Chapter 1
Introduction

The uncontested and unparalleled importance of polymers made a drastic advancement in the field of polymer science during the past few decades. In order to meet the requirements of sophisticated applications, the production of new materials is always required. The term ‘new materials’ implies not only the newly synthesised materials but the modified form of existing ones also. The modified polymers have significantly superior properties than their homopolymer counterparts. This led to the introduction of polymer hybrids. Recent years have witnessed great developments in the field of polymer hybrids. Specific material requirements for specified applications prompted the development of these materials. They include polymer blends, polymer alloys, copolymers, IPN network etc. Blends and copolymers gained significance and a vast number of such materials have emerged for applications ranging from general purpose to high performance areas.

Factors which led to the greater significance of polyblends are their ease of preparation and the ease of getting a specific set of properties. Copolymers on the other hand, achieved importance owing to the fact that the specific set of properties is inherently built into the molecular structure of the polymers which is a single moiety.
1.1 Physical blends

Physical blends are mixtures of two or more polymers without any chemical bonding between them. This is the most versatile, inflexible and commercially important method for the production of polymer hybrids. Any two polymers can form a blend. It may be either two plastics, two elastomers or combinations of the two types.

The properties of physical blends strongly depend on the degree of compatibility of the components which in turn is related to the degree of phase separation that varies theoretically from zero to unity. In a strict sense, however, both theoretical limits may never be attained. Blends are divided into three classes based on the extent of versatility of the two components. They are miscible blends, compatible blends and incompatible blends.

1.1.1 Miscible blends

Truly miscible pairs of polymers are very rare. Such a system is characterised by homogenous phase morphology and transparency and exhibits properties intermediate to those of the components. The most familiar example is that of polystyrene and poly-2,6-dimethyl-1,4-phenylene oxide.

1.1.2 Compatible blends

Components having limited extent of miscibility form this type of blends. Owing to thermodynamic and kinetic factors the components exist as different phases with interfacial adhesion. Example of compatible blend is polystyrene and poly-o-methyl styrene.

1.1.3 Incompatible blends

This is characterised by the absence of any factor which leads to interfacial adhesion in the blend system. Examples of incompatible blends are 1) polymethyl methacrylate and
polymethyl acrylate, 2) polymethyl acrylate and polyethyl acrylate, 3) poly-o-methyl styrene and poly-m-methyl styrene.

For most pairs of polymers, molecular mixing is not favoured thermodynamically, since there is only little entropy gain on mixing, compared to the mixing of small molecules. Thus most blends are two-phase systems.

1.1.4 Polymer alloys

In general, polymer alloy is an alternate name for polymer blend. The term is sometimes used to refer to a blend of two miscible components. Now it is commonly used to refer to a compatible blend system with high extent of interfacial adhesion. This is achieved with the help of interfacial modifiers. An example is the blend formed from polystyrene and polyethylene in which polystyrene-b-hydrogenated butadiene is used as interfacial modifier.

The mechanical properties of these polymer systems depend on the interphase adhesion. The thermal properties are related to those of the component polymers.

1.2 Interpenetrating network polymers.

Interpenetrating network polymers are chemically homogenous (on a sufficiently large scale binary systems), which could be conveniently prepared by swelling first the loosely cross-linked component in a suitably chosen monomer and subsequently cross-linking the latter. This procedure of chemical blending offered the possibility to avoid the hazards of imminent phase separation which were present in physical blending of linear polymers, due to topological constraints (permanently entangled, chemically different macrocycles) on IPN unmixing.
IPN materials have been studied extensively on polymer alloys with synergistic physical properties of technological interest. The polyurethane with epoxy resin is the first reported simultaneous interpenetrating network (SIN).

1.3 Copolymers

The simultaneous polymerization of chemically different species yields copolymers. The properties of the resulting copolymers depend on the pattern of distribution of the different types of monomer molecules along the copolymer chain structure. Copolymers are classified into four groups according to the pattern of intermolecular distribution of like and unlike unit.

1.3.1 Alternating copolymers

In an alternating copolymer, the monomers alternate regularly along the chain, regardless of the composition of the monomer feed. An example is the alternating styrene–maleic anhydride copolymer. The highly selective addition of the monomers governed by the respective reactivity ratios. However, these copolymers are quite few in number.
1.3.2 Random copolymers

Random copolymers are characterised by a statistical placement of the monomer repeating units along the backbone of the chain. They are the most versatile, economical, and easily synthesised type of copolymers\(^4\). A typical example of this type is styrene-acrylonitrile copolymers (Scheme 2) formed by free radical initiation.

\[
\text{---CH₂-CH-CH₂-CH-CH₂-CH-CH₂-CH-CH₂-CH-CH₂-CH-CH₂---}
\]

\[
\begin{array}{cccc}
\text{Ph} & \text{Ph} & \text{CN} & \text{Ph} \\
\end{array}
\]

Scheme 2 Random styrene – acrylonitrile copolymer.

Random and alternating copolymers display properties representing a weighted average of the two repeating units. They exhibit single phase morphology, controllably reduced crystallinity and hence greater transparency. Another example is the set of copolymers formed from ethylene and propylene ranging from crystalline plastics to amorphous elastomers.

1.3.3 Graft copolymers

In a graft copolymer the sequence of one monomer is grafted on to a backbone of the second monomer (Scheme 3). The formation of an active site at a point on a polymer

\[
\begin{array}{cccc}
\text{A A A} & \text{A A A} & \text{A A A} \\
\text{B} & \text{B} & \text{B} \\
\text{B} & \text{B} & \text{B} \\
\end{array}
\]

Scheme 3 Graft copolymer architecture.
molecule other than its end, and exposure to a second monomer results in graft copolymerization. An important commercial example of graft copolymerization is the grafting of polystyrene or styrene-acrylonitrile copolymer onto polybutadiene or acrylonitrile-butadiene copolymer in the production of ABS resins. Another example is the NR-g-PMMA polymer. The methods for the production of polymer radicals are the initiation involving ultraviolet or ionising radiation or redox initiators.

Graft copolymers exhibit properties of each of the components than the resultant properties. They are characterised by single as well as two-phase morphology that occurs on a microscale rather than the macroscale dimension of the incompatible blends. Like incompatible physical blends, graft copolymers display two distinct glass transition temperatures. However, because of the presence of the inter-segment linkage, they display a finer morphology. As a result, an amorphous system free of homopolymers shows optical clarity. The component present in excess forms the continuous phase and have greater influence on the physical properties of the copolymer. The individual glass transition temperatures observed in graft copolymers support two-phase morphology and this makes the blending easier with their respective homopolymer. By virtue of this property they can be employed as interfacial emulsifying and compatibilising agents.

1.3.4 Block copolymers

Block copolymers are macromolecules that consist of chemically different monomer sequences. The monomer sequences are called the blocks. Block copolymers with two types of blocks are common (scheme 4) but with a third type of block is very rare. Some examples of block copolymers are styrene-b-butadiene, styrene-b-isoprene, polyurethane block copolymers, polyether-co-polyesters.
Graft and block copolymers possess similarity in their properties. Both of them exhibit properties characteristic of the components. This is the main advantage of these copolymers. Block copolymers have resemblance towards all other forms of copolymers, viz., graft, and random and even towards incompatible polymer blends. Block and graft copolymers are basically similar due to the presence of inter-segment linkages in both. They exhibit two-phase morphology, but this occurs on a microscale rather than the macroscale dimension of incompatible physical blends. The microscale morphology can be attributed to the influence of the inter-segment linkage, which restricts the extent of phase separation. The small domain size and the excellent interphase adhesion can produce a high degree of transparency and a good balance of mechanical properties which are characteristic of homogeneous copolymers.

The thermal properties of block and graft copolymers are similar to those of physical blends. They exhibit multiple thermal transitions such as glass transitions and or crystalline melting points characteristic of each of the components. But homogeneous random copolymers display a single, compositionally dependent glass transition temperature. Unlike random systems, where chain regularity is disrupted, crystallinity is possible in block and graft copolymers due to long sequences. The forthcoming section of this chapter deals with a detailed review of the block copolymers.
1.4 A review on block copolymers

The various aspects of block copolymers which commanded considerable academic and industrial importance are reviewed with special reference to structure-property relations existing in them.

