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Poly(butylene terephthalate)/Glycerol-based Vitrimers via Solid-State Polymerization

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S Supporting Information

ABSTRACT: A new type of semicrystalline vitrimer was prepared via the incorporation of glycerol into the amorphous phase of poly(butylene terephthalate) (PBT) by solid-state (co)polymerization (SSP). A near quantitative incorporation of the glycerol was confirmed by NMR spectroscopy. Wide-angle X-ray diffraction, differential scanning calorimetry (DSC), and temperature-modulated DSC showed that the PBT/glycerol-based vitrimers maintain the crystallization characteristics of normal PBT. By a change in the cross-link density of the PBT/glycerol-based vitrimers, a wide range of thermal, rheological and mechanical properties were obtained; e.g., the rubbery plateau modulus at 270 °C could be tuned from 0.07 to 3 MPa. The characteristic vitrimer behavior was demonstrated by stress relaxation and oscillatory frequency sweep experiments. In addition, these semicrystalline vitrimers can be recycled multiple times by compression molding without a substantial loss in dynamic mechanical and thermal properties.

■ INTRODUCTION

Vitrimers, pioneered by Leibler and co-workers,^{1–3} are a new class of chemically cross-linked polymers in which thermally stimulated exchange reactions permit the change of the network topology while keeping the number of bonds and cross-links constant. The vitrimer chemistry was initially based on transesterification reactions,^{4–10} but has been broadened since the vitrimer concept was introduced,^{11–20} and was recently reviewed by Du Prez and co-workers.²¹ Since their invention, vitrimers have been shown to be useful in a variety of practical applications, such as liquid-crystalline elastomer actuators,⁹ multishape memory polymers,¹⁰ and rubber recycling.^{22,23}

In the current work, we focus on poly(butylene terephthalate), which is a semicrystalline polyester of great commercial importance and widely used in injection-molding applications due to its high crystallization rate and good solvent resistance.²⁴ However, commercial PBT, with M_n ranging from 5000 to 45 000 g/mol, is hardly entangled.²⁵ Its lack of entanglements inherently gives the material a low melt strength, leading to processing challenges for techniques that involve elongational flows, such as blow molding, foaming, film, or sheet extrusion.^{26,27} In practice, the melt strength describes the resistance of the polymer to extensional deformation and the melt must have a sufficiently high viscosity to withstand the high strain. In general, there are several ways to improve the melt strength of PBT.²⁸ The first one is increasing the molecular weight and polydispersity index by solid-state

polymerization or chain extension by reactive extrusion with bifunctional chain extenders, such as diepoxies²⁹ and pyromellitic dianhydride.³⁰ Increasing the molecular weight of PBT above its critical molecular weight (M_c) is, however, very difficult. A second option would be to change the molecular topology, such as introducing branching points (if the branches are few and long enough to entangle, the melt viscosity will be higher than that of a corresponding linear polymer of the same molecular weight due to the strain hardening).³¹ A third option is the introduction of multiphasic structures, such as in microphase-separated PBT-based blends²⁴ and thermoplastic elastomers.³² Here, we propose a fourth method via introducing dynamic cross-links to increase the melt strength, while maintaining processability.

In this study, a new type of semicrystalline vitrimer is developed by incorporation of glycerol (i.e., the ring-opened analogue of an epoxy group)^{1,33} into PBT via a solid-state (co)polymerization method in the presence of zinc(II) acetylacetonate hydrate as the transesterification catalyst. Often, reactive extrusion is used to incorporate comonomers, as for example done in the accompanying paper.³³ However, the volatility of glycerol at the typically high temperatures and gas flow rates make reactive extrusion less suitable and, therefore, we used solid-state (co)polymerization (SSP). This

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has the additional benefit of maintaining a high degree of crystallinity when high quantities of cross-linker are used. The transesterification reaction between the glycerol and the PBT segment in the amorphous phase in the presence of Zn^{2+} during SSP would initially lead to branching and ultimately to a network. The preparation, morphology, and vitrimer behavior of the cross-linked copolyesters are discussed in this article.

EXPERIMENTAL SECTION

Materials. Special grade poly(butylene terephthalate) pellets ($M_n = 21.2$ kg/mol, $M_w = 46.6$ kg/mol against poly(methyl methacrylate) (PMMA) standards in 1,1,1,3,3,3-hexafluoroisopropanol (HFIP)) were provided by SABIC (Bergen op Zoom, The Netherlands) and used as received. Glycerol ($\geq 99.5\%$), zinc(II) acetylacetonate hydrate ($\text{Zn}(\text{acac})_2$) (powder), terephthaloyl chloride ($\geq 99\%$), trimethylamine ($\geq 99.5\%$), magnesium sulfate (anhydrous, $\geq 99.5\%$), potassium nitrate (BioXtra, $\geq 99.0\%$), sodium nitrate ($\geq 99.0\%$), and sodium nitrite ($\geq 97.0\%$) were all obtained from Sigma-Aldrich. Hydrochloric acid, anhydrous dichloromethane, methanol, 1,1,1,3,3,3-hexafluoroisopropanol (HFIP, 99%) and Milli-Q water (LC-MS grade) were obtained from Biosolve. Deuterated chloroform (CDCl_3 , 99.8 atom % D) and deuterated trifluoroacetic acid (TFA-*d*, 99 atom % D) were obtained from Cambridge Isotope Laboratories. All chemicals were used as received unless denoted otherwise.

