

**SYNTHESIS OF ABA TYPE TRIBLOCK COPOLYMERS
BY RING OPENING POLYMERIZATION AND
INVESTIGATION OF THE STRUCTURE PROPERTY
BEHAVIOR OF THE COPOLYMERS**

by

Mehmet Işık

**A Thesis Submitted to the
Graduate School of Engineering
in Partial Fulfillment of the Requirements for
the Degree of**

**Master of Science
in
Materials Science and Engineering Program**

Koç University

August 2011

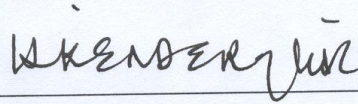
Koç University
Graduate School of Sciences and Engineering

This is to certify that I have examined this copy of a master's thesis by

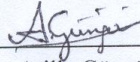
Mehmet Işık

and have found that it is complete and satisfactory in all respects,
and that any and all revisions required by the final
examining committee have been made.

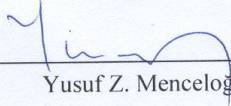
Committee Members:



İskender Yılğör, Ph. D. (Advisor)



Atilla Güngör, Ph. D.



Yusuf Z. Menciloğlu, Ph. D.

Date:

Aug. 15, 2011

ABSTRACT

Poly(ϵ -caprolactone)–polydimethylsiloxane–poly(ϵ -caprolactone) (PCL-PDMS-PCL) and poly(ϵ -caprolactone)-poly(ethylene oxide)-poly(ϵ -caprolactone) (PCL-PEO-PCL) triblock copolymers having a wide range of mid-block and end-block lengths (1000 – 32000 g/mol) were synthesized by the ring-opening polymerization of caprolactone using functionally terminated PDMS and PEO oligomers.

Effect of the polymer composition and the average lengths of the mid and end blocks on;

- (i) extent of microphase separation and polymer morphology,
- (ii) crystallization of PCL segments
- (iii) thermal properties of copolymers and
- (iv) surface properties of the polymers, were investigated.

Materials were characterized by FTIR spectroscopy, gel permeation chromatography (GPC), atomic force microscopy (AFM), temperature-dependent optical microscopy (OM), X-Ray Diffraction analyses (XRD), differential scanning calorimetry (DSC) and static water contact angle measurements. PCL-PDMS-PCL copolymers displayed well microphase separated morphologies. The extent of microphase separation was strongly dependent on the lengths of both PCL and PDMS segments. It was seen that the hydrophobicity of the copolymer surfaces was enhanced with increasing PDMS molecular weight. Crystallization of PCL blocks was affected by the amount and the molecular weight of the PDMS mid-block as revealed by DSC, OM and XRD analyses. PCL-PEO-PCL copolymers exhibited competitive crystallization due to presence of two crystallizable segments within the same copolymer. DSC analysis showed the presence of different crystal structures which were reflected as multiple melting peaks in the thermograms. PCL end-blocks overwhelmed the crystallization of PEO mid-block and the extent of suppression of PEO crystallization increased with increasing PCL fraction as determined by XRD and OM.

ÖZET

Farklı orta blok ve uç blok uzunluklarına sahip poli(kaprolakton)-polidimetilsilikon-poli(kaprolakton) (PCL-PDMS-PCL) ve poli(kaprolakton)-poli(etilen oksit)-poli(kaprolakton) (PCL-PEO-PCL) üç bloklu kopolimerleri sentezlendi ve karakterize edildi. Orta blok ve uç blok uzunluğunun mikrofaz ayırımına, poli(kaprolakton) kristallenmesine ve polimerin yüzey özelliklerine olan etkileri araştırıldı. Malzemelerin karakterizasyonu için atomik kuvvet mikroskopu (AFM), optik mikroskopu (OM), diferansiyel taramalı kalorimetre (DSC) ve X-ışını kırınımı (XRD) teknikleri uygulandı. PCL-PDMS-PCL kopolimerleri çok iyi mikrofaz ayırımı gösterdi. Mikrofaz ayırımının hem PCL hem de PDMS bloklarının uzunluğuna bağlı olduğu anlaşıldı. PDMS zincirlerinin ortalama molekül ağırlığı arttıkça kopolimer yüzeylerinin su iticiliğinin arttığı gözlemlendi. PCL bloklarının kristallenmesi PDMS orta bloğundan etkilendi ve bu durum OM ve XRD analizleriyle gösterildi. İki tane kristalleşebilen blok varlığından dolayı, PCL-PEO-PCL kopolimerleri yarışmalı kristallenme gösterdiler. Bu özellikten dolayı DSC ile çoklu erime noktaları tespit edildi. PCL uç bloklarının kristallenmesi, PEO orta bloğunun kristallenmesini baskıladı ve XRD ve OM analizleriyle gösterildiği gibi bu etki PCL fraksiyonu arttıkça daha da arttı.

ACKNOWLEDGEMENTS

I would first like to express my sincere gratitude to my thesis advisors Prof. İskender Yılğör and Emel Yılğör for their help and guidance in all aspects during my undergraduate and graduate research. It was a precious opportunity for me to study and learn in their research team under their supervision.

I also would like to thank to all faculty members of Materials Science and Engineering program at Koç University for their help and teaching throughout my graduate life, especially to Asst. Prof. Özgür Birer and Asst. Prof. Uğur Ünal for their very kind approach.

I especially would like to thank to Sevilay Bilgin for her endless help and support throughout my graduate life. I also like to thank to Sedef Pırıl Ertem for her kind friendship and all current and graduate members of Polymer Research Laboratory for providing me an enjoyable environment.

Lastly, I would like to thank to my family and friends from home, who always supported me in the decisions that I have made.

TABLE OF CONTENTS

List of Tables	ix
List of Figures	x
Nomenclature	xvii
Chapter 1: Introduction	1
1.1 Block Copolymers.....	2
1.1.1 Types of Block Copolymers.....	5
1.1.1.1 Diblock Copolymers.....	6
1.1.1.1.1 Synthesis.....	6
1.1.1.2 Triblock Copolymers	11
1.1.1.2.1 Synthesis of Symmetrical Triblock Copolymers.....	11
1.1.1.2.2 Synthesis of Nonsymmetrical Triblock Copolymers.....	16
1.1.1.3 Morphology and Properties of Block Copolymers.....	19
1.2 Principles of Ring Opening Polymerization.....	28
1.2.1 General Mechanisms in Ring Opening Polymerization.....	29
1.2.1.1 Anionic Ring Opening Polymerization.....	29
1.2.1.2 Cationic Ring Opening Polymerization.....	32
1.2.1.3 Radical Ring Opening Polymerization.....	34
1.2.1.4 Organocatalytic Ring Opening Polymerization.....	36
1.3 Applications of Block Copolymers.....	37
1.3.1 Biological Applications.....	38
1.3.2 Nanofabrication.....	40
Chapter 2: Experimental	45
2.1 Materials.....	45
2.2 Reaction Procedures.....	47

2.2.1 Synthesis of polycaprolactone-polydimethylsiloxane-polycaprolactone (PCL-PDMS-PCL) Triblock Copolymers.....	47
2.2.2 Synthesis of polycaprolactone-poly(ethylene oxide)-polycaprolactone (PCL-PEO-PCL) Triblock Copolymers.....	48
2.3 Characterization Methods.....	51
2.3.1 Spectroscopic Analysis.....	51
2.3.2 Spin Coating.....	51
2.3.3 Gel Permeation Chromatography (GPC) Analysis.....	51
2.3.4 Static Water Contact Angle (SWCA) Measurements.....	52
2.3.5 Optical Microscopy (OM) Analysis.....	52
2.3.6 Atomic Force Microscopy (AFM) Analysis.....	52
2.3.7 X-Ray Diffraction (XRD) Analysis.....	53
2.3.8 Differential Scanning Calorimetry (DSC) Analysis	53
Chapter 3: Results and Discussion	54
3.1. PCL-PDMS-PCL Triblock Copolymers.....	55
3.1.1 Monitoring the Polymerization Reactions by FTIR Spectroscopy.....	56
3.1.2 Gel Permeation Chromatography Characterization (GPC) of PCL-PDMS-PCL Block Copolymers	57
3.1.3 Morphologies of PCL-PDMS-PCL Block Copolymers.....	59
3.1.4 Differential Scanning Calorimetry Analysis of PCL-PDMS-PCL Triblock Copolymers	76
3.1.5 Optical Microscopic Investigation of the Crystallization of PCL-PDMS-PCL Triblock Copolymers	77
3.1.6 Surface Properties of PCL-PDMS-PCL Block Copolymers.....	88
3.1.7 X-Ray Diffraction Analysis of PCL-PDMS-PCL Block Copolymers.....	91
3.2 PCL-PEO-PCL Triblock Copolymers.....	96
3.2.1 Gel Permeation Chromatography Characterization of PCL-PEO-PCL Block Copolymers.....	97
3.2.2 Differential Scanning Calorimetry Analysis of PCL-PEO-PCL Block Copolymers...	99
3.2.3 Crystallization and Crystal Structures of PCL-PEO-PCL Copolymers.....	102

3.2.4 X-Ray Diffraction Analysis of PCL-PEO-PCL Block Copolymers.....	128
Chapter 4: Conclusions	132
Bibliography	134
Vita	144

LIST OF TABLES

Chapter 1: Introduction

Table 1.1 Examples of AB diblock copolymers by sequential addition of monomers.....	7
--	---

Chapter 2: Experimental

Table 2.1 Chemical structures of reactants used during the synthesis.....	46
--	----

Table 2.2. Characteristics of the starting oligomers.....	46
--	----

Chapter 3: Results and Discussion

Table 3.1 Composition and yields of PCL-PDMS-PCL copolymers synthesized.....	56
---	----

Table 3.2 Solubility parameters used to calculate the interaction parameter.....	60
---	----

Table 3.3 Calculated χ_N values for PCL-PDMS-PCL block copolymers.....	61
--	----

Table 3.4 The solvents used to dissolve PCL-PDMS-PCL copolymers for AFM analysis.....	64
--	----

Table 3.5 Static water contact angle values of PCL-PDMS-PCL block copolymers.....	89
--	----

Table 3.6 Compositions and yields of PCL-PEO-PCL copolymers synthesized.....	97
---	----

Table 3.7 Solvents and homopolymers and their solubility parameters.....	102
---	-----

LIST OF FIGURES

Chapter 1: Introduction

Figure 1.1 Phase separation in a multiblock copolymer having hard and soft domains.....	4
Figure 1.2 Different architectures of block copolymers.....	5
Figure 1.3 Sequential monomer addition for the synthesis of AB diblock copolymer.....	6
Figure 1.4 Simple synthesis route for the production PS-PB copolymer.....	8
Figure 1.5 Anionic copolymerization of styrene and ethylene oxide.....	9
Figure 1.6 ATRP synthesis of 2-[(methacryloyloxy)ethyl]trimethylammonium chloride based diblock copolymers via sequential monomer addition	10
Figure 1.7 Sequential addition synthesis of ABA symmetrical block copolymers.....	12
Figure 1.8 Synthesis of PS-PI-PS copolymer through coupling of living AB chains.....	13
Figure 1.9 Synthesis of symmetrical ABA block copolymer via dilithium initiator.....	14
Figure 1.10 Synthesis of symmetrical ABA triblock copolymer having perfluorinated outer blocks and styrene inner block via ATRP	15
Figure 1.11 Synthesis of ABC block copolymer through sequential monomer addition.....	16
Figure 1.12 Synthesis of PS-PI-P2VP block copolymer via anionic sequential polymerization.....	17
Figure 1.13 ATRP synthesis pathway for the preparation of PS-PtBA-PMMA terblock copolymer	18
Figure 1.14 Block copolymer morphologies. Morphologies are shown in increasing red-block (decreasing blue) composition of a copolymer of red-blue monomers. (S) BCC spheres, (C) hexagonally packed cylinders, (G) gyroid, (L) lamellae	22
Figure 1.15 A) Microphase separation in PS-PB-PS triblock copolymer B) Change in orientation of blocks upon heat treatment	23

Figure 1.16 Phase separated morphologies of LDL symmetrical block copolymers.....	24
Figure 1.17 Polarized optical microscope images of PCL-PEO-PCL triblock copolymers	25
Figure 1.18 TEM images of SBM terblock copolymers in various solvents.....	26
Figure 1.19 SEM images of SVT terblock copolymers.....	27
Figure 1.20 Commercially available polymers obtained via ring opening polymerization	28
Figure 1.21 General anionic ROP mechanism	29
Figure 1.22 Anionic ring opening polymerization of ϵ -caprolactone	30
Figure 1.23 Reaction mechanism for the synthesis of poly(ϵ -caprolactam).....	32
Figure 1.24 General cationic ROP reaction mechanism.....	33
Figure 1.25 Cationic ROP of THF through SN2 mechanism	34
Figure 1.26 Radical ring opening polymerization of vinyl cyclopropane	35
Figure 1.27 Polymerization of rac-lactide with PEO-(NH ₂) ₂ as the initiator in the presence of 1 as the catalyst	37
Figure 1.28 SEM images of PS-PDMS thin films. a) Exposure to O ₂ plasma for 1 min	41
Figure 1.29 AFM height images of a) PLA-PDMS-PLA thin film b) After exposure to 20s SF ₆ plasma	42
Figure 1.30 PS-PLA block copolymer a) fast evaporation resulting in perpendicular cylinders b) parallel cylinder orientation due to slow evaporation	43

Chapter 2: Experimental

Figure 2.1 Reaction scheme for the synthesis of poly(ϵ -CL)-PDMS-poly(ϵ -CL) triblock Copolymers	49
Figure 2.2 Reaction scheme for the synthesis of poly(ϵ -CL)-PEO-poly(ϵ -CL) triblock copolymers	50

Chapter 3: Results and Discussion

Figure 3.1 FTIR spectra of 3-3-3 PCL-PDMS-PCL copolymer	57
Figure 3.2 GPC signals of three different copolymer compositions	58
Figure 3.3 Two different orientations of ABA molecules two form the lamella a) Lamellae perpendicular b) Lamellae parallel to the substrate	62
Figure 3.4 Possible orientations of molecules on the substrate surface	63
Figure 3.5 3x3 μm AFM images of PCL-PDMS-PCL copolymer with 2-2.5-2 composition ..	65
Figure 3.6 1.5x1.5 μm AFM phase and height images of PCL-PDMS-PCL with 3-3-3 composition	66
Figure 3.7 Height profile of PCL-PDMS-PCL copolymer with a composition of 3-3-3	67
Figure 3.8 Possible cylinder orientation of PCL-PDMS-PCL copolymer	68
Figure 3.9 Semi-cylindrical orientation of PCL-PDMS-PCL copolymer	68
Figure 3.10 3x3 μm AFM a) phase and b) height images of 6-11-6 copolymer in hard- tapping mode	70
Figure 3.11 10x10 μm AFM a) phase and b) height images of 6-11-6 copolymer in soft tapping mode	71
Figure 3.12 Height profile of 6-11-6 copolymer surface measured from 10x10 μm AFM height image	71
Figure 3.13 10x10 μm AFM images are provided for PCL-PDMS-PCL copolymer of 16-32-16 composition	72
Figure 3.14 3x3 μm AFM a) phase and b) height images of 16-32-16 copolymer	73
Figure 3.15 Height profile of PCL-PDMS-PCL copolymer with 16-32-16 composition	74
Figure 3.16 3x3 μm AFM a) phase and b) height images of 32-32-32 copolymer	74

Figure 3.17 Height profile of 32-32-32 PCL-PDMS-PCL copolymer	75
Figure 3.18 DSC thermograms of three different mid-block lengths of PCL-PDMS-PCL copolymers at a heating rate of 20°C/min	76
Figure 3.19 a) non-polarized and b) polarized OM images of homo-PCL at 10X magnification	78
Figure 3.20 a) Non-polarized and b) polarized OM images of 1-1-1 copolymer at 5X magnification	79
Figure 3.21 a) Non-polarized and b) polarized OM images of 1-3-1 copolymer at 10X magnification	80
Figure 3.22 a) Non-polarized and b) polarized OM images of 3-3-3 copolymer at 20X magnification	81
Figure 3.23 a) Non-polarized and b) polarized OM images of 3-11-3 PCL-PDMS-PCL copolymer at 10X magnification	82
Figure 3.24 a) Non-polarized and b) polarized OM images of 6-11-6 PCL-PDMS-PCL copolymer at 10X magnification	83
Figure 3.25 a) Non-polarized and b) polarized OM images of 3-32-3 copolymer at 10X magnification	84
Figure 3.26 a) Non-polarized and b) polarized OM images of 6-32-6 PCL-PDMS-PCL copolymer	85
Figure 3.27 a) Non-polarized and b) polarized OM images of 16-32-16 PCL-PDMS-PCL copolymer	86
Figure 3.28 a) Non-polarized and b) polarized OM images of 32-32-32 PCL-PDMS-PCL copolymer	87
Figure 3.29 Sessile water drops on the PCL-PDMS-PCL triblock copolymer surfaces with compositions: (a) 1-1-1, (b) 2-2.5-2, (c) 1-3-1, (d) 3-3-3, (e) 3-11-3, (f) 6-11-6, (g) 3-32-3, (h) 6-32-6, (i) 16-32-16, (j) 32-32-32, (k) virgin PCL	89

Figure 3.30 XRD pattern of homo-PCL showing the two ‘*’ labeled major crystal	91
Figure 3.31 XRD diagrams of PCL-PDMS-PCL copolymers for different copolymer compositions	92
Figure 3.32. XRD patterns of 3-11-3 and 6-11-6 PCL-PDMS-PCL copolymers	93
Figure 3.33 XRD patterns of 3-32-3, 16-32-16 and 32-32-32 PCL-PDMS-PCL copolymers	94
Figure 3.34. XRD diagrams of 3-3-3, 3-11-3 and 3-32-3 PCL-PDMS-PCL copolymers	95
Figure 3.35 GPC signals of three different copolymer compositions	98
Figure 3.36 DSC thermograms of 2-2-2, 2-4-2, and 4-4-4 PCL-PEO-PCL triblock Copolymers	100
Figure 3.37. DSC thermograms of 4-8-4, 8-8-8 and 16-8-16 triblock copolymers	101
Figure 3.38 OM images of homo-PCL and homo-PEO4K at 10X magnification	104
Figure 3.39 Non-polarized optical images of 2-2-2 copolymer crystallized from 20% solid solution of a) THF b) THF-DMF (1:1) c) chloroform and d) DMF at 10X magnification	105
Figure 3.40 a) Non-polarized and b) polarized OM images of 2-2-2 copolymer spincoated from DCM-IPA (1:1 by w) mixture	106
Figure 3.41 Non-polarized 10X magnified OM images of 2-2-2 copolymer on heating stage; heating process a) 24.5°C, b) 55.6°C, c) 63.1°C, cooling process d) 55.1°C and e) 38.9°C	107
Figure 3.42 Non-polarized optical images of 2-4-2 copolymer crystallized from 20% solid solution of a) THF b) THF-DMF (1:1) c) DMF and d) toluene at 10X magnification	108
Figure 3.43. a) Non-polarized and b) polarized OM images of 2-4-2 copolymer spincoated from chloroform solution at 10X magnification	110
Figure 3.44 Non-polarized 20X magnified OM images of 2-4-2 copolymer on heating stage;	

heating process a) 25.0°C, b) 66.3°C, c) 67.3°C, d) 68.0°C cooling process e) 59.0°C and f) 52.0°C	111
Figure 3.45 30x30 µm AFM a) phase and b) height images of 2-4-2 copolymer	112
Figure 3.46 Non-polarized optical images of 4-4-4 copolymer crystallized from 20% solid solution of a) THF, b) DMF, c) IPA-DCM (1:1) and d) toluene at 10X magnification	113
Figure 3.47 a) Non-polarized and b) polarized OM images of 4-4-4 copolymer spincoated from chloroform solution at 20X magnification	114
Figure 3.48 Non-polarized 20X magnified OM images of 4-4-4 copolymer on heating stage at a rate of 3°C/min; heating process a) 35.7°C, b) 63.4°C, c) 66.3°C, d) 68.1°C cooling process e) 62.7°C and f) 37.6°C	115
Figure 3.49 3x3 µm AFM a) phase and b) height images of 4-4-4 PCL-PEO-PCL copolymer	116
Figure 3.50 Non-polarized optical images of 4-8-4 copolymer crystallized from 20% solid solution of a) DMF b) IPA-DCM (1:1) and C) toluene at 10X magnification	117
Figure 3.51 a) Non-polarized and b) polarized OM images of 4-8-4 copolymer spincoated from chloroform solution at 10X magnification	118
Figure 3.52 Non-polarized 20X magnified OM images of 4-8-4 copolymer on heating stage; heating process a) 29.0°C, b) 69.3°C, c) 71.9°C, d) 72.4°C cooling process e) 65.0°C and f) 25.6°C	119
Figure 3.53 Non-polarized optical images of 8-8-8 copolymer crystallized from 20% solid solution of a) chloroform, b) DMF, c) IPA-DCM (1:1) and d) toluene at 10X magnification	120
Figure 3.54 a) Non-polarized and b) polarized OM images of 8-8-8 copolymer spincoated from THF solution at 20X magnification	121
Figure 3.55 Non-polarized 20X magnified OM images of 8-8-8 copolymer on heating stage; heating process a) 27.0°C, b) 66.0°C, c) 71.1°C, d) 73.1°C cooling process e)	

63.0°C and f) 50.3°C	122
Figure 3.56 30x30 μm AFM images of 8-8-8 copolymer taken from different locations on the sample surface a,c) phase and b,d) height images	123
Figure 3.57 Non-polarized optical images of 16-8-16 copolymer crystallized from 20% solid solution of a) toluene (10X), b) IPA-DCM (1:1) (10X), c) DMF (5X) and d) chloroform (10X)	124
Figure 3.58 a) Non-polarized and b) polarized OM images of 16-8-16 copolymer spincoated from THF solution at 50X magnification	125
Figure 3.59 Non-polarized 20X magnified OM images of 16-8-16 copolymer on heating Stage	126
Figure 3.60 30x30 μm AFM a,c) phase and b,d) height images of 16-8-16 copolymer scanned from different locations on the sample surface	127
Figure 3.61. XRD patterns of PEO having three different molecular weights and PCL for comparison	129
Figure 3.62 XRD patterns of PCL-PEO-PCL block copolymers of three different compositions	130
Figure 3.63 XRD diagrams of 4-8-4, 8-8-8 and 16-8-16 copolymer compositions	131

NOMENCLATURE

1	1,3,4-triphenyl-4,5-dihydro-1H-1,2,4-triazol-5-ylidene
δ	solubility parameter
χ	interaction parameter
AFM	Atomic Force Microscopy
BCC	Body centered cubic
CL	ϵ -Caprolactone
DCM	Dichloromethane
DMF	Dimethyl formamide
DSC	Differential Scanning Calorimetry
FDA	Food and Drug Administration
FTIR	Fourier transform infrared spectroscopy
GPC	Gel Permeation Chromatography
IPA	Isopropyl alcohol
M_n	Number average molecular weight
N	Degree of polymerization
OM	Optical microscopy
P2VP	Poly(2-vinylpyridine)
PB	Polybutadiene
PCL	Poly(ϵ -caprolactone)
PDI	Polydispersity Index
PDMS	Poly(dimethylsiloxane)
PEO	Poly(ethylene oxide)
PI	Polyisoprene
PLA	Poly(L-lactide)
PMMA	Poly(methyl methacrylate)
PPO	Poly(propylene oxide)
PS	Polystyrene
PSLi	Polystyrene-lithium
R_g	Radius of gyration
RAFT	Radical addition fragmentation transfer

ROP	Ring opening polymerization
SEM	Scanning electron microscopy
SWCA	Static water contact angle
TEM	Transmission electron microscopy
THF	Tetrahydrofuran
XRD	X-Ray Diffractometry

Chapter 1

INTRODUCTION

Triblock copolymers are interesting materials which combine properties of two different polymers on the same macromolecule. As a result they have received widespread attention both from academic and industrial researchers since their discovery about 50 years ago. Recently, biocompatible and biodegradable triblock copolymers obtained by ring-opening polymerization, which have potential use in various biomedical applications, such as; scaffolds in tissue engineering, matrix resins for time-release drugs, become been the focus of attention.

The major goal of this study was to investigate the synthesis, characterization and structure-morphology-property behavior of symmetrical triblock copolymers obtained by ring-opening polymerization. For this purpose, we mainly focused on symmetrical triblock copolymers, where end blocks were poly (ϵ -caprolactone) (PCL) and center or middle blocks were either poly(dimethylsiloxane) (PDMS) or poly(ethylene oxide) (PEO). A series of PCL-PEO-PCL and PCL-PDMS-PCL triblock copolymers, with block lengths varying

between 1,000 and 32,000 g/mol were synthesized, characterized and their morphologies were investigated together with their bulk properties. The properties of homopolymers were also investigated for comparison.

The introduction part of the dissertation was planned to cover a literature search on;

- (i) types of block copolymers, basic synthetic strategies and properties of various block copolymers,
- (ii) basic principles and types of ring opening polymerization of cyclic monomers,
- (iii) applications of block copolymers in different fields.

1.1. Block Copolymers

Block copolymers are a class of polymers in which there are at least two different constituent blocks which are linked together by covalent bonds [1]. Block copolymers having two different types of blocks are named as diblock copolymers. Similarly block copolymers having three constituent blocks are called triblock copolymers. Depending on the composition and the intrinsic properties of constituent blocks, block copolymers display a wide range of periodic nanostructures such as spheres, cylinders and lamellas, which are extensively discussed in the literature [2]. Block copolymers also display very different properties compared to alternating and statistical copolymers, as a result of their microphase separated morphologies. The property which is present in the corresponding homopolymer is interestingly displayed by each type of block within the block copolymer.

This phenomenon is observed unless the constituent blocks are too short to be able to display their self intrinsic properties [3]. Another interesting class of block copolymers is multiblock or segmented copolymers in which there are chemically linked alternating hard and soft segments. Segmented polyurethanes, polyamides, polyesters can be listed in this class [4]. One of the most important properties displayed by multiblock copolymers is strong segregation within the segments, which in turn leads to a microphase separated morphology, where hard domains are generally well dispersed within the soft matrix [5]. The main reasons for phase separation include; (i) hydrogen bonding that takes place between the hard domains, (ii) crystallization of the hard domains, or (iii) both hydrogen bonding and crystallization. The microphase separated morphology induced by strong incompatibility between hard and soft domains is illustrated in Figure 1.1., as well-dispersed hard domains in the matrix of soft segments. The influence of this microphase separated morphology is reflected in the thermal and mechanical properties of these materials. While hard domains contribute to the mechanical strength and thermal stability, soft domains make up the flexibility of the material. Therefore, the properties of these materials are strongly dependent on chemical structure and composition [4].

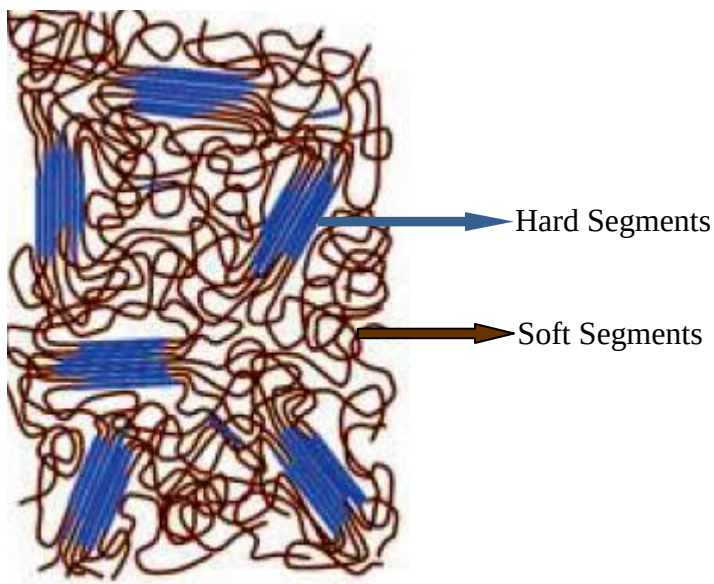


Figure 1.1. Phase separation in a multiblock copolymer having hard and soft domains [6].

Due to very interesting properties of block copolymers, they are subjected to intensive research over the past few decades [7]. There are various synthetic pathways for the production of block copolymers. Controlled free radical polymerization, polymerization techniques such as anionic and cationic polymerizations, step growth polymerization are the well known synthetic routes for the production of block copolymers with controlled architecture and block lengths. Even though anionic and controlled radical polymerization methods are the widely accepted techniques, depending on the monomer type different synthetic approaches can be applied [8].

1.1.1. Types of Block Copolymers

Polymers are long chain molecules in which there are large numbers of repeat units. Sometimes the desired properties are given by mixing two different polymer types. Those physical mixtures are called as blends. However, one major drawback of physically mixed polymer blends is possibility of macrophase separation leading to poor performance, if the constituent polymers are strongly incompatible. Therefore, it is mostly intended to have a chemical bond between the constituent blocks in order not to have macrophase segregation [9]. Different architectures of block copolymers can be synthesized. These structures can vary from simple diblock copolymers to complex mixed multiarm star block copolymers. Possible architectures of block copolymers are schematically shown in Figure 1.2 [8].

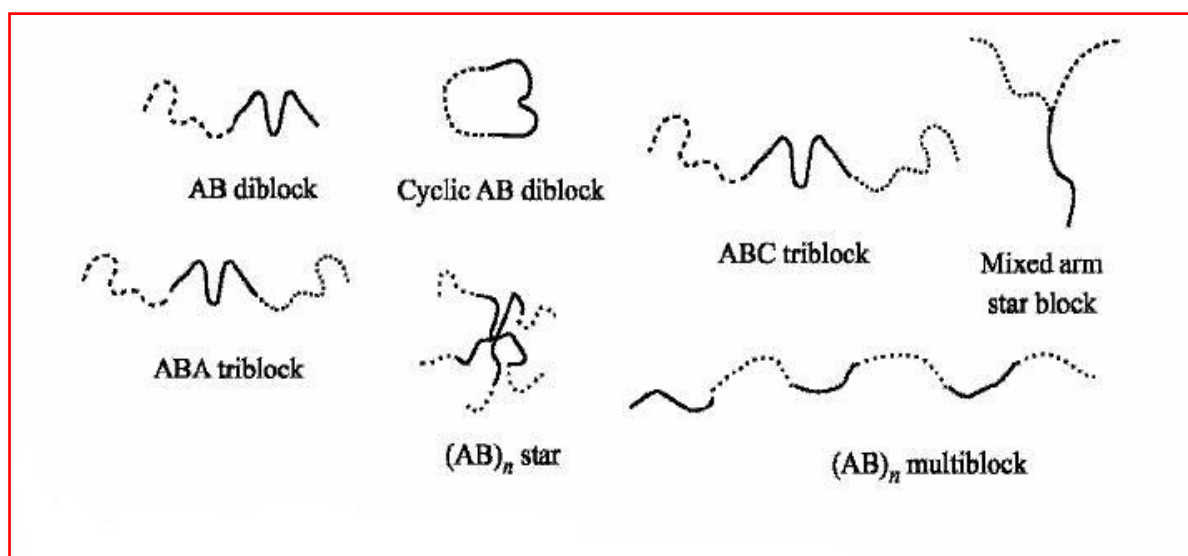


Figure 1.2. Different architectures of block copolymers

1.1.1.1. Diblock Copolymers

1.1.1.1.1. Synthesis

AB diblock copolymers are the simplest linear block copolymers with two different constituent blocks, which are chemically linked through covalent bonding [10]. Well defined AB diblock copolymers can be synthesized by anionic polymerization or controlled free radical polymerization (such as ATRP) using sequential monomer addition. First, one of the monomers is polymerized and then the other monomer is added for copolymerization. The basic formulation is given in Figure 1.3.

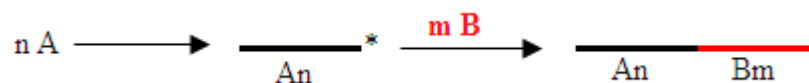


Figure 1.3. Sequential monomer addition for the synthesis of AB diblock copolymer.

(* represents the reactive site for copolymerization).

In order to make such a reaction proceed properly, (i) the first monomer carbanion must be able to initiate the copolymerization of the second monomer, meaning that the first monomer should form a carbanion, which is a stronger nucleophile than that of the second monomer, (ii) the rate of propagation of monomer B must be less than the rate of polymerization of the second monomer by the anion of the first, therefore a narrow molecular weight distribution can be obtained for the second block, (iii) the second monomer purity must be very high in order to prevent the termination of first monomer

reactive sites [10]. The anionic copolymerization of block copolymers were first conducted in as early as 1956 [11]. There are numerous examples of AB diblock copolymers which are synthesized through sequential monomer addition as shown in Table 1.1.

Table 1.1. Examples of AB diblock copolymers synthesized by sequential addition of monomers [10].

1 st monomer	2 nd monomer	Reference
Styrene	Isoprene	[12]
	Butadiene	[13]
	Cyclohexadiene	[14]
	Methylmethacrylate	[15]
	<i>tert</i> -Butyl methacrylate	[15]
	<i>tert</i> -Butyl acrylate	[16]
	2,3-glycidyl methacrylate	[17]
	2-Vinylpyridine	[18]
	Ethylene Oxide	[19]
	ϵ -caprolactone	[20]
	Hexamethylcyclotrisiloxane	[21]
α -Methyl styrene	Butadiene	[22]
Isoprene	2-Vinyl pyridine	[23]
	Ethylene Oxide	[24]
	Hexamethylcyclotrisiloxane	[25]
Butadiene	ϵ -caprolactone	[26]
	Ethylene Oxide	[24]
Methyl methacrylate	<i>tert</i> -Butyl methacrylate	[27]
2-Vinyl pyridine	ϵ -caprolactone	[28]
	Ethylene Oxide	[29]

As can be seen from Table 1.1, plenty of research is carried out for sequential addition synthesis of AB diblock copolymers of styrene monomer. Copolymers of styrene monomer with isoprene or butadiene have been synthesized through anionic polymerization with narrow molecular weight and compositional distributions. A simple synthesis route is given in Figure 1.4 [30,31]. Styrene is first polymerized in the presence of sec-butyl lithium catalyst and then the diene is added to the reaction mixture. It is well known that dienes are efficiently polymerized in the hydrocarbon solvents in the presence of polystyrene-lithium (PSLi) active centers.

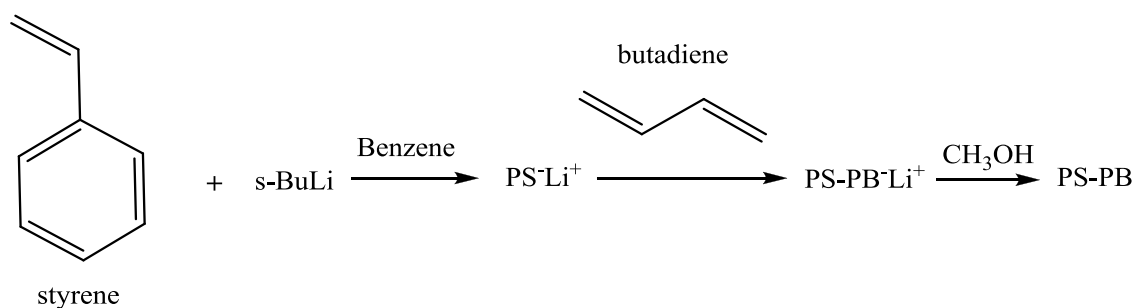


Figure 1.4. Simple synthesis route for the production PS-PB copolymer.

Prescribed anionic polymerization of diblock copolymers can be applied to wide range of monomers such as dienes, styrenes, acrylates, cyclic ethers and lactones [3]. Polystyrene-poly(ethylene oxide) diblock copolymers were prepared through anionic polymerization in

the presence of different types of initiators having Na^+ or K^+ counterions [31,32]. The reaction scheme is given in Figure 1.5.

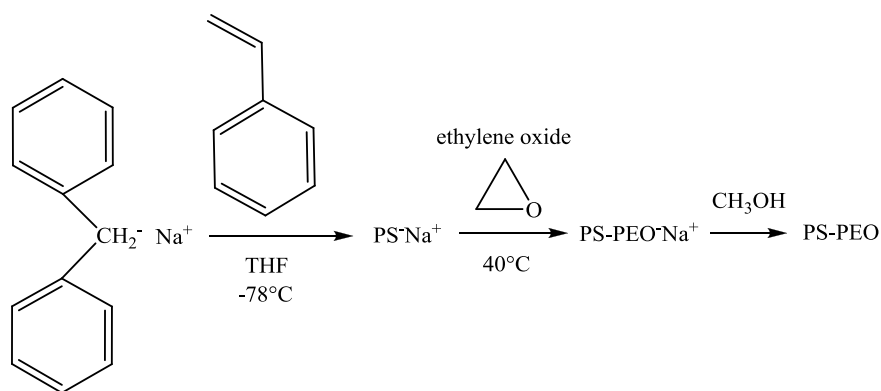


Figure 1.5. Anionic copolymerization of styrene and ethylene oxide.

Another well-known and somewhat recent method for the synthesis of diblock copolymers is living radical polymerization in which a dynamic equilibrium between growing free radicals and dormant species is established. Atom-transfer radical polymerization (ATRP) is the most widely used method among living polymerization techniques. In this method, a halogen atom is abstracted from the dormant species causing a one-electron oxidation of the transition metal complex which catalyzes the reversible redox process for the generation of the radicals [8,33]. ATRP has been used for the synthesis of AB diblock copolymers. A synthesis route for the synthesis of a diblock copolymer is given in Figure 1.6 [34].

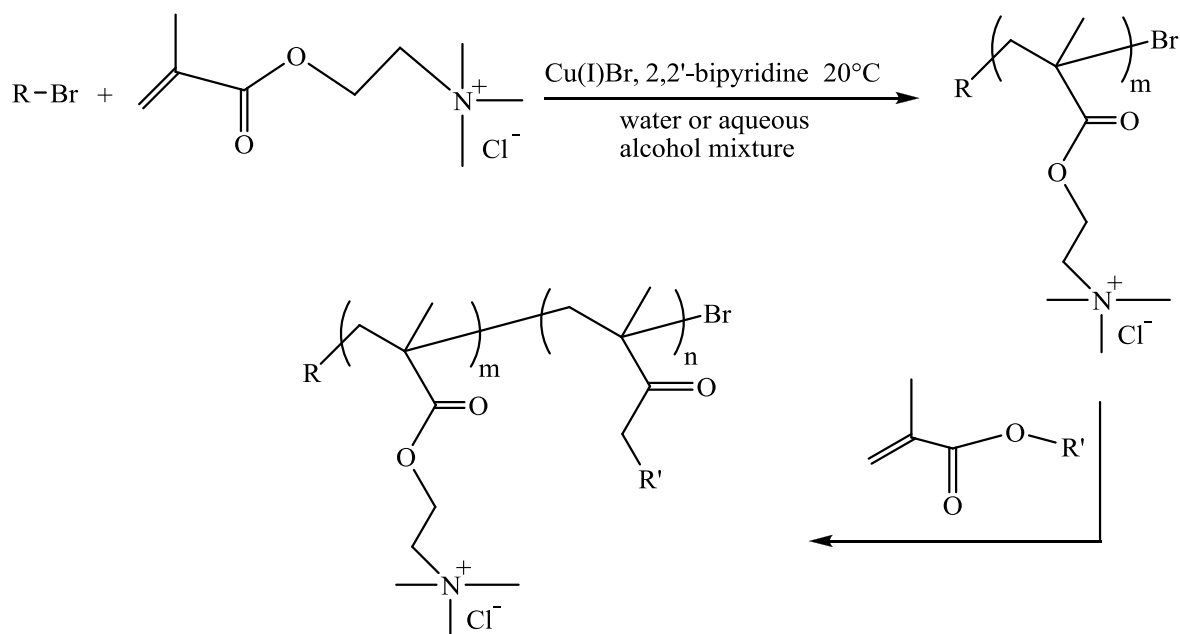


Figure 1.6. ATRP synthesis of 2-[(methacryloyloxy)ethyl]trimethylammonium chloride based diblock copolymers via sequential monomer addition

In this synthesis, 2-(methylamino) ethyl methacrylate is quaternized with methyl chloride prior to polymerization. Quaternized monomer and the initiator are dissolved in water. In the presence of 2,2'-bipyridine ligand, the homopolymerization occurs. The subsequent addition of the second monomer results in the formation of well-defined AB diblock copolymer [34].

1.1.1.2. Triblock Copolymers

Another class of block copolymer family is the triblock copolymers, which are usually denoted as ABA copolymers. ABA Triblock copolymers are the most widely investigated block copolymer systems. There are two types of triblock copolymers. Symmetrical triblocks are composed of one middle block and two end blocks of the same monomer units, whereas asymmetrical triblocks consist of three distinct monomer units. Both types display different properties depending on the chemical composition and architecture.

