

TABLE OF CONTENTS

Abstract	ii
Acknowledgements	iv
Table of contents	v
List of tables	x
List of figures	xiii
1. Introduction	1
2. Literature review on polymer solutions, polymerizations and polymer processing at high pressures in dense fluids	15
2.1 Polymer solutions in binary fluid mixtures	16
2.2 Polymerization in high-pressure dense fluids	20
2.2.1 Chain-growth polymerization in supercritical fluids	21
2.1.2 Step-growth polymerization in supercritical fluids	29
2.2 Polymer processing in high-pressure dense fluids	30
2.2.1 Polymer particle formation	31
2.2.2 Polymer impregnation	32
2.2.3 Polymer blending and polymer composite preparation	34
2.2.4 Microporous polymer formation	35
3. Literature review on polymer solution viscosity at high pressures ...	39
3.1 High-pressure viscometers	39
3.1.1 Capillary tube viscometer	39
3.1.2 Falling-body/ rolling-body viscometer	40
3.1.3 Rotational viscometer	42
3.1.4 Magnetoviscometer	43
3.1.5 Magnetically levitated sphere rheometer	44
3.1.6 Extrusion slit die rheometer	44
3.1.7 Sliding plate viscometer	45
3.2 Polymer solution viscosity at high pressures	45

3.3 Viscosity of polymer melts containing SCFs at high pressure	49
4. Experimental methodology	55
4.1 View cell system	55
4.1.1 Solvent delivery system	56
4.1.2 High-pressure variable volume view cell	56
4.1.3 Data acquisition units	57
4.1.4 Operational procedures	57
4.1.5 Accuracy and precision of the measurements	60
4.2 Viscometer system	60
4.2.1 Measurement principle and apparatus	60
4.2.2 Solvent delivery system	61
4.2.3 Viscometer	61
4.2.4 Control and data acquisition units	62
4.2.5 Data processing software package	62
4.2.6 Operational procedures	63
4.2.7 Accuracy and precision of measurement	67
4.3 Other characterizations	67
5. Acetone + carbon Dioxide mixtures at high pressures	80
5.1 Experimental procedures	82
5.2 Results and discussion	83
5.2.1 Density	83
5.2.2 Viscosity	84
5.2.3 Flow activation volume and flow activation energy	85
5.2.4 Viscosity – density correlation and close-packed volume	85
5.2.5 Excess volume	86
5.2.6 Correlations for mixture viscosity	88
5.2.7 Excess viscosity	89
5.3 Further discussion. Recent advances on free volume theory for viscosity	94
5.4 Summary and conclusions	98
6. Viscosity and density of PMMA in acetone + carbon dioxide mixtures	127
6.1 Experimental	131

6.1.1 Materials	131
6.1.2 Viscometer and operational procedure	131
6.2 Results and discussion	133
6.2.1 Acetone	133
6.2.2 Polymer solutions	134
6.2.3. Effect of pressure on viscosity	135
6.2.4 Effect of temperature on viscosity	136
6.2.5. Correlation of viscosity with density	137
6.2.6 Effect of concentration on viscosity	138
6.3 Summary and conclusion	139
7. Viscosity and density of poly (ϵ-caprolactone) in acetone + carbon dioxide mixtures	170
7.1 Experimental	172
7.1.1 Materials	172
7.1.2 Apparatus and operational procedure	173
7.2 Results and Discussion	174
7.2.1 PCL + Acetone	174
7.2.2 PCL + Acetone + CO ₂	174
7.2.3 Miscibility and the effect of phase separation	175
7.2.4 Correlation of viscosity with pressure, temperature and density ...	176
7.2.5 Comparison of PCL + Acetone + CO ₂ system with PMMA + Acetone + CO ₂ system	178
7.3 Summary and conclusions	179
8. Acetone + carbon dioxide as tunable mixture solvents for poly (ϵ-caprolactone)	199
8.1 Experimental	201
8.1.1 Materials	201
8.1.2 Determination of demixing pressures and densities	202
8.2 Results and discussion	202
8.2.1 Phase behavior	202
8.2.2 Volumetric properties. Density	205

8.2.3 Isothermal compressibility and isobaric expansivity. Polymer solutions <i>versus</i> solvent mixtures	207
8.3 Summary and conclusions	213
9. High-pressure solution blending of poly (ϵ-caprolactone) with poly (methyl methacrylate) in acetone + carbon dioxide	247
9.1 Introduction	247
9.2 Experimental	251
9.2.1 Materials	251
9.2.2 Determination of liquid-liquid phase boundary	251
9.2.3 Preparation of PCL/PMMA blends	251
9.3. Results and discussion	252
9.3.1 Liquid-liquid phase boundary	252
9.3.2 Polymer blend characterizations	254
9.4 Summary and conclusions	257
10. Density and viscosity as real-time probes for the progress of high-pressure polymerization. Polymerization of methyl methacrylate in acetone ...	286
10.1 Introduction	286
10.2 Experimental	289
10.3 Polymerization conditions and product recovery	290
10.4 Variations of density and viscosity with time during polymerization ...	291
10.5 Comparisons with density and viscosity of reference polymer solutions	294
10.6 Assessment of the rate of change of monomer (MMA) concentration during polymerization from viscosity and density measurements	295
10.7 Summary and conclusions	300
11. Homopolymerization and copolymerizations of 2-methylene-1,3-dioxepane (MDO) in carbon dioxide at high pressures	326
11.1 Experimental	331
11.2 Results and Discussion	332
11.2.1 Homopolymerization of 2-methylene-1,3-dioxepane (MDO).....	332
11.2.2 Copolymerization of MDO	335
11.3 Summary and conclusions	340

12. Major accomplishments, conclusions and recommendations	...	362
References	366
Vita	393