

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

NAURAH BINTI MAT ISA

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Doctor of Philosophy

School of Chemical and Energy Engineering
Faculty of Engineering
Universiti Teknologi Malaysia

MAY 2019

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.

ACKNOWLEDGEMENT

In the name of Allah, the Most Gracious and the Most Merciful.

Alhamdulillah. All praises to Allah for giving me the strength, knowledge, ability and opportunity to undertake this research study and to persevere and complete it satisfactorily.

My gratitude also goes to many people who involved directly and indirectly in my work. It is with immense gratitude that I acknowledge the support and help of my fellow researchers, academicians, and practitioners in the process of completing this thesis either from Universiti Teknologi Malaysia or from Malaysian Nuclear Agency. My sincere appreciation goes to both of my supervisors, Dr. Rohah A. Majid and Associate Professor Dr. Wan Aizan Wan Abdul Rahman for equipping me with a lot of encouragement, guidance, motivation and friendship. Without their continued support and interest, this thesis would not have been the same.

I am also indebted to Jabatan Perkhidmatan Awam (JPA) for funding my PhD study under Hadiah Latihan Persekutuan (HLP) program. Malaysian Nuclear Agency also deserve special thanks for their complete radiation facilities (SINAGAMA and Biobeam Gamma Cell) and laboratories (Makmal Teknologi Sinaran and Materials Technology Group).

Finally, my sincere appreciation extends to my husband, Mohd Yusof Hamzah. Without his support and persistent help, this thesis would not be possible. To all my family members and close friends, thank you for all your love, views, tips and assistance at various occasions. Wish me luck, as the journey continues.

Thank you.

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.

TABLE OF CONTENTS

	TITLE	PAGE
	DECLARATION	ii
	DEDICATION	iii
	ACKNOWLEDGEMENT	iv
	ABSTRACT	v
	ABSTRAK	vi
	TABLE OF CONTENTS	vii
	LIST OF TABLES	xi
	LIST OF FIGURES	xii
	LIST OF ABBREVIATIONS	xix
	LIST OF SYMBOLS	xxi
	LIST OF APPENDICES	xxiii
CHAPTER 1	INTRODUCTION	1
1.1	Background	1
1.2	Problem Statement	2
1.3	Research Objectives	3
1.4	Scope of the Study	4
1.5	The Novelty of the Study	5
CHAPTER 2	LITERATURE REVIEW	7
2.1	Introduction	7
2.2	Polymer in Radiation Sensing	7
2.2.1	Electronic Properties for Radiation Sensing	8
2.2.2	Optical Properties for Radiation Sensing	9
2.3	Change Mechanism of Conjugate Polymer for Optical Shifts	12
2.3.1	Topochemical Reaction	12
2.3.2	Conjugation Length	16

2.4	Pentacosanoic Acid for Radiation Sensitive Material	21
2.5	Functionalized Microsphere for Radiation Sensing	23
2.5.1	Microsphere for Polymer Support	24
2.5.2	Factors Affecting the Size of Microsphere	26
2.5.3	Pentacosanoic Acid for Deposition	29
2.5.3.1	Preparation Method	30
2.5.4	Deposition of Conjugated Material onto Polymer Microsphere	32
2.5.4.1	Surface Deposition via Physical Immobilization	33
2.5.4.2	Simple Mixed Solvent	33
2.5.4.3	Layer-by-layer Assembly	34
2.5.4.4	Surface Modification via Covalently Attached Molecules	38
2.6	Polymer Characterisation	40
2.6.1	Chemical Structure Verification	40
2.6.1.1	Nuclear Magnetic Resonance	42
2.6.2	Particle Size and Distribution	44
2.6.3	Polydispersity Index	45
2.6.4	Particle Stability	47
2.6.5	Polymer Morphology	49
2.6.6	Optical Properties Analysis	50
CHAPTER 3	RESEARCH METHODOLOGY	55
3.1	Introduction	55
3.2	Materials	55
3.3	Emulsion Copolymerisation of Poly (Styrene-co-Butyl Acrylate)	56
3.4	Layer-by-Layer (LbL) Deposition of Polyelectrolytes on PSBA	59
3.5	Preparation of PCDA Liposome	63
3.6	Deposition of PCDA onto PSBA-PEL	64
3.7	Dose-Response Study of Radiation Indicator (Field Test)	66

3.7.1	Volume Ratio Against Dose Sensitivity	66
3.7.2	The Effect of Polyelectrolyte Layer Against Dose Sensitivity	67
3.8	Material Characterisation	68
3.8.1	Chemical Analysis	68
3.8.1.1	Fourier Transform Infra-Red (FTIR)	68
3.8.1.2	Nuclear Magnetic Resonance (NMR)	69
3.8.2	Static Light Scattering (SLS)	69
3.8.3	Differential Scanning Calorimeter (DSC)	70
3.8.4	Morphology and Size Distribution Study	70
3.8.4.1	Dynamic Light Scattering (DLS)	70
3.8.4.2	Transmission Electron Microscopy (TEM)	71
3.8.4.3	Field Emission Scanning Electron Microscopy (FESEM)	71
3.8.5	Zeta Potential Analyser	71
3.8.6	Colorimeter	72
CHAPTER 4	RESULT AND DISCUSSION	75
4.1	Introduction	75
4.2	Polymerisation of Poly(Styrene-Butyl Acrylate) as Core Support	75
4.2.1	Chemical Structure Confirmation	75
4.2.2	Effect of Butyl Acrylate Composition on PSBA Thermal Analysis	80
4.2.3	Morphology of Polymerised PSBA Particle	81
4.2.4	Effect of Radiation Dose on PSBA Particle Development	84
4.2.5	Effect of Monomer in Water (m/w) Ratio for PSBA Particle	87
4.3	Deposition of Polyelectrolyte	91
4.3.1	Modification on the Outer Surface Charge	91
4.4	Deposition of PCDA on PSBA/PEL	99
4.4.1	Physical Stability of PCDA for Adsorption	99

4.4.2	Effect of PSBA Amount on Sample Colour Lightness (L*)	104
4.4.3	Effect of PCDA Deposition on the Stability of PSBA	105
4.4.4	Surface Morphology of PCDA/PSBA Particle	110
4.5	Radiation Exposure Test on PCDA/PSBA Latex	114
4.5.1	Changes in Optical Properties as a Function of Irradiation Dose	114
4.5.2	Post-irradiation Characteristics and Its Optical Stability	121
4.5.3	Effect of Storage Time on Colour Stability	128
CHAPTER 5	CONCLUSIONS AND RECOMMENDATIONS	135
5.1	Conclusions	135
5.2	Recommendations for Future Work	136
REFERENCES		139

LIST OF TABLES

TABLE NO.	TITLE	PAGE
Table 2.1	Correlation between conjugation length (N), molecular weight (M_w) and absorbance (λ_{max}) for polyene oligomers	17
Table 3.1	Chemicals involved in preparing the PSBA/ PCDA-PEL latex.	55
Table 3.2	Material composition used for emulsion polymerisation of styrene-butyl acrylate (PSBA) in weight fraction unit	57
Table 3.3	Samples of different PCDA to PSBA ratios assigned for irradiation using ^{137}Cs	67
Table 3.4	Samples of different polyelectrolyte layers assigned for irradiation using ^{60}Co	68
Table 4.1	Data obtained by measurements against the theoretical value calculated using the Fox-flory equation	80

