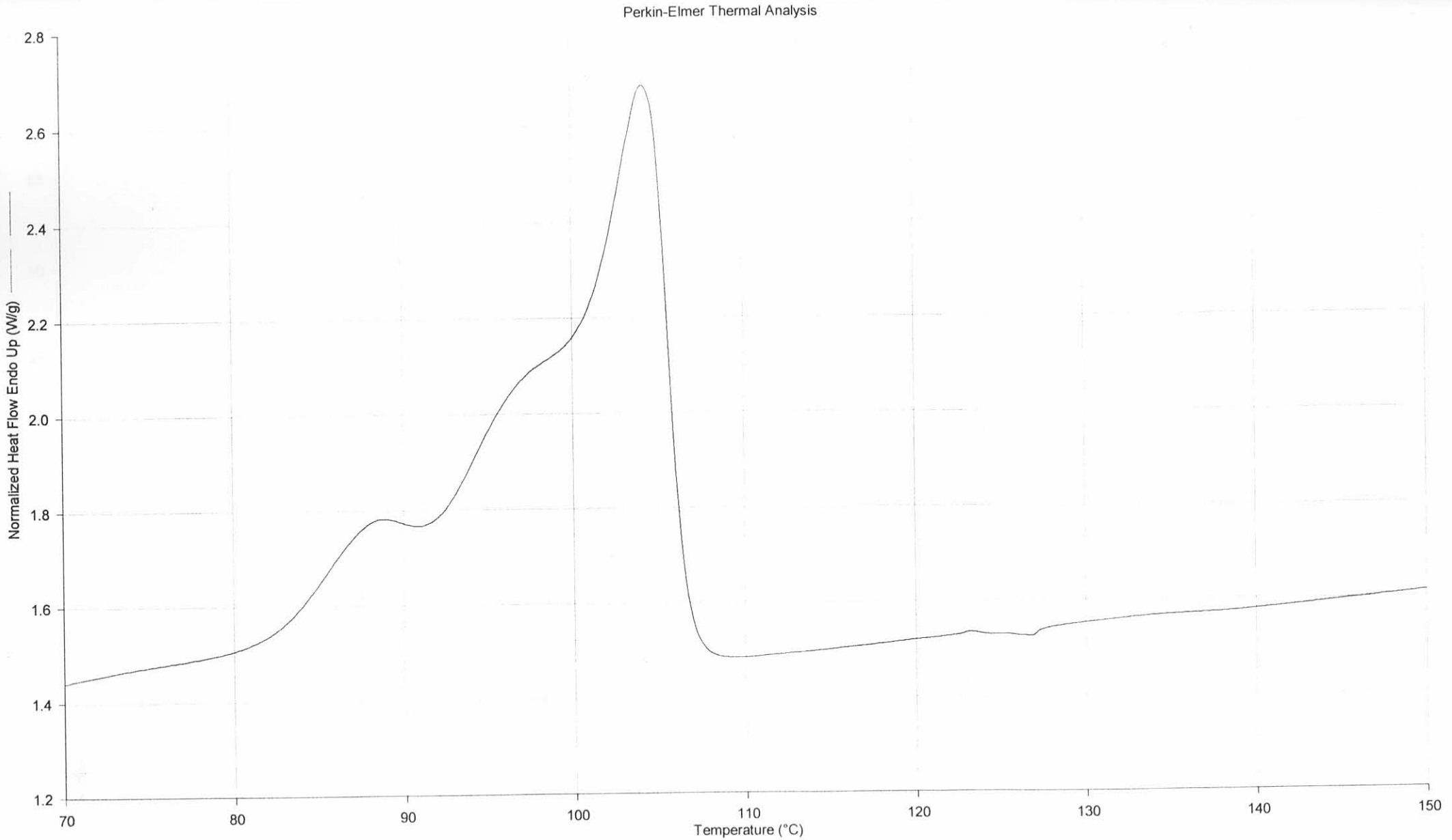


Figure A10 Melting scan for copolymer of stearic acid with N,HE-METHYL-TAA-01

Sample Weight: 10.930 mg
Comment:



Sample ID: Buta
Sample Weight: 20.170 mg
Comment: Samples for Walter



Sample ID: Butol
Sample Weight: 12.170 mg
Comment: Samples for Walter

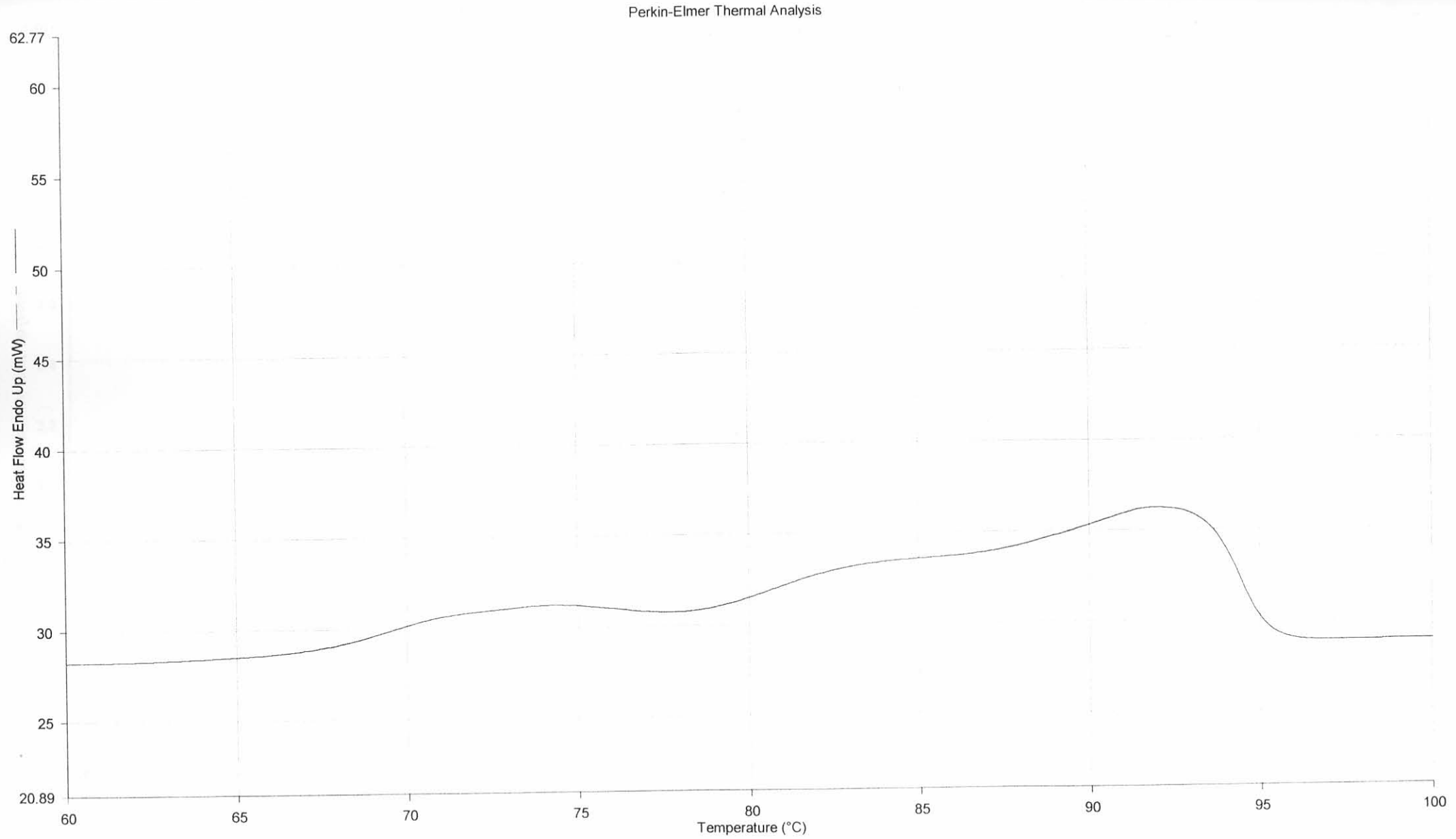
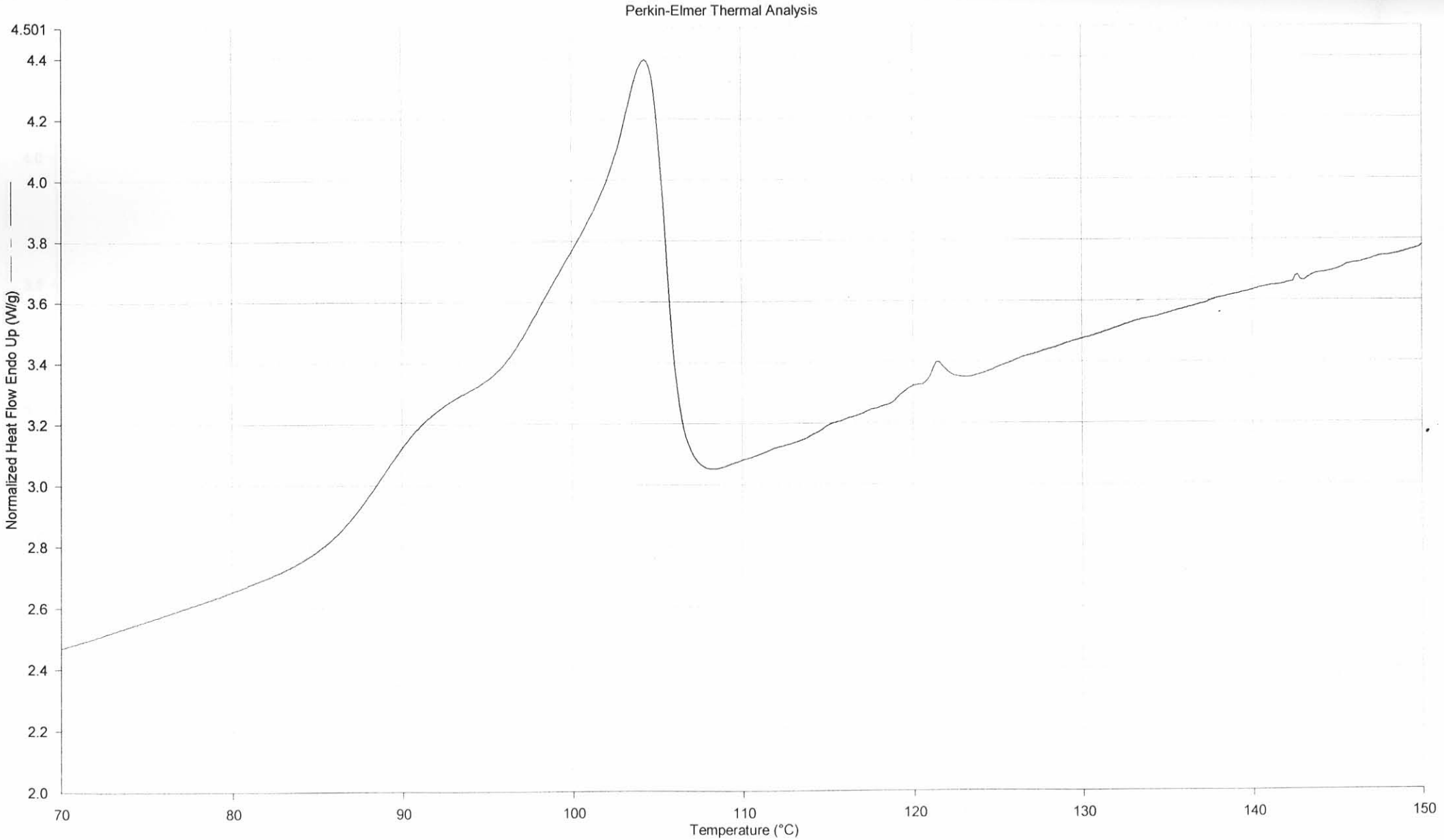


Figure A.13 Melting scan for copolymer of polybutylene succinate with

9/29/00 1:42:02 PM

Sample ID: BUMA
Sample Weight: 11.640 mg
Comment: Samples for Walter



Sample Weight: 14.850 mg
Comment: Samples for Walter

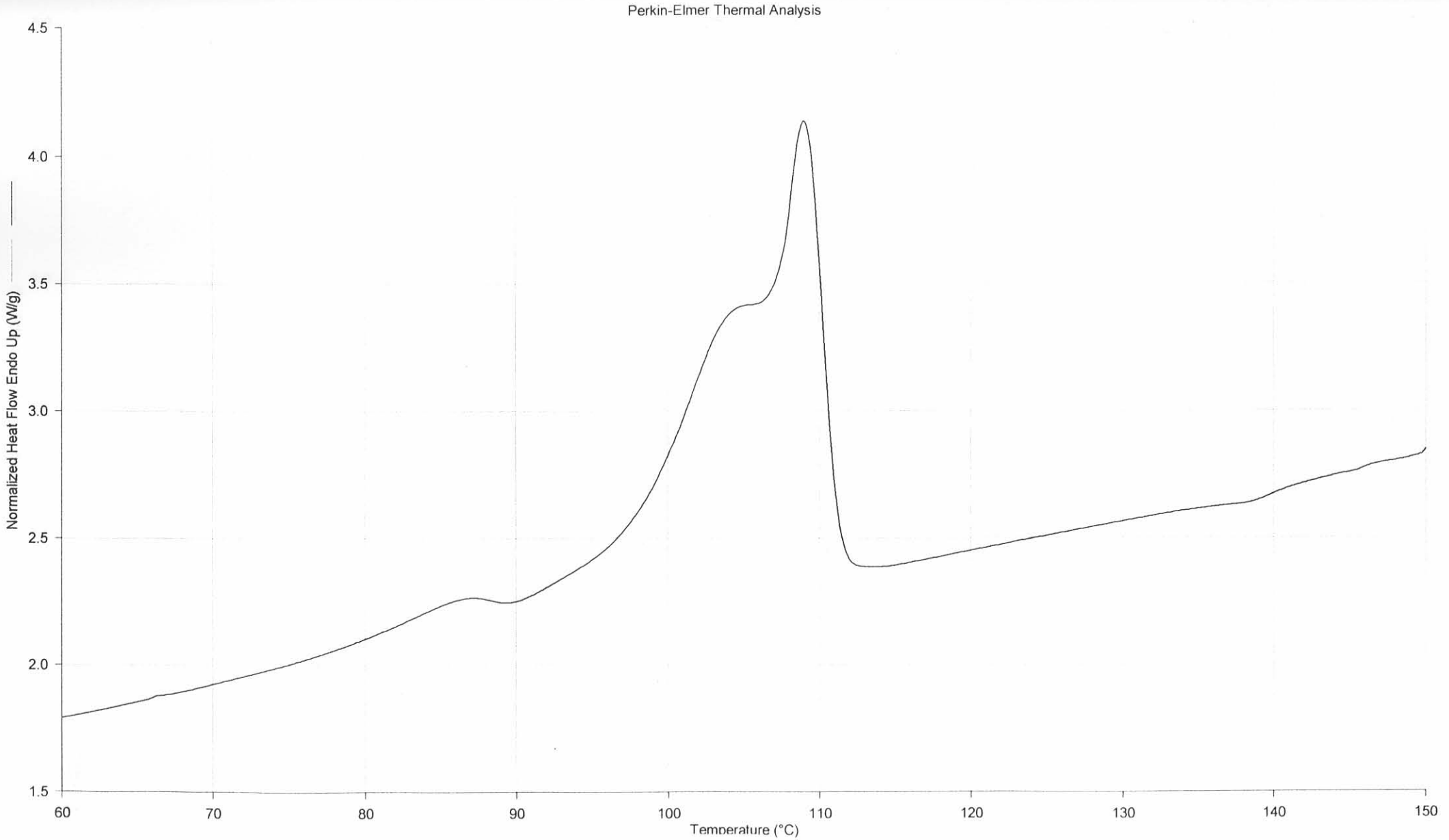
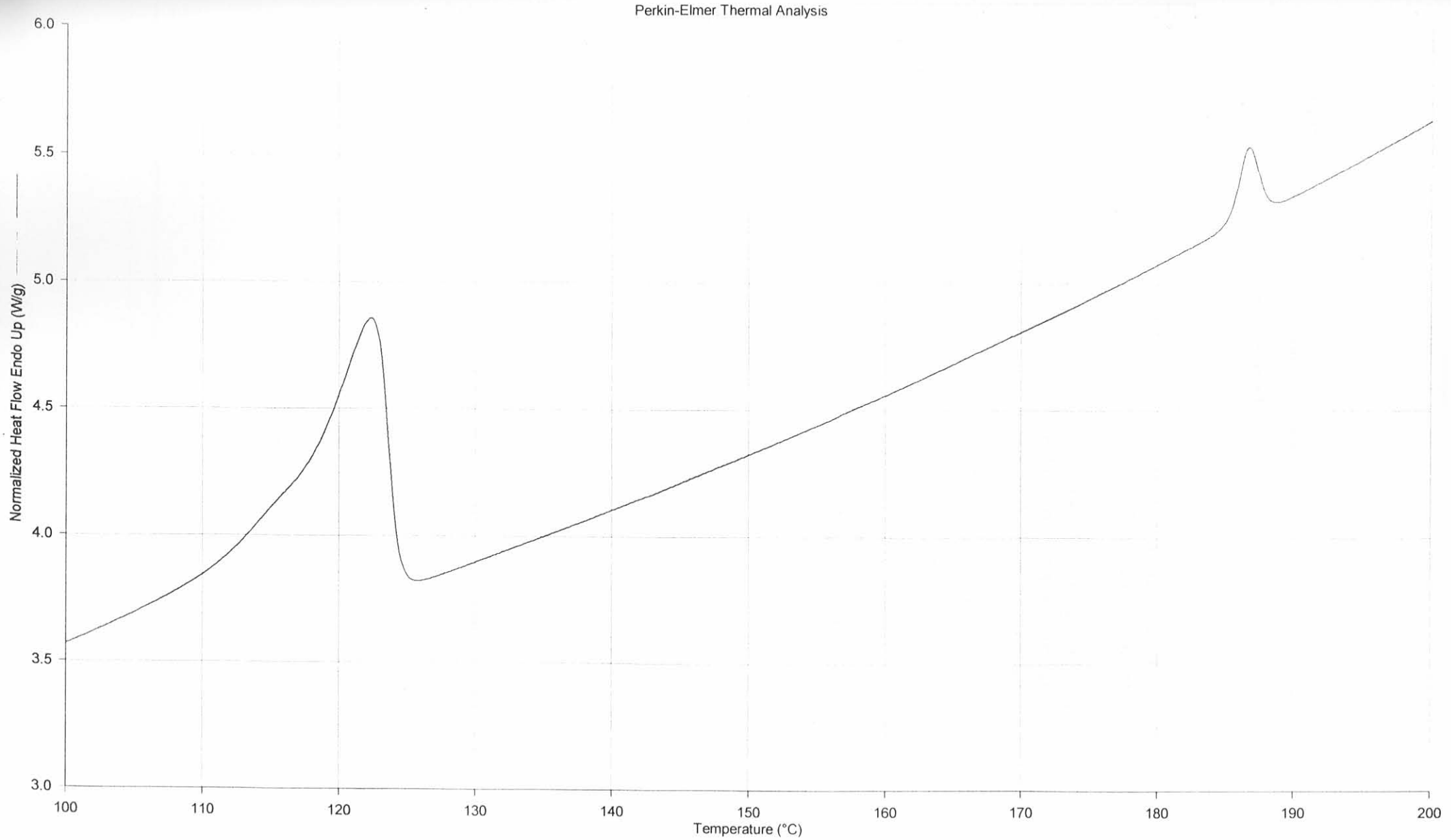


