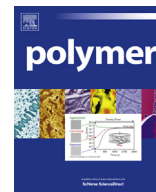




Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

A systematic study of the effect of the hard end-group composition on the microphase separation, thermal and mechanical properties of supramolecular polyurethanes

Daniel Hermida Merino ^a, Antonio Feula ^a, Kelly Melia ^a, Andrew T. Slark ^b, Ioannis Giannakopoulos ^c, Clive R. Siviour ^c, C. Paul Buckley ^c, Barnaby W. Greenland ^d, Dan Liu ^e, Yu Gan ^a, Peter J. Harris ^a, Ann M. Chippindale ^a, Ian W. Hamley ^a, Wayne Hayes ^{a,*}

^a Department of Chemistry, University of Reading, Whiteknights, Reading, RG6 6AD, UK

^b Henkel UK Limited, 957 Buckingham Avenue, Slough, SL1 4NL, UK

^c Department of Engineering Science, Oxford University, Parks Road, Oxford, OX1 3PJ, UK

^d The Reading School of Pharmacy, University of Reading, Whiteknights, Reading, RG6 6AD, UK

^e Department of Physics, University of Surrey, Guildford, Surrey, GU2 7XH, UK

ARTICLE INFO

Article history:

Received 11 May 2016

Received in revised form

7 July 2016

Accepted 10 July 2016

Available online xxx

Keywords:

Supramolecular polymer

Self-assembly

Polyurethane

Phase separation

Rheology

ABSTRACT

This paper reports a systematic study on a series of supramolecular polyurethanes that possess microphase separated morphologies which afford elastic materials at room temperature. Combinations of urea and/or urethane linkers in addition to a phenyl spacer have been used to study the effect of the rigidity of the hard end group segments as well as the hydrogen bonding capability of the urethane-urea linker units. Small angle X-ray scattering (SAXS) experiments have revealed characteristic microphase separated morphologies. Wide angle X-ray scattering (WAXS) was used to probe the lateral packing of the urethane and/or urea within the hard segments. Differential scanning calorimetry (DSC) analysis confirmed that unsymmetrical soft/hard segment phases have been achieved by varying the urethane/urea content. Transmission electron microscopy (TEM) and atomic force microscopy (AFM) determined that a 1-D fibrillar structure was obtained when the hard segment featured ureas whereas a 3-D structure was achieved when a combination of urea and urethane groups was used, giving rise to enhanced elongation properties. Finally, we present mechanical testing data in which oscillatory rheology at a range of frequencies and temperatures has revealed the effect of the connectivity of the hard segments on the relaxation times of the supramolecular chains. Tensile tests showed that end groups with ureas or a combination of a urea and urethane yielded elastic materials with strengths of ca. 5 MPa at room temperature.

© 2016 Published by Elsevier Ltd.

1. Introduction

Polyurethane and polyurea (PU) based materials [1,2] have found widespread applications in the industrial scale production of synthetic rubbers, adhesives, protective coatings, foams, fibers and elastomers as well as in biomaterials [3,4] and semi-permeable membranes [5]. The extensive use of PUs has been facilitated by their ease of synthesis from relatively inexpensive starting

materials [6–8]. In addition, the mechanical properties of PUs are intimately related to their chemical composition [9,10]. The structure/property relationships that exist between the monomeric components and bulk material provide wide scope for tailoring and optimisation of the physical properties of the PUs to target specific applications [11–15].

One of the most intriguing properties of PUs is their elastomeric behaviour [16,17], which arises from the segmented nature of the chemical composition within each polymer chain [18,19]. In the solid state, PUs are observed to phase-separate into soft domains (containing flexible polymeric components) and hard domains which contain a high proportion of urea and/or urethane

* Corresponding author.

E-mail address: w.c.hayes@reading.ac.uk (W. Hayes).

linkages [9,20,21]. The urea and urethane components are closely associated through hydrogen bonding interactions [2,8,22,23], thereby providing physical crosslinking between the soft segments. Thus these PUs behave similarly to conventional, covalently crosslinked rubbers, except that disruption of the hydrogen bonding by elevating the temperature, permits melt-processing [24].

