# Polystyrene Hybrid-Vitrimer Based on the Hemiacetal Ester Exchange Reaction

David Boucher, Jeppe Madsen, Liyun Yu, Qian Huang, Nicolas Caussé, Nadine Pébère, Vincent Ladmiral, Claire Negrell

## To cite this version:

David Boucher, Jeppe Madsen, Liyun Yu, Qian Huang, Nicolas Caussé, et al.. Polystyrene Hybrid-Vitrimer Based on the Hemiacetal Ester Exchange Reaction. Macromolecules, 2021, 54 (14), pp.6772-6779. 10.1021/acs.macromol.1c00948 . hal-03320319

# Polystyrene hybrid-vitrimer based on hemiacetal ester exchange reaction

David Boucher,[†,‡] Jeppe Madsen,[⊥] Liyun Yu,[⊥] Qian Huang,[⊥] Nicolas Caussé,[‡] Nadine Pébère,[‡]
Vincent Ladmiral,[†*] and Claire Negrell[†]

[†] ICGM, Univ Montpellier, ENSCM, CNRS, Montpellier, France.

[‡] CIRIMAT UMR 5085-CNRS, UT, INPT, UPS, ENSIACET, 4 allée Emile Monso, CS 44362, 31030 Toulouse.

[⊥] Danish Polymer Centre, Department of Chemical and Biochemical Engineering, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark.

*KEYWORDS (Word Style "BG_Keywords"). If you are submitting your paper to a journal that requires keywords, provide significant keywords to aid the reader in literature retrieval.*

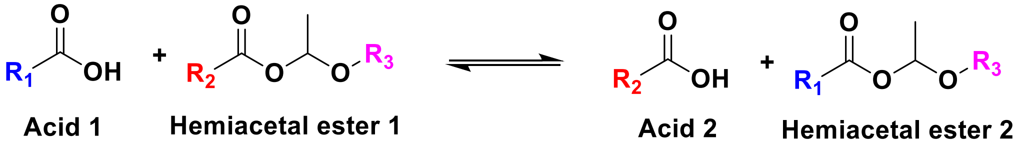
---

**ABSTRACT:** Vitrimer materials, which are permanently cross-linked but reshapable polymers, are a class of materials of growing interest due to their potential in recycling and sustainable development. More precisely, vitrimers derived from commodity polymers could have a drastic impact on plastic consumption in the upcoming years. Here, the development of a polystyrene-based vitrimer harnessing the recently discovered hemiacetal ester exchange reaction of carboxylic acid is presented. 1,4-cyclohexanedimethanol divinyl ether was reacted with 4-vinylbenzoic acid to form a divinyl species containing two hemiacetal ester functions. This dimer was then copolymerized with styrene, butyl acrylate and 4-vinylbenzoic acid to form a cross-linked material presenting pendent acid groups. This material exhibited three distinct behaviors at different temperature regimes: below 80 °C, despite the ability of exchange reactions to occur, the cross-linked material behaved as a frozen material due to hydrogen bonding formed by carboxylic acid pendent groups. Between 80 °C and 130 °C vitrimer behavior was demonstrated by rheological creep experiments. At higher temperature, the dissociation of the hemiacetal ester groups led to the loss of the covalent cross-linking.

---

## Introduction

Vitrimers constitute a very interesting class of materials, since their inception in 2011 by Leibler's group[1] as reprocessable, permanently cross-linked materials. This feat was made possible by the integration of associative exchange reactions in the matrix, namely catalyzed transesterification reactions. These associative exchanges allowed the reorganization of covalent bonds under thermal treatment. Such materials differ from most dissociative covalent adaptable networks, where exchange reactions occur through the dissociation-reformation of covalent bonds, because vitrimers possess a rheological behavior similar to that of glass (evolution of the relaxation time, or of zero-shear viscosity, with temperature following an Arrhenius equation), indicating a conservation of the amount of cross-link nodes during reshaping.[1] Due to this ability to be reshaped without breaking the crosslinks, and thus keeping their mechanical properties, a high potential for sustainable economy (by recycling of cross-linked material) was attributed to these materials. Since this first proof of concept, vitrimers based on a wide range of exchange reactions have been reported.[2–4] The search for new vitrimer materials led to the classification of numerous systems as vitrimers only based on the fact that the evolution of their relaxation time, or zero-shear viscosity, with temperature followed an Arrhenius equation.[2,4] However, it was recently demonstrated that some dissociative covalent adaptable networks may also be described by an Arrhenius equation.[4,5] This behavior is attributed to a faster formation than dissociation of the covalent bonds in a temperature range, leading to a quasi-constant cross-link density.[5,6] In addition *Breuillac et al.*[7] demonstrated that a vitrimer with few cross-links can show solubility in good solvents at temperatures where the exchange reactions take place sufficiently fast. This additional understanding of dissociative covalent adaptable networks and vitrimer behavior indicates that determination of solubility[7,8] or rheological behavior[4] is not sufficient to classify a novel material as a vitrimer.[9] In the present article, a vitrimer is thus considered as a cross-linked system where reprocessability and glass-like rheological behavior are brought by associative exchange reactions. Vitrimer properties can also be sometimes combined with other properties that affect the material flow, such as reversible physical interactions. In this case, the material is defined as hybrid-vitrimer.[3]



Scheme 1. Hemiacetal ester exchange

Due to the sometimes low compatibility of catalysts with the matrix[3,10] and potential negative environmental impact,[10] significant effort has been devoted to developing catalyst-free vitrimer materials.[3,5] Another, and more recent, research trend is the development of vitrimers from commodity plastics.[5] This path was first explored by *Leibler's* group[11,12] with the development of polyethylene, poly(methyl methacrylate) and polystyrene vitrimers based on dioxaborolane metathesis. These systems were prepared in two steps: first the synthesis of linear chains with pendent dioxaborolane functions by Reversible Addition-Fragmentation chain Transfer (RAFT) polymerization and then the resulting linear polymers were cross-linked using bis-dioxaborolane cross-linker. The resulting materials showed, in addition to vitrimer behavior, similar mechanical properties as the commodity plastics used as references and reshaping did not alter their properties. The authors presented the development of such materials as an important step to shift vitrimers from academic research to industrial applications due to the position of commodity plastics in the global annual plastic production (more than 75%).[11] Since this seminal work, other commodity vitrimer materials were developed, such as the silyl ether-based polystyrene vitrimer reported by *Nishimura et al.*[13] and the vinylogous amine polyurethane-based vitrimer materials reported by *Sumerlin et al.*[14,15] The development of different chemistries able to induce vitrimer properties in a material affords more control over specific parameters such as the flow activation energy, the viscosity and the temperature at which the material can be reshaped.[3]

Here, the development of a polystyrene-based vitrimer using for the first time the hemiacetal ester exchange (Scheme 1) is presented. Hemiacetal esters were recently shown to undergo associative acid exchange at room temperature without the need for any catalyst.[16] They also possess a dissociation temperature, $T_{dis}$ (depending on their structure), above which the hemiacetal ester function dissociates.[17–19] A material based on this exchange chemistry is therefore expected to present two behaviors depending on the temperature range: below$T_{dis}$, associative exchanges would occur and lead to vitrimer behavior, whereas above $T_{dis}$ the dissociation of the cross-links should lead to the loss of the material's vitrimeric properties. Here, a poly(styrene-*co*-vinylbenzoic-acid-*co*-butylacrylate) copolymer cross-linked using a difunctional hemiacetal esters cross-linker was synthesized. Its rheological profile with temperature was examined and compared with three reference materials of similar composition but either without pendent acid groups, without crosslinks or without hemiacetal ester groups. Particular attention was given to $T_{dis}$ in order to characterize the rheological behavior of the material in its cross-linked state.