The first reported academic work on block copolymers was that of Bolland and Melville in the year 1938. Their work was on polymethyl methacrylate and chloroprene. Melville in another work showed that the trapped free radicals in the polymethyl methacrylate can form a high molecular weight multiblock copolymer. In 1951 Lundsted studied low molecular weight triblock copolymers, where nonionic detergents based on polyethylene oxide and polypropylene oxide were used as the two types of blocks. These studies accelerated the rapid developments in the field of block copolymers during the succeeding decades. Bayer et al. reported in the early 1950s on (AB)n type polyurethane multiblock networks formed by linking polyesters and other prepolymer through diisocyanate links. Szwarc and co-workers synthesised polystyrene-b-polyoxyethylene copolymers by living anionic polymerization method. After this work the Strasbourg school investigated mesomorphic structures formed by block copolymers in a systematic manner using the technique of X-ray diffraction. Lyotropic mesophases formed by soaps were also being investigated at that time by X-ray diffraction and a connection between the two types of materials was quickly established, both forming similar structures. The anionic polymerization improved the field of block copolymerization markedly. For example, noteworthy invention of alkyl lithium initiators by Stavely and co-workers helped the synthesis of high cis-polydienes, in the preparation of block copolymers from styrene and butadiene as well as styrene and isoprene. In 1965, Shell brought on the market a number of polystyrene-b-polybutadiene-b-polystyrene and polystyrene-b-polyisoprene-b-polystyrene
copolymers. These ABA type copolymers show high tensile strength and rubber elasticity similar to vulcanized rubber, when they are in chemically uncross-linked state.

Legge et al. used styrene to modify the cold-flow rheology of alkyl lithium-initiated polybutadiene. A paper dealing with the structure-property relationships of these materials was presented at the International Rubber conference held in UK in 1967. The results presented at the conference stimulated many groups to enter the block copolymer field.

Hytrel is a new type block copolymer from polyesters and polyethers manufactured by Dupont in the year 1972. In the succeeding years other manufacturing companies developed products similar to Hytrel.

Another significant contribution in the field of block copolymers is the development of polyurethane block copolymers in which non polar segments are used as the soft blocks. The prominent advantage of these systems is the complete phase separation existing in them which helps in the studies of the structure-property relationship.

1.4.1 Architectural variation

Several structural variations are possible in the general category of block copolymers due to the arrangement of blocks along the copolymer chain. There are three basic architectural forms for the block copolymers. The simplest arrangement is (A-B) diblock architecture. The second form is the triblock or (A-B-A) and third is the multiblock copolymer (A-B)$_n$. These different forms are shown in Figure 1.1

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A blocks
/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\/~\ ~/B-blocs
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A-B architecture
Another but less common variation is the radial block copolymer. This structure takes the form of a star-shaped macromolecule in which three or more diblock sequences radiate from a central hub (Figure 1.2).
1.4.2 Synthetic methods

The block copolymers can be prepared by several methods. They are generally categorised into living addition polymerization and step-growth (condensation) polymerization. Living polymerization techniques can be used to achieve all three types of block copolymer architecture \([A-B, A-B-A, (A-B)_n]\). On the other hand the step growth process yields \((A-B)_n\) architecture with the advantage of a much wider selection of polymeric types.

1.4.2.1 Living polymerization (sequential addition process)

By far the most important synthetic method of block copolymers is the anionic polymerization. In this method the first step is to produce an exhausted monomer. Addition of a second monomer to this living polymer leads to a block copolymer uncontaminated with homopolymer and with blocks of accurately known and controlled length. These are the essential requirements of a polymer with certain anticipated properties.

The best example of a well-defined block copolymer synthesised by anionic living technique is the alkyl lithium initiated polymerization of styrene and butadiene\(^{17}\). This technique is carried out by the polymerization of styrene followed by the sequential addition and polymerization of butadiene as in Scheme 7.

**Initiation**

\[
R\text{Li} \rightarrow CH_2 = CH \quad \rightarrow \quad R - CH_2 - CH\text{Li}^+ 
\]
First propagation

\[
R - CH_2 - \overline{CH} - Li^+ \quad CH_2 = CH \quad R \left\{ CH_2 - CH \right\}_{a-1} CH_2 - \overline{CH} - Li^+ 
\]

Cross initiation

\[
R \left\{ CH_2 - CH \right\}_{a-1} CH_2 - \overline{CH} - Li^+ + CH_2 = CH - CH = CH - CH_2
\]

\[
\rightarrow R \left\{ CH_2 - CH \right\}_a CH_2 - CH = CH - \overline{CH}_2 \quad Li^+
\]

Second propagation

\[
R \left\{ CH_2 - CH \right\}_a \left( CH_2 - CH = CH - CH_2 \right)_b CH_2 - CH = CH - \overline{CH}_2 \quad Li^+
\]
\[
\left( \text{CH}_2 - \text{CH}_3 \right)_a \left( \text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 \right)_b \text{CH}_2 - \text{CH} = \text{C} \text{H}_2 \text{ Li}^+
\]

Scheme 5  Alkyl lithium initiated polymerization of styrene and butadiene.

Absence of termination reaction has several advantages. The block length can be controlled by merely controlling monomer initiator ratio. Another advantage is the ability to achieve a very high degree of monodispersity. If initiation is rapid compared to propagation, \( \frac{M_w}{M_n} \) approaching unity can be achieved.

Anionic living polymerization techniques can also be applied to both olefinic and heterocyclic monomers such as acrylcs, vinyl pyridines, siloxanes, lactones, epi sulphides and epoxides. However, these systems generally produce block copolymers with a less ideal structure due to a greater susceptibility to terminating side reactions.

1.4.2.2 Step-growth polymerization (Interactions of functionally terminated oligomers)

In this method of block copolymer synthesis, only the inter-segment linkage is formed during the block copolymerization. When oligomers bearing mutually reactive end groups are used, a perfectly alternating sequence distribution is obtained, (Scheme 6).

\[
X \quad \quad \quad X + Y \quad \longrightarrow \quad Y
\]

\[
\downarrow
\]

\[
\left( \quad / \quad \longrightarrow \right)_n + X Y
\]

Scheme 6
This technique is used for the synthesis of polysulfone-polydimethyl siloxane block copolymers\textsuperscript{18}. The polydispersity of the block copolymer is a function of both the oligomer forming and block copolymer forming reactions.

When two oligomers with the same functional end group are coupled via reaction with a third component, a block copolymer with less control of segment sequence is obtained. An example of this type is the coupling of hydroxyl terminated polyethylene oxide and hydroxyl terminated liquid natural rubber by toluene diisocynate\textsuperscript{19}. If the reactivity of both oligomers are similar towards the coupling agent, their arrangement in block copolymer molecule would be in a statistical or random fashion (Scheme 7).

\[
\begin{align*}
X & \quad X + X \quad \text{X} + \text{Y R Y} \\
\text{[} & \quad \text{[} \quad \text{[} \quad \text{[} \quad \text{[} \quad \text{[} \\
\text{X} & \quad \text{Y} \quad \text{R} \quad \text{Y} \quad \text{]} \quad \text{]} \quad \text{]} \quad \text{]} \quad \text{]} \quad \text{]} \\
\end{align*}
\]

\textbf{Scheme 7}

In the alternating systems, chemical composition is directly proportional to the oligomer molecular weight and hence equimolar quantities of the functional oligomers are required in order to fulfil stoichiometric requirements. But in statistically coupled systems any combination of the two oligomers can be stochiometrically satisfied by the use of appropriate quantity of coupling agent and hence these systems have the advantage that compositions can be easily controlled.
1.4.2.3 Polymer growth from oligomer end groups

This technique is a combination of the two methods already described. In general, this route allows the possibility of bulk polymerization and so this is more economical than the oligomer-oligomer approach. Bulk polymerization is not normally possible with the oligomer-oligomer process due to the phenomenon of polymer-polymer incompatibility. Solution polymerization of block copolymer containing both amorphous and crystalline segments is difficult to achieve by the oligomer-oligomer process due to the insolubility of the crystalline segment. This can be achieved by the growth of the crystallising polymer initiated by the end group of a preferred soluble oligomer.

All the three block copolymer architectural types can be synthesised by the oligomer monomer approach. The reaction of addition or ring opening monomers with monofunctional oligomers produces A-B structure (Scheme 8) while difunctional oligomers produce A-B-A structure (Scheme 9).

![Scheme 8](image1)

**Scheme 8**

![Scheme 9](image2)

**Scheme 9**
Under conditions of perfect stoichiometry, step-growth monomers can interact with monofunctional and difunctional oligomers to produce principally A-B-A and \( (A-B)_n \) structures respectively (Scheme 10).

![Scheme 10](#)

**1.4.3 Morphology of block copolymers**

Block copolymers possess complex morphological structures due to the assembling of segments. Assembling of like segments leads to phase separation. The major component will exist as the continuous phase and forms the matrix and the phase which is present in low proportion forms the domains. The core factor for domain formation is the incompatibility of the two segment types. When the segments are compatible due to structural and compositional similarity, miscibility of the phases occurs resulting in a single phase morphology.

