

Mechanochemical synthesis of polypropylene-based macromolecular stabilizers

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ABSTRACT

A mechanochemical process is proposed as an innovative approach to the synthesis of polypropylene-based macromolecular stabilizers with outstanding thermal behavior. Properly designed butylated hydroxytoluene antioxidants (BHT) and hindered amine light stabilizers (HALS) are covalently linked to polypropylene grafted with maleic anhydride (PP-g-MA) using a ball-mill apparatus under mild and solvent-free conditions. The study reports a quantitative evaluation of the degree of functionalization based on ATR-FTIR quantification technique and the solid-state NMR spectroscopy characterization of the ensuing materials. This strategy is a significant step towards safe and sustainable chemical synthesis in the field of macromolecular materials.

1. Introduction

Polyolefins are the plastic materials most frequently used in the entire agrifood production chain, from the greenhouses for agriculture production to food contact materials, playing a major role in sustaining quality and safety of modern lifestyle [1].

Meeting the needs of today's society also means pursuing sustainable development. Moving economy and society on a sustainable pathway and green economy means turning towards a zero pollution/toxic-free production. Crucial to this social transformation will be the transition to a safe and sustainable-by-design approach, so that chemicals and materials are designed, produced, used, and recycled without harming people and the environment. In this perspective increasing the recycled polyolefins content is pivotal in a strategy of circular economy for plastics [2–12].

Among the key limits of the use and recycling of polyolefin materials is the thermo- and/or photo-oxidative degradation which takes place at all stages of their life cycle (*i.e.*, during processing, storage, and use). The highly reactive free radicals that are generated by heat, radiation, and mechanical shear (often intensified by the presence of metallic impurities) react with the polymer chains leading to chain cracking and loss

of physical and mechanical properties, such as color changes, reduction of impact and tensile strength, and elongation capacity [13–14].

This degradation process is accelerated by UV radiation, therefore exposure to sunlight and artificial lights can have adverse effects on integrity and durability of plastic materials. Greenhouse films are exposed to high UV radiation as well as to heat build-up on the greenhouse supports. In food packaging, the oxidation processes increase with exposure to high temperatures, including contact with hot foodstuff, retort processing and microwave heating.

During the processing, various chemical substances, known as stabilizer additives, are added to the polyolefin material to extend its shelf-life, by inhibiting or retarding the degradation processes [15]. Moreover, structural inhomogeneities built up in thermo- and photo-aged samples have an accelerating role in degradation during subsequent reprocessing, being therefore mandatory to apply proper re-stabilizing additives prior to re-processing [16–17].

Hindered phenol antioxidants, such as butylated hydroxytoluene (BHT) and hindered amine light stabilizers (HALS), like 2,2,6,6-tetramethylpiperidine (TMP) and their derivatives, are widely employed stabilizers, normally added to polyolefins by melt blending [18–20]. The compatibility between polyolefins and additives is closely related to

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their chemical structures and physical properties. The commonly used antioxidants/UV-light stabilizers are relatively low molar mass compounds, structurally different from the apolar polyolefinic matrix. This causes poor additives vs polyolefin compatibility, with consequent stabilizers physical loss by migration, which results in reduced material stability and, in case of food packaging, potential contamination and improper food storage [21–27]. Furthermore, the migration of chemical additives and contaminants from plastic packaging could represent a potential risk to ecosystems [28].

Increasing stabilizers persistence in the polymer bulk by reducing migration phenomena is therefore crucial for enhancing the protection of the plastic artifact and its safety. In the last decade we have developed a new class of non-releasing macromolecular stabilizer additives for polyolefin materials [29–36]. Such additives were obtained using ethylene or propylene-based copolymers containing tuned amounts of suitable olefinic comonomers bearing a stabilizing functional unit (Scheme 1). These macromolecular antioxidants bring together the useful proprieties of both polymeric materials and antioxidant components.

The role of the polymer backbone of the macromolecular additives is to improve the compatibility and, likewise, the miscibility of the additives in polymer matrices with constitutionally similar backbones. In fact, the polymeric nature of the so-obtained macromolecular stabilizer additives with about 1% mol of stabilizing moieties covalently linked to the polymer backbone ensures their good dispersion into polyolefin matrices, and, practically, sets to zero their loss by migration due to the intrinsically non-releasing character, while guaranteeing a very good protection to oxidation [29–36].