Solution Preparation of a Physical PBT/Glycerol Mixture. Physical mixtures of PBT and glycerol were prepared from solution using a common solvent approach.^{34–44} As a representative example, for the physical mixture containing 14.1 mol % of glycerol and 2 mol % $\text{Zn}(\text{acac})_2$, the dried PBT powder (9.14 g, 41.55 mmol), glycerol (0.64 g, 6.92 mmol) and $\text{Zn}(\text{acac})_2$ (0.22 g, 0.83 mmol) as the transesterification catalyst were dissolved in 20 mL of HFIP at 55 °C. After complete dissolution of all compounds, the HFIP was distilled off. As soon as the material started to precipitate, a vacuum ($p = 10^{-2}$ mbar) was applied for complete removal of HFIP. Finally, the obtained lump residue was dried under vacuum for 24 h at 30 °C, vitrified in liquid nitrogen, and subsequently ground into powder using an IKA A11 Basic Analytical mill. This powder was subsequently dried under vacuum for a period of 24 h at 30 °C. The molecular weight of the polymer in the mixture was then checked to ascertain that no undesirable reactions, such as transesterification or degradation, occurred during the preparation procedure.

Preparation of PBT/Glycerol-Based Copolyesters. PBT/glycerol-based copolyesters were synthesized by a two-step solid-state (co)polymerization method. Typically, in the first step, 5 g of PBT/GLY powder containing 2 mol % $\text{Zn}(\text{acac})_2$ was placed in a closed vial,⁴³ and pressurized with argon ($p < 3$ bar) to avoid the evaporation of glycerol. After 24 h at 160 °C, the mixture was transferred to the SSP reactor,³⁷ which was a glass tube (inner diameter = 2.4 cm) with a sintered glass plate at the bottom. A heat exchange glass coil (inner diameter = 0.5 mm) surrounded the reactor and entered the inner glass tube at the bottom just below the glass plate. The nitrogen gas was heated by passing through this coil prior to entering the reactor and its flow was controlled by a flow meter. The powder bed was fixed by addition of glass pearls (diameter = 2 mm) on top of the powder, and the reactor was purged with a nitrogen flow of 0.5 L/min for 30 min. After flushing, the reactor was placed in a heated salt bath ($T = 180$ °C). When the temperature inside the reactor reached 180 °C, the measurement of the reaction time (t_{ssp}) was initiated, and the composition and molecular weight were followed until the gel point. After the reaction, the product was cooled down to room temperature under a continuous nitrogen flow, discharged from the reactor, and the obtained polymer dried under vacuum at 120 °C for 6 h. The prepared PBT/GLY-based copolyesters will be abbreviated as C_x, where *x* indicates the mol % of glycerol (calculated based on the amount of PBT repeat units). The composition as determined by ^1H NMR spectroscopy is used for the abbreviations in this paper.

Characterization. Proton and Carbon Nuclear Magnetic Resonance Spectroscopy. ^1H and ^{13}C NMR spectroscopy were

performed on a 400 MHz Bruker Avance III spectrometer at 25 °C. For the ^1H NMR experiments, the spectral width was 6402 Hz, the delay time was 5 s, and the number of scans was 64. For the ^{13}C NMR experiments, the spectral width was 24 154 Hz, the delay time was 2 s, and the number of scans was between 2000 and 5000. Samples were prepared by dissolving ~15–50 mg of the crude polyester in 0.8 mL of an 80:20 vol % CDCl_3 :TFA-*d* mixture. Chemical shifts are reported in ppm relative to the residual solvent peak of CDCl_3 ($\delta = 77.0$ ppm).

Size Exclusion Chromatography (SEC). Molecular weight distributions, the number-average molecular weight (M_n) and polydispersity index ($\bar{D}$) of the copolyesters were measured on a system equipped with a Waters 1515 isocratic HPLC pump, a Waters 2414 refractive index detector (40 °C), a Waters 2707 autosampler, and a PSS PFG guard column followed by a 2PFG-linear-XL (7 μm , 8 $\times$ 300 mm) columns in series at 40 °C. HFIP with potassium trifluoroacetate (3 g L^{-1}) was used as eluent at a flow rate of 0.8 mL min^{-1} . The molecular weights were determined relative to PMMA standards (Polymer Laboratories, $M_p = 580$ Da up to $M_p = 7.1 \times 10^6$ Da).

