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DSC STUDY OF POLYURETHANES OBTAINED FROM 4,4'-BIS(10-HYDROXYDECAOXY)BIPHENYL

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Abstract

The melting and crystallization of a series of polyurethanes derived from poly(1,6-hexylene adipate)diol (PHA), 4,4'-dicyclohexylomethane diisocyanate (HMDI) and 4,4'-bis(10-hydroxydecaoxy)biphenyl (BHDBP) as a chain extender were investigated by using DSC. Thermal properties of the polyurethanes were found to be strongly influenced by the hard segment content.

Keywords: 4,4'-bis(10-hydroxydecaoxy)biphenyl, DSC, phase transitions, polyurethanes

Introduction

Segmented polyurethanes with 4,4'-bis(ω-oxyalkyloxy)biphenyl moieties in the main chain, containing mesomorphous structures, were investigated by a number of authors [1–9]. In our previous investigation on segmented block polyurethanes and on a hard segment polyurethane, obtained from 4,4'-bis(6-hydroxyhexyloxy)biphenyl (BHHBP), 4,4'-dicyclohexylomethane diisocyanate (HMDI) and poly(1,6-hexylene adipate)diol, we have found that polyurethanes obtained from HMDI with the 16% *trans*-*trans*, 52% *cis*-*trans* and 32% *cis*-*cis* HMDI isomer content are characterized by considerably lower phase transition temperatures than analogues polyurethanes obtained from HMDI with higher *trans*-*trans* isomer content [10].

In this paper the influence of 4,4'-bis(10-hydroxydecaoxy)biphenyl, a novel chain extender from the group of 4,4'-bis(ω-oxyalkyloxy)biphenyls, on the thermal properties of synthesized polyurethanes, will be discussed.

Experimental

Segmented polyurethanes were synthesized from poly(1,6-hexylene adipate)diol (PHA), 4,4'-dicyclohexylomethane diisocyanate (HMDI) and 4,4'-bis(10-hydroxydecaoxy)biphenyl (BHDBP) as a chain extender.

BHDBP was synthesized from 10-chloro-1-decanol and 4,4'-dihydroxybiphenyl. It is a white, crystalline substance with the melting temperature range of 151–155°C. For the syntheses of polyurethanes reagent grade HMDI (Aldrich) was taken, which is a mix-

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ture of the three stereoisomers (*trans-trans*, *cis-trans*, *cis-cis*) (90%), the remaining 10% incorporates other isocyanates. PHA (3000 g mol^{-1}) was delivered by Zakłady Chemiczne 'Zachem' (Bydgoszcz – Poland) from a pilot scale production.

A series of 8 polyurethanes with different hard segment (HS) content was obtained and investigated. The HS content, estimated as a sum of equimolar mass amounts of BHDBP and HMDI, was set as 12, 19.2, 29.5, 40.4, 49.5, 60.6, 79.4 and 100%. The synthesized polyurethanes were marked as PUR1, PUR2, PUR3, PUR4, PUR5, PUR6, PUR7 and PUR8, respectively.

DSC measurements were performed using a differential scanning calorimeter DSC7 (Perkin Elmer) from –20 to 200°C in nitrogen atmosphere at a heating/cooling rate of 10 K min^{-1}.

Results and discussion

The chemical structure of BHDBP was confirmed by NMR measurements end elemental analysis. Phase transitions for BHDBP as investigated by DSC are shown in Fig. 1. First heating run (curve 1) shows only one peak Tt1 of melting of BHDBP. The second heating run (curve 2) of the previously crystallized sample shows a broad endothermic peak Tn2, probably due to some transition of the mesomorphic phase and the melting peak Tt2. The cooling from the isotropic liquid is represented by the curve 3, which shows three exotherm peaks: Tc1 for primary crystallization from the melt, Tb1 and Ta1 for transitions of mesomorphic phase of BHDBP, like observed by some liquid crystal polymers [11, 12].

The melting transitions of the investigated polyurethanes are shown in Fig. 2. Heating runs for PUR1, PUR2, PUR3 and PUR4 show transitions corresponding to separate melting of hard segments (HS) or soft segments (SS). Therefore these polyurethanes are phase-separated, whereas for polyurethanes PUR5, PUR6, PUR7 and PUR8 only single peaks attributed to the melting of the hard segment phase were found.

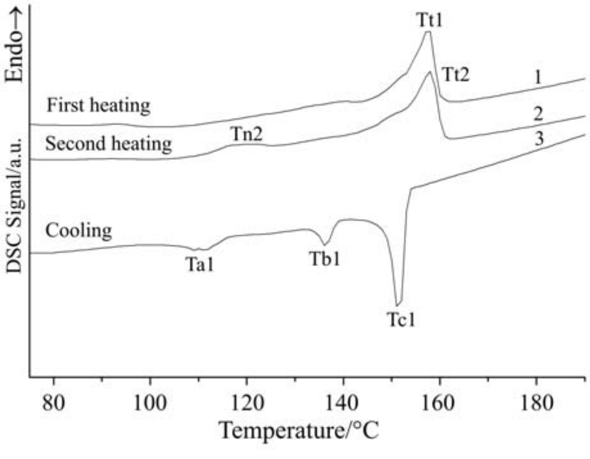

Fig. 1 DSC heating and cooling curves 4,4'-bis(10-hydroxydecaoxy)biphenyl (BHDBP)

