

Contents

1	Introduction and Basic Theory	1
1.1	Nonlinear Optics	1
1.1.1	Introduction to Nonlinear Optical Phenomena	1
1.1.2	Microscopic Origin of the Nonlinear Susceptibility	2
1.1.3	Nonlinear Polarization	4
1.1.4	Second Harmonic Generation	5
1.1.5	Relationship Between Microscopic and Macroscopic Nonlinearities	16
1.2	Materials for Nonlinear Optics	18
1.2.1	Introduction	18
1.2.2	Organic Materials for SHG. Donor- π -Acceptor Chromophores	18
1.2.3	Liquid-Crystalline Polymers with Azobenzene	22
	References	30
2	Experimental Methods	35
2.1	Sample Preparation	35
2.1.1	Synthesis and Basic Characterization of the Materials	35
2.1.2	Film Preparation and Thickness Measurement	36
2.2	Optical Measurements	37
2.2.1	Optical Absorption Spectroscopy (UV-vis-NIR)	37
2.2.2	Refractive Index Measurement	39
2.3	Nonlinear Response Characterization	42
2.3.1	Electric Field Induced Second Harmonic Generation	42
2.3.2	Thin Films: SHG in Thin Films Oriented by Corona Discharge	50
2.4	Nonlinear Gratings	62
2.4.1	Recording of Diffraction Gratings	62
2.4.2	Recording of Nonlinear Gratings	64
	References	65
3	Nonlinear Optical Molecular Response	67
3.1	Study of NLO Chromophores with Azo Groups	68

3.2	Characterization of Highly Efficient Chromophores	71
3.2.1	Merocyanines with Dicyanothiazole as a Proaromatic Acceptor	73
3.2.2	Merocyanines with 1,3-Dithiol-2-ylidene as a Proaromatic Donor	75
3.2.3	Merocyanines with Pyran Derivatives as Proaromatic Donors	78
3.2.4	Merocyanines with Isophorone, Pyran and Dihydropyran Spacers	83
3.2.5	Merocyanines with Thiophene Spacers: Influence of Chain Lengthening on Both Sides of the Thiophene	85
3.3	Conclusions	88
	References	89
4	Piperazine Azopolymer Thin Films	91
4.1	Homopolymers	91
4.1.1	Optical Study	92
4.1.2	Nonlinear Response	108
4.2	Copolymers	125
4.2.1	Optical Study	125
4.2.2	Nonlinear Response	128
4.3	Conclusions	131
	References	133
5	Films of Doped Low Polar Azopolymers	135
5.1	Description of the Guest–Host (Chromophore–Polymeric Matrix) Systems	136
5.2	Optical Study	138
5.2.1	Azopolymer Films	138
5.2.2	Azopolymer/Chromophore Films	141
5.3	Nonlinear Optical Response	142
5.3.1	Thermal Poling	142
5.3.2	Photoassisted Poling	145
5.4	Conclusions	150
	References	151
6	Nonlinear Optical Gratings	153
6.1	Recording Procedures	154
6.2	Results	155
6.2.1	Recording of Gratings	156
6.2.2	Recording of Nonlinear Gratings	157
6.3	Conclusions	160
	References	160
7	General Conclusions	161

**Appendix A: Expression for the Second Harmonic Intensity
at the Exit of the Nonlinear Planar Surface. 165**

**Appendix B: Expression for the Second Harmonic Intensity
at the Exit of the EFISH Cell. 179**

Appendix C: Order Parameters 183

Appendix D: NLO Parameter Units 191

Curriculum Vitae 195

Photoinduced Modifications of the Nonlinear Optical
Response in Liquid Crystalline Azopolymers

Alicante, R.

2013, XX, 200 p., Hardcover

ISBN: 978-3-642-31755-2