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
Figure 2.1	Molecule structure of conjugated polymers	8
Figure 2.2	Absorbance spectra of conjugated polymers upon exposure to radiation (a) Optical shift for γ -irradiated PANI ⁴⁰ (b) Optical shift for neutron irradiated PANI ⁴⁰ (c) Blue-shifts in the absorption spectra of γ -irradiated MEH-PPV ⁴⁸	11
Figure 2.3	Distance of double bonds for diacetylene monomer that allows for the topochemical reaction ⁸	13
Figure 2.4	Illustration of polydiacetylene backbone conformation that cause changes in chromatic properties upon prolonged UV irradiation ⁶³	14
Figure 2.5	The change in absorption spectra as the result of temperature change (a) hypsochromic effect on polydiacetylene from red to blue (b) hyperchromic effect on P ₃ HT from yellow to magenta with denomination of a to f was -23°C, 5.5°C, 9.5°C, 24.5°C, 38°C, 65°C ⁶⁵	14
Figure 2.6	Schematic representation of the shape of polydiacetylene chains in different solvent type. a) planar (fully conjugated chain), b) Kuhn model (limited conjugated chain), c) Worm-like chain (continuous curvature) ⁸	15
Figure 2.7	(A) Cotton effect manipulated by solvent variation. (B) Single helical strand of polyacetylene stabilized by intrachain and (C) double helical strands of polyacetylene stabilized by interchain hydrogen bonds ⁶⁷	16
Figure 2.8	Illustration of Cl radical attacks on MEH-PPV that leads to chain scission ⁴⁸	18
Figure 2.9	Absorption spectra of polythiophene irradiated with various dosage of γ -ray under SF ₆ gas ⁷²	19
Figure 2.10	Optical difference of polymer after substitution of alkyl and alkoxy side chain. a) Molecular structure of PININE and its derivatives and (b) UV-visible absorption spectra of the polymer in thin films ⁷⁴	20
Figure 2.11	Absorption spectra of (a) 10,12-pentacosadiynoic acid (PDA) and (b) its mixture with PDATAZ after exposure to UV irradiation from 10 to 400 second and from 100 to 1000 second respectively. (c) Hydrogen bonding network between PDATAZ and its components ⁶³	21

Figure 2.12	Chemical structure of pentacos-10,12-diyonic acid (PCDA) and its chromatic properties resulted from polymerisation of C1 and C4 carbon atom ⁷⁶	22
Figure 2.13	Growth plots of polystyrene particle as the result of different initiator type ⁹⁰	26
Figure 2.14	Effect of water-soluble initiator (V-501) concentration (a) $c = 0.7$ mM (b) $c = 1.4$ mM (c) $c = 2.0$ mM on the particle size, and (d) its particle size-concentration relationship ⁹¹	27
Figure 2.15	Size of microcapsule for particle development depends on the size of droplet dispersed in emulsion ⁹⁴	28
Figure 2.16	Molecule structure of pentacos-10,12-diyonic acid (PCDA)	29
Figure 2.17	Classification of liposome based on vesicle size and lamellarity system	30
Figure 2.18	A schematic representation of the formation of MLV upon the hydration of the dry phospholipid film ¹⁰⁵	31
Figure 2.19	Liposome retention at different lipid composition, lamellarity structure and storage condition ¹⁰⁸	32
Figure 2.20	Schematic illustration of simple mixed solvent method, (a) modification process on PS microspheres with K ⁺ -selective sensing components (b) Microscopic images for K ⁺ -selective PS microspheres with 0.8 mm diameter, (c) with 2.4 mm diameter, in aqueous ⁸³	34
Figure 2.21	Schematic flow of procedure used for preparing PANI-containing melamine formaldehyde (MF) core-shell particles and its hollow capsules ¹¹¹	36
Figure 2.22	(a) Increment of absorbance curves observed at different numbers of adsorption cycles (k) during the preparation of a PSS/PAH multilayer (b) Plot of the absorbance of the PSS band at 225 nm shows a constant increment against the addition of layer ¹¹⁴	37
Figure 2.23	Example of microspheres prepared with LbL method (a) Transmission electron micrographs of individual gold colloids stabilized by sodium citrate up to 19 layers of polyelectrolytes (from upper left to lower right corner) (b) Overview transmission electron micrograph showing individual colloids covered by 13 layers ¹¹⁵	37
Figure 2.24	Evolution of the ζ potential during the build-up of a PSS/PAH, the polyelectrolyte multilayer ¹¹⁶	38
Figure 2.25	Scheme for the covalent immobilisation of spiropyran on the surface of the polystyrene microbeads ⁵⁰	39

Figure 2.26	IR spectra of polystyrene (PS) labelled as <i>a</i> and polystyrene-co-butyl acrylate (PS-co-BA) labelled as <i>b</i> ¹²¹	41
Figure 2.27	IR spectra of pure poly-PCDA in blue phase (top) and pure poly-PCDA in red phase (bottom) ¹²²	42
Figure 2.28	¹ H-NMR of styrene monomer ¹²³	43
Figure 2.29	¹ H-NMR of butyl acrylate monomer ¹²³	43
Figure 2.30	Particle size distribution curves using DLS technique for uncoated PS particles and PPy-Pd nanocomposite-coated PS particles synthesized at various pyrrole concentrations. Inset: magnified laser diffraction particle size distribution curves for uncoated PS particles and PPy-Pd nanocomposite-coated PS particles (pyrrole: 2.5, 5.0, and 10 wt %) ¹²⁵	45
Figure 2.31	Correlation of particle size distribution to particle dispersity, (a) monodisperse and (b) polydisperse size distribution	46
Figure 2.32	Potential energy of interaction against distance between centers of two spherical particles based on DLVO theory ¹³¹	48
Figure 2.33	Zeta-potential (ζ) of ligand-free gold nanoparticles at different pH values for the determination of the isoelectric point ¹³²	48
Figure 2.34	SEM images of uncoated PS particles and PPy-Pd nanocomposite-coated PS particles synthesized at various pyrrole concentrations ¹²⁵	49
Figure 2.35	Example of TEM images of Laponite-armored latexes synthesized by surfactant-free emulsion polymerisation of styrene and BuA ¹³³	50
Figure 2.36	CIE (1931) chromatic diagram showing the influence of blue-light radiation on the colour coordinates of MEH-PPV chloroform solutions with different mass concentrations (a) 25 μ g/ml, (b) 50 μ g/ml ¹³⁵	51
Figure 2.37	Three-dimensional model of CIEL*a*b* scale ¹³⁴ .	52
Figure 2.38	Colorimetric data obtained from spectroelectrochemical switching study in CIEL*a*b* system ($C/2^\circ$) (projected on isosurface colour at level $L^* \frac{1}{4}$). P3-OMe (blue, plain line), P3-H (dash), P3-F (dots), P3-COOMe (dash dot), P3-CN (short dot)	53
Figure 2.39	Image of spiropyran-coated-polystyrene spheres (a) in the presence of Cu^{2+} and in the presence of Ca^{2+} upon exposure to UV lights; (b) its reflectance spectra ⁵⁰	54
Figure 3.1	Molecular structure of styrene (a) and butyl acrylate (b); two important monomers in the copolymerisation process	56

Figure 3.2	Workflow of preparation and selection of polystyrene butyl acrylate (PSBA) latex	58
Figure 3.3	The molecular structure of selected polyelectrolyte, (a) poly (sodium 4-styrenesulfonate) (PSS) and (b) poly (diallyldimethylammonium chloride) (PDADMAC)	59
Figure 3.4	Illustration of the polyelectrolyte's deposition via LbL assembly technique	61
Figure 3.5	Workflow of layer-by-layer deposition	62
Figure 3.6	Method of PCDA liposome preparation: (a) PCDA powder weighed to the desired amount, (b) dissolution of PCDA in THF solvent, (c) thin film formation by moderate heating and (d) liposome formation by the addition of deionised water and heating	63
Figure 3.7	Standard curve of PCDA concentrations measured using a UV/Vis spectrophotometer (at 560nm)	64
Figure 3.8	Workflow of PCDA adsorption for field test study	65
Figure 3.9	Summary of the field test study and material characterisation	73
Figure 4.1	FTIR spectra of polymerised poly styrene-co-butyl acrylate in comparison to polystyrene	76
Figure 4.2	¹ H-NMR spectrum of polymerised PSBA with possible molecule structure according to the peak assignment	77
Figure 4.3	Suggested mechanism of copolymerisation of poly(styrene-co-butyl acrylate) (PSBA)	79
Figure 4.4	Glass transition temperature (T_g) of the copolymers as a function of composition expressed by weight fraction	81
Figure 4.5	Micrographs taken using TEM at 10K magnification for polymers radiated with 25 kGy where (a) 100% PS, (b) 100% polyBA and (c) poly (60% styrene – 40% BA)	83
Figure 4.6	Hydrodynamic diameter (D_h) of polymerised particles of different PS-BA compositions at elevated γ -radiation dosage (0.6 Gy/s)	84
Figure 4.7	Polydispersity of PS, PBA and PSBA latex in the aqueous phase	86
Figure 4.8	Molecular weight of PSBA as measured against radiation dose	87
Figure 4.9	Average hydrodynamic diameter (D_H) of PSBA against the radiation dosage for various monomers in the water ratio	88
Figure 4.10	Illustration of inter- and intramolecular bonds of PSBA particle formation	89

