Depolymerization behavior of thermoplastic poly(urethane) (TPU) and its dependence on initial molecular weight

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ABSTRACT

The quantitative and qualitative depolymerization behavior of thermoplastic poly(urethane) (TPU) consisting of 4,4′-methylenediphenyldiisocyanate (MDI), 1,6-hexanediol (HD) and 1-hexanol (HEX) was described using temperature-modulated differential scanning calorimetry and Fourier transform infrared (FT-IR) spectroscopy. The depolymerization behavior could be altered by lowering the starting molecular weight. This resulted not only in a higher ceiling temperature, but also in a faster decrease of the molecular weight as a function of temperature once the depolymerization has started. The increase in the ceiling temperature for low molecular weight TPUs is attributed to the lower entropy of polymerization for these compounds compared to high molecular weight TPUs.

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1. Introduction

Chemical reactions that involve aggregation of a large number of molecules, such as polymerization reactions, can be characterized by a temperature above which no aggregation occurs, the so-called ceiling temperature (T_{cl}) [1–4]. Above this temperature, a (partial) disaggregating or depolymerization of the material occurs. For polymers, the practical implications of this phenomenon are, for instance, illustrated by the obtainment of a residual monomer content or no polymerization at all after polymerization at high temperatures for anionic ring-opening polymerization of caprolactam or the polymerization of α-methyl styrene [5]. Furthermore, the thermal instability of (meth)acrylates [6] and polyurethanes [7] and the formation of cyclic oligomers from linear polymers at high temperatures [8–10] can be ascribed to this phenomenon. Although

this depolymerization is in most cases unfavorable, it can also be used in some processes. An example of this can be found in the solid-state modification of poly(ethylene terephthalate) (PET) or poly(butylene terephthalate) (PBT). In this process, PET/PBT is depolymerized to some extent to create more reactive groups for the modification [11–14]. Another example is thermoplastic poly(urethane) (TPU) consisting of short building blocks only, i.e. 4,4′-methylene diphenyldiisocyanate (MDI) and 1,6-hexanediol (HD), which is depolymerized during processing to yield lower processing viscosities without affecting the mechanical properties due to the build-up of the molecular weight upon cooling after the processing step [15].

The ceiling temperature of a polymer is directly related to the free energy change of the polymerization reaction. At equilibrium, the free energy change is zero and the ceiling

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temperature can then be defined as shown in Eq. (1):

$$T_{cl} = \frac{\Delta H_{pol}}{\Delta S_{pol}} \qquad (1)$$

A number of physical factors such as monomer concentration, solvent medium, crystallization or pressure as well as the type of substituents and the number of atoms in cyclic monomers have an effect on either the enthalpy of polymerization, ΔH_{pol}, or the entropy of polymerization, ΔS_{pol} [2,7]. In this way, the ceiling temperature can be influenced. For instance, the extent of polymerization for cyclic oligomers depends on the number of atoms in the ring [2]. For ring-opening polymerization of small rings, ΔH_{pol} is largely negative due to the high bond strain, resulting in essentially complete reactions, while for polymerization of larger rings, ΔH_{pol} is much smaller giving rise to partial or no reaction. The polymerization of very large rings results in a positive change in ΔS_{pol}, consequently yielding a high extent of polymerization again. In this respect, the molecular weight of the final polymer should also have a significant effect on the ceiling temperature, as ΔS_{pol} is substantially influenced by the obtained molecular weight, especially for low molecular weights. However, such dependency has to our knowledge never been reported.