1.1.1.2.1. Synthesis of Symmetrical Triblock Copolymers

Symmetrical triblock copolymers generally denoted as ABA type block copolymers. A and B units are arranged in a way that the first and the third blocks have the same molecular weights [10]. As it is the case for AB diblock copolymers, ABA triblock copolymers can also be synthesized through many synthetic pathways. The monomers can be polymerized via sequential addition of each monomer. The A monomer is first polymerized then the B monomer is added resulting in AB* active diblock. Finally, the A monomer is introduced giving symmetrical ABA block copolymer [45]. There are a couple of drawbacks for this type of synthesis route. The first one is the increase in the probability of termination due to three monomer addition. This increases the partial termination of growing chains due to impurities which may be present in the monomers. The second one is that there may be differences in the amounts of monomers introduced, therefore resulting in the asymmetry

of the block copolymer. The monomers of choice are also important. The monomer A should be able to polymerize the B monomer and vice versa. Otherwise, there will be non-uniform products at the end [10]. A simple synthesis pathway is provided in Figure 1.7.



Figure 1.7. Sequential addition synthesis of ABA symmetrical block copolymers

In order to synthesize exactly symmetric triblock copolymers, living AB chains are coupled. In this method, a living AB copolymer with half of the molecular weight of the final copolymer is synthesized through sequential addition. Then, a coupling agent, which is able to react with the reactive end of the AB diblock and have two functional end groups, is introduced into the reaction medium. As a result, exactly symmetric ABA block copolymer is obtained [46]. Usually excess amount of living anion is used to guarantee the complete reaction of both end groups of the coupling agent, therefore a fractionation step is required to separate the excess AB blocks from the ABA block copolymer. For this reason, it becomes more time consuming than the sequential addition method [10]. A representative reaction scheme is given in Figure 1.8. [10,31].

First, the styrene monomer is polymerized and the diene is added resulting in reactive AB diblock copolymer. Then, the living diblocks are coupled using dimethyldichlorosilane. The coupling reaction usually does not lead to complete coupling as a result the system usually has diblock impurities which are very difficult to remove from the system.

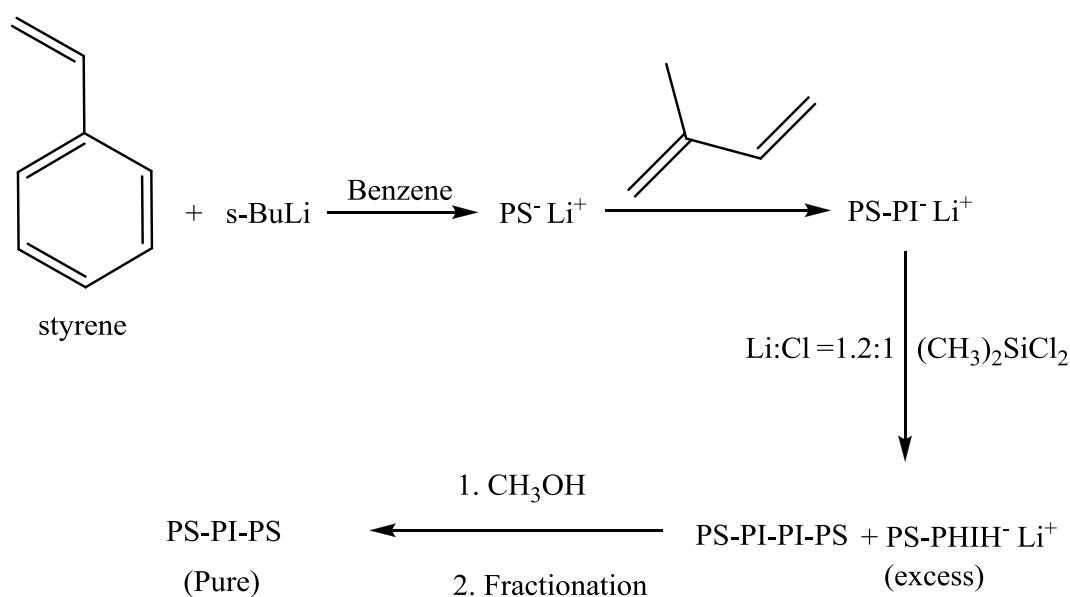


Figure 1.8. Synthesis of PS-PI-PS copolymer through coupling of living AB chains.

Another method to synthesize symmetrical triblock copolymers is to use a difunctional initiator [10]. In this method, a difunctional initiator is used and the polymerization proceeds from both ends resulting in a symmetrical triblock copolymer. In this technique first, the middle block is synthesized, and then the end blocks are polymerized [47]. A representative reaction scheme is provided in Figure 1.9. [48,49,50].

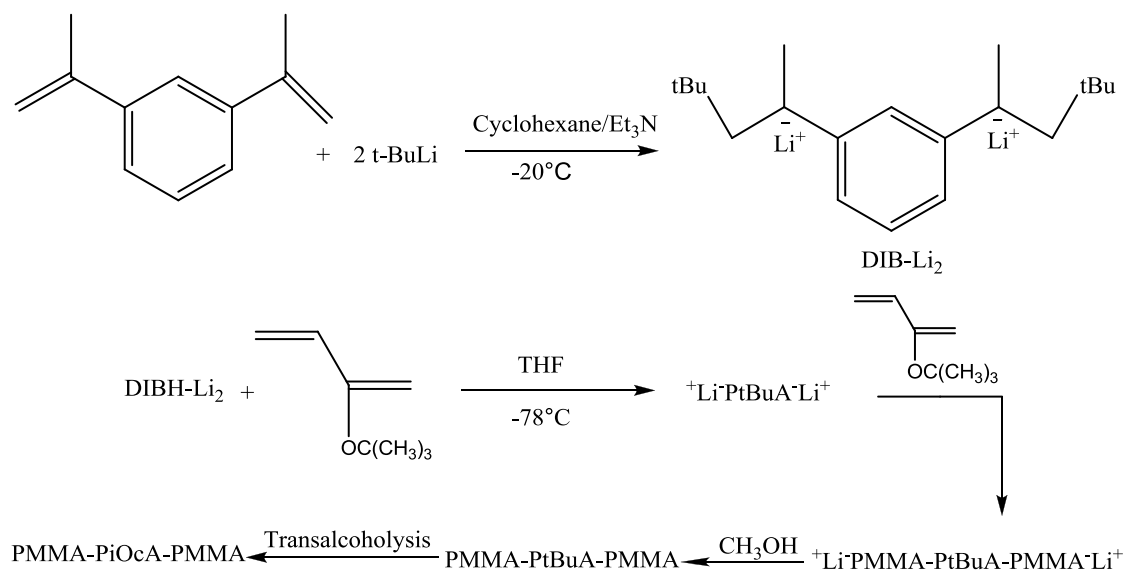


Figure 1.9. Synthesis of symmetrical ABA block copolymer via dilithium initiator.

In addition to anionic synthesis of ABA triblock copolymers, ATRP is another widely used method. ATRP synthesis of triblock copolymers having perfluorinated outer blocks was reported earlier [36]. As the difunctional initiator, dibromo or dichloromethylbenzene was used in the presence of CuX catalyst ($\text{X} = \text{Br}, \text{Cl}$) and 2-2'-bipyridine (bpy) as the ligand. The reaction scheme is provided in Figure 1.10 [10].

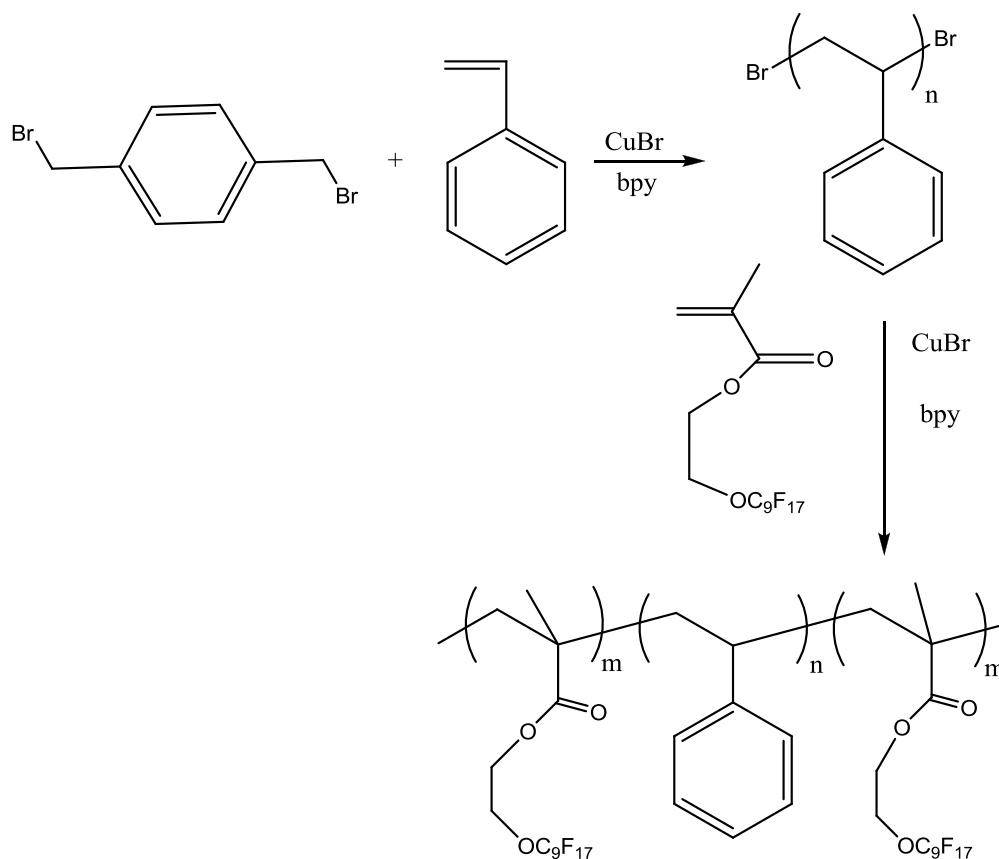


Figure 1.10. Synthesis of symmetrical ABA triblock copolymer having perfluorinated outer blocks and styrene inner block via ATRP.

In this synthesis pathway, styrene inner block is first synthesized having halogenated end groups. Then, this macroinitiator is used for the polymerization of perfluorinated acrylate outer blocks. Polydispersities of the products were between 1.27 and 1.49 [10].

1.1.1.2.2. Synthesis of Nonsymmetrical Triblock copolymers

Block copolymers having three distinct constituent blocks are called nonsymmetrical triblock copolymers which are generally denoted as ABC triblock copolymers. The synthesis of such copolymers can be achieved through sequential addition of monomers. First, the living diblock chains are synthesized, then the third block is polymerized with the living AB^* chain, giving ABC block copolymer [59,60]. A simple synthesis pathway is provided in Figure 1.11.

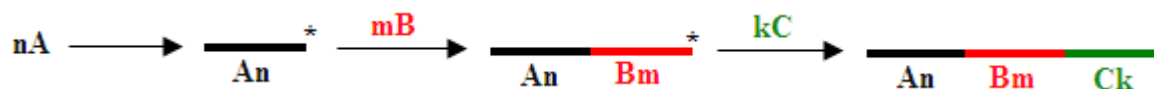


Figure 1.11. Synthesis of ABC block copolymer through sequential monomer addition.

A large number of ABC block copolymers were synthesized in order to investigate the morphologies and properties of such materials. One example can be given as poly(styrene)-poly(isoprene)-poly(2-vinylpyridine) (PS-PI-P2VP) synthesis through sequential addition method [61,62,63]. The synthesis scheme is given in Figure 1.12 [10].

As it is for other types of block copolymerization techniques, the purity of each monomer and the amount of monomer addition is crucial. The addition sequence of styrene and isoprene can be switched, but 2-vinylpyridine is always added as the final monomer. The

molecular weight distribution of the final block copolymer is narrow which indicates a well controlled polymerization [10].

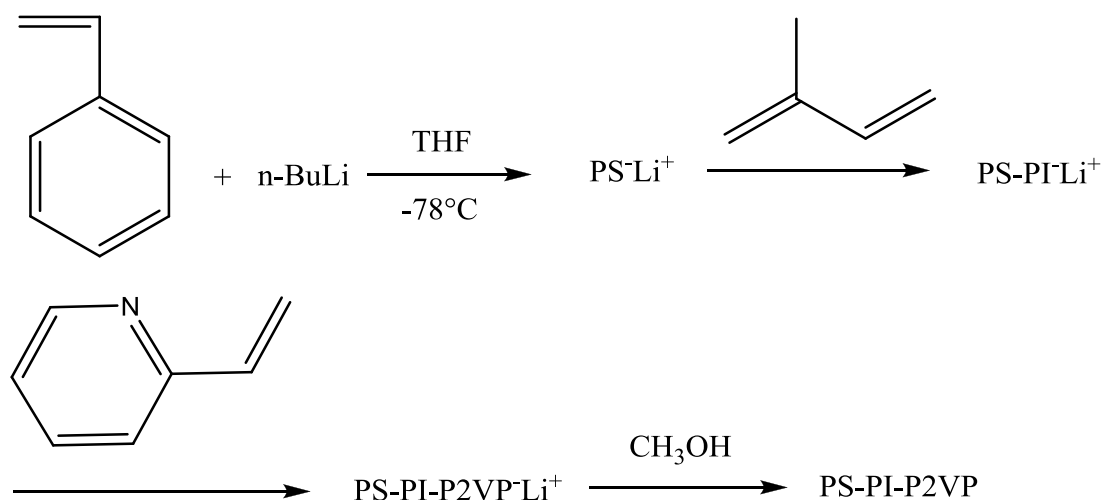


Figure 1.12. Synthesis of PS-PI-P2VP block copolymer via anionic sequential polymerization.

Most recently, ATRP has been applied for the synthesis of ABC terblock copolymers. In order to obtain well-defined block copolymers through ATRP, high chain end functionality has to be maintained. This can be achieved by limiting the termination and side reactions and also adjusting the reactivity of the end group with the monomer, namely having a rapid initiation [36]. For a typical ABC terblock copolymer synthesis through ATRP, first the halogenated AB diblock copolymer (X-AB , $\text{X}=\text{Br}, \text{Cl}$) is synthesized and then the third monomer is polymerized by using the X-AB ATRP active copolymer [36]. Synthesis of

poly(styrene)-poly(t-butylacrylate)-poly(methylmethacrylate) ABC terblock copolymer via ATRP was reported in the literature. The reaction mechanism is provided in Figure 1.13 [37].

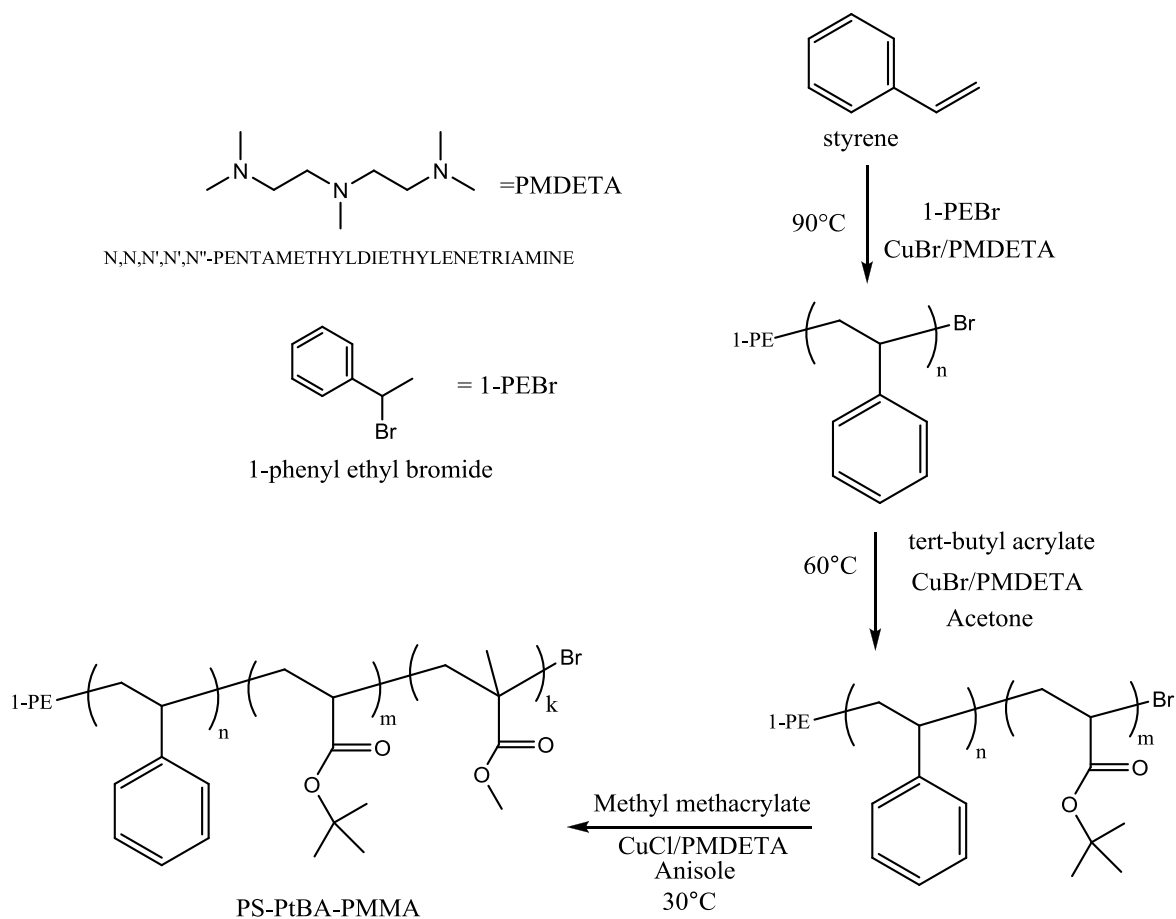


Figure 1.13. ATRP synthesis pathway for the preparation of PS-PtBA-PMMA terblock copolymer

Styrene monomer is first polymerized in the presence of CuBr/PMDETA cocatalyst and 1-PEBr initiator resulting in Br terminated macroinitiator, which is used to initiate the copolymerization of tert-butyl acrylate. Methyl methacrylate monomer is introduced as the third monomer which is polymerized with PS-PtBA-Br diblock macroinitiator. The resulting ABC terblock copolymer had a reasonably low polydispersity index which is measured as ~ 1.15 [37].

1.1.1.3. Morphology and Properties of Block Copolymers

Block copolymers are interesting materials since different polymeric properties can be incorporated into a single macromolecule. Therefore, block copolymers may possess combination of a wide variety of properties. Incorporation of immiscible polymer blocks into a copolymer system results in diverse morphologies [1]. In a diblock copolymer, two different blocks tend to segregate from each other due to immiscibility of constituent blocks. The existence of covalent bond between the two blocks prevents the macrophase separation, therefore leading to microphase separated morphology [38]. The segregation between the blocks is driven by the interaction parameter χ_{AB} which was introduced by Flory [39]. The energetic interactions between different polymers are described according to Eq. 1.1 [39]:

$$\Delta G_m = RTV_c [(\phi_A/N_A) \ln \phi_A + (\phi_B/N_B) \ln \phi_B + \chi_{AB} \phi_A \phi_B],$$

where ΔG_m is the Gibbs free energy of mixing, ϕ_A and ϕ_B are the volume fractions of polymers A and B, and N_A and N_B are the number of reference units with the molar volume V_c of a given reference unit.

Different methods are described to obtain the interaction parameter χ_{AB} , (i) directly from the phase diagram by simply plotting N versus ϕ [40,41], (ii) from the behavior of a block copolymer in small angle light scattering [42], (iii) from polymer-solvent interactions, and (iv) through contact angle and segregation isotherm determination [43]. Determination of interaction parameter is mostly applied through solvent-polymer interaction. The determination through phase diagram, small angle light scattering and contact angle and segregation isotherms require the knowledge of mean-field theory and the whole phase diagram. Therefore, it is restricted both from the theoretical and experimental point of view [44]. Polymer-solvent interaction is investigated and solubility parameter, δ , is found out for each type of polymer system. The solubility parameters, δ_A and δ_B of two different polymers are correlated to the interaction parameter, χ_{AB} according to Eq. 1.2 [45]

$$\chi_{AB} = (\delta_A - \delta_B)^2 V_c / RT$$

where V_c represents the reference unit volume which is arbitrarily set to 100 cm³/mol, R is the gas constant and T is the temperature [46]. Another parameter affecting the behavior of

block copolymers is the total degree of polymerization, N [10]. As the total degree of polymerization gets higher, the A-B monomer contacts decrease due to the loss of translational and configurational entropy, thus it leads to local ordering. Therefore, interaction parameter multiplied with N , χN , is taken into account to determine block copolymer phase state [10]. When χN is greater than 100, it is said to be strong segregation regime, while weak segregation regime is defined for χN , smaller than 10. Between 10 and 100, the interaction strength is in the intermediate regime [10]. The extent of segregation is dependent on the magnitude of χN . For small values of χN , that is to say in weak-segregation regime, the composition is almost regular throughout the material. The blocks are strongly separated and almost pure domains are observed for χN values which are termed in strong segregation regime [8]. The copolymer phase morphology depends on both composition and architecture [1]. The lamellar morphology is observed for symmetrical block copolymers where fraction of one component is equal to 0.5 ($f=0.5$). As the asymmetry of constituent blocks increases, the morphology observed is altered to hexagonally packed cylinders and spherical structures. Possible morphologies are given in Figure 1.14 [47]

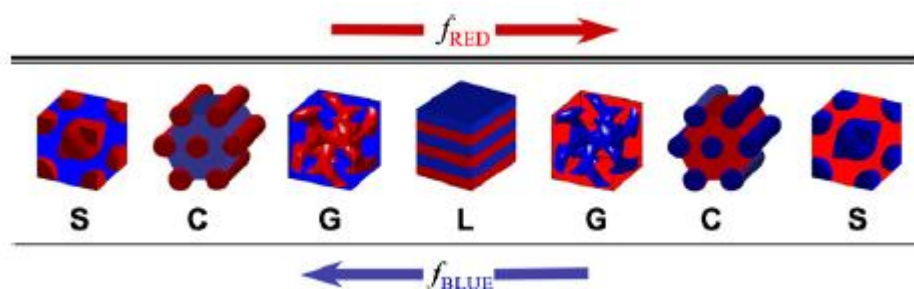


Figure 1.14. Block copolymer morphologies. Morphologies are shown in increasing red-block (decreasing blue) composition of a copolymer of red-blue monomers. (S) BCC spheres, (C) hexagonally packed cylinders, (G) gyroid, (L) lamellae.

Among various types of block copolymers, triblock copolymers are the most widely studied materials. Symmetrical triblock copolymers display a wide range of properties. Commercially available and important ABA block copolymers are poly(styrene)-poly(butadiene)-poly(styrene) (PS-PB-PS) and poly(styrene)-poly(isoprene)-poly(styrene) (PS-PI-PS) block copolymers and their hydrogenated versions. Such ABA type block copolymers are generally synthesized through living anionic polymerization resulting in high molecular weight polymers. Poly(styrene) in the end blocks act as the hard domain, therefore it is incompatible with the middle block. At room temperature hard domains act as the physical crosslinks through chain entanglement, and those physical crosslinks can be broken at high temperatures giving the opportunity to be used with conventional molding techniques. When the softened material is cooled down, physical crosslinks are reestablished. Therefore, such materials can be used as thermoplastic elastomers [3]. The

microphase morphology and thermoplasticity of PS-PB-PS triblock copolymer is illustrated in Figure 1.15. [54, 55].

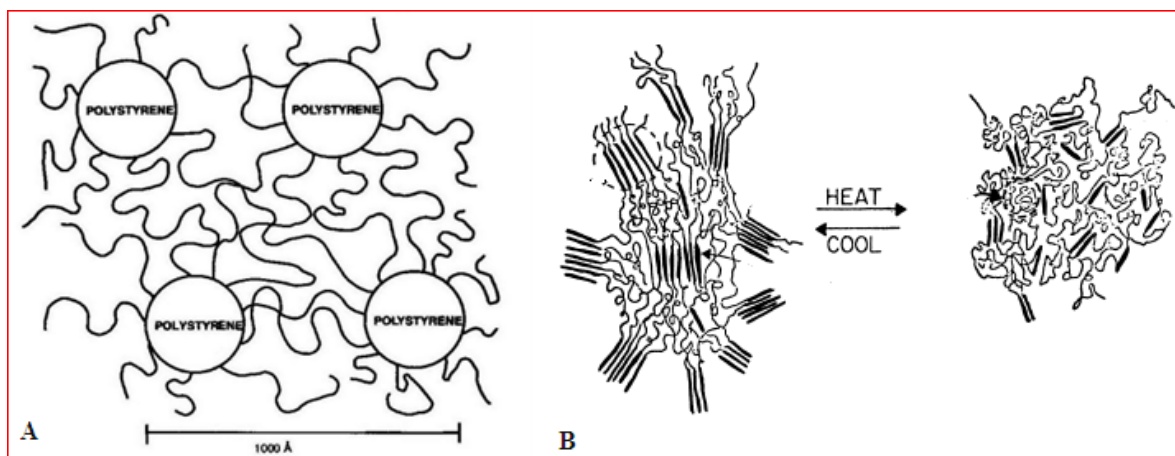


Figure 1.15. A) Microphase separation in PS-PB-PS triblock copolymer B) Change in orientation of blocks upon heat treatment.

Similar to the morphology observed in most of the block copolymer systems, triblock copolymers which have two different monomer units can self assemble into microphase separated structures which are strongly dependent on the segregation strength χN , and the volume ratio of the constituent blocks. Incorporation of crystallizable species within the block copolymer increases the diversity of the observed morphologies. The morphology of semicrystalline polymers depends on the thermodynamic incompatibility of constituent blocks and the crystallization of the crystallizable block [56, 57]. Hillmyer et. al. studied

the bulk morphology of symmetrical ABA block copolymers of poly(l-lactide)-poly(dimethylsiloxane)-poly(l-lactide) (LDL) for possible multifunctional nanolithographic applications. It was found out that due to strong segregation within the constituent blocks, the block copolymers displayed different morphologies depending on the monomer fraction. The observed morphologies are given in Figure 1.16. [2].

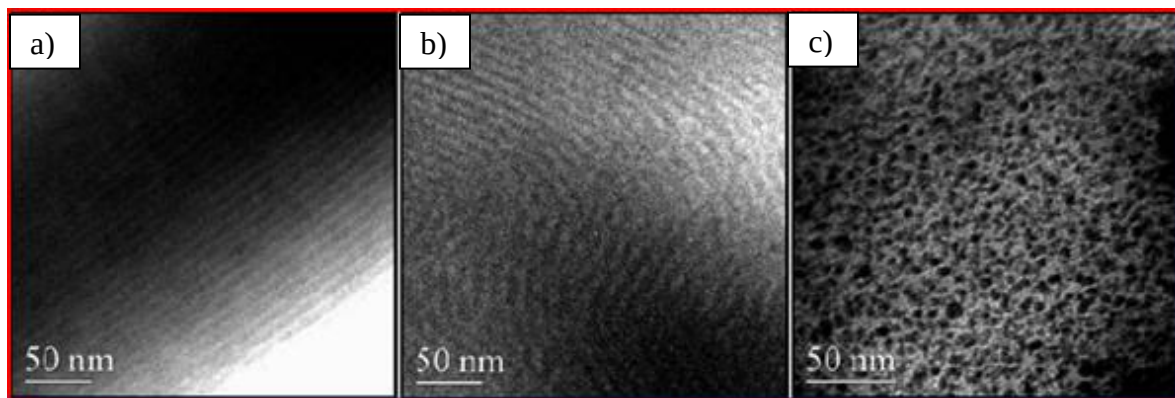


Figure 1.16. Phase separated morphologies of LDL symmetrical block copolymers.

- a) Lamellar morphology LDL (2.2-5-2.2) b) Cylindrical morphology LDL (3.7-5-3.7)
c) Spherical morphology LDL (7.0-5-7.0).

The volume fraction of A monomer in ABA block copolymer determines the morphology. For very low concentrations of A monomer, the two blocks will mix homogeneously resulting in phase-mixed morphology. Increasing the fraction of monomer A to roughly equal amounts of monomer B will result in the formation of alternating layered sheets

called lamellae (Figure 1.16.a). Further increasing the fraction of A monomer will give rise to a cylindrical morphology where B is dispersed in the A matrix (Figure 1.16.b). The higher fractions of A will result in spherical morphologies where spheres of B domains is formed within the A matrix (Figure 1.16.c) [58, 59].

For the block copolymers having at least two crystallizable units, the competitive crystallization of different components is an important factor for the block copolymer morphology. Such crystallization may result in high order structure of crystals having double spherulites like concentric circles. The crystal structures observed for PCL-PEO-PCL block copolymers are given in Figure 1.17.[60].

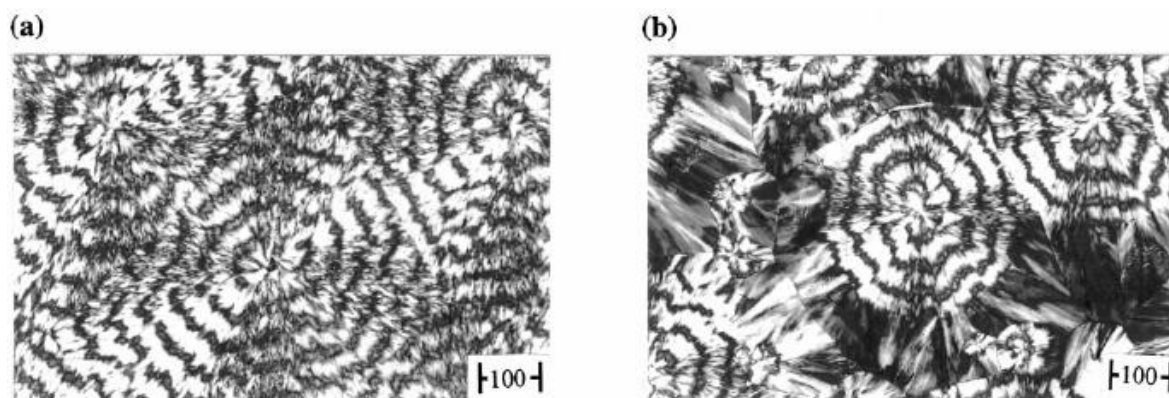


Figure 1.17. Polarized optical microscope images of PCL-PEO-PCL triblock copolymers
a) Single circle spherulites b) Concentric spherulites

As another class of block copolymer family, ABC terblock copolymers display much richer phase behaviors compared to diblock or triblock copolymers, which are composed of two monomer units [66]. The enrichment of phase behavior is a result of multiple interaction parameters which are χ_{AB} , χ_{AC} , and χ_{BC} due to the presence of a distinct third block [8]. Thomas et. al. [61] studied the phase behavior of polystyrene-polybutadiene-poly(methyl methacrylate) (SBM) terblock copolymers with various solvents by using transmission electron microscopy (TEM). TEM results showed that solvent-polymer and polymer-polymer interactions are the key points for the establishment of the phase morphology. The observed morphologies are provided in Figure 1.18. [61].

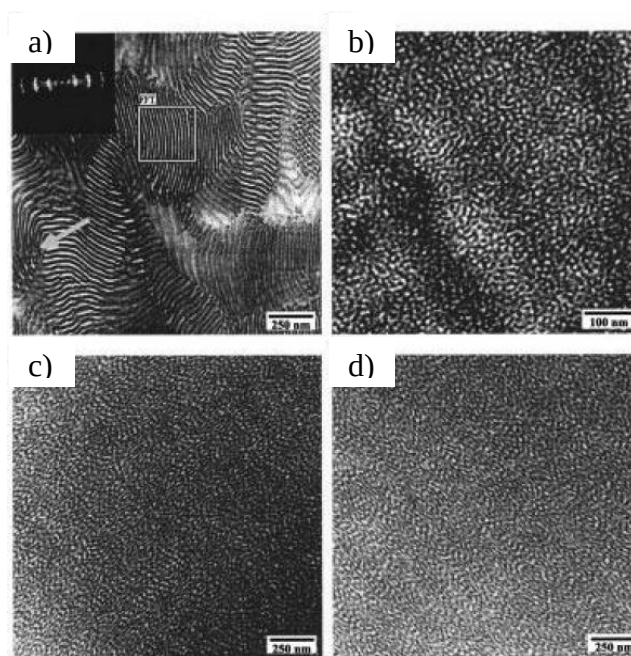


Figure 1.18. TEM images of SBM terblock copolymers in various solvents (a) chloroform, (b) toluene, (c) benzene/cyclohexane (50:50), (d) benzene/cyclohexane (70:30) [61].

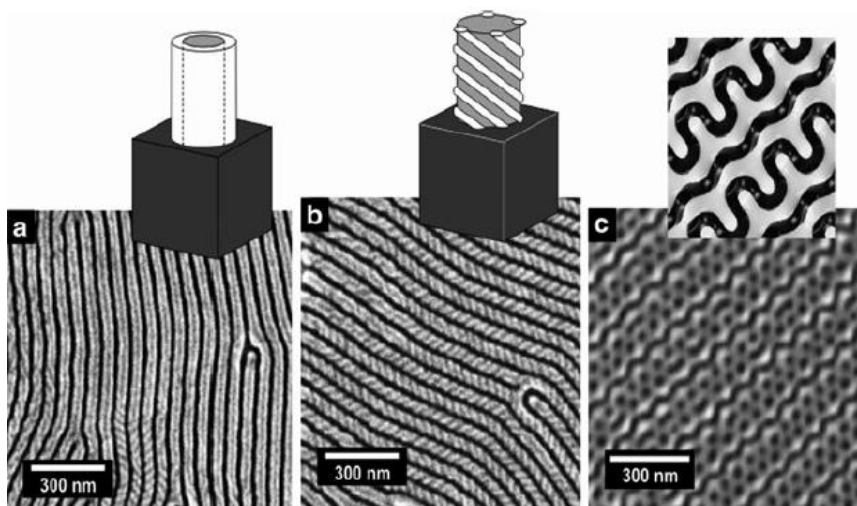


Figure 1.19. SEM images of SVT terblock copolymers. (a) core-shell cylinders, (b) helices wound around a cylindrical core, (c) (112) plane of an ideal double gyroid structure [7].

Chloroform cast films displayed lamellar morphology. Close to grain boundaries lamellae rupture to form cylindrical morphologies (Figure 1.18.a). Toluene cast SBM films displayed phase separated morphologies but did not exhibit any long range order (Figure 1.18.b). In order to further investigate the effect of solvent on the morphology, benzene-cyclohexane mixtures were used. Benzene is a good solvent for all three blocks like toluene, but cyclohexane is a nonsolvent for PMMA and θ -solvent for PS. For solvent ratio of 1:1, similar morphology was observed (Figure 1.18.c) as in the case of toluene, whereas 30:70 mixture of benzene-cyclohexane cast films displayed hexagonally packed cylinders (Figure 1.18.d) [62]. Elbs et. al. studied the phases of poly(styrene)-poly(2-vinylpyridine)-poly(tert-butylmethacrylate) (SVT) terblock copolymers which were exposed to different

solvent vapors. It was found out that morphology strongly depends on annealing vapor and drying conditions. SEM images are provided in Figure 1.19. [7].

1.2. Principles of Ring Opening Polymerization

Ring opening polymerization (ROP) is an important technique for the polymerization of cyclic monomers such as; cyclic ethers, lactams, lactones and siloxanes. Ring opening polymerization is used commercially for the polymerization of oxirane, trioxane, ϵ -caprolactam and octamethylcyclotetrasiloxane as shown in Figure 1.20 [3].

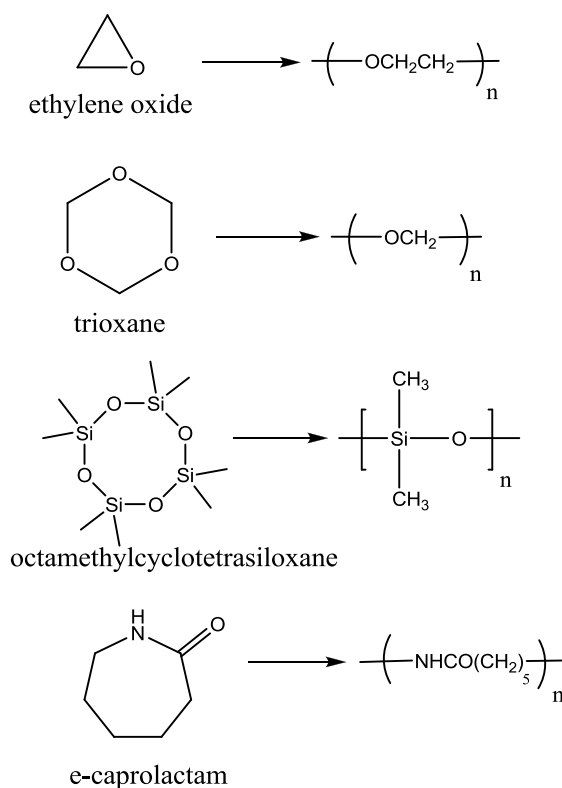


Figure 1.20. Commercially available polymers obtained via ring opening polymerization.

Most of the cyclic monomers are heterocyclic; therefore the functional group in the ring undergoes heterolysis due to its highly polarized nature. For this reason, a wide range of nucleophiles and electrophiles can react with cyclic monomers to initiate their polymerizations [67].

1.2.1. General Mechanisms in Ring Opening Polymerization

1.2.1.1. Anionic Ring Opening Polymerization

When nucleophilic initiators are used in the ring opening polymerizations, these reactions can be called as “Anionic ring opening polymerization”. A general reaction scheme is given in Figure 1.21 [67].

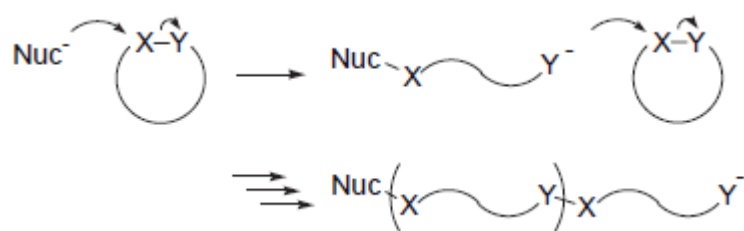


Figure 1.21. General anionic ROP mechanism

Generally organometallic reagents such as alkyl lithium and alkyl magnesium bromide, metal amides, alkoxides, amines, alcohols and water are used as the nucleophilic reagents. In order to be polymerizable through ring opening techniques, the cyclic monomers have to

possess polarized bonds such as ether, ester or amide bonds so that the corresponding polyethers, polyesters or polyamides can be synthesized. The functional group in the cyclic monomer is represented as X-Y where X is electron deficient (or positively charged) due to electron withdrawing nature of Y, which is generally oxygen, nitrogen or sulfur. Therefore, the ROP will proceed with the nucleophilic attack of the initiator to the electron deficient center which will release Y^- anion. These species will further attack electron deficient centers in other monomers and will lead to polymer formation [67]. Alkoxide initiated ring opening polymerization of ϵ -caprolactone can be given as an example to this type of polymerization. ROP mechanism of ϵ -caprolactone is provided in Figure 1.22 [68,69]. One major drawback of ϵ -caprolactone ROP is the alkoxide back biting reaction with the ester linkage in the main chain. This side reaction leads to the formation of macrocyclic oligomers [67].

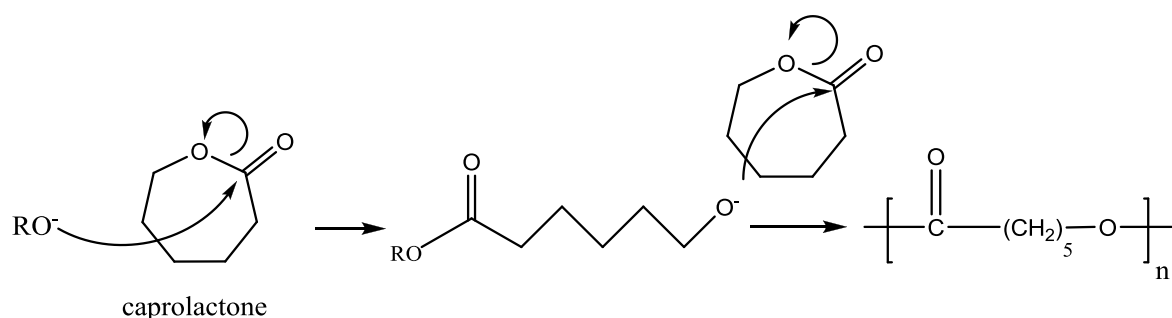


Figure 1.22. Anionic ring opening polymerization of ϵ -caprolactone.

Another type of anionic ring opening polymerization is “the activated monomer mechanism”, where nucleophilic attack of activated monomer takes place to polymer chain end. Polymerization of ϵ -caprolactam can be given as a good example for such mechanism. First the monomer is activated by abstracting an acidic N-H proton in basic conditions. The activated monomer attacks to another lactam releasing a highly basic amide anion which activates another monomer by abstracting the acidic N-H proton. Thus, the reaction medium consists of activated monomer and N-acylated lactam. The activated monomer eventually reacts with N-acylated lactam in the chain end of the polymer. The reaction mechanism is provided in Figure 1.23 [67].

