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Synthesis of Polyester Thermosets via Internally Catalyzed Michael-addition of methylene compounds on a 2-(Trifluoromethyl)acrylate-derived building block

Dimitri Berne^a, Sylvain Caillol^a, Vincent Ladmiral^{a,*}, Eric Leclerc^{a,*}

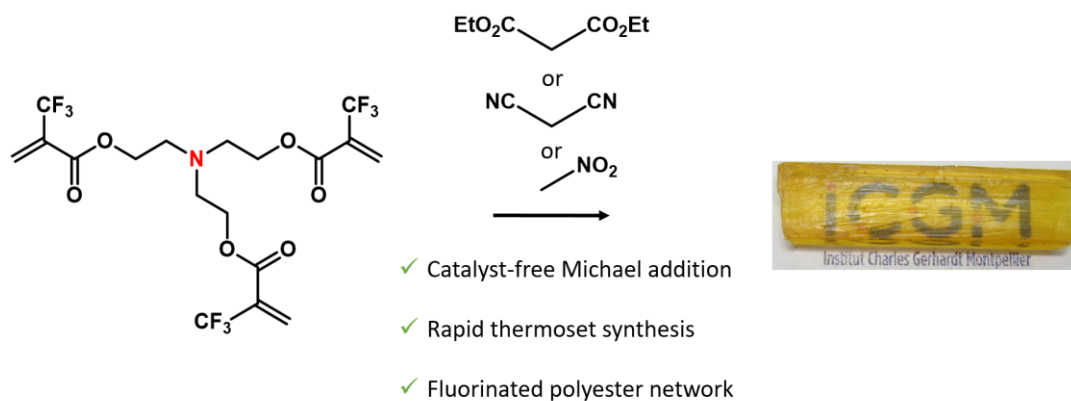
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Keywords

Michael-addition, fluorine, fluorinated polyester thermosets, internal catalysis, 2-trifluoromethyl)acrylate

Abstract

The Michael-addition reaction of methylene compounds has been known and used for more than 120 years in organic chemistry synthesis. We report herein a new type of application for this reaction: the preparation of thermosets by **catalyst-free bis-Michael addition**. In this study, the addition of various methylene C-nucleophiles on *tert*-butyl 2-(trifluoromethyl)acrylate in presence of a tertiary amine was preliminary evaluated. Then, a *tris*-2-(trifluoromethyl)acrylate monomer incorporating a tertiary amine was synthesized and used with methylene monomers to prepare innovative polyester networks **at temperature going from 25 °C to 100 °C**. Finally, the resulting fluorinated carbon-Michael networks were characterized by FTIR, **differential scanning calorimetry, thermal gravimetry, dynamic mechanical and swelling analyses**. These thermosets exhibited high gel content (**>86 %**) and good thermo-mechanical properties with a rubbery plateau above 7 MPa and a glass transition temperature above 44 °C. The material thermal properties could be adapted to a targeted application (**binder or coating**) by the choice of the methylene compound used in the thermoset formulation.



Introduction

The Michael-addition reaction originally consists in the addition of a malonate to an activated α - β unsaturated ester *via* a base-promoted mechanism.^{1,2} The "Michael addition" naming has since then been attached to any addition of active methylene compounds or enol-type nucleophiles (Michael donor) to electron-poor olefins (Michael acceptor such as α - β unsaturated esters or vinylsulfones, nitroolefins, ...) and such reactions have been used as a synthetic step in a wide range of applications in organic chemistry.^{3,4} The extension of this reaction to heteronucleophiles such as alcohols,^{5,6} amines^{7,8} or thiols⁹⁻¹¹ is also well documented. Moreover, aza and thia-Michael reactions have also been used in materials science¹² for the production of a large range of monomers,¹³ dendrimers¹⁴ and particles.¹⁵

Crosslinked networks were also synthesized by thia-Michael^{16–22} and aza-Michael^{23–25} and some of these networks also demonstrated reprocessability under thermal stimulus *via* Michael exchange.^{26–28} While Michael addition of active methylene compounds on acrylate enabled the synthesis of some crosslinked networks under catalyzed or UV-promoted conditions,^{29–32} no crosslinked network based on a catalyst-free *bis*-carbon-Michael addition has been described to the best of our knowledge, although the use of this reaction should allow the preparation of useful materials.