## Experimental section

### Materials

Dichloromethane (DCM), tetrahydrofuran (THF), diethyl ether, 3Å molecular sieves, n-butyl acrylate (99 %), styrene (99 %), 1-4 cyclohexanedimethanol divinyl ether (mixture of isomers 98 %)(CDDVE), butylvinyl ether (98 %), cyano-2-propyldodecyl trithiocarbonate (97 %), trifluoroacetic acid (99 %), magnesium sulfate, basic alumina and deuterated chloroform were purchased from Sigma-Aldrich. 4-Vinylbenzoic acid (VBA) (97 %) and n-dodecyl dihydrogen phosphate (90 %) were purchased from TCI Europe and Abcr GmbH, respectively.

Polymerization inhibitors contained in styrene and butyl acrylate were removed using a column of basic alumina.

### Polymer synthesis

Drying of the materials

300 mg of 4-vinyl benzoic acid was dissolved in 50 ml of DCM and the solution was dried on $MgSO_4$ for 30 minutes before filtration. The filtrate was then kept in the presence of 3Å molecular sieves and under nitrogen for 1 h before evaporation of DCM under vacuum. The resulting solid 4-vinyl benzoic acid was then used immediately. Water traces contained in styrene and n-butyl acrylate were removed using 3Å molecular sieves under inert atmosphere. n-Dodecyl dihydrogen phosphate (200 mg; 7 $10^{-4}$ mol) was dissolved into styrene (5.0 g; 4.8 $10^{-2}$ mol) and kept in the presence of 3Å molecular sieves and under nitrogen for 1 h before use. THF was dried using first $MgSO_4$ followed by storage in the presence of 3Å molecular sieves under nitrogen.

Synthesis of the cross-linked material with pendent acid groups (CMA)

180 mg (1.2 $10^{-3}$ mol) of 4-vinylbenzoic acid, 53 mg (2.7 $10^{-4}$ mol) of 1,4-cyclohexanedimethanol divinyl ether, along with 1040 mg of the n-dodecyl dihydrogen phosphate/styrene solution [i. e. approximately 40 mg (1.4 $10^{-4}$ mol) of n-dodecyl dihydrogen phosphate and 1.0 g (9.6 $10^{-3}$ mol) of styrene] and 2.1 mg (6.1 $10^{-6}$ mol) of cyano-2-propyldodecyl trithiocarbonate, were placed in a 10 ml glass flask, dried at 130 °C in an oven for at least 5 minutes and closed with a septum. The resulting solution was purged with nitrogen for 10 minutes before being stirred for 15 h at 25 °C to convert the vinyl ether functions into hemiacetal esters. After 15 h, the conversion of VBA into hemiacetal ester was monitored using $^1$H NMR in deuterated chloroform. 600 mg (4.7 $10^{-3}$ mol) of n-butyl acrylate were then added to the main solution and the RAFT polymerization was initiated by heating the solution to 100 °C. After 21 h, the glass flask was cooled down to room temperature for 1 h and then broken to recover the solid material. Residual monomers and catalyst were then extracted by successive immersion of the material in anhydrous DCM (around four times the material volume), one time overnight and twice for 2 h. After a drying step of 4 h at 100 °C in a vacuum oven the resulting material was a transparent colorless solid.

Synthesis of the cross-linked reference (CR)

This material was prepared using the protocol used for the synthesis of the CMA with some modifications. Briefly, 180 mg (1.2 $10^{-3}$ mol) of 4-vinylbenzoic acid, 106 mg (5.4 $10^{-4}$ mol) of 1,4-cyclohexanedimethanol divinyl ether, along with 1040 mg of the n-dodecyl dihydrogen phosphate/styrene solution [i. e. approximately 40 mg (1.4 $10^{-4}$ mol) of n-dodecyl dihydrogen phosphate and 1.0 g (9.6 $10^{-3}$ mol) of styrene] and 3.8 mg (1.1 $10^{-5}$ mol) of cyano-2-propyldodecyl trithiocarbonate were mixed in a 10 ml glass flask, dried at 130 °C in an oven for at least 5 minutes and closed with a septum. After 15 h of mixing, at 25 °C 70 mg (3.36 $10^{-4}$ mol) of 1,4-cyclohexanedimethanol divinyl ether and 600 mg (4.7 $10^{-3}$ mol) of n-butyl acrylate were added to the reaction medium and the resulting solution was mixed for 6 additional h. The RAFT polymerization was then carried out at 100 °C for 21 h and the materials was recovered following the protocol described above for CMA. The CR material was again a transparent colorless solid.

Synthesis of the non-cross-linked reference (NR)

This material was prepared using the protocol used for the synthesis of the CMA with some changes to reagents and their amounts, as well as some modifications of the extraction protocol. Briefly, 180 mg (1.2 $10^{-3}$ mol) of 4-vinylbenzoic acid were mixed with 200 mg (2 $10^{-3}$ mol) of butylvinyl ether, 1040 mg of the n-dodecyl dihydrogen phosphate/styrene solution [i. e. approximately 40 mg (1.4 $10^{-4}$ mol) of n-dodecyl dihydrogen phosphate and 1.0 g (9.6 $10^{-3}$ mol) of styrene], 600 mg (4.7 $10^{-3}$ mol) of n-butyl acrylate, and 3.8 mg (1.1 $10^{-5}$ mol) of cyano-2-propyldodecyl trithiocarbonate. Residual monomers and catalyst were then extracted by immersion of the material in diethyl ether, in which the material was not soluble. After a drying step of 4 h at 100 °C in a vacuum oven the recovered material was again a transparent and uncolored solid.

Synthesis of the acid dissociated reference (AR)

300 mg of the CMA were immersed in 100 ml of THF containing 4 ml of trifluoracetic acid. This reaction mixture was then stirred for 24h at ambient temperature (ca. 25 °C). After 24h, the THF was evaporated under vacuum and the material was purified by extraction with diethyl ether as NR. After a drying step of 4 hours at 100 °C in a vacuum oven the recovered material was again a transparent colorless solid.

Formation of disk samples for rheology experiments

Disk samples (8 mm in diameter and about 1.5 mm in thickness) were obtained by molding 40 mg of material under a pressure of 16.2 N/cm$^2$, and at a temperature of 90 °C, for 1.5 h.