The major factor which determines the compatibility of the segment types is their chemical dissimilarity. This can be measured in terms of the differential solubility
parameter difference $\Delta = (\delta A - \delta B)$. The value of $\Delta$ and extent of phase separation are directly proportional. As the value of $\Delta$ increases, greater is the possibility of phase separation. The additional factors which affect the degree of micro phase separation are the segment length, crystallisability of either segment, compositional heterogeneity of the segments, hydrogen bonding and the method of sample processing. The segment segregation is affected by the molecular weight of the block copolymer and mainly that of soft segments$^{20,21}$. Thus a low molecular weight block copolymer will display two-phase behaviour only if the $\Delta$ value is relatively large, whereas two high molecular weight segments can produce two-phase systems even when $\Delta$ value is small. This assessment is mainly applicable to amorphous systems. The phase separation is also improved by the crystalline nature of one or both segments. In this case phase separation will occur even when the blocks are chemically similar and the block molecular weight is low. The various intramolecular interactions influence the morphological structures of block copolymers, both the short range and long range supermolecular structures and determine the end use properties. The morphology strongly depends also upon the casting solvent. The segment least soluble in a particular solvent will tend to precipitate out first. These segments form discrete domains that become dispersed in the continuous matrix of the other component. The morphology can be inverted simply by choosing a casting solvent that is preferred for the other component.

Spheres, cylinders and lamellae are the three general morphological structural components. The minor components assume spherical shapes at very low volume fraction, e.g., $\sim 30\%$ of the total volume and cylindrical shape at some what higher level. When the two segments are present in nearly equivalent volume fraction, they can exist in co-continuous phases with lamellar structures.
1.4.4 Commercial importance of block copolymers

Block copolymers of commercial importance are classified into three types. They are toughened plastics, thermoplastic elastomers and surfactants. Toughened plastics or rigid block copolymers consist either of two hard segments or one hard segment together with a minor fraction of a soft segment. The mechanical properties such as creep or stress relaxation can be improved by the copolymerization of two hard segments. The inherent flexibility of the segments is retained due to the fine dispersion of the phases. Toughness of an inherently rigid polymer can be improved by block copolymerization with a soft segment.

Figure 1.3  Morphological variation of block copolymer as a function of composition: (a) lower, (b) equivalent, (c) higher volume fractions of hard segments.
The best example of the above is the Philips K resin\textsuperscript{22,23} which is a radial block copolymer of styrene and butadiene containing 75 weight % of polystyrene. The second example is the polyallomers of Eastman\textsuperscript{24}.

Block copolymers of elastomeric types contain soft segment as the major component. They display A-B-A or (A-B)$_n$ architecture. They have the mechanical properties of cross-linked rubber with the processing characteristics of linear thermoplastic polymers. So the block copolymers which exhibit the behaviour of both thermoplastics and elastomers are known as thermoplastic elastomers. The best examples of this type are the polyurethane elastomers and styrene-butadiene block copolymers.

Surfactants, the third category of block copolymers were formed by segments of different activities towards water. One segment is hydrophobic and the other is hydrophilic. The pluronics of Wyandotte\textsuperscript{25} are examples of surfactants and are very useful as emulsifiers of aqueous and non aqueous components. A second type of surfactant is the silicone-alkylene oxide block copolymers, mainly used as polyurethane foam stabilisers. Another class of biologically important block copolymers is hydrophobic and hyrophilic polyurethanes and they are characterised by their selectivity in absorbing oily lipids (e.g., cholesterol).

W. Marconi et al.\textsuperscript{26} synthesised polymers containing both hydrophobic and hydrophilic group (consisting of long alkyl chain) in the monomeric unit. These type of biocompatible polymers have uses in surface grafting of molecules possessing an anticoagulant activity such as heparin, albumin, platelet antiaggregants or prostaglandins.

Among the three classes of block copolymers described above thermoplastic elastomers have gained greater significance due to wide range of commercial applications. The prominent outcome of block copolymer technology is the development of thermoplastic
elastomers. Hence it is worth discussing them in detail. The following sections deal with various aspects of these materials.

### 1.5 Thermoplastic elastomers (TPE)

Thermoplastic elastomers are materials which possess, at normal temperatures, the characteristic resilience and recovery from extension of cross-linked elastomers but which exhibit plastic flow at elevated temperatures and can be fabricated by the usual techniques applied to thermoplastics.

The thermoplastic elastomers are similar to linear polymers containing segments which give rise to interchain attraction. These interactions are susceptible to temperature. At ambient temperature these interactions have the effects of conventional covalent cross-links and confer elasticity but at elevated temperatures the secondary forces are inoperative and the material shows thermoplastic behaviour. So the key requirement for this behaviour is the ability to develop two intermingled polymeric systems, each with its own phase and softening temperature. The system is composed of minor fraction of a hard block and major fraction of a soft block arranged in A-B-A or (A-B)$_n$ structural forms. The hard phase thus anchors the chains of the soft phase and the material is elastomeric.

The diblock copolymer does not show the elastomeric property. It rather behaves as unvulcanized rubber. This is caused by the fact that one end of the copolymer chain bears the soft segment which remains as a loose end. The glass transition temperature of the hard phase is above room temperature and that of soft phase is below room temperature. At temperatures above the softening temperature of the hard phase, the restrictions imposed by the hard phase disappear and the material behaves as a liquid. On cooling, the hard phase resolidifies and the material recaptures its elastomeric properties. The hard domains serve as
physical cross-linking and reinforcement sites which provide strength to the material. The reinforcement is possible due to small, uniform and discrete nature of the hard segments and the chemical linkages between the segments as it provides maximum interface adhesion.

1.5.1 Commercial grade thermoplastic elastomers

Thermoplastic elastomers of commercial interest are mainly of three types. (i) Styrene-based thermoplastic elastomers such as the styrene-diene A-B-A triblock and radial block copolymers and their hydrogenated derivatives. Examples are the Kraton of Shell chemical Co.\textsuperscript{27,28} and Solprene of Phillips Petroleum Co.\textsuperscript{29} (ii) Ester-Ether (A-B)\textsubscript{n} block copolymers. Example is the Hytrel of Dupont Co.\textsuperscript{30,31} (iii) Polyurethane (A-B)\textsubscript{n} block copolymers. Examples are the Estanes of BF Goodrich Co.\textsuperscript{32} and Texins of Mobay Co.\textsuperscript{33}.

1.5.1.1 Styrene-based block copolymers

One of the essential components of these type of copolymers is polystyrene. The second segment may be either polybutadiene, polyisoprene, or an alkenyl aromatic polymer.

In 1961, the triblock copolymers of styrene and butadiene/isoprene were first synthesised at the Synthetic Rubber Research Laboratory of Shell Chemicals\textsuperscript{34,35}. These block copolymers were marked by their very high tensile strength, ultimate elongation and resilience. The development of triblock TPE opened new markets for elastomeric products such as injection moulded shoe soles. The economical importance of injection moulded TPE makes it more advantageous than thermoset rubbers. Another application of triblock TPE is as solvent-based adhesives.

Solprene\textsuperscript{29} is a radial block copolymer of styrene and butadiene produced by Phillips Petroleum Company. Polymerization of styrene is initiated by alkyl lithium initiators in the
first stage of formation of Solprene. This is followed by the addition of butadiene to form a midblock and then linking with a multifunctional linking agent to form a radial block copolymer.

Among the same molecular weight triblock copolymers, the linear block copolymers have higher melt and solution viscosities. The radial styrene-diene block copolymers such as the \((S-B)_{4}X\) and the linear \((S-B-S)\) triblock copolymers are examples of the above type. These radial copolymers were reported\(^{36-38}\) to be more desirable on adhesive applications than those of the linear \(S-B-S\) types. With the same triene/diene ratio, the linear block copolymers have significantly higher ultimate tensile strength and higher elongation at break than radial block copolymers\(^{39}\).

1.5.1.2 Polyether-ester

The multiblock copolymers of this type are composed of polyether segments such as polyethylene oxide or polysulphone and polyester segments such as polyethylene terephthalate, polyethylene adipate and polycaprolactone.

