



Catalyst-Free α -Acetyl Cinnamate/Acetoacetate Exchange to Enable High Creep-Resistant Vitrimers

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Abstract: Vitrimers represent an emerging class of polymeric materials that combine the desirable characteristics of both thermoplastics and thermosets achieved through the design of dynamic covalent bonds within the polymer networks. However, these materials are prone to creep due to the inherent instability of dynamic covalent bonds. Consequently, there are pressing demands for the development of robust and stable dynamic covalent chemistries. Here, we report a catalyst-free α -acetyl cinnamate/acetoacetate (α -AC/A) exchange reaction to develop vitrimers with remarkable creep resistance. Small-molecule model studies revealed that the α -AC/A exchange occurred at temperatures above 140 °C in bulk, whereas at 120 °C, this reaction was absent. For demonstration in the case of polymers, copolymers derived from common vinyl monomers were crosslinked with terephthalaldehyde to produce α -AC/A vitrimers with tunable thermal and mechanical performance. All resulting α -AC/A vitrimers exhibited high stability, especially in terms of creep resistance at 120 °C, while retaining commendable reprocessability when subjected to high temperatures. This work showcases the α -AC/A exchange reaction as a novel and robust dynamic covalent chemistry capable of imparting both reprocessability and high stability to cross-linked networks.

Vitrimers offer a promising avenue for tackling the formidable challenge of recycling thermosets.^[1] Although a diverse array of vitrimers, utilizing various dynamic covalent bonds, has been developed,^[2] an ongoing design challenge lies in achieving an optimal equilibrium between thermal reprocessability in the context of material flow and stability during usage, particularly in terms of dimensional stability.^[3] When it comes to applications in engineering plastics or structural materials, it is essential to underscore the significance of creep resistance for materials.^[4] This necessity has led to an explosion in research dedicated to innovative vitrimers that exhibit enhanced creep-resistant characteristics.^[5]

The fundamental mechanism behind creep of vitrimers is mainly attributed to dynamic bond exchange at temperatures lower than the service temperatures. In other words, the upper limit temperature of vitrimers for use seems to be dictated by the topology freezing temperature (T_v).^[6] Therefore, the strategic approach to mitigating creep is to impede or even halt the chemical bond exchanges within vitrimers at their usage temperatures. For this purpose, several strategies have been explored to enhance bond reactivity control and material robustness. These strategies predominantly focus on catalyst control,^[7] phase separation,^[5b,8] metal coordination networks,^[9] and the combination of permanent and dynamic bonds^[5a,10] to prevent material deformation at lower temperatures. However, these methodologies usually sacrifice the reprocessability of the material and increase the system's complexity.^[11] An ideal vitrimer material should

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combine a high T_v to avoid creep at operational temperatures with a high activation energy (E_a) to enable rapid acceleration in dynamic bond exchange and material flow at elevated temperature beyond T_v .^[5c] Currently, designing vitrimers with such characteristics remain a significant challenge.

Here, we report a catalyst-free α -acetyl cinnamate/acetoacetate (α -AC/A) exchange, discovered through small molecule model studies between an acetoacetate and an α -acetyl cinnamate (α -AC). As shown in Figure 1a, an equimolar amount of methyl acetoacetate (MA) and ethyl 2-benzylidene-3-oxobutanoate (EBO) were dissolved in anhydrous deuterated dimethyl sulfoxide (DMSO- d_6) solvent. Initially, ^1H NMR (400 MHz, DMSO- d_6 , 22 °C) showed the proton signals of $-\text{CH}=\text{C}-$ of EBO (isomers) at about 7.75 ppm and 7.59 ppm (Figures S1 and S2). Upon heating the solution at different temperatures for various durations, two additional proton signals emerged at approximately 7.77 ppm and 7.61 ppm, corresponding to the proton signals in $-\text{CH}=\text{C}-$ of the exchange product methyl 2-benzylidene-3-oxobutanoate (MBO, isomer, Figures 1b and S1). The exchange reaction can reach equilibrium after reaction at 80 °C for about 6 h in DMSO- d_6 (Figure 1b). Further evidence of the exchange reaction was obtained from gas chromatography-mass spectrometry (GC-MS) (Figure 1c). As exchange proceeded at 80 °C, two additional peaks appeared with the masses (m/z) matching the exchange products MBO and ethyl acetoacetate (EA), respectively (Figures 1c, S3 and S4). The intensity of the new peaks grew with time until the reaction reached equilibrium after 6 h (Figure 1c).