Figure A15 Melting scan for copolymer of polybutyle succinate with 2,2-(2,2,6,6-

Sample Weight: 10.480 mg
Comment: Samples for Walter



APPENDIX B

UV spectra for additives synthesised

Figure	Additives synthesised
B1	TAA-OL and stearic acid
B2	N-METHYL-TAA-OL and stearic acid
B3	Imino-bis ethanol and stearic acid
B4	TAA-OL and polybutyle succinate
B5	N-HE-TAA-OL and polybutylene succinate
B6	N-METHYL-TAA-OL and polybutylene succinate
B7	Imino-bis ethanol and polybutylene succinate
B8	Ferric stearate
B9	Nickel methyl glyoxime

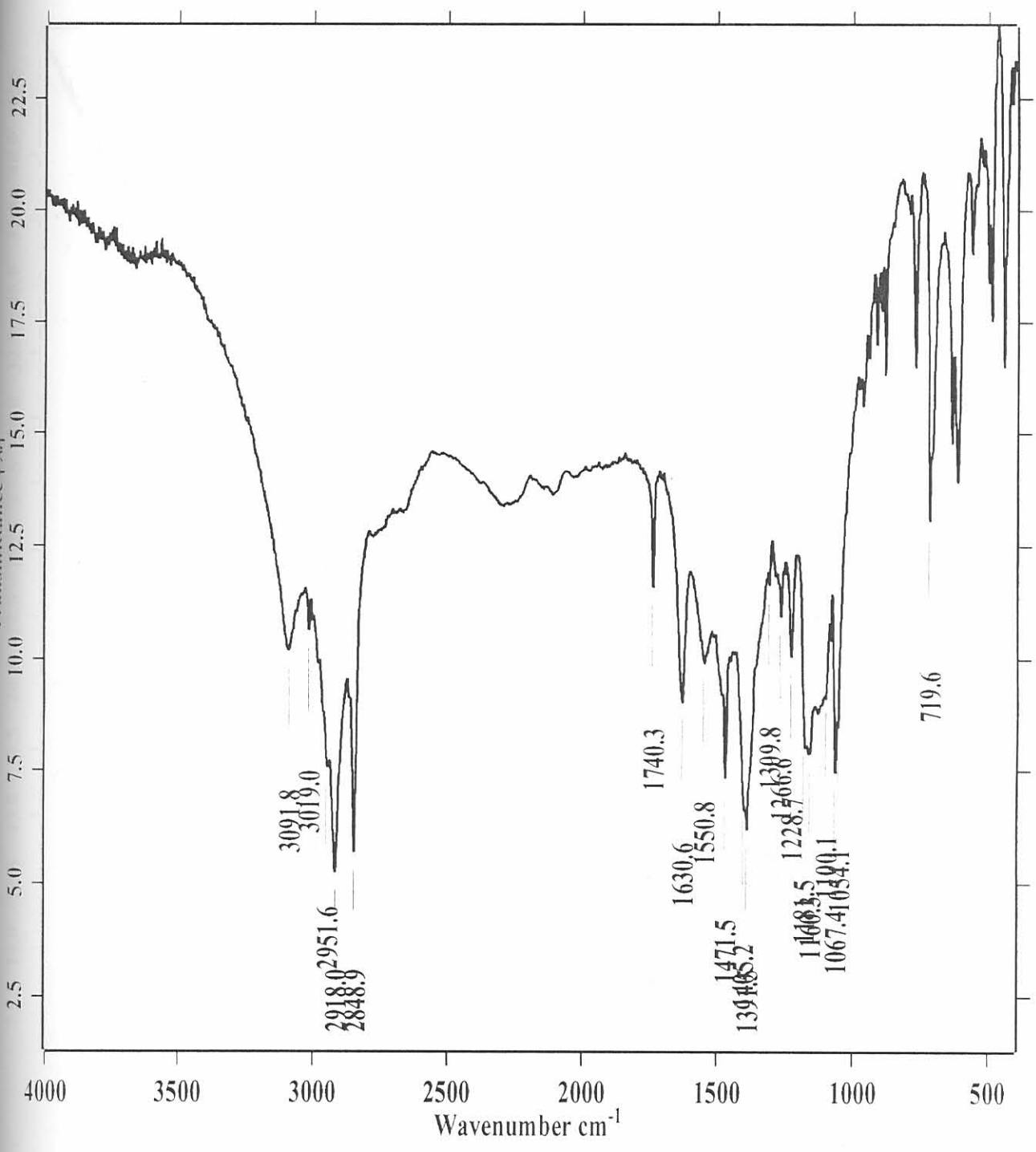


Figure B1 UV spectra for copolymer of stearic acid with TAA-OL (STETA)

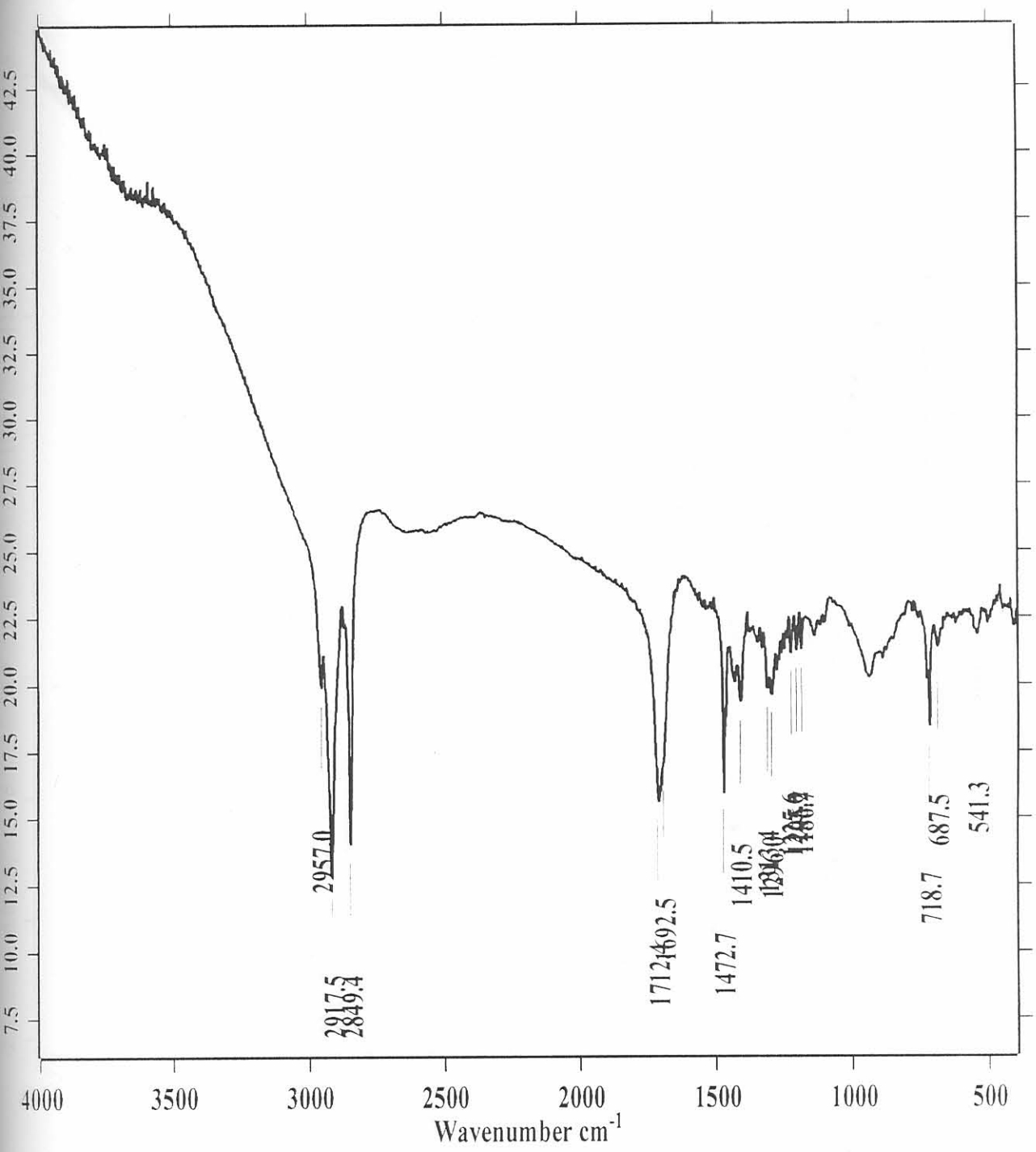


Figure B2 UV spectra for copolymer of stearic acid with N-METHYL-TAA-OL (STEMA)

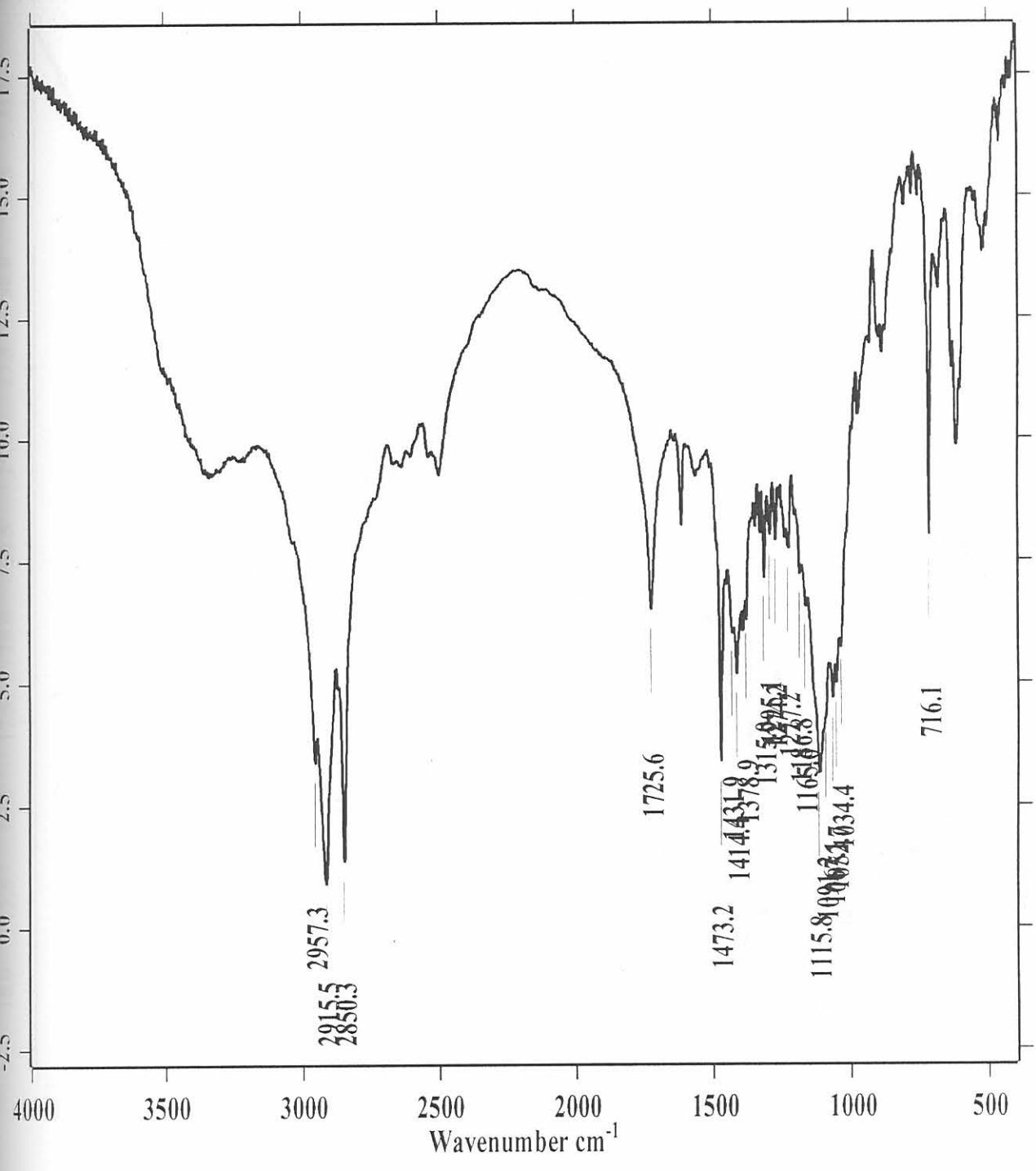


Figure B3 UV spectra for copolymer of stearic acid with 2,2-(2,2,6,6-Tetramethyl-4-piperidinyl)imino)bis(Ethanol) (STEDIOL)

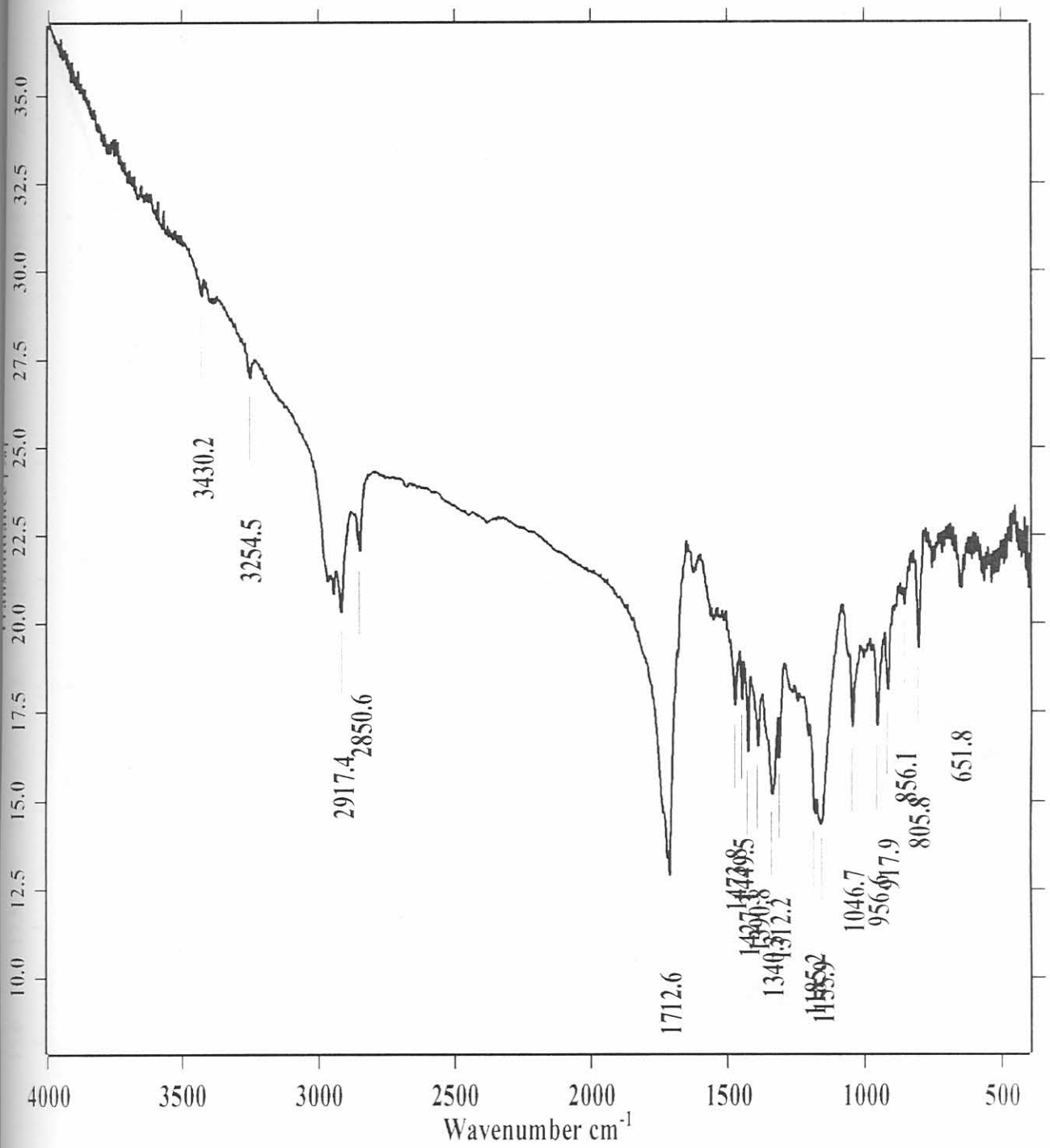


Figure B4 UV spectra for copolymer of polybutylene succinate with TAA-OL (BUTA)