Such a strategy allowed us to successfully develop several types of non-releasing antioxidant additives, specifically dedicated to stabilizing the most common families of commercial polyolefins [29–36]. Usually, the procedure requires two synthetic steps: i) the synthesis of olefinic comonomers bearing the stabilizing functionality and ii) the copolymerization or, even better, terpolymerization of the synthesized comonomers with ethylene or propylene (and other common olefins as suitable termonomers) in the presence of a metallocene catalyst (Scheme 1) [29–36].

Clearly, the latter synthetic step can exclusively be conducted in laboratories specialized and equipped for co-polymerization procedures carried out with transition metal-based catalysts. Additionally, these catalysts are often not compatible with the functional moieties required to exert the stabilizing activity on the final material.

The field of polymeric materials showing antioxidant properties is not limited to food packaging but is a research area of great industrial applications, ranging from biomedical, pharmaceutical, cosmetic to materials science [37]. However, the incorporation of functional groups into polyolefins via metal-catalyzed copolymerization remains a difficult

task on an industrial scale. To skip these drawbacks, in this work we have explored a different synthetic strategy to access to polymeric stabilizers under a green and sustainable synthetic approach minimizing the use of hazardous and difficult to handle substances.

When designing and evaluating chemicals and materials, which might be alternative choices to already existing solutions, safety and sustainability considerations should be integrated to ensure transition towards safer and more sustainable products.

Inspired by the “12 principles of green chemistry” and growing environmental concerns [38], mechanochemical methods [39], such as reactive extrusion and ball milling, have recently emerged as simple and effective solvent-free synthesis routes [40–43], and have been identified by IUPAC as one of the 10 technologies that could change the world [44].

The acronym PRODUCTIVELY well describes the spirit of the twelve principles of green chemistry [45–46]. In this framework, mechanochemistry offers the possibility of obtaining useful synthetic methods with low environmental impact, in mild conditions and without organic solvents, exploiting the frictional power as the promoter of chemical reactions in a very efficient way, from the energetic, the timing and atom economy points of view [47].

Post-polymerization functionalization of polypropylene, by grafting reaction in the extruder via melt mixing or less commonly via a solid-state shear extrusion pulverization method, are known [48–51], as well as polymer modifications conducted in solution [52–53]. Few examples of post-polymerization modifications under mechanochemical ball-milling conditions were recently reported, but not on polypropylene [54–55].

Maleic anhydride (MA) grafted polyolefins are an important class of reactive-modified polymers, commonly employed as functional derivatives to form graft copolymers during reactive processing. In view of the above, the aim of this work was an innovative strategy which implies the covalent linking of suitable active stabilizing moieties (ASM) to a polypropylene grafted with maleic anhydride by a mechanochemical process carried out in a ball mill (Scheme 2), working under mild and solvents free conditions.

Specifically, we have projected and synthesized a new family of macromolecular stabilizers, by reactions of polypropylene-graft-maleic anhydride (PP-g-MA 1) with derivatives of BHT (2–3) and TMP (4) run in a ball mill at room temperature (Scheme 2). Therefore, the active stabilizing moieties (ASM) were opportunely decorated with a primary alcohol or amine residue to react with the succinic anhydride portion pending from the polymer backbone of 1 (Scheme 2). Actually, the most common reaction of the anhydride group is with a primary amine giving a β -carboxamide, or with an alcohol to form a β -carboxyester [56] but was reported to occur in solution under hard and not eco-friendly condition i.e. xylene at 125–145 °C under a nitrogen atmosphere for 15 h [56].

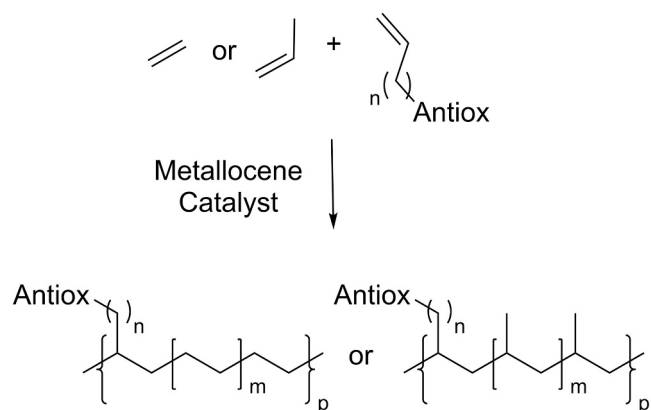
New polymeric radical scavengers based on hindered phenols and hindered amines have been extensively explored in recent years and have demonstrated their effectiveness [29–36,57–62].