In this research, for the synthesis of symmetrical triblock copolymers, α,ω -aminopropyl terminated poly(dimethylsiloxane) (PDMS) and hydroxyl terminated poly(ethylene oxide) (PEO) difunctional oligomers were used in order to initiate the polymerization of ϵ -caprolactone. Reaction schemes for both of the macroinitiator systems are provided in Chapter 2.

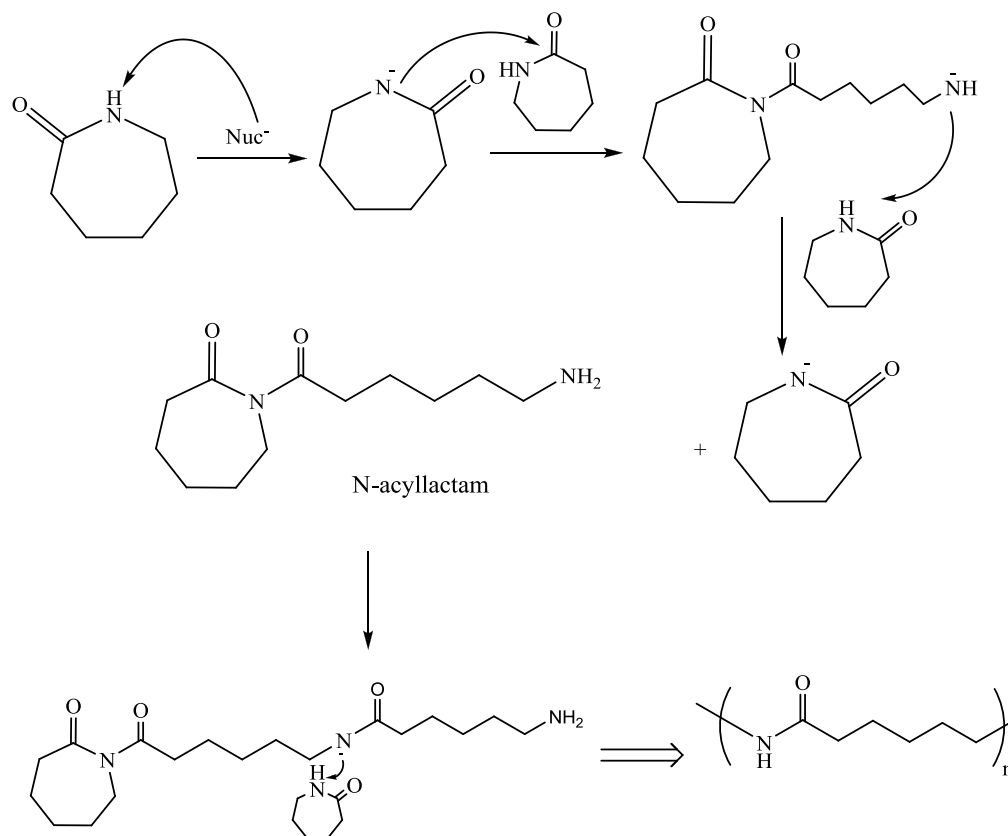
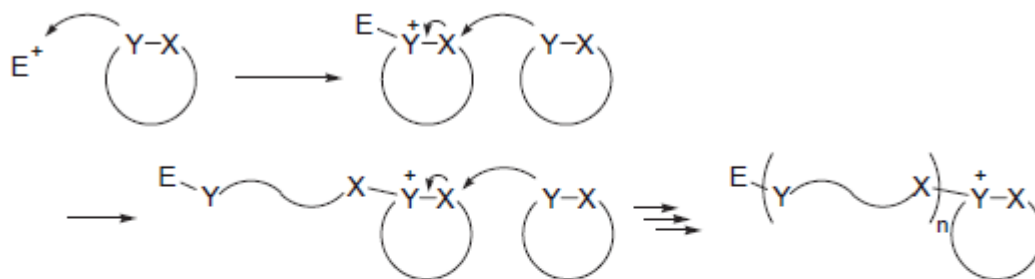
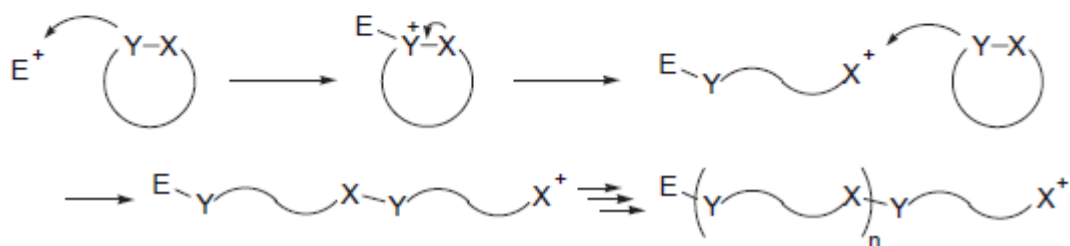


Figure 1.23. Reaction mechanism for the synthesis of poly(ϵ -caprolactam)

1.2.1.2. Cationic Ring Opening Polymerization

Another class of ring opening polymerization is cationic ROP in which electrophilic initiators are used. The initiators of cationic ROP are often Brønsted acids, Lewis acids and alkyl esters of strong acids. A general reaction mechanism is given in Figure 1.24 [67].

S_N2 Mechanism**S_N1 Mechanism****Figure 1.24.** General cationic ROP reaction mechanism.

Monomers of cationic ring opening polymerization have polarized bonds represented as $Y-X$, where Y is the functional group or the atom. (Y) has a lone electron pair; therefore it is capable of acting as a Lewis base in order to react with electrophiles. (X) atom needs to be electron rich since it will become the cationic center at the end of ring opening polymerization. Nucleophilic attack of (Y) towards the electrophilic initiator will trigger the ring opening polymerization of the monomer. Cationic cyclic species in the reaction medium can be attacked by (Y) in another molecule through S_N2 mechanism; or they can undergo ring opening polymerization through S_N1 mechanism where acyclic cationic species are produced and will be attacked by the monomer. The superiority of one

mechanism over the other mechanism is regulated by the stability of the X^+ cation. Electron donating neighboring groups to X^+ will increase the stability and lifetime of the cation; therefore the S_N1 mechanism will be dominant. The vice versa is valid for S_N2 mechanism [67,70]. Polymerization of tetrahydrofuran (THF) is a good example to cationic ring opening polymerization through S_N2 mechanism for which the mechanism is provided in Figure 1.25 [70].

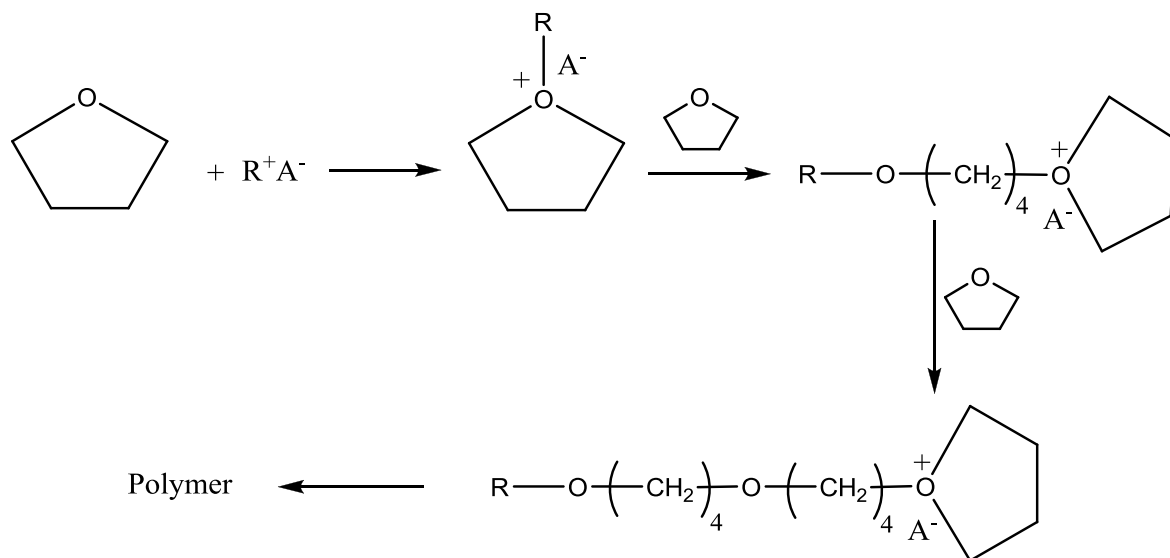


Figure 1.25. Cationic ROP of THF through S_N2 mechanism.

1.2.1.3. Radical Ring Opening Polymerization

Free-radically induced ring opening polymerization is another mechanism to polymerize cyclic monomers. Since the cyclic monomers undergo homolytic dissociation in radical ROP, the requirement for highly polarized functional groups are not essential as in the ionic

types of ROPs. Radical ring opening polymerization of vinyl cyclopropane is given in Figure 1.26 [71].

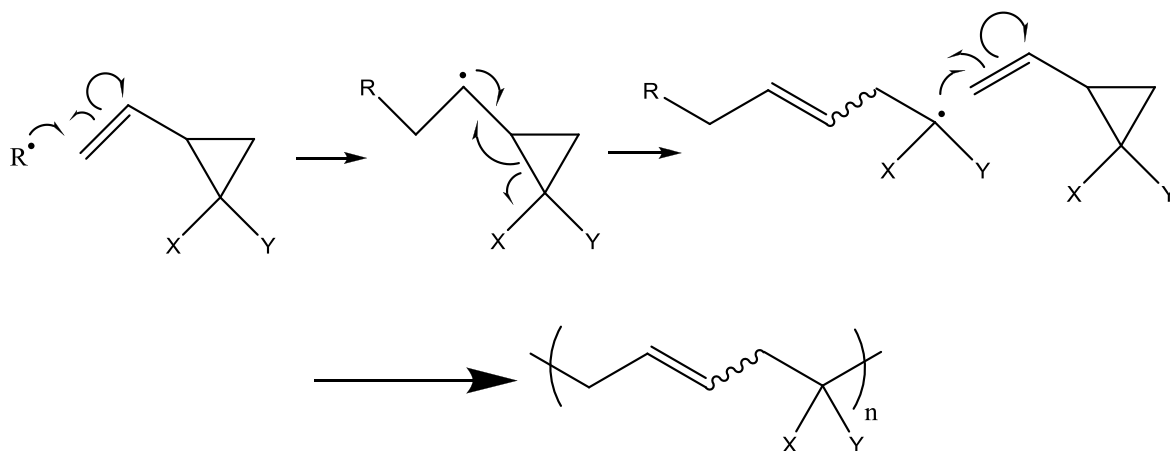


Figure 1.26. Radical ring opening polymerization of vinyl cyclopropane.

In the radical ring opening polymerization mechanism of vinyl cyclopropane, vinyl group first accepts a radical and then a carbon radical is created by the transformation of this newly formed radical. The carbon radical is stabilized by (X) and (Y) substituents, which can be halogens, aromatic units or ester groups. In order to synthesize polymers which have functional groups that cannot be produced by the traditional chain polymerization of vinyl monomers, radical ring opening polymerization is a very good method [67]. Polymer chains with predictable molecular weights can now be synthesized due to advances in controlled radical polymerization methods [72]. Radical addition fragmentation transfer

(RAFT) polymerization technique is a good example to controlled radical polymerization methods [73].

1.2.1.4. Organocatalytic Ring Opening Polymerization

For materials which are used in biomedical and microelectronic fields, one important parameter is the use of nontoxic and metal free catalysts. In order to do so, organocatalytic ring opening polymerization of cyclic monomers is established and is a hot topic in recent years. Hedrick et. al. studied the ring opening polymerizations of cyclic esters such as lactones, lactide, cyclic silyl ethers with completely metal-free catalyst systems [74]. 1,3,4-triphenyl-4,5-dihydro-1H-1,2,4-triazol-5-ylidene (**1**) is a commercially available organic material which enables H-shaped and super-H-shaped architectures via its unique reactivity [75]. It was found out that primary amines function as bifunctional initiators in the presence of (**1**) for ring opening polymerization. Creation of imide end groups and two chains per initiating amine provides the introduction of branch points within the block copolymer [76,77]. Racemic mixture of lactide is polymerized with poly(ethylene oxide)-bis(3-aminopropyl) ($\text{H}_2\text{N-PEO-NH}_2$) as the initiator and (**1**) as the catalyst. The reaction scheme is given in Figure 1.27. [78].

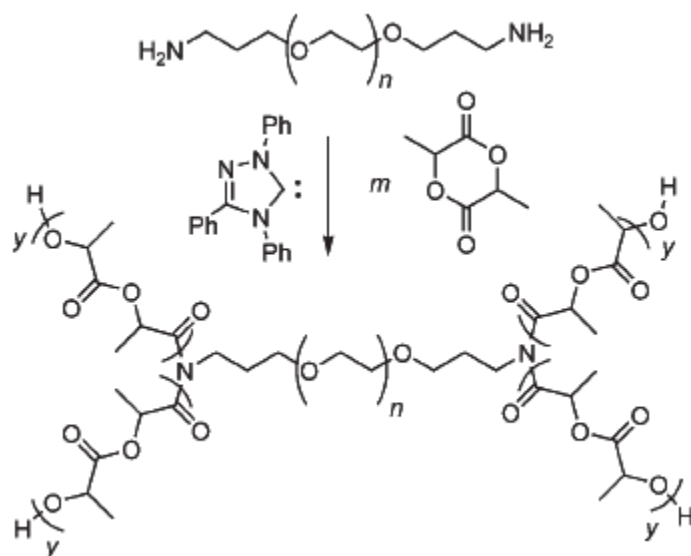


Figure 1.27. Polymerization of racemic lactide with H_2N -PEO- NH_2 as the initiator in the presence of **(1)** as the catalyst.

After 71 h reaction 85% conversion was reached. ^1H NMR spectrum revealed that as a result of the polymerization, [poly(lactide)]-poly(ethylene oxide)-[poly(lactide)] triblock copolymer is obtained with an average degree of polymerization of 48 and with narrow molecular weight distributions ($M_w/M_n < 1.1$) [78].

1.3. Applications of Block Copolymers

Block copolymers attracted much attention in recent years due to their versatile properties. Block copolymers of different monomers display the properties of each constituent block due to covalent bonding even if they are not miscible by means of physical mixing.

Therefore, it gives us the great opportunity to produce materials with hybrid properties. These materials are used in many applications and fields such as biodegradable and biocompatible elastomers, drug delivery systems, tissue engineering, medical implants and nanofabrication [2,8,79].

1.3.1. Biological Applications

Poly(ϵ -caprolactone) (PCL) which is biodegradable and biocompatible belongs to the family of aliphatic polyesters. First poly(ϵ -caprolactone) was synthesized in the early 1930s by Carothers' group [80]. Due to its beneficial properties such as good solubility, low melting point (54-64°C) and blend compatibility, PCL is subjected to extensive research in biomedical field [81,82]. PCL and its copolymers were used in a number of drug delivery devices. The advantages of such copolymers over other copolymers were tailorable degradation and mechanical properties, pore sizes that allow conduction to tissue in-growth. Due to slower degradation rate of PCL and its copolymers, they are used in drug delivery systems which can serve for over 1 year. Therefore, there are a number of drug delivery devices made of PCL, which already have FDA approval [83]. Some important parameters of a biodegradable material can be categorized as non-toxicity of the material and the degradation products, acceptable shelf-life and appropriate mechanical property [82]. Medical applications for poly(ethylene oxide) are also widely investigated. They are generally utilized for improved drug delivery. Ethylene oxide/propylene oxide block

copolymers are successfully applied to help in the cure of cancer treatment. Compositional tuning of these block copolymers allowed to improve targeted delivery of therapeutic agents [8]. Genetic material containing at least 15% PEO/PPO block copolymer is employed to introduce genetic material into living cells and is patented as Poloxamer 407 [84]. Viegas et. al. showed that ethylene oxide/propylene oxide block copolymers can be used for wound care and surgical dressings [85,86]. Li et. al. studied the block copolymers of ethylene oxide/ ϵ -caprolactone as a new class of biomaterials for controlled drug delivery [88]. Poly(ethylene oxide)-poly(ϵ -caprolactone) block copolymers displayed promising results for drug carriers in medical applications. These block copolymers showed high loading efficiency of human serum albumin which is a liver-produced protein found in human blood. Results indicate that the properties can be tailored by adjusting copolymer composition. Therefore, those block copolymers are good candidates for controlled protein delivery [89]. When a natural tissue bed is weakened by an injury, a disease or a surgery, it generally requires an artificial support. In such a case, a degradable implant would provide the temporary support until the natural tissue bed retrieves its initial strength. Therefore, there should be a gradual stress transfer; meaning that as the natural tissue heals, the temporary support device should weaken. This is achieved through tailored degradation behavior of polymeric materials. One of the first examples of such materials is the block copolymer of poly(glycolic acid) and poly(lactic acid) which is commercially known as “Vicryl” suture [90].

The chemistry and resulting properties of polymeric materials are highly relevant to the performance and functionality of those materials. Therefore, polymers are very useful with the diversity of their compositions and properties to be used in bio-related applications. In this research, a series of triblock copolymers of ϵ -caprolactone with PDMS and ϵ -caprolactone with PEO are synthesized. Their surface properties, crystal structures and thermal properties are investigated in order to understand their function and performance to be used as precursors to biodegradable and biocompatible block copolymers with tailored properties and functionalities.

1.3.2. Nanofabrication

Block copolymers have attracted much attention due to their self assembly at nanoscale. When the repulsive interaction between the constituent blocks is large, the architecture of the block copolymer leads to microphase separation into ordered structures since two or more homopolymers are covalently bonded to each other [91]. It is well known that strongly segregated block copolymers display morphologies in the order of 10 nm which is suitable for block copolymer lithography. The morphology developed can be tailored by adjusting the composition and process conditions [2]. Poly(styrene)-poly(methyl methacrylate) (PS-PMMA) diblock copolymers are the first examples of block copolymers used in lithographic applications. One block (PMMA) is removed and then the structure, which is made from the other block, generally PS, is preserved. This pattern is used as a

mask for pattern transfer. One drawback of such system is that PS is a poor mask having a low etch resistance with remaining defects in the systems. In order to obtain a defect-free system with a long range order, strong segregation strength, a high repulsion between the constituent blocks, is necessary. Therefore PDMS containing block copolymers have attracted increasing interest. PS-PDMS block copolymers have extremely high etch contrast due to high density of Si within the PDMS backbone and relatively long range order since the segregation strength between the blocks is very strong. Ross et. al. studied PS-PDMS diblock copolymers in order to produce masks for nanolithography. SEM images of PS-PDMS thin films are provided in Figure 1.28 [92].

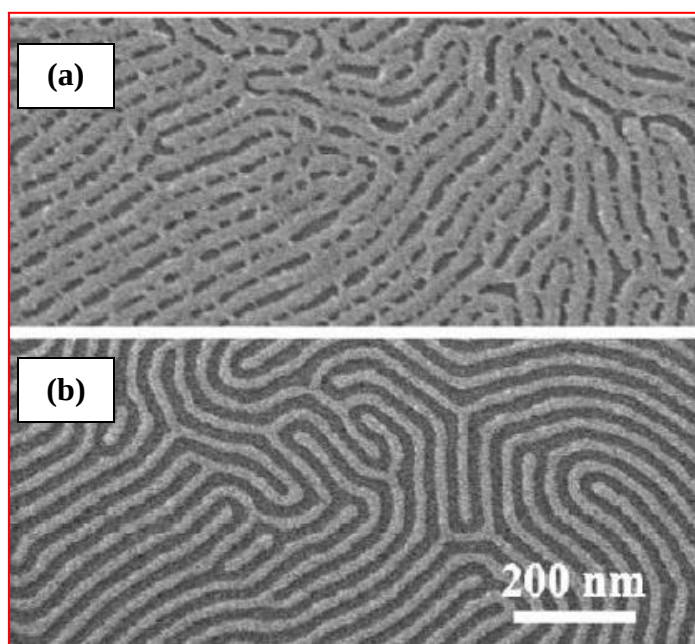


Figure 1.28. SEM images of PS-PDMS thin films. a) Exposure to O_2 plasma for 1 min
b) Exposure to CF_4 plasma (5 s) followed by O_2 plasma (1 min) [92].

PDMS surface layer is resistant to oxygen plasma; therefore O_2 plasma alone does not provide sharp patterns (Figure 1.24.a). In order to overcome this problem, initially the surface is exposed to CF_4 plasma to etch away the very top PDMS surface layer, and then the O_2 plasma is applied to etch the PS domains. As a result, sharp domain patterns are obtained (Figure 1.24.b) [92]. Triblock copolymers of PDMS with poly(L-lactide) (PLA), which self assemble into ordered structures in bulk, have also been investigated for nanolithography applications. PLA is susceptible to O_2 plasma and resistant to fluorinated etchants and vice versa is valid for PDMS backbone. Therefore, it is possible to obtain both dot and antidot arrays due to selective etchability of block copolymer domains. AFM height images of dot arrays are provided in Figure 1.29 [2].

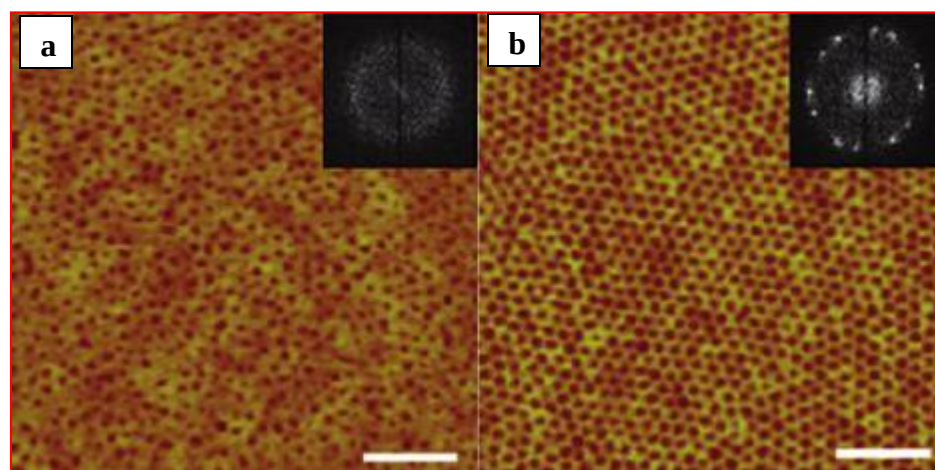


Figure 1.29. AFM height images of a) PLA-PDMS-PLA thin film b) After exposure to 20s SF_6 plasma. Scale bar 200 nm. [2]

Block copolymers are also used in order to produce improved ultrafiltration membranes. It is known that a certain composition of poly(styrene-*b*-lactide) (PS-PLA) self assembles into cylindrical morphologies where PLA block forms the cylinders in PS matrix. The evaporation rate of the solvent determines whether the orientation will be perpendicular or parallel to the substrate surface. Fast evaporation results in perpendicular orientation which is the desired architecture for an ultrafiltration membrane. Selective etching of PLA domain in basic medium results in a porous selective layer with monodisperse pores having 24 nm diameters. Poly(ethylene oxide) molecules of varying molecular weights are dissolved in water and fluxed through the produced membranes. Rejection of PEO molecules showed the selective filtration ability of nanoporous membranes. The perpendicular orientation of cylinders is provided in Figure 1.30. [93].

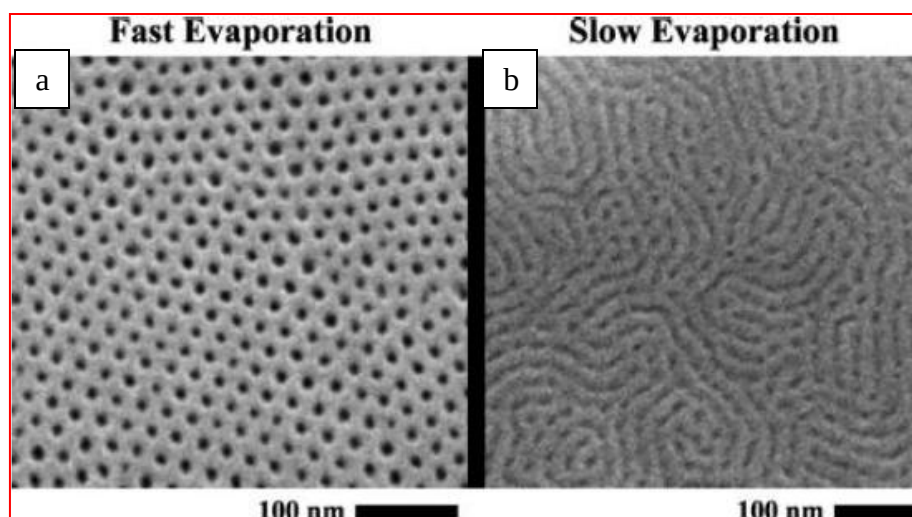


Figure 1.30. PS-PLA block copolymer a) fast evaporation resulting in perpendicular cylinders b) parallel cylinder orientation due to slow evaporation [93].

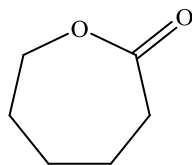
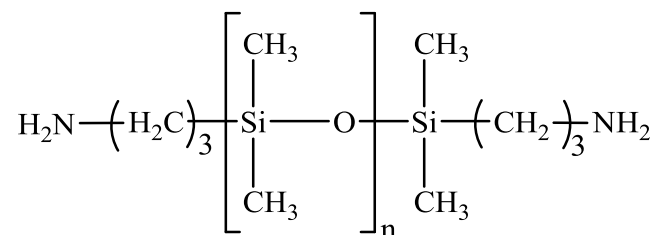
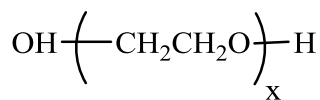
In this study, PCL-PDMS-PCL crystalline-amorphous and PCL-PEO-PCL crystalline-crystalline triblock copolymers were synthesized and their morphologies were studied.

Chapter 2

EXPERIMENTAL

2.1. Materials

ϵ -Caprolactone (ϵ -CL) was purchased from Aldrich. α,ω -Aminopropyl terminated Poly(dimethylsiloxane) (PDMS) oligomers with number average molecular weights $\langle M_n \rangle$ of 1000 g/mol, 3200 g/mol, 10800 g/mol and 31500 g/mol were kindly supplied by Wacker Chemie, Germany and were used as received. Poly(ethylene oxide) glycol (PEO) oligomers (Aldrich) with $\langle M_n \rangle = 2000$ g/mol, 4600 g/mol, and 8500 g/mol were used as received. Stannous octoate (T-9) was obtained from Air Products. All chemicals were reagent grade and were used without further purification. Reagent grade xylene (mixtures of isomers) (Merck), n-hexane, toluene, 2-butanone, chloroform, dichloromethane, isopropyl alcohol, tetrahydrofuran and N,N-dimethyl formamide were used without further purification. Technical grade methanol was used in polymer coagulation. Number average molecular weights of amine terminated oligomers were determined by end group titration using standard hydrochloric acid and bromophenol blue indicator in methanol. Chemical structures of the reactants used during the synthesis are provided in Table 2.1. Various characteristics of the oligomers, such as number average molecular weights, numbers of repeat units are provided on Table 2.2.

Table 2.1. Chemical structures of reactants used during the synthesis ϵ -Caprolactone α,ω -Aminopropyl terminated poly(dimethylsiloxane)

Poly(ethylene oxide) glycol

Table 2.2. Characteristics of the starting oligomers

Oligomer Code	$\langle M_n \rangle$ (g/mol)	Av. repeat units (n)
PEO-2.0K	2000	45
PEO-4.6K	4600	104
PEO-8.5K	8484	192
PDMS-1.0K	1000	11
PDMS-3.2K	3200	41
PDMS-11.0K	10800	143
PDMS-32.0K	31500	423

2.2. Reaction Procedures

2.2.1. Synthesis of polycaprolactone-polydimethylsiloxane-polycaprolactone (PCL-PDMS-PCL) Triblock Copolymers

Ring opening polymerization reactions of ϵ -caprolactone were conducted in 250 mL, three-neck round bottom Pyrex flasks equipped with an overhead stirrer and a thermometer. Calculated amounts of ϵ -caprolactone, α,ω -aminopropyl terminated PDMS, stannous octoate and xylene were introduced into the flask. The homogeneous mixture was heated slowly to $127^{\circ}\text{C} \pm 5^{\circ}\text{C}$ and kept at this temperature for about 24 hours. Due to the increase in the viscosity as the polymerization reaction proceeded, additional appropriate amounts of xylene were added for dilution. The polymer was coagulated in methanol or n-hexane under strong agitation depending on the composition of the copolymer. The resulting precipitate was filtered and dried in an 50°C air oven until constant weight. The yields of the reactions were calculated as the ratio between the weight of recovered polymeric material and the total weight of reactants. Reaction scheme is given in Figure 2.1.

A typical procedure used for the preparation of PCL-PDMS-PCL with average block lengths of 3000 g/mol each was as follows: 3.00 g of ϵ -caprolactone monomer, 1.60 g of PDMS-3.2K macroinitiator, 0.023 g of T-9 catalyst and 1.84 g of xylene were weighed into the reaction flask. The catalyst and solvent amounts were 0.5% (by weight) and 40% (by weight) of the reactants, respectively. The system was heated up to $\sim 130^{\circ}\text{C}$ and kept at this temperature for 24 hours. As the reaction proceeds, the viscosity of the medium increased.

Therefore, additional solvent was introduced into the reactor whenever necessary. After 24 hours of heating, the system was quenched to room temperature and diluted with xylene to obtain a solution of 20% solid by weight. The resulting solution was coagulated by dropwise addition onto methanol under strong agitation. The recovered polymer was dried and the yield of the reaction was calculated as described above.

2.2.2. Synthesis of polycaprolactone-poly(ethylene oxide)-polycaprolactone (PCL-PEO-PCL) Triblock Copolymers

The same experimental setup described in section 2.2.1. was used. Calculated amounts of ϵ -caprolactone, poly(ethylene oxide)glycol and stannous octoate were introduced into the flask and the mixture was heated up to $127^{\circ}\text{C} \pm 5^{\circ}\text{C}$ in the presence of xylene as the solvent. The reactions were conducted for about 24 hours. Highly viscous polymer solutions obtained were further diluted with appropriate amounts of xylene. The copolymer was coagulated in hexane under strong agitation. The precipitate was washed with hexane several times, filtered and dried in oven at 50°C until constant weight. The yields of the reactions were calculated as described earlier in section 2.2.1. Reaction scheme is given in Figure 2.2. A typical procedure used for the preparation of PCL-PEO-PCL with average block lengths of 2000 g/mol each was as follows:

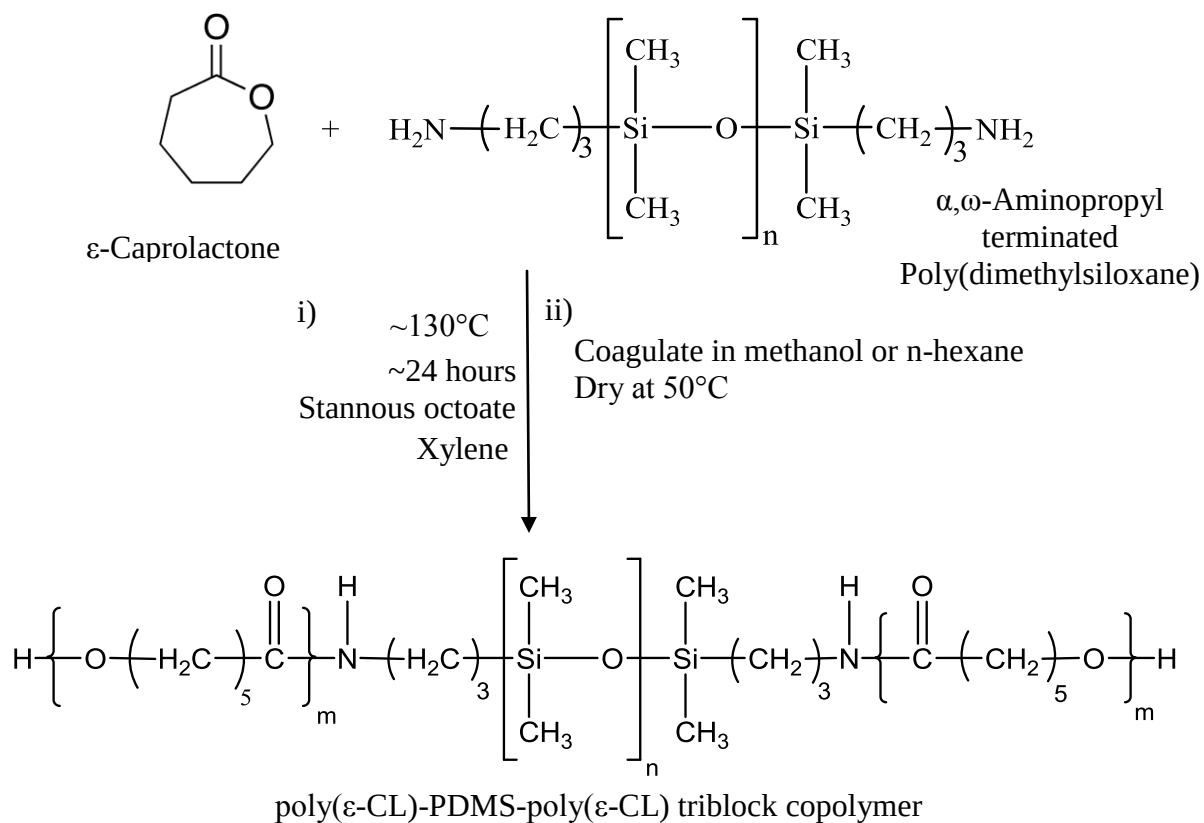


Figure 2.1. Reaction scheme for the synthesis of poly(ϵ -CL)-PDMS-poly(ϵ -CL) triblock copolymers

2.00 g of ϵ -caprolactone monomer, 1.00 g of PEO-2.0K macroinitiator, 0.015 g of T-9 catalyst and 1.20 g of xylene were weighed into reaction flask. The catalyst and solvent amounts were 0.5% (by weight) and 40% (by weight) of the reactants, respectively. The medium was heated to 130°C and kept at this temperature for 24 hours. Additional solvent was added to control the viscosity throughout the reaction. After 24 hours, the system was

quenched to room temperature and diluted with xylene to obtain a solution of 20% solid by weight. The resulting solution was coagulated dropwise onto hexane under strong agitation. The recovered polymer was dried and the yield of the reaction was calculated as described earlier.

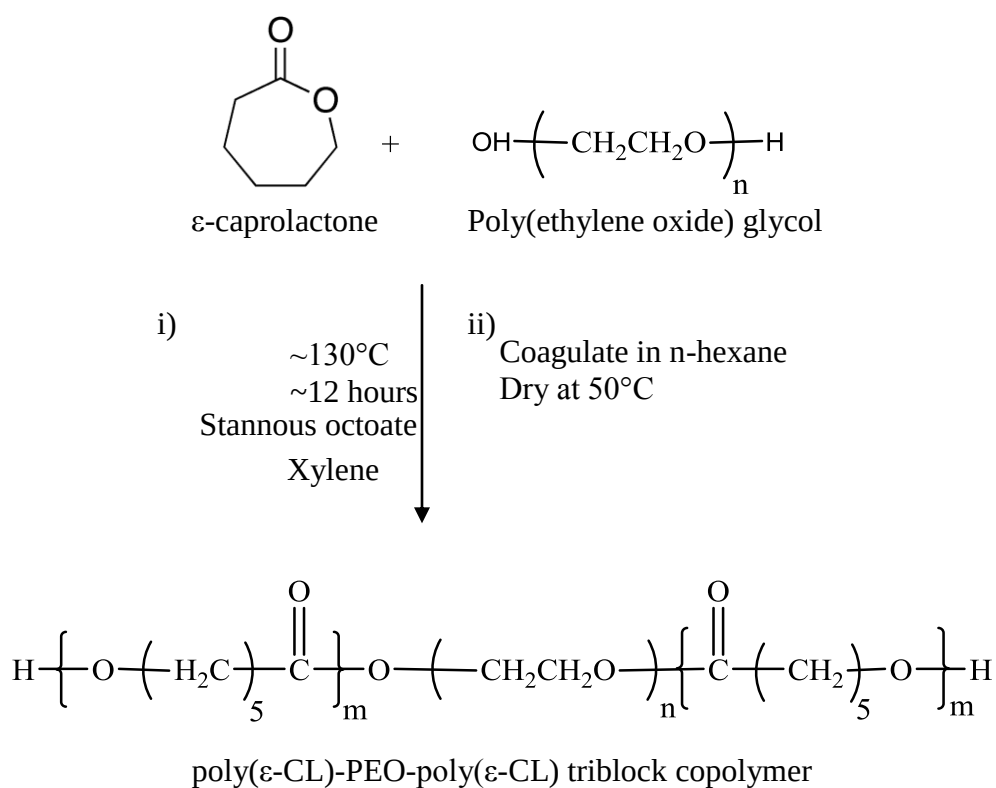


Figure 2.2. Reaction scheme for the synthesis of poly(ε-CL)-PEO-poly(ε-CL) triblock copolymers

2.3. Characterization Methods

2.3.1. Spectroscopic Analysis

Fourier transform infrared spectroscopy (FTIR) analysis of solution cast thin films on KBr pellets were performed by using a Nicolet Impact 400 D spectrometer equipped with a DTGS-KBr detector. 32 scans were taken for each spectrum with a resolution of 2 cm^{-1} .

2.3.2. Spin Coating

Polymer solutions were prepared at concentrations of 10% solid by weight and 10 mg mL^{-1} in different solvents. Polymer solutions were spin coated at 2000 rpm for approximately 60 seconds onto either glass or silicon substrates by using Specialty Coating System P6200 Spincoater. Substrates were rinsed with isopropanol prior to spin coating. Spin coated samples were dried in a vacuum oven below the melting temperature of the copolymers.

2.3.3. Gel Permeation Chromatography (GPC) Analysis

Gel permeation chromatography was performed on a Viscotek VE 2001 series instrument equipped with a VE3580 refractive index detector. THF was used as the mobile phase at 35°C flowing at a rate of 1 mL/min . Polymer samples were prepared at a concentration of $1\text{--}2\text{ mg/mL}$ in THF. Molecular weights were determined from calibration curves plotted from narrow molecular weight polystyrene standards purchased from Viscotek.

2.3.4. Static Water Contact Angle (SWCA) Measurements

Polymer films spin coated from 10% solid (w/w) solutions on glass substrates were used to determine the static water contact angles of PDMS containing triblock copolymers. The contact angles were measured by using Kruss Goniometer with 20 μL deionized water drop at room temperature. At least five measurements were taken from different points on the sample surface.

2.3.5. Optical Microscopy Analysis

Spin coated polymer samples were used for optical microscopy analysis. Nikon Eclipse ME 600 optical microscope was used to capture the images of the spin coated samples at ambient temperature. In order to observe the melting and recrystallization behavior of spin coated samples, Linkam THMS 600 heating stage was attached to the optical microscope. The samples were heated above 5°C of their melting temperatures with 3°C/min heating rate. The images of the samples were recorded continuously while heating and cooling.

2.3.6. Atomic Force Microscopy (AFM) Analysis

Atomic Force Microscopy images were taken by using Nanomagnetics Instruments Multimode Atomic Force Microscope with spin coated samples from 10 mg mL⁻¹ solutions. AFM images were taken in dynamic mode by using Bruker MPP21100 silicon tip with a force constant of 3 N/m and resonance frequency of 75 KHz and MPP12100 silicon tip

with a force constant of 5 N/m and a resonance frequency of 150 KHz. Engagement set points between 0.5 and 0.9 of the free amplitude oscillation were used.

2.3.7. X-Ray Diffraction (XRD) Analysis

X-Ray diffraction studies were conducted by using Bruker D2 Phaser X-ray Diffractometer. 0.1542 nm Cu-K α radiation was used as the X-ray beam and slit length was 1 mm. The scans were performed from 5° up to 80° in 3700 steps. The XRD intensities obtained were plotted against scattering angle 2θ .

2.3.8. Differential Scanning Calorimetry (DSC) Analysis

Thermal properties of triblock copolymers were studied using a TA Q100 DSC instrument. Standard indium was used for temperature and enthalpy calibration. All measurements were made under helium atmosphere at a heating rate of 20°C/min. The samples were heated above their melting temperature (90°C) to erase the thermal history and slowly cooled down to -90°C. The DSC thermograms provided in the dissertation are the signals collected in the second heating runs.

