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On sustainable vitrimers based on polycaprolactones

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Abstract. Vitrimers represent an environmentally friendly class of materials, which behave like thermosets at room temperature but exhibit thermoplastic flow behaviour when heated, making them processable and recyclable, thus extending material life and reducing waste. However, to fully meet the current demand for a sustainable economy, biodegradability at the end of the material life should also be considered, a property that not all vitrimers possess. Based on the above issues, this work aimed to develop biodegradable vitrimers based on polycaprolactone (PCL), a biodegradable polyester, potentially derived from biomass fermentation. In detail, three different *ad-hoc* synthesized star-shaped acrylated PCLs, characterized by different number of arms and molecular weight, were synthesized and used to prepare vitrimeric systems. Indeed, the above polymers were crosslinked with a fast exchangeable diboronic ester dithiol ([2,2′-(1,4-phenylene)-bis[4-mercaptan-1,3,2-dioxaborolane], DBEDT), in solventless conditions. The formation of a dynamic network was proven by FT-IR, DSC, TGA, gel fraction, rheological and DMA measurements. In particular, the activation energies for the relaxation process of these materials were verified by rheological measurements in the range of 44-62 kJ/mol. Moreover, all vitrimers, which were completely degraded by enzymatic hydrolysis within 12 days, exhibited excellent recyclability and self-healing properties when heated to 180 °C before processing.

KEYWORDS: Vitrimers; Polycaprolactone; Polymer Recycling; Enzyme Degradation; Self-healing.

1. INTRODUCTION

Covalent Adaptable Networks (CANs) have gained considerable attention because they combine some of the properties of thermosets, such as creep and solvent resistance, with the reprocessability typical of thermoplastic-like materials, thus bridging the gap between these two classes of materials.[1] Indeed, CANs have the unique ability to chemically break, reshape or reform their covalent network when exposed to external stimuli and may represent one of the possible solutions to the thermoset recycling problem. These systems can be divided into dissociative or associative, depending on how the density of cross-links changes following the stimulus application.[2] In dissociative CANs, which present variable cross-link density, dissociation of the cross-links after application of the stimulus leads to partial or complete depolymerization. In contrast, associative CANs are characterized by a fixed cross-link density because a bond formation process occurs prior to bond breaking, resulting in a dynamic and rapid exchange that softens the material when the stimulus is applied.[3] The concept of associative CANs was further extended by the introduction of vitrimers, which are characterized by an Arrhenius-like viscosity variation with temperature. Indeed, as with CANs in general, the reprocessability of vitrimers enables easy mechanical recycling, thus extending the life of the material and reducing its overall environmental impact.[4] Despite the above property, vitrimers may be exposed to similar scenarios as conventional plastics at the end of their life cycle, leading to their potential disposal in landfills or dispersion in the environment, and raising concerns about visual and chemical pollution, due to the release of toxic species or the formation of macro and microplastics.[5] To reduce the environmental impact, many vitrimers are designed by exploiting the use of biobased building blocks,[6] but this does not guarantee their biodegradability. Therefore, the development of sustainable systems is crucial to fully solve the problem of their dispersion in the environment. In this context, the use of polycaprolactone

(PCL), an aliphatic polyester, is very interesting because it is not only biodegradable, but also potentially produced from 5-hydroxymethylfurfural (5-HMF), a molecule obtained by fermentation of biomass, thus closing the material's carbon loop.[7]

In the literature, the majority of PCL-based CANs are mainly of dissociative type and are generally prepared by exploiting the Diels-Alder reaction.[8–10] Defize et al. used the above mechanism to prepare PCL-based dissociative networks starting from different furan/anthracene systems and maleimide-bearing star-shaped PCLs.[9–11] Despite the dynamicity of the formed network, some drawbacks should be highlighted, such as the time-consuming synthesis, the toxicity of the maleimides,[12] and the decrease of cross-linking density with temperature, leading to a relevant worsening of the rheological properties.

For PCL-based vitrimers, a few examples were described in the literature, where the formation of a dynamic system was ensured by exchange reactions involving the ester bond of the polyester[13,14]. Thus, Vallin et. al developed a covalent associative nanocomposite network by combining star-shaped hydroxyl-terminated PCL and methylene diphenyl diisocyanate (MDI) in presence of reduced graphene oxide (rGO) by exploiting transesterification and transcarbamoylation reactions.[15] It was demonstrated that the rheological behaviour of the above material can be controlled by adjusting the OH:NCO ratio and by incorporating rGO as nanofiller. Similarly, Joe et al. prepared PCL-based 4D printable PCL-based, shape memory vitrimers by reacting a PCL printing resin with polyhexamethylene diisocyanate (PHMDI) and poly(styrene-co-allyl alcohol) (PSA) promoting the transesterification with Zn(acac)$_2$.[16] In another work, linear commercial PCL was used together with thermoplastic polyurethane (TPU), cellulose nanocrystals (CNC) and a vitrimer (ESO-S) prepared by mixing epoxidized soybean oil (ESO) with 4,4′-diaminodiphenyldisulfide (APD). The presence of ESO-S was found to improve the interfacial compatibility between TPU, PCL, and CNC, while increasing tensile strength and thermal stability of the material.[17]