## Characterization

NMR analyses

$^1$H NMR analyses were performed using a 300 MHz Bruker spectrometer. The acquisition parameters were as follows : Pulse angle : 90°, acquisition time : 4 seconds, relaxation delay : 1 second and scan number : 16, temperature : 20 °C. Chemical displacement are reported in part per millions (ppm) relative to tetramethylsilane. All samples were prepared in deuterated chloroform.

In the case of CR and NR samples, 40 µl of trifluoroacetic acid (TFA) was added to the NMR tube and the mixture was agitated for 24h to ensure complete substitution of the hemiacetal ester functions by TFA.

Gel permeation chromatography analyses

GPC analyses were performed using a Viscotek VE 2001 GPC instrument equipped with a refraction index detection Viscotek Model 302 and two PL gel mixed-D columns. All analyses were achieved using THF as eluent with a 1 ml/min rate flow. The instrument was calibrated with narrow polystyrene standards.

GPC sample preparation: Prior to analysis, 2 mg of copolymer was dissolved in 1 ml of THF containing 40 µl of TFA, except for AR where the absence of crosslinks and pendent acid groups made the addition of TFA unnecessary.

Differential scanning calorimetry analyses

DSC analyses were performed on a Discovery DSC apparatus from TA instruments. The temperature program scanned the 20 - 100 °C range with a 10 °C/min ramp in a nitrogen atmosphere.

Thermogravimetry coupled with mass spectrometry analyses

TGA-MS experiments were performed using a Discovery TGA apparatus coupled with a Discovery MS instrument also from TA instruments. After an isotherm of 60 min at 100 °C aimed to evaporate all residual solvent and water, a temperature ramp of 10 °C/min was applied from 100 to 350 °C in an air atmosphere.

Isothermal thermogravimetry analyses

Isothermal TGA experiment were performed using a Discovery TGA apparatus from TA instruments. A heating ramp of 10 °C/min was applied to reach the temperature of the first isotherm. Then each isotherm was maintained for 5 h and a heating ramp of 2 °C/min was applied between each of the isotherms. These experiments were performed under air atmosphere.

Creep experiments

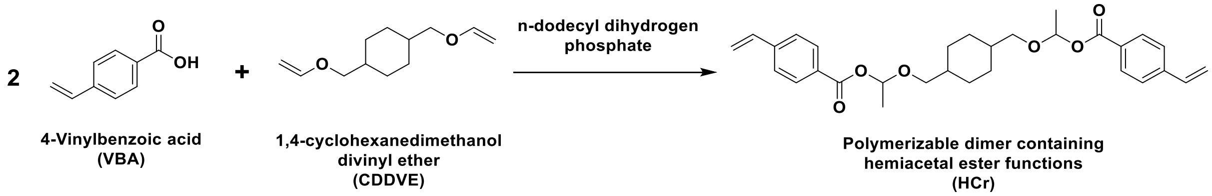
Creep experiments were performed using an Ares G2 rheometer from TA instruments, equipped with an 8 mm parallel plate measuring system. The experiments proceeded by successive measurements every 10 °C from 80 to 130 °C under nitrogen. Before every measurement, the temperature was allowed to stabilize for 5 min. The strain was monitored by applying a stress of 2 kPa during 600 s, and then the stress was removed.

## Results and discussion

### Polymer syntheses

The poly(styrene-*co*-vinylbenzoic acid-*co*-butylacrylate) copolymer cross-linked via hemiacetal linkage was synthesized using a two-step one-pot procedure. The first step consisted in the synthesis of the cross-linker containing two hemiacetal ester functions and two vinyl functions (HCr). This dimer was prepared by reacting 1,4-cyclohexanedimethanol divinyl ether (CDDVE) with 4-vinylbenzoic acid (VBA) in the presence of n-dodecyl dihydrogen phosphate as catalyst (Scheme 2) directly in the polymerization mixture. In the case of the vitrimer candidate (CMA), the aim was to convert 53% of VBA into cross-linker to keep carboxylic acid groups available for the exchange reaction. This conversion was monitored by $^1$H NMR (Figure S1) by comparing the signals of the hemiacetal ester and of the divinyl ether (CDDVE) (Equation S1). A conversion of 87 % of the vinyl ether functions was reached, the remaining 13% corresponding to a side reaction with water leading to the formation of alcohol and acetal (Figure S1 and S2),[20–22] indicating a functionalization of around 46 % of the initial VBA amount. The second step was the RAFT copolymerization (see Table S1) of styrene, n-butyl acrylate and VBA in the presence of HCr. The polymerization was promoted by self-initiation of styrene[23] at 100 °C and controlled using cyano-2-propyldodecyl trithiocarbonate as the RAFT chain transfer agent (CTA). This copolymer, cross-linked by hemiacetal ester linkage and comprising available carboxylic acid functions able to engage in hemiacetal ester exchange reaction, is called "cross-linked material with acid pendent groups" (CMA, Figure 1, CMA). This material was expected to behave like a vitrimer.

In addition to CMA, three other copolymers were also synthesized as reference materials: 1) A cross-linked copolymer (CR, Figure 1, CR) prepared by copolymerization of styrene and n-butyl acrylate in the presence of HCr. For this material, the functionalization of the VBA into hemiacetal esters proceeded with a small excess of divinyl ether to ensure that all acid functions were converted into hemiacetal esters. A small proportion of mono-functional hemiacetal ester derivative of VBA was also likely produced under the conditions used. However, the presence of this monofunctional VBA did not impair its use as a fully cross-linked material devoid of any available carboxylic acid groups. The amount of CDDVE involved in HCr was estimated to represent between 6 and 12 wt% of the total mass of CR, with 6 wt% corresponding to the case where no mono-functional derivative of VBA was produced, and 12 wt% corresponding to the case where only mono-functional derivative was produced. 2) A non-cross-linked copolymer prepared by copolymerization of styrene, n-butyl acrylate, and a monofunctional hemiacetal ester derivative of VBA. This copolymer designated as non-cross-linked reference (NR, Figure 1, NR) possessed neither cross-links nor carboxylic acid functions. 3) A copolymer that only presented carboxylic acid functions prepared by treating CMA with excess trifluoroacetic acid (able to fully substitute the hemiacetal ester linkages) thus generating the acid-dissociated reference (AR, Figure 1, AR).



Scheme 2. Preparation of dihemiacetal ester cross-linker (HCr).