Differential Scanning Calorimetry (DSC). Thermal properties were measured using a DSC Q1000 from TA Instruments. The measurements were carried out from -50 to $+250$ °C with heating and cooling rates of 10 °C/min under a nitrogen flow of 50 mL min^{-1} . The mobile amorphous fraction (MAF) was determined via the heat capacity increase at half-step (ΔC_p) in modulated DSC (TMDSC) mode using the same DSC equipment. An oscillating heat flow signal with a period of 60 s and amplitude of 0.5 °C was used with an underlying heating rate of 2 °C/min. The copolyester samples, prepared by SSP, were measured in the temperature range from 0 to 180 °C.

Compression Molding. The materials were compression molded at 250 °C and 100 bar for 25 min in a Collin Press 300G and subsequently cooled with water.

Dynamic Mechanical Thermal Analysis (DMTA). Compression-molded samples (ca. 10.0 (length) $\times$ 5.0 (width) $\times$ 1.0 (thickness) mm) were measured on a DMA Q800 (TA Instruments) with a film tension setup. A temperature sweep from -50 to 270 °C was performed with a heating rate of 3 °C/min at a frequency of 1 Hz. A preload force of 0.01 N, an amplitude of 10 μm and a force track of 125% were used. The storage modulus and loss modulus were recorded as a function of temperature. The glass transition temperature was calculated from the peak maximum in the loss modulus.

Rheometry. Dynamic shear measurements were performed on a stress-controlled AR-G2 Rheometer (TA Instruments) by using a 25 mm parallel plate geometry and disk-shaped specimens (25 mm diameter; 1 mm thick). Frequency sweeps from 0.01 to 500 rad s^{-1} were performed at a temperature range between 230 and 270 °C with a strain of 1%, which is in the linear viscoelastic regime. Stress relaxation experiments were performed at a temperature range between 230 and 270 °C with a strain of 1% and the relaxation modulus was monitored as a function of time. A constant normal force of 20 N was applied to ensure a good contact with the plates.

Wide-Angle X-ray Diffraction (WAXD). Wide-angle X-ray diffraction measurements were performed on a Rigaku Geigerflex Bragg–Brentano powder diffractometer using Cu radiation, wavelength 1.54056 Å, at 40 kV and 30 mA. The scans were performed with 0.02° steps in 2θ and a dwell time of 3–15 s in the 2θ range from 5° until 40°. The analyses were performed on the powder samples directly after SSP and pellet samples directly after compression molding of the powder prepared by SSP.

RESULTS AND DISCUSSION

In general, solid-state (co)polymerization of PBT is performed with a continuous flow of nitrogen in order to remove the condensate (1,4-butanediol). However, due to the volatility of glycerol at high temperatures under the continuous nitrogen flow, the evaporation rate of glycerol is much faster than its incorporation rate. In order to optimize the preparation method, we compared the built-in glycerol concentrations of three different preparation strategies, of which the details are

discussed in the [Supporting Information](#). The best method is schematically shown in [Scheme 1](#) and includes a two-step

Scheme 1. Synthesis of Poly(butylene terephthalate)/Glycerol-Based Vitrimers by Solid-State (Co)Polymerization (SSP)

copolymerization strategy. First, a prepolymerization step was performed at 160 °C in a closed glass vial which was pressurized with inert gas to avoid the evaporation of glycerol. After the total incorporation of the glycerol (24 h for ca. 13 mol % glycerol and 2 mol % Zn^{2+}), the mixture was transferred to a SSP reactor, and the reaction was continued at 180 °C with a N_2 flow of 0.5 $\text{L} \cdot \text{min}^{-1}$.

Incorporation of Glycerol into PBT. The general observations on the molecular weight evolution as a function of reaction time during the two-step SSP method is shown in [Figure 1](#). During the prepolymerization step at 160 °C, an initial drop in M_n due to chain scission was observed for all the compositions studied in this paper (see [Figure S2](#) in the [Supporting Information](#) for the other compositions). The chain scission is caused by the alcoholysis of the PBT chains by the free hydroxyl groups from the glycerol. The data in [Figure 1](#) show that the molecular weight shifts to lower M and the molecular weight distribution becomes broader after prepolymerization. The M_n drops from 21.2 to 3.4 kg/mol for the material containing 13 mol % glycerol catalyzed by 2 mol % Zn^{2+} , and the $\bar{D}$ is increased from 2.2 (physical mixture) to 2.5 (after prepolymerization at 160 °C for 24 h). No cross-linked copolyesters were formed at 160 °C after 24 h with 2 mol % $\text{Zn}(\text{acac})_2$.

