

SYNTHESIS AND CHARACTERISATION OF PENTACOSA-10,12-DIYNOIC
ACID – POLY(STYRENE-BUTYL ACRYLATE) LATEX FOR GAMMA
RADIATION INDICATOR

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To my parent.... Who taught me that being strong and persevere are part of victory,

To my husband... Who has been the tower of my strength,

To Milo Shera and kids... Who filled my life with all the colourful dots.

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ABSTRACT

Pentacosanoic acid (PCDA) is one of the most highly used polymeric materials in radiation sensing applications. It is quintessential for its ability to indicate ionising radiation by colour transition. The PCDA monomer forms lipid vesicles in aqueous mediums that closely align themselves. This alignment enables polymerisation of the monomer upon irradiation. The polymerisation is visibly identified by the polymer colour transition from colourless to bluish-violet. However, the indication of radiation is hampered by the vesicle's instability and low colour reflectance from its transparent body. Therefore, an opaque polystyrene-butyl acrylate (PSBA) latex was fused into the transparent PCDA vesicles to promote the stability while simultaneously enhancing the colour reflectance. The PSBA was copolymerised using the radiation route to avoid the presence of unwanted chemical residues, especially from the initiator. The fusion of PCDA and PSBA was accomplished by the hydrophobic-hydrophobic interaction. The effect of ionic layers on the PSBA surface against the effectiveness of PCDA immobilisation was also investigated. The ionic layers from polyelectrolytes (PEL), namely, poly(sodium 4-styrenesulfonate) (PSS) and poly(diallyldimethyl-ammonium chloride) (PDADMAC), were applied layer-by-layer onto the PSBA surface for up to five layers prior to PCDA adsorption. The performance of all stable latexes (PCDA/PSBA-PEL_{0,1,3,5}) as radiation indicators was evaluated using gamma ray source from Cesium 137 (0.662 MeV) and Cobalt 60 (1.17 MeV). Colour transitions demonstrated by the latex were measured and reported as total colour difference (dE*). Results from the analysis confirm that PSBA-filled PCDA is responsive against gamma radiation from 1 to 50 kGy. The optimum colour transition response by irradiated samples compared to unirradiated samples is noted after 7 kGy of ¹³⁷Cs and 10 kGy of ⁶⁰Co. Moreover, the difference of colour measured for PSBA-filled PCDA is 50% higher than non-filled PCDA, suggesting that high colour reflectance was achieved by the presence of the opaque PSBA. All latex particles were stable during pre and post-irradiation up to 60 days of storage. Variation of colours was noted on the irradiated non-filled PCDA. However, the variation reduced with the presence of PSBA core inside PCDA envelope due to less available room between PCDA and PSBA, which usually allows for PCDA molecule relaxation.

ABSTRAK

Asid pentakosa-10,12-dainoik (PCDA) adalah merupakan satu bahan polimer yang kerap digunakan dalam aplikasi pengesanan sinaran. Ianya adalah bahan yang penting disebabkan oleh kebolehnya memberi petunjuk kepada sinaran mengion berdasarkan perubahan warna. Monomer PCDA ini membentuk vesikel lipid yang tersusun rapat di dalam medium akueus. Penyusunan ini membolehkan pempolimeran berlaku apabila monomer itu terdedah terhadap penyinaran. Pempolimeran dapat dikenalpasti secara tampak melalui perubahan warna bahan dari tiada warna kepada warna biru-ungu lembayung. Bagaimanapun, penunjukkan sinaran ini terhalang oleh faktor ketidakstabilan vesikel PCDA dan pembalikan warna yang rendah oleh badan lutcahaya tersebut. Oleh itu, lateks daripada bahan poli(stirena-butil akrilat) (PSBA) dimasukkan ke dalam vesikel PCDA untuk menambah kestabilan sambil menambah baik pantulan warna secara serentak. PSBA ini telah dihasilkan secara pengkopolimeran melalui kaedah sinaran bagi mengelakkan kehadiran sisa bahan kimia yang tidak diinginkan, khususnya dari bahan pemula. Percantuman PCDA dan PSBA telah disempurnakan melalui interaksi hidrofobik-hidrofobik. Kesan lapisan ion pada permukaan PSBA terhadap keberkesanan imobilisasi turut dikaji. Lapisan-lapisan ion daripada polielektrolit (PEL), iaitu poli(natrium 4-stirenasulfonat) (PSS) dan poli(dialildimetil-ammonium klorida) (PDADMAC), dikenakan secara berlapis-lapis di atas permukaan PSBA sehingga mencapai maksima 5 lapisan sebelum penjerapan PCDA. Prestasi kesemua lateks yang stabil (PCDA/PSBA-PEL_{0,1,3,5}) telah dinilai sebagai penunjuk sinaran dengan menggunakan sinaran gamma dari sumber Cesium 137 (0.662 MeV) dan Cobalt 60 (1.17 MeV). Peralihan warna yang ditunjukkan oleh lateks diukur dan dilaporkan sebagai jumlah perbezaan warna (dE^*). Hasil analisa mengesahkan bahawa PCDA terisi PSBA memberi tindakbalas terhadap sinaran gamma bermula 1 hingga 50 kGy. Tindakbalas peralihan warna yang optima bagi sampel yang disinari tersebut dikenalpasti sebaik sahaja mencecah 7 kGy bagi ¹³⁷Cs dan 10 kGy bagi ⁶⁰Co. Tambahan pula, perbezaan warna yang diukur bagi PCDA terisi PSBA adalah 50% lebih tinggi berbanding PCDA tanpa isi, mencadangkan bahawa pantulan warna yang tinggi telah dicapai dengan kehadiran PSBA yang legap. Kesemua partikel lateks stabil semasa pra dan selepas penyinaran sehingga 60 hari penyimpanan. Variasi warna dikenalpasti pada sampel PCDA tidak terisi yang disinari. Variasi ini bagaimanapun menyusut dengan kewujudan teras PSBA dalam sampul PCDA yang disebabkan oleh kurang ruang antara PCDA dan PSBA, di mana selalunya membolehkan perehatan molekul PCDA.

