

Preface

Everything connects to everything else. (Leonardo da Vinci)

Things are always changing, while everything connects together to everything else, to form a balance of our chances, experiences and things, so to maintain *a structure*. From letters that build the word to language, from the relationship between our actions to their consequences, everything is connected. From social networking to digit communication, or from neuron networks in the brain to chemical neuromediators generating thoughts and viewpoints of people, everything is connected.

They all work together, while each relationship is a discrete thing in itself.

The overwhelming majority of research studies rely on the opinions of individuals, but all of them are linked.

The connections go beyond human relationship. Various systems of interacting things act together to perform a common goal. The details make the product. In this picture, polyurethanes architecture is a small world where everything is linked to everything too by a two — phase microstructure consisting of hard and soft domains. The overall properties of polyurethanes depend on the intrinsic properties of each of the phases, which in turn depend on details of molecular packing of the constituents within the phases, including the density of hydrogen bonds.

There are no hard and fast rules for obtaining the optimum polyurethane elastomers end products, success depends on good formulation selection with well chosen and appropriate processing parameters. Polyurethane elastomers are polymers with remarkable versatility. Through suitable choice of the diisocyanates and diols combined in their synthesis, a huge range of physical properties are achievable. For example, these may be varied from those typical of soft elastomers to those of hard plastics, simply by varying the dominant diol from a flexible long-chain molecule to a small molecule such as ethylene glycol.

This versatility is combined with the processing advantages of a thermoplastic. It is therefore understandable that the polyurethane elastomers are employed in an exceptionally wide range of manufactured products.

An important feature of polyurethane elastomers is that their elastomeric behaviour is highly sensitive to chemical and physical structure of the material, that are potentially under the control of the synthesist. For this advantage to be exploited more effectively, however, there is a need for deeper understanding of the mechanisms by which structure determines the properties of importance.

The present book aims to advance this understanding, by means of a systematic study of the effects of varying chemical composition of model polyurethane elastomers on: (a) their physical structure at the important nanometre length-scale, and (b) the resulting mechanical properties of interest.

The book reviews aspects from the up-to-date literature focused on these topics including our research. In addition the book records selected results from an international NATO project collaboration between The Department of Engineering Science, University of Oxford and our Romanian laboratory at the Institute of Macromolecular Chemistry “Petru Poni”, Iasi. This has made possible an unusually comprehensive study of the structure and important physical properties of polyurethane elastomers—a class of polymer of such great industrial importance.

A particular topic approached in this book is new insight into the physical origin of inelastic effects in reinforced elastomers, to assist with the development of physically-based constitutive models.

In the book, a study was made of how aspects of the constitutive responses of polyurethane elastomers vary with composition: the polyaddition procedure, the hard segment, soft segment and chain extender (*mostly diols*) were varied systematically in a large number of systems of model and novel materials. Results were related to: microstructural changes, on the basis of evidence from X-ray scattering, scanning and transmission electron microscopy, atomic force microscopy, and also dynamic mechanical analyses, differential scanning calorimetry and IR dichroic measurements.

The book covers aspects from the morphology to mechanical aspects focused on the elasticity and inelasticity of amorphous to crystalline polyurethane elastomers, in relation to their sensitivity to chemical and physical structure. In such polymers, resilience of the material is an important attribute. In many applications they are in commercial competition with other, relatively soft, elastomeric materials. The choice of material for any given application then hinges on a spectrum of key properties offered by relatively soft polymers—stiffness and strain recovery characterizing their elasticity, but also inelastic effects such as hysteresis and stress relaxation. In these respects the mechanical properties of polyurethane elastomers are similar to those of other elastomers.

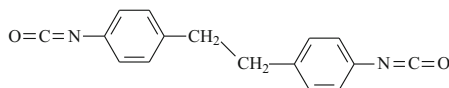
In this book, inelastic effects correlated with systematically varying the chemical structure, were also investigated by including quantitative correlations between the magnitude of the Mullins effect and the fractional energy dissipation by hysteresis under cyclic straining, giving common relations approached by all the materials studied.

A major structural feature that was explored in this book is the relationship between the nature of the hard segment (crystallizing or not) and that of the soft segments. Crystallinity has been sometimes observed in the commercial polyurethane

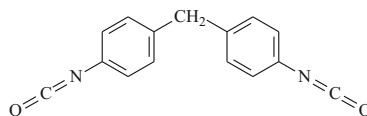
elastomers hard phase but this is usually limited to only a few percent for most hard segment structures when solidified from the melt.

But there is one particular diisocyanate, 4,4'-dibenzyl diisocyanate (DBDI) that, in the presence of suitable chain extenders (diols or diamines), gives rise to significant degrees of crystallinity and this is included in the present work.

