New methodologies for covalently modifying pigments

A thesis
Submitted for the Degree of Doctor Philosophy
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DECLARATION

The work presented in this thesis is, to the best of my knowledge and belief, original except where acknowledged in the text. I hereby declare that I have not submitted this material, either in whole or in part, for a degree at this or any other institution. Furthermore, parts of this work have been patented under WO 2006/082352A2.

University of Edinburgh

Abstract

Faculty of Engineering, Science and Mathematics

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New methodologies for covalently modifying pigments

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Pigments are widely used materials in inkjet inks and their surface properties are an important factor in their performance. The aim of this project was to devise methodologies for covalently modifying the surfaces of pigments in order to modulate their properties. This was achieved by activating the surface of pigments with either gamma or plasma irradiation and then covalently grafting polymers onto their surfaces. The four pigments used were: Pigment red 122, Pigment blue 15:3, Pigment yellow 155 and Carbon black, which are already used in Kodak inks. It was demonstrated that dispersibility in water or DMF could be greatly improved by grafting polymers onto pigments. After dispersion tests over two weeks, poly(*N,N*-dimethylacrylamide) was found to be the best polymer to graft onto pigments in order to improve pigment dispersibility in water, while polystyrene allowed dispersion of pigments in DMF. Further modifications were attempted by copolymerisation, cross-linking and esterification reactions. The optimised pigments were analysed using filtration, UV/Vis measurement, contact angle and SEM to determine their particle sizes and properties. They were used in basic ink formulations, printed onto paper and tested against light and ozone fading.

Preface

The research described in this thesis was carried out under the supervision of Prof. Mark Bradley at the University of Southampton between February 2003 and February 2005 then at the University of Edinburgh between March 2005 and February 2006.

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I would first of all to thank my supervisor Professor Mark Bradley for all his advice during these three years of my PhD. I would like to thank Dr John Goddard from Kodak for my project, its funding, and his enormous amount of advice and encouragement.

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I would like to thank Derek and Annette's family for taking care of my little cat Filou. I would like to thank my parents and my little brother for their patience and support thoughout my study. Finally, I would like to thank Laurent for his love and everlasting support.

ABBREVIATIONS

AAC	acryloyl chloride
acPR122	activated pigment red 122
AIBN	2, 2'-azo-*bis*-isobutyronitrile
B	becquerel
BMA	*n*-butyl methacrylate
br	broad
°C	degrees celsius
CB	carbon black
δ	chemical shift in ppm downfield from tetramethylsilane
DMAA	*N,N'*-dimethylacrylamide
DMAP	4-(dimethylamino)pyridine
DMF	*N,N*-dimethylformamide
d	doublet
DPPH	2,2-diphenyl-1-picrylhydrazyl
DSC	differential scanning calorimetry
EDTA	ethylenediaminetetraacetic acid
EGDMA	ethylene glycol dimethylacrylate
EMA	ethyl methacrylate
EPR	electron paramagnetic resonance
ESCA	electron spectroscopy for chemical analysis
FTIR	Fourier transform infrared
g	grams
HBA	hydroxybutyl acrylate
HBMA	hydroxybutyl methacrylate
HEA	2-hydroxyethyl acrylate
HEMA	2-hydroxyethyl methacrylate
HPMA	hydroxypropyl methacrylate
h	hour
Hz	hertz
J	coupling constant
kC	kilocuries

MAA	methacrylic acid
MEA	2-methoxyethyl acrylate
MEMA	2-methoxyethyl methacrylate
MMA	methyl methacrylate
min	minutes
m	multiplet
MW	molecular weight
NMR	nuclear magnetic resonance
Pa	Pascal
PB15:3	pigment blue 15:3
ppm	parts per million
PR122	pigment red 122
PVA	poly(vinyl alcohol)
PY155	pigment yellow 155
RMCS	royal military college of science
RT	room temperature
SEM	scanning electron microscopy
s	singlet
St	styrene
T	temperature, torr
THF	tetrahydrofuran
UDC	10-undecenoyl chloride
XPS	X-ray photoelectron spectroscopy

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1 Introduction

1.1 Pigments and Dyes

1.1.1 What is a pigment?

Pigments are solid colorants used in inks and are an aggregation of molecules that typically range in size from 0.1 to 1.0 μm. [1] Pigments usually consist of planar molecules which contain functional groups such as amides and carbonyls that participate in hydrogen bonding. These molecular features give strong intermolecular attractive forces which lead to stable "crystals" with high lattice energies which are difficult to disrupt by solvents. Thus pigments are solid particles, practically insoluble in any solvent, and to be dispersed require a dispersant to act as a "bridge" between the solvent of the ink and the pigment. Unlike dyes, pigments do not dissolve in the ink's solvents but remain as distinct particles. They are used to improve coverage on certain substrates while offering better fade resistance and humidity stability than dyes.

1.1.2 What is a dye?

Like pigments, dyes are colorants but may contain solubilising groups such as sulfonic and carboxylic acids. [1] Dye "crystals" are less stable than pigment particles due to the fact that their intermolecular forces are weaker than thoses found in pigments, they are thus easily broken up by solvents to give rise to solutions. Therefore, dyes can be applied to various substrates from a liquid in which they are soluble, although they must possess an affinity for the media, such as paper, for which they are used.

1.1.3 Pigments used

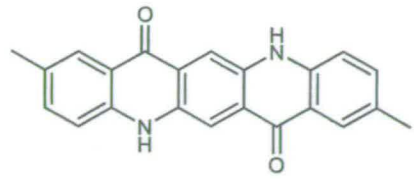
The choice of the pigments to be used in an ink formulation depends on a large number of factors. [1] The selection is a compromise between the hue of the material, that is the major wavelength reflected from the material (the color), the intensity of the colour, the cost of the pigment and the manufacturing ease of the pigment.

In this project four pigments: Pigment Red 122, Pigment Blue 15:3 and Pigment Yellow 155 (manufactured by Clariant) and Carbon Black (manufactured by Degussa) were used because:

a) They were all on the market and used in commercial Kodak inks.
b) They are chemically inert and are highly symmetrical uncharged molecules which form relatively rigid, planar or near planar structures with strong intermolecular bonding forces (hydrogen bonds) providing protection of the pigments from chemical reactions. [2]

1.1.3.1 Pigment red 122

Pigment red 122 **1** also known as 2,9-dimethylquinacridone belongs to the quinacridone pigment family (Figure 1.1).



1

Figure 1.1: Pigment red 122

The quinacridone structure is a linear system of five rings. The molecule consists of a central benzene ring which is bridged to two peripheral six-membered aromatic rings by two 4-pyridone rings. Quinacridones exist in the angular forms **2** and **3**, as well as in two linear arrangements **4** and **5** (Figure 1.2). [3]

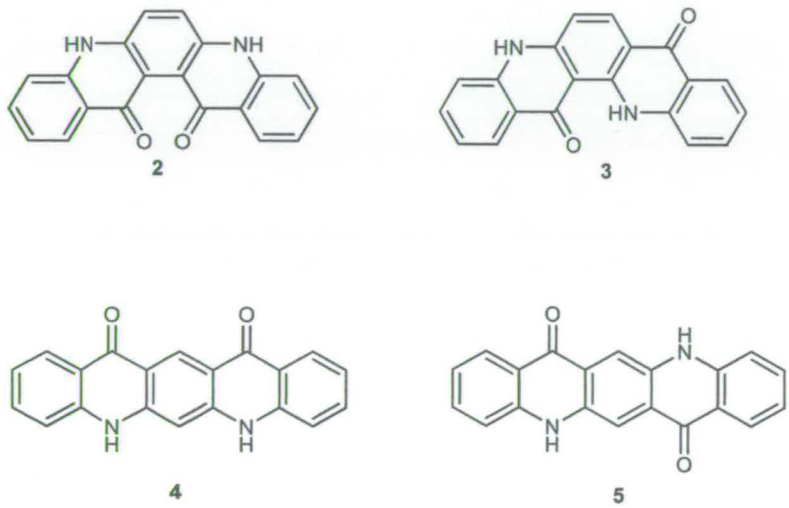


Figure 1.2: Quinacridone molecules

Among the four isomers only quinacridone **5,** named linear trans quinacridone, has stimulated commercial interest because of its high tinctorial strengh.

1.1.3.1.1 Synthesis of pigment red 122

Four general methods have been used to prepare pigment red 122. [4, 5]

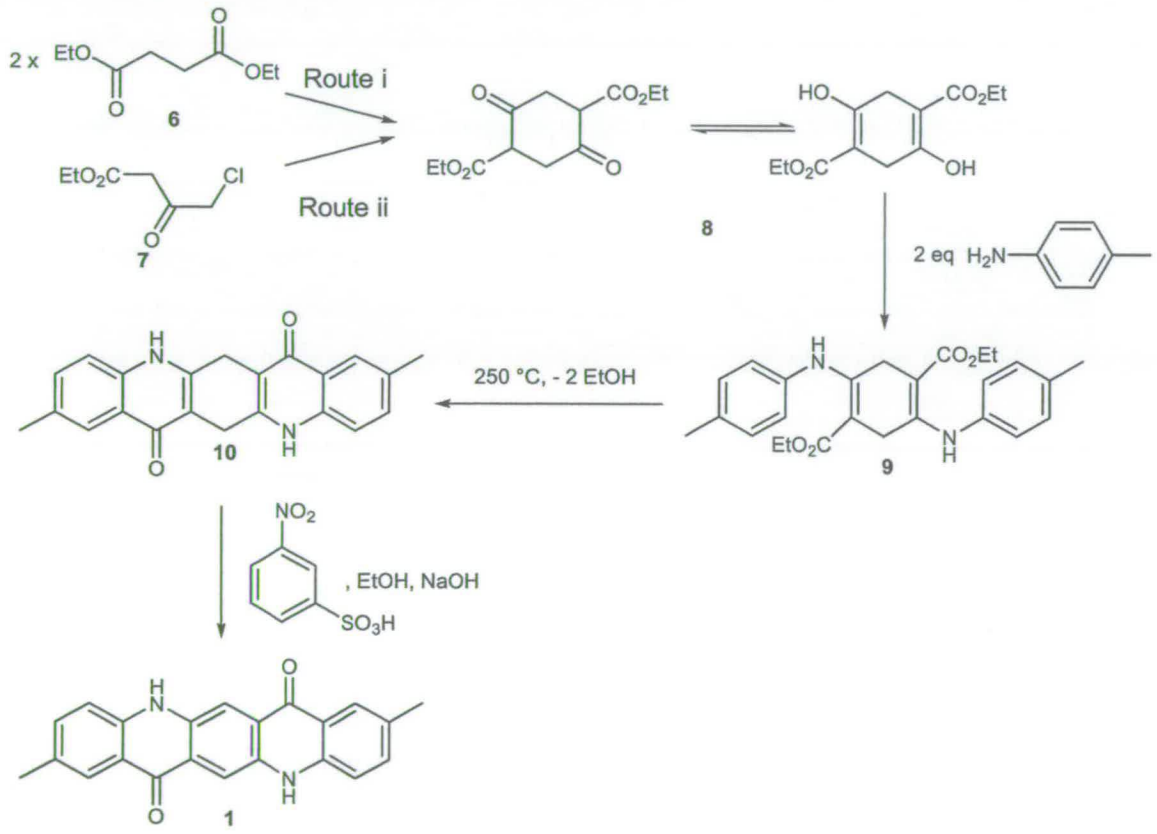
a) Thermal ring closure processes via the succinylosuccinic dialkylester. [6]

The succinylosuccinic dialkylester **8** can be made in two different ways:

i. Cyclisation of succinic dialkylesters **6** using sodium alkoxide. [7]

ii. Condensation of ethyl-γ-chloroacetoacetate **7**. [8]

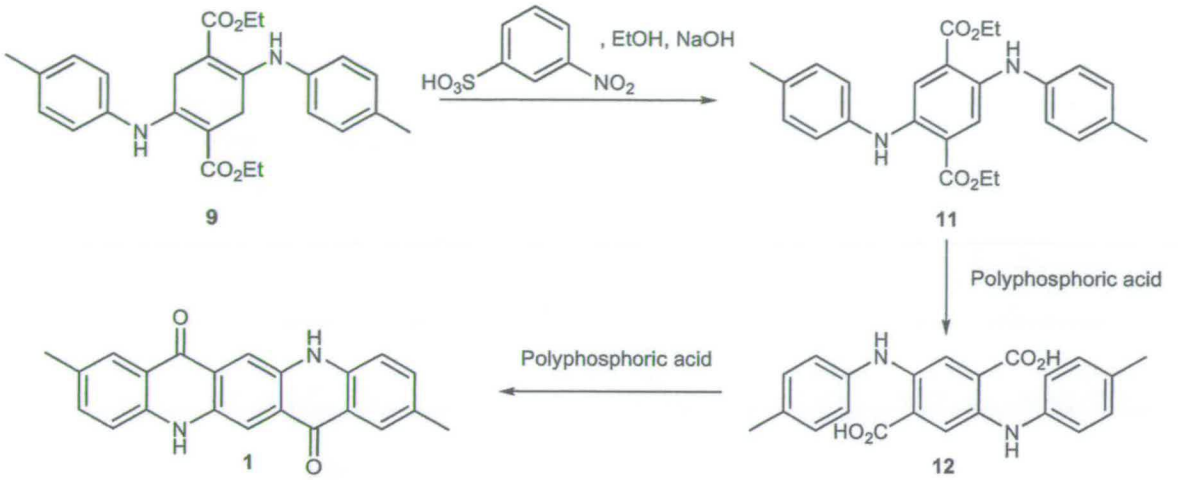
Succinylosuccinic dialkylester **8** is treated with two equivalents of *p*-tolylamine to form the diethyl-2,5-bis-(*p*-tolylamino)-cyclohexa-1,4-diene-1,4-dicarboxylate **9**. Thermal ring closure forms the dihydroquinacridone **10** which is oxidised to give rise to **1**. [9]



Scheme 1.1: Synthesis of pigment red 122

b) Acid mediated ring closure

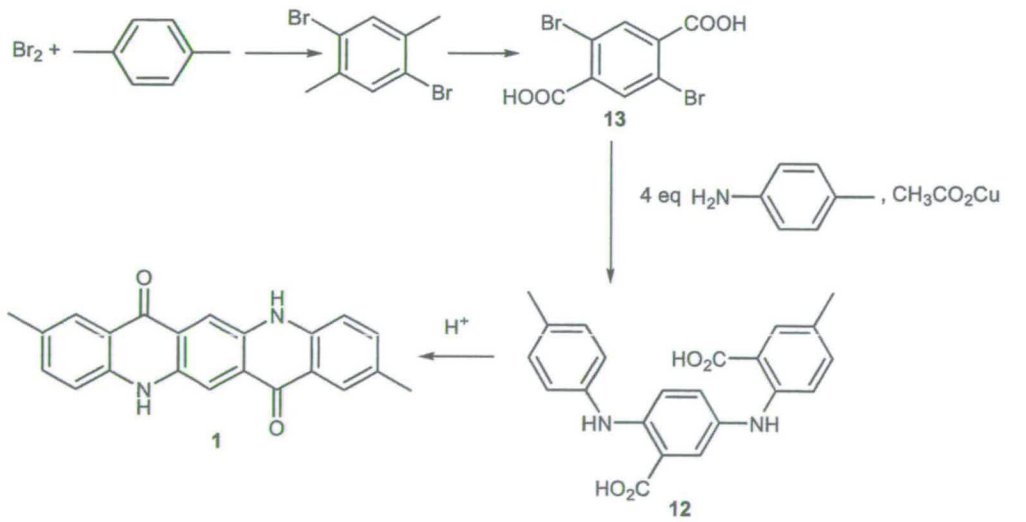
Diethyl-2,5-bis-(*p*-tolylamino)-cyclohexa-1,4-diene-1,4-dicarboxylate **9** is oxidised to diethyl-2,5-bis-(*p*-tolylamin)-o-terephthalate **11**. Hydrolysis and cyclisation in polyphosphoric acid produces pigment red 122 **1**. [10]



Scheme 1.2: Second synthesis of pigment red 122

c) Dihalogenterephthalic acid process

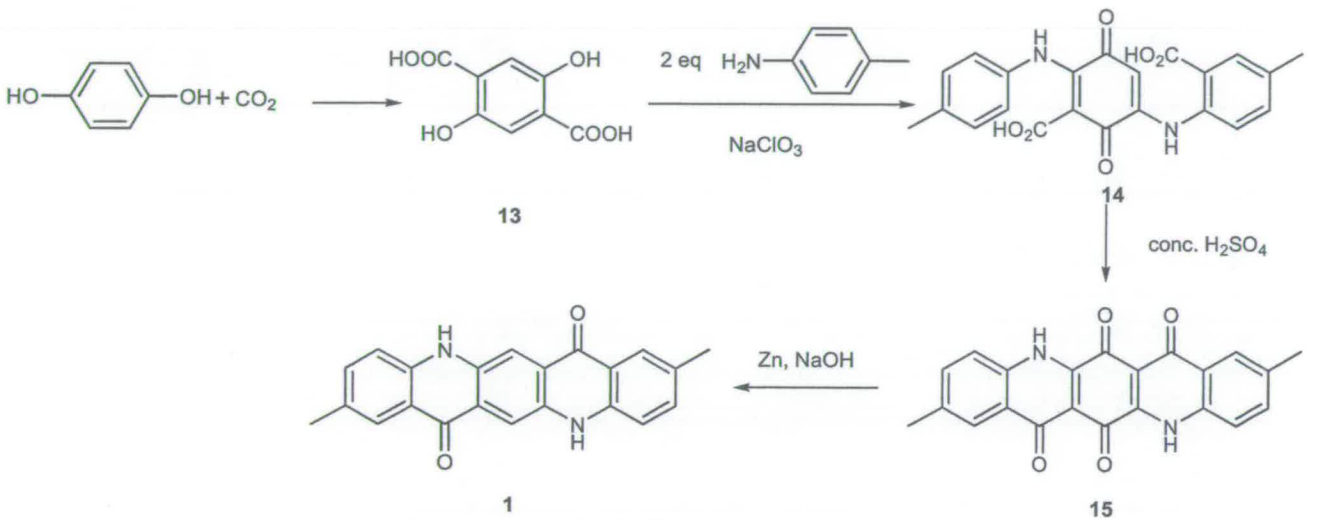
2,5-dibromo-1,4-xylene obtained by bromination of 1,4-xylene using Br_2 followed by oxidation gives 2,5-dibromoterephthalic acid **13**. Reaction with *p*-tolylamine gives 2,5-ditolyaminoterephthalic acid **12**, which cyclises to form pigment red 122 under acidic conditions as above. [11]



Scheme 1.3: Third synthesis of pigment red 122

d) Hydroquinone process

The hydroquinone process was developed by BASF. [12, 13] Hydroquinone-2,5-dicarboxylic acid is prepared by a modified Kolbe-Schmitt synthesis from hydroquinone and carbon dioxide. Subsequent reaction with *p*-tolylamine affords 2-(5-carboxy-3,6-dioxo-4-*p*-tolylamino-cyclohexa-1,4-dienylamino)-5-methyl-benzoic acid **14** which after ring closure using concentrated sulphuric acid affords 2,9-dimethyl-5*H*,12*H*-quino[2,3-*b*]acridine-6,7,13,14-tetraone **15** which is reduced with zinc in dilute sodium hydroxide solution under pressure to form pigment red 122 **1** (Scheme 1.4).



Scheme 1.4: Hydroquinone process

1.1.3.2 Carbon black

Carbon black refers to particles of essential pure carbon composed of complex aggregates with quasi-graphitic structure produced by gas phase polymerisation. Small parts of carbon black are like graphite, and the overall structure of carbon black is believed to consist of a folded version of the graphite network. [14]

1.1.3.2.1 Preparation

Carbon black used in inks is produced following the Degussa gas black process. [15] This process is based on the principle of thermal oxidative decomposition which means that combustion occurs in the presence of air and operates as an open system where the carbon black is formed in diffusion flames meaning that oil and the carrier gas are initially separated and combustion will occur when they are mixed together. The process uses vaporized oil with coal tar distillates being the preferred feedstock. These oils are heated in a vaporizer, and the resultant vapours are carried by a hydrogen-rich gas to the burners, the flames from which are allowed to impinge on water cooled rollers.

1.1.3.2.2 Other uses of carbon black

The Chinese were the first to use carbon black in order to produce water colours and inks. The Greeks and Romans used it in black paint for painting the walls of buildings. Nowadays carbon black is prevalent in cars, from the engine compartment (seals, engine mounting, hoses, fan belts) to the interior (such as the dashboard), in coatings for the exterior and in tyres and special rubber items and rubber mixtures.[16, 17, 18, 19] Much smaller amounts of carbon black are used in inks [20] and paints [21] and in plastics [17]. A new aspect of carbon black is that it is being studied for its electro-conductor capabilities to be used in electrodes and other cell components for batteries. [22]

1.1.3.2.3 Characteristics of carbon black

Carbon black does not exist as primary particles. [23, 24] During the manufacture of carbon black the primary particles fuse to form aggregates. The shape and degree of aggregate branching is referred to as structure. Typical carbon black primary particle size ranges from 8 nanometers to 300 nanometers.

Carbon black and graphite have similar structures, the difference between them are:

a) The particle size of graphite (micro-sized) is bigger than the one of carbon black (nano-sized).
b) The surface area of graphite (8 to 250 m^2/g) is typically smaller than the surface area of carbon black (50 – 770 m^2/g).
c) Graphite has a high crystallinity whereas carbon black has a low crystallinity.
d) Carbon black has a similar structure to graphite, just with less order.

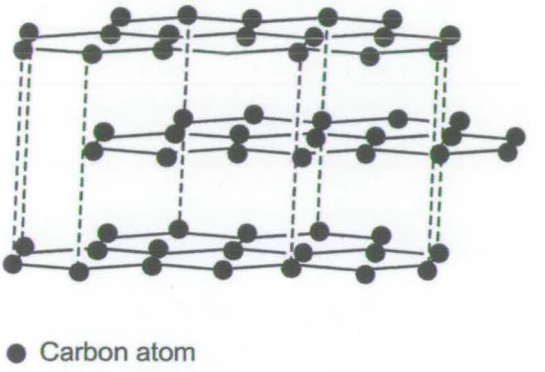
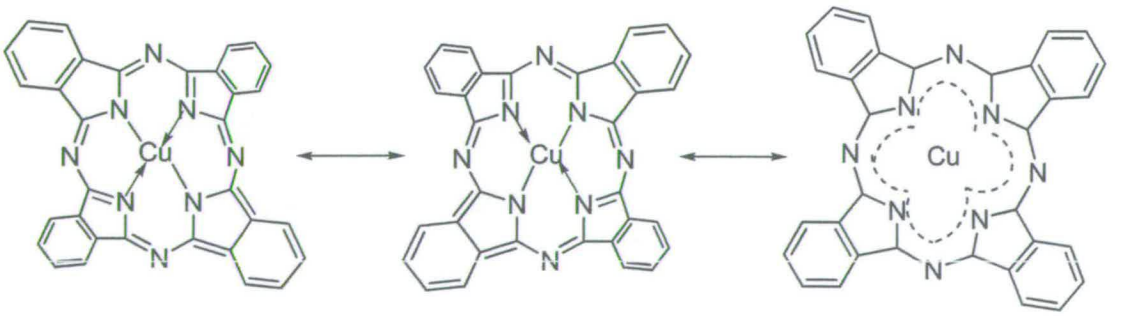


Figure 1.3: Graphite crystal structure

1.1.3.3 Pigment Blue 15:3

Copper phthalocyanine blue is the copper (II) complex of tetraazatetrabenzoporphine. The molecule adopts a planar and fully conjugated structure which exhibits exceptional stability. The unit cell contains two centrosymmetric molecules. The mesomeric structures indicate that all of the pyrrole rings simultaneously contribute to the aromatic system.



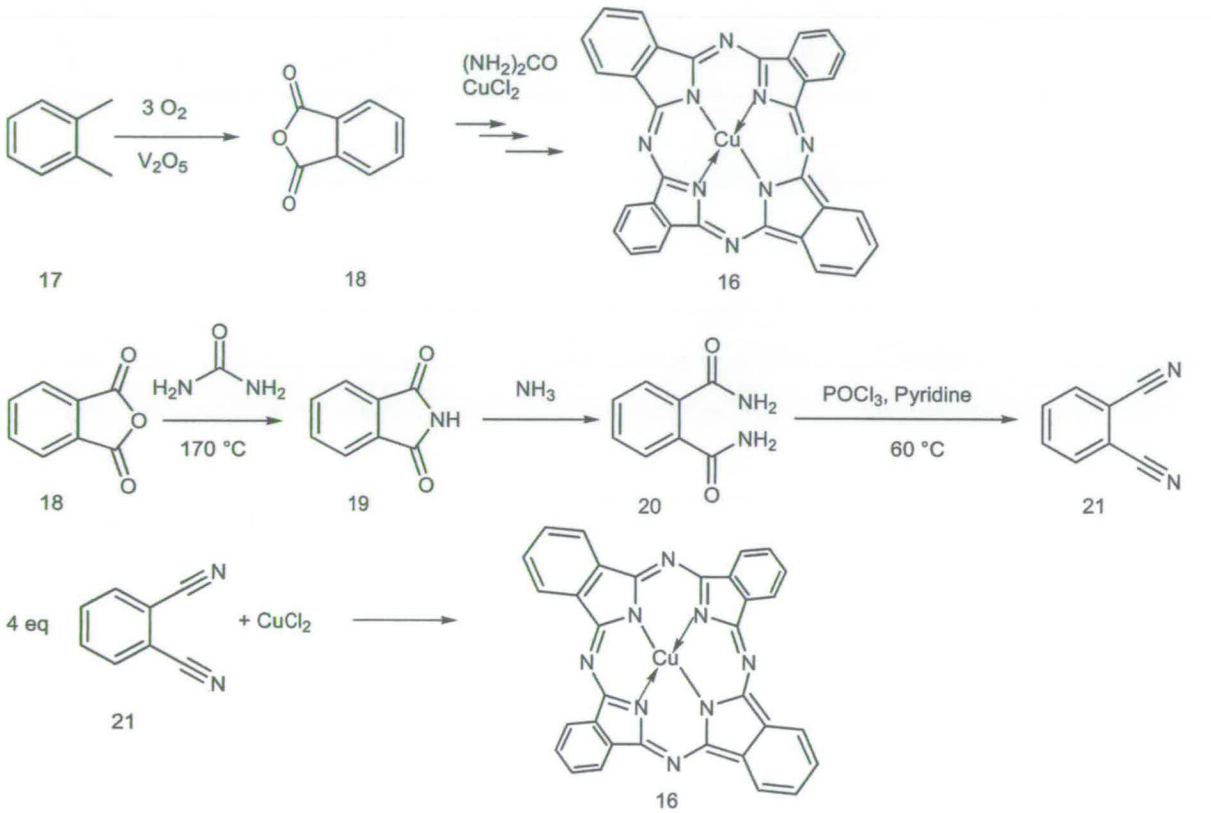
16 16a 16b

Scheme 1.5: The mesomeric structures of PB 15:3

Phthalocyanines were independently studied in three groups between 1907 and 1933 with R. P. Linstead [25] analysing and naming the molecules.

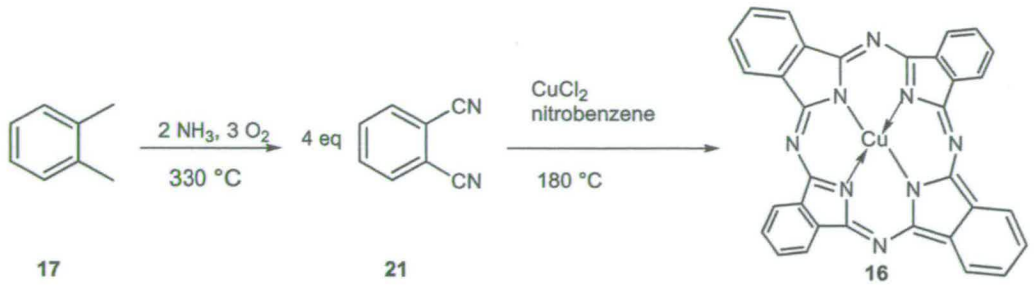
1.1.3.3.1 Methods of preparation

Two main methods can be used in the production of Pigment blue 15:3. [26] The synthesis [27, 28] can be achieved by high temperature cyclotetramerisation of phthalic anhydride **18** which is prepared by oxidizing *o*-xylene in the gas phase with vanadium peroxide as a catalyst. Phthalic anhydride was converted into phthalimide **19** by heating it to 170 °C with an excess of urea. Using a large excess of concentrated ammonia, phthalimide **19** is converted to phthalamide **20**, which by dehydration using phosphorous oxychloride in pyridine at 60 °C, is converted to phthalonitrile **21**. The phthalonitrile **21** reacts with copper (II) chloride at 200 °C to give copper phthalocyanine **16** (Scheme 1.6).

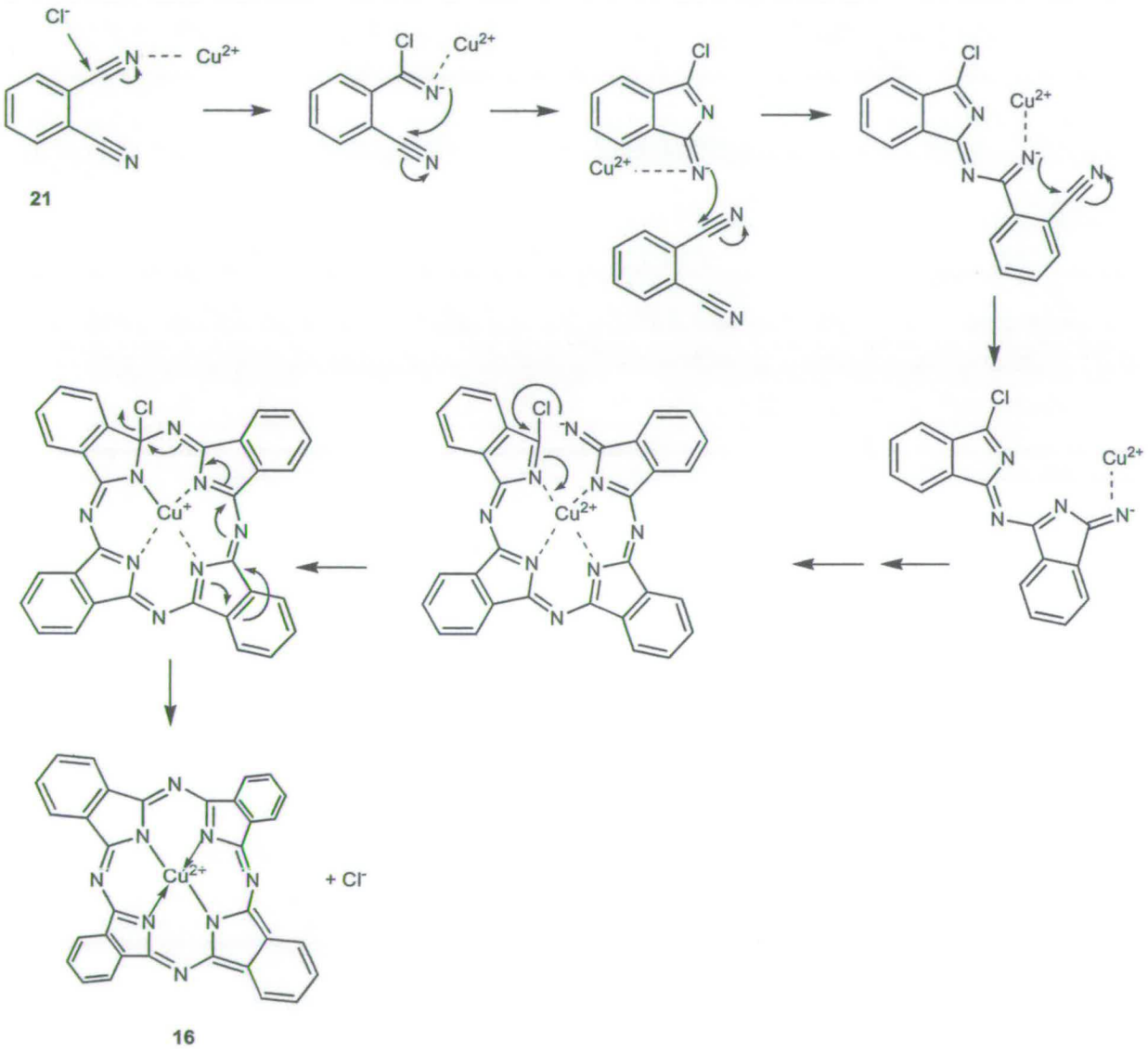


Scheme 1.6: Production of Pigment Blue 15:3 by BASF

The synthesis [27] of Pigment blue 15:3 **16** can also be achieved by high temperature cyclotetramerisation of phthalimide **19** which is obtained by oxidizing *o*-xylene with ammonia at 330 °C. Subsequently a cyclisation reaction to an isoindoline derivate takes place which is shown in Scheme 1.8. These steps are repeated to give a CuPc ring intermediate. Finally, the counter-ion Cl^- ion is eliminated and CuPc is formed.



Scheme 1.7: Synthesis of copper phthalocyanine (II)



Scheme 1.8: Mechanism of copper phthalocyanine (II) synthesis

1.1.3.3.2 Properties

In general, all the phthalocyanine pigments exhibit excellent lightfastness, heat stability, chemical and bleed resistance, processing capabilities and durability. Copper phthalocyanine blue is polymorphous and has five different crystal forms but the α and β forms (Figure 1.4) are the only ones to have commercial interest. The formation of these crystal forms is controlled by the finishing of the crude pigment such as use of acid or mechanical treatment. Pigment blue 15:3 is the β-form of copper phthalocyanine blue which is the most stable. It affords a clean shade of turquoise and displays good dispersibility. [29]

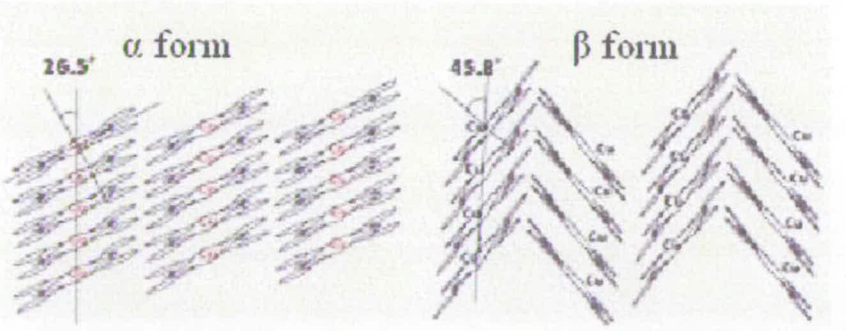
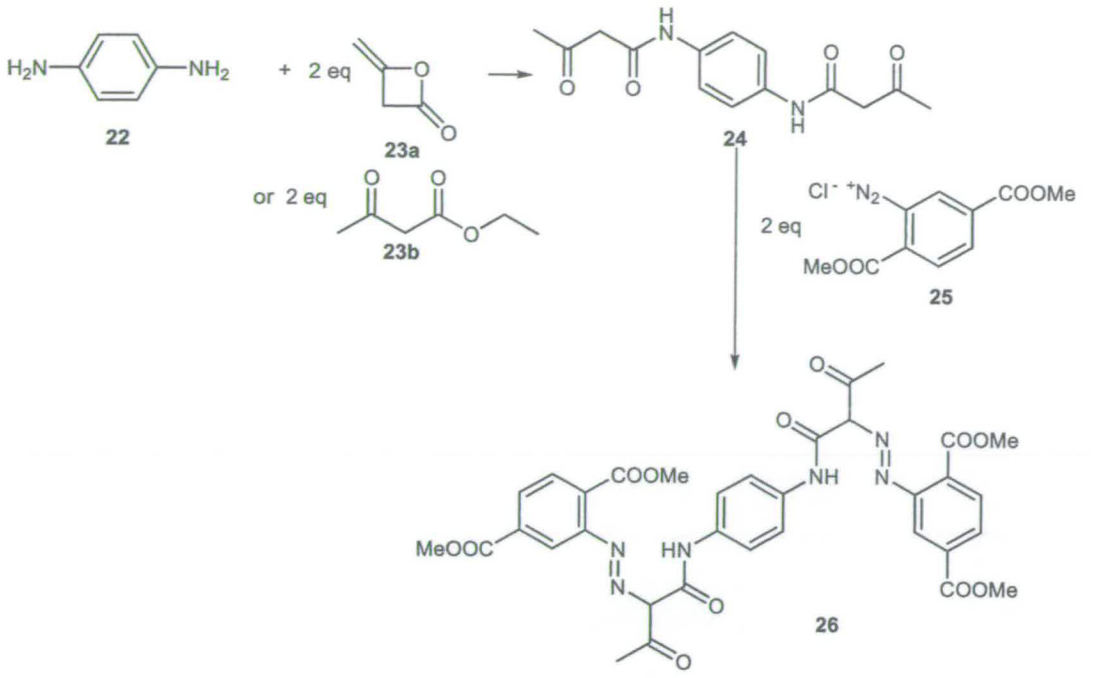


Figure 1.4: Arrangements of molecular stacks in α and β forms [29](reproduced with permission)

1.1.3.4 Pigment Yellow 155

Pigment Yellow 155 comes from the family of the bisacetoacetarylide pigments. One method to synthesise pigment yellow 155 **26** is described in Scheme 1.9. [30] Condensation of 1,4-phenylenediamine **22** and 2 equivalents of diketene or acetoacetic ester **23** gives *N,N'*-p-phenylene-bis-acetoacetamide **24** which reacts with coupling to 2,5-bis-methoxycarbonylbenzenediazonium chloride **25** to form Pigment yellow 155 **26**.



