The term morphology is a Greek derived word meaning study of shape. It can be found in reference to many disciplines such as archaeology where it is used to describe the shapes or forms of artifacts, or in biology where it is used to describe the form or shape of organisms or parts of organisms and their function, or in linguistics to describe the study of words and how they are formed and their relationship to other words. For the purpose of this article and the study of polyurethanes we will define morphology as the structure of polyurethane blocks or segments. One of the unique aspects of polyurethane chemistry is that we are able to construct molecules of different types for different functions by combining different isocyanates and different polyols. Unlike other polymers like polyethylene which is derived from ethylene monomer or polystyrene which is derived from styrene monomer, there is no one urethane monomer that is used to create polyurethane polymers. Polyurethanes are “made-to-order” polymers which are created in the manufacturing process for a particular product. There are a variety of isocyanate types and polyl types that can be combined to make polyurethane polymers. These include a variety of aliphatic and aromatic isocyanates which differ in molecular structure and functionality. There is an even larger variety of polyols which can be either aliphatic or aromatic and further vary in molecular weight, branching and functionality. This variety of reacting components is why polyurethanes are used in so many different applications, as can be seen in Figure-1 below.
Figure-1: Relative percentages of major polyurethane applications.  
(Source: The Center of Industry Education and Collaboration, University of York, 2016)

Getting back to chemistry and morphology, it is important to remember that all molecules have shapes. They are not two dimensional structures as we draw them on paper, they are three dimensional structures. This fact is illustrated in Figure-2 which shows the structure of 4,4’-methylene diphenyl diisocyanate (MDI).

Figure-2: Illustration of 4,4’-methylene diphenyl diisocyanate (MDI) as drawn chemically, as a ball and stick model, and as a space filled model.
4,4’-MDI molecules have a different size and a different shape as compared to the higher oligomer analogs found in polymeric MDI (PMDI) as can be seen in Figure-3.

![Figure-3: Typical composition of polymeric methylene diphenyl diisocyanate as depicted by space filled models.](image)

It is also important to remember that molecules can only react if they get close enough to one another. Therefore, the size and shape of the isocyanate and the polyol molecules are important factors associated with polyurethane chemical reactions and the rates of these reactions. In addition, it is important to remember that molecules move. We have all learned that for gases and liquids, the positions of individual molecules are random and associated with all dimensions in space. Solid molecules have defined positions in space, but still have the ability to move via thermal motion or can move if a force is applied to a solid, like a polyurethane. When designing a polyurethane for a particular application it is important to think about the structure (morphology) and the associated motions of the polyurethane molecules. For example, if we want to impart flexibility into a polyurethane we often incorporate a long chain, low functionality, aliphatic diol into the formulation. These long chain diol molecules can move more easily in the solid polymer matrix when a force is applied to the solid polyurethane as compared to a highly branched and high functionality polyol.

To illustrate the idea of how morphology can affect performance from a rigid or hard domain perspective, we can consider the example given in Figure-4. In this example two different diisocyanates are reacted with polyethylene glycols (PEG) of different molecular weights. From these data, we see that by changing the isocyanate at any specific PEG molecular weight we can observe a shift in the endothermic transition as measured with differential scanning calorimetry (DSC).
Figure-4: Differential Scanning Calorimetry (DSC) analysis of LDI and HDI polyurethanes made with polyethylene glycol (PEG) of differing molecular weights. Source: Soft Matter, Issue 7, 2011, The Royal Society of Chemistry

The size, shape and symmetry of the isocyanate group will impact how rapidly it will react in a polyurethane system and it will also impact how it will order or “pack” with other isocyanate moieties. This packing will also establish the extent of the hydrogen bonding network in the rigid or hard domain of the polyurethane. As can be observed in these data in Figure-4, the symmetrical HDI samples have a higher endothermic transition (melt transition) for any given molecular weight of PEG as compared to the LDI counterpart. The change in morphology thus has an impact on the molecular motion of these polyurethanes. That is, the symmetrical HDI will pack more efficiently and hydrogen bond more efficiently and thus it will take more thermal energy to cause the molecules to move giving rise to the higher melt transitions for the HDI polyurethanes in this example.

It is the ability of the polyurethane formulator to design a molecular architecture which allows polyurethanes to be used in so many different applications. Just as an architect needs to consider the type of structural elements necessary for a specific kind of building project, so too must the chemist or formulator consider the molecular architecture necessary to achieve the defined performance for a particular application. The morphology of the reacting polyurethane components, the size and shape of those components and how those components will move while reacting and in the solid polymer must be considered when designing any polyurethane. Remember, the morphology and motion of the molecules are what makes a rigid polyurethane foam rigid, a flexible polyurethane foam flexible, a polyurethane coating tough, or a polyurethane elastomer elastic.