Recyclable, degradable and high-performance citric acid-based vitrimers using vinylogous urethane chemistry

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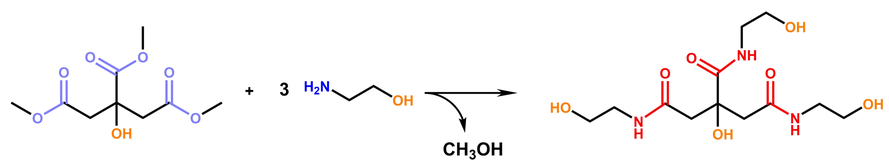
Introduction

Citric acid is a widely distributed biobased monomer, and its polyfunctionality makes its derivatives a potential choice as crosslinker for thermosets. The utilization of bio-based precursors to prepare polymers is very beneficial for environmental protection and sustainable development. However, thermosets usually lack reprocessability and recyclability due to their permanent chemical cross-linking. To achieve sustainable recycling, design and modification of citric acid as a precursor for vitrimer is a promising strategy. In this work, we synthesized a new cross-linker that incorporated acetoacetate groups onto citric acid and performed the synthesis and evaluation of citric acid-based vitrimers. A series of bio-based vitrimers with different dynamic bond contents were prepared by adjusting the ratio of the reactants and their properties were characterized. The process adopted melt polymerization without additional catalyst, which was green and environmentally friendly and avoided the problem of catalyst escape or decomposition during reprocessing. The incorporation of the amide segment enhanced the mechanical properties and the thermal stability, whereas vinyl urethane bonds provided reprocessability, degradability, and self-healing capabilities. At the same time, it was physically and chemically recycled and showed excellent stability in terms of chemical structure and physical properties. Chemical recycling by acid-catalyzed degradation also provides a route for monomer recovery.

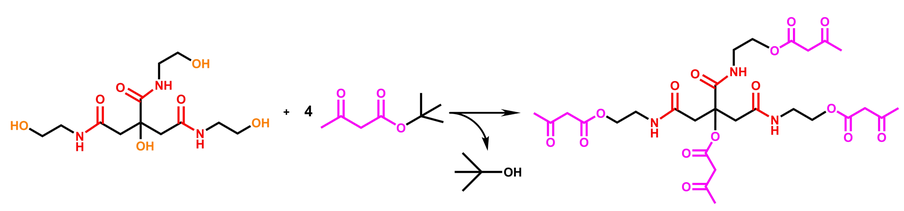
Experimental Section

Preparation of VUCAs

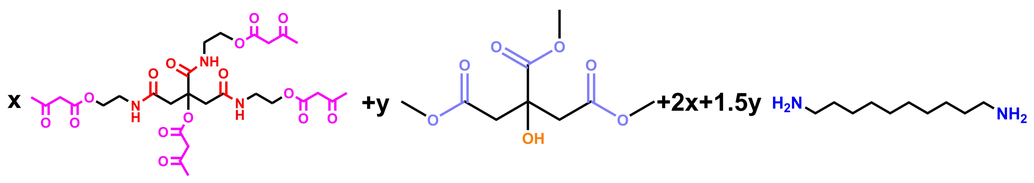
1. Synthesis of QHTA



2. Synthesis of QAATA



3. Synthesis of VUCAs

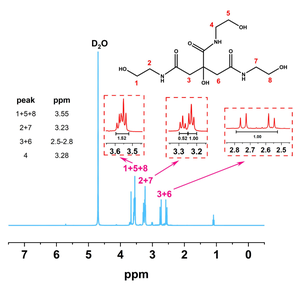


	x	y	2x+1.5y
VUCA-1	0.5	1	2.5
VUCA-2	1	1	3.5
VUCA-3	1.5	2/3	4
VUCA-4	1	0	2

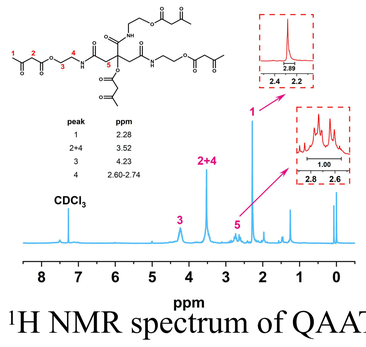
Characterizations

^{1}H NMR, Fourier transform infrared (FT-IR) spectroscopy, differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), tensile testing, gel content (GC) test, swelling ratio (SR) test, stress-relaxation test, degradation and reprocessing tests were conducted.

