The study of model reactions occurring in the synthesis of adaptive multiblock polyurethanes

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Abstract. In the paper a study of formation process of linear polyurethane on the basis of 4,4'-diphenylmethane diisocyanate, poly(1,4-butylene adipate) diol and 1,4-butanediol is presented. The kinetics of the first stage of macrodiisocyanate formation reaction was studied by IR spectroscopy. Experimental and calculated values of the rate constant of the first reaction stage were obtained. The influence of the solvent on the polyurethane structure was defined. The conditions to fabricate polymer with a maximum crystallinity degree have been determined. Important results for the synthesis of the shape memory multiblock polyurethane thermoplastic elastomer have been obtained.

1.Introduction

A detailed study of the properties and synthesis methods of biodegradable and biocompatible polymers with shape memory effect (SME), one of which is a thermoplastic polyurethane block-copolymer (TPU), consisting of soft, crystallizable polyester blocks, and hard diol-urethane segments, is currently being conducted. Such polymers are used in medicine for drug-release systems, for manufacture of prostheses, implants, also there is the widespread application in textile, automobiles and aircrafts industry [1]. A wide range of materials based on these polymers applications is associated with their specific structure, the possibility of varying mechanical properties by changing the ratio of reagents during synthesis [2].

It is important to note that properties of TPU with shape memory effect (SME) depend on the method and conditions of synthesis, stoichiometry of functional groups of reagents, molecular and weight parameters, which are defined by a kinetics of reaction that occurs during the formation of these polymers.

Analysis of literature on the synthesis of TPU based on 4,4'-diphenylmethane diisocyanate (MDI), which, in fact, is one of the most popular diisocyanates used in the production of polyurethanes, it should be noted that, mainly, results of the research of properties and structure of TPU based on it are presented, and there is practically no information on the kinetics of synthesis.

In the literature about the kinetics of reaction, there are studies of stoichiometric reaction of MDI with low molecular weight diols in chloroform [3], the formation of macrodiisocyanate (MDC) with polypropylene oxide carried out in THF [4] and polypropylene glycol carried out in bulk at 60°C [4] with an excess of NCO-groups is discussed.

As assumed, the reaction has second-order kinetics and two reaction rate constants were presented in accordance with the first stage of MDC formation and the second final stage after adding a chain...
extension. It is important to note that the synthesis of multiblock thermoplastic polyurethanes with SME is usually carried out in a methylene chloride solution. However, this reaction was not described in details.

In this paper, the formation process of linear polyurethane based on hydroxyl-containing poly(1,4-butylene adipate) diol (PBA), MDI and a chain extender 1,4-butandiol (BD) in the presence of a methylene chloride solvent and a tin dibutyltin dilaurate catalyst, as a model reaction that occurs during synthesis of TPU with SME has been studied.

2. Experimental part

2.1. Materials
Poly(1,4-butylene adipate) diol (PBA), Mn ~ 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 [5] was 1.76%

4,4’-diphenylmethane diisocyanate (MDI) by Alfa Aesar and dibutyltin dilaurate catalyst (DBTDL), were used without prior purification.

1,4-butanediol (1,4-BD), methylene chloride (purity 99.9%) and THF (purity 99.9%) were used preliminarily purified according to the standard method [6], equals to 99.9% of the theoretical one.

2.2. Fourier Transform Infrared Absorption Spectroscopy (FTIR)
IR spectra for the identification of the reagents and the synthesized TPU were recorded on an Alpha Bruker spectrometer under the following conditions: measurement range 4000 cm⁻¹ - 360 cm⁻¹; measurement step 2 cm⁻¹; the number of scans per spectrum 56; samples were obtained in a film from a methylene chloride solution on KBr glass.

The kinetics of the catalytic reaction of urethane formation was studied by IR spectroscopy by the total consumption of NCO-groups and the accumulation of urethane groups. At certain intervals after the start of the reaction of PBA with MDI taken in the ratio [NCO] / [OH] = 2, samples of the reaction mixture were taken. Then, the IR spectra of solutions of the reaction mixture in methylene chloride were recorded on a spectrometer.

The current concentration of isocyanate groups was determined by changing the intensity of the absorption peak corresponding to the antisymmetric vibration of the NCO-groups of MDI (ʋNCO = 2275-2260 cm⁻¹) and the stretching vibration of the urethane group carbonyl (ʋC=O = 1720 cm⁻¹).

To obtain the molar extinction coefficient of MDI, MDI solutions in various concentrations of methylene chloride were prepared, after which a calibration dependence of the optical density of the analytical band on the concentration of isocyanate groups was constructed. The molar extinction coefficient of MDI was determined by equation (1).

\[
\varepsilon = \frac{\Delta D}{\Delta l \cdot C} \tag{1}
\]

where:
- \( \varepsilon \) is the molar extinction coefficient of MDI
- \( \Delta D \) is the optical density
- \( \Delta l \) is the cuvette thickness, cm
- \( C \) is the concentration of the solution, g-eq/l.

