

Contents

Abstract	iii
Acknowledgements	v
1 Background	1
1.1 Introduction	1
1.2 Liquid crystals	3
1.2.1 The nematic mesophase	3
1.2.2 Liquid crystal elasticity	5
1.2.3 Dynamic properties of the nematic director	5
1.3 Liquid crystalline elastomers and gels	7
1.3.1 LC polymers: anisotropic chains	7
1.3.2 LC elastomers	8
1.3.3 LC gels	8
1.3.4 Block copolymer self-assembly for LC elastomers and gels	10
1.4 The molecular theory of nematic rubber elasticity	10
1.4.1 Soft elasticity	12
1.4.2 Semi-softness	12
1.5 Objectives	13
Bibliography	15

2 Liquid Crystalline Gels by Self-Assembly of Triblock Copolymers	19
2.1 Abstract	19
2.2 Introduction	20
2.3 Experimental	21
2.3.1 Gel permeation chromatography (GPC)	21
2.3.2 Nuclear magnetic resonance	22
2.3.3 Liquid crystal phase identification	22
2.3.4 Conoscopic imaging	22
2.3.5 Rheometry	22
2.3.6 Electro-optic measurements	23
2.3.7 Synthesis of SGLCPs: homopolymers and triblocks	23
2.3.8 Mixing of nematic gels	26
2.4 Results	26
2.4.1 Polymer characteristics	26
2.4.2 Monodomain alignment of LC gels	28
2.4.3 Dynamic mechanical analysis	29
2.4.4 Reversible electro-optic response	30
2.5 Discussion	33
Bibliography	36
3 Buckling Instability in Physical LC Gels	40
3.1 Abstract	40
3.2 Introduction	41
3.3 Experimental	42
3.4 Results	43
3.4.1 Details of the stripe texture	43
3.4.2 Mathematical model	44

3.5 Discussion	49
Bibliography	53
4 Director Dynamics in Liquid Crystal Physical Gels	56
4.1 Abstract	56
4.2 Introduction	57
4.3 Experimental	58
4.4 Results	62
4.5 Discussion	71
4.6 Conclusions	74
Bibliography	75
5 Micellar Structure of Block Copolymers in an LC Solvent	79
5.1 Abstract	79
5.2 Introduction	80
5.3 Experimental	81
5.3.1 Preparation of nematic gels	81
5.3.2 LC phase identification	81
5.3.3 Rheometry	82
5.3.4 SANS	82
5.4 Results	82
5.4.1 Polymer characteristics and phase behavior	82
5.4.2 Neutron scattering	84
5.4.3 Rheometry	88
5.5 Discussion	91
5.6 SANS of diblock and triblock gels	94
5.7 Rheometry of diblock and triblock mixtures	98

Bibliography	114
6 Covalent Liquid Crystal Networks via “Click” Chemistry	117
6.1 Introduction	117
6.2 Experimental	118
6.2.1 Synthesis of 5,6-disubstituted cyclooctene-based mesogen 2	119
6.2.2 Polymerization via ROMP and end-group functionalization	120
6.2.3 Crosslinking of telechelic polymers by “click” chemistry	121
6.3 Results	121
6.3.1 Synthesis of covalent LC network	121
6.3.2 Temperature-dependent swelling of covalent LC networks in liquid crystal . .	123
6.3.3 Electro-optical properties of LC gels	123
6.4 Discussion	127
6.5 Conclusions	128
Bibliography	129
7 Outlook	135
Bibliography	136
A Transient Electro-Optic Properties of Liquid Crystal Gels	137

List of Figures

1.1	Image and schematic of the nematic mesophase	4
1.2	Chemical structure of 5CB	4
1.3	Elastic distortions of the nematic phase	6
1.4	Schematic of different types of liquid crystal polymers	8
1.5	Schematic for method of preparing an LCE	9
1.6	Schematic of a soft elastic distortion in a nematic elastomer	12
2.1	Chemical structure and NMR of ABASiBB	24
2.2	Synthesis of LC side-group mesogen	24
2.3	Preparation of SiBB by attachment of siloxane spacer to LC side-group mesogen . . .	25
2.4	Coupling reaction to attach LC side-group mesogen to ABA polymer	25
2.5	Schematic of LC triblock gel	27
2.6	Conoscopic images of gel during shear	29
2.7	Triblock gel rheology	31
2.8	Voltage sweep of LC triblock gel	32
2.9	Electric field threshold for LC triblock gels	33
2.10	Dynamic electro-optical behavior of LC triblock gels	34
3.1	Chemical structure of 5CB and LC triblock ABASiBB	42
3.2	Stripes in a 5 wt % LC gel	44
3.3	Data and model fit for the buckling instability	45
3.4	Schematic of buckling instability	46

