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In Situ Network Formation in PBT Vitrimers via Processing-Induced Deprotection Chemistry

Yanwu Zhou, Johannes G. P. Goossens,* Sjarco van den Bergen, Rint P. Sijbesma, and Johan P. A. Heuts*

Although the network dynamics and mechanical properties of poly(butylene terephthalate) vitrimers can to some extent be controlled via chemical and physical approaches, it remains a challenge to be able to process PBT vitrimers with the same processing conditions via, for example, injection molding as neat PBT. Here, it is shown that the use of protected pentaerythritol as a latent cross-linker and the use of a Zn(II) transesterification catalyst allows for the in situ dynamic network formation in PBT during processing, with a delayed onset of gelation. This process can be controlled by adjusting the processing temperature, (protected) cross-linker content, and the type of protection group. This solvent-free deprotection strategy opens the way to high production rates of PBT vitrimer products via injection molding with the combination of low viscosity during processing and vitrimer characteristics in the final product.

Vitrimers form a relatively new class of materials which bridge the traditional thermosets and thermoplastics via the incorporation of covalent adaptable networks in cross-linked polymers.[1–3] These dynamic cross-linked networks follow an associative exchange mechanism, in which exchange reactions under certain stimuli permit the change of network topology while keeping the number of bonds and cross-links constant.[4–7] Since their discovery, research has been directed toward the development of new types of associative exchangeable chemistries,[8–24] and practical applications for high-performance or functional material innovations.[25–51] Previously, we developed poly(butylene terephthalate) (PBT) vitrimers via the incorporation of glycerol into PBT in the solid state.[38,45] In general, the terminal relaxation behavior of PBT vitrimers above the melting temperature was rarely observed at angular frequencies down to $10^{-2}$ s$^{-1}$ in the temperature range from 250 to 270 °C.[37,38,45] Considering that typical shear rates during injection molding are as high as 10 000 s$^{-1}$ and the viscosity of PBT vitrimers can be up to 10$^7$ Pa s at 250 °C, these PBT vitrimers cannot be processed like neat PBT during the short residence times typical for extrusion and injection molding.[52] Here, we propose a controllable way to process PBT vitrimers (based on transesterification exchange reactions) via controlling the network formation with the help of protection–deprotection chemistry. In this way, we can overcome the relatively long relaxation times and high viscosities associated with PBT vitrimers and maintain the high production rates of final parts by injection molding as for neat PBT. The strategy is schematically shown in Scheme 1: pentaerythritol is first converted into 5,5-bis(hydroxymethyl)-2-phenyl-1,3-dioxane (BPO, melting point 135–137 °C) via benzaldehyde protection chemistry.[53] Subsequently, this diol is incorporated into the PBT backbone via solid-state (co)polymerization to form a linear copolyester in line with earlier work from our group on PBT modification in the solid state.[54–59] The linear polymer chain is then transformed into a network via deprotection of the benzal group to afford a linear polymer chain with pendant-free hydroxyl groups for further thermal transesterification of the linear copolyester catalyzed by the Zn(II) catalyst. If deprotection and subsequent cross-linking takes place during processing, we can combine an initial low viscosity with final vitrimer characteristics.

Normally, the deprotection step to obtain the linear copolyester with pendant hydroxyl groups, as shown in Scheme 1, involves an acid-promoted deprotection of the benzal group at room temperature and an acid used often is trifluoroacetic acid (TFA).[54] Accidentally we discovered that compression molding of the linear copolyester with benzal protection groups resulted in a cross-linked material with vitrimer characteristics, even without deprotection with TFA. This observation is in contrast to results previously reported by Collard et al.[54] who obtained thermoset materials after incorporation of BPO into PBT and poly(ethylene terephthalate) (PET) and repeated subsequent cycling to 300 °C in differential scanning calorimetry (DSC). Driven by this intriguing result and its practical relevance, we investigated the in situ network formation in more...
Detail and compared the dynamic network formed by this novel processing-induced method with that from a common TFA-promoted deprotection method.

