Study of the effect of crystallization conditions on the structure of polyurethane block copolymer based on poly-ε-caprolactone diol and isophoron diisocyanate

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Abstract. In the paper a study of isothermal crystallization kinetics of polyurethane on the basis of poly-ε-caprolactone diol, isophoron diisocyanate and 1,4-butandiol is presented. The process of isothermal crystallization in the temperatures range from -15 to 30ºС was studied by DSC method. Analysis of total melting enthalpy and degree of crystallinity of the polyurethane allows to obtain material with one or two melting points of polyester block at desired temperature. These results will help in design of new thermoplastic elastomers with one- or two-stage shape memory effect.

1. Introduction

Shape memory polymers (SMPs) attract a lot of attention of researchers because of their ability to obtain a temporary shape and restore their initial shape under the influence of external factors. In most cases, polymers with SME are thermosensitive, i.e. they recover to their original shape after local heating. Among polymers with SME, particular interest is given to semi-crystalline multi-block thermoplastic polyurethanes (TPU) with thermodynamically incompatible soft and rigid blocks, which lead to microphase separation. Rigid blocks are built from urethane groups forming a network of hydrogen bonds, providing physical cross-links. Soft blocks are crystallizing hydroxyl-containing polyesters and the crystals play the role of additional units of the physical network, providing high strength of the material. Therefore, a rigid block is responsible for the strength of the material, while a soft block is responsible for its elasticity and ability to take a temporary shape.

For applications, it is important to control switching temperature of heat-sensitive TPUs, i.e. the temperature at which the material changes its temporary shape. For TPU with crystallizing soft blocks the switching temperature is the melting point of polyester crystal phase [1]. Nowadays one of the most popular oligoether diols used as a soft block is biodegradable poly-ε-caprolactone (PCL), which has a melting point close to physiological environment temperature, which allows to use such TPU in medicine [2]. It is known that crystallization of PCL significantly changes the structure and properties of TPU. The size of crystals and the growth rate depend on the crystallization conditions and determine switching temperature. In such way, control of thermal properties of PCL-based TPU, particularly, switching temperature can be done by adjustment of crystallization conditions in soft
block domains without changing the polymer composition. The choice of optimal crystallization conditions allow to fabricate materials with desired properties which is important for practical applications.

In this paper, the structure of a model block copolymer based on PCL, isophoron diisocyanate (IPDI) and 1,4-butanediol (1,4-BD) has been studied by the DSC method depending on the crystallization conditions. The presented results are aimed at the development of multi-block urethane and urethanurea copolymers with programmable shape memory effect for medical applications.

2. Experimental part

2.1. Materials

Poly-ε-caprolactone diol (PCL), M_n~ 2000 Da, by Aldrich, was used after pre-drying at 60°C on a rotary evaporator. The content of hydroxyl groups determined by the chemical method [3] was 1.9%.

Isophoron diisocyanate (IPDI), 1,4-butanediol (1,4-BD) by Aldrich company, methylene chloride (purity ~ 99.9%) were used preliminarily purified according to the standard method [4]. The content of isocyanate groups in IPDI and hydroxyl groups of 1,4-BD, determined by the chemical method [4], equals to 99.9% of the theoretical one.

Dibutyltin dilaurate catalyst by Aldrich was used without additional purification.

2.2. Synthesis of polyurethane

Linear polyurethane block copolymer was obtained by a two-stage method through the stage of formation of macromdiisocyanate in methylene chloride solution in the presence of dibutyltin dilaurate catalyst. At the first stage, IPDI interacted with PCL at [NCO]_{IPDI}/[OH]_{PCL} = 2, then the chain extension 1,4-BD was added to the stoichiometric ratio of functional groups. Upon reaching the degree of transformation in the groups of NCO ~ 98%, the reaction mass was poured into a flat form of Teflon and dried at 40°C for a day to a constant weight.

2.3. Methods

Polyurethane crystallization kinetics was investigated by DSC method in isothermal conditions using DSC 30 Mettler Toledo calorimeter. The samples (10±0.2 mg) were placed in an aluminium pan, rapidly cooled down to -20°C and further heated at rate to 10°C/min in a nitrogen atmosphere to 70°C. After 2 minutes at 70°C, the samples were cooled down to isothermal crystallization temperature (-15 to +30°C). After holding for period of time from 15 to 960 minutes at given temperature, the samples were heated up to 70°C to determine the melting enthalpy of crystal phase.

The degree of crystallinity (X) was determined by the formula (1):

$$ X = \frac{\Delta H_m}{\Delta H_{100\%}^{100\%}} $$

where $\Delta H_m$ – total melting enthalpy measured from DSC curves, $\Delta H_{100\%}^{100\%} = 243$ J/g - equilibrium melting enthalpy of PCL, taking into account that crystallinity of Poly-ε-caprolactone diol determined by X-ray diffraction is about 40%.

Microscopic images of thin films with thickness of 10-30 microns were obtained with optical microscope Carl Zeiss AxioScope A1 POL in polarized light with 100x objective. The films were applied to cover glasses made of THF solution, heated up to 70°C, then crystallized at room temperature and at -10°C during twenty-four hours. To heat the films, a Linkam LTS420 heating stage with a working temperature range from -196°C to 420°C was used. Images were exported to the PC using 5 MP CMOS camera.