In the second step, solid-state (co)polymerization was performed at 180 °C with a N_2 flow of 0.5 $\text{L} \cdot \text{min}^{-1}$ in order to remove the condensate 1,4-butanediol. The M_n increases as a function of t_{ssp} before the gel point, it increased from 3.7 kg/mol ($t_{\text{ssp}} = 0$ h at 180 °C) to 6.8 kg/mol ($t_{\text{ssp}} = 1$ h) and the $\bar{D}$ increased from 2.5 to 3.0. This increase in M_n is a result of the polymer chain recombination by transesterification (polycon-

Figure 1. Evolution of the molecular weight distribution of C13 as a function of t_{ssp} . Molecular weights are reported relative to PMMA standards.

densation) that takes place between end groups of the chains with elimination of 1,4-butanediol. When $t_{\text{ssp}} \geq 3$ h, a cross-linked copolyester was obtained, which is confirmed by insolubility in HFIP. In general, after $t_{\text{ssp}} = 7$ h, all the compositions are cross-linked.

In order to determine the glycerol content, NMR chemical shifts of the soluble polymer were compared to a model branched copolyester (poly(glycerol-co-terephthalate) (PGT) that was synthesized and characterized via different NMR techniques (see [Supporting Information](#) for further details in [Figure S3](#)). On the basis of the assignments of this model branched PGT and the study by Gross et al.,⁴⁵ integration of the peaks at $\delta = 8.10$ ppm (1,4-phenylene) against the peaks from glycerol at $\delta = 4.72$ –4.95 ppm (CH_2 – $\text{O}(\text{C}=\text{O})$) and $\delta = 6$ ppm (CH – $\text{O}(\text{C}=\text{O})$) allowed for determination of the glycerol composition before the gel point during solid-state (co)polymerization by ^1H NMR in a deuterated solvent mixture (CDCl_3 :TFA- $d = 5:1$). The results are summarized in [Table 1](#) and the ^1H NMR data are presented in [Figure S4](#) ([Supporting Information](#)). It is evident from [Table 1](#) that a high degree of incorporation of the glycerol with this two-step solid-state (co)polymerization method is obtained. Since the reaction continues after the gel point, the reported values in [Table 1](#) can be considered a lower bound of the real amount of incorporated glycerol.

Thermal Properties and Morphology during Solid-State (Co)Polymerization. One of the benefits of the solid-state (co)polymerization method is that the modification only occurs in the amorphous phase and the crystalline phase is largely retained,⁴⁶ implying that one can obtain a cross-linked copolyester with a PBT-like degree of crystallinity and crystallization behavior.

In order to investigate the semicrystalline character of the cross-linked PBT-based copolyester, DSC and temperature-modulated DSC (MDSC) were employed to follow the thermal properties (melting temperature (T_m), crystallization temperature (T_c) and degree of crystallinity ($\chi_{c,\text{heating}}$) and morphology (rigid amorphous fraction (α_{rigid}), mobile amorphous fraction (α_{mobile}), and crystalline fraction ($\chi_{c,\text{heating}}$)) as a function of t_{ssp} respectively. The uncertainty for the different fractions is about 5%. The DSC and MDSC thermograms are presented in [Figure S5](#) ([Supporting Information](#)). The thermograms were analyzed by using the first heating run in order to obtain information on

Table 1. Overview of the PBT/Glycerol Copolyesters Prepared by Solid-State (Co)Polymerization (SSP)

entry	t_{ssp} (h) ^a	Zn(acac) ₂ ^b (mol %)	glycerol content (mol %) ^c		M_n^d (kg/mol)	M_w^d (kg/mol)	cross-linked copolyesters ^e		
			feed	$t_{\text{ssp}} \approx t_{\text{gel}}$			T_m (°C) ^f	T_c (°C) ^f	$\chi_{c,\text{heating}}$ (%) ^f
PBT	0	0	0	0	21.2	46.6	222	194	40
C2	7	2	2.2	2.2	15.2	48.3	219	192	39
C4	7	2	6.1	4.0	12.7	31.9	216	192	36
C7	3	2	8.9	7.0	13.2	35.6	212	183	36
C13	1	2	14.1	13.0	6.8	17.0	209	173	32
C18	1	2	18.6	18.0	6.4	12.8	205	170	31