Chapter 3

RESULTS AND DISCUSSION

The major goals of this study were the synthesis, characterization and investigation of the morphology and various physicochemical properties of ABA type triblock copolymers with polycaprolactone (PCL) end blocks and polydimethylsiloxane (PDMS) and poly(ethylene oxide) (PEO) center blocks. Copolymers with a wide range of block lengths were synthesized by ring-opening polymerization of caprolactone, using amine terminated PDMS and hydroxyl terminated PEO as the macroinitiators, in the presence of catalytic amount of tin octoate.

Symmetrical PCL-PDMS-PCL triblock copolymers consisted of crystalline PCL end blocks and amorphous PDMS center blocks, whereas PCL-PEO-PCL systems consisted of crystalline center and end blocks. The properties that were investigated included:

- i) Polydispersities of PCL-PDMS-PCL triblock copolymers via gel permeation chromatography (GPC)
- ii) Morphologies of PDMS containing triblock copolymers with Atomic Force Microscopy (AFM)

- iii) Thermal properties of triblock copolymers with differential scanning calorimetry
- iv) Crystal structures of triblock copolymers with Optical Microscopy
- v) Crystallization of poly(caprolactone) blocks with X-ray Diffractometry (XRD)
- vi) Surface properties of triblock copolymers with static water contact angle measurements (SWCA)

3.1. PCL-PDMS-PCL Triblock Copolymers

ϵ -Caprolactone was polymerized by using aminopropyl terminated PDMS macroinitiators with number average molecular weights of 1000 g/mol, 3200 g/mol, 10800 g/mol and 31500 g/mol. The reaction is initiated with the attack of amine group to the carbonyl carbon of the ϵ -caprolactone. The resulting species propagate until termination, which is mainly due to depletion of the caprolactone monomer. The detailed reaction mechanism was already provided in Figure 1.19. The list of PCL-PDMS-PCL copolymers is given in Table 3.1. together with the block lengths, yields of polymerization reactions and the solvents used.

Table 3.1. Composition and yields of PCL-PDMS-PCL copolymers synthesized

Code	Composition	Block Lengths	Yield	Solvent	Coagulation Solvent
MI-62	PCL-PDMS-PCL	1-1-1	88.2	bulk	Hexane
MI-99		2-2.5-2	94.7		DI H ₂ O
MI-64		1-3-1	90.6		No coagulation
MI-72		3-3-3	87.5	Xylene	methanol
MI-71		3-11-3	87.8		
MI-67		6-11-6	92.0		
MI-70		3-32-3	89.8		
MI-68		6-32-6	92.5		
MI-69		16-32-16	90.3		
MI-102		32-32-32	92.1		

3.1.1. Monitoring the Polymerization Reactions by FTIR Spectroscopy

Syntheses of PCL-PDMS-PCL copolymers were performed by following the procedure provided in the experimental section. When amine terminated PDMS reacts with the caprolactone monomer, an amide linkage is formed. The formation of this linkage can be monitored by FTIR spectroscopy. The FTIR spectrum of PCL-PDMS-PCL (3-3-3) copolymer is given in Figure 3.1. as a general example. It is clearly seen from Figure 3.1. that when amine terminated PDMS is used as an initiator for ϵ -caprolactone polymerization, the peaks arising from the amide linkages formed within the copolymer are observed around 1650 cm^{-1} (amide I or C=O stretching) and 1550 cm^{-1} (amide II bands).

The presence of these peaks clearly indicates that the amine end groups are initiating the polymerization of the caprolactone monomer.

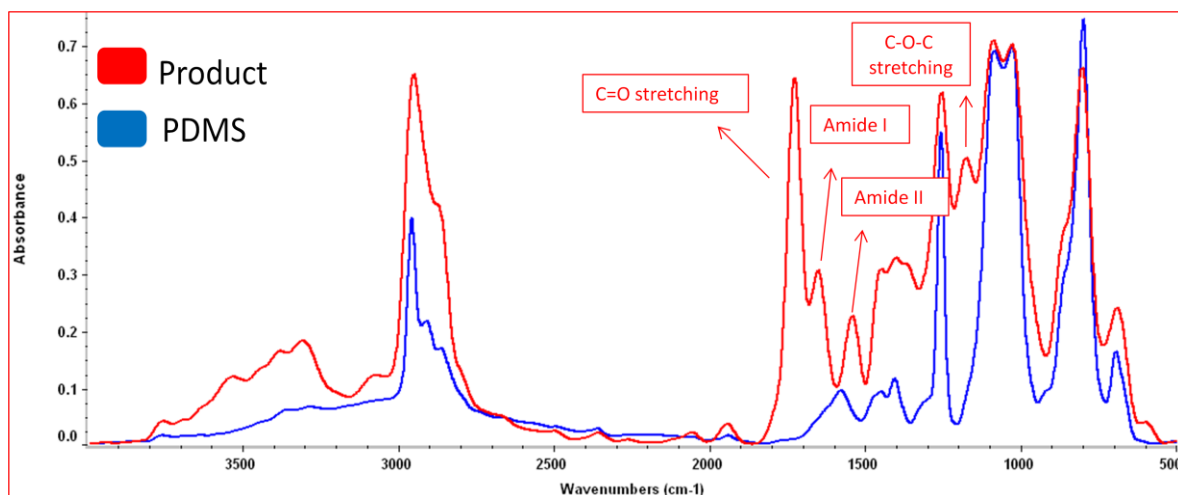


Figure 3.1. FTIR spectra of PCL-PDMS-PCL (3-3-3) copolymer

3.1.2. Gel Permeation Chromatography on PCL-PDMS-PCL Block Copolymers

In order to confirm the formation of PCL-PDMS-PCL triblock copolymers and to determine their average molecular weights and polydispersities, gel permeation chromatography (GPC) was employed. The GPC chromatograms for all copolymer compositions are reproduced in Figure 3.2.

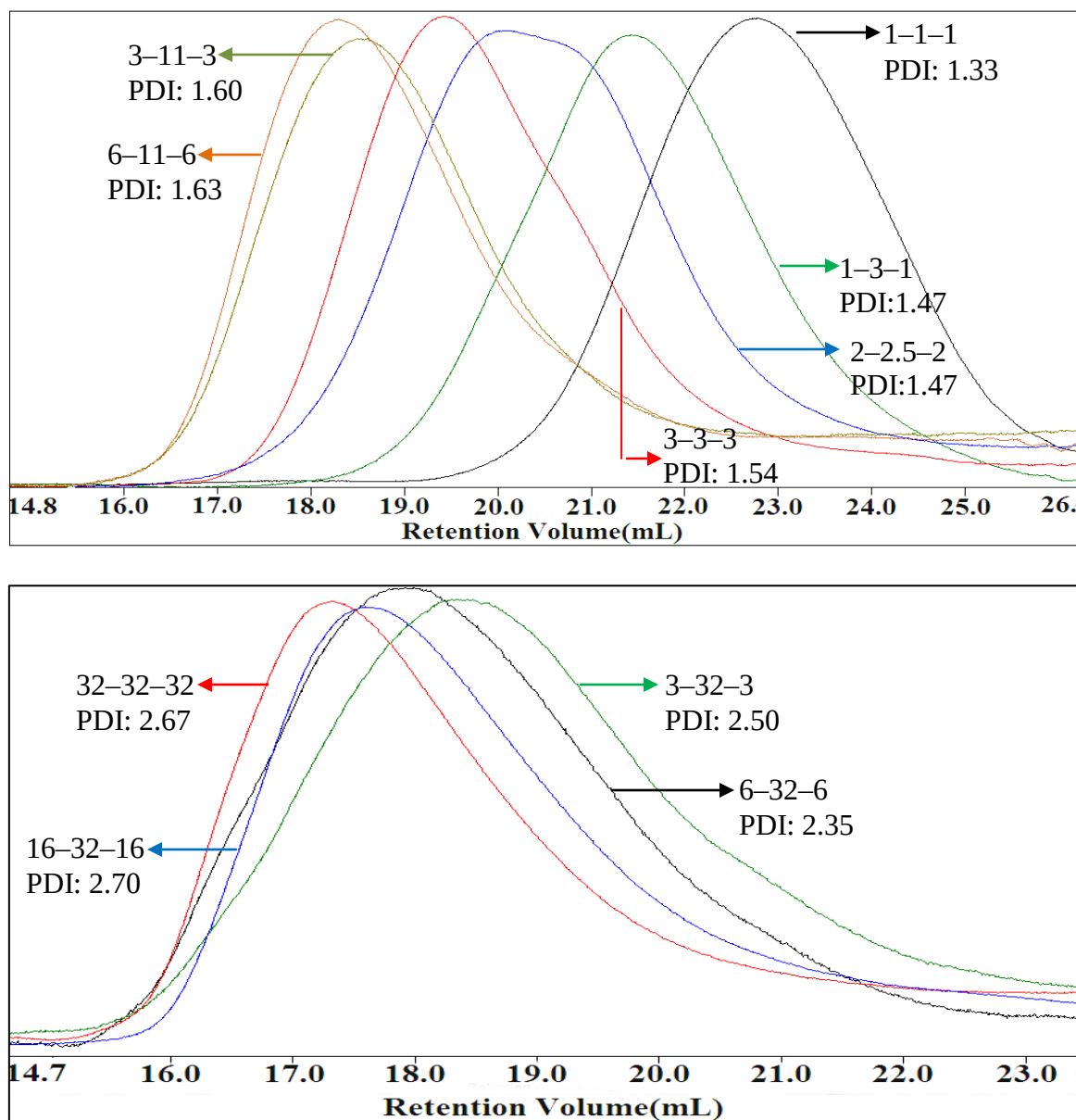


Figure 3.2. GPC chromatograms of PCL-PDMS-PCL copolymers

As expected, as the average molecular weight of the PCL-PDMS-PCL triblock copolymers increase, gradual shifts to lower retention volumes are observed. Polydispersity index (PDI) (or molecular weight distribution) values are also provided on the plots. For copolymers prepared by using PDMS initiators with number average molecular weights of 1K, 2.5K, 3K and 11K, fairly low PDI values (between 1.33 and 1.63) were obtained. Interestingly, as the overall molecular weight of the copolymer increased PDI values also increased. On the other hand fairly high PDI values were measured for PDMS32K initiated copolymer compositions. The high PDI values may be arising from the low initiation efficiency of the macroinitiator or irregular PCL arm growth due to very low concentration of amine end groups present in PDMS32K. However, GPC results clearly confirm the initiation efficiency of all of PDMS macroinitiators and the propagation of ϵ -CL monomer to form PCL-PDMS-PCL triblock copolymers.

3.1.3. Morphologies of PCL-PDMS-PCL Block Copolymers

Block copolymers display different morphologies depending on the nature of the constituent blocks and their molecular weight. When two incompatible blocks are chemically linked together, they tend to microphase separate. The nature and extent of the phase separation can be explained through Flory-Huggins interaction (χ) parameter, which is defined earlier in the introduction part of the dissertation. By multiplying the interaction parameter with the average degree of polymerization (N), a numerical value χN is obtained.

This value can be used to estimate the degree or the extent of phase separation within the block copolymer. According to computational studies, χN value must be greater than 10.5 in order to obtain a phase separated morphology [10]. Below this value entropy gains over the energetic penalty of mixing, therefore a disordered morphology is obtained. The Hildebrand solubility parameters used to determine the interaction parameter are provided in Table 3.2.

Table 3.2. Solubility parameters used to calculate the interaction parameter [94]

Name	Hildebrand solubility parameter (δ) [(cal/cm ³) ^{1/2}]
PDMS	7.30
PCL	8.55

The χ values are calculated using equation 1.2. which is given as $\chi_{AB} = (\delta_A - \delta_B)^2 V_c / RT$, where V_c represents the reference unit volume, which is arbitrarily set to 100 cm³/mol, R is the gas constant and T is the temperature. The calculated χN values are provided in Table 3.3. for theoretical molecular weights of block copolymers, which are calculated from the yields of polymerization reactions.

Table 3.3. Calculated χN values for PCL-PDMS-PCL block copolymers

Composition		Theoretical <Mn> for PCL blocks	Theoretical <Mn> for PDMS block	# repeat units for PCL blocks	# repeat unit for PDMS block	N (effective degree of pzn)	χ	χN
PCL-PDMS-PCL	1-1-1	1764	1000	15.5	11.2	27.6	0.60	16.5
	2-2.5-2	3787	2500	33.2	31.4	65.7	0.60	39.3
	1-3-1	1932	3200	16.9	40.9	54.6	0.60	32.7
	3-3-3	5248	3200	46.0	40.9	88.8	0.60	53.1
	3-11-3	5268	10500	46.2	146.3	178.6	0.60	106.8
	6-11-6	11044	10500	96.8	146.3	238	0.60	142.4
	3-32-3	5388	31500	47.2	430.1	421	0.60	251.8
	6-32-6	11094	31500	97.2	430.1	479.8	0.60	286.9
	16-32-16	28880	31500	253.0	430.1	662.9	0.60	396.4
	32-32-32	58969	31500	516.6	430.1	972.6	0.60	581.6

The degree of incompatibility increases with increasing molecular weight of the block copolymer. It can also be seen that as the length of PDMS block increases, the χN value increases dramatically. To summarize, it can be estimated that PCL-PDMS-PCL block copolymers should display microphase separated morphologies.

It was reported that PCL-PDMS-PCL block copolymer with a composition of 2-2.5-2 exhibits lamellar morphology [95]. In general, there are two possible orientations of molecules in order to form the lamellar structure [98]. These orientations are given in Figure 3.3.

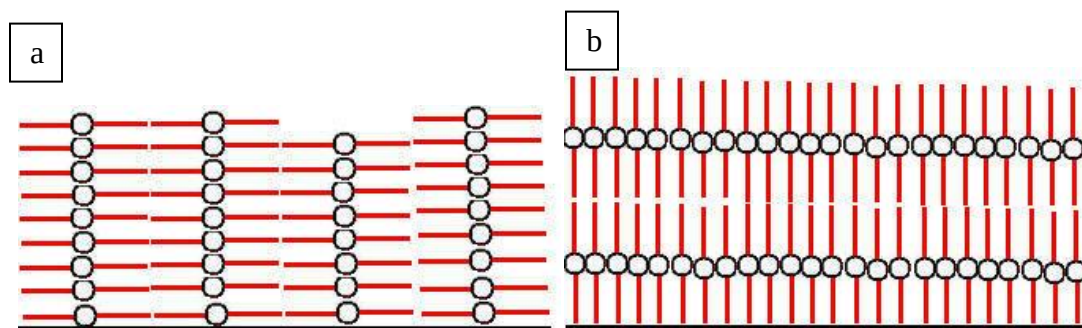


Figure 3.3. Two different orientations of ABA molecules two form the lamella (a) Lamellae perpendicular, (b) Lamellae parallel to the substrate

If the affinities of constituent blocks toward the substrate are equal, the molecules are aligned horizontally and form the lamellae perpendicular to the substrate surface (Figure 3.3.a). If one of the blocks has a higher preference for the substrate surface, the molecules are aligned normal to the surface resulting in a parallel lamellar orientation (Figure 3.3.b). These estimations can be accepted if there are non-bendable and inflexible blocks present within the block copolymer. In the case of PCL-PDMS-PCL, it can be foreseen that the PCL blocks will bend over the PDMS backbone due to very high flexibility of silicone at room temperature [96]. The orientation of molecules on the substrate will be determined by the affinity of constituent blocks towards the surface. As shown in Figure 3.3 the orientations will be the same. The estimated orientations of once folded PCL-PDMS-PCL block copolymer on the substrate surface are provided in Figure 3.4.

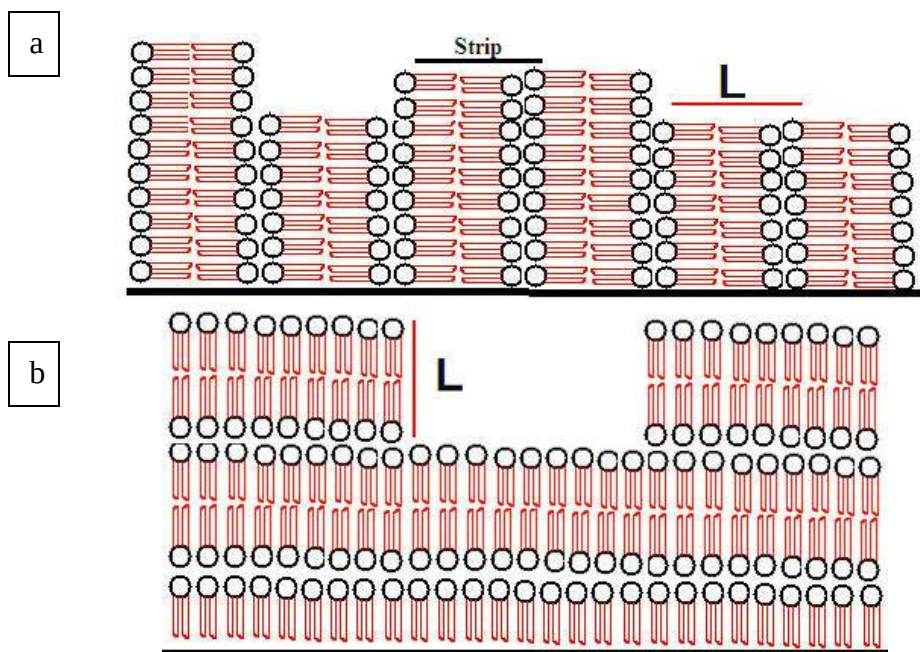


Figure 3.4. Possible orientations of molecules on the substrate surface a) Lamellae perpendicular to the substrate b) Lamellae parallel to the substrate (Note that the circle represents the PDMS block, the straight lines represent PCL blocks)

The compositional difference due to strip formation (Fig. 3.4.a) on the surface can be analyzed through atomic force microscopy (AFM) phase imaging in case of lamellae perpendicular to the substrate surface (Fig 3.4.a). While the phase image will reflect the strips on the surface as a phase contrast, there will be no significant contrast in the height image since there is no layer formation. For lamellae parallel to the substrate surface (Fig 3.4.b), AFM phase image will give no phase contrast since the surface composition is the

same, but the layer formation can be obtained from AFM height images. In brief, the lamellar spacing can be obtained from AFM for both cases of lamellae formation.

The copolymers were dissolved (10 mg/mL) in appropriate solvents that can dissolve both PCL and PDMS and spin coated on silicon substrates by using the recipe provided in Chapter 2. The solvents used to dissolve the copolymers are given in Table 3.4.

Table 3.4. The solvents used to dissolve PCL-PDMS-PCL copolymers for AFM analysis

Composition	Solvent
2-2.5-2	Methyl ethyl ketone
3-3-3	
6-11-6	Toluene
16-32-16	
32-32-32	

AFM phase and height images of PCL-PDMS-PCL block copolymer with 2-2.5-2 composition are given in Figure 3.5. It is clearly seen that there is a significant phase contrast in the AFM phase image (Fig 3.5.a). The strip formation due to two different phases on the surface can be seen in the phase image, which is an indication of lamellae perpendicular to the substrate surface. The measured layer thickness is around 25 nm from the phase image. In addition there is no significant contrast in the AFM height image (Fig 3.5.b). By using the calculated theoretical molecular weight of PCL block (Table 3.3) within 2-2.5-2 block copolymer, the length of expanded PCL can be calculated as 15.24

nm. If the PCL block is accepted to be once folded over the PDMS mid-block, the length of once-folded PCL chain becomes 7.62 nm. In order to estimate the radius of gyration (R_g) of PDMS mid-block, the formula $\langle R^2 \rangle_g = 0.274 \times M_w^{0.53}$ can be used [97]. The R_g of the PDMS mid-block is calculated as 4.16 nm. By using the estimated values for once-folded PCL length and R_g of PDMS mid-block, the strip size can be calculated as $(2 \times 7.62 + 2 \times 4.16)$ 23.56 nm. This value is in agreement with the measured value from AFM phase images. Therefore, it can be estimated that the lamellae is formed perpendicular to the substrate surface which resulted in strip formation with an average periodicity of 25 nm and a contact angle value between that of PDMS and PCL (Figure 3.5.a).

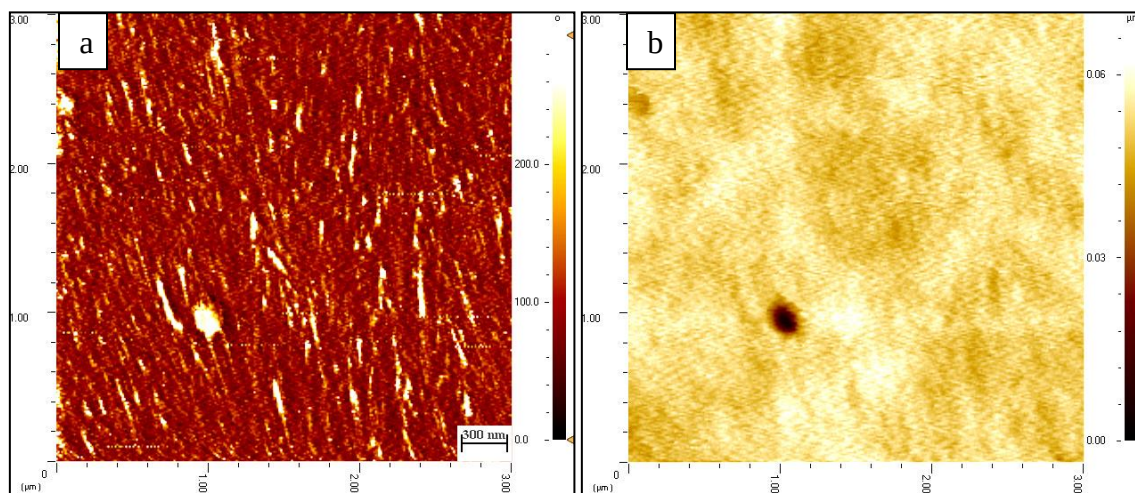


Figure 3.5. 3x3 μm AFM images of PCL-PDMS-PCL copolymer with 2-2.5-2 composition
a) phase image, b) height image

The AFM phase and height images of PCL-PDMS-PCL with the composition 3-3-3 are given in Figure 3.6. When the same calculations are done for PCL-PDMS-PCL copolymer with 3-3-3 composition, the length of expanded PCL chain is found to be 21.09 nm for the theoretical molecular weight of PCL block. The radius of gyration is calculated as 4.44 nm by using the given formula earlier. Therefore, the lamellar thickness becomes $(2 \times 10.54 + 2 \times 4.44)$ 29.97 nm if lamellar morphology is being accepted with once-folded PCL chains. The size of each period within the AFM phase image is ~ 20 nm (Fig 3.6.a). There should be no contrast in the height image if the lamellar morphology is being accepted. On the contrary, there is a contrast in the height image. In order to analyze if there is any layer formation, the height profile of a wider surface scan ($20 \times 20 \mu\text{m}$) is provided in Figure 3.7.

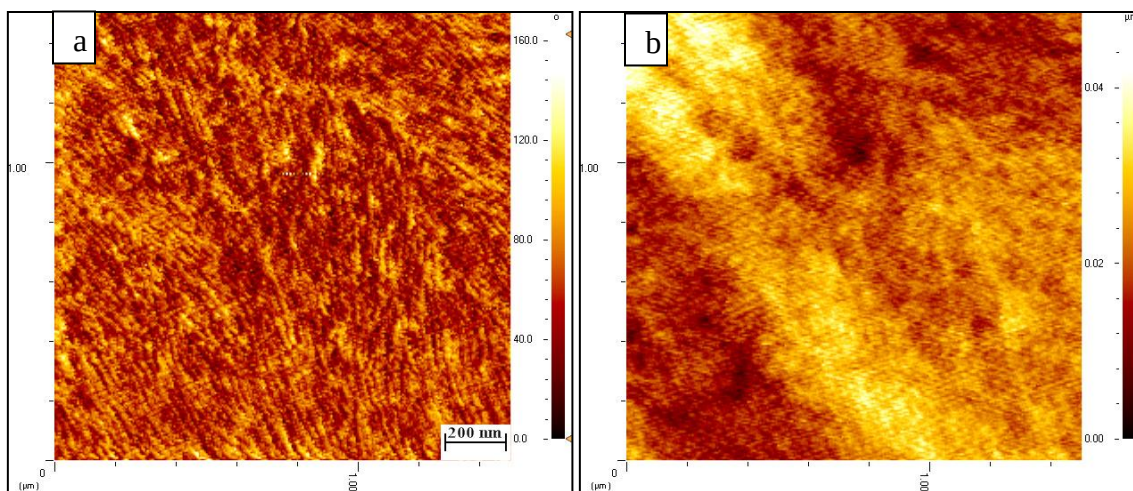


Figure 3.6. 1.5x1.5 μm AFM phase and height images of PCL-PDMS-PCL with 3-3-3 composition

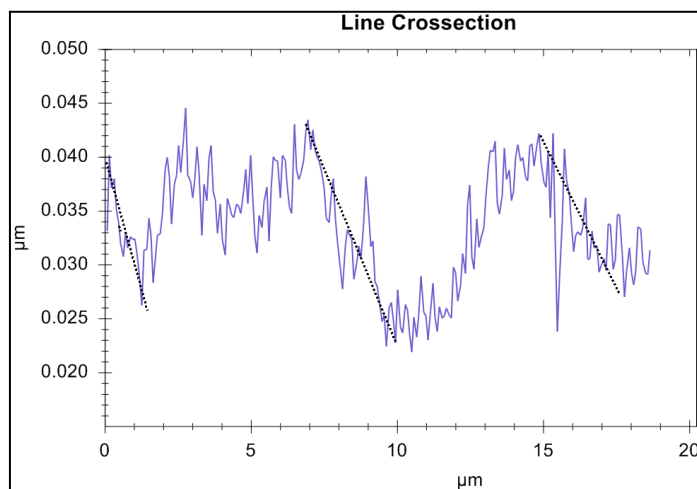


Figure 3.7. Height profile of PCL-PDMS-PCL copolymer with a composition of 3-3-3

The layer thickness is found to be approximately 20 nm from the profile provided above. Therefore, the calculated and measured layer thickness values are contradictory for lamellar orientation. The other possibility that this composition can display is the cylindrical orientation. In a cylindrical morphology, both strips and layers can be observed [76]. For a perfect cylinder to form, the blocks will form a concentric structure in which the PCL domains are stacked inside the cylinder and PDMS block covers the outermost layer. The illustration is given in Figure 3.8.

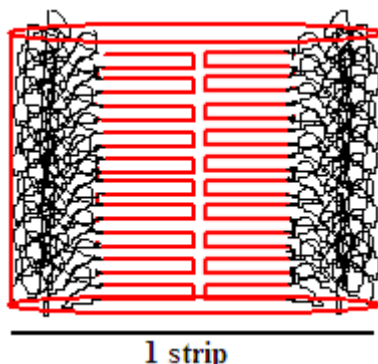


Figure 3.8. Possible cylinder orientation of PCL-PDMS-PCL copolymer

The cylindrical orientation given in Figure 3.8 will have a size of $(2 \times 10.54 + 2 \times 4.44)$ 29.96 nm which is not consistent with the measured layer thickness. Therefore, the cylinder that is formed should have a different structure. Instead of a perfect cylinder, the structure can have a semi-cylinder structure in which PCL blocks are aligned forming a line and PDMS block can be at any position. Therefore, while some regions of cylinder are PCL rich, some will be PDMS rich resulting in phase contrast in the AFM. The orientation is illustrated in Figure 3.9.

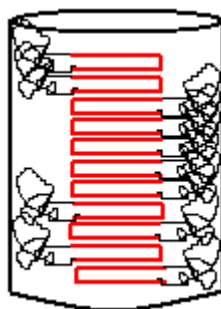


Figure 3.9. Semi-cylindrical orientation of PCL-PDMS-PCL copolymer

The size of the cylinder becomes $(1 \times 10.54 + 2 \times 4.44)$ 19.42 nm for such an orientation proposed in Figure 3.9. The calculated cylinder size for the PCL-PDMS-PCL copolymer with 3-3-3 composition is in good agreement with the measured value (~ 20 nm) from AFM. Therefore, the morphology can be accepted as cylindrical for which an illustration is provided in Figure 3.9.

When the length of PDMS is further increased up to 10500 g/mol, the strength of segregation is almost tripled for 6-11-6 copolymer with respect to the previous copolymer composition (Table 3.3). Therefore, stronger phase segregation is expected to take place. One important thing that should be taken account is the enhanced migration of silicone towards the surface upon the increase in the PDMS length. Material surfaces with high PDMS content are difficult to image with AFM. When PCL-PDMS-PCL copolymer with 6-11-6 composition is scanned by applying hard tapping to the surface, the contrast in the phase image is lost. The hard-tapping AFM phase and height images of 6-11-6 copolymer are provided in Figure 3.10.

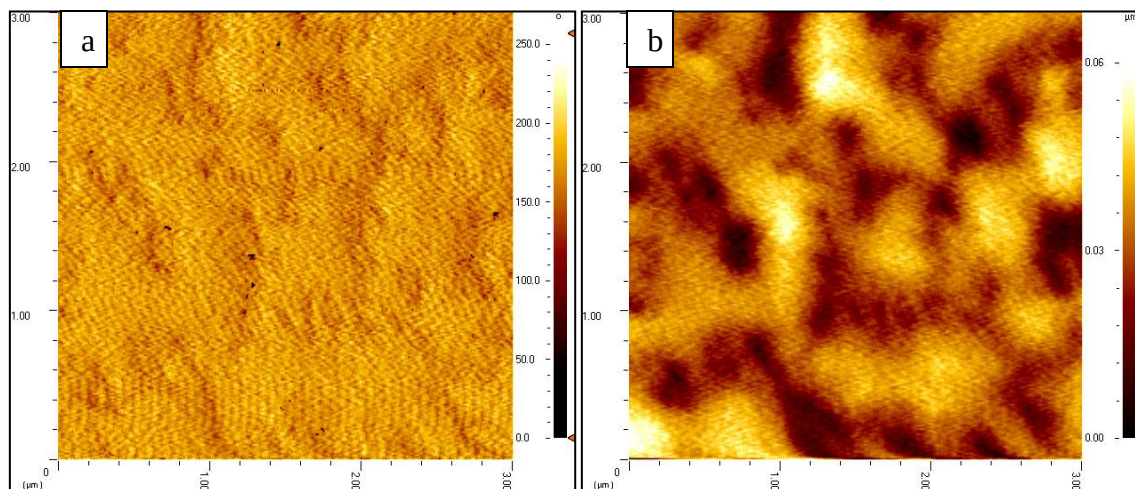


Figure 3.10. 3x3 μm AFM a) phase and b) height images of 6-11-6 copolymer in hard-tapping mode

As clearly seen from the AFM images, while the contrast is almost lost in the phase image due to PDMS coverage on the surface, the segregated morphology can be observed in the height image. When soft tapping is applied on the surface of the same copolymer, the phase separated morphology can be observed explicitly. Therefore, the rest of the AFM images that will be shown are taken in soft tapping mode. The AFM images of 6-11-6 copolymer taken in soft-tapping mode are provided in Figure 3.11.

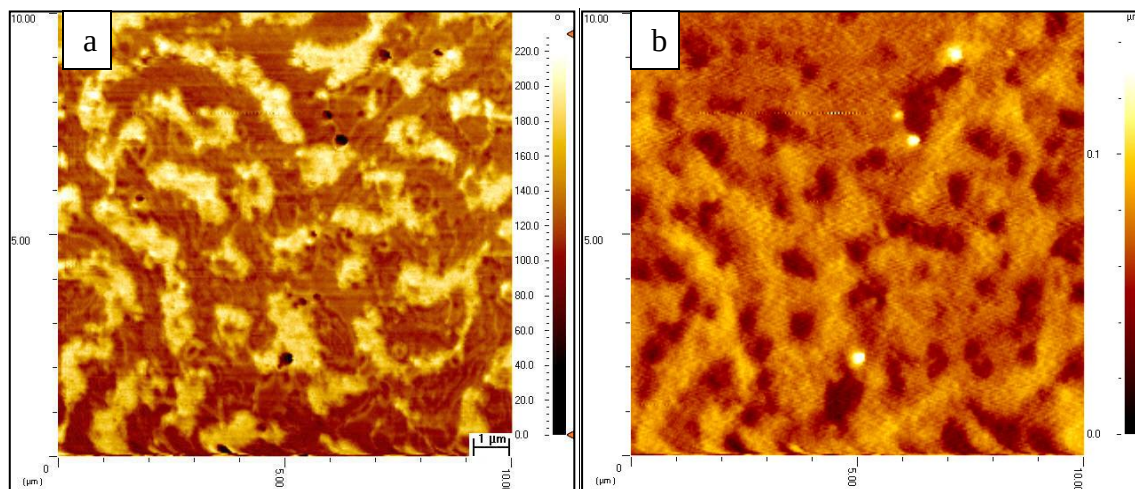


Figure 3.11. 10x10 μ AFM a) phase and b) height images of 6-11-6 copolymer in soft tapping mode.

The darker areas in the phase image are brighter in the height image (Figure 3.11. a,b). This indicates that the darker regions in the phase image are at a higher position than their surroundings. The average altitude of bright regions is measured as ~ 35 nm from the height profile which is given in Figure 3.12.

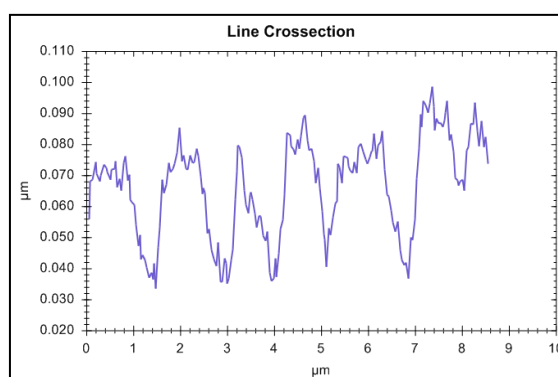


Figure 3.12. Height profile of 6-11-6 copolymer surface measured from 10x10 μ AFM height image

Therefore, dark regions in the phase image represent PDMS rich domains which are accumulated as mounds due to high chain mobility and compressibility of silicone at room temperature. The measurable domain sizes are between 100 nm and 500 nm. However, it is difficult to estimate the orientation of copolymer chains by using the AFM phase and height images. Additional analysis such as small angle x-ray scattering measurements should be performed for exact determination of copolymer morphology.

When the molecular weight of PDMS is increased up to 31500 g/mol by keeping PCL fraction constant, the strength of segregation is doubled for 16-32-16 copolymer composition as seen from Table 3.3. AFM images for 10 x 10 μm scan are given in Figure 3.13 for 16-32-16 copolymer composition.

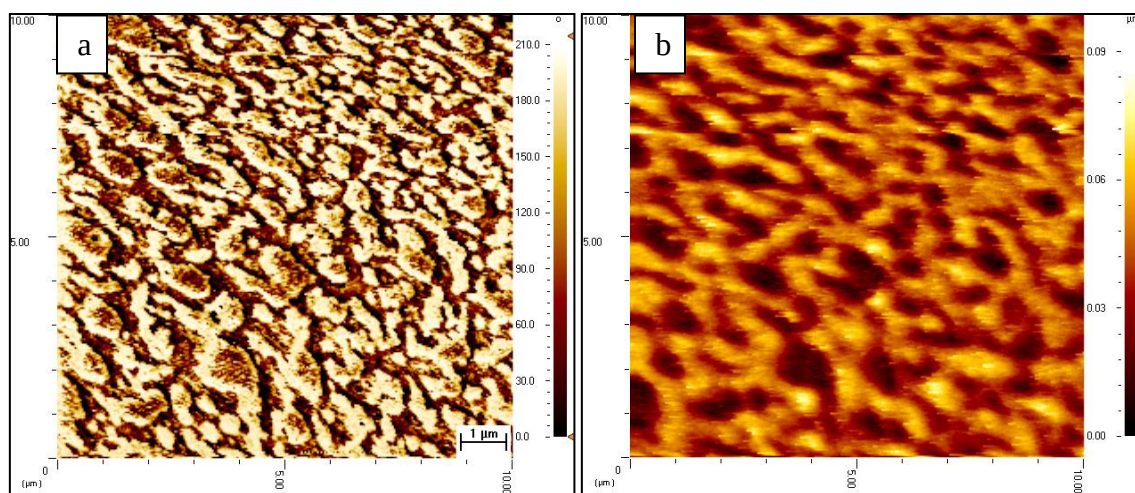


Figure 3.13. 10x10 μm AFM images are provided for PCL-PDMS-PCL copolymer of 16-32-16 composition, a) phase image, b) height image

It is seen that the darker regions in the AFM phase image correspond to PDMS rich domains due to the reason explained earlier. The surface of the material is strongly segregated having nonhomogeneous domain sizes. When a smaller surface area is scanned, microphase separation is better observed. The 3x3 μm AFM phase and height images are provided in Figure 3.14.

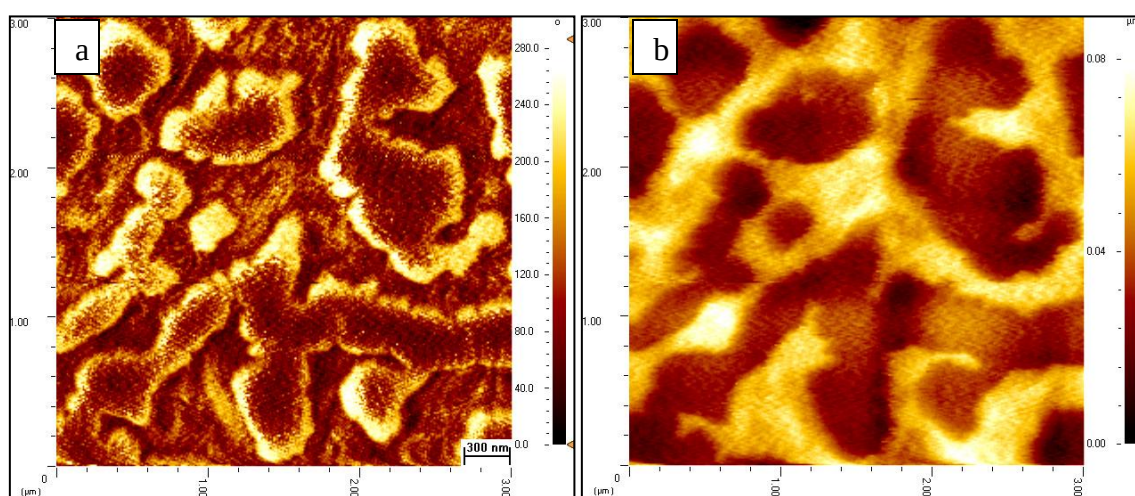


Figure 3.14. 3x3 μm AFM a) phase and b) height images of 16-32-16 copolymer

The darker regions in the phase image are PDMS rich domains which are ~ 40 nm higher with respect to their surroundings as indicated in height profile given in Figure 3.15. However, it is clearly seen that there is a thin PDMS wetting layer which hinders the imaging of actual domain sizes and morphology. Therefore, the orientation of molecules cannot be determined from AFM images. As indicated earlier, further analysis should be performed.

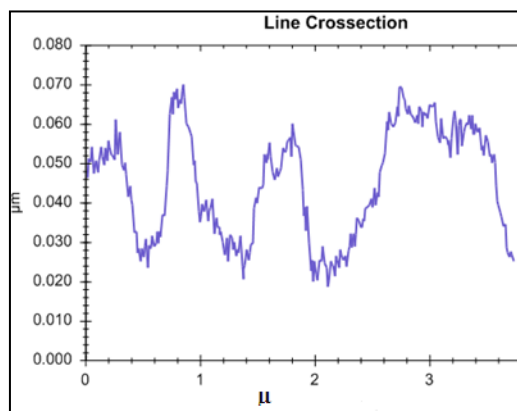


Figure 3.15. Height profile of PCL-PDMS-PCL copolymer with 16-32-16 composition

The highest molecular weight PCL-PDMS-PCL copolymer studied in this study has a 32-32-32 composition. Due to increase in the molecular weight of the copolymer, the strength of segregation is further increased (Table 3.3). AFM images of 32-32-32 PCL-PDMS-PCL copolymer are shown in Figure 3.16.

