

**STUDIES ON THE COPOLYMERIZATION OF METHYL
METHACRYLATE WITH N-ARYLSUBSTITUTED
ITACONAMIC ACIDS/ ITACONIMIDES**

by

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Submitted

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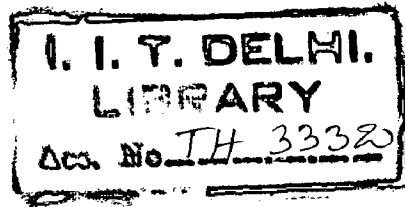
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CERTIFICATE

This is to certify that the thesis entitled “**Studies on the Copolymerization of Methyl Methacrylate with N-arylsubstituted Itaconamic Acids/ Itaconimides**” submitted by **Ms. Rashmi Chauhan**, to the **Indian Institute of Technology, Delhi** for the award of degree of Doctor of Philosophy, in Polymer Science and Technology is a record of bonafide research work carried out by her. Ms. Rashmi Chauhan 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 are original and have not been submitted in partial or full, to any other University or Institute for the award of any degree (or) diploma.



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Dedicated
to
My Parents

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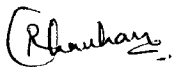
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(Rashmi Chauhan)

ABSTRACT

The thesis deals with the synthesis and characterization of N-arylsubstituted itaconamic acid monomers such as N-(4-carboxyphenyl) itaconamic acid (CPA), N-(2-methoxy-5-chlorophenyl) itaconamic acid (OMCPA), N-(4-methoxy-3-chlorophenyl) itaconamic acid (MCPA) and the corresponding N-arylsubstituted itaconimides i.e. N-(4-carboxyphenyl) itaconimide (CPI), N-(3-methoxyphenyl) itaconimide (MAI), N-(4-methoxyphenyl) itaconimide (PAI), N-(4-methoxy-3-chlorophenyl) itaconimide (MCPI), and N-(2-methoxy-5-chlorophenyl) itaconimide (OMCPI). Structural and thermal characterization was done using FT-IR, ¹H-NMR, differential scanning calorimetry (DSC) and thermogravimetry (TGA).

To investigate systematically the copolymerization behavior of these monomers with MMA, free radical copolymerisation was carried out in 10-30 % solution, at 60°C, using AIBN (1% w/w) as an initiator in dry THF or dimethyl acetamide (DMAc) as solvent under nitrogen atmosphere. Feed compositions having varying mole fractions of N-arylsubstituted itaconamic acid monomers ranging from 0.05 to 0.5 were taken to prepare the copolymers. For N-arylsubstituted itaconimide monomers, the range was varied from 0.1-0.5. Copolymerization was terminated at low percentage conversion (< 20%).

Structural characterization of copolymers was done by FT-IR, ¹H-NMR and elemental analysis. Percent nitrogen content was used to calculate the copolymer composition. The monomer reactivity ratios were calculated from the copolymer composition using Fineman-Ross and Kelen Tüdös methods. The reactivity ratios of the monomers were found to be $r_{\text{MMA}} = 0.46 \pm 0.06 / r_{\text{CPA}} = 0.68 \pm 0.06$; $r_{\text{MMA}} = 0.32 \pm 0.03 / r_{\text{MCPI}} = 1.54 \pm 0.05$; $r_{\text{MMA}} = 0.15 \pm 0.02 / r_{\text{OMCPI}} = 1.23 \pm 0.18$; $r_{\text{MMA}} = 1.00 \pm 0.01 / r_{\text{MAI}} = 0.99 \pm 0.07$ and $r_{\text{MMA}} = 0.93 \pm 0.02$

$r_{PAI} = 1.11 \pm 0.10$. The monomer reactivity ratios for the N-arylsubstituted itaconimide monomers were higher as compared to MMA monomer. In case of MMA-MAI and MMA-PAI copolymer systems, reactivity ratios of the two comonomers were ~ 1 thus making it a system close to azeotropic. The monomer reactivity ratios for the MMA-N-arylsubstituted itaconamic acid systems were not determined due to the low incorporation of the itaconamic acid in the backbone.

The molecular characterisation of the copolymers was done using gel permeation chromatography and for MMA-N-arylsubstituted itaconimides the molecular weight was found in the range of 0.9×10^3 - 64.4×10^3 (\overline{M}_n) and 3.3×10^3 - 101.8×10^3 (\overline{M}_w) with polydispersity index in the range of 1.5 - 4.1. The molecular weight decreased with increasing mole fraction of itaconimide in the feed.

