CONCLUTIONS

This research project has been concerned, in the first part, with the preparation of methyl methacrylate-styrene (MMA-ST) copolymers of varying composition via free radical copolymerization using benzoyl peroxide as the initiator. Subsequent copolymerization studies of these materials have been able to relate copolymer composition, as determined spectroscopically, with that predicted by copolymer composition theory. The ultimate value of such a study is, of cause, in extending this to the optimisation of copolymer properties, from either a chemical, physical and/or mechanical stand-point, with respect to varying composition.

From IR spectroscopic analysis, the presence of ester groups (from MMA) is evident from the carbonyl stretching peak at 5.8 μm whilst a further sharp, but much weaker, aromatic band (from ST) appears characteristically at 6.25 μm. Additionally, the relationship between predicted copolymer composition (see eq.4 on p.4) and the observed IR absorbance ratio is found to be essentially linear. As a result, the hither to unknown compositions of MMA-ST copolymers prepared from anionic and cationic copolymerization techniques, using butyl lithium (BuLi) in benzene and aluminium trichloride ($AlCl_3$) in nitrobenzene as the initiator respectively, were also able to be determined from their IR spectra. These latter spectra showed that the positions of the carbonyl and aromatic bands were the same as those for free radical copolymerization. Thus, the linear relationship between the theoretical free radical copolymer compositions of MMA-ST and the observed spectral data for the prepared materials enables calibration of the cationic and anionic copolymers to be carried out with a view to determining their associated monomer reactivity ratios.

In addition to studying the free racical copolymers by IR spectroscopy, NMR spectroscopy was also used, the NMR spectra clearly showing the positions of the methoxy proton resonances (from MMA) at 3.6 ppm. and the aryl proton resonances (from ST) at 6.3-7.3 ppm. The relationship between predicted copolymer composition of MMA-ST and their corresponding observed NMR resonance area ratios is also found to be experimentally linear. The determination of molar fractions of MMA-ST in the prepared copolymers from NMR spectroscopy gave good agreement with those values predicted by the copolymer composition equation. In the case of copolymers prepared from anionic copolymerization, the NMR spectra exhibited much stronger methoxy proton resonances than aryl proton resonances. This is a clear indication of the preference which MMA has over ST for anionic copolymerization using BuLi in benzene as initiator. This is only to be expected from elementary considerations of the relative electronic structures of those two vinyl monomers. Consequently, the anionic copolymers prepared consisted mainly of MMA whilst, conversely, copolymers perpared from cationic copolymerization using $AlCl_3$ in nitrobenzene as initiator were composed mainly of ST units, as also confirmed by NMR analysis. It was also noted that the NMR spectra relating to copolymers from both anionic and cationic copolymerization consisted of similarly positioned resonance peaks to those from free radical copolymerization.

Finally, acylonitrile-styrene (ACN-ST) copolymers from free radical copolymerization, again using benzoyl peroxide as initiator, were also prepared, as indeed they were via other routes-except, that is, via cationic copolymerization due to the strongly electron-withdrawing (i.e., cationically deactivating) nature of the $C\equiv N$ group in ACN which much prefers anionic initiation. These copolymers were also studied by IR and NMR spectroscopy, their IR spectra showing a $C\equiv N$ peak at 4.4 μm together with an aromatic band at 6.25 μm. However, the NMR spectra failed to show aryl parallel response, apparently due to insolubility of the copolymer samples in the NMR solvent (deuterochloroform) used as the acrylonitrile content increased.

In conclution, it can be said that a study of the copolymerization of two different monomers, such as has been carried out here, is of particular interest and commercial significance because of the important practical improvements in a wide range of material properties which can be brought about in a homopolymer by copolymerization with a modifying species. Further than this, of cause, terpolymerization is also very important nowadays as this whole field of co-and higher polymerization at last enjoys the amount of research interest commensurate with its obvious techndogical importance.