W.K. Witsiepe\(^{40}\) of Dupont studied the copolyesters derived from terephthalic acid, tetramethylene glycol and polytetramethylene oxide glycol. In 1972 Dupont marketed a new TPE, Hytrel\(^{16}\), from the investigation of W.K. Witsiepe. Hytrel is a randomly segmented copolymer containing polytetramethylene oxide soft segments and multiple tetramethylene terephthalate hard segments. Another copolymer of the Hytrel-type is the Pelprene\(^{16}\) of Toyoba, Japan. The copolyesters are characterised by their good melt flow properties, melt stability, low mould shrinkage and rapid crystallisation rate. They exhibit high strength, resilience and resistance to flex, fatigue and impact\(^{41,42}\). The polyether soft blocks provide
the flexibility due to their low glass transition temperatures, and the polyester hard blocks provide the physical cross-linking due to their crystallisation.

1.5.1.3 Polyurethane block copolymers.

The first commercial PU product was developed by Bayer and Associates in the late 1930s at I.G. Farben Industrie. It was based on 1,6-hexane diisocyanate and 1,4-butane diol and exhibited polyamide-type properties. As Perlon U, they gained temporary importance in the manufacture of bristles. Idamid U was the trade name for the corresponding injection moulded grades. Later this field has developed greatly and a diverse and versatile group of economically important polymers which consists of foams, rigid or semi-rigid solids, films, elastomers, adhesives and thermoplastics has emerged.

A major breakthrough in the field of polyurethane products occurred when the first polyurethane elastomer was developed by Prof. Otto Bayer with polyester of adipic acid $\overline{M_n}$ (2000), naphthalene diisocyanate and ethylene glycol. Their market expanded when these polymers were introduced in the 1950’s by Shollen Berger et al. The progress in this field of polyurethane elastomers is so great that now the term is almost synonymous with polyurethane block copolymers. Solid polyurethane elastomers can be divided into three main categories. They are cast, millable and polyurethane thermoplastic elastomers.

(i) Cast elastomers

Cast elastomers are prepared by casting technique, the technique in which a liquid reaction mixture comprising of low molecular weight material is poured into a heated mould, wherein, the material is converted into a solid of high molecular weight elastomeric product. Elastomers of this kind are slightly branched. The cast polyurethane elastomers are generally characterised by high tensile strength, abrasion resistance and tear strength.
Polyethylene adipate and toluene diisocyanate-based cast elastomers are extensively used in making printing rollers.

(ii) **Millable elastomers**

These are elastomers to which the conventional techniques of mill compounding and vulcanization can be applied. Examples of this type are the polyurethane elastomers made from stable polyesters (commonly adipates) or polyethers commonly polyoxytetramethylene glycol with diisocyanates. Another distinct feature of them is their outstanding resistance towards aliphatic hydrocarbon fuel oils, oxygen and ozone. Because of these advantageous properties they have also been used as solid tyres and bearings. These are extensively used for making printing rollers.

(iii) **Polyurethane thermoplastic elastomers**

They are segmented block copolymers of the type (A-B)<sub>n</sub> with an intermittent arrangement of hard and soft blocks. The two-phase structure of a block copolyurethane consists of soft segment usually an oligomeric polyol and hard segment formed from diisocyanate and a simple diol. The soft segment as its name implies is soft, extensible rubber at ambient and has a glass transition temperature (T<sub>g</sub>) below ambient. The hard segment is usually crystalline or glassy material. The glass transition temperature or crystalline melting point of these segments is significantly above ambient.

The soft segment generally used is a polyether or polyester of molecular weight (M<sub>n</sub>) between 1000 and 5000 possessing a glass transition temperature (T<sub>g</sub>) well below ambient temperature. Examples are polytetramethylene oxide and polybutylene adipate. Hard segments are generally formed by the reaction of diisocyanate such as diphenyl methane diisocyanate (MDI) or toluene diisocyanate (TDI) with low molecular weight diol.
such as 1,4-butanediol, propylene glycol etc. or diamine such as ethylene diamine. The diamine gives polyureas.

The properties of the polyurethane elastomers can be tailored as desired according to the applications. The elastic or rigid nature of the material is related to its chemical constituents. A desired product can be obtained by simply varying them. Rigid foam is formed if the diisocyanate/polyol mixture is highly cross-linked, whereas flexible foam is obtained for a lightly cross-linked system. Usually linear polyethers are used for thermoplastic elastomers while slightly branched for flexible form and highly branched for rigid foams manufacture. The isocyanate usually used for thermoplastic elastomers is diphenyl methane diisocyanate.

a. Synthesis of polyurethane elastomers

The synthesis of copolyurethanes is generally carried out by two methods. They are one-shot and two-shot processes.

One-shot method

In the one-shot process, the chain extender diol and oligomeric polyol are blended and reacted simultaneously with all of the diisocyanate. It leads to a more polydisperse block copolymer.

Two-shot method

The two-shot process involves first the reaction between polyol and diisocyanate followed by the chain extension with a simple diol or diamine. Schematic representation of polyurethane block copolymer is shown in Scheme 11.
Scheme 11 Schematic representation of polyurethane block copolymer.

The synthesis can be carried out in bulk or solution. The diol–diisocyanate reaction is catalysed by tertiary amines or organotin compounds.

In general copolyurethanes formed from one-shot process, compared to two-shot process, possess hard segments of longer sequence length, although their distribution is broader. The important polyols used for the preparations are polytetramethylene oxide (polytetrahydrofuran), polypropylene oxide, polyester polyols such as poly-1,4-butylene adipate and poly-1,4-butylene terephthalate.

b. Properties

Phase separation and domain formation were observed in both the cases. The polytetramethylene oxide soft segment and hard segment based on MDI and butane diol have got very good tensile strength, modulus, tear strength, toughness, very excellent abrasion resistance and high melting transition. Polyester-based polyols have some
disadvantage over polyether-based polyols due to their high rate of moisture absorption and poor hydrolitic stability.

c. **Morphological features of block copolyurethanes**

Segmented copolyurethanes have complex microstructures and morphological features and therefore their study is very important. The hard and soft block composition and the processing details have direct influence on microstructure of these types of materials. The mechanical properties of segmented copolyurethanes depend strongly on micromorphology which is determined by the nature and extent of phase separation. Several authors46-49 have studied the structure-property relations and morphology of copolyurethanes.

Two incompatible segments always result in phase separation. The interurethane hydrogen bonds in polyurethane increase phase separation further. Shollenberger and coworkers50 first proposed the concept of hydrogen bonding of polyurethanes to explain high tensile strength. Cooper and Tobolsky51 studied the viscoelastic response of selected polyurethanes with that of other polymers. The above study together with the detection of more than oneTg led to the conclusion that two phases existed in the polyurethanes.

The phase separation results in aggregation of hard domains into extensively hydrogen bonded rigid domains (Figure 1.4). The hard segment domain size, cohesive strength of domains and their ability to orient during copolymerization are the factors affecting the nature of microstructure, which is responsible for materials properties at a given hard segment content.
Figure 1.4 Schematic morphology of polyurethane thermoplastic elastomer.

Hard segments have powerful effect on morphologies and physical properties. The effect of diisocyanate structure on the physical properties and morphologies has been studied by several authors. The copolyurethanes based on MDI in comparison with TDI show a higher extent of phase separation between the segments. This is due to the perfectly ordered domains of polyurethanes based on MDI. Bonart et al. studied the phase separation of polyether versus polyester urethanes and polyurethanes differing only in the length of the aliphatic chain extender. They calculated a number of parameters such as phase boundary diffuseness, width of diffuse transition zones, domain size, specific internal surface area and fraction of sharp boundaries.
Harell investigated polyurethanes based on piperazine. Even though these types of polymers are incapable of forming hydrogen bonds they still exhibit phase segregation and desirable mechanical properties.

The aromatic hard segments and aliphatic soft segments are thermodynamically incompatible. This incompatibility increases the phase separation. Li et al. investigated a series of polyurethanes from aliphatic and aromatic hard segments. They obtained results in contrast to thermodynamic viewpoint, but is valid from a kinetic viewpoint. Due to the increased mobility of aliphatic hard segment, the phase separation becomes more complete.

The extensively studied polyurethane series is that of polyether/MDI/BDO systems. The microstructure of these block copolymers is generally divided into three categories. They are globules spherulites and fibrils depending on the proportion of hard segments. Hard segment content and its miscibility have strong influence on the microstructure.

Gengchao et al. have synthesised a series of polyurethanes from a system consisting of ethylene oxide-endcapped polypropylene oxide polyol, MDI and ethylene glycol by one-shot process. The morphology of these copolyurethanes has been investigated by a variety of techniques. Hard segment rich spherulites with sizes 10 μm in diameter consisting of fibrils, have been observed. The melting point of these spherulites lies in the range 220-260°C. The degree of microphase separation and the crystallinity of polyurethanes increase with increase in hard segment content. The percentage of hard segment is in the range of 11 to 47.

