STUDIES ON THE COPOLYMERISATION OF METHYL METHACRYLATE WITH N-ARYL ITACONIMIDES

by

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Dedicated to My Parents

CERTIFICATE

This is to certify that the thesis entitled **"STUDIES ON THE COPOLYMERISATION OF METHYL METHACRYLATE WITH N-ARYL ITACONIMIDES"** being submitted by ***Vishal Anand*** 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 him. Vishal Anand 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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ABSTRACT

Copolymerisation of MMA with *N*-aryl substituted maleimides has been extensively investigated in the past with an aim to improve their thermal performance. Since maleimides have a very low tendency for homopolymerisation due to the presence of 1,2-disubstituted double bond, the propagation step is extremely slow due to the steric interactions between the β-substitutent of the propagating species and the two substituents of the incoming monomer molecule. Itaconimides on the other hand contain 1,1-disubstituted double bond, thereby rendering it more reactive. Secondly the dwindling petrochemical feed stocks have necessitated the need to focus attention on developing polymers based on annually renewable resources. Maleimides obtained from maleic anhydride are based on petrochemical resources whereas itaconimides are prepared from itaconic acid, obtained from easily renewable resources such as corn starch by fermentation process using *Aspergillus itaconicus* or *Aspergillus terreus fungi*.

Earlier studies in our laboratories has shown that the position as well as the nature of substituent i.e. electron withdrawing or releasing group in maleimides affected the copolymerisation and thermal behaviour of MMA copolymers. The main focus of present investigation was therefore to investigate the copolymerisation behaviour of *N*-(phenyl) itaconimide / *N*-(*o*-/*m*-/*p*-chlorophenyl) itaconimides / *N*-(*p*-tolyl) itaconimide monomers with methyl methacrylate using conventional and controlled free radical polymerisation. The effect of comonomer structure and copolymer composition on the glass transition temperature, thermal stability and microstructure of the copolymers was also evaluated.

N-aryl itaconimide monomers having electron releasing and electron withdrawing groups was synthesized according to the procedure reported by Searle using acetone as a solvent. A two step procedure was employed for the synthesis of *N*-aryl itaconimide monomers. 0.25 moles of itaconic anhydride were dissolved in minimum amount of dry acetone and 0.25 moles of amine solution was added slowly with vigorous stirring. The reaction was carried out at 20-25°C. The itaconamic acid precipitated out from the solution. Cyclodehydration of the itaconamic acid was done using acetic anhydride and anhydrous sodium acetate as cyclodehydrating agents at 60°C. Purification of monomers was done by passing a chloroform solution of the monomer through silica gel column and the solution was concentrated under reduced pressure and imide crystallised out on cooling. Monomers were characterised using elemental analysis, FTIR, ^{1}H-NMR and ^{13}C{^{1}H}-NMR spectroscopy. The results of elemental analysis for monomers agree well with the theoretical values. The mole fraction of citraconimide in various itaconimide monomers was calculated from the ratio of intensity of methyl protons at $\delta = 2.17 \pm 0.03$ ppm (citraconimide) to the vinylidene protons at $\delta = 5.76 \pm 0.03$ ppm in ^{1}H-NMR and was found to be in the range of 0.06-0.11.

Conventional free radical polymerisation was carried out by using AIBN as an initiator and THF as solvent at 60°C under nitrogen atmosphere. The mole fraction of N-aryl itaconimides in the initial feed was varied from 0.1 to 0.5 for the preparation of copolymers. Polymerisation was carried out by taking 30% (w/v) solution of monomers in THF using 0.5% of AIBN as an initiator. The reaction was stopped at low conversion (≤15%) by pouring the contents of the flask into large excess of methanol.

Molecular characterisation of polymers was done by GPC using polystyrene as calibration standards. Monomers having electron-withdrawing group (PI/MI/OI) gave copolymers having low molecular weight as compared to the copolymers prepared from I and PTI monomers. Molecular weight in copolymers decreased with increasing amount of N-aryl itaconimide in the copolymers. Termination due to chain transfer to monomer may be responsible for the formation of low molecular weight polymers. The copolymers had molecular weight in the range of $2.2 \times 10^3 - 61.8 \times 10^3$ (M_n) and $5.1 \times 10^3 - 108.2 \times 10^3$ (M_w) with polydispersity index in the range of 1.5-3.0. All the homopolymers of N-aryl itaconimides i.e. sample PI, PPI, PMI, POI and PPTI had molecular weight in the range of $1 \times 10^3 - 8.7 \times 10^3$ (M_n) and $1.6 \times 10^3 - 18.7 \times 10^3$ (M_w) with polydispersity index in the range of 1.5-2.2.

