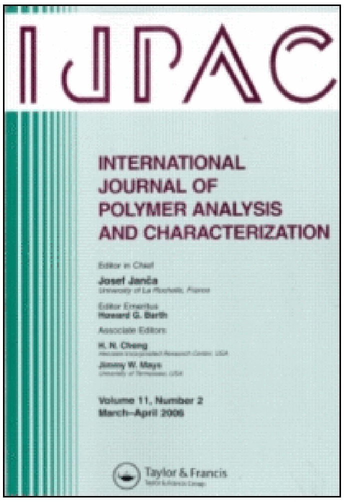

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

Influence of Macrodiol on Phase Separation and Crystallization Processes in Hard-Phase Reinforced Polyurethane Elastomers Based on Isocyanates of Variable Conformational Mobility

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To cite this Article Prisacariu, Cristina and Scortanu, Elena(2010) 'Influence of Macrodiol on Phase Separation and Crystallization Processes in Hard-Phase Reinforced Polyurethane Elastomers Based on Isocyanates of Variable Conformational Mobility', International Journal of Polymer Analysis and Characterization, 15: 5, 277 — 286

To link to this Article: DOI: 10.1080/1023666X.2010.493268

URL: http://dx.doi.org/10.1080/1023666X.2010.493268

International Journal of Polymer Anal. Charact., 15: 277–286, 2010

ISSN: 1023-666X print
DOI: 10.1080/1023666X.2010.493268

INFLUENCE OF MACRODIOL ON PHASE SEPARATION AND CRYSTALLIZATION PROCESSES IN HARD-PHASE REINFORCED POLYURETHANE ELASTOMERS BASED ON ISOCYANATES OF VARIABLE CONFORMATIONAL MOBILITY

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An investigation was performed to determine how aspects of microstructural changes in polyurethane elastomers vary with composition: the hard segment and soft segment were varied in a family of six segmented copolyurethane elastomers. Two hard segments were compared, based on the rigid model diisocyanate 4,4′-methylene bis(phenyl isocyanate) (MDI) or a novel flexible 4,4′-dibenzyl diisocyanate (DBDI). The hard segment fraction was held constant at approximately 40%. The soft segment macrodiols were polyesteric poly(butylene adipate) (PBA) and poly(caprolactone) glycol (PCD), or polyetheric polytetrahydrofuran (PTHF). The molar masses were $2000 \pm 50\,g\,mol^{-1}$ for PBA and PTHF and $1250 \pm 50\,g\,mol^{-1}$ for PCD. For all materials, the chain extender used in the synthesis was butylene glycol (BG). Materials were studied using wide-angle X-ray scattering (WAXS) and small-angle X-ray scattering (SAXS). There was no indication of crystallinity arising from the soft segments in these materials. The broad WAXS peaks measured for the elastomers found no crystalline domains for the hard segments with MDI, while for the materials achieved with DBDI, high crystallinity is observed. All materials with PTHF showed much higher intensity in SAXS. Due to less hydrogen bonding, irrespective of the type of diisocyanate, all the materials with PTHF displayed higher phase segregation (quantified in terms of the SAXS peak areas).

Keywords: Hydrogen bonding; Macrodiols; Polyurethanes; Structural studies

INTRODUCTION

The morphology of thermoplastic polyurethane materials (TPU) is very complicated not only because of the two-phase structure, but also because of other physical phenomena such as phase separation, crystallization, and hydrogen bonding in such systems. It is well known that the segmented polyurethane elastomers

Submitted 9 February 2010; accepted 15 April 2010.

This work was supported by NATO Collaborative Linkage Grant CBP.EAP.CLG.981805. The authors are grateful to Professor C. P. Buckley, Department of Engineering Science, University of Oxford, and to Dr. C. M. Martin, Manchester University, for helpful assistance in the processing and interpretation of data.

