Synthesis of Polyurethanes and Study of Their Surface Morphology

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Abstract: A series of polyurethanes comprising of varying molar ratio of 1,4-butane diol (BD) and 1,1,2,2-tetraphenylenethanediol (TPED) were synthesized. Tetraphenyl ethane and its derivatives having a sterically hindered carbon-carbon single bond are known to act as thermal iniferters in free radical polymerization. Polyurethanes having such sterically hindered carbon-carbon bonds may also act as thermal macroiniferters. Such polyurethane macroiniferters based on 4,4’-diphenylmethane diisocyanate (MDI), polypropylene glycol (PPG, M.W. 1000), 1,4-butane diol (BD) and 1,1,2,2-tetraphenylenethanediol (TPED) were synthesized by the prepolymer method. The molar ratio maintained in all the synthesis was MDI:PPG:short chain diol( 3:1:2). MDI and PPG were reacted first thermally followed by chain extension with short-chain diols BD and TPED. These thermal polyurethane macroiniferters were used to prepare polyurethane-block polyvinyl copolymers. N, N-diethyl dithiocarbamato group is known to act as photoiniferter. When a new diol N,N-diethyl dithiocarbamato-(1,2)-propane diol(DCPD) is incorporated into polyurethane backbone then it can be used to synthesize polyurethane-graft-polyvinyl copolymers. The surface morphology of both the polyurethanes and their corresponding vinyl block and graft copolymers were studied by scanning electron microscopy (SEM).

Index Terms: Block copolymer, macroiniferters, polyurethane, radical polymerization, SEM.

I INTRODUCTION

Polyurethanes are a broad class of polymers having only one aspect in common – the presence of the urethane linkages [–NH–COO–] in their repeat units. The structure has some resemblance to polyamides because both of them contain – CONH – groups. The presence of additional oxygen in the chain increases its flexibility and thus, the melting point of polyurethane is much less than that of the corresponding poliamide. Segmented polyurethanes are block copolymers of the (AB)n type consisting of alternating rigid and flexible segments. They are an important subclass of the family of thermoplastic elastomers. Due to the different polarity and chemical nature of these segments, they tend to separate into two phases usually referred to as soft and hard phases. Hard segments usually associate into hard domains because of the rigidity of the molecules and their intermolecular hydrogen bonding. Hard domains act as physical crosslinks while at the same time they serve as reinforcing fillers, an effect similar to that of carbon black in conventional rubbers. Thus segmented polyurethanes consist of two phases and their properties are strongly affected by the degree of phase separation into hard domains and the soft phases. The soft segments of segmented polyurethanes are usually derived from linear polyester or polyester macrodiacols having molecular weights between 600 and 3000, while the hard segments are formed from disiocyanate chain extended with low-molecular weight diols or diamines.

The extent of phase separation is directly related to the degree of interaction between the soft and hard segments. It has been reported that in polyester and polyether-based polyurethanes, some of the urethane N-H groups could form hydrogen bonds with the oxygen atoms of ether or ester linkages causing partial phase mixing. Polyvinyls are polymers of vinylic monomers, like styrene, methyl methacrylate (MMA), methyl acrylate, acrylic acid, acrylonitrile (AN) etc.

The scope of utility of polyurethanes can be widened by its modifications. One way of modification may be its block and graft copolymerization with vinyl monomers. Graft copolymers (Ceresa, 1976; Cavagnaro, 1977; Folkes, 1985) are considered promising heteropolymeric functional materials. These compounds are widely used to control the stability of disperse
systems, as compatibilizers for improving the compatibility of polymer mixtures, thickeners, film forming coatings, protective coatings and so on.

A number of review articles have appeared (Bruins, 1969; Buist & Gudgeon, 1968; Ionesc, 2019) to deal with the chemistry and technology of linear, branched, grafted, network polyurethanes. Linear segmented polyurethanes, which are essentially block copolymers made up of hard and soft chain segments in an alternating fashion, exhibit many of the properties of crosslinked elastomers and are of particular importance (Koutsuy & Hien, 1970).