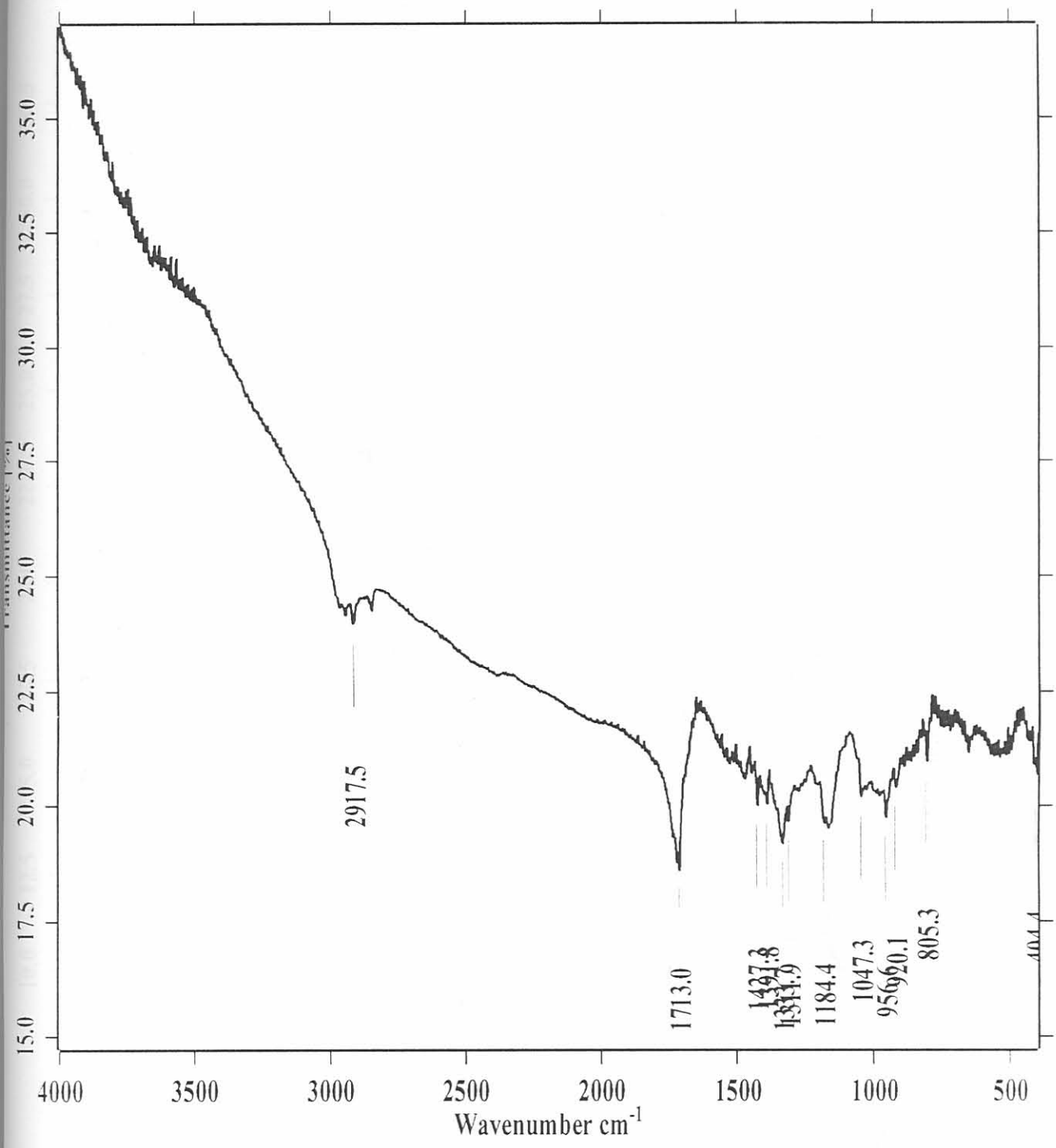


Figure B5 UV spectra for copolymer of polybutylene succinate with N-HE-TAA-OL (BUTOL)

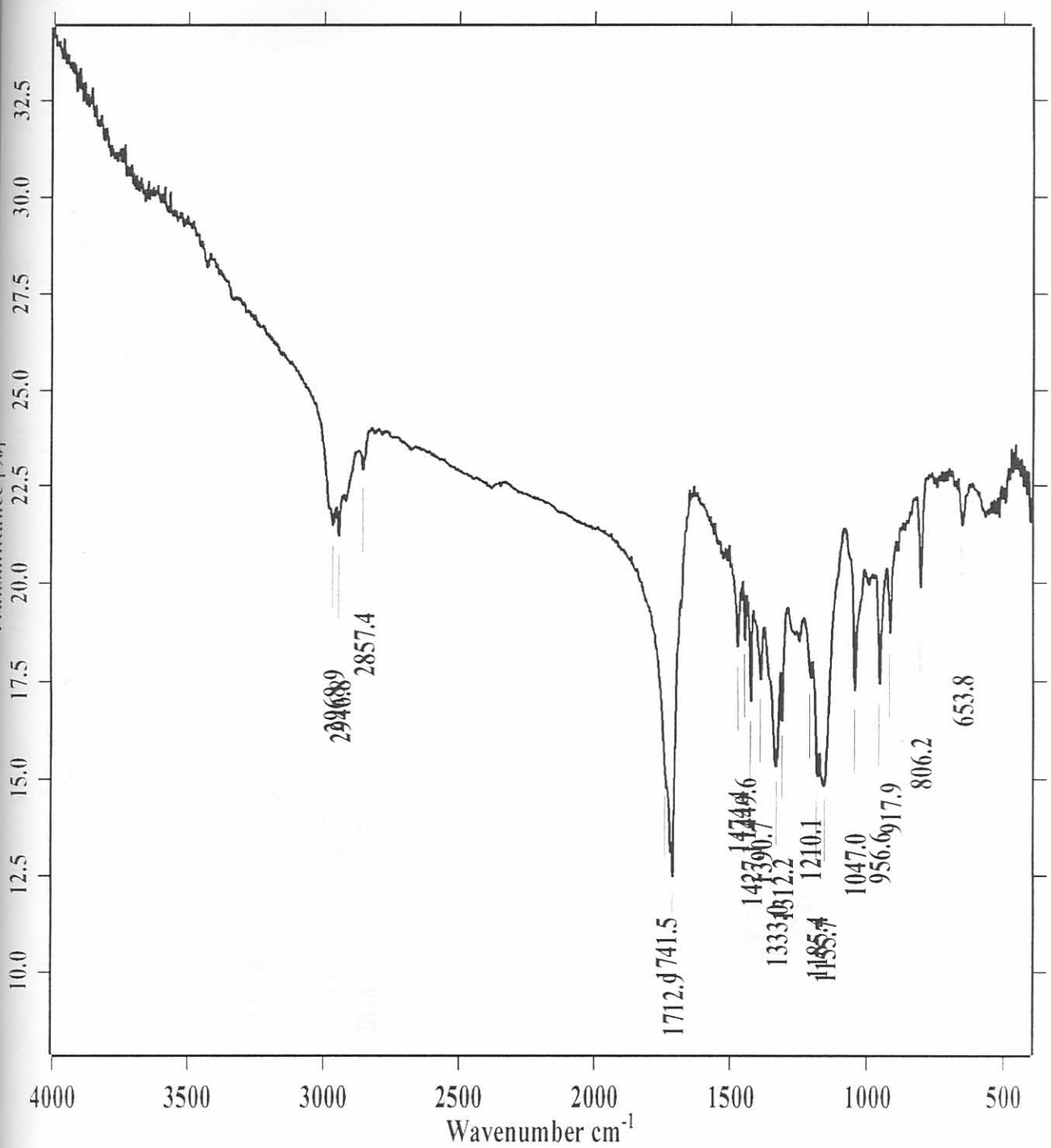


Figure B6 UV spectra for copolymer of polybutylene succinate with N-METHYL-TAA-OL (BUMA)

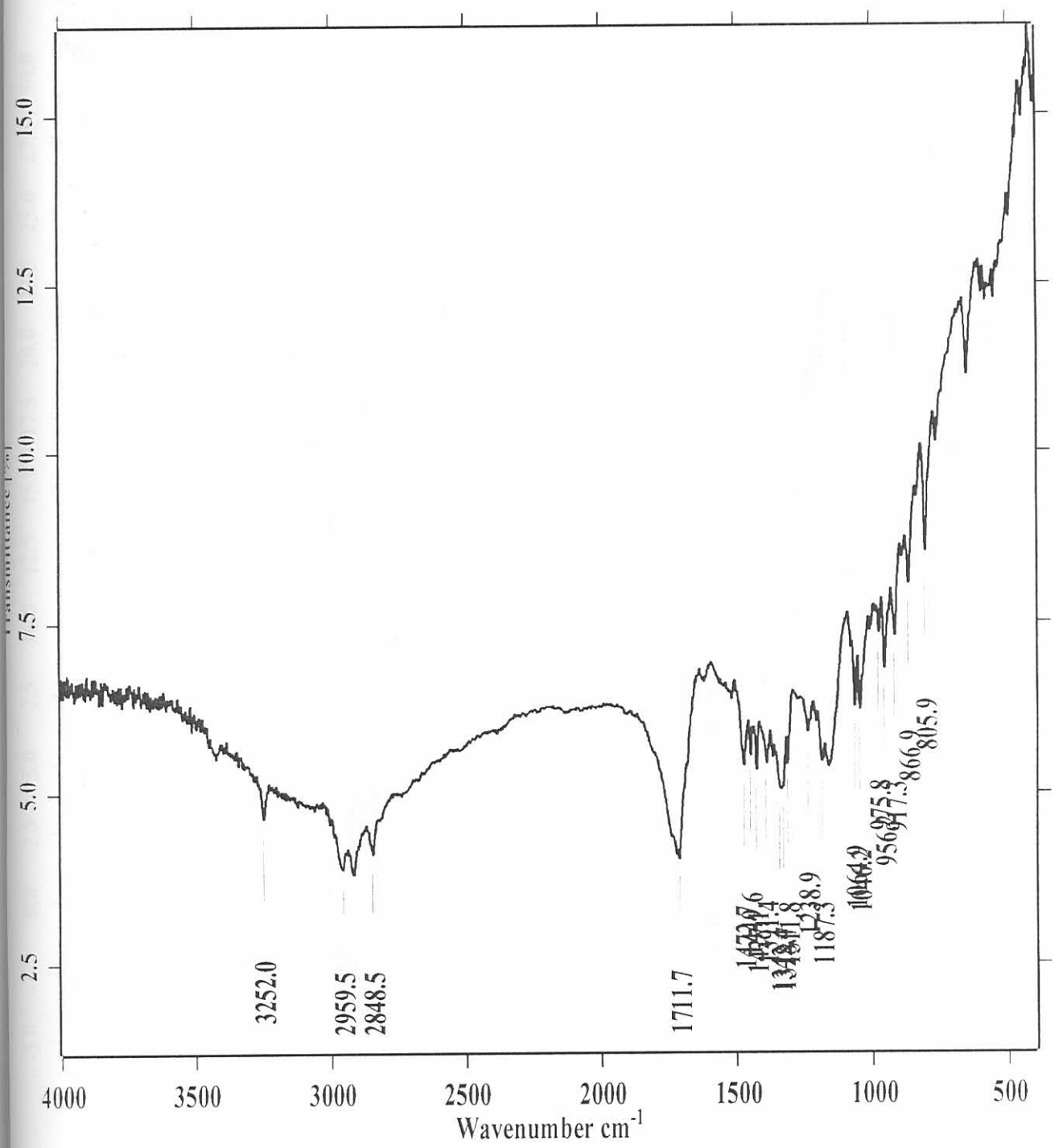


Figure B7 UV spectra for copolymer of polybutylene succinate with 2,2-(2,2,6,6-Tetramethyl-4-piperidinyl)imino)bis(Ethanol) (BUDIOL)