The materials containing 1.0, 2.4, 3.5, and 9.0 mol% of BPO were prepared by using the solid-state polymerization method as reported in our previous work (see Supporting Information for details), using a constant Zn(II) catalyst loading of 0.2 mol% with respect to the PBT repeat unit. In Scheme 2, the subsequent treatment of the polymer samples before rheology and dynamic mechanical thermal analysis (DMTA) measurements is schematically shown, using the sample containing 1.0 mol% BPO cross-linker as an example. This scheme also serves to define the notation we used for our samples: pC1 is the initially protected linear copolymer with 1.0 mol% BPO units. This sample was treated in two different ways. First, by compression molding to a different shape at 250 °C with a total heating time of around 25 min; this material is named compression-molded pC1. Second, by removing the benzal groups by treatment with TFA yielding the linear copolyester with pendant hydroxyl groups, that is, deC1, which was subsequently compression molded at 250 °C for 25 min. Both compression-molded samples underwent a further curing step resulting in fully cured samples, that is, pX1 and deX1, respectively.

In order to investigate in situ network formation during processing, oscillatory time sweep experiments with 1% strain at different temperatures were used to monitor the molecular structure changes of the material (pC1) directly after SSP or after debenzalation (deC1). A ring-shaped melting chamber setup surrounding the lower plate was charged with the materials (see Figure S3, Supporting Information) and the time dependence of the storage ($G'$) and loss ($G''$) moduli of the material after SSP was measured. The results for pC1 and deC1 at 250 °C are shown in Figure 1A and from the observation that $G'$ crosses $G''$ it can be concluded that cross-linking takes place in both experiments, that is, also in the case of the initially protected polymer pC1. Furthermore, it is clear that this happens significantly sooner in the case of the deprotected polymer (deC1); the initial complex viscosities for pC1 and deC1 were about 2.1 kPa s and 3.6 kPa s at 250 °C and clear crossover (gel) points ($G' = G''$) were observed around 65 min and 17 min for pC1 and deC1, respectively. After the crossover point ($G' = G''$), both samples were insoluble in 1,1,1,3,3,3-hexafluoropropanol (HFIP) at room temperature and a gel fraction of approx. 76% was obtained for both materials (Figure S4, Supporting Information).

Increasing the BPO content results in a decrease in the crossover time (see Figure 1B); for example, the crossover times of pC1, pC2.4, and pC3.5, respectively, were found to be 65, 6.5, and 4.3 min. Also an increase in temperature results in shorter crossover times; for example a temperature increase from 250 to 270 °C leads to a decrease from 65 to 36 min for pC1 (Figure S3, Supporting Information).

The results presented thus far are consistent with a processing-induced debenzalation process, which is probably catalyzed by the terminal carboxylic acid groups in the material. Furthermore, it is clear that this process (with a “delayed” cross-linking) allows the material to be processed as a thermoplastic with a low viscosity for a controllable cross-linking time, which is beneficial for a processing technique such as injection molding. It should be noted here that the linear material prepared by SSP possesses similar thermal properties as neat PBT, such as $T_m$, $T_c$, and degree of crystallinity ($\chi_c$).
linear pC1, $T_m = 221.5 \, ^\circ C$, $T_c = 193.3 \, ^\circ C$, and $\chi_{cr} = 38.3%$; neat PBT, $T_m = 221.6 \, ^\circ C$, $T_c = 193.7 \, ^\circ C$, and $\chi_{cr} = 42%$.

Having established that the initially protected linear polymer undergoes a “delayed” cross-linking during processing, it is fundamentally interesting and practically important to investigate whether the properties of the final cured materials originating from the TFA deprotection and processing-induced deprotection methods differ.

Figure 2A shows the frequency dependence of $G'$ and $G''$ at 250 °C measured for pX1 and deX1. The fully cured pX1 and deX1 both exhibit a solid-like gel behavior over the entire measured frequency range (i.e., $G' > G''$), with pX1 displaying a slightly lower plateau modulus ($G_p$, taken at the minimum of $G''$) of 0.035 MPa versus 0.14 MPa for deX1. It is important to note that pX1 in the presence of different amounts of Zn(II)—including no Zn(II)—displays a solid-like gel behavior after curing ($G' > G''$) as well (Figure S6, Supporting information). The solid-like mechanical responses of the cured materials were also demonstrated by the frequency dependence of the complex viscosity ($|\eta^*|$, Pa·s). Linear relationships between log $|\eta^*|$ and log $\omega$ with a slope of $-1$ were observed (Figure 2A), and this behavior corresponds to a perfectly elastic solid, such as an ideal chemically cross-linked network.\[61,62\]