3. Results and discussion

Synthetic polyurethane is a block copolymer consisting of a soft block of PCL and a rigid block formed by IPDI and chain extenderer 1,4-BD (Figure 1).
Figure 1. Scheme of reaction of two-stage synthesis of polyurethane based on IPDI and PCL using 1,4-BD as a chain extender.

Figure 2 shows DSC-thermograms of the studied samples heated from crystallization temperature from -15°C to 25°C. At the crystallization temperature -15°C two endothermic melting peaks are observed during heating, that can be associated with the melting of crystals of different perfection – less regular $T_{m_1}(1)$ and more regular $T_{m_2}(2)$, respectively. With the increase of the crystallization temperature, the intensity of endothermic melting peaks changes due to the difference in the nucleation rate. With the increase of crystallization time up to 960 minutes the area of peaks gradually increases with a shift of the first peak to higher temperatures (Table 1). This is probably related to the improvement of the PCL crystal quality during heating.
The increase of the crystallization temperature to 25°C results in decrease of the nucleation and crystallization rate and formation of perfect thick crystals due to homogeneous nucleation. This is represented on the DSC-thermogram as single endothermic melting peak. On the DSC curves of sample crystallized at higher temperature the endothermic peaks do not appear indicating the absence of crystallization because of very slow nucleation rate.

Table 1 shows the degree of crystallinity of TPU depending on crystallization temperature and time, calculated from area of endothermic melting peaks at certain temperature intervals using equation (1). Table 1 shows that the maximum degree of crystallinity of the TPU is obtained after crystallization at 5°C.

The influence of crystallization conditions on the TPU structure is confirmed by the results of optical microscopy (Figure 3).
Table 1. The dependence of the change in the degree of crystallinity on the holding time at different crystallization temperatures.

| Crystallization temperatures (°C) | Crystallization time (min) | X (%) | -ΔH (J/g) | T_{melt}(1) (°C) | T_{melt}(2) (°C) |
|----------------------------------|---------------------------|-------|-----------|-----------------|-----------------|
| -15                              | 15                        | 0.06  | 0.09      | -               | 30.4            |
|                                  | 480                       | 17.1  | 27.3      | 0.6             | 29.3            |
|                                  | 960                       | 20.7  | 33.1      | 2.3             | 29.1            |
| -10                              | 15                        | 0.06  | 0.10      | -               | 30.5            |
|                                  | 480                       | 19.3  | 30.9      | 5.7             | 29.9            |
|                                  | 960                       | 22.2  | 35.5      | 7.2             | 29.7            |
| -5                               | 15                        | 0.06  | 0.06      | -               | 29.6            |
|                                  | 480                       | 20.4  | 32.6      | 10.2            | 30.2            |
|                                  | 960                       | 21.3  | 34.0      | 11.4            | 30.2            |
| 0                                | 15                        | 0.11  | 0.11      | -               | 30.5            |
|                                  | 480                       | 16.3  | 32.8      | 14.6            | 15.5            |
|                                  | 960                       | 22.8  | 36.5      | 15.5            | 31.2            |
| 5                                | 15                        | 0.07  | 0.10      | -               | 31.2            |
|                                  | 480                       | 21.5  | 34.3      | 19.0            | 32.3            |
|                                  | 960                       | 24.9  | 39.8      | 20.2            | 32.5            |
| 10                               | 15                        | 0.07  | 0.12      | -               | 32.3            |
|                                  | 480                       | 12.5  | 19.9      | 23.4            | 33.6            |
|                                  | 960                       | 22.5  | 35.9      | 24.2            | 33.8            |
| 15                               | 15                        | 0.04  | 0.03      | -               | 31.1            |
|                                  | 480                       | 8.5   | 13.6      | 27.8            | 34.8            |
|                                  | 960                       | 18.1  | 28.8      | 30.0            | 34.9            |
| 20                               | 15                        | 0.02  | 0.03      | -               | 36.9            |
|                                  | 480                       | 10.8  | 17.2      | 32.4            | 36.7            |
|                                  | 960                       | 10.8  | 17.4      | 32.8            | 36.6            |
| 25                               | 15                        | -     | -         | -               | -               |
|                                  | 480                       | 0.17  | 0.27      | -               | 37.1            |
|                                  | 960                       | 0.99  | 1.6       | -               | 42.0            |

The microphotographs show the change in the size of the crystalline domains depending on the crystallization conditions. At the image of TPU crystallized at 25°C one can observe the presence of "Maltese cross" type texture with the size of objects of about 20-50 microns. These objects represent radially growing spherulites which are typical for crystallizing block copolymers [5]. In contrast, crystallization at -10°C results in formation of smaller spherulites of 10-20 microns. The obtained results indicate changes in nucleation rate which affects the total degree of crystallinity of the polymer and crystals quality.
4. Conclusions
Using combination of DSC and optical microscopy the effect of crystallization conditions on thermal behavior of PCL-based TPU was studied. It was shown that increasing of crystallization temperature leads to decrease of nucleation and growth rate. In the result, total degree of crystallinity decreases with improvement of crystal quality. In addition, variation of crystallization conditions allows varying switching temperature of the model linear polyurethane block copolymer from 30 to 42 °C for the same sample. This result is very important for fabrication of heat-sensitive TPU with controllable shape memory effect for particular medical application.

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