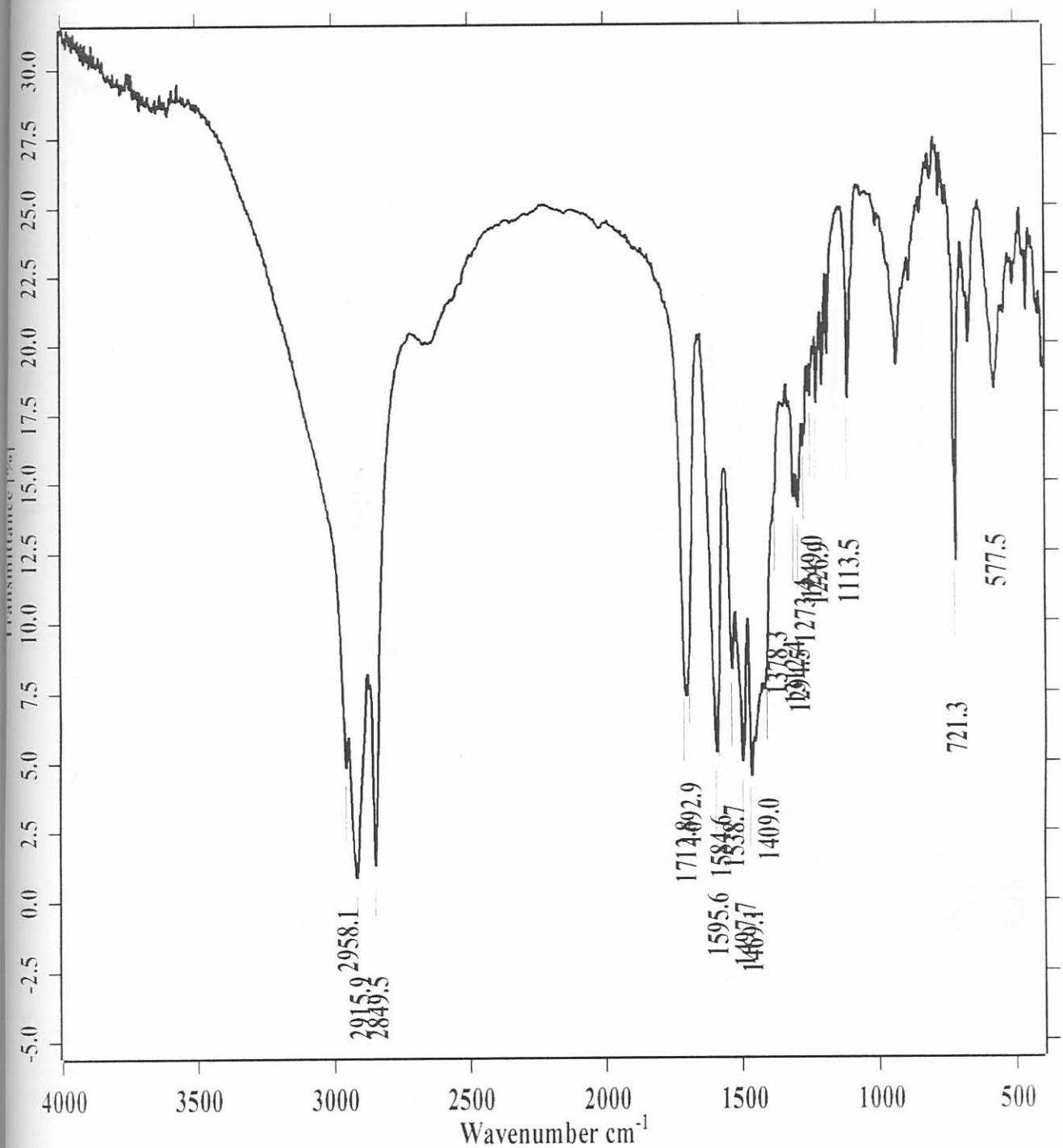


Figure B8 UV spectra for copolymer of ferric stearate

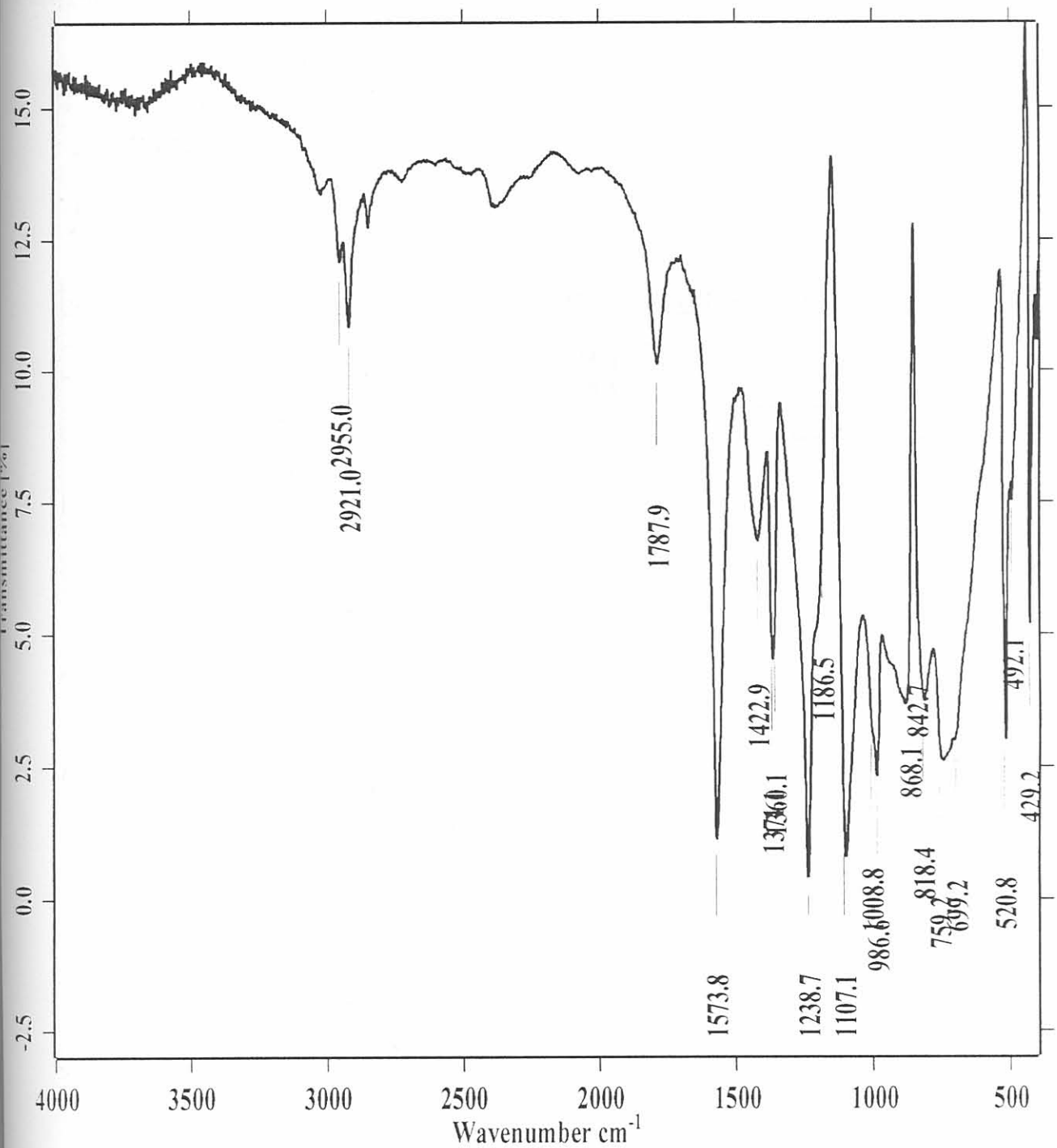


Figure B9 UV spectra for nickel methyl glyoxime

APPENDIX C

DSC/TGA traces for additives synthesised

Figure	Additives synthesised
C1	TOTA
C2	TOTOL
C3	STETA
C4	STEMA
C5	STEDIOL
C6	OTMQ
C7	BUTA
C8	BUTOL
C9	BUMA
C10	BUDIOL

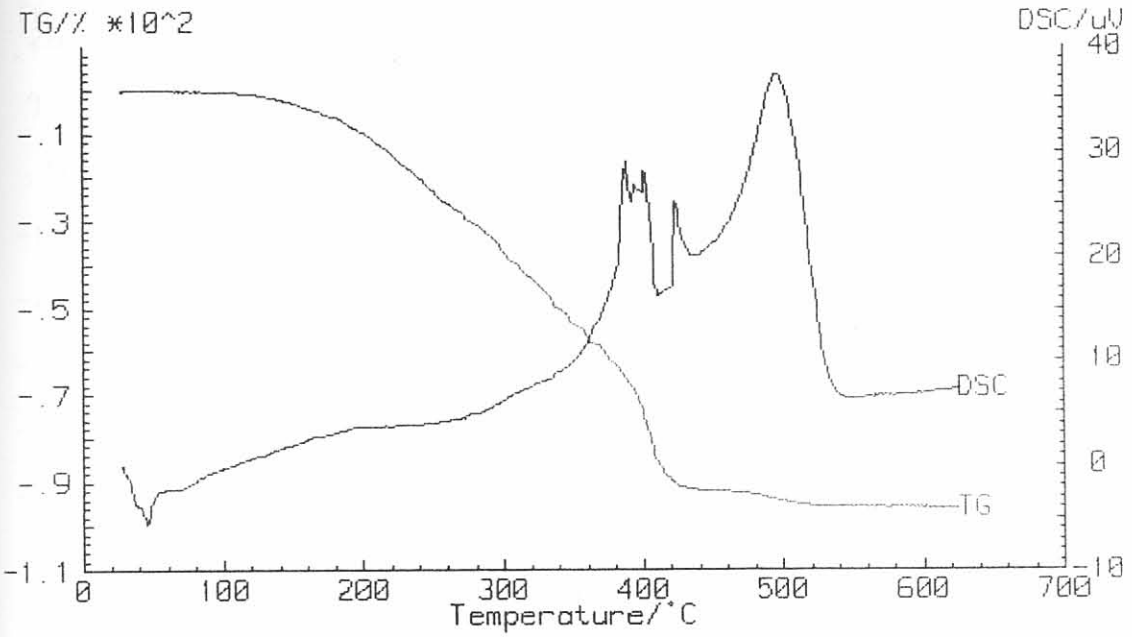


Figure C1 DSC/TGA traces for copolymer of caprolactone with TAA-OL (TOTA)

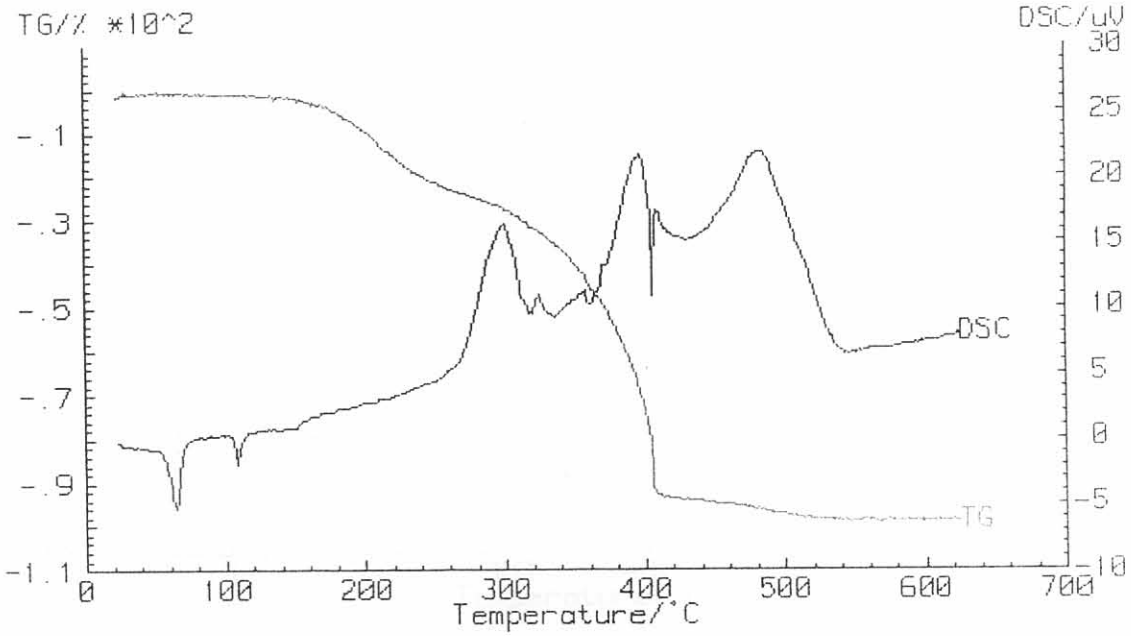


Figure C2 DSC/TGA traces for copolymer of caprolactone with N-HE-TAA-OL (TOTOL)

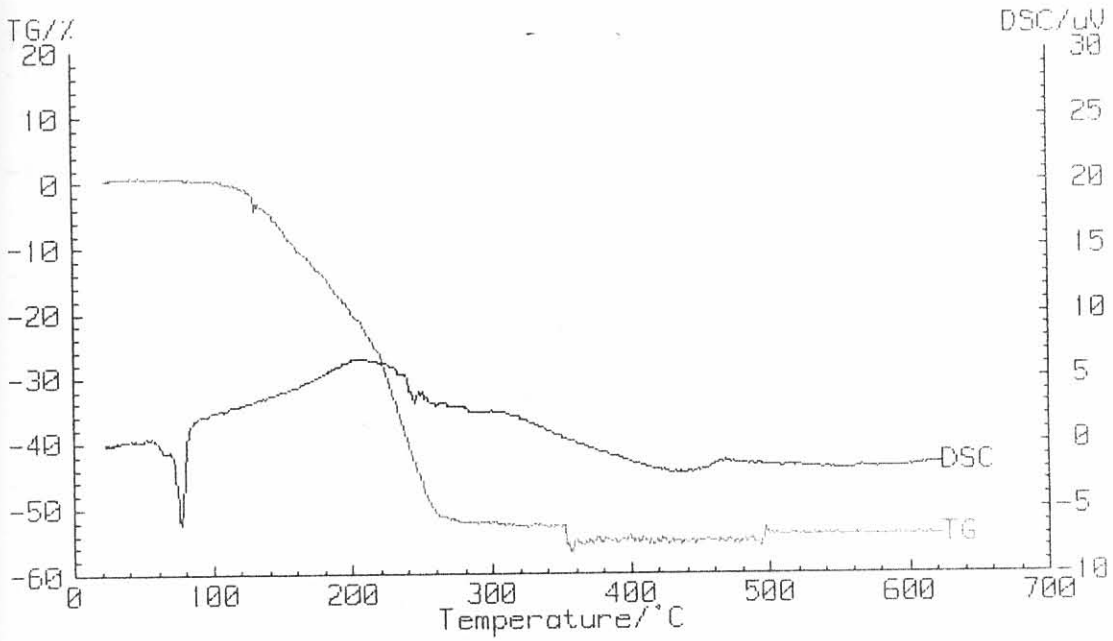


Figure C3 DSC/TGA traces for copolymer of stearic acid with TAA-OL (STETA)

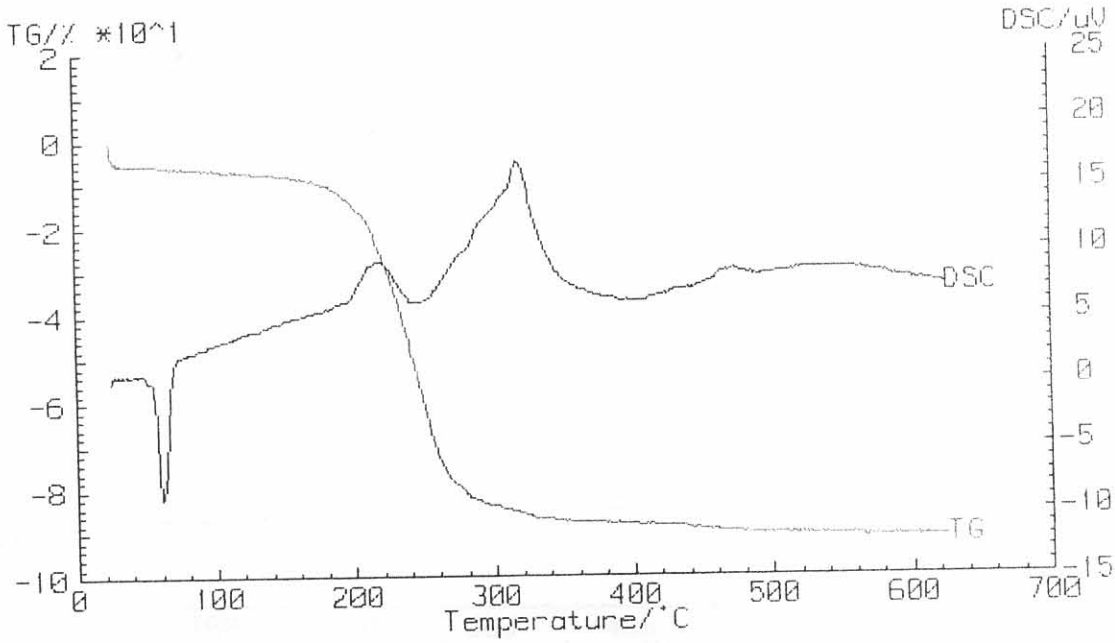


Figure C4 DSC/TGA traces for copolymer of stearic acid with N-METHYL-TAA-OL (STEMA)

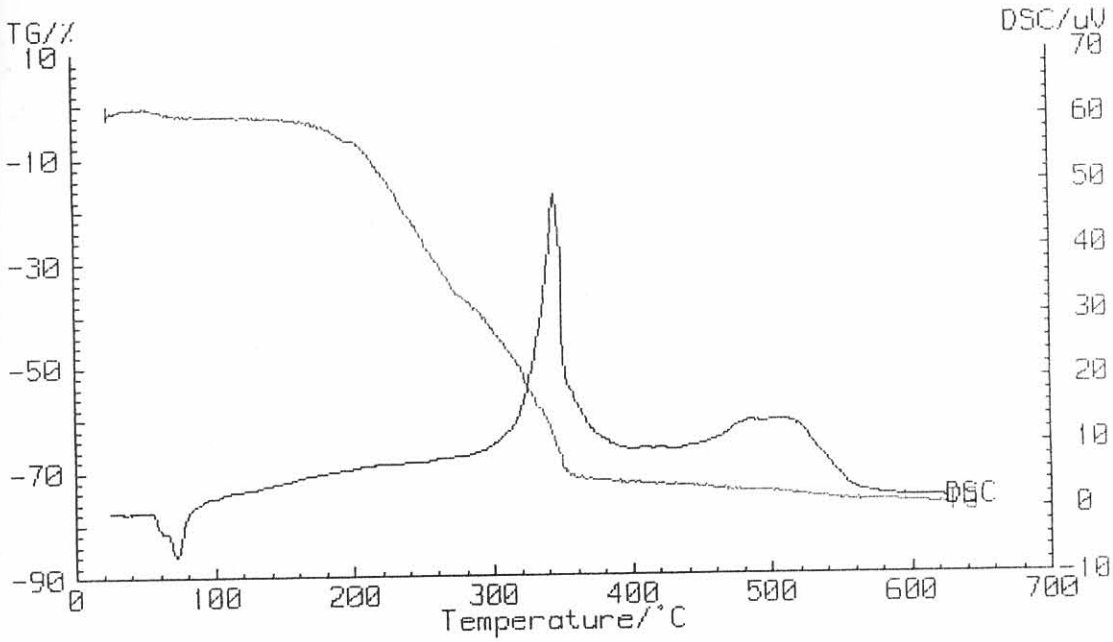


Figure C5 DSC/TGA traces for copolymer of stearic acid with 2,2-(2,2,6,6-Tetramethyl-4-piperidinyl)imino)bis(Ethanol) (STEDIOL)

