COPOLYMERIZATION OF 2-HYDROXYETHYL METHACRYLATE WITH ALKYL METHACRYLATES

by

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DEDICATED TO

MY PARENTS

CERTIFICATE

This is to certify that the thesis entitled "COPOLYMERIZATION OF 2-HYDROXYETHYL METHACRYLATE WITH AIKYL METHACRYIATES" being submitted by Mr. Manjeet Singh Choudhary to the Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy in Polymer Chemistry, is a record of bonafide research work carried out by him. Mr. Choudhary has worked under my guidance and supervision and has fulfilled the requirement for the submission of this thesis, which to my knowledge, has reached 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

The present thesis deals with the copolymerization of 2-hydroxy ethyl methacrylate (HEMA) with methyl methacrylate (MMA) ethyl methacrylate (EMA) and butyl methacrylate (BMA) and the structure-property relationship of the resulting polymers.

The thesis has been divided into seven chapters. Chapter I deals with the literature survey of HEMA and its copolymers. The properties and application of these polymers are also discussed.

Chapter II is concerned with copolymerization of HEMA with alkyl methacrylates using free radical initiators in nitrogen atmosphere. The copolymer composition was evaluated by estimation of the hydroxyl group. Mole fraction of HEMA in these random copolymers could be altered by changing the monomer ratios in the initial monomer feed. An increase in HEMA content in the feed resulted in an increase in HEMA in copolymers. Monomer reactivity ratios were calculated by several methods and a reasonable agreement was observed between the values of r_1 and r_2 determined by these methods. The temperature

had only a marginal effect on the reactivity ratios. The reactivity ratios were not affected by the presence of water or dimethylformamide in the feed upto a 30% of these additives (V/V).

HEMA-alkyl methacrylate copolymers were characterized by intrinsic viscosity $[\eta]$ determination and infra-red spectroscopy.

Number average molecular weight ($\bar{M}_n$) was determined by membrane osmometry. The $\bar{M}_n$ values ranged from $1.33\text{-}3.5\times10^5$ in these polymers. In the copolymers of HEMA-EMA following relationship was found to exist between intrinsic viscosity (in DMF at 35°C) and number average molecular weight :

$$[\eta] = 6.342\times10^{-1} [M]^{0.875}$$

The cohesive energy density (c.e.d.) determined by swelling measurements increased with a decrease in alkyl methacrylate content.

Fractionation of HEMA-alkyl methacrylate copolymers was done by fractional precipitation technique using DMF as solvent and water as precipitant. These fractions were characterized by ir, nmr and intrinsic viscosity evaluation. Fractions having higher intrinsic viscosity were present in larger quantities in these copolymers. A narrow molecular weight distribution was observed in HEMA-EMA copolymers.

Thermal behaviour of these copolymers was investigated by dynamic thermogravimetry (TGA) and differential scanning calorimetry (DSC) and the results are presented in Chapter V. These copolymers were stable upto a temperature of $\sim 200^{\circ}C$ and started loosing weight above this temperature which is clearly evident in the primary thermograms. Above $250^{\circ}C$ these polymer fractions decomposed at a faster rate and total weight loss was observed around $420\text{-}450^{\circ}C$. A two step degradation was observed in these copolymers in nitrogen atmosphere. A decrease in $[\eta]$ and consequently in molecular weight did not change the thermal characteristics of various fractions obtained in these copolymers. However, an increase in HEMA content resulted in a increase in initial decomposition temperature and integral procedural decomposition temperatures. The structural changes taking place in HEMA-EMA and HEMA-BMA copolymers during thermal degradation were evaluated by ir spectroscopy. Glass transition temperatures (T_g) of these copolymers determined from DSC thermograms were found to be higher for HEMA-EMA copolymers ($84\text{-}92^{\circ}C$) than HEMA-BMA copolymers ($52\text{-}65^{\circ}C$).

Results of the mechanical properties evaluation of some HEMA-MMA, HEMA-EMA and HEMA-BMA copolymer films are given in Chapter VI. Breaking stress, breaking elongation, initial modulus and toughness were calculated from the stress-strain curves. The tensile strength and initial modulus of HEMA-MMA copolymers were better than HEMA-EMA and HEMA-BMA copolymers. Subcutaneous implants of HEMA-BMA and HEMA-EMA copolymers were tested in rats to evaluate the biocompatibility of the copolymers. Negligible tissue reaction was observed upto 30 days implantation.

Summary of the work and suggestion for future work are given in Chapter VII. References are indexed at the end of the thesis.

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