The chemical kinetics of small molecules was investigated through ^1H NMR (400 MHz, DMSO- d_6) spectra recorded at temperatures ranging from 70 to 100 °C for various durations (Figure S5). The rate constants of this reaction at different temperatures were obtained by mon-

itoring the changes in the ratio of reactants (EBO) to products (MBO) in the reaction system (Figures S6 and S7, Table S2). Accordingly, the relationship between the reaction rate constant k_{exp} and the temperature obeyed the Arrhenius equation, with the activation energy of the reaction calculated to be 43.7 kJ mol⁻¹ (Figure S8).

To simulate the polymer environment, the exchange reaction was conducted under solvent-free conditions. In contrast to the aforementioned reaction system employing DMSO- d_6 as a solvent, where the exchange reaction can occur even at room temperature (Figure S1), the exchange reaction remains undetectable at 120 °C for 6 h in a solvent-free reaction system (Figures 1d and S9). The exchange product can be observed only after raising the temperature to 140 °C (Figures 1d and S9). This is mainly attributed to the inherent β -ketoester structure of ethyl acetoacetate, which facilitates keto-enol tautomerism.^[12] In polar solvents, the resulting enol structure is stabilized through the formation of hydrogen bonds, leading to a lower pK_a compared to that in non-polar solvents.^[13] To further prove this, non-polar tetrachloroethane- d_2 was used as the reaction solvent. As shown in Figure S10, the products could not be detected even when the temperature was increased to 140 °C and heated for 6 h.

Based on above results, we propose an associative Michael addition-elimination mechanism for the α -AC/A exchange reaction (Figure 2a): The MA_t produced by MA through keto-enol tautomerization performs a nucleophilic attack on the β -carbon atom of EBO to generate the intermediate anion INT1, which can undergo an intramolecular proton transfer reaction to form anionic INT3. A new saturated carbonyl compound (anionic INT2) generates from the intramolecular proton transfer reaction. E1cB elimination then occurs where INT3 dissociates into EA_t and MBO. Eventually, EA_t undergoes keto-enol tautomerization to form EA. This catalyst-free Michael addition-