Scheme 1.9: Synthesis of Pigment Yellow 155 [30]

1.1.4 Current uses of these pigments in Kodak inkjet inks

Kodak uses a water based formulation comprising a humectant and a composite of colorant polymer particles, which have a pigment phase and a polymer phase. [31] The principle difference between this ink and other available formulations resides in the colorant composition. An aqueous colorant mixture is dispersed in an aqueous medium under agitation to give very finely divided colorant particles having a particle size less than 80 nm. Then, to this mixture is added a polymerisation initiator such as AIBN and a monomer such as an acrylate to form a composite colorant having a colorant phase and a polymer phase. This formulation has the following properties:

a) Compatibility with water and solvents such as ethylene glycol, ethanol and diethylene glycol,
b) Stability in ink jet compositions (no formation of aggregates, particle size of the components does not change),
c) When such an ink composition is printed, the resultant images on the surface of an ink jet recording element have improved image quality and physical durability such as scratch and smudging resistance.

Another advantage of this ink composition is the formation of a concentrate which can be diluted with an appropriate solvent to an ideal working concentration in terms of viscosity, colour, hue, saturation density and print area coverage for a particular application.

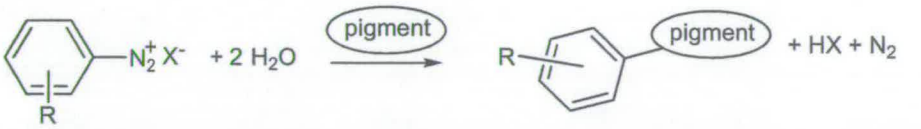
Furthermore, this ink composition is compatible with the organic solvents used in the formulation and maximises the interaction with the substrate where the ink is applied. This results in an improvement in the adhesion, and/or the smudge resistance of the image area. [31]

1.1.5 General methods used to modify or activate the surface of pigments

Only a few methods are already used to modify the surface of pigments in order to improve their performances.

1.1.5.1 Diazonium coupling reaction

Surface modification by diazonium coupling of pigments can result in "enhanced" pigment characteristics and is achieved by coupling either an aromatic group or a C1-C12 alkyl chain, an ionic, ionizable group or mixture of both. [32] This is commonly used with carbon black in order to produce surface modified carbon black. [33]



R = CO_2H, SO_3H, polymer

Scheme 1.10:Diazonium coupling reaction

1.1.5.2 Impregnation, adsorption and precipitation methods

The impregnation method[34] is effectively impregnation of polymers onto pigment. This involves pre-treatment of pigment surface using for example nitric acid and then grafting of polymer by heating overnight of the pigment – polymer mixture.

For the adsorption method[35], the polymer is absorbed onto a carbon black surface by heating. Upon irradiation with a ^{60}Co source, fixation of the polymer onto the carbon black surface occurs.

In the case of the precipitation method, two ways can be used. Firstly, the dispersion consisting of pigment particles and polymer in a water immiscible organic solvent can be dispersed in water to form an emulsion. The solvent is then distilled off and the emulsion droplets convert into solid particles. [36] Alternatively, the polymer can be dispersed in a first solvent (methanol for example) and then added to a pigment dispersion in a second solvent where the polymer is not soluble (water for example). With this method precipitation of the polymer occurs, thereby covering the pigment particles. [37]

1.2 Inks

An ink is defined as a fluid used in writing or printing. Two main types of ink formulations are used in the market today: dye based and pigmented inks. Their uses are determined by the mode of printing and the required performance. [38]

1.2.1 Performance requirements for inks

In addition to matching the colour, others specifications are required for ink formulation which are summarised in Table 1.1 below. [38]

Table 1.1: Ink formulation requirements [38]

Ink	Media compatibility	Drop ejection	Print
Good stability	Non-corrosive	Uniform drop size	High optical density
Low viscosity	Plastic compatible	High drop velocity	Colour quality
High surface tension	Adhesive compatible	High drop frequency	Fading resistance
Conductivity	No particulate formation	No orifice wetting	Lightfastness
Long shelf life		No crusting	Waterfastness
Non flammable		No clogging	Solvent resistance
Non toxic			Smear resistance
No biological growth			Crack resistance
			Media sensitivity
			Spreading
			Feathering
			Dry time

1.2.2 Ink Formulation

The formulation of an ink is an important step of the printing process. Not only it will determine the drop ejection characteristics and the reliability of the printing system but also the quality of the printed image. Below are described the majority of the common compounds used to formulate the ink. [39, 40, 41, 42]

a) **Colorant**: normally a dye or a pigment. Usually 2-8 % wt of the total ink.
b) **Solvent**: Primary ink vehicle that dissolves or suspends the colourant. The typical solvents used are water, alcohols and methyl ethyl ketone. Usually 35-80 wt%.
c) **Surfactants and penetrants**: the former are used to lower the surface tension of the ink and the latter to promote penetration (wetting) into the substrates. For example surfynol (0.1-2 wt%) is used as a surfactant while isopropyl alcohol (1-5 wt%) is used as a penetrant.
d) **Solubilizing agent**: to promote dye solubility in the primary solvent. This is also called a co-solvent and can be used to increase the loading of the dye, which enhances the ink's optical density. Furthermore it should hold the dye in solution in case of increasing concentration e.g. due to nozzle evaporation N-methyl pyrrolidine can be used. Usually 2-5 wt%.
e) **Dispersant**: to assist the colloidal suspension of a pigment. For example Tween 80, which is also named polysorbate 80, can be used. Usually 3-8 wt%.
f) **Humectant**: to inhibit evaporation. Glycols are used for aqueous inks. Usually 13-30 wt%.
g) **Viscosity modifier**: to raise the inks viscosity. For example glycols can be used for aqueous inks. Usually 1-3 wt%.
h) **pH buffer**: pH adjustement toward the basic side is typically used for improving ink metal compatibility (less corrosion of the printer's metal parts). Further pH changes induces colour shifts. Usually 0.1-1 wt%.
i) **Chelating agent**: to complex metal ions to prevent scale build-up where ink may evaporate. A typical material is EDTA (ethylenediaminetetraacetic acid). Usually 0.1-0.5 wt%.
j) **Bioacid**: to kill bacteria and other organisms. An example is Thioethylene glycol. Usually 0.1-0.3 wt%.
k) **UV-blocker, antioxidant, free radical inhibitor**: to promote lightfastness or to prevent degradation of long chain dye molecules. Usually 1-5 wt%.
l) **Fixative**: to promote image permanence, improving the smear resistance. For example a water-based soluble latex, 1-3 wt%.

A typical ink formulation used by Kodak is described in Table 1.2. [43]

Table 1.2: Example of an ink formulation

Component	Concentration (wt %)		Purpose
Dye or pigment	Dye based 1.5 %	Pigment based 0 – 10 %	Colourant (Gloss inks contain polymer only)
Humectant (mixture)	15 % (thermal drop on demand) Mixture of pyrrolidinone, hexanediol, glycerol, (ethylene-, diethylene-, triethylene-, polyethylene-glycol).	50 % (piezo drop on demand)	Viscosity (3.2 cps)
Polymer	n/a	2 – 6 %	Rubability
Surfactant	As needed	As needed	Surface tension (27 dynes/cm)
Buffer	As needed (for example triethanolamine)	As needed	pH= 8 - 9
Bioacid	As needed	As needed	Stability
Deionised water	Balance	Balance	Adjust volume and density (usually d=1.05g/cm^3)

When the best formulation in terms of density and viscosity is obtained the ink / media interaction needs to be studied in order to know the best media for a given ink.

1.3 Media

Due to the variety of applications where inkjet printing is used, a range of media can be used such as "film", canvas, vinyl-, textiles and papers. The media can be any material which is capable of absorbing the ink and can be fed though the printer. [44]

1.3.1 Plain paper

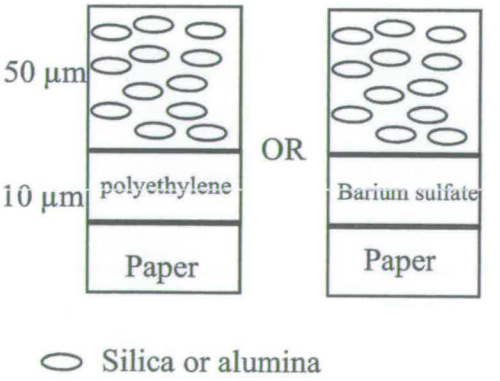
This is the paper typically used in photocopy machines in the office environment. [45] It consists mainly of cellulose fibres and is not recommended for liquid ink jet printing because the ink wicks along these fibre structures decreases sharpness of the image. Fillers, such as calcium carbonate or titanium dioxide, are added to the paper composition to improve the brightness and whiteness, fill voids and increase mechanical stability. Sizing agents, such as starches and gelatine, are added to the paper at a later stage in order to modify the characteristics of the paper by sealing the surface fibres.

1.3.2 Coated media

With modern printers becoming faster there is a need of media which are able to absorb inks as quickly as possible in order to avoid problems such as bleeding. [45] Two sorts of media can be used which are either a porous systems (absorption of the ink by capillarity) or a non porous systems (Swellable Polymer Papers). And both of these systems can be coated in two different ways which give either a resin coated media or a glossy paper media.

1.3.2.1 Porous media (absorption of the ink by capillarity)

The ink is absorbed by capillary action into the micro- or nano- capillaries created by alumina and silica particles (Scheme 1.11).



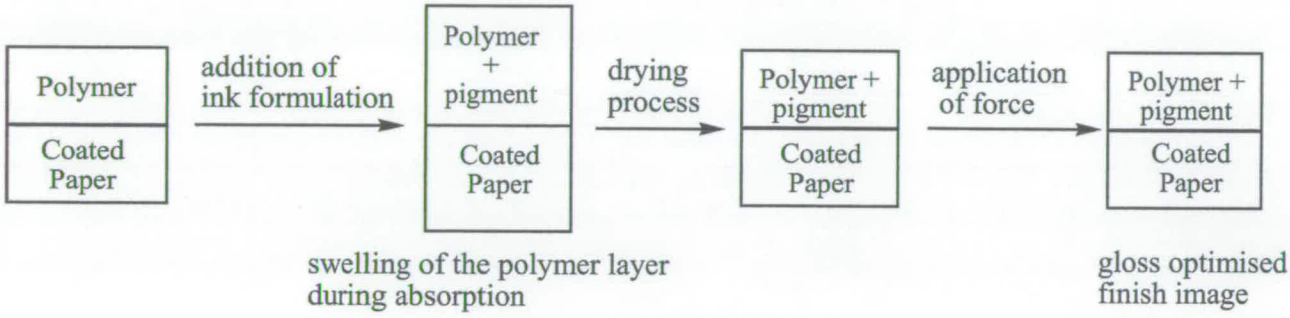
Scheme 1.11: Microporous media

The advantages are that the media dries instantly so it can be handled immediately after printing, it has a good resistance to water and high speed printing modes are possible.

However the media is environmental sensitive: air can be absorbed onto the first layer which means that pollutant and oxidants can be absorbed too. Because of the absence of polymer the surface is quite fragile and can be easily scratched which can results in cracking and slow the speed of coating.[44]

1.3.2.2 Non porous media (swellable polymer papers)

The ink is absorbed and diffuses in to the polymer layers which are typically gelatine, polyvinylalcohol (PVOH), polyvinylpyrrolidone (PVP) or combinations of these polymer systems creating an expansion of the first layer of the media. Then, the solvents evaporate and the media goes back to its original size. At the end of the process, the media will be compressed in order to generate a smoother surface which optimises the gloss of the image (Scheme 1.12).



Scheme 1.12: Swellable polymer paper

The advantages using this type of media is that no gas fading can occur because colourants are protected from the atmosphere and a good glossy appearance results with anti abrasion protection. However, significant problems also arise, puddling can occur because of the bad absorption of ink into the media and coalescence can occur if the paper does not dry enough. [44]

In summary, a good interaction between inks and media is required. The next step is to find the ideal printhead that can be used to spray ink onto the media for a specific application. This part of the procedure is of great significance as it affects the quality of the final image. [44]

1.4 Ink Jet Printing

Ink jet printing can be classed as a digital process. [46, 47] Digital data is converted into a printed product without using any physical image carrier or plate. The ink is ejected though very small orifices to form droplets that are directed onto the media. It is for this reason that this process is called a "non impact printing process". Two main printhead technologies exist: one that produces drops continuously and one that produces drops on demand.

1.4.1 Continuous ink jet printing (CIJ)

CIJ printing (Figure 1.5) means that the ink supply is pressurized sufficiently to create a jet. The jet will break up into a varying drop sizes based on surface waves produced by a piezoelectric vibrator (for example a piezoelectric crystal). These droplets which are charged electrostatically will be ejected from an orifice in the direction of the receptive media. The drops which are not meant to reach the substrate are intercepted and recycled. The drops which will form an image are deflected in mid flight by passing an interceptor (a detector) and flying onwards to finally hit the media, forming an ink dot, which is the smallest image forming entity in an ink jet print. [46]

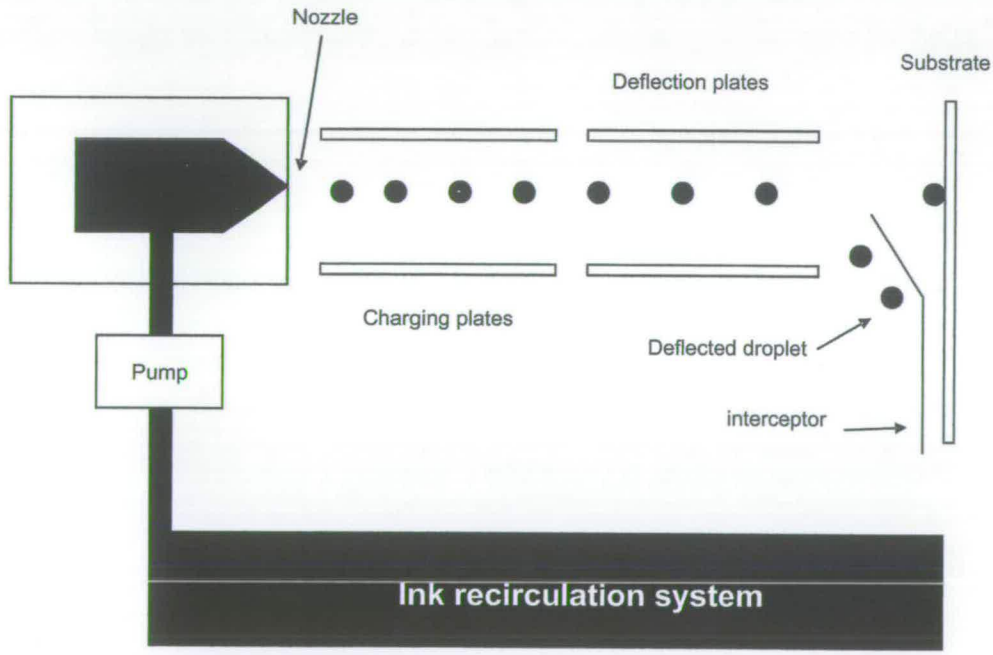


Figure 1.5: Continuous jet printing

1.4.2 Drop on demand ink jet printing (termed DOD and impulse jet)

The drop on demand printhead design is categorized into two methods: piezoelectric and thermal ink jet. The ink is held in a small chamber and forms a meniscus at the orifice. The ink droplet is only produced when it is required to form a dot on the medium. There is no deflection needed and the drops do not need to be charged.[46]

In piezoelectric ink jet printing (Figure 1.6), a piezoelectric element is used to squeeze individual drops out of a small chamber by changing its shape. When an electric field is applied to a piezoactivated wall chamber, the wall's dimension changes a minute amount proportionally to the applied voltage. Depending on the polarity of the applied voltage, it is either a minute contraction or a minute expansion which pushes the ink through the nozzle.

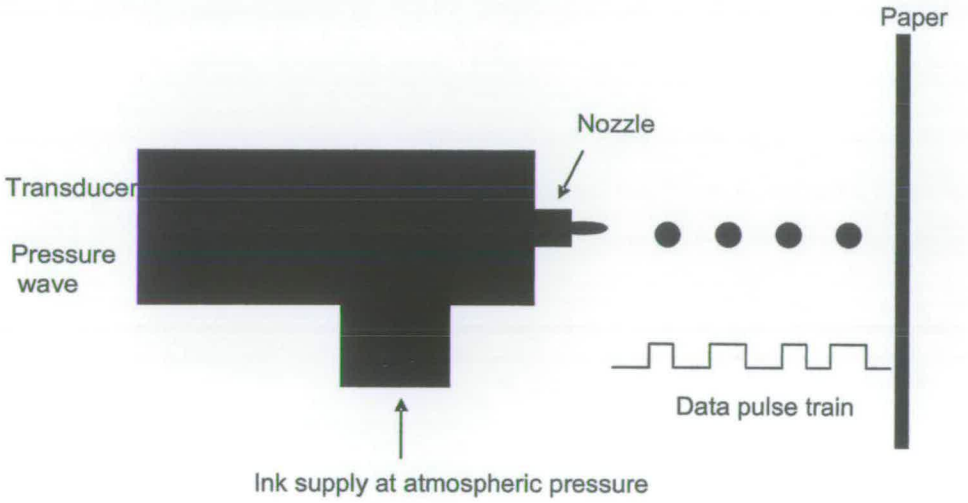


Figure 1.6: piezoelectric ink jet printing

In thermal ink jet printing (Figure 1.7), the printhead is heated up by a resistor, and a vapor bubble is formed, which, as it grows, increases the pressure inside the printhead, thus forcing a droplet of ink though the orifice. As the heat is suddenly cut off, the bubble shrinks, and the resulting pressure shockwave forces the droplet to break off from the orifice and fly towards the substrate. Due to the sudden decrease of pressure, the printhead refills with ink drawn in from the reservoir, and the cycle can begin again.

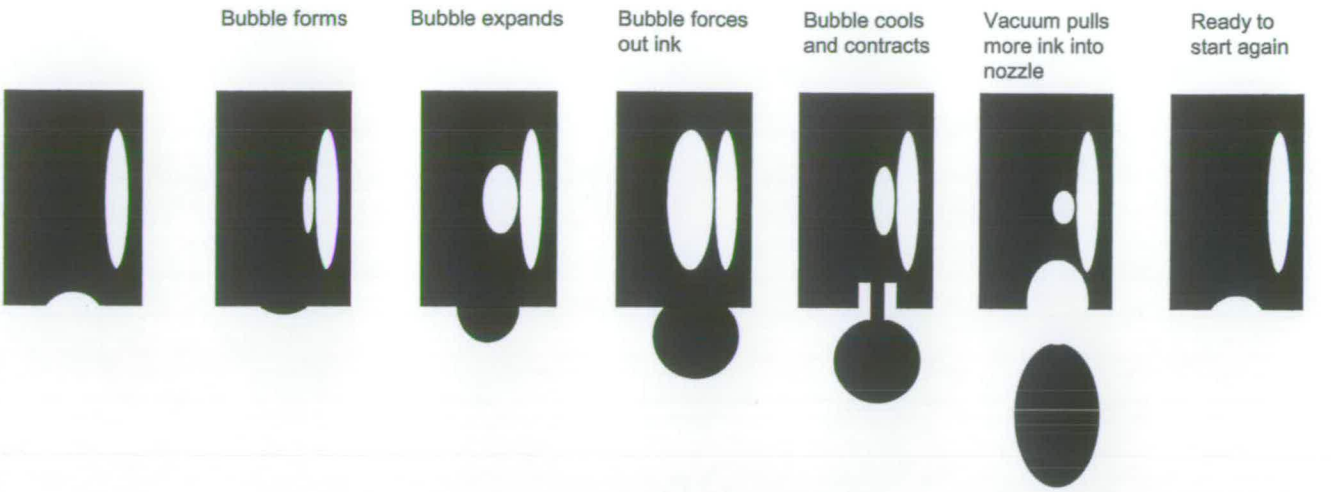


Figure 1.7: Thermal jet technology

In the ideal case, if all the criteria have been respected (perfect ink which does not fade and interacts perfectly with the media chosen, perfect printhead which eject tiny drops of ink with the perfect speed and power) a good quality and permanent image should be obtained. However this is an ideal situation and many parameters have to be optimised to reach this state.

1.5 Problems encountered using inkjet inks

The main problem using dyes in inks is the stability of the image over time. By using pigments in inks, this problem is improved but not completely resolved and other problems result from using pigments. Their industrial synthesis is very difficult and expensive; pigments are generally not soluble in water and therefore require dispersants and/or other additives to render them "printable" in water. The stability of the formulation using pigments in the cartridge is often poor and additionally fading still occurs, if after a longer time.

1.6 Aims of the project

The aims of this project were to improve a range of key properties by modifying the surface of the pigments. The properties to be addressed included:

a) The stability of the ink in the cartridge. This can be improved using "water-soluble pigments" so they will not form any deposit at the bottom of the cartridge.

b) The stability of the image on the paper. When the paper is touched, the ink must not run. The pigments need to be well absorbed by the paper. This can be done by using "water-soluble pigments" which will penetrate better into the first layer of the paper.

c) The stability of the image over time. Damage of the image is due to: [48]

i. light fading caused by visible light or ultraviolet radiation which causes the dye to fade,

ii. ozone absorbed into the pores of the prints which causes the dye to fade and yellow,

iii. temperature which causes the dye to fade, to migrate and allows yellowing,

iv. humidity which allows the dye to migrate.

The idea was to make a protective barrier at the surface of the pigments using polymers which could act as light stabilisers, absorbers of UV and antiozonants.

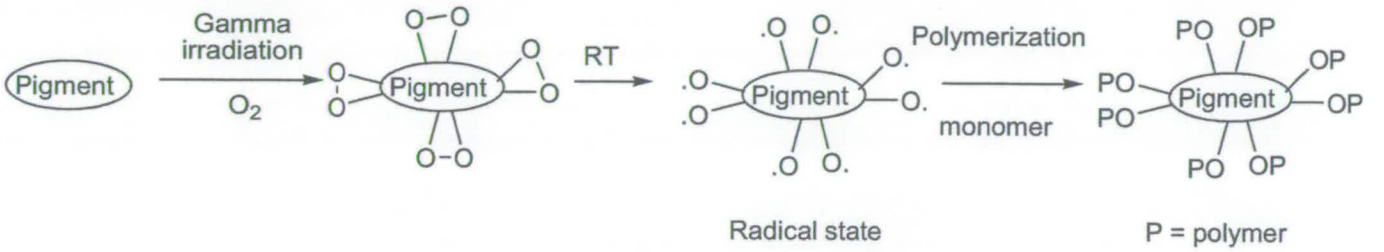
In summary, the inkjet system performances depend on the co-optimisation of the software, the hardware, the ink and the media. The printhead will influence the selection of the ink and the ink will influence the choice of the media. The main concerns for pigment based inks are reliability (to avoid nozzle clogging, misdirect jets), image quality and durability of the image. One of the previous solutions to improve the ink was to absorb polymers onto the pigment surface.

The actual method which will be described in this thesis involves covalent attachment of polymers onto the pigment surfaces. This method improves the dispersibility of the pigment in water, which means that the stability of the ink inside the cartridge, and the stability of the image on the media increase. Then because the pigment is covered by polymers and other additives, it is protected and will provide enhanced resistance against fading.

2 Gamma irradiation and grafting

2.1 The concept

Four pigments (PR122, PY155, PB15:3 and CB) were exposed to gamma radiation, in the presence of oxygen, so that the free radicals created on the pigment by C-H fission would combine with oxygen to form bridged peroxide species. These peroxides decompose at room temperature to yield oxygen radicals that can undergo reactions with monomers such as acrylates or acrylamides for example (Scheme 2.1). [49, 50]



Scheme 2.1: Principle of irradiation & grafting

The treatment of pigments by gamma irradiation provides a clean and convenient method of functionalisation that avoids the difficult and unpleasant chemistries typically associated with pigment functionalisation. [49] Attachment of a variety of functionalities (for example esters and acids) can be readily achieved using free radical methodologies. The aim of this work was to determine the levels of radicals generated on pigment surfaces by gamma irradiation and to optimise the grafting conditions in order to obtain polymers grafted onto pigments and to keep the colour strength of the initial pigment.

2.2 Gamma irradiation

2.2.1 Source of gamma irradiation

The formation of ^{60}Co is carried in a nuclear reactor by bombarding a lighter nucleus such as ^{59}Co with neutrons. [51]

$$^{59}_{27}Co + ^{1}_{0}n \longrightarrow ^{60}_{27}Co$$

Scheme 2.2: Formation of ^{60}Co

^{60}Co is radioactive, which means that its nucleus is not stable and has a tendency to disintegrate. One of its neutrons converts to a proton, electron and anti-neutrino. The electron picks up the disintegration energy and is emitted from the ^{60}Co atom at almost the speed of the light. [52] The emergence of the electron is accompanied by energy photons called gamma rays. The nucleus of the ^{60}Co atom, in this process, converts to a nucleus with 28 protons and 32 neutrons which is a stable nucleus of nickel (^{60}Ni).

$$^{60}_{27}Co \longrightarrow ^{60}_{28}Ni + ^{0}_{-1}e + 2\,^{0}_{0}\gamma$$

β particle γ particle

Scheme 2.3: Gamma rays formation

2.2.2 The instrument

The Royal Military College of Science (RMCS) ^{60}Cobalt Gamma Radiation Source is retractable enabling the radioactive material to be moved from the irradiation space to a shielded position by remote control. This, coupled with an interlocking door, ensures that the cell can only be entered when the source is shielded. The source is made up of 20 rods of ^{60}Co encapsulated in steel tubes and retained in an open cylindrical arrangement. In the shielded position, the source is housed in a lead and steel flask which incorporates a sliding shutter. In the equipment, the can is visible as an aluminium structure on the bench top. When the source is in the up position, therefore irradiating, a cylinder of cobalt rods is raised into the hollow can. [53]

The typical activity of a new source is 3.7 10^4 B (Becquerel) which is equivalent to 10 kC (kilocuries) with a maximum dose rate of 33 kGy/h (kilogray per hour) or 3.3 Mrad/h occurring at the centre of the cylindrical can and has a half life of 5.2 years. The RMCS source activity while this work was performed was approximately 6 kGy/h.

According to the inverse square rule (Equation 2.1) dose rate drops off with distance r from the source, therefore the dose rate received by a sample can be controlled by positioning the sample with respect to the can.

$$D = ME / 6r^2$$

Where: D is dose rate in μSvh^{-1}, M is activity in MBq, E is energy/disintegration in MeV and r is distance from source in metres

Equation 2.1: inverse square rule

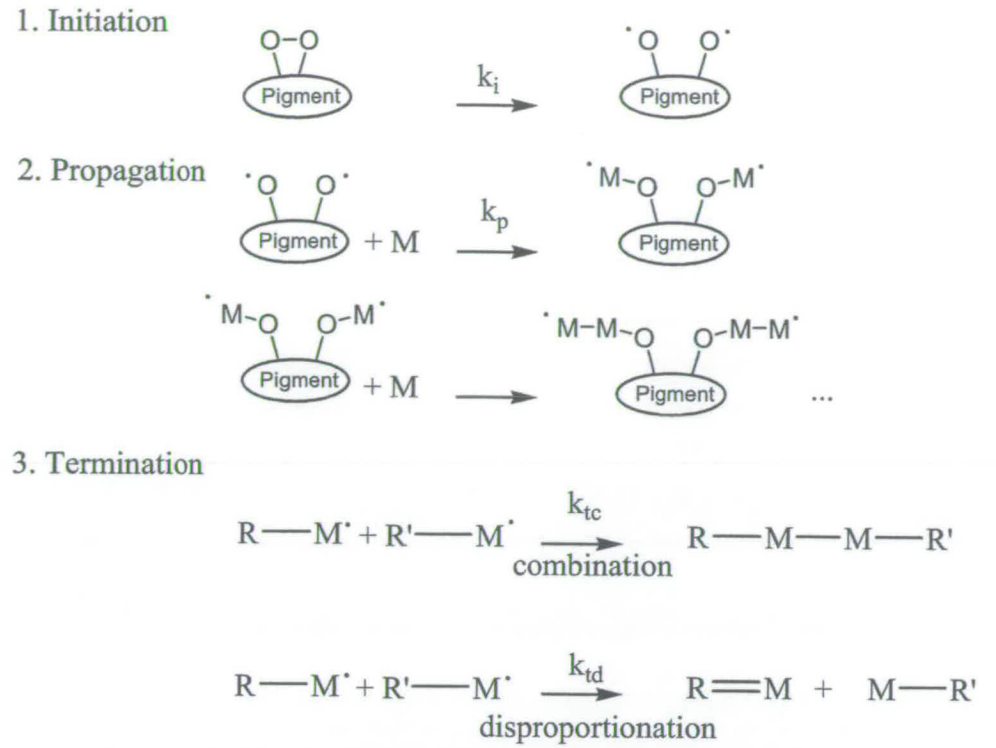
The total dose received by a sample can be controlled by the length of time the sample is left in the activated source in combination with the distance from the can, which dictates the dose rate. In this project, the sample was placed on the bench top in the height range of 3 – 12 cm above the work surface at a distance of 15.4 cm from the centre of the source. To achieve this, the small sample bottles were placed on top of lead bricks. Then irradiated samples were kept at - 20 °C until required.

2.2.3 Free radical polymerization

Free radical polymerization is the most common method to synthesize polymers with high molecular weight due to the number and diversity of monomers available,[54] while radicals formed have a variety of advantages such as tolerance to other functional groups and relatively non-demanding reaction conditions. Radical chemistry does not require reagents of high purity and is relatively insensitive to water, although reactions are often carried out with an atmosphere of nitrogen, since oxygen is a quencher of free-radicals.

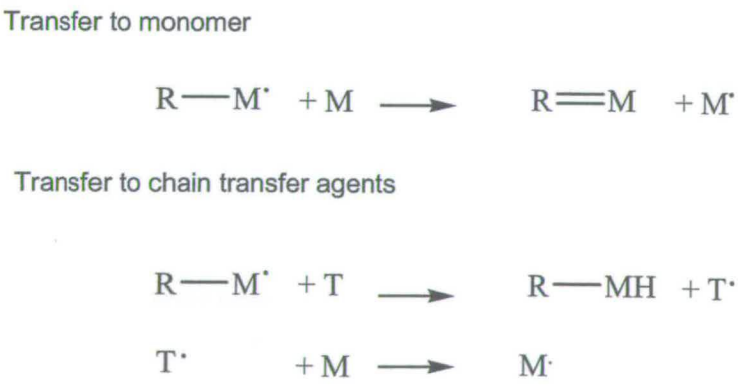
Mechanism of radical polymerization

Free radical polymerizations take place via three steps: initiation, propagation and termination (Scheme 2.4). The initiation step involves homolytic cleavage of the initiator with heat, light or a catalyst, although in our case, the peroxide species synthesized during gamma irradiation will have the role of the initiator. In the propagation step, radicals formed attack the monomer and transfer the radical to the monomer, which is followed by a series of reactions increasing the chain length. Termination of polymer chains is obtained via various mechanisms such as combination and disproportionation.[55]



Scheme 2.4: The three stages in free radical polymerization

Transfer reactions may also occur during polymerization; which includes transfer of the radical from the growing chain to the monomer, transfer to another polymer chain as well as intramolecular transfer. The later two may lead to branching and cross-linking of the polymer (Scheme 2.5). Transfer reactions also occur when radicals of a growing chain are trapped by a transfer agent, which ultimately controls the overall degree of polymerization (DP).



Scheme 2.5: Various types of transfer reactions involved in termination of radical polymerization

2.2.4 Irradiation of pigments

The initial samples were irradiated at a total dose of 25 kGy at 1 kGy/h. Higher doses of 50 kGy and above were irradiated at a dose rate of 2.5 kGy/h. The dose was varied in order to control the number of radicals formed.

2.2.5 Measurement of the relative level of radicals formed on pigment surfaces

Electron paramagnetic resonance (EPR) was used to determine the level of radicals on pigment surfaces. [56]

2.2.5.1 Principle of EPR

The energy differences between atomic or molecular states studied by EPR are predominantly due to interactions of unpaired electrons in the sample with a static magnetic field $\mathbf{B}_0$ produced by an electromagnet (typical values of $\mathbf{B}_0$ in EPR are between 0.1 T and 5 T).

This effect is called the *Zeeman effect*, and because the electron has a magnetic moment μ, it acts like a compass when placed in a magnetic field. This magnetic moment is quantized, it can take only discrete values while the energy differences between the levels are proportional to $\mathbf{B}_0$. The free electron has a spin S=1/2, which means it can take two different states. [56]

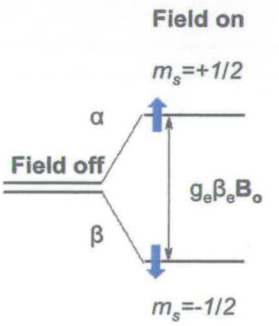


Figure 2.1: For a free electron: two projections, $m_s = \pm 1/2$

The energy between those states for a free electron is given by

$$\Delta E = h\nu = g_e \beta_e B_0$$

$$Where\ \beta_e = 9.27402e^{-24}\ JT^{-1}\ and\ g_e = 2.00232.$$

Equation 2.2: Energy between two states

For real samples, g is an often orientation-dependent proportionality factor which depends on the electronic configuration of the radical or ion being studied and is one of the main information sources in EPR. The interaction between the unpaired electron and nuclear spins is called *hyperfine coupling* and is also obtained by EPR.

It provides orientation dependent information about the electron density at the nucleus, the distance and orientation of the nucleus to an ion carrying the unpaired electron, or the number of equivalent nuclei coupling to the electron. Further interactions influencing the EPR spectrum are the *zero-field splitting* for systems with $S > 1/2$, the *nuclear quadrupole interaction* due to a quadrupole moment for nuclei with $I > 1/2$, and the *nuclear Zeeman interaction*. [57, 58, 59]

2.2.5.2 Results and discussion

The first experiment was done using 2,2-diphenyl-1-picrylhydrazyl (DPPH) as a standard. [60, 61] A specific amount of activated pigment red 122 and a capillary tube containing a specific amount of DPPH were placed inside the quartz tube and analyzed by EPR.

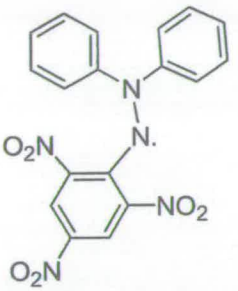
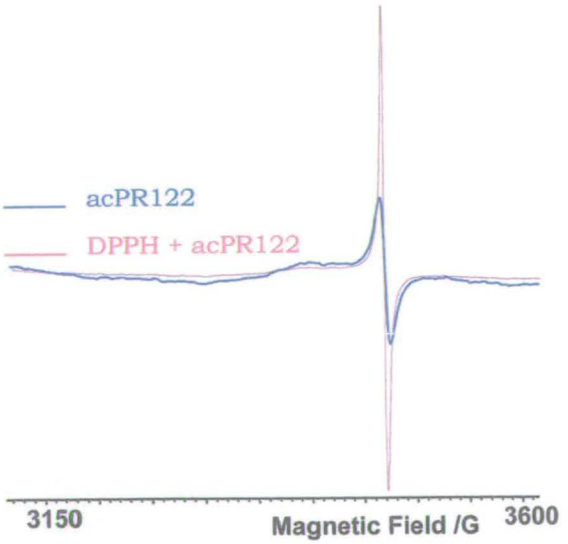


Figure 2.2: DPPH structure

Unfortunately, the signal of DPPH overlapped the signal of activated PR122 which made the determination of the level of radicals impossible. However, the single signal of activated PR122 gave information on the radicals formed suggesting it was a C·, O· or a radical not coupled to any nucleus.



acPR122: activated pigment red 122

Figure 2.3: EPR spectrum of acPR122 and DPPH

An alternative standard used was manganous sulfate tetrahydrate. This time, the signals did not overlap and by integrating and comparing the signals, a qualitative correlation of radicals formed on the surface of pigments could be deduced. The signal which is circled represents the pigment signal. The six other signals represent manganese sulfate tetrahydrate which has a spin of 5/2.

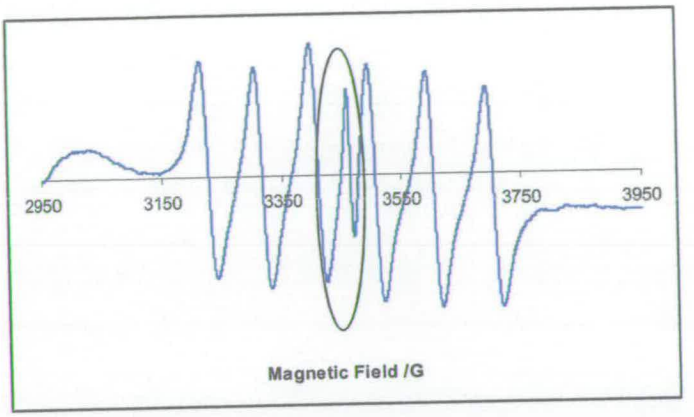


Figure 2.4: EPR spectrum of activated PR122 and $MnSO_4$, $4H_2O$

This experiment was conducted for the four pigments using the same procedure. The EPR spectra are shown in Figure 2.4 to Figure 2.7. Carbon black absorbs all microwaves, therefore, no signal could be detected. In Figure 2.5 and Figure 2.6, only a part of the EPR spectrum focusing on the pigment peak is shown, therefore, not all the $MnSO_4$ signals are visible.