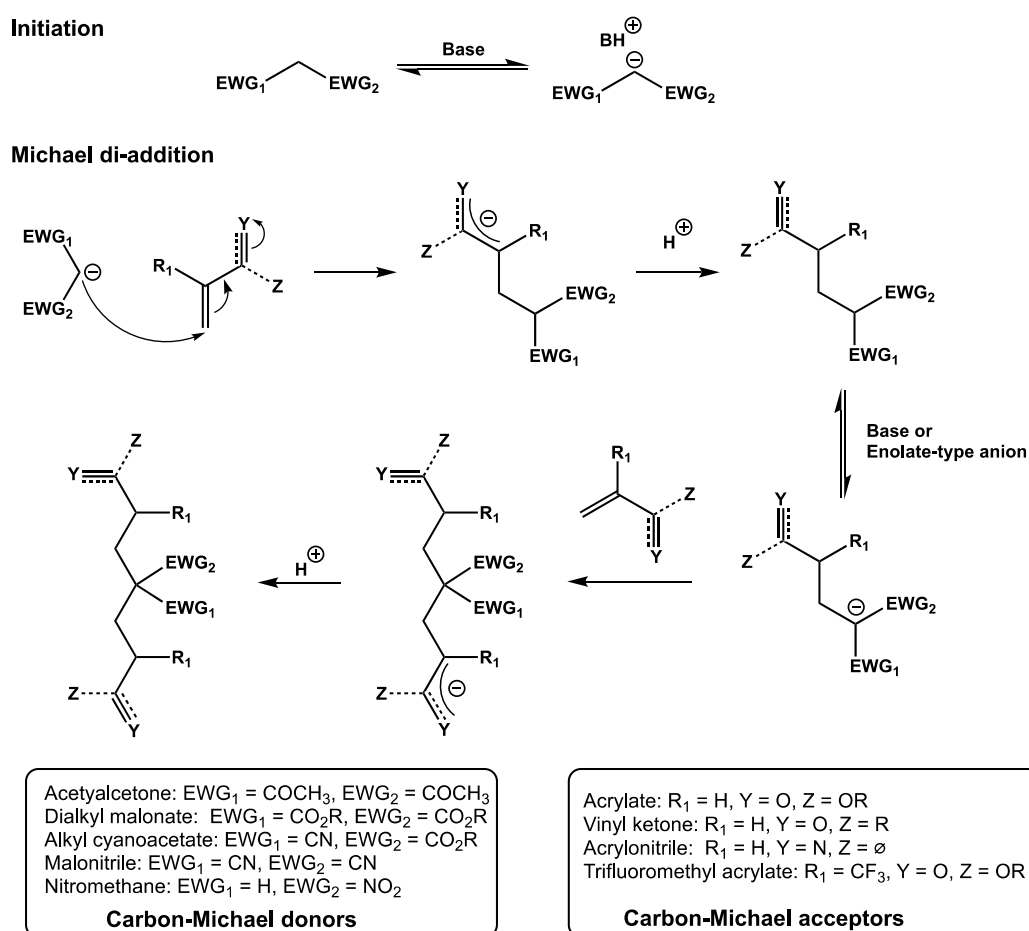
The mechanism of the Michael addition consists in three steps, beginning with the formation of the Michael nucleophile by a base-mediated deprotonation. This nucleophile then adds to the β -position of the Michael acceptor through a 1,4-conjugate addition mechanism, leading to a delocalised enolate-type anion. Depending on the reaction conditions, the latter can react with different kinds of electrophiles but a simple proton transfer affords the standard Michael adduct (Scheme 1). If the product of a first Michael addition has a remaining activated hydrogen, it can possibly undergo a second addition following the same mechanism. However, it is important to note that the second pK_a is expected to be higher than the initial pK_a of the activated methylene compound. For instance, it has been reported that the pK_a of the first adduct is expected to have a value of 13 (vs 12 for the initial donor) for the addition of ethyl acetoacetate to methyl acrylate.³³

In order to perform a Michael *bis*-addition, specific acceptors such as acrylonitrile, acrylates or vinyl ketones and activated methylene compounds such as acetylacetone, dialkyl malonate, alkyl cyanoacetate or malonitrile have to be used. In 1963, the addition of different methylene compounds onto acrylonitrile catalyzed by triethylamine was reported.³⁴ Following this early research, a wide range of catalysts has been developed, including for instance ruthenium complexes and enolatoiron(II) compounds.^{34–38} 1-methyl-3-butylimidazolium hydroxide (an ionic liquid) has also been used as the reaction medium to promote different Michael additions, leading exclusively to *bis*-adducts.^{39,40} Synthesized basic cesium-beta zeolite proved as well to be an effective catalyst for the addition of malonitrile to terpenoid acceptors.⁴¹ Methyl vinyl ketone, one of the most activated acceptors, can undergo Michael addition under mild reaction conditions. These reactions were generally catalyzed by metal complexes acting as Lewis acid catalyst such as palladium,^{42,43} platinum⁴⁴ and ruthenium⁴⁵ complexes. In this case, the Lewis acid coordinates to the pronucleophile (ligand exchange with a nitrile group of the Michael donor), lowering its pK_a and allowing the use of a weak base such as Hünig's base to promote the two successive addition reactions to the acceptor. Organosilicates have also been used to catalyze such Michael additions, in this specific case the silicate might act as both a Lewis acid catalyst and a Brønsted base catalyst.⁴⁶ The reactive enolate (Michael donor) can also be generated through electrochemical methods to perform a metal- and strong base-free Michael addition.⁴⁷