Figure 4.11	Influence of radiation dose on PSBA latex in terms of (a) total solid content and (b) particle count rate (intensity)	90
Figure 4.12	Illustration of all possible potentials on the PSBA latex (a), and simplified version with only zeta potential shown on its surface (b)	93
Figure 4.13	Illustration of PSS and PDADMAC layers on PSBA latex particle; (a) 0 layer, (b) PSBA with 1 PSS layer, (c) PSBA with 1 PSS layer and 1 PDADMAC layer, (d) PSBA with 3 layers of polyelectrolytes where PSS is at the outermost layer	94
Figure 4.14	Zeta potential stability of PSBA latex before and after deposition of polyelectrolyte layers	95
Figure 4.15	Diameter of PSBA and PSBA/PEL particles with different outer surface charges	96
Figure 4.16	Transmission electron micrograph of individual colloid after addition of polyelectrolyte layers (marked by arrow); (a) 4 layers of polyelectrolytes, (b) 5 layers of polyelectrolytes	98
Figure 4.17	Structure of PCDA liposome in an aqueous medium	100
Figure 4.18	PCDA liposome diameter after days of storage at room temperature	101
Figure 4.19	Expansion of PCDA liposome size due to the fusion of two or more vesicles	102
Figure 4.20	Unimodal distribution of PCDA liposome at three interval storage times, and particularly stored at room temperature	102
Figure 4.21	Multimodal distribution of PCDA liposome after 20 days of storage	103
Figure 4.22	Change in lightness on PCDA/PSBA sample with different percentages of PSBA	104
Figure 4.23	Illustration of adsorption of PCDA on the PSBA surface by hydrophobic interaction	105
Figure 4.24	Stable PCDA liposome dispersion in aqueous medium, and after its adsorption on the PSBA latex	106
Figure 4.25	Particle size distribution of PSBA and PCDA before and after PCDA deposition	107
Figure 4.26	Increment of PCDA/PSBA size upon PCDA adsorption on 1 ml PSBA latex	107
Figure 4.27	Zeta potential (ζ) of PCDA/PSBA latex at different compositions of PSBA	108

Figure 4.28	Deposition of PCDA on PSBA/PEL of various PEL layers: (L0) 0 layer, (L1) 1 layer, (L2) 2 layers, (L3) 3 layers, (L4) 4 layers and (L5) 5 layers	109
Figure 4.29	Shift of zeta potential after PCDA adsorption on PSBA/PEL	110
Figure 4.30	Morphology of (a) neat PSBA latex, (b) PCDA on uncoated PSBA, (c) PSBA with 5 layers of polyelectrolyte, and (d) PCDA on polyelectrolyte coated PSBA.	112
Figure 4.31	Change of PSBA/PCDA latex colour upon exposure γ -ray (^{137}Cs) at different ratios of PCDA attached on the PSBA latex	115
Figure 4.32	Shift in L^* , a^* and b^* of PCDA/PSBA sample upon exposure to ^{137}Cs	116
Figure 4.33	Total colour difference (dE^*) of PCDA/PSBA sample upon exposure to low dose irradiation range (^{137}Cs)	117
Figure 4.34	Difference of Dose-response curve of PCDA (2:0), and PCDA/PSBA samples (2:0.5) at low dose range (^{137}Cs) and high dose range (^{60}Co)	119
Figure 4.35	Dose response curve of PCDA samples incorporated onto different polyelectrolyte layers	120
Figure 4.36	Change in chemical structure of PCDA after exposure to gamma ray (^{137}Cs)	122
Figure 4.37	Proposed structure of polymerised PCDA based on peak assignment from ^1H NMR	123
Figure 4.38	Size consistency of irradiated PCDA/PSBA latex against storage time; (a) measured immediately after irradiation, (b) measured 30 days after irradiation	124
Figure 4.39	Morphology of PCDA/PSBA (L0) sample after exposure to 10 kGy of ^{60}Co viewed using FESEM; (a) PSBA only, (b) PSBA with PCDA before irradiation, (c) PSBA with PCDA after irradiation	127
Figure 4.40	Colour shift of PCDA/PSBA latex with and without polyelectrolyte layers immediately after γ -ray exposure (^{60}Co)	129
Figure 4.41	Irradiated PCDA/PSBA latex with and without polyelectrolyte layers after 60 days of post-irradiation storage	129
Figure 4.42	Colour drift on PCDA/PSBA samples kept for 60 days: (a) samples irradiated with 5 kGy, (b) samples irradiated with 50 kGy	131
Figure 4.43	Influence of polyelectrolyte layers on colour variation of PCDA/PSBA latex during storage time	132

Figure 4.44 Low colour variation of PCDA/PSBA(L0) compared to non-filled PCDA for consistent colour dosimeter (a) non-filled PCDA, (b) PCDA/PSBA(L0)

133

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

LIST OF APPENDICES

APPENDIX	TITLE	PAGE
Appendix A	Monomers' Composition	155
Appendix B	Glass transition temperature	156

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.

REFERENCES

1. Kim. M.J., Ki. H.A., Kim. W.Y., et al. Development of Radiation Indicators to Distinguish between Irradiated and Non-Irradiated Herbal Medicines Using HPLC and GC-MS. *Anal Bioanal Chem.* 2010, 398(2): 943–53.
2. Dutta. J., Chatterjee. T., Dhara. G., and Naskar. K. Exploring the Influence of Electron Beam Irradiation on the Morphology, Physico-Mechanical, Thermal Behaviour and Performance Properties of EVA and TPU Blends. *RSC Advances.* 2015, 5(52): 41563–41575.
3. Burns. J. Standards and Codes of Practice in Medical Radiation Dosimetry. Proceedings of an International Symposium, Vienna, 25-28 November 2002. Volumes 1-2. Pp Ii+ 483, 497, 2003 (IAEA, Vienna, Austria).€130. ISBN 92-0-111403-6. 2005.
4. Podgorsak. E., and others. Radiation Oncology Physics. *a handbook for teachers and students/EB Podgorsak.-Vienna: International Atomic Energy Agency.* 2005, 657.
5. Flakus. F. Detecting and Measuring Ionizing Radiation- A Short History. *IAEA bulletin.* 1982, 23(4): 31–36.
6. Williams. M., and Metcalfe. P. Radiochromic Film Dosimetry and Its Applications in Radiotherapy. *AIP Conference Proceedings.* 2011, 1345(1): 75–99.
7. Bässler. H. Photopolymerization of Diacetylenes. *Polydiacetylenes.* 1984, 1–48.
8. Enkelmann. V. Structural Aspects of the Topochemical Polymerization of Diacetylenes. *Polydiacetylenes.* 1984, 91–136.
9. Lieser. G., Tieke. B., and Wegner. G. Structure, Phase Transitions and Polymerizability of Multilayers of Some Diacetylene Monocarboxylic Acids. *Thin Solid Films.* 1980, 68(1): 77–90.
10. Nasr. A. Modeling and Development of Three Dimensional Gel Dosimeters. 2014.
11. Nasr. A., Olding. T., Schreiner. L., and McAuley. K. Evaluation of the Potential for Diacetylenes as Reporter Molecules in 3D Micelle Gel Dosimetry. *Physics in medicine and biology.* 2013, 58(4): 787.