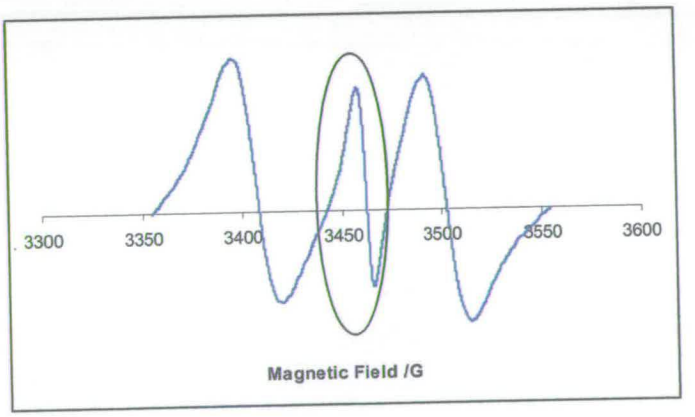


Figure 2.5: EPR spectrum of activated PR122 and $MnSO_4.4H_2O$ (C =4.5 mmol.L^{-1})

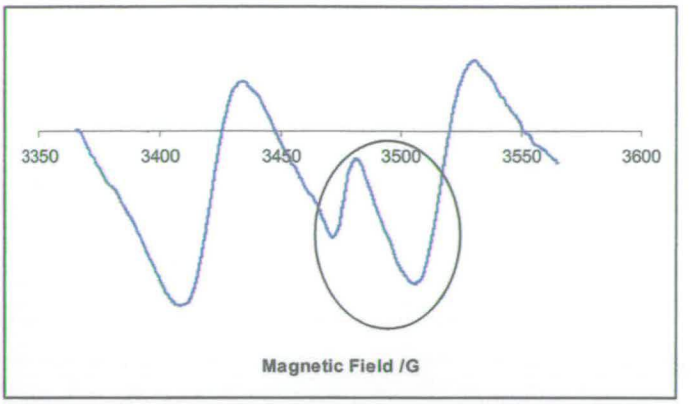


Figure 2.6: EPR Spectrum of activated PY155 and $MnSO_4.4H_2O$ (C = 0.25 mmol.L^{-1})

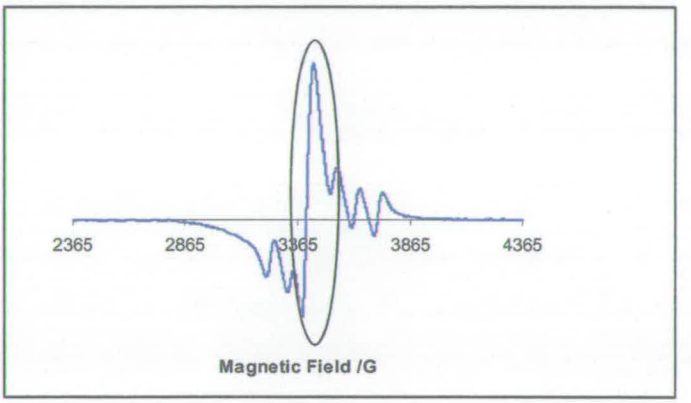


Figure 2.7: EPR spectrum of activated PB15:3 and $MnSO_4.4H_2O$ (C = 0.11 mmol.L^{-1})

The relative levels of radicals on the pigment surfaces was determined by comparing the area of the integrated signal of manganese, which corresponded to a known concentration of manganous sulfate tetrahydrate, with the area of the integrated signal of the pigment (Table 2.1).

Following this procedure the area of the peak of the pigment spectra was calculated and gave a qualitative level of radicals on activated pigment red 122, activated pigment blue 15:3 and activated pigment yellow 155 surfaces. PB15:3 showed the highest signal, PR122 had a moderate signal and PY155 had a very weak signal.

Table 2.1: relative levels of radicals generated on the pigments

Pigment	Relative level of radicals
activated PR122	0.075
activated PB15:3	0.43
activated PY155	0.0155

Three samples of PR122 were irradiated at different dose rates (10, 100 and 200 kGy) and therefore should have different levels of radicals on their surface. EPR results showed an increase, demonstrating that a higher dose rate gave higher levels of radicals on the pigment surfaces (Table 2.2).

Table 2.2: Radical amount on PR122 surface for different dose rates

Dose rate (kGy)	Relative level of radicals Average
10	0.0048
10	
10	
100	0.0123
100	
100	
200	0.0278
200	

In conclusion, EPR has been used to confirm the presence of radicals on pigment surfaces and allows comparison of the radical levels, which increased with higher dose rates.

2.3 Grafting

The grafting of polymers onto pigment surfaces was achieved by radical polymerization of various monomers initiated by the radicals present on the pigment surface. The polymerizations in these studies were carried out in up to twelve parallel reactions, in a Radleys Carousel Station™ with water cooling and under a nitrogen atmosphere. The degree of grafting was calculated as follows: [62]

$$\%Graft = 100\ (W_2 - W_1)/W_2$$

Where: W_1 is the initial weight of activated pigment and W_2 is the weight of the modified pigment

2.3.1 Preliminary studies

PR122 was used for the optimisation of the grafting process. As optimisation of all the parameters was carried out at the same time, graft percentage of poly(*N,N*-dimethylacrylamide) onto PR122 could vary due to the different changes applied during modification.

For each experiment, a degassing time of 2 hrs prior to grafting was carried out, in order to avoid any inhibition of the polymerization reactions due to oxygen, as it reacts with chain radicals to form relatively unreactive species. [62]

2.3.1.1 Temperature

The polymerization of *N,N*-dimethylacrylamide (DMAA) in DMF, the solvent in which the activated pigment red 122 was "most soluble" and gave a well dispersed solution without any agglomeration of pigment particles, was investigated at several temperatures.

At 80 °C no detectable polymerisation occurred. At higher temperatures (120 °C) polymerization was detected by the increase of the mass recovered (Table 2.3).

Table 2.3: Influence of temperature on grafting

Activated pigment (mg)	36	36
DMF (mL)	3	3
DMAA (mL)	1	1
Temperature (°C)	80	120
Graft weight (%)	0	1900

2.3.1.2 Use of water as solvent

It can be advantageous if the grafted polymers can be added in water, due to ease of industrialisation. However, significantly higher grafting yields were obtained with DMF used as a solvent compared to water (Table 2.4).

Table 2.4: Influence of solvent on graft weight

Activated pigment (mg)	31	31
DMF (mL)	-	3
H_2O (mL)	3	-
DMAA (mL)	1	1
T (°C)	120	120
Graft weight (%)	16	2212

By observing a difference between the graft weight of pDMAA-PR122 obtained in Table 2.3 and Table 2.4, it was concluded that the degassing time had an effect on the amount of polymer grafted onto pigment red 122, therefore this parameter was studied.

2.3.1.3 Reaction time

Nine reactions were carried out and stopped at different times of polymerisation (2, 6 and 21 hrs). Reactions were carried out in DMF at 120 °C under nitrogen and DMAA was used as the monomer. The best grafting was obtained after 21 hrs, as shown in Figure 2.8. Longer reaction times did not affect the amount of grafting.

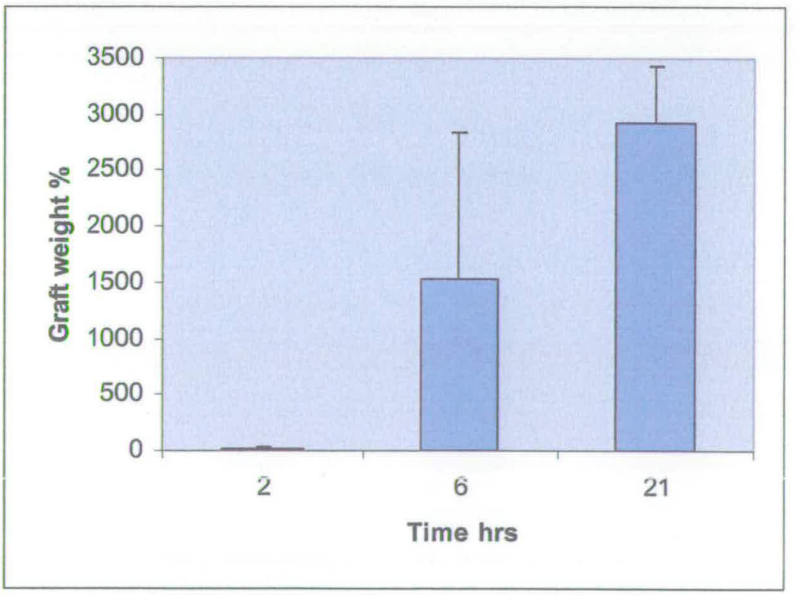


Figure 2.8: Effect of time on graft weight

2.3.1.4 Negative control

In order to ensure that the grafting was occurring due to activation by gamma irradiation, grafting was carried out using non irradiated pigment red 122 for 21 hrs. No polymerization took place at any temperature, showing that it was the process of radical formation on the surface of the irradiated pigment that initiates the radical polymerization.

Table 2.5: Negative control

Pigment red 122 (mg)	33	-
Activated pigment (mg)	-	36
DMAA (mL)	1	1
DMF (mL)	3	3
Graft weight (%)	0	200

2.3.2 Influence of total dose

In order to determine the relation between total dose, which determines the number of radicals [63], and the resulting degree of grafting, four samples were irradiated at different dose rates, which were 10, 50, 150 and 200 kGy, and then used in the grafting process. Reactions were carried out in a Radley Carousel Station™ in parallel in DMF at 120 °C under nitrogen for 7 hrs and DMAA was used as the monomer. Results are summarised in Table 2.6.

Table 2.6: Effect of total dose on graft weight

Total dose (kGy)	Activated Pigment (mg)	DMAA (mL)	DMF (mL)	Graft weight (%)
10	36	1	3	1700
50	36	1	3	1922
150	36	1	3	2148
200	36	1	3	2615

Table 2.6 shows that the higher the total dose, the higher the degree of grafting which is in accordance with the results obtained by EPR (Table 2.2).

2.3.3 Stability of the irradiated compounds

The stability of the irradiated pigments over time was investigated by reacting the activated pigments with DMAA under the same conditions over 12 months beginning 6 months after irradiation. Two types of activated pigments were studied, one group had been stored at RT and the other one had been stored at -20 °C (Figure 2.9). The optimised procedure used for pigment red 122 was used for the three other pigments to check the stability of their activation.

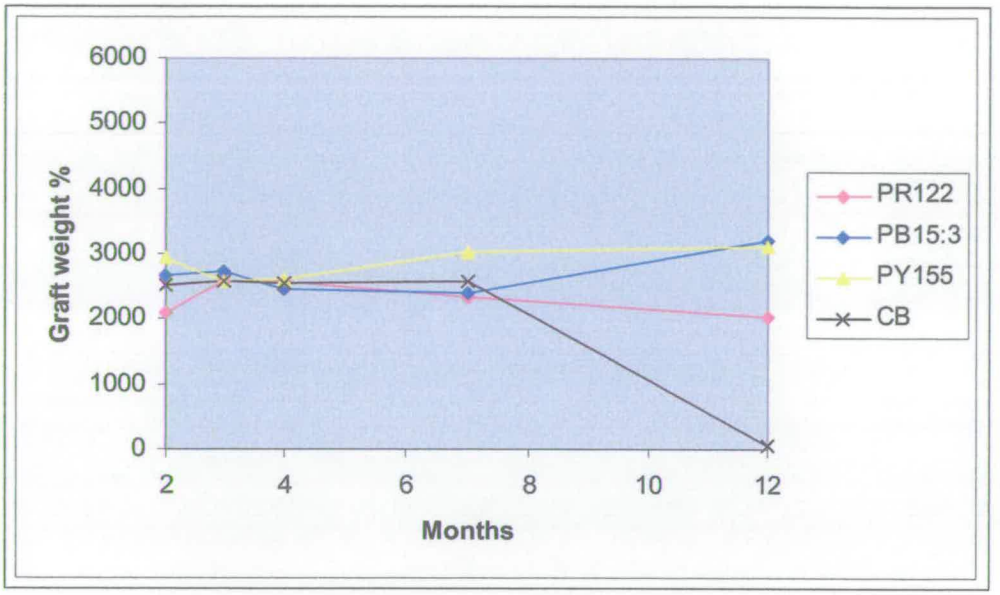


Figure 2.9: Stability of irradiated pigments stored at -20 °C

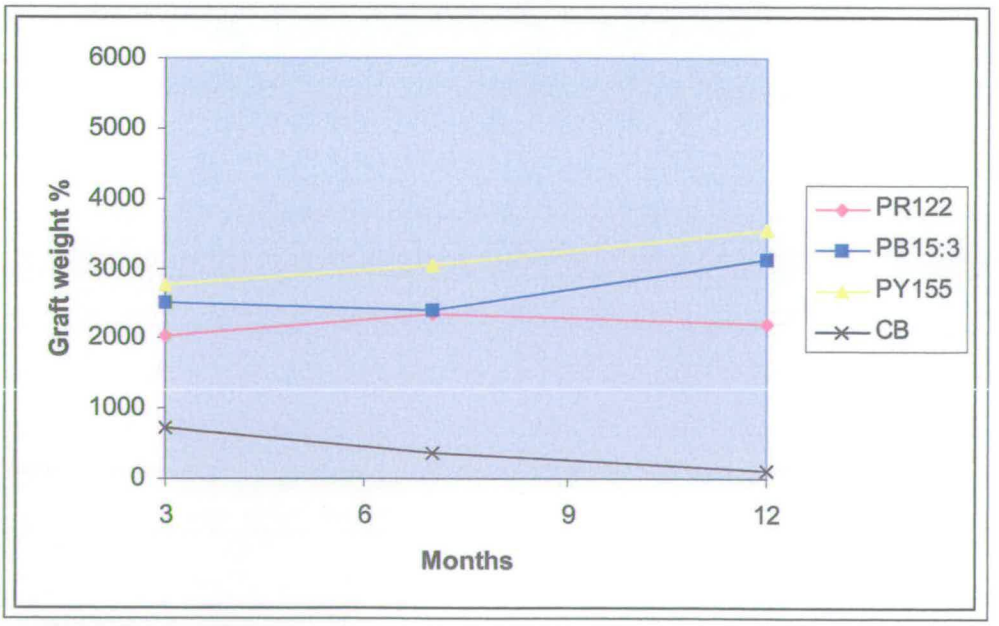


Figure 2.10: Stability of irradiated pigments stored at room temperature

Figure 2.9 and Figure 2.10 show that the activated pigments are stable over 12 months except for activated carbon black which exhibits a decrease in its reactivity. Activated pigments kept at room temperature have a similar reactivity after a year as activated pigments kept in the fridge.

2.3.4 Effect of monomer concentration

This effect was investigated to control the grafting of polymer onto pigment surface. A polymer library was prepared by using different ratios of DMAA and activated pigment red 122 in order to see the effect of monomer concentration on grafting yield, solubility and color of the grafted polymer. Reactions were carried out in DMF at 120 °C under nitrogen overnight. Most of the grafted polymers were obtained in good yield. As Table 2.7 and Figure 2.11 illustrate, the higher the monomer concentration the greater the grafting percentage.

Table 2.7: Monomer concentration effect

	AcPR122 (mg)	DMF (mL)	DMAA (%vol)	Graft weight (%)
1	30	3	0.0003	31
2	30	3	0.003	34
3	30	3	0.01	36
4	30	3	0.03	36
5	30	3	0.16	36
6	30	3	0.3	53
7	30	3	1.6	50
8	30	3	3	104
9	30	3	14	239
10	30	3	25	4976

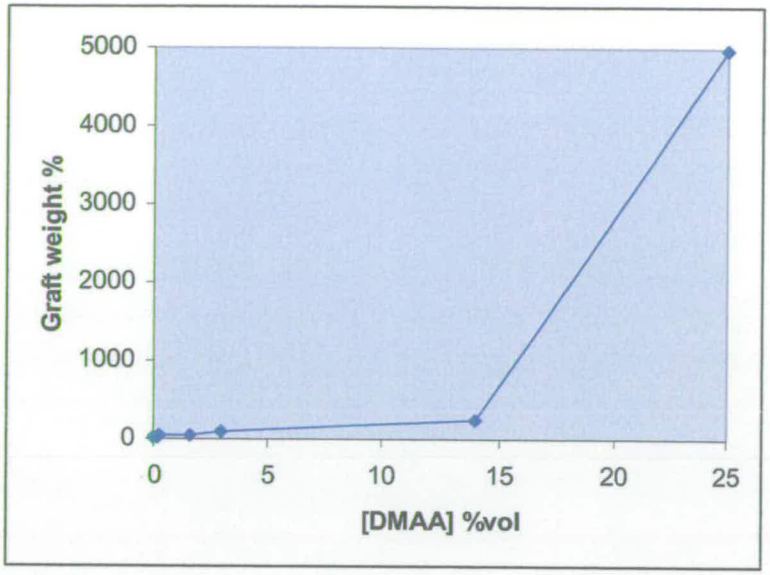


Figure 2.11: Correlation between the graft weight percentage and monomer concentration

Figure 2.12 shows the dispersibility of the aqueous solutions of grafted polymers (1 mg/mL). It was observed that solutions with high grafting weight had a paler colour, which is not ideal, as high quantities of modified pigments will be needed when formulating the ink, as well as good dispersibility in water. After one week, solutions with high graft weights did not sediment which was not the case for low graft weight solutions. In any case, the modified pigments were more dispersible in water than PR122.

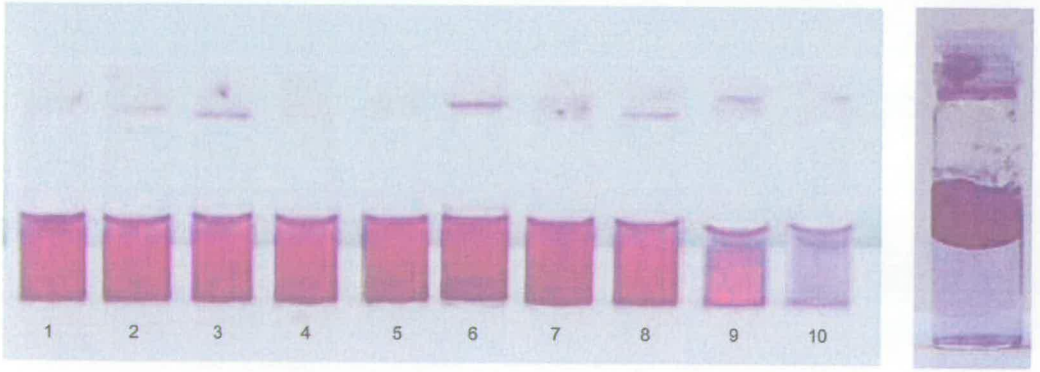


Figure 2.12: Dispersibility of modified pigments *1* to *10* (see Table 2.7) and PR122

2.4 Conclusions

Gamma irradiation was used to graft polymers onto pigment surfaces by surface radical generation and reaction with DMAA. It was possible to verify presence of radicals by EPR. Preliminary experiments were done using PR122 to optimise the grafting via free radical polymerization.

It was noted that pigments modified using DMAA were more dispersed in water than pigment PR122. It was observed that a high percentage of graft weight lead to better dispersibility and less intensity of colour in the formulation. Therefore, it would be best to have a low percentage of graft weight, while still giving a good dispersibility in water. With the concept proved, further grafting was undertaken.

3 Advanced Grafting

The aim of this work was to extend and optimize the process discussed in Chapter 2. In order to do this, different monomers were tested to find the most suitable monomer for grafting and subsequently make a combination of the best monomers to further improve the performance of the pigments. This could be either done by copolymerization or by cross-linking reactions. Finally, modification of the polymers grafted on the pigment was attempted via esterification. This may improve the performance of the pigment and also prove covalent bonding between the polymer and the pigment had taken place.

3.1 Homopolymerisation

Polymerisations were attempted using seventeen different monomers to improve the dispersibility of the four pigments (PR122, Carbon black, PB15:3 and PY155) in water and/or organic solvents. The reaction conditions used were identical and most grafted polymers were obtained in good yields as described in Table 3.1, Table 3.2, Table 3.3 and Table 3.4. Monomers such as acrylamide, 2-acrylamido-2-methylpropane sulfonic acid, DMAA, HEA, methacrylic acid, PVA and 4-Styrenesulfonic acid were used to enhance the solubility of the pigments in water as they are known to produce water soluble polymers. Whereas monomers such as BMA, EMA, HBA, HBMA, HEMA, HPMA, maleic anhydride, methyl acrylate, styrene and 4-vinylbenzylchloride were used to enhance the solubility of pigments in different organic solvents. [64] This also introduced new alcohol groups allowing post polymerisation modification of the grafted species.

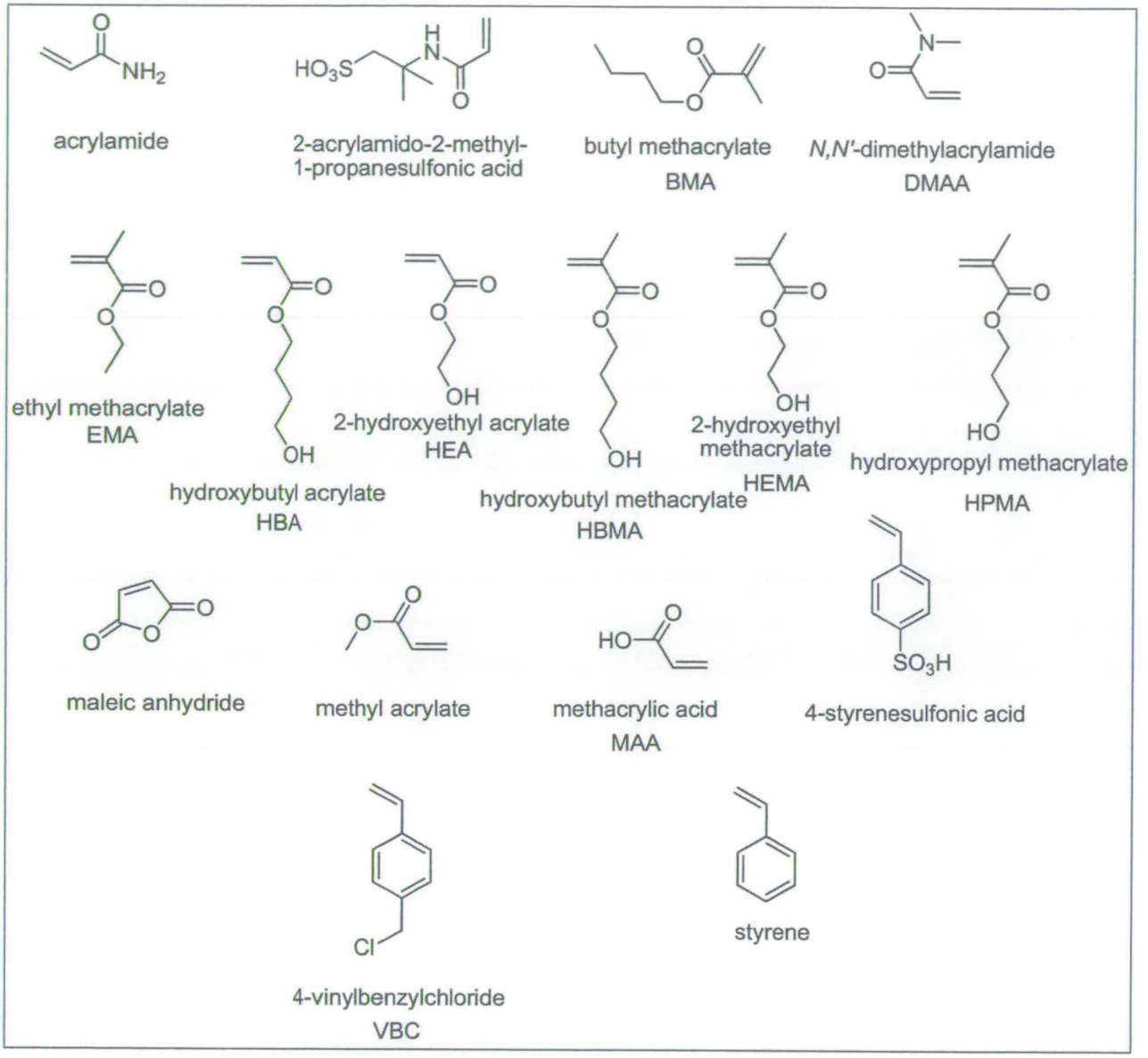


Figure 3.1: Monomers used in homopolymerisation

In order to test dispersibility, each pigment (1 mg) was suspended or dissolved in water (1 mL). The dispersibility of the modified pigments was studied by following the time it took for the pigments to settle when left undisturbed.

3.1.1 Results for PR122

Seventen samples of activated pigment red 122 were treated with monomer, suspended in DMF and degassed using oxygen free nitrogen. The mixtures were heated for 21 h at 120 °C and, after cooling, they were added to a solution of cyclohexane:ether (1:1). The modified pigments precipitated and were filtered and dried under vacuum. It was observed that in the case of methacrylic acid no modification occurred. Table 3.1 shows the graft weight percentage obtained and the dispersibility of the modified pigment in water.

Table 3.1: Homoplymerisation on PR122

Entry	Monomer	Graft weight (%)	Time taken to settle (days)
1	Acrylamide	17	5
2	2-Acrylamido-2-methylpropane sulfonic acid	121	6
3	BMA	88	0
4	DMAA	2594	14
5	EMA	100	0
6	HBA	781	0
7	HBMA	521	0
8	HEA	58	1
9	HEMA	4304	2
10	HPMA	1109	14
11	Maleic anhydride	70	14
12	Methyl acrylate	1148	14
13	Polyvinyl alcohol	136	2
14	St	291	0
15	4-Styrenesulfonic acid	77	14
16	4-Vinylbenzene chloride	411	0

^{1}H NMR was recorded for all the compounds dispersed in $CDCl_3$ and D_2O. In the case of 4-styrenesulfonic acid, only the monomer was detected by NMR as evidenced by the presence of the alkene signals at 6.75, 5.95 and 5.37 ppm. 2-Acrylamido-2-methylpropane sulfonic acid, Maleic anhydride, HBA, HEA, methyl acrylate, PVA and 4-vinylbenzene chloride were poorly dispersed so IR analysis was performed to prove that modification of pigment surfaces had occurred.

^{1}H NMR of the pigment grafted with DMAA could not be analyzed properly despite changes of solvent and temperature. However ^{1}H NMR of commercial polydimethylacrylamide was performed and compared to the NMR of the modified pigment. The two spectra were almost identical meaning that polydimethylacrylamide was well grafted onto the surface of pigment red 122 (Figure 3.2). The same results were obtained for the three others pigments (carbon black, pigment blue 15:3 and pigment yellow) modified using N,N-dimethylacrylamide as the monomer.

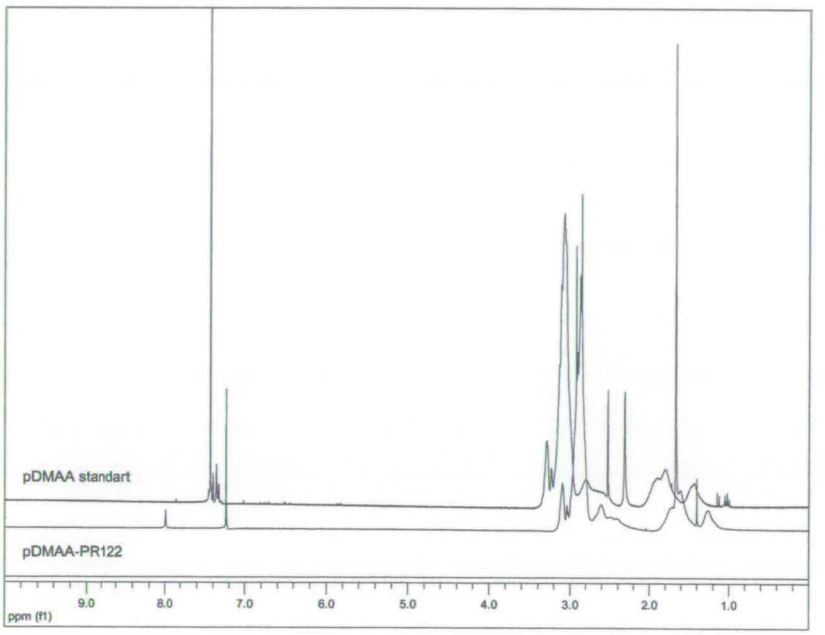


Figure 3.2: pDMAA spectra

It was observed in the majority of cases that modified pigments had improved dispersibility in water (1 mg/mL) (Figure 3.3). With PR122, the best results were obtained using DMAA (4), maleic anhydride (11), methyl acrylate (12) or HPMA (10). However in the case of DMAA (4) the color intensity of the dispersion had diminished, due to the high grafting level.

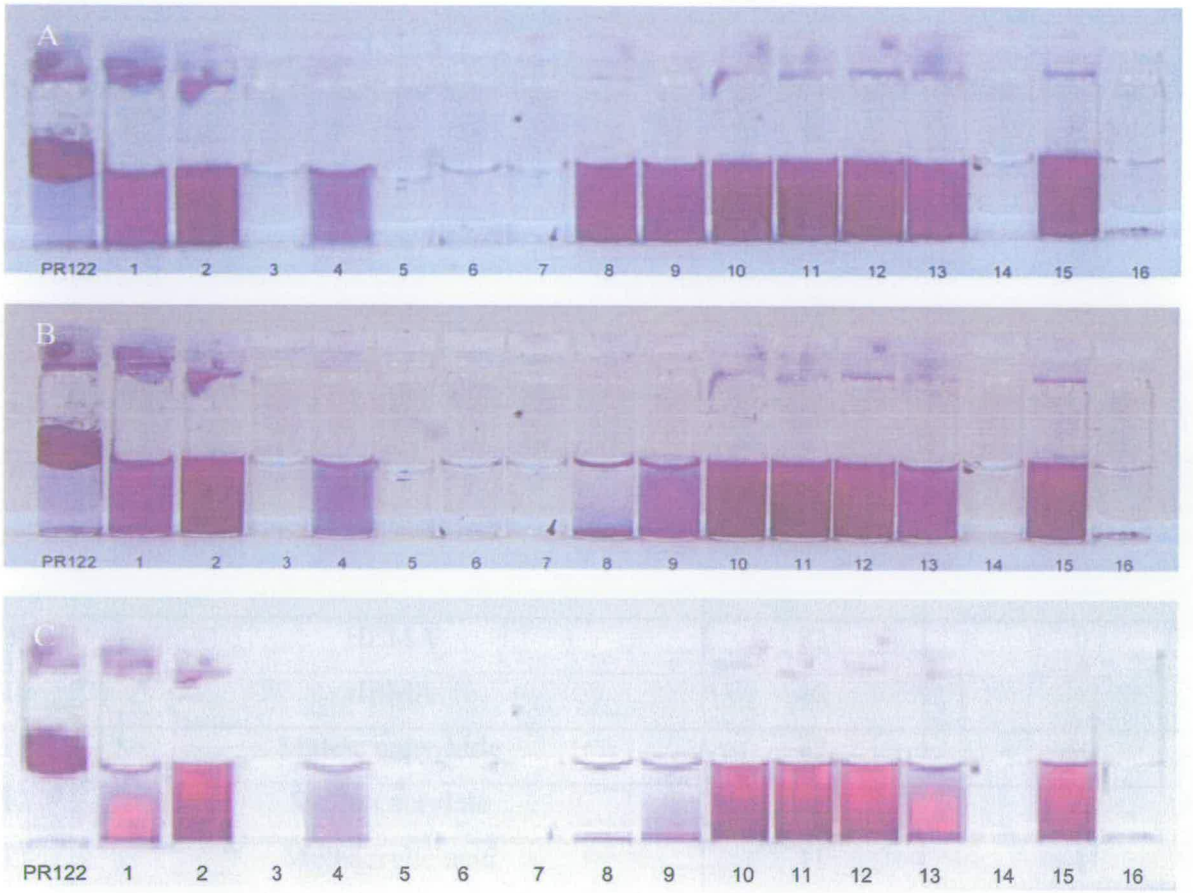


Figure 3.3: Dispersibility study on modified PR122 *1* to *16* (see Table 3.1); A: image taken after 1 h; B: 24 h; C: 48 h

3.1.2 Results for carbon black

The same protocol, described in section 3.1.1, was applied to carbon black (Table 3.2). One additional monomer was tested (methacrylic acid (17)), but this did not improve the dispersibility of pigment black in water. Like pigment red 122 the modified carbon blacks were analysed either by NMR or IR depending on their solubility in either $CDCl_3$ or D_2O. These analyses proved the presence of polymers on the pigments except for 4-styrenesulfonic acid.

Table 3.2: Homopolymerisation on carbon black

Entry	Monomer	Graft weight %	Time taken to settle (days)
1	Acrylamide	125	1
2	2-Acrylamido-2-methylpropane sulfonic acid	125	30
3	BMA	533	0
4	DMAA	2427	30
5	EMA	4500	0
6	HBA	71	14
7	HBMA	175	0
8	HEA	77	5
9	HEMA	83	0
10	HPMA	18	4
11	Maleic anhydride	42	30
12	Methyl acrylate	3489	0
17	Methacrylic acid	11	1
13	PVA	138	0
14	St	1066	0
15	4-Styrenesulfonic acid	105	30
16	4-Vinylbenzyl chloride	655	0

Dispersibility studies in water (1mg/mL) showed an improvement for the majority of the modified pigments (Figure 3.4). The best dispersions were obtained using DMAA (4), 2-acrylamido-2-methylpropane sulfonic acid (2), maleic anhydride (11).

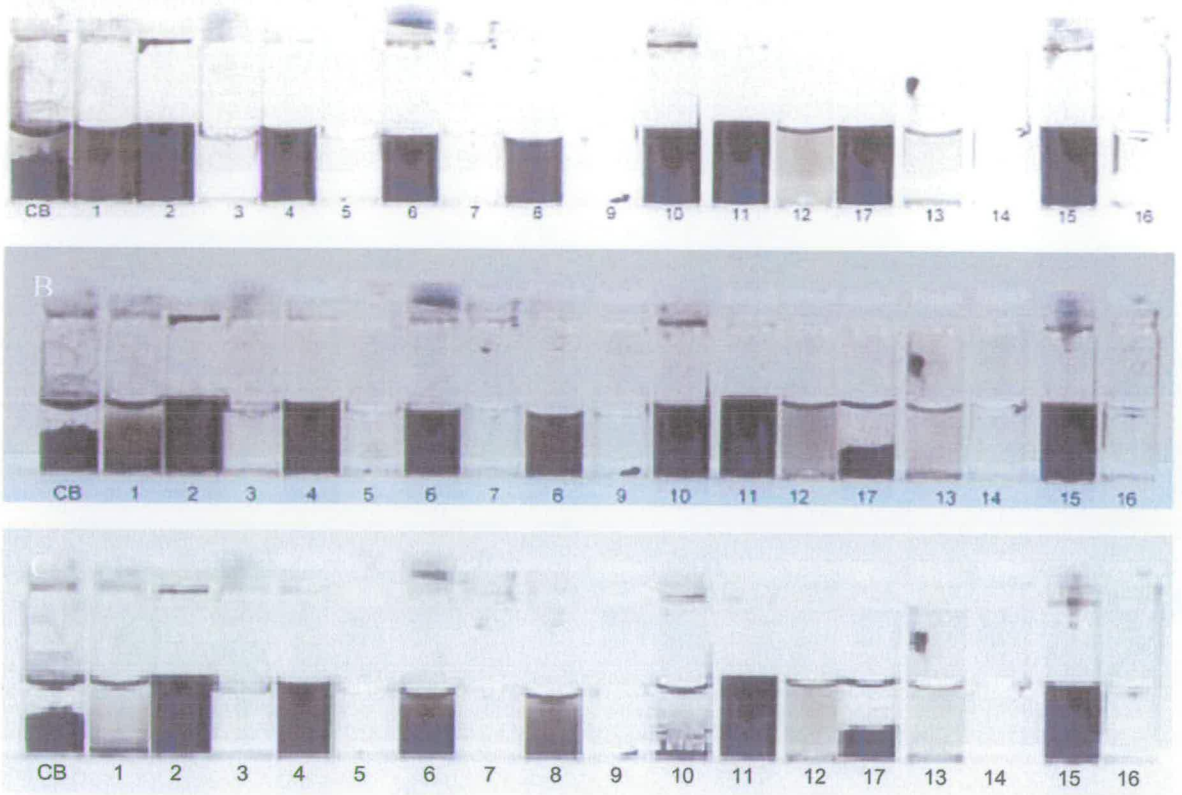


Figure 3.4: Dispersibility study on modified CB *1* to *17* (see Table 3.2); A: image taken after 1h; B: 24 h; C: 48 h

3.1.3 Results for PB15:3

Polymerisations were achieved by following the protocol described in section 3.1.1 (Table 3.3). In the case of 2-acrylamido-2-methylpropane sulfonic acid (2), HEMA (9), HPMA (10), maleic anhydride (11), PVA (13), 4-vinylbenzyl chloride (16), the products were not soluble enough to obtain ^{1}H NMR but the IR spectra of these compounds showed modification of the pigment. All other compounds were analysed by NMR which proved the presence of the polymers except for 4-styrenesulfonic acid which only showed the presence of the monomer. Modification using DMAA (4), maleic anhydride (11) and methyl acrylate (12) as monomers gave an improvement in dispersibility in water (1 mg/mL) (Figure 3.5).