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LIST OF ABBREVIATIONS

ATR	-	attenuated total reflection
AuNP	-	gold nanoparticle
BuA or BA	-	butyl acrylate
CIE	-	Commission Internationale de l'Eclairage
CMC	-	critical micelle concentration
DHOTBT	-	bis (4-hexyl-2-thienyl)-2,1,3-benzothiadiazole
DHTBT	-	bis (4-hexyl-2-thienyl)-2,1,3-benzothiadiazole
DI	-	dionized water
DLS	-	Dynamic Light Scattering
DLVO	-	Derjaguin-Landau-Verwey-Overbeek
DSC	-	Differential Scanning Calorimetry
DTBT	-	di-2-thienyl-2,1,3 – benzothiadiazole
EBT	-	external beam therapy
EDC	-	ethylcarbodiimide
FESEM	-	field emission scanning electron microscopy
FTIR	-	Fourier Transform Infra-Red
GUV	-	giant unilamellar vesicles
HOMO	-	higher occupied molecular orbital
IEP	-	isoelectric point
IR	-	Infrared
LB	-	Langmuir-Blodgett
LbL	-	layer-by-layer
LED	-	light emitting diode
LiPCDA	-	lithium salt of pentacosanoic acid
LUMO	-	lower unoccupied molecular orbital
LUV	-	large unilamellar vesicles
MEH	-	2-méthoxy-5-(2-éthyl-hexyloxy)
MF	-	melamine formaldehyde
MLV	-	multilamellar vesicles
NMR	-	neutron magnetic resonance

OSL	-	optically stimulated luminescence
PA	-	polyacetylene
PANI	-	polyaniline
PCCS	-	photon cross-correlation spectroscopy
PCDA or PDA	-	pentacos-10,12-dienoic acid
PDA	-	polydiacetylene
PDADMAC	-	poly(diallyldimethyl-ammonium chloride
PDI	-	polydispersity index
PEL	-	polyelectrolyte
PF	-	polyfuran
PFO	-	poly(9,9-dioctyl fluorene)
PhV	-	polyheteroaromatic vinylene
PININE	-	poly(2,7-dihydroindeno[2,1-a]indene-co-4,7)
PMMA	-	polymethyl methacrylate
PPP	-	polyparaphenylene
PPV	-	polyphenylenevinylene
PPy	-	polypyrrole
PS	-	polystyrene
PSBA	-	poly (styrene-co-butyl acrylate)
PSS	-	poly(sodium 4-styrenesulfonate)
PT	-	polythiophene
PVA	-	polyvinyl alcohol
SAM	-	self-assembly material
SEM	-	Scanning Electron Microscopy
SF ₆	-	sulfur hexafluoride gas
SUV	-	small unilamellar vesicles
TAZ	-	triaminotriazine
TEM	-	Transmission Electron Microscopy
THF	-	tetrahydrofuran
UV	-	ultraviolet