^a t_{ssp} , the sample was taken at the time when $t_{\text{ssp}} \approx t_{\text{gel}}$ (when the material becomes insoluble in HFIP). ^bZn(acac)₂ mole percentage based on the amount of PBT repeat units. ^cThe feed compositions and the minimum glycerol content obtained at $t_{\text{ssp}} \approx t_{\text{gel}}$ were determined using ¹H NMR spectroscopy and the ratio between the glycerol/PBT repeat units is expressed in mol % and the uncertainty is estimated to be around 5%. ^dThe molecular weight of the PBT samples measured with relative to PMMA standards in HFIP. ^eCross-linked copolyesters were the powder sample directly after SSP for 24 h under 0.5 L/min N₂ flow. ^f T_m , melting temperature, and T_c , crystallization temperature, values are the peak values of the melting endotherms and crystallization exotherms from the second heating and first cooling run, respectively. $\chi_{c,\text{heating}}$, degree of crystallinity, was determined by dividing the melting enthalpy (ΔH_m) of the heating run (obtained via DSC measurements) by the melting enthalpy (ΔH_m^0) for 100% crystalline PBT. For ΔH_m^0 values of 142 J/g⁴⁹ were used in this study.

Figure 2. (A) Development of T_m , T_c as a function of t_{ssp} measured by DSC at a heating rate of 10 °C/min from −50 to +250 °C. The reported data at $t_{\text{ssp}} = 0$ h refer to the material after prepolymerization at 160 °C for 24 h. (B) Morphology development during SSP of C13.

the thermal properties of the copolyesters obtained directly after SSP.

As shown in Figure 2A, the onset T_m increases with increasing t_{ssp} , which changes from 186 to 209 °C for C13 after prepolymerization at 160 °C for 24 h and solid-state polymerization at 180 °C for 24 h, respectively. Since the relation between the lamellar thickness and T_m is well known via the Gibbs–Thomson relation,⁴⁷ we can conclude that lamellar thickening occurs simultaneously during the cross-linking process due to the thermal annealing, and this lamellar thickening was also observed during the chain extension of linear PBT/diol copolyesters in the solid state by Jansen et al.³⁷ T_m , T_c , and degree of crystallinity are maintained although the molecular architecture of copolyester changes from a branched ($t_{\text{ssp}} < 3$ h) to a cross-linked ($t_{\text{ssp}} \geq 3$ h) structure due to the thermal annealing step. Normally, crystal perfectioning does not lead to an increased T_c but to a sharper melting peak and sometimes a higher melting temperature.⁴⁸ Here, the rise of T_c by 15 °C in comparison to the value of T_c at $t_{\text{ssp}} = 0$ and 0.5 h is probably more related to the presence of the heterogeneities in the melt in the form of glycerol-enriched microdomains with a higher cross-link density that act as nucleation sites. In order to erase the effect of thermal

annealing and compare the T_m and $\chi_{c,\text{heating}}$ as a function of glycerol content, the data from the second heating run were analyzed. The overview of the influence of glycerol contents on the thermal properties of cross-linked PBT/glycerol-based copolyester are summarized in Table 1. The T_m and $\chi_{c,\text{heating}}$ of the obtained cross-linked copolyester decreases with increasing glycerol contents, and the differences between T_m and $\chi_{c,\text{heating}}$ are about 17 °C and 9% for PBT and C18, respectively. However, for T_c a constant plateau is observed for glycerol content ≤ 4 mol %. A sharp decrease of 9 °C is observed from C4 to C7, and it reaches another plateau around 170 °C when glycerol contents are further increased from C7 to C18.

To demonstrate that glycerol is exclusively incorporated into the amorphous phase of PBT during SSP, the morphology of C13 as a function of t_{ssp} is studied as an example.

Generally, the morphology of a semicrystalline polymer is described with a two-phase model. This two-phase model comprises a crystalline and an amorphous phase. As reported by Jansen et al.,⁴⁶ a small fraction of the amorphous phase is confined by the chain segments in the crystal and is, therefore, not accessible for the transesterification reactions during SSP. Thus, it is more appropriate to describe the morphology of PBT/glycerol-based copolyester by a three-phase model,⁵⁰ in

which the amorphous phase is subdivided into a rigid amorphous fraction (α_{rigid}) and a mobile amorphous fraction (α_{mobile}). The MDSC data in Figure 2B show that the α_{rigid} is not converted into α_{mobile} during prepolymerization at 160 °C; the material still exclusively consists rigid amorphous and crystalline fractions. During the solid-state (co)polymerization at 180 °C, two processes occur simultaneously due to increased chain mobility. Up to the gel point, one process involves the transformation of α_{rigid} into α_{mobile} and the other is the crystal perfectioning by transformation of rigid amorphous chain segments into the crystal phase. After gel point ($t_{\text{ssp}} > 3$ h), the α_{mobile} decreases from about 35% to 28% but α_{rigid} increases from about 13% to 20%. This divergent phenomenon is due to the limited mobility within the mobile amorphous fraction when a cross-linked network is formed during the SSP.