Among Michael acceptors, 2-trifluoromethylacrylates (MAF) demonstrated a high reactivity towards Michael additions due to the strong inductive effect of the trifluoromethyl group on the double bond. For instance, thiols were added to CF_3 -substituted acrylic acids under catalyst-free conditions by Fokin et al.⁴⁸ 3-(2,2,2-Trifluoroethylidene)oxindoles also showed the ability to easily react in the catalyst-free addition of aryl thiols.⁴⁹ A new α - CF_3 -tetracid used for epoxy-vitrimer application was also obtained via a catalyst-free thia-Michael addition of a tetra-thiol on MAF.⁵⁰ The specific electronic withdrawing character of the CF_3 group was also used to activate an alkyne-derived acceptor, allowing the synthesis of fluorinated polythioether by DBU catalyzed thia-Michael addition.⁵¹ The reactivity of MAF towards carbanions in Michael additions was already observed in the anionic copolymerisation of MAF with methyl methacrylate.^{52,53} Narita has extensively studied the high reactivity of fluorinated vinyl compounds towards the addition of anionic and radical species.⁵⁴ In particular, Narita *et al.* synthesized linear polymers by the anionic double Michael

addition of ethyl cyanoacetate to a *bis*-functional MAF-derivative.⁵⁵ In this initial study, the potential of sodium hydroxide as a catalyst for the double Michael addition was first demonstrated on model molecules before being used in the synthesis of linear polymers. In contrast, to the best of our knowledge, no polymer has been synthesized by **catalyst-free double** Michael addition to *bis*-vinylketones or *bis*-acrylates.

In the objective to broaden the use of MAF, the synthesis of 3D networks was attempted by a double-Michael addition on a new *tris*-MAF monomer. An internal catalyst for the Michael addition was integrated into this network to avoid the use of external catalyst. **The latter can indeed accelerate material degradation with time or temperature or leach out from the polymer matrix.** According to this strategy, the bulk synthesis of these different networks was made possible. Prior to the chemical and mechanical study of these newly formed materials, the addition of three different methylene compounds in the presence of triethylamine was assessed.



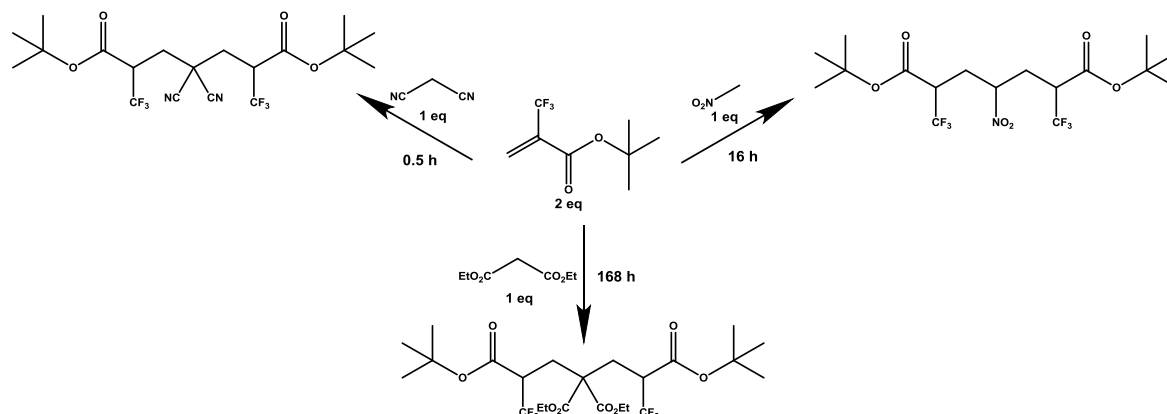
Scheme 1. Mechanism of the double Michael addition of methylene compound on activated Michael acceptors.

Results and discussion

Addition of model molecules catalyzed by triethylamine

The addition of different methylene compounds on *tert*-butyl 2-(trifluoromethyl)acrylate (MAF-TBE) (Scheme 2) was assessed under different conditions summarized in Table 1. The conversion of the double bond was monitored by ¹⁹F-NMR and confirmed by ¹H-NMR when the reaction conditions allowed it. Dichloromethane and **Et₃N** were not removed from the system as MAF-TBE could potentially also evaporate during vacuum treatment, which could have biased the determination of

the conversion. The *bis*-addition products were obtained in high yields for malonitrile, diethylmalonate and nitromethane, their corresponding NMR characterizations are respectively presented in Figure S1, Figure S2 and Figure S3.



Scheme 2. Addition of malonitrile, diethylmalonate or nitromethane on MAF-TBE. Reactions were performed in dichloromethane in presence of 0.1 eq. of Et_3N .

Table 1. Synthesis conditions of the different experiments performed on model molecules.

Entry	Methylene compound	Ratio MAF-TBE/methylene/ Et_3N	Solvent	T (°C)	Time (h)	MAF-TBE conversion (%) ^a
1	Malonitrile	2/1/0	-	25	24	0
2	Malonitrile	2/1/0.1	DCM	25	0.5	100
3	Diethyl malonate	2/1/0.1	DCM	25	0.5	4
4	Diethyl malonate	2/1/0.1	DCM	25	168	100
5	Diethyl malonate	2/1/0.1	-	60	24	100
6	Nitromethane	2/1/0.1	DCM	25	0.5	16
7	Nitromethane	2/1/0.1	DCM	25	16	100
8	Nitromethane	4/1/1 (<i>tris</i> -addition)	DCM	25	72	75