The depolymerization behavior of a polymer depends on its polymerization mechanism, i.e. chain-growth and step-growth. Step-growth polymers will randomly break up into smaller fragments upon depolymerization, while chain-growth polymers release successive monomer units from their chain ends, a literal unzipping of the chain [5]. Due to this direct release of monomer, the depolymerization of chain-growth polymers is of much more importance. Moreover, the accompanying equations to describe the depolymerization can be easily simplified resulting in the monomer concentration as the single remaining concentration influencing the ceiling temperature, while for step-growth polymerizations the concentrations of all the constituents involved have to be taken into account. Therefore, most studies on depolymerization consider chain-growth polymers only. One of the most studied step-growth polymer which clearly shows depolymerization phenomena is poly(urethane) and its thermal instability has been reported by many authors [16–21]. However, none of these studies described the molecular weight of the TPU fragments upon depolymerization in order to be able to predict the molecular weight at a certain temperature. The curve of the molecular weight as a function of temperature is called the depolymerization curve.

This depolymerization curve of TPU is of critical importance in the use of TPU as reactive 'solvent' to improve the processing of intractable polymers [22]. Intractable polymers can be processed using reactive solvents which are polymerized in situ after the processing step. Due to this polymerization, the reactive solvent phase separates from the intractable polymer to form a constituent of the final material. In this way, the properties of the intractable polymer can be retained without solvent removal. However, the thus far used reactive solvents, such as epoxy resin [23] or styrene [24], are polymerized at high temperatures, which can lead to premature polymerization during the homogenization step.

This intrinsic problem can be circumvented by using reactive 'solvents' which possess a practically accessible ceiling temperature. These 'solvents' depolymerize during processing to yield small fragments which can act as a solvent for the polymer to be processed. During the shaping step, the system is cooled down below the ceiling temperature, inducing a repolymerization of fragments and a subsequent phase separation between polymer and 'solvent', similar to the conventional reactive solvent systems.

In this paper, we report on the depolymerization behavior of TPU consisting of short building blocks of MDI, HD and 1-hexanol. Due to the short building blocks which repolymerize very fast upon cooling, monitoring of the depolymerization reaction is restricted to in situ techniques, since it is impossible to quench to a particular state of (de)polymerization. Only when poly(glycols) are incorporated, the repolymerization can be slowed down to such an extent that quenching is possible [25]. Recently, Dickie [26] used temperature-modulated differential scanning calorimetry (TM-DSC) to investigate the depolymerization behavior of TPU, but the molecular weight determination as a function of temperature was based on an empirical approach. Therefore, Fourier transform infrared (FT-IR) spectroscopy is used in this study to construct the depolymerization curve, while TM-DSC is only used to qualitatively determine the ceiling temperature. Furthermore, as the starting molecular weight of the TPU had to be lowered in order to improve the miscibility of TPU with the intractable polymer [22], the effect of the starting molecular weight on the depolymerization behavior is investigated.

2. Experimental

2.1. Materials

Thermoplastic poly(urethane) (TPU) consisting of alternating 4,4′-methylenediphenyldiisocyanate (MDI) and 1,6-hexanediol (HD) building blocks was supplied by the DOW Chemical Company (ISOPLAST^{TM} 2530 resin). This compound will be referred to as TPU-0%. Three low molecular weight TPUs containing MDI and HD were synthesized using 2, 4 and 8 wt.% of 1-hexanol (Hex) as chain stopper based on the total weight [27]. The three reactants were simultaneously fed to a Berstorff model ZE40X47D 40-mm twin-screw extruder, operated at a screw speed of 450 rpm and a temperature of 100 °C. The output of the extruder was set to 135 kg h^{-1} and the extrudate was chopped under water into small granules. The compounds will be referred to as TPU-2%, TPU-4% and TPU-8% depending on the amount of 1-hexanol added. The absolute molecular weights of the TPUs are determined via triple detection size exclusion chromatography (Triple-SEC) using hexafluorisopropanol (HFIP) as the mobile phase. The important parameters for all TPUs are summarized in Table 1.

2.2. Fourier transform infrared (FT-IR) spectroscopy

All samples were analyzed using a high temperature sample holder equipped with a 3-mm thick crystal carrier of potassium bromide (KBr). The high molecular weight TPU-0% was solution cast from N,N'-dimethylformamide (DMF) and the