In order to gain information on the crystal morphology, X-ray measurements were performed on powder samples directly after SSP and pellet samples directly after compression molding of the powder prepared by SSP. Figure 3 shows that α -crystals

Figure 3. Wide-angle X-ray diffraction patterns of obtained cross-linked copolyesters before and after compression molding. The samples are listed as follows: (1) neat PBT (treated with HFiP); samples obtained directly after SSP, (2) C2, (3) C4, and (4) C13; samples obtained directly after compression molding, (5) C2, (6) C4, (7) C13.

are unambiguously identified by the position of the 010, $\bar{1}01$, and 100 diffraction peaks detected at scattering angles 2θ of 17.19, 20.6, and 23.37°, respectively, on using Cu $K\alpha$ radiation.⁵¹ No cocrystallization of glycerol with PBT was observed. As expected, the diffraction peaks become broader after compression molding, which is due to a reduced lateral crystal size caused by a lower degree of crystallinity. These results corroborate that all the cross-linked copolyesters are semicrystalline, as observed by DSC.

Dynamic Thermomechanical Properties. The thermal stability and insolubility were characterized by TGA and swelling experiments, for details see Supporting Information. In general, the cross-linked copolyesters show a similar thermal stability as neat PBT as determined by TGA (Figure S6). The gel fractions of the compression-molded samples determined by room-temperature swelling tests in HFiP increase with increasing glycerol contents (Figure S7, Supporting Information).

The thermomechanical properties of the compression-molded samples were characterized by dynamic mechanical

thermal analysis (DMTA) and the samples were dried at 120 °C under vacuum for 6 h prior to the test. The DMTA results on the materials with different glycerol contents (see Table 1) are presented in Figure 4 (only 2, 4, and 13 mol % for clarity reasons) and Figure S8A (7 and 18 mol %), Supporting Information.

Figure 4. DMTA curves of neat PBT and cross-linked copolyester with different amounts of glycerol catalyzed by 2 mol % Zn^{2+} , heating rate = 3 °C/min, and $\omega = 1$ Hz.

The storage modulus (E') as obtained by DMTA of the neat PBT exhibits the expected behavior of a semicrystalline polyester.²⁴ After the glass transition region (T_g), it shows a plateau between T_g and T_m , where the crystalline domains act as physical cross-links, and its modulus depends on the molecular weight between entanglements (M_e) and degree of crystallinity. On continued heating, PBT reaches the terminal region and it flows above T_m .²⁴ The DMTA curves of the cross-linked PBT/glycerol-based copolyesters are similar to that of PBT below T_m , but above T_m , a second plateau, which originates from the cross-linked network is observed. From PBT to cross-linked semicrystalline copolyesters (C18), the plateau moduli (at 270 °C) of the materials increased from 0 to 3 MPa, and the T_g increased from 56 to 82 °C, respectively (Figure 4 and Figure S8). Furthermore, we would like to point out two phenomena, first, the DMTA curve of 13 mol % glycerol shows a strong temperature-dependent plateau modulus above the melting temperature; this is probably caused by the randomization of the chemical microstructure and is subject of further study. Second, all cross-linked semicrystalline copolyesters show a drop of modulus in the temperature window between 120 and 165 °C. This drop is probably caused by a melting transition, and further investigation is ongoing to explain this phenomenon. In general, the modulus in the rubbery plateau increases and melting transition temperature decreases with increasing glycerol content.

Rheological Behavior. The dynamic nature of the cross-linked copolyesters was studied by oscillatory frequency sweep experiments in the molten state. Each sample listed in Table 1 was tested at sufficiently low strain amplitudes (1%) to probe only the linear viscoelastic properties. The dynamic storage (G') and loss moduli (G'') were measured at various temperatures over an angular frequency range of 500–0.01 rad/s. Three representative compositions are presented in

Figure 5. (A) Storage (open symbols) and loss (filled symbols) moduli and (B) complex viscosity versus angular frequency for PBT/glycerol-based vitrimers catalyzed by 2 mol % Zn^{2+} at 240 °C by 25 mm plate–plate geometry with 1% strain applied.

Figure 6. (A) Nontreated stress relaxation curve for C13 catalyzed with 2 mol % $\text{Zn}(\text{acac})_2$ catalyst at 250 °C. Normalized stress relaxation curves with respect to (B) temperature with C18 and (C) glycerol content at 270 °C. (D) Variation of the stress relaxation time versus inversed temperature for C_x catalyzed by 2 mol % Zn^{2+} , where x is ca. 7, 13, and 18 mol % glycerol.

Figure 5A, and the data for C18 and C7 are presented in Figure S9, Supporting Information.