3.5	Model predictions for the threshold free energy of the buckling instability	51
4.1	Chemical structure of LC block copolymers	59
4.2	Schematic of light scattering setup	61
4.3	$g_2(t)$ for 5CB, homopolymer, and triblock gels	63
4.4	Average relaxation rates for homopolymer solutions	63
4.5	$g_2(t)$ for 5 wt % end-on homopolymer and gel	65
4.6	$g_2(t)$ for 5 wt % side-on homopolymer and gel	66
4.7	$g_2(t)$ for 5 wt % end-on and side-on gels in the P orientation	66
4.8	$g_2(t)$ for 5, 10, 15, and 20 wt % end-on gels	67
4.9	Temperature dependence of $g_2(t)$ for 5 wt % end-on homopolymer and gel	68
4.10	Temperature dependence of $g_2(t)$ for 5 wt % side-on homopolymer and gel	69
4.11	$g_2(t)$ for 5 wt % side-on homopolymer and gel at 31.5 °C	70
4.12	Schematic of slow and fast network relaxation processes	72
4.13	Schematic of network deformations	73
5.1	Neutron scattering pattern for a monodomain solution of SGLCP homopolymer in D5CB	85
5.2	Neutron scattering pattern for shear-aligned 1320(60)ABA gel	85
5.3	Neutron scattering patterns at 25 °C	86
5.4	Neutron scattering trace for 590(40)AB gel	94
5.5	Neutron scattering trace for 530(60)AB gel	95
5.6	Neutron scattering trace for 890(70)AB gel	95
5.7	Neutron scattering trace for 620(80)AB gel	96
5.8	Neutron scattering trace for 450(120)AB gel	96
5.9	Neutron scattering trace for 840(190)AB gel	97
5.10	Neutron scattering trace for 1320(60)ABA gel	97
5.11	Storage and loss moduli of 5 wt % 590(40)AB gel	98
5.12	Temperature sweep of 5 wt % 590(40)AB gel	98

5.13	Storage and loss moduli of 5 wt % 530(60)AB gel	99
5.14	Temperature sweep of 5 wt % 530(60)AB gel	99
5.15	Storage and loss moduli of 5 wt % 890(70) AB gel	100
5.16	Temperature sweep of 5 wt % 890(70) AB gel	100
5.17	Storage and loss moduli of 5 wt % 620(80)AB gel	101
5.18	Temperature sweep of 5 wt % 620(80) AB gel	101
5.19	Storage and loss moduli of 5 wt % 450(120)AB gel	102
5.20	Temperature sweep of 5 wt % 450(120)AB gel	102
5.21	Storage and loss moduli of 5 wt % 840(190) AB gel	103
5.22	Temperature sweep of 5 wt % 840(190) AB gel	103
5.23	Storage and loss moduli of 5 wt % 1320(60)ABA gel	104
5.24	Temperature sweep of 5 wt % 1320(60)ABA gel	104
5.25	Storage and loss moduli of 5 wt % 800(20)ABA gel	105
5.26	Temperature sweep of 5 wt % 800(20)ABA gel	105
5.27	Storage and loss moduli of 10 wt % 590(40)AB gel	106
5.28	Temperature sweep of 10 wt % 590(40)AB gel	106
5.29	Storage and loss moduli of 10 wt % 530(60)AB gel	107
5.30	Temperature sweep of 10 wt % 530(60)AB gel	107
5.31	Storage and loss moduli of 10 wt % 890(70) AB gel	108
5.32	Temperature sweep of 10 wt % 890(70) AB gel	108
5.33	Storage and loss moduli of 10 wt % 620(80)AB gel	109
5.34	Temperature sweep of 10 wt % 620(80) AB gel	109
5.35	Storage and loss moduli of 10 wt % 450(120)AB gel	110
5.36	Temperature sweep of 10 wt % 450(120)AB gel	110
5.37	Storage and loss moduli of 10 wt % 840(190) AB gel	111
5.38	Temperature sweep of 10 wt % 840(190) AB gel	111
5.39	Storage and loss moduli of 10 wt % 1320(60)ABA gel	112

5.40	Temperature sweep of 10 wt % 1320(60)ABA gel	112
5.41	Storage and loss moduli of 10 wt % 800(20)ABA gel	113
5.42	Temperature sweep of 10 wt % 800(20)ABA gel	113
6.1	Synthesis of substituted octene monomer	119
6.2	Reaction scheme for ROMP of substituted cyclooctene	122
6.3	Crosslinking of telechelic LC polymers by “click” chemistry	123
6.4	Optical micrograph of covalent LC gels	124
6.5	Temperature dependent swelling of covalent LC networks	124
6.6	Optical micrograph of covalent LC gels under an electric field	125
6.7	Dynamic electro-optical behavior of covalent LC gels	126
A.1	Electro-optical behavior of 5 wt % gel	138