The morphology of segmented copolyurethanes was studied using electron microscopy by J. Foks et al. The polymers were prepared by prepolymer method from polyethylene adipate, 4,4′-diphenyl methane diisocyanate and 1,4-butane diol. Unstained
samples show the presence of spherulites with radially distributed fibrillar elements. Suitable staining of the sample enables observation of lamellae. The studies revealed that hard segment lengths vary greatly from one another in PU investigated and that they differ considerably from the stoichiometry of the raw materials. The morphology and thermal properties of polyester copolyurethanes were investigated under different casting conditions. Authors arrived at the conclusion that the final morphology is very complicated and strongly depends on the temperature of the prepolymer and the mould. The size and melting point of spherulite was related to the temperature of the mould.

Schneider and Rustard have conducted studies on polyether and polyester-based series with 1000 and 2000 polyl molecular weight. They obtained better phase separated product with polyether-based series of 2000 molecular weight. The molecular weight of the polyl influence & phase separation. If the molecular weight of the polyl is below 1000, phase mixing is possible and for a molecular weight above 2000 phase separation is more or less complete.

The microphase structure and microphase separation kinetics of the segmented copolyurethanes was studied by Chu et al. The hard segment moiety was obtained from MDI and 1,4-BDO and the soft segments were polytetramethylene oxide and polypropylene oxide endcapped with polyethylene oxide. The result indicates that the extent of phase separation is more in PTMO-based samples even though PTMO and PPO-PEO have identical solubility parameters. The phase separation behaviour is explained by the kinetic factor. A single relaxation process is observed for the PTMO–based sample and a double relaxation time process in PPO–PEO-based samples.

Chee and Farris studied the phase separation in segmented copolyurethanes and obtained the result that it obeys first order kinetics. The mechanism involves two elementary
steps which can be characterised by two discrete relaxation times. The polyether-based polyurethanes recover their original domain structure faster than a polyester-soft segment material. The activation energy obtained for the demixing of polyether polyurethanes is found to be about 23 KJ mol\(^{-1}\) and is not influenced by hydrogen bonding.

d. Effect of hard segment on the properties of polyurethane elastomers

The effect of hard segment content on the physical, mechanical, thermal and dynamic-mechanical properties of a series of polyether-based thermoplastic polyurethanes have been studied by Zdrahala et al.\(^8\) A two-phase morphology was prominent within the limit of the hard segment concentration studied. As the hard segment content increases, the hardness, tensile strength, tear strength and flexural modulii increase. Inversion or mixing of the hard and soft segments was observed at 60 weight percentage of hard segment. Thus hard segment content alters the nature of the copolyurethane from a tough elastomer to a more brittle high modulus plastics.

Harris et al.\(^9\) studied the effects of variation of MDI/1,4-BDO-based hard segment content on the properties of polyurethane elastomers, while holding the polyethylene-ether-carbonate diol soft segment and block size constant. The properties such as rubber plateau modulus, solvent resistance, melting point, hardness, and tensile strength all improve with increasing hard segment content. Impact properties suffer at the highest hard segment concentration (60 and 65.2 wt %), DMA and DSC data indicate a partially phase-mixed morphology. However, phase mixing must occur at domain boundaries since the soft segment Tg is nearly invariant with hard segment content. The polyethylene-ether-carbonate diol blocks show a high compatibility with any amorphous hard segment blocks present.
The mechanical properties of polyether urethanes were studied by Wang and Cooper. They observed that it depends primarily upon the hard segment content of the sample. The interchain hard domain hydrogen bonding leads to strong hard domain cohesion. At a lower hard segment content, the morphology changes from interconnected to isolated hard domains.

Wilkes et al. investigated the structure-property relations in segmented polyether-polyurethanes based on polytetramethylene oxide, MDI and 1,4-BDO. The phase separation is related to hard segment level. Increase in hard segment content results in microcrystallinity, phase inversion and domain continuity. Thermal treatment favours phase mixing due to the domain disruption. The recovery of structure is a time-dependent phenomenon. The samples with microcrystalline domain structure recover faster than others.

The effect of hard segment content on morphology of a series of segmented polyurethanes synthesised from polyethylene adipate glycol soft segment and a hard segment derived from MDI and BDO has been investigated by electron and optical microscopy. With increase in hard segment content, changes in morphology have been observed. The number of grain aggregates at the fracture surface of the sample is directly proportional to the hard segment content. The copolyurethanes with hard segment content of 22% are not crystalline and have no grain aggregate on the fracture surface. The polymers with hard segment content above 50% are anisotropic. Those with 32-50% hard segment have two types of grain aggregates dispersed in spherulite-like matrix.

Wang et al. studied the effect of hard segment on morphology and properties of thermoplastic polyurethanes. The degree of phase mixing, hardness and strength increase with an increase in hard segment content.
6. **Effect of chain extenders**

The effect of different chain extenders on the morphology and properties was described by Wang et al.\textsuperscript{53} and Bonart et al.\textsuperscript{85}. Diols and diamines are the most commonly employed chain extenders in block copolymer preparation. Extension with diols leads to polyurethane and diamine to polyurea formation. Diamine extended materials usually possesses a higher level of physical properties due to the strong hydrogen bonded interaction of the urea groups. The effect of diol chain extenders was studied by Wang et al.\textsuperscript{53} using 1,4-butane diol, 1,5-pentane diol and 1,3-butane diol. The soft segment was polytetramethylene oxide of molecular weight $\langle$Mn$\rangle$2000. The tensile strength and Young's modulus increased, while elongation at break decreased when the chain extender changed from 1,3-butane diol to 1,5-pentanediol and to 1,4-butane diol.

Blackwell et al.\textsuperscript{96} investigated the effect of chain extender length on the structure of MDI-based copolyurethanes. It is found that for butane diol to octane diol chain extenders the structure depends on the number of CH\textsubscript{2} groups in the diol. The diols with even number of CH\textsubscript{2} groups have fully extended conformation that allows hydrogen bonding which is not possible for odd diol-containing polymers. The even diol polymers have higher crystalline order than odd diol-bearing polymers. The lower members of the series, i.e., ethylene glycol and propylene glycol are exceptions to the above behaviour and adopt contracted unstaggered structures. These low diols are so short that they cannot permit packing of the MDI units in the same way as for longer chain extenders.

Polyether copolyurethanes based on polypropylene glycol, MDI and different extenders such as 1,5-pentane diol(P), diethylene glycol(D), triethylene glycol(T) and 1,3-bis(N,N\textsuperscript{1} -methyl-N,N\textsuperscript{1}-2-hydroxyethyl) isophthalamide (BIM) were synthesised by Hong et al.\textsuperscript{49}. The hard segment crystallinity varies in the order extended polymer. Besides
crystallinity, the other factors which control phase separation are chain length and flexibility and aromatic content of the applied chain extender.

Mevlida et al. studied the effect of chemical structure of chain extenders and hard segment content on the properties of polymers. Elastomers from symmetrical and rigid difunctional chain extenders have better mechanical and physical properties than cross-linked elastomers.

The influence of chain extender length on copolymer properties was investigated by Pandya et al. The Tg of the polyurethane–based on the homologous series of α,ω-saturated diols decreases from lower to higher members, ie., Tg of hexane diol is lower than that of ethane diol. Tg is found to increases from butane diol to butyne diol extended polymers, ie., unsaturation in the chain extender increases Tg.

f. **Effect of diisocyanate.**

The diisocyanate used for the synthesis has prominent influence on properties of polyurethanes. Although most widely used, the aromatic diisocyanates lead to polyurethanes which turn yellow on exposure to the UV light. These defects can be rectified by using diisocyanates in which the NCO groups are aliphatic or not attached directly to an aromatic nucleus such as hexamethylene diisocyanate (HDI), 4,4′-dicyclohexylmethane diisocyanate (based on the mixed stereoisomers obtained on hydrogenation of 4,4-diaminodiphenyl methane), 70:30 meta/paraxyylene diisocyanate and 2,2,4-trimethyl-1,6-hexamethylene diisocyanate.

Wang et al. studied the properties of MDI and H₁₂MDI-based series of copolyurethanes. In their study they observed that MDI-based copolyurethanes have a higher
soft segment $T_g$, a higher hard segment softening temperature, a higher tensile strength and Young's modulus in comparison with $H_{12}$MDI-based materials.

