EFFECT OF STRUCTURE ON PROPERTIES OF METHYL METHACRYLATE COPOLYMERS

BY

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Thesis submitted in fulfilment of
the requirements for the degree of
DOCTOR OF PHILOSOPHY

Centre for Materials Science & Technology
INDIAN INSTITUTE OF TECHNOLOGY, DELHI
NOVEMBER, 1991

Dedicated

To

My Parents

CERTIFICATE

This is to certify that the thesis entitled "**EFFECT OF STRUCTURE ON PROPERTIES OF METHYL METHACRYLATE COPOLYMERS**" being submitted by Mr. Manoranjan Patnaik 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. Mr. Manoranjan Patnaik has worked under our guidance and supervision and has fulfilled the requirements for the submission of this thesis which to our 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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ACKNOWLEDGEMENT

I express my heart-felt gratitude and indebtedness to my supervisors Prof. (Mrs.) I.K. Varma and Dr. (Mrs.) Veena Choudhary for their guidance, encouragement and cooperation throughout the duration of this work.

I am thankful to Prof. S. Krishnamoorty and Prof. Ashok Mishra, Head, CMST for providing necessary facilities for carrying out this work.

I wish to thank the management of Gujarat State Fertilizers Company Limited (Polymers Unit), Baroda for providing necessary facilities for preparation and testing of polymer sheets. I owe my gratitude to Dr. T.J.M. Sinha, Manager R&D, GSFC (PU), Baroda for his immense help and keen interest in this work. I am also thankful to Dr. G.H. Patel, Akshya Bhai, Ravi Bhai for their cooperation and help during my stay at GSFC (PU), Baroda.

Mr. Appa Rao, Dr. A.K. Gupta, Dr. A.K. Tuli, Mr. V. Kagdiyal and Ms. Mary of Indian Oil Corporation, Faridabad are acknowledged for providing GPC facility and Dr. (Mrs.) Veena Koul of CBME, IIT, Delhi for recording electronic spectra.

I am thankful to all the faculty and staff of Centre for Materials Science and Technology for their help and cooperation during this work.

I wish to thank my friends, Dr. H.S. Varma, Dr. R. Anand Kumar, Dr. G.S. Kapoor, Krishnan, Srinivasan, Suneeta, Meenakshi, Ratnam, Radhakrishnan and other colleagues for providing me a friendly atmosphere and a timely help.

I am also thankful to the Eagle Computer Centre for typing the manuscript and Mr. Suresh Chandra for tracing the figures.

Financial assistance provided in the form of Junior Research Fellowship and then Senior Research Fellowship by the Council of Scientific and Industrial Research, New Delhi is gratefully acknowledged.

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ABSTRACT

The aim of the present work was to study the copolymerization of methyl methacrylate (MMA) with (meth)acrylates derived from straight chain and branched chain alcohols. Comonomers, 2-ethylhexyl methacrylate (EHMA), n-hexyl methacrylate (HMA), 2-ethylhexyl acrylate (EHA) and n-hexyl acrylate (HA) were selected to study the effect of structure on properties of MMA copolymers.

The thesis has been divided into six chapters. Chapter I deals with the general introduction and literature survey on copolymerization of MMA with alkyl (meth)acrylates.

Bulk polymerization of MMA with EHMA, HMA, EHA and HA is described in Chapter II of the thesis. The copolymers of MMA have been designated as EM, HM, E and H respectively. Bulk polymerization was carried out to low conversion (~10%) using 0.2% (w/w) benzoyl peroxide as an initiator at 78°C. After the desired interval of time the copolymers were precipitated in methanol and purified by reprecipitation from chloroform/methanol. Several copolymer samples were prepared by changing the mole fraction of alkyl (meth)acrylates from 0 to 1 in the initial feed. The rate of homopolymerization decreased with an increase in alkyl chain length while the rate of copolymerization also depended on the composition of the feed. The rate of copolymerization increased by an increase in temperature.

Two copolymer samples of MMA and EHMA were also prepared by suspension polymerization method taking 0.05 and 0.25 mole fraction of EHMA in the initial feed. Polymerization was carried out using 1% (w/w) AIBN at a temperature of 78°C to high conversion (98%). These copolymers have been designated as EM-A and EM-B respectively.

From the copolymer composition determined by ^{1}H-NMR spectroscopy reactivity ratios r_1 (MMA) and r_2 (comonomer) were calculated using Fineman-Ross and Kelen-Tudos method. The values of r_1 and r_2 obtained in copolymers EM, HM, E and H were 0.75 and 0.54; 1.05 and 1.01; 1.86 and 0.42; 4.32 and 0.56 respectively. The reactivity ratios for EM copolymerization at 70°C were found to be 0.86 (r_1) and 0.67 (r_2) respectively. From the knowledge of reactivity ratios and Q and e values of MMA reported in the literature, the Q and e values for EHMA and EHA were calculated and were found to be 1.062, -0.551 (EHMA) and 0.343, -0.097 (EHA) respectively.