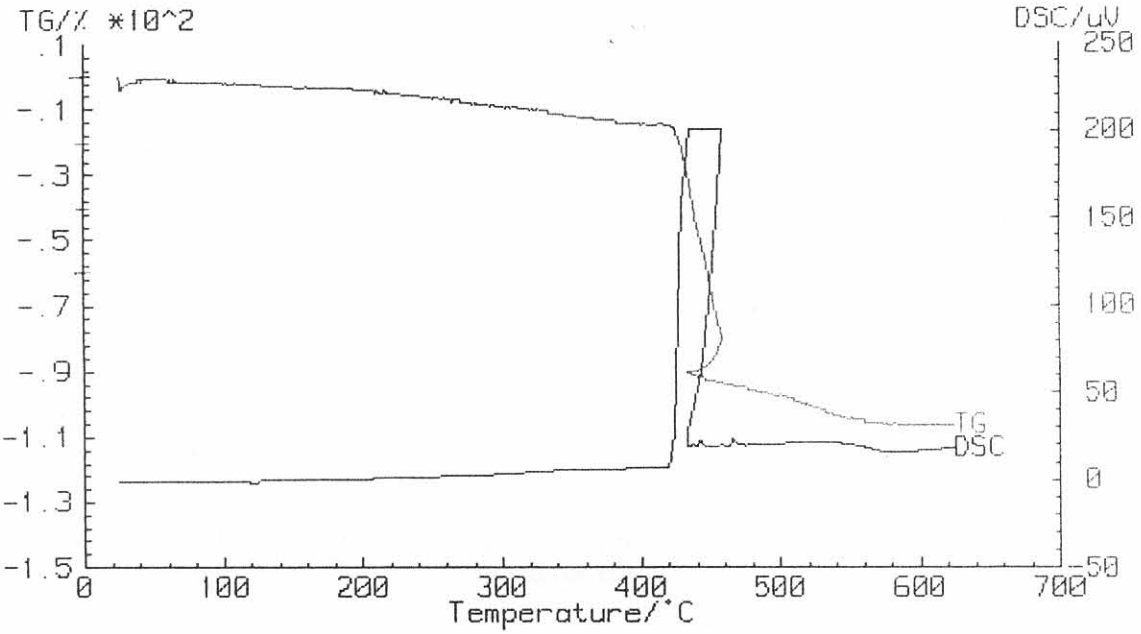


Figure C6 DSC/TGA traces for) Poly(1,2-dihydro-2,2,4-trimethylquinone)(OTMQ

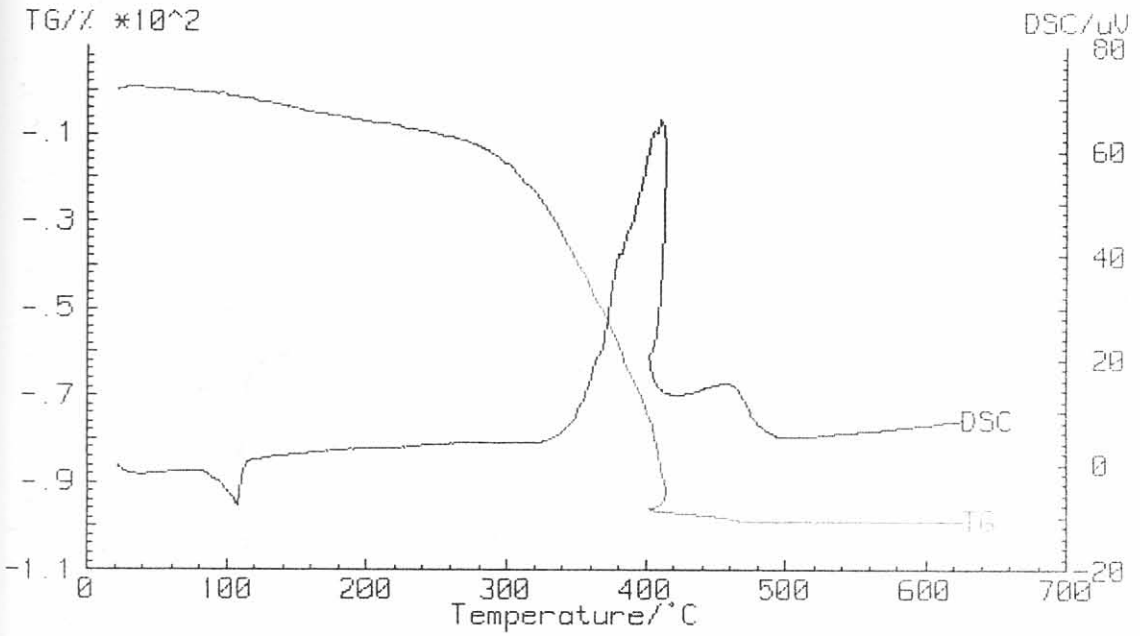


Figure C7 DSC/TGA traces for copolymer of polybutylene succinate with TAA-OL (BUTA)

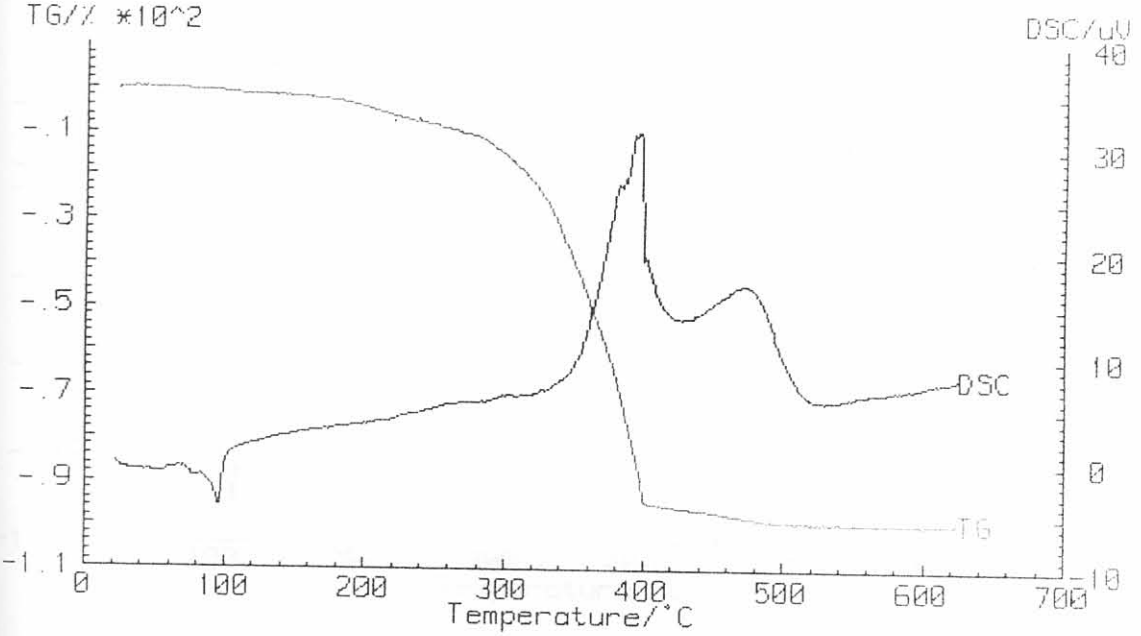


Figure C8 DSC/TGA traces for copolymer of polybutylene succinate with N-HE-TAA- OL (BUTOL)

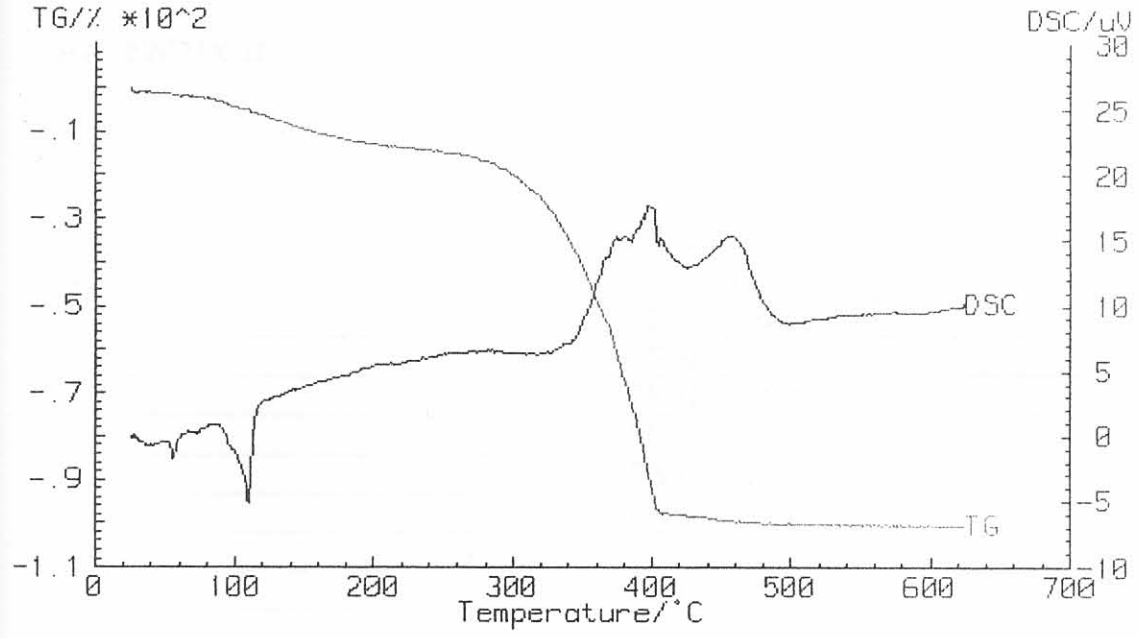


Figure C9 DSC/TGA traces for copolymer of polybutylene succinate with N-METHYL-TAA-OL (BUMA)

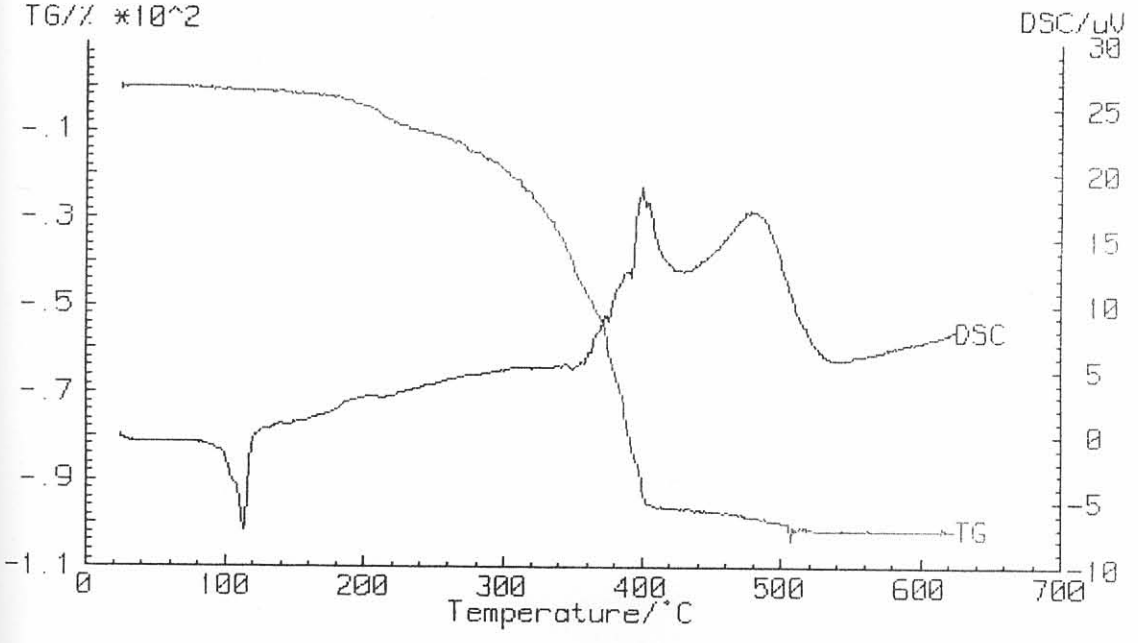


Figure C10 DSC/TGA traces for copolymer of polybutylene succinate with 2,2-(2,2,6,6-Tetramethyl-4-piperidinyl)imino)bis(Ethanol) (BUDIOL)

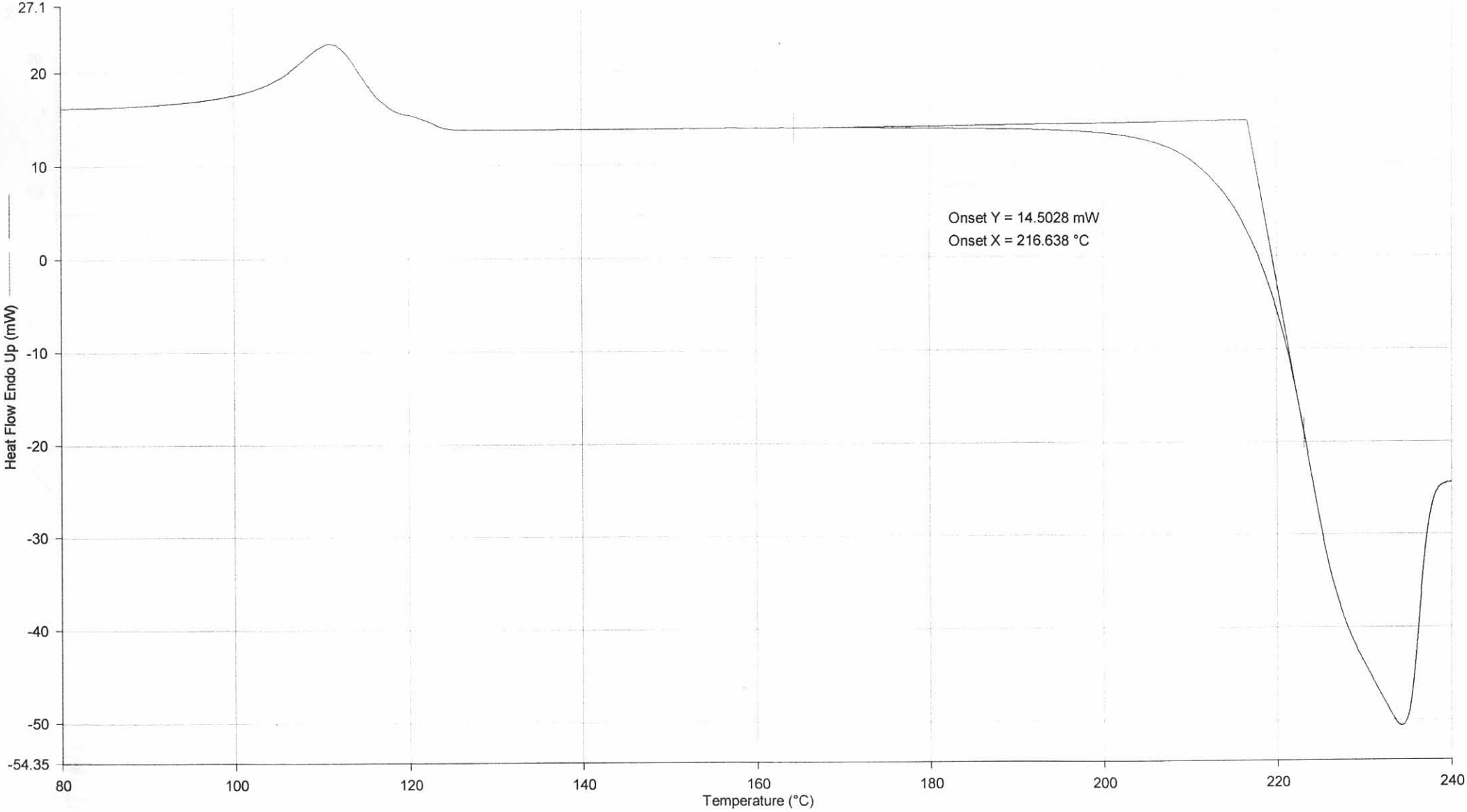
APPENDIX D

DSC/OIT scans

Figure	Film
D1	Polyethylene
D2	PE (Cu Acac)
D3	PE (Al Acac)
D4	PE (Fe-Stea)
D5	PE (Phetln)
D6	PE (Ni-dmg)
D7	PE (OTMQ)
D8	Polypropylene
D9	PP (Fe-Stea)
D10	PP (Cu Acac)
D11	PP (Al Acac)
D12	PP (Ni-dmg)
D13	Pp (OTMQ)

Operator ID: walter
Sample ID: Polyethylene film
Sample Weight: 10.100 mg
Comment: OIT measurements