Our contribution on the preparation of macromolecular additives perfectly deals with sustainability. As it has been clearly shown by us and by others, the use of macromolecular additives eliminates the releasing of small molecular weight stabilizers while maintaining the stabilization ability of the additive. This is healthy and safe when the polyolefin is used as food or drug contact material and, at the same time, environmental benign since, ensuring a long-lasting stability and an increased shelf life to the polymer, decreases the demand of the production of new plastic material.

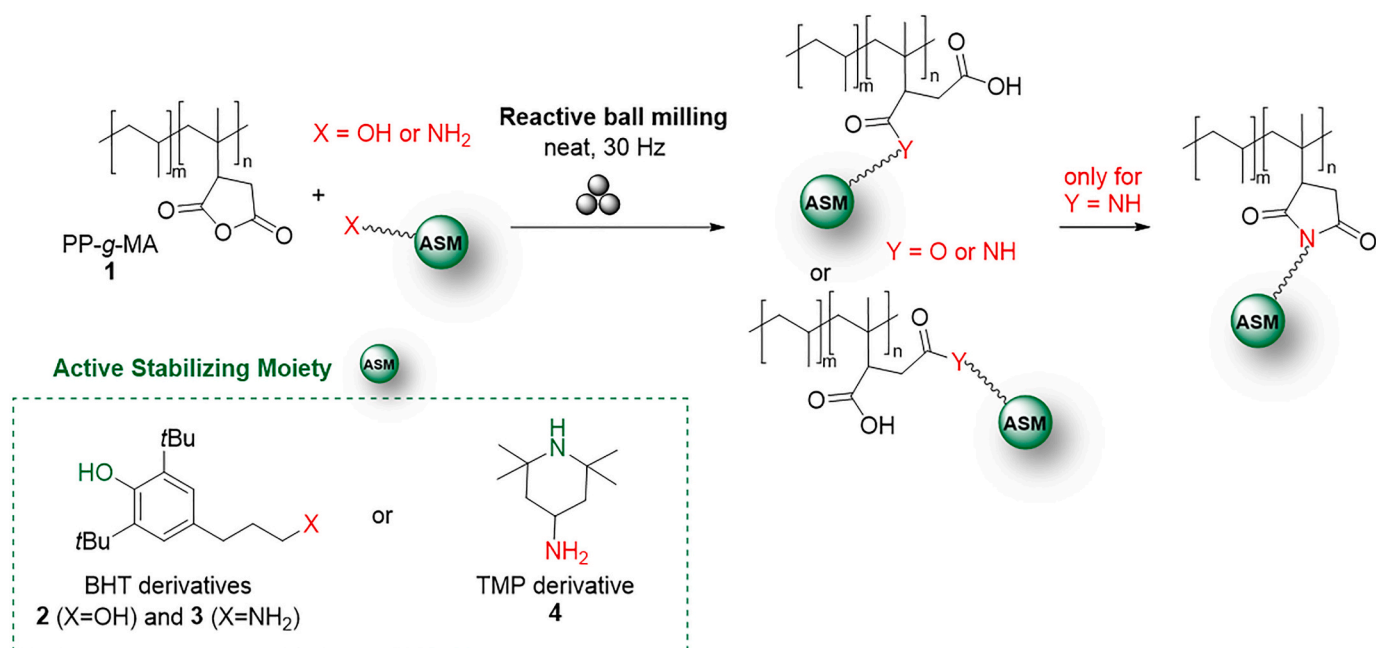
2. Experimental section

2.1. Materials and methods

^1H and ^{13}C NMR spectra were recorded on a Varian Mercury Plus 400



Scheme 1. Copolymerization of ethylene or propylene with olefinic comonomers bearing an antioxidant functionality.



