Supplementary Information

Sustainable Polyester Vitrimer Capable of Fast Self-healing and Multiple Shape-programming via Efficient Synthesis and Configuration Processing

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Figure S1. Torque curves of samples 0BT3PMDA, 0BT6ADR, 0.8BT3PMDA, and 0.8BT6ADR obtained by the internal mixer.

Figure S1 revealed the corresponding viscosity change in the synthesis process of samples 0BT3PMDA, 0BT6ADR, 0.8BT3PMDA, and 0.8BT6ADR. It was found that sample 0BT3PMDA with linear chain structure has the lowest torque value, while sample 0BT6ADR with crosslinking structure has the highest torque value. Due to the viscous-flow behavior of vitrimers and the shorter molecular chains after transesterification with BIS-TRIS, samples 0.8BT3PMDA and 0.8BT6ADR possess lower torque values than sample 0BT6ADR but are still much higher than sample 0BT3PMDA. Meanwhile, sample 0.8BT3PMDA possesses a lower torque value than sample 0.8BT6ADR, due to the lower melt strength resulting from the faster exchange reaction rate.



Figure S2. Swelling tests of various samples: (a) 0.8BT3PMDA, (b) 0.8BT6ADR, and (c) 0BT6ADR.

After being swollen in the suitable solvent of PET at room temperature for 48 hours, the samples' images were shown in Figure S2. It was found that samples 0BT6ADR,

0.8BT3PMDA, and 0.8BT6ADR could not dissolve in the solvent, demonstrating the formation of crosslinking networks in samples. Samples 0.8BT3PMDA and 0.8BT6ADR have a much lower swelling ratio than sample 0BT6ADR, ascribing to 0.8BT3PMDA and 0.8BT6ADR larger crosslinking density.



Figure S3. Strain-temperature curves of vitrimer 0.8BT3PMDA and vitrimer 0.8BT6ADR.

The strain-temperature curves of vitrimer 0.8BT3PMDA and vitrimer 0.8BT6ADR were plotted in Figure S3. In the covalent adaptable network, an exchange reaction is activated above Tv, which endows the vitrimer's viscous-flow behavior. Based on the strain-temperature curve, Tv was calculated to be 247.4°C and 242.9°C for samples 0.8BT6ADR and sample 0.8BT3PMDA, respectively.



Figure S4. The creep resistance of samples 0BT3PMDA, 0BT6ADR, 0.8BT3PMDA, and 0.8BT6ADR at various temperatures ranging from 225°C to 245°C.

The creep resistance of all samples was characterized at different temperatures ranging from 225°C to 245°C, as shown in Figure S4. Due to the linear structures, 0BT3PMDA possesses the worst creep resistance at all temperatures. In contrast, the rest samples with

crosslinking structures possess much better creep resistance. Specifically, vitrimer 0.8BT6ADR possesses the best creep resistance, ascribing to two aspects: (1) the denser crosslinking networks than 0BT6ADR, and (2) the slower exchange reaction rate than 0.8BT3PMDA. Although has a larger crosslinking density, 0.8BT3PMDA possesses poorer creep resistance than 0BT6ADR, which is attributed to the obvious viscous-flow behavior resulting from the fast exchange reaction. With decreasing temperature, it was found that the creep resistance of all samples is getting better.



Figure S5. Images of samples obtained in extensional rheological experiment at different extensional rates: (a) 0.8BT3PMDA at 0.2 s⁻¹, (b) 0.8BT6ADR at 0.05 s⁻¹, and (c) 0BT6ADR at 2 s⁻¹.

As shown in Figure S5, 0BT6ADR presents a brittle failure while 0.8BT6ADR presents a ductile failure at all extensional rates, ascribing to 0BT6ADR's larger crosslinking density than that of 0.8BT6ADR. In contrast, 0.8BT3PMDA presents a ductile failure below 0.2 s⁻¹ but a brittle failure above 0.5 s⁻¹, ascribing to the viscoelastic transition resulting from the fast exchange reaction.



Figure S6. Stress relaxation of sample 0.8BT3PMDA and sample 0.8BT6ADR at temperatures ranging from 245° C to 275° C

Relaxation time (τ^*) is defined as $G_t/G_0 = (1/e) \approx 0.37$. Based on the stress relaxation curves in Figure S6, it was found that 0.8BT3PMDA has an extremely fast τ^* of 4.8 seconds at 270°C, while that of 0.8BT6ADR was 31.2 seconds, demonstrating that 0.8BT3PMDA has a much fast exchange reaction rate than 0.8BT6ADR.



Figure S7. Thermogravimetric differential curves of samples 0BT3PMDA, 0BT6ADR, 0.8BT3PMDA, and 0.8BT6ADR.

Thermogravimetric differential curves of all samples were plotted in Figure S7. Since easy to hydrolysis, pyrolysis, and shear degradation, PET possesses poor thermal stability. With the formation of crosslinking networks and the consumption of carboxyl groups, the thermal stability of vitrimer 0.8BT6ADR increases significantly, which has a degradation temperature of 388.5°C, a value much higher than that of 0BT3PMDA.



Figure S8. SEM images of foam samples 0BT3PMDA, 0BT6ADR, 0.8BT3PMDA, and 0.8BT6ADR, which are foamed at 250°C, 260°C, and 270°C, respectively.