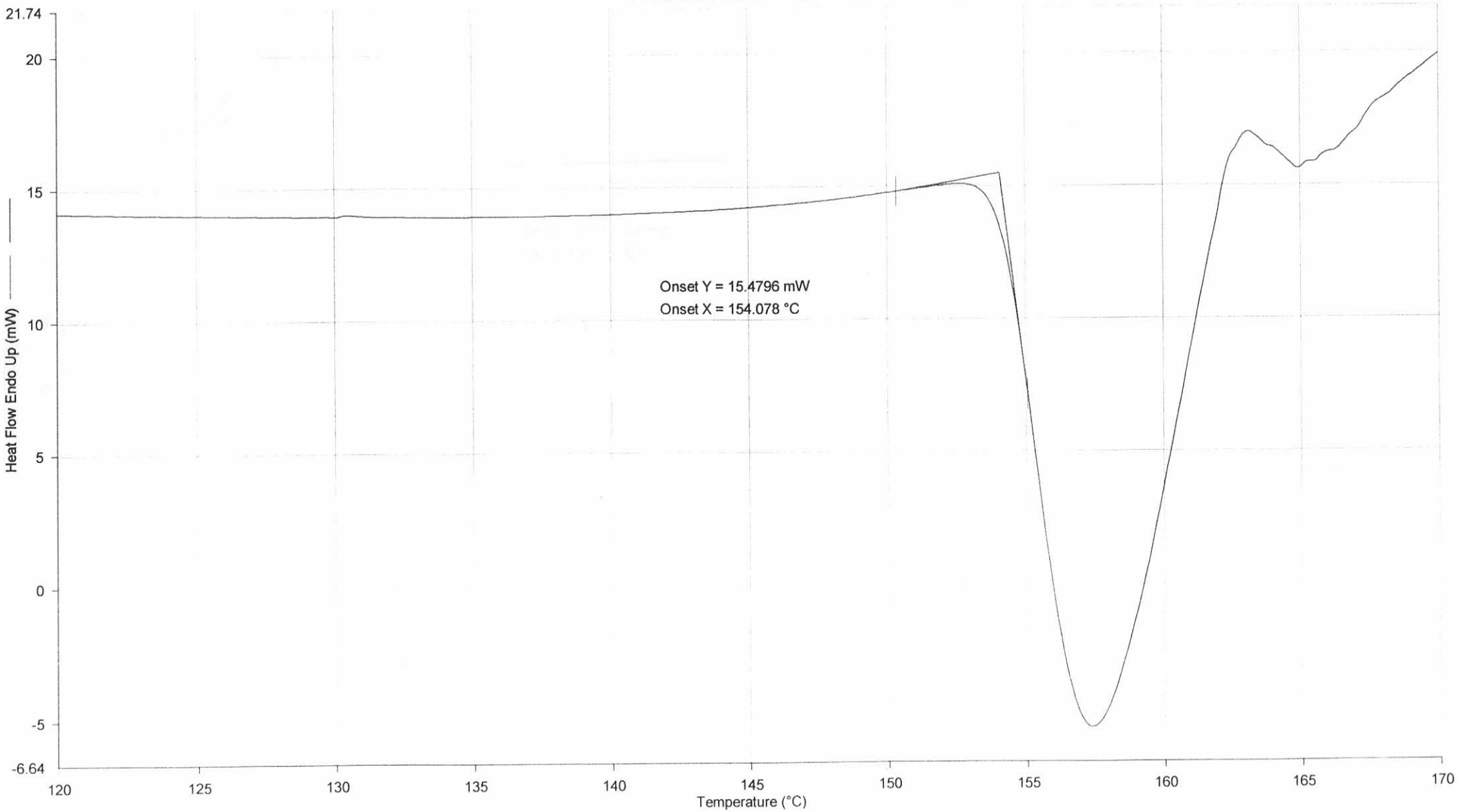
Perkin-Elmer Thermal Analysis



12/20/00 10:27:40 AM

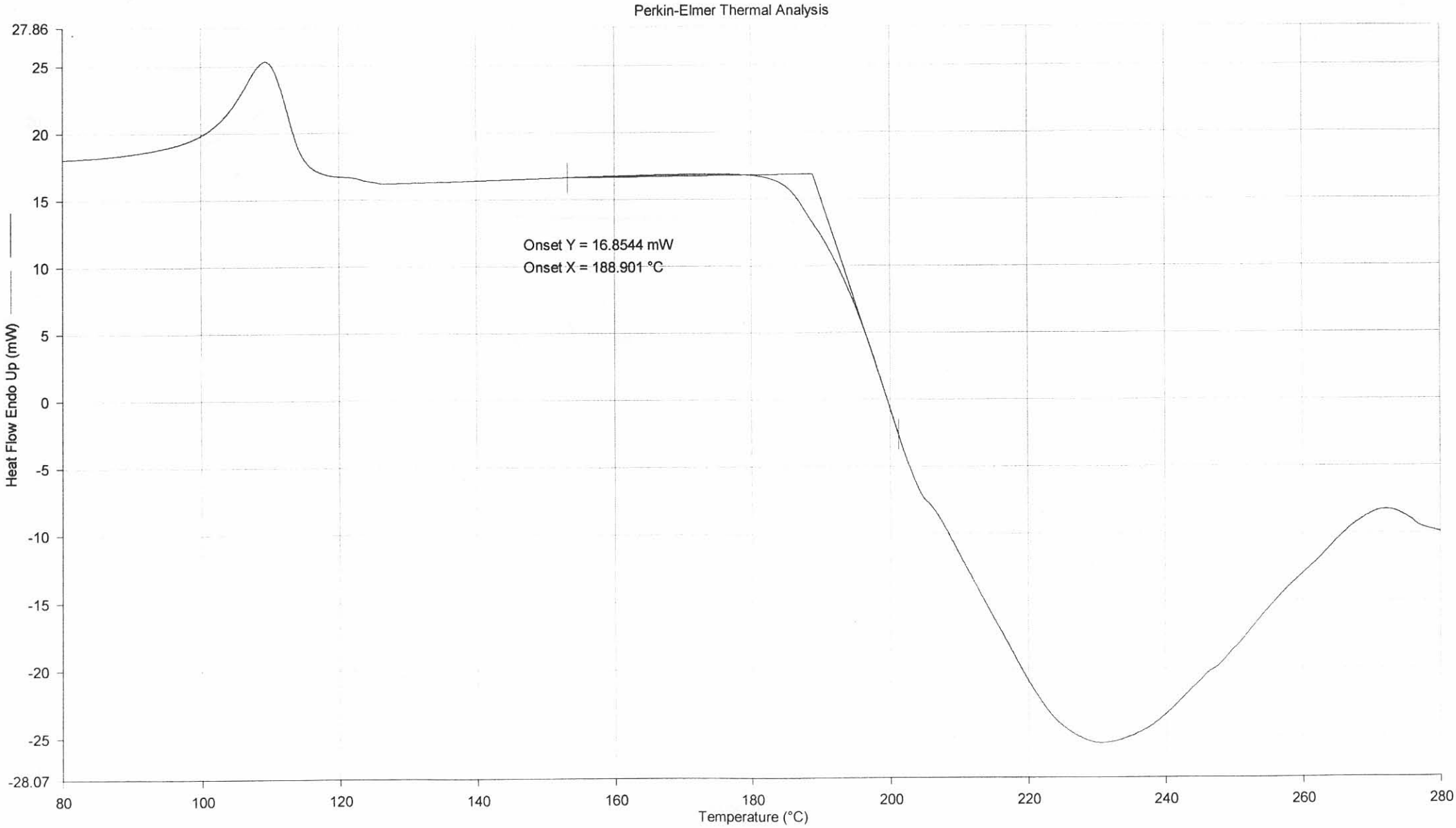
Filename:
Operator ID: walter
Sample ID: Polypropylene-Cu-acac_0.5%
Sample Weight: 10.400 mg
Comment: OIT measurements

Perkin-Elmer Thermal Analysis



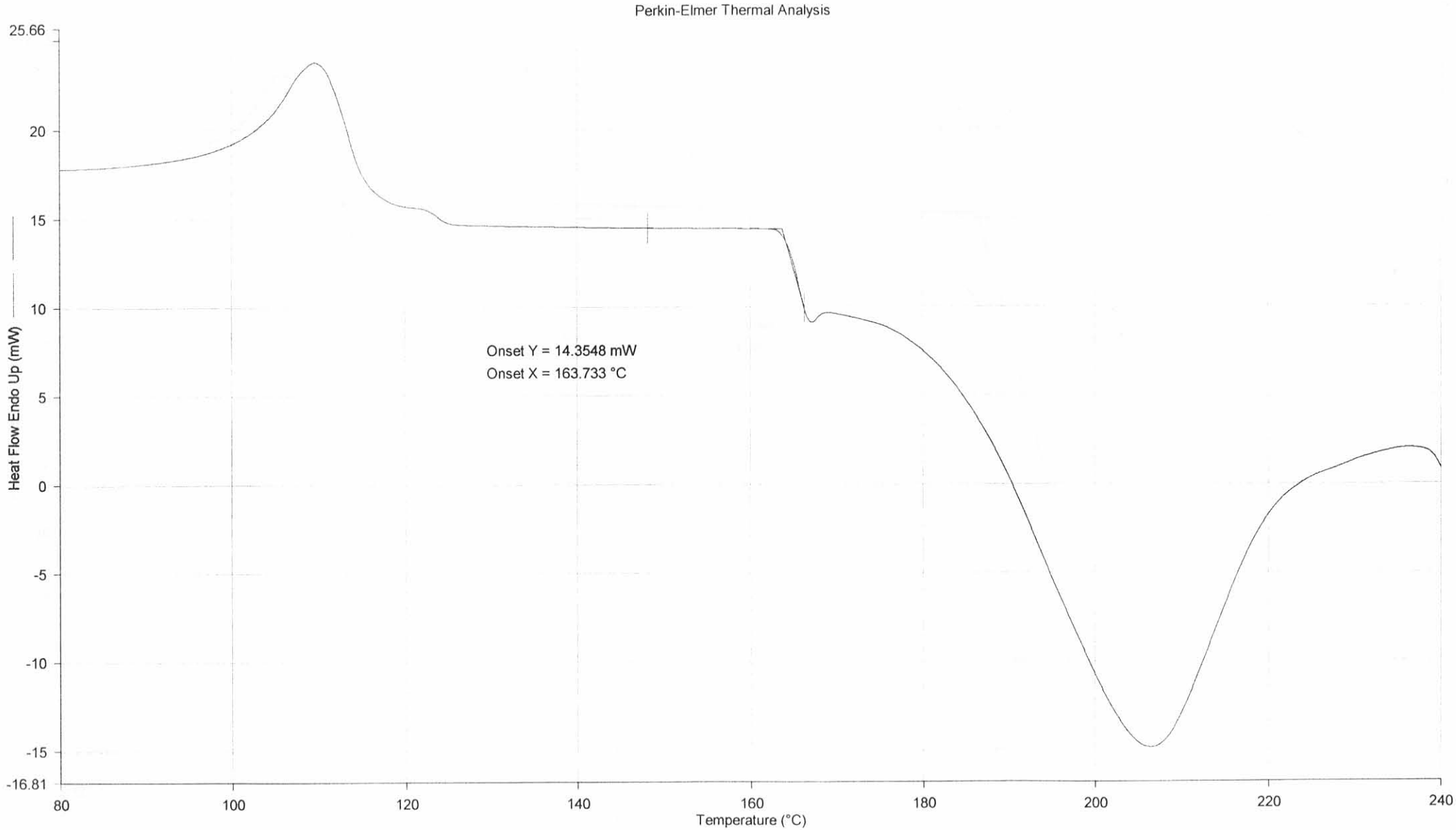
12/20/00 3:49:17 PM

Filename: C:\PE\Data\Walter\PE05.dsc
Operator ID: walter
Sample ID: Polyethylene film_Al-AcAc_0.5%
Sample Weight: 10.330 mg
Comment: OIT measurements



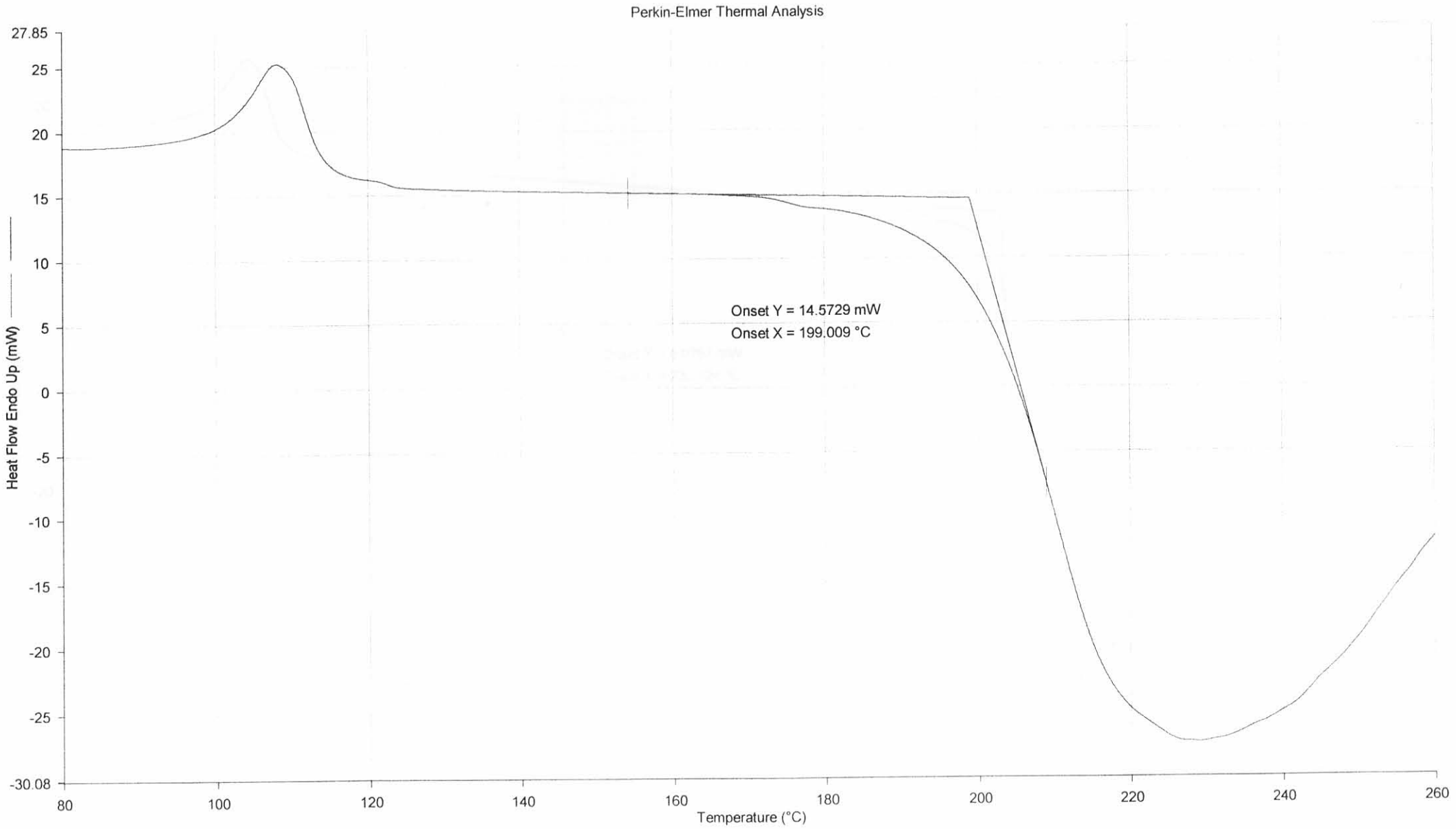
12/20/00 12:04:02 PM

Operator ID: walter
Sample ID: Polyethylene film_Ferric_Stearate_0.5%
Sample Weight: 10.450 mg
Comment: OIT measurements



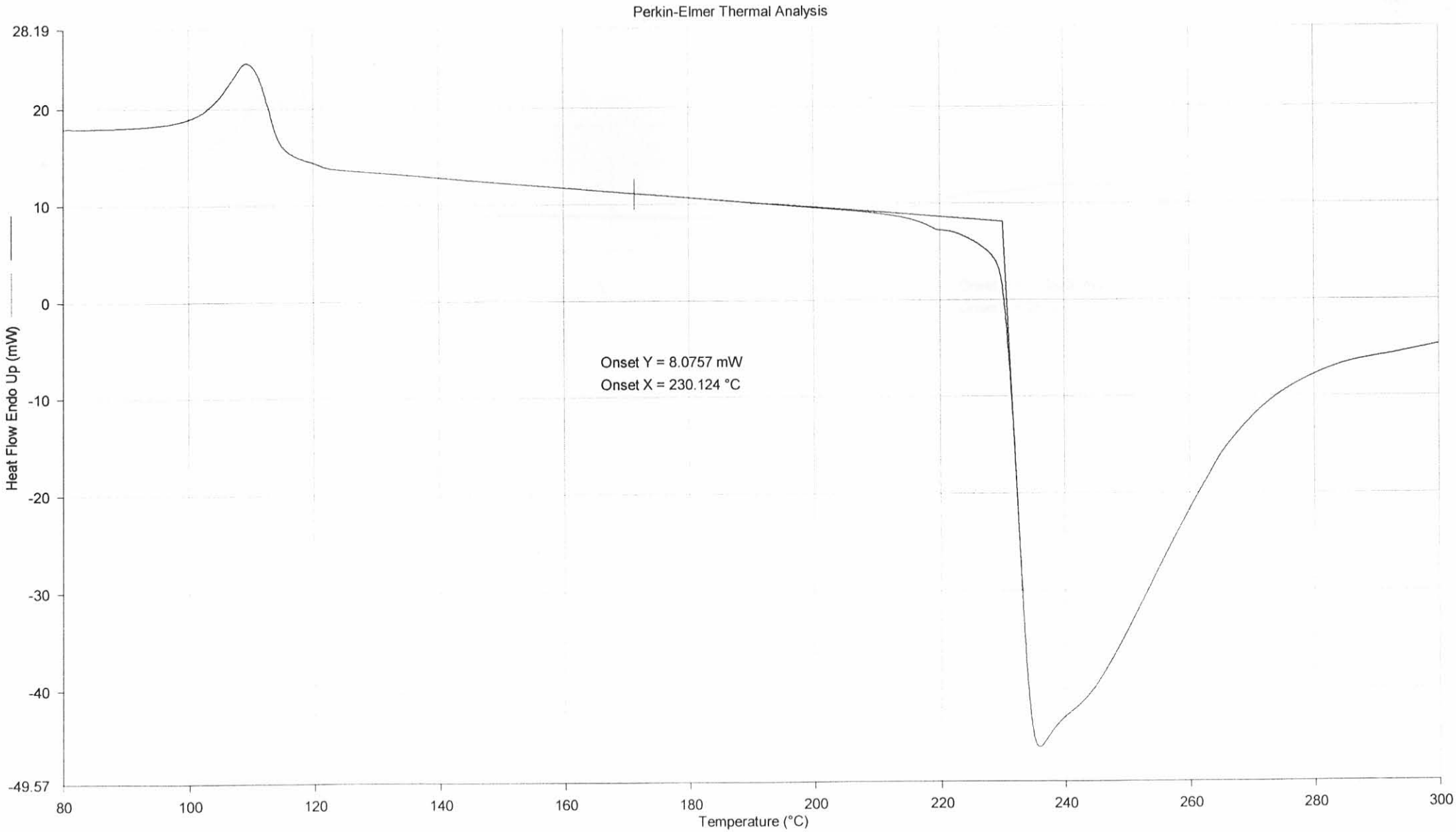
12/20/00 11:33:45 AM

Filename: C:\PE-Pyris\Data\B68_PE68.dsc
Operator ID: walter
Sample ID: Polyethylene film_phenolphthalein_0.5%
Sample Weight: 10.440 mg
Comment: OIT measurements