12. Patel. G. Diacetylenes as Radiation Dosage Indicators. *Radiation Physics and Chemistry (1977)*. 1981, 18(5-6): 913–925.
13. Wenz. G., and Wegner. G. Molecular Weight Distribution and Solution Properties of a Poly (diacetylene). *Macromolecular Rapid Communications*. 1982, 3(4): 231–237.
14. Ogawa. K. Control of Polymerization Processes of 10, 12-Pentacosadiynoic Acid LB Films. *Polymer international*. 1992, 28(1): 25–33.
15. Semaltianos. N., Araujo. H., and Wilson. E. Polymerization of Langmuir-Blodgett Films of Diacetylenes. *Surface science*. 2000, 460(1-3): 182–189.
16. Kauffman. J.S. Incorporation of Polydiacetylene Sensors into Commercial Polymers. 2008.
17. Sun. P., Fu. Y.-C., Hu. J., et al. Electron Irradiation Effects of Radiochromic PCDA Vesicle Gel Dosimeters. *Nucl. Sci. Tech*. 2015, 26: 050301.
18. Beckham. H., and Rubner. M. On the Origin of Thermochromism in Cross-Polymerized Diacetylene-Functionalized Polyamides. *Macromolecules*. 1993, 26(19): 5198–5201.
19. Jonas. U., Shah. K., Norvez. S., and Charych. D.H. Reversible Color Switching and Unusual Solution Polymerization of Hydrazide-Modified Diacetylene Lipids. *Journal of the American Chemical Society*. 1999, 121(19): 4580–4588.
20. Rubner. M. Synthesis and Characterization of Polyurethane-Diacetylene Segmented Copolymers. *Macromolecules*. 1986, 19(8): 2114–2128.
21. Chuang. F.-S. Analysis of Thermal Degradation of Diacetylene-Containing Polyurethane Copolymers. *Polymer Degradation and Stability*. 2007, 92(7): 1393–1407.
22. Harano. I., Okano. C., Takayama. Y., et al. Color Transition Properties of Water Dispersible Polydiacetylene Particles Conjugated with the Thermosensitive Polymer. *Applied Mechanics and Materials*. 2017, 863: 38–43.
23. Lewis. D. Gafchromic HD-810 Radiochromic Dosimetry Film and D-200 Pre-Formatted Dosimeters for High-Energy Photons: Configuration, Specifications and Performance Data.
24. Soliman. Y., Bayomi. A., Abdel-Fattah. A., and Abdel-Khalek. A. Radiochromic Label Dosimeter Based on a Synthesized Monomer of 2, 4-Hexadiyn-1, 6-Bis (n-Butyl Urethane). *Sensors and Actuators B: Chemical*. 2014, 200: 109–116.

25. Feast. W.J., Cacialli. F., Koch. A.T., et al. Control of Luminescence in Conjugated Polymers through Control of Chain Microstructure. *Journal of Materials Chemistry*. 2007, 17(9): 907–912.
26. Yadav. A., Murthy. M., Shete. A., and Sakhare. S. Stability Aspects of Liposomes. *Indian Journal Of Pharmaceutical Education And Research*. 2011, 45(4): 402–413.
27. Kaneto. K., Yoshino. K., and Inuishi. Y. Electrical and Optical Properties of Polythiophene Prepared by Electrochemical Polymerization. *Solid state communications*. 1983, 46(5): 389–391.
28. Hattori. T., Hayes. W., Wong. K., Kaneto. K., and Yoshino. K. Optical Properties of Photoexcited and Chemically Doped Polythiophene. *Journal of Physics C: Solid State Physics*. 1984, 17(29): L803.
29. Yoshino. K., Hayashi. S., Inuishi. Y., Hattori. K., and Watanabe. Y. Photoluminescence of Cis-and Trans-Polyacetylene. *Solid state communications*. 1983, 46(7): 583–585.
30. Heeger. A.J., Kivelson. S., Schrieffer. J., and Su. W.-P. Solitons in Conducting Polymers. *Reviews of Modern Physics*. 1988, 60(3): 781.
31. Tanaka. K., Koike. T., Ohzeki. K., Yoshikawa. K., and Yamabe. T. Photoisomerization of Cis-Polyacetylene. *Solid state communications*. 1983, 47(2): 127–129.
32. Lambert. K.P., and Van de Voorde. M. High Radiation Dose Luminescent and Optical Dosimetry Systems. *The International Journal of Applied Radiation and Isotopes*. 1974, 25(2): 69–79.
33. Chance. R., and Patel. G. Solid-State Polymerization of a Diacetylene Crystal: Thermal, Ultraviolet, and Gamma-Ray Polymerization of 2, 4-Hexadiyne-1, 6-Diol Bis-(p-Toluene Sulfonate). *Journal of Polymer Science Part B: Polymer Physics*. 1978, 16(5): 859–881.
34. Stumpel. J.E., Broer. D.J., and Schenning. A.P. Stimuli-Responsive Photonic Polymer Coatings. *Chemical Communications*. 2014, 50(100): 15839–15848.
35. Bai. H., and Shi. G. Gas Sensors Based on Conducting Polymers. *Sensors*. 2007, 7(3): 267–307.
36. Brahim. S., Narinesingh. D., and Guiseppi-Elie. A. Amperometric Determination of Cholesterol in Serum Using a Biosensor of Cholesterol Oxidase Contained

- within a Polypyrrole-Hydrogel Membrane. *Analytica Chimica Acta*. 2001, 448(1): 27–36.
37. Natali. D., and Sampietro. M. Detectors Based on Organic Materials: Status and Perspectives. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*. 2003, 512(1-2): 419–426.
 38. Boroumand. F., Zhu. M., Dalton. A., et al. Direct X-Ray Detection with Conjugated Polymer Devices. *Applied Physics Letters*. 2007, 91(3): 033509.
 39. Binda. M., Natali. D., Sampietro. M., Agostinelli. T., and Beverina. L. Organic Based Photodetectors: Suitability for X-and Gamma-Rays Sensing Application. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*. 2010, 624(2): 443–448.
 40. Sonkawade. R., Kumar. V., Annapoorni. S., Vaijapurkar. S., and Dhaliwal. A. Effects of Gamma Ray and Neutron Radiation on Polyaniline Conducting Polymer. 2010, .
 41. Intaniwet. A., Keddie. J.L., Shkunov. M., and Sellin. P.J. High Charge-Carrier Mobilities in Blends of Poly (triarylamine) and TIPS-Pentacene Leading to Better Performing X-Ray Sensors. *Organic Electronics*. 2011, 12(11): 1903–1908.
 42. Suzuki. T., Miyata. H., Katsumata. M., et al. Organic Semiconductors as Real-Time Radiation Detectors. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*. 2014, 763: 304–307.
 43. El Ghazaly. M., Aydarous. A., and Al-Thomali. T.A. Photoluminescence Properties of PADC Irradiated with Ultraviolet Radiation of Short Wavelength (UVC). *Int. J. Electrochem. Sci*. 2014, 9: 3650–3657.
 44. Mills. C.A., Chan. Y.-F., Intaniwet. A., et al. Direct Detection of 6 MV X-Rays from a Medical Linear Accelerator Using a Semiconducting Polymer Diode. *Physics in Medicine & Biology*. 2013, 58(13): 4471.
 45. Birer. O., Suzer. S., Sevil. U., and Guven. O. UV-Vis, IR and XPS Analysis of UV Induced Changes in PVC Composites. *Journal of molecular structure*. 1999, 482: 515–518.
 46. Beckerle. P., and Ströbele. H. Charged Particle Detection in Organic Semiconductors. *Nuclear Instruments and Methods in Physics Research Section*