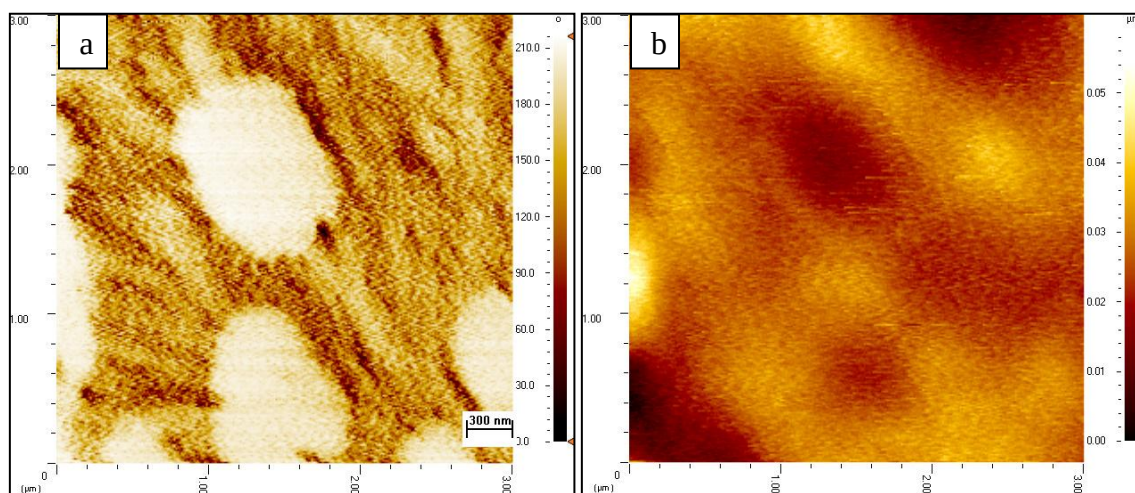


Figure 3.16. 3x3 μm AFM a) phase and b) height images of 32-32-32 copolymer

The brighter regions in the phase image correspond to PCL rich domains. As a result of the increase in the segregation strength, the domains are now better resolved compared to other compositions of PDMS 31500 g/mol. Different than the previous copolymer compositions the height difference between the bright and dark regions is smaller. The height profile of 32-32-32 PCL-PDMS-PCL copolymer is provided in Figure 3.17.

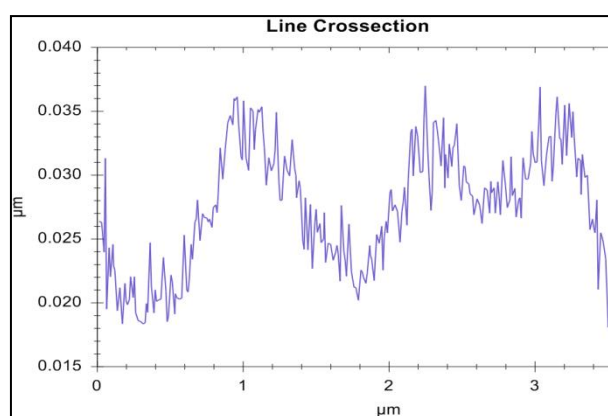


Figure 3.17. Height profile of 32-32-32 PCL-PDMS-PCL copolymer

The measured height difference from Figure 3.17 is ~15 nm. This means that the accumulation of PDMS rich domains is not as strong as they were for the previous cases of PDMS with 31500 g/mol. Therefore, it can be attributed to the increase in the molecular weight of PCL end blocks which reduces the mobility of PDMS domains upon crystallization which is enhanced with increasing chain length. As PCL blocks are better aligned and packed, the chains become stiffer resulting in a decrease in the chain mobility.

The nature of the orientation of the copolymer chains remains unknown, so more detailed analysis should be carried out in order to determine the morphology of the copolymer.

3.1.4. Differential Scanning Calorimetry Analysis of PCL-PDMS-PCL Triblock Copolymers

DSC analysis was performed on PCL-PDMS-PCL triblock copolymers in order to understand the effect of PDMS mid-block length on the crystallization of PCL end-blocks. Representative DSC thermograms showing PCL melting are provided in Figure 3.18.

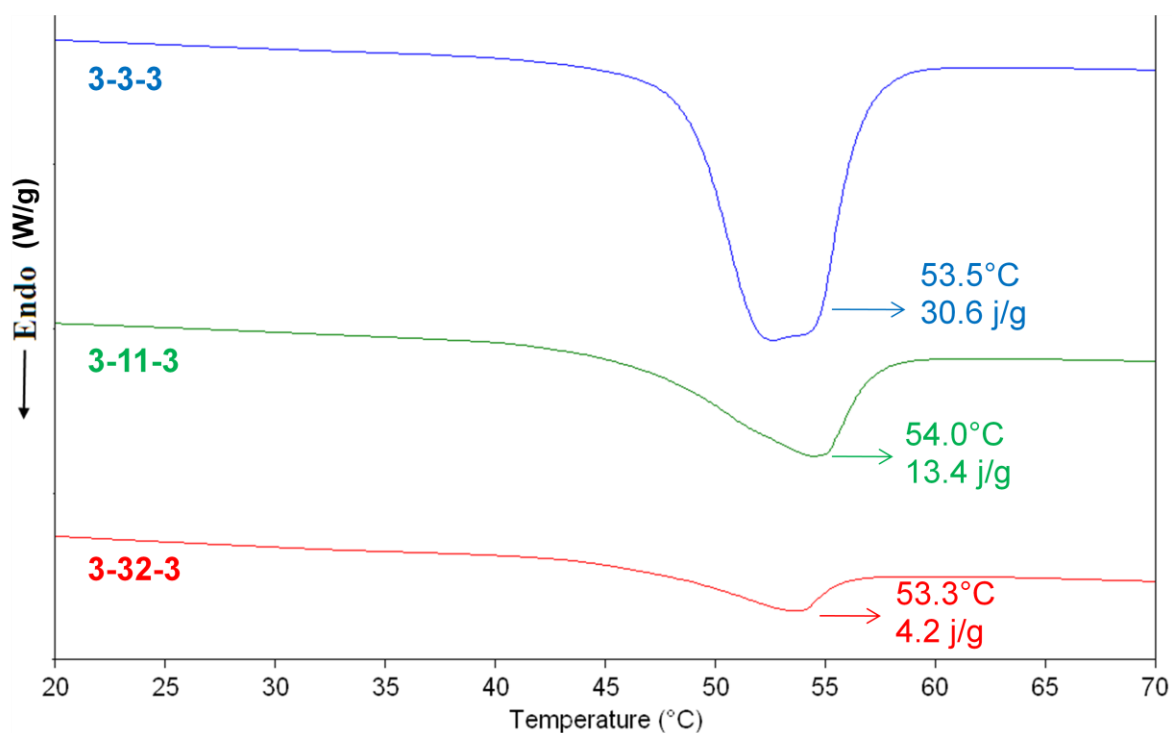


Figure 3.18. DSC thermograms of three different mid-block lengths of PCL-PDMS-PCL copolymers at a heating rate of 20°C/min

The melting of crystalline PCL domains takes place at around 53.5°C for the three copolymer compositions (Figure 3.18.). The main difference between the copolymers with different PCL content is in the absolute value of the enthalpy of fusion, which is expected. However, it is interesting to observe that even in PCL-PDMS-PCL (3-32-3) a crystalline PCL phase is observed, clearly indicating presence of excellent microphase separation in the copolymers.

3.1.5. Optical Microscopic Investigation of the Crystallization of PCL-PDMS-PCL Triblock Copolymers

Crystalline-amorphous block copolymers display interesting properties since one component can crystallize and the other cannot. The crystallization of the crystalline domain will be strongly dependent on the presence of the amorphous domain and the extent of compatibility between the constituent blocks. The crystal structure that is formed by the crystalline domain can be analyzed by using optical microscopy (OM) imaging. The extent of crystallization is associated with the PDMS mid-block and PCL end-blocks molecular weights.

Homo-PCL has small crystal domains which can be observed under optical microscopy. Polarized and non-polarized optical microscopy images of PCL are provided in Figure 3.19.

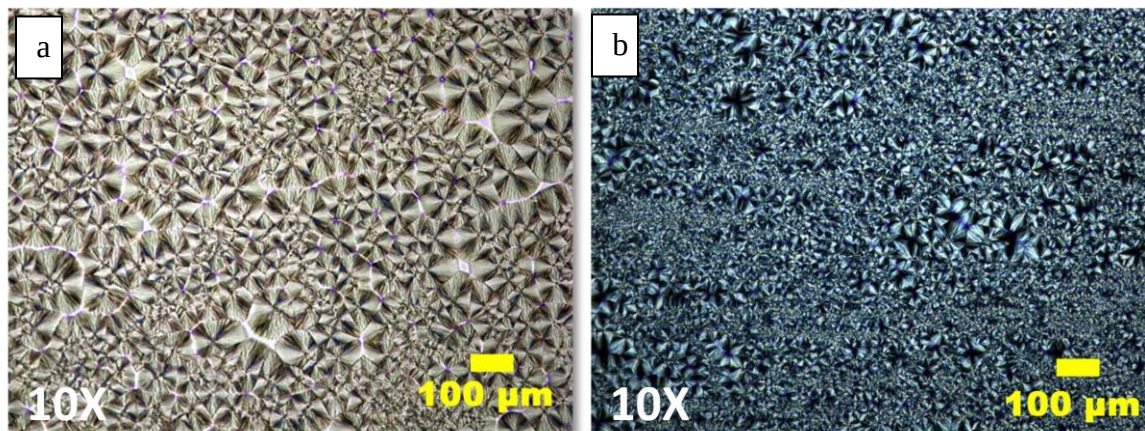


Figure 3.19. a) non-polarized and b) polarized OM images of homo-PCL at 10X magnification

PCL homopolymer has completely space filling crystalline spherulites as an intrinsic property [100]. Therefore, the crystal structure of homopolymer can be used as a reference in order to investigate the effect of copolymerization with PDMS which is used as the mid-block. The OM images for PCL-PDMS-PCL copolymer of 1-1-1 composition are provided in Figure 3.20.

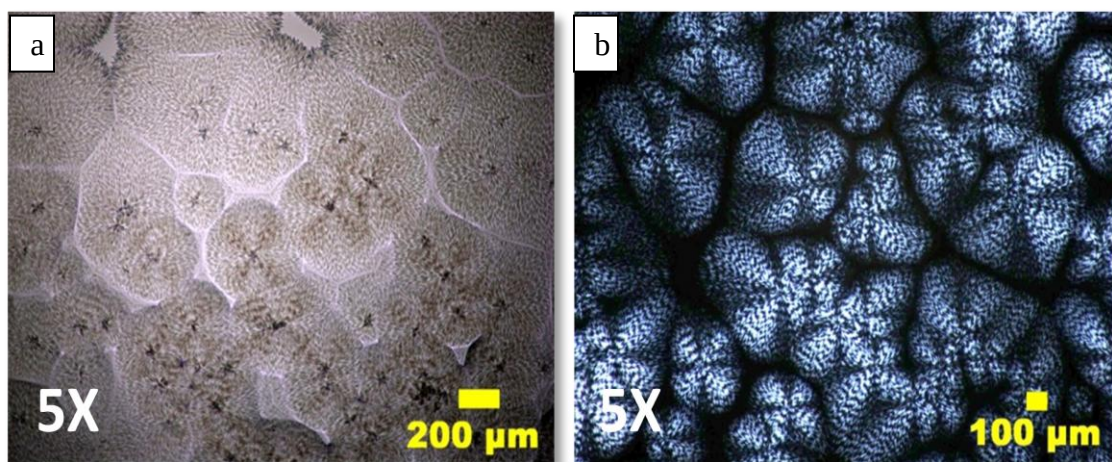


Figure 3.20. a) Non-polarized and b) polarized OM images of 1-1-1 copolymer at 5X magnification

As distinct from the PCL homopolymer crystal structure, the crystal spherulites are larger and they are apart from each other as seen from the Figure 3.20. A possible reason for such a crystal formation can be the short length of PCL domains which reduces the packing ability of polymer chains. Another factor that should be taken into account is the presence of PDMS as the mid-block which interferes to the crystallization of PCL and eventually reducing the extent of crystallization. The effect of PDMS molecular weight can be further investigated by increasing the length of PDMS mid-block. The OM images of 1-3-1 PCL-PDMS-PCL copolymer are given in Figure 3.21

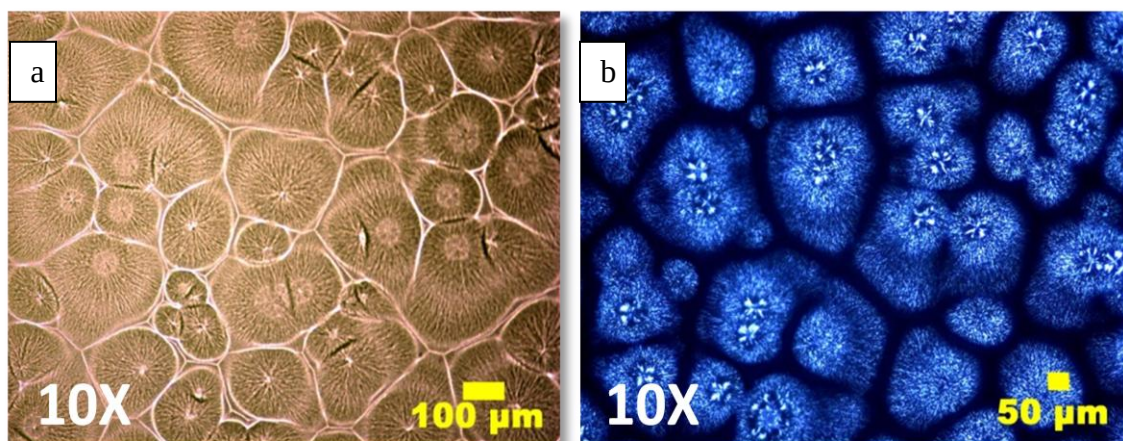


Figure 3.21. a) Non-polarized and b) polarized OM images of 1-3-1 copolymer at 10X magnification

The PCL length is kept constant and PDMS length is tripled for 1-3-1 block copolymer. The crystal size is a bit smaller and the crystal domains are more segregated compared to the previous copolymer composition. The interesting thing that takes place is crystal domains can form stronger crystals as seen from Figure 3.21.b. This phenomenon can be attributed to the increase in the segregation strength upon the increase in the PDMS mid-block length, which results in a better phase separation and eventually a better crystallization of the crystalline domain. Therefore, when PCL block length is increased, the crystallization should be enhanced due to increased block length of PCL and segregation strength. The OM images of PCL-PDMS-PCL copolymer of 3-3-3 composition are provided in Figure 3.22.

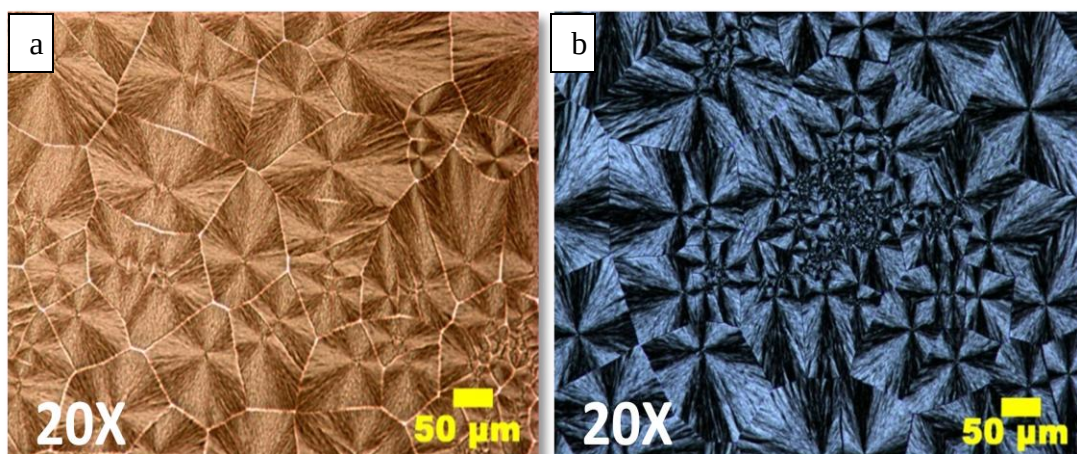


Figure 3.22. a) Non-polarized and b) polarized OM images of 3-3-3 copolymer at 20X magnification

The sizes of the crystals are smaller than the previous copolymer in which the PCL fraction is less. As the length of PCL block increases, the crystallization is enhanced and the structures of the crystals better resemble that of homo-PCL. Although there is a non-uniform size distribution, the domains are all cohesive to each other. This means that there should be PDMS rich phase separated micro-regions which are dispersed between the crystal domains of the PCL rich phase. When 1-3-1 and 3-3-3 compositions are compared, it is comprehended that as the PCL fraction increases within the copolymer, the crystallization of PCL is steadier and favorable. In order to analyze the effect of mid-block length on the crystallization of PCL block, PCL block length is kept constant and PDMS mid-block length is increased. The OM images of 3-11-3 PCL-PDMS-PCL copolymer composition are given in Figure 3.23.

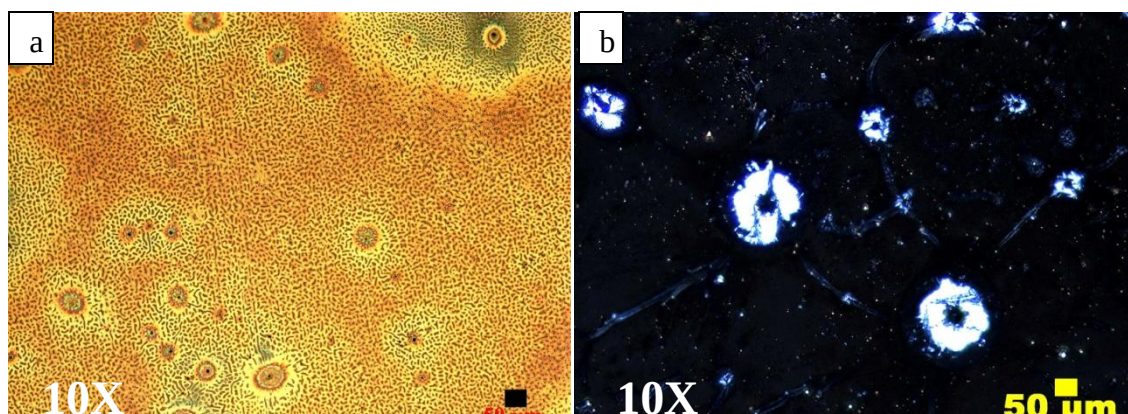


Figure 3.23. a) Non-polarized and b) polarized OM images of 3-11-3 PCL-PDMS-PCL copolymer at 10X magnification

Crystallization of PCL blocks is considerably reduced with the increase in the molecular weight of PDMS mid-block. It is seen PCL rich domains are distributed within the copolymer surface like small water globules within an oil matrix (Figure 3.23.a). Some of the PCL blocks are accumulated together and formed crystals which are around $\sim 100\ \mu\text{m}$. The crystals that are observed comprise crystalline PCL domains together with amorphous PDMS mid-block. The most probable reason for the formation of large crystal domains is the strength of segregation due to which the constituent blocks tend to come together. For further analysis, the length of PCL block is doubled by keeping the PDMS length constant and OM images are given in Figure 3.24

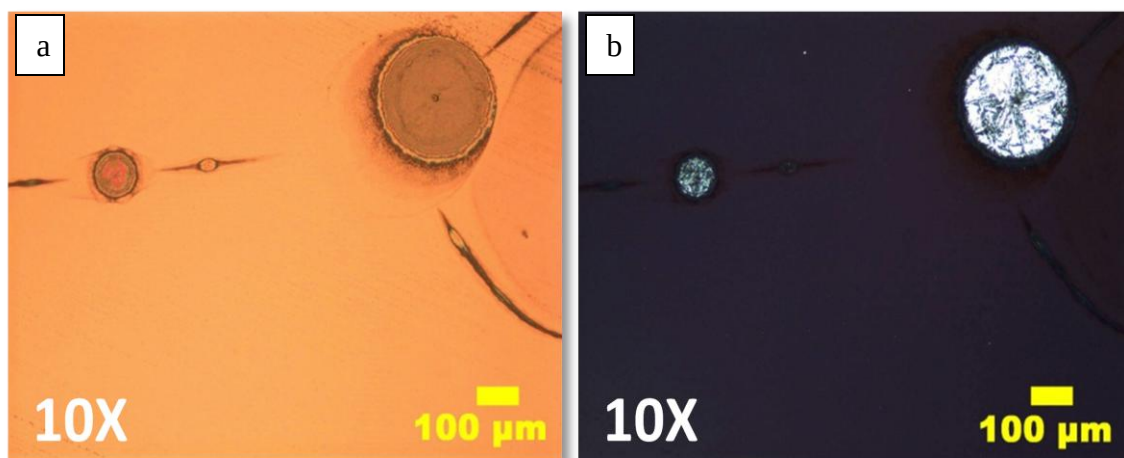


Figure 3.24. a) Non-polarized and b) polarized OM images of 6-11-6 PCL-PDMS-PCL copolymer at 10X magnification

Increase in the molecular weight of PCL block results in higher segregation strength, therefore PCL domains are either crystalline or amorphous. The non-crystalline or partially crystalline PCL domains are confined within the PDMS domains which cannot be monitored through OM imaging. Since the extent of segregation is enhanced, the crystalline copolymer domains form huge crystal regions which are $\sim 200\ \mu\text{m}$ in size. Those crystal domains contain the crystallized PCL domains together with the PDMS mid-block.

In this study, PDMS mid-block molecular weight is increased up to 31500 g/mol in order to further investigate and understand the effect of mid-block length on the crystallization of PCL end-blocks. The OM images of 3-32-3 PCL-PDMS-PCL copolymer are given in Figure 3.25.

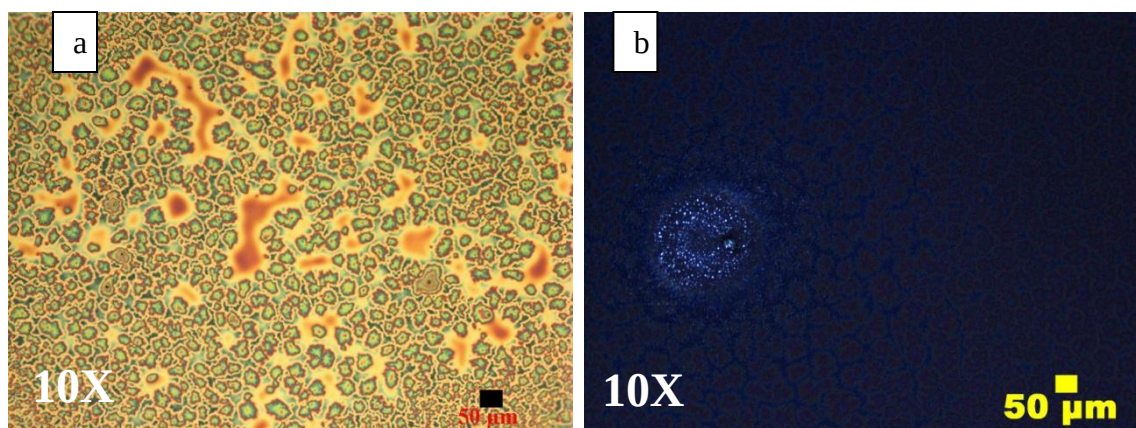


Figure 3.25. a) Non-polarized and b) polarized OM images of 3-32-3 copolymer at 10X magnification

As clearly seen from the OM images, PCL domains cannot crystallize or partially crystallize due to strong precluding of long PDMS mid-block. Some of the PCL end-blocks tend to crystallize (Figure 3.25.b) but the extent of crystallization is very limited. In spite of the fact that 3-3-3 copolymer composition can form strong crystal domains which are all connected; upon the increase in the mid-block molecular weight the crystallization is almost suppressed. Therefore, in order to obtain well-defined crystals, the PCL length should also be increased gradually with increasing PDMS mid-block molecular weight. The OM images of 6-32-6 PCL-PDMS-PCL copolymer are provided in Figure 3.26.

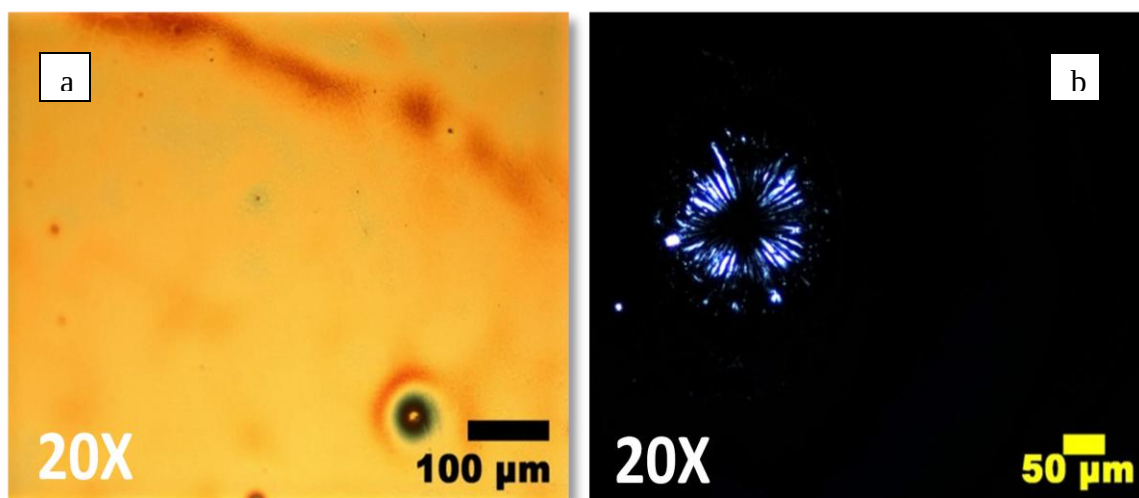


Figure 3.26. a) Non-polarized and b) polarized OM images of 6-32-6 PCL-PDMS-PCL copolymer

The increase in the segregation strength upon the increase in the molecular weight of the copolymer causes the constituent blocks to be as separate as possible from each other. Therefore, the PCL blocks are confined within the matrix or tend to crystallize forming weak crystal domains. Compared to 6-11-6 copolymer, increase in the PDMS mid-block molecular weight further prevents the crystallization as expected. It is now clear that for PCL to form strong and continuous crystal matrix, the length has to be increased more, so that the prohibitive effect of PDMS mid-block can be minimized. The OM images for PCL-PDMS-PCL copolymer of 16-32-16 composition are presented in Figure 3.27.

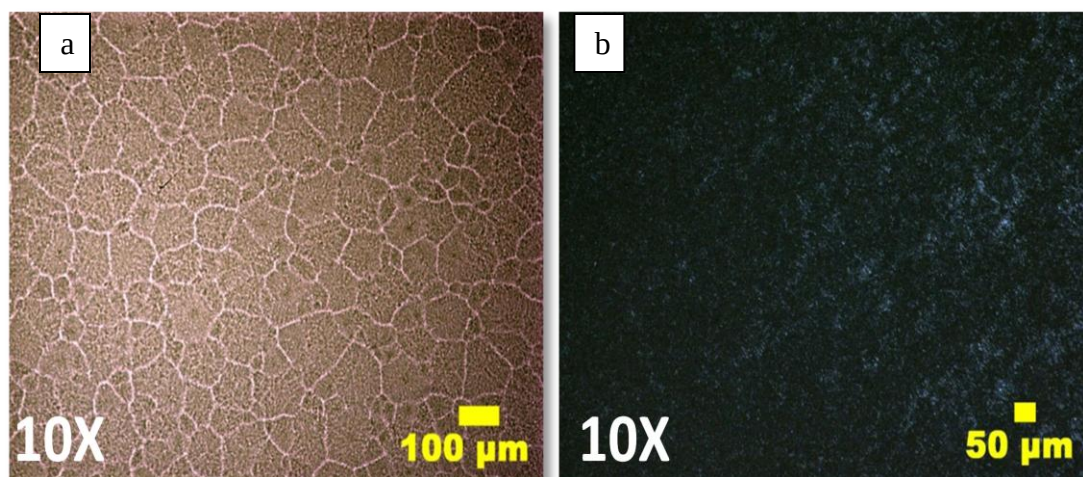


Figure 3.27. a) Non-polarized and b) polarized OM images of 16-32-16 PCL-PDMS-PCL

The increase in the length of PCL block apparently increases the crystallization of crystallizable blocks. Although the crystallization is still somewhat limited, the crystal or partially crystalline domains can form a connected network giving a homogeneous view. It can be now clearly understood that the extent of PCL fraction is crucial for the alignment and the packing of the crystallizable copolymer domains. Therefore, it is expected that the crystallization should be enhanced with further increase in the PCL block length. The OM images of 32-32-32 PCL-PDMS-PCL copolymer are provided in Figure 3.28.

Upon the increase in the molecular weight of PCL end-blocks, there is an observable enhancement in the crystallization as seen from Figure 3.28. The PCL blocks are able to pack more decent resulting in continuous and strong PCL crystal matrix which more or less resembles that of homo-PCL. It is expected that the microphase separation should take

place between the crystalline segments of PCL rich domains. It can be concluded that PCL crystallization within the PCL-PDMS-PCL copolymer is strongly dependent on the fraction of PCL domain. The analyzed copolymer compositions revealed the fact that the PCL fraction should be kept around 65% in order to have a continuous network of crystalline PCL copolymer domains.

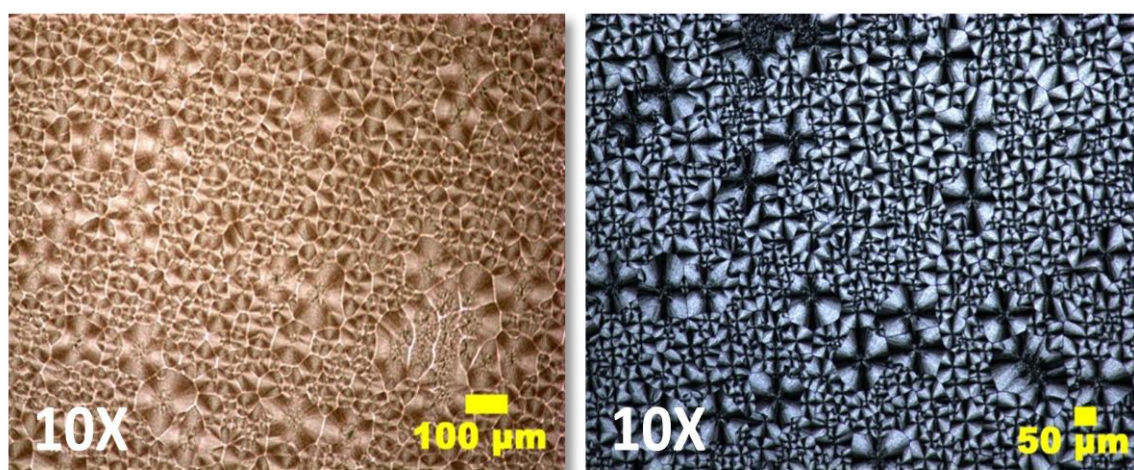


Figure 3.28. a) Non-polarized and b) polarized OM images of 32-32-32 PCL-PDMS-PCL

3.1.6. Surface Properties of PCL-PDMS-PCL Block Copolymers

Triblock copolymers display different surface properties depending on the composition and the properties of constituent blocks. Poly(dimethylsiloxane) migrates towards the surface leading to an enhancement in the hydrophobicity due to its low surface energy which is 20.3 mN/m [94]. Low glass transition temperature of PDMS gives rise to high chain mobility increasing the rate of migration. Therefore, incorporation of PDMS within a

material will result in a hydrophobic surface and the extent of hydrophobicity is dependent on the composition of the polymer and molecular weight of the constituent PDMS block. In this study, PDMS mid-block molecular weight was ranging from 1000 g/mol up to 31500 g/mol. Surface properties of triblock copolymers were investigated and results were analyzed with respect to PDMS and end block PCL molecular weights. The images of 20 μ L water drop on the sample surfaces are provided in Figure 3.29.

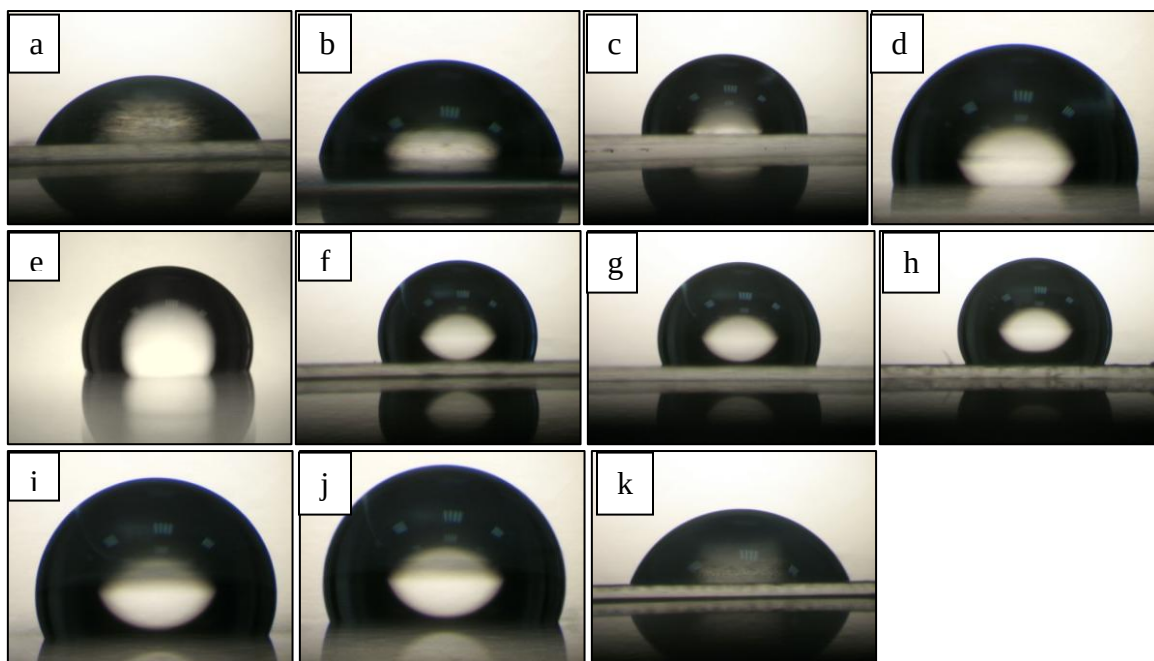


Figure 3.29. Sessile water drops on the PCL-PDMS-PCL triblock copolymer surfaces with compositions: (a) 1-1-1, (b) 2-2.5-2, (c) 1-3-1, (d) 3-3-3, (e) 3-11-3, (f) 6-11-6, (g) 3-32-3, (h) 6-32-6, (i) 16-32-16, (j) 32-32-32, (k) virgin PCL

As clearly seen from the contact angle images of PCL-PDMS-PCL copolymers, the hydrophobicity of the surface increases with increasing PDMS fraction within the block copolymer. The measured static contact angle values are provided in Table 3.2.

Table 3.5. Static water contact angle values of PCL-PDMS-PCL block copolymers

Copolymer Composition	Static Water Contact Angle (Degrees)
1-1-1	68.1 ± 1.7
2-2.5-2	81.1 ± 2.7
1-3-1	86.1 ± 1.9
3-3-3	98.3 ± 1.3
3-11-3	110.3 ± 2.7
6-11-6	100.2 ± 1.5
3-32-3	108.6 ± 0.9
6-32-6	114.1 ± 1.0
16-32-16	110.2 ± 1.2
32-32-32	108.0 ± 0.9
Virgin PCL	70.1 ± 1.4

The ultimate static water contact angle that can be obtained from PCL-PDMS-PCL block copolymers is around 110° which is around the maximum value for bulk PDMS surface [94]. These measurements clearly indicate that as the fraction and length of PDMS increases within the block copolymer, its tendency to migrate to the surface increases. Therefore, the surfaces of block copolymers are fully covered by PDMS after a certain fraction and molecular weight. For PDMS mid-block molecular weight of 31500 g/mol, the water contact angle values are measured between $\sim 108^\circ$ and $\sim 114^\circ$, which are in the range

of PDMS. Lower PDMS molecular weights displayed hydrophobic character having values between $\sim 81^\circ$ and $\sim 110^\circ$. Those values are higher compared to that of virgin PCL, which indicates the partial accumulation of PDMS on the surface as a wetting layer.

3.1.7. X-Ray Diffraction Analysis of PCL-PDMS-PCL Block Copolymers

X-Ray diffraction (XRD) is another method in order to analyze the crystallization of crystallizable species. PCL is a semicrystalline material with an orthorhombic unit cell structure [71]. Therefore, crystallization of PCL end-blocks within the block copolymers is analyzed with XRD. PCL has two sharp 2θ peaks at around 21.5° and 23.5° and two weak peaks at 22° and 29.5° . The XRD pattern for homo-PCL is provided in Figure 3.30.

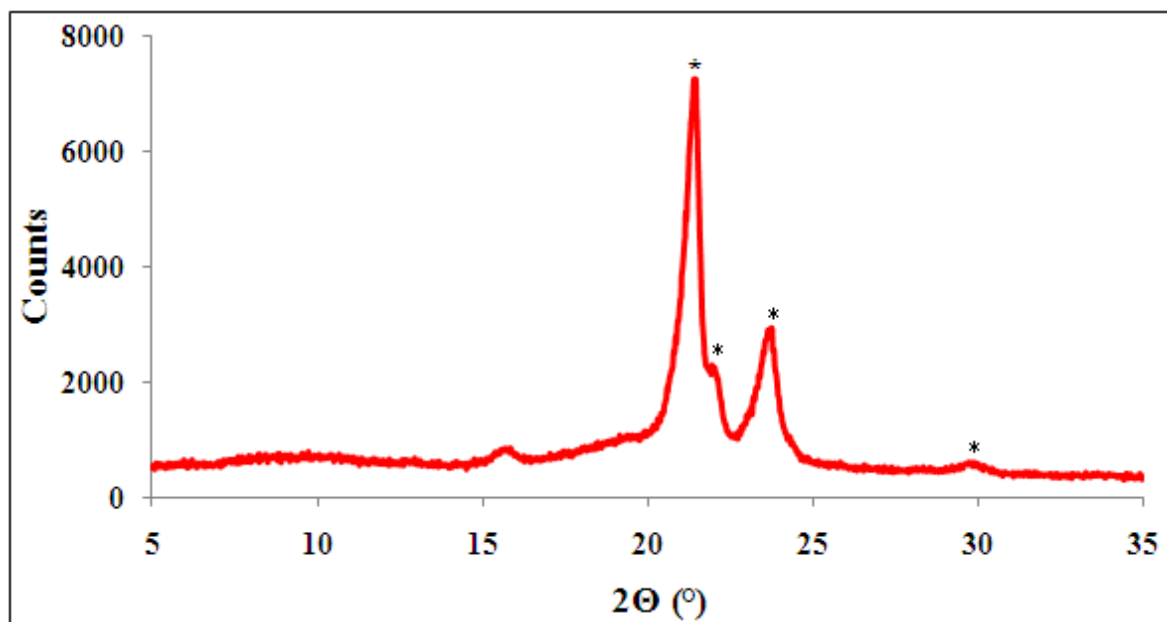


Figure 3.30. XRD pattern of homo-PCL showing the two ‘*’ labeled major crystal peaks

Crystallization of PCL domains is strongly affected by the copolymerization with PDMS since the prohibitive effect of mid-block on crystallization will differ depending on the PCL fraction. The XRD diagram for 1-1-1, 1-3-1 and 3-3-3 PCL-PDMS-PCL copolymers are given in Figure 3.31.