Table 3.3: Homopolymerisation on PB15:3

Entry	Monomer	Graft weight %	Time taken to settle (days)
1	Acrylamide	1	1
2	2-Acrylamido-2-methylpropane sulfonic acid	65	1
3	BMA	121	0
4	DMAA	2730	30
5	EMA	147	0
6	HBA	966	0
7	HBMA	358	0
8	HEA	164	1
9	HEMA	2317	0
11	Maleic anhydride	51	1
12	Methyl acrylate	439	1
17	Methacrylic acid	1	0
13	PVA	169	1
14	St	248	0
15	4-Styrenesulfonic acid	92	1
16	4-Vinylbenzyl chloride	269	0

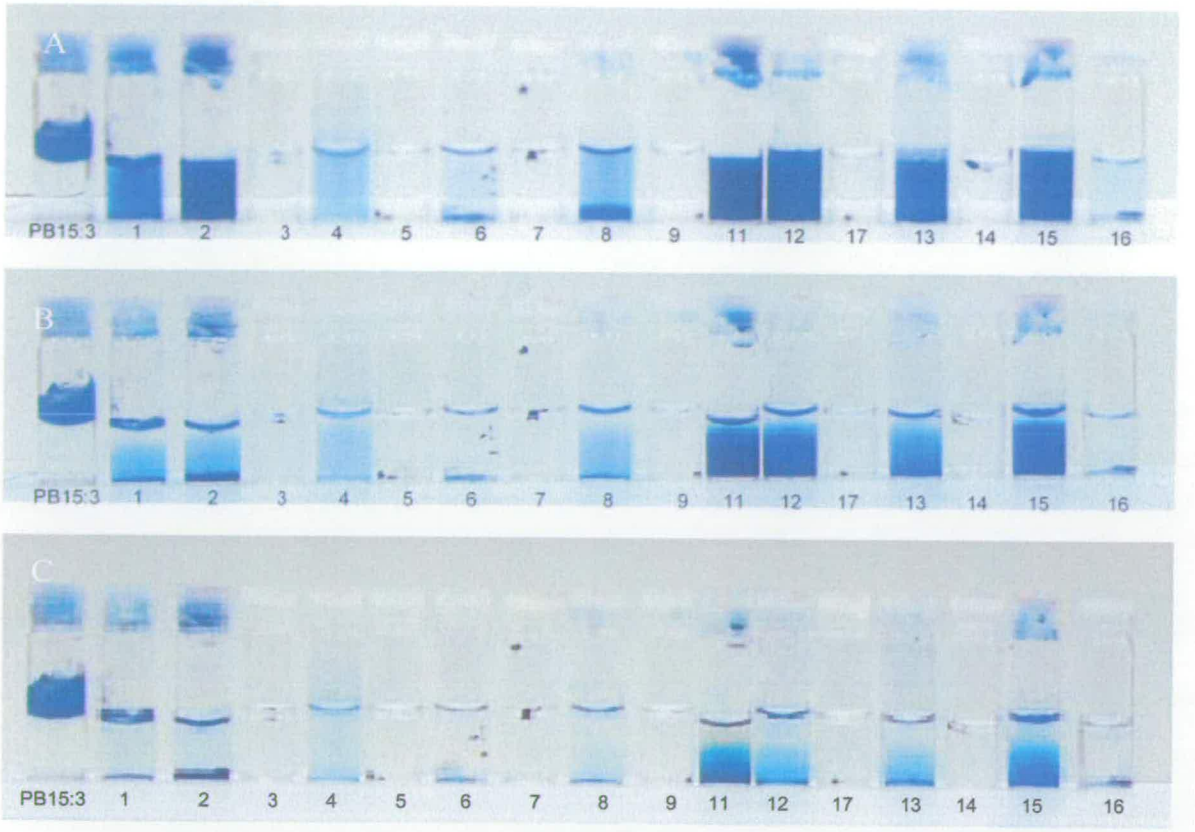


Figure 3.5: Dispersibility study on modified PB15:3 *1* to *17* (see Table 3.3); A: image taken after 1h; B: 1 day; C: 2 weeks

3.1.4 Results for PY155

Like for the three others pigments, the protocol described in section 3.1.1 was used for the polymerisations (Table 3.4). ^{1}H NMR and IR were performed on pigment yellow 155 and similar conclusions were obtained. All the modified pigments showed the presence of polymer grafted onto pigment by NMR or IR except for 4-styrenesulfonic acid. DMAA (4), 2-acrylamido-2-methylpropane sulfonic acid (2), HEA (8), maleic anhydride (11), PVA (13) and 4-Styrenesulfonic acid (15) gave an improvement in the dispersibility of the pigment yellow 155.

Table 3.4: Homopolymerisation on PY155

Entry	Monomer	Graft weight %	Time taken to settle (days)
1	Acrylamide	64	1
2	2-Acrylamido-2-methylpropane sulfonic acid	121	30
3	BMA	300	0
4	DMAA	2594	5
5	EMA	285	0
6	HBA	532	0
7	HBMA	233	0
8	HEA	774	8
9	HEMA	677	0
10	HPMA	833	1
11	Maleic anhydride	64	14
12	Methyl acrylate	1000	0
17	Methacrylic acid	1	3
13	PVA	141	5
14	Styrene	258	0
15	4-Styrenesulfonic acid	102	14
16	4-Vinylbenzyl chloride	205	0

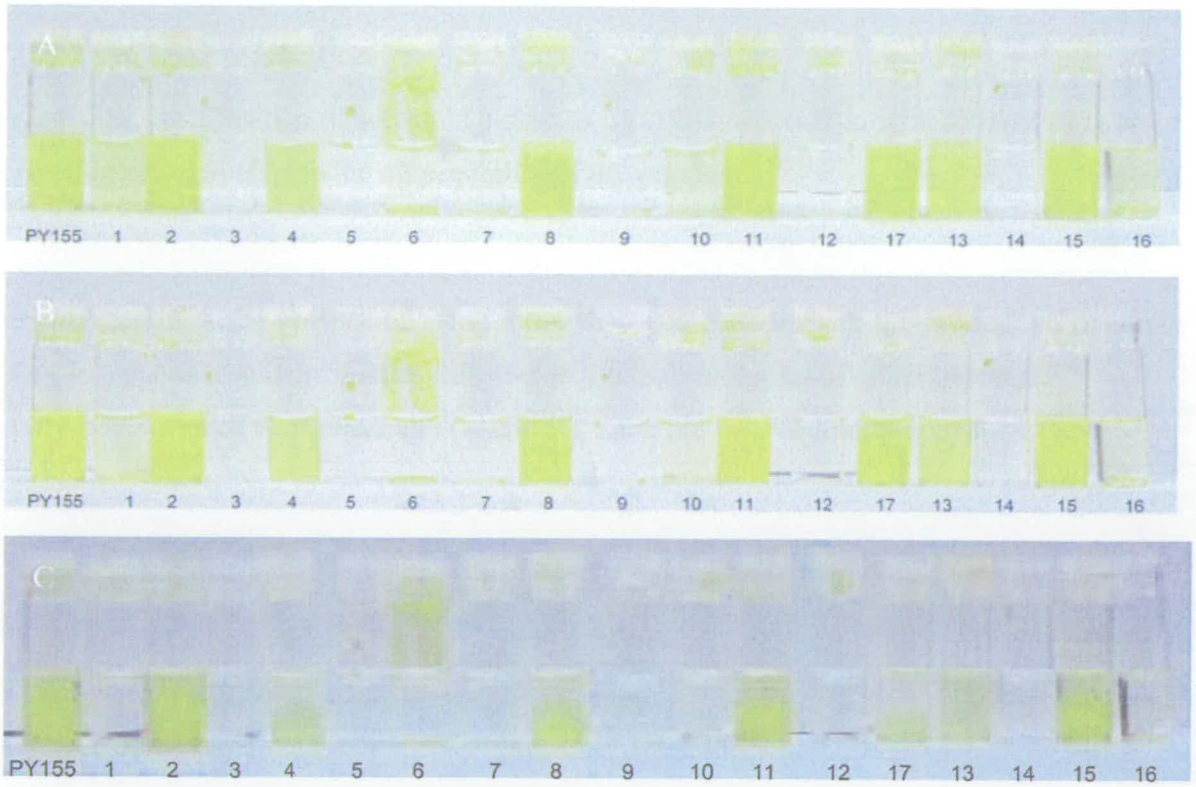


Figure 3.6: Dispersibility study on modified PY155 *1* to *17* (see Table 3.4); A: image taken after 1h; B: 1 day; C: 2 weeks

In conclusion, the modification of the four pigments using different monomers were analysed either by NMR when "pigments" were soluble enough. In case of insoluble compounds, IR, SEM or contact angle were used to show the modifications of the pigments. These results will be discussed in chapter 4 and 8. The best polymers obtained for the four pigments, taking into account only dispersibility, were DMAA and maleic anhydride. The only disadvantage using DMAA was that a high percentage of polymer was grafted onto the pigment surface which gave a decrease of the intensity of the color.

3.2 Copolymerization

In this section, modification of activated pigments by copolymerization with different monomers was performed in order to change the dispersibility of the pigments. [65]

3.2.1 Principle of copolymerization

Copolymerization is the process of using more than one monomer in the production of a polymer, resulting in a product with properties different to the homopolymer of either monomer. [66]

In copolymerization of two monomers (A and B), there are four distinct propagation steps:

$$IA_m^{\cdot} + A \xrightarrow{k_{AA}} IA_{m+1}^{\cdot}$$

$$IA_m^{\cdot} + B \xrightarrow{k_{AB}} IA_mB^{\cdot}$$

$$IB_n^{\cdot} + A \xrightarrow{k_{BA}} IB_nA^{\cdot}$$

$$IB_n^{\cdot} + B \xrightarrow{k_{BB}} IB_{n+1}^{\cdot}$$

Figure 3.7: Copolymerization propagation steps

Figure 3.7 shows that two homo-propagation and two cross-propagation reactions exist and can create copolymers which can differ in:

a) their composition (the amount of each monomer unit incorporated into the copolymer can vary).
b) their microstructure (alternative copolymers, block copolymers and random copolymers can be synthesised).
c) their chain end composition.

The specific polymerisation rates of monomers A and B are given by: [67, 68]

$$-(d(V[A])/dt) = K_{AA}[P_A^*][A] + K_{BA}[P_B^*][A]$$

$$-(d(V[B])/dt) = K_{AB}[P_A^*][B] + K_{BB}[P_B^*][B]$$

where $[P_A^*]$ and $[P_B^*]$ are the total concentrations of active centers of type A and B with:

$$[P_A^*] = \Sigma\,[IAm^{\cdot}]\,,\ m = [1, \infty]$$

$$[P_B^*] = \Sigma\,[IBn^{\cdot}]\,,\ n = [1, \infty]$$

And if the stationary state hypothesis is applied to $[P^*]$:

$$k_{BA}[P_B^*][A] = k_{AB}[P_A^*][B]$$

The instantaneous copolymer composition equation gives:

$$F_AF_B = (-d(V[A]))/ (-d(V[B])) = ([A](r_A[A]+[B]))/([B]([A]+r_B[B]))$$

where F_A and F_B are the mole fractions of monomers A and B

$$\text{or } F_A = (r_Af_A^2+f_Af_B)/(r_Af_A^2+2f_Af_B+r_Bf_B^2)$$

where f_A and f_B are the mole fractions of unreacted monomer

The reactivity ratio are defined by:

$$r_A = k_{AA}/k_{AB}$$

$$r_B = k_{BB}/ k_{BA}$$

In free radical copolymerisation r_Ar_B is generally less than one unit, indicating a higher alternating tendency. [67] For example the styrene – DMAA system is an example where $r_Ar_B = 0.64$

3.2.2 Modification of Pigment red 122 by copolymerization

A library was prepared by copolymerization using PR122 and combinations of 8 monomers (Styrene, HPMA, HBMA, HEMA, MMA, DMAA, EMA and BMA) (Figure 3.8). The majority of grafted polymers were obtained in good yields (Table 3.5), however none of them were dispersible in water but in DMF (1 mg/mL) for one day but not any longer four days except for p(HEMA-*co*-EMA) (12) (Figure 3.9 and Figure 3.10). In contrast to these results, high dispersibility in DMF had been observed with pDMAA modified PR122 (Table 3.1, entry 4), which means that pDMAA was still the best modified pigment.

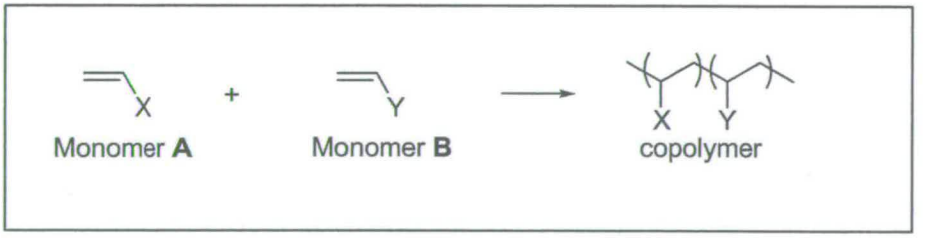


Figure 3.8: copolymerization using PR122

Table 3.5: Copolymerization on PR122

	Monomers		Ratio (mol. %)	Graft weight (%)
	A	B	A/B	
1	Styrene	DMAA	50/50	2800
2	Styrene	MMA	50/50	2880
3	HPMA	DMAA	50/50	5100
4	HPMA	MMA	50/50	1940
5	HPMA	EMA	50/50	1500
6	HPMA	BMA	50/50	950
7	HBMA	DMAA	50/50	1990
8	HBMA	MMA	50/50	250
9	HBMA	EMA	50/50	1230
10	HBMA	BMA	50/50	950
11	HEMA	DMAA	50/50	4000
12	HEMA	EMA	50/50	272
13	HEMA	BMA	50/50	1090

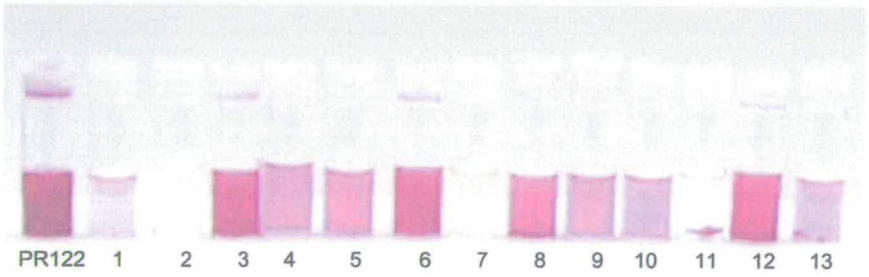


Figure 3.9: Dispersibility of copolymers in DMF after 1 h

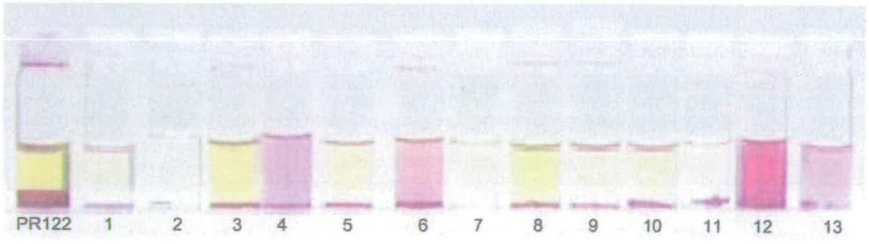


Figure 3.10: Dispersibility of copolymers in DMF after 4 days

NMR analysis for the copolymers gave spectra that were not resolved and gave broad signals that could not be assigned to specific protons. One example is given in Figure 3.11 for p(styrene-*co*-DMAA)-PR122 (1). It is clear from the spectrum that both polymers (ratio 50/50) are present but no further information could be gained.

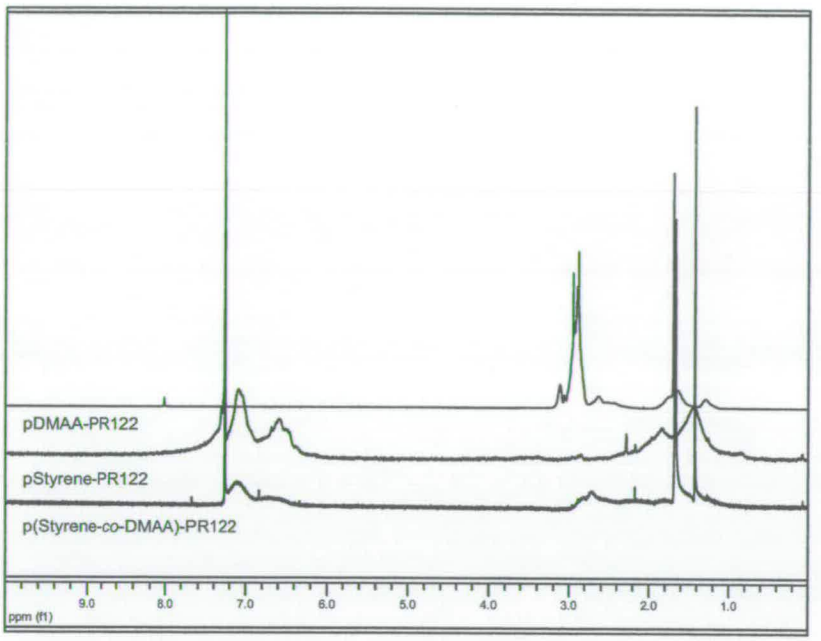


Figure 3.11: ^{1}H NMR Spectra of pDMAA-PR122, pStyrene-PR122 and p(Styrene-co-DMAA)-PR122

3.2.3 Modification of carbon black by copolymerization

A library was prepared using carbon black and a combination of styrene and 3 other monomers (MMA, BMA and EMA) in order to increase the dispersibility of carbon black in water. The grafted polymers were obtained with high graft weights (Table 3.6) but none of the products were dispersible in water (1 mg/mL) but in DMF (1 mg/mL) for 3 weeks (Figure 3.13), and, they showed a similar dispersibility to carbon black in DMF (Figure 3.12 and Figure 3.13, carbon black is entry 0).

Table 3.6: Copolymerization on CB with styrene

	Ratio (mol. %) MMA/EMA/BMA	Graft weight (%)
1	20/0/0	1666
2	50/0/0	2222
3	100/0/0	2722
4	0/0/0	4000
5	0/50/0	2566
6	0/100/0	2370
7	0/0/0	4010
8	0/0/50	2848
9	0/0/100	2222

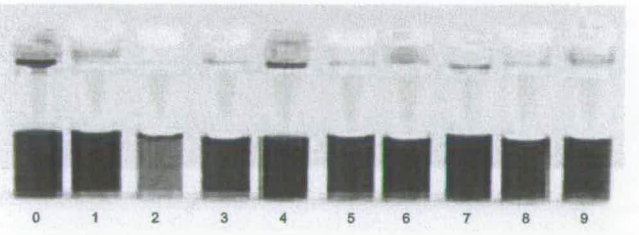


Figure 3.12: Dispersibility of copolymers in DMF after 1 h

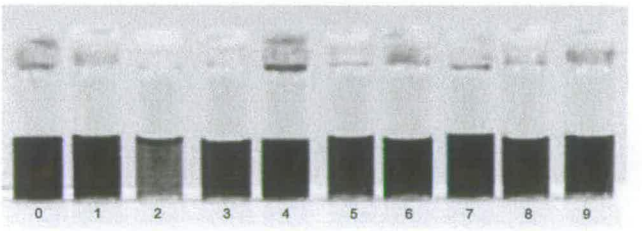


Figure 3.13: Dispersibility of copolymers in DMF after 3 weeks

3.2.4 Control of dispersibility of pigments in water by copolymerization

In order to control the dispersibility of pigments in water, a library was prepared by co-polymerization using the four pigments and different ratios of DMAA and MAA (Figure 3.14, Table 3.7). These monomers were chosen from the observation made during the dispersibility studies in section 3.1 (DMAA, when grafted onto the pigments, was improving their solubility in water whereas MAA was keeping them insoluble).

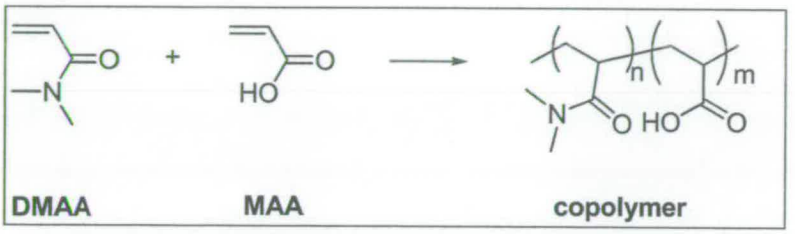


Figure 3.14: Copolymerization using DMAA/MAA

Table 3.7: Copolymerization using DMAA/MAA

Entry	Pigment	Ratio (mol. %) MAA/DMAA	Graft weight (%)
1	PR122	0/100	3643
2	PR122	10/90	580
3	PR122	50/50	138
4	PB15:3	0/100	3645
5	PB15:3	10/90	3
6	PB15:3	50/50	0.3
7	PY155	0/100	642
8	PY155	10/90	164
9	PY155	50/50	121
10	PY155	100/0	535
11	CB	0/100	4526
12	CB	10/90	1452
13	CB	50/50	215
14	CB	100/0	157

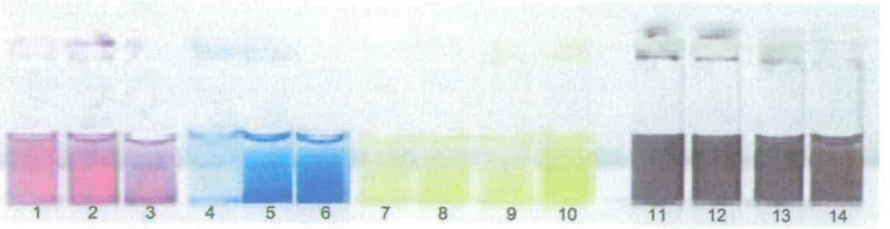


Figure 3.15: dispersibility of copolymers after a week

Figure 3.15 shows that in the case of pigment red 122, pigment blue 15:3 and carbon black the more the amount of MAA the less dispersed are the pigments (1 mg/mL) in water. It was also observed that using DMAA gave a better grafting level than using MAA. If dispersibility is the most important factor, pDMAA grafted onto pigment red 122 still appears to be the best modified pigment to use in the ink formulation but a high graft weight gives poor color intensity.

3.3 Cross-linking

Cross-linking was envisaged as a potential solution against fading pigment, by adding a layer of polymers cross-linked on its surface to form a barrier against fading agents such as ozone.

3.3.1 Principle of cross-linking

A cross linking polymer consists of a three-dimensional network, formed by copolymerization of a system where at least one of the monomers has two free radically polymerizable double bonds. As the amount of cross linking increases, the polymer becomes less flexible. [69]

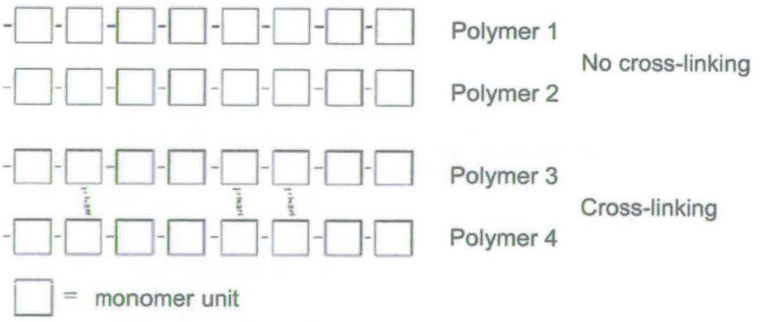


Figure 3.16: Cross-linking

3.3.2 Studies on activated pigments

3.3.2.1 Preliminary study

The preliminary experiments using pigment red 122 and carbon black were run concurrently in order to study the effect of the order of addition of monomer and cross-linker. Therefore, three protocols were applied:

Protocol A: Addition of both monomer and cross-linker at the same time at the beginning of the polymerisation,

Protocol B: Addition of the monomer and 5h later the cross linker,

Protocol C: Addition of the cross-linker and 5h later the monomer.

In the case of pigment red 122, DMAA, which was observed to be the best monomer to use in section 3.1.1, was used and ethylene glycol dimethacrylate (EGDMA) was selected as cross linker due to its similar reactivity compared to DMAA in polymerisation (Figure 3.17). For carbon black, styrene was used as monomer and divinylbenzene (DVB), which has a similar reactivity to styrene in polymerisation, was selected.

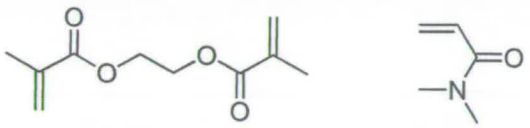


Figure 3.17: EGDMA and DMAA

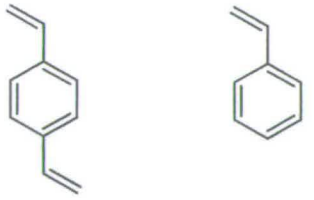


Figure 3.18: DVB and styrene

Table 3.8: Cross linking experiments with PR122

Entry	Pigment	Method	Ratio (mol %) DMMA/EGDMA	Graft weight %	Product appearance
1	PR122	A	1/0.1	1355	Magenta powder
2	PR122	A	1/0.2	4116	light magenta powder
3	PR122	A	1/0.3	4761	light magenta powder
4	PR122	A	1/0.4	5316	light magenta powder
5	PR122	A	1/0.5	7400	magenta powder
6	PR122	B	1/0.005	2522	magenta gum
7	PR122	B	1/0.02	2733	magenta gum
8	PR122	B	1/0.05	4642	magenta compact gum
9	PR122	B	1/0.2	3455	light magenta powder
10	PR122	B	1/0.5	4678	light magenta powder
11	PR122	C	1/0.005	2094	magenta compact gum
12	PR122	C	1/0.02	2516	magenta compact gum
13	PR122	C	1/0.05	4066	magenta compact gum
14	PR122	C	1/0.2	4344	light magenta powder
15	PR122	C	1/0.5	6233	light magenta powder

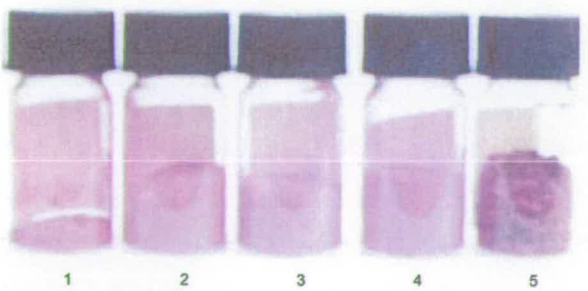


Figure 3.19: Modified-PR122 using protocol A

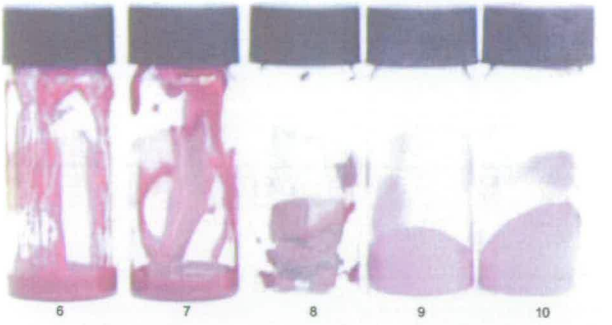


Figure 3.20: Modified-PR122 using protocol B

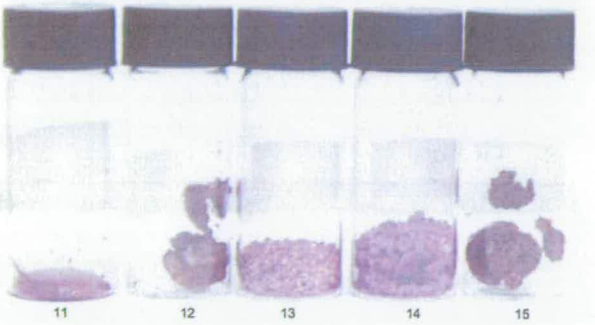


Figure 3.21: Modified-PR122 using protocol C

During the polymerisation process, formation of a gel was observed which indicated that cross linking reactions were successful. Because none of the products were soluble in either water or organic solvents (1 mg/mL) it was impossible to perform NMR studies. All powders obtained consisted of a mixture of grafted compounds and excess cross-linked polymer which had not been grafted onto PR122 (Figure 3.19, Figure 3.20 and Figure 3.21). No work-up strategy managed to separate the grafted compounds from the excess of polymerised cross-linker.

Table 3.9: CB on cross linking

Entry	Pigment	Method	Ratio (mol %) Styrene/DVB	Graft weight %	Product appearance
1	CB	A	1/0	11	black powder
2	CB	A	1/0.1	2650	black powder
3	CB	A	1/0.3	3956	black powder
4	CB	A	1/0.4	4150	grey powder
5	CB	A	1/0.6	5372	grey powder
6	CB	A	1/0.8	5456	grey powder
7	CB	B	1/0.0008	427	black powder
8	CB	B	1/0.03	1355	black gum
9	CB	B	1/0.08	3003	black gum
10	CB	B	1/0.4	3419	grey powder
11	CB	B	1/0.8	2458	grey powder
12	CB	C	1/0.03	2050	black gum
13	CB	C	1/0.08	2427	black gum
14	CB	C	1/0.4	2797	grey powder
15	CB	C	1/0.8	4500	grey powder

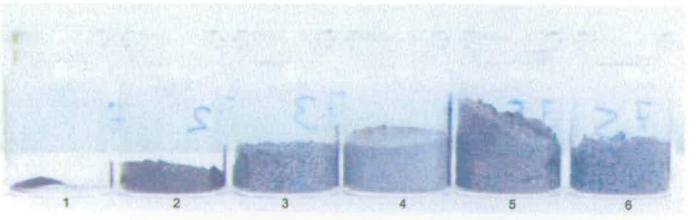


Figure 3.22: Compounds via protocol A

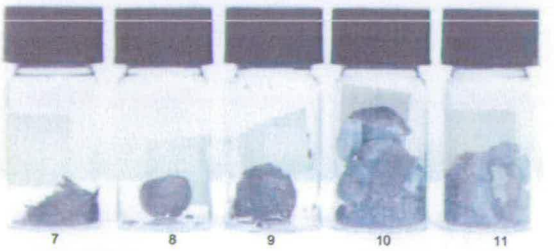


Figure 3.23: Compounds via protocol B

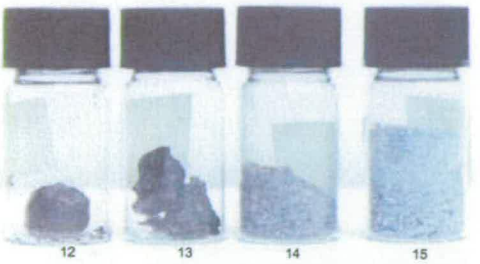


Figure 3.24: Compounds via protocol C

The same conclusions as for PR122 were obtained by using CB. None of the products were soluble in DMF (1 mg/mL) and the products obtained were a mixture of grafted compounds and free polymers.

3.3.2.2 Use of the four pigments

Knowing that the cross linking reaction was possible but decreased the dispersibility of pigment red 122 and carbon black, a library was made using the four pigments (PR122, CB, PB15:3 and PY155) and reduced amounts of cross-linker. The reactions were done by adding either DMAA or styrene (depending on the pigment) and 2 h later the corresponding cross-linker.

Table 3.10: Cross-linking

	Pigments	Monomers	Cross-linkers	Ratio (mol) Monomer/CL	Graft weight %
1	PR122	DMAA	EGDMA	1/0.001	1168
2	PR122	Styrene	DVB	1/0.001	332
3	PY155	DMAA	EGDMA	1/0.001	1275
4	PY155	Styrene	DVB	1/0.001	305
5	PB15:3	DMAA	EGDMA	1/0.001	5191
6	PB15:3	Styrene	DVB	1/0.001	345
7	CB	DMAA	EGDMA	1/0.001	1497
8	CB	Styrene	DVB	1/0.001	662

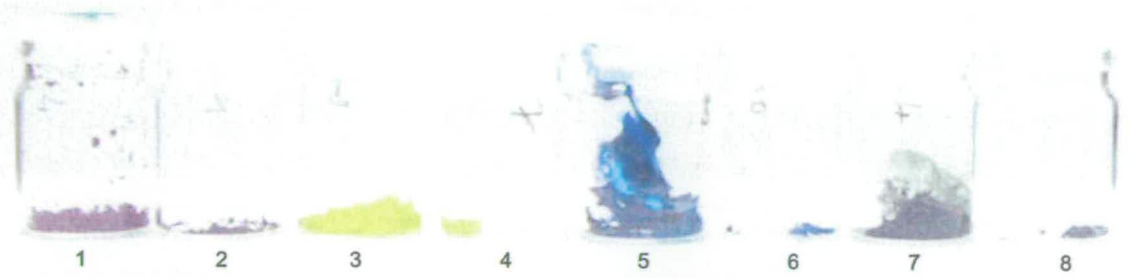


Figure 3.25: Cross-linking

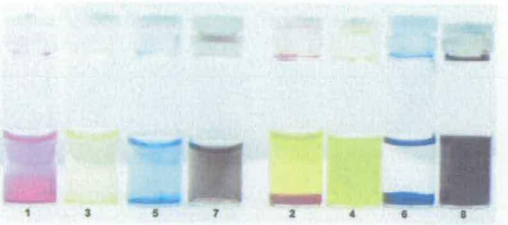
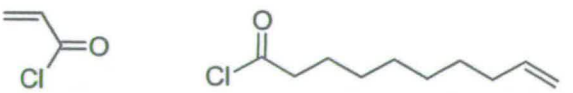


Figure 3.26: Dispersibility of cross-linked compounds in water for (1, 3, 5, 7) and DMF for (2, 4, 6, 8) (1 mg/mL) after 2 weeks

As shown in Figure 3.26, the dispersibility of the majority of the compounds improved a little by comparison with the dispersibility of the unmodified pigments, which means that adding a very small amount of cross-linker does not affect the dispersibility of compounds in water or DMF (1 mg/mL).

3.4 Esterification

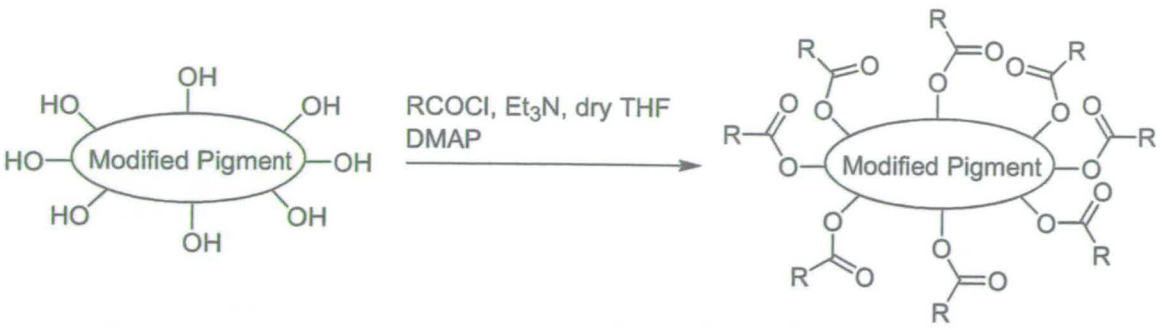
The aim of this work was to prove the covalent bonding between pigment and polymer and to improve the solubility of pigments. pHEMA modified PR122 was esterified using two different acid chlorides, acryloyl chloride (ACC) and 10-undecenoyl chloride (UDC).



Acryloyl chloride 10-Undecenoyl chloride

Figure 3.27: Acid chlorides used during esterification

The reactions were carried out in THF at room temperature under nitrogen using triethylamine as a base and DMAP as a catalyst. During addition of the acid chlorides, the pigments became insoluble in THF and the solution became pink / orange (Scheme 3.1). 10-Undecenoyl-modified PR122 had the biggest improvement in dispersibility in $CDCl_3$ (1 mg/mL). This is probably due to the length of the alkyl chain (Figure 3.28). However, 10-Undecenoyl-modified PR122 was still not soluble enough to obtain a clear ^1H NMR spectrum.



Scheme 3.1: Esterification

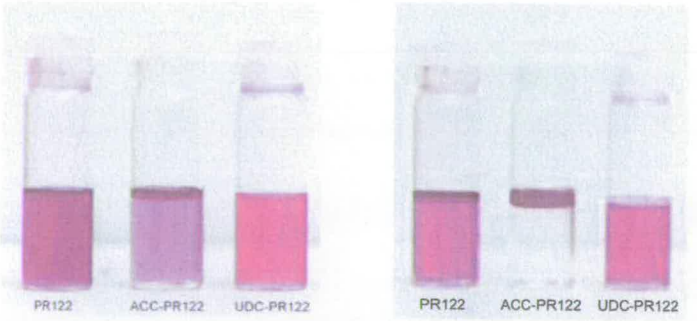


Figure 3.28: dispersibility of PR122 and the esterified compounds: ACC-PR122 and UDC-PR122 in $CDCl_3$ after 2 days

Further modification using five modified pigments (pHBA-PR122, pHEA-PR122, pHBA-CB, pHEA-CB and pHEA-PY155) was carried out using 10-Undecenoyl chloride under the same esterification conditions (Scheme 3.1). All reactions gave improvements in solubility (Table 3.11, Figure 3.29 and Figure 3.30).