- A: Accelerators, Spectrometers, Detectors and Associated Equipment*. 2000, 449(1): 302–310.
47. Bai. Y., Chen. X., Zhang. D., Wan. X., and Zhou. Q. A DSC Study of Photopolymerization of Polyesters Containing Conjugated Diacetylenes. *Chinese Journal of Polymer Science*. 2000, 18(4): 351–356.
 48. Bronze-Uhle. E., Batagin-Neto. A., Lavarda. F.C., and Graeff. C.F. de O. Ionizing Radiation Induced Degradation of Poly (2-Methoxy-5-(2'-Ethyl-Hexyloxy)-1, 4-Phenylene Vinylene) in Solution. *Journal of applied physics*. 2011, 110(7): 073510.
 49. Bronze-Uhle. E., Batagin-Neto. A., Fernandes. D., et al. Poly [1, 1'-Bis (ethynyl)-4, 4'-Biphenyl (bis-Tributylphosphine) Pt (II)] Solutions Used as Low Dose Ionizing Radiation Dosimeter. *Applied Physics Letters*. 2013, 102(24): 241917.
 50. Scarmagnani. S., Walsh. Z., Slater. C., et al. Polystyrene Bead-Based System for Optical Sensing Using Spiropyran Photoswitches. *Journal of Materials Chemistry*. 2008, 18(42): 5063–5071.
 51. Ciferri. A. Supramolecular Polymers. CRC press; 2005.
 52. Patterson. J., and Bailey. B. Solid-State Physics. *Solid-State Physics: Introduction to the Theory*, ISBN 978-3-642-02588-4. Springer-Verlag Berlin Heidelberg, 2010. 2010, .
 53. Cohen. M., and Schmidt. G. 383. Topochemistry. Part I. A Survey. *Journal of the Chemical Society (Resumed)*. 1964, 1996–2000.
 54. Schmidt. G. Photodimerization in the Solid State. *Pure and Applied Chemistry*. 1971, 27(4): 647–678.
 55. Baughman. R., and Shacklette. L. Conductivity as a Function of Conjugation Length: Theory and Experiment for Conducting Polymer Complexes. *Physical Review B*. 1989, 39(9): 5872.
 56. Bloor. D. Experimental Studies of Polydiacetylene: Model Conjugated Polymers. *Recent Advances in the Quantum Theory of Polymers*. 1980, 14–34.
 57. Wegner. G. Topochemical Reactions of Monomers with Conjugated Triple-Bonds. IV. Polymerization of Bis-(p-Toluene Sulfonate) of 2.4-Hexadiin-1.6-Diol. *Macromolecular Chemistry and Physics*. 1971, 145(1): 85–94.

58. Yang. Y., Lu. Y., Lu. M., et al. Functional Nanocomposites Prepared by Self-Assembly and Polymerization of Diacetylene Surfactants and Silicic Acid. *Journal of the American Chemical Society*. 2003, 125(5): 1269–1277.
59. Matsuzawa. H., Okada. S., Sarkar. A., Matsuda. H., and Nakanishi. H. Synthesis of Polydiacetylenes from Novel Monomers Having Two Diacetylene Units Linked by an Arylene Group. *Polymer journal*. 2001, 33(2): 182–189.
60. Hirshfeld. F., and Schmidt. G. Topochemical Control of Solid-State Polymerization. *Journal of Polymer Science Part A: Polymer Chemistry*. 1964, 2(5): 2181–2190.
61. Spagnoli. S., Schott. M., Johnson. M., and Toupet. L. Structural Study of Two Reactive Diacetylenes. *Chemical physics*. 2007, 333(2): 236–245.
62. MacGillivray. L.R., and Papaefstathiou. G.S. Solid-State Reactivity/topochemistry. *Encyclopedia of supramolecular chemistry*. Dekker, New York. 2004, 1316–1319.
63. Huo. Q., Russell. K., and Leblanc. R.M. Chromatic Studies of a Polymerizable Diacetylene Hydrogen Bonding Self-Assembly: A “self-Folding” Process to Explain the Chromatic Changes of Polydiacetylenes. *Langmuir*. 1999, 15(11): 3972–3980.
64. Rink. A., Lewis. D.F., Varma. S., Vitkin. I.A., and Jaffray. D.A. Temperature and Hydration Effects on Absorbance Spectra and Radiation Sensitivity of a Radiochromic Medium. *Medical physics*. 2008, 35(10): 4545–4555.
65. Rughooputh. S., Hotta. S., Heeger. A., and Wudl. F. Chromism of Soluble Polythienylenes. *Journal of Polymer Science Part B: Polymer Physics*. 1987, 25(5): 1071–1078.
66. Burns. A.R., Sasaki. D.Y., Carpick. R., Shelnett. J.A., and Brinker. C.J. Functional Materials for Microsystems: Smart Self-Assembled Photochromic Films: Final Report; FINAL. 2001, .
67. Lam. J.W., and Tang. B.Z. Functional Polyacetylenes. *Accounts of chemical research*. 2005, 38(9): 745–754.
68. Rissler. J. Effective Conjugation Length of Pi-Conjugated Systems. *Chemical physics letters*. 2004, 395(1): 92–96.
69. Kuzmany. H., and Kürti. J. The Physical Meaning of the Conjugation Length in Polymers. *Synthetic Metals*. 1987, 21(1-3): 95–102.

70. Samuel. I.D., Ledoux. I., Dhenaut. C., et al. Saturation of Cubic Optical Nonlinearity in Long-Chain Polyene Oligomers. *Science*. 1994, 265(5175): 1070–1072.
71. Foot. P., and Simon. R. Electrochromic Properties of Conducting Polyanilines. *Journal of Physics D: Applied Physics*. 1989, 22(11): 1598.
72. Yoshino. K., Hayashi. S., Kaneto. K., et al. Radiation Effect in Conducting Polymers. *Molecular Crystals and Liquid Crystals*. 1985, 121(1-4): 255–258.
73. Saion. E., Shaari. A., Ali. M., et al. Syntheses of Conducting Polymers and Metal Nanoparticles by Using Ionizing Radiation. *Solid State Science and Technology*. 2008, 16(1): 114–123.
74. Cho. S., Seo. J.H., Kim. S.H., et al. Effect of Substituted Side Chain on Donor-Acceptor Conjugated Copolymers. *Applied Physics Letters*. 2008, 93(26): 450.
75. Feast. W.J., Tsibouklis. J., Pouwer. K.L., Groenendaal. L., and Meijer. E.W. Synthesis, Processing and Material Properties of Conjugated Polymers. *Polymer*. 1996, 37(22): 5017–5047.
76. Kim. Y.-R., Jung. S., Ryu. H., et al. Synthetic Biomimetic Membranes and Their Sensor Applications. *Sensors (Basel)*. 2012, 12(7): 9530–50.
77. Song. J., Cisar. J.S., and Bertozzi. C.R. Functional Self-Assembling Bolaamphiphilic Polydiacetylenes as Colorimetric Sensor Scaffolds. *Journal of the American Chemical Society*. 2004, 126(27): 8459–8465.
78. Devic. S., Seuntjens. J., Sham. E., et al. Precise Radiochromic Film Dosimetry Using a Flat-Bed Document Scanner. *Medical physics*. 2005, 32(7Part1): 2245–2253.
79. Thomas. G.L., Böhner. C., Ladlow. M., and Spring. D.R. Synthesis and Utilization of Functionalized Polystyrene Resins. *Tetrahedron*. 2005, 61(51): 12153–12159.
80. Yusilawati. A., Maizirwan. M., Hamzah. M., Ng. K., and Wong. C. Surface Modification of Polystyrene Beads by Ultraviolet/ozone Treatment and Its Effect on Gelatin Coating. *American Journal of Applied Sciences*. 2010, 7(6): 724.
81. Breed. D.R., Thibault. R., Xie. F., et al. Functionalization of Polymer Microspheres Using Click Chemistry. *Langmuir*. 2009, 25(8): 4370–4376.
82. Odian. G.G., and Odian. G. Principles of Polymerization. Wiley-Interscience New York; 2004.