Despite the interesting properties of the obtained materials, the described approaches, generally applied for the preparation of PCL-based vitrimers, present some drawbacks mainly related to the use of organic- or metal-based catalyst, which can be harmful, and to the uncontrolled changes in the starting polymer topology towards random structures due to the transesterification exchange reactions on the polyester backbone.[18]

On this basis, the incorporation of a biopolymer in a vitrimer preparation that does not use catalysts or solvents for its preparation, while maintaining the degradability of the system is highly desirable. In this context, a promising reaction for vitrimer production is the one based on boronic esters, compounds first used by Cromwell et al.[19] to prepare exchangeable networks by boronic ester transesterification and later by Röttger et al. based on boronic ester metathesis.[1] These boron-based systems have the advantage of being easily hydrolysed through the B-O bond by the action of water or alcohols, producing a hydrolysate that can be recovered and reused to form a polymer.[20] Nevertheless, boronic esters, which are also easy to prepare and exhibit low toxicity, have not yet been employed in combination with PCL-based systems, which may be potentially advantageous given the combination of the low melting temperature of this material (< 60 °C) and the fast metathesis exchange rate of boronic esters.

The aim of this work was to develop biodegradable vitrimers, combining for the first time PCL with a boronic ester cross-linker, using an approach that does not require the use of solvents and catalysts. To verify the influence of polymer architecture and molecular weight on the final material properties, three different star-shaped PCLs with acrylate end groups, characterized by four and six arms and different molecular weights were synthesized and applied in the formulation of vitrimer systems. In detail, the star-shaped PCL were synthesized by ring opening polymerization of ε-caprolactone using pentaerythritol and dipentaerythritol as initiators (**Figure 1)**. The acryloyl-terminated star-shaped PCLs, prepared by acrylation of the hydroxyl end groups, were cross-linked through a thiol-acrylate reaction without solvents with a boronic ester cross-linker, i.e., [2,2′-(1,4-phenylene)-bis[4-mercaptan-1,3,2-dioxaborolane] (DBEDT). The systems were characterized in terms of their thermal and rheological properties as well as their enzymatic degradation and recyclability.

