Chapter II

Aims and Objectives
2.1 Aims

Prime aim of this thesis is the synthesis and study of novel high refractive index polymers. For biomedical optical articles, high refractive index polymers having low birefringence, high transparency and good biocompatibility are needed.

Transparent acrylic materials are becoming increasingly important in optical design. Amongst several optical properties, refractive index is the most important criteria for selection of materials suitable for application in optics. One of the possible candidates for this purpose is plastic materials. Other than the essential properties like light transmission, transparency and refractive index (RI), plastics are also known for their light weight. High refractive index is important for transparent synthetic polymers to be suitable as optical materials. Polymers with high refractive index will need to be thinner than those having lower refractive index, for the same focal length. The use of thin lenses contributes to reducing the volume of space occupied by lenses in optical assemblies, which can advantageously make an optical apparatus light weight and small sized. Additional requirement for greater through-put during operative procedures is the material’s flexibility. This is addressed by tweaking the polymer back-bone to lower the glass transition temperature. While thin lenses reduce the space occupied by lenses in optical assemblies, flexible materials require shorter operative lengths for insertion.

Optical products can be prepared from high index of refraction materials, including high index of refraction (meth)acrylates monomers. The monomers can be polymerised to take the form of a product capable of modifying or controlling the flow of light. The refractive index of materials can be increased by increasing the polarisability of
substituent groups. High refractive index polymers can be obtained by incorporating oxygen and sulphur containing groups as well as aromatic rings.

Current high RI plastics include polyurethanes, polyesters, epoxy and episulphide resins. Most of the high RI plastics use thiourethane and episulphide chemistries with highly polarisable chemical moieties such as aromatics and sulphur. However, optical articles produced from these materials suffer from after-cure yellowing and strong odours during lens processing. In addition, these monomers have inherently long production cycles due to prolonged curing times needed to maintain optical homogeneity. There is, therefore, a need for monomers which offer fast cure, high RI, low colour, and low odour when cured or upon cutting and grinding, while maintaining optical homogeneity.

Copolymerisation is the most successful and powerful method for effecting systematic changes in polymer properties. The incorporation of two different monomers, having diverse physical and chemical properties in the same polymer molecule in varying proportions leads to the formation of new materials with scientific technical importance. Copolymerisation modulates both the intramolecular and intermolecular forces exercised between like and unlike polymer segments and consequently properties such as glass transition temperature, refractive index, melting point, solubility, crystallinity, permeability, adhesion, elasticity and chemical reactivity may be varied within wide limits. Co- and terpolymerisation are used effectively to increase the amorphous character of the polymer which increases the transparency and the flexibility of the polymer chains. Copolymers tend to have a set of properties uniquely their own, setting them apart from that of their parent homopolymers. In copolymers, the sequence distribution of the different monomers is a key parameter to ensure homogeneity. Copolymerisation studies
and estimation of reactivity ratios are of utmost importance due to the need of predicting, designing, and properly controlling polymeric material properties. Therefore, having a good knowledge of polymerization parameters, among which reactivity ratios are the most important ones, would be very helpful.

In human contact applications it is an intrinsic requirement that the level of residual monomers to be extremely low. One way to ensure this is to follow polymerisation kinetics till the very end so as to ensure sufficient time is given for all the monomers to be converted into polymers. However, since both monomers in a copolymerisation will have differing relative rate of addition to the copolymer chain, one of the monomers will be depleted ahead of the other and the final several percentage of the copolymerisation will be essentially homopolymerisation of the less reactive monomer. In such a case the copolymer and homopolymer may phase separate leading to inhomogenity, thereby affecting transparency. Thus, investigation of copolymerisation kinetics is of paramount importance.

Cataract is the opacification of the lens due to age or other causes such as ocular trauma or inflammation which do not allow light rays to pass through the eye. It is a common surgical procedure for the cataract treatment to remove the opaque natural crystalline lens and replace it with an intraocular lens (IOL). Despite the enormous success of the intraocular lens, there is considerable opportunity for newer polymers with higher refractive index and lower glass transition temperature. Higher refractive index would allow for the use of the thinner IOLs. This, coupled with lower glass transition temperature (and hence greater flexibility), will allow for smaller incision and quicker healing after surgery, generating higher through-puts and lower costs.
In the present investigation a thorough study was carried out to synthesise different, new high refractive index (meth)acrylate monomers. This was followed by study of solution and bulk polymerisation, characterisation and evaluations.