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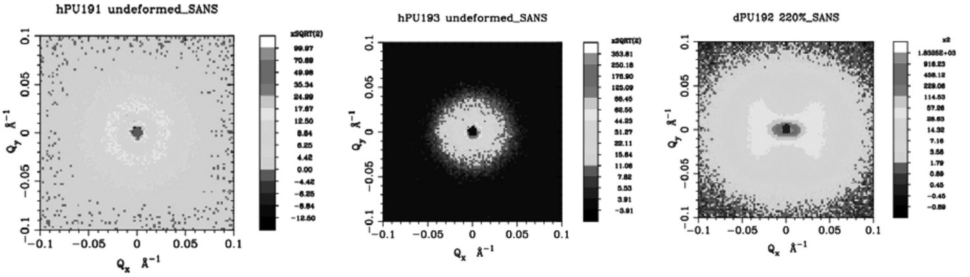
tend to exhibit phase separation.[1,2] It is energetically favorable for the soft segments (SS) and hard segments (HS) not to mix. To achieve elastomeric performance, the SS must be the majority constituent by mass, and the phase structure then takes the form of discrete hard domains dispersed within a soft matrix. Such a phase structure impacts elastomeric properties,[3] and, therefore, a structural parameter of further importance is the degree of phase separation. The overall properties depend upon the relative volume fractions of soft and hard phases and on the intrinsic properties of each of the phases. These in turn depend on details of molecular packing of the constituents within the phases, including the density of hydrogen bonds.

Polyurethanes are extensively hydrogen bonded, which involves the N-H group as the proton donor and the urethane carbonyl, the ester carbonyl (in polyester materials), or the ether oxygen (in polyether polyurethanes) as proton acceptor. Hydrogen bonding can be detected and studied by means of IR spectroscopy. The hydrogen bonded and free N-H and urethane carbonyl C=O are the peaks of interest.[1] Hydrogen bonding is related to the phase separation, and its extent is affected by the polyurethane structure, composition, and temperature. The degree of phase separation, the crystallinity of phases, and the size of domains along with the molecular composition control the PU's morphology and macroscopic properties. Crystallinity has been observed in the soft phase when the macrodiol (MD) chain is long enough,[1] and it is also sometimes present in the hard phase. The latter is usually limited to only a few percentages for most HS structures when solidified from the melt, but there is one particular diisocyanate (DI), 4,4′-dibenzyl diisocyanate (DBDI), that, in the presence of suitable chain extenders (CE), gives rise to significant degrees of crystallinity,[4,5] and this is included in the present work. As reported by ourselves[4,5] and Lyman and coworkers,[6] the MDI molecule introduces the rigid $–Ph–CH_2–Ph–$ moiety in the elastomeric PU hard segments. In contrast, when using DBDI, the specific $–Ph–CH_2–CH_2–Ph–$ moiety introduces a variable geometry into the hard segments due to the possibility of internal rotation of this isocyanate around the $–CH_2–CH_2–$ ethylene bridge. This leads to the appearance of both "syn" and "anti" rotational conformations, which coexist in the DBDI-based PU macromolecules. As a result, in this latter case the PU macromolecules can adopt a more compact packing, which enhances significantly the ability to order in crystalline structures involving predominantly the "anti" form.[4]

A conformational mobility of the DI as it is DBDI may cause an unusually wide range of mechanical, physical, and chemical properties, associated with a higher tendency to crystallization and self-association by hydrogen bonding[4] and with the possibility of pronounced phase separation into a domain-matrix morphology (Figure 1). The anisotropy of the structures relative to the strain direction was clearly visible in the 2-D images in deformed TPUs. Samples were strained to up to 300% levels of extension. Depending on the type of DI (crystallizing or not), they showed various degrees of anisotropy, with the highest values corresponding to the DBDI-based materials. Macroscopic deformation was present in the molecular levels that were probed with neutrons.[7]

Hard domains having a higher flow stress in the presence of the diisocyanate DBDI have been associated with increased hydrogen bonding, which was enhanced in numerous cases by HS crystallinity.[4,5] The primary effect of employing flexible HS in PU synthesis was shown to be a closer self-association of hard segments by



(a) (b) (c)

Figure 1. 2-D scatterring plots from the TPU small-angle neutron scattering (SANS) measurements from two bulk PU elastomers based on MDI and DBDI: (a) undeformed PU (MDI:BG:PTHF)[12]; (b) undeformed PU (DBDI:BG:PTHF); (c) PU (DBDI:BG:PTHF) stretched to a 220% level of extension. Courtesy of Dr. D. Bucknall, Virginia Tech University.

hydrogen bonding. In such polymers, there is a clear indication from the data that the physical origin of the flow stress must be relative displacement of the hydrogen-bonded HS.

