Crystallization and Properties of Novel Polyurethanes Based on the Chain Extender Ethylene Glycol and Aromatic Diisocyanates of Variable Flexibility

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Summary: Novel polyurethane elastomers (PUs) were synthesized with ethylene glycol (EG) as a chain extender. The macrodiol was poly(ethylene adipate) (PEA), MW = 2000 ± 50. Two isocyanates were employed: 4,4′-methylene bis(phenyl isocyanate) (MDI) and 4,4′-dibenzyl diisocyanate (DBDI). The conformational mobility of 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 higher tendency to crystallization and self-association by hydrogen bonding. Materials were characterized by wide angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC), dynamic mechanical analyses (DMA), and mechanical measurements. Results were discussed in terms of the effect of PUs crystallinity. In the case where the chain extender–diisocyanate couple was EG-DBDI, the hard segments were observed to crystallize. The DBDI based PUs displayed higher flow stress in the hard phase caused by stronger phase segregation.

Keywords: crystallinity; diisocyanates; physical-mechanical properties; polyurethanes

Introduction

The present paper is part of a wider study that has been made of numerous block copolyurethanes (PUs), based on several diisocyanates (DI), macrodiols (MD) and chain extenders (CE), with the aim of improving the understanding of the relationship between molecular/supramolecular architecture at the nm-scale and macroscopic mechanical properties in such systems.[1–9] As shown in previous papers, a novel diisocyanate (4,4′-dibenzyl diisocyanate (DBDI)) and a triol chain extender (1,1,1-trimethylol propane (TMP)) were included as well as more widely-used components, in order to widen the range of structures achievable beyond those normally available.[5,6] In previous studies a systematic investigation was made of the effects of varying the chemistry of hard and soft segment and CE, and the preparation procedures employed, on mechanical response of the PUs. In polymers with diol chain CE, there were tendencies to phase separation, with a characteristic length of ca. 20 nm, and, when DBDI was employed with certain CE, to crystallization of the hard phase. In polymers prepared with the triol TMP as CE a crosslinked system was obtained, preventing phase separation.[5,6]

In the present study the two polymers were designed as shown in Table 1, to reveal the roles of choice of flexible or rigid DI, and of chain extender EG in determining the performance as an elastomer. The soft segment (SS) was built using PEA of molar mass 2000 ± 50 as MD.

To obtain better elastomeric properties, reactive PUs with a small excess of isocyanic NCO groups was prepared, by using a deficit of CE with molar concentrations such as DBDI:PEA:EG = 4:1:2.64, giving isocyanic index I = 110 as shown in our previous publications.[2,3,9] The synthesis

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Table 1.
Casted PU Adopted Structure.

PU #	DI	MD	CE	DI:MD:CE
1	DBDI	PEA	EG	4:1:2.64
2	MDI	PEA	EG	4:1:2.64

Isocyanic index was I = 110 where I (isocyanic index %) = 100 × $[NCO]/([OH]_{MD} + [OH]_{CE})$.

was complete only after performing the total consumption of the isocyanate group excess by postcuring with water present in ambient atmospheric humidity.

As reported,[2] the MDI molecule introduces the rigid - Ph-CH_2-Ph- moiety in the elastomeric PU hard segments (HS). In contrast, when using DBDI, the specific - Ph-CH_2-CH_2-Ph- moiety introduces a variable geometry into HS due to the ability 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 shown in Figures 1 and 2. As a result, in this latter case the PU macromolecules can adopt a more compact packing structure which enhances significantly the ability to order in crystalline structures involving predominantly the "anti" form.[2,3]

Experimental Part

Synthesis

Materials

Two hydroxyl-terminated components, PEA_{2000} commercial product (Bayer) as MD and the anhydrous EG (p.a., Aldrich) as CE were used. The isocyanates were DBDI (an experimental product from CIFC Savinesti, Romania) which was recrystallized twice from anhydrous cyclohexane m/p/ 89–89.5 °C) and commercial MDI (Bayer)