The thermomechanical properties of the studied $pX$ and $deX$ vitrimers are shown in Figure 2B and in all cases a rubbery plateau is observed above $T_g$; consistent with our previous work. The rubbery plateau modulus increases with cross-linker content.\[18\] Differences in rubbery plateau moduli are observed for the material obtained via TFA-promoted and processing-induced debenzalation, even though the numbers of cross-links in both systems are expected to be similar. This difference in rubbery plateau modulus is most likely caused by different distributions of the dynamic cross-links in the two materials. The powder after SSP of the TFA-deprotected material possesses a nonrandom distribution of dynamic cross-links, while the materials obtained via processing-induced deprotection are cross-linked in the melt and possess a more random distribution of cross-links. The observed decrease in modulus at temperatures between $T_g$ and $T_m$ with increasing cross-linker content is related to a slight decrease in degree of crystallinity (see Supporting Information).

Shear stress relaxation experiments were used to compare the dynamics of the networks obtained by processing-induced deprotection and TFA-deprotection procedures. In Figure 3A, the stress relaxation curve ($G(t) = \sigma(t)/\gamma_0$ vs time) of $pX3.5$ is shown as an example and it is clear that full stress relaxation occurs, which is indicative of a truly dynamic network. As expected,\[38,45\] the stress relaxation time depends on temperature and amount of cross-linker. The temperature dependence of the stress relaxation is illustrated in Figure 3B for cured $pX2.4$ and it is immediately clear that an increase in temperature leads to a faster stress relaxation. Analogous to what has been done in other vitrimer studies,\[1–3,17,18,22–27,35,36\] we use the relaxation time $\tau$, which is defined as the time it takes for the modulus to relax to $1/e$ of its original value, as a characteristic measure for stress relaxation. The data in Figure 3B show that an increase in temperature from 230 to 260 °C leads to a
decrease in $\tau$ from $5 \times 10^3$ s to $3 \times 10^2$ s. The effects of BPO content and debenzalation strategies are shown in Figure 3C.

For the materials with the same BPO content, the results indicate that the material obtained via the processing-induced debenzalation has a slightly longer stress relaxation time than the one prepared via the TFA-promoted debenzalation, which is consistent with a higher cross-link density (and thus a higher rubbery plateau modulus, see Figure 2B). For the materials obtained via the same debenzalation process, the higher the BPO content (i.e., the higher the cross-link density), the longer the stress relaxation time, in accordance with what we observed previously for PBT/glycerol vitrimers.  

It should also be noted here that the stress relaxation of the materials with fewer cross-links ($pX1$ and $deX1$) cannot be described by the Maxwell model with a single characteristic stress relaxation time. This was also observed previously in PBT/glycerol vitrimers. Therefore we only used the data of materials with a well-developed network (nearly $\omega$-independent

![Figure 2. A) Storage (open symbols) moduli, loss (filled symbols) moduli and complex viscosity ($|\eta^*|$) (half-open symbols) versus frequency at 250 °C for the cured $pX1$ and $deX1$. B) Comparison of DMTA curves for X1 and X3.5 vitrimers obtained by processing-induced (bold line) deprotection and TFA protection (thin line) (heating rate = 3 °C min$^{-1}$, frequency = 1 Hz). For clarity reasons, the DMTA curves of C2.4 are shown in Figure S5, Supporting Information.](image1)

![Figure 3. A) Stress relaxation curve for $pX3.5$ catalyzed with 0.2 mol% Zn(II) obtained at 290 °C and B) different temperatures for $pX2.4$. C) Normalized stress relaxation curves for different BPO contents. Relaxation times are measured for a 63% relaxation. D) Variation of the stress relaxation time for X3.5 versus inverse temperature obtained via different curing processes. For clarity reasons, the complete normalized stress relaxation curves of $pX1$, $deX1$, $pX3.5$, and $deX3.5$ are presented in the supporting information (Figure S8, Supporting Information).](image2)
G’ and small G″), that is, ϕX3.5 and ϕX3.5, to derive an activation energy for stress relaxation from the obtained stress relaxation times. Since the relaxation times are controlled by associative exchange reactions, the temperature dependence of the relaxation time can be described by the Arrhenius equation (Equation (1)).

