CONTENTS

I. INTRODUCTION AND OBJECTIVES .................................................. 1

II. POLYMERIC REAGENT CONCEPT - AN OVERVIEW ............................. 8

A. POLYMER-SUPPORTED REACTIONS: CONCEPTS AND CHARACTERISTICS ... 9

1. Structure and Properties of Reactive Polymers ......................... 11
   (a) Nature of the Polymer Support .................................. 12
   (b) Solvation behaviour of Functional Polymers ................. 18
   (c) Characterization of Functional Polymers .................. 22

2. Advantages and Limitations of Polymer-Supported Strategy .......... 25

B. CHARACTERISTIC EFFECTS OF THE POLYMER MATRIX ON SOLID-PHASE REACTIONS ......................................................... 28

1. Microenvironmental Effects ............................................... 29

2. Immobilization and Mutual Inaccessibility Effect ................. 33

3. Diffusional and Molecular Sieving Effects .......................... 38

4. Kinetics and Mechanism of Polymer-Aided Reactions ............. 41

5. Effect of Spacer .................................................................. 47

6. Effect of Crosslink Density .............................................. 51

C. POLYMER-SUPPORTED OXIDISING REAGENTS ............................... 55
1. Oxidation-Reduction Polymers
2. Peracids, Peroxides and Periodate-Type Reagents
3. Halogen-Containing Reagents
4. Reagents Based on Ion Exchange-Type Resins
5. Polymer-Bound Oxidising Metal Compounds
6. Miscellaneous Oxidising Reagents

III. DESIGN AND APPLICATIONS OF POLYMER-SUPPORTED t-BUTYL HYPOHALITES
A. RESULTS AND DISCUSSION
1. Preparation and Characterization of Polymer-Supported t-Hypohalites
2. Role of Solvents in the Extent of Functionalisation in the Polymer-Analogous Reactions
3. Physical Nature and Stability of the Polymer-Supported Hypohalites
4. Comparison of the Polymer-Analogous Reactions with the Low-Molecular Weight Reactions
5. Synthetic Reactions of Polymer-Supported Hypohalites
   (a) Oxidation of Alcohols
      (i) Halogenation vs Oxidation
      (ii) Comparison with Low-Molecular Weight Oxidants
      (iii) Monitoring the Course of the Reaction
   (b) Halogenations with the Polymeric Hypohalite Reagents
      (i) Comparison with Other Polymeric Halogenating Reagents
      (ii) Reactions with Polymeric Hypoiodite Reagent
B. EXPERIMENTAL

1. Preparation of 2-Oxopropyl Resin 106
2. Preparation of \textit{t}-Alcohol Resin 108
3. Preparation of \textit{t}-Butyl Hypochlorite Resin 108
4. Estimation of Hypochlorite Function 109
5. Preparation of \textit{t}-Butyl Hypobromite Resin 110
6. Preparation of \textit{t}-Butyl Hypoiodite Resin 110
7. Estimation of the Hypoiodite Function 110
8. Oxidation of Alcohols with the Hypohalite Resins 111
9. \textit{\alpha}–Halogenation of Ketones and N-Halogenation of Amides 111
10. Decarboxylation Reactions using the Hypoiodite Resin 111
11. Recycling of the Spent Hypohalite Resins 112

IV. SPACER-MODIFIED POLYMER-SUPPORTED HYPOHALITES: POLYMER-ANALOGOUS SYNTHETIC APPROACHES 113

A. RESULTS AND DISCUSSION 115

1. General Synthetic Approach to Spacer-Modified Polymer-Supported Hypohalite Resins 115
2. Synthesis and Characterization of Spacer-Modified Hypochlorite Reagents 116
3. Analytical Procedures for the Different Functional Groups 120
4. Synthesis of Hypohalite Resins having no Spacer Group 125
5. Preparation of the Low-Molecular Weight Analogue 128
6. Effect of Spacer  

7. Effect of Reaction Conditions on the Extent of Functional Group Conversion: Effect of Solvents  

B. EXPERIMENTAL  

1. Preparation of Spacer-Modified Hypochlorite Reagents  

2. Analytical Procedures  

3. Preparation of Hypohalite-Resins with the Hypohalite Function Attached Directly to the Carbon Nearest to the Polystyrene Matrix  

4. Preparation of Dimethylbenzyl Hypochlorite  

V. STRUCTURAL CHARACTERISTICS OF THE POLYMER MATRIX AND REACTIVITY OF THE ATTACHED HYPOHALITE FUNCTION  

A. RESULTS AND DISCUSSION  

1. Effect of Crosslink Density  
   (a) Functionalisation Reactions for the Preparation of the Hypochlorite Reagent without Spacer  
   (b) Functionalisation Reactions for the Preparation of the Hypochlorite Reagent with One Spacer  
   (c) Functionalisation Reactions for the Preparation of the Hypochlorite Reagent with Three, Four and Five Spacers  
   (d) Effect of Crosslink Density on Oxidation Reactions with the Hypochlorite Reagents  
   (e) Comparison with Other Systems  
   (f) Crosslink Density, Mechanical Stability and Reaction Workup
2. Effect of Spacer Grouping

B. EXPERIMENTAL

1. Study of the Effect of Crosslink Density
2. Study of the Effect of Spacer Grouping

VI. REACTION PARAMETERS IN HALOGENATION AND OXIDATIONS WITH POLYMER-SUPPORTED HYPOCHLORITES

A. RESULTS AND DISCUSSION

1. Influence of Reaction Temperature
   (a) Oxidation vs Halogenation
   (b) Extent of Reaction and Temperature
   (c) Halogenation Reactions: Effect of Temperature

2. Nature of the Solvent
   (a) Hydrophilic/Hydrophobic Nature
   (b) Solvation of Reactive Function through Spacer Mediation
   (c) Crosslinking, Polarity, and Solvent Effect

3. Concentration of the Reagent Function
4. Duration of the Reaction

B. EXPERIMENTAL

1. Investigation of the Effect of Solvents on Reactivity of the Hypohalite Reagents
2. Study of the Dependence of the Reaction Rate on Temperature of the Reaction 199

3. Study of the Dependence of the Reaction Rate on the Concentration of the Reagent 200

4. Study of the Effect of Duration of the Reaction in the Extent of Synthetic Reactions 201

VII. SUMMARY AND OUTLOOK 203

REFERENCES 213