Polyaddition Procedure

The polyaddition was perfomed via the prepolymer route. 50.0 g (0.025 mol of PEA was dehydrated by stirring at 110 °C under vacuum (<1 mm Hg) for 2 hours. 25.0 g (0.10 mol) of MDI or respectively 26.4 g (0.10 mol) of DBDI, was added to the anhydrous macrodiol with intense mixing, and vacuum was restored. After 30 minutes of mixing under vacuum at 100 °C the temperature was reduced to 90 °C and vacuum was removed. A reactive prepolymer was obtained with final NCO groups in a mixture with the excess of isocyanate. Then 4.09 g (0.0659 mol) mol of EG was added quickly with rapid stirring. The mixing was continued for a maximum of 30–40 seconds. After addition of the CE the prepolymer melt was poured into a sheet mould and cured by heating for 24 h. at 110 °C. In the case of sheets up to 2 mm thick, PUs prepared with stoichiometric deficit of CE (I = 110) were postcured by holding for two weeks under ambient humidity, so as to obtain a further increase of the molecular weight as a result of the NCO excess transforming into urea linkages and allophanate crosslinks. The description of the synthesis of the homopolyurethanes was made elsewhere.[3]

WAXD Measurements

WAXD measurements were made using a TUR M62 diffractometer on films, using Cu Kα radiation (36 kV, 20 mA).

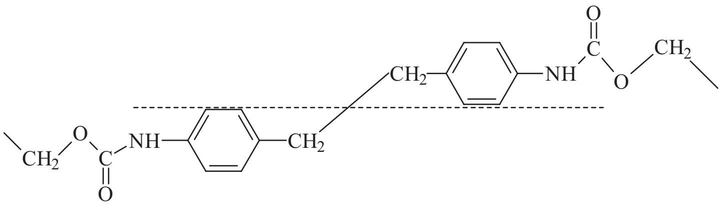

Figure 1.
Geometry of the extended linear anti DBDI form.

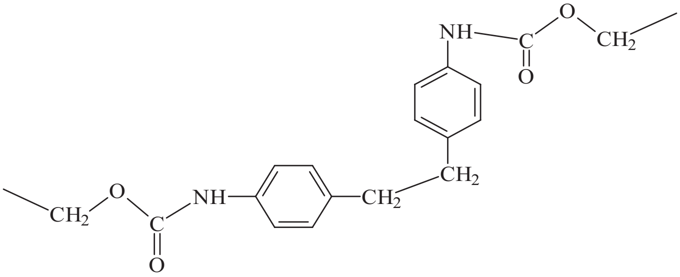

Figure 2.
Geometry of the contorted sin DBDI form.

Mechanical Tests

The study of the mechanical properties was made in accordance with standard procedures from the stress-strain curve data of simple uniaxial tension. The specimens for the testing were cut from films using dimension given in ASTM D1708, i.e. a dumbbell-shaped specimen with a gauge length of 20 mm, a width of 58 mm, and 0.3 up to 2 mm thickness. To investigate mechanical hysteresis, cyclic tensile tests were carried out, cycling between a fixed strain limit and zero load, with the same magnitude of strain-rate for loading and unloading. The stress-strain and hysteresis data were obtained using an Instron 4204 Testing Machine or Schopper MZ Gip Testing Machine, at room temperature (T ≈ 25 °C).

DSC Measurements

DSC measurements were performed by a Mettler TA instrument DSC 12 E with a heating rate of 20 °C/min, in nitrogen.

DMA Tests

The DMA measurements were carried out with a Gabo Qualimeter Eplexor 150 N. The samples were tested in tensile mode with a starting distance between the clamps of 45 mm. The cross section area of the specimen was 5 mm × 1–2 mm. The samples were placed in the temperature chamber and cooled down to the starting temperature of −140 °C. The cooling conditions were: room temperature till −60 °C cooling rate of 10 Kelvin/minute, −60 °C to −120 °C 3,5 K/min and −120 °C to −140 °C 2 K/min.