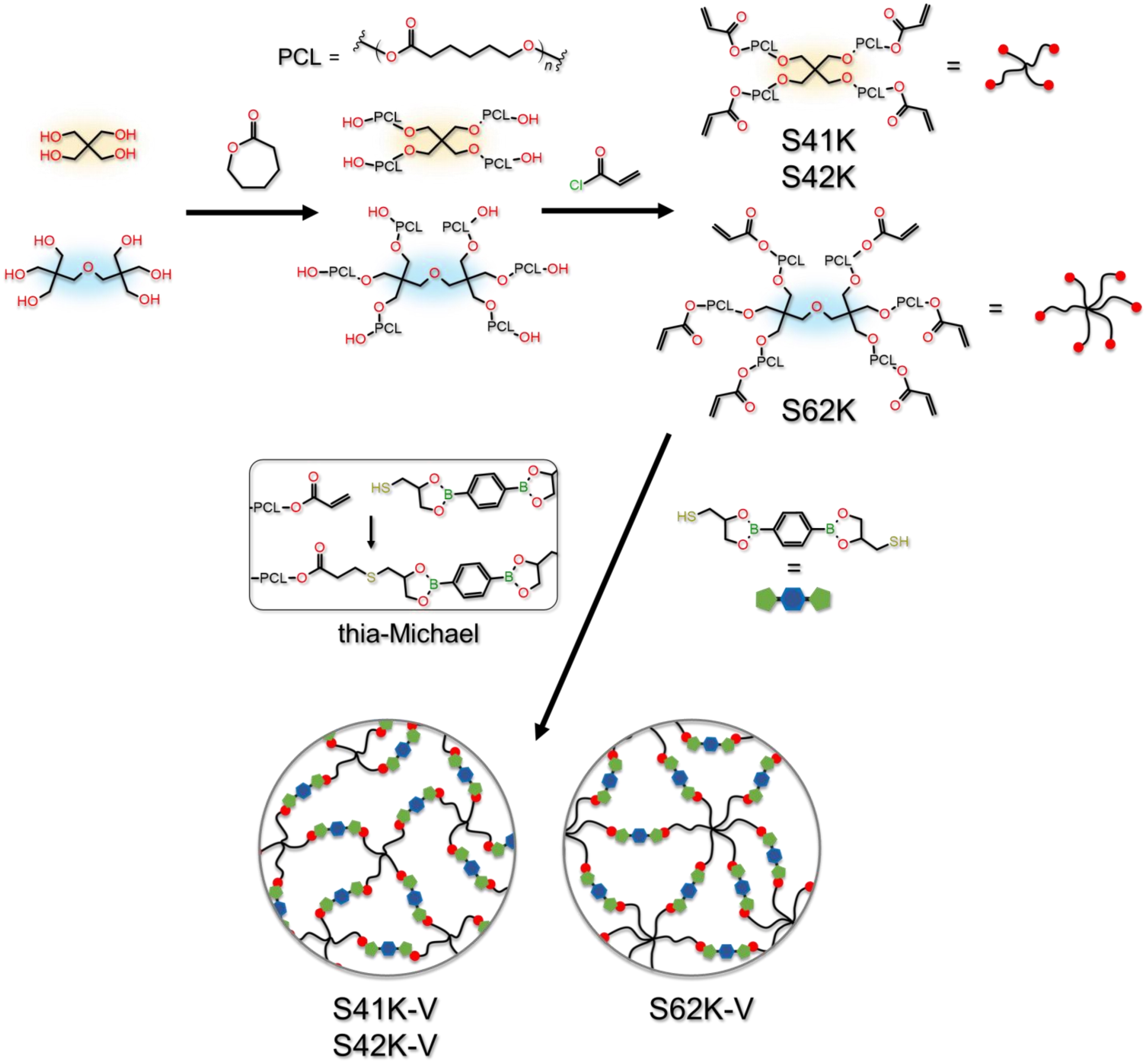

Figure 1. Preparation of PCL-based vitrimeric networks starting from pentaerythritol or dipentaerythritol as initiators.

2. EXPERIMENTAL SECTION

Materials. ε-caprolactone (ε-CL, purity = 97%), pentaerythritol (purity = 99%), tin octoate ($Sn(Oct)_2$, purity ≥ 96%), methanol (purity = 99.9%), acryloyl chloride (purity ≥ 99%), toluene (purity = 99.8%, anhydrous), dichloromethane (DCM, purity ≥ 99.8%, stabilized with amylene), thioglycerol (purity ≥ 97%), benzene-1,4-diboronic acid (purity ≥ 97%), ethanol (purity ≥ 99.8%), potassium carbonate (purity ≥ 99%) were purchased from Sigma Aldrich. High molecular weight commercial PCL, CAPA 6500® (M_w = 50000 g/mol) (PCL-L) was purchased from Perstorp. ε-caprolactone and DCM were purified prior to use by vacuum distillation over CaH_2 and stored under Ar atmosphere. Pentaerythritol and benzene-1,4-diboronic acid were dried in vacuum oven at 40 °C prior use. All the other reagents were of analytical grade and used without further purification. Cutinase Novozym 51032 was purchased from STREM chemicals.

Preparation of the boronic ester crosslinker, the star-shaped PCLs and vitrimers. [2,2′-(1,4-Phenylene)-bis[4-Mercaptan-1,3,2-Dioxaborolane] (DBEDT) was prepared according to the procedure reported by Zych et al. by condensation of thioglycerol and benzene-1,4-diboronic acid in ethanol.[21] Acrylated polymers were synthesized according to a previously reported two-step procedure, starting from the synthesis of star-shaped PCL with hydroxyl end groups[22–24] using pentaerythritol or dipentaerythritol as initiators (**Figure S1**). The details of the polymer and vitrimers preparation (**Figure S2**) are reported in the supporting information. The acrylated polymers were defined by specifying the number of arms and molecular weight in the code. The example S41K indicates a star-shaped polymer (S) prepared using pentaerythritol as initiator with 4 arms (4) and characterized by a molecular weight of 1000 g/mol (1K). The coding of vitrimers follows that of the corresponding acrylates, i.e., the vitrimers prepared using S41K are coded S41K-V.

Characterization measurements. ^{1}H-NMR spectra of hydroxyl and acrylated PCLs were recorded using a Jeol ECZ400R/S3 400 MHz using 10 mm NMR tubes and $CDCl_3$ as solvent. All the samples were dissolved in $CDCl_3$ at a concentration of 15 mg/mL and analyzed at room temperature.

FT-IR spectra of the materials were acquired using a Bruker "Vertex 70$^{®}$" in ATR mode from 400 to 4000 cm^{-1}. Thermal analysis was performed using a DSC1/TGA STAR^{e} System$^{®}$. In detail, DSC thermograms were recorded in the range -100/+150 °C, using heating/cooling rates of ±10 °C/min under 20 mL/min nitrogen flow.

The crystallinity degree of the prepared materials (χ_c) was calculated based on their PCL content, Φ_{PCL}, by applying **Equation 1**, using the melting enthalpy values (ΔH_m) measured from the second heating scan.

$$\chi_c = \frac{\Delta Hm}{\Delta H_m^0 \cdot \Phi PCL} \quad \mathbf{(1)}$$

where ΔH_m is the measured melting enthalpy, Φ_{PCL} is PCL weight fraction in the vitrimer and ΔH_m^0 is the melting enthalpy of the 100% crystalline PCL (139 J/g).[25]

TGA measurements were performed from 30 to 800 °C under a nitrogen flow of 80 mL/min.