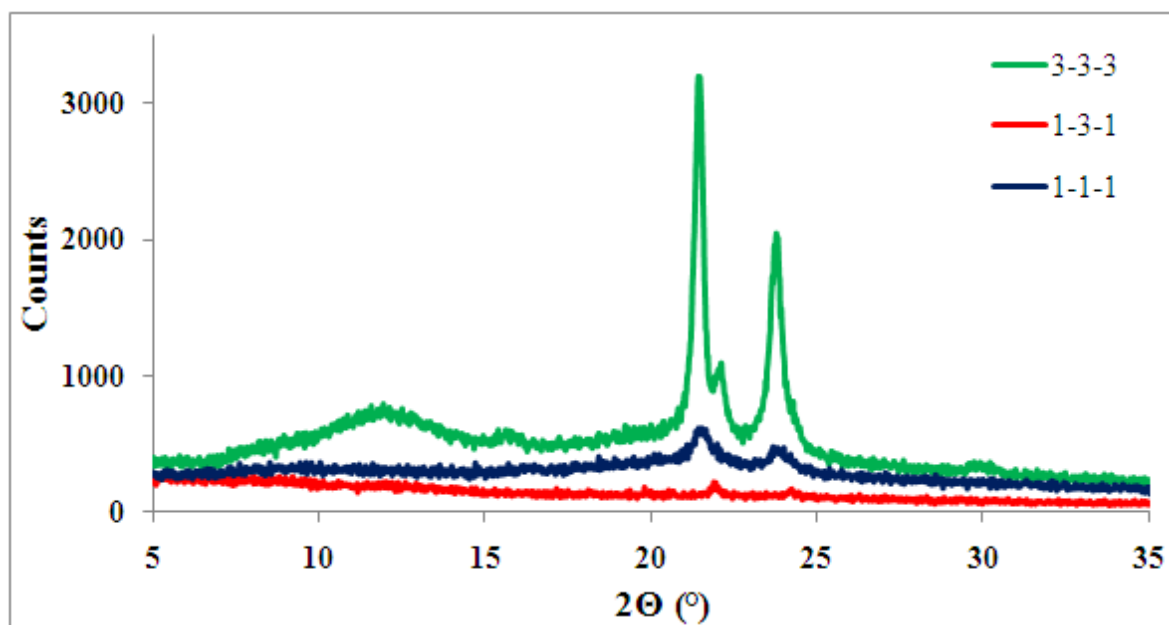


Figure 3.31. XRD diagrams of PCL-PDMS-PCL copolymers for different copolymer compositions

The effects of PCL end-block length and PDMS mid-block length on crystallization are clearly observed from Figure 3.31. 1-1-1 copolymer shows two weak peaks at around 22° and 24°. This can be explained through combination of two reasons; i) PCL end-blocks may be too short to have an effective packing and ii) the crystallization is prevented by the presence of PDMS mid-block. As it was already revealed by OM analysis given in the

previous section, PCL chain length has to be above a certain value in order to have an effective crystallization. The effect of PDMS mid-block length on PCL crystallization can be seen from the XRD pattern of 1-3-1 copolymer. The increase in the PDMS length further decreased the packing of PCL rich segments having almost no regular crystallization. The crystallization is prominently enhanced when the composition is 3-3-3 having a PCL fraction of 67%. The intensity of peaks is increased displaying the entire characteristic peaks of homo-PCL. In addition, there is a broad amorphous background with a maximum at $\sim 12^\circ$ which is not observed for the previous copolymer compositions. Irregular packing of PDMS mid-blocks is the main reason for the presence of this peak. Both peaks coming from amorphous and crystalline segments suggest that there is a microphase separation between PDMS rich amorphous and PCL rich crystalline domains. 3-11-3 and 6-11-6 copolymers are analyzed with XRD in order to further investigate the effect of mid-block length on the crystallization of PCL blocks. XRD patterns for those copolymers are provided in Figure 3.32. The peaks that are displayed by both of the block copolymer compositions demonstrate the presence of crystallized PCL rich domains. However, the intensities of these crystal peaks are reduced with respect to 3-3-3 copolymer case indicating a decrease in the extent of crystallization of PCL domains. At the same time, the peak intensity of 6-11-6 copolymer is higher with respect to 3-11-3 copolymer meaning that higher PCL fraction is more prone to crystallization. The broad amorphous peaks that are observed at $\sim 12^\circ$ can be accounted for the microphase separated morphology

of block copolymers. The highest PDMS molecular weight that was used as the mid-block was 31500 g/mol. The same trend is observed for 3-32-3, 16-32-16, and 32-32-32 PCL-PDMS-PCL copolymers. The XRD patterns of these copolymers are shown in Figure 3.33.

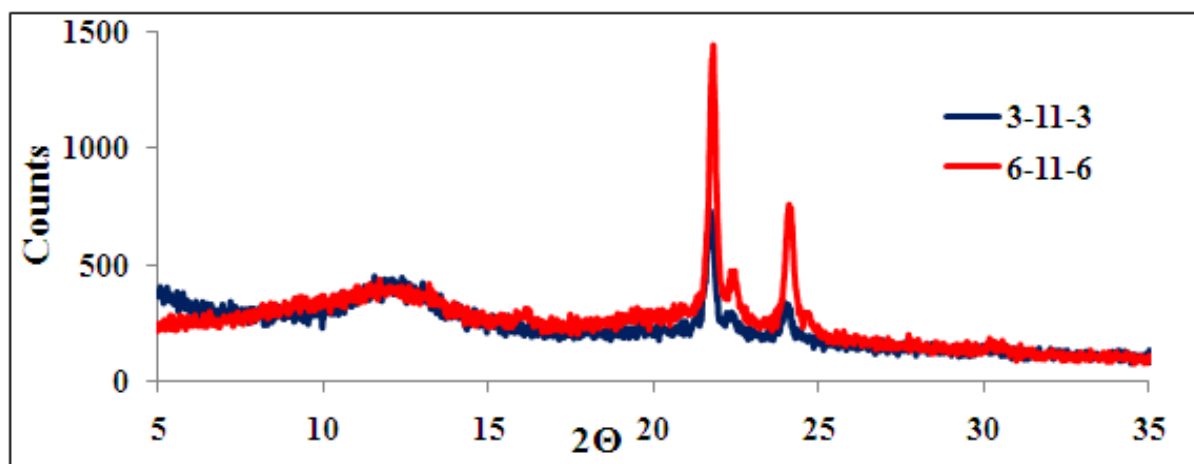


Figure 3.32. XRD patterns of 3-11-3 and 6-11-6 PCL-PDMS-PCL copolymers

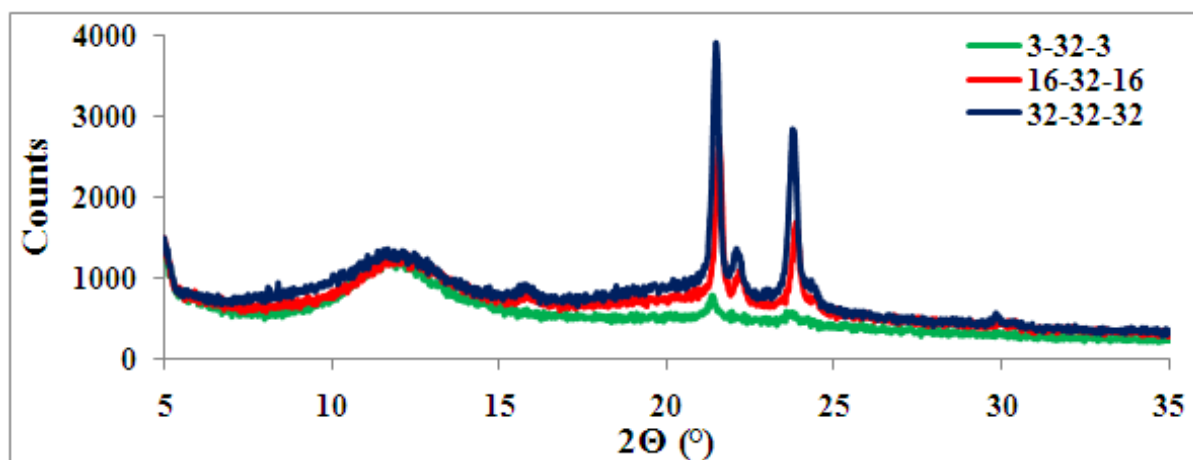


Figure 3.33. XRD patterns of 3-32-3, 16-32-16 and 32-32-32 PCL-PDMS-PCL polymers

The increase in PDMS mid-block molecular weight greatly affects the packing of PCL domains. As seen from Figure 3.33, 3-32-3 copolymer barely crystallizes giving two weak crystal peaks. As the fraction of PCL increases, the extent of crystallization also increases as indicated by the presence of the strong crystal peaks. The strongest crystallization is obtained when the PCL fraction is equal to 0.67. In addition to sharp crystal peaks, broad curves originating from PDMS mid-block amorphous region are also observed at $\sim 12^\circ$. As stated earlier, the presence of both amorphous and crystal peaks clearly indicate the microphase separated morphology of constituent blocks. This is an expected result arising from the increased segregation strength and length of PCL blocks. In order to better see the effect of mid-block length on the crystallization, the XRD patterns of 3-3-3, 3-11-3 and 3-32-3 copolymers are compared in Figure 3.34.

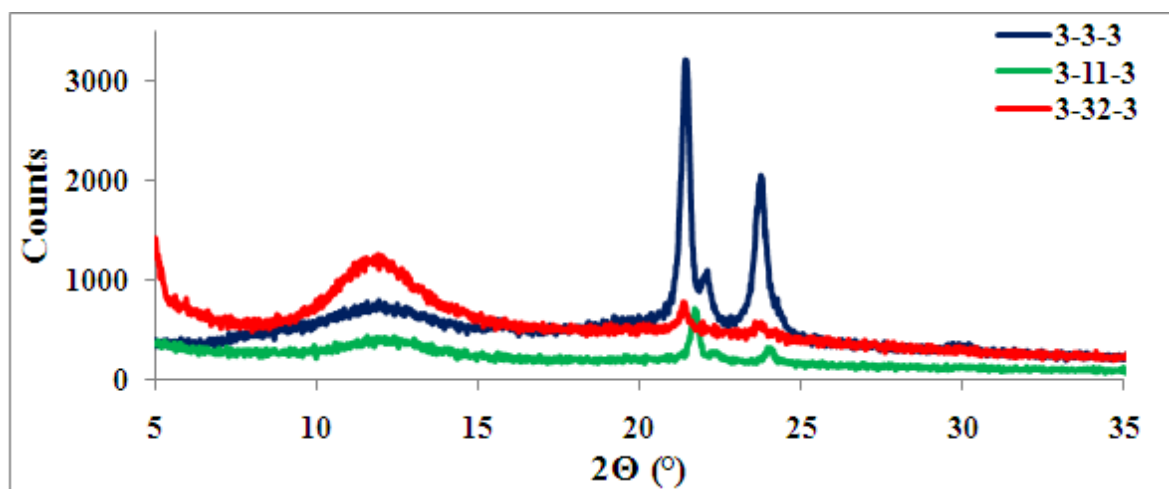


Figure 3.34. XRD diagrams of 3-3-3, 3-11-3 and 3-32-3 PCL-PDMS-PCL copolymers

The effect of mid-block length on the crystallization of PCL blocks is clearly seen in Figure 3.34. The intensities of crystal peaks are greatly reduced with increasing mid-block length which has a strong prohibitive effect on the crystallization of PCL blocks. Therefore, in order to have a better crystallization the PCL fraction should also be increased with increasing PDMS molecular weight. The curves originating from the PDMS rich amorphous regions have an increasing pattern with increasing PDMS fraction. Existence of both amorphous and crystal peaks reveals that the materials display microphase separated morphologies in all three compositions.

3.2. PCL-PEO-PCL Triblock Copolymers

ϵ -Caprolactone was polymerized by using difunctional hydroxyl terminated poly(ethylene oxide) macroinitiator with number average molecular weights of 2000 g/mol, 4436 g/mol and 8484 g/mol. The reaction scheme is provided in Figure 2.2. The properties that were investigated included:

- i) Polydispersities of PCL-PEO-PCL copolymers with gel permeation chromatography (GPC).
- ii) Thermal properties of PCL-PEO-PCL copolymers with differential scanning calorimetry (DSC)
- iii) Crystallization and crystal structures of PCL-PEO-PCL copolymers with optical and atomic force microscopy
- iv) The extent of crystallization of PCL-PEO-PCL copolymers with X-ray Diffractometry (XRD)

PCL-PEO-PCL copolymers having different compositions were synthesized and characterized. A list of PCL-PEO-PCL copolymers synthesized is given in Table 3.6.

Table 3.6. Compositions and yields of PCL-PEO-PCL copolymers synthesized

Code	Composition	Block Lengths	Yield	Solvent	Coagulation Solvent
MI-105	PCL-PEO-PCL	2-2-2	93.7	Bulk	Hexane
MI-104		2-4-2	98.0	Xylene	
MI-103		4-4-4	92.0		
MI-106		4-8-4	96.5		
MI-107		8-8-8	96.0		
MI-108		16-8-16	97.8		

3.2.1. Gel Permeation Chromatography Characterization of PCL-PEO-PCL Block Copolymers

In order to follow the formation of PCL-PEO-PCL triblock copolymers gel permeation chromatography (GPC) was employed. GPC chromatograms for starting PEO oligomers and all copolymer compositions are provided in Figure 3.35.

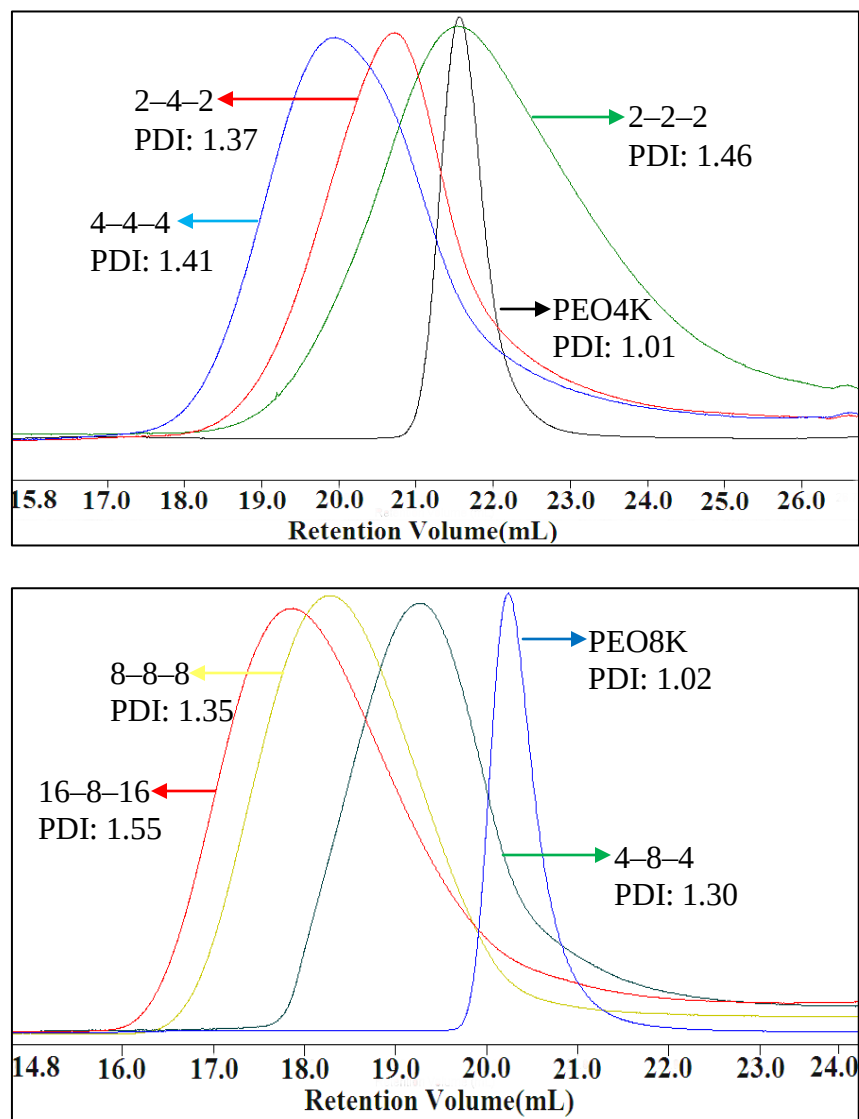


Figure 3.35. GPC signals of PCL-PEO-PCL copolymer compositions

As it can be seen from the GPC signals of the PCL-PEO-PCL triblock copolymers, the peaks shift to lower retention volumes with increasing molecular weight of the triblock

copolymer and increasing PEO mid-block length relative to the signal of the PEO macroinitiator used. Therefore, it can be concluded that GPC ensures the initiation of hydroxyl terminated PEO macroinitiator and the formation of PCL-PEO-PCL triblock copolymers. The polydispersity index (PDI) values are between 1.30 and 1.55 indicating the formation of well defined triblock copolymers.

3.2.2. Differential Scanning Calorimetry Analysis of PCL-PEO-PCL Block Copolymers

DSC analysis was performed in order to understand the effect of composition on the melting behavior of PCL-PEO-PCL triblock copolymers. Copolymers were heated at a heating rate of 20°C/min to 90°C to erase the thermal history and then were cooled down to -90°C with the same rate. The second run melting peaks of three copolymer compositions are provided in Figure 3.36.

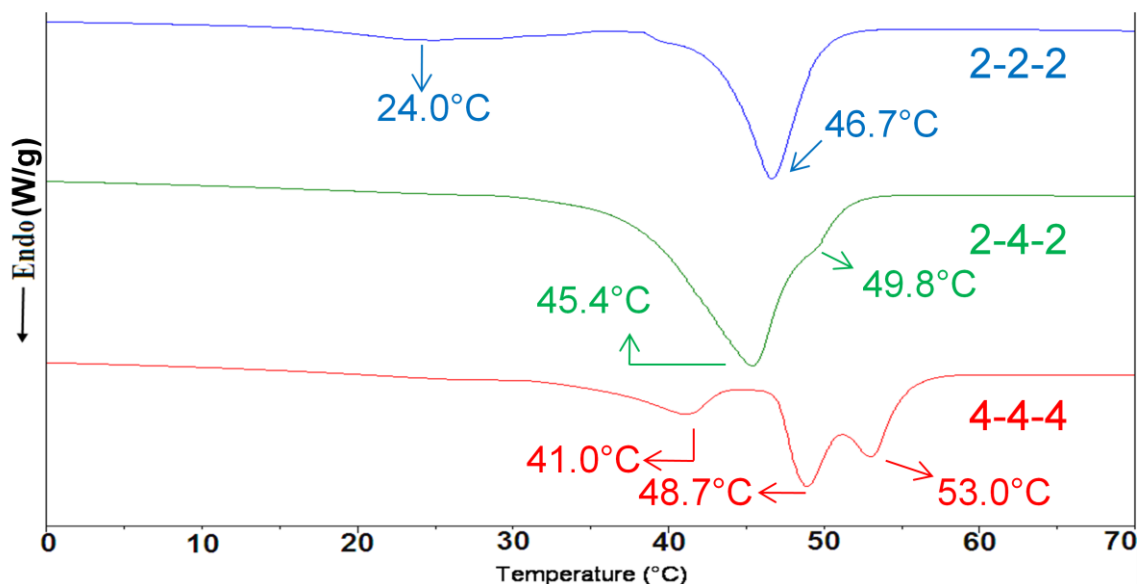


Figure 3.36. DSC thermograms of 2-2-2, 2-4-2, and 4-4-4 PCL-PEO-PCL triblock copolymers

2-2-2 copolymer displays a single, sharp and fairly symmetrical melting peak, with a maximum at 46.7°C together with a much smaller, broad peak centered at 24.0°C. Two different melting peaks indicate the presence of two different crystal structures. In order to tell which melting corresponds to which component of the copolymer, further analysis is required. When PEO4K was used as the mid-block, the position of the sharp melting peak shifts to 45.4°C with a shoulder at 49.8°C. As it is in the previous copolymer composition, further analysis is necessary in order to clarify the basis of the melting peaks. When PCL fraction is increased (4-4-4), three different melting peaks are detected in 30 - 60°C range with peak maxima at 41, 48.7 and 53.0 °C as shown in Figure 3.36. The presence of three

different melting peaks can be arising from a mixture of crystal structures having different number of foldings. Detailed analysis should be performed for further interpretations.

DSC thermograms of PEO8K initiated triblock copolymers are provided in Figure 3.37.

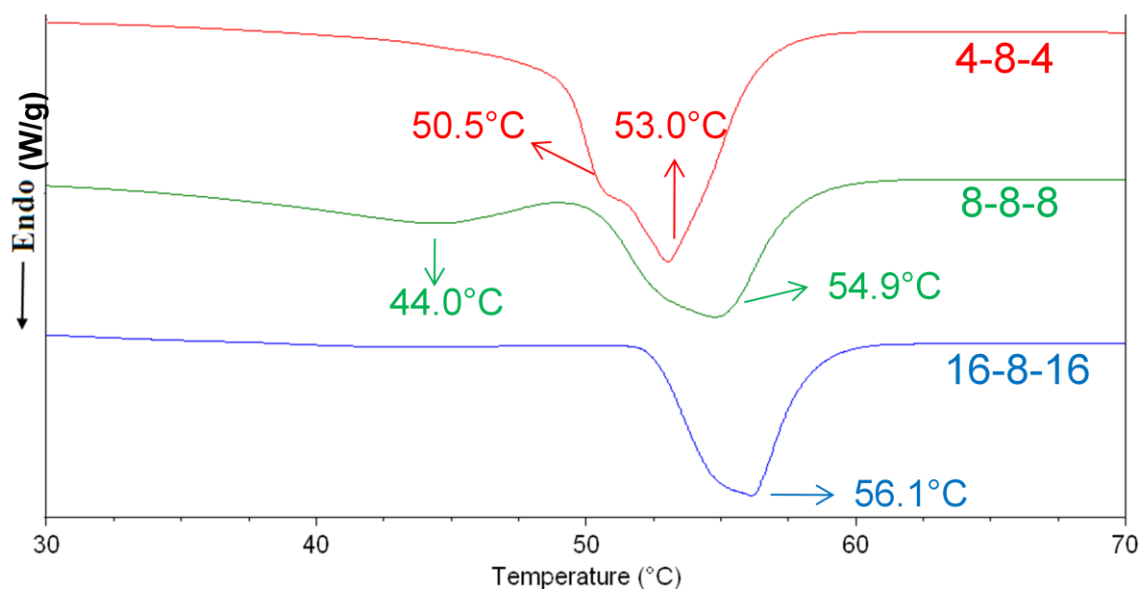


Figure 3.37. DSC thermograms of 4-8-4, 8-8-8 and 16-8-16 triblock copolymers

4-8-4 triblock copolymer displays a sharp melting peak at 53.0°C together with a shoulder at 50.5°C. When PCL length is doubled, the single melting peak shifts to 54.9°C and the previous shoulder is further confined within. In addition, a broad melting peak is detected at 44.0°C. For 16-8-16 copolymer the melting maxima of the melting endotherm shifts to 56.1°C. The increasing trend in the melting point for the three copolymer compositions can be attributed to PCL blocks since the melting point increases with increasing PCL fraction.

To sum up our observations, DSC analysis of PCL-PEO-PCL triblock copolymers showed that the thermal behavior of the copolymers is strongly dependent on the composition of the copolymer and more detailed examination is required to understand the nature of the crystallization of the constituent blocks.

3.2.3. Crystallization and Crystal Structures of PCL-PEO-PCL Copolymers

Copolymers having two crystallizable constituent blocks display different crystal structures depending on the composition. The richness of crystal structures comes from the competitive crystallization between two different units [100]. Crystallization of one component strongly affects the crystallization of the other units. In order to see the effect of composition on the crystal structures of those block copolymers, different copolymer compositions are analyzed with optical microscopy (OM) and atomic force microscopy (AFM). The copolymers were dissolved in different solvents and crystal structures are observed upon the removal of the solvent with spin coating process. Therefore, the effects of solvents on the crystal structures are also investigated. The solvents that are used are given in Table 3.5 together with the solubility parameters.

Table 3.7. Solvents and homopolymers and their solubility parameters [101]

Chemical	Solubility Parameter (cal/cm³)^{1/2}
Tetrahydrofuran (THF)	9.52
Chloroform	9.21
Dimethyl formamide (DMF)	12.14
Isopropyl alcohol (IPA)	11.50
Dichloromethane (DCM)	9.70
Toluene	8.90
PCL	8.55
PEO	9.88

Prior to analysis of copolymers, crystal structures of homopolymers should be examined.

OM images of homo-PCL and homo-PEO are provided in Figure 3.38.

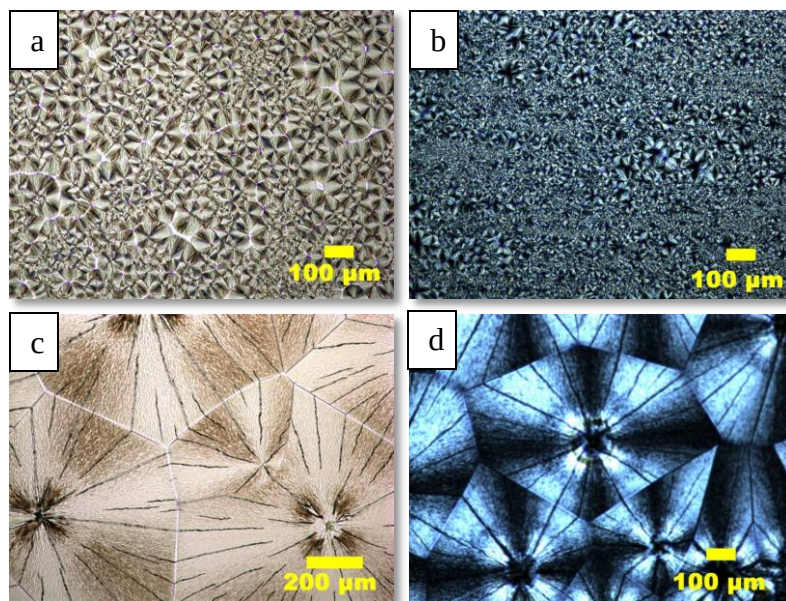


Figure 3.38. OM images of homo-PCL and homo-PEO4K at 10X magnification a) homo-PCL non-polarized, b) homo-PCL polarized, c) homo-PEO4K non-polarized, d) homo-PEO4K polarized

PCL homopolymers display small size crystal spherulites whereas PEO homopolymers display large crystal domains. In addition, it is known that PCL crystallization takes place slowly and that of PEO takes place rapidly [100]. Therefore, copolymers of PCL and PEO display competitive crystallization and the extent of competition is determined by the composition. Crystal images of 2-2-2 triblock copolymer observed by optical microscopy are given in Figure 3.39.

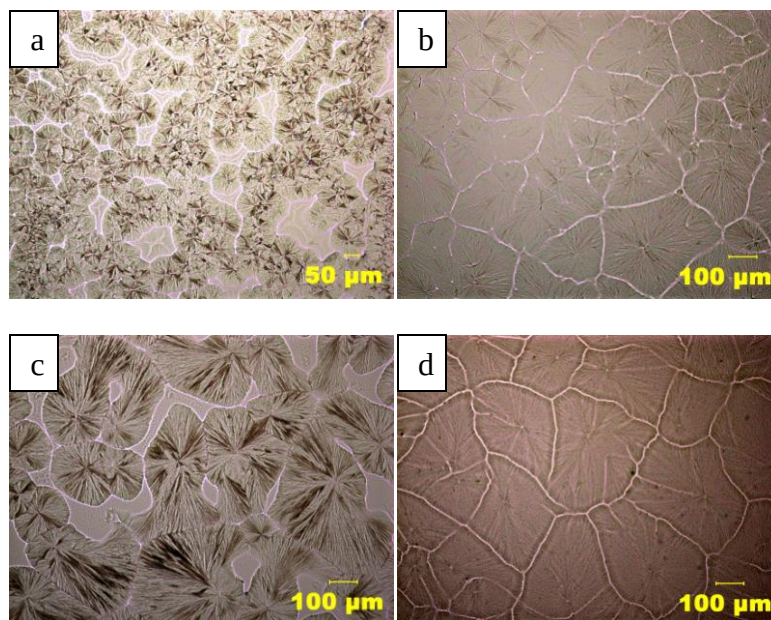


Figure 3.39. Non-polarized optical images of 2-2-2 copolymer crystallized from 20% solid solution of a) THF b) THF-DMF (1:1) c) chloroform and d) DMF at 10X magnification

The crystallization of the copolymer is dependent on the solubility in the solvent and also to the boiling point of the solvent used. The time that is required for the evaporation of the solvent during spin coating process is strongly affiliated to the boiling point of that material. When the 2-2-2 copolymer is crystallized from THF, THF-DMF and chloroform the crystals that are formed are separated from each other, therefore giving immature crystal structures. For THF-DMF solvent system, DMF can dissolve PEO mid-block but PCL is not soluble in it. Since the boiling point of DMF is quite higher than THF, DMF is present in the system even after THF is evaporated. Hence, PEO can somewhat crystallize

but PCL blocks cannot. At the same time, the shape of the crystals resembles the shape of PEO crystal domains rather than that of PCL. The same effect is valid for the case ‘d’ in which DMF is the only solvent. As mentioned earlier both solubility and boiling point of the solid determine the crystal structure. The same copolymer is dissolved in DCM-IPA (1:1 by w) mixture and further analyzed. The optical microscopy images are given in Figure 3.40.

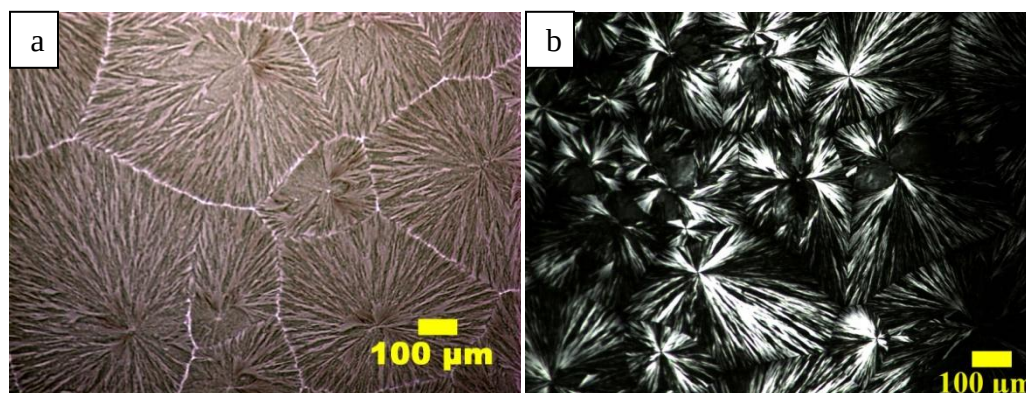


Figure 3.40. a) Non-polarized and b) polarized OM images of 2-2-2 copolymer spincoated from DCM-IPA (1:1 by w) mixture

DCM is a good solvent for PCL end-blocks and IPA can better dissolve PEO mid-block. Therefore, the crystal structure that is observed under OM is a co-crystal system in which both components are somewhat crystallized even for such a small molecular weight copolymer. In order to further analyze the crystallization of this composition, the copolymer is melted on a heating stage under OM at a heating rate of 3°C/min. OM images

of heating and cooling cycles are given in Figure 3.41. It should be noted that the given temperature values are the recorded temperatures from the heating stage, therefore they may not represent the exact temperature of the bulk material heated.

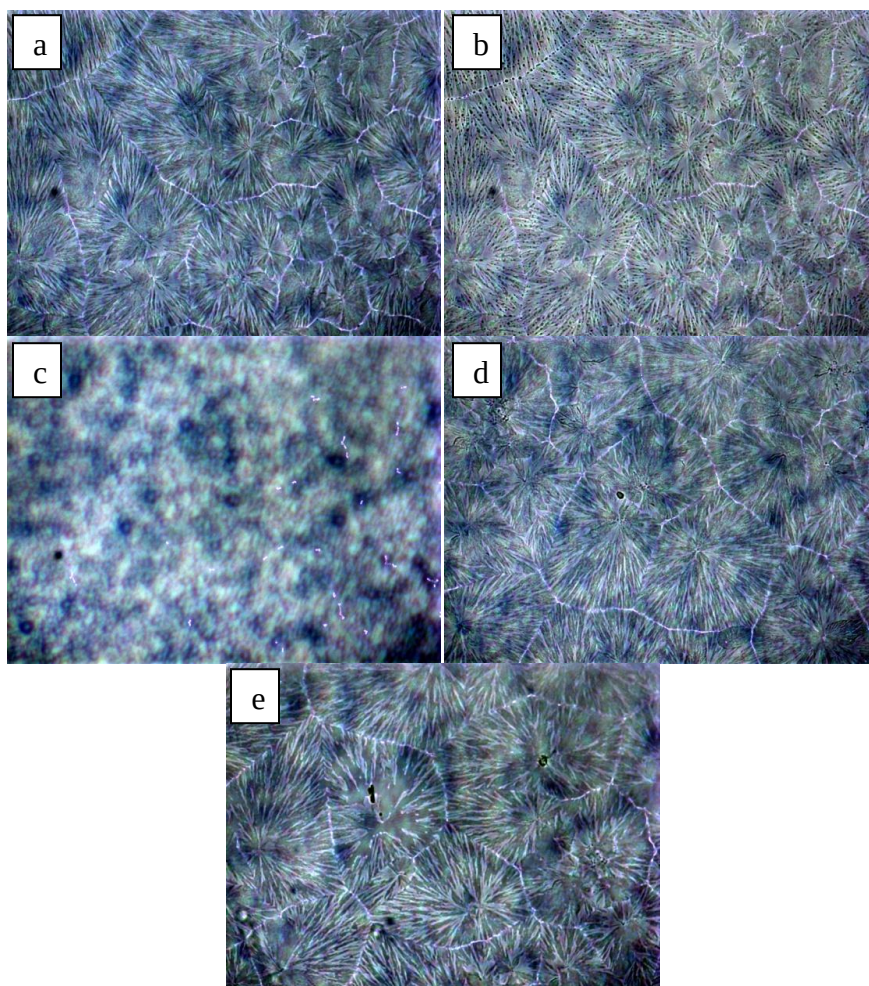


Figure 3.41. Non-polarized 10X magnified OM images of 2-2-2 copolymer on heating stage; heating process a) 24.5°C, b) 55.6°C, c) 63.1°C, cooling process d) 55.1°C and e) 38.9°C

It is clearly seen that the melting starts homogeneously within the copolymer (Figure 3.41.b). This can be attributed to the co-crystallization of the constituent blocks or dominance of crystallinity of one domain over the other. When the temperature is increased to 63.1°C, all the material is melted. The recrystallization of the copolymer starts around 56°C and as seen from the image (Figure 3.41.d) the crystal domains are formed homogeneously. At a lower temperature, the crystal morphology is reestablished (Figure 3.41.e).

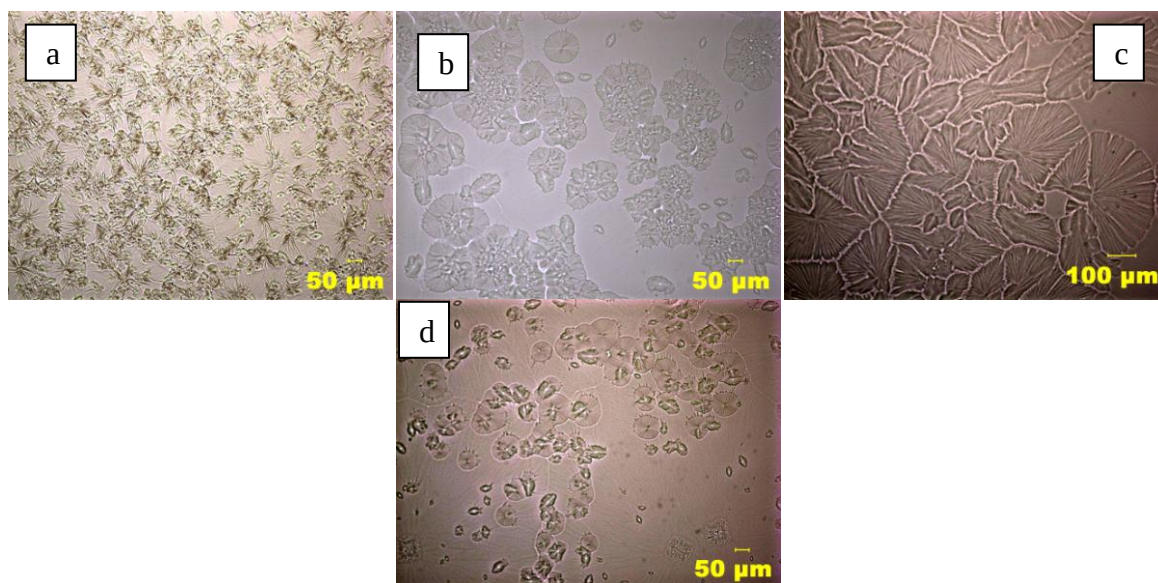


Figure 3.42. Non-polarized optical images of 2-4-2 copolymer crystallized from 20% solid solution of a) THF b) THF-DMF (1:1) c) DMF and d) toluene at 10X magnification

The same analysis was performed for 2-4-2 copolymer in which the PCL end-block length was kept constant by increasing the length of PEO mid-block. The OM images are provided in Figure 3.42 for different solvent systems.

When THF is the solvent system for 2-4-2 copolymer, the spherulites observed resemble that of homo-PCL, therefore it can be concluded that PEO mid-block cannot crystallize effectively. Introduction of DMF into THF system is not sufficient for the formation of mature crystal domains. Due to its high boiling point, DMF remains in the system for a longer time than THF resulting in a decrease in the extent of packing of PCL end-blocks. When DMF is the only solvent that is present in the system, it is seen that the crystal domains appear to be immature and crystal spherulites peculiar to PCL domains are not observed. Toluene is a better solvent for PCL domains but it is not appropriate for PEO mid-blocks. Therefore, the structures that are observed are inchoate. Better crystal morphology is observed when 2-4-2 copolymer is spin casted from chloroform solution. OM images are shown in Figure 3.43.

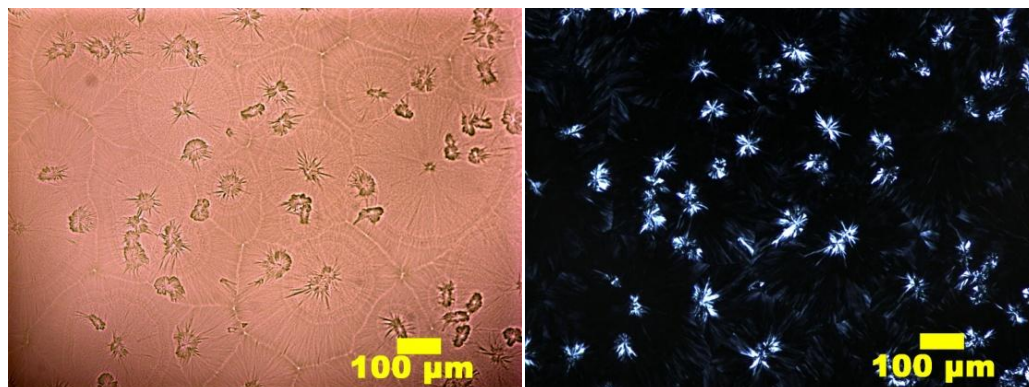


Figure 3.43. a) Non-polarized and b) polarized OM images of 2-4-2 copolymer spincoated from chloroform solution at 10X magnification

Chloroform was found to be a better solvent for crystallization of 2-4-2 copolymer. It is observed that the smaller size spherulites, which are like PCL crystal domains, are homogeneously distributed along the surface. The other crystal phase that is present in the image belongs to PEO mid-block which is not as strongly crystallized as the PCL end-blocks. This is further analyzed on the heating stage under optical microscope at a heating rate of $3^{\circ}\text{C}/\text{min}$ for which the images are shown in Figure 3.44.

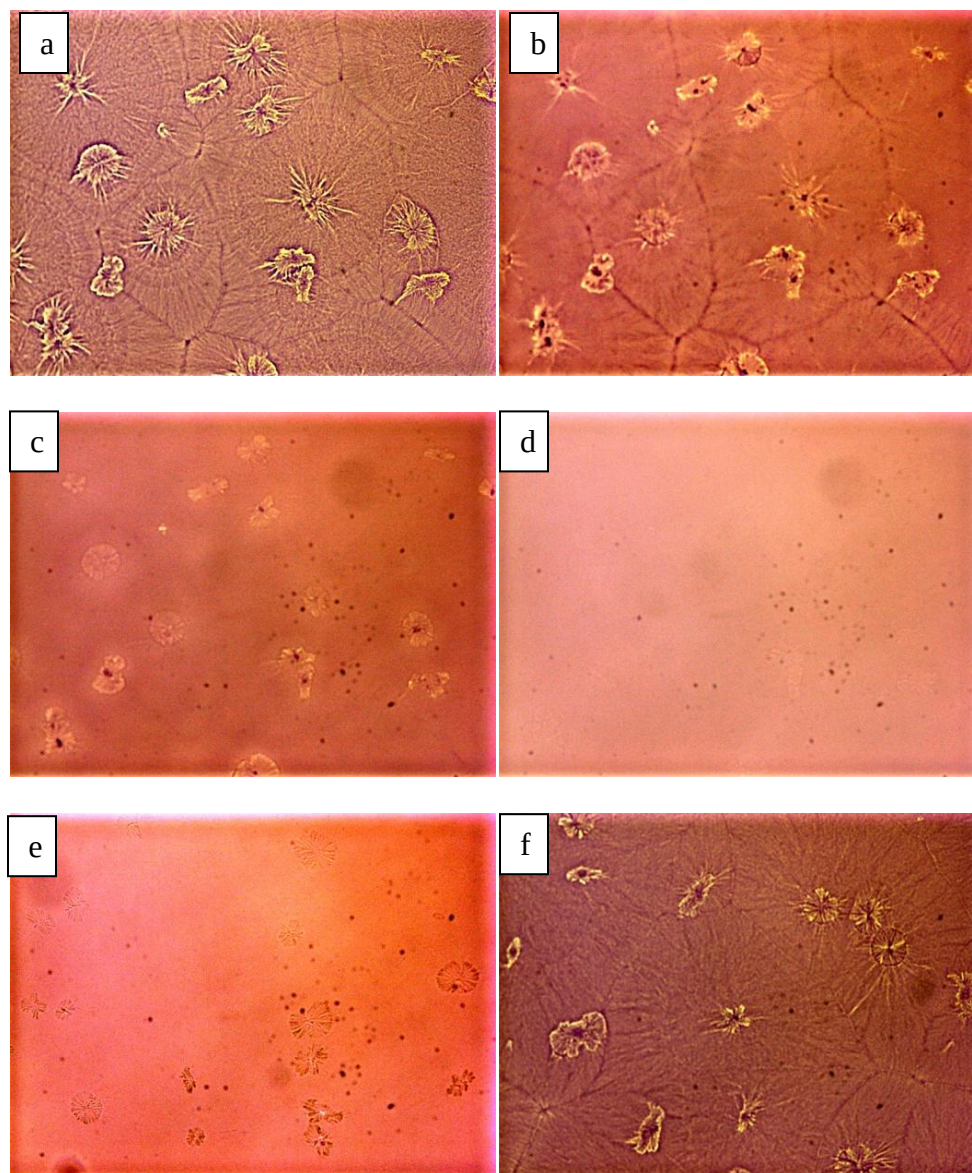


Figure 3.44. Non-polarized 20X magnified OM images of 2-4-2 copolymer on heating stage; heating process a) 25.0°C, b) 66.3°C, c) 67.3°C, d) 68.0°C cooling process e) 59.0°C and f) 52.0°C

The melting of the copolymer first starts from the wider crystalline regions which are composed of PEO rich domains of the copolymer. The integrity of small crystal spherulites are partially preserved until 67.3°C then all the copolymer is observed to be in molten state. The reestablishment of the previous crystalline structure starts with the PCL rich domains which act as the nucleation points of the other crystal domains. As the material cools down, the crystalline morphology is reestablished. AFM also revealed the presence of two different crystal domains on the surface. AFM height and phase images are provided in Figure 3.45.