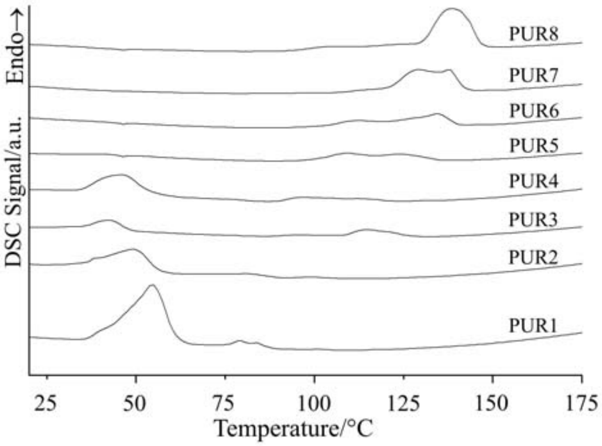

Fig. 2 DSC heating curves for the investigated polyurethanes

The heating curve for the polyurethane with 12% HS content (PUR1) shows an intensive transition representing melting of the soft segments with the peak maximum at 55°C. The subsequent two small peaks are connected with melting of small domains of the hard segment phase.

The melting of the polyurethane PUR2 is mainly characterized by the melting peak of the soft segments. The transitions which may be attributed to the hard segment phase are broad and of low intensity. For polyurethane PUR3 the melting endotherm shows two peaks: well visible at 45.6°C for SS melting and a broad band with a peak at 111.9°C for HS melting. The next curve for polyurethane PUR4 shows similar transitions for the HS with peaks at 95.5 and 114.7°C.

For the polyurethanes PUR5, PUR6 and PUR7 only peaks typical for melting of hard segment phase were observed. It may be explained by phase inversion to the structure with continuous hard segment phase. The dispersed and not able to undergo separate crystallization soft segments influence crystallization of the hard segment phase, causing shifts of HS melting peaks. The melting curve of the polyurethane PUR8, containing only hard segment building units, shows symmetric peak with a maximum at 138.3°C, which represents transition in an isotropic state and at lower temperature a less distinct peak with a maximum at 105°C. The existence of the multiple peaks connected with melting of the hard segment phase may be explained by different crystallization patterns of hard segments build from different HMDI isomers.

Because glass transitions at DSC melting runs were hardly visible, the more sensitive DMTA method was additionally applied. For the samples PUR1–PUR7 loss tangent peaks, for the glass transition of the soft segment phase, were found at temperature range from –10 to –12°C. The PUR7 and PUR8 samples showed additional glass transition for the amorphous hard segment phase at 53.4 and 82.1°C, respectively. The loss tangent peaks extended over broad temperature range, what explains absence of the usual heat flow ‘jump’ at T_g at DSC heating runs and is also typical for partially miscible systems.

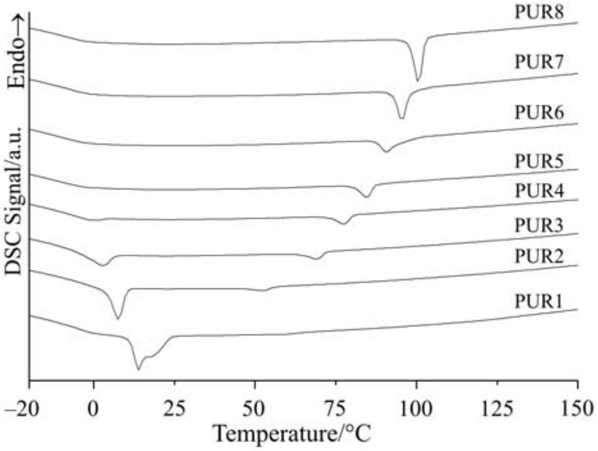

Fig. 3 DSC crystalization curves of investigated polyurethanes

DSC curves of the polyurethanes crystallization from the melt are shown in Fig. 3. The crystallization curves for the polyurethanes PUR1, PUR2, PUR3 and PUR4 show two separate peaks for the transitions of the soft segment phase and the hard segment phase, what confirms occurrence of the phase separation on cooling for these polymers.

Increasing of the HS content up to 49.5% for the polyurethanes PUR1–PUR4 causes a decrease of the crystallization temperature of the soft segment phase. For the polyurethanes with higher HS content PUR5–PUR8 only single peaks for the crystallization of the hard segments were observed. Shifts of the hard segment crystallization peaks to the lower temperatures for polyurethanes with greater soft segment content is probably caused by partial segment miscibility at the molten state.

Conclusions

DSC study of the polyurethanes derived from PHA, HMDI and BHDBP as a chain extender reveal presence of ordered, crystalline or mesomorphic, structures. Obtained block polyurethanes comprise separated phases with partial miscibility of hard segments inside soft segment microphases. Ordered structures occur in both kinds of microphases.

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