The gel fraction (GF) of vitrimers was measured using anhydrous toluene, being a good solvent for both reagents. In detail, 50 mg of the samples were accurately weighed and immersed in 2 mL of solvent until constant weight. Then, the samples were dried at 25 °C for 24 h followed by another 24 h at 30 °C under vacuum. After this phase, the samples were weighed, and the GF was calculated using **Equation 2**.

$$GF = \frac{M_d}{M_i} \cdot 100 \qquad (2)$$

where: M_d = weight of the dried sample, M_i = initial weight.

Dynamic mechanical analysis (DMTA) was carried out on bars (nominal size 6x1.5x30 mm^3) working in tensile mode on a TA Instruments Q800 using a heating rate of 3°C/min in the range from 25 to 200 °C, in strain-controlled mode (frequency = 1 Hz, deformation amplitude = 0.05%, preload = 0.01 N).

Plate-plate rheological analysis of the materials was performed using an ARES rheometer, using 25 mm diameter x 1 mm thickness disks. Specimens for both DMTA and rheology were obtained by curing the vitrimers within silicone molds with suitable geometries and keeping the materials in the desiccator until the tests. Dynamic strain sweep measurements were performed to confirm the linearity of the viscoelastic region up to 1% strain. Frequency sweeps measurements were carried out to measure the complex viscosity (η*), storage modulus (G') and dissipative modulus (G'') in the frequency range of 0.1–100 rad/s, between 90 °C and 210 °C with 30 °C steps. Isothermal relaxation tests were also carried out using 1% strain. Stress G(t) was normalized on G_0, namely the stress recorded at t = 0.5 s to get rid of instrumental transitory at the begin of the relaxation test. All the rheological measurements were performed under nitrogen flow to avoid oxidative and hydrolytic degradation of the materials.

Enzymatic hydrolysis of materials was performed by placing small rectangular vitrimer specimens (dimensions = 6x2x2 mm^3, initial weight = 25 mg, n = 4) in a 1.5 mL Eppendorf safe-lock tube followed by 1 mL of a 5 µM solution of cutinase in 0.1 M phosphate buffer solution (KPO), pH 8. Samples were incubated at 50 °C for 1, 3, 6 and 12 days, until complete degradation was observed. At the desired time point, the samples were removed from the enzyme solution, washed three times with an excess of milliQ water and then dried at 30 °C in vacuum oven until constant weight before performing the gravimetric measurement of the weight loss using an analytical scale (±0.0001 g).

3. RESULTS AND DISCUSSION

Study of the cross-linking reaction. The thiol-acrylate reaction (**Figure 1**) between the star-shaped acrylated PCLs and DBEDT was monitored by comparing the FT-IR spectra of the starting polymers with those of the respective cross-linked systems (**Figure S3**). The neat polymers exhibited typical signals associated with PCL chains at 2950 cm^{-1} and 2870 cm^{-1} (υ Csp^3- H methylenic unit), 1725 cm^{-1} (υ C=O), at 1295 cm^{-1} (υ C–O and C–C), 1242 cm^{-1} and 1171 cm^{-1} (υ C–O–C asymmetric/symmetric). Moreover, two additional bands were found at 1640 and 814 cm^{-1}, which can be attributed to C=C stretching and $CH=CH_2$ twisting of acrylate units, respectively, as previously reported in other works.[24,26] As shown in Figure 2, the above mentioned two signals disappeared in the FT-IR spectra of the polymers after reaction with DBEDT. Indeed, as previously reported by Zych et al., this finding proves the successful of the thiol-acrylate reaction. Moreover, some shoulders around 1211 cm^{-1} and peaks at 652 cm^{-1} were found in the spectra of the cross-linked PCL, which can be attributed to the presence of B-O and B-O-B bonds of the boronic ester, respectively and which can be also observed as distinct peaks in the DBEDT spectrum (**Figure S4**).[27] Macroscopically, the crosslinking process was evidenced by an increase in the system’s viscosity, over time, while the mixture was being heated up. For all the systems, the transition from liquid, pourable mixtures (**Figure S5a**), having viscosity comparable to those of melted PCL acrylates, to rubbery transparent solids (**Figure S5c**), able to slowly crystallize at room temperature (**Figure S5b**) was observed. Moreover, the gel fraction (GF) measurements performed on the materials (**Table S4**) showed values of 79%, 78% and 83% for S41K-V, S42K-V, S62K-V vitrimers respectively. These were comparable to the GF found for a similar system (81.9 ± 1.4%) reported in the literature,[21] and previously confirmed results obtained by FT-IR analysis. The GF values, which are high enough to confirm a positive outcome of the curing reaction as reported in other works,[21] but the fact that they did not reach 100% may be explained by considering the peculiar structure and molecular weight of the star-shaped PCLs, which could limit their diffusion and thus the cross-linking reaction.