Chapter III deals with the molecular characterisation of copolymers. Intrinsic viscosity $[\eta]$ was determined in chloroform at 30°C using Ubbelhode suspension level viscometer. Molecular weight and molecular weight distribution (MWD) of these copolymers was determined by using Gel Permeation Chromatography (GPC). PMMA standards were used for calibration. All the polymers had high molecular weight and MWD ranged from 1.24 to 1.32 in EM copolymers. In all other copolymer samples, MWD was found to be greater than two. Higher MWD values of PEHA and PHA were obtained in acrylates which may be due to branching.

Fractionation of suspension polymerized samples (EM-A and EM-B) was carried out at 30 ± 1°C in nitrogen atmosphere using acetone as solvent and methanol as non-solvent. Four fractions were obtained from each sample. Fractionation yielded copolymer samples with narrow molecular weight distribution (1.08-1.15). The weight average molecular weight of these fractions ranged from 2,81,000 to 1,19,000 (EM-A) and 2,67,300 to 97,000 (EM-B).

The 'K' and 'α' values of Mark-Houwink-Sakurada equation were calculated from the intrinsic viscosity (in THF at 25°C) and hydrodynamic volume of fractions having 0.92 and 0.75 mole fraction of MMA. An α value of 0.81 ± 0.01 while 'K' value which is a measure of polymer-solvent interaction, was found to be 3.465×10^{-3} and 2.748×10^{-3} mL/g respectively.

Results of thermal characterisation of MMA copolymers form the basis of Chapter IV of the thesis. A three step degradation was observed in PMMA sample with T_{max} at 250, 306 and 378°C. Head-to-head linkages degrade at lower temperature followed by chain-end initiated depolymerization and random chain scission. Activation energy for the first, second and third steps of PMMA degradation was found to be 39.7, 129 and 184.9 kJ/mol. A single step decomposition was observed in poly (2-ethylhexyl acrylate) (PEHA) and poly(n-hexyl acrylate) (PHA) whereas poly(2-ethylhexyl methacrylate) (PEHMA) and poly(n-hexyl methacrylate) (PHMA) showed a two step degradation. The effect of molecular weight on thermal behaviour of EM-A and EM-B copolymer was evaluated by using fractions of narrow MWD. Chain-end initiated degradation reactions slightly increased with a decrease in molecular weight of EM-A fractions. No such effect was observed in EM-B fractions.

Chapter V deals with the fabrication of cast acrylic sheets and evaluation of their mechanical properties. For this purpose known quantity of prepolymer syrup of MMA (~7-8% solid content), comonomer (EHMA, HMA, EHA, HA), initiator (lauroyl peroxide + peroxydicarbonate, 0.05%) and UV stablizer (0.005%) were mixed thoroughly followed by filtration and degassing. The total quantity of mixture taken was approximately 1.5 kg for preparing a sheet of one composition. The clear syrup thus obtained was poured into a glass mould having a pvc gasket so as to obtain sheets of 60 cm x 60 cm dimension and 3 mm thickness. The polymerization was carried out at 75°C in water bath for 4 h followed by heating in an air oven at 90-120°C for 3h. Several copolymer sheets were prepared by taking 1,3,5,10,15 and 20 weight % of comonomer in the feed. These copolymer sheets are designated as EMS (MMA - EHMA), HMS (MMA - HMA), ES (MMA-EHA) and HS (MMA - HA).

The % light transmittance and % haze of PMMA sheet was found to be 92.3 and 1.6 respectively. The addition of ≈ 15 weight % of comonomers did not affect % light transmittance. Further increase in the comonomer content resulted in a marginal decrease in % light transmittance.

Tensile strength and modulus decreased with increasing weight % of comonomer. A little effect on % elongation was observed in EMS and HMS whereas in ES and HS samples, a significant increase in % elongation was observed. The toughness of polymeric sheets was also determined from area under the stress-strain curve. Rockwell hardness (M-scale) decreased with increase in comonomer content. EMS and HMS samples showed better hardness values than ES and HS samples. The DMTA studies showed a decrease in softening point of copolymer sheets on increasing comonomer content. The decrease in softening point was more in ES and HS as compared to EMS and HMS sheets. Activation energy (ΔH^*) of ß-relaxation process was calculated by recording DMTA traces at a frequency of 1 Hz and 10 Hz. An increase in ΔH^* with increase in comonomer content was observed in EMS and HS samples. In HMS and ES samples no definite trend was observed.

General discussion and summary of the work is given in Chapter VI. Suggestions for future work are also made. References are given at the end of the thesis.

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