



Time resolved characterization of the solid-state reaction between polycarbonate and primary amine



Cordelia Zimmerer^{a,*}, Lisa Ziegler^a, Gert Heinrich^a, Gerald Steiner^b

^a Leibniz Institute of Polymer Research Dresden, P.O. Box 120 411, D-01005 Dresden, Germany

^b Dresden University of Technology, Faculty of Medicine Carl Gustav Carus, Clinical Sensing and Monitoring, Fetscher Str. 74, D-01307 Dresden, Germany

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ABSTRACT

Polycarbonate can be functionalized with specific moieties such as amino groups. A novel approach for functionalization is based on a process integrated surface modification, e.g. during the injection molding process. However, the solid-state reaction routes are complex, not well investigated and difficult to control. In this study the solid state reaction of polycarbonate with octadecylamine was studied by using infrared spectroscopy and 2D correlation analysis. The infrared spectrum taken after 20 min reaction time shows the formation of urethane as an interfacial linker between polycarbonate and octadecylamine. Furthermore, bisphenol-A, also formed initially, indicates a degradation of polycarbonate. The solid-state reaction during 360 min processing time was investigated by 2D correlation analysis. The 2D correlation maps indicate a progress in the degradation of polycarbonate and the formation of biuret and urea. No more urethane is formed during longer processing time. This study demonstrates that a surface modification of polycarbonate with octadecylamine requires a very short reaction time in order to ensure an optimized interfacial link and to minimize the degradation of the materials.

1. Introduction

Polymer surface modification is a useful method for creating functional polymer surfaces combined with the advantageous properties of the bulk polymer [1]. Many different chemical and physical methods for polymer surface modification have been developed during the last decades. The chemical methods developed for such purpose are either direct reactions of the polymer with the surface modifier component in solution or postpolymerization modifications. While postpolymerization needs the presence of monomers, direct chemical reactions can be used to modify a polymer surface with different components [2]. Direct reactions for surface modification are usually solid-state reactions which lead to the formation of different structures making the surface modification process complex. Solid-state reactions are mostly limited to the grain boundaries and, therefore, require elevated temperatures for a longer period of time to provide sufficient diffusion of functional groups and to bring reactive groups in proximal distance and reactive orientation [3]. They are generally much slower, more complex and more difficult to interpret than reactions in solution state [4]. This is in particular true for the solid – solid boundary condition.

An example of surface modification is the covalent coupling of

amino groups of a primary amine on the surface of bisphenol-A based polycarbonate (PC), also called as aminolysis. PC is a widely used engineering polymer with excellent optical and mechanical properties. However, PC has a hydrophobic surface and is therefore less suitable for biochemical application. A primary amine with functionalized end groups can be used to modify surfaces of PC in order to alter hydrophilicity, hydrophobicity and to prepare biocompatible surfaces [5]. For example, the surface modification of PC with octadecylamine (ODA) makes PC more hydrophobic.

The surface modification of PC with ODA during the forming process, e.g. injection molding, is a very promising approach because the melt heat can be simultaneously used to initiate chemical solid-state reactions between a carbonate and amino group.

Although few papers were published that examined and debated the reaction of carbonate groups with amino groups to create urethane bonds [6–8], detailed knowledge about the chemical reaction mechanisms, including intermediates and side products, is still lacking. Fig. 1 shows the expected reaction mechanism between PC and ODA: an initial PC backbone scission at carbonate groups is followed to a coupling of amino groups. Urethane groups are finally formed.

This general mechanism and the formation of urethane groups have

Abbreviations: PC, polycarbonate; ODA, octadecylamine; IR, infrared; ATR, attenuated total reflection; mp, melting point; BPA, bisphenol-A; DODU, 1,3-Dioctadecylurea; ODA-U, Propane-2,2-diylbis(4,1-phenylene) bis(octadecylcarbamate); TOD-B, 1,3,5-Trioctadecylbiuret; FT, Fourier Transform

* Corresponding author.

E-mail address: zimmerer@ipfdd.de (C. Zimmerer).

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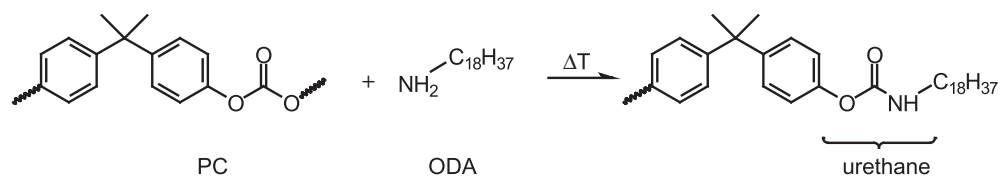


Fig. 1. Expected reaction of PC with ODA.

been confirmed by a similar study [9]. However, several other reaction products and structural units were also identified. In order to translate modification of PC surface by primary amines to practical applications, it is necessary to understand the chemical reaction in detail. This is in particular important as both reactants, PC and ODA, are solid-state materials. Unfortunately, mechanism of the solid-state reaction and related molecular processes within and across interfacial structures are not directly accessible from experimental measurements. Although several studies of polymer interfacial macroscopic structures were performed, for example atomic force microscopy [10] and other microscopic methods [11,12], the sensitive characterization of molecular processes remains a challenge. Among all analytical methods infrared (IR) spectroscopy is the most convenient to provide molecular information about interfacial structures or reactive processes [13,14].