The extent of hydrogen bonding is affected by the nature of the soft segments. Eisenbach and Gronski found that 40% of carbonyls in polyether urethanes are hydrogen bonded, which is much less than with polyester urethanes on the same basis but at a higher hard segment content.[8] Their results are in agreement with the findings of other authors.[9–11]

In the present study, TPU crystallinity and segregation behavior has been investigated by means of structural studies by using wide-angle X-ray scattering (WAXS) and small-angle X-ray scattering (SAXS). Orientation of the HS and SS monitored by means of infrared dichroism or scanning electron microscopy (SEM) was previously reported for analogous structures but achieved as cross-linked materials.[4,13]

EXPERIMENTAL METHODS

Materials

A family of six thermoplastic polyurethanes was synthesized by the authors in the Romanian laboratory. They were all three-component systems combined in stoichiometric proportions, consisting of: (1) a diisocyanate (DI) generating hard segment HS (MDI or DBDI); (2) a soft segment macrodiol (MD): poly(butylene adipate) (PBA), poly(caprolactone) glycol (PCD), or polytetrahydrofuran (PTHF); and (3) a small molecule diol as chain extender (CE), anhydrous butylene glycol (BG). The macrodiols were of molar masses $2000 \pm 50\,\mathrm{g\,mol^{-1}}$ for PBA and PTHF and $1250 \pm 50\,\mathrm{g\,mol^{-1}}$ for PCD. The three components were always mixed in the proportions HS:CE:MD = 4:3:1, giving hard segment mass fractions in the region of 30% and isocyanic index I = 100.

The synthesis procedure followed was the pre-polymer route described previously by Prisacariu et al.[4] The HS and MD components reacted together with vigorous mixing under vacuum at 100°C to give a pre-polymer terminated by HS.

Table I. Compositions of the family of polyurethane elastomers Pu1–Pu6 prepared and studied in this work

		PTHF $M_W = 2000 \pm 50\,\text{g mol}^{-1}$	PBA $M_W = 2000 \pm 50\,\text{g mol}^{-1}$	PCD $M_W = 1250 \pm 50\,\text{g mol}^{-1}$
MDI	BG	Pu1	Pu3	Pu5
DBDI	BG	Pu2	Pu4	Pu6

This was then thoroughly mixed with the CE at 90°C and cast into closed sheet molds for curing at 110°C for 24 h. The final result was a polymer with M_w in the range 60–120 kg mol^{-1}, in the form of sheets with thickness in the range 0.3–0.6 mm. The sheets were stored at room temperature for at least one month before testing. They were labeled Pu1–Pu6 according to their combination of HS, MD, and CE, as indicated in Table I.

Structural Studies

Information on the microstructures of the materials was gained by X-ray scattering, using synchrotron radiation at the Daresbury Laboratory. Wide-angle X-ray scattering (WAXS) studies were carried out using Station 16.2 SMX, with X-ray wavelength of 82 pm. Small-angle X-ray scattering (SAXS) studies were carried out using Station 16.1 with the RAPID 2-dimensonal detector, with X-ray wavelength of 141 pm. Phase separation, crystallization, and orientation phenomena in the present materials were also studied by means of a WAXS experiment using Cu K_α radiation; and also differential scanning calorimetry (DSC), IR dichroism, and SEM, from which results were reported elsewhere.[5]

In some of the materials with DBDI as hard segment, sharp peaks were observed in the WAXS intensity versus 2θ scans, indicating phase separation and crystallization in the hard domains. The scattering was separated into amorphous halo (I_a) and crystal diffraction peak (I_c) components and a "crystallinity index" was calculated:

$$\text{Crystallinity index} = \int I_c \mathrm{d}\theta \Big/ \int (I_a + I_c)\mathrm{d}\theta \tag{1}$$

HS crystallinity was observed only in the DBDI-based materials Pu2, Pu4, and Pu6. In each scan of SAXS intensity versus q, there was evidence for a peak in intensity (indicating long spacings in the range 15–23 nm), associated with the preferential wavelength of density fluctuations expected from the spinodal decomposition that occurs in these materials as they phase-separate during preparation. In those cases where a separate peak could be resolved and fitted, the peak area was computed and expressed in arbitrary units. This gave a measure of the degree of phase separation.