Study of the thermal properties. The thermal properties of the acrylated polymers and the corresponding cross-linked systems are reported in **Table 1**, while DSC and TGA traces are given in the Supporting Information (**Figure S6** and **Figure S7**). In particular, when comparing the DSC data of the different acrylated starting materials, it was found that the molecular weight as well as the number of arms of the star-shaped PCL affected the systems' thermal properties. In particular, the crystallinity (χ_c) of the acrylated polymers increased with increasing the molecular weight and the number of arms, from 40 % for S41K to 52% and 53 % for S42K and S62K, respectively. These samples show a different trend compared to linear high molecular weight polymers, where, in general, an increase in molecular weight leads to a decrease in crystallinity.[28] Indeed, in the case of branched or star-shaped polymers, the chain length enhances the structuring, at least at low molecular weights, showing an inverse behavior compared to linear polymers.[29] This could be due to the fact that the structuring of the linear fraction predominates with increasing chain length compared to the crystallization disorder that develops around the branched core and could explain the same crystallinity of the 4-armed and 6-armed sample, S42K and S62K, respectively, characterized by the same molecular weight per single arm. In contrast, all the cross-linked samples seemed to maintain the same χ_c, which was lower than that of the pristine polymers for S42K-V and S62K-V. A slight difference among the samples was observed in the T_c, which decreased especially for S42K after the cross-linking process. The decrease in crystallinity and T_c in the cross-linked samples, which was observed mainly in the samples characterized by the highest molecular weights, namely S42K and S62K, could be related to a decrease in the mobility of the macromolecular chains caused by the introduction of bonds at the ends of the star-shaped structures. Therefore, the above findings appear to support the formation of a network when the star-shaped polymers are reacted with DBEDT at high temperature. Although the crystallinity decreases in the cross-linked systems, it is worth underlining that all the samples retain some degree of structuration even after the treatment with the cross-linking agent, a characteristic which may affect the final material's properties.

Table 1. DSC characterization of acrylated polymers and vitrimers.

Sample code	T_c [°C]	$\Delta H_{c\ CORR}$ [J/g]	T_m [°C]	$\Delta H_{m\ CORR}$ [J/g]	$\chi_{c\ CORR}$ [%]	$T_{onset\ 5\%}$* [°C]	T_{max}** [°C]
S41K	16	-52	43	55	40	399	427
S42K	23	-67	47	72	52	393	427
S62K	27	-68	48	73	53	398	427
S41K-V	13	-56	46	58	42	356	407
S42K-V	14	-56	48	59	42	359	416
S62K-V	20	-58	46	60	43	346	412

The subscript m CORR and c CORR indicate the values measured during melting and crystallization, respectively, considering the mass fraction of PCL contained in the materials. *: $T_{onset\ 5\%}$ was extrapolated from TGA curves as the point where the mass loss was equal to 5%. **: T_{max} was extrapolated from DTG curves as the points where the mass loss rate was at its maximum.

The results of thermogravimetric analysis of the acrylated polymers revealed similar onset degradation temperatures ($T_{onset\ 5\%}$), which were around 390 °C, and equal temperatures of maximum rate of degradation (T_{max}) of 427 °C, in agreement with the values observed in other previous works for acrylated PCL[24,30] and related to a statistical chain scission by a β-elimination mechanism. In contrast, a noticeable decrease in the thermal stability, in terms both of $T_{onset\ 5\%}$ and T_{max}, was observed after the cross-linking reaction. The magnitude of the T_{max} alteration directly correlates with the presence of DBEDT in the system. Considering the lower degradation temperature observed for neat DBEDT compared to the PCL acrylated polymers (**Figure S8** and **Table S5**), this can be possibly attributed to its thermal degradation within the network structure.

DMTA and rheological analyses. Thermomechanical properties of vitrimers were investigated by dynamic mechanical thermal analyses on a heating ramp (**Figure S9**). At room temperature, storage moduli in the range of 0.4±0.1 GPa were measured, which are consistent with that of a linear high molecular weight, PCL-L (**Figure S10**). Beside the expected fall in stiffness across the melting of PCL, the storage modulus at high temperature can be correlated with the crosslinking of the PCL. Indeed, a fully stable storage modulus plateau was observed for all vitrimeric formulations, in the range of 1 MPa, with limited differences between the formulations. Such plateau confirms the crosslinked nature of the material, maintaining the shape of the specimens well above the melting temperature (**Figure S11**). To further investigate the bond exchange at high temperature, rheological measurements were carried out in frequency sweep at different temperatures (**Figure S12**), ranging from 90 to 210°C. At 90°C, S41K-V displayed a fully solid like behaviour, characterized by a constant value of storage modulus, higher than G'' over the whole frequency range. Similarly, rheological behaviour for S42K-V and S62K-V is dominated by the elastic component, with only a slight decrease in the storage modulus at frequencies below 1 rad/s. At higher temperatures, the decay in storage modulus at low ω expectedly becomes progressively more important for all formulations, while the peak in loss modulus shift to higher frequencies. This suggests the relaxation of the vitrimers becomes significant at low frequency (i.e. long timescale) and high temperature, in good agreement with previously reported vitrimers based on DBEDT.[21] However, within the explored frequency range, crossover between G' and G'' was observed only for S62K-V at 210°C (at 0.2 rad/s), whereas for lower temperatures it appears to fall below the minimum frequency applied. Similarly, crossover was not observed in the explored frequency range for both S41K-V and S42K-V.