Table 3.11: Esterification

Starting modified pigment	Grafting % After esterification	Solubility (1 mg/mL)
pHBA-PB15:3	3	$CDCl_3$
pHBA-PR122	6	$CDCl_3$
pHEA-PY155	16	DMF
pHEA-PB15:3	3	DMF
pHEA-PR122	33	DMF

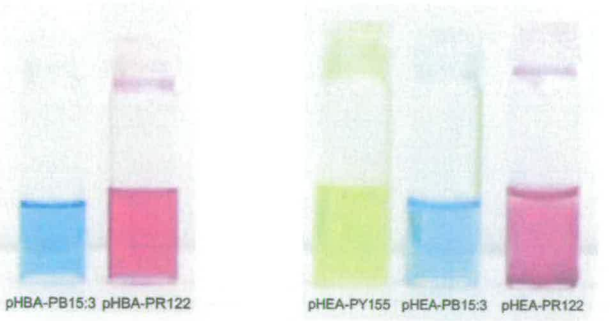


Figure 3.29: dispersibility of esterified compounds after 1 day in either $CDCl_3$ or DMF

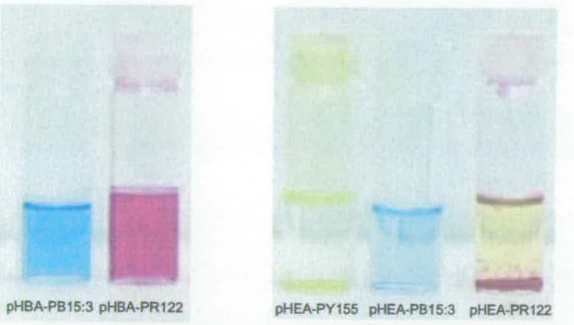


Figure 3.30: Dispersibility of esterified compounds after 4 days

The improvement of solubility shows the bonding between pigments and polymers was stable to further elaboration such as esterification. It was observed that esterified pigments synthesised from pHBA-pigments were more soluble in organic solvents than the esterified pigments synthesised from pHEA-pigments (Figure 3.30). Furthermore, ^1H NMR spectra (Figure 3.32, Figure 3.34, Figure 3.31 and Figure 3.33) were obtained, (except for modified pigment yellow which was not enough soluble in $CDCl_3$), and showed the formation of the esterified modified pigments.

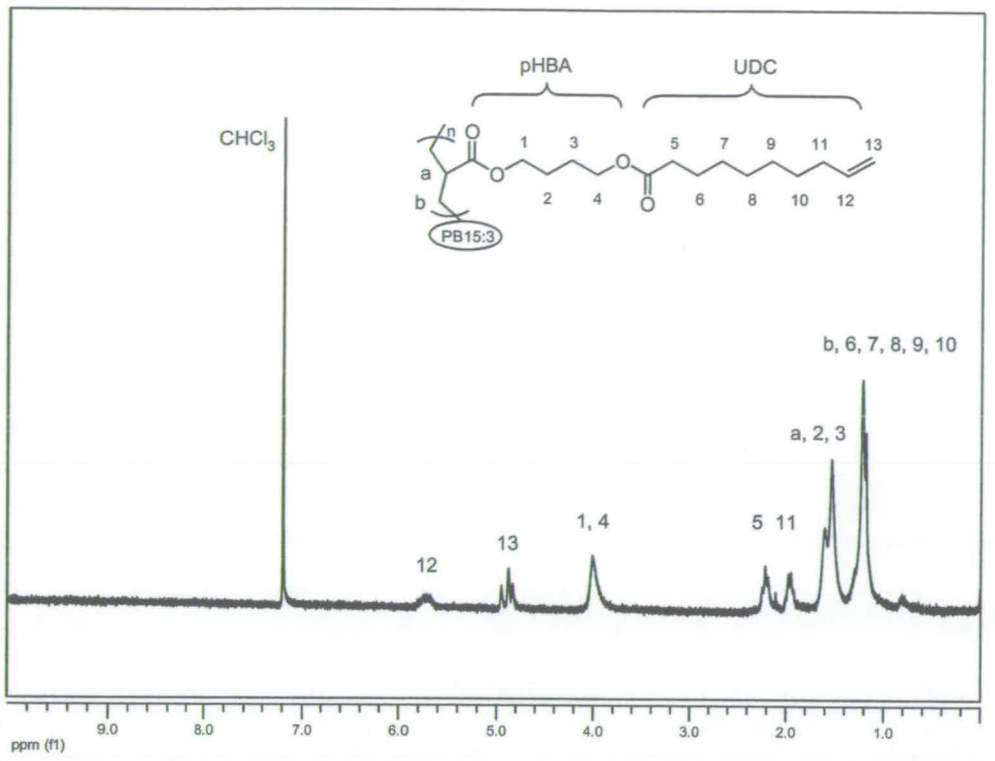


Figure 3.31: ^{1}H NMR of pHBA-PB15:3 esterified with 10-Undecenoyl chloride

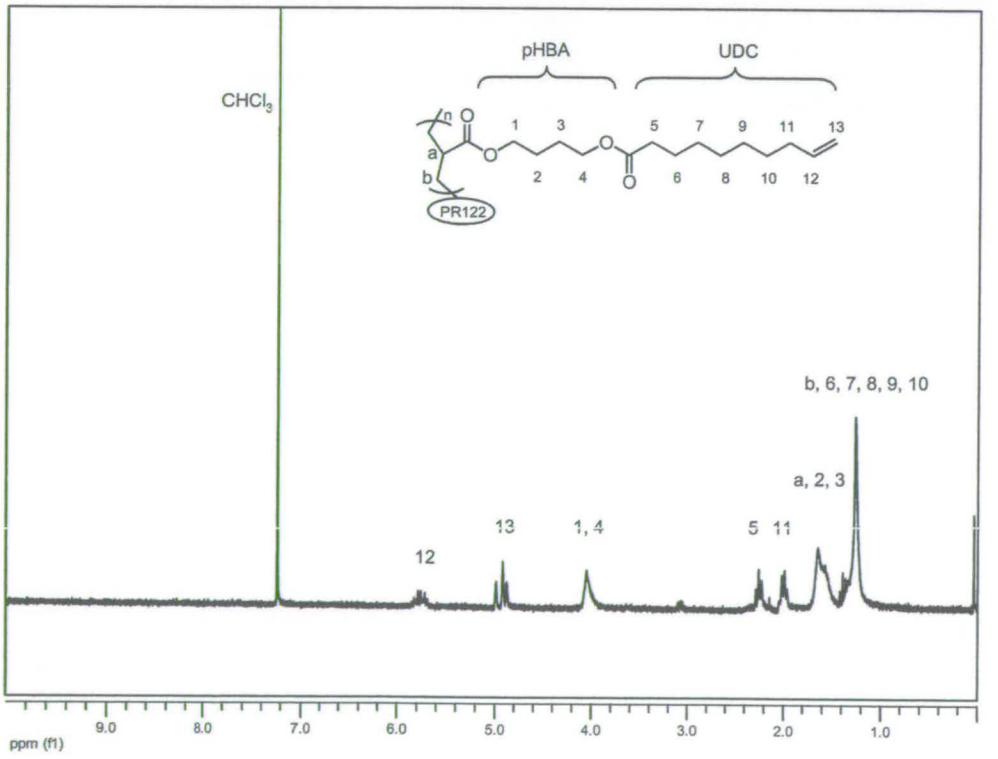


Figure 3.32: ^{1}H NMR of pHBA-PR122 esterified with 10-Undecenoyl chloride

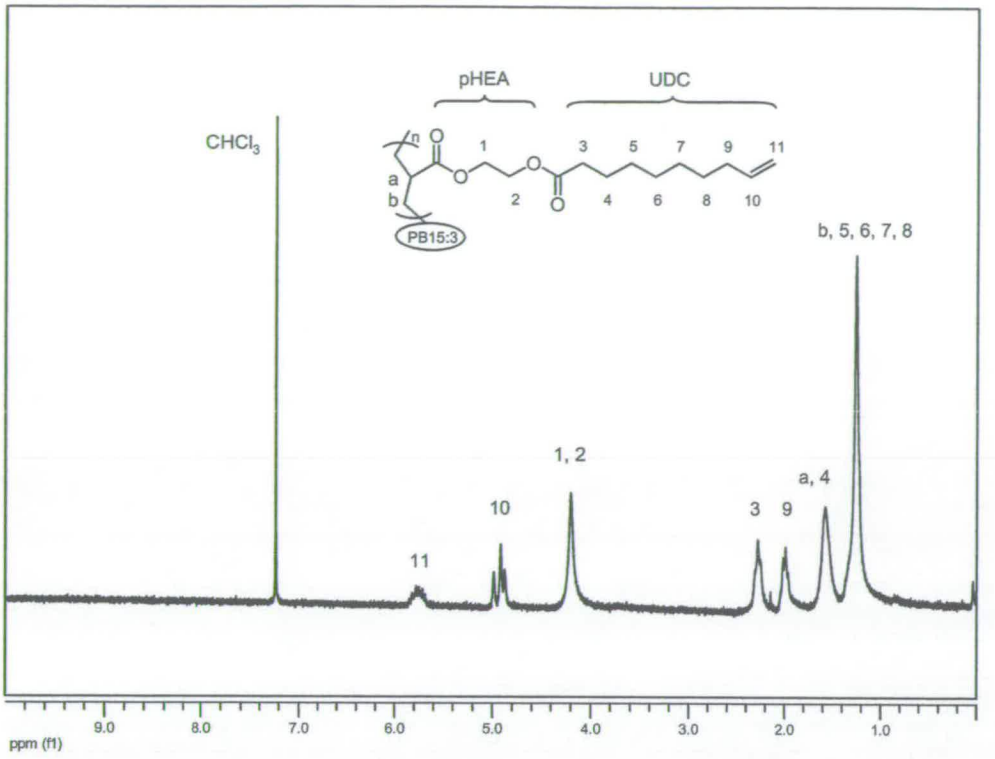


Figure 3.33: ^{1}H NMR of pHEA-PB15:3 esterified with 10-Undecenoyl chloride

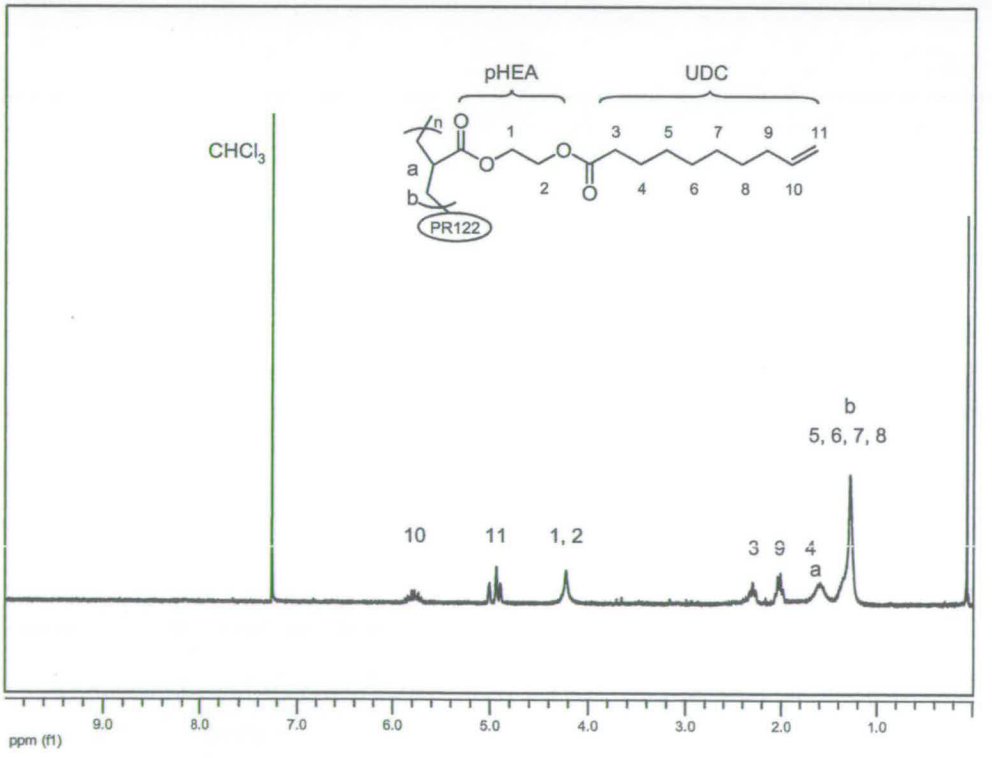
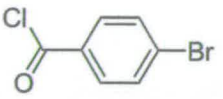


Figure 3.34: ^{1}H NMR of pHEA-PR122 esterified with 10-Undecenoyl chloride

As for the solubility, the clearest spectra were obtained for esterified pigments synthesised from pHBA-pigments. Additionally, a reaction was carried out using 4-Bromobenzoyl chloride to esterify pHBA-PR122. A good improvement of solubility (1 mg/mL) was noticed (Figure 3.35). Synthesis of this compound is interesting, as allows the possibility of reactions such as palladium catalyst halogen exchange.



Scheme 3.2: Structure of acid chloride

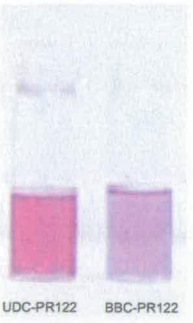


Figure 3.35: Difference of dispersibility between 10-Undecenoyl-modified PR122 (UDC-PR122) and 4-Bromobenzoyl-modified PR122 (BBC-PR122) after 4 days

3.5 Conclusions

Homopolymerisation on pigment red 122, pigment yellow 155, pigment blue 15:3 and carbon black were performed with a number of different monomers. It was observed in the majority of cases that modified pigments had improved dispersibility in water (1 mg/mL) and it appeared that DMAA was one of the most suitable monomers to use to improve the dispersibility of these pigments in water. To control the dispersibility of the pigments and to understand more their behaviour, copolymerisation reactions were carried out using DMAA and carbon black. The results showed that DMAA in case of PR122 and styrene in case of carbon black gave better improvement of the dispersibility of the pigments in water (1 mg/mL) compare to the copolymer compounds. Then, cross-linking reactions were carried out in order to prevent pigments from fading. The reactions were successful but the dispersibility of the products obtained did not improve significantly either in water or DMF (1 mg/mL) and the presence of free polymers was observed. Finally, in order to check that covalent bonding between pigment and monomer had taken place, esterification reactions were successfully achieved on modified pigments and the dispersibility of the esterified pigments was improved in organic solvents (1 mg/mL).

4 Physical characterization of modified pigments

4.1 General

Pigments are insoluble compounds which make their characterisation challenging. Modification of their surfaces can alter their properties and a range of techniques can be used to evaluate these changes such as filtration, UV/Vis measurements, contact angle measurements, SEM and XPS.

4.2 Filtration

The aim of these experiments was to determine whether or not the modified pigments had increased dispersibility. This was complicated by the physical nature of the starting pigments and the fact that the grafted materials had to be ground by hand.

pDMAA grafted onto pigment red 122 was dispersed in water (0.1 mg/mL). During filtration using a whatman syringe filter (hydrophilic, pores size = 0.2 μm), it was observed that the filter became blocked due to the particle sizes of modified pigments exceeded 0.2 μm. Using another filter of greater pore size (0.45 μm), it was observed that the suspension passed though without problem. Therefore, it can be assumed that pDMAA particles in water had a size between 0.2 - 0.45 μm. These experiments demonstrated that pDMAA grafted PR122 was not soluble in water but very well dispersed compared to starting PR122, which dispersed in water at the same concentration had blocked filters of 20 μm. This observation confirms that grafting DMAA onto PR122 surface improves the solubility of PR122 in water (cf. dispersibility studies in Chapter3.1).

Filtration using filters with pore sizes of 0.45 μm and 20 μm were used to study the modified and unmodified pigment dispersions in water. The pigments used were the ones that showed the best dispersibility in Chapter 3.1. They were ground by hand, dissolved in water (0.1 mg/mL), sonicated and filtered though the 20 μm filters and then though the 0.45 μm filters in order to determine their dispersibility. All unmodified pigments dispersions (PR122, CB, PB15:3 and PY155) did not get through the 20 μm at the opposite of the modified pigment dispersions. However, not all modified pigment dispersions went through the 0.45 μm filters (Table 4.1). In the majority of the cases, only modified pigments synthesised using DMAA as monomer had particle sizes below 0.45 μm. This result confirmed that DMAA was the best monomer to use in order to improve dispersibility of any pigments in water.

Table 4.1: Filtration of modified pigments

Modified pigment	Particle size (μm)
pDMAA-PR122	X < 0.45
pHPMA-PR122	0.45< X <20
pMaleic anhydride-PR122	X < 0.45
pMethyl acrylate-PR122	0.45< X <20
pStyrenesulfonic acid-PR122	0.45< X <20
pAAMPSA-CB*	0.45< X <20
pDMAA-CB	X < 0.45
pVBC-CB	0.45< X <20
pDMAA-PB15:3	X < 0.45
pAAMPSA-PY155*	0.45< X <20
pMaleic anhydride-PY155	0.45< X <20
pVBC-PY155	0.45< X <20

Where X= particle size, pAAMPSA = poly(2-acrylamido-2-methylpropane sulfonic acid), pVBC = poly(vinylbenzyl chloride).

4.3 UV/Vis measurements

The aim was to determine if the pigment were, after modification, behaving as a dye or still as a pigment. If the modified pigment was behaving like a dye, its UV/Vis spectrum should change when using different type of solvents. If no change could be observed it would suggest that the modification did not change the properties of the initial pigment. [70]

4.3.1 Pigment red 122

Four dispersions in water or DMF were prepared at 0.1 mg/mL using PR122, which was used as a control, pDMAA-PR122 and esterified pHBA-PR122, which were chosen due to their high dispersibility.

In the case of PR122 and pDMAA-PR122 dispersed in water (Figure 4.1), both spectra gave the same overall shape, which suggests that pDMAA-PR122 is still a pigment and that modification only occurred at some of the sites of the pigment because it did not modify the hue as the spectrum of the modified pigment would have had different peaks if this were the case. The difference of intensity is due to the fact that the amount of "pigment" in the grafted sample is less in mass than PR122, due to polymer.

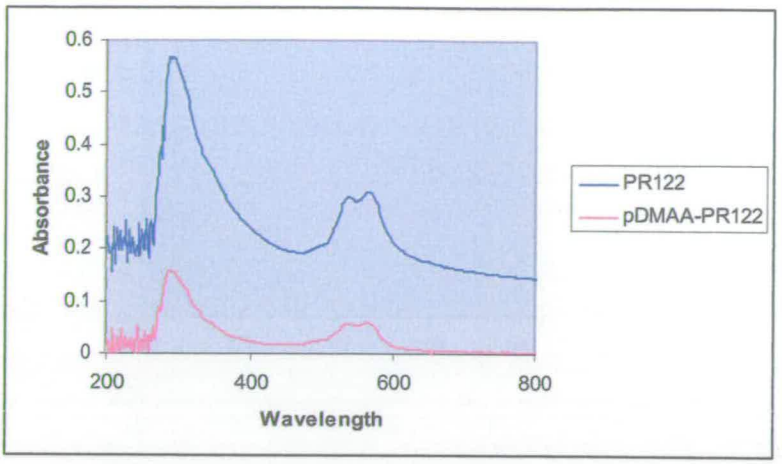


Figure 4.1: UV/Vis spectra of PR122 and pDMAA-PR122 dispersed in water

In the case of PR122 and esterified pHBA-PR122 dissolved in DMF (Figure 4.2), the overall shape of the spectra did not change either. The absorbance profiles of the two samples were similar to those measured in water confirming that that the four samples are pigments and not dyes.

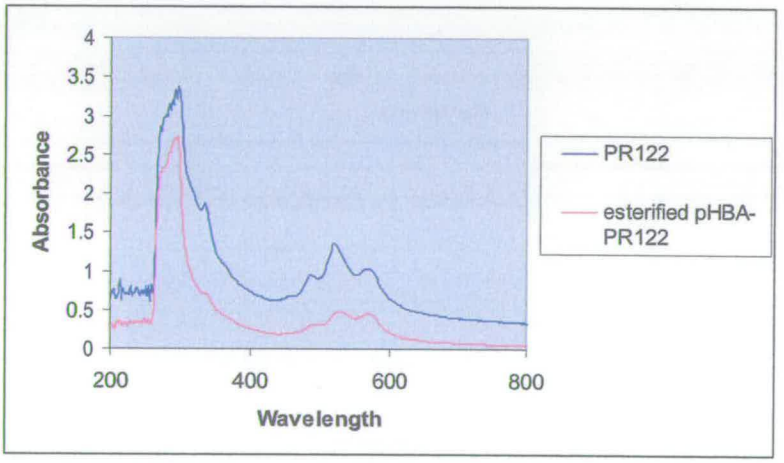


Figure 4.2: UV/Vis spectrum of PR122 and esterified pHBA-PR122 dispersed in DMF

4.3.2 Carbon Black

Carbon black, pDMAA-CB and pStyrene-CB were analysed by UV/Vis following the same procedure. In each case, UV/Vis spectra gave the same overall shape, suggesting that even after modification carbon black behaved as a pigment. (Figure 4.3 and Figure 4.4). Modified CB had the smallest intensity due to the large graft weight of 2400 %.

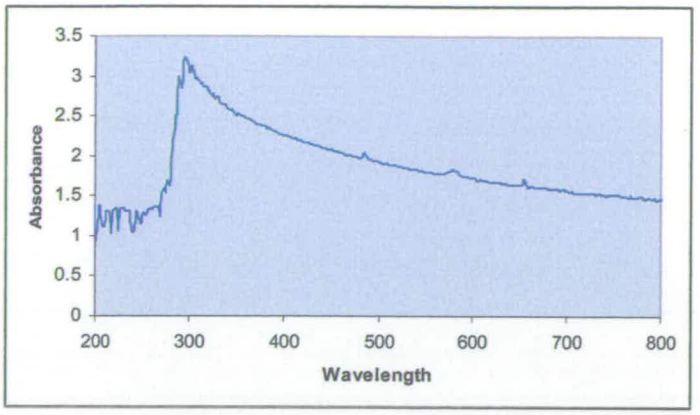


Figure 4.3: UV/Vis spectrum of CB dispersed in water

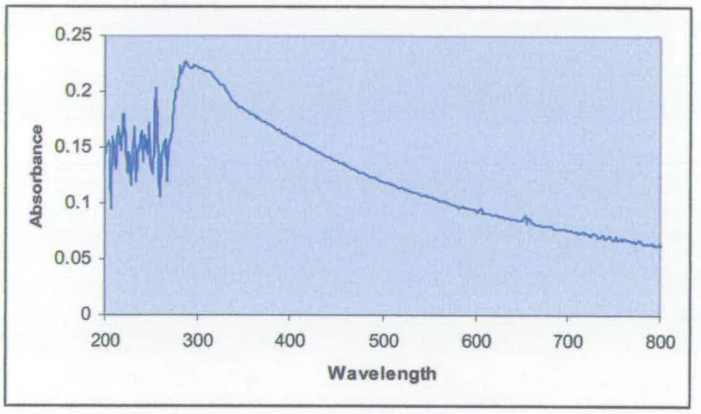


Figure 4.4: UV/Vis spectrum of pDMAA-CB dispersed in water

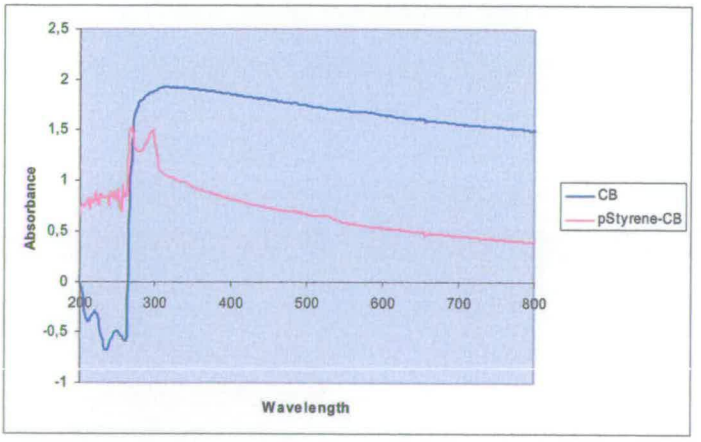


Figure 4.5: UV/Vis spectra of CB and polystyrene-CB dispersed in DMF

4.3.3 Pigment blue 15:3

PB15:3, pDMAA-PB15:3 and polystyrene-PB15:3 were the most dispersed pigments in either water or DMF (0.1mg/mL). Figure 4.6 and Figure 4.7 show that pigment blue 15:3, pDMAA-PB15:3 and polystyrene-PB15:3 dispersed in DMF (0.1 mg/mL) had similar overall spectral shapes.

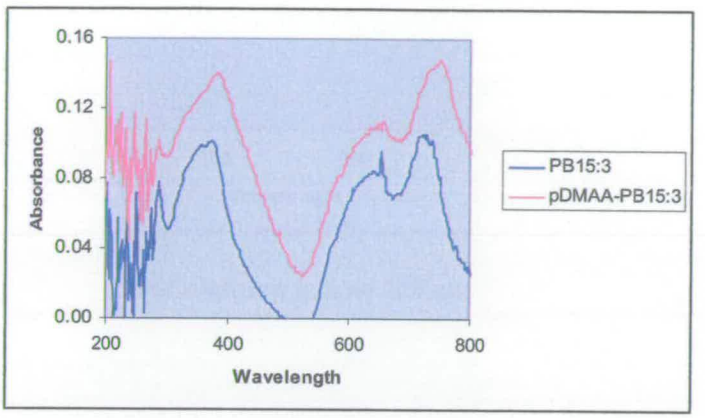


Figure 4.6: UV/Vis spectra of PB15:3 and pDMAA-PB15:3 dispersed in water

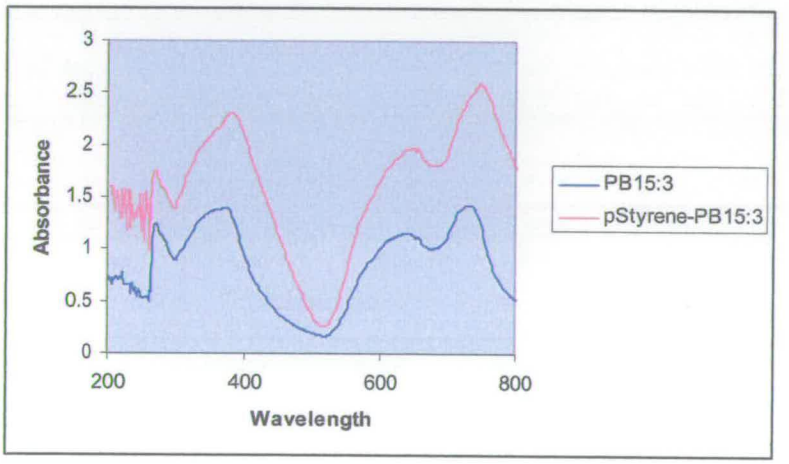


Figure 4.7: UV/Vis spectrum of PB15:3 and pStyrene-PB15:3 dispersed in DMF

4.3.4 Pigment yellow 155

UV/Vis measurements were also done using PY155, pDMAA-PY155 and polystyrene-PY155, which were dispersed either in water or DMF (0.1mg/mL) and also gave similar spectra (Figure 4.8 and Figure 4.9).

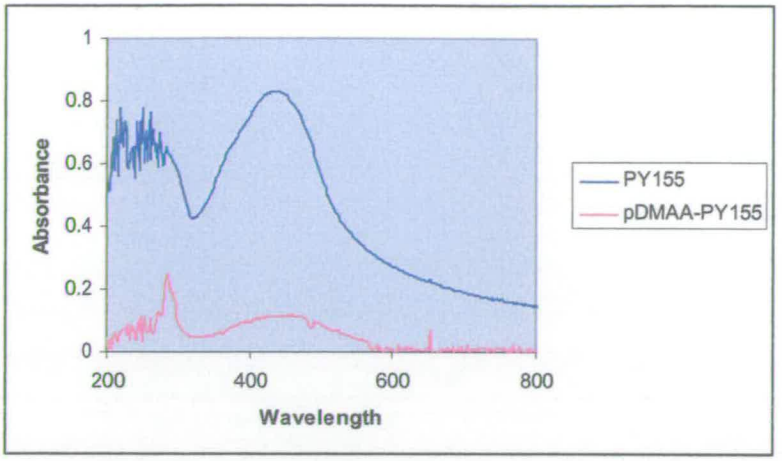


Figure 4.8: UV/Vis spectrum of pigment yellow 155 and pDMAA-PY155 dispersed in water

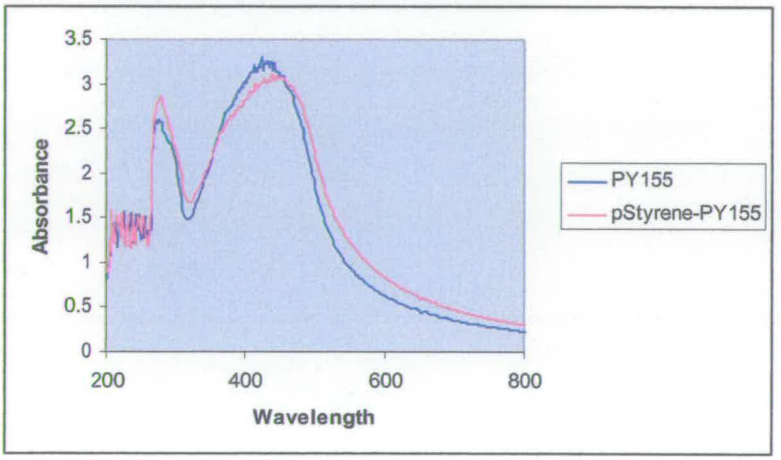


Figure 4.9: UV/Vis spectrum of pigment yellow 155 and pStyrene-PY155 dispersed in DMF

These experiments suggest that the modified pigments are still behaving as a pigment even if their solubility properties have improved.

4.4 Wetting measurements

Contact angle is defined as the angle formed at the interface between a liquid and a substrate when a liquid droplet is placed on a sample surface. By definition, a fluid which 'beads up' on a surface droplet is described as non-wetting and a high contact angle is displayed. When the droplet 'wets out' across the surface the contact angle is low.

Figure 4.10: Schematic representation of contact angle measurement

Using a method developed in our laboratory [71], it was possible to determine the spreading area of water on our coated samples, which was proportional to the contact angle of the spin coated pigments. Coating of the modified pigments on cover glasses was carried out by spin coating. Dispersions of modified pigments in THF (1 mg/mL) were prepared and placed onto the cover glass during spin coating. After drying, a drop of water (dyed red) was placed onto each coated cover glass using a robotic liquid handing system. An image was taken 20 seconds after placing the droplet and analysed by Image Pro-Plus (Media cybernetics) to calculate the area of the drop. The spreading area of the drop on the coated glass could be measured, which is known to be proportional to the contact angle of the coated glass.

4.4.1 Preliminary analyses

Poly(*N,N*-dimethylacrylamide) grafted onto PR122 (pDMAA-PR122, Graft weight = 1894 %), polystyrene and polyhydroxyethylmethacrylate (pHEMA) were coated separately onto cover glasses and the droplet sizes measured. Knowing that polystyrene is considered hydrophobic and pHEMA hydrophilic it was concluded that pDMAA-PR122 was very hydrophilic as expected (Figure 4.11).

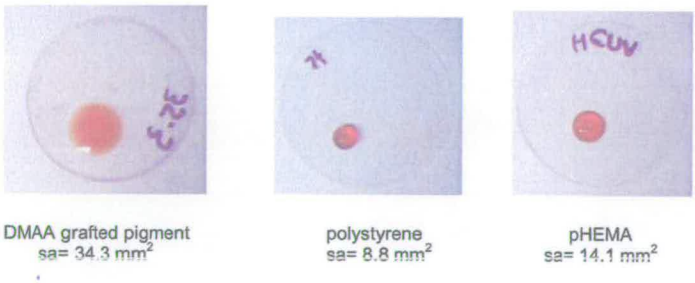


Figure 4.11: Comparison between area of droplets of pDMAA-PR122, pStyrene and pHEMA on spin coater

4.4.2 Wetting studies of modified pigments

In each case, three cover slips of the same modified pigment were prepared and analysed by Image Pro Plus to obtain an average value of the area of these pigments. However, it was difficult to get reproducible results for some modified pigments, which had a poor dispersibility in THF.

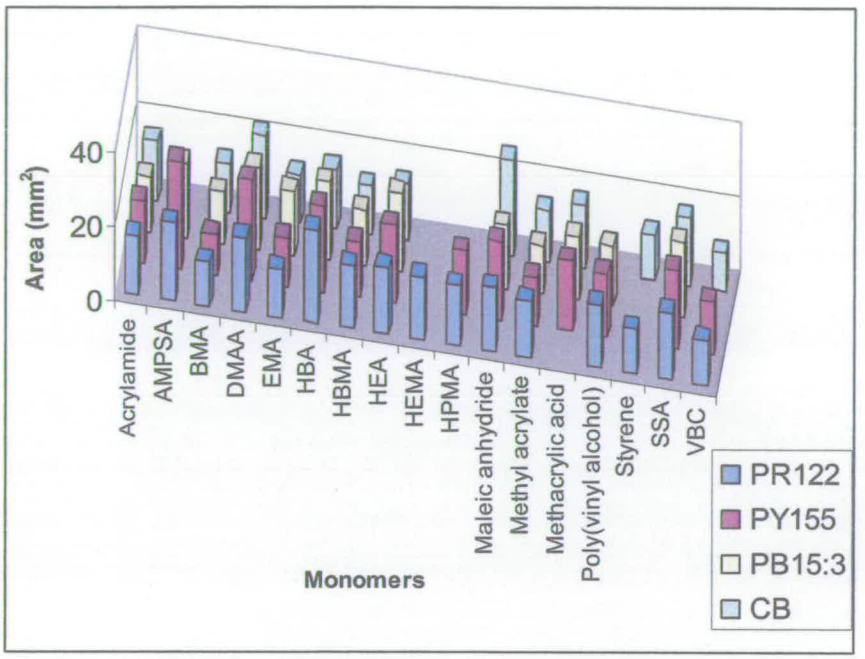


Figure 4.12: Area screening on modified pigments

where AMPSA is -acrylamido-2-methylpropane sulfonic acid, SSA is 4-Styrenesulfonic acid and VBC is 4-Vinylbenzylchloride

Table 4.2: Area screening on modified pigments

Monomers	Area (mm^2)				Graft weight (%)			
	PR122	PY155	PB15:3	CB	PR122	PY155	PB15:3	CB
Acrylamide	16	17	15	16	17	64	1	125
AMPSA	21	29	20	*	121	121	65	125
BMA	12	11	14	13	88	300	121	533
DMAA	20	27	22	22	2594	2594	2730	2427
EMA	13	13	17	13	100	285	147	4500
HBA	25	23	21	16	781	532	966	71
HBMA	17	15	15	13	521	233	358	175
HEA	18	21	21	15	58	774	164	77
HEMA	17	*	*	*	4304	677	2317	83
HPMA	16	17	*	*	1109	833	955	18
Maleic anhydride	17	21	17	26	70	64	51	42
Methyl acrylate	15	13	13	14	1148	1000	439	3489
Methacrylic acid	*	19	17	17	1	1	1	11
PVA	17	17	16	*	136	141	169	138
Styrene	12	*	*	12	291	258	248	1066
SSA	18	21	20	18	77	102	92	105
VBC	12	14	*	10	411	205	269	655

** Modified pigment was not dispersed in THF (1 mg/mL), therefore no measurements were made.*

Three main conclusions can be drawn from these results:

a) Monomers with hydroxyl groups such as HBA, HBMA, HEA, HEMA and HPMA and monomers with sulfonic acid group such as 2-acrylamido-2-methylpropane sulfonic acid transferred hydrophilicity to the pigments.

b) DMAA, which has an amide group, transferred hydrophilicity to pigments due to hydrogen bonding between the amide group and water.

c) The choice of monomer can control the hydrophilicity of the grafted pigments.

4.5 SEM

Scanning electron microscopy (SEM) analyses the surface structure by bombarding the sample with a scanning beam of electrons and then collecting secondary electrons. A Jeol JSM-5600 was operated with an accelerating voltage of 10KeV and a resolution of 3.5 nm. The aim of these experiments was to understand how grafting had modified the pigment surface. Analysis was performed on four pigments.

4.5.1 Results on Pigment red 122

By comparing images of pigment red 122, activated pigment red 122, pDMAA-PR122 (Graft weight = 2594 %) and pStyrene-PR122 (Graft weight = 291 %) taken by SEM (Figure 4.13, Figure 4.14, Figure 4.15, Figure 4.16), it was observed that modifications using DMAA as a monomer gave a smoother surface to pigment red 122. In the case of pStyrene grafted onto PR122, the appearance of the modified pigment was similar to pigment red 122.