LIST OF SYMBOLS

α	-	alpha
\AA	-	angstrom
δ	-	wavelength
D	-	diameter
D_h	-	hydrodynamic diameter
γ	-	gamma
Gy	-	Gray
kcps	-	kilo count rate per second
kV	-	kilovolt
λ	-	optical absorbance wavelength
π	-	pi
m/w	-	monomer in water ratio
N	-	conjugation length
nm	-	nanometer
σ	-	standard deviation
ζ	-	zeta
Z	-	average size
ΔE	-	total colour difference
L^*	-	lightness
a^*	-	green-red component
b^*	-	blue-yellow component
T_g	-	glass transition temperature
$^{\circ}\text{C}$	-	degree Celsius
K	-	Kelvin
w	-	mass fraction
wt%	-	weight percentage
k	-	adsorption cycle
M	-	molar
M_w	-	molecular weight

$<$	-	less than
$>$	-	more than
Φ	-	angle

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CHAPTER 1

INTRODUCTION

1.1 Background

Radiation dose indication and determination is an important subject that has received global recognition in the contemporary world. Irradiation has applications in the sanitary and phytosanitary treatment of food¹, polymer modification², medical treatment^{3,4} and national security⁵. The emerging application propelled the development of a new dosimeter and indicators from various types of substances to meet the radiation energy and range.

Radiochromic polymers are among the materials studied for use as radiation indicators and dosimeters. They are useful for radiation indication because their chromic response against radiation allows for quantification of the dose absorbed. Their high spatial resolution, minor energy dependence and near tissue-equivalence makes radiochromic dosimeters appropriate for dose distribution measurements⁶. They are either made from a combination of radiation/pH sensitive leuco dyes with a halogen containing compound or from a colourless photo-initiated monomer molecule such as the conjugate polymer.

Pentacosanoic acid (PCDA) is an example of a conjugate material under the diacetylene group with radiochromic ability⁷⁻¹². It has a pi-conjugated electron in its structure that efficiently reacts against radiation, transforming its optical properties in a visible region. It has been tested in the form of a solution¹³, Langmuir-Blodgett film^{14,15}, polymer blends¹⁶, 3D gel^{10,11,17} and modified structures¹⁸⁻²². PCDA is seldom used alone due to its instability in aqueous mediums and brittleness in its dried form. As such, conventional polymers are typically added to PCDA via direct mixing or blending for ease of film casting. Common polymers used for film aid include polyester²³, polyvinyl alcohol (PVA)²⁴ and gelatine^{10,17}. A drawback of

blending an amphiphilic material such as PCDA with another polymer is the ability of the monomer to stay in proximity for the topochemical reaction. In some cases the blend does not respond to radiation until the PCDA precipitates reaction, suggesting that oligomerisation only occurs after PCDA phasing is outside the matrix¹⁰. PCDA in gelatine also experiences a turbidity effect from the gelation of the matrix upon irradiation¹¹. This inhibits the colour change of the PCDA itself, causing less colour to be reported by the indicator.

One way to retain PCDA in a conventional polymer while keeping it functional for radiation indication is by avoiding high interaction between it and the conventional polymer. The introduction of conventional polymer colloids as a core for radiochromic vesicles is one alternative for retaining the original orientation of the amphiphile material. When PCDA is attached to a polymer latex, it can also be called a radiochromic latex.

1.2 Problem Statement

Colour visibility is an important property for indicating the radiation absorption. The higher the response against low doses of radiation, the better the sensitivity of the radiochromic material as an indicator. Pentacosanoic acid (PCDA) is a radiochromic material with high sensitivity to radiation^{10,17}. It is colourless in the monomer form and violet-bluish in the polymerised form¹¹. The shift in colour depends upon the molecular orientation of PCDA for topochemical reactions. The basic requirements for the reaction are a minimum molecular stacking distance of $d \approx 5\text{\AA}$ and an angle of $\Phi \approx 45^\circ$ to enable 1, 4-additions of adjacent PCDA units to form a backbone for the polyPCDA⁸. The longest backbone generated from polymerisation contributes to the maximum colour transition due to the extension of the pi-conjugation length. The higher the degree of conjugation, the larger the nonlinear optical susceptibility²⁵.

The drawback of using the PCDA monomer is that its vesicles are short-lived at room temperature²⁶, reducing the possibility of polymerisation and colour shifts.

Mixing other polymers with the PCDA monomer to aid dry-casting also contributes to the disintegration of the vesicle wall, releasing PCDA monomers freely in between the polymer matrix. This causes the distance between molecules to increase and in turn, disrupts the minimum arrangement required for a topochemical reaction. Due to increased distance, fewer chains are polymerised; thus, low colour (low intensity) is produced for radiation indication^{10,11}.