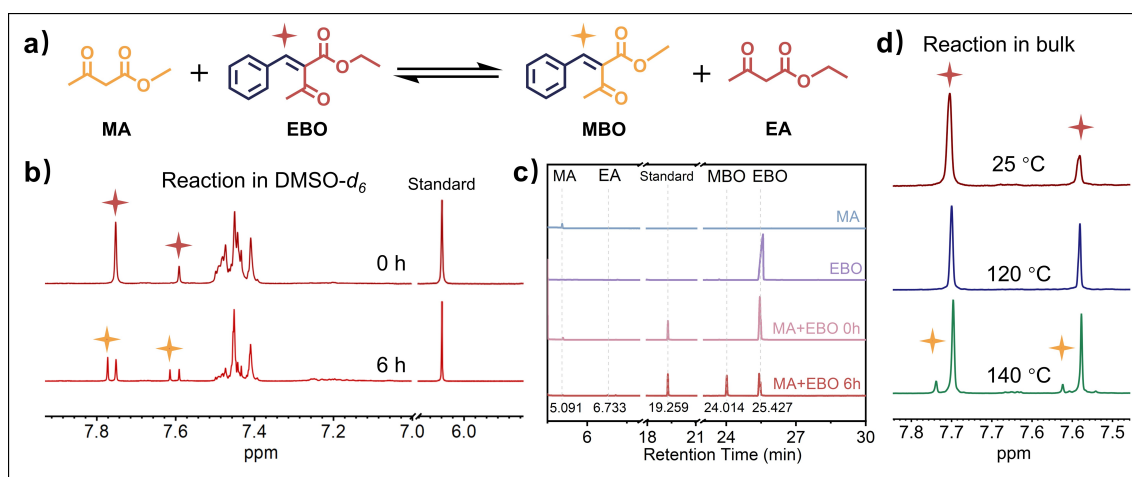


Figure 1. Model reactions for α -acetyl cinnamate/acetoacetate (α -AC/A) exchange. (a) Model reactions of α -AC/A exchange between methyl acetoacetate (MA) and ethyl 2-benzylidene-3-oxobutanoate (EBO) to produce methyl 2-benzylidene-3-oxobutanoate (MBO) and ethyl acetoacetate (EA); (b) ^1H NMR (400 MHz, DMSO- d_6 , 22 °C) traces and (c) gas chromatography (GC) traces of the α -AC/A exchange reaction between MA and EBO before and after a 6 h reaction in DMSO- d_6 at 80 °C. (d) ^1H NMR (400 MHz, DMSO- d_6 , 22 °C) traces of the α -AC/A exchange model reaction between MA and EBO before and after a 6 h reaction in bulk at different temperatures.

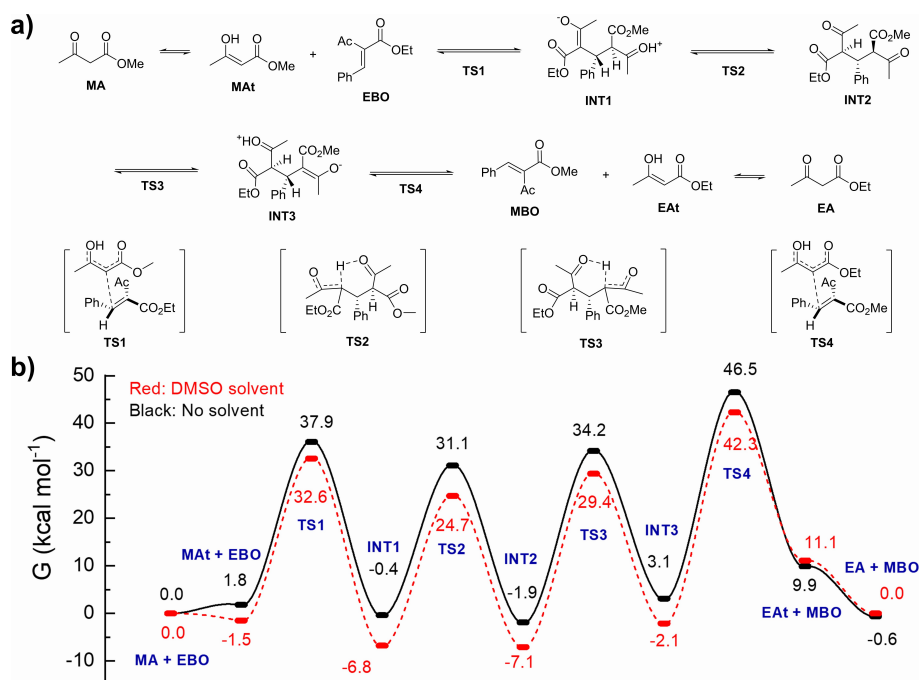


Figure 2. α -AC/A exchange reaction mechanism. (a) Proposed associative Michael addition-elimination mechanism for α -AC/A exchange reaction; (b) Reaction energy profile of the α -AC/A exchange reaction from DFT calculations in both DMSO solvent and solvent-free conditions, where TS and INT represent transition states and intermediates, respectively.

elimination mechanism was further supported by DFT theoretical calculations on M06-2X combined with the 6-31+G (d, p) basis set, which demonstrated its feasibility in DMSO and bulk states (Figure 2b). The optimized geometric configuration of the molecule is detailed in Table S1.