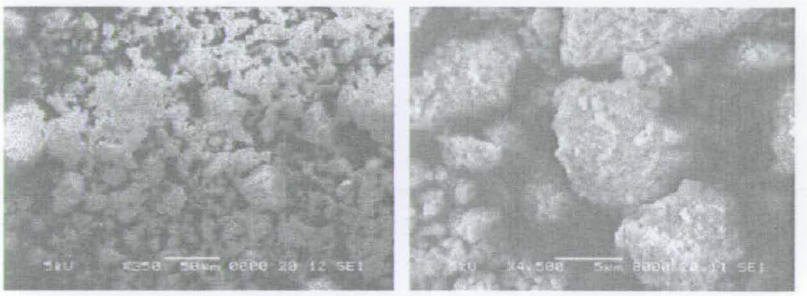


Figure 4.13: SEM images of PR122

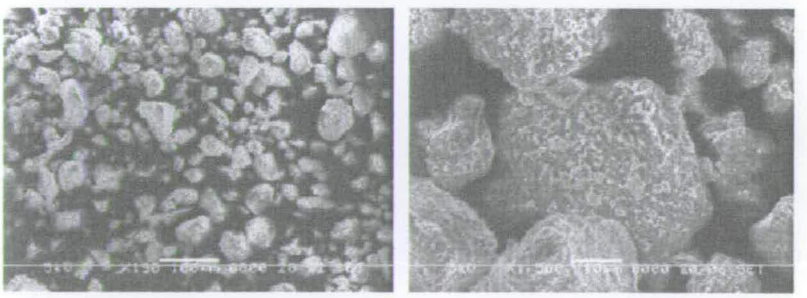


Figure 4.14: SEM images of activated PR122

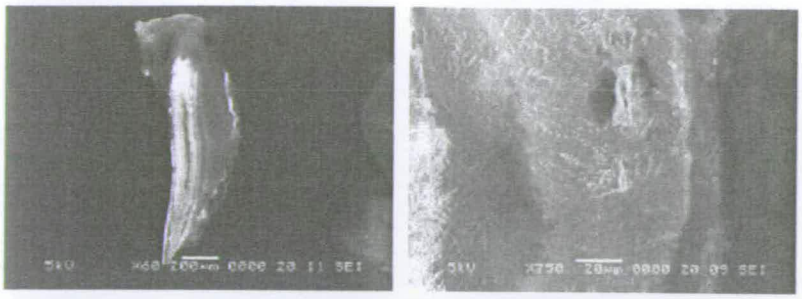


Figure 4.15: SEM images of pDMAA-PR122

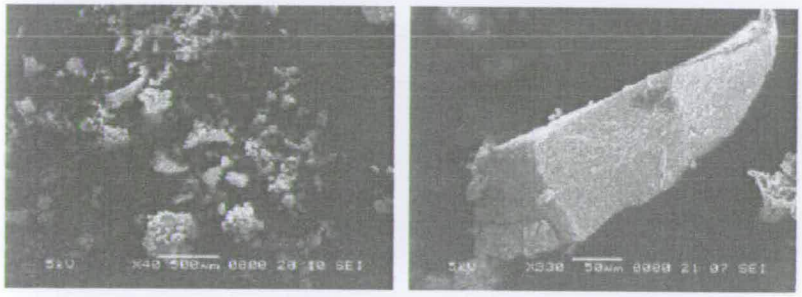


Figure 4.16: SEM images of pStyrene-PR122

4.5.2 Results on Pigment blue 15:3, Pigment yellow 155 and Carbon Black

Similar results were obtained for the three other pigments. pDMAA-PB15:3 (Graft weight = 2730 %) had a smoother surface than PB15:3, activated PB15:3 and pStyrene-PB15:3 (Graft weight = 92 %) due to the large amount of polymer grafted onto the pigments surface (Figure 4.17). In the case of pigment yellow 155 the modification did not change the surface of the pigment even if a large amount of polymer was grafted onto the pigment (Graft weight of pDMAA-PY155 = 2954 % and Graft weight of pStyrene-PY155 = 258 %) as shown in Figure 4.18. By using DMAA to modify the surface of CB (Graft weight = 2427 %) the pigment became a gum and by using styrene (Graft weight = 1066 %) its surface became also very smooth (Figure 4.19).

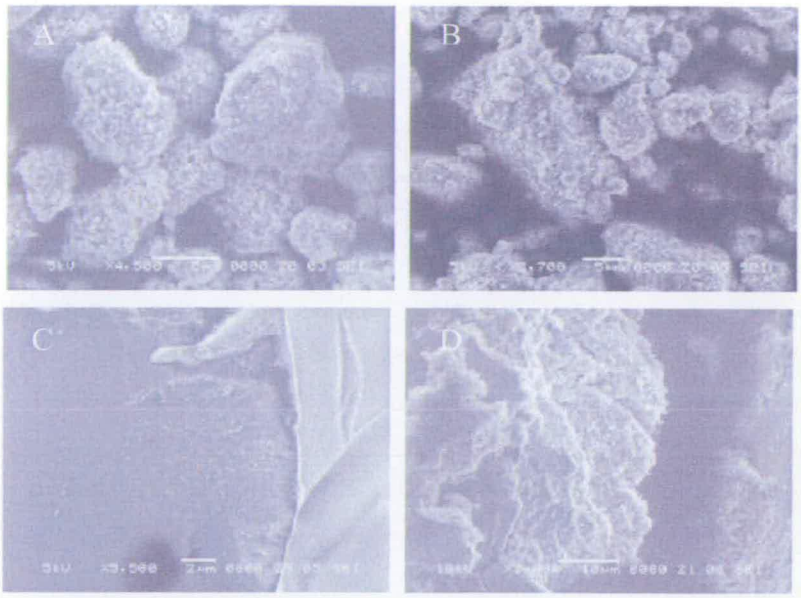


Figure 4.17: SEM images of PB15:3 (A), activated PB15:3 (B), pDMAA-PB15:3 (C) and pStyrene-PB15:3 (D)

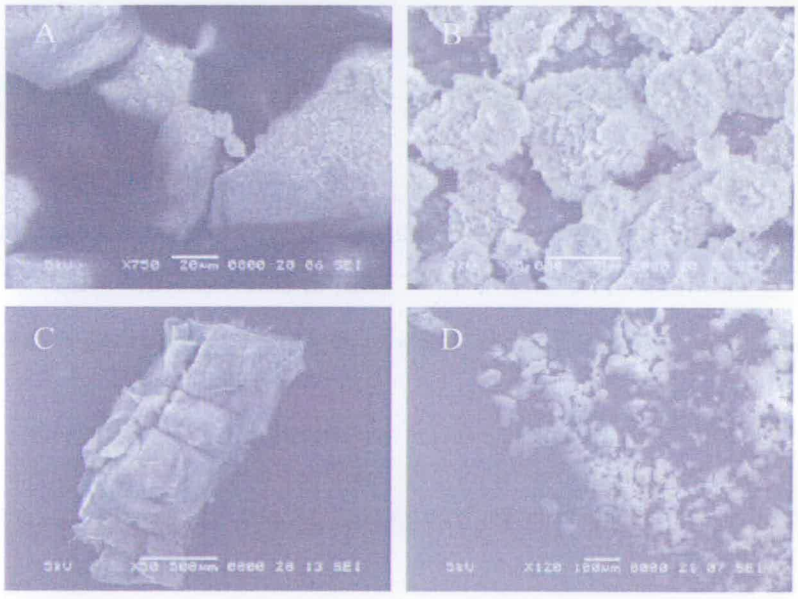


Figure 4.18: SEM images of PY155 (A), activated PY155 (B), pDMAA-PY155 (C) and pStyrene-PY155 (D)

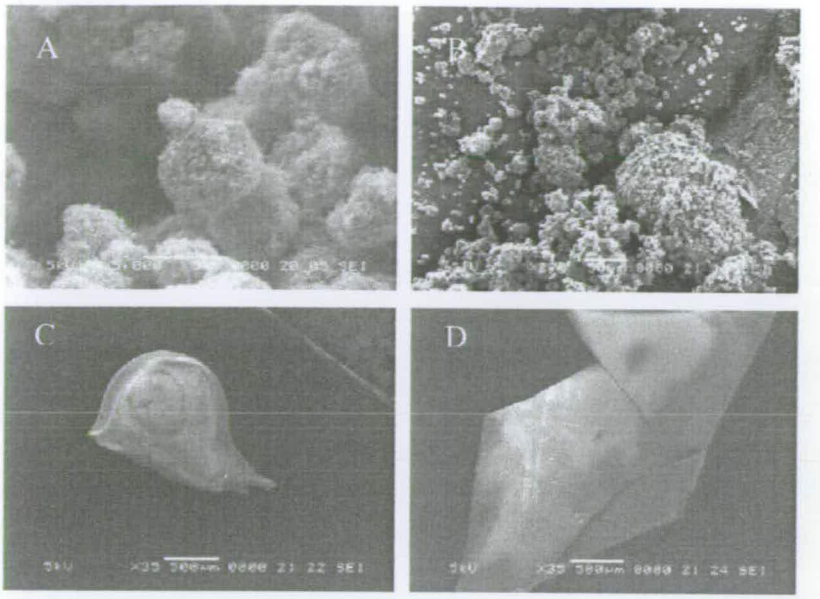


Figure 4.19: SEM images of CB (A), activated CB (B), pDMAA-CB (C) and pStyrene-CB (D)

4.6 X-ray Photoelectron Spectroscopy[72]

Photoelectron spectroscopy uses photoionization and energy-dispersive analyses of the emitted photoelectrons to study the composition and electronic state of the surface region of a sample. X-ray photoelectron spectroscopy (XPS) [72] is using soft X-ray (200 – 2000 eV) radiation to examine core – levels. The energy of a photon is given by the Einstein relation:

$$E=h\upsilon$$

Where: υ: frequency of radiation (Hz) and h: Planck constant ($6.62\ 10^{-34}$ J.s)

The photon is absorbed by an atom in a molecule, leading to ionisation and the emission of a core electron. The kinetic energy distribution of the emitted photoelectrons can be measured using an appropriate electron energy analyser and a photoelectron spectrum can thus be recorded.

Looking at the overall process as follows:

$$A + h\upsilon = A^{+} + e^{-}$$

Conversion of energy requires that:

$$E(A) + h\upsilon = E(A^{+}) + E(e^{-})$$

And since the electron's energy is present as kinetic energy (KE), this can be rearranged to give:

$$KE = h\upsilon - (E(A^{+}) - E(A))$$

Where $(E(A^{+}) - E(A))$ represents the difference in energy between the ionised and neutral atoms, which is generally called the binding energy (BE) of the electron. Therefore, the above equation can be simplified to:

$$KE = h\upsilon - BE$$

To summarize, for each element, there will be a characteristic binding energy associated with each core orbital. Each element will give rise to a characteristic set of peaks in the photoelectron spectrum at kinetic energies determined by the photon energy and the respective binding energies. The presence of the peaks at particular energies will indicate the presence of a specific element in the sample under study and the intensity of the peaks is related to the concentration of the element within the sampled region. [73]

For this experiment only one monomer, 4-vinylbenzylchloride (VBC), was used for the four pigments, because it contains chlorine, which is easily detected by XPS. The results for the four pigments showed the presence of chlorine on the four modified pigments but not on the unmodified pigments used as controls, which suggest grafting of poly(4-vinylbenzylchloride) on pigment surfaces.

Table 4.3: XPS results for PR122, Modified PR122, PB15:3 and modified PB15:3

Atoms	PR122 Atom %	pVBC-PR122 Atom %	PB15:3 Atom %	pVBC-PB15:3 Atom %
Cl 3p	0	1.7	0	2.1
C 1s	86.91	92.6	73.88	81
N 1s	6.22	0.2	15.59	10.5
O 1s	6.87	5.4	10.53	6.4

Table 4.4: XPS results for PY155, modified PY155, CB and modified CB

Atoms	PY155 Atom %	pVBC-PY155 Atom %	CB Atom %	pVBC-CB Atom %
Cl 3p	0	4.3	0	4.7
C 1s	73.88	88	81.69	86.6
N 1s	15.59	2	0	3.5
O 1s	10.53	5.7	18.31	5.2

4.7 Conclusions

Physical characterization showed that covalent grafting of polymers had occurred on the pigments, that in the majority of cases, modified pigments were not soluble but dispersed in water or DMF (1 mg/mL) depending on the monomer used and the level of grafting on the pigments, that surfaces of modified pigments were different from the surfaces of the initial pigments and that their surfaces were smoother.

5 Plasma activation and grafting

5.1 The concept

The concept of plasma activation is similar to gamma irradiation [74, 75, 76] and was already used for activating the pigment surfaces. [77, 78, 79, 80] The four pigments (PR122, PY155, PB15:3 and CB) were exposed to N_2 and O_2 plasmas in the absence of monomers in order to create free radicals on the pigment surface. This is a gentle technique and should modify only the pigment surfaces. [81] Like gamma irradiation, grafting occurs by free radical polymerisation.

5.2 Principle of plasma activation

Plasma is a partially ionised gas containing ions, electrons, atoms and neutral species and plasma treatment is becoming increasingly used in industry. A few applications are described below [82]:

a) Adhesive promotion [82]

Oxygen plasma is used to modify the surfaces of materials to maximize contact with the adhesive or coating. This technique is not only used in printing and painting procedures but also in medical applications, which include surface preparation for adhesive bonding of catheters and balloon catheters as an example.

b) Cleaning [82]

Plasma treatment will remove microscopic rust and contaminant films. Ultra fine cleaning of medical consumables, connectors and needles can also be achieved.

c) Biocompatibility [82]

Gas plasma prepares surfaces for cell growth or protein bonding. Already, petri dishes and microtiter plates for laboratory experiments or drug production are treated using plasma. This process can be used to enhance the biocompatibility of implants, for example by treating the surface of the device to increase the adherence of hemocompatible coating.

d) Sterilization [82]

Gas plasmas are already used to sterilize the surfaces of medical components

5.2.1 Formation of the plasma

A gas, which is enclosed in a vacuum chamber at low pressure (26 Pa) is subjected to an electric field (2.45 GHz) in order to create an electric gas discharge that causes gas molecule excitation and the acceleration of free electrons. Free electrons gain enough energy from the imposed radio frequency field for reactions such as ionization and fragmentation of the gas molecules, which will collide with neutral gas molecules and transfer energy, dissociation of molecules to form numerous reactive species (excited atomic, molecular, ionic, and free radical species). [83], [84]

5.2.2 Modification of surface

It is the interaction of the excited species formed by the plasma with the material surface that results in the chemical and physical modification of its surface. The effect of the plasma on a given material is determined by the chemistry of the reactions between the surface and the reactive species present in the plasma. Resulting surface changes depend on the composition of the surface and the gas used. The process of plasma treatment can be divided into thee mechanisms:

a) Ablation [83]

This is generally achieved using oxygen plasma. The process, called "cold burning", is able to break weak covalent bonds though bombardment with high energy particles. Therefore, surface contaminations are transformed into typical "burning products" such as water and carbon dioxide.

b) Activation [83]

This process consists of replacing surface polymer groups with chemical groups from the plasma.

c) Deposition [83]

A thin polymer coating is formed at the surface of the material though polymerization of the process gas.

5.3 Plasma activation

Using a Junior Plasma System (Europlasma NV), as a plasma irradiation source, samples of pigments (PR122, PB15:3, PY155 and CB) were placed individually inside quartz tubes and subjected to O_2 or N_2 plasma activation. The resulting activated pigment samples were stored at - 20 °C until required.

Figure 5.1: Junior Plasma System

5.3.1 Measurement of the levels of radicals formed onto pigment surfaces

EPR analysis was used to determine the level and the characteristics of the radicals created on the pigment surfaces. For each pigment, the samples activated either by N_2 or O_2 plasma, were analysed.

Initially, an experiment was performed to determine whether or not radicals were present on the pigment surfaces. EPR analysis of PB15:3 (Figure 5.2 and Figure 5.4) and PR122 (Figure 5.3 and Figure 5.5) proved the presence of radicals on their surfaces, while no radicals could be detected on the surface of PY155.

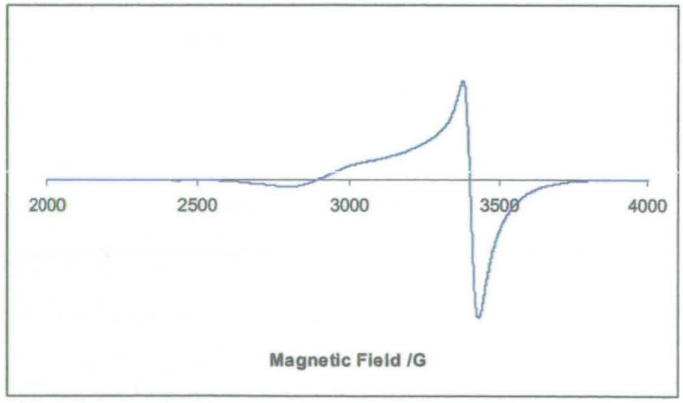


Figure 5.2: EPR spectrum of PB15:3 activated by O_2 Plasma

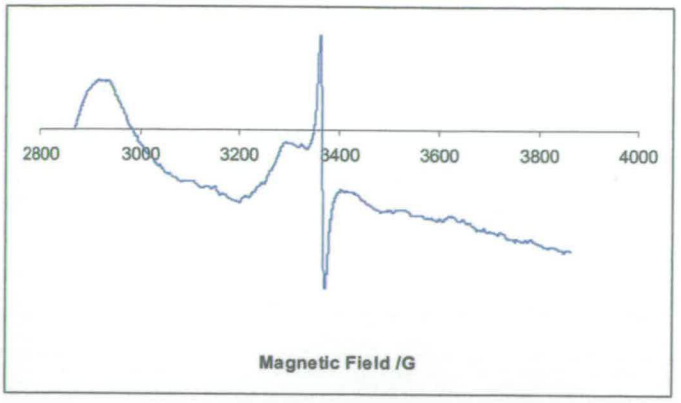


Figure 5.3: EPR spectrum of PR122 activated by O_2 Plasma

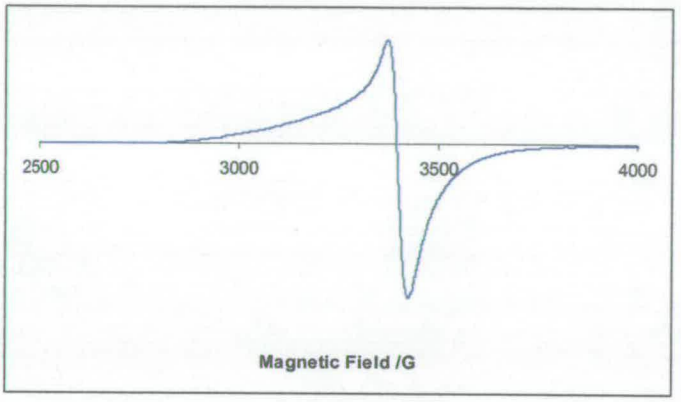


Figure 5.4: EPR spectrum of PB15:3 activated by N_2 Plasma

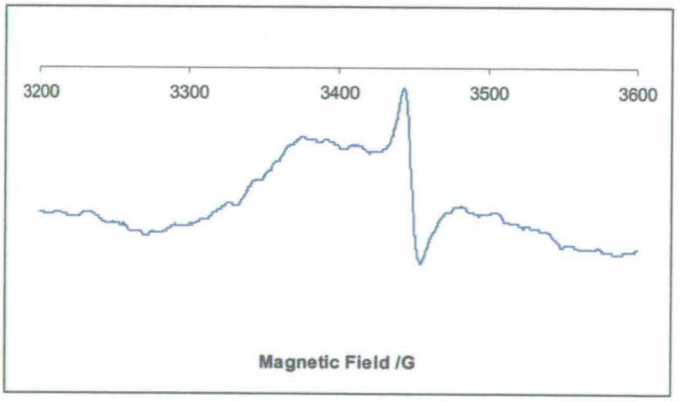


Figure 5.5: EPR spectrum of PR122 activated by N_2 Plasma

It was observed that the same type of signal was obtained for compounds synthesised via both O_2 (Figure 5.2 and Figure 5.3) and N_2 Plasmas (Figure 5.4 and Figure 5.5) and was characteristic of $C^{\cdot}$ or $O^{\cdot}$ radicals.

A second experiment using EPR was carried out to determine the levels of radicals present on the pigment surfaces using different concentrations of manganous sulfate as a calibrator. Table 5.1 shows that PB15:3 was the pigment with the highest levels of radicals on its surface and that the O_2 Plasma was responsible for the highest levels that the longer the process time, the higher the radical content.

Table 5.1: Level of radicals present onto pigment surfaces

Pigments	Time of irradiation (s)	Gas used	Relative level of radicals
PR122	500	N_2	0.0000016
PR122	1000	N_2	0.000003
PR122	2000	N_2	0.0000045
PR122	200	O_2	0.0000074
PR122	1000	O_2	0.00003
PB15:3	200	N_2	0.0139
PB15:3	500	N_2	0.085
PB15:3	2000	N_2	0.078
PB15:3	200	O_2	0.045

5.4 Grafting

Four libraries were prepared by homopolymerisation using either DMAA or styrene as monomers and using either pigment red 122 or pigment blue 15:3 activated by N_2 or O_2 plasma. The monomers giving the best results in terms of gamma irradiation and improvement of solubility were chosen (see Chapter 3) (Table 5.2). In order to check the reproducibility of the grafting, three identical batches were synthesized at the same time. The reactions were carried out at 120 °C under nitrogen overnight, using DMF as a solvent. The product was then precipitated by dropwise addition into cyclohexane / diethyl ether (1/1) to obtain a solid or rubber. The product was washed with cyclohexane / diethyl ether (1/1) and dried under vacuum at 40 °C for 7 h.

Table 5.2: Homopolymersiation using DMAA as monomer

Entry	Pigment	Type of Plasma	Time of irradiation (s)	Graft weight % Average
1	PR122	O_2	500	7753
2	PR122	O_2	1000	7749
3	PR122	O_2	2000	7916
/	PB15:3	O_2	500	0
/	PB15:3	O_2	1000	0
/	PB15:3	O_2	2000	0
4	PR122	N_2	500	5469
5	PR122	N_2	1000	5395
6	PR122	N_2	2000	6477
7	PB15:3	N_2	500	5679
8	PB15:3	N_2	1000	5966
9	PB15:3	N_2	2000	6225

Using the O_2 plasma, free polymers were obtained. Figure 5.6 shows that the pigment is located at the surface of the polymer only. The reactions were repeated, and the same results were observed.

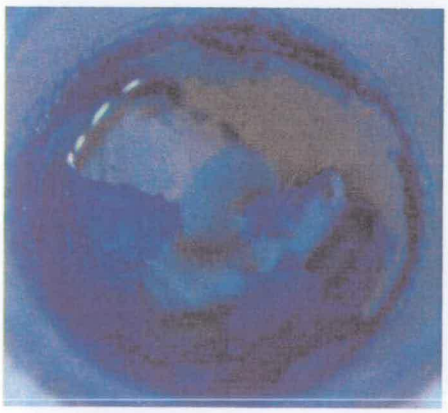


Figure 5.6: Unsuccessful grafting on PB15:3 activated by O_2 plasma

In a second set of experiments, styrene was used as a monomer (Table 5.3). A small grafting percentage was obtained for each compound (Table 5.2).

Table 5.3: Homopolymersiation using styrene as monomer

	Pigment	Type of Plasma	Time of irradiation (10^3 s)	Graft weight % Average
10	PR122	O_2	0.5	114
11	PR122	O_2	1	156
12	PR122	O_2	2	129
13	PB15:3	O_2	0.5	151
14	PB15:3	O_2	1	116
15	PB15:3	O_2	2	124
16	PR122	N_2	0.5	103
17	PR122	N_2	1	148
18	PR122	N_2	2	130
19	PB15:3	N_2	0.5	379
20	PB15:3	N_2	1	359
21	PB15:3	N_2	2	385

The dispersibility of pigments obtained for plasma activation was investigated next (Figure 5.7 and Figure 5.8). Following observations were made:

a) Modified pigment blue 15:3 (pigments 7, 8, 9, 13, 14, 15, 19, 20 and 21) was not dispersed in either water or DMF after one day (1 mg/mL).

b) Pigment red activated by either O_2 or N_2 plasma and modified using DMAA as monomer was soluble in water for days (pigments 1, 2, 3, 4, 5 and 6).

c) Pigment red activated by either O_2 or N_2 plasma and modified using styrene as monomer (pigments 10, 11, 12, 16, 17 and 18) was soluble in DMF for 2 days except for compound 15 which was only dispersed in DMF for 1 day.

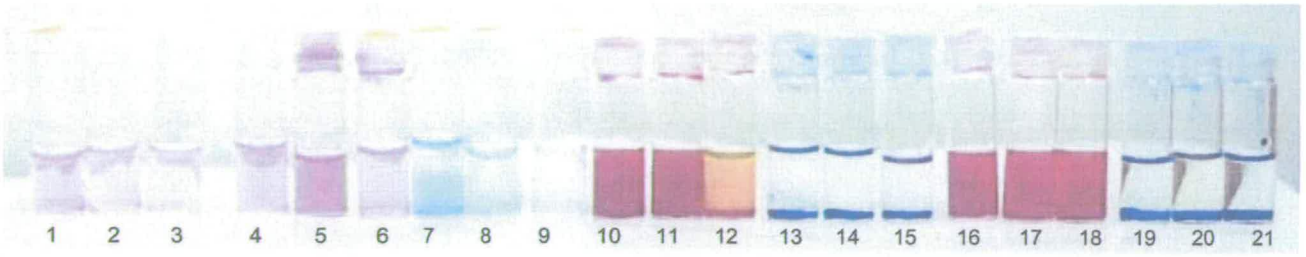


Figure 5.7: Dispersibility of modified pigments after one day

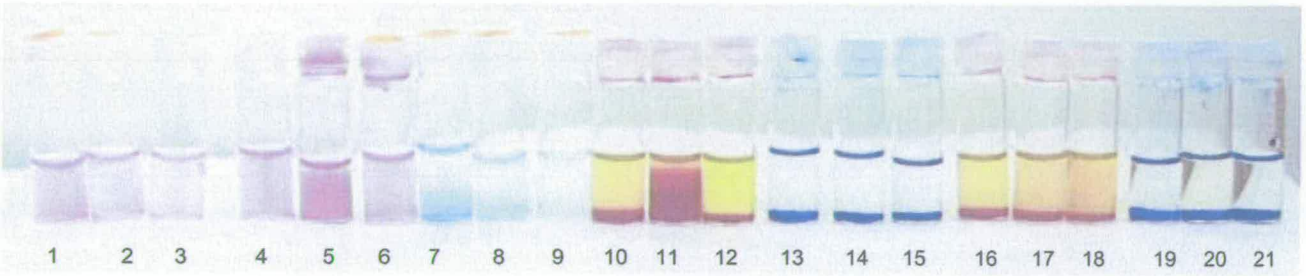


Figure 5.8: Dispersibility of modified pigments after two days

Finally, modification of PR122 by plasma activation at different times of irradiation (500, 1000 and 2000 s) using DMAA as monomer were analysed by UV/Vis spectroscopy in water and DMF. All spectra gave the same overall shape, suggesting that the modified PR122 are still pigments and not dyes (Figure 5.9, Figure 5.10 and Figure 5.11).

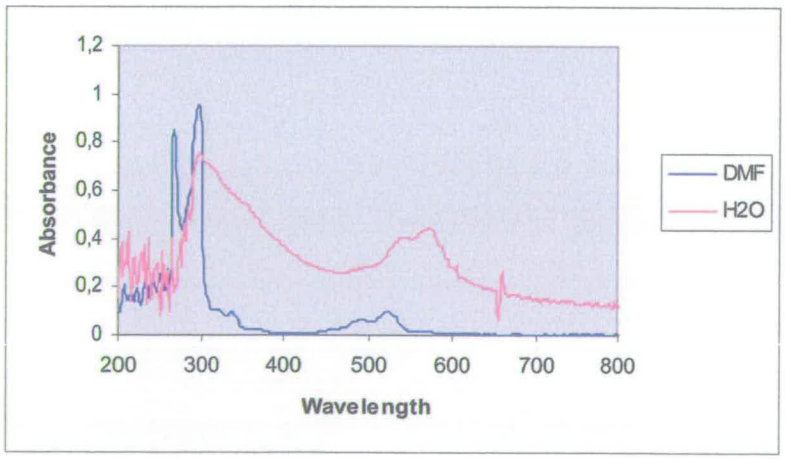


Figure 5.9: UV spectra of PR122 modified by plasma irradiation (T = 500 s)

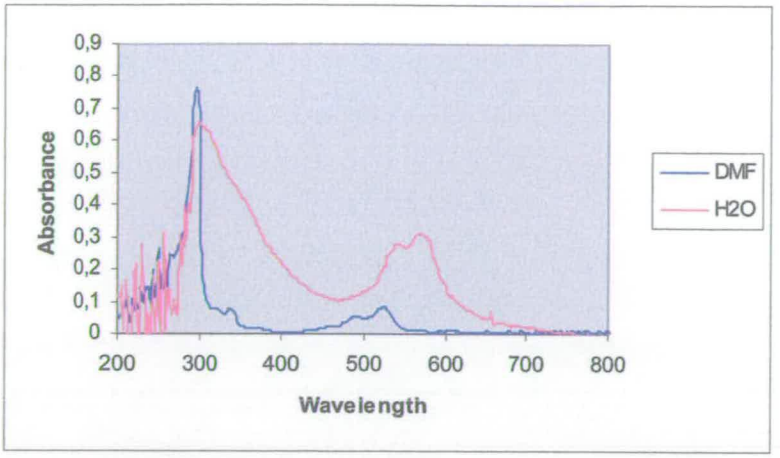


Figure 5.10: UV spectra of PR122 modified by plasma irradiation (T = 1000 s)

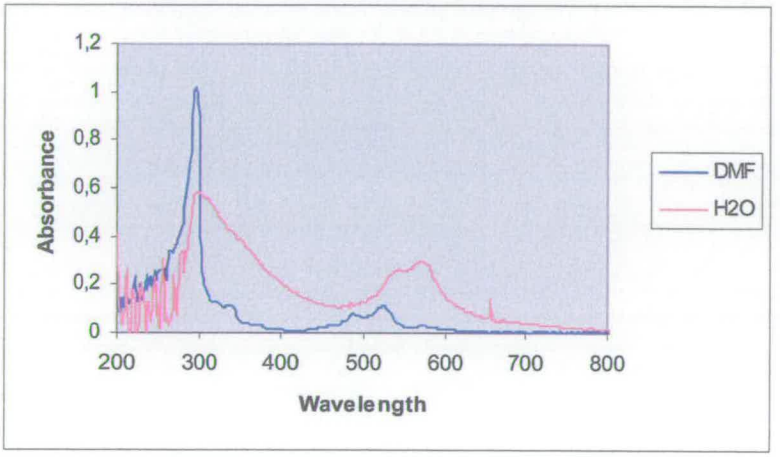


Figure 5.11: UV spectra of PR122 modified by plasma irradiation (T = 2000 s)

5.5 Conclusions

The plasma activation technique gave good results and could be industrialised after further optimisation. Not only it is a simple and easy technique to use but it also allows activation of only the first layer of the pigment's surface which means that the body of the pigment was not altered.

6 Ink formulation and testing

In this part of the project, the aim was to prepare, print and check the stability of different formulations using the optimized pigments described in the earlier chapters.

6.1 Formulation of the ink

Kodak gave us a general Dell formulation [85] in order to test a simple formulation. The composition of this formulation consisted of:

a) 2-Pyrrolidininone (7.8 %), which is used as an humectant,
b) Polyethylene glycol (PEG, 400 MW, 6.1 %), which is also an humectant and a modifier of viscosity,
c) 1,2-Hexanediol (1.2 %), which is used as co-solvent humectant,
d) Surfynol 465 (0.1 – 1 %), which is a non ionic surfactant and is used to reduce the surface tension of the ink which should be between 30 and 35 mN/m,
e) Solids (pigment and any acetonitrile insoluble polymers, 5.8 % including around 2 to 4 % of pure pigment),
f) Water, used as a solvent (78 %).

A Canon printer (S450) was used because of access into the cartridges. Thus the density and viscosity of the Canon yellow formulation were analyzed (density of 1.0736 g/mL and viscosity of 2.2954 mPa.s at 20 °C). In the setup used for printing (Chapter 6.2), density and viscosity influence largely the quality of the printing. Therefore, a set of formulations was made by varying the amount of the additives in the Dell formulation (Table 6.1).

Table 6.1: Formulations

pyrrolidinone (mL)	PEG 400 MW (mL)	hexanediol (mL)	Surfynol (mL)	water (mL)	density (g/mL)	T °C	viscosity (mPa.s)
0.3	4	0.05	0.5	0.15	1.0131	25.03	1.3079
0.1	4.5	0.05	0.2	0.15	1.0132	24.54	1.3245
0.5	3.5	0.1	0.5	0.4	1.0124	24.18	1.3327
1	3	0.1	0.5	0.4	1.016	21.98	1.491
1.5	2.5	0.1	0.5	0.4	1.0211	21.4	1.5787
2	2	0.1	0.5	0.4	1.0236	23	1.6203
2.5	1.5	0.1	0.5	0.4	1.0258	22.44	1.736

By varying the ratio of 2-pyrrolidinone to PEG-400, only a small increase in viscosity could be obtained (Table 6.1). In order to obtain higher viscosities close to the canon formulation, it was decided to use a new type of PEG that had a greater molecular weight. A stock solution of polyethylene glycol (10,000 MW) was prepared and then tested in different formulations (Table 6.2).

Table 6.2: Formulations

pyrrolidinone (mL)	PEG 400 MW (mL)	PEG 10,000 MW (mL)	hexanediol (mL)	Surfynol (mL)	Water (mL)	Density (mg/l)	T ° C	viscosity (mPa.s)
2.5	1.5	0	0.1	0.5	0.4	1.0274	20.78	1.835
3	1	0	0.1	0.5	0.4	1.0339	20.66	2.0901
2.5	0	1.5	0.1	0.5	0.4	1.0261	20.73	2.889
3.5	0.5	0	0.1	0.5	0.4	1.0339	22.01	1.9759
2.5	0	1	0.1	0.5	0.9	1.0246	21.69	2.3454
3	0	1	0.1	0.5	0.4	1.0294	21.91	2.6054

Using PEG (10,000 MW) a formulation close to the Canon parameters could be synthesized. This formulation was made on a large scale in order for pigments to be printed onto paper using a Canon S450 printer.

6.2 Printing

The Canon printer used was a thermal ink jet (Chapter 1.4.2). In this type of printer, the ink drops are ejected from the nozzle by the growth and collapse of a water vapour bubble on the top surface of a small heater located near the nozzle (Figure 1.7). The whole printing system is located within the printer and not on the cartridge itself, which is a great advantage meaning that the cartridge could be modified without damaging the whole printing system.

The "home-made cartridge" (Figure 6.1) was made by cutting off the top of the Canon cartridge, emptying its inner contents (sponges and ink) and glueing a syringe to the inside to give a smaller reservoir. This was followed by the placement of a hard sponge at the cartridge outlet. The ink formulation (2 mL) was added through the top of this new cartridge. The major disadvantage of this cartridge is that it is not under pressure. Consequently, the viscosity of the formulation is really the most important parameter ensuring that enough ink can get though the cartridge and enter the print head in time to allow good printing.

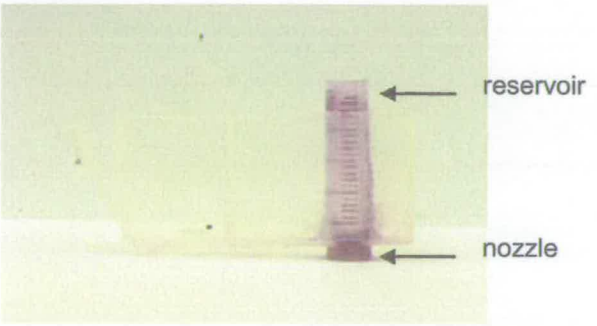


Figure 6.1: Home-made cartridge

The first printing attempt was achieved using pDMAA grafted on PR122 (Graft weight = 485 %). A formulation containing a pigment concentration of 29 mg/mL was tested without success. It appeared that the nozzle was blocked by undispersed pigment particles. After several attempts using different concentrations of pigments, a light print was achieved using a formulation with a pigment concentration of 2.9 mg/mL. Although the first color printing on paper was very light, after repeating the printing four times using the same paper, a magenta color print was obtained. Once the paper had been saturated, further printing proved futile as the color did not get stronger. Canon inkjet photography paper for pigments was then used to get a high quality print but, unfortunately, the color did not fix onto the paper. Similar printing results (appendix) were obtained for pDMAA grafted on PY155 (graft weight = 355 %), pDMAA grafted onto PB 15:3 (Graft weight = 952 %) and pDMAA grafted onto CB (Graft weight = 300 %), all prints out done with these formulations were not stable onto photographic papers under physical treatment.

In order to get a stronger color after the first print, it was decided to use modified pigments with a smaller graft weight (less than 100 %), which had been ground by hand and decreased in size by attrition using glass beads. Unfortunately, these pigments were not dispersed. Nozzles blocked, the print head was broken and no print was obtained. To use these types of pigments a dispersant needs to be added to the formulation.

During all these experiments many problems occurred demonstrating how difficult it is to set up a perfect formulation. A few examples are given below:

a) Bleeding problems occurred when solutions were not viscous enough,
b) Formulations that were too viscous did not print because the ink was taking too much time to reach the printhead,
c) Air bubbles in the print head were also a problem and occurred when the formulations were emulsions,
d) The nozzle blocked because of the large particle sizes of the pigments.

To conclude, pDMAA modified pigments were put into formulation and showed reasonable results in printing; The best prints were kept and exposed to a light fading test.

6.3 Light fading

Before exposing the prints to light fading their color was examined using the Munsell book of color [86] to determine their hue (the quality by which one color is distinguished from another), their value (refering to the gray level of the color, ranging from white to black) and their choma numbers (quality to distinguish between a pure hue from a grey shade) (Table 6.3). These parameters were then used to evaluate fading.