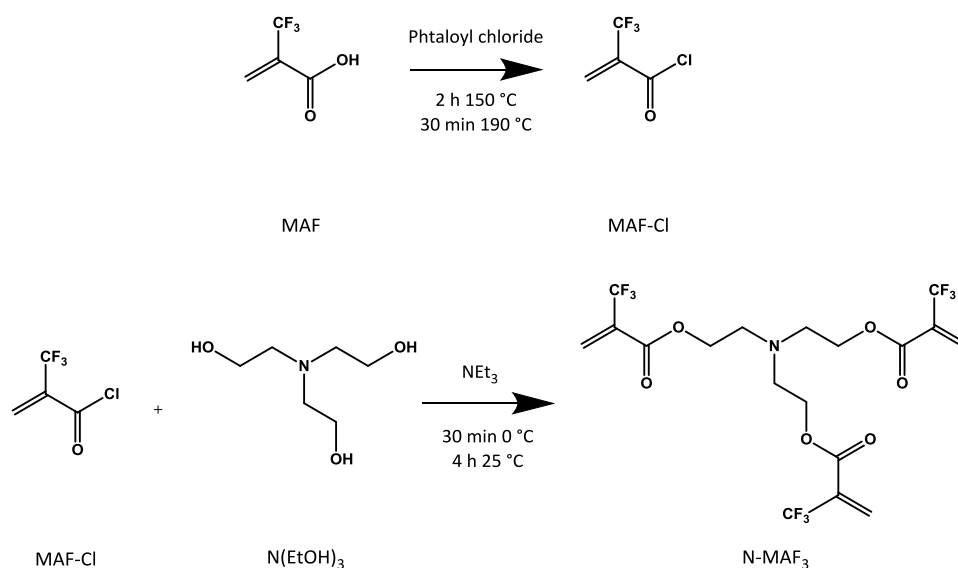
^a Conversion was determined from the integration of the ^{19}F -NMR spectrum of the crude mixture

The first observation is that, without Et_3N , the Michael addition does not occur with malonitrile at 25 °C even under solvent-free conditions (Table 1, entry 1). Hence, the presence of a base is required to initiate the reaction. For a 2/1/0.1 (MAF-TBE/methylene/ Et_3N) molar ratio, high *bis*-addition yields were obtained under different conditions, depending on the involved methylene compound. Particularly, malonitrile was highly reactive since a quantitative conversion was achieved after 30 mn in DCM at room temperature (Table 1, entry 2). Under the same conditions and reaction time, diethylmalonate and nitromethane led only to relatively low conversion of 4 % and 16 %, respectively (Table 1, entry 3 and 6). A full conversion of the MAF-TBE can however be obtained after 168 h and 16 h of reaction (Table 1, entry 4 and 7) respectively for the addition on diethylmalonate and nitromethane. In the case of malonitrile and diethylmalonate, these differences in reactivity can be related to the stronger electron withdrawing ability of a cyano group compared to an ester, and to the resulting difference in pK_a of the activated methylenes (11.2 for malonitrile and 12.9 for diethyl malonate).⁵⁶ The nitro group is, however, generally classified as a more powerful electron-withdrawing group than the cyano group, which is reflected by the lower pK_a of nitromethane (10.2) compared to malonitrile (11.2) despite the presence of only one nitro group. The difference in reaction time observed might therefore be related to the difference in reactivity of the resulting anion. The reaction conditions can however be adapted to reduce the reaction time. Indeed, under

neat conditions at 60 °C, full conversion was obtained for diethylmalonate after 24 h (entry 5). Finally, it should be noted that, in this study, nitromethane was considered as a divalent molecule to keep the focus on the *bis*-Michael addition. However, entry 8 demonstrated the possibility to use nitromethane as a trivalent monomer. Indeed, in presence of an excess of MAF-TBE and a stoichiometric amount of triethylamine, a total disappearance of the nitromethane proton was noticed (Figure S4), indicating the efficient *tris*-addition of nitromethane to MAF-TBE.

Material synthesis

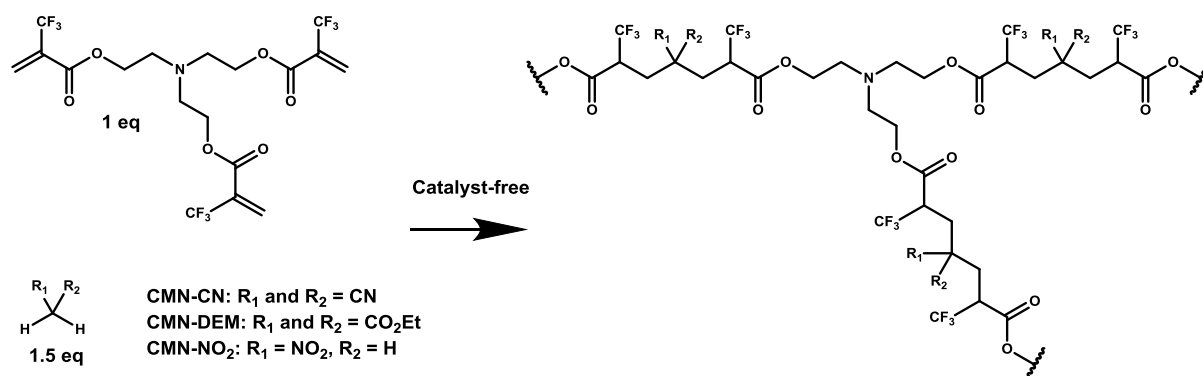
In order to perform a network synthesis via double Michael addition without the use of an external catalyst, a tertiary amine could interestingly be present on one of the monomers to act as an internal catalyst. This strategy was previously employed for the synthesis by thia-Michael addition of polymer networks, used as hydrophilic microfluidic devices.⁵⁷ This mechanism of internal catalysis was previously observed for amine/epoxy or anhydride system.^{58,59} However, for these systems, tertiary amines were generally directly synthesized during the curing process. Similar effect was probably also at play for thermosets involving tertiary amine production such as materials synthesized by aza-Michael addition for instance.^{23,24} Following this strategy, a novel trifunctional monomer possessing 2-(trifluoromethyl)acrylate moieties (N-MAF₃) was simply synthesized from triethanolamine (N(EtOH)₃) and the acyl chloride derived from MAF (Scheme 3). This monomer features a tertiary amine that can act as a catalyst for the Michael addition, like Et₃N did in the model reactions described above. N-MAF₃ was obtained in good yield (77 %) as a brown viscous liquid and was characterized by ¹H, ¹³C and ¹⁹F-NMR (Figure S5).