Pandya et al.\textsuperscript{88} studied the influence of diisocyanate on the thermal stability of materials. Their result shows that the thermal stability varies in the order MDI > TDI > IPDI > HDI > TMDI. The tensile strength of MDI-based polyurethanes is higher than others. The influence of the diisocyanate structure on domain size and properties with two series of polyurethane block copolymers was studied by Shneider et al.\textsuperscript{89} The isocyanates used were isomers of TDI, i.e., 2,4-TDI and 2,6-TDI. The polyurethanes based on 2,4-TDI series are transparent and amorphous and the properties varied progressively with urethane concentration, whereas the 2,6-TDI series is opaque, semicrystalline and hard but tough. In 2,4-TDI series $T_g$ is a strong function of urethane concentration indicating extensive phase mixing but in 2,6-TDI series, $T_g$ is generally independent of urethane concentration and the domains are highly ordered and therefore phase mixing is minimum.

When polyurethanes are produced in the presence of excess diisocyanate in a two-step process, extensive allophanate linkages are formed\textsuperscript{90}, (Scheme 8).

\begin{center}
\begin{tikzpicture}
    \node at (0,0) [left] {HN\textsuperscript{=}};
    \node at (1,0) [right] {CH\textsubscript{2}};
    \node at (2,0) [right] {NH\textsuperscript{-}};
    \node at (3,0) [right] {CO\textsuperscript{=}};
    \node at (4,0) [right] {NCO\textsuperscript{-}};
    \node at (0.25,0.5) [right] {NCO\textsuperscript{-}};
    \node at (0.5,0.5) [right] {NCO\textsuperscript{-}};
    \node at (0.75,0.5) [right] {NCO\textsuperscript{-}};
    \node at (1,0.75) [right] {NCO\textsuperscript{-}};
    \node at (1.25,0.75) [right] {NCO\textsuperscript{-}};
    \node at (1.5,0.75) [right] {NCO\textsuperscript{-}};
    \node at (1.75,0.75) [right] {NCO\textsuperscript{-}};
    \node at (2,0.75) [right] {NCO\textsuperscript{-}};
    \node at (2.25,0.75) [right] {NCO\textsuperscript{-}};
    \node at (2.5,0.75) [right] {NCO\textsuperscript{-}};
    \node at (2.75,0.75) [right] {NCO\textsuperscript{-}};
    \node at (3,0.75) [right] {NCO\textsuperscript{-}};
    \node at (3.25,0.75) [right] {NCO\textsuperscript{-}};
    \node at (3.5,0.75) [right] {NCO\textsuperscript{-}};
    \node at (3.75,0.75) [right] {NCO\textsuperscript{-}};
    \node at (4,0.75) [right] {NCO\textsuperscript{-}};
\end{tikzpicture}
\end{center}

\textit{Scheme 8}
The allophanate linkages lead to the formation of branched or cross-linked products. The gelation in polyurethanes with excess isocyanate has been described by M. Spirkova et al. and D. Karel.

G. Spathis et al. studied the morphological changes induced in the segmented polyurethane elastomers by varying the NCO/OH ratio during the second step of polymerization, while keeping constant total hard segment content at 30%, by means of FTIR, DSC and thermally stimulated depolarization current method (TSDC). The DSC results gave evidence for the existence of phase separation in thermoplastic polyurethanes and a homogeneous network in elastomeric ones. The FTIR measurements were used to detect the strength of hydrogen bonds and hence phase separation. An attempt was also made to study the influence of ester and urethane carbonyls on hydrogen bonding by FTIR. The TSDC results gave relaxation mechanism that is due to interfacial polarisation, providing evidence of the existence of one interfacial phase. The introduced secondary chemical cross-links were found to affect mainly the irregularly packed hard domains and to form a more homogeneous network at higher value of the NCO/OH ratio.

Y.M. Song et al. have investigated the effect of isocyanate on the crystallinity and thermal stability of polyurethanes synthesised from polyester diol with three different diisocyanates, i.e., MDI, m-xylene diisocyanate (XDI) and TDI. They have observed that the hard segment crystallinity decreases in the order MDI > XDI > TDI and thermal stability decreases in the order XDI > MDI > TDI. The copolyurethanes from MDI have higher thermal stability than polyurethanes from TDI because of their higher degree of hard segment crystallinity.

Chen and Chan have studied the structure-property relationships of copolyurethane cationomers prepared using polytetramethylene oxide and N-methyl-diethanolamine as
chain extender. The diisocyanates used are MDI, hexamethylene diisocyanate (HDI) and TDI. The level of order in the synthesised polyurethanes fall in the sequence HDI > MDI > TDI.

Chen and Chan\textsuperscript{96} have investigated the effect of phase inversion on physical properties. MDI, HDI and TDI are the diisocyanates used for the preparation of polyether-copolyurethane cationomers. The phase inversion mechanism depends on the structure of the hard segment, ionic content and dispersion temperature. The dispersion process can be divided into three steps involving separation of hard segments, entering water into disordered and then ordered hard segments and finally formation of microspheres. The dispersion can disrupt the order in hard domains leading to an increased phase separation for the MDI system and to a slightly increased phase mixing for the HDI and TDI systems.

g. Effect of hydrogen bonding

Fu Cai Wang et al.\textsuperscript{97} have investigated the influence of temperature on hydrogen bonding in amorphous linear aromatic copolyurethanes by FTIR. Hydrogen bonding was checked in the N-H stretching (3347 cm\textsuperscript{-1}) and the bending (1535 cm\textsuperscript{-1}) regions, using the bond decomposition technique. The ratio of the absorptivity coefficients for the hydrogen-bonded N-H to the free N-H vibrations is used to study the influence of temperature. This ratio is found to be independent of temperature. The enthalpy and entropy of hydrogen bond dissociation are also obtained as 9.6 KJ mol\textsuperscript{-1} and 44.8 J mol\textsuperscript{-1} K\textsuperscript{-1} respectively. Two \text{C}=\text{C} in plane vibrational bands of the aromatic rings at 1614 and 1598 cm\textsuperscript{-1} were studied at different temperatures. The integrated absorbance for both bands decreases clearly and regularly with increasing temperature and both bands shift to lower wave numbers. This
strongly suggests a specific interaction of the aromatic rings in forming the hydrogen bands, probably the N-H-...π hydrogen bonds.

Fu Cai Wang et al.\textsuperscript{98} have studied the influence of styrene solvent on hydrogen bonding in amorphous linear aromatic copolyurethanes by FTIR in a range of 30-90\textdegree C w. w of styrene. N-H vibrations were studied in the stretching and bending regions. The results demonstrated that the N-H groups of the polyurethane can hydrogen bond not only with the C=O groups but also with other groups in this system. The investigation of the vibrations of the monosubstituted aromatic rings confirms that some aromatic rings of the styrene are hydrogen bonded with the N-H groups of the copolyurethane. These results are useful in elucidating why a physical gel appears in this system.

Luo Ning et al.\textsuperscript{99} have investigated crystallinity and hydrogen bonding of hard segments in segmented polyurethane urea copolymers from MDI, 3, 5-diethyl toluene diamine (DETDA) and ethylene oxide–capped polypropylene oxide polyether diol (PPO). By analysis of model compounds crystallisation of DETDA-MDI hard segments was confirmed and relationships between urea hydrogen bonding with morphological changes were suggested. The crystallisation, however, was not complete in the copolymers even when the hard segments were high. FTIR analysis suggested that the equilibrium of urea hydrogen bonding between crystalline region and amorphous region was affected mainly by morphological changes (phase inversion) and was almost independent of chemical composition of the segmented polyurethane–urea copolymers under certain morphological conditions both before and after phase inversion.

Chen and Chan\textsuperscript{96} have studied the effect of phase inversion on physical properties. The extent of penetration of water into ordered hard domains depend on the dissociation temperatures of urethane–urethane hydrogen bonds.
h. **Effect of soft segment on the properties of the polyurethane elastomers**

The soft segment characteristics such as structure, length, functionality etc. largely influence the properties and performance of the corresponding block copolymers.

**Segment length**

The effect of soft segment molecular weight on the properties of conventional polyurethanes has been extensively studied. The optimum properties were obtained when the molecular weight ($M_n$) is in the range of 2000-3000. Lower molecular weight materials, i.e., materials with molecular weight below 2000 exhibit lower degree of phase separation and are unable to crystallise under strain.

T.L. Smith studied the strength of elastomers and suggested that smaller hard segment domains at equivalent volume fraction should be more effective at stopping catastrophic crack growth through the soft segment matrix. Molecular weight affects hard segment domains. Materials with lower hard segment molecular weight have small hard segment domains. Materials with high soft segment molecular weight would tend to possess poorer tensile properties. From the foregoing studies, optimum tensile properties are observed at molecular weight values given above.

