Microwave technology is emerging as an alternative energy source powerful enough to accomplish chemical transformation in minutes, instead of hours or even days. For this reason, microwave irradiation is presently seeing an exponential increase in acceptance as a technique for enhancing chemical synthesis. A growing number of investigators are adopting microwave-assisted synthesis as a means of increase their productivity. There is no doubt that microwaves can be used to great effect in organic synthesis; the ‘in situ’ generation of heat is very efficient and can be used to significantly reduce reaction times of numerous synthetically useful organic transformations. Thus microwave assisted organic synthesis has advantages over conventional technology: it is more energy efficient and it can lead to improved isolated yields of products. The obvious application of this approach to organic synthesis should provide a major impetus for further development in this area; a particularly important feature will be the continued development of microwave assisted solid phase reactions. Avoiding organic solvents during the reactions in organic synthesis leads to a clean, efficient, and economical technology (green chemistry). There is an increasing interest in the use of environmentally benign reagents and procedures. The absence of solvents coupled with the high yields and short reaction times often associated with reactions of this type make these procedures very attractive for synthesis. In the present work, we describe the
advantages of dry reaction techniques coupled with microwave activation and their applications to organic synthesis using polyvinylpyrrolidone-bromine complex. These solvent free microwave assisted reaction provide an opportunity to work with open vessels, thus avoiding the risk of high-pressure development and increasing the potential of such reactions to upscale. The theme of the work presented in this thesis is concerned with the design and development of a polymeric reagent and illustration of their application as efficient oxidizing and halogenating agent under microwave conditions. A thermal comparison for each reaction was also carried out by performing reactions under conventional heating conditions. Keeping the aim of introducing a polymer support, the crosslinked polymers of N-vinylpyrrolidone was synthesized by varying the amount of the crosslinker used between 3 to 20 mole percentages in the feed polymerization. The crosslinker tried in this present work are DVB, NN MBA and EGDMA. The criteria for selecting these crosslinking agents are the difference in their relative rigidity/flexibility and polarity. These polymers were functionalized with bromine in order to investigate their efficiency in oxidation and halogenation reactions.

The crosslinked polymers were synthesized by free radical suspension polymerisation in a saturated aqueous solution of Na$_2$SO$_4$ containing a little NaH$_2$PO$_4$ maintained at 80 °C. To avoid any chance of decomposition of NVP into acetaldehyde and pyrrolidone even in a slightly acidic medium, the polymerisation was carried out in a slightly basic medium using NaH$_2$PO$_4$. The polymers synthesized were purified from linear polymers formed during polymerisation by washing with hot water and
Soxhlet extraction with methanol and acetone. The yield of the crosslinked polymer was found to increase as the amount of the crosslinker, DVB, NNMB and EGDMA increases from 3 to 20 mole percentage. As the amount of the crosslinker increases, the degree of crosslinking increases and the extent of linear polymerisation decreases and hence the yield of the crosslinked product increases with increasing the amount of the crosslinker from 3 to 20 mole percentage. These crosslinked polymers on treatment with bromine in carbon tetrachloride at room temperature afforded the dark orange colored beads of polyvinylpyrrolidone-bromine complexes. The polyvinylpyrrolidone-bromine complexes were stable under ordinary laboratory conditions and could be stored for a long period without much loss in capacity. The hygroscopic nature of the polymer was reduced on complexing with bromine. The bromine content of polyvinylpyrrolidone-bromine complexes prepared from different crosslinking agents were found to decrease with increase in crosslink density. As the degree of crosslinking increases the extent of swelling decreases and hence the diffusion of low molecular weight molecules into the interior of the polymer matrix becomes reduced and so the capacity decreases with increasing crosslinking density.

When the stability of polyvinylpyrrolidone-bromine complexes with different crosslinking agents and crosslink densities towards microwave irradiation were compared, it was observed that, in all cases the bromine content of the reagent decreased with increase in crosslink density. The release of bromine is more vigorous in the case NNMBA-crosslinked polyvinylpyrrolidone-bromine complex under microwave irradiation when compared to DVB- and EGDMA- crosslinked polyvinylpyrrolidone-bromine
complexes. It may be due to the increased bromine content coupled with high microwave activation of NNMBA-crosslinked polyvinylpyrrolidone-bromine complexes. Moreover, out of the different mole percentage of crosslinker used, 3% crosslinked reagent showed maximum stability towards microwave irradiation.