In recent years, a number of polymeric system based on reversible termination of growing radicals were reported in order to improve the radical polymerization, such as iniferter where the same species served the purpose of initiator, transfer agent and/or terminator. For controlled incorporation of vinyl blocks into polyurethane blocks, iniferter concept developed by Otsu (Otsu & Yoshida, 1982; Otsu & Kuriyama, 1985) can be employed.

Two types of iniferter, one is thermally and another is photochemically active, are used for block and graft copolymerization process. The C – C bond in tetraphenyl ethane moiety is sterically hindered, thermally labile and acts as a thermal iniferter group. Polyurethane with this thermally labile group behaves as thermal macrinoiferter which can be used for block copolymerization process with other vinyl monomers. Again, C – S bond is photo chemically ruptured at around 254 – 366 nm and if such photo labile moieties are incorporated into polyurethane backbone then it may act as macrophotoiniferter. N, N-diethyl dithiocarbamato group is known to act as photoiniferter. When a diol with pendent N, N-diethyl dithiocarbamato group is incorporated into polyurethane backbone then it can be used to synthesise polyurethane-graft-polyvinyl copolymers. Most of the thermal inifers containing carbon-carbon bonds are symmetrically disubstituted tetraphenylethane derivatives which were reported in the earlier work (Xiao & Kun, 2000).

The surface study plays a major role in the characterisation of polymeric materials. At present scanning electron microscopy (SEM) offers a possibility of directly viewing the surface morphology of bulk specimens. Electron microscopy is an indispensable analytical instrument for investigating the morphology of multiphase polymers. Multiphase polymers contain a soft elastomeric or rubbery phase and a hard glassy or thermoplastic phase. Scanning electron microscopy (SEM) offers a possibility of directly viewing the surface morphology of bulk specimens. However, in SEM the image contrast depends largely on variations in surface topography. In case of solution cast or melt cast multiphase polymers and copolymers fractured surface study is found to be more useful in evaluating the surface morphology of the polymer. The features of major interest have been the two phase morphologies including the size, shape and complexity of the phase within a phase structure. The domains are formed by nucleation and growth mechanisms (Paul & Barlow, 1992; Mark, Bikales, Overberger, & Menges, 1987) and they are modified by diffusion to lower energy structures.

Multiphase polymers containing polyurethane are common toughened polymers in which it has long been known that phase separation is important in determining the structure-property relationship (Cooper & Tobolsky, 1966). A review of structure of segmented polyurethane has shown incompatibility to be a key factor in determining morphology. Chen et al. (1983) used both optical microscopy with a hot-stage and electron microscopy to assess the morphology of segmented polyurethane. Koutsuy, Hien & Cooper (1970) carried out the electron microscopic investigation of polyether-urethane and polyester-urethane block copolymers. They observed two phase structures with hard aromatic-urethane microphase having width 30–100Å. Electron microscopic investigations (Fridman, & Thomas, 1980; Foks & Michler, 1986; Li & Cooper, 1990; Thomas, 1977) carried out on different types of polyurethanes revealed two phase morphology with spherulitic or granular structure originating from hard aromatic-urethane microphase dispersed in the soft elastomeric phase of polyether or polyester segments. Wilkes & Samuels (1974) carried an exhaustive scanning and transmission electron microscopic studies on a model series of spherulitic segmented polyurethanes. They observed that spherulitic structure size depended on hard segment content. When a polyurethane with higher hard segment content was blended with another sample of lower hard segment content, greater coalescence among the spherulites was observed leading to marring (Madaleno & Pyrz, 2013) of well defined spherulitic boundaries.

In the present study scanning electron microscopic investigations were carried out on the polyurethane thermal and photo macrinoiferter and their corresponding block and graft copolymers. Besides revealing the different morphologies of the block and graft from that of the macrinoiferter, the scanning electron micrograph also provided a direct proof of the successful block and graft copolymerisation processes. This indicates that different polymers have different surface morphology.