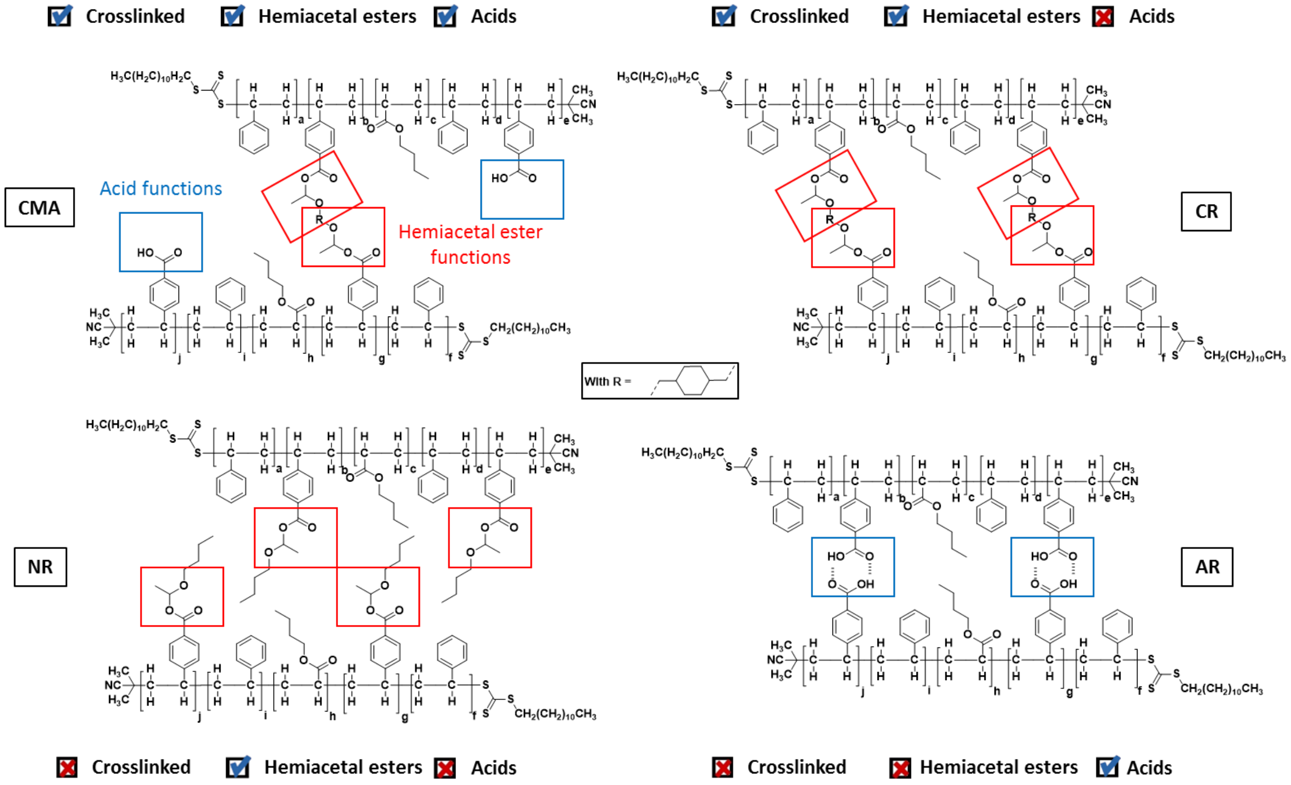


Figure 1. Schematic and ideal representation of CMA, CR, NR and AR.

The copolymers were characterized by ¹H NMR and gel permeation chromatography (GPC). Prior to these analyses, all the hemiacetal ester linkages were cleaved by substitution with TFA (except for AR which does not contain any hemiacetal ester functions). The ¹H NMR spectra of AR, and of the TFA-treated CR and NR are shown in Figure S3, Figure S4 and Figure S5, respectively (note that AR is the purified product resulting from the treatment of CMA with TFA). The compositions of the copolymers were calculated using Equation S2, Equation S3 and Equation S4, and are reported in Table S1 along with the molar masses measured by GPC. The GPC chromatograms of the copolymers are presented in Figure S6.

¹H NMR analyses indicated molar fractions ranging from 6 to 7.5 %, from 64 to 68 % and from 26 to 28 % for vinyl benzoic acid, styrene and n-butyl acrylate respectively for the various copolymers. Table S1 indicates relatively low dispersities of the CMA and NR polymers (1.3 and 1.2 respectively). The higher value (Đ = 1.55) measured for CR is probably due to incomplete cleavage of the hemiacetal ester bonds. These GPC analyses thus suggest a fairly good control of the RAFT terpolymerization process. This is remarkable given the high monomer to CTA ratios used for these syntheses (ranging between 1400/1 and 2500/1).

Importantly, assuming similar reactivity for VBA and for HCr, these results show that each of the CMA chains should contain around 1.8 mol % of cross-linker. CMA thus features a fairly low cross-linking density.

### Thermal characterization

All copolymers were analyzed by differential scanning calorimetry (DSC) and thermogravimetry coupled with mass spectrometry (TGA-MS) to determine their glass transition temperature ($T_g$), as well as $T_{dis}$. The DSC thermograms are presented in Figure 2.