We suggest that this high-temperature induced α -AC/A exchange reaction can be effectively used in the preparation of highly creep-resistant vitrimers. To verify our hypothesis, two types of copolymers, poly (ethylene glycol monoacetoacetate monomethacrylate-co-ethyl acrylate/methyl methacrylate) (AAEM-co-EA and AAEM-co-MMA), containing acetylacetone side chains, were synthesized by free radical polymerization (Figures S11–S13). The α -AC/A vitrimers (CAEs and CAM) were prepared by cross-linking AAEM-co-EA/MMA with various loadings of terephthalaldehyde (TPA, used as crosslinker) (Figure 3a and Table S3). The free AAEM motifs in the AAEM-co-EA/MMA backbone facilitate the α -AC/A exchange reaction.

FTIR spectra of the α -AC/A vitrimers (Figure S15) revealed notable reductions in the absorbance at 2750 to 2850 cm^{-1} ($-\text{CH}=\text{O}$ stretching frequency), alongside with the appearance of the $\text{C}=\text{C}$ stretching vibration in α -AC/A vitrimers at 1602 cm^{-1} after curing, indicating the successful formation of α -AC bond during the curing process. This process activated the transformation of the soluble linear polymers into cross-linked networks, which was confirmed by gel contents and swelling tests. The gel content of the α -AC/A vitrimers, determined via Soxhlet extraction in THF for 48 hours, was found to exceed 95%, indicative of a high cross-link degree within these materials (Figure 3b). Besides, CAE-50 was used as a representative sample to test the

swelling behavior, which exhibited a tendency to swell (without dissolution) in various solvents (Figure S16). α -AC/A vitrimers also exhibit remarkable water stability; CAE-50 maintained its original appearance and chemical structure after being submerged in hot water (95 °C) for 7 days (Figure 3c). Moreover, a broad range of glass transition temperatures (T_g) and mechanical properties for α -AC/A vitrimers were observed (Figures 3d, 3e and S17, Tables S4 and S5), with these tendencies consistently aligning with their crosslinking density and polymer rigidity.^[14] These results demonstrate the successful synthesis of cross-linked networks with highly tunable properties.

Next, we set out to study the dynamic characteristics of α -AC/A exchange within bulk polymers. As illustrated in Figure 4a, the topological network rearrangement of α -AC/A vitrimers can be achieved in the presence of free acetoacetate via α -AC/A exchange without a catalyst. Stress relaxation tests were conducted for α -AC/A vitrimers to evaluate these exchange dynamics at elevated temperatures (160–190 °C). As depicted in Figures 4b, S19 and S20, α -AC/A vitrimers exhibit temperature-dependent stress relaxation behavior. At higher temperature (190 °C), all samples can achieve rapid stress relaxation with the relaxation time within 200 s. Besides, the relaxation time ($\ln \tau^*$) displayed a linear relationship with the inverse temperature (Figure 4c), indicative of the Arrhenius flow characteristics and vitrimeric nature of the α -AC/A networks. The calculated activation energy (E_a) values for α -AC/A vitrimers, ranging from 141 to 200 kJ mol^{-1} , are higher than those of most previously reported vitrimers based on various dynamic covalent bonds (Figure 4c and Table S6). This suggests a

