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

by

RASHMI CHAUHAN

Centre for Polymer Science and Engineering

Submitted

in fulfillment of the requirements of the degree of Doctor of Philosophy

To the

Indian Institute of Technology, Delhi

JULY, 2006

polymers — Itaconimides

polymerization (methyl methacrylate) - Itaconamic acids

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.

Prof. (Mrs.) Veena Choudhary
Professor and Head,
Centre for Polymer Science & Engineering
Indian Institute of Technology, Delhi
Hauz Khas, New Delhi-110016

Dedicated

to

My Parents

ACKNOWLEDGEMENT

It has been an exceptional journey-one that I had never dreamt of. It involves the use of a chemist's mind to the challenges of polymer chemistry led by my supervisor Prof. Veena Choudhary. I am deeply indebted to her for her able guidance, disciplined freedom, inspiration to achieve higher heights and invaluable planning and execution, which made this work a fruitful one. I truly appreciate her patience and tolerance during my numerous misadventures and her help in developing my confidence and sense of autonomy. My demands on her valuable time and energy were excessive. But I am grateful to her for the many hours of discussions we had in which she showed her enthusiasm and positive attitude towards this study. I owe my thanks to her for providing necessary facilities to complete this venture and especially for her faith in me which gave me the confidence to carry out my research work. Her enthusiasm, down to earth nature, dedication for work and integral view on research has made a deep impression on me.

I am thankful to Prof. I.K.Varma, Prof. A.K. Gupta, Prof. S.N. Maiti, Prof. A.K. Ghosh and Dr. Josemon Jacob for their constructive criticism and valuable suggestions at various stages of the work.

My special thanks are due to Mr. Surender Sharma and Mr. Shivkant for their immediate help whenever needed. I extend my thanks to Mr. Ashok Kapoor, Mr. Devender Singh and all official staff of CPSE. I am thankful to Mr. Munna Lal and Mr. R.K.Singh for recording my NMR spectras, Mr. Singhal and Mr. Virendra Sharma for fabricating the glasswares, I needed as well as Mr. Prabhunath for tracing the figures. I am grateful to all those who have done that extra bit in one form or the other so that I could meet the deadline.

My sincere thanks are due to Prof. H.M. Chawla and Prof. A.S. Brar for their help to come out from the difficult times during my research career. I am thankful to Dr. N.G.Ramesh for teaching me different aspects of the research.

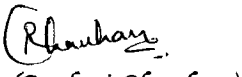
I express my most sincere thanks to Dr. A.S. Sarpal and Dr. A.K. Gupta, of Indian Oil Corporation, Faridabad and Prof. Martin Moeller of RWTH Aachen and Prof. H.A.J.Adler TU Dreseden for providing NMR and GPC facilities. I am thankful to Dr. G. Jayakrishna and Dr. Anil Yadav of Indian Oil Corporation, Faridabad, for recording the C-13 spectra and GPC chromatograms of my samples.

I wish to thank Dr. Sulakshana Jain for not only bearing my repeated tales of problems but also for her invaluable suggestions to come out of them. I am thankful to Dr. (Mrs.) Meenakshi Khemka and Mrs. Sudakshina Sahoo for making my hostel life memorable. I am thankful to Ruchi Gaur for her nice company during the last days of my stay in hostel. I wish to thank Rashmi Rawat, Mrs. Mamata, Mrs. Dipti Gupta and Dr. Chetna for being kind, helpful and trustful friends. I extend my thanks to S. Vengetesan, Titto and Vipin for always being ready to help. I am grateful to Dr. Vishal Anand, Mrs. Sujata Mishra, Mr. Vitthal Sawant, Mrs. Punita and Mr. Praveen and Mr. Rangarao for their timely help. I am thankful to my colleagues Rakesh Kumar, Dr. Anantha Padmanabha, Dr. Joy K. Paul, Dr. Muthulakshmi R.T.S., D. Purnima, Nimisha, Neetu, Kavita, Dipti, Pooja, Sangita, Bala, Dilip and Senthil for providing a nice working environment in the laboratory.

I am indebted to my beloved parents who are at the back of my each and every movement. I wish to record my sincere appreciation and thanks to them for their ceaseless and tireless support, patience and encouragement. The blind trusts of my father which keeps me going and makes me feel more responsible and his understanding the value of education is truly beyond my comprehension. I am grateful to my mother for her love and care which always comforted me and the good things she taught me that really matters. Though physically she is not with me but I know somewhere she is seeing me and will always be with me. I am thankful to my brother Deepak who in spite of being younger to me had always been a helping hand.

The financial assistance provided by Indian Institute of Technology, Delhi and Council of Scientific and Industrial Research, Government of India for carrying out the research work is gratefully acknowledged.

Last but not the least I thank the ALMIGHTY who always made his presence felt in my life and gave me the strength to come out of my toughest times and continue to inspire me towards the right path.



(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, ^{1}H-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, ^{1}H-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 Tüdos methods. The reactivity ratios of the monomers were found to be r_{MMA} = 0.46± .06/ r_{CPA} = 0.68±0.06 ; r_{MMA} = 0.32±0.03/ r_{MCPI} = 1.54±0.05 ; r_{MMA} =0.15±0.02 / r_{OMCPI} = 1.23±0.18 ; r_{MMA} =1.00±0.01 / r_{MAI} =0.99±0.07 and r_{MMA} =0.93±0.02

/ r_{PAI} = 1.11±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 X 10^3- 64.4 X 10^3 ($\overline{M}_n$) and 3.3 X 10^3-101.8 X 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}C {^1H}-NMR spectra. In the ^{13}C {^1H}-NMR spectra of MMA-MCPI and MMA-OMCPI copolymers, the carbonyl carbon of MMA was observed in the region δ = 176.0-178.8 ppm and of N-aryl itaconimide in the region δ = 179.0-182.0 ppm ($>^1C=O$) and δ = 172.7-175.0 ppm ($>^2C=O$) 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 ($\overline{N}_M$ and $\overline{N}_I$) which are the reciprocals of the conditional probabilities has been calculated. The average sequence length containing MMA monomer units ($\overline{N}_M$) 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 ^{1}H-NMR and GPC. The molecular weight was observed in the range of 0.7 X 10^5- 10.0 X 10^5 ($\overline{M}_n$) and 1.0 X 10^5-15.0 X 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.

TABLE OF CONTENTS