

## CHAPTER IV

## CONCLUSION

Four copolymer systems, MMA-PCPA copolymer, MMA-2,4,5-TCPA copolymer, MMA-2,4,6-TCPA copolymer were successfully synthesized by two steps of reactions. Firstly, the fungicidal monomers, i.e., pentachlorophenyl acrylate (PCPA), 2,4,5-trichlorophenyl acrylate (2,4,5-TCPA), 2,4,6-trichlorophenyl acrylate (2,4,6-TCPA) and 4-chloro-3-methylphenyl acrylate (4-Cl-3-MPA) were obtained in high percentage yield by the reaction between the corresponding chlorophenolic fungicides and acryloyl chloride. Then copolymerization of these fungicidal monomers with methyl methacrylate were carried out in benzene at 50°C using  $\alpha, \alpha'$ -azobisisobutyronitrile (AIBN) as the initiator. Various monomer feeding ratios were used.

In order to analyze the number of the fungicidal monomer units in the copolymer, the corresponding homopolymers were prepared by solution polymerizations. During purification, all the polymers were subjected to thin layer chromatography to monitor any fungicidal monomer which might be trapped in the polymer. The formation of all copolymers and homopolymers are confirmed by comparison of their IR spectra with those of corresponding fungicidal monomers. The absorption bands at 1640  $\text{cm}^{-1}$  (C=C), 1350 and 900  $\text{cm}^{-1}$  ( $\text{CH}_2$  of olefinic end group) disappears. Simultaneously, a characteristic band of the  $\text{CH}_2$  group in the polymer chain appears at 750  $\text{cm}^{-1}$ .

In order to determine the monomer reactivity ratios by the Fineman and Ross method, the composition of low conversion copolymer

must be considered. In this research work, each copolymer composition was determined by UV-Visible spectroscopic technic. It was compared to the absorbance of the corresponding homopolymer, except the MMA-PCPA copolymer which PCPA monomer was used instead of poly (PCPA). The monomer feed composition at the start and end of copolymerization experiments were also determined by using quantitative gas chromatographic technic, to evaluate the monomer reactivity ratios using an integrated form of the copolymer equation, the Mayo and Lewis equation for high conversion.

The monomer reactivity ratios determined by both methods are listed in Table 4.1.

**Table 4.1** Monomer reactivity ratios of methyl methacrylate ( $M_1$ ) and the chlorophenyl acrylate ( $M_2$ )

| $M_2$      | Fineman-Ross method |                 | Mayo-Lewis method |       |
|------------|---------------------|-----------------|-------------------|-------|
|            | $r_1$               | $r_2$           | $r_1$             | $r_2$ |
| PCPA       | 1.07 $\pm$ 0.04     | 0.08 $\pm$ 0.11 | 1.00              | 0.08  |
| 2,4,5-TCPA | 0.84 $\pm$ 0.01     | 0.36 $\pm$ 0.05 | 0.92              | 0.42  |
| 2,4,6-TCPA | 0.58 $\pm$ 0.01     | 0.20 $\pm$ 0.05 | 0.63              | 0.12  |
| 4-Cl-3-MPA | 0.67 $\pm$ 0.02     | 0.33 $\pm$ 0.02 | 0.64              | 0.37  |

The reactivity ratios, as determined by both methods, are in good agreement and indicate similar tendencies of these monomers toward alternation and random.