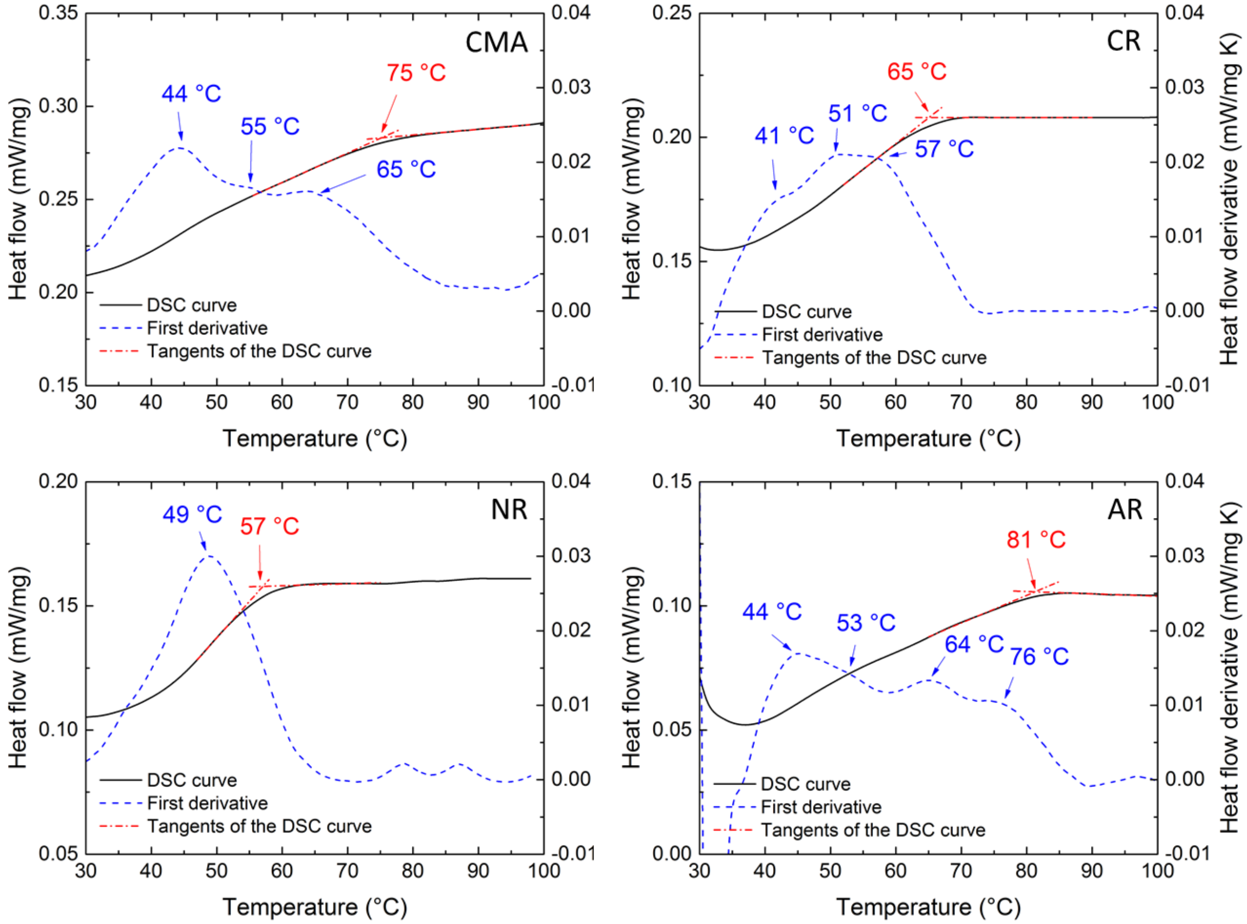


Figure 2. DSC thermograms and their derivatives for CMA, CR, NR and AR.

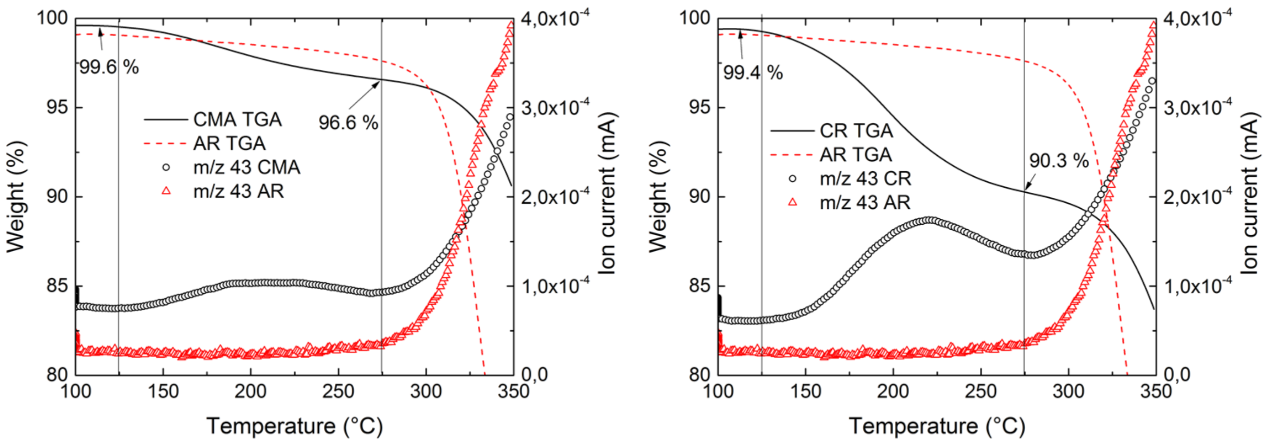


Figure 3. Comparison of the TGA-MS results of CMA compared to AR, and of CR compared to AR. A temperature ramp of 10 °C/min was used in both cases.

The DSC derivative of NR (Figure 2), that does not contain cross-links or acid functions, present one major peak at 49 °C which was attributed to its $T_g$. This is consistent with the $T_g$ calculated (45 °C) from the composition determined by NMR using Fox equation (Equation S5). However, the DSC derivatives of CR, CMA, and AR (Figure 2) present several peaks which made the determination of a unique $T_g$ impossible. The samples were therefore compared using the end of the transition phenomenon, determined by the tangents method. Although the transition upon heating seems to start at a lower temperature of around 35 °C for all samples, the upper temperature varies from one sample to the other. Thus, the upper temperature is 57 °C for NR and 65 °C for CR. This slight broadening of the transition phenomenon is ascribed to the low cross-link density of CR (amount of HCr in the structure estimated between 2 and 4 mol%), which decreases the mobility of the system at a given temperature. AR is the sample for which the broadening of the transition phenomenon is the most pronounced (end of phenomenon = 81 °C). This was attributed to the presence of numerous acid functions capable of forming a hydrogen-bonded network.[24–26] Finally, in the case of CMA (end of phenomenon = 75 °C) the broadening lies between those of CR and AR. This was ascribed to the lower amount of acid functions in CMA compared to AR.

The dissociation temperature of the hemiacetal ester function (temperature at which the hemiacetal ester function dissociate) was determined from TGA-MS experiments performed on CMA, CR and AR (Figure 3). These experiments indicated that while AR did not show significant mass loss below 300 °C, CMA and CR did show a distinct mass loss between 125 and 275 °C. Importantly, this mass loss was different for the two materials; CMA lost 3 % of its initial mass, which corresponds to the mass fraction of linked CDDVE in CMA. In comparison, CR, which contains between 6 and 12 wt% of CDDVE, lost around 9 % of its initial mass. These mass losses were thus ascribed to the evaporation of vinyl ether, which was confirmed by the analysis of the exhausted gas by mass spectrometry. As shown in Figure 3, between 125 and 275 °C, a compound with m/z = 43 was observed for CMA and CR but not for AR. This m/z value corresponds to acetaldehyde, which is a typical product of the thermal degradation of vinyl ethers.[22,27,28] In addition, this mass loss appeared at temperatures higher than the evaporation temperature of CDDVE (Figure S8 and Figure S9) further confirming that the mass losses observed for CMA and CR were resulting from the dissociation of hemiacetal ester functions.

The feasibility of the characterization of the materials by rheology experiments at elevated temperature without significant degradation was checked by isothermal thermogravimetric analyses of CMA (Figure S10). These experiments (Table S2) showed that the relative loss at 140°C represented less than 17 % of the initial CDDVE in 5 h, or approximately 3.5 % per hour. The rheology experiments carried out under nitrogen atmosphere and at different temperatures did not last more than 15 min. The thermal degradation of CMA during these rheological characterizations was thus negligible.

## Vitrimer behavior demonstration

8 mm diameter disks of the copolymer materials were prepared in a mold at 90 °C for 1.5 h prior to rheology experiment. The formation of such a disk from CMA is illustrated in Figure 4. In contrast, this shaping step was impossible for CR at 90 °C. For CR, the shaping process required extended exposure to high temperatures (5 h at 150 °C), at which the hemiacetal ester functions dissociate. This was expected since CR is fully cross-linked and does not possess any carboxylic acid groups able to engage into exchange reactions with hemiacetal ester. Since CR could not be shaped without thermal degradation, no further characterization was performed on this material.

To demonstrate unambiguously the vitrimer behavior of CMA, creep experiments of CMA, NR and AR were performed every 10 °C between 80 °C and 130 °C.