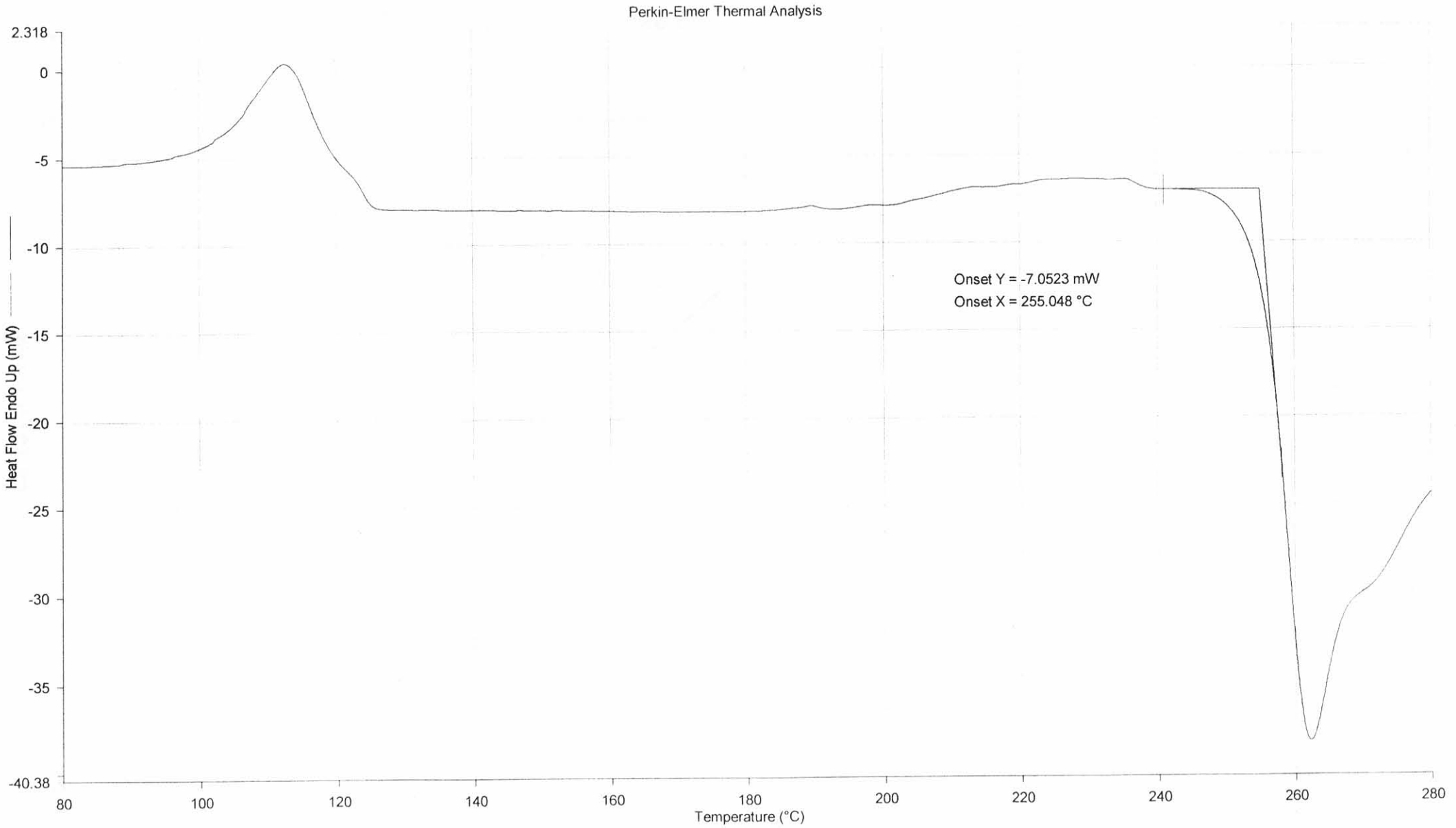
12/20/00 12:41:49 PM

Operator ID: walter
Sample ID: Polyethylene film_Ni-dimethylglyoxi_0.5%
Sample Weight: 10.020 mg
Comment: OIT measurements



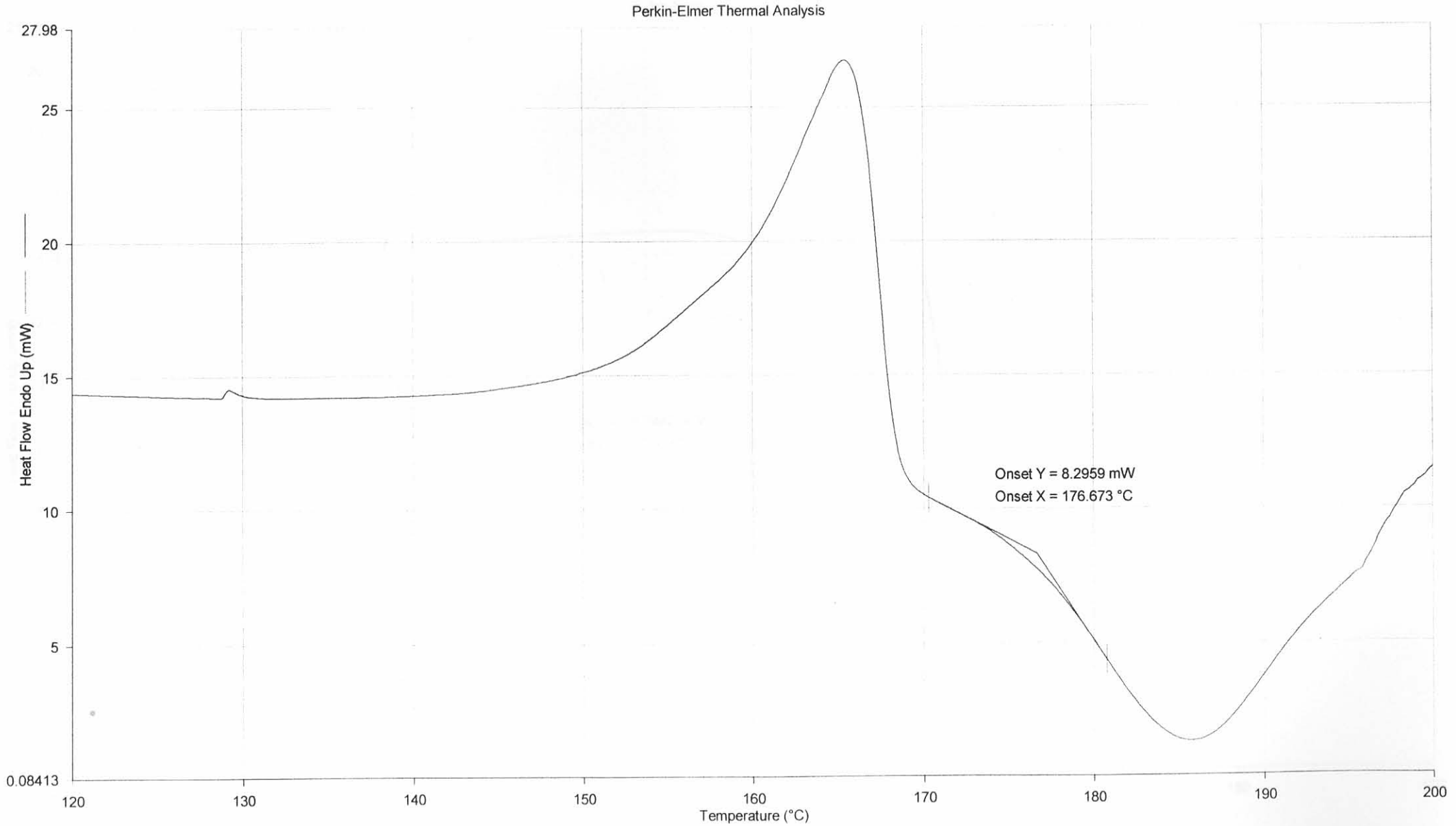
12/20/00 2:02:12 PM

Filename: [illegible]
Operator ID: walter
Sample ID: Polyethylene film_OroxPK_0.4%
Sample Weight: 10.730 mg
Comment: OIT measurements



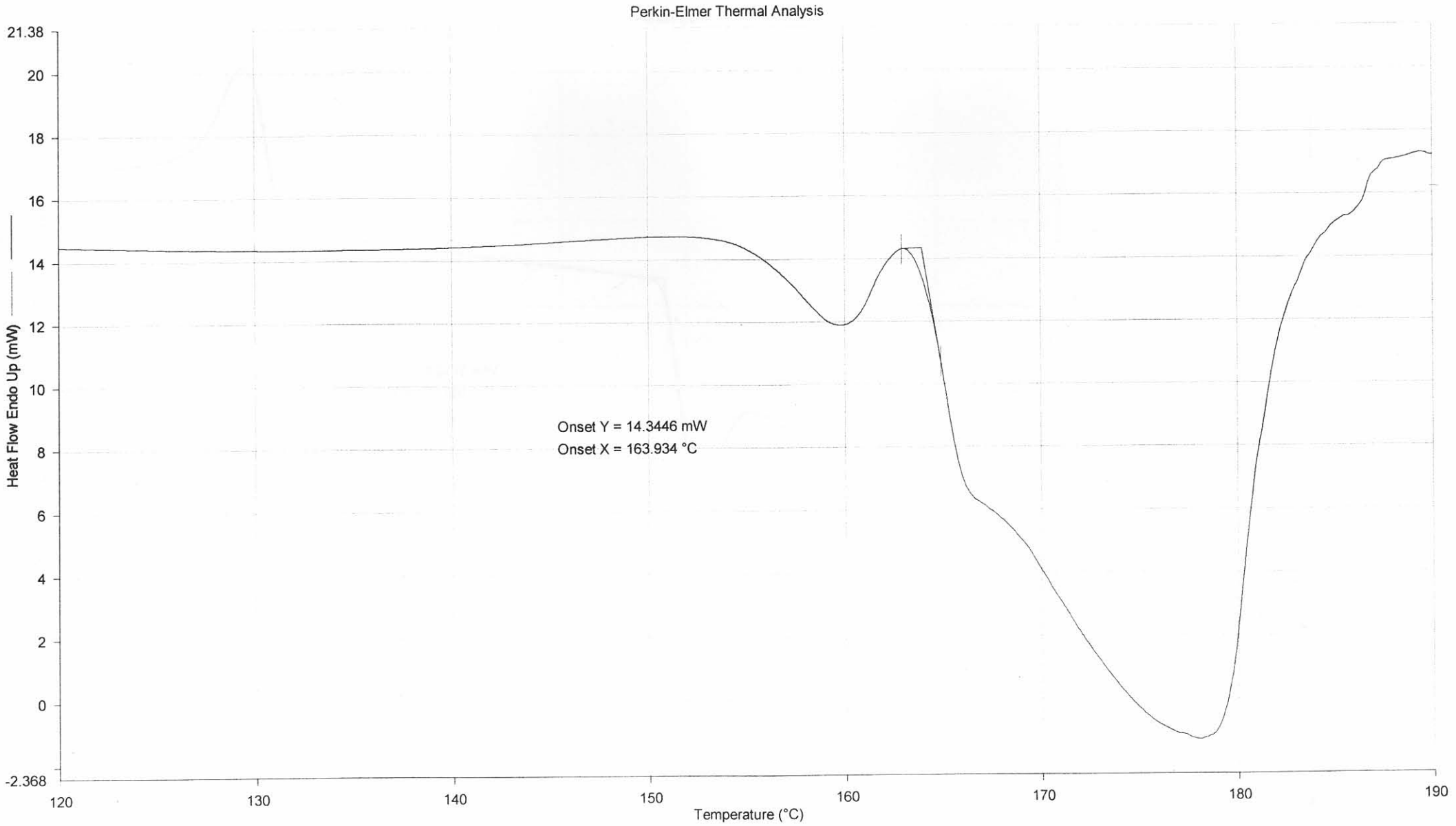
12/20/00 11:07:48 AM

Filename:	C:\PE\Pyris\Data\Bob_PP01.dsd
Operator ID:	walter
Sample ID:	Polypropylene-film-virgin
Sample Weight:	10.240 mg
Comment:	OIT measurements



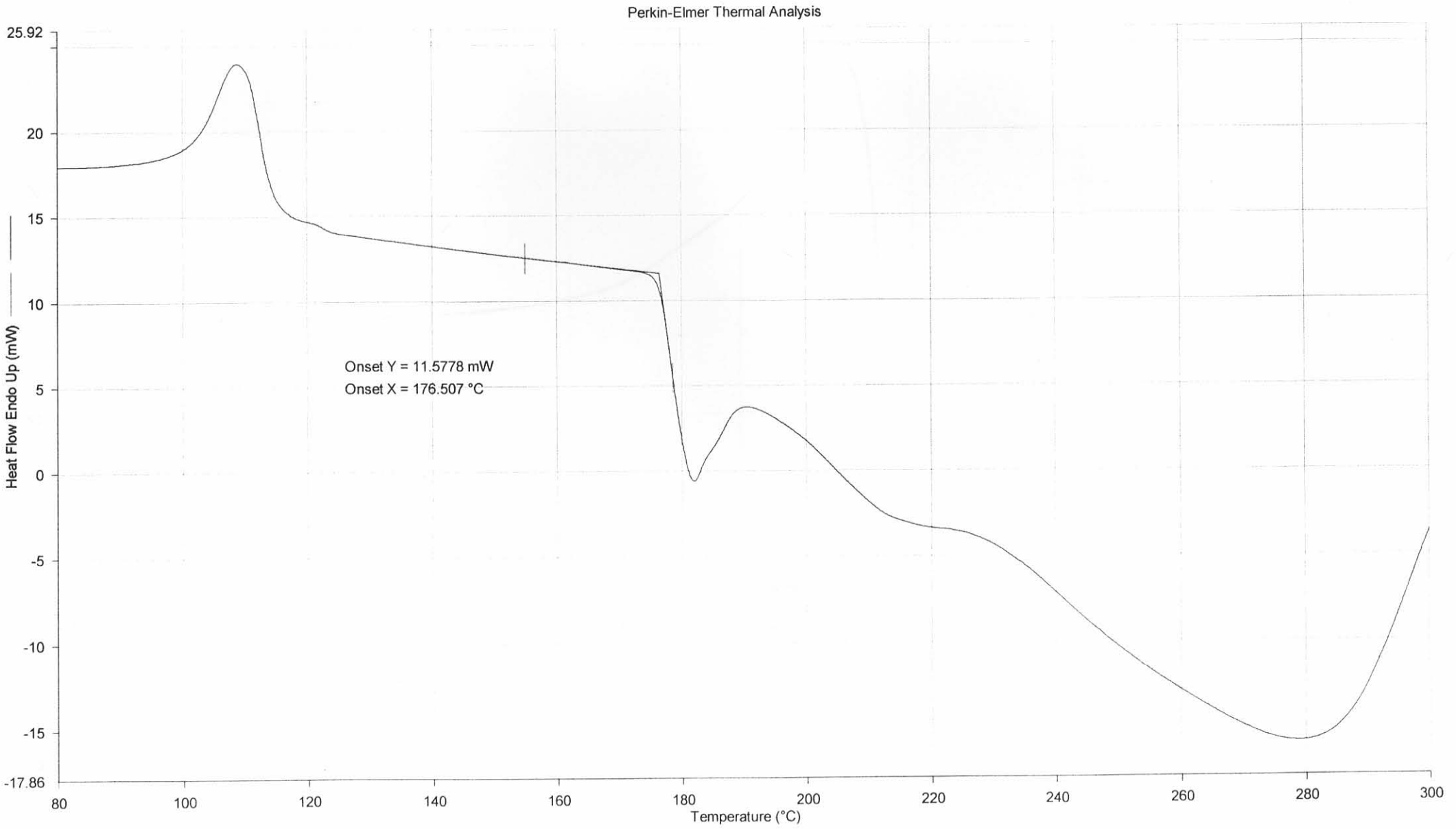
12/20/00 2:25:52 PM

Filename:
Operator ID: walter
Sample ID: Polypropylene-Fe(III)Stearate_0.5%
Sample Weight: 10.410 mg
Comment: OIT measurements