83. Xie. X., Crespo. G.A., Zhai. J., Szilágyi. I., and Bakker. E. Potassium-Selective Optical Microsensors Based on Surface Modified Polystyrene Microspheres. *Chemical Communications*. 2014, 50(35): 4592–4595.
84. Ballantine. D., Glines. A., Metz. D., et al. G Values of Gamma-Ray Initiation of Vinyl Polymerization and Their Relation to Graft Copolymer Formation. *Journal of Polymer Science Part A: Polymer Chemistry*. 1956, 19(91): 219–224.
85. Lukhovitskii. V., Lebedeva. A., and Karpov. V. Radiation Emulsion Polymerization of Styrene at High Latex-Particle Concentrations. *Polymer Science USSR*. 1973, 15(11): 2791–2797.
86. Stannett. V., Gervasi. J., Kearney. J., and Araki. K. Radiation-Induced Emulsion Polymerization of Vinyl Acetate and Styrene. *Journal of Applied Polymer Science*. 1969, 13(6): 1175–1189.
87. Moore. P., Clouston. J., and Chaplin. R. Gamma Radiation-Initiated Polymerization of Styrene at High Pressure. III. Emulsion Polymerization with Anionic Emulsifiers. *Journal of Polymer Science Part A: Polymer Chemistry*. 1983, 21(8): 2491–2501.
88. Wanxi. Z., and Jiazhen. S. Radiation-Induced Emulsion Polymerization of Styrene in Soap-Free System. *Polymer communications*. 1985, 3(1): 11–16.
89. Chern. C. Emulsion Polymerization Mechanisms and Kinetics. *Progress in polymer science*. 2006, 31(5): 443–486.
90. Liu. B., Wang. Y., Zhang. M., and Zhang. H. Initiator Systems Effect on Particle Coagulation and Particle Size Distribution in One-Step Emulsion Polymerization of Styrene. *Polymers*. 2016, 8(2): 55.
91. Yamamoto. T., Kawaguchi. K., and Takahashi. Y. Particle Size Control in the Soap-Free Emulsion Polymerization of Styrene by an Oil-Soluble Initiator with a Weakly Acidic Water-Soluble Initiator. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2016, 502: 1–5.
92. Yamamoto. T., Nakayama. M., Kanda. Y., and Higashitani. K. Growth Mechanism of Soap-Free Polymerization of Styrene Investigated by AFM. *Journal of colloid and interface science*. 2006, 297(1): 112–121.
93. Tauer. K., Hernandez. H., Kozempel. S., Lazareva. O., and Nazaran. P. Towards a Consistent Mechanism of Emulsion Polymerization—new Experimental Details. *Colloid and polymer science*. 2008, 286(5): 499–515.

94. Liu. B., Zhang. M., Liu. Y., et al. Particle Nucleation and Growth in the Emulsion Polymerization of Styrene: Effect of Monomer/water Ratio and Electrolyte Concentration. *Journal of Macromolecular Science, Part A*. 2015, 52(2): 147–154.
95. Hawket. B.S., Napper. D.H., and Gilbert. R.G. General Solution to the Smith-Ewart Equation for Emulsion Polymerization Kinetics. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*. 1977, 73: 690–698.
96. Akbarzadeh. A., Rezaei-Sadabady. R., Davaran. S., et al. Liposome: Classification, Preparation, and Applications. *Nanoscale Res Lett*. 2013, 8(1): 102.
97. Bangham. A. Properties and Uses of Lipid Vesicles: An Overview. *Annals of the New York Academy of Sciences*. 1978, 308(1): 2–7.
98. Deamer. D.W. Preparation and Properties of Ether-Injection Liposomes. *Annals of the New York Academy of Sciences*. 1978, 308(1): 250–258.
99. Szoka. F., and Papahadjopoulos. D. Procedure for Preparation of Liposomes with Large Internal Aqueous Space and High Capture by Reverse-Phase Evaporation. *Proceedings of the national academy of sciences*. 1978, 75(9): 4194–4198.
100. Zumbuehl. O., and Weder. H.G. Liposomes of Controllable Size in the Range of 40 to 180 Nm by Defined Dialysis of Lipid/detergent Mixed Micelles. *Biochim. Biophys. Acta*. 1981, 640(1): 252–62.
101. Huang. Z., Li. X., Zhang. T., et al. Progress Involving New Techniques for Liposome Preparation. *asian journal of pharmaceutical sciences*. 2014, 9(4): 176–182.
102. Saunders. L., Perrin. J., and Gammack. D. Ultrasonic Irradiation of Some Phospholipid Sols. *Journal of Pharmacy and Pharmacology*. 1962, 14(1): 567–572.
103. Hope. M., Bally. M., Webb. G., and Cullis. P. Production of Large Unilamellar Vesicles by a Rapid Extrusion Procedure. Characterization of Size Distribution, Trapped Volume and Ability to Maintain a Membrane Potential. *Biochimica et Biophysica Acta (BBA)-Biomembranes*. 1985, 812(1): 55–65.
104. Tan. Y.-C., Cristini. V., and Lee. A.P. Monodispersed Microfluidic Droplet Generation by Shear Focusing Microfluidic Device. *Sensors and Actuators B: Chemical*. 2006, 114(1): 350–356.

105. Lasic. D.D. The Mechanism of Vesicle Formation. *Biochemical Journal*. 1988, 256(1): 1.
106. Hargreaves. W.R., and Deamer. D.W. Liposomes from Ionic, Single-Chain Amphiphiles. *Biochemistry*. 1978, 17(18): 3759–3768.
107. Enoch. H.G., and Strittmatter. P. Formation and Properties of 1000-Å-Diameter, Single-Bilayer Phospholipid Vesicles. *Proceedings of the National Academy of Sciences*. 1979, 76(1): 145–149.
108. Szoka. F., and Papahadjopoulos. D. Comparative Properties and Methods of Preparation of Lipid Vesicles (liposomes). *Annual review of biophysics and bioengineering*. 1980, 9(1): 467–508.
109. Kelly. T.L., and Wolf. M.O. Template Approaches to Conjugated Polymer Micro- and Nanoparticles. *Chemical Society Reviews*. 2010, 39(5): 1526–1535.
110. Prulliere. F., Leem. G., Reisinger. N.C., and Lee. T.R. Preparation and Characterization of Conducting Polymer Shell/core Composite Nanoparticles. *Curr. Top. Colloid Interface Sci*. 2006, 7: 19–34.
111. Shi. X., Briseno. A.L., Sanedrin. R.J., and Zhou. F. Formation of Uniform Polyaniline Thin Shells and Hollow Capsules Using Polyelectrolyte-Coated Microspheres as Templates. *Macromolecules*. 2003, 36(11): 4093–4098.
112. Chen. W., and McCarthy. T.J. Layer-by-Layer Deposition: A Tool for Polymer Surface Modification. *Macromolecules*. 1997, 30(1): 78–86.
113. Decher. G. Layer-by-Layer Assembly (putting Molecules to Work). *Multilayer Thin Films: Sequential Assembly of Nanocomposite Materials, Second Edition*. 2012, 1–21.
114. Decher. G., Hong. J., and Schmitt. J. Buildup of Ultrathin Multilayer Films by a Self-Assembly Process: III. Consecutively Alternating Adsorption of Anionic and Cationic Polyelectrolytes on Charged Surfaces. *Thin solid films*. 1992, 210: 831–835.
115. Schneider. G., and Decher. G. From Functional Core/shell Nanoparticles Prepared via Layer-by-Layer Deposition to Empty Nanospheres. *Nano Letters*. 2004, 4(10): 1833–1839.
116. Ladam. G., Schaad. P., Voegel. J., et al. In Situ Determination of the Structural Properties of Initially Deposited Polyelectrolyte Multilayers. *Langmuir*. 2000, 16(3): 1249–1255.