Result and Discussion



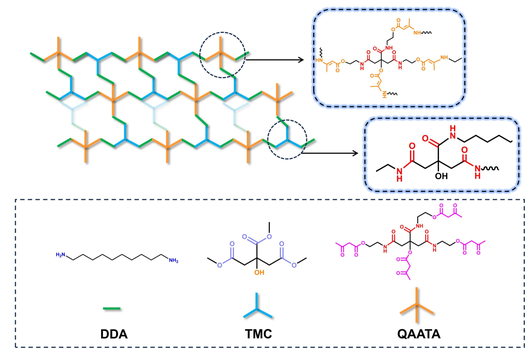
^{1}H NMR spectrum of QHTA



^{1}H NMR spectrum of QAATA

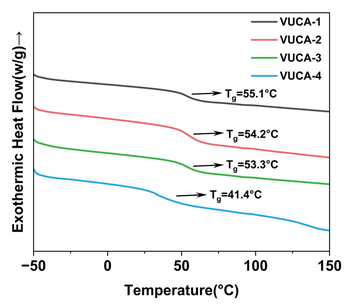
The above characterization results confirm that the monomer has been successfully synthesized.

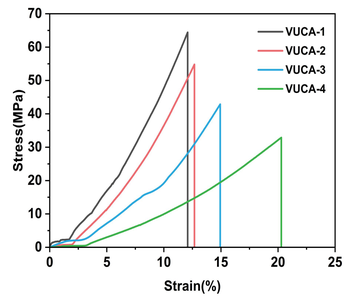
Synthesis and characteristics of VUCAs



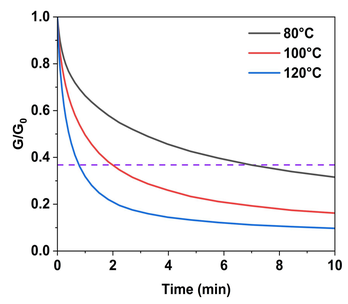
Schematic diagram of VUCAs network structure

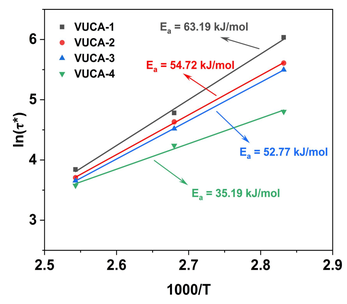
By adjusting the ratio of the three components, a series of citric acid-based vitrimers were prepared by a facile one-pot method. Among these, the amount of amino groups was in excess by 5%. Although excessive amino groups can lead to a decrease in crosslinking density, which was crucial for the dynamic exchange of vinylogous urethane bonds and the rearrangement of the crosslinked networks.



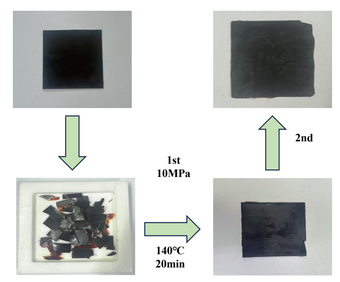


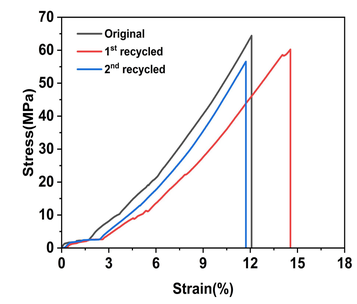
The second heating DSC curves were presented in Figure 3b. The glass transition temperature (Tg) of VUCAs were 41.4 to 55.1 °C, displaying an upward trend with the increase content of TMC. VUCAs displayed excellent mechanical property with tensile strength (σb) reaching 64.4MPa, due to the high amide bonds content, which increased hydrogen bond density and enhanced the intermolecular interaction.





The stress relaxation curves of VUCAs exhibited that the modulus of all VUCAs can relax to 1/e at different temperatures due to dynamic VU bonds. It was found that they adhered well to Maxwell model .





The incorporation of dynamic bonds enables vitrimers to possess reprocessability characteristic under specific temperatures, similar to thermoplastic polymers. The mechanical properties of VUCAs remained well after multiple reprocessing cycles.

Conclusions

In summary, a novel tetrafunctional acetoacetate (QAATA) based on citric acid and related citric acid-based vitrimers (VUCAs) with excellent mechanical properties, reprocessability, and degradability were successfully prepared. Amide bonds enhanced the mechanical properties and thermal stability of polymers, while VU bonds conferred reprocessability and degradability.

References

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