Results and Discussion

Structural Studies

Previous structural studies illustrated the general point that a DBDI based PU may crystallize, while the corresponding MDI based PU does not.[2–4] In the present paper X-ray diffraction patterns showed significant capacity to crystallize for the PU materials based on DBDI-EG HS. The degree of crystallization was controlled by changing the molar ratio between EG/PEA. Figure 3, shows WAXD diffractograms for the DBDI based material derived from PEA and EG, with the molar ratios EG/PEA = 3 (curve 2), and EG/PEA = 2.64 respectively (curve 3) (PU_1). PU_1 of molar ratio equal to 2.64 (curve 3) was compared to a linear PU previously detailed[2–4] with a higher molar ratio equal to 3 (curve 2) and to the corresponding

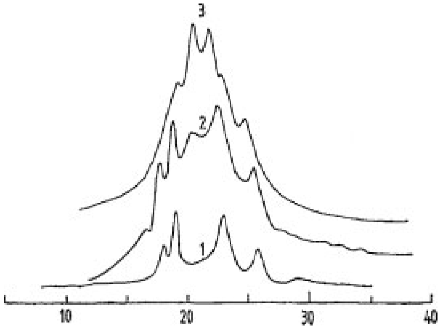

Figure 3.
Wide-angle X-ray diffraction from: (1) homopolymer EG-DBDI; (2) – PU (DBDI:PEA:EG) with molar ratio EG/PEA = 3;[2–4] (3) – PU (DBDI:PEA:EG) with molar ratio EG/PEA = 2.64 (PU_1).

homopolyurethane [EG-DBDI] based on hard segments only (curve 1).

As seen, curve (2) for the material with molar ratio EG/PEA = 3, was very much alike to curve (1) corresponding to the homopolymer, and proportional to HS content from PUs. Reducing the number of HS by lowering of molar ratio from 3 to 2.64 has as a result significant changes in the shapes of the diffractograms. There appeared crystalline structures of other types, within which the SS were involved also. A convenient means to reduce the DBDI based PUs crystallinity was to use the flexible diethylene glycol (DEG) as a CE which inhibited crystallization.[2] As earlier reported, combining the flexible DBDI with a conventional rigid DI like MDI also reduced significantly the PU crystallinity.[3]

Tensile Test Results

Typical results of uniaxial tensile load/unload cycles and stress relaxation were described elsewhere for a large range of materials based on DBDI.[2–9] The strain-recovery data for the two polymers based on EG, DBDI and MDI, are shown in Figures 4 and 5. They included load-unload cycles at constant rate of extension, with measurement of hysteresis and strain recovery, and stress relaxation tests. The presence of DBDI HS instead of MDI led systematically to increases in: the input strain energy to a given elongation, hysteresis and residual strain under cyclic loading, and stress relaxation. Polymers based on DBDI HS, displayed higher stiffness and strength than the conventional MDI based PU. Both features of the response were attributed to differences in hard phase plastic flow stress, resulting from crystallinity in the DBDI phase. Lower strain recovery and strain energy recovery on cycling (hysteresis) were observed in the case of PU derived from DBDI. Material PU_1 based on DBDI, displayed higher Young Modulus values and higher residual elongation than did the conventional MDI based PU_2. In such materials the stiffness, hysteresis, residual elongation and stress relaxation were all increased relative to the corresponding MDI based PU.

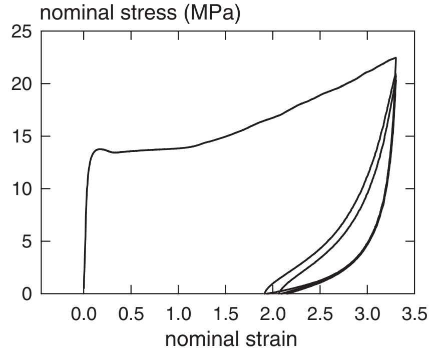

Figure 4.
Tensile load/unload cycles for material based on DBDI:PU_1(EG-PEA-DBDI,I = 110) at strain rate 0.03 s^{-1}.

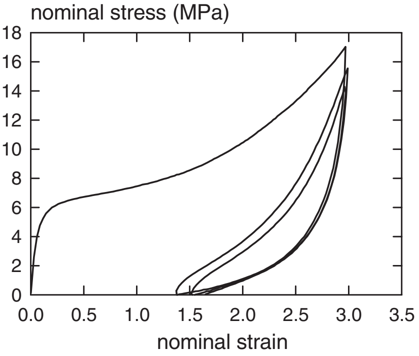

Figure 5.
Tensile load/unload cycles for material based on MDI:PU_2(EG-PEA-MDI,I = 110), at strain rate 0.03 s^{-1}.