Block copolymers of MMA and *N*-aryl itaconimides were also prepared using atom transfer radical polymerisation (ATRP) technique. In the first step, PMMA-Cl (macroinitiator) was prepared by bulk polymerisation of MMA at 85°C using AIBN/$FeCl_3.6H_2O$/PPh_3 in 1:4:12 molar ratio as an initiator. In the second step, polymerisation of *N*-aryl itaconimides was carried out in toluene at 85°C using PMMA-Cl/CuBr/Bpy in the molar ratio of 1:1:3 as an initiating system.

M_n and polydispersity index of PMMA prepared from ATRP was also determined using GPC and was found to be $1.27X10^4$ and 1.29 respectively which is in good correlation with the value calculated from $M_{n,cal} = ([M]_0/[I]_0) \times MW_{MMA} \times conversion$. Unimodal curve for all PMMA-b-Poly (*N*-aryl itaconimide) copolymers were obtained in GPC. M_n and polydispersity index of copolymer were calculated and it was found that there is an increase in molecular weight for all the block copolymers without much effect on

polydispersity. Only oligomeric blocks of *N*-aryl itaconimides could be incorporated in the PMMA backbone. However high molecular weight PMMA i.e. M_n of 4.8 x 10^4 with narrow PDI (1.17) could be prepared by using PMMA-X macroinitiator (M_n = 1.27 x 10^4 and PDI = 1.29). Isomerisation of *N*-aryl itaconimides to *N*-aryl citraconimides or termination due to chain transfer reaction i.e. chain transfer to monomer may be responsible for the low molecular weight of the second block (homopolymer of itaconimides). In order to investigate this fact, *N*-aryl itaconimide monomers were heated separately in toluene at 85°C for different time intervals. The % isomerisation was found to be 32%, 21% and 23% in case of MI, PI and I monomers repectively after 4 days. On the other hand, ~40% isomerisation was observed in case of PTI monomer after 6 days.

Structural characterisation of homo/copolymers was done using ^{1}H-NMR, ^{13}C{^{1}H}-NMR and elemental analysis. ^{1}H-NMR spectroscopy and elemental analysis was used for the determination of copolymer composition. A good agreement was observed between the values obtained using ^{1}H-NMR and elemental analysis in all the copolymers. In the copolymerisation of MMA with *N*-aryl itaconimides, an increase in mole fraction of itaconimide in feed (m_1) did not show a linear increase in the mole fraction of itaconimide in copolymer (M_1). All the copolymerisations showed deviation from linearity i.e. ideal polymerisation and the copolymers were richer in M_1, thus showing that the *N*-aryl itaconimide monomers are more reactive in propagation compared to MMA.

The reactivity ratios of the monomers were calculated from the knowledge of copolymer composition using Fineman-Ross, Kelen Tüdos and RREVM methods. The RREVM reactivity ratios of the monomers were found to be r_1 (I) = 1.32 / r_2 (MMA) = 0.36; r_1 (PI)

= 1.26 / r_2 (MMA) = 0.35; r_1 (MI) = 1.21 / r_2 (MMA) = 0.34; r_1 (OI) = 0.78 / r_2 (MMA) = 0.34 and r_1 (PTI) = 1.18 / r_2 (MMA) = 0.23. This clearly shows that *N*-aryl itaconimides are more reactive than MMA (i.e., $\kappa_{11} > \kappa_{12}$ and $\kappa_{21} > \kappa_{22}$) towards homopropagation and cross-propagation. The values of Q and e for *N*-aryl itaconimide monomers were calculated from Alfrey and Price equation using the value of Q and e for MMA as 0.78 and 0.4 respectively. The Q and e values of the monomers were found to be Q = 2.74 / e =1.16; Q = 3.12 / e =1.27; Q = 3.64 / e =1.4; Q = 3.64 / e =1.55 and Q = 4.98 / e = 1.47 for I, PI, MI, OI and PTI respectively.

In order to clarify the substituent effect on the copolymerisation, Hammett's equation was applied to the copolymerisation and ρ value was calculated. The negative ρ-value suggests that the relative reactivity ($1/r_2$) of itaconimide toward an attack by PMMA radicals tends to increase as the electron donating nature of the substituents in itaconimide becomes greater. Q and e values were also plotted against the σ constants of the substituents in itaconimide. The large Q values thus observed in case of PPTI can be explained on the basis of resonance stabilization due to the presence of electron releasing substituent (-CH_3) at p-position, which may not be possible in case of itaconimide monomers having electron-withdrawing substituent (-Cl group).