This is in agreement with other boronic ester-crosslinked vitrimers, displaying crossover points below 0.1 rad/s.[1] To investigate the kinetics of the relaxation phenomena, stress relaxation tests were carried out at different temperatures (**Figure 2**). While the relaxation of vitrimers based on the star-shaped polymers are expected to result in multiple relaxation modes, owing to possible dangling chains and non-crosslinked fractions,[31] the relaxation times obtained are very well fitted by the Arrhenius plots, yielding activation energy for the relaxation process in the range of 60 kJ/mol for both S41K-V and S42K-V, while a lower value was obtained for S62K-V. As already observed for the rheological behavior, it is possible to hypothesize that the 6-arm PCL structure allows greater mobility, and the corresponding network is consequently characterized by a lower activation energy compared to systems prepared from 4-arm PCL. Overall, the activation energies for the relaxation of PCL boronic ester vitrimers are in agreement with previously reported results for similar systems.[1,21,32]

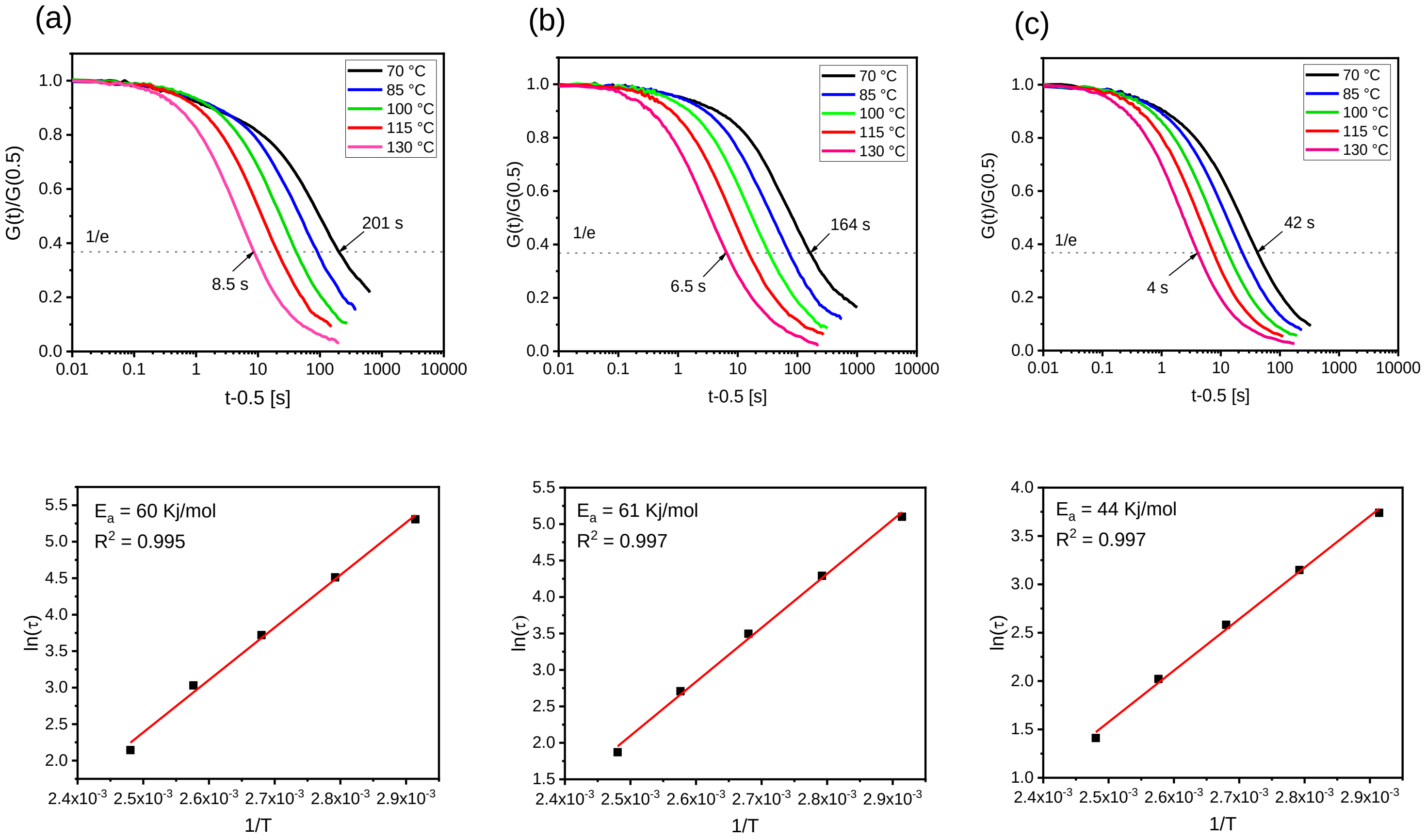

Figure 2. Stress relaxation plots (top) for (a) S41K-V, (b) S42K-V and (c) S62K-V, along with the corresponding Arrhenius plots (bottom).

Recyclability and self-healing test. To assess the recyclability of the developed systems (**Figure S13a**), a 0.5 g segment of the cross-linked film was manually cut into smaller pieces. These fragments were subsequently positioned within a rectangular mold, measuring 3.0 x 3.5 cm² and inserted into the hot press for compression molding. The sample was preheated to 180 °C for 3 minutes and then pressed at the same temperature for 5 minutes with a very low force (300 kgf). It is worth underlining that the above temperature was chosen to adequately reduce the viscosity of the system in order to fill all empty cavities in the mold and to ensure sufficient interdiffusion kinetics of the macromolecular chain segments, i.e., to promote good grain adhesion in a short time interval. After this procedure, a homogeneous film, without any apparent defects, identical to the original material was successfully recovered. The self-healing test was similarly performed by cutting the film sample into two parts and using the same temperature without preheating (**Figure S13b**). To ensure ideal contact between the cut edges and prevent distortion caused by heat, a small glass slide was used to secure the sample within the mold. This technique effectively produced an uninterrupted film without any visible cut marks. These observations clearly demonstrate that the bond exchange and macromolecular interdiffusion, as well as the viscosity of the materials under the conditions used for both tests, were sufficient to ensure good adhesion between the different pieces confirming the vitrimeric behaviour possessed by this class of materials. Furthermore, the thermochemical stability of the materials was proved by the unchanged FT-IR spectra and TGA curves of the samples before and after