Scattering intensities were determined,[15] and they were radially averaged to obtain 1-D patterns of intensity versus $q = (4\pi/\lambda)\sin\theta$. Wide variations were observed in the scattering intensity for the different materials, indicating differing degrees of phase separation. For each scattering pattern, the measured intensity (in arbitrary units) was normalized for specimen thickness and incident beam intensity.[14] Then the high q tail of the curve of normalized intensity $I_n(q)$ was fitted to Porod's law for scattering by a two-phase system with sharp phase boundaries $I_n = K/q^4 + I_b$ to obtain the background intensity I_b and Porod constant K. The corrected intensity $I = I_n - I_b$ was then employed in determining the relative scattering invariant Q from the relation

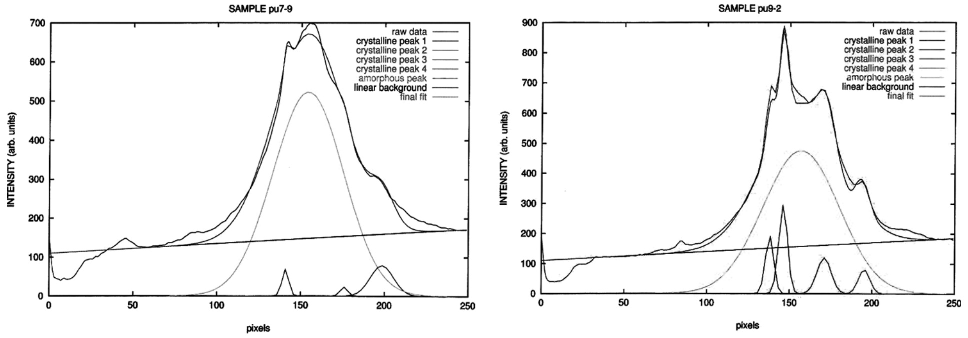
$$Q = \int_0^\infty q^2 I(q) \mathrm{d}q \tag{2}$$

where the upper end of the range of integration, beyond where data were available, was obtained with the extrapolation $I = K/q^4$. Where the scattering patterns obtained showed a distinct peak, (at a position q^* in the region of $0.3\,\mathrm{nm}^{-1}$), a "long period" d was calculated from $d = 2\pi/q^*$, representing a dominant repeat distance of the two-phase structure causing the scattering.

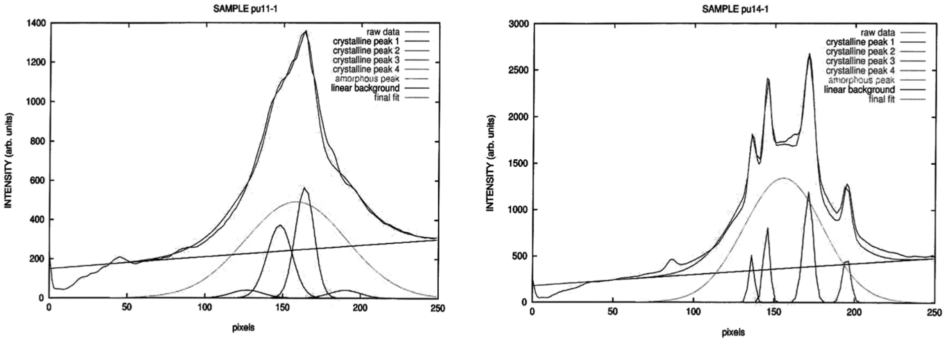
RESULTS AND DISCUSSION

Investigations carried out using WAXS and SAXS showed that the morphology developed in the TPU system listed in Table I was strongly dependent on the hard block nature (crystallizing or not). WAXS patterns gave evidence of hard phase crystallinity in the DBDI-based materials Pu2, Pu4, and Pu6, irrespective of the type macrodiol (polyesteric PBA or PCD or polyetheric PTHF). This is shown in Figures 2–4, which illustrate examples of the range of types of pattern obtained for the PTHF and PBA series: DBDI-based polymers with intense sharp peaks indicating significant crystallinity ($\chi = 0.15$ for Pu2 and $\chi = 0.18$ for Pu4), MDI-based polymers with low intensity sharp peaks indicating very slight crystallinity ($\chi = 0.01$ for Pu1 and $\chi = 0.03$ for Pu3). Similar observations were made for the materials achieved with PCD: while the MDI-based polymer based on PCD and MDI showed only an amorphous halo ($\chi = 0$ for Pu5), the DBDI-based polymer with PCD showed an intense sharp peak indicating significant crystallinity ($\chi = 0.12$).