It was well documented in the comprehensive review on covalent adaptable networks by Kloxin and Bowman⁵² that materials formed by permanent covalent bonds display a frequency-independent storage (G') modulus, while frequency-dependent G' and loss moduli (G'') are observed for materials containing covalent adaptable networks. As shown in Figure 5A, at 240 °C, for neat PBT, the loss modulus is constantly higher than the storage modulus ($G'' > G'$) in the entire

frequency range available and it is right in the terminal regime as shown by the typical $G''(\omega) \sim \omega^1$ and $G'(\omega) \sim \omega^2$ variation. When 2 mol % of glycerol is incorporated, the viscous modulus is still greater than the elastic modulus, characteristic of a viscous liquid, showing a much lower resistance to flow consistent with rapid exchange kinetics. Only at higher frequencies, the storage modulus is higher than the loss modulus. These results corroborate the absence of a rubber plateau modulus in DMTA (see Figure 4), where the material above T_m loses its resistance to the small stress around 230

Figure 7. (A) Frequency sweep data for C4, and the crossover frequency is indicated by the dotted arrow line. (B) Variation of the average relaxation time versus inversed temperature for samples C2 and C4.

°C; the DMTA experiment (Figure 4) is carried out at 1 Hz and C2 exhibits a crossover frequency around 12 Hz at 230 °C (Figure 5). When the glycerol content is increased to 4 mol %, the material exhibits a power-law behavior ($G'' \sim G' \sim \omega^n$)^{57,58} and it is similar to the rheological behavior of reversible Diels–Alder networks below the gel point.⁵⁵ A drop-off in the low-frequency modulus occurs, and a crossover in the elastic and viscous moduli is observed for this sample at 250 °C as will be seen below, demonstrating liquid-like behavior and relaxation at long time scales (Figure 7A). Moreover, the crossover frequency of G' and G'' at 240 °C for the sample C4 is beyond the lowest frequency tested (0.0016 Hz), which is several orders of magnitude lower than the ~25 Hz crossover frequency of the sample with 2 mol % glycerol. When the glycerol content increases from 4 to 13 mol %, a densely cross-linked network is formed and the plateau modulus (G_0) increases from 0.006 to 0.2 MPa. In the examined frequency range the sample does not exhibit an ω -dependent G' and shows much smaller G'' values; the relaxation times of the dynamic network at 240 °C are relatively long compared to the probed time scales. Thus, in the range of frequencies tested, it behaves like a solid-like gel ($G' > G''$) and shows a plateau modulus (G_0), taken at the minimum point of G'' of around 0.2 MPa. These aforementioned frequency-dependent mechanical phenomena originate from the transesterification catalyzed by the catalyst present in the system. Above the melting temperature, the exchange reactions enable the movement of the cross-links through the network leading to stress relaxation. A similar frequency-dependent G' and G'' behavior is also observed for chemical gels containing reversible covalent bonds.^{53–56} On the basis of the dynamic nature of the cross-links above T_m , we called this material a PBT vitrimer.

One of the aims of this work is to increase the melt strength of PBT, because a higher melt strength is essential for processing techniques such as film blowing, foaming and thermoforming. Normally, the melt strength is characterized by uniaxial extensional viscosity, but there is also a power law relationship between the melt strength and the zero-shear viscosity, η_0 , which is the value taken from the Newtonian plateau from the complex viscosity in the terminal region. As reported by Ghijssels et al.,^{28,59} the melt strength is proportional to η_0 . We can see from Figure 5B, although the sample C2 shows a similar rheological behavior as neat PBT (G''

dominates in the tested frequency region), its complex viscosity at $\omega = 0.1 \text{ rad s}^{-1}$ is 2 orders of magnitude higher than neat PBT at 240 °C. When the glycerol content increases from 4 to 13 mol %, the complex viscosity at $\omega = 0.01 \text{ rad s}^{-1}$ increases 3 orders of magnitude at 240 °C, which is expected with increasing cross-link density. These results are consistent with the DMTA data in Figure 4 and indicate that a PBT vitrimer with higher melt strength is obtained at higher glycerol contents in the presence of 2 mol % Zn^{2+} .