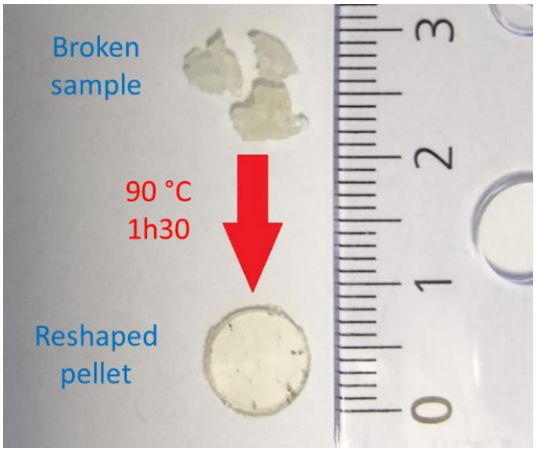


Figure 4. Shaping of CMA into a disk sample by heating at 90 °C, under a pressure of 16.2 N/cm$^2$, for 1.5 h.

The results from the creep experiments, presented in Figure 5, show that in contrast to NR, neither AR nor CMA showed any strain at 80 °C and a 2KPa stress. These results can be linked to previous DSC results that showed broadening of the transition phenomenon at around 80 °C for AR and CMA. As AR does not present any covalent cross-links, this absence of strain and the broadening of the transition penomenon oberved in DSC were ascribed to the hydrogen bonding generated by the carboxylic acid groups.[24] Hydrogen bonds have already been exploited to prevent the movement of polymer chains at temperatures where exchange reactions can occur in so-called hybrid-vitrimer materials.[3,29] Above 80 °C, viscoelastic deformation was observed in the first few seconds of the experiment. This deformation was recovered when stress was released. Then, plastic deformation was observed. The plastic deformation of CMA indicates that the material can flow even though the material is cross-linked. This phenomenon was attributed to the ability of the hemiacetal ester cross-links to undergo exchange reactions with the carboxylic acid groups. Between 90 and 110 °C, the influence of temperature onto the plastic deformation was lower for CMA than for AR. However, at 130 °C, the plastic deformation of CMA was similar to that of AR. This was attributed to the acceleration of the exchanges with increasing temperature, which were not anymore the limiting factor of the plastic deformation at 130 °C.

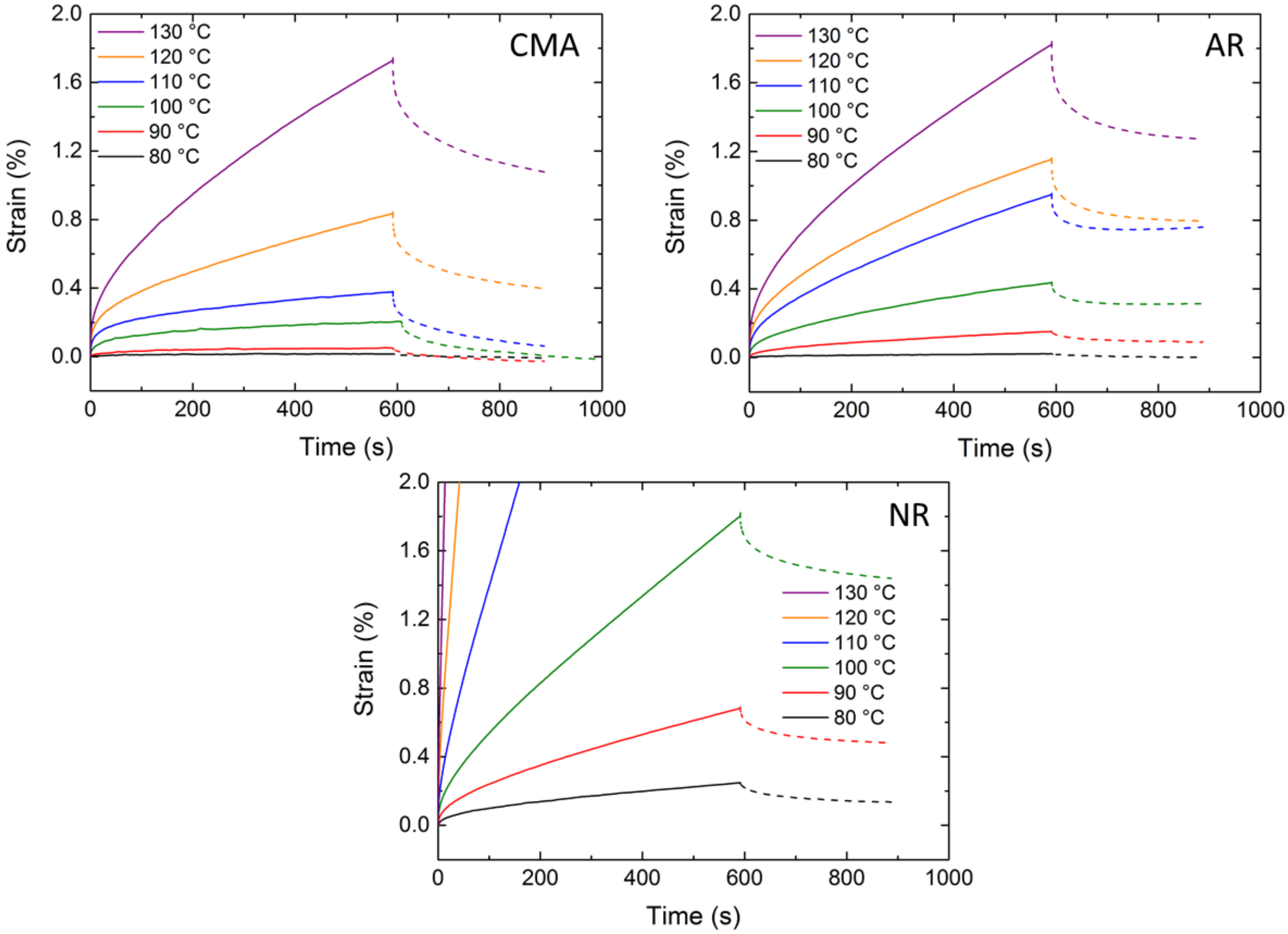


Figure 5. Strain curves obtained from creep experiments between 80 and 130 °C for CMA, AR and NR. Plain curves represent strain when a stress of 2 kPa was applied while dashed curves represent strain when the stress was released.

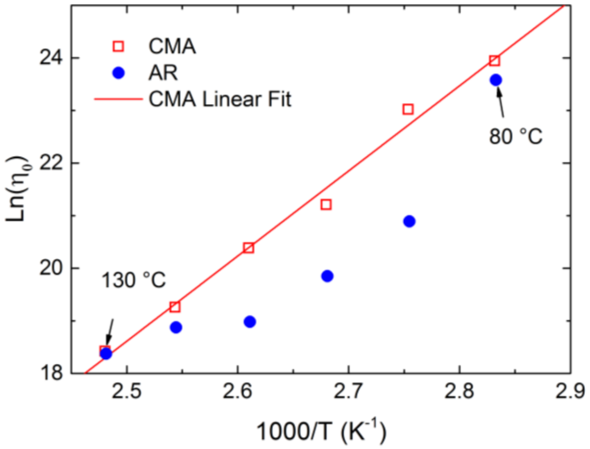


Figure 6. Variation of zero shear viscosity (ηo) as function of temperature for CMA and AR.