Scheme 3. Synthesis of N-MAF₃ from MAF.

Three carbon-Michael networks (CMN) were respectively synthesized from the polyaddition of nitromethane (CMN-NO₂), malonitrile (CMN-CN) and diethyl malonate (CMN-DEM) on N-MAF₃ (Scheme 4). For the synthesis of CMN-NO₂, nitromethane was considered as divalent to facilitate the comparison between CMN. Due to the stoichiometry of the reagents, to the increasing pK_a of the addition products and the probable slower rate of the third addition, it was assumed that the network was mostly formed from *bis*-addition of nitromethane and that the third addition occurred only marginally.³³ The reaction conditions for the polyaddition of the CMN are summarized in Table 2. The same order of reactivity was observed for the network formation as in the preliminary study on model molecules. Indeed, a solid was directly obtained for CMN-CN after mixing the components

for 1 min in the speed mixer, whereas curing at 80 °C and 100 °C was required for CMN-NO₂ and CMN-DEM, respectively, to obtain a rigid material. For CMN-CN, a post-curing at 75 °C was required to reach complete conversion of the reactive functions since an enthalpy reaction peak around 75 °C could still be detected in DSC analysis after the initial curing at 25 °C. Despite this, it can be noticed that a solid material was readily obtained at 25 °C. The polyaddition presumably followed the same mechanism as the model reactions, the tertiary amine present in N-MAF₃ acting as triethylamine in the model reactions but as an internal catalyst. Compared to the stoichiometry used for the model reactions for which only 0.1 eq of Et₃N was used, the tertiary amine was present as 0.66 eq. for 1 eq. of methylene group in the CMN preparation, resulting in a higher catalyst loading and an increased rate of the polymerization reaction.



Scheme 4. Synthesis of carbon-Michael networks from reaction N-MAF₃ with a methylene monomer in external catalyst-free conditions.

Table 2. Curing conditions and characterizations of carbon-Michael networks.

CMN	Curing conditions	T _g (°C)	T _α (°C)	T _d ^{5%} (°C)	E' _{glassy} ^a (GPa)	E' _{rubbery} ^a (MPa)	Swelling index (%)	Gel Content (%)
CMN-CN	25 °C 2 h +75 °C 30 min	51	79	206	2.95	8.93	178 ± 12	86 ± 1
CMN-NO ₂	80 °C 12 h	46	72	205	1.25	9.64	123 ± 25	88 ± 2
CMN-DEM	100 °C 3h	44	70	207	1.32	7.31	240 ± 33	93 ± 1

^a Determined at T_α - 50 °C; ^b Determined at T_α + 50 °C

FTIR measurements have been performed on the three synthesized CMNs (Figure S6-8). Some specific bonds related to the nature of the methylene monomer are noticeable in the CMN. For instance, an elongation band associated to a nitro group at 152 cm⁻¹ and a band at 2200 cm⁻¹ corresponding to a nitrile group can be observed for CMN-NO₂ and CMN-CN respectively. Network formation was confirmed by the insolubility tests carried out on the three CMN. High gel contents were obtained (>86 %) for each material, demonstrating the synthesis of highly cross-linked materials. Swelling index were slightly impacted by the nature of the starting methylene compound and followed the expected trend. Indeed, the larger the electron-withdrawing group, the higher the swelling index was.

The glass transition and the alpha transition temperatures were hardly affected by the monomers used. Indeed, T_g values were comprised between 44 and 51 °C and T_α values ranged from 70 to 79 °C for all CMN. From DSC (Figure S9) and DMA (Figure 1) curves, the glass transition window appeared to be broader for CMN-DEM and CMN-NO₂ compared to CMN-CN. This could be related to the higher curing temperature used for the first materials which induces some heterogeneity in these materials

compared to CMN-CN. Finally, the storage moduli on the rubbery plateaus were of the same order of magnitude for the three samples and no clear trend dependent on the methylene used could be found. Nevertheless, it appears that CMN-CN was more rigid than CMN-NO₂ and CMN-DEM at low temperatures as its glassy plateau storage modulus was higher than the ones of the two other materials. Finally, the degradation thermograms of the three CMN were similar and the mass loss temperature at 5 % was above 200 °C for all materials (Figure S10). The three synthesized CMN exhibited relatively similar physical properties.