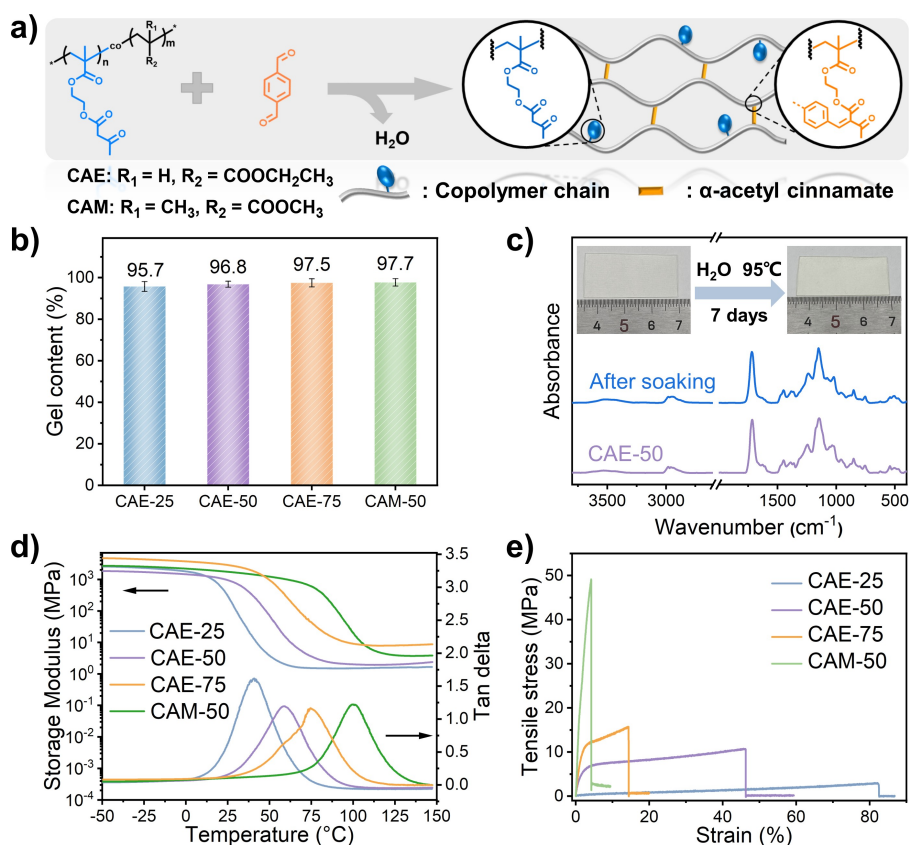


Figure 3. Synthesis and properties of the α -AC/A vitrimers. (a) Schematic diagram of the synthesis of α -AC/A vitrimers through the reaction between linear copolymers derived from common vinyl monomers with acetylacetone side chains and terephthalaldehyde; (b) Gel content data of α -AC/A vitrimers by extraction in THF for 48 h; (c) FTIR spectra and images of CAE-50 before and after being placed in H_2O at 95°C for 7 days; (d) Storage modulus and $\tan \delta$ as a function of temperature for α -AC/A vitrimers from DMA temperature sweep tests; (e) Representative stress-strain curves of α -AC/A vitrimers.

comparatively higher temperature dependence of the α -AC/A exchange reaction compared to other developed vitrimers.^[15] A theoretical value for the topology freezing transition temperature (T_v) can be extracted from the Arrhenius relationship yielding values of 93°C , 113°C , 129°C and 123°C for CAE-25, CAE-50, CAE-75 and CAM-50, respectively, in close alignment with the onset temperatures of the α -AC/A exchange reaction observed in the small molecule studies. Furthermore, frequency sweep measurements, revealing a constant rubbery plateau modulus in α -AC/A vitrimers, underscore the associative dynamic nature of the α -AC/A exchange in polymer systems (Figure S21).

The observed rapid stress relaxation at elevated temperatures endows α -AC/A vitrimers with reprocessability. As exemplified by CAE-50, the chopped CAE-50 samples, subjected to 180°C and 3 MPa pressure, can be reprocessed, producing complete and transparent reprocessed samples (Figure 4d). The isothermal TGA measurement revealed the thermal stability of CAE-50 at reprocessing temperature (Figure S22). The chemical structures, T_g , and thermal stability of the CAE-50 after two-cycles reprocessing are highly comparable to the original one, as evidenced by FT-IR spectroscopy, differential scanning calorimetry (DSC)

analysis, and thermogravimetric analysis (TGA) (Figures S23–S25). In term of mechanical properties, an elevation in Young's modulus, coupled with a reduction in tensile strength and elongation at break after two cycles reprocessing were observed (Figure 4e). The difference in mechanical properties could be ascribed to the irreversible chain scissions or the formation of permanent cross-links occurring within the networks from the side reactions during the repetitive chopping and hot-press molding processes. Moreover, the stress relaxation behavior comparison of the original and 1st cycle reprocessed CAE-50 at 160°C confirms consistently high exchange dynamics of the reprocessed sample (Figure S26).