The effect of microwave power level on the efficiency of synthetic reactions were investigated using 3% crosslinked polyvinylpyrrolidone-bromine complexes prepared from different crosslinking agents like DVB, NNMBA and EGDMA. The oxidation of benzoin to benzil was taken as the model reaction. The polymeric reagent and the adsorbed low molecular weight substrate molecule was subjected to microwave irradiation at different power levels ranging from 80 to 800 W for 10 minutes. The results showed that oxidizing efficiency of the reagents prepared from DVB, NNMBA and EGDMA crosslinkers, increases upto a microwave power of 320 W and then decreases. The decrease in the percentage of product at a microwave power level above 320 W may be due to the sudden release of bromine from the polymeric reagent due to the high temperature attained at this power level. Therefore microwave power level of 320 W was found to be the most suitable condition for the reactions under microwave irradiation.

The polyvinylpyrrolidone-bromine complexes was found to be effective for the oxidation of alcohols to the corresponding carbonyl compounds, dihalogenation of olefinic compounds, α-halogenation of ketones, bromination of activated aromatic compounds and oxidative coupling of thiols in high yields. All the synthetic reactions using polyvinylpyrrolidone-bromine complexes (3%) were carried out under
microwave condition and also under conventional thermal heating condition. In microwave condition, the reactions take place in the solid phase, and the products are then extracted from the reaction mixture using an appropriate solvent, as these reactions were carried out in a solvent free condition. In conventional thermal heating the reactions were carried out by heating of a solution of low molecular weight substrate in cyclohexane with the polymeric reagent at refluxing temperature for 5h. The results revealed that reactions conducted under microwave condition dramatically enhances the reaction rates and achieves high conversion within minutes compared to reactions conducted under conventional thermal conditions in the presence of cyclohexane. This might be because microwaves couples directly with the molecules of the entire reaction mixture, leading to a rapid rise in temperature. However conventional heating is a slow and inefficient method of transforming heat energy into the reacting system because the heat driven into the substance first passes through the wall of the vessel before reaching the solvent and reactants. The greatest saving, therefore, is the reduced reaction time and solvent volumes for the microwave assisted processes. It was found that DVB-crosslinked polyvinylpyrrolidone-bromine complex is more reactive when compared to NNMA- or EGDMA-crosslinked polyvinylpyrrolidone-bromine complexes. This result cannot be explained by the effect of rapid heating alone. The high reactivity of DVB-crosslinked polyvinylpyrrolidone-bromine complex may be due to the good swelling of the reagent during impregnation with a solution of substrate in dichloromethane, which in turn depends on the hydrophobic-hydrophilic balance attained by the polymeric reagent. This swelling nature coupled with
the effect of microwave heating enhances the reactivity of DVB-crosslinked polyvinylpyrrolidone-bromine complex.

The reactivity of polymeric reagents depends on many factors like nature of the polymer support, extent of crosslinking and molecular character. They have significant influence on the kinetics and extent of functional group conversions in polymer aided reactions. The nature of the polymer support can be varied by changing the crosslinking agents. The topographical nature of the polymeric backbone varies widely with the extent of crosslinking. The binding of an active species to a polymer chain results in a new reagent with different structure, reactivity and selectivity. Knowledge of the dependence of the topographical nature of the polymer backbone on the reactivity of the attached functional groups requires a study of the effect of the crosslink density in solid phase polymer supported reactions. Thus bromo polymers with varying mole percentage of crosslinker (3-20%) were prepared from crosslinking agents like DVB, NN MBA and EGDMA and their oxidation efficiencies were compared under microwave and conventional heating conditions. Oxidation of benzoin to benzil was taken as the model reaction for this comparative study. The results revealed that, under microwave heating, 6% crosslinked polymeric reagent showed higher oxidizing efficiency in all the cases. As the mole percentage of the crosslinker increases the extent of swelling during impregnation decreases and hence the rate of diffusion of substrate molecule into and out of the crosslinked polymeric reagent decreases as the crosslink density increases.