Microstructure analysis of MMA-MCPI and MMA-OMCPI copolymers was done by recording their $^{13}\text{C} \{^1\text{H}\}$ -NMR spectra. In the $^{13}\text{C} \{^1\text{H}\}$ -NMR spectra of MMA-MCPI and MMA-OMCPI copolymers, the carbonyl carbon of MMA was observed in the region $\delta = 176.0$ - 178.8 ppm and of N-aryl itaconimide in the region $\delta = 179.0$ - 182.0 ppm ($>^1\text{C}=\text{O}$) and $\delta = 172.7$ - 175.0 ppm ($>^2\text{C}=\text{O}$) and shows multiplicity due to tacticity. The concentration of various compositional triad fractions was calculated from the relative areas of the resonance signals which were determined using a non-linear shape deconvoluting program. In all these cases the fitting was considered valid only when $\chi^2 < 1$. Assuming the Alfrey-Mayo model (first-order Markov terminal model) to be valid at low-conversion of the copolymers, the triad fractions were calculated using the terminal model reactivity ratio of the monomers using Harwoods statistical model program. There is a good agreement between the calculated and the experimentally determined triad concentrations. Thus the copolymer formation follows the first order Markov model. From the results of the composition with

respect to various I- and M-centered triads, the conditional probabilities P_{IM} , P_{II} , P_{MI} and P_{MM} and the number average sequence lengths (\bar{N}_M and \bar{N}_I) which are the reciprocals of the conditional probabilities has been calculated. The average sequence length containing MMA monomer units (\bar{N}_M) decreases with decrease of MMA in the polymer backbone. Similarly, the average sequence length containing the itaconimide monomer units increases with increase of the itaconimide in the polymer backbone.

Glass transition temperature (T_g) and thermal stability of the copolymers were determined using DSC and TGA. The T_g was found to be dependent on the copolymer composition, nature of substituents, molecular weight, etc. For homopolymers of N-arylsubstituted itaconamic acid and itaconimides, softening points were determined theoretically using Gordon and Taylor equation. There was a good agreement with the experimentally determined values for N-arylsubstituted itaconimide homopolymers whereas for N-arylsubstituted itaconamic acid homopolymers the calculated T_g values were lower than expected. The softening points of MMA-N-arylsubstituted itaconimide copolymers as determined from DSC scans were found to increase with increasing amounts of N-arylsubstituted itaconimides in copolymers but for MMA-N-arylsubstituted itaconamic acid copolymers the copolymer composition had little effect on T_g . Also, T_g for MMA-N-arylsubstituted itaconimide copolymers were calculated theoretically using Fox equation. The softening points calculated using Fox equation were lower than the experimentally obtained values. It could be due to the fact that homopolymerization of itaconimides gave low molecular weight homopolymer which has not reached the limit where it is independent of molecular weight. The T_g for all the copolymers was higher when the substituent was present on the *p*-position as compared to that at *m*- or *o*-position.

Thermal stability of homopolymers and copolymers was determined by recording TG/DTG traces in nitrogen atmosphere. The relative thermal stability of the copolymers was assessed by comparing the mass loss in the temperature range of 150–250°C, 250–350°C, 350–700°C, percent char yield at 700°C and by calculating integral procedural decomposition temperature (IPDT) according to the procedure of Doyle in the temperature range of 100°C to 700°C. An increase in thermal stability was observed with the incorporation of the N-arylitaconamic / itaconimide in the copolymer backbone. A significant improvement in the char yield as determined by thermogravimetry was observed upon copolymerization.

Preparation of MMA-N-arylsubstitued itaconimide copolymer sheets by bulk polymerization using prepolymer syrup was also carried out to investigate the effect of copolymer structure and composition on the performance properties. The prepolymer syrup, prepared by polymerisation at 60°C and using AIBN as an initiator, was poured in a mould made of two toughened glass plates separated by a PVC gasket of diameter 3mm. Nine copolymer sheets were prepared by taking varying amounts MCPI, OMCPI and PAI in the feed ranging from 0.5- 4 mol percent. The structural and molecular characterisation of the sheets was done by ¹H-NMR and GPC. The molecular weight was observed in the range of 0.7×10^5 - 10.0×10^5 (\overline{M}_n) and 1.0×10^5 - 15.0×10^5 (\overline{M}_w) with polydispersity index in the range of 1.4-6.1. The density of the copolymer sheets was observed in the range 1.28-1.39 for MMA-MCPI sheets, 1.33-1.52 for MMA-OMCPI sheets and 1.22-1.27 for MMA-PAI sheets and for PMMA it was 1.23. The density of the copolymer samples was also calculated from the group contribution method. The calculated densities are higher than the

theoretically calculated values. T_g of all the copolymer sheets was higher as compared to PMMA (122°C) and was observed in the range of 123-134°C.

The relative thermal stability of the copolymers was also assessed by comparing initial decomposition temperature (T_i), final decomposition temperature (T_f), temperature of maximum rate of mass loss (T_{max}) and integral procedural decomposition temperature (IPDT) in the temperature range of 100°C to 500°C. All the copolymers were stable upto 300°C and started degrading after that. Mechanical and dynamic mechanical properties of the sheets were investigated using ASTM standards. Optical properties and chemical resistance of the sheets were also determined.

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