Schematic of the flexible
4,4'-dibenzyl diisocyanate
DBDI crystallizing



Schematic of a conventional
rigid diisocyanate,
4,4'-diphenylmethane
diisocyanate (MDI)
non-crystallizing



Recent developments in polyurethane materials have been made in our Romanian laboratory, by producing and studying polymers based on the diisocyanate DBDI giving dibenzyl based hard segments (only available from Romania), that allows the variation of hard domain crystallinity as a key structural variable. The conformational mobility of the novel DBDI causes an unusually wide range of mechanical, physical and chemical properties, associated with the possibility of pronounced phase separation into a domain-matrix morphology, and with a high tendency to crystallization and self-association by hydrogen bonding, which is not available with the conventional diisocyanates in traditional melt-cast polyurethanes.

Thus, new polymers were achieved by us, with a controlled ordering of copolymer hard segment blocks on the macromolecular chain.

This book concerns with the study of a large series of systems of PUs based on the aromatic DBDI diisocyanate as compared to materials derived from conventional diisocyanates, mainly 4,4'-diphenylmethane diisocyanate (MDI), as one of the most representative and commonly used aromatic diisocyanates.

The present book is organized into 6 chapters. Chapter 1 describes general aspects on the chemistry of polyurethane elastomers: their origins and development, the principles and synthesis mechanisms, as well as general considerations on the main chemical parameters that define such materials, i. e. diisocyanate, macrodiol and chain extender. Selected considerations regarding the reactivity of diisocyanates, the hydrogen bonding and its dynamic and quantum aspects are also discussed in this chapter.

In chapter 2, there are investigated aspects regarding the morphology and phase separation on two large categories of polyurethane elastomers: materials based on *single* diisocyanates, and materials derived from *mixtures* of diisocyanates. Results are discussed in terms of the structural studies: wide and small angle X-ray scattering (WAXS) and (SAXS), and transmission and scanning electron microscopy

(TEM and SEM) revealing particularities on the polyurethane elastomers morphology. Conventional materials derived from rigid diisocyanates (*mainly MDI*) are compared with the relatively recent polyurethane elastomers obtained by us, that contain crystallizing hard segments generated by DBDI which displays a variable geometry. *Such materials have higher flow stress in the hard phase caused by stronger phase segregation.*

Thermal techniques such as differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) used to describe the thermal behaviour of the materials are also detailed in this book. A comparison is made in chapter 3, between the thermal behaviour of conventional materials and those derived from dibenzyl structures, from the perspective of the *materials with single diisocyanates as compared to those based on mixtures of diisocyanates*. The thermal behaviour of a series of novel polyurethane blends obtained with the isocyanate DBDI has also been described in chapter 3.

The mechanical performance of polyurethane elastomers is strongly affected by the higher-ordered structure of hard segments on the macromolecular chain, and this is also discussed to a large extent in the present book. Inelastic features in the polyurethane elastomers constitutive response are investigated in chapter 4. Their constitutive responses are sensitive to microstructural detail on length scales of order nm and the hard-domain crystallinity exerts a strong effect on inelasticity of the elastomers and this is largely discussed in chapter 4. Tensile properties and the cyclic tensile responses are investigated and the correlation between the Mullins response and hysteresis is made for a large number of polyurethane elastomers with varying systematically the chemical structure: diisocyanates, macrodiols and chain extenders. A comparison has been made between the mechanical response of elastomers achieved without and with excess of isocyanate NCO groups. For the latter, a study of the kinetics and postcure reaction mechanisms has been devoted.

Special consideration was given to the investigation of polyurethane elastomers deformation induced morphological developments and crystallization. In chapter 5, a brief review has been made of selected research in this area, by including materials with hard segments crystallizing or non-crystallizing, based on diisocyanates of variable geometries.

Chapter 6 is dedicated to a detailed description of a new family of crosslinked polyurethanes, with regard to their thermorheological characterization as shape memory materials and the prediction of their shape-memory performance.

Recent progress has been done by us, in the field of PUs chain extended with diols. For this reason, in the present book I have mainly focused on this category of materials.

Understanding the reaction pathways involved, in resolving the subtle morphological evolution at the nanometre level, and capturing mathematically the complex, large-deformation nonlinear viscoelastic mechanical behaviour are assumed to bring new important insights in the world basic research in polyurethanes and towards applied industrial research in this area, and this is the overall target of this book.

Which is why, this book is addressed not only to chemists from both academia and industry, but to all those who are interested in the latest developments in the science of elastomeric materials.

I started from simple to complex approaches so that hopefully this book is also useful and of interest for graduate students and in general for younger audience.

However, while doing so, undoubtedly I am aware that the road to success is always “under construction” ☺.

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