Despite their high reprocessability, the developed α -AC/A vitrimers display a remarkable resistance to creep. The creep behavior of vitrimers is profoundly influenced by two critical factors: E_a and T_v .^[16] Enhanced E_a and T_v typically show greater resistance to creep. This arises from the increased energy demand for creep and the restriction of molecular chain movement below the T_v .^[15a,17] Consequently, due to the high E_a (ranging from 141 to 200 kJ mol^{-1}) (Figure 4c) and T_v values (spanning from 93 to 129°C) (Table S4), all α -AC/A vitrimers exhibited significant resistance to creep at 120°C with various degrees of deformation

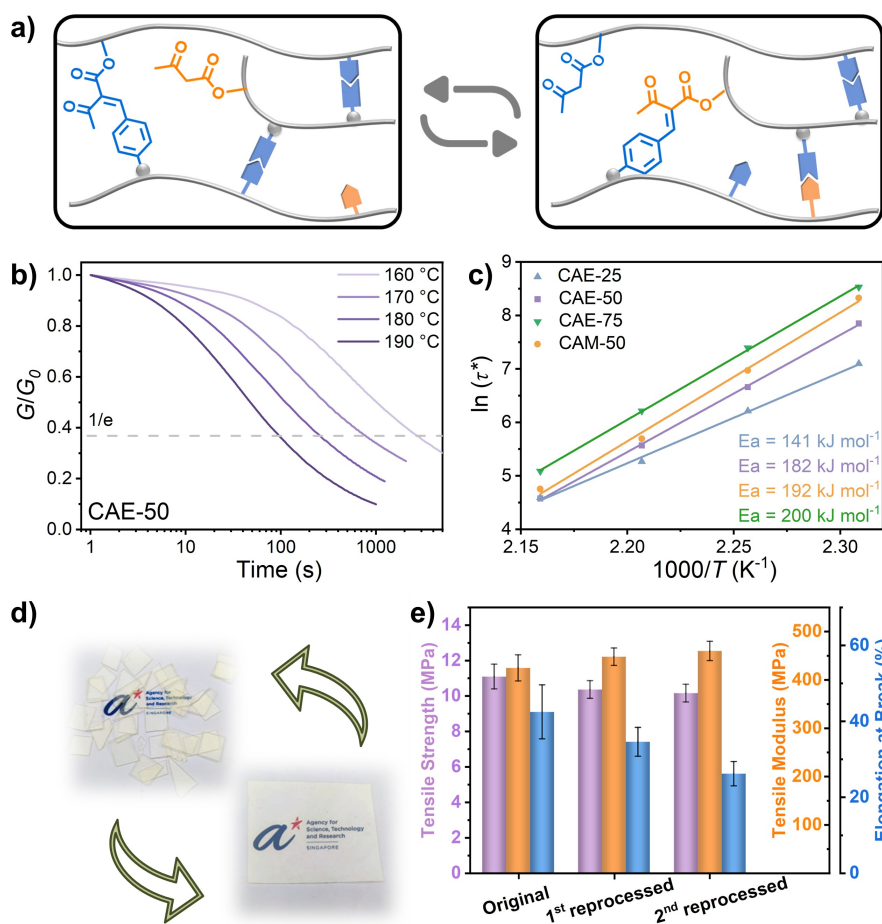


Figure 4. Reprocessability of α -AC/A vitrimers. (a) Schematic representation of the topological network rearrangement in the presence of free cyanoacetate via α -AC/A exchange; (b) Normalized stress relaxation curves of CAE-50 at different temperatures; (c) Arrhenius plots and the linear fitting of α -AC/A vitrimers; (d) Schematic diagram of the hot-press reprocessing for CAE-50 at 180 °C for 30 min; (e) Mechanical properties of CAE-50 after two cycles of hot-press reprocessing.

becoming apparent with further increases in temperature (Figures 5, S27 and S28). Upon external loading at 140 °C and 160 °C, increased creep was observed. The significant viscoelastic response is attributed to the triggered dynamic exchange reactions of the α -AC/A motif at elevated temperature, facilitating the topological rearrangement of the cross-linked networks. At lower temperatures, the exchange reactions are inferior and even frozen, and therefore the stiff networks behave like classic thermosets. Moreover, CAE-25 with reduced cross-link density also demonstrates an ability to suppress creep below 120 °C (Figure 5), further indicating that the intrinsic α -AC/A dynamic exchange is crucial to achieve this creep resistance.