One et al. have investigated the effect of soft segment molecular weight on properties. They have selected 3000 to 1350 range for their study and found that many properties such as doubling of tensile strength (from 5 to 10 Mpa) was observed as the molecular weight decreased. Since they have used a constant hard segment to soft segment ratio which raises the hard segment content to 75%, the effect on tensile strength may not be attributed solely to the effect of soft segment molecular weight.

Speckhard et al. have studied the effect of soft segment molecular weight on the properties of PIB copolyurethanes. They have selected 1800-11000 range for their studies.
and arrived at the conclusion that tensile property decreased with increasing soft segment molecular weight. Thus some improvement in the tensile properties may be obtained by using lower soft segment molecular weights (< 1500) than the generally reported values. In conventional copolyurethanes, phase separation and strain-induced crystallization increases with increasing soft segment molecular weight. But this is not the case with the materials studied by Speckhard et al. Schollenberger and Dinbergs\textsuperscript{106,107} have obtained the result that decreasing the total molecular weight below a certain threshold value leads to a reduction in tensile properties.

The average functionality and functionality distribution of soft segment polyols have marked influence on the tensile properties of copolyurethanes\textsuperscript{108}. Segments with less than two functional groups retard chain extension. On the other hand segments with more than two functional groups promote cross-linking and led to increased phase mixing which results in poorer tensile properties\textsuperscript{109}.

But a small extent of cross-linking is a desirable property. Soft segment with a number average functionality two but a broad distribution contain many segments with functionalities both greater and less than two, therefore, suffer from a combination of the above effects.

Properties were studied by Petrov and Lykin\textsuperscript{109} and Schneider et al\textsuperscript{110-112}. Petrov and Lykin obtained materials with improved mechanical properties when the average functionality of polyol approaches two. The studies done by Schneider et al have shown that broad distribution of functionalities affects the properties of the material due to gel formation and low molecular weight fractions. However, PBD polyol with a narrow distribution\textsuperscript{111} of functionality (about 1.97) gives lower value of tensile strength and higher values of elongation at break due to fewer cross-links in the material.
Studies\textsuperscript{102,111} revealed that the differences in soft segment glass transition temperatures affect material properties. Generally the non polar soft segments have lower glass transition temperatures than conventional polyurethanes. The glass transition temperatures of conventional polyurethanes can change with hard segment content, soft segment molecular weight and other factors such as degree of phase separation. The $T_g$ of non polar hydrocarbon-based polyurethanes due to the incompatibility of segments, is independent of changes in hard segment content, soft segment molecular weight and hard segment type\textsuperscript{104}.

**Strain-induced crystallisation**

The strain-induced crystallisation is a characteristic feature of conventional copolyurethanes and results in an upturn in the stress-strain curve. This is not a general phenomenon among copolyurethanes based on non polar soft segments. The strain-induced crystallisation imparts strength to the materials. Speckhard et al\textsuperscript{113} studied the tensile properties of PBD and PPO-based samples and that of PTMO and PEO based materials. The result indicate higher tensile strength to PTMO and PEO-based materials due to the strain-induced crystallisation.

**Copolyurethanes with non polar soft segments**

The soft segment of conventional $(A-B)_n$ block copolyurethanes is usually polyether or polyester polyol. Much work has also been carried out using other polyols including hydrocarbon polyols such as polyisobutylene\textsuperscript{104,105,114,115} polybutadiene\textsuperscript{116-123} polydimethyl siloxane\textsuperscript{115,124-126} polymyrcene\textsuperscript{127,128} and natural rubber\textsuperscript{19,129-131}. When compared with polyester polyurethanes, these materials demonstrate superior hydrolytic stability. Higher
oxidative stability, improved low temperature flexibility and variations in gas permeability are other advantages of this type of materials.

The studies have shown that these materials exhibit higher degree of phase separation. The non polar nature of the soft segment inhibits them from phase mixing with the polar polyurethane hard segments.

T.A. Speckhard et al. have investigated a series of four polyurethanes formed from, 4,4'-diphenyl methane diisocyanate (MDI) and polyisobutylene (PIB). The mechanical properties have improved by using PIB glycol prepared via the 'inifer' technique and had a narrow functionality distribution with a number average functionality 2. However, the mechanical properties were still low compared with conventional polyurethanes. The effect of hard segment content and soft segment molecular weight on the properties of the materials has been investigated. Stress-strain studies, DSC, DMA, wide-angle X-ray scattering and small angle X-ray scattering were the characterisation methods. Increasing hard segment content resulted in improved dynamic and tensile modulus, lower elongation at break and larger hard segment domains. Increasing soft segment molecular weight led to larger domains and reduced mechanical properties. The degree of phase separation as measured by the soft segment Tg and the amount of interfacial mixing measured by small angle X-ray scattering (SAXS) were unaffected by hard segment content and soft segment molecular weight and were indicative of a high degree of phase separation compared with conventional copolyurethanes.

B. Fu et al. investigated the thermal stress-strain properties as functions of the hard segment length and the type of soft segment. The soft segments were hydroxyl terminated PBD, polytetramethylene ether glycol and polycaprolactone (PCL) with close to 2000. Both PTMEG and PCL are crystallisable where as PBD is not. The strength and amount of
interphase hydrogen bonding is in the decreasing order polyester > polyether. PBD-based copolyurethanes do not exhibit interphase hydrogen bonding. The hard segments are formed from TDI / 1,4-BDO and TDI / HBPA (hydrogenated bisphenol A). This study demonstrates that the hard segment length plays an important role in phase segregation; although the degree of phase segregation is also affected by the type of soft segment. The tensile strength is determined by the degree of phase segregation and the melting temperature of the crystallisable segments. PBD polyurethanes show nearly complete phase segregation by DSC. The hard segment glass transition temperatures increase as the hard segment length increases. The short (2 units) and the long (6 units) hard segments in a blend of PBD polyurethanes are found to be compatible.

K. Ono et al.\(^{103}\) have studied the relationship between the molecular weight of liquid hydroxyl terminated polybutadiene (HTPB) and the physical properties of the elastomers. MDI was the diisocyanate used. The tensile strength, modulus, tear strength and hardness decreased with increase in the molecular weight of HTPB and this phenomenon was remarkable in the low molecular weight of HTPB (below 3000). On the other hand, the ultimate elongation increased linearly with increase in molecular weight of HTPB. The incorporation of short–chain diol, viz., N, N-bis(2-hydroxypropyl)aniline (HPA) increases stiffness of the product due to the presence of the aromatic ring (from HPA).

M. Xu et al.\(^{117}\) have studied the influence of incompatibility on hard–segment sequence length among a series of PBD/MDI/1,4-BDO segmented polyurethanes by means of solvent extraction. The results indicate that the molecules of the original polyurethanes are quite dissimilar in chemical composition and average hard segment length. These polyurethanes are just blends of two fractions of segmented copolymer with very different average hard segment content and average hard–segment length. These copolyurethanes are
phase segregated systems. Two hard segment Tgs are observed and it indicates compositional non uniformity which results from poor compatibility between the components of the system. This result is a common phenomenon for segmented copolymers, but is especially obvious in the case of PBD-based copolyurethanes owing to the extremely poor compatibility between their segments.

M. Serrano et al.\textsuperscript{118} have investigated the transport–morphology relationships in segmented PBD polyurethanes. The diisocyanate used was TDI and the chain extender 1,4-BDO. This system constitutes a model segmented polyurethane copolymer composed of amorphous rubbery and glassy domains. Evidence for the presence of phase separation is inferred from the scattering and phase contrast mechanisms of imaging. However, it is not possible to assign specific domain morphologies such as spherical, lamellar or cylindrical, based solely on the results of TEM. Complimentary evidence of the domain presence is provided from the transport results; in particular, phase inversion and domain connectivity. Incomplete phase separation was indicated from the combined transport-morphology results for samples with less than 33\% hard segment.

M. Serrano et al.\textsuperscript{122} have correlated the transport-morphology relationships in segmented PBD polyurethanes with effective medium theory (EMT) and simple transport models involving ordered microstructures. The 75 wt\% hard segment (HS) sample is assigned a dispersed morphology of soft segment (SS) spheres in a glassy matrix of hard segment. A lamellar morphology is indicated at 55 wt \% HS by all methods of analysis. Based on sorption studies and the results from SAXS, cylindrical domains of hard segment in a rubbery matrix of soft segment are believed to exist in the dilute range (< 40 wt\%) of hard segment content. Complex sorption kinetics indicates the inadequacy of Fick’s law to describe the transport in copolymer samples of rubbery and glassy materials.
effects dominate the transport of CO₂ in PBD copolyurethanes. In this case, a simple transport model using EMT involving coupled diffusion and relaxation is used to describe the anomalous sorption kinetics.