Table 6.3: Munsell measurement on the prints

Ink Formulation	Hue	Value	Choma
Canon red	7.5 RP	4	12
pDMAA-PR122 (Graft weight = 2000 %) printed 4 times	2.5 RP	7	10
pDMAA-PR122 (Graft weight = 2000 %)	2.5 RP	8	6
pDMAA-PY155 (Graft weight = 1030 %) printed 4 times	10 Y	9	4
Canon yellow	Y-6	6.25Y	-
pDMAA-CB (Graft weight = 300 %) printed 4 times	Neutral	7	-
pDMAA-CB (Graft weight = 300 %)	P.RP	8	10 P
pDMAA-PB15:3 (Graft weight = 952 %) printed 4 times	2.5 PB	9	2
Canon blue	2.5 PB	6	10

The samples were exposed to an intense light consisting of 16 fluorescent lights with a total intensity of 4180 mW/m^2. These lights are used to emulate residential indoor and commercial application daylight window fade conditions (Figure 6.2).

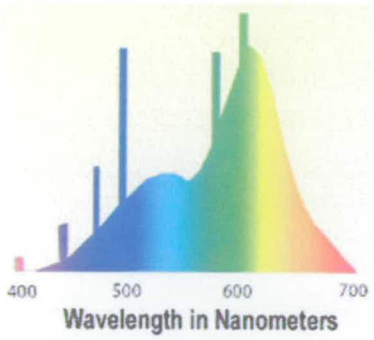


Figure 6.2: Spectrum of fluorescent light (reproduced with permission by Mrs Martin)[87]

The prints exposed to this accelerated fading test were:

a) Canon red,
b) pDMAA-PR122 printed 4 times on the same paper,
c) pDMAA-PR122 printed once on the paper,
d) pDMAA-PY155 printed 4 times on the same paper,
e) Canon yellow,
f) pDMAA-CB printed 4 times on the same paper,
g) p DMAA-CB,
h) pDMAA-PB15:3 printed 4 times on the same paper,
i) Canon blue.

Two prints of each were used to ensure reproducibility of the test (Figure 6.3). The prints were exposed to fading conditions over three weeks and no fading was observed.

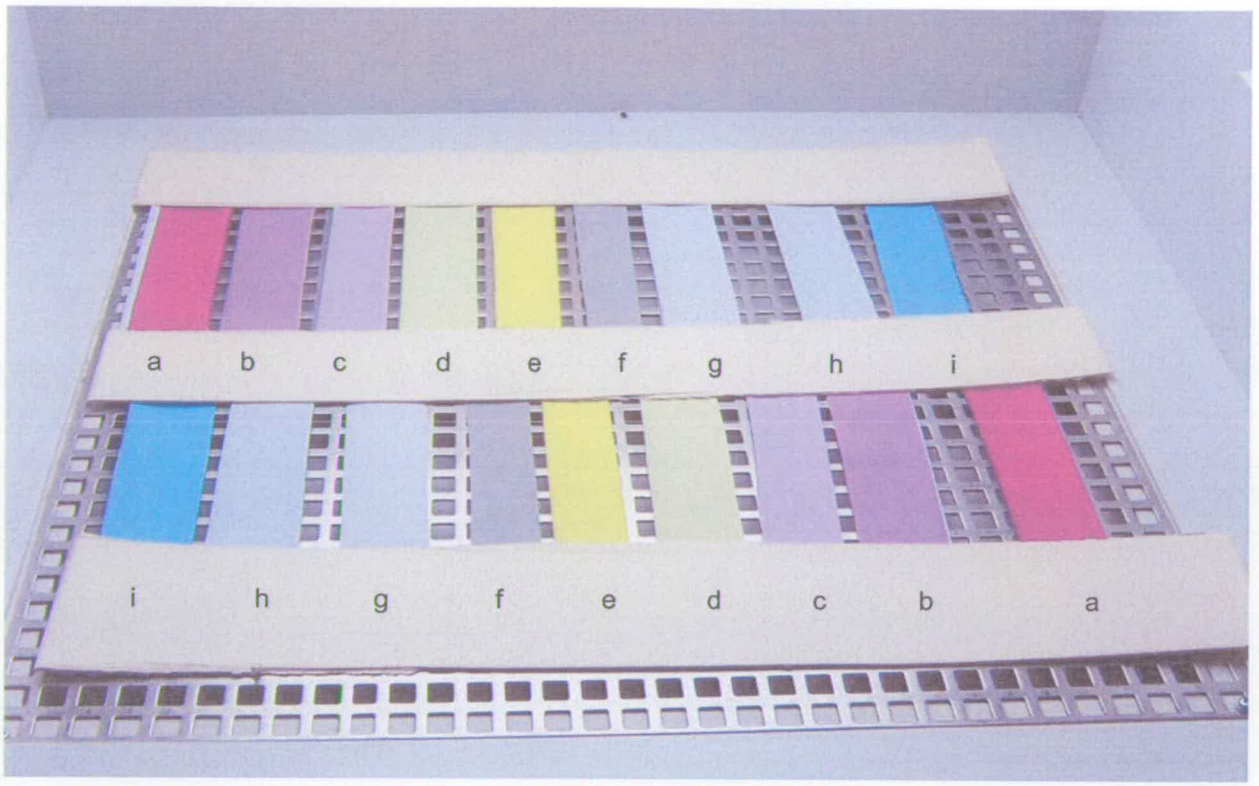


Figure 6.3: light fading test

6.4 Ozone fading

The ozone fading test was done by Kodak in Rochester (NY, USA). Therefore, no detailed explanation of this test can be given due to restrictions on information. Two samples of pDMAA-PR122 with different graft weights (10-15 % and 100-200 %) were compared with a control formulated in two different ways. Results are summarized in Figure 6.4 and shows that modified pigments had good resistance against ozone fading.

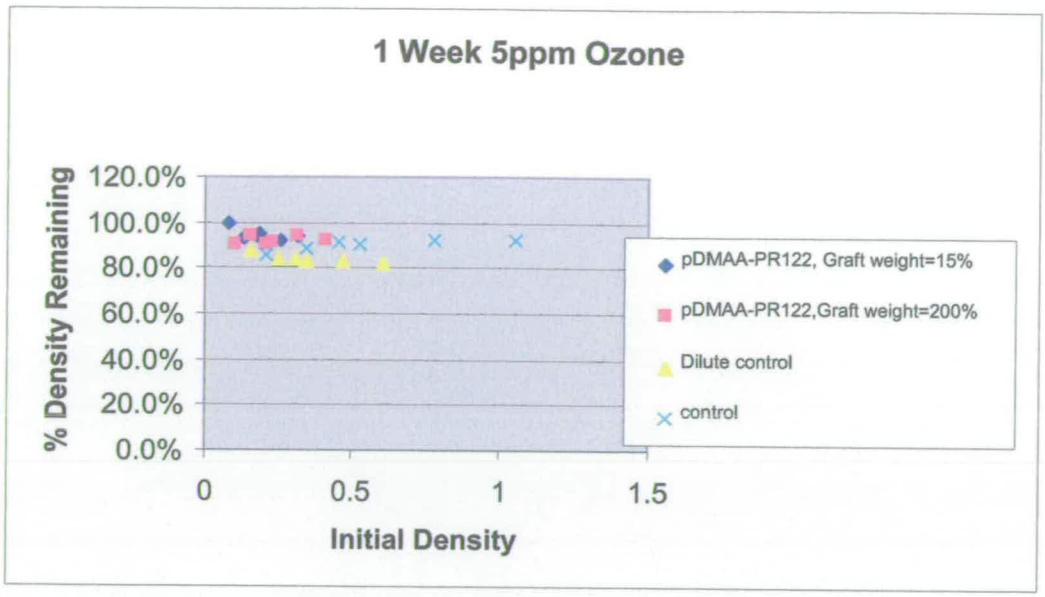


Figure 6.4: Ozone fading test over a week

6.5 Conclusions

Formulations of modified pigments synthesized using pDMAA including PEG (MW 10 000) were found enabling successful printing onto paper with a modified Canon printer cartridge and the printing showed high resistance to light and ozone fading for all modified pigments (pDMAA-PR122, pDMAA-PY155, pDMAA-PB15:3, pDMAA-CB).

7 CONCLUSION

Pigment red 122, carbon black, pigment blue 15:3 and pigment yellow 155 were modified using gamma irradiation followed by polymer grafting. The presence of radicals created on the pigment surface was detected by EPR. Dispersibility studies revealed that *N,N*-dimethylacrylamide was the best monomer to graft onto the pigment surface to improve its water dispersibility; polystyrene was grafted onto pigments to disperse them in DMF. Further modifications like copolymerization, cross-linking and esterification reactions did not improve the properties of the pigments significantly by comparison with the properties of the modified pigments obtained using poly(*N,N*-dimethylacrylamide) and polystyrene. New physical properties of modified pigments were evaluated either by filtration, UV/Vis, contact angle, SEM and XPS. Filtration results showed that pDMAA modified pigments had small particles sizes (0.2 – 0.45 μm) even if pigments were not ground before the experiments; UV/Vis measurements showed that no change in the absorbance profile had occurred as the hue of the pigments had not changed. Contact angle measurements revealed the improvement in the hydrophilicity of the pigments was due to the type of polymer rather than the quantity of polymer grafted onto pigment surfaces. SEM showed that in the majority of the cases the surfaces of the pigments were smoother than the surfaces of the initial pigments. XPS was able to detect the percentage of chlorine on the surface of poly(4-vinylbenzyl chloride) grafted onto pigments. An alternative technique was tested to activate the surface of pigments: plasma irradiation, which is a milder technique compared to gamma irradiation. Successful surface activation and grafting were achieved using pigment red 122 and pigment blue 15:3. This should allow the introduction of new types of functionalities onto the pigment surfaces. Finally, by using a basic formulation, printing using the optimized pigments was accomplished successfully. Fading and ozone tests were done on these prints and revealed good stability of the images over time. The work presented here should open up new opportunities to improve further the properties of pigments. For example, zwitterionic polymers could be grafted onto pigments making possible to manipulate the dispersibility of the pigments by varying the pH of the ink. Furthermore, by synthesizing metal complexes, the problem of light fading could be hopefully resolved.

8 Experimental part

8.1 General information

8.1.1 Materials

All chemicals were reagent grade obtained from commercial sources and were used without further purification. All reactions, requiring an inert atmosphere, were carried out under dry nitrogen.

8.1.2 Characterizations

8.1.2.1 Contact angle

Contact angle measurements were carried out using a Robotic Liquid Handling system. Solutions of modified pigments dispersed in THF (1 mg/mL) were coated on cover glass by spin coating and three cover slips (24 mm) of the same modified pigment were tested by adding a drop of water (dyed red) onto the surface of the coated glass and by analysing the spreading of the drop by Image pro plus to get an average value of the contact angle of these pigments.

8.1.2.2 Density measurement

Density analyses were carried out using a liquid density transmitter named L-DENS from ANTON PAAR.

Before sampling, the device was calibrated with water giving a density of 0.999 g/mL. Then, the sample was injected inside the device through a propylene pipe. The sample (5 mL), which was the formulation, once was stirred, was absorbed with a plastic syringe and was allowed to flow inside the device from one extreme to the other extreme of the pipe in order to avoid the bubble formation inside the device and give a steady state flow through the outcome liquid. When the liquid occupies the whole inner double U-shape device, a screening of data of density as a function of temperature was visualized on a computer. The device was washed with ethanol (2 x 5 mL) and water (2 x 5 mL) and dried with nitrogen stream, until the value o density decayed nearly to zero.

8.1.2.3 Electron paramagnetic resonance (EPR) spectroscopy

X-band EPR data were recorded on an X-band Bruker ER 200-D SRC spectrometer and processed with EPR acquisition System version 2.42. Samples were added to EPR quartz tubes and were not heated prior the analysis. DPPH was used as standard and non-irradiated pigments tested without giving any signals.

block which rotates at ± 70 °C. The computer record the different parameters such as kinematic viscosity, dynamic viscosity and a rolling time of the ball were done. Finally, the capillary was washed by injecting water (2 mL) and then with EtOH (2 mL) following a nitrogen stream until the ball was able to fall freely at small angles of inclination.

8.1.2.10 X-ray photoelectron spectroscopy (XPS)

XPS was performed on a Thermo VG Scientific Sigma Probe under the following conditions:

X-ray source: Alkα

Analysis area: 400 micron radius

Pass energy: 40 eV for individual scans

80 eV for full scan

Step size (resolution): 0.2 eV for individual scans

0.5 eV for full scan

8.2 Experimental to Chapter 2

8.2.1 Gamma irradiation

Samples of pigment red 122 (1 g per vial of 5 mL) were irradiated in air in a ^{60}Co gamma irradiation source to give a dose of 25 kGy, 50 kGy and 100 kGy. Samples of 25 kGy were irradiated at 1 kGy/h and the higher doses of 50 kGy and above were irradiated at a dose rate of 2.5 kGy/h. The central dose rate of the RMCS source (activity of the source) was about 6 kGy/h during the course of the research programme. The samples were kept at – 20 °C until required.

8.2.2 Measurement of the percentage of radicals formed onto pigment surfaces

Activated pigment powders (40 mg approximately) were poured into EPR quartz tubes, which were placed inside the analytical cell. After, observation of the radicals on the pigments, a tube containing 1 cm of a specific solution of manganous sulphate tetrahydrate (standard solution) was placed inside the quartz tube containing the activated pigment, and then a second measurement was takento determine the ratio of peaks area. Different concentrations of manganous sulphate tetrahydrate ($3\ 10^{-4}$, $4.5\ 10^{-4}$, $6\ 10^{-4}$, $9\ 10^{-4}$, $2.7\ 10^{-3}$, $5.5\ 10^{-3}$, $2.5\ 10^{-2}$ and $7.7\ 10^{-2}$ mol/L) were prepared to determine the levels of radicals on the surface of the pigments.

8.2.3 Grafting

8.2.3.1 General procedure for grafting

Samples of activated pigment red 122 were placed in glass vessels with a specific monomer (1 mL) and a specific solvent (3 mL). The mixtures were degassed by bubbling with oxygen free nitrogen for a specific time (0, 0,5, 1 or 2 h). The mixtures were heated during a specific time (2, 6 or 21 h) at a determined temperature (80 or 120 °C). After cooling, the mixtures were added to a solution of cyclohexane:ether (1:1) (40 mL), and precipitation occurred. The precipitate was isolated by centrifugation and washed with cyclohexane:ether (2 x 40 mL), then dried under vacuum. The residue was purified by Soxhlet extraction using cyclohexane:ether (1:1) and dried to constant weight.

8.2.3.2 Temperature experiments

Samples of activated pigment red 122 (36 mg each, 25 kGy) were treated with DMAA (2.4 M), suspended in DMF (3 mL) and degassed for 1 h using oxygen free nitrogen. The mixtures were heated for 21 h at either 80 °C or 120 °C. After cooling, they were washed and treated as described in 8.2.3.1.

Table 8.1: Temperature effect

Temperature (°C)	Graft weight (%)
80	0
120	1900

8.2.3.3 Solvent experiments

Samples of activated pigment red 122 (31 mg each, 25 kGy) were treated with DMAA (2.4 M), suspended either in H_2O or DMF (3 mL) and degassed for 2 h using oxygen free nitrogen. The mixtures were heated for 21 h at 120 °C and treated as described in 8.2.3.1.

Table 8.2: Solvent effect

Solvent	Graft weight (%)
H_2O	16
DMF	2212

8.2.3.4 Reaction time experiments

Nine samples of activated pigment red 122 (33 mg each, 25 kGy) were treated with DMAA (2.4 M), suspended in DMF (3 mL) and degassed for 2 h using oxygen free nitrogen. The mixtures were heated for either 2 h, 6 h or 21 h at 120 °C and treated as described in 8.2.3.1 (Table 8.4).

Table 8.3: Reaction time effect

Reaction time (h)	Graft weight (%)
2	29
2	24
2	14
6	2492
6	2068
6	36
21	2787
21	3484
21	2500

8.2.3.5 Negative control experiment

Pigment red 122 (33 mg) and activated pigment red 122 (36 mg, 25 kGy) were each treated with DMAA (2.4 M), suspended in DMF (3 mL) and degassed for 1 h using oxygen free nitrogen. The mixtures were heated for 21 h at 120 °C and treated as described in 8.2.3.1 (Table 8.5).

Table 8.4: Negative control

Starting material	Graft weight (%)
Pigment red 122	0
Activated pigment red 122	200

8.2.3.6 Influence of total dose

Samples of activated pigment red 122 with different doses 10, 50, 150 or 200 kGy (36 mg each) were treated with DMAA (2.4 M), suspended in DMF (3 mL) and degassed for 2 h using oxygen free nitrogen. The mixtures were heated for 21 h at 120 °C and treated as described in 8.2.3.1 (Table 8.6).

Table 8.5: Total dose effect

Dose rate of activated pigments (kGy)	Graft weight (%)
10	1700
50	1922
150	2148
200	2615

8.2.3.7 Stability of the irradiated pigments

One sample of each activated pigment (pigment red 122, pigment blue 15:3, pigment yellow 155 and carbon black, 32 mg each, 25 kGy), stored at - 20 °C, were treated with DMAA (2.4 M), suspended in DMF (3 mL) and degassed for 2 h using oxygen free nitrogen. The mixtures were heated for 21 h at 120 °C and treated as described in 8.2.3.1. This procedure was repeated at 2, 3, 4, 7 and 12 months beginning 6 months after irradiation (Table 8.7).

Table 8.6: Study of the stability of activated pigments stored at - 20 °C

Activated pigment	Month	Graft weight (%)
PR122	2	2115
PB15:3	2	2682
PY155	2	2952
CB	2	2530
PR122	3	2594
PB15:3	3	2730
PY155	3	2594
CB	3	2566
PR122	4	2579
PB15:3	4	2460
PY155	4	2596
CB	4	2550
PR122	7	2353
PB15:3	7	2402
PY155	7	3038
CB	7	2579
PR122	12	2041
PB15:3	12	3196
PY155	12	3131
CB	12	64

One sample of each activated pigment (pigment red 122, pigment blue 15:3, pigment yellow 155 and carbon black, 32 mg each, 25 kGy), stored at room temperature, were treated with DMAA (2.4 M), suspended in DMF (3 mL) and degassed for 2 h using oxygen free nitrogen. The mixtures were heated for 21 h at 120 °C and treated as described in 8.2.3.1. This procedure was repeated at 3, 4, 7 and 12 months beginnig 6 months after irradiation (Table 8.8).

Table 8.7: Study of the stability of activated pigments stored at room temperature

Activated pigment	Month	Graft weight (%)
PR122	3	2025
PB15:3	3	2503
PY155	3	2761
CB	3	729
PR122	4	2900
PB15:3	4	2722
PY155	4	2776
CB	4	1903
PR122	7	2353
PB15:3	7	2402
PY155	7	3038
CB	7	349
PR122	12	2210
PB15:3	12	3131
PY155	12	3557
CB	12	124

8.2.3.8 Effect of monomer concentration

Ten samples of activated pigment red 122 (30 mg each, 25 kGy) were treated with different amounts of DMAA, suspended in DMF (3 mL) and degassed for 2 h using oxygen free nitrogen. The mixtures were heated for 21 h at 120 °C and treated as described in 8.2.3.1 (Table 8.9).

Table 8.8: Monomer concentration effect

DMAA % vol/vol	$M_{monomer}$ (M)	Graft weight (%)
$1.6\ 10^{-3}$	0.00016	31
$3.3\ 10^{-3}$	0.00032	34
3.310^{-2}	0.0016	36
0.13	0.0032	36
0.16	0.016	36
0.33	0.032	53
1.6	0.16	50
3	0.32	104
14	1.4	239
25	2.4	4976

8.3 Experimental to Chapter 3

8.3.1 Homopolymerisation

8.3.1.1 Experimental Conditions

Sixteen samples of activated pigment red 122 (25 kGy, stored at –20 °C) were treated with monomer (1 mL), suspended in DMF (3 mL) and degassed for 2 h using oxygen free nitrogen. The mixtures were heated for 21 h at 120 °C and treated as described in 8.2.3.1 (Table 8.10).

Table 8.9: Homopolymerisation on PR122

Monomers	$m_{activated\ pigment}$ (mg)	$M_{monomer}$ (M)	Graft weight (%)
Acrylamide	36	3.5	17
2-Acrylamido-2-methylpropane sulfonic acid	33	0.2	121
BMA	30	1.6	88
DMAA	30	2.4	2594
EMA	30	2.0	100
HBA	33	1.8	781
HBMA	36	1.6	521
HEA	32	2.2	58
HEMA	36	2.1	4304
HPMA	36	1.8	1109
Maleic anhydride	30	2.5	70
Methyl acrylate	36	2.8	1148
PVA	36	2.1	136
St	34	2.2	291
4-Styrenesulfonic acid	36	1.3	77
4-Vinylbenzylchloride	20	1.8	411

Seventeen samples of activated carbon black (25 kGy, stored at –20 °C) were treated with monomer (1 mL), suspended in DMF (3 mL) and degassed for 2 h using oxygen free nitrogen. The mixtures were heated for 21 h at 120 °C and treated as described in 8.2.3.1 (Table 8.11).

Table 8.10: Homopolymerisation on Carbon black

Monomer	$m_{activated\ pigment}$ (mg)	$M_{monomer}$ (M)	Graft weight (%)
Acrylamide	36	3.5	125
2-Acrylamido-2-methylpropane sulfonic acid	33	0.2	125
BMA	33	1.6	533
DMAA	30	2.4	2427
EMA	36	2.0	4500
HBA	33	1.8	71
HBMA	36	1.6	175
HEA	33	2.2	77
HEMA	36	2.1	83
HPMA	36	1.8	18
Maleic anhydride	36	2.5	42
Methyl acrylate	36	2.8	3489
Methacrylic acid	36	2.9	11
PVA	36	2.1	138
St	36	2.2	1066
4-Styrenesulfonic acid	36	1.3	105
4-Vinylbenzylchloride	20	1.8	655

Sixteen samples of activated pigment blue 15:3 (25 kGy, stored at –20 °C) were treated with monomer (1 mL), suspended in DMF (3 mL) and degassed for 2 h using oxygen free nitrogen. The mixtures were heated for 21 h at 120 °C and treated as described in 8.2.3.1 (Table 8.12).

Table 8.11: Homopolymerisation on pigment blue 15:3

Monomer	$m_{activated\ pigment}$ (mg)	$M_{monomer}$ (M)	Graft weight (%)
Acrylamide	36	3.5	1
2-Acrylamido-2-methylpropane sulfonic acid	33	0.2	65
BMA	37	1.6	121
DMAA	30	2.4	2730
EMA	40	2.0	147
HBA	33	1.8	966
HBMA	36	1.6	358
HEA	33	2.2	164
HEMA	36	2.1	2317
Maleic anhydride	36	2.5	51
Methyl acrylate	36	2.8	439
Methacrylic acid	36	2.9	1
PVA	36	2.1	169
St	36	2.2	248
4-Styrenesulfonic acid	36	1.3	92
4-Vinylbenzylchloride	20	1.8	269

Sixteen samples of activated pigment yellow 155 (25 kGy, stored at –20 °C) were treated with monomer (1 mL), suspended in DMF (3 mL) and degassed for 2 h using oxygen free nitrogen. The mixtures were heated for 21 h at 120 °C and treated as described in 8.2.3.1.

Table 8.12: Homopolymerisation on pigment yellow 155

Monomer	$m_{activated\ pigment}$ (mg)	$M_{monomer}$ (M)	Graft weight (%)
Acrylamide	36	3.5	64
2-Acrylamido-2-methylpropane sulfonic acid	33	0.2	121
BMA	37	1.6	300
DMAA	30	2.4	2594
EMA	32	2.0	285
HBA	33	1.8	532
HBMA	36	1.6	233
HEA	33	2.2	774
HEMA	36	2.1	677
HPMA	36	1.8	833
Maleic anhydride	36	2.5	64
Methyl acrylate	36	2.8	1000
Methacrylic acid	36	2.9	1
PVA	36	2.1	141
St	36	2.2	258
4-Styrenesulfonic acid	36	1.3	102
4-Vinylbenzylchloride	20	1.8	205

8.3.1.2 NMR analyses

Proton NMR was done on all compounds which were well dispersed in either $CDCl_3$ or D_2O. The results are given below.

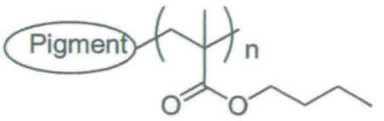


Figure 8.1: Pigment modified using pBMA

pBMA standard

^{1}H-NMR ($CDCl_3$, 250 MHz): δ 3.91 (brs, 2 H, $C\underline{H_2}$-O), 1.78 – 1.92 (m, 4 H, $C\underline{H_{2a}}$, $C\underline{H_{2b}}$), 1.38 – 1.58 (m, 6 H, $(C\underline{H_2})_2$-CH_2O), 1.36 – 1.38 (m, 3 H, $C\underline{H_3}$), 0.84 – 0.95 (m, 3 H, $C\underline{H_3}$)

pBMA-PR122

^{1}H-NMR ($CDCl_3$, 250 MHz): δ 3.89 - 3.94 (brs, 2 H, $C\underline{H_2}$-O), 1.76 – 1.91 (m, 4 H, $C\underline{H_{2a}}$, $C\underline{H_{2b}}$), 1.54 – 1.61 (m, 4 H, $(C\underline{H_2})_2$-CH_2O), 1.32 – 1.43 (m, 3 H, $C\underline{H_3}$), 0.85 – 0.95 (m, 3 H, $C\underline{H_3}$)

pBMA-CB

^{1}H-NMR ($CDCl_3$, 250 MHz): δ 3.88 - 3.93 (brs, 2 H, $C\underline{H_2}$-O), 1.89 (m, 4 H, $C\underline{H_{2a}}$, $C\underline{H_{2b}}$), 1.53 – 1.54 (m, 7 H, $(C\underline{H_2})_2$-CH_2O, $C\underline{H_3}$), 0.85 – 0.94 (m, 3 H, $C\underline{H_3}$)

pBMA-PY155

^{1}H-NMR ($CDCl_3$, 250 MHz): δ 3.89 - 3.93 (brs, 2 H, $C\underline{H_2}$-O), 1.86 – 1.89 (m, 2 H, $C\underline{H_{2a}}$), 1.76 – 1.78 (m, 2 H, $C\underline{H_{2b}}$), 1.35 – 1.39 (m, 7 H, $(C\underline{H_2})_2$-CH_2O, $C\underline{H_3}$), 1.35 – 1.34 (m, 3 H, $C\underline{H_3}$)

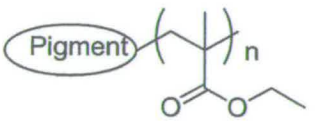


Figure 8.2: Pigment modified using pEMA

pEMA standard

^{1}H-NMR ($CDCl_3$, 250 MHz): δ 3.98 – 4.02 (m, 2 H, $C\underline{H_2}$-O), 1.88 – 1.89 (m, 2 H, $C\underline{H_{2a}}$), 1.79 (m, 2 H, $C\underline{H_{2b}}$), 1.22 (brs, 3 H, $C\underline{H_3}$-CH_2O), 1.00 – 1.01 (brs, 3 H, CH_{3a}), 0.85 (brs, 3H, CH_{3b})

pEMA-PR122

^{1}H-NMR ($CDCl_3$, 250 MHz): δ 3.99 – 4.02 (m, 2 H, $C\underline{H_2}$-O), 1.87 – 1.90 (m, 2 H, $C\underline{H_{2a}}$), 1.79 – 1.80 (m, 2 H, $C\underline{H_{2b}}$), 1.54 (brs, 3 H, $C\underline{H_3}$-CH_2O), 0.96 – 1.06 (m, 3 H, CH_{3a}), 0.79 – 0.88 (m, 3H, CH_{3b})

pEMA-CB

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 4.02 – 4.04 (m, 2 H, $C\underline{H_2}$-O), 1.94 (m, 2 H, $C\underline{H_{2a}}$), 1.82 (brs, 2 H, $C\underline{H_{2b}}$), 1.25 (m, 3 H, $C\underline{H_3}$-CH_2O), 1.03 (m, 3 H, CH_{3a}), 0.88 (m, 3H, CH_{3b})

pEMA-PB15:3

^{1}H-NMR ($CDCl_3$, 250 MHz): δ 3.99 (s, 2 H, $C\underline{H_2}$-O), 1.87 – 1.91 (m, 2 H, $C\underline{H_{2a}}$), 1.78 (s, 2 H, $C\underline{H_{2b}}$), 1.21 (m, 3 H, $C\underline{H_3}$-CH_2O), 0.99 (brs, 3 H, $C\underline{H_{3a}}$), 0.84 (brs, 3 H, $C\underline{H_{3b}}$)

pEMA-PY155

^{1}H-NMR ($CDCl_3$, 250 MHz): δ 3.969 – 4.015 (m, 2 H, O-$C\underline{H_2}$), 1.89 (s, 2 H, $C\underline{H_{2a}}$), 1.88 – 1.89 (s, 2 H, $C\underline{H_{2b}}$), 1.20 – 1.24 (m, 3 H, $C\underline{H_3}$-CH_2O), 0.99 – 1.00 (brs, 3 H, $C\underline{H_{3a}}$), 0.84 – 0.85 (brs, 3 H, $C\underline{H_{3b}}$)

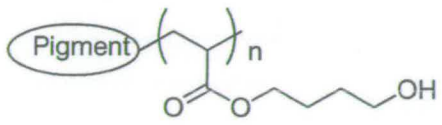


Figure 8.3: Pigment modified using pHBA

pHBA-PB15:3

^{1}H-NMR ($CDCl_3$, 250 MHz): δ 4.03 – 4.10 (m, 2 H, $C\underline{H_2}$-O), 3.60 – 3.68 (m, 2 H, $C\underline{H_2}$-OH), 1.80 – 1.86 (m, 4H, $(C\underline{H_2})_2$-CH_2O), 1.65 – 1.70 (m, 1 H, $C\underline{H}$), 0.82 -0.86 (m, 2 H, $C\underline{H_2}$)

pHBA-PY155

^{1}H-NMR ($CDCl_3$, 250 MHz): δ 4.01 – 4.09 (m, 2 H, $C\underline{H_2}$-O), 3.59 – 3.64 (m, 2 H, $C\underline{H_2}$-OH), 1.50 – 1.63 (m, 7 H, $(C\underline{H_2})_2$-CH_2O, $C\underline{H_2}$, $C\underline{H}$)

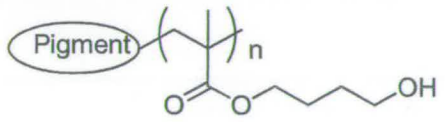


Figure 8.4: Pigment modified using pHBMA

pHBMA-PR122

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 4.10 (brs, 2 H, $C\underline{H_2}$-O), 3.58 (brs, 2 H, $C\underline{H_2}$-OH), 1.94 (m, 2 H, $C\underline{H_2}$-CH_2O), 1.84 (m, 2 H, $C\underline{H_2}$-CH_2OH), 1.06 (brs, 2 H, $C\underline{H_2}$), 0.90 (brs, 3 H, $C\underline{H_3}$)

pHBMA-PB15:3

^{1}H-NMR ($CDCl_3$, 250 MHz): δ 4.00 – 4.06 (m, 2 H, $C\underline{H_2}$-O), 3.78 – 3.79 (m, 2 H, $C\underline{H_2}$-OH), 1.89 – 2.03 (m, 2 H, $(C\underline{H_2})_2$ CH_2O), 0.92 – 1.11 (m, 5 H, $C\underline{H_3}$, $C\underline{H_2}$)

pHBMA-PY155

^{1}H-NMR ($CDCl_3$, 250 MHz): δ 3.68 – 3.96 (m, 4 H, $C\underline{H_2}$-O, $C\underline{H_2}$-OH), 1.85 – 1.99, (m, 4 H,$C\underline{H_2})_2$ CH_2O), 1.48 – 1.53 (m, 2 H, $C\underline{H_2}$), 0.91 – 1.00 (m, 3 H, $C\underline{H_3}$)

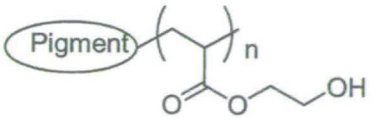


Figure 8.5: Pigment modified using pHEA

pHEA-PB15:3

^{1}H-NMR ($CDCl_3$, 250 MHz): δ 4.10 – 4.18 (m, 2 H, C<u>H</u>$_2$-O), 3.72 – 3.82 (m, 2 H, C<u>H</u>$_2$-OH), 1.73 – 1.82 (m, 1 H, C<u>H</u>), 0.79 -0.83 (m, 2 H, C<u>H</u>$_2$)

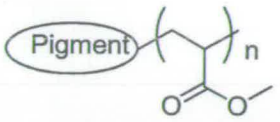


Figure 8.6: Pigment modified using poly(methylacrylate)

pMethylacrylate-PR122

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 3.61 (brs, 3 H, C<u>H</u>$_3$), 1.87 – 1.88 (m, 1 H, C<u>H</u>), 1.63 (m, 2 H, C<u>H</u>$_2$)

pMethylacrylate-PB15:3

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 3.65 (brs, 3 H, C<u>H</u>$_3$-O), 1.92 (m, 1 H, C<u>H</u>), 1.67 (m, 2 H, C<u>H</u>$_2$)

pMethylacrylate-PY155

^{1}H-NMR ($CDCl_3$, 250 MHz): δ 3.63 (brs, 3 H, C<u>H</u>$_3$), 2.24 – 2.44 (m, 1 H, C<u>H</u>), 1.65 – 1.93 (m, 2 H, C<u>H</u>$_2$)

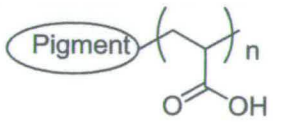


Figure 8.7: Pigment modified using poly(methacrylic acid)

pMethacrylic acid-CB

^{1}H-NMR ($CDCl_3$, 250 MHz): δ1.45 -1.56 (brs, 2 H, C<u>H</u>$_2$), 1.19 (brs, 1 H, C<u>H</u>)

pMethacrylic acid-PB15:3

^{1}H-NMR ($CDCl_3$, 250 MHz): δ1.82 -1.91 (m, 2 H, C<u>H</u>$_2$), 1.47 – 1.62 (m, 1 H, C<u>H</u>)

pMethacrylic acid-PY155

^{1}H-NMR ($CDCl_3$, 250 MHz): δ 1.59 – 1.62 (brs, 2 H, C<u>H</u>$_2$), 1.22 (brs, 1 H, C<u>H</u>)

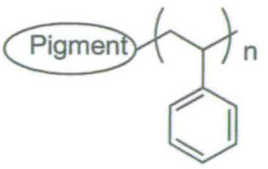


Figure 8.8: Pigment modified using polystyrene

polystyrene-PR122

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.04 – 7.10 (m, 3 H, Ar-*o*H, Ar-*p*H), 6.48 – 6.68 (m, 2 H, Ar-*m*H), 1.75 – 1.85 (m, 1 H, CH), 1.41 – 1.47 (m, 2 H, CH_2)

polystyrene-CB

^{1}H-NMR ($CDCl_3$, 250 MHz): δ 7.29 – 7.33 (m, 3 H, Ar-*o*H, Ar-*p*H), 6.69 – 6.918 (m, 2 H, Ar-*m*H), 2.20 – 2.15 (m, 1 H, CH), 1.62 – 1.68 (m, 2 H, CH_2)

polystyrene-PY155

^{1}H-NMR ($CDCl_3$, 250 MHz): δ 6.91 – 7.10 (m, 3 H, Ar-H), 6.46 – 6.59 (m, 2 H, Ar-H), 1.33 – 1.48 (m, 1 H, CH), 1.22 – 1.24 (m, 2 H, CH_2)

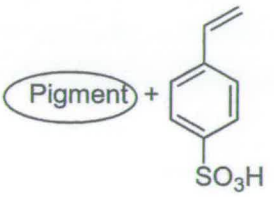


Figure 8.9: Pigment modified using 4-styrenesulfonic acid as monomer

4-Styrenesulfonic acid mixed with PR122

^{1}H-NMR (D_2O, 250 MHz): δ 7.60 – 7.72 (m, 4H, Ar-H), 6.75 – 6.86 (dd, 1 H, J = 10 Hz, J = 17 Hz, CH), 5.89 – 5.95 (d, 1 H, J = 18 Hz, CH-H), 5.37 – 5.41 (d, 1 H, J = 11 Hz, CH-H)

4-Styrenesulfonic acid mixed with CB

^{1}H-NMR (D_2O, 250 MHz): δ 7.55 – 7.73 (m, 4H, Ar-H), 6.73 – 6.84 (dd, 1 H, J = 11 Hz, J = 17 Hz, CH), 5.86 – 5.93 (d, 1 H, J = 17 Hz, CH-H), 5.35 – 5.39 (d, 1 H, J = 10 Hz, CH-H)

4-Styrenesulfonic acid mixed with PB15:3

^{1}H-NMR (D_2O, 250 MHz): δ 7.57 – 7.76 (m, 4H, Ar-H), 6.73 – 6.87 (m, 1 H, CH), 5.86 – 5.98 (m, 1 H, CH-H), 5.35 – 5.43 (m, 1 H, CH-H)