The effect of molar concentration of the reagent on the reactivity of polyvinylpyrrolidone-bromine complexes were studied by conducting the
oxidation of benzoin to benzil at different reagent-to-substrate ratios under microwave heating. An excess amount of polymeric reagent can increase the rate of a reaction, since the rate of a reaction is directly proportional to the concentration of the reactants. In all cases it was observed that a high molar excess of the polymeric reagent resulted in enhanced rate of reaction.

In order to study the effect of solvents on the extent of oxidation reactions of crosslinked polyvinylpyrrolidone-bromine complexes under conventional heating conditions, solvents of varying polarity such as carbon tetrachloride, cyclohexane, tetrahydrofuran, dichloromethane and ethyl acetate were used. The polarity and boiling points of the solvents are the factors which decide the extent of oxidation. During the reaction using a crosslinked polymeric reagent, the accessibility of the reactive functions anchored on the crosslinked matrix depends on the extent of swelling of the matrix in which the reaction is carried out. As the degree of swelling of the matrix increases the rate of diffusion of substrate molecules into the interior of the matrix, where the active functions are buried, also increases. At elevated temperature easy penetration of the solvent and extensive swelling of the polymer matrices takes place. Hence rate of the reaction increases with swelling and rise of temperature. For a hydrophobic DVB-crosslinked polymer, the non-polar cyclohexane was found to be the most suitable solvent. For hydrophilic NNMA- and EGDMA-crosslinked polymeric reagent, the reactions were more efficient in polar solvents like ethyl acetate and tetrahydrofuran.

The effect of crosslink density on the extent of oxidation reaction under conventional heating condition was carried out by refluxing polymeric
reagent with benzoin in cyclohexane for 5h. Here the rate of the reaction depends on the extent of swelling of the polymer matrix. The reactive functions attached on the polymer support are more accessible to the substrate molecules present in the solvent, if the polymer matrix is in a swelled state. The swelling of the polymer matrix in a solvent depends on the degree of crosslinking as well as the nature of the solvent. Thus the mole percentage of the crosslinker present in the crosslinked polymeric reagent plays an important role while performing synthetic reactions with it. When divinylbenzene was used as the crosslinker, it was found that 6% crosslinked polyvinylpyrrolidone bromine complex was most efficient in terms of the yield of the product. The increased reactivity of the 6% crosslinked polyvinylpyrrolidone bromine complex is attributable to the hydrophilic-hydrophobic balance of the polymer backbone which makes it compatible with the low molecular weight substrate. As the percentage of the rigid and hydrophobic divinylbenzene crosslinker increases above six, the accessibility of the attached bromo function to the substrate molecules present in the solvent becomes difficult. The access of reactive groups on highly crosslinked networks is considerably diminished as they are flanked by a large frequency of crosslinking leading to decreased reactivity. In the case of NN MBA-and EGDMA-crosslinked polymers, the reactivity decreases gradually with increase in crosslink density from 3% to 20%. The decrease in reactivity of NN MBA-and EGDMA-crosslinked polymers as compared to DVB crosslinked polymers may be due to the decreased swelling of these polymeric reagents in cyclohexane which is a non polar solvent. For highly crosslinked polymers the penetration of low molecular weight substrate in to
the polymer matrix becomes more difficult and hence the reactivity decreases.

In general, the polyvinylpyrrolidone-bromine complexes were found to be suitable for various synthetic conversions under microwave heating. The use of microwave irradiation drastically reduces the reaction time when compared to conventional methods of heating. Moreover the polymeric reagent has the advantage of increased shelf-life, operational simplicity, possibility of regeneration and reuse.

The entry of microwave oven in the chemistry laboratory has made it possible to carry out many transformations with greater efficiency and ease of workup. We believe that in the future many more microwave assisted reactions will be developed which will simplify time consuming conventional procedures. It is also hopped that appropriate technology will develop so that some of these fascinating microwave assisted transformation could be done on industrial scales thereby increasing the overall efficiency of the processes and reducing pollution of the environment through the use of solvent free reaction protocols.