recycling. **Figure S14** and **Figure S15** show the characteristic FT-IR spectra and TGA profiles, respectively, of S41K-V before and after the rycling tests. As demonstrated by this test, the high network dynamicity introduced by boronic ester metathesis provides a key advantage in terms of reprocessability, making these materials easily moldable and recycable without the use of catalysts (**Figure S16**). It is worth underlining that some of these catalysts, used in previous works, especially the metal-based ones, such as tin octoate or zinc acetylacetonate, which are widely used in polyester/polyurethane vitrimers to promote transesterification and transcarbamoylation exchange reactions,[15,33] are toxic or harmful even when employed in very low concentration.[34,35] Moreover, their presence could lead to a decrease in the thermal stability of the system, since they are able to promote degradation by depolymerization or, in presence of water, by hydrolytic processes under the recycling conditions generally used.[36,37] Considering these aspects, the developed approach is promising when considered from the point of view of producing sustainable materials with lower environmental impact.

Enzymatic Degradation. The enzymatic degradation of the PCL vitrimers was carried out using a cutinase, a highly active hydrolytic enzyme belonging to the serin-hydrolases family known for its activity on polyesters.[22,38] To investigate the effect of crosslinking on the hydrolytical stability of the PCL-based vitrimers, PCL-L, was used as the reference material (**Figure 3**). Not surprisingly, complete hydrolysis of PCL-L was observed after 3 days, demonstrating the effective depolymerization activity of this enzyme for PCL, as also reported in our previous work.[22] In contrast, the vitrimers exhibited slower degradation times, requiring 12 days to be completely degraded. Considering the melting behaviour of the linear PCL and vitrimers, a faster degradation rate could be expect for the latter systems, as the reaction temperature (50 °C) was above the T_m of the PCL crystalline phase of the vitrimers but below the melting temperature reported in other works for PCL-L (57 °C).[22,39] On this basis, the results suggest that the presence of cross-links in the polymer matrix is the main factor influencing the degradation rate of PCL at that temperature. Moreover, no significant differences in the degradation profile of the different vitrimers were observed, probably due to the limited differences in molecular weight and number of functionalities of the studied star-shaped polymers. Although a different degradation rate of the vitrimers compared to the linear polymer was observed, it was still possible to degrade the cross-linked PCL network in shorter times. LC-MS analyses confirm that the enzymatic hydrolysis reaction releases 6-hydroxyhexanoic acid, the ring-opened derivative of ε-caprolactone, as major products (Figure S17) and that the DBEDT monomer is hydrolyzed and converted to 1,4-phenylenediboronic acid (Figures S18 and S19).