II. EXPERIMENTAL

All solvents and chemicals were purified according to the methods given in a standard text (Perrin, 1966).

A. Synthesis of polyurethane thermal macrinoiferter based on MDI, PPG, BD and / or TPED

MDI (2.0002 g), PPG (2.6602 g), varying amount of BD and / or TPED were taken in the molar ratio 3:1:2 respectively to synthesize a number of polyurethane macrinoiferter (PU-100%, PU-80% etc.). MDI and PPG were reacted first at 70°C for 1 ½ h under dry nitrogen-atmosphere. The reaction mixture was cooled below to 50°C and BD and/or TPED dissolved in 20 ml methyl ethyl ketone (MEK) was added drop wise through the pressure
equalising funnel. This was followed by the addition of catalyst dibutyl tin dilaurate. The reaction mixture was then again heated at 50°C for 5 hours and finally the polymer was precipitated from water. It was then dried in a vacuum oven for several days.

B. Synthesis of polyurethane macrophotoinitiators based on MDI, PPG, BD and/or DCPD

MDI (2.0002 g), PPG (2.6602 g), varying amount of BD and/or DCPD were taken in the molar ratio of 3:1:2 to synthesize polyurethane macrophotoinitiators (PU-SR). MDI and PPG were reacted at 70°C for 1½ h under nitrogen atmosphere. Then the temperature of the reaction mixture was lowered below to 50°C. The chain extender mixture of BD and DCPD at different compositions were dissolved in 20 ml dimethyl sulphoxide (DMSO) and slowly added from a pressure equalising funnel to the reaction mixture. This was followed by the addition of catalyst dibutyl tin dilaurate and then the reaction mixture was again heated at 90°C. At the end of five hours the reaction mixture was poured into water to precipitate the resultant polymer. It was then dried in a vacuum oven for several days.

C. Polyurethane- block-polyvinyl copolymers

Tetraphenyl ethane and its derivatives having a sterically hindered carbon-carbon single bond are known to act as thermal iniferter in free radical polymerization. They are used to synthesize a number of polyurethane-polyvinyl block copolymers. The vinyl monomers used were acrylonitrile (AN) and 2-hydroxyethyl methacrylate (HEMA). A mixture of polyurethane macroiniferter(PU-100%, 1.2026 g) and AN (2.0662 g) in 20 ml DMF were heated under nitrogen atmosphere at 75°C for 10 hours and then the products were precipitated by pouring the mixture into large volume of water. The block copolymers were then freed from polyacrylonitrile (PAN) homopolymers by partial dissolution technique using DMF and ethanol as solvent and non-solvent respectively. Finally these were then Soxhlet extracted with acetone to remove any impurity. The purified product, PU100%-b-PAN copolymer was then dried under vacuum for several days.

Further, a mixture of polyurethane macroiniferter(PU-100%, 1.2026 g) and HEMA (2.0662 g) in 20 ml DMF were heated separately under nitrogen atmosphere at 80°C for 10 hours and then the products were precipitated by pouring the mixture into large volume of water. The block copolymers were then freed from poly 2-hydroxyethyl methacrylate (PHEMA) homopolymers by Soxhlet extraction with methanol. The purified product PU100%-b-PHEMA copolymer was dried under vacuum for several days.

D. Polyurethane-graft-polyvinyl copolymers

Polyurethane macrophoto initiators (PU-SR) having such pendant N,N-diethyl dithiocarbamate group were used to synthesize polyurethane-graft-polyvinyl copolymers. This photopolymerization process was carried out in a Heber multilamp photochemical reactor (COMPACT-LP-MP 88) at 254 nm to synthesize polyurethane-graft-polydimethyl methacrylate.