Until now, several robust chemistry platforms, such as acetal bond,^[2h] S,O-thioacetal bond,^[18] transalkylation reaction,^[19] have been developed to create vitrimers with excellent dimensional stability. Compared with these well-established systems (Table S6), the α -AC/A vitrimers show superiority in an excellent combination of high T_v , and E_a . This synergy results in a desired temperature transition window between stability and reprocessability, enhancing the sustainability and durability of the materials.

In conclusion, we report a α -AC/A exchange reaction and its application to the development of vitrimers with remarkable creep resistance. Our small molecule investigations revealed an interesting mechanism for α -AC/A exchange reaction, where the carbanion intermediate species, resulting from acetoacetates, undergoes nucleophilic attack on the α -AC compounds, leading to subsequent exchange reactions through an associative mechanism. Furthermore, we discovered that the stability of these carbanion intermediate species is closely related to the reaction environment. In bulk, the formation of these carbanion intermediates requires higher temperatures, thus enabling the exchange reactions to occur predominantly at elevated temperatures while remaining stable at lower temperatures. This distinctive property holds significant promise for the development of high creep-resistant vitrimers. The designed networks are reprocessable but were shown not to creep under prolonged exposure below 120 °C due to their high E_a and T_v . We believe that the presented α -AC/A exchange and corresponding vitrimers represent a significant advance in the field of polymeric materials, in the light of the creep vs recycling of thermosets.

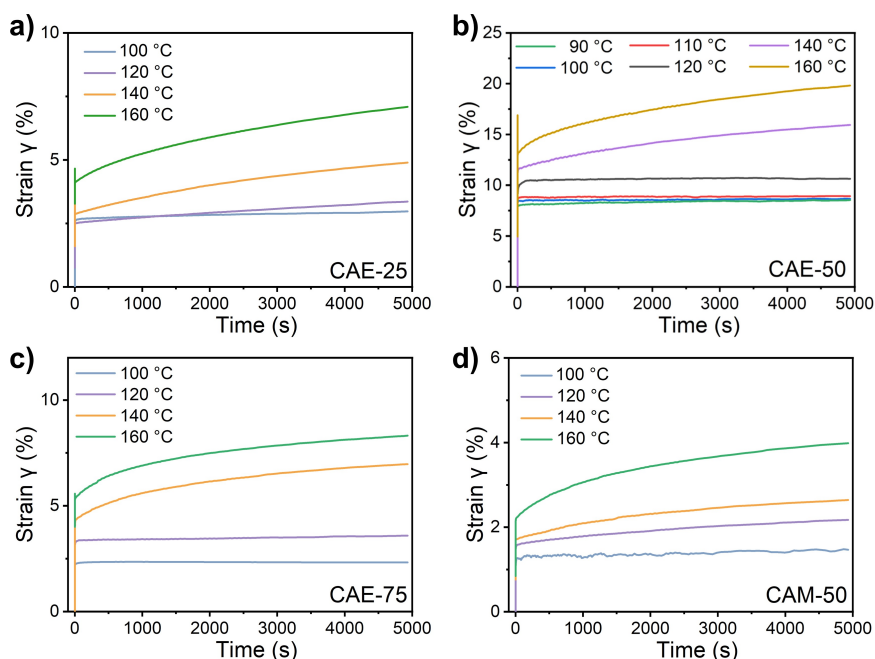


Figure 5. Creep behavior of α -AC/A vitrimers. Creep curves of (a) CAE-25, (b) CAE-50, (c) CAE-75 and (d) CAM-50 at different temperatures under a stress of 2 kPa tested by rheology.

Supporting Information

The authors have cited additional references within the Supporting Information.^[20–47]

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Vitrimers · α -acetyl cinnamate/acetooacetate dynamic covalent chemistry · Creep resistance · Sustainability · Plastic recycling

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