Scheme 2. Graphic representation of the eco-design of the new class of macromolecular stabilizers.

spectrometer using CDCl₃ as solvent. Residual CHCl₃ at $\delta = 7.26$ ppm and central line of CDCl₃ at $\delta = 77.16$ ppm were used as the reference of ¹H and ¹³C NMR spectra, respectively. Solid-state NMR spectra were recorded on a Bruker Avance II 700 MHz NMR spectrometer and compared with literature data [63–64]. Infrared spectra were recorded with a PerkinElmer Spectrum Two FTIR Spectrometer. GC/MS spectra were recorded with a QMD 100 Carlo Erba. ESI-MS spectra were recorded with a JEOL MStation JMS700. Elemental analysis was measured with Elemental Analyzer 2400 series II PerkinElmer. Melting points were measured with Stuart SMP50 Automatic Melting Point Apparatus. All the reactions were monitored by TLC on commercially available precoated plates (silica gel 60 F 254) and the products were visualized with acidic vanillin solution. Silica gel 60 (230–400 mesh) was used for column chromatography. Anhydrous solvents were obtained by the PureSolv Micro Solvent Purification System. The mechanochemical reactions were carried out by mechanical milling using a Micro Ball Mill GT 300 operating at room temperature and in the absence of solvent. The horizontal oscillations in high frequency (30 Hz) performed by the grinding jars and balls result in the intensive grinding and mixing of the samples.

The melting and crystallization behavior of the synthesized polymers was analyzed by differential scanning calorimetry (DSC) using a DSC TA Instruments Q-2000 calorimeter under a nitrogen atmosphere (heating and cooling rate: 10 °C/min). All samples were treated as follows: a first heating run was conducted up to 180 °C, the specimens were then cooled down to –100 °C, and a second heating up to 180 °C was imposed.

Thermal stabilities of the prepared terpolymers were investigated under N₂ atmosphere (flow rate 40 mL min⁻¹) with a PerkinElmer TGA7 analyzer in dynamic mode (heating rate 10 °C/min) from 50 up to 750 °C.

Isothermal experiments TGA were carried out to determine the oxygen induction time (OIT) at 230 °C. To achieve this, the samples are heated at a constant rate in an inert gas atmosphere (nitrogen flow). When the defined temperature is reached, the inert atmosphere is replaced by oxygen. The sample is then held at a constant temperature until the oxidative reaction takes place, indicated by the loss of weight due to sample decomposition. The isothermal OIT value is the time interval between the start of the oxygen flow and the beginning of the oxidation reaction.

Polypropylene-*graft*-maleic anhydride (PP-*g*-MA 1), a PP grade grafted with 8–10 wt% of MA (1×10^{-3} mol/g), was bought from Merck chemical company and used as received.

4-(3-hydroxypropyl)-2,6-di-*tert*-butylphenol (BHT-OH, 2), 4-(3-aminopropyl)-2,6-di-*tert*-butylphenol (BHT-NH₂, 3) were synthesized in our laboratories. BHT-OH 2 is the result of LiAlH₄ reduction of Irganox 1010, a commercial molecular antioxidant widely used as polyolefins stabilizer. Moreover, to obtain a more reactive nucleophile, the conversion of the hydroxyl group of BHT-OH 2 into the amino group of BHT-NH₂ 3 was considered. In fact, derivative 2 was transformed into 3 in two steps by tosylation with *p*-Toluenesulfonyl chloride (TsCl) in pyridine and reaction with NH₄OH at 70 °C for 18 h (Scheme 1S). Additional details and characterization are in the Supporting Information.