It is notable that all the MDI-based polymers showed no, or only slight, crystallinity (maximum 3%), whereas those with DBDI had degrees of crystallinity up to 18%. The only polymers that had significant crystallinity were those based on DBDI. This is consistent with previous reports of comparisons between melt-processed polyurethanes based on these two DI and other CE like EG.[10,13] The presence of DBDI does not always lead to crystallinity: it depends on the choice of chain extender. As shown elsewhere, the DBDI-based polymers with DEG as chain extender can be seen to have no detectable crystallinity.[5] The relative ease of crystallization in DBDI as compared to MDI is readily explained in terms of greater flexibility of the DBDI molecule, arising from its $-(CH_2)_2-$ bridge between the phenyl rings, compared to only $-CH_2-$ in MDI.[4] Thus, DBDI hard segments can adopt a linear conformation facilitating packing and inter-chain hydrogen bonding. MDI hard segments, however, are intrinsically kinked in shape, reducing



(a) (MDI:BG:PTHF) (b) (DBDI:BG:PTHF)



(c) (MDI:BG:PBA) (d) (DBDI:BG:PBA)

Figure 2. Examples 1-D WAXS patterns for: (a) material Pu1 based on MDI, slightly crystalline (1.3%); (b) material Pu2 based on DBDI, significantly crystalline (16%); (c) material Pu3 based on MDI, amorphous (0%); (d) material Pu4 based on DBDI (DBDI+EG), significantly crystalline (18%).

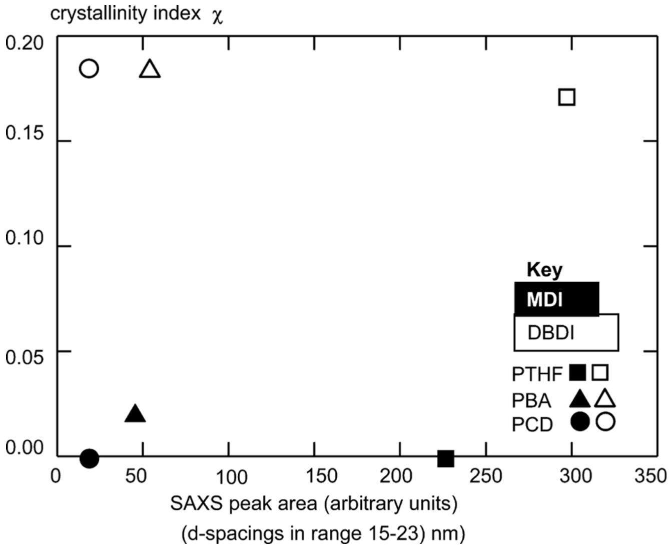


Figure 3. X-ray characterization of the nanoscale structure for the materials listed in Table I.

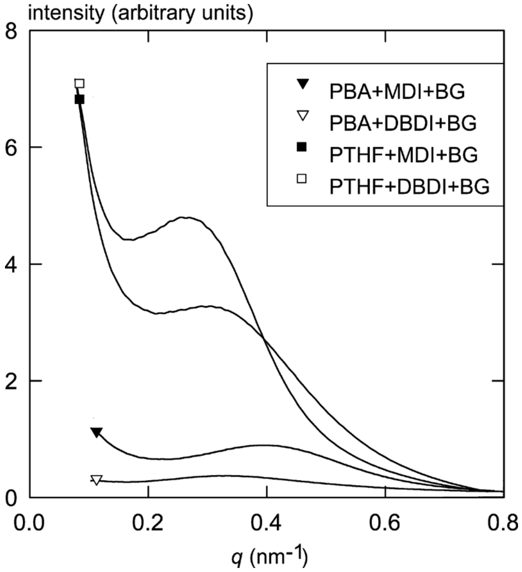


Figure 4. Example of 1-D SAXS patterns for four of the materials listed in Table I.

conformational mobility and thereby hindering close packing and achievement of hydrogen bonding.

Now consider the role of phase separation. In Figure 3, this was quantified in terms of the SAXS peak area. The peak area was computed and expressed in arbitrary units. This gave a measure of the degree of phase separation.

A striking feature of the results was that all materials with PTHF as soft segment showed much higher intensity in SAXS than the corresponding polymers with the other soft segments. The crystallinity index (χ) was higher for polyesteric TPUs with DBDI and PCD or PBA at lower SAXS peak areas, irrespective of the value of the SS molar mass; BG led to distinct diffraction peaks. Polymers with MDI were amorphous ($\chi = 0$), or showed very slight crystallinity ($\chi = 0.01$). Their SAXS peak areas ranged within the values of $25 \div 225$ arbitrary units. There was no indication of crystallinity arising from the soft segments in these materials.