DSC Measurements

As reported, previous DSC studies achieved by us on PUs based on mixtures of DBDI with MDI have revealed systematic differences resulting from changing the PUs copolymeric ordering.[3] Thermal analysis have also shown evidence of profound differences in structure brought about by changing the type of DI (flexible DBDI or conventional rigid MDI), along with changing the type of CE.[2,3]

The DSC events observed for the two PUs based on EG with varying the type of DI are summarized in Table 2. In this work the resulting polymers were compared

Table 2.
DSC Events for the PU Studied Initially, After Stretching to 300% and 600% Elongation.

PU #	Structure	Melting Peaks [°C]			Heat of Fusion [J/g]		
		Soft segment (SS) zone			Hard segment (HS) zone		
		$t_{max}/\Delta H$			$t_{max}/\Delta H$		
		initially	300%	600%	initially	300%	600%
1	DBDI:PEA:EG (4:1:2.64)	–	40°/3.46	54°/5.58	277°/18.21	277°/25.22	277°/16.4
2	MDI:PEA:EG (4:1:2.64)	–	–	62°/0.5	173°/8.3	168°/6.7	152°/2.94
3	DBDI:EG homopolymer	without soft segments			287°/91.83	–	–
4	MDI:EG homopolymer	without soft segments			237°/41.7	–	–

to the corresponding homopolyurethanes [EG-DBDI] and [EG-MDI] based on HS only. It is observed that there coexist two fields of temperatures: 40 °C up to 62 °C when the melting of the SS occurred and 168 °C up to 277 °C characteristic to the HS melting zones.

As shown in Table 2, after stretching from a 300% up to a 600% limit of elongation, the SS crystallized in both of the material with DBDI and MDI. The degree of crystallinity increased with increasing the strain level. The HS crystallinity was not significantly influenced by the degree of elongation. When compared to the sub-set of homopolymers (materials 3 and 4 in Table 2), made up only by HS, it is observed that PU_1 and PU_2 displayed lower values of the melting peaks. In the case of PU_2 with MDI, the HS – SS interaction within the so-called mesophases[3] was preponderant, which affected the position of the PU melting peaks against models (homopolyurethanes). An interesting observation could be made in the case of PU_1. For this polymer, the melting peak ($t_{max} = 277$ °C) was very close to the melting peak value ($t_{max} = 287$ °C) of the corresponding homopolyurethane $[EG\text{-}DBDI]_n$. Due to the special spatial structure of DBDI, the HS crystallization of the EG-DBDI couple in the material PU2 occured in a high proportion (88.7%). This process was not affected by the presence of the SS. As a

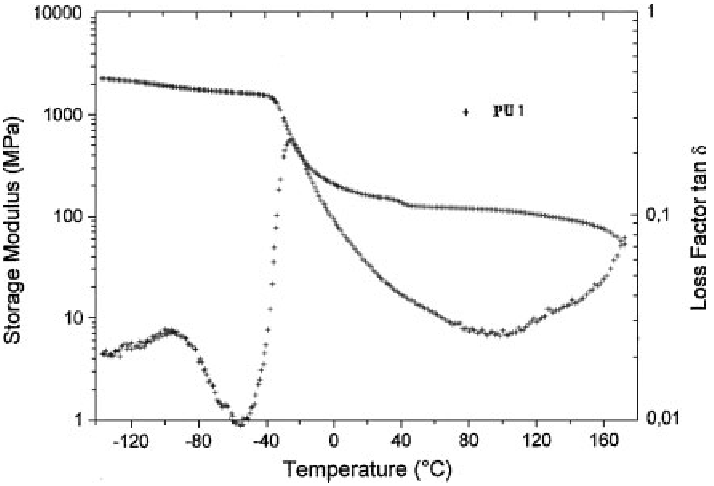

Figure 6.
Storage modulus and Loss Factor as a function of temperature for PU_1 based on DBDI.