The mixture of PU-SR (1.5245 g) and MMA (1.0667 g) in 10 ml DMSO was first purged with dry nitrogen. The reaction tubes were then sealed and photolirradiated in a Heber multilamp photocatalytic reactor at 254 nm for 9 h. The resultant polymers were isolated by precipitation in water and filtered. The polymers were Soxhlet extracted with acetone to remove the PMMA homopolymer.

III. CHARACTERIZATION BY SEM

Scanning electron microscopy (SEM) was performed using LEO 1430 VP electron microscope operating at 15 KV. The instrument has maximum resolution of 3.5 nm and maximum magnification of 300 KX. To make conducting, the polymer surface was coated with a thin film of gold by a gold sputtering method under vacuum condition. The polymer samples were then ready for investigation under the above mentioned scanning electron microscope. In the present study scanning electron microscopic investigations were carried out on the polyurethane thermal and photo macroiniferter and their corresponding block and graft copolymers.

![Fig.1 Scanning electron micrograph of PU-100% macrothermal iniferter](image)

Fig.1 shows the scanning electron micrograph of PU-100% macroiniferter. The use of TPED as chain extender diol increased the size of the hard domain structure in comparison to polyurethane hard domains from MDI and BD. Thus spherulitic hard domain structures with the width (1.74 to 3.48 μm) was observed while granular structure of 0.5 to 3 μm was reported in polyurethane hard domain formed from MDI and BD.

The scanning electron micrograph of PU100%-b-PAN copolymer (shown in Fig. 2) is different from that of the polyurethane macroiniferter (PU-100%) which indicated a change in morphology as a result of block copolymerization. The domain structure observed in case of the iniferter was replaced by continuous, layered structure. It seems that the nucleation process of the polyurethane hard segment was influenced by the growing chain of the polycrylonitrile. This resulted in higher coalescence along the spherulitic structures leading to the marring of the well defined spherulitic boundaries.
In scanning electron micrograph of PU100-b-PAN copolymer (shown in Fig. 3), the surface appeared to have a layer of spherulites of various sizes superimposed on a larger coalesced spherulitic underlying material. The morphology of the PU100-b-PHEMA was observed to be different from that of PU100-b-PAN. This is because PHEMA exhibits amphiphilic properties. The backbone polymer chains and the α-methyl groups are hydrophobic and the hydroxyl groups are hydrophilic. As a result the growing PHEMA chain undergoes complex interactions with the soft (hydrophilic) and hard (hydrophobic) segments of the polyurethane macroinitiator. Such interactions appeared to augment the domain formation as well as the coalescence among the spherulites leading to the observed morphology.

Fig. 4 shows the scanning electron micrograph of the polyurethane macrophotoinitiator (PU-SR) where the chain extender diol (Bhuyan & Kakati, 2005), diethylidithiocarbamato-(1,2)-propane diol (DCPD) replaced the 1,4-butane diol (BD). The scanning electron micrograph showed a two-phase morphology though the sizes of the hard segment spherulites are smaller (0.87 to 2.61 μm) than what was observed in case of the thermal iniferter based on the 1,1,2,2-tetraphenylethane diol (TPED) as the chain extender. The scanning electron micrograph of (PU-SR)-g-PMMA copolymer (shown in Fig. 5) revealed a different morphology from that of the starting macroinitферter (PU-SR). The PMMA is an amorphous polymer. The nucleation process of the hard segment spherulites in the polyurethane segment was influenced by the growing PMMA chain. The spherulite formation by the hard segment of polyurethane started earlier but undoubtedly incorporated some of the growing chains of PMMA into it. This resulted in the deformation of the spherulites which led to increased coalescence and a resultant continuous morphology.

**CONCLUSION**

The scanning electron microscopy revealed that hard-soft domain segregation of the polyurethane macoiniferter was influenced as a result of block and graft copolymerization of vinyl monomers on to it. Besides revealing the different morphologies of the block and graft from that of the macroiniferter, the scanning electron micrograph also provided a direct proof of the successful block and graft copolymerisation processes. This indicates that different polymers have different surface morphology.

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