In this study, a tailor-made polymer latex, poly (styrene-co-butyl acrylate) also known as PSBA, was introduced to the PCDA monomer without altering its minimum molecular stacking using the non-covalent method. The advantage of PSBA is its adaptability in terms of glass transition temperature for film formation. It was prepared via radiation method as a safety measure because ready-made latex may contain unwanted chemical residues that would interrupt the PCDA's attachment to the latex. The hydrophobic surface of PSBA latex has functions to hold the PCDA monomer onto it via hydrophobic-hydrophobic interaction and ionic bond. Besides additional interaction between the PCDA and PSBA surfaces, the incorporation of PSBA into PCDA vesicles can cause them to hold PCDA molecular stacking longer by reducing the osmotic force on the lipid wall. The PSBA latex is formulated for glass transition temperatures (T_g) below 25°C, thus making dry-casting possible. This combination of PCDA and PSBA can provide a better radiation-sensitive indicator in the form of latex while being applicable as a coating material for indication. The lowest and highest radiation doses that caused colour shifts in the PCDA/PSBA latex were assessed and evaluated along with other characteristics. A conclusion of the findings was drawn concerning the dose response curve of the latex and its stability during pre and post irradiation.

1.3 Research Objectives

The main objective of this study is to develop a radiochromic latex from a combination of the pentacosanoic acid (PCDA) monomer and the poly (styrene-co-butyl acrylate) (PSBA) latex. The PCDA/PSBA latex is intended for the

indication of gamma radiation. In order to achieve this goal, four objectives are highlighted below:

- (a) To formulate and optimize a uniform size poly (styrene-co-butyl acrylate) (PSBA) latex as a function of irradiation dose and monomer in water ratio.
- (b) To study the surface charge density on the PSBA surface by the deposition of polyelectrolytes (PSS and PDADMAC) through the layer-by-layer method.
- (c) To diffuse the PCDA monomer onto the modified PSBA surface at different volume ratios.
- (d) To characterise the optical response of PCDA/PSBA upon exposure to gamma radiation.

1.4 Scope of the Study

The first part of this study began with the preparation of the poly (styrene – butyl acrylate) polymer in the form of a latex. The preparation involved the radiation-induced synthesis of the copolymer in emulsion. Gamma irradiation was used only to produce uniform latex particles with an average diameter between 100-300 nm. The range of PSBA size was chosen to fit inside PCDA vesicle as a polymer core without distorting the original assembly. The ratio of styrene to butyl acrylate in the copolymer was formulated for a T_g lower than 25°C to allow for particle coalescence during water removal at room temperature when required. The optimum formulation for particle recovery was identified for the next objective.

The development of polyelectrolyte (PEL) multilayers on the PSBA sphere created additional interaction between the PCDA and PSBA cores besides the existing hydrophobic-hydrophilic interaction. Multiple layers were built through the layer-by-layer deposition method. This method involves the deposition of poly (sodium 4-styrenesulfonate) (PSS) as a polyanion, and poly (diallyldimethyl-ammonium chloride) (PDADMAC) as a polycation on the PSBA surface at five different layers (L1, L2, L3, L4 ad L5). Their stability in colloidal form (zeta potential) and particle sizes were monitored and characterised.

The PCDA, which was prepared in vesicle form, was introduced to the PSBA/PEL via an aqueous medium. The colloidal stability of the latex after the PCDA deposition was then monitored and evaluated. The unstable colloid that formed agglomerates as a result of the deposition was terminated. At this stage, the background optical absorbance of every latex was measured as a reference for the next step.

Radiation exposure was carried out in series on the PCDA/PSBA-PEL to evaluate their performance as radiation indicators. The field test was limited to a gamma-ray source obtained from Cobalt 60 (^{60}Co) and Cesium 137 (^{137}Cs). The radiation dose for low energy ^{137}Cs is between 5 Gy to 7 kGy and the radiation dose for high energy ^{60}Co is between 5-50 kGy. The minimum dose of radiation that stimulates the optical response of the PCDA/PSBA-PEL was identified using the CIElab colour space within a visible region of 400-700 nm. An evaluation of the PCDA/PSBA-PEL optimum response against radiation exposure was also conducted to determine its limitations for application.

1.5 The Novelty of the Study

The novelty of this study lies in the addition of the white PSBA core into PCDA for polymer support and reflectance enhancement. Unlike the blending method, the PCDA in this study was deposited on the outer surface of individual PSBA particles and maintains its colloidal stability for radiation indication. The advantage of this technique is the possibility of the PCDA to self-assemble on the PSBA surface. In terms of colour response, the true colour of PCDA can be seen directly upon radiation exposure for it always stays on top of the surface.

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