2.2 Objectives

- Synthesis of new (meth)acrylic monomers with potentially higher refractive indices.
- Synthesis of homopolymers and evaluation of their optical and thermal properties.
- Copolymerisation studies of newer monomers to determine reactivity ratios.
- Synthesis and evaluation of new cross-linked (meth)acrylate polymer networks.
- Bulk polymerisation kinetics of 2-phenylethyl (meth)acrylate using photo and thermal initiators.

Objectives of thesis explored in detail were as follows:

Standard procedure for synthesising novel high refractive index monomers was established. Initially, reaction of achiral styrene oxide with phenol was conducted to synthesise aromatic based alcohols. Newly synthesised alcohol was thoroughly purified, reacted with acryloyl and methacryloyl chloride to obtain respective acrylates and methacrylates. Sulphur containing aromatic based alcohol was synthesised by reacting thiophenol with styrene oxide and converted to corresponding acrylate and methacrylate by reacting with acryloyl and methacryloyl chloride, respectively. 2-Phenylethyl acrylate and 2-phenylethyl methacrylate were synthesised using 2-phenylethanol and corresponding acid chlorides. Characterisation of newer monomers was carried out using $^1$H NMR, $^{13}$C NMR, IR and mass spectroscopic techniques to confirm their structure.
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Homopolymers of newer monomers were prepared by free radical solution polymerisation using 2,2’-azobisisobutyronitrile (AIBN). Newer monomers were characterised for their thermal and optical properties.

Copolymerisation studies of newer monomers were done by free radical solution polymerisation using 2,2’-azobisisobutyronitrile (AIBN). \(^1\)H NMR spectroscopy was used to determine compositions of copolymers. Chain copolymerisation is important to study the relationship between the chemical structure and reactivity of monomer. Estimation of reactivity ratios was done using Fineman-Ross (FR), Kelen-Tudos (KT), extended Kelen-Tudos (Ex KT) and Mao-Huglin (MH) graphical methods. From estimated reactivity ratios of the monomer combinations, azeotropic composition for some monomer sets were calculated. Structural parameters of the copolymers were obtained by calculating dyad monomer sequence fractions and the mean sequence length. Optical properties of copolymers like refractive index (RI) and transmittance was determined by Abbe refractometer and spectrophotometer, respectively. Solubility of copolymers was tested in common solvents. The molecular weights [weight-average molecular weight (\(M_w\)) and number-average molecular weight (\(M_n\))] of the polymers were determined with gel permeation chromatography (GPC). Thermal data was obtained with a DSC and TGA instruments.

Novel polymeric flexible, high refractive index systems of chemically cross-linked aromatic and sulphur containing aromatic based acrylate/methacrylate copolymer networks were developed and characterised. Glass moulds were designed and fabricated for polymerisation. Binary copolymer networks based on different compositions were
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synthesised by radical copolymerisation in bulk using bifunctional radical initiator like Luperox–256. Various divinyl monomers were used as cross-linkers.

The thermomechanical properties, refractive index, transparency, and surface wettability as well as cytotoxicity were systematically evaluated to mimic the in vivo situation by differential scanning calorimetry (DSC), tensile tester, Abbe refractometer, spectrophotometer, contact angle measurements, and MTT assay, respectively.

Photopolymerisation of 2-phenylethyl (meth)acrylates were carried out to estimate their kinetic parameters. Different compositions of photoinitiators were used to study the effect of concentration of photoinitiator on cure kinetics. These compositions obtained were tested for photo-curing performance using differential photocalorimetry (DPC) or photo DSC under polychromatic radiation. Rates of polymerisation as well as the percentage conversions were estimated. Other parameters such as induction time, maximum rate and conversion attained as well as the time to attain peak maximum were obtained.

Thermal free radical bulk polymerisation kinetics of 2-phenylethyl acrylate and 2-phenylethyl methacrylate monomers were carried out. Free radical bulk polymerisation kinetics of 2-phenylethyl (meth)acrylate were determined by differential scanning calorimetry in the non-isothermal mode. The polymerisation was investigated with varying ramp rate at different monomer to initiator concentrations. Kissinger and Ozawa methods were applied to determine the activation energy ($E_a$).