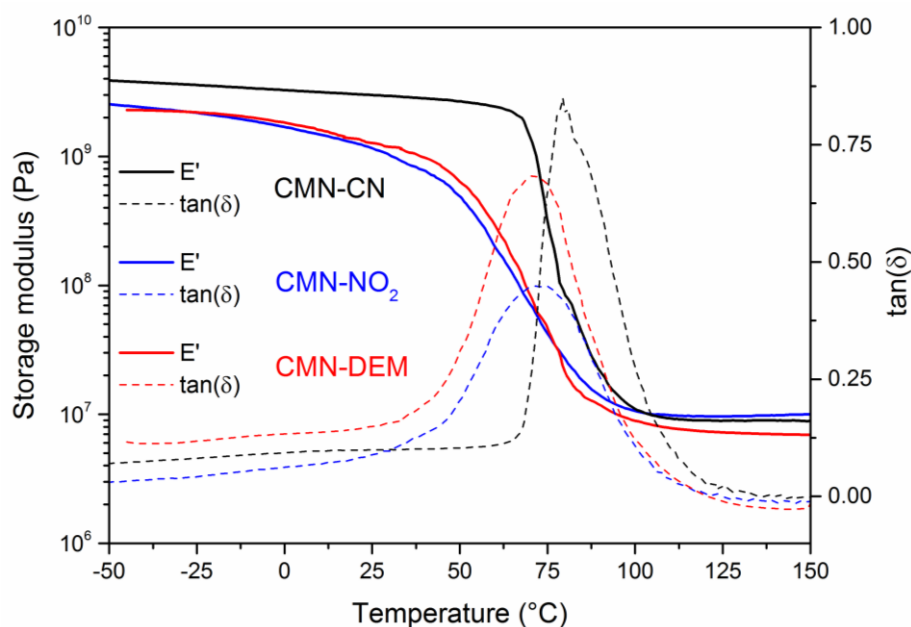


Figure 1. Storage modulus (full curves) and $\tan(\delta)$ of CMN-CN (black curves), CMN-NO₂ (blue curves) and CMN-DEM (red curves) from DMA analyses.

Similarly to the curing of epoxy/amine systems,^{60,61} thermosets polymers can easily be obtained by *bis*-Michael addition. Moreover, the reactivity of the Michael system can be tuned by the choice of a specific electron-withdrawing group on the methylene monomer. Finally, the mechanical properties of CMN are similar to the ones already observed for epoxy/amine systems,⁶²⁻⁶⁴ and the glass transition could be adapted by designing new 2-(trifluoromethyl)acrylate monomers including, for instance, aromatic groups.

Conclusion

The preliminary study of the addition of different active methylene compounds as Michael addition donors on a 2-(trifluoromethyl) acrylic ester (Michael acceptor) demonstrated the efficient catalytic role of triethylamine. Moreover, these reactions on model molecules allowed to determine the reactivity order between the methylene compounds (malonitrile > nitromethane > diethylmalonate) in the Michael addition on 2-(trifluoromethyl)acrylate. Following these encouraging results, a new trivalent monomer featuring 2-(trifluoromethyl)acrylate moieties and incorporating a tertiary amine was synthesized. This novel monomer was reacted with the previously studied methylene compounds to provide carbon-Michael addition networks. These polyester thermosets demonstrated relatively similar physical and chemical properties compared to existent epoxy/amine systems.

Their high glass transition temperatures, coupled with their capability to form at relatively low temperature and without an external catalyst, make these carbon-Michael addition networks interesting for future application as binders or coatings. This study represents a first step in the

synthesis of thermosets by Michael addition on methylene groups and paves the way to further applicative studies on these materials.

Materials & Methods

Materials

Triethylamine (99 %), Triethanolamine (99 %), Phthaloyl dichloride (> 95 %), Dichloromethane (DCM), THF were purchased from Sigma-Aldrich Merck (Darmstadt, Germany). Malonitrile (99 %) was purchased from Alfa Aesar (Kandel, Germany). Diethylmalonate (99 %) was purchased from Abcr (Karlsruhe, Germany). Nitromethane (99 %) was purchased from Acros Organics (Geel, Belgium). 2-(Trifluoromethyl)acrylic acid (MAF) (> 98%), tert-Butyl 2-(Trifluoromethyl)acrylate (MAF-TBE) (> 98 %) were purchased from SynQuest Labs (Alachua, FL, USA). All materials were used as received. The NMR solvents CDCl₃ was purchased from Eurisotop (Saint-Aubin, France).

Characterizations

Nuclear Magnetic Resonance

Proton Nuclear Magnetic Resonance (¹H, ¹³C, ¹⁹F-NMR) analyses were carried out in deuterated chloroform (CDCl₃, 99.50% isotopic purity) using Bruker Avance III 400 MHz NMR spectrometer at a temperature of 25 °C.

Fourier Transform Infrared Spectroscopy

Infrared (IR) spectra were recorded on a Nicolet 210 Fourier transform infrared (FTIR) spectrometer. The characteristic IR absorptions mentioned in the text are reported in cm⁻¹. Materials analyses were recorded using an ATR accessory.