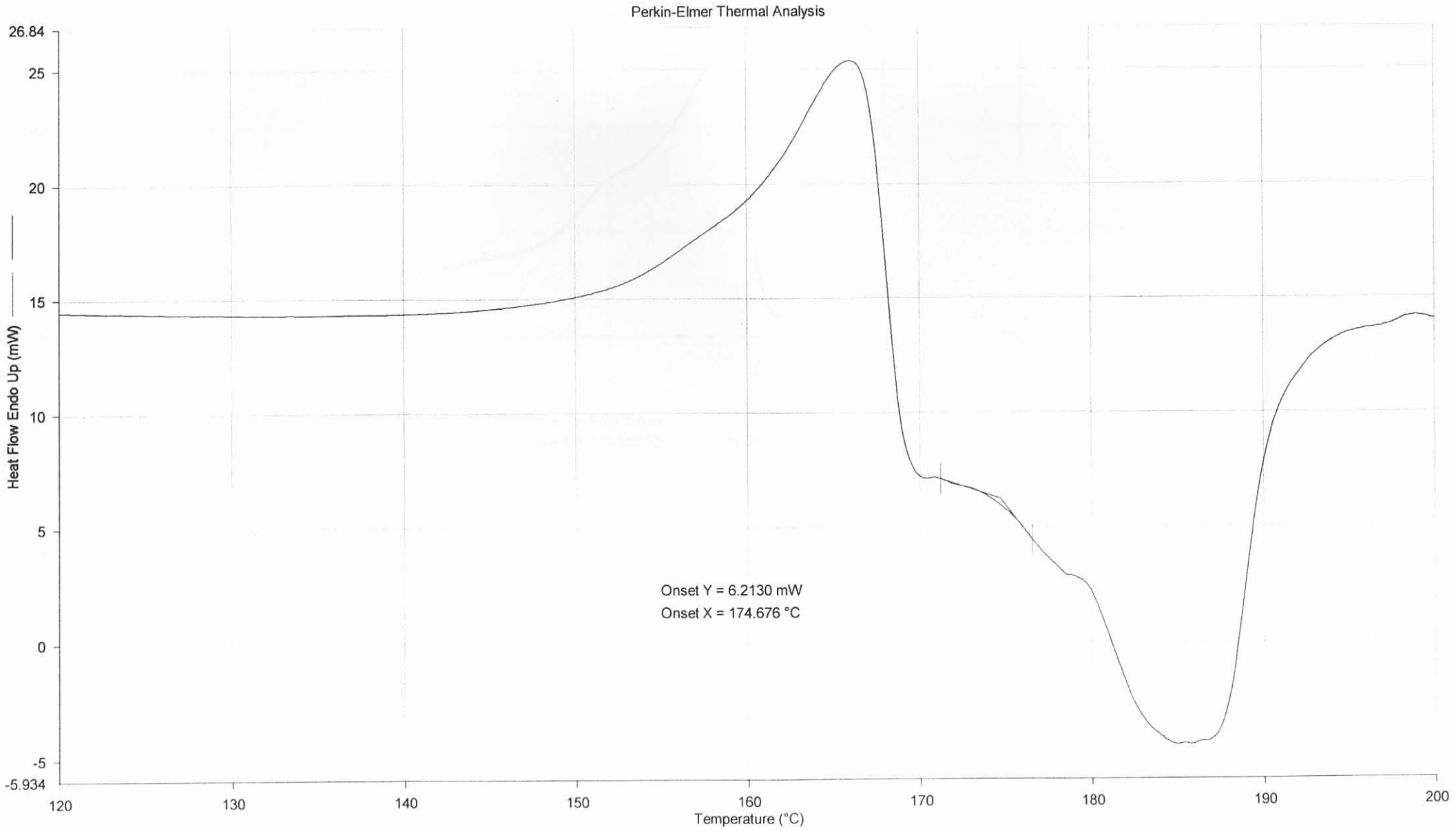
12/20/00 3:11:51 PM

Filename:	C:\PE\Pyris\Data\Bob_PE07.dsd
Operator ID:	walter
Sample ID:	Polyethylene film_Cu-acac_0.5%
Sample Weight:	10.530 mg
Comment:	OIT measurements



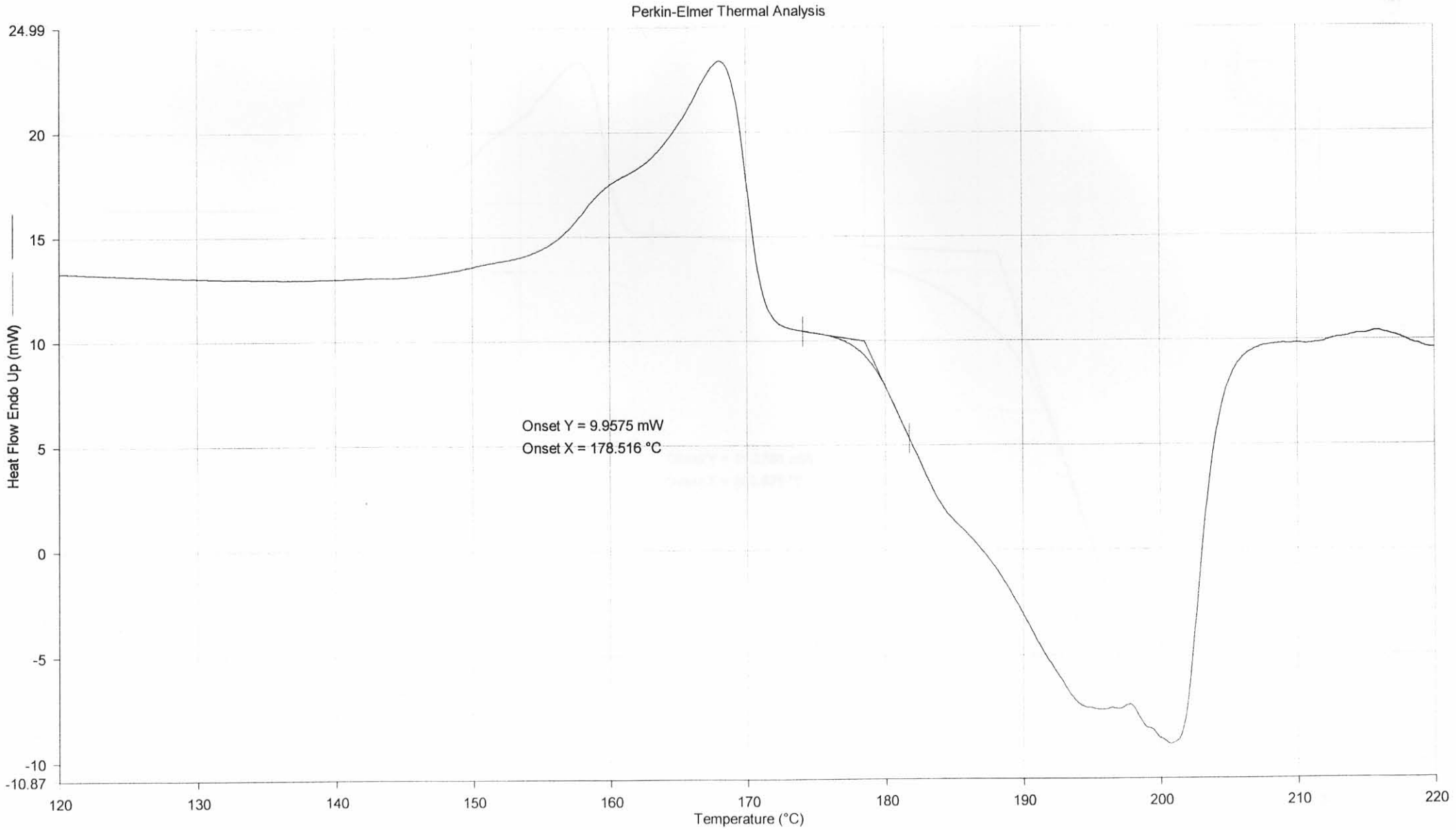
12/20/00 1:20:41 PM

Filename: C:\PE\Pyris\Data\Bob_PP04.dsc
Operator ID: walter
Sample ID: Polypropylene-AL-acac_0.5%
Sample Weight: 10.420 mg
Comment: OIT measurements



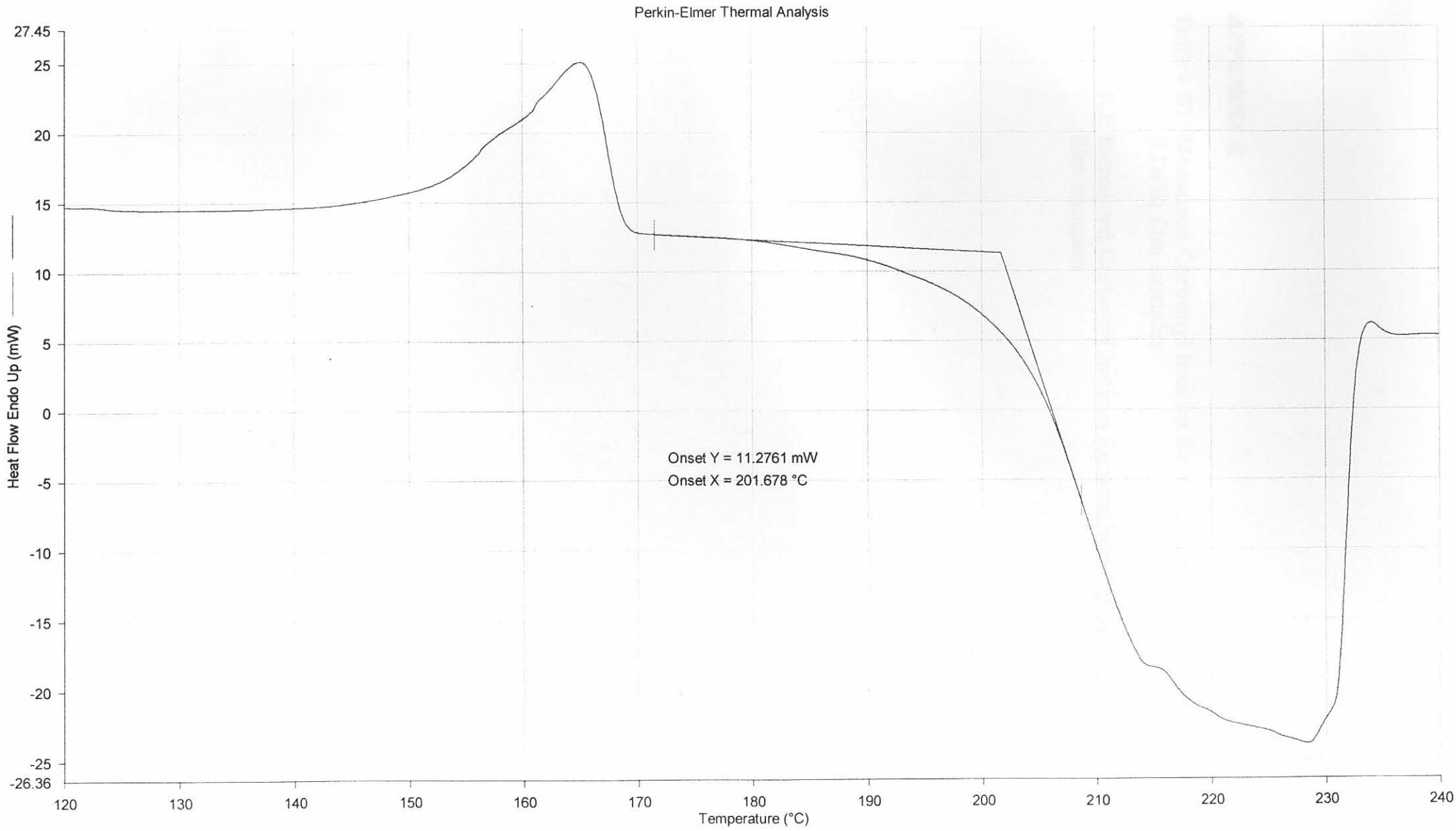
12/20/00 3:31:27 PM

Filename: C:\PE\Pyris\Data\Sos_PP 06.dsc
Operator ID: walter
Sample ID: Polypropylene-Ni-DMGlyoxime_1%
Sample Weight: 10.120 mg
Comment: OIT measurements



12/20/00 4:11:47 PM

Operator ID: walter
Sample ID: Polypropylene-OroxPK_0.5%
Sample Weight: 10.070 mg
Comment: OIT measurements



12/20/00 2:50:56 PM

Figure D13 DSC OIT scan for Poly(1,2-dihydro-2,2,4-trimethylquinoline)

APPENDIX E

Tables E1: Measured Carbonyl Indices for weathered polyethylene (LDPE) film samples

Tables E2: Measured Carbonyl Indices for weathered polypropylene film samples

HOURS	PE	TOTA	TOTOL	STETA	STEMA	STEDIOL	BUTA	BUTOL	BUMA	BUDIOL	Ni-dmg	Chimasorb 944
0	0	0	0	0	0	0	0	0	0	0	0	0
100	0	0	0	0	0	0	0	0	0	0	0	0
200	0	0	0	0	0	0	0	0	0	0	0	0
300	0	0	0	0	0	0	0	0	0	0	0	0
400	0	0	0	0	0	0	0	0	0	0	0	0
500	0	0	0	0	0	0	0	0	0	0	0	0
600	0	0	0	0	0	0	0	0	0	0	0	0
700	0	0	0	0	0	0	0	0	0	0	0	0
800	0	0	0	0	0	0	0	0	0	0	0	0
900	0	0	0	0	0	0	0	0	0	0	0	0
1000	0	0	0	0	0	0	0	0	0	0	0	0
1100	0	0	0	0	0	0	0	0	0	0	0	0
1200	0.21	0	0	0	0	0	0	0	0	0	0	0
1300	0.23	0	0	0	0.21	0.04	0.07	0.01	0.21	0.10	0	0
1400	0.28	0	0	0	0.25	0.09	0.08	0.01	0.21	0.18	0	0
1500	0.33	0	0	0.06	0.27	0.12	0.14	0.17	0.24	0.19	0	0
1600	0.35	0	0.07	0.06	0.33	0.15	0.19	0.18	0.25	0.19	0.04	0
1700	0.35	0.01	0.09	0.07	0.39	0.18	0.20	0.18	0.27	0.20	0.04	0
1800	0.41	0.01	0.09	0.07	0.33	0.21	0.22	0.19	0.34	0.20	0.05	0
1900	0.51	0.03	0.10	0.14	0.41	0.30	0.30	0.26	0.37	0.25	0.05	0
2000	0.68	0.07	0.10	0.16	0.44	0.32	0.33	0.27	0.45	0.31	0.06	0
2100	------	0.09	0.11	0.17	0.47	0.33	0.36	0.28	0.50	0.38	0.08	0
2200		0.13	0.13	0.19	0.50	0.34	0.37	0.28	0.55	0.40	0.08	0
2300		0.14	0.19	0.25	0.54	0.38	0.47	0.37	0.56	0.43	0.08	0
2400		0.19	0.20	0.29	0.61	0.46	--------	--------	0.59	0.50	0.08	0
2500		0.21	--------	0.34	0.62	0.46			0.61	0.57	0.08	0
2600		0.22		0.35	----------	0.47			-------	----------	0.09	0
2700		0.25		-------		0.58					0.13	0
2800		-------				0.75					0.16	0
2900						0.78					0.22	0
3000						--------					0.25	0
3100											----------	0

Table E1 Measured Carbonyl Indices for weathered LDPE film samples.

HOURS	PP	TOTA	TOTOL	STETA	STEMA	STEDIOL	BUTA	BUTOL	BUMA	BUDIOL	Ni-dmg	Ni-dmg & Anox20	Chimasorb 944
0	0	0	0	0	0	0	0	0	0	0	0	0	0
100	0	0	0	0	0	0	0	0	0	0	0	0	0
200	0.32	0	0	0	0	0	0.03	0	0.01	0.08	0	0	0
300	0.38	0	0	0	0	0	0.04	0	0.03	0.12	0	0	0
400	------	0	0	0	0.13	0	0.06	0.016	0.04	0.17	0	0	0
500		0	0	0	0.29	0	0.08	0.08	0.04	0.13	0	0	0
600		0	0	0	0.49	0	0.16	0.14	0.12	0.13	0	0	0
700		0.06	0.10	0	----------	0.07	0.17	0.14	0.17	0.13	0	0	0
800		0.07	0.15	0		0.09	0.18	0.26	0.19	0.16	0	0	0
900		0.08	0.15	0		0.26	0.30	0.32	0.30	0.26	0	0	0
1000		0.15	0.22	0		0.27	0.47	0.46	0.49	0.25	0	0	0
1100		0.22	0.33	0.02		----------	---------	---------	-------	0.39	0	0	0
1200		0.29	---------	0.04						----------	0	0	0
1300		0.36		0.05							0	0	0
1400		0.46		0.08							0	0	0
1500		-------		0.10							0	0	0
1600				0.16							0	0	0
1700				0.22							0.04	0.02	0
1800				0.27							0.07	0.03	0
1900				---------							0.19	0.03	0
2000											0.19	----------	0
2100											0.23		0
2200											--------		0

Table E2 Measured Carbonyl Indices for weathered polypropylene film samples.