From CMA and AR data, compliance curves were also plotted (Figure S11 and Figure S12, respectively) and the zero shear viscosities were determined from linear fittings of the parts corresponding to plastic deformation ($J(t) = t/\eta_0$). The determined zero shear viscosities are presented in the Arrhenius plots in Figure 6.

Figure 6 clearly shows a linear evolution of viscosity ($R^2 = 0.99$) for CMA. On the contrary, the evolution of the viscosity of AR was far from linear (Figure 6). This difference indicates that, contrary to AR, CMA behave as a vitrimer and that the evolution of its viscosity is governed by associative hemiacetal ester exchange reaction. The slope of the linear fit, which corresponds to the flow activation energy of the material, was 16.2 ± 0.8 kJ mol$^{-1}$. This value is low compared to values between 60 and 150 kJ mol$^{-1}$ reported in other studies of vitrimer materials.[3,10,11,30] This relatively low flow activation energy can in part be explained by the low cross-link density[3] and the excess of carboxylic acid functions compared to the hemiacetal ester linkages which promote the exchange reaction.[10,31] The low value is also likely related to the fact that these acid exchange reactions can take place at ambient temperature at a significant rate as showed in a previous publication.[16] This would imply a low activation energy of the exchange reaction itself (not measured), which would in turn favor viscous flow.[5] In addition, the presence of two hemiacetal ester groups per cross-link is likely to further increase the probability of encounter between carboxylic acid group and hemiacetal ester function.

## Conclusion

The aim of this paper was to study the feasibility of synthesizing a vitrimer based on the recently reported hemiacetal ester exchange reaction. The material was prepared by copolymerizing a cross-linker containing two hemiacetal ester functions, with styrene, vinyl benzoic acid and n-butyl acrylate. The synthesis of the cross-linker and the copolymerization were performed using an easy and efficient, solvent-free two-step one-pot procedure. The properties of this material were then compared with materials that did not possess carboxylic acid groups able to participate into exchange reactions with hemiacetal ester, and with non-cross-linked materials. Although model hemiacetal ester exchange reactions were previously shown to occur at ambient temperature in solution,[16] rheological experiments demonstrated that the vitrimer candidate material did not present any strain at and below 80 °C, likely due to hydrogen bonding formed by the pendent carboxylic acid groups. In contrast, at 90 °C and above the material presented typical vitrimer flow behavior. In addition to the room temperature vitrification by hydrogen bonding, TGA experiments demonstrated that this vitrimer material was decross-linkable by heat treatment at elevated temperatures (significant dissociation of the cross-links was observed above 140 °C). This work highlighted that the vitrimer was frozen due to hydrogen bonding at temperatures below 80 °C, making it a “hybrid-vitrimer”. The novel hybrid-vitrimer thus presents three temperature domains: Below 80 °C, the material is frozen due to hydrogen bonding despite the ability of the exchange reaction to occur. At moderate temperatures (between 80 °C and 140 °C), hydrogen bonds dissociate, hemiacetal ester exchange reactions take place and the material show vitrimer flow behavior. Finally, at elevated temperatures (above 140°C), the hemiacetal ester cross-links dissociate and the material loses its vitrimer properties. Ongoing studies in our laboratory aim at designing hemiacetal ester linkage with higher thermal dissociation to expand the reshaping temperature range and suppress undesired degradation of the linkage entirely. In this study, a copolymer of styrene and butyl acrylate, presenting a moderate transition temperature, was used to demonstrate the vitrimer behavior of the material. However, a similar approach should be applicable for other vinylic monomers, including styrene, which is used for the production of commodity plastics and therefore relatively inexpensive.

## ASSOCIATED CONTENT

**Supporting Information**. Detailed information about $^1$H NMR, gel permeation chromatography, thermal and rheological characterizations. Vinyl ether side reaction with water and the equations used are also presented. This material is available free of charge via the Internet at http://pubs.acs.org.

## AUTHOR INFORMATION

### Corresponding Author

* vincent.ladmiral@enscm.fr

## Author Contributions

All authors have given approval to the final version of the manuscript.

## Funding Sources

This project was supported by the Chimie Balard Cirimat Carnot institute through the ANR programme N°16 CARN 0008-01 and by the I-SITE MUSE (ANR managed "Investissements d'avenir" programme N° ANR-16-IDEX-0006) Explore#2 mobility grant.

## ACKNOWLEDGMENT

The authors warmly thank Marc Guerre (CNRS Researcher - Paul Sabatier University Toulouse) for sharing is experience in vitrimer chemistry and for his valuable advices about rheology experiments.

## ABBREVIATIONS

AR, Acid-dissociated reference; CDDVE, 1-4 cyclohexanedimethanol divinyl ether; CMA, Cross-linked material with acid pendent groups; CR, Cross-linked reference; DCM, Dichloromethane; NR, Noncross-linked reference; RAFT, Reversible Addition-Fragmentation chain Transfer; $T_{dis}$, Dissociation temperature at which hemiacetal ester functions dissociate; THF, Tetrahydrofuran; VBA, 4-Vinylbezoic acid.

## REFERENCES

1. Montarnal D, Capelot M, Tournilhac F, Leibler L. Silica-Like Malleable Materials from Permanent Organic Networks. *Science* 2011; **334**: 965–968. doi:10.1126/science.1212648.
2. Denissen W, Winne JM, Du Prez FE. Vitrimers: Permanent organic networks with glass-like fluidity. *Chem Sci* 2016; **7**: 30–38. doi:10.1039/c5sc02223a.
3. Guerre M, Taplan C, Winne JM, Du Prez FE. Vitrimers: directing chemical reactivity to control material properties. *Chem Sci* 2020; **11**: 4855–4870. doi:10.1039/D0SC01069C.
4. Jourdain A, Asbai R, Anaya O, Chehimi MM, Drockenmuller E, Montarnal D. Rheological Properties of Covalent Adaptable Networks with 1,2,3-Triazolium Cross-Links: The Missing Link between Vitrimers and Dissociative Networks. *Macromolecules* 2020: acs.macromol.9b02204. doi:10.1021/acs.macromol.9b02204.
5. Scheutz GM, Lessard JJ, Sims MB, Sumerlin BS. Adaptable Crosslinks in Polymeric Materials: Resolving the Intersection of Thermoplastics and Thermosets. *J Am Chem Soc* 2019; **141**: 16181–16196. doi:10.1021/jacs.9b07922.
6. Hayashi M. Implantation of Recyclability and Healability into Cross-Linked Commercial Polymers by Applying the Vitrimer Concept. *Polymers* 2020; **12**: 1322. doi:10.3390/polym12061322.
7. Breuillac A, Kassalias A, Nicolaÿ R. Polybutadiene Vitrimers Based on Dioxaborolane Chemistry and Dual Networks with Static and

Dynamic Cross-links. *Macromolecules* 2019; **52**: 7102–7113. doi:10.1021/acs.macromol.9b01288.