Thermogravimetric Analyses

Thermogravimetric Analyses (TGA) were carried out using TG 209F1 apparatus (Netzch). Approximately 10 mg of sample were placed in an aluminum crucible and heated from room temperature to 580 °C at a heating rate of 20 °C/min under nitrogen atmosphere (60 mL/min).

Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) analyses were carried out using a NETZSCH DSC200F3 calorimeter, which was calibrated using indium, *n*-octadecane and *n*-octane standards. Nitrogen was used as purge gas. Approximately 10 mg of sample were placed in a perforated aluminum pan and the thermal properties were recorded between -150 °C and 150 °C at 20 °C/min to observe the glass transition temperature. The *T_g* values were measured on the second heating ramp to erase the thermal history of the polymer. All the reported temperatures are average values.

Dynamic mechanical analyses

Dynamic mechanical analyses (DMA) were carried out on Metravib DMA 25 with Dynatest 6.8 software. Samples were tested in the uniaxial tension mode at a frequency of 1 Hz with a fixed strain of 10⁻⁵ m, while applying a temperature ramp at a rate of 3 °C/min from -100 °C to +150 °C. The *T_α* was determined as the maximum of the loss modulus *E''*.

Swelling index

Three samples from the same material, of around 20 mg each, were separately immersed in THF for 24 h. The swelling index (SI) was calculated using Equation 1, where m_2 is the mass of the swollen material and m_1 is the initial mass. Reported swelling index are average values of the three samples.

$$\text{Equation 1} \quad SI = \frac{m_2 - m_1}{m_1} \times 100$$

Gel content

Three samples from the same material, of around 20 mg each, were separately immersed in THF for 24 h. The samples were then dried in a ventilated oven at 70 °C for 24 h. The gel content (GC) was calculated using Equation 2, where m_2 is the mass of the dried material and m_1 is the initial mass. Reported gel content are average values of the three samples.

$$\text{Equation 2} \quad GC = \frac{m_2}{m_1} \times 100$$

Synthesis

Synthesis of CN-MAF₂

Malonitrile (3 mmol, 0.20 g, 1 eq., [1 M]) was mixed with *tert*-butyl 2-(trifluoromethyl)acrylate (MAF-TBE) (6 mmol, 1.18 g, 2 eq.) in dichloromethane at 25 °C. A catalytic amount of triethylamine (Et₃N) (0.3 mmol, 30 mg, 0.1 eq) was then added to the solution at 0 °C. After 30 min of stirring at 25 °C, *bis*-addition product was then obtained in good yield.

¹H NMR (400 MHz, CDCl₃): δ/ppm = 1.53 (s, O-C-(CH₃)₃), 2.27-2.33 (m, C-CH₂-CH), 2.80-2.88 (m, C-CH₂-CH), 3.33-3.43 (m, CF₃-CH-CH₂).

¹³C NMR (101 MHz, CDCl₃): δ/ppm = 27.6 (O-C-(CH₃)₃), 33.7 (C-CH₂-CH), 34.6 (C-CH₂-CH), 48.0-48.9 (CF₃-CH-CH₂), 85.3 (O-C-(CH₃)₃), 112.5-113.5 (C-CN), 119.5-127.9 (q, ¹J = 281 Hz, CF₃), 163.8-163.9 (q, ³J = 2.7 Hz, C=O)

¹⁹F NMR (377 MHz, CDCl₃): δ/ppm = -68.5

Synthesis of DEM-MAF₂

Diethylmalonate (3 mmol, 0.48 g, 1 eq.) was mixed with *tert*-butyl 2-(trifluoromethyl)acrylate (MAF-TBE) (6 mmol, 1.18 g, 2 eq.) at 25 °C. A catalytic amount of triethylamine (Et₃N) (0.3 mmol, 30 mg, 0.1 eq) was then added to the solution. The solution was stirred at 60 °C for 24 h and the *bis*-addition product was obtained in good yield.

¹H NMR (400 MHz, CDCl₃): δ/ppm = 1.22-1.25 (m, CH₂-CH₃), 1.43-1.44 (m, O-C-(CH₃)₃), 2.17-2.22 (m, C-CH₂-CH), 2.45-2.55 (m, C-CH₂-CH), 3.15-3.24 (m, CF₃-CH-CH₂), 4.10-4.18 (m, CH₂-CH₃)

¹³C NMR (101 MHz, CDCl₃): δ/ppm = 13.7 (CH₂-CH₃), 27.6 (O-C-(CH₃)₃), 29.6-30.0 (C-CH₂-CH), 47.2-48.2 (CF₃-CH-CH₂), 55.1-55.2 (C-CH₂-CH), 62.0-62.1 (CH₂-CH₃), 83.2 (O-C-(CH₃)₃), 119.53-127.90 (q, ¹J = 281 Hz, CF₃), 165.8-165.9 (CH-C=O), 169.5-169.8 (C-C=O)

¹⁹F NMR (377 MHz, CDCl₃): δ/ppm = -69.7

Synthesis of NO₂-MAF₂

Nitromethane (3 mmol, 0.18 g, 1 eq., [1 M]) was mixed with *tert*-butyl 2-(trifluoromethyl)acrylate (MAF-TBE) (6 mmol, 1.18 g, 2 eq.) in dichloromethane at 25 °C. A catalytic amount of triethylamine (Et₃N) (0.3 mmol, 30 mg, 0.1 eq) was then added to the solution. After 16 h of stirring at 25 °C, the *bis*-addition product was then obtained in good yield.