Stress Relaxation Experiments. The time- and temperature-dependent stress relaxation properties of the semicrystalline PBT vitrimers were studied by stress relaxation experiments. The experiments were performed on all of the materials in the linear viscoelastic regime (1% strain) and the stress relaxation times (τ^*) were determined at $G_t/G_0 = 0.37$ ($=1/e$).³ A typical raw stress relaxation curve ($G(t) = \sigma(t)/\gamma_0$) is shown in Figure 6A, for C13 heated at 250 °C. It is clear from this Figure, that although the PBT/glycerol-based vitrimers are cross-linked, they are able to fully relax stresses ($G(t) \approx 0$) at longer times, indicating that the network is indeed fully dynamic and that any residual stress is negligible. For further analyses the stress relaxation data were normalized by the apparent plateau value G_0 as indicated in Figure 6A. As is clear from Figure 6B the normalized relaxation modulus G_t/G_0 decreases as a function of time for C13 at the temperature range from 230 to 270 °C (for complete stress relaxation curves of C7 and C18 as a function of temperature, see Figure S10). The relaxation is significantly shifted toward shorter time-scales upon increasing temperature, which enhances the rearrangement reaction kinetics with a decrease in relaxation time (τ^*) from 814 s at 230 °C to only 57 s at 270 °C. Thus, the semicrystalline vitrimer is able to relax stress at temperature above T_m . Decreasing the cross-link density has a similar effect as increasing the temperature (Figure 6C); the stress relaxes faster when there are fewer cross-links. The temperature dependence of the relaxation time can be described by the Arrhenius eq 1.

$$\tau^* = \tau_0^* \exp\left(\frac{E_a}{RT}\right) \quad (1)$$

Where τ_0^* is the pre-exponential factor (s), E_a is the activation energy (J mol^{-1}), R is the ideal gas constant (J mol^{-1}).

K^{-1}) and T is the temperature (K). The activation energy E_a is determined from the slope of the data in Figure 6C. An excellent fit is observed in Figure 6C, and comparable activation energies of ~ 155 , ~ 153 , and ~ 138 kJ/mol were determined from the slopes for the samples containing 7 mol %, 13 mol %, and 18 mol % Zn^{2+} , respectively.

Stress relaxation experiment on the samples with glycerol content below 7 mol % exhibited remarkably fast relaxation as we can see from the representative normalized stress relaxation curves at 250 °C for C13, C4, and C2 in Figure S10 (Supporting Information). Thus, it is impossible to determine the relaxation times by stress relaxation experiments. Here, we use oscillatory frequency sweep tests to characterize the average relaxation time (τ_d) of the samples possessing faster relaxation kinetics. The average relaxation time (τ_d) is determined by the crossover frequency (ω_c) at $G' = G''$, $\tan \delta = 1$. (Figure 7A and Figure S11). The activation energy (E_a) of C2 and C4, as determined from the average relaxation times obtained from frequency sweeps at the crossover points (Figure 7) is in the same order of magnitude with C13 determined from stress relaxation experiments. However, the correlation between these two techniques needs further investigation.

Reprocessing Ability of the PBT/Glycerol-Based Semicrystalline Vitrimers. Since the dynamic cross-links could allow for reprocessing of the materials, the recyclability of the semicrystalline vitrimers was tested with the vitrimer sample (C18) containing 18 mol % glycerol and 2 mol % Zn^{2+} as an example. The sample was cut into small pieces and then compression molded at 250 °C for four times (Figure 8A).

Figure 8. (A) Recycling of the broken pieces by compression molding and (B) storage modulus of the recycled samples.

Before performing dynamic mechanical thermal analysis (DMTA) measurements, the recycled samples were thermally treated at 120 °C for 6 h under vacuum to remove possible moisture. Afterward, the moisture-free recycled samples were subjected to DMTA for comparing the dynamic mechanical properties as a function of cycle number. DMTA experiments

demonstrate nearly full recovery of the dynamic mechanical properties (see Figure 8B).

CONCLUSIONS

Semicrystalline vitrimers were obtained by the incorporation of volatile glycerol into PBT via a two-step solid-state (co)-polymerization protocol. Near quantitative incorporation was confirmed via 1H NMR spectroscopy up to the gel point. During the first step of this protocol, i.e. a prepolymerization at 160 °C the glycerol is incorporated into the linear polymer chains after which network formation takes place in the second step, i.e., the solid-state (co)polymerization at 180 °C. DSC revealed that the semicrystalline character of PBT was maintained in the PBT/glycerol-based vitrimers in the solid state and modulated DSC confirmed that the cross-linked points are exclusively located in the amorphous phase. Additionally, WAXD showed that the triclinic α -crystal of neat PBT was maintained in the PBT/glycerol-based vitrimers and that no cocrystallization of glycerol took place. In DMTA, two plateaus were found for this type of semicrystalline vitrimers: one between T_g and T_m and which is due to the physical cross-links from the crystalline part of PBT, and the other one above T_m , i.e. the rubber plateau, which is due to the cross-links. Tunable rheological behavior, ranging from a typical thermoplastic to a solid-like gel, and stress relaxation times were achieved by controlling the glycerol content while keeping the Zn^{2+} concentration constant. Finally, it was found that several recycling steps did not significantly alter the thermomechanical properties of the materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge via the Internet at The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.7b01142.

Comparison of three different types of synthetic routes, synthesis and characterization of branched poly(glycerol terephthalate), thermal stability before and after compression molding, and insolubility after compression molding(PDF)

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Notes

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