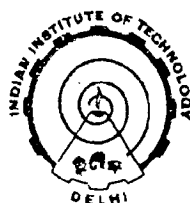


**STUDIES ON THE COPOLYMERISATION OF
METHYL METHACRYLATE WITH VINYL
MONOMERS**

By

ALPANA MISHRA

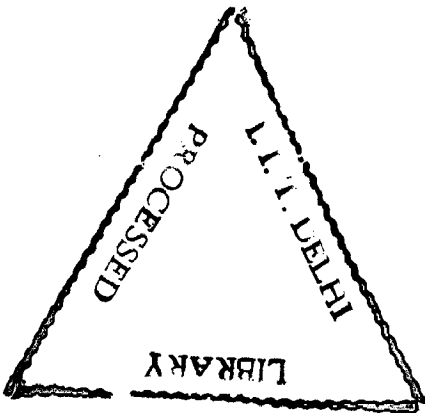
*THESIS SUBMITTED
IN FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY*



**CENTRE FOR POLYMER SCIENCE AND ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY, DELHI
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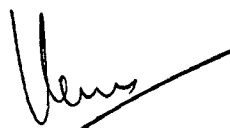
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CERTIFICATE

This is to certify that the thesis entitled "**STUDIES ON THE COPOLYMERISATION OF METHYL METHACRYLATE WITH VINYL MONOMERS**" being submitted by **Ms. Alpana Mishra** to the Indian Institute of Technology, Delhi, for the award of degree of **Doctor of Philosophy** is a record of bonafide research work carried out by her. Ms. Alpana Mishra has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis which to my knowledge has reached the requisite standard.

The results contained in this thesis have not been submitted, in part or full, to any other University or Institute for the award of any degree or diploma.



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Alpana Mishra
(ALPANA MISHRA)

ABSTRACT

The thesis deals with the synthesis of various vinyl monomers: *N*-*o*-chlorophenyl maleimide (OC), *N*-*m*-chlorophenyl maleimide (MC), *N*-*p*-chlorophenyl maleimide (PC), *N*-(*p*-carboxyphenyl) methacrylamide (CPMA) / acrylamide (CPA) and 2-cinnamoyloxyethyl methacrylate (COEMA) monomers, their characterization and investigation of homopolymerisation and copolymerization of these monomers with methyl methacrylate.

Thirty copolymer samples having varying mole fraction of these monomers were prepared by solution/bulk polymerisation in nitrogen atmosphere using AIBN as an initiator and THF/DMF as a solvent. Molecular characterisation of the copolymers was done by intrinsic viscosity $[\eta]$ and gel permeation chromatography (GPC). $[\eta]$ decreased with increasing concentration of *N*-chlorophenyl maleimides in the copolymers. In case of MMA-COEMA copolymers, $[\eta]$ increased with increasing COEMA content. \bar{M}_n , \bar{M}_w determined by GPC also showed a similar trend. All the copolymers were polydisperse and had a polydispersity index in the range of 1.85-1.97 in MMA-*N*-chlorophenyl maleimides and 2.80-2.99 in MMA-COEMA copolymers. Structural characterisation of the copolymers was done by recording ¹H-NMR spectra using CDCl₃/DMSO-d₆ as solvent. Copolymer composition was determined by taking the ratio of the intensity of signals due to methoxy protons of MMA and aromatic protons of maleimides/CPA/CPMA. On the other hand, in case of MMA-COEMA copolymers, copolymer composition was determined by taking the

ratio of intensities of the signals due to (i)-OCH₃ protons of MMA and -OCH₂CH₂O- protons of COEMA and (ii)-OCH₃ protons of MMA and C₆H₅-CH=CH- proton of COEMA. From the knowledge of copolymer composition, reactivity ratios for various monomer pairs were calculated using Fineman-Ross and Kelen Tüdös methods. *Q* & *e* values for these vinyl monomers were also determined using Alfrey-Price equation. ¹H-NMR and ¹³C[¹H] NMR spectroscopy was used to determine stereochemical parameters and sequence distribution in some of the copolymer samples.

Thermal characterisation of the homopolymers and copolymers was done by using differential scanning calorimetry in static air atmosphere and dynamic thermogravimetry in nitrogen atmosphere. From the DSC scans the effect of monomer structure and copolymer composition on the glass transition temperature was investigated. *T_g* increased with increasing amount of N-chlorophenyl maleimides. All the homopolymers had *T_g* of 217 ± 1°C. However in case of copolymers the position of substituents showed an effect on *T_g*. In case of MMA-COEMA copolymers, *T_g* decreased with increasing COEMA content in the copolymer.

Relative thermal stability was compared by comparing *T_i*, *T_f*, *T_{max}*, decomposition temperature at various % weight loss and weight loss in different temperature ranges. Activation energy of decomposition for copolymers was higher than PMMA.

Fabrication of copolymer sheets was done by casting technique using prepolymer syrup. Twenty copolymer sheets were prepared by taking varying mole fractions of comonomers (OC, MC, PC and COEMA) in the initial feed. Copolymer sheets using monomers having amide linkage in the side chain could not be prepared

as it was insoluble in MMA monomer. Characterisation of the sheets was done by density, viscosity, GPC, T_g , vicat softening temperature (VST). Mechanical and dynamic mechanical properties of the sheets was also investigated. Optical characterisation was also carried out. All the sheets were transparent. A yellow tinge was observed in the cast sheets having higher weight fraction of the comonomers. Solar transmittance, tensile and flexural properties of copolymer sheets having low mole fraction of comonomers were comparable to PMMA. A marginal decrease in the properties was observed for copolymer samples having higher mole% of comonomers. T_g , determined from DSC and DMA, increased in the presence of N-chlorophenyl maleimides whereas it decreased in the presence of COEMA. A similar trend was observed in VST.

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