117. Rempp. P., and Franta. E. Grafting and Branching of Polymers. *Pure and Applied Chemistry*. 1972, 30(1-2): 229–238.
118. Blacha. A., Krukiewicz. K., and Zak. J. The Covalent Grafting of Polymers to the Solid Surface. *Chemik*. 2011, 65(1): 11–19.
119. Barrios. V.A.E., Méndez. J.R.R., Aguilar. N.V.P., Espinosa. G.A., and Rodr'iguez. J.L.D. FTIR-An Essential Characterization Technique for Polymeric Materials. *Infrared Spectroscopy-Materials Science, Engineering and Technology*. 2012, .
120. Bhargava. R. Infrared Spectroscopic Imaging: The next Generation. *Applied spectroscopy*. 2012, 66(10): 1091–1120.
121. Deng. K., Zhang. Y., Liu. Y., Shi. Z., and Wang. Y. Atom Transfer Radical Polymerization of Styrene Catalyzed by Iron II chloride/EDTA. *Chem J Intern*. 2002, 4: 59–65.
122. Patlolla. A., Zunino. J., Frenkel. A.I., and Iqbal. Z. Thermochromism in Polydiacetylene-Metal Oxide Nanocomposites. *Journal of Materials Chemistry*. 2012, 22(14): 7028–7035.
123. Sasaki. S. Handbook of Proton-NMR Spectra and Data. Academic Press; 1985.
124. Choi. H., Bae. Y.M., Yu. G.S., Huh. K.M., and Choi. J.S. Synthesis of Poly(ethylene Glycol)-Polydiacetylene Conjugates and Their Micellar and Chromic Characteristics. *J Nanosci Nanotechnol*. 2008, 8(10): 5104–8.
125. Fujii. S., Matsuzawa. S., Nakamura. Y., et al. Synthesis and Characterization of Polypyrrole- Palladium Nanocomposite-Coated Latex Particles and Their Use as a Catalyst for Suzuki Coupling Reaction in Aqueous Media. *Langmuir*. 2010, 26(9): 6230–6239.
126. Koppel. D.E. Analysis of Macromolecular Polydispersity in Intensity Correlation Spectroscopy: The Method of Cumulants. *The Journal of Chemical Physics*. 1972, 57(11): 4814–4820.
127. Arzensek. D. Dynamic Light Scattering and Application to Proteins in Solutions. *Seminar, Department of Physics, University of Ljubljana*. 2010, 1–18.
128. ISO. 22412. Particle Size Analysis—Dynamic Light Scattering (DLS). 2017, .
129. Sabin. J., Prieto. G., Ruso. J., Hidalgo-Alvarez. R., and Sarmiento. F. Size and Stability of Liposomes: A Possible Role of Hydration and Osmotic Forces. *The European Physical Journal E: Soft Matter and Biological Physics*. 2006, 20(4): 401–408.

130. Hamaker. H. The London—van Der Waals Attraction between Spherical Particles. *physica*. 1937, 4(10): 1058–1072.
131. Verwey. E.J.W., Overbeek. J.T.G., and Overbeek. J.T.G. Theory of the Stability of Lyophobic Colloids. Courier Corporation; 1999.
132. Pfeiffer. C., Rehbock. C., Hühn. D., et al. Interaction of Colloidal Nanoparticles with Their Local Environment: The (ionic) Nanoenvironment around Nanoparticles Is Different from Bulk and Determines the Physico-Chemical Properties of the Nanoparticles. *Journal of The Royal Society Interface*. 2014, 11(96): 20130931.
133. Bourgeat-Lami. E., Guimaraes. T.R., Pereira. A.M.C., et al. High Solids Content, Soap-Free, Film-Forming Latexes Stabilized by Laponite Clay Platelets. *Macromolecular rapid communications*. 2010, 31(21): 1874–1880.
134. Harold. R. An Introduction to Appearance Analysis. *GATFWORLD*. 2001, 13(3): 5–12.
135. De Vasconcelos. C., and Bianchi. R.F. A Blue-Light Dosimeter Which Indicates the Dose Accumulation by a Multicoloured Change of Photodegraded Polymer. *Sensors and Actuators B: Chemical*. 2009, 143(1): 30–34.
136. Ingle. G., and Rudick. L. A Comparison of the MacAdam and the Adams-Nickerson Indexes of Color Differences. *JOSA*. 1953, 43(6): 501–504.
137. International. A. Standard Practice for Computing the Colors of Objects by Using the CIE System. 2006, .
138. Hunter. R.S., and Harold. R.W. The Measurement of Appearance. John Wiley & Sons; 1987.
139. Fagour. S., Thirion. D., Vacher. A., et al. Understanding the Colorimetric Properties of Quinoxaline-Based Pi-Conjugated Copolymers by Tuning Their Acceptor Strength: A Joint Theoretical and Experimental Approach. *RSC Advances*. 2017, 7(36): 22311–22319.
140. Instruments. M. Dynamic Light Scattering: An Introduction in 30 Minutes. 2015. *Documnet No. MRK656-01*. 2016.
141. Ahmadian-Alam. L., Haddadi-Asl. V., Roghani-Mamaqani. H., Hatami. L., and Salami-Kalajahi. M. Use of Clay-Anchored Reactive Modifier for the Synthesis of Poly (styrene-Co-Butyl Acrylate)/clay Nanocomposite via in Situ AGET ATRP. *Journal of Polymer Research*. 2012, 19(1): 9773.

142. Matyjaszewski. K., and Davis. T.P. Handbook of Radical Polymerization. John Wiley & Sons; 2003.
143. Dispenza. C., Grimaldi. N., Sabatino. M.A., Soroka. I.L., and Jonsson. M. Radiation-Engineered Functional Nanoparticles in Aqueous Systems. *Journal of Nanoscience and Nanotechnology*. 2015, 15(5): 3445–3467.
144. Fox Jr. T.G., and Flory. P.J. Second-Order Transition Temperatures and Related Properties of Polystyrene. I. Influence of Molecular Weight. *Journal of Applied Physics*. 1950, 21(6): 581–591.
145. Rieger. J. The Glass Transition Temperature of Polystyrene: Results of a Round Robin Test. *Journal of Thermal Analysis and Calorimetry*. 1996, 46(3-4): 965–972.
146. Kim. S.H., Son. W.K., Kim. Y.J., et al. Synthesis of Polystyrene/poly (butyl Acrylate) Core-Shell Latex and Its Surface Morphology. *Journal of applied polymer science*. 2003, 88(3): 595–601.
147. Wang. W., and Zhang. Q. Synthesis of Block Copolymer Poly (n-Butyl Acrylate)-B-Polystyrene by DPE Seeded Emulsion Polymerization with Monodisperse Latex Particles and Morphology of Self-Assembly Film Surface. *Journal of colloid and interface science*. 2012, 374(1): 54–60.
148. SIDS. O. SIDS Initial Assessment Report For SIAM 10. 2000, .
149. Ballard. N., Hamzehlou. S., and Asua. J.M. Intermolecular Transfer to Polymer in the Radical Polymerization of N-Butyl Acrylate. *Macromolecules*. 2016, 49(15): 5418–5426.
150. Yamamoto. T. Synthesis of Micron-Sized Polymeric Particles in Soap-Free Emulsion Polymerization Using Oil-Soluble Initiators and Electrolytes. *Colloid and Polymer Science*. 2012, 290(11): 1023–1031.
151. Khaddazh. M., Litvinenko. G., and Gritskova. I. A Theoretical Study of the Emulsion Polymerization of Styrene: The Effect of the Initial Dispersion of the System on the Molecular-Mass Distribution of Polystyrene. *Polymer Science Series B*. 2011, 53(5): 283–291.
152. Chapiro. A. Radiation Chemistry of Polymers. *Radiation Research Supplement*. 1964, 4: 179–191.
153. Ulanski. P., and Rosiak. J.M. Polymeric Nano/microgels. *Encyclopedia of nanoscience and nanotechnology*. 2004, 8(871): 845–871.