T.A. Speckhard et al.¹⁰⁸ have investigated the ultimate tensile properties of polyurethanes based on non polar soft segments. Copolyurethanes based on non polar soft segments are likely to suffer from premature phase separation during polymerization leading to low molecular weight product with compositional heterogeneity, especially if the reaction is done in bulk. The lower soft segment glass transition temperature of, in particular, the polydimethyl siloxane copolyurethanes can also contribute to their lower tensile properties at room temperature. However, if differences in the soft segment glass transition temperatures are accounted for by comparing samples at equivalent values, T-Tg and other parameters are optimised, it appears that only lack of soft segment crystallisability under strain and possibly an exclusively high degree of phase separation are inherently limiting the tensile properties of non polar soft segment-based polyurethane block copolymer.

Teng Ko Chen et al.¹³² have studied the first high temperature endotherm of copolyurethane based on PBD. MDI is the diisocyanate and 1,4-BDO is the chain extender used in this study.

Brunette et al.¹¹¹ have studied copolyurethane with varying hard segment content viz., 20-60 wt %, HTPB was used as soft segment. The material exhibits individual soft and hard segment Tg indicating phase separation.

C.H.Y. Chen-Tsai et al.¹³³ have studied the structure and morphology of segmented HTPB polyurethanes by electron microscopy and small-angle x-ray scattering. Microscopy results indicate that meandering cylinders of the soft segment phase are present in the 74% hard segment sample. An alternating plate-like structure is found in the 52% sample.
Modelling results and mechanical behaviour of these samples lead to the conclusion that discrete hard segment domains of anisotropic shape are present in the soft segment matrix. This conclusion is also supported by the results from calculation of specific area of domains. A spectrum of morphologies varying with sample composition is thus obtained for this particular system of copolyurethanes.

B. Bengtson et al.\textsuperscript{134} studied the thermal and mechanical properties of solution polymerized segmented polyurethanes with HTPB. The values of hard segment glass transition increase with the average hard segment length following a Fox–Flory type relationship. Single hard segment T\textsubscript{g} observed indicate homogeneous nature.

R. Benrashid et al.\textsuperscript{135} have synthesised new siloxane urethane block copolymers and analysed the effect of a siloxane moiety on microphase segregation in soft/hard block copolymers. Of particular interest is the fact that the data also show that the solvents from which the polymers were cast, have a significant influence on microphase segregation. The films cast from tetrahydrofuran have higher silicone concentration at the surface as compared to polymers cast from dimethyl acetamide/dichloro methane or dioxane.

R. Benrashid and G.L. Nelson\textsuperscript{136} have synthesised siloxane urethane block with varying soft segment molecular weights and studied their properties. Surface studies including ESCA, EDS and FTIR show well-segregated block copolymers with enhanced siloxane on the surface. DSC studies show a low mp (\textdegree 44\textdegree C) for the soft segment and above room temperature T\textsubscript{g} for hard segment. These materials show higher thermal stability compared to polyether urethane block copolymers. These copolymers also show relatively good resistance to exposure to oxygen plasma and show improved flame retardancy compared to nonsiliconated, polyether polyurethane block copolymers.
Yu-Chin Lai and E.T. Quinn\textsuperscript{137} have synthesised and characterised UV-curable polysiloxane-based copolyurethanes. Isophorone diisocyanate, hydroxybutyl terminated polysiloxane and 2-hydroxyethyl methacrylate with diethylene glycol or neopentyl glycol are the materials used for the synthesis.

Characterisation methods are high resolution NMR, FTIR and gel permeation chromatography. The cured films from these prepolymers gave a wide range of mechanical properties and high oxygen permeability, providing opportunities for many applications.

J.L. Cawse et al.\textsuperscript{127} prepared a range of hydroxyl terminated poly(myrcene). The polyols so prepared and purified had number average molecular weights \( \bar{M}_n \) between 4000 and 2000 gm mol\(^{-1} \) at low and high concentration respectively. The corresponding number average functionalities \( \langle \text{fn} \rangle \) were between 1.3 and 2.3 and polydispersity \( \frac{M_w}{M_n} \) was \(~1.3.\) The microstructure of polyols was investigated using NMR spectroscopy from which the main mode of propagation during polymerization of myrcene was deduced to be 1,4-addition across the conjugated double bonds. Glass transition temperatures of the polymyrcenes measured by DSC were in the range \(-50 \) to \(-60^\circ \)C.

Francis et al.\textsuperscript{129} have synthesised a series of polyurethane elastomers containing natural rubber (NR). The NR soft segment has been provided by hydroxyl terminated liquid natural rubber (HTNR). A simple and efficient method for the production of hydroxyl terminated liquid natural rubber has been reported recently\textsuperscript{138,139}. The method involves the photochemical degradation of natural rubber in solution with the help of aqueous hydrogen peroxide. This provides hydroxyl end groups which are essential for the reaction with diisocyanates. For a tropical country like India the method is very economical since the labour and machinery requirements are low as it utilises solar energy. Moreover natural rubber is an easily available material, from natural sources. The hard segment was formed
from 1,4-butanediol and toluene diisocyanate. The closeness of soft segment glass transition temperature to that of HTNR indicates that the system is a phase separated one. The properties of the block polymers were found to vary from soft to rigid elastomers and to rubber toughened plastics with the variation in hard segment content.

Ravindran et al.\textsuperscript{19} studied the block copolymers from HTNR and polyethylene oxide. TDI was used as a coupling agent for combining the two segments. The materials were hydrophilic in nature.

C.J. Paul\textsuperscript{140} studied the polyurethane block copolymers based on HTNR and different diols. TDI was the diisocyanate used for the synthesis. The diols are 1,2-ethane diol, 1,2-propane diol, 1,3-butane diol, 1,4-butane diol and bisphenol-A. The characterisation techniques are IR, NMR, DSC, TGA, DMA, tensile analysis and microscopy. The materials possess phase-separated morphology with amorphous characteristics. As hard segment increases the tensile strength and modulus show an increase with a decrease in elongation at break. The properties varied from soft to rigid elastomers and then to rubber toughened plastics with hard segment content. This variation in behaviour was consistent with sample morphology, which in fact depended upon the relative fractions of the soft and hard segments.

1.6 Scope of the present work

It is found that block copolymers bearing NR soft segments possess similar characteristics as that of the polybutadiene and polyisobutylene-based block copolymers described earlier. The use of NR as the soft segment gains significance because of its availability from renewable natural sources and also due to its ecofriendly characteristics. As a completely phase separated system NR-based copolymers could be used as a model
polymeric material for following the structure property relationship in block copolymers.

It is to be noted that the characteristics of the block copolymers could be varied with the type of hard segments. The above studies used hard segments either formed from polyethers or from TDI and various diols. The TDI was an 80:20 mixture of the 2,4- and 2,6-isomers. The 2,4-isomer present in three quarter proportion determines the overall product characteristics. Because of the unsymmetrical disposition of the isocyanate groups in the 2,4-isomer the resulting hard segments lack crystallisability and hence remain as amorphous.

In this context it is interesting to study the possible modification in properties when a symmetric diisocyanate is used for the formation of polyurethane segments. Hence the present work envisages the studies on a few series of block copolymers based on NR soft segment and polyurethane hard segment made from diphenyl methane diisocyanate and a number of diols.

1.6.1 Objectives of the work

The study aims at the following objectives.

1. To synthesise different series of block copolymers in which the soft segment is hydroxyl terminated liquid natural rubber (HTNR) of molecular weight 4500 (number average) and hard segments are polyurethanes derived from various diols such as ethylene glycol (EG), 1,2-propane diol (PG), 1,3-butane diol (1,3-BDO) 1,4-butane diol (1,4-BDO) and bisphenol–A (BPA) by reaction with the diisocyanate-MDI.

2. To follow the course of reactions involving the formation of block copolymers and to analyse the structure of the products.

3. To study the thermal properties of the samples.

4. To investigate mechanical properties such as tensile properties, tear strength, hardness etc.

5. To carry out morphological studies of the various samples.
6. To interpret the characteristic properties of the block copolymers on the basis of the chemical structure of the hard segments.

7. To study the effect of aromatic ring systems present in the chain extender on the properties of the block copolymers.

8. To investigate the effect of symmetric diisocyanate on the properties.

1.7 References

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