This result opens up the possibility of exploiting this process in the formation of monomers/oligomers through enzymatic depolymerization, that can be subsequently reused in the *ex novo* synthesis of polymers/vitrimers, making these materials appealing from a circular economy perspective.[40]

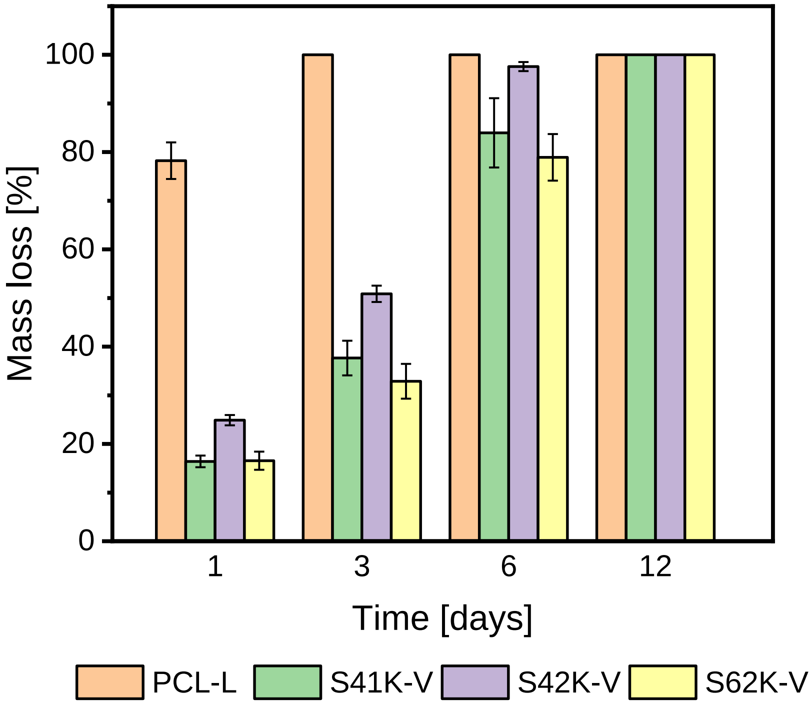

Figure 3. Enzymatic hydrolytic degradation profile of: PCL-L polymer, S41K-V, S42K-V and S62K-V vitrimers in 5 μM cutinase solution in 0.1 M KPO buffer pH 8.

4. CONCLUSIONS

In this work, vitrimer systems based on PCL were successfully developed. In the design of the formulation, various aspects related to both the manufacturing approach and the final properties of the material were considered to make the whole process environmentally friendly. First, starting from ad-hoc synthesized star-shaped PCL, a polymer potentially produced from renewable sources, a crosslinker was used that allowed the vitrimer production without the use of solvents and catalysts, it being based on a simple thiol-acrylate reaction.

The behavior of the vitrimers, common to all systems produced and slightly influenced by the number of arms and the length of the star-shaped polymers, allowed easy recycling through a simple shaping process. In addition, an analysis of enzymatic hydrolysis highlighted the ability of the materials to degrade despite the formation of the network, a phenomenon due to the construction of the systems based on PCL, a highly biodegradable polymer. The above property, which generally does not apply to all vitrimer systems, may clearly be of great interest for the end of life of the developed material.

ASSOCIATED CONTENT

Supporting Information: Star-shaped PCLs and vitrimers preparation description; Scheme of the synthesis and properties of the star-shaped polymers; FT-IR and ^{1}H-NMR signals of a four-arm star-shaped polymer; Scheme and conditions of vitrimers preparation; FT-IR spectra of PCL acrylates and vitrimers; FT-IR spectrum of DBEDT powder; Gel fractions of PCL-based vitrimers; Photos of the prepared materials; DSC thermograms of PCL acrylates and respective vitrimers; TGA curves of PCL acrylates and respective vitrimers; TGA thermogram of DBEDT; DBEDT thermal properties; DMTA of PCL-based vitrimers; DMTA analysis of high molecular weight linear PCL; Photo of a vitrimer sample, above PCL T_m, during DMTA analysis; Rheological plots of vitrimers; Photos of recyclability and self-healing tests; FT-IR spectra of vitrimers before and after recycling test; TGA thermograms of a vitrimer before and after recycling test; Photos a vitrimer specimen; LC-MS analysis of the vitrimer sample S41K-V after 3 days of hydrolysis carried out in positive mode; LC-MS analysis of the vitrimer sample S41K-V after 3 days of hydrolysis, the 1,4-phenylenediboric acid standard and a mixture of S41K-V and 1,4-phenylenediboric acid standard; MS spectra at 6.5 min for the 1,4-phenylenediboronic acid standard and for the S41K-V hydrolysate.

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Notes

The authors declare no competing financial interest.

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