In this contribution the solid-state reaction of PC with ODA was characterized by attenuated total reflection (ATR) IR spectroscopy. The spectroscopic results are discussed with respect to the injection molding process of PC with integrated surface modification by primary amines. The scope of the study refers to the parameter under which injection molding operates and is closely connected to the problem of an optimized processing time.

2. Experimental section

2.1. Chemicals

All substances used in this study, their specification and suppliers are summarized in Table 1. The substances were used as received.

2.2. Synthesis of reference materials

2.2.1. 1,3-Dioctadecylurea (DODU)

A mixture of diphenyl carbonate (50 mmol) and octadecylamine (110 mmol) was heated at 110 °C for 225 min in a three-necked flask under nitrogen. The product was recrystallized in chloroform. DODU was obtained as white solid with a yield of 65% and a melting point (mp) of 115 °C.

¹H NMR (CDCl₃, 500 MHz, 323 K): δ (ppm): 4.13 (s, 1 H, NH), 3.15 (q, 2 H, CH₂), 1.5 (t, 3 H, CH₃).

2.2.2. Propane-2,2-diylbis(4,1-phenylene) bis(octadecylcarbamate) (ODA-U)

BPA (1.25 mmol) and dibutyltin dilaurate (0.05 mmol) were solved in 20 ml dry acetonitrile. The resulting solution was added dropwise to a solution of octadecyl isocyanate (2.85 mmol, solved 20 ml dry

acetonitrile) at room temperature. The reaction mixture was stirred for 24 h. Subsequently, a solution of octadecyl isocyanate (1.2 mmol) solved in 8 ml dry acetonitrile was added. After 24 h stirring acetonitrile was evaporated under reduced pressure. The resulting residue was purified via column chromatography. The column with a length of 42 cm and an inner diameter of 3 cm was packed with silica gel as the stationary phase. A mixture of chloroform:acetonitrile (6:0.1) was used as eluent. ODA-U was eluted first and had a retardation factor of 0.93. A recrystallization from chloroform gave the pure product. ODA-U was obtained as white crystals with a yield of 49% and mp of 109 °C.

¹H NMR (CDCl₃, 500 MHz, 300 K): δ (ppm): 7.18 (d, 2 H, CH_{ar}), 7.02 (d, 2 H, CH_{ar}), 4.94 (s, 1 H, NH), 3.26 (q, 2 H, N-CH₂) and 1.65 (s, 3 H, C-(CH₃)₂-).

2.2.3. 1,3,5-Trioctadecylbiuret (TOD-B)

A mixture of 1,3-dioctadecylurea (0.846 mmol) and octadecyl isocyanate (6.77 mmol) was refluxed at 105 °C for 44 h. After reflux the solid was recrystallized from chloroform and purified by column chromatography under the same conditions as described above. The product was found in the second fraction with a retardation factor of 0.88. TOD-B was obtained as a white solid product with a yield of 60% and mp of about 77 °C.

¹H NMR (CDCl₃, 500 MHz, 300 K): δ (ppm): 7.03 (s, 1 H, NH), 3.65 (t, 2 H, N-CH₂) and 3.24 (q, 4 H, NH-CH₂).

2.3. Preparation PC - ODA composite

An equimolar ratio of PC and ODA was mixed in a glass tube. The mixture with a mass of approx. 1 g was homogenized and then transferred into a three-necked flask equipped with a stirrer, heated to 180 °C for 7 h and purged with nitrogen and temperature control. The schematic diagram of the experimental set-up is shown in Fig. 2. Totally seven samples, each approx. 1 mg, were taken in an interval of 60 min from the hot PC-ODA mixture. As ODA is a low viscous liquid at a temperature of 180 °C only a thin layer of ODA envelop the solid PC particles when a sample is taken. During the cooling time of approx. 5 min remaining ODA reacts with PC and primary reaction products. This procedure ensures that the film of reaction products comes directly in contact to the ATR crystal surface as it is schematically illustrated in Fig. 2. The sampling procedure was repeated two times. IR spectroscopy revealed that PC and ODA were always present.

2.4. Fourier Transform (FT)-IR spectroscopy and data analysis

IR spectra of PC, ODA, of the PC-ODA mixtures and of the reference

Table 1
Materials used in this study.

Substance	Abbreviations	Specifications/Purity	Suppliers
Polycarbonate	PC	Makrolon 2207	Bayer, Germany
Octadecylamine	ODA	99%, mp 50–52 °C	Sigma-Aldrich, Germany
Bisphenol-A	BPA	97%, mp 158–159 °C	Sigma-Aldrich, Germany
Octadecyl isocyanate		98%	Sigma-Aldrich, Germany
Diphenyl carbonate		99%	Sigma-Aldrich, Germany
Chloroform		99%	Acros Organics, Belgium
Acetonitrile		99.8%	Merck KGaA, Germany
Silica gel 60		0.02–0.045 mm	Carl Roth, Germany

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