\[
\tau = \tau_0 \exp \left( \frac{E_a}{RT} \right)
\]

In this equation, τ0 is the pre-exponential factor (s), Ea is the activation energy (J mol⁻¹), R is the ideal gas constant (J mol⁻¹ K⁻¹), and T is the temperature (K). An excellent fit is observed in Figure 3D yielding similar activation energies for the materials obtained using both debenzalation approaches; values of Ea are ≈230 and ≈250 kJ mol⁻¹ for ϕX3.5 and ϕX3.5, respectively, which are significantly higher than the 150–170 kJ mol⁻¹ obtained for PBT/glycerol vitrimers. We can conclude that the PBT vitrimers obtained via the (solvent-free) processing-induced debenzalation process have similar networks as those obtained via the TFA-promoted debenzalation approach; this in turn suggests that similar cross-linking chemistries are involved.

Finally, we believe that processing-induced debenzalation proceeds via a similar mechanism as the acid-promoted debenzalation process and this hypothesis was confirmed by model reactions (Figure S9, Supporting Information). Benzoic acid and 5,5-bis(phenylcarboxymethyl)-2-phenyl-1,3-dioxane were used to mimic the end group of PBT and the protected PBT/BPO copolyester, respectively. Infrared spectroscopy shows the appearance of the OH group and the vanishing of benzylic ring after thermally heating the mixture to 180 °C for 2 h (Figure S9, Supporting Information).

Having clearly demonstrated that PBT vitrimers can be produced by an in situ cross-linking approach in which the onset of cross-linking can be delayed by the use of a protection group (and a processing-induced deprotection), we wanted to investigate whether it is possible to adjust the onset of cross-linking by using different protection groups (the chemical structure of the cross-linkers with different protection groups is shown in Scheme 3).

In order to do so, we also used p-anisaldehyde (resulting in the p-methoxybenzylidene-pentaerythritol, MBPO, cross-linker) and 2,2-dimethoxy propane (resulting in the 2,2-dimethyl-1,3-dioxane-5,5-dimethanol, APO, cross-linker) as protection groups (for synthesis details, see Supporting Information). Copolymers with 1.2 mol% of cross-linker were produced using the same procedure as used for BPO, again using 0.2 mol% of Zn(II) catalyst, followed by the processing-induced deprotection approach.

The thermal properties of these copolymers were similar to those obtained for the BPO-containing copolymers (see Figure S10, Supporting Information) and above the melting temperature (at T = 250 °C), all polymers exhibited a solid-like gel behavior (see Figure 4A), just as was observed for the BPO-containing copolymers (see Figure 2A).

The APO and MBPO containing polymers just after SSP and before compression molding, however, were not fully soluble in HFIP, suggesting that cross-linking had already occurred during the copolymerization reaction. This can also be concluded from Figure 4B, in which we compare the time dependence of the storage and loss moduli during processing for the three different protection groups at 250 °C. From the start onward, the APO-containing polymer is characterized by G’ > G″, but further cross-linking takes place for longer times. The MBPO-containing polymers very quickly show gelation after starting the processing, and only the BPO-containing polymers show a significant delay in the onset of gelation.

**Scheme 3**. The chemical structure of the cross-linkers with different protection groups.

**Figure 4.** A) Storage (open symbols) and loss (filled symbols) moduli versus frequency at 250 °C for the networks resulting from linear (○) APO, (△) MBPO, and (■) BPO—protected PBT/pentaerythritol copolymers. B) Time dependence of the storage (open symbols) and loss (filled symbols) moduli at 250 °C for the in situ network formation in linear (○) APO, (△) MBPO, and (■) BPO—protected PBT/pentaerythritol copolymers.
In summary, the use of protected pentaerythritol as a latent cross-linker and the use of a Zn(II) transesterification catalyst allows for the in situ dynamic network formation in PBT during processing, with a delayed onset of gelation. The resulting vitrimers have similar properties as those obtained using a common TFA-promoted deprotection method. It was shown that cross-link density of the final network can be tuned by adjusting the processing temperature and (protected) cross-linker content. The duration of the pregel period (i.e., the low-viscosity processing window) also depends on these two parameters in addition to the type of protection group that was used. Practically, this in situ network formation paves the way for fast processing using current extrusion or injection molding equipment of PBT vitrimers.

Supporting Information
The supporting information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Keywords
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