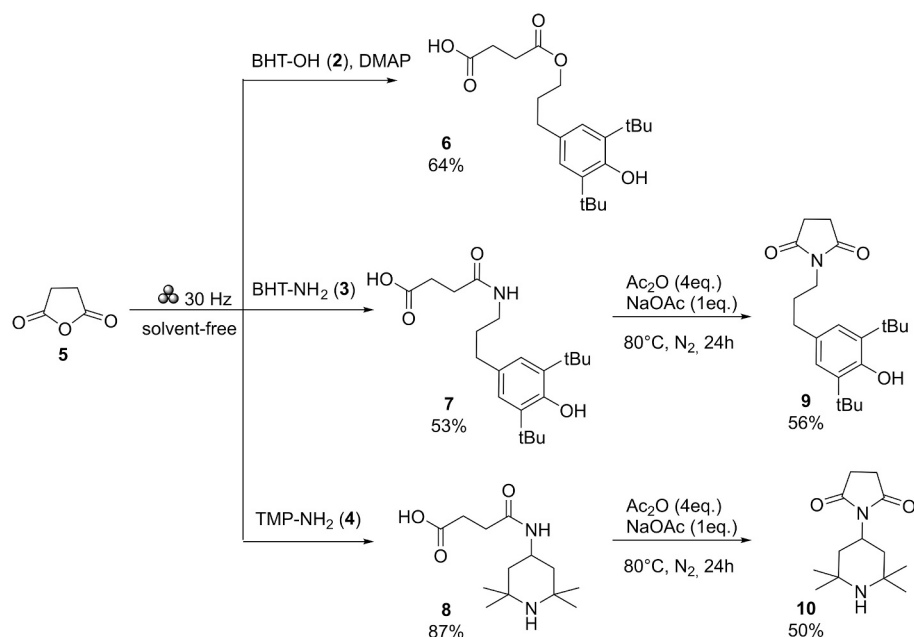
4-amino-2,2',6,6'-tetramethylpiperidine (TMP-NH₂, 4), pentaerythritol tetrakis(3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate) commonly known as Irganox 1010, 4-dimethylaminopyridine (DMAP), *N,N*-diisopropylcarbodiimide (DIC), TsCl, Succinic anhydride 5, were bought from Merck chemical company and used as received without further purifications. Derivates 6–10 (Scheme 3) were synthesized in our laboratories, relative procedure and characterization are in the Supporting Information.

The macromolecules samples PP@OBHT 11, PP@NHBHT 12 and PP@NHTMP 13 obtained after reaction of PP-*g*-MA 1 with 2, 3, and 4, respectively, (Scheme 4) contain the corresponding active stabilizing moieties (ASM) 2,6-di-*tert*-butylphenol (BHT) or tetramethylpiperidine (TMP). All details about their synthesis were reported in the next subsection 2.2 and in the Supporting Information.

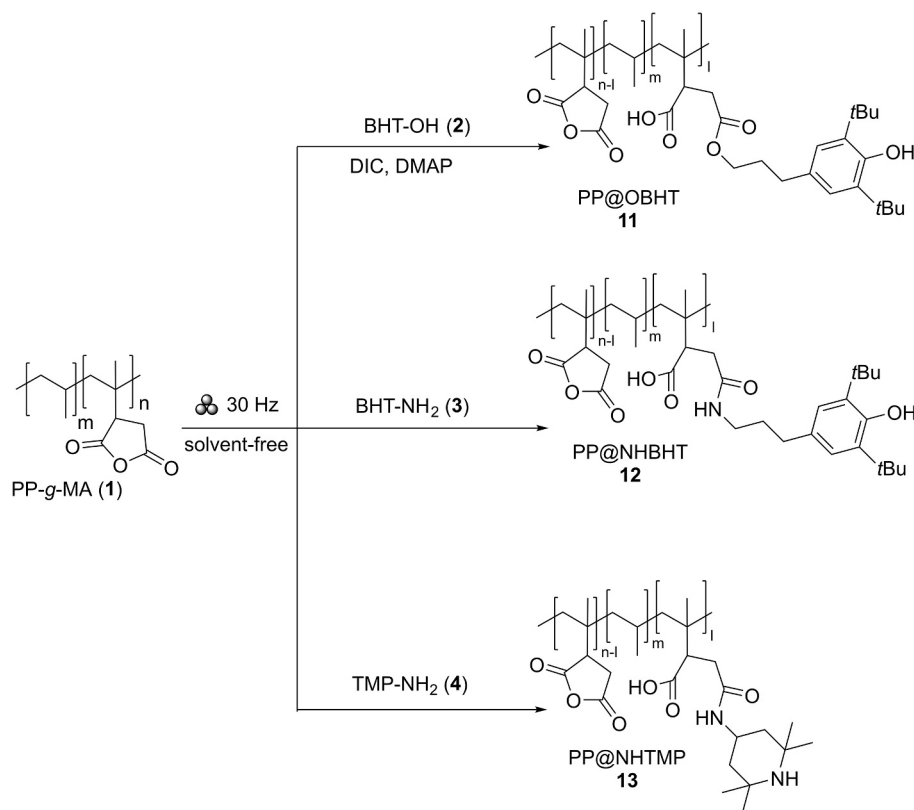
2.2. Mechanochemical functionalization of PP-*g*-MA

PP-*g*-MA 1 (200 mg, ~0.2 mmol of MA), and the active stabilizing moieties (ASM) 2, 3, or 4, respectively, were mixed in a grinding jar (stainless steel, 5 mL) without solvent. The reactions were conducted by reactive ball milling, working at the maximum frequency of 30 Hz (1800 rpm, revolutions per minute with 6 grinding balls (stainless steel, Φ 5 mm).