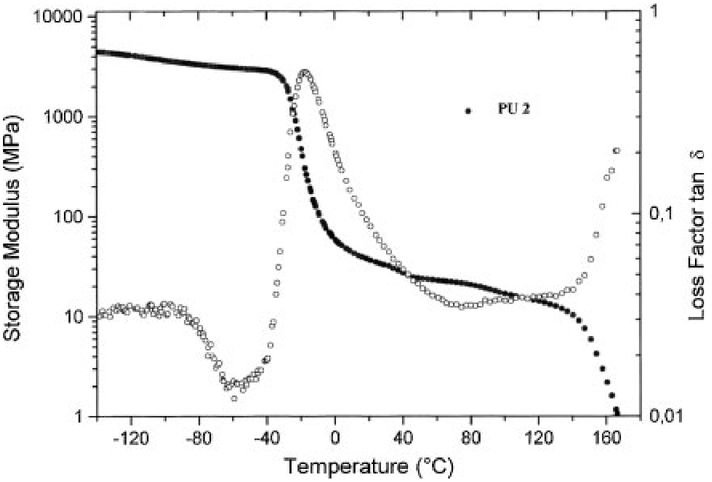

Figure 7.
Storage modulus and Loss Factor as a function of temperature for PU_2 with a similar structure but based on MDI.

result, in this polymer unexpected high phase separations were achieved which were confirmed by the X-ray experiments.

DMA Measurements

The tests started at $-140\,^{\circ}C$. The complex modulus (E^*), storage modulus (E'), loss modulus (E'') and the loss factor ($\tan\delta$) were measured as a function of temperature at a heating rate of 1 K/min (Figures 6 and 7). The instrument was operated with controlled sinusoidal force with a frequency of 1 Hz. Depending on the type of DI (rigid or variable geometry), significant differences of the Storage Modulus (E'), and consequently differences in softening were found between the two polymers. The glass transition temperature (T_G) was influenced by the mobility of the macromolecular chain. PU_1 with DBDI displayed a higher tendency to crystallize. The DMA results are presented in Figures 6 and 7. The storage modulus (E') in the temperature range above the glass transition region is the highest for the DBDI-based PU_1 which is controlled by the crystalline content of HS given by the stronger tendency of the DBDI-BG HS to self-associate in a coplanar packing.[2,3] The decrease of the modulus is connected with the softening/melting of the samples. T_G in the maximum of the loss factor at $f = 1$ Hz ranged among $-10\,^{\circ}C$ to $21\,^{\circ}C$, and the lowest T_G value corresponded to PU_1, based on HS of conformational mobility. T_G in the maximum of the loss factor at $f = 1$ Hz were: for PU_1, $T_G = -24\,^{\circ}C$. Tan $\delta = 0.198$; for PU_2, $T_G = -16\,^{\circ}C$, with Tan $\delta = 0.418$.

Conclusions

Two segmented PUs were designed and synthesized based on two isocyanates of different geometries: the conventional 4,4′-methylene bis(phenyl isocyanate) (MDI) with a rigid geometry, and the flexible 4,4′-dibenzyl diisocyanate (DBDI). Rotation around the central $–CH_2\text{-}CH_2–$ bridge in DBDI allows alignment of aromatic rings and hence crystallization within the hard phase, which is not available with MDI in melt –cast polyurethanes.

Wide angle X-ray diffraction and DMA experiments revealed clearly the strong influence of the DBDI on the formation of hard domains with a pronounced crystallinity, particularly in the case when EG was employed as a CE. The DSC measurements have shown that once the temperature is raised sufficiently the polymer matrix becomes more mobile and allows the CE – DI segments to move and crystallize in self-associations, especially in the case of the EG-DBDI couple. Due to the DBDI special spatial variable geometry, in such polymers the HS crystallization occured in a high proportion of up to 90%. This process was not influenced by the presence of the SS. This was in contrast to the almost general situation characteristic to classical PUs with lower values of the melting peaks, when the interaction between the HS and SS was preponderant.

The presence of DBDI HS instead of MDI led systematically to increases in: the input strain energy to a given elongation, hysteresis and residual strain under cyclic loading, and stress relaxation. Polymers based on DBDI HS, displayed higher stiffness and strength than the conventional MDI based PU. Lower strain recovery and strain energy recovery on cycling (hysteresis) were observed in the case of PU derived from DBDI. PU based on DBDI displayed higher Young Modulus values and higher residual elongation than the conventional MDI based material did.

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