The effective reaction rate constant was determined by equation (2), based on equal reactivity of both of the isocyanate groups of MDI with a twofold excess of them relative to the hydroxyl groups of PBA:

\[
\ln \frac{[OH]_0 + [OH]}{2[OH]} = k \Delta t \tag{2}
\]

where:
- \( k \) is the reaction rate constant, l/g-eq·s
- \( \Delta t \) is the change in the reaction time, s
\[ [\text{OH}] \] - the current concentration of hydroxyl groups of PBA during the reaction, g-eq/l
\[ [\text{OH}]_0 \] is the concentration of hydroxyl groups at a time \( t = 0 \).

2.3. Theoretical calculation of the kinetics of the studied reactions of urethane formation
The experimental values of the effective rate constant of the first stage of the MDC formation were confirmed by solving direct kinetic equations by means of standard Kinet program using numerical Gear method [7]. For the calculation, the following assumptions were made: the reaction mixture is homogeneous throughout the urethane formation process, and the reactivity of hydroxyl and isocyanate groups does not change during the reaction.

For the studied PBA-MDI system with equal reactivity of the functional groups, a system of equations describing the interaction of the functional groups is written. As a result of the calculation, the value of the kinetic constant is obtained, which characterizes the interaction between the functional groups of PBA and MDI. The proof of the obtained value of the rate constant was made by comparison of the calculated and experimental kinetic curve, the deviation between which does not exceed 1-2%.

The calculation of the rate constant was carried out according to the following parallel-sequential reaction scheme (Scheme 1):

\begin{align*}
  &I + \text{OH} \rightarrow U_1 + I_2 \\
  &I + \text{OH} \rightarrow U_2 + I_1 \\
  &I_1 + \text{OH} \rightarrow U_1 \\
  &I_2 + \text{OH} \rightarrow U_2 \\
\end{align*}

where:
- \( I \) is the concentration of MDI at the initial time
- \( \text{OH} \) is the concentration of OH groups of PBA at the initial time
- \( U_1 \) is the concentration of urethane groups formed by OH-groups of PBA and NCO-group MDI in position 4-
- \( U_2 \) is the concentration of urethane groups formed by OH-groups of PBA and NCO-group MDI in position 4’-
- \( I_1 \) - concentration of NCO-groups of MDI in position 4-
- \( I_2 \) - concentration of NCO-groups of MDI in position 4’-

2.4. DSC method
The structure of TPU was investigated by DSC using DSC 30 Mettler Toledo calorimeter in dynamic mode. The sample (10.0 ± 0.2 mg) were placed in an aluminium pan, rapidly cooled down to -20°C and further heated at rate 10°C/min in a nitrogen atmosphere to 70°C. The degree of crystallinity (CD) of TPU was determined by the formula (3):

\[
CD = \frac{\Delta H_m}{\Delta H_{m(100\%)} \cdot \omega} \\
\]  

where:
- \( \Delta H_m \) - total melting enthalpy measured from DSC curves;
- \( \omega \) - mass fraction of PBA in the polymer;
- \( \Delta H_{m(100\%)} = 95 \text{ J/g} \) - equilibrium melting enthalpy of PBA at its 100% crystallinity.

2.5 Synthesis of polyurethane
Linear polyurethane block copolymer was obtained by a two-stage method through the stage of formation of macrodiisocyanate in methylene chloride solution (or THF) at a room temperature in the presence of DBTDL catalyst from PBA oligoether diol, MDI and BD as chain extender (figure 1). At the first stage, MDI interacted with PBA at \([\text{NCO}]_{\text{MDI}} / [\text{OH}]_{\text{PBA}} \approx 2\), then the chain extension 1,4-BD
was added to the stoichiometric ratio of functional groups ([NCO]_{MDI} / [OH]_{PBA + BD} = 1). 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.

Figure 1. TPU scheme.

3. Results and discussion
The synthesis of TPU based on MDI, according to published data, is usually carried out in DMSO, DMAA or DMF [8]. However, the disadvantage of these solvents for the synthesis of the polymer is their high boiling point, which complicate removing solvents from the polymer matrix, as well as the difficulties in the study of kinetics by IR spectroscopy due to strong absorption in this wave range. To avoid above-mentioned problems, in the presented study the formation of TPU was carried out in methylene chloride and THF. For identification and purity of the starting compounds, their IR spectra were recorded for a film from a methylene chloride solution (figure 2).

Figure 2. IR spectra of films of PBA (a) and MDI (b) in methylene chloride solution.

In the IR spectrum of PBA (figure 2a), absorption bands of hydroxyl groups (3670-3580 cm\(^{-1}\)) and carbonyl C = O (1730 cm\(^{-1}\)) which belong to the functional groups of diols based on esters, are observed, which confirms the chemical composition of polyether diol used in the work. On the IR spectrum of MDI (figure 2b), characteristic bands of isocyanates are observed in the region of absorption of stretching vibrations of NCO groups at 2270 cm\(^{-1}\), a characteristic absorption band at 1511 cm\(^{-1}\) corresponding to stretching vibrations of the aromatic ring is also visible, which confirms the presence of the C\(_6\)H\(_5\)- group in the MDI isocyanate. Thus, from figure 2, we can conclude that IR spectra correspond to the proposed structures.