154. Tauer. K., Ramirez. A.G., and López. R.G. Effect of the Surfactant Concentration on the Kinetics of Oil in Water Microemulsion Polymerization: A Case Study with Butyl Acrylate. *Comptes Rendus Chimie*. 2003, 6(11): 1245–1266.
155. Ishigure. K., O’neill. T., Stahel. E., and Stannett. V. The Radiation-Induced Polymerization and Copolymerization of Butadiene in Emulsion. *Journal of Macromolecular Science—Chemistry*. 1974, 8(2): 353–372.
156. Whitesides. G.M., Kriebel. J.K., and Mayers. B.T. Self-Assembly and Nanostructured Materials. *Nanoscale assembly*. 2005, 217–239.
157. Salgin. S., Salgin. U., and Bahadir. S. Zeta Potentials and Isoelectric Points of Biomolecules: The Effects of Ion Types and Ionic Strengths. *Int. J. Electrochem. Sci*. 2012, 7(12): 12404–12414.
158. Hückel. E., and Debye. P. The Theory of Electrolytes: I. Lowering of Freezing Point and Related Phenomena. *Phys. Z*. 1923, 24: 185–206.
159. Zan. X., Peng. B., Hoagland. D.A., and Su. Z. Polyelectrolyte Uptake by PEMs: Impact of Salt Concentration. *Polymer Chemistry*. 2011, 2(11): 2581–2589.
160. Perry. S.L., Li. Y., Priftis. D., Leon. L., and Tirrell. M. The Effect of Salt on the Complex Coacervation of Vinyl Polyelectrolytes. *Polymers*. 2014, 6(6): 1756–1772.
161. Rojas. O.J., Claesson. P.M., Muller. D., and Neuman. R.D. The Effect of Salt Concentration on Adsorption of Low-Charge-Density Polyelectrolytes and Interactions between Polyelectrolyte-Coated Surfaces. *Journal of colloid and interface science*. 1998, 205(1): 77–88.
162. Hanske. C., Schneider. C., Drechsler. M., Wittmann. A., and Fery. A. Salt-Regulated Attraction and Repulsion of Spherical Polyelectrolyte Brushes towards Polyelectrolyte Multilayers. *Phys Chem Chem Phys*. 2012, 14(12): 4196–203.
163. Knoll. W. Self-Assembled Microstructures at Interfaces. *Current Opinion in Colloid & Interface Science*. 1996, 1(1): 137–143.
164. Caruso. F., and Möhwald. H. Preparation and Characterization of Ordered Nanoparticle and Polymer Composite Multilayers on Colloids. *Langmuir*. 1999, 15(23): 8276–8281.
165. Volodkin. D., and von Klitzing. R. Competing Mechanisms in Polyelectrolyte Multilayer Formation and Swelling: Polycation-Polyanion Pairing vs. Polyelectrolyte-Ion Pairing. *Current Opinion in Colloid & Interface Science*.

- 2014, 19(1): 25–31.
166. Porcel. C., Lavalle. P., Ball. V., et al. From Exponential to Linear Growth in Polyelectrolyte Multilayers. *Langmuir*. 2006, 22(9): 4376–4383.
 167. Kazakova. L.I., Shabarchina. L.I., Anastasova. S., et al. Chemosensors and Biosensors Based on Polyelectrolyte Microcapsules Containing Fluorescent Dyes and Enzymes. *Anal Bioanal Chem*. 2013, 405(5): 1559–68.
 168. Zijlstra. P., van der Molen. K.L., and Mosk. A.P. Spatial Refractive Index Sensor Using Whispering Gallery Modes in an Optically Trapped Microsphere. *Applied physics letters*. 2007, 90(16): 161101.
 169. Kwon. J.H., Song. J.E., Yoon. B., Kim. J.M., and Cho. E.C. Role of Gel to Fluid Transition Temperatures of Polydiacetylene Vesicles with 10, 12-Pentacosadiynoic Acid and Cholesterol in Their Thermochromisms. *Bull. Korean Chem. Soc*. 2014, 35(6): 1809.
 170. Su. Y., Li. J., and Jiang. L. Effect of Amphiphilic Molecules upon Chromatic Transitions of Polydiacetylene Vesicles in Aqueous Solutions. *Colloids Surf B Biointerfaces*. 2004, 39(3): 113–8.
 171. Laouini. A., Jaafar-Maalej. C., Limayem-Blouza. I., et al. Preparation, Characterization and Applications of Liposomes: State of the Art. *Journal of colloid Science and Biotechnology*. 2012, 1(2): 147–168.
 172. Toh. M.-R., and Chiu. G.N. Liposomes as Sterile Preparations and Limitations of Sterilisation Techniques in Liposomal Manufacturing. *Asian Journal of Pharmaceutical Sciences*. 2013, 8(2): 88–95.
 173. Cox. M.M., and Nelson. D.L. Principles of Biochemistry. WH Freeman; 2008.
 174. Van Swaay. D., and others. Microfluidic Methods for Forming Liposomes. *Lab on a Chip*. 2013, 13(5): 752–767.
 175. Tominaga. S., and Wandell. B.A. Standard Surface-Reflectance Model and Illuminant Estimation. *JOSA A*. 1989, 6(4): 576–584.
 176. Walde. P., and Ichikawa. S. Enzymes inside Lipid Vesicles: Preparation, Reactivity and Applications. *Biomolecular engineering*. 2001, 18(4): 143–177.
 177. Pellegrino. T., Kudera. S., Liedl. T., et al. On the Development of Colloidal Nanoparticles towards Multifunctional Structures and Their Possible Use for Biological Applications. *small*. 2005, 1(1): 48–63.

178. Petersen. S., Barchanski. A., Taylor. U., et al. Penetratin-Conjugated Gold Nanoparticles- Design of Cell-Penetrating Nanomarkers by Femtosecond Laser Ablation. *The Journal of Physical Chemistry C*. 2010, 115(12): 5152–5159.
179. Szilagyí. I., Trefalt. G., Tiraferri. A., Maroni. P., and Borkovec. M. Polyelectrolyte Adsorption, Interparticle Forces, and Colloidal Aggregation. *Soft Matter*. 2014, 10(15): 2479–502.
180. Karabacak. R.B., and Türk. H. Preparation of PS Colloids with DMA and MMA Comonomers and Suitability of P (S/DMA) for Colloidal Silica Deposition. *Journal of Macromolecular Science, Part A*. 2012, 49(8): 680–688.
181. Johnston. S.F. A History of Light and Colour Measurement: Science in the Shadows. CRC Press; 2015.
182. Ji. E.-K., Ahn. D.J., and Kim. J.-M. The Fluorescent Polydiacetylene Liposome. *Bulletin-Korean Chemical Society*. 2003, 24(5): 667–670.
183. Small. D., Penkett. S., and Chapman. D. Studies on Simple and Mixed Bile Salt Micelles by Nuclear Magnetic Resonance Spectroscopy. *Biochimica et Biophysica Acta (BBA)-Lipids and Lipid Metabolism*. 1969, 176(1): 178–189.
184. Ernst. R.R., Bodenhausen. G., Wokaun. A., and others. Principles of Nuclear Magnetic Resonance in One and Two Dimensions. Clarendon Press Oxford; 1987.
185. Mattler. S.J. Studying Topochemistry of Solid State Photoreactions Using Solid State Nuclear Magnetic Resonance Spectroscopy. Washington University in St. Louis; 2012.
186. Walsh. S.P. Investigations of the Structures and Molecular Processes in Polar Langmuir-Blodgett Superlattices. 1992, .
187. Murphy. M.K., Kovács. A., Miller. S.D., and McLaughlin. W.L. Dose Response and Post-Irradiation Characteristics of the Sunna 535-Nm Photo-Fluorescent Film Dosimeter. *Radiation Physics and Chemistry*. 2003, 68(6): 981–994.
188. A. Kovacs. M.B.L.W. Characterization of Fluorimetric, Calorimetric, Oscillometric and Radiochromic Dye Film Dosimeters Under Processing Conditions at Electron Accelerators. *Dosimetry for radiation processing*. 2000.