All materials with PTHF showed much higher intensity in SAXS, irrespective of the type of diisocyanate, MDI or DBDI. PUs with PTHF displayed higher phase segregation (quantified in terms of the SAXS peak areas). This is because such PU has fewer H bondings: as shown,[8] only 40% of the carbonyl in polyether urethanes are hydrogen bonded compared to polyester urethanes (PCD, PBA) with the same HS content.

Scattering intensities were determined. Figure 4 shows an example of SAXS patterns for the PBA and PTHF-based materials listed in Table I, providing evidence of phase separation in the present series of materials. As can be seen, the SAXS intensity, indicating the degree of phase separation, varies greatly between the materials. Again, the polymers with strongest scattering are those with PTHF as macrodiol, irrespective of the type of DI (crystallizing or not).

Significantly lower scattering was observed in the polyesteric materials based on PBA. Similar observations were made when the polyesteric macrodiol PBA of molar mass 2000 was replaced by the polyesteric macrodiol PCD, with soft segment molar mass of 1250.

The observation that polyetheric PTHF-based TPUs phase-separate to a greater extent than the corresponding polyesteric PBA- and PCD-based polymers is consistent with previous studies of polyurethanes that showed polyether macrodiols to give greater phase separation than polyester macrodiols.[1] The reason is the availability of a >C=O group on each monomer in a polyester for possible hydrogen bonding with the >N-H groups on the hard segments. This lowers the free energy of mixing of hard and soft segments that drives phase separation, relative to those macrodiols where this is absent, such as the polyethers.

Figure 4 also shows that the SAXS patterns of the PTHF-based polymers had pronounced peaks in intensity, indicating a dominant repeat distance for the two-phase structure. As quantified by the long period *d*, this varied from 15 to 23 nm.

For the polyesteric materials, the values of Q (the relative SAXS scattering invariant defined in the text in arbitrary units) ranged between 5.3 and 4.4 for the PCD series and between 5.5 and 5.6 for the PBA series. Higher Q values were found for the PTHF-based materials, irrespective of the type of HS: 28.7 for the MDI-based TPUs and 34.4 for the DBDI-based material.

Polyethers such as PTHF promote phase-separation from the DI, while polyesters such as PBA and PCD have a greater affinity for the DI through hydrogen bonding to their ester groups and hence are more miscible with the DI and phase segregation is less pronounced.

CONCLUSION

A study was made of structural features (phase segregation and degree of crystallinity) of a family of TPU elastomers, in which hard segment fractions were held constant at approximately 40%. The DI and MD were varied and the CE was the same, BG. The DI was: a rigid model diisocyanate MDI and a flexible diisocyanate DBDI. The conformational mobility of DBDI is associated with the possibility of pronounced phase separation into a domain-matrix morphology and with a higher tendency to crystallization and self-association by hydrogen bonding.

One prominent result from this study is the strong influence that hard-domain type exerts on the degree of crystallinity of the elastomers. An increased hard phase degree of crystallinity was primarily achieved by the use of DBDI instead of MDI as diisocyanate. In the cases where the CE-DI couple was $[\text{BG-DBDI}]_n$, the hard segments were observed to crystallize. WAXS patterns gave evidence of hard phase crystallinity in all the DBDI-based materials, irrespective of the type of the macrodiol (polyesteric PBA or PCD or polyetheric PTHF). This capacity for crystallization is characteristic not only for the $[\text{BG-DBDI}]_n$ structure, but also for similar materials produced by changing the glycol as, for example, in the case of a $[\text{EG-DBDI}]_n$ structure.[5]

All the MDI-based polymers showed no, or only slight, crystallinity (maximum 3%), whereas those with DBDI had degrees of crystallinity up to 18%.

The crystallinity index (χ) was higher for polyesteric TPUs with DBDI and PCD or PBA at lower SAXS peak areas, irrespective of the value of the SS molar mass.

All materials with PTHF showed much higher intensity in SAXS. Due to fewer hydrogen bondings, irrespective of the choice of diisocyanate (MDI or DBDI), all the materials with PTHF displayed higher phase segregation. Materials derived from DBDI and PTHF showed both crystallinity and high phase segregation. This was in contrast with the analogous structures but achieved with MDI where crystallinity was absent, but the materials also showed high phase segregation.

Polyethers such as PTHF promote phase-separation from the DI, while polyesters such as PBA and PCD have a greater affinity for the DI through hydrogen bonding to their ester groups and hence are more miscible with the DI and phase segregation is less pronounced.

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