SEM images of samples foamed at 250°C, 260°C, and 270°C are presented in Figure S8. It is found that 0BT3PMDA possesses good foamability at 250°C. Nevertheless, the cells would coalesce and collapse at a higher temperature, ascribing to the low melt strength. In contrast, 0.8BT6ADR fails to achieve a larger expansion ratio at all temperatures; because the melt strength is too strong. On the other hand, 0BT6ADR possesses fine cell morphology at all tested temperatures. However, its cell diameter is decreased at 250°C, due to the suppression of excess crystals. With a suitable crosslinking density and fast exchange reaction rate (that is suitable melt strength at all temperatures), vitrimer 0.8BT3PMDA has fine cell morphology and uniform cell diameter at all foaming temperatures.



Figure S9. Self-healing behavior of solid 0.8BT3PMDA sample at 245°C for 20min.

Due to the fast exchange reaction rate, the fractured solid 0.8BT3PMDA could self-heal efficiently at 245°C in 20 minutes, which endows the recovered material with mechanical strength from fraction, as shown in Figure S9.



Figure S10. Swelling tests and relaxation experiment of sample 0.8BT3PMDA, 1.2BT3PMDA, and 1.4BT3PMDA: (a) gel content and swelling ratio; (b) images of samples immersed in trifluoroacetic acid for 48 h; (c), (d) stress relaxation curves of sample 1.2BT3PMDA, and 1.4BT3PMDA.

Constructed in PET macromolecular chains, the covalent adaptable networks of the PETbased vitrimer inevitably have a smaller crosslinking density than that of normal crosslinked networks synthesized from monomers or prepolymers. To further promote the get content, different contents of PMDA and BIS-TRIS were used to synthesize PET-based vitrimer. The results are shown in Figure S10. It is found that the gel content of PET-based vitrimer could increase effectively through the regulation of amounts of additives and could reach 68.5%. Most importantly, the increase of gel content does not compromise relaxation performance, indicating the vitrimer with higher gel content also possesses a fast exchange reaction rate. Hence, the gel content of the vitrimer could be well regulated.



Figure S11 Degradation evolution in the moding process: (a) tensile strength; (b) thermal stability; (c) and (d) DMA curves of storage modulus and tan(δ) for 0.8BT3PMDA samples of molding for 4 min and 12 min, respectively.

To understand the extent of degradation during the molding process, various properties of samples 0.8BT3PMDA with different moding times were characterized, as shown in Figure S11. The coincidence of thermogravimetric curves suggests that the thermal stability does not change after molding for 12 min. As mechanical properties were one of the most important indicators after recycling, DMTA analysis and tensile properties were applied to examine the

thermomechanical properties, as shown in Figure S11 (a, c, d). E' and tensile strength of the sample molding for 12 min were almost the same as that of the original one, suggesting the degradation in the molding process is minor. Besides, T_g obtained from DMTA also maintained constant after molding for 12 min, implying no change of the crosslinking structure. Therefore, the sample has minor degradation in the molding process.



Figure S12. Stress relaxation of sample 0.8BT3PMDA (a) and sample 0.8BT6ADR (b) at temperatures ranging from 235°C to 270°C; (c) fitting of Ea for sample 0.8BT3PMDA and 0.8BT6ADR.

The deviation of *Ea* values would be larger if the relaxation time is too fast. But it should be noted that the PET-based vitrimer has a melting point of around 240°C, as shown in Figure S12. Therefore, it should be firstly heated to 270°C to erase crystalline, then cooled to the desired temperatures for the relaxation experiment. On the other hand, PET may crystallize at 230°C after a long period of isothermal time.¹ Therefore, the lowest relaxed temperature of 235°C is chosen for vitrimer 0.8BT3PMDA, at which vitrimer 0.8BT3PMDA fully relaxes over a period of 2100 s. Besides, to reduce the deviation, five points acquired at lower relaxed temperatures are utilized for the fitting of E_a value for vitrimer 0.8BT3PMDA. Differently, vitrimer 0.8BT6ADR exhibits a much lower exchange reaction rate than 0.8BT3PMDA, making it fully relaxed over a period of 2500 s at its lowest relaxed temperature of 245°C. Therefore, the E_a values for samples 0.8BT3PMDA and 0.8BT6ADR are calculated as 104.1 KJ/mol and 125.4 KJ/mol, respectively. The R^2 values for the fitting are both higher than 0.99, indicating that the E_a values are reliable.



Figure S13. (a) Schematic illustration of the heat-triggered shape memory test procedure by fold-deploy test;² (b) The shape fixity (Rf) and recovery ratios (Rr) of sample 0.8BT3PMDA; (c).the quantification process of shapememory behavior for sample 0.8BT3PMDA.

The quantification of shape memory behavior is indeed meaningful. However, DMTA analysis is not quite suited for PET. On one hand, PET is brittle and its elongation at break is commonly lower than 5%. Although elongation at break could be improved through the increase in temperature, it is still not enough for the DMTA analysis at 105°C. On the other hand, considering bending is the main deformation in the programmed shape, DMTA analysis is not quite suited to this work. Therefore, the fold-deploy test was employed to quantify the shape memory behavior, as shown in Figure S13. It is found that the R_f and R_r of PET-based vitrimer are 90.2% and 98.9%, respectively.

References

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