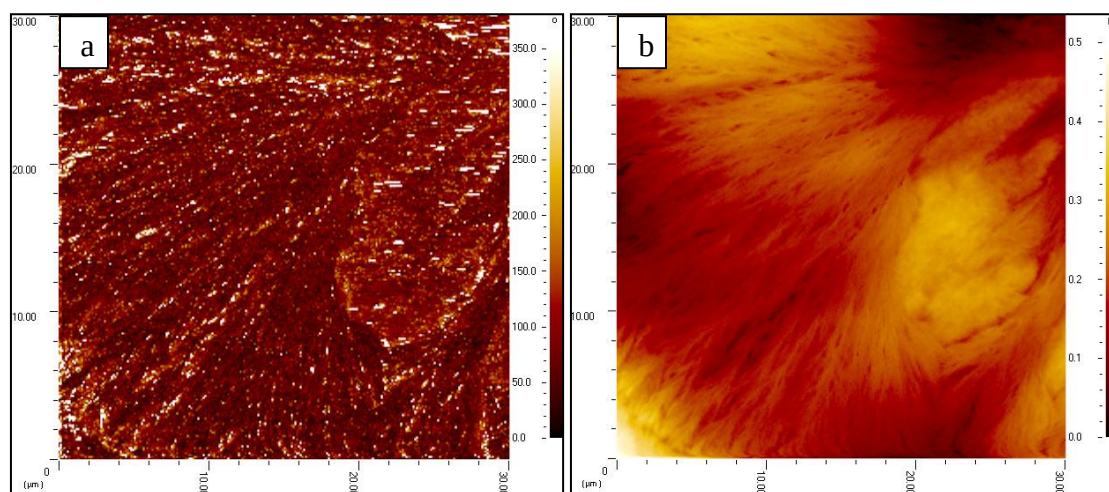


Figure 3.45. 30x30 μm AFM a) phase and b) height images of 2-4-2 copolymer

Although the phase image (Figure 3.45.a) does not provide significant contrast, the existence of two crystal domains can be observed from the height image (Figure 3.45.b). The smaller domain which is higher in position compared to the surroundings is composed

of PCL rich crystalline domain and crystalline fibrils of the other segment are aligned at a certain direction as seen from the image.

In order to further analyze the effect of composition on the crystal morphology of PCL-PEO-PCL, 4-4-4 copolymer is examined through the same processes. The OM images of 4-4-4 copolymer spin coated from different solvents are given in Figure 3.43.

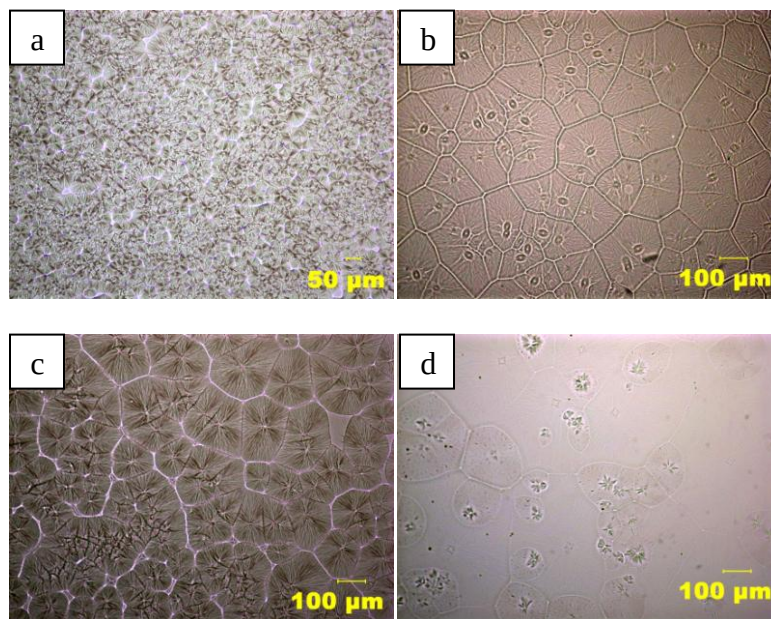


Figure 3.46. Non-polarized optical images of 4-4-4 copolymer crystallized from 20% solid solution of a) THF, b) DMF, c) IPA-DCM (1:1) and d) toluene at 10X magnification

When the copolymer is crystallized from THF solution, the crystalline-like structure formed is composed of very small domains (Figure 3.46.a) resembling the shape of homo-PCL. DMF gives a domain structure which was like the previously observed structure from

the other copolymer compositions. PCL rich domains may be confined within the PEO rich partially crystalline domains which are seen from the OM image (Figure 3.46.b). Crystal structure of the copolymer from IPA-DCM solvent pair is given in Figure 3.46.c. The size distribution of the crystal domains is nonhomogeneous and the domains are separated from each other. When toluene is used as the solvent, crystalline morphology that is observed is poor in which PCL domains may be partially crystallizing and almost no strong PEO crystal domains are observed.

Better crystalline morphology is observed when chloroform is the solvent for this copolymer for which the OM images are shown in Figure 3.47.

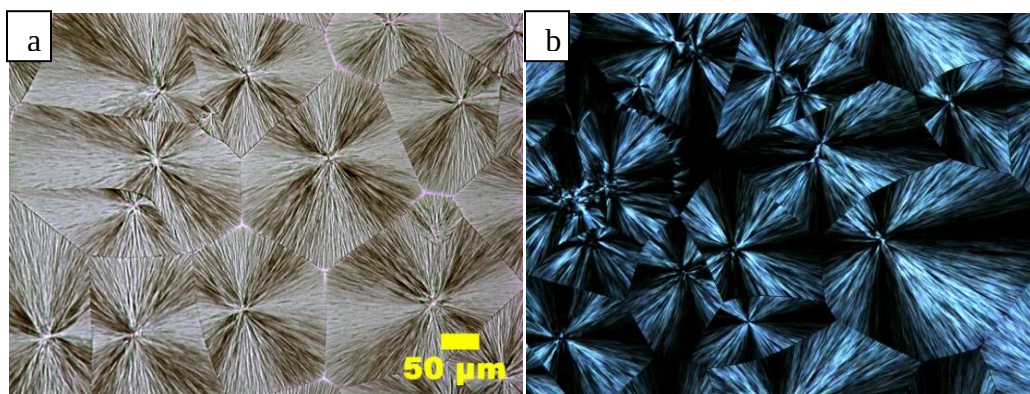


Figure 3.47. a) Non-polarized and b) polarized OM images of 4-4-4 copolymer spincoated from chloroform solution at 20X magnification

The crystal domains that are observed in Figure 3.44 are stronger and all bound to each other. The size of the domains is in between the size of homo-PCL and that of homo-PEO.

Therefore, it can be concluded that the domains may be crystallizing together forming concentric crystalline spherulites or one of the copolymer component is dominant in the crystallization. In order to further analyze the crystal structure that is formed, the sample is melted under OM and images are provided in Figure 3.48.

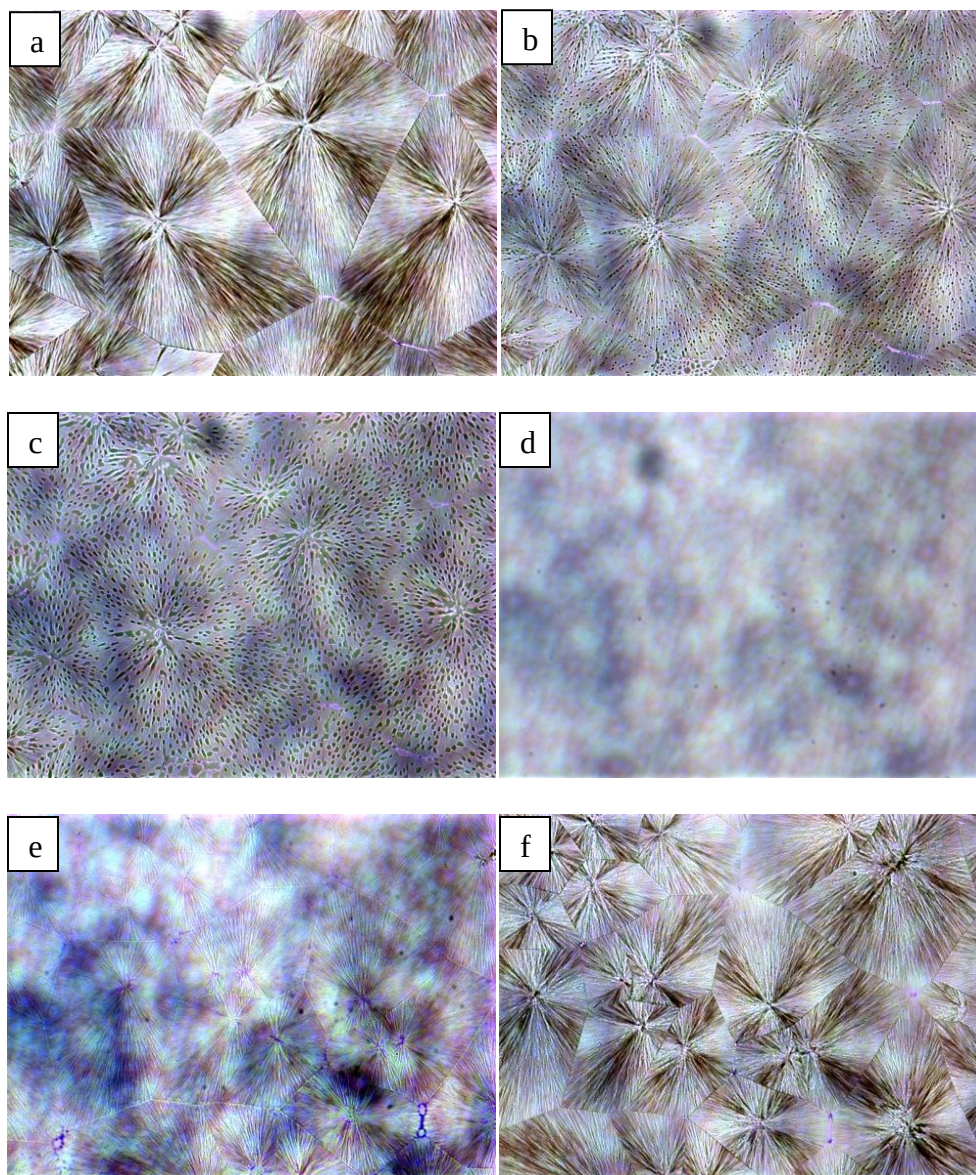


Figure 3.48. Non-polarized 20X magnified OM images of 4-4-4 copolymer on heating stage at a rate of 3°C/min; heating process a) 35.7°C, b) 63.4°C, c) 66.3°C, d) 68.1°C cooling process e) 62.7°C and f) 37.6°C

Melting of the copolymer starts homogeneously throughout the whole crystalline morphology which is in fact an indication of homogeneous crystallization of the of the copolymer. The process continues uniformly (Figure 3.48.c) and all the copolymer is melted at 68.1°C. Reestablishment of the crystal morphology takes place in an agreement with the idea that the crystal domains are composed of both components of the 4-4-4 copolymer. When the material is further cooled down to 37.6°C, the morphology is reestablished. Crystalline fibrils of 4-4-4 copolymer are also revealed by AFM images which are given in Figure 3.49.

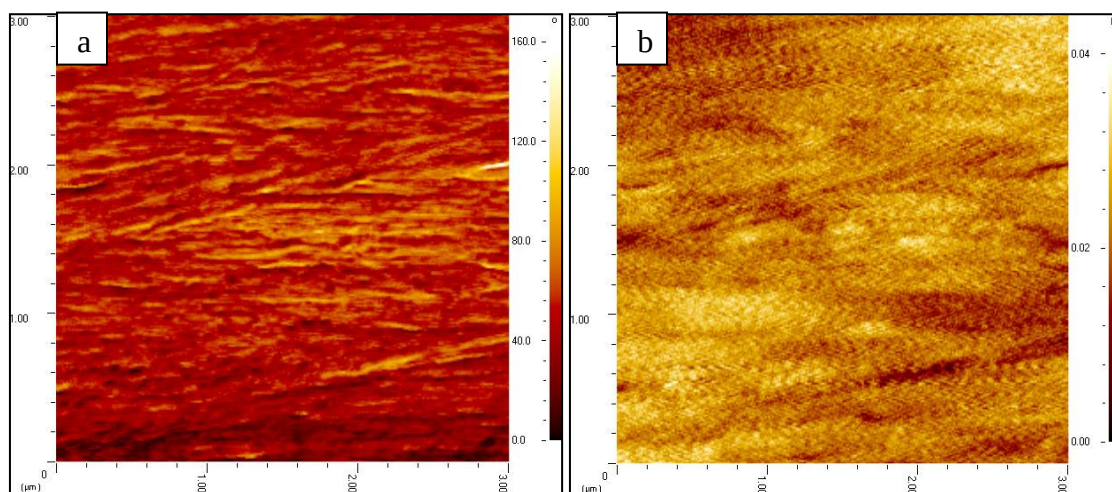


Figure 3.49. 3x3 μm AFM a) phase and b) height images of 4-4-4 PCL-PEO-PCL copolymer

When the surface of 4-4-4 copolymer is analyzed with AFM, it is seen from the phase image that the crystal fibrils are aligned at a certain orientation on the surface (Figure

3.49.a). The alignment of the crystal domains are comparable to the ones that are observed in a larger scale in OM images (Figure 3.47).

Copolymer composition was modified and mid-block length was doubled by keeping the length of end-blocks constant. Detailed analysis was performed for 4-8-4 PCL-PEO-PCL copolymer composition. OM images for spincoated samples from different solvents are provided in image 3.50.

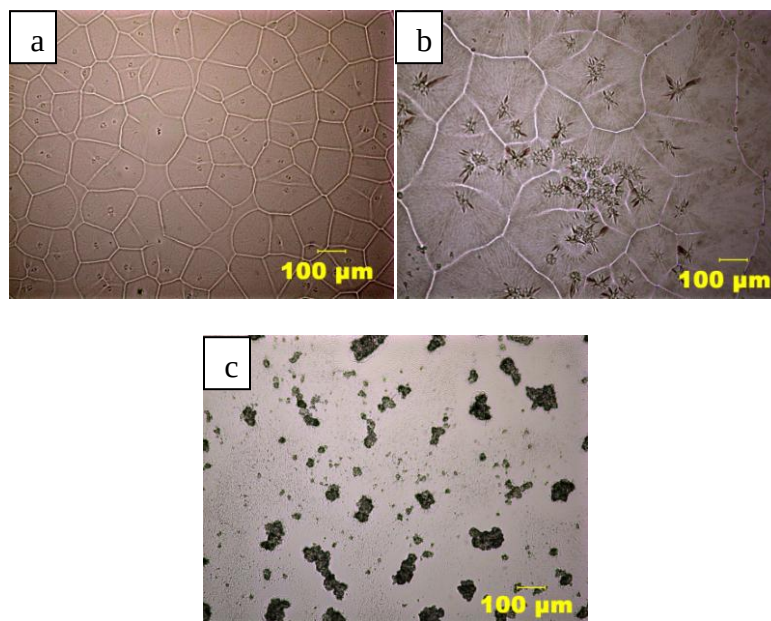


Figure 3.50. Non-polarized optical images of 4-8-4 copolymer crystallized from 20% solid solution of a) DMF b) IPA-DCM (1:1) and C) toluene at 10X magnification

When the copolymer is dissolved in DMF, the structure that is observed resembles those of the previous ones in which weak and large domains are observed (Figure 3.50.a). This may

be arising from the better alignment of PEO mid-blocks in DMF than PCL blocks. Therefore, mid-block may be better packing while the end-blocks are confined within the amorphous domains of the copolymer. IPA-DCM solvent pair displays a mixed crystalline structure in which both end and mid-blocks can partially crystallize (Figure 3.50.b). When toluene is used as the solvent, no crystalline domains are observed (Figure 3.50.c). The best crystalline morphology was obtained when the copolymer was dissolved in chloroform. The OM images are given in Figure 3.51.

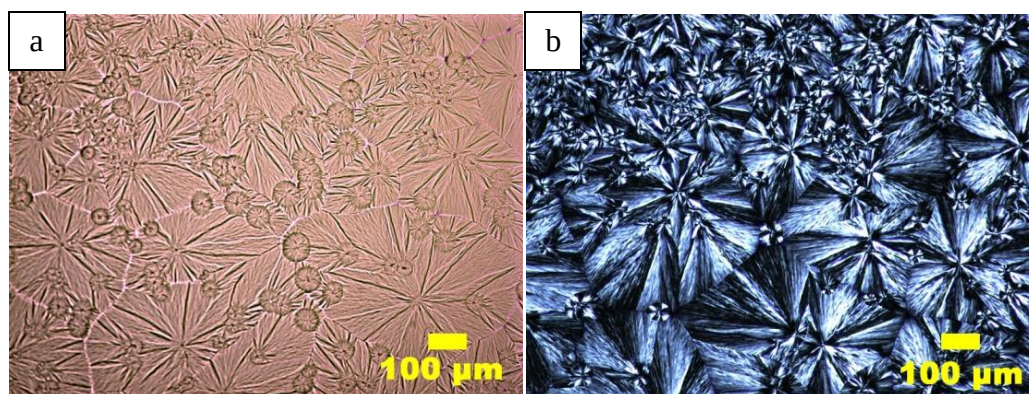


Figure 3.51. a) Non-polarized and b) polarized OM images of 4-8-4 copolymer spincoated from chloroform solution at 10X magnification

When chloroform was used as the solvent, it is seen that both components of the block copolymer are crystallized. While some of the domains displayed concentric crystal structures, for some the domains were separate from each other. PCL end-blocks formed spherical and small crystal domains and PEO mid-block filled the space left from the spherulites of PCL rich domains. In order to further analyze the crystal structure observed

when chloroform is the solvent, the copolymer is melted on a heating stage under OM. The images are shown in Figure 3.52.

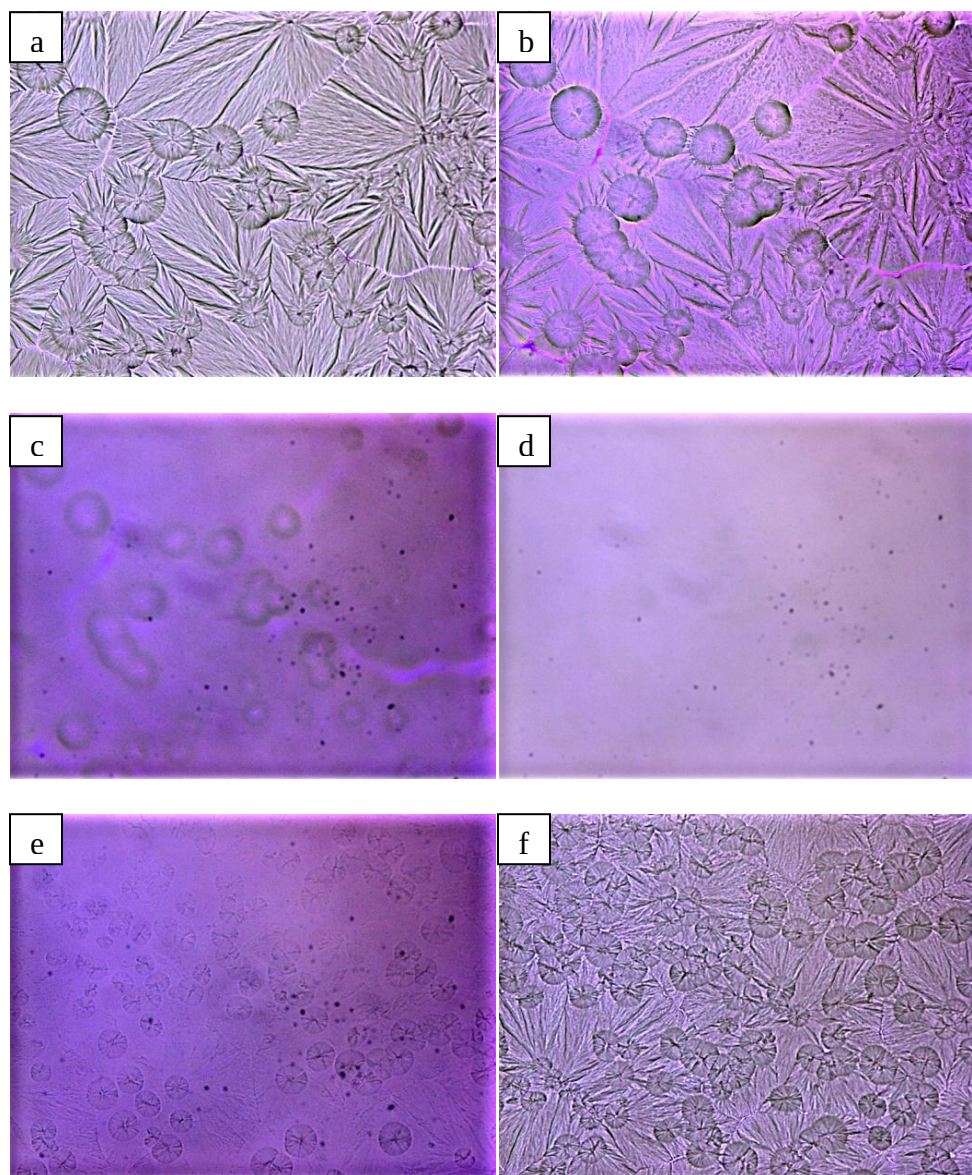


Figure 3.52. Non-polarized 20X magnified OM images of 4-8-4 copolymer on heating stage; heating process a) 29.0°C, b) 69.3°C, c) 71.9°C, d) 72.4°C cooling process e) 65.0°C and f) 25.6°C

As clearly seen from the images, melting starts within the larger crystal domains and spherulites of PCL rich domains can be observed up to 71.9°C (Figure 3.52.c). Then all the components are melted (Figure 3.52.d). Crystallization of the copolymer is initiated with the formation of PCL rich spherulites (Figure 3.52.e) and reestablishment of the crystal morphology is completed with the packing of PEO rich mid-block (Figure 3.52.f).

Another copolymer composition analyzed was 8-8-8 PCL-PEO-PCL copolymer in which the length of PCL was doubled with respect to previous composition. Different solvents were used for the crystallization studies and OM images of this copolymer were provided in Figure 3.53.

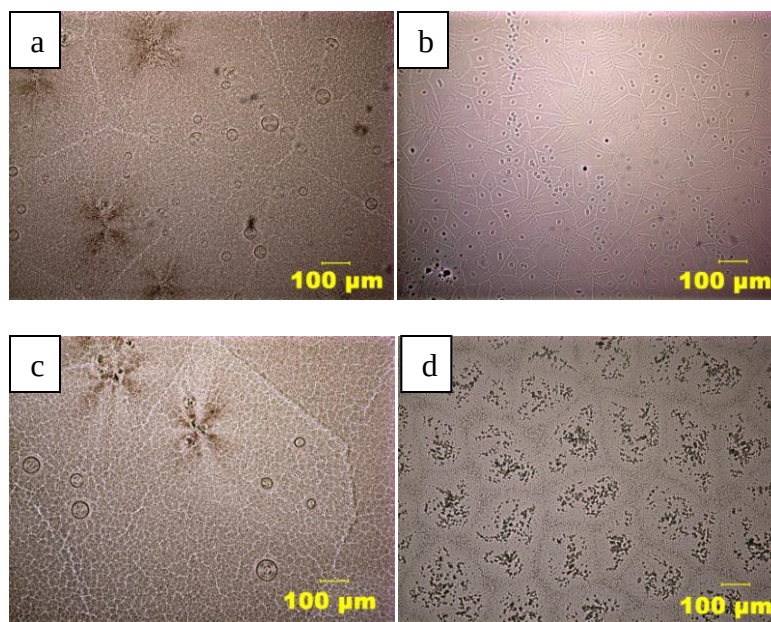


Figure 3.53. Non-polarized optical images of 8-8-8 copolymer crystallized from 20% solid solution of a) chloroform, b) DMF, c) IPA-DCM (1:1) and d) toluene at 10X magnification

Although chloroform was a good solvent for crystallization of the previous copolymer composition, the structure that is obtained for 8-8-8 copolymer is very weak and the domains are barely distinguished (Figure 3.53.a). DMF as expected gave crystal domains which are weak (Figure 3.53.b). Similar to the case of chloroform, IPA-DCM solvent pair resulted in crooked structures that are barely crystalline or non-crystalline (Figure 3.53.c). When toluene was used as the solvent no ordered crystal structure was observed (Figure 3.53.d).

Better crystal morphology was obtained, when the copolymer was crystallized from THF. The OM images are provided in Figure 3.54.

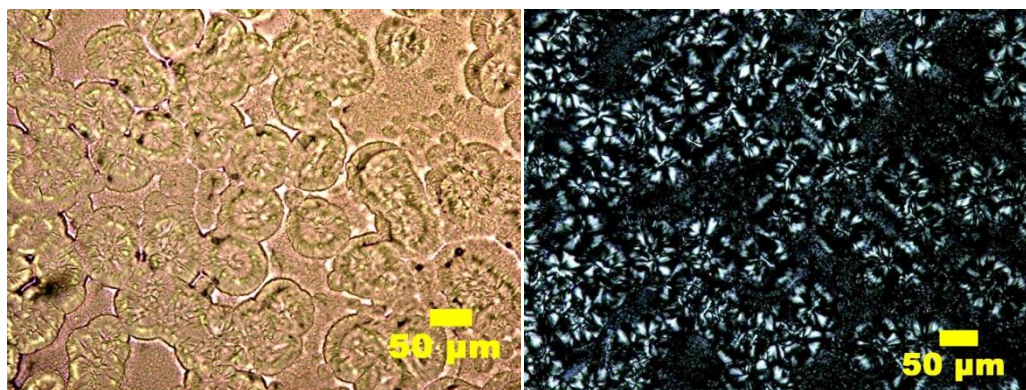


Figure 3.54. a) Non-polarized and b) polarized OM images of 8-8-8 copolymer spincoated from THF solution at 20X magnification

As revealed from the OM images, while the spherulites of PCL end-blocks are clearly observed, PEO mid-block partially crystallizes without any observable order. The reason for this may be the dominance of PCL blocks over PEO mid-block in length, therefore

decreasing the extent of packing of the mid-block. The same copolymer is melted on heating stage under OM. The images are given in Figure 3.55.

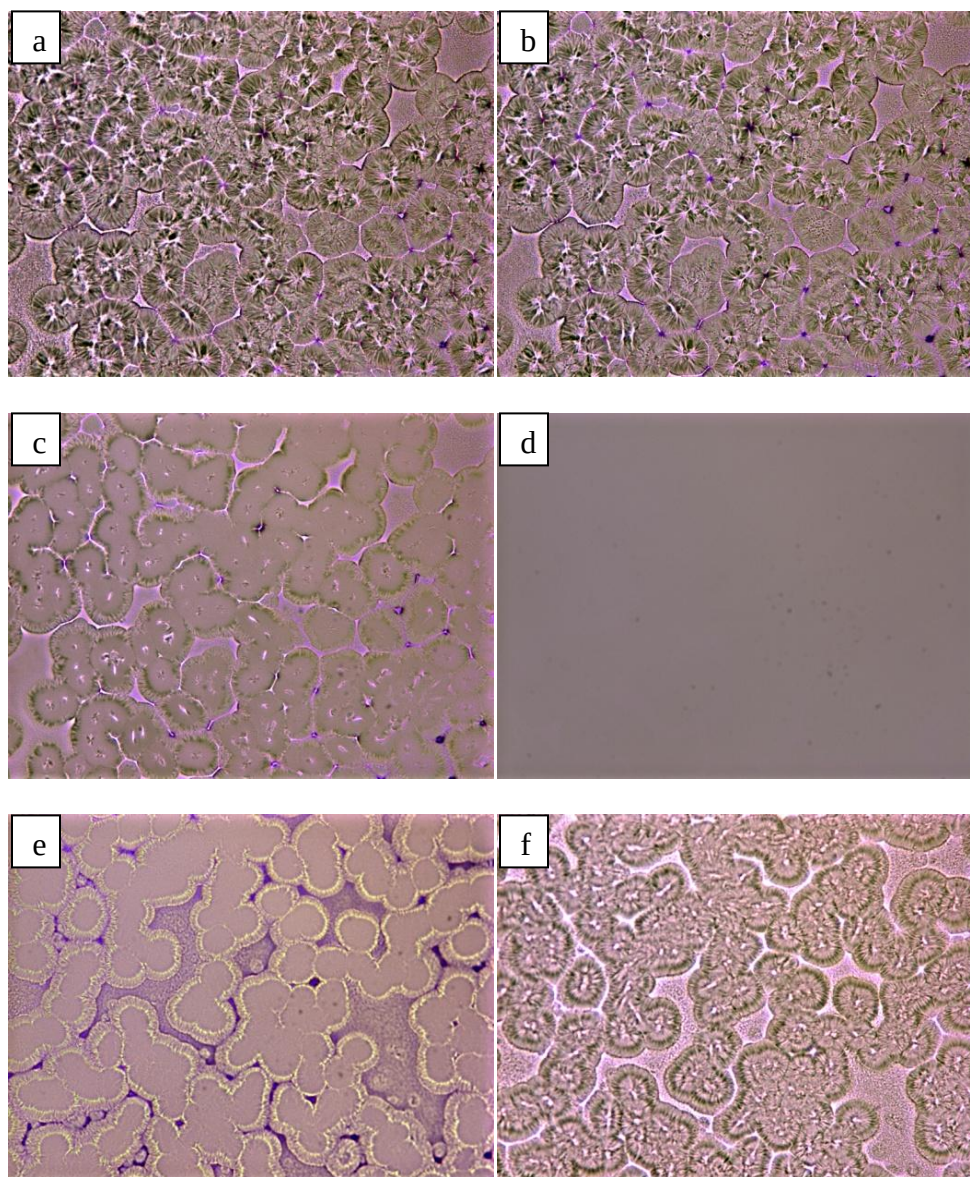


Figure 3.55. Non-polarized 20X magnified OM images of 8-8-8 copolymer on heating stage; heating process a) 27.0°C, b) 66.0°C, c) 71.1°C, d) 73.1°C cooling process e) 63.0°C and f) 50.3°C

Melting of 8-8-8 copolymer starts within the disordered crystalline regions of the mid-block. PCL spherulites preserve their integrities up to 71.1°C (Figure 3.55.c). At 73.1°C all the components are melted. Recrystallization of the copolymer starts within the PCL rich domains resulting in the formation of PCL crystalline spherulites (Figure 3.55.e). At lower temperatures, the crystalline morphology is reestablished (Figure 3.52.f). Crystalline morphology of the copolymer is further investigated with AFM for which the images are shown in Figure 3.56.

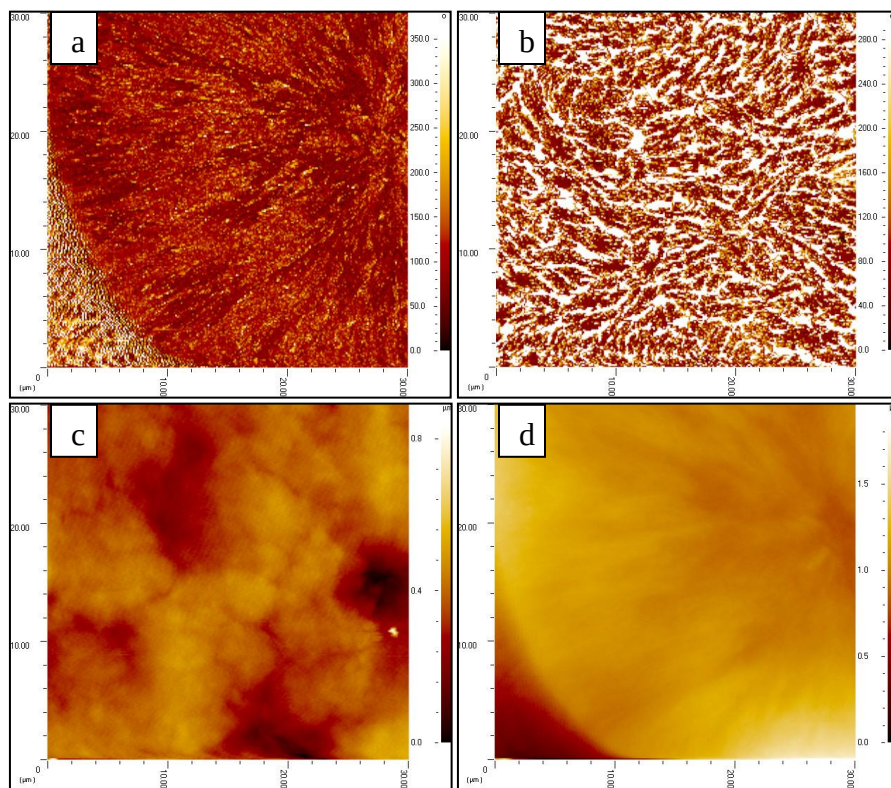


Figure 3.56. 30x30 μm AFM images of 8-8-8 copolymer taken from different locations on the sample surface a,c) phase and b,d) height images

AFM images support the findings that are obtained with OM. Figure 3.56.a,b belongs to regions where PEO mid-block is crystallized. As revealed by OM images, these regions do not have a certain orientation since they are crystallized after PCL spherulites. AFM also showed that those regions are crystalline regions; however they do not show a specific crystal structure. One of the PCL spherulites on the surface was scanned with AFM. The spherulite was clearly revealed in Figure 3.56.c,d showing a certain phase separation with the other crystalline region. The reason why there is a significant separation between two constituent blocks is obviously competitive crystallization in which one component prevents the crystallization of the other component.

The length of PCL end-blocks are doubled by keeping the length of PEO mid-block constant. OM images of 16-8-16 PCL-PEO-PCL copolymer crystallized from different solvents are given in Figure 3.57.

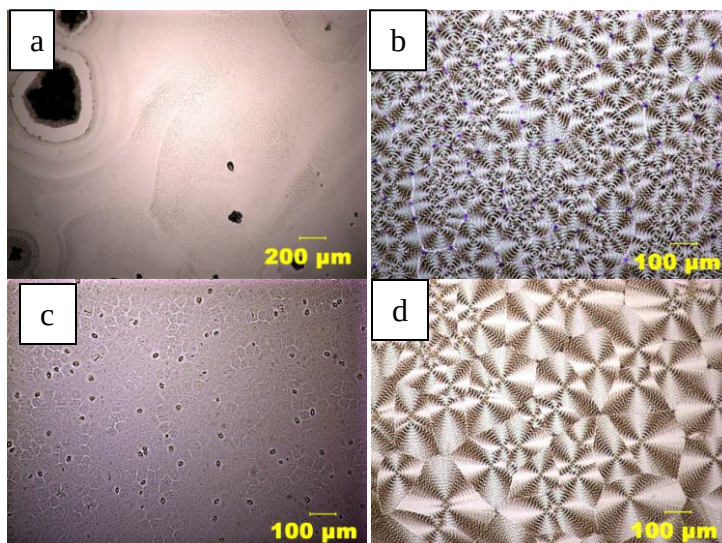


Figure 3.57. Non-polarized optical images of 16-8-16 copolymer crystallized from 20% solid solution of a) toluene (10X), b) IPA-DCM (1:1) (10X), c) DMF (5X) and d) chloroform (10X)

When toluene was used as the solvent no crystalline morphology was observed due to hindered crystallinity of copolymer chains in the medium (Figure 3.57.a). IPA-DCM solvent pair resulted in ring-banded crystal domains in which both components can be co-crystallized (Figure 3.57.b). No ordered structure is observed when copolymer is spincoated from DMF solution (Figure 3.57.c). Chloroform resulted in ring-banded crystal domains resembling that of IPA-DCM solvent pair, however the domain size is larger and more uniform (Figure 3.57.d).

The copolymer is crystallized from THF solution. The images are shown in Figure 3.58.

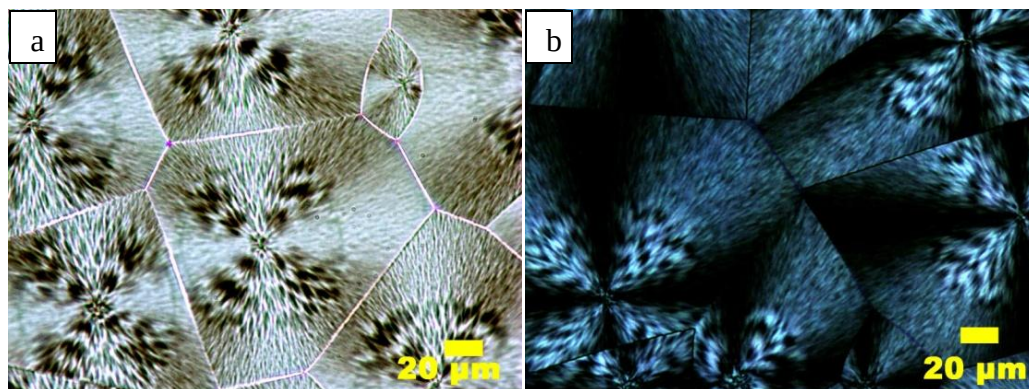


Figure 3.58. a) Non-polarized and b) polarized OM images of 16-8-16 copolymer spincoated from THF solution at 50X magnification

Crystallization of the copolymer from THF solution resulted in concentric spherulites which are uniform and distinctive (Figure 3.58). As seen from the images, there are two different components within the same spherulite. PCL domains are seen as ring-like structures in the spherulite and PEO mid-block fills the domain following the PCL domain.

This prudence is further investigated on heating stage under OM and the images are provided in Figure 3.59.