Figure 3 illustrates the change in the intensity of the absorption band of the NCO group of MDI in the solutions of various concentrations in methylene chloride (figure 3a). Using this dependence, a calibration plot of the optical density of the analytical band on the concentration of isocyanate groups was calculated (figure 3b). As a result, the value of the molar extinction coefficient for MDI in methylene chloride was calculated, which amounts to 872 l/g-eq.cm.

The kinetics of the catalytic reaction of the first stage of the synthesis - PBA with MDI in the presence of a dibutyltin dilaurate catalyst with a ratio of NCO/OH = 2 was studied by changing the
intensity of the absorption band corresponding to the antisymmetric stretching vibrations of the NCO groups of MDI (figure 4a). The concentration of the catalyst was 0.003 mol/l; the initial concentration of MDI isocyanate groups was 0.86 g-eq/l.

Figure 3. IR spectra of MDI solutions in methylene chloride at 0.006 (1), 0.015 (2), 0.029 (3) g-eq/l in the absorption region of NCO groups, Δl = 0.078 cm (a) and typical calibration dependence (b).

Figure 4. IR spectra of the reaction media, showing the change in the concentration of the NCO group in the process of urethane formation, where 1 is the end of the first stage of urethane formation (a) and the dependence of the change in the concentration of MDI, mol/l (1), the concentration of OH-groups of PBA, g-eq/l (2), the concentration of MDC, mol/l (3) and the concentration of urethane groups, g-eq/l (4) of the reaction time of urethane formation (b).

It was found that the catalytic reaction was almost completed in 60 minutes after the beginning of the synthesis. The conversion of OH groups of PBA was 98%. Based on the results obtained, the kinetic constant of urethane formation, calculated by the formula (1), was estimated to be 1.09⋅10⁻³ l/g-eq⋅s. The calculation by the numerical method using the Kinet program confirmed the validity of this value for the kinetic constant and made it possible to determine the structural composition of the obtained prepolymer (figure 4b).

The curves presented in figure 4b make it possible to estimate the concentration of reagents and the structural composition of the reaction mass at any time during synthesis. After the OH-groups of PBA
completely reacted, a 1,4-BD (chain extender) was added to the prepolymer to the stoichiometric ratio of the reacting groups.

As it can be seen from the IR spectra (figure 5), the absorption band corresponding to the stretching vibration of the NCO group of MDI in the region of 2270 cm\(^{-1}\) and the appearance of peaks in the absorption region of hydrogen-bonded NH groups at 3420 cm\(^{-1}\) and absorption bands are observed at 1780 cm\(^{-1}\), corresponding to the C=O free group, characterizing the formation of urethane bonds.

**Figure 5.** IR spectra of PBA (1) and TPU synthesized in a solution of methylene chloride (2) and THF (3).

The IR spectrum of TPU obtained in a THF solution shows a small shoulder in the region of free OH groups of water, which is probably due to the high hydrophilicity of the solvent. The presence of moisture in the sample will affect the formation of the structure of TPU and its properties.

The obtained kinetic results were used in the synthesis of TPU carried out in methylene chloride and THF.

The synthesized polyurethane is a phase-separated linear block copolymer consisting of thermodynamically incompatible soft block of PBA and a hard block based on MDI and BD. The polymer is opaque under normal conditions, which indicates its heterogeneous structure (figure 6).

**Figure 6.** TPU synthesized in methylene chloride solution (a) and in THF (b).

The results of the DSC analysis of polymers, depending on the type of solvent in which the polymers were synthesized, showed differences in their structure (figure 7). In the DSC thermogram of samples immediately after synthesis, multiple melting peaks of crystals of the soft polyester block are observed. Such behavior is typical for which melting of imperfect crystals of different thicknesses [9]. It was established that TPU synthesized in methylene chloride solution shows higher degree of crystallinity (33.8%) in comparison with TPU synthesized in THF (23.05%). It is important to note
that in the synthesis of multiblock TPUs with SME, phase separation and crystallization processes will determine thermal and mechanical parameters of adaptive materials.

**Figure 7.** DSC heating thermograms of TPU synthesized in methylene chloride (1) and THF (2)

### 4. Conclusions

The formation of linear polyurethane based on PBA, MDI, and 1,4-BD in the presence of a catalyst in different solvents was studied. Based on the kinetics data, the optimal conditions for the synthesis of TPU were proposed. Using a combination of IR and DSC methods, the influence of a solvent on the formation of the structure of TPU was shown. A polymer synthesis strategy that allows to obtain TPU without side reactions with a maximum degree of crystallinity has been developed. The results will help for the synthesis of thermoplastic polyurethanes with SME.

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