4-Styrenesulfonic acid mixed with PY155

^{1}H-NMR (D_2O, 250 MHz): δ 7.73 – 7.55 (m, 4H, Ar-H), 6.73 – 6.84 (dd, 1 H, J = 10 Hz, J = 17 Hz, CH), 5.93 – 5.94 (d, 1 H, J = 18 Hz, CH-H), 5.35 – 5.39 (d, 1 H, J = 11 Hz, CH-H)

8.3.1.3 IR analyses

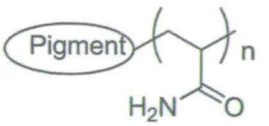


Figure 8.10: Pigment modified using poly(acrylamide)

Poly(acrylamide)-PR122: IR (neat): υ_{max}: 3184 (N-H), 1650 (N-C=O) cm^{-1}

Poly(acrylamide)-CB: IR (neat): υ_{max}: 3184 (N-H), 1650 (N-C=O) cm^{-1}

Poly(acrylamide)-PB15:3: IR (neat): υ_{max}: 3184 (N-H), 1650 (N-C=O) cm^{-1}

Poly(acrylamide)-PY155: IR (neat): υ_{max}: 3185 (N-H), 1659 (N-C=O) cm^{-1}

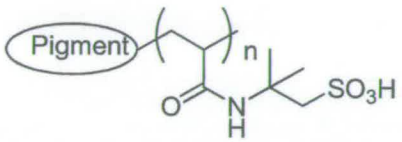


Figure 8.11: Pigment modified using poly(2-Acrylamido-2-methylpropane sulfonic acid)

poly(2-Acrylamido-2-methylpropane sulfonic acid)-PR122: IR (neat): υ_{max}: 1725 (C=O), 1215 (C-N) cm^{-1}

poly(2-Acrylamido-2-methylpropane sulfonic acid)-PB15:3: IR (neat): υ_{max}: 1725 (C=O), 1288 (C-N) cm^{-1}

poly(2-Acrylamido-2-methylpropane sulfonic acid)-PY155: IR (neat): υ_{max}: 3053 (N-H), 1732 (C=O), 1265 (C-N) cm^{-1}

p(HBA)-PR122: IR (neat): υ_{max}: 3053 (OH), 1732 (C=O) cm^{-1}

p(HBA)-CB: IR (neat): υ_{max}: 3154 (OH), 1732 (C=O) cm^{-1}

p(HBMA)-CB: IR (neat): υ_{max}: 3380 (OH), 1712 (C=O), 1155 (C-O) cm^{-1}

p(HEA)-PY155: IR (neat): υ_{max}: 3054 (OH), 1731 (C=O), 1263 (C-OH), 1165 (C-O) cm^{-1}

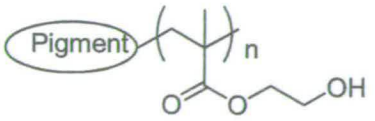


Figure 8.12: Pigment modified using poly(HEMA)

p(HEMA)-PR122: IR (neat): υ_{max}: 3053 (OH), 1732 (C=O) cm^{-1}

p(HEMA)-CB: IR (neat): υ_{max}: 3053 (OH), 1732 (C=O)cm^{-1}

p(HEMA)-PB15:3: IR (neat): υ_{max}: 3393 (OH), 1720 (C=O), 1153 (C-O) cm^{-1}

p(HEMA)-PY155: IR (neat): υ_{max}: 3193 (OH), 1727 (C=O), 1184 (C-O) cm^{-1}

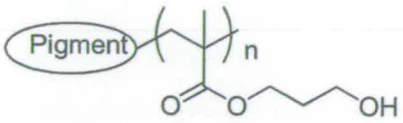


Figure 8.13: Pigment modified using poly(HPMA)

p(HPMA)-PR122: IR (neat): υ_{max}: 3053 (OH), 1732 (C=O) cm^{-1}

p(HPMA)-PB15:3: IR (neat): υ_{max}: 3393 (OH), 1731 (C=O), 1164 (C-O) cm^{-1}

p(HPMA)-PY155: IR (neat): υ_{max}: 1732 (C=O), 1183 (C-O) cm^{-1}

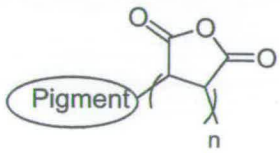


Figure 8.14: Pigment modified using p(maleic anhydride)

p(maleic anhydride)-PR122: IR (neat): υ_{max}: 1732 (C=O) cm^{-1}

p(maleic anhydride)-PB15:3: IR (neat): υ_{max}: 1736 (C=O) cm^{-1}

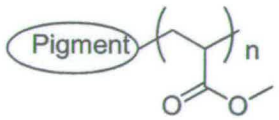


Figure 8.15: Pigment modified using p(methyl acrylate)

p(methyl acrylate)-CB: IR (neat): υ_{max}: 1655 (C=O), 1159 (C-O) cm^{-1}

polystyrene-PB15:3: IR (neat): υ_{max}: 907, 730, 650 (aromatic mono-substituted) cm^{-1}

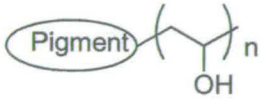


Figure 8.16: Pigment modified using polyvinyl alcohol

polyvinyl alcohol-PR122: IR (neat): υ_{max}: 3053 (OH), 1170 (CH-O) cm^{-1}

polyvinyl alcohol-CB: IR (neat): υ_{max}: 3053 (OH), 1157 (CH-O) cm^{-1}

polyvinyl alcohol-PB153: IR (neat): υ_{max}: 3053 (OH), 1157 (CH-O) cm^{-1}

polyvinyl alcohol-PY155: IR (neat): υ_{max}: 3053 (OH), 1157 (CH-O) cm^{-1}

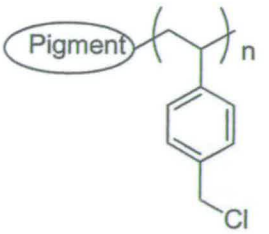


Figure 8.17: Pigment modified using pVBC

pVBC-PR122: IR (neat): υ_{max}: 724 (C-Cl) cm^{-1}

pVBC-CB: IR (neat): υ_{max}: 746 (C-Cl) cm^{-1}

pVBC-PB15:3: IR (neat): υ_{max}: 720 (C-Cl) cm^{-1}

pVBC-PY155: IR (neat): υ_{max}: 722 (C-Cl) cm^{-1}

8.3.2 Copolymerisation

Thirteen samples of activated pigment red 122 were treated with two monomers (1:1 ratio), suspended in DMF (3 mL) and degassed for 2 h using oxygen free nitrogen. The mixtures were heated for 21 h at 120 °C and treated as described in 8.2.3.1.

[monomer] = 25 % vol/vol

Table 8.13: Copolymerization on PR122

Entry	$m_{activated\ pigment}$ (mg)	Monomers A	Monomers B	$M_{A/B}$ (M)	Graft weight (%)
1	27	Styrene	DMAA	1.5/1.6	2800
2	27	Styrene	MMA	1.5/1.6	2880
3	25	HPMA	DMAA	1.4/1.5	5100
4	25	HPMA	MMA	1.4/1.4	1940
5	23	HPMA	EMA	1.2/1.4	1500
6	20	HPMA	BMA	1.2/1.1	950
7	24	HBMA	DMAA	1.1/1.5	1990
8	24	HBMA	MMA	1.1/1.4	250
9	22	HBMA	EMA	1.1/1.2	1230
10	20	HBMA	BMA	1.1/1.1	950
11	27	HEMA	DMAA	1.6/1.5	4000
12	24	HEMA	EMA	1.4/1.4	272
13	21	HEMA	BMA	1.2/1.2	1090

None of the modified pigments were soluble enough to get clear ^{1}H NMR data therefore IR was used to check the presence of copolymers on the pigments. **IR (neat): (1)** υ_{max}: 3053 (ArC-H), 1636 (C=O) cm^{-1}; **(2)** υ_{max}: 3054 (ArC-H), 1726 (C=O) cm^{-1}; **(3)** υ_{max}: 1721 (C=O), 1632 (C=O) cm^{-1}; **(4)** υ_{max}: 1726 (C=O) cm^{-1}; **(5)** υ_{max}: 1725 (C=O) cm^{-1}; **(6)** υ_{max}: 1725 (C=O) cm^{-1}; **(7)** υ_{max}: 1721 (C=O), 1625 (C=O) cm^{-1}; **(8)** υ_{max}: 1726 (C=O) cm^{-1}; **(9)** υ_{max}: 1730 (C=O) cm^{-1}; **(10)** υ_{max}: 1725 (C=O) cm^{-1}; **(13)** υ_{max}: 1725 (C=O) cm^{-1}.

Nine samples of activated carbon black (36 mg each) were treated with four monomers having different ratios, suspended in DMF (3 mL) and degassed for 2 h using oxygen free nitrogen. The mixtures were heated for 21 h at 120 °C and treated as described in 8.2.3.1.

Table 8.14: Copolymerization on CB

Entry	$m_{Carbon\ Black}$ (mg)	$M_{styrene}$ (mol)	Ratio (mol. %) MMA/EMA/BMA	Graft weight (%)
1	36	2.2	20/0/0	1666
2	36	2.2	50/0/0	2222
3	36	2.2	100/0/0	2722
4	36	2.2	0/0/0	4000
5	36	2.2	0/50/0	2566
6	36	2.2	0/100/0	2370
7	36	2.2	0/0/0	4010
8	36	2.2	0/0/50	2848
9	36	2.2	0/0/100	2222

IR (neat): **(1)** υ_{max}: 3053 (ArC-H), 1725 (C=O) cm^{-1}; **(2)** υ_{max}: 3053 (ArC-H), 1725 (C=O) cm^{-1}; **(3)** υ_{max}: 3054 (ArC-H), 1726 (C=O) cm^{-1}; **(4)** υ_{max}: 3053 (ArC-H) cm^{-1}; **(5)** υ_{max}: 3053 (ArC-H), 1718 (C=O) cm^{-1}; **(6)** υ_{max}: 3053 (ArC-H), 1719 (C=O) cm^{-1}; **(7)** υ_{max}: 3053 (ArC-H) cm^{-1}; **(8)** υ_{max}: 3054 (ArC-H), 1717 (C=O) cm^{-1}; **(9)** υ_{max}: 3053 (ArC-H), 1717 (C=O) cm^{-1}.

Fourteen samples of activated pigments were treated with two monomers in different ratios, suspended in DMF (3 mL) and degassed for 2 h using oxygen free nitrogen. The mixtures were heated for 21 h at 120 °C and treated as described in 8.2.3.1.

Table 8.15: Copolymerization using DMAA/MAA

Entry	Pigment	Activated pigment (mg)	Ratio (mol. %) MAA/DMAA	Grafting (%)
1	PR122	30.8	0/100	3643
2	PR122	31.6	10/90	580
3	PR122	31.4	50/50	138
4	PB15:3	30.6	0/100	3645
5	PB15:3	31.9	10/90	3
6	PB15:3	31.9	50/50	0.3
7	PY155	31.6	0/100	642
8	PY155	30.6	10/90	164
9	PY155	30.7	50/50	121
10	PY155	31.1	100/0	535
11	CB	31.8	0/100	4526
12	CB	31.8	10/90	1452
13	CB	31.2	50/50	215
14	CB	31.3	100/0	157

IR (neat): (1) υ_{max}: 1667 (C=O), 1627 (C=O) cm^{-1}; **(2)** υ_{max}: 1673 (C=O) cm^{-1}; **(3)** υ_{max}: 1603 (C=O) cm^{-1}; **(4)** υ_{max}: 1674 (C=O), 1641 (C=O) cm^{-1}; **(5)** υ_{max}: 1604 (C=O) cm^{-1}; **(6)** υ_{max}: 1604 (C=O) cm^{-1}; **(7)** υ_{max}: 1604 (C=O) cm^{-1}; **(8)** υ_{max}: 1672 (C=O), 1642 (C=O) cm^{-1}; **(9)** υ_{max}: 1731 (C=O), 1674 (C=O), 1642 (C=O) cm^{-1}; **(10)** υ_{max}: 1674 (C=O) cm^{-1}; **(11)** υ_{max}: 1673 (C=O), 1642 (C=O) cm^{-1}; **(12)** υ_{max}: 1638 (C=O) cm^{-1}.

8.3.3 Cross-linking

Protocol A: Activated pigments were treated with a specific monomer (1 mL) and the corresponding cross-linker in different quantities (from 0.005 to 0.5 moles), suspended in DMF (3mL) and degassed for 2 h using oxygen free nitrogen. The mixtures were heated for 21 h at 120 °C and treated as described in 8.2.3.1.

Protocol B: Activated pigments were treated with a specific monomer (1 mL), suspended in DMF (3 mL) and degassed for 2 h using oxygen free nitrogen. The mixtures were heated for 5 h, then the corresponding cross-linker was added, in the same quantity than used in protocol A, and the mixtures heated at 120 °C overnight and treated as described in 8.2.3.1.

Protocol C: Activated pigments were treated with a specific amount of cross-linker, suspended in DMF (3 mL) and degassed for 2 h using oxygen free nitrogen. The mixtures were heated for 5 h, then the corresponding monomer (1 mL) was added and the mixtures heated at 120 °C overnight and treated as described in 8.2.3.1.

Experiments on pigment red 122

For each reaction, activated pigment red 122 (36 mg) was modified using DMAA (1 mL) as a monomer and EGDMA as a cross linker.

Entry	Method	Ratio EGDMA/ DMAA	Graft weight %
1	A	0.1 mol %	1355
2	A	0.2 mol %	4116
3	A	0.3 mol %	4761
4	A	0.4 mol %	5316
5	A	0.5 mol %	7400
6	B	0.005 mol %	2522
7	B	0.02 mol %	2733
8	B	0.05 mol %	4642
9	B	0.2 mol %	3455
10	B	0.5 mol %	4678
11	C	0.005 mol %	2094
12	C	0.02 mol %	2516
13	C	0.05 mol %	4066
14	C	0.2 mol %	4344
15	C	0.5 mol %	6233

IR (neat): (1) υ_{max}: 3165 – 3267 ($N(CH_3)_2$),1722 (C=O), 1625 (C=C) cm^{-1}; **(3)** υ_{max}: 1725 (C=O), 1627 (C=C) cm^{-1}; **(4)** υ_{max}: 1724 (C=O), 1631 (C=C) cm^{-1}; **(5)** υ_{max}: 1723 (C=O), 1637 (C=C) cm^{-1}; **(6)** υ_{max}: 3471 ($N(CH_3)_2$), 1619 (C=C) cm^{-1}; **(7)** υ_{max}: 3470 ($N(CH_3)_2$), 1624 (C=C) cm^{-1}; **(8)** υ_{max}: 1673 (C=C) cm^{-1}; **(9)** υ_{max}: 1737 (C=O), 1619 (C=C) cm^{-1}; **(10)** υ_{max}: 1737 (C=O), 1623 (C=C) cm^{-1}; **(1&)** υ_{max}: 3478 ($N(CH_3)_2$), 1624 (C=C) cm^{-1}; **(12)** υ_{max}: 3466 ($N(CH_3)_2$), 1626 (C=C) cm^{-1}; **(13)** υ_{max}: 1726 (C=O), 1631 (C=C) cm^{-1}; **(14)** υ_{max}: 1724 (C=O), 1630 (C=C) cm^{-1}; **(15)** υ_{max}: 1737 (C=C), 1677 (C=C) cm^{-1}.

Experiments on Carbon black

In each case, activated pigment carbon black (36 mg) was modified using styrene (1 mL) as monomer and DVB as a cross linker using protocol A.

Entry	Method	Ratio DVB/Styrene	Graft weight %
1	A	0 mol %	11
2	A	0.1 mol %	2650
3	A	0.3 mol %	3956
4	A	0.4 mol %	4150
5	A	0.6 mol %	5372
6	A	0.8 mol %	5456
7	B	0.0008 mol %	427
8	B	0.03 mol %	1355
9	B	0.08 mol %	3003
10	B	0.4 mol %	3419
11	B	0.8 mol %	2458
12	C	0.03 mol %	2050
13	C	0.08 mol %	2427
14	C	0.4 mol %	2797
15	C	0.8 mol %	4500

IR (neat): **(1)** υ_{max}: 2923 (ArC-H) cm^{-1}; **(2)** υ_{max}: 2923 (ArC-H), 1678 (C=C) cm^{-1}; **(3)** υ_{max}: 2921 (ArC-H), 1672 (C=C) cm^{-1}; **(3)** υ_{max}: 2923 (ArC-H), 1673 (C=C) cm^{-1}; **(4)** υ_{max}: 2922 (ArC-H), 1670 (C=C) cm^{-1}; **(5)** υ_{max}: 2922 (ArC-H), 1679 (C=C) cm^{-1}; **(6)** υ_{max}: 2920 (ArC-H), 1680 (C=C) cm^{-1}; **(7)** υ_{max}: 2920 (ArC-H), 1675 (C=C) cm^{-1}; **(8)** υ_{max}: 2928 (ArC-H), 1676 (C=C) cm^{-1}; **(9)** υ_{max}: 2920 (ArC-H), 1680 (C=C) cm^{-1}; **(10)** υ_{max}: 2920 (ArC-H), 1679 (C=C) cm^{-1};**(11)** υ_{max}: 2918 (ArC-H), 1677 (C=C) cm^{-1}; **(12)** υ_{max}: 2917 (ArC-H), 1679 (C=C) cm^{-1}; **(13)** υ_{max}: 2921 (ArC-H), 1680 (C=C) cm^{-1}; **(14)** υ_{max}: 2923 (ArC-H), 1682 (C=C) cm^{-1}.

Experiments on the four pigments

Eight samples of activated pigments were treated with monomer (1 mL), suspended in DMF (3 mL) and degassed for 2 h using oxygen free nitrogen. The mixtures were heated for 2 h, then a specific amount of cross-linker was added and the mixtures heated at 120 °C and treated as described in 8.2.3.1.

Table 8.16: Cross-linking

Activated Pigment	$m_{activated\ pigment}$ (mg)	Monomers	CL	Ratio (mol %) CL/Monomer	Graft weight %
PR122	21	DMAA	EGDMA	0.001	1168
PR122	21	St	DVB	0.001	332
PY155	21	DMAA	EGDMA	0.001	1275
PY155	21	St	DVB	0.001	305
PB15:3	21	DMAA	EGDMA	0.001	5191
PB15:3	21	St	DVB	0.001	345
CB	21	DMAA	EGDMA	0.001	1497
CB	20	St	DVB	0.001	662

IR (neat): (1) υ_{max}: 3491 ($N(CH_3)_2$), 1633 (C=C) cm^{-1}; **(2)** υ_{max}: 1605 cm^{-1}; **(3)** υ_{max}: 3465 ($N(CH_3)_2$), 1714 (C=O), 1635 (C=C) cm^{-1}; **(4)** υ_{max}: 1636 (C=C) cm^{-1}; **(5)** υ_{max}: 3465 ($N(CH_3)_2$), 1640 (C=C) cm^{-1}; **(6)** υ_{max}: (ArC-H) cm^{-1}; **(7)** υ_{max}: 1640 (C=C) cm^{-1}; **(8)** υ_{max}: 3053 (ArC-H) cm^{-1}.

8.3.4 Esterification

8.3.4.1 General procedure for esterification

Grafted pigments (pHEMA-PR122, pHBA-PR122, pHEA-PR122, pHBA-PB15:3, pHEA-PB15:3, pHEA-PY155) were dissolved in dry THF (10 or 12 mL) then sonicated. Triethylamine (9,3 mmol, 2 eq or 1,14 mmol, 2,5 eq) was added to the mixtures followed by either 10-undecenoyl chloride (1 mL), acryloyl chloride (1 mL) or 4-bromobenzoyl chloride (37.4 mg). 4-Dimethylaminopyridine (DMAP, 2,3 mmol, 0,5 eq or 4,6 mmol, 1 eq) was added and the mixtures were sonicated. The solutions were stirred at room temperature for 4 or 20 h. Methanol (10 mL) was added drop wise to quench the reactions. The solutions were centrifuged and the solids dried under vacuum to constant weight.

Table 8.17: Esterification conditions

Entry	Grafted pigment (mg)	Acid used	Et_3N (mL)	DMAP (g)	THF (mL)	Reaction Time (h)	m_{final} (mg)
1	pHEMA-PR122 29	10-undecenoyl chloride	1.3	0.28	10	4	79
2	pHEMA-PR122 29.1	acryloyl chloride	1.3	0.28	10	4	28
3	pHBA-PR122 30.9	10-undecenoyl chloride	1.3	0.28	10	20	33
4	pHEA-PR122 19.5	10-undecenoyl chloride	1.3	0.28	10	20	26
5	pHBA-PB15:3 32.8	10-undecenoyl chloride	1.3	0.28	10	20	15
6	pHEA-PB15:3 35.5	10-undecenoyl chloride	1.3	0.28	10	20	14
7	pHEA-PY155 37.9	10-undecenoyl chloride	1.3	0.28	10	20	44
8	pHBA-PR122 67.8	4-bromobenzoyl chloride	1.6	0.56	12	20	79

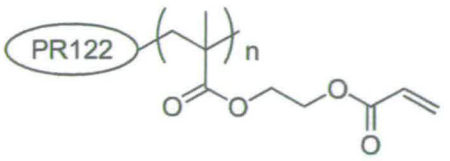


Figure 8.18: esterified pHEMA-PR122 using ACC

2- **IR (neat):** υ_{max}: 1717 (C=O) cm^{-1}.

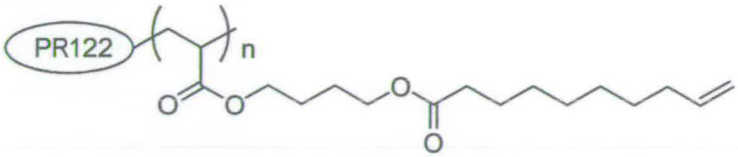


Figure 8.19: esterified pHBA-PR122 using UDC

3- pHBA grafted on pigment red 122: **^{1}H-NMR** ($CDCl_3$, 250 MHz): δ 5.69 – 5.81. (m, 1 H, C<u>H</u>=CH_2), 4.87 - 4.99 (m, 2 H, C<u>H_2</u>=CH), 3.97 - 4.08 (m, 4 H, OC<u>H_2</u>CH_2CH_2C<u>H_2</u>O), 2.21 – 2.28 (m, 2 H, C<u>H_2</u>-CO), 1.95 – 2.02 (m, 2 H, C<u>H_2</u>-CH), 1.57 – 1.66 (m, 5 H, C<u>H</u> and C<u>H_2</u>-CH_2OCO), 1.26 – 1.29 (m, 12 H, C<u>H_2</u> and $(C\underline{H_2})_5$-CH_2). **IR (neat):** υ_{max}: 1731 (C=O), 1646 (C=C) cm^{-1}.

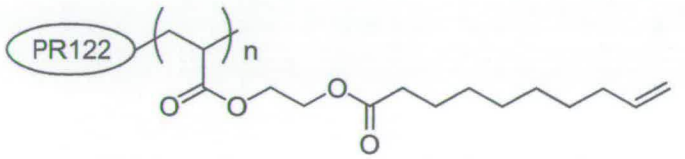


Figure 8.20: esterified pHEA-PR122 using UDC

4- pHEA grafted on pigment red 122: **^{1}H-NMR** ($CDCl_3$, 250 MHz): δ 5.74 – 5.85 (m, 1 H, C<u>H</u>=CH_2), 4.89 – 5.02 (m, 2 H, C<u>H_2</u>=CH), 4.20 – 4.26 (m, 4 H, OC<u>H_2</u>CH_2CH_2C<u>H_2</u>O), 2.27 – 2.33 (m, 2 H, C<u>H_2</u>-CO), 1.99 – 2.04 (m, 2 H, C<u>H_2</u>-CH), 1.55 – 1.64 (m, 3 H, C<u>H</u> and C<u>H_2</u>-CH_2CO), 1.29 – 1.36 (m, 10 H, C<u>H_2</u> and CH2$(C\underline{H_2})_4$-CH_2). **IR (neat):** υ_{max}: 1737 (C=O) cm^{-1}.

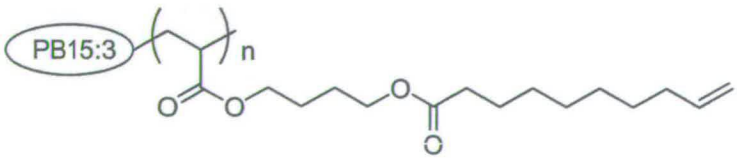


Figure 8.21: Esterified pHBA-PB15:3 using UDC

5- pHBA grafted on pigment blue 15:3: **^{1}H-NMR** ($CDCl_3$, 250 MHz): δ 5.65 – 5.82 (m, 1 H, C<u>H</u>=CH_2), 4.82 – 5.04 (m, 2 H, C<u>H_2</u>=CH), 4.04 – 3.94 (m, 4 H, OC<u>H_2</u>CH_2CH_2C<u>H_2</u>O), 2.18 – 2.22 (m, 2 H, C<u>H_2</u>-CO), 1.94 – 1.98 (m, 2 H, C<u>H_2</u>-CH), 1.56 – 1.61 (m, 5 H, C<u>H</u> and C<u>H_2</u>-CH_2OCO), 1.15 – 1.27 (m, 12 H, C<u>H_2</u> and $(C\underline{H_2})_5$-CH_2). **IR (neat):** υ_{max}: 1674 (C=O) cm^{-1}.

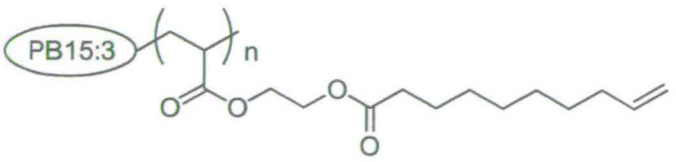


Figure 8.22: Esterified pHEA-PB15:3 using UDC

6- pHEA grafted on pigment blue 15:3: **^{1}H-NMR** ($CDCl_3$, 250 MHz): δ 5.61 – 5.84 (m, 1 H, C<u>H</u>=CH_2), 4.84 - 4.96 (m, 2 H, C<u>H_2</u>=CH), 4.13 – 4.20 (m, 4 H, OC<u>H_2</u>CH_2CH_2C<u>H_2</u>O), 2.22 – 2.29 (m, 2 H, C<u>H_2</u>-CO), 1.93 – 1.98 (m, 2 H, C<u>H_2</u>-CH), 1.51 – 1.59 (m, 3 H, C<u>H</u> and C<u>H_2</u>-CH_2CO), 1.16 – 1.31 (m, 10 H, C<u>H_2</u> and (C<u>H_2</u>)$_4$-CH_2). **IR (neat):** υ_{max}: 1674 (C=O) cm^{-1}.

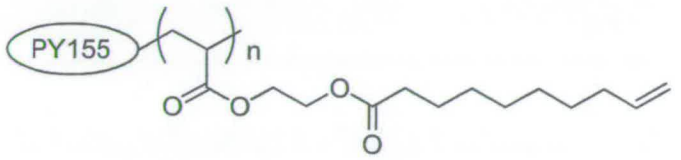


Figure 8.23: Esterified pHEA-PY155 using UDC

7- pHEA grafted on pigment yellow155: **^{1}H-NMR** ($CDCl_3$, 250 MHz): δ 5.72 – 5.83 (m, 1 H, C<u>H</u>=CH_2), 4.87 - 4.99 (m, 2 H, C<u>H_2</u>=CH), 4.17 – 4.21 (m, 4 H, OC<u>H_2</u>CH_2CH_2C<u>H_2</u>O), 2.23 – 2.31 (m, 2 H, C<u>H_2</u>-CO), 1.96 – 2.02 (m, 2 H, C<u>H_2</u>-CH), 1.47 – 1.58 (m, 3 H, C<u>H</u> and C<u>H_2</u>-CH_2CO), 1.14 – 1.32 (m, 10 H, C<u>H_2</u> and (C<u>H_2</u>)$_4$-CH_2). **IR (neat):** υ_{max}: 1736 (C=O) cm^{-1}.

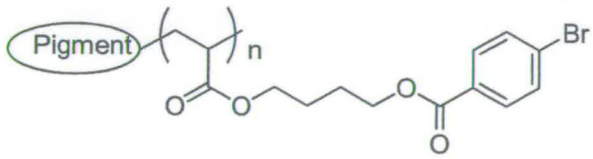


Figure 8.24: Esterified pHBA-PR122 using BBC

8- pHBA grafted on pigment red 122: **^{1}H-NMR** ($CDCl_3$, 250 MHz): δ 7.79 – 7.83 (m, 2 H, C<u>H</u>*o*), 7.48 – 7.55 (m, 2 H, C<u>H</u>*m*), 4.25 – 4.30 (m, 2 H, C<u>H_2</u>-OCO), 4.02 – 4.08 (m, 2 H, C<u>H_2</u>-OCO), 1.71 – 1.93 (m, 7 H, C<u>H</u> and C<u>H_2</u>). Excess of acid chloride was observed on the spectra due to the following signals: 7.94 – 7.97 (d, 2 H, J = 8 Hz, C<u>H</u>*o*), 7.55 – 7.59 (d, 2 H, J = 11 Hz, C<u>H</u>*m*), and the signals: 8.29 – 8.32 (d, 2 H, J = 7 Hz, C<u>H</u>*o*), 6.57 – 6.69 (d, 2 H, J = 7 Hz, C<u>H</u>*m*) indicated formation of a by-product. **IR (neat):** υ_{max}: 3053 (ArC-H), 1719 (C=O) cm^{-1}.

8.4 Experimental to Chapter 5

Eleven samples of activated pigment red 122 and twelve samples of activated pigment blue 15:3 were treated with DMAA (2.4 M), suspended in DMF (3 mL) and degassed for 2 h using oxygen free nitrogen. The mixtures were heated for 21 h at 120 °C and treated as described in 8.2.3.1.

Table 8.18: Homopolymerisation using DMAA as monomer

Entry	Pigment	$m_{activated\ pigment}$ (mg)	Type of Plasma	Activation Time (s)	Graft weight %
1	PR122	12	O_2	500	7675
2	PR122	12.1	O_2	500	7783
3	PR122	11.9	O_2	1000	7832
4	PR122	12.5	O_2	1000	8284
5	PR122	12.4	O_2	2000	7214
6	PR122	12.1	O_2	2000	7916
7	PB15:3	12.2	O_2	500	/
8	PB15:3	12.8	O_2	500	/
9	PB15:3	12.7	O_2	1000	/
10	PB15:3	13	O_2	1000	/
11	PB15:3	12.5	O_2	2000	/
12	PB15:3	12.6	O_2	2000	/
13	PR122	20.6	N_2	500	5914
14	PR122	20.8	N_2	500	5025
15	PR122	20.1	N_2	1000	4944
16	PR122	20.5	N_2	1000	5846
17	PR122	20.1	N_2	2000	6477
18	PB15:3	19.8	N_2	500	5046
19	PB15:3	20.1	N_2	500	6312
20	PB15:3	20.2	N_2	1000	5612
21	PB15:3	20.3	N_2	1000	6320
22	PB15:3	20.6	N_2	2000	6225
23	PB15:3	20.7	N_2	2000	4816

^{1}H NMR spectra were obtained for every modified PR122 in $CDCl_3$ and compared to the ^{1}H NMR spectra of pDMAA standard to check the presence of grafting. IR spectra were obtained for every modified PB15:3 and gave the same results. One example is given: **IR (neat): (18)** υ_{max}: 2931 ($N(CH_3)_2$), 1638 (C=O) cm^{-1}.

Eleven samples of activated pigment red 122 and eleven samples of activated pigment blue 15:3 were treated with Styrene (2.2 M), suspended in DMF (3 mL) and degassed for 2 h using oxygen free nitrogen. The mixtures were heated for 21 h at 120 °C and treated as described in 8.2.3.1.

Table 8.19: Homopolymerisation using Styrene as monomer

Entry	Pigment	$m_{activated\ pigment}$ (mg)	Type of Plasma	Activation Time (s)	Graft weight %
1	PR122	20.7	O_2	500	127
2	PR122	20.7	O_2	500	102
3	PR122	20.1	O_2	1000	1
4	PR122	19.9	O_2	1000	156
5	PR122	20.5	O_2	2000	129
6	PR122	20.5	O_2	2000	130
7	PB15:3	19.8	O_2	500	142
8	PB15:3	20	O_2	500	160
9	PB15:3	20.2	O_2	1000	103
10	PB15:3	20	O_2	1000	130
11	PB15:3	20.5	O_2	2000	124
12	PB15:3	20.5	O_2	2000	124
13	PR122	20.1	N_2	500	103
14	PR122	20.5	N_2	500	104
15	PR122	19.7	N_2	1000	142
16	PR122	19.6	N_2	1000	155
17	PR122	21.7	N_2	2000	130
18	PB15:3	19.8	N_2	500	394
19	PB15:3	19.5	N_2	500	365
20	PB15:3	19.8	N_2	1000	327
21	PB15:3	19.7	N_2	1000	392
22	PB15:3	20.2	N_2	2000	385

^{1}H NMR analysis of all compounds soluble in $CDCl_3$ was carried out. Modified pigment blue were not soluble enough in $CDCl_3$ and other NMR solvents for good NMR analysis.

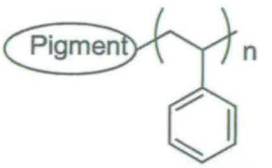


Figure 8.25: polystyrene grafted onto pigment

(2) ^{1}H-NMR ($CDCl_3$, 250 MHz): δ 7.16 – 7.24 (m, 3 H, Ar-*o*H, Ar-*p*H), 6.76 – 6.58 (m, 2 H, Ar-*m*H), 1.72 – 1.66 (m, 3 H, CH, CH_2), **(3) ^{1}H-NMR** ($CDCl_3$, 250 MHz): δ 7.09 – 6.97 (m, 3 H, Ar-*o*H, Ar-*p*H), 6.59 – 6.42 (m, 2 H, Ar-*m*H), 1.57 – 1.50 (m, 3 H, CH, CH_2), **(4) ^{1}H-NMR** ($CDCl_3$, 250 MHz): δ 7.09 – 6.99 (m, 3 H, Ar-*o*H, Ar-*p*H), 6.61 – 6.43 (m, 2 H, Ar-*m*H), 1.55 – 1.53 (m, 3 H, CH, CH_2), **(5) ^{1}H-NMR** ($CDCl_3$, 250 MHz): δ 7.09 – 6.97 (m, 3 H, Ar-*o*H, Ar-*p*H), 6.59 – 6.51 (m, 2 H, Ar-*m*H), 1.56 – 1.50 (m, 3 H, CH, CH_2), **(6) ^{1}H-NMR** ($CDCl_3$, 250 MHz): δ 7.10 – 7.01 (m, 3 H, Ar-*o*H, Ar-*p*H), 6.62 – 6.47 (m, 2 H, Ar-*m*H), 1.91 – 1.70 (m, 1 H, CH), 1.58 – 1.51 (m, 2H, CH_2), (17) **^{1}H-NMR** ($CDCl_3$, 250 MHz): δ 7.10 – 7.02 (m, 3 H, Ar-*o*H, Ar-*p*H), 6.61 – 6.44 (m, 2 H, Ar-*m*H), 1.95 – 1.77 (m, 1 H, CH), 1.55 – 1.40 (m, 2H, CH_2).

IR spectra were obtained for every modified PB15:3 and showed the same peak which confirmed the grafting of polystyrene onto pigments: **IR (neat): (7)** υ_{max}: 3154 (ArC-H) cm^{-1}.

8.5 Experimental to Chapter 6

8.5.1 Stock solution preparations

Stock solutions of 1,2-hexanediol, polyethylene glycol (PEG 400 MW), 2-pyrrolidinone and surfynol were prepared in order that their density approached the density of water (Table 8.20).

Table 8.20: Stock solutions preparations

	1,2-hexanediol	PEG (400 MW)	PEG (10,000 MW)	2-pyrrolidinone	Surfynol
C (g/l)	48.82	103.6	80	385	100
d (g/mL)	0.9974	0.938	1.010	1.049	1.005
T (°C)	21.77	22.27	20.00	22.00	20.00

8.5.2 Preparation of the ink

A standard formulation (100 mL) was prepared by mixing pyrrolidinone (50 mL), PEG 10,000 (20 mL), 1,2-hexanediol (2 mL), surfynol 465 (10 mL) and water (18 mL) and sonicated for 3 hrs.

A first experiment was achieved to determine the optimal pigment concentration. Modified pigment red 122 (290 mg) was added to the formulation (10 ml) to obtain a saturated solution, which was sonicated for 2 hrs and then centrifugated for 2 min. The top layer of the solution (4 mL) was added to the cartridge and a print was tried but was not successful. A second printing was attempted using modified pigment red 122 (29, 50 and 100 mg) dispersed in the standard formulation (10 mL). The solutions were sonicated for 1 h. Only the solution containing 29 mg of pigment was well dispersed and put into the cartridge to give a successful print.

Every ink tested on the Canon S450 printer was made using the standard formulation (20 ml) and a pigment concentration of 29 mg/mL.

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ANNEX

Comparison between the developed ink formulations and Canon ink formulations

Page 1: pDMAA-PR122 (Graft weight = 485 %) vs Canon magenta ink.

Page 2: pDMAA-PB15:3 (Graft weight = 952 %) vs Canon cyan ink.

Page 3: pDMAA-PY155 (Graft weight = 355 %) vs Canon yellow formulation.

Page 4: pDMAA-CB (Graft weight = 300 %) vs Canon black formulation.

In each case, the top box was made by printing once the new ink formulation, the middle box was obtained after printing 4 times the new ink formulation and the last box was made by printing Canon formulation once.