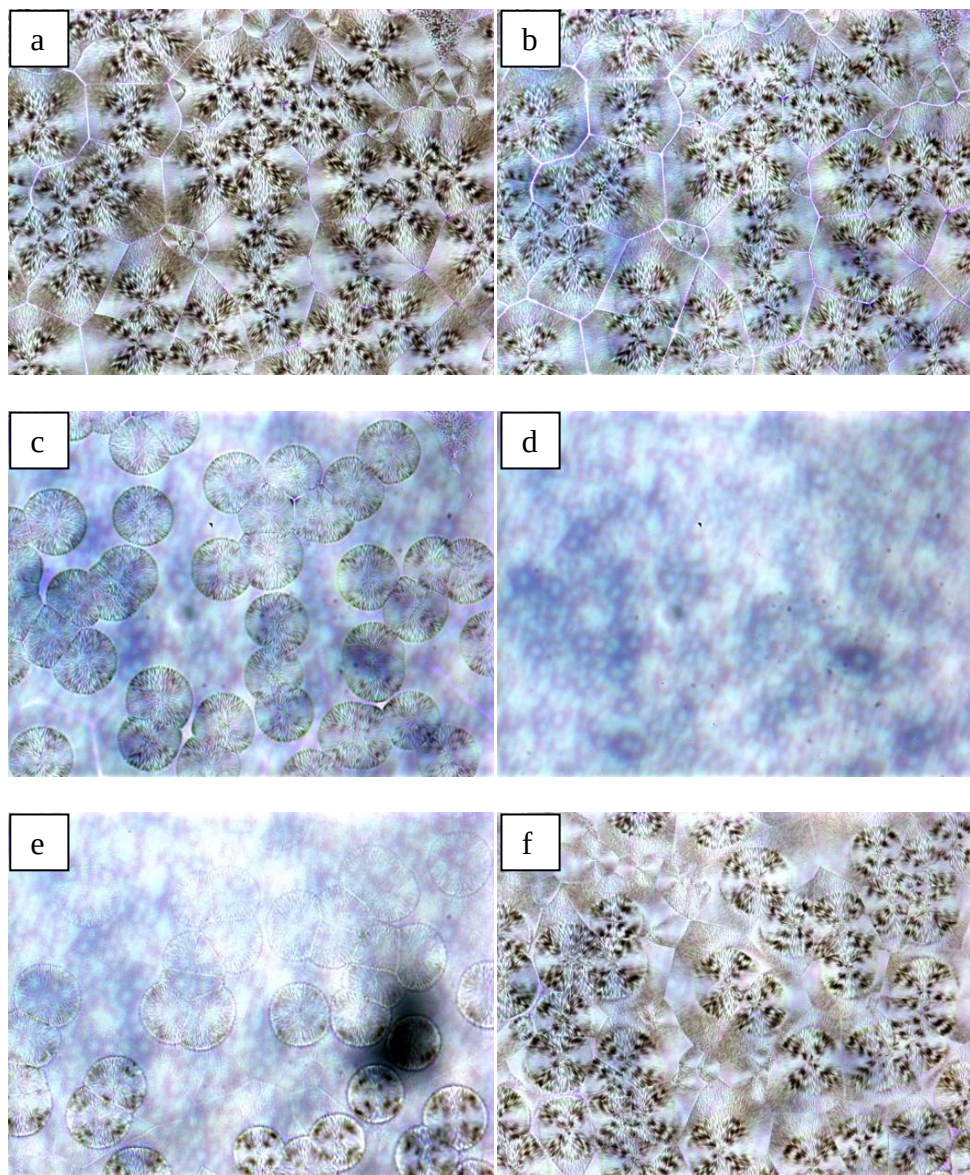


Figure 3.59. Non-polarized 20X magnified OM images of 16-8-16 copolymer on heating stage; heating process a) 25.0°C, b) 71.7°C, c) 74.6°C, d) 75.3°C cooling process e) 58.3°C and f) 35.0°C

Melting of the copolymer starts with the melting of the PEO rich crystal domains and PCL rich spherulites are preserved until 74.6°C. After all the components are melted, recrystallization of the copolymer starts with the formation of ring-like PCL rich crystal structure (Figure 3.59.e). The concentric crystal structure is completed with the crystallization of PEO mid-block within the same spherulite (Figure 3.59.f). Presence of two different components within the concentric spherulite was also revealed with AFM analysis. The phase and height images are provided in Figure 3.60.

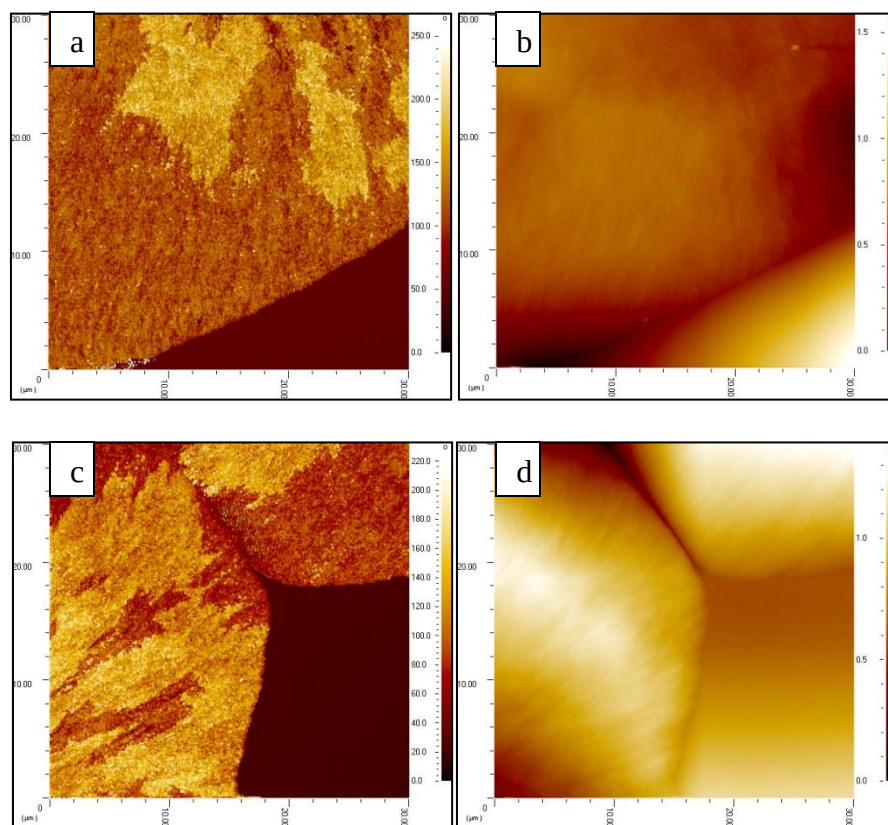


Figure 3.60. 30x30 μm AFM a,c) phase and b,d) height images of 16-8-16 copolymer scanned from different locations on the sample surface

AFM phase images of 16-8-16 copolymer show the phase difference within a crystal spherulite for which the OM images indicated the presence of two different domains. As explained earlier, PCL domains crystallize as the first component of the spherulite and then PEO mid-block crystallizes within the same spherulite. PCL blocks act as nucleation points for the other component. AFM clearly showed that there are two different phases in a single spherulite domain for which the brighter and darker regions belong to PCL rich and PEO rich domains, respectively (Figure 3.60.a,c).

3.2.4. X-Ray Diffraction Analysis of PCL-PEO-PCL Block Copolymers

Poly(caprolactone) and poly(ethylene oxide) polymers are semicrystalline materials with orthorhombic and monoclinic unit cell structures, respectively. As the extent of crystallinity increases, two major crystalline peaks are observed for PEO. The XRD diagrams for PEO having three different molecular weights are provided in Figure 3.61 including the pattern of PCL for comparison.

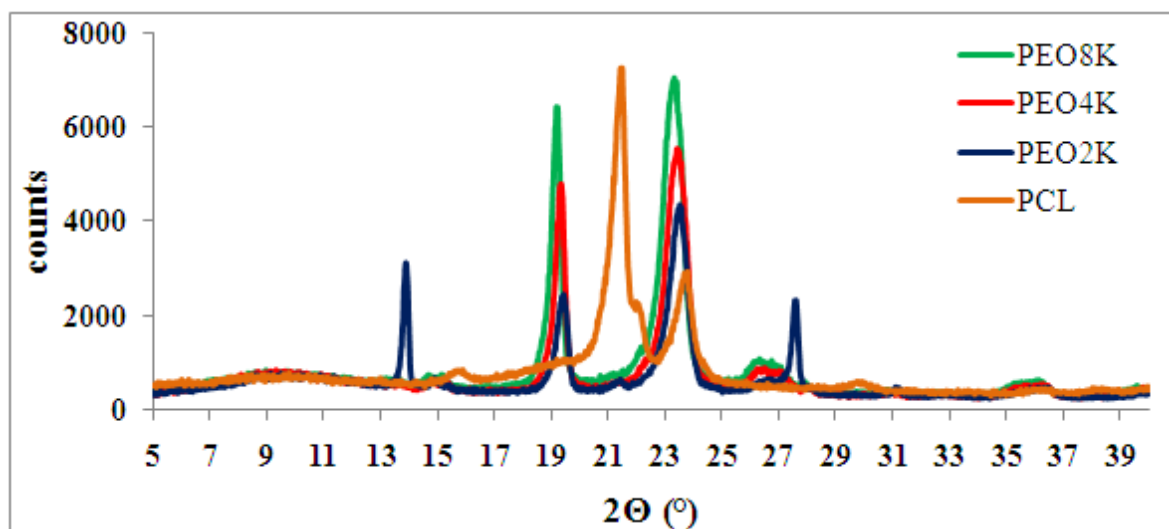


Figure 3.61. XRD patterns of PEO having three different molecular weights and PCL for comparison

As observed from the XRD patterns, PEO displays two major peaks at $\sim 19^\circ$ and $\sim 23^\circ$ as the molecular weight increases. When PEO is copolymerized with PCL, two crystalline peaks of both at $\sim 23^\circ$ overlaps; therefore it is more reasonable to make comparison with respect to other crystalline peaks which are at $\sim 19^\circ$ and $\sim 21.5^\circ$.

It is known that PCL and PEO components of the copolymer display competitive crystallization [100]. Depending on the length of each constituent block, the extent of crystallization of the segments is determined. In order to compare the extent of crystallization of the components of the copolymer, the XRD patterns are shown in Figure 3.62 for three different copolymer compositions.

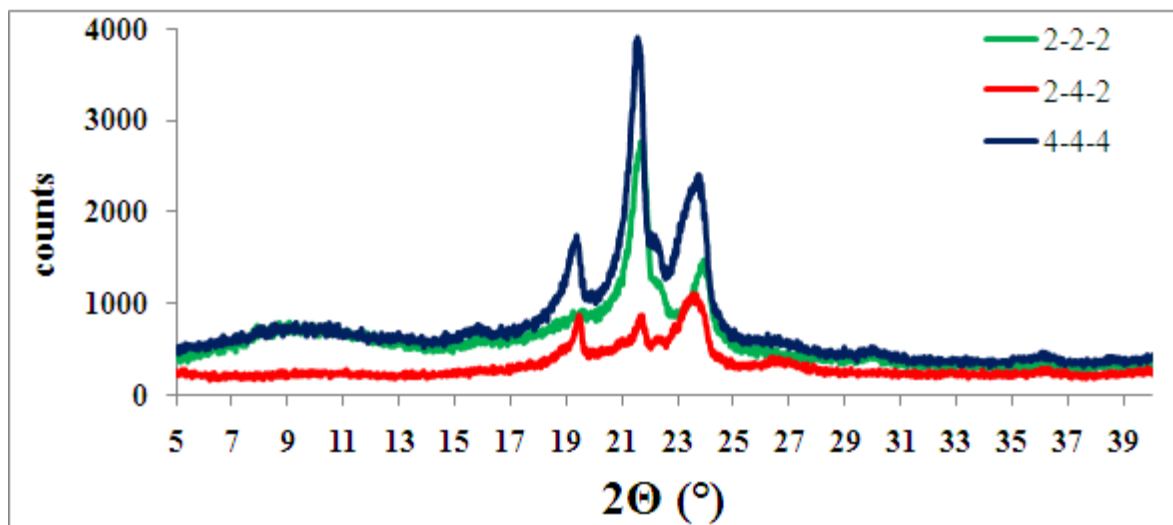


Figure 3.62. XRD patterns of PCL-PEO-PCL block copolymers of three different compositions

It is clearly seen that the crystallization of copolymer is strongly dependent on the length of the constituent blocks (Figure 3.62). Almost no crystal peaks arising from PEO mid-block is observed for 2-2-2 copolymer composition. It is most probably due to deterring effect of PCL crystallization on the packing of PEO mid-block. PEO segment is barely crystallized and its amorphous domains are confined within the amorphous regions of the copolymer for which the amorphous XRD peak is observed at $\sim 10^{\circ}$. When PEO mid-block length is doubled by keeping PCL end-block length constant, it is clearly seen that the crystallization of PCL is strongly prevented. At the same time, crystal peaks emerging from PEO mid-block are becoming clear. This indicates that increase in the PEO mid-block length decreases the extent of packing of PCL end-blocks for 2-4-2 copolymer. As PCL fraction

increases within the copolymer, the extent of crystallinity which reflects itself as an increase in the peak intensity at $\sim 21.5^\circ$ increases. The crystal peaks of 4-4-4 copolymer arising from PCL and PEO domains are prominent compared to previous compositions. This may be attributed to the enhanced crystallization of the copolymer domains due to increase in the molecular weight of constituent blocks which promotes the degree of packing of the polymer chains.

XRD patterns of the other copolymer compositions having the same mid-block length are analyzed together. The XRD diagrams are shown in Figure 3.63.

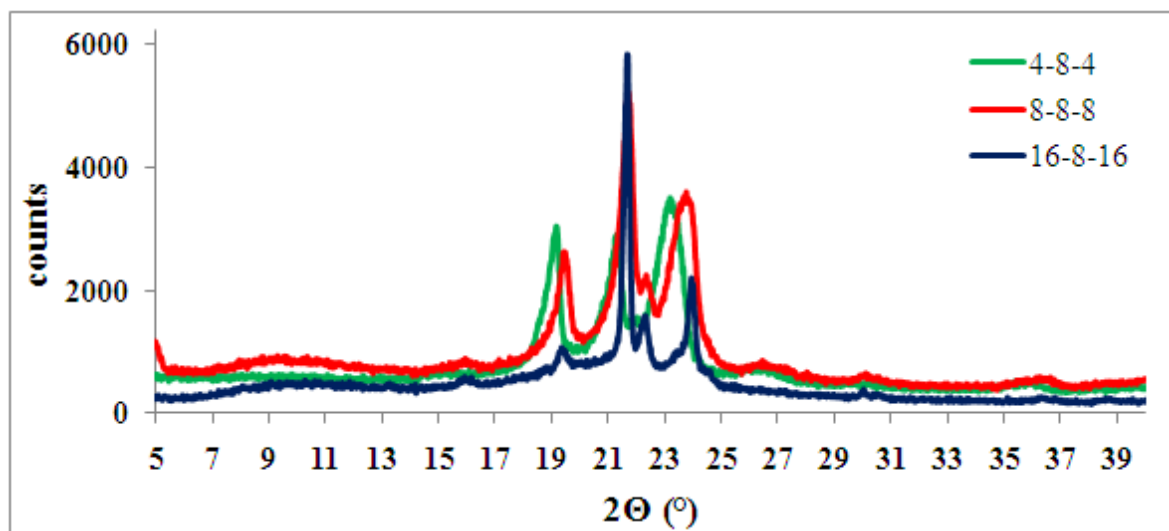


Figure 3.63. XRD diagrams of 4-8-4, 8-8-8 and 16-8-16 copolymer compositions

It is expected that an increase in the fraction of one component within the copolymer should enhance the crystallization of that copolymer component. Therefore, the enhancement of crystallinity has to be monitored as an increase in the peak intensity of the

crystal peak of the component. The XRD pattern of 4-8-4 copolymer reveals that both components are crystallized having comparable peak intensities. This means that even though there is competitive crystallization between the components, all of the constituent blocks of the copolymer can align and pack up to a certain degree. When PCL fraction is doubled by keeping the mid-block length constant, it is seen that the crystallization of PCL is enhanced compared to previous copolymer composition. Crystal peak intensity of PCL block increased and peak intensity of PEO mid-block is slightly decreased in 8-8-8 copolymer as an indication of better packing of the PCL end-blocks. 16-8-16 block copolymer composition has the highest PCL fraction which is 0.8. As expected, the extent of PCL crystallization is the highest for this copolymer composition. While the crystal peak intensity of PEO mid-block is decreased, PCL peak intensity is increased very much. It was previously explained that the PCL block is the first crystallizing component within the block copolymer. Therefore, PEO mid-block crystallizes within a confined space which is dependent on the crystalline PCL blocks. An increase in the PCL fraction enhances the crystallization of PCL which eventually decreases the space left for PEO mid-block. As a result, the crystallization of PEO mid-block is the lowest and that of PCL is the highest in 16-8-16 copolymer compared to other two previously discussed compositions.

Chapter 4

CONCLUSIONS

A series of PCL-PDMS-PCL and PCL-PEO-PCL ABA type copolymers were successfully synthesized with different mid-block and end-block lengths and were characterized. Surface properties, microphase separation and crystallization of triblock copolymers were investigated by using static contact angle measurements, atomic force microscopy, optical microscopy and X-Ray Diffractometry.

PCL-PDMS-PCL triblock copolymers displayed hydrophobic surface characters due to migration of PDMS to the surface. The extent of hydrophobicity was found to be strongly dependent on the molecular weight of the PDMS macroinitiator. PCL-PDMS-PCL copolymers displayed microphase separated morphologies which were determined by the length of each constituent block. Crystallization of PCL end-blocks was also dependent on the length of both PCL and PDMS segments. Crystallization is generally decreased with increasing mid-block length.

PCL-PEO-PCL triblock copolymers demonstrated competitive crystallization which was dependent on the length of each constituent copolymer segment. Thermal properties of triblock copolymers were also dependent on the composition of the copolymers. It was found out that the crystallization of PEO mid-block was strongly affected by the presence of PCL end-blocks for which the crystallization was enhanced with increasing PCL fraction within the copolymer.

BIBLIOGRAPHY

- [1] Hamley, Ian W. *The Physics of Block Copolymers*. Oxford: Oxford Univ., 1998.
- [2] Hillmyer, Marc A., Marc D. Rodwogin, Charles S. Spanjers, and C. Leighton. "Polylactide-Poly(dimethylsiloxane)-Polylactide Triblock Copolymers as Multifunctional Materials for Nanolithographic Applications." *ACS Nano* 4.2 (2010): 725-32.
- [3] Odian, George G. *Principles of Polymerization*. Hoboken [N.J.]: Wiley-Interscience, 2004.
- [4] Yilgor, Iskender, and Emel Yilgor. "Structure-Morphology-Property Behavior of Segmented Thermoplastic Polyurethanes and Polyureas Prepared without Chain Extenders." *Polymer Reviews* 47.4 (2007): 487-510.
- [5] Klinedinst, Derek B., Emel Yilgör, Iskender Yilgör, Frederick L. Beyer, and Garth L. Wilkes. "Structure-property Behavior of Segmented Polyurethaneurea Copolymers Based on an Ethylene-butylene Soft Segment." *Polymer* 46.23 (2005): 10191-0201.
- [6] Kojio, Ken, Mutsuhisa Furukawa, Suguru Motokucho, Makoto Shimada, and Machiko Sakai. "Structure-Mechanical Property Relationships for Poly(carbonate Urethane) Elastomers with Novel Soft Segments." *Macromolecules* 42 (2009): 8322-327.
- [7] Müller, Axel H. E., and Hans-Werner Schmidt. *Complex Macromolecular Systems*. Heidelberg: Springer, 2010.
- [8] Hamley, Ian W. *Developments in Block Copolymer Science and Technology*. Chichester, West Sussex: J. Wiley, 2004.
- [9] Bahadur, Pratap. "Block Copolymers – Their Microdomain Formation (in Solid State) and Surfactant Behaviour (in Solution)." *Current Science* 80.8 (2001): 1002-007.
- [10] Hadjichristidis, Nikos, Stergios Pispas, and George Floudas. *Block Copolymers: Synthetic Strategies, Physical Properties, and Applications*. Hoboken, NJ: Wiley-Interscience, 2003.
- [11] Szwarc, M., M. Levy, and R. Milkovich. "A simplified route to a key intermediate in the total synthesis of reserpine." *J.Am.Chem.Soc.* 78 (1956): 2656.

- [12] Corbin, N., and J. Prud'Homme. "Multiblock Copolymers of Styrene and Isoprene. I. Synthesis and Characterization." *Journal of Polymer Science: Polymer Chemistry Edition* 14.7 (1976): 1645-659.
- [13] Quirk, Roderic P., and Bumjae Lee. "Experimental Criteria for Living Polymerizations." *Polymer International* 27.4 (1992): 359-67.
- [14] Hong, Kunlun, and Jimmy W. Mays. "1,3-Cyclohexadiene Polymers. 3. Synthesis and Characterization of Poly(1,3-cyclohexadiene--styrene)." *Macromolecules* 34.11 (2001): 3540-547.
- [15] Varshney, S. K., J. P. Hautekeer, R. Fayt, R. Jerome, and P. Teyssie. "Anionic Polymerization of (meth)acrylic Monomers. 4. Effect of Lithium Salts as Ligands on the "living" Polymerization of Methyl Methacrylate Using Monofunctional Initiators." *Macromolecules* 23.10 (1990): 2618-622.
- [16] Hautekeer, J. P., S. K. Varshney, R. Fayt, C. Jacobs, R. Jerome, and P. Teyssie. "Anionic Polymerization of Acrylic Monomers. 5. Synthesis, Characterization and Modification of Polystyrene-poly(tert-butyl Acrylate) Di- and Triblock Copolymers." *Macromolecules* 23.17 (1990): 3893-898.
- [17] Hild, G., and J. P. Lamps. "Diblock Copolymers, Triblock Copolymers and Model Networks Synthesized by Sequential Anionic Polymerization of Styrene and 2,3-epoxypropyl Methacrylate." *Polymer* 39.12 (1998): 2637-649.
- [18] Schindler A., Williams J. L. (1969) *Polym. Prepr.* 10(2), 832.
- [19] Finaz G., Rempp P., Parrod J. (1962) *Bull. Soc. Chim. Fr.* 262.
- [20] D. R. Paul and J. W. Barlow, "Polymer Blends (or Alloys)," *J. Macromol. Sci. - Rev. Macromol. Chem.*, **C18**, 109 (1980).
- [21] Zilliox, J. G., J. E. L. Roovers, and S. Bywater. "Preparation and Properties of Polydimethylsiloxane and Its Block Copolymers with Styrene." *Macromolecules* 8.5 (1975): 573-78.
- [22] Elgert K. F., Seiler E., Puschendorf G., Kantow H. J. (1973) 165, 245.

- [23] Matsushita Y., Shimizu N., Nakao Y., Choshi H., Nagasawa M. (1986) *Polymer J.* 18, 361.
- [24] Förster, Stephan, and Eckart Krämer. "Synthesis of PB-PEO and PI-PEO Block Copolymers with Alkylolithium Initiators and the Phosphazene Base-BuP." *Macromolecules* 32.8 (1999): 2783-785.
- [25] Almdal, Kristoffer, Kell Mortensen, Anthony J. Ryan, and Frank S. Bates. "Order, Disorder, and Composition Fluctuation Effects in Low Molar Mass Hydrocarbon-Poly(dimethylsiloxane) Diblock Copolymers." *Macromolecules* 29.18 (1996): 5940-947.
- [26] Balsamo, Vittoria, A. J. Müller, Friederike Von Gyldenfeldt, and Reimund Stadler. "Ternary ABC Block Copolymers Based on One Glassy and Two Crystallizable Blocks: Polystyrene-block-polyethylene-block- Poly(ϵ -caprolactone)." *Macromolecular Chemistry and Physics* 199.6 (1998): 1063-072.
- [27] Allen, R. D., T. E. Long, and J. E. McGrath. "Preparation of High Purity, Anionic Polymerization Grade Alkyl Methacrylate Monomers." *Polymer Bulletin* 15.2 (1986): 127-34.
- [28] Duivenvoorde, Francis L., J. J. G. Steven Van Es, Cornelus F. Van Nostrum, and Rob Van Der Linde. "Novel Block Copolymers of 2-vinylpyridine and ϵ -caprolactone: Synthesis and Characterization." *Macromolecular Chemistry and Physics* 201.6 (2000): 656-61.
- [29] Martin, Thomas J., K. Procházka, P. Munk, and S. E. Webber. "PH-Dependent Micellization of Poly(2-vinylpyridine)-poly(ethylene Oxide)." *Macromolecules* 29.18 (1996): 6071-073.
- [30] Hsieh, Henry L., and Roderic P. Quirk. *Anionic Polymerization Principles and Practical Applications*. New York: M. Dekker, 1996.
- [31] Morton, Maurice. *Anionic Polymerization: Principles and Practice*. New York: Academic, 1983.
- [32] Barker, Martyn C., and Brian Vincent. "The Preparation and Characterisation of Polystyrene/poly(ethylene oxide) AB Block Copolymers." *Colloids and Surfaces* 8.3 (1984): 289-95.

- [33] Matyjaszewski, Krzysztof, and Jianhui Xia. "Atom Transfer Radical Polymerization." *Chemical Reviews* 101.9 (2001): 2921-990.
- [34] Li, Yuting, Steven P. Armes, Xiaoping Jin, and Shiping Zhu. "Direct Synthesis of Well-Defined Quaternized Homopolymers and Diblock Copolymers via ATRP in Protic Media." *Macromolecules* 36.22 (2003): 8268-275.
- [35] Zhang, Z. B., S. K. Ying, and Z. Q. Shi. "Synthesis of Fluorine-containing Block Copolymers via ATRP 2. Synthesis and Characterization of Semifluorinated Di- and Triblock Copolymers." *Polymer* 40 (1999): 5439-444.
- [36] Davis, Kelly A., and Krzysztof Matyjaszewski. "ABC Triblock Copolymers Prepared Using Atom Transfer Radical Polymerization Techniques." *Macromolecules* 34.7 (2001): 2101-107.
- [37] Ramakrishnan, A., and R. Dhamodharan. "Facile Synthesis of ABC and CBABC Multiblock Copolymers of Styrene,-Butyl Acrylate, and Methyl Methacrylate via Room Temperature ATRP of MMA." *Macromolecules* 36.4 (2003): 1039-046.
- [38] Weiyu, Cao, Kohji Tashiro, Makoto Hanesaka, Shinichi Takeda, Hiroyasu Masunaga, Sono Sasaki, and Masaki Takata. "Relationship between Morphological Change and Crystalline Phase Transitions of Polyethylene–Poly(ethylene Oxide) Diblock Copolymers, Revealed by the Temperature-dependent Synchrotron WAXD/SAXS and Infrared/Raman Spectral Measurements." *The Journal of Physical Chemistry B* 113.8 (2009): 2338-346.
- [39] Flory, Paul J. *Principles of Polymer Chemistry*. Ithaca: Cornell UP, 1953.
- [40] Bates, F. S., and G. H. Fredrickson. "Block Copolymer Thermodynamics: Theory and Experiment." *Annual Review of Physical Chemistry* 41.1 (1990): 525-57.
- [41] Flory, Paul J. "Thermodynamics of High Polymer Solutions." *The Journal of Chemical Physics* 10.1 (1941): 51-62.
- [42] Mori, K. "Small-angle X-ray Scattering from Block Copolymers in Disordered State: 2. Effect of Molecular Weight Distribution." *Polymer* 30.8 (1989): 1389-398.
- [43] Clarke, C. J., A. Eisenberg, J. La Scala, M. H. Rafailovich, J. Sokolov, Z. Li, S. Qu, D. Nguyen, S. A. Schwarz, Y. Strzhemechny, and B. B. Sauer. "Measurements of the

Flory–Huggins Interaction Parameter for Polystyrene–Poly(4-vinylpyridine) Blends." *Macromolecules* 30.14 (1997): 4184-188.

[44] Pospiech, Doris, Antje Gottwald, Dieter Jehnichen, Peter Friedel, Andreas John, Christina Harnisch, Dieter Voigt, Galina Khimich, and Alexander Bilibin. "Determination of Interaction Parameters of Block Copolymers Containing Aromatic Polyesters from Solubility Parameters Obtained from Solution Viscosities." *Colloid & Polymer Science* 280.11 (2002): 1027-037.

[45] Hildebrand, Joel Henry, and Robert L. Scott. *The Solubility of Nonelectrolytes*. New York: Reinhold Pub., 1950.

[46] Arnal, M. "Coincident or Sequential Crystallization of PCL and PEO Blocks within Polystyrene-*b*-poly(ethylene Oxide)-*b*-poly(?-caprolactone) Linear Triblock Copolymers." *European Polymer Journal* 40.7 (2004): 1461-476.

[47] Lynd, N., A. Meuler, and M. Hillmyer. "Polydispersity and Block Copolymer Self-assembly." *Progress in Polymer Science* 33.9 (2008): 875-93.

[48] Avgeropoulos, Apostolos, Benita J. Dair, Nikos Hadjichristidis, and Edwin L. Thomas. "Tricontinuous Double Gyroid Cubic Phase in Triblock Copolymers of the ABA Type." *Macromolecules* 30 (1997): 5634-642.

[49] Pitsikalis, Marinos, Stella Sioula, Stergios Pispas, Nikos Hadjichristidis, Daniel C. Cook, Jianbo Li, and Jimmy W. Mays. "Linking Reactions of Living Polymers with Bromomethylbenzene Derivatives: Synthesis and Characterization of Star Homopolymers and Graft Copolymers with Polyelectrolyte Branches." *Journal of Polymer Science Part A: Polymer Chemistry* 37.23 (1999): 4337-350.

[50] Lo, G. Y.-S., E. W. Otterbacher, A. L. Gatzke, and L. H. Tung. "Studies on Dilithium Initiators.3. Effect of Additives and Seeding." *Macromolecules* 27.8 (1994): 2233-240.

[51] Tong, J. D., and R. Jerome. "Synthesis of Poly(methyl Methacrylate)-*b*-poly(n-butyl Acrylate)-*b*-poly(methyl Methacrylate) Triblocks and Their Potential as Thermoplastic Elastomers." *Polymer* 41 (2000): 2499-510.

[52] Tong, Jiang-Dong, Shaoru Ni, and Mitchell A. Winnik. "Synthesis of Polyisoprene--Polystyrene Block Copolymers Bearing a Fluorescent Dye at the Junction by the

Combination of Living Anionic Polymerization and Atom Transfer Radical Polymerization." *Macromolecules* 33.5 (2000): 1482-486.

[53] Tong, Jiang-Dong, and Robert Jérôme. "Dependence of the Ultimate Tensile Strength of Thermoplastic Elastomers of the Triblock Type on the Molecular Weight between Chain Entanglements of the Central Block." *Macromolecules* 33.5 (2000): 1479-481.

[54] Morton M., Synthetic Elastomers, Kirk-Othmer Encyclopedia of Chemical Technology, vol. 9 (2000) 550-567.

[55] Bogart, V., A. Lilaonitkul, and S. L. Cooper. "Morphology and Property of Segmented Copolymers." *Multiphase Polymers* (1979): 4-30.

[56] Loo, Yueh-Lin, Richard A. Register, Anthony J. Ryan, and Gregory T. Dee. "Polymer Crystallization Confined in One, Two, or Three Dimensions." *Macromolecules* 34.26 (2001): 8968-977.

[57] Hamley, I. W., P. Parras, V. Castelletto, R. V. Castillo, A. J. Müller, E. Pollet, P. Dubois, and C. M. Martin. "Melt Structure and Its Transformation by Sequential Crystallization of the Two Blocks within Poly(L-lactide)-block-Poly(ϵ -caprolactone) Double Crystalline Diblock Copolymers." *Macromolecular Chemistry and Physics* 207.11 (2006): 941-53.

[58] Geckeler, Kurt E. *Advanced Nanomaterials*. Weinheim: Wiley-VCH, 2010.

[59] Ho, C. H., G. W. Jang, and Y. D. Lee. "Crystallization of Poly(L-lactide-dimethyl Siloxane-L-lactide) Triblock Copolymers and Its Effect on Morphology of Microphase Separation." *Polymer* 51 (2010): 1639-647.

[60] Shiomi, T., K. Imai, K. Takenaka, H. Takeshita, H. Hayashi, and Y. Tezuka. "Appearance of Double Spherulites like Concentric Circles for Poly(ϵ -caprolactone)-block-poly(ethylene Glycol)- Block-poly(ϵ -caprolactone)." *Polymer* 42 (2001): 3233-239.

[61] Brinkmann, Susanne, Reimund Stadler, and Edwin L. Thomas. "New Structural Motif in Hexagonally Ordered Cylindrical Ternary (ABC) Block Copolymer Microdomains." *Macromolecules* 31.19 (1998): 6566-572.

- [62] Stadler, Reimund, Clemens Auschra, Joerg Beckmann, Udo Krappe, Ingrid Voight-Martin, and Ludwik Leibler. "Morphology and Thermodynamics of Symmetric Poly(A-block-B-block-C) Triblock Copolymers." *Macromolecules* 28.9 (1995): 3080-097.
- [63] Mogi, Yasuhiro, Hiroyuki Kotsuji, Yuji Kaneko, Katsuaki Mori, Yushu Matsushita, and Ichiro Noda. "Preparation and Morphology of Triblock Copolymers of the ABC Type." *Macromolecules* 25.20 (1992): 5408-411.
- [64] Matsushita, Yushu, Masaki Tamura, and Ichiro Noda. "Tricontinuous Double-Diamond Structure Formed by a Styrene-Isoprene-2-Vinylpyridine Triblock Copolymer." *Macromolecules* 27.13 (1994): 3680-682.
- [65] Hückstädt, H. "Influence of the Block Sequence on the Morphological Behavior of ABC Triblock Copolymers." *Polymer* 41.26 (2000): 9089-094.
- [66] Bates, Frank S., and Glenn H. Fredrickson. "Block Copolymers—Designer Soft Materials." *Physics Today* 52.2 (1999): 32.
- [67] Dubois, Philippe, Olivier Coulembier, and Jean-Marie Raquez. *Handbook of Ring-opening Polymerization*. Weinheim: Wiley-VCH, 2009.
- [68] Biela, Tadeusz, Adam Kowalski, Jan Libiszowski, Andrzej Duda, and Stanisław Penczek. "Progress in Polymerization of Cyclic Esters: Mechanisms and Synthetic Applications." *Macromolecular Symposia* 240.1 (2006): 47-55.
- [69] Keul, Helmut, and Hartwig Höcker. "Expected and Unexpected Reactions in Ring-opening (co)polymerization." *Macromolecular Rapid Communications* 21.13 (2000): 869-83.
- [70] Chanda, Manas. *Introduction to Polymer Science and Chemistry: a Problem Solving Approach*. Boca Raton, FL: CRC/Taylor & Francis, 2006.
- [71] Endo, Takashi, and Katsufumi Suga. "Radical Ring-opening Polymerization Behavior of Vinylcyclopropanes Derived from Dienes and Chloroform." *Journal of Polymer Science Part A: Polymer Chemistry* 27.6 (1989): 1831-842.
- [72] Yuan, Jin-Ying, Cai-Yuan Pan, and Ben Zhong Tang. "'Living' Free Radical Ring-Opening Polymerization of 5,6-Benzo-2-methylene-1,3-dioxepane Using the Atom Transfer Radical Polymerization Method." *Macromolecules* 34.2 (2001): 211-14.

- [73] Mori, Hideharu, Shigeki Masuda, and Takeshi Endo. "Ring-Opening RAFT Polymerization Based on Aromatization as Driving Force: Synthesis of Well-Defined Polymers Containing Anthracene Units in the Main Chain." *Macromolecules* 39.18 (2006): 5976-978.
- [74] Nederberg, Fredrik, Bas G. G. Lohmeijer, Frank Leibfarth, Russell C. Pratt, Jeongsoo Choi, Andrew P. Dove, Robert M. Waymouth, and James L. Hedrick. "Organocatalytic Ring Opening Polymerization of Trimethylene Carbonate." *Biomacromolecules* 8.1 (2007): 153-60.
- [75] Enders, Dieter, Klaus Breuer, Gerhard Raabe, Jan Runsink, J. Henrique Teles, Johann-Peter Melder, Klaus Ebel, and Stefan Brode. "Preparation, Structure, and Reactivity of 1,3,4-Triphenyl-4,5-dihydro-1H-1,2,4-triazol-5-ylidene, a New Stable Carbene." *Angewandte Chemie International Edition in English* 34.9 (1995): 1021-023.
- [76] Kowalski, Adam, Jan Libiszowski, Tadeusz Biela, Marek Cypryk, Andrzej Duda, and Stanislaw Penczek. "Kinetics and Mechanism of Cyclic Esters Polymerization Initiated with Tin(II) Octoate. Polymerization of ϵ -Caprolactone And-Lactide Co-initiated with Primary Amines." *Macromolecules* 38.20 (2005): 8170-176.
- [77] Cai, Qing, Youliang Zhao, Jianzhong Bei, Fu Xi, and Shenguo Wang. "Synthesis and Properties of Star-Shaped Polylactide Attached to Poly(Amidoamine) Dendrimer." *Biomacromolecules* 4.3 (2003): 828-34.
- [78] Coulembier, Olivier, Matthew K. Kiesewetter, Andrew Mason, Philippe Dubois, James L. Hedrick, and Robert M. Waymouth. "A Distinctive Organocatalytic Approach to Complex Macromolecular Architectures." *Angewandte Chemie International Edition* 46.25 (2007): 4719-721.
- [79] Wong, Joyce Y., and Joseph D. Bronzino. *Biomaterials*. Boca Raton: CRC, 2007.
- [80] Natta, Frank J.V., Julian W. Hill, and Wallace H. Carothers. "Studies of Polymerization and Ring Formation. XXIII. Epsilon-Caprolactone and Its Polymers." *Journal of American Chemical Society* 56 (1934): 455-57.
- [81] Chandra, R., and R. Rustgi. "Biodegradable Polymers." *Prog. Polym. Sci.* 23 (1998): 1273-335.

- [82] Nair, L., and C. Laurencin. "Biodegradable Polymers as Biomaterials." *Progress in Polymer Science* 32.8-9 (2007): 762-98.
- [83] Woodruff, Maria Ann, and Dietmar Werner Hutmacher. "The Return of a Forgotten Polymer—Polycaprolactone in the 21st Century." *Progress in Polymer Science* 35 (2010): 1217-256.
- [84] K. L. March, "Use of polyols for improving the introduction of genetic material into cells", U. S. Patent 5,552,309 to Indiana University Foundation (1996).
- [85] T. X. Viegas, L. E. Reeve and R. L. Henry, "Medical uses of in situ formed gels", U. S. Patent 5,587,175 to MDV Technologies Inc. (1996).
- [86] T. X. Viegas, L. E. Reeve and R. L. Henry, "Method of making thermoreversible polyoxyalkylene gels", U. S. Patent 5,593,683 to MDV Technologies Inc. (1997).
- [87] T. X. Viegas, L. E. Reeve and R. L. Henry, "Body cavity drug delivery with thermo-irreversible polyoxyalkylene and ionic polysaccharide gels", U. S. Patent 6,346,272 to MDV Technologies Inc. (2002).
- [88] Petrova, Ts., N. Manolova, I. Rashkov, Suming Li, and Michel Vert. "Synthesis and Characterization of Poly(oxyethylene)-poly(caprolactone) Multiblock Copolymers." *Polymer International* 45.4 (1998): 419-26.
- [89] Ye, W. "In Vitro Degradation of Poly(caprolactone), Poly(lactide) and Their Block Copolymers: Influence of Composition, Temperature and Morphology." *Reactive and Functional Polymers* 32.2 (1997): 161-68.
- [90] Ratner, B. D. *Biomaterials Science: an Introduction to Materials in Medicine*. Amsterdam: Elsevier Academic, 2004.
- [91] Kim, H. C., S. M. Park, and W. D. Hinsberg. "Block Copolymer Based Nanostructures: Materials, Processes, and Applications to Electronics." *Chem. Rev.* 110 (2010): 146-77.
- [92] Jung, Yeon Sik, and C. A. Ross. "Orientation-Controlled Self-Assembled Nanolithography Using a Polystyrene–Polydimethylsiloxane Block Copolymer." *Nano Letters* 7.7 (2007): 2046-050.

- [93] Philip, W. A., B. O'Neill, M. Rodwogin, M. A. Hillmyer, and E. L. Cussler. "Self-Assembled Block Copolymer Thin Films as Water Filtration Membranes." *Applied Materials and Interfaces* 2 (2010): 847-53.
- [94] Mark, James E. *Polymer Data Handbook*. New York: Oxford UP, 1999.
- [95] Lovinger, Andrew J., B. J. Han, Frank J. Padden, and Peter A. Mirau. "Morphology and Properties of Polycaprolactone-poly(dimethylsiloxane)-polycaprolactone Triblock Copolymers." *Journal of Polymer Science: Part B: Polymer Physics* 31 (1993).
- [96] Matsen, M. W., and R. B. Thompson. "Equilibrium Behavior of Symmetric ABA Triblock Copolymer Melts." *Journal of Chemical Physics* 111.15 (1999).
- [97] Gagliardi, S., V. Arrighi, A. Dagger, and A. J. Semlyen. "Conformation of Cyclic and Linear Polydimethylsiloxane in the Melt: a Small-angle Neutron-scattering Study." *Applied Physics A* 74 (2002).
- [98] Fasolka, M. J., and A. M. Mayes. "Block Copolymer Thin Films: Physics and Applications." *Annu. Rev. Mater. Res.* 31 (2001): 323-55.
- [99] Hamley, I. W. "Nanostructure Fabrication Using Block Copolymers." *Nanotechnology* 14.10 (2003): R39-54.
- [100] Cho, Heui Kyoung, Kwang Soo Cho, Jin Hun Cho, Sung Wook Choi, Jung Hyun Kim, and In Woo Cheong. "Synthesis and Characterization of PEO-PCL-PEO Triblock Copolymers: Effects of the PCL Chain Length on the Physical Property of W1/O/W2 Multiple Emulsions." *Colloids and Surfaces B: Biointerfaces* 65.1 (2008): 61-68.
- [101] Smallwood, Ian M. *Handbook of Organic Solvents*. New York: John Wiley & Sons Inc., 1996.

VITA

Mehmet Işık was born in Kütahya, Turkey in 1985. He completed the high school in İMKB Tavşanlı Anatolian Teacher High School, Kütahya in 2004. He received his B.S. degree in Chemistry from Koç University, İstanbul, in June 2009. He has been working towards his M.S. degree in Materials Science and Engineering at Koç University since September 2009. He will continue his academic career in Materials Science and Engineering Ph.D program at Koç University, Turkey.