Yilgör and co-workers have investigated extensively the structure-property relationship in segmented PUs including the local packing of the urea moieties, which results in a high degree of microphase separation [16,25]. In addition, phase separation may be promoted by using apolar soft segments with low surface energies such as polydimethyl siloxane (PDMS) [5,26–28]. During extensive studies by Bouteiller and co-workers [29], PDMS with bis-urea motifs were synthesised, the resulting materials exhibited a 3D network of hard domains, as a consequence of the partial crystallisation of the hard segments. In a related study, Sijbesma and co-workers have investigated [30] the influence of increasing the length of the PDMS soft segments. They found that it was possible to obtain fibrillar structures by increasing the incompatibility of the soft and hard segments [31]. Such fibrillar structures were not observed in PUs that contained PEB [32] or PCL [33]. An interesting spherical morphology was observed when longer soft segment chains were used as a result of a transition of cylindrical to micellar ordering along with the enlargement of the volume fraction of the external segment, as predicted by Flory-Huggins [34]. Detailed studies conducted by Thurn-Albrecht et al. have established [35] that for a series of telechelic polyisobutylenes equipped with complementary hydrogen-bonding groups, interactions between micellar aggregates leads to network formation and solid-like properties at lower temperatures induced by gelation without any specific ordering. Recent studies have not just been restricted to low molecular weight polymers with functionalised chain ends, for example Creton et al. have shown that the viscoelastic characteristics of a series poly(*n*-butyl)acrylates whose central units feature pendant hydrogen bonding motifs can be tailored by the loading of the self-complementary recognition groups [36,37]. Meijer and co-workers have introduced monodisperse hard segments within PUs, and these hard segments were found to undergo crystallisation, and thus achieve a higher degree of microphase separation [38]. It was found that the polymers, which featured two urea groups, displayed a useful balance between high toughness and low melting temperature, the latter of which is key to aiding processability. In agreement with recent studies by Rowan and co-workers [39–41], we have found [42–44] that tough materials could be formed by addition of hydrogen bonding end-groups with low binding constants (between 1 and 45 M⁻¹) [45] to relatively low molecular weight PUs (between 10,000 and 20,000 g/mol). These materials possess interesting temperature responsive properties whereby the degree of phase separation within the materials, and the temperature at which the polymers started to weaken, correlated to the binding constant of the end-group [2,7,22,46,47].

Herein we describe the systematic design and synthesis of four novel, low molecular weight ($M_n \approx 6600$ g/mol, $\bar{D} \approx 1.8$) PUs which vary in the nature of their end-groups. The effect that systematically changing chemical structure and relative % composition of the hard end group has on the morphology of the new materials has been studied using multiple techniques. In addition we have investigated the mechanical properties of these novel materials by oscillatory rheometry and tensile testing. These extensive studies provide new insights into the structure property relationships that underpin this important class of materials.

2. Results and discussion

2.1. Design

The aim of this study was to gain a deeper understanding of the relationship between the structure of the end-groups of linear supramolecular PU based materials and resulting morphological and mechanical properties in the solid state. It was predicted that an increase in the rigidity and the number of possible hydrogen bonding interactions within the polymer end-group would generate materials with advantageous rheological properties under ambient conditions, whilst still permitting facile processing at elevated temperatures.

2.2. Synthesis

Prior to commencing polymer synthesis, two novel polymer end-groups (**1** and **2**) were synthesised *via* a two-step route by initial addition of morpholine derivatives **3** and **4** to 4-nitrophenyl isocyanate to produce urethane **5** and urea **6** followed by reduction of the nitro groups (Scheme 1, see also the Supporting Information (SI), Figs. S1–8).

With the end groups in hand, the targeted supramolecular polymers were generated through a two-step protocol [8,42,43]. Briefly, this involves the synthesis of pre-polymer **7** by the addition of MDI to hydroxyl-terminated poly(ethylene-*co*-butylene) (Krasol) in the bulk state at 120 °C (NCO:OH ratio of 2:1). Subsequent addition of the endgroups (either **1**, **2**, **3** or **4**) to **7** results in the formation of supramolecular PUs **8**, **9**, **10** and **11**, respectively (Table 1). The supramolecular PUs were isolated in good yields (>84%) after several precipitations into methanol.

All four of the supramolecular polymers exhibited comparable molecular weights and polydispersity as measured by GPC analysis (M_n 6600 g/mol \pm 10% and $\bar{D} = 1.8 \pm 0.1$). This increase in molecular weight compared to the starting Krasol material ($M_n = 1730$ g/mol, $\bar{D} = 1.2$) demonstrates that the conditions used to produce the prepolymer **7** result in repeatable degrees of chain extension centred around 3 repeating units of Krasol/MDI.

The resulting polymers were structurally related, possessing identical morpholine end-groups but varying numbers of urea groups (see comparison of **8** and **9** or **10** and **11**), with polymers **10** and **11** featuring two additional urea groups when compared to polymers **8** and **9** (see Table 1). Maintaining the composition of the hydrophobic block whilst changing the end group enabled the study of the changes in phase separation on the mechanical properties to be investigated in isolation from changes incurred through altering the soft segments of the PUs.

2.3. Solid state structures of end group mimics

In order to provide an insight into how end groups of this type may aid the assembly of polyurethanes in the bulk, the end group mimics **12** and **13** (Fig. 1) were generated (see Figs. S17–20) and solid state structures obtained from single-crystal X-ray diffraction analysis (see Fig. 1, Table S1 and Figs S21–22).

The dominant intermolecular interaction evident for urethane **12** was found to be a strong hydrogen bond (2.142 Å and 139.73°) between the morpholine oxygen and urethane hydrogen (see Fig. 2a) whereas bifurcated hydrogen bonds [48] between urea moieties dominated in the solid state structure of urea **13** as shown (see Fig. 2b).

2.4. Morphology

Variable temperature SAXS has revealed that each member of

Download English Version:

<https://daneshyari.com/en/article/5178760>

Download Persian Version:

<https://daneshyari.com/article/5178760>

[Daneshyari.com](https://daneshyari.com)