^1H NMR (400 MHz, CDCl_3): δ/ppm = 1.42-1.43 (m, $\text{O-C}(\text{CH}_3)_3$), 2.03-2.34 (m, $\text{CH-CH}_2\text{-CH}$), 2.49-2.67 (m, $\text{CH-CH}_2\text{-CH}$), 3.10-3.31 (m, $\text{CF}_3\text{-CH-CH}_2$), 4.25 (s, $\text{NO}_2\text{-CH-CH}_2$)

^{13}C NMR (101 MHz, CDCl_3): δ/ppm = 27.4 ($\text{O-C}(\text{CH}_3)_3$), 31.6-32.7 ($\text{C-CH}_2\text{-CH}$), 46.3-47.4 ($\text{CF}_3\text{-CH-CH}_2$), 84.4-84.7 ($\text{O-C}(\text{CH}_3)_3$), 88.2-88.7 ($\text{NO}_2\text{-CH-CH}_2$), 120.1-128.5 (q, $^1\text{J} = 281$ Hz, CF_3), 165.8-165.9 (CH-C=O), 165-1-165.3 (C-C=O)

^{19}F NMR (377 MHz, CDCl_3): δ/ppm = -69.8

Synthesis of $\text{NO}_2\text{-MAF}_3$

Nitromethane (3 mmol, 0.18 g, 1 eq., [0.5 M]) was mixed with tert-butyl 2-(trifluoromethyl)acrylate (MAF-TBE) (12 mmol, 2.36 g, 4 eq.) in dichloromethane at 25 °C. A catalytic amount of triethylamine (Et_3N) (3 mmol, 0.30 g, 1 eq) was then added to the solution. After 24 h of stirring at 25 °C, the tri-addition product was obtained in good yield.

^1H NMR (400 MHz, CDCl_3): δ/ppm = 1.42-1.43 (m, $\text{O-C}(\text{CH}_3)_3$), 2.04-2.31 (m, $\text{CH-CH}_2\text{-CH}$), 2.51-2.69 (m, $\text{CH-CH}_2\text{-CH}$), 3.10-3.41 (m, $\text{CF}_3\text{-CH-CH}_2$)

^{19}F NMR (377 MHz, CDCl_3): δ/ppm = -69.8

Synthesis of MAF-Cl

2-Trifluoromethylacryloyl chloride (MAF-Cl) was synthesized by the reaction of 2-trifluoromethylacrylic acid (MAF) (29.1 g, 208 mmol) with phthaloyl dichloride (63.2 g, 311.3 mmol) at 150 °C for 2 h and then 190 °C for 30 min. The product was collected by distillation during reaction. Yield: 72 %, 23.8 g. Boiling point: 82 °C.

Synthesis of N-MAF₃

Triethanolamine (2.49 g, 1 eq) was dissolved in 100 mL of dichloromethane in the presence of triethylamine (8.43 g, 5 eq). MAF-Cl (9.5 g, 3.6 eq) was added dropwise at 0 °C for 10 min and the reactive mixture was stirred for 2 hours at room temperature. The reaction mixture was filtered, washed with a saturated aqueous sodium hydrogen carbonate solution and twice with brine, twice with distilled water, dried over MgSO_4 , filtered and evaporated under reduced pressure to afford the pure N-MAF₃ as a viscous brown liquid. Yield: 77 %, 6.58 g.

^1H NMR (400 MHz, CDCl_3): δ/ppm = 2.95-2.98 (t, $^3\text{J} = 5.8$ Hz, 6H, $\text{N-CH}_2\text{-CH}_2$), 4.31-4.34 (t, $^3\text{J} = 5.8$ Hz, 6H, $\text{N-CH}_2\text{-CH}_2$), 6.46 (m, 6.74, 3H, $\text{CH}_2=\text{C}$), 6.74-6.75 (q, 6.74, $^4\text{J} = 1.7$ Hz, 3H, $\text{CH}_2=\text{C}$)

^{13}C NMR (101 MHz, CDCl_3): δ/ppm = 53.0 ($\text{N-CH}_2\text{-CH}_2$), 64.0 ($\text{N-CH}_2\text{-CH}_2$), 117.2-125.3 (q, CF_3 , $^1\text{J} = 272.5$ Hz), 130.8-131.8 (q, C-CF_3 , $^2\text{J} = 32.2$ Hz), 133.1-133.2 (q, $\text{CH}_2=\text{C}$, $^3\text{J} = 5.1$ Hz), 161.2 (C=O)

^{19}F NMR (377 MHz, CDCl_3): δ/ppm = -65.6

Synthesis of Carbon Michael Addition Networks (CMN)

CMNs were synthesized by mixing 1.5 eq of N-MAF₃ (2.06 g) with 1 eq. of methylene compound in a SpeedMixer. Malonitrile (0.40 g), diethylmalonate (0.96 g) and nitromethane (0.37 g) were used for the synthesis of CMN-CN, CMN-DEM and CMN-NO₂ respectively.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

All data included in this study are available from the corresponding author upon reasonable request.

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