Structural characterisation of block copolymers obtained by using AIBN/$FeCl_3.6H_2O$/PPh_3 initiating system was done using ^{1}H-NMR and $^{13}C\{^1H\}$-NMR. Mole fraction of *N*-aryl itaconimides in copolymers calculated using ^{1}H-NMR and CHN analysis was very low i.e. 0.03 and 0.06 for PTI and I monomers respectively even after 9 days of reaction. Polymerisation for *N*-(*o*-/*m*-/*p*-chlorophenyl) itaconimides was also

carried out but no signal due to aromatic protons was detected in ^{1}H-NMR even after 7 days of reaction.

Structural characterisation of block copolymers obtained by PMMA-Cl/CuBr/Bpy initiating system was also done using ^{1}H-NMR and ^{13}C{^{1}H}-NMR. Mole fraction of *N*-aryl itaconimides in copolymers calculated using ^{1}H-NMR and CHN analysis are in good correlation with each other.

For microstructural analysis, ^{13}C{^{1}H}-NMR spectra of PMMA, homopolymers of *N*-aryl itaconimide and MMA : *N*-aryl itaconimide copolymers were recorded. In copolymers the carbonyl carbon of MMA resonate at δ = 175.0-178.4 ppm and of *N*-aryl itaconimide at δ = 171.9-174.2 ppm and 178.6-180.9 ppm. The carbonyl carbon signals of MMA (M) (δ = 175.0-178.4 ppm) as well as *N*-aryl itaconimide (I) (δ = 171.9-174.2 ppm) in copolymers show multiplet indicating that it is sensitive to compositional and configurational sequences and hence were used for the determination of sequence distribution of M- and I- centered triads. The concentration of various compositional triad fractions was calculated from the relative area of the resonance signals. The relative area of resonance signals were determined using a non-linear least square Lorentzian line shape deconvulating program. Assuming the Alfrey-Mayo statistical model (first-order Markov terminal model) to be valid at any moment of the low-conversion copolymers, the triad fractions can be calculated using the terminal model reactivity ratio of the monomers using Harwood's statistical model program. There was a good agreement between the experimentally determined values and theoretical values obtained from Alfrey Mayo statistical model. The Monte Carlo (MC) simulation method was also used to monitor the changes in copolymer sequence behavior during the course of

polymerisation and the M- and I-centered triads obtained from this method are also in good agreement with the experimental values calculated from $^{13}C\{^{1}H\}$-NMR.

DSC scans of various homopolymers and copolymers were recorded to study the effect of copolymer structure and composition on the glass transition temperature of the copolymers. In order to have a similar thermal history second heating scans were used to determine the glass transition temperature. The powdered samples were first heated to 120°C and then quench cooled and the DSC scans were re-recorded at a heating rate of 10°C/min. T_g of PI, PPI, PMI and PPTI homopolymers was found to be 220°C, 238°C, 227°C and 232°C respectively whereas PMMA prepared under similar conditions had T_g of 109°C. Copolymers having 0.21 ± 0.01 mole fraction of itaconimide monomers of varying structure showed an increase in T_g of 15-53°C. The position of the substituent on the phenyl ring (*o*-,*m*-,or *p*-) in *N*-aryl itaconimides affected the glass transition temperature. T_g was maximum in case of OI copolymers and was lowest in MI copolymers. Glass transition temperature of copolymers increased with increasing amounts of *N*-aryl itaconimides in the copolymer.

Thermal stability of the copolymers was determined by recording TG/DTG traces in the nitrogen atmosphere. The relative thermal stability of the homopolymers and copolymers was compared by comparing the initial decomposition temperature (T_i), temperature of maximum rate of weight loss (T_{max}), final decomposition temperature (T_f) and percent char yield at 700°C. One or two step degradation was observed in all the copolymers whereas PMMA showed three-step decomposition. This shows that the incorporation of *N*-aryl itaconimide in PMMA backbone restricts the formation of H-H linkages. A significant increase in the percent char yield i.e. in the range of 5-35% at 700°C was

observed upon incorporation of *N*-aryl itaconimides in the PMMA backbone. Percent char yield in case of PI and PPTI homopolymers and copolymers was lower as compared to *N*-(*o*-/*m*-/*p*-chlorophenyl) itaconimide homo/copolymers. Position of chloro substituent also affected the char yield and showed a trend of PPI>POI>PMI.

Thermal characterisation of block copolymers prepared by ATRP was also carried out using DSC and thermogravimetry. Second heating scans were used to determine the glass transition temperature. Two transitions were seen in the DSC scans of block copolymers. First transition corresponds to glass transition temperature of PMMA and second transition corresponds to the glass transition temperature of *N*-aryl itaconimides. All copolymers showed broad single step degradation and were stable up to 245°C.

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