8. Ricarte RG, Tournilhac F, Cloître M, Leibler L. Linear Viscoelasticity and Flow of Self-Assembled Vitrimers: The Case of a Polyethylene/Dioxaborolane System. *Macromolecules* 2020; **53**: 1852–1866. doi:10.1021/acs.macromol.9b02415.

9. Van Zee NJ, Nicolaÿ R. Vitrimers: Permanently crosslinked polymers with dynamic network topology. *Prog Polym Sci* 2020; **104**: 101233. doi:10.1016/j.progpolymsci.2020.101233.

10. Han J, Liu T, Hao C, Zhang S, Guo B, Zhang J. A Catalyst-Free Epoxy Vitrimer System Based on Multifunctional Hyperbranched Polymer. *Macromolecules* 2018; **51**: 6789–6799. doi:10.1021/acs.macromol.8b01424.

11. Röttger M, Domenech T, van der Weegen R, Breuillac A, Nicolaÿ R, Leibler L. High-performance vitrimers from commodity thermoplastics through dioxaborolane metathesis. *Science* 2017; **356**: 62–65. doi:10.1126/science.aah5281.

12. Ricarte RG, Tournilhac F, Leibler L. Phase Separation and Self-Assembly in Vitrimers: Hierarchical Morphology of Molten and Semicrystalline Polyethylene/Dioxaborolane Maleimide Systems. *Macromolecules* 2019; **52**: 432–443. doi:10.1021/acs.macromol.8b02144.

13. Nishimura Y, Chung J, Muradyan H, Guan Z. Silyl Ether as a Robust and Thermally Stable Dynamic Covalent Motif for Malleable Polymer Design. *J Am Chem Soc* 2017; **139**: 14881–14884. doi:10.1021/jacs.7b08826.

14. Sims MB, Lessard JJ, Bai L, Sumerlin BS. Functional Diversification of Polymethacrylates by Dynamic β-Ketoester Modification. *Macromolecules* 2018; **51**: 6380–6386. doi:10.1021/acs.macromol.8b01343.

15. Lessard JJ, Garcia LF, Easterling CP, *et al.* Catalyst-Free Vitrimers from Vinyl Polymers. *Macromolecules* 2019; **52**: 2105–2111. doi:10.1021/acs.macromol.8b02477.

16. Boucher D, Madsen J, Caussé N, Pébère N, Ladmiral V, Negrell C. Hemiacetal Ester Exchanges, Study of Reaction Conditions and Mechanistic Pathway. *Reactions* 2020; **1**: 89–101. doi:10.3390/reactions1020008.

17. Otsuka H, Endo T. Poly(hemiacetal ester)s: New class of polymers with thermally dissociative units in the main chain. *Macromolecules* 1999; **32**: 9059–9061. doi:10.1021/ma9909408.

18. Otsuka H, Fujiwara H, Endo T. Fine-tuning of thermal dissociation temperature using copolymers with hemiacetal ester moieties in the side chain: Effect of comonomer on dissociation temperature. *React Funct Polym* 2001; **46**: 293–298. doi:10.1016/S1381-5148(00)00071-7.

19. Kovash CS, Pavlacky E, Selvakumar S, Sibi MP, Webster DC. Thermoset coatings from epoxidized sucrose soyate and blocked, bio-based dicarboxylic acids. *ChemSusChem* 2014; **7**: 2289–2294. doi:10.1002/cssc.201402091.

20. Cho CG, Feit BA, Webster OW. Initiation of vinyl ether polymerization by trimethylsilyl triflate, dimethyl sulfide, and adventitious water. *Macromolecules* 1992; **25**: 2081–2085. doi:10.1021/ma00034a004.

21. Fife TH. Vinyl Ether Hydrolysis. The Facile General Acid Catalyzed Conversion of 2-Ethoxy-1-Cyclopentene-1-carboxylic Acid to Cyclopentanone. *J Am Chem Soc* 1965; **87**: 1084–1089. doi:10.1021/ja01083a026.

22. Gallucci RR, Going RC. Reaction of hemiacetal esters, acetals, and acylals with alcohols or acetic acid. *J Org Chem* 1982; **47**: 3517–3521. doi:10.1021/jo00139a026.

23. Khuong KS, Jones WH, Pryor WA, Houk KN. The Mechanism of the Self-Initiated Thermal Polymerization of Styrene. Theoretical Solution of a Classic Problem. J. Am. Chem. Soc. 2005; **127**: 1265–1277. doi:10.1021/ja0448667.

24. Lewis CL, Stewart K, Anthamatten M. The Influence of Hydrogen Bonding Side-Groups on Viscoelastic Behavior of Linear and Network

Polymers. *Macromolecules* 2014; **47**: 729–740. doi:10.1021/ma402368s.

25. Bershtein VA, Yegorov VM, Razgulyayeva LG, Stepanov VA. The use of differential scanning calorimetry for evaluating the intermolecular reaction changes in glass-like polymers. *Polym Sci USSR* 1978; **20**: 2560–2568. doi:10.1016/0032-3950(78)90192-2.
26. Bershtein VA, Razgulyayeva LG, Gal'perin VM, *et al.* Molecular interaction and conformation of molecules in polystyrene and styrene-methacrylic acid copolymers. *Polym Sci USSR* 1978; **20**: 2118–2127. doi:10.1016/0032-3950(78)90339-8.
27. Blades AT. The kinetics of the thermal decomposition of vinyl isopropyl ether. *Can J Chem* 1953; **31**: 418–421. doi:10.1139/v53-057.
28. Shimofuji K, Saito K, Imamura A. Unimolecular thermal decomposition of ethyl vinyl ether and the consecutive thermal reaction of the intermediary product acetaldehyde: shock wave experiment and ab initio calculation. *J Phys Chem* 1991; **95**: 155–165. doi:10.1021/j100154a032.
29. Azcune I, Odriozola I. Aromatic disulfide crosslinks in polymer systems: Self-healing, reprocessability, recyclability and more. *Eur Polym J* 2016; **84**: 147–160. doi:10.1016/j.eurpolymj.2016.09.023.
30. Van Herck N, Maes D, Unal K, Guerre M, Winne JM, Du Prez FE. Covalent Adaptable Networks with Tunable Exchange Rates Based on Reversible Thiol–yne Cross-Linking. *Angew Chemie Int Ed* 2020; **59**: 3609–3617. doi:10.1002/anie.201912902.
31. Wu J-B, Li S-J, Liu H, Qian H-J, Lu Z-Y. Dynamics and reaction kinetics of coarse-grained bulk vitrimers: a molecular dynamics study. *Phys Chem Chem Phys* 2019; **21**: 13258–13267. doi:10.1039/C9CP01766F.