After ball milling, the polymer material was transferred in a 25 mL solid phase extraction (SPE) polypropylene tube with PE frit, 20 μ m porosity, directly connected through a needle to a two-neck round-



Scheme 3. Reaction of succinic anhydride 5 with derivatives 2–4.



Scheme 4. Synthesis of macromolecular additives 11–13.

bottom flask (Fig. 1). To completely remove unreacted reagents the polymers were washed with very-low-toxic solvents such as ethanol and ethyl acetate (2×5 mL each one) at the top of the list of green solvents and listed as environmentally safe in the industrial solvent selection guidelines (SSGs) [65]. Liquid poured into the tube passes through the filter, which retains the solid polymer, and the filtrate unreacted reagents are collected into the round-bottom flask. Applying vacuum

reduces process time compared to gravity flow. After this fast and easy workup, the recovered macromolecules samples PP@OBHT 11, PP@NHBHT 12 and PP@NHTMP 13 were dried under vacuum. Considering the loading of grafted maleic anhydride in 1 (10 wt%, 1×10^{-3} mol/g of PP-g-MA), the amount of stabilizers insertion was expressed as yield of MA functionalization (see Tables 1–3).

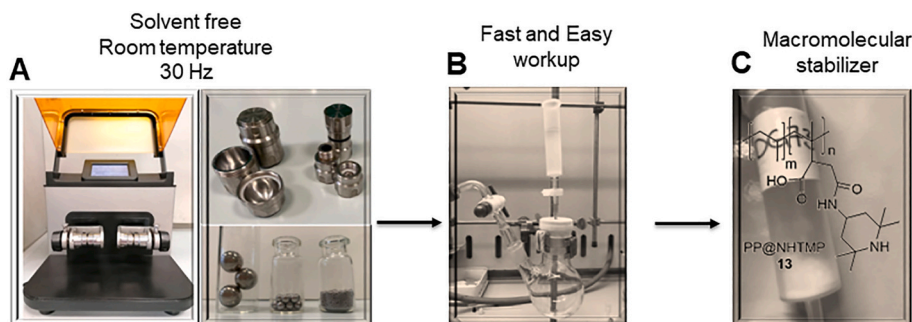


Fig. 1. Mechanochemical process: (A) ball mill system, (B) washing and filtering system, (C) isolated macromolecular HALS 13.

Table 1

Grafting reaction of PP-g-MA 1 (200 mg, ~0.2 mmol of MA) with BHT-OH 2 and estimated MA functionalization (%) for each macromolecular antioxidants PP@OBHT 11.

Entry	Sample	2 ^[a] eq.	DIC ^[a] eq.	DMAP ^[a] eq.	min	(%) MA functionalization
1	MDM33	2	–	2	180	2
2	MDM44	1	1	–	180	5
3	MDM43	1	1	2	180	15
4	MDM48	2	1	0.5	180	11
5	MDM45	2	2	0.5	240	16
6	MDM46	2	2	1	180	17
7	MDM50	2	2	1	60	15

[a] Equivalents considering 0.2 mmol of MA.

Table 2

Grafting reaction of PP-g-MA 1 (200 mg, ~0.2 mmol of MA) with BHT-NH₂ 3 and estimated MA functionalization (%) for each macromolecular antioxidant PP@NHBHT 12.

Entry	Sample	3 ^[a] (eq.)	min	(%) MA functionalization
1	DG79	1	60	1.5
2	MDM27	2	120	15.5
3 ^[b]	MDM28	1.5	240	10
4	DG78	2	30	7.5
5 ^[c]	MDM71	2	120	15.5

[a] Equivalents considering 0.2 mmol of MA. [b] The recovered reagent by MDM27 was reprocessed. [c] (600 mg, ~0.6 mmol of MA).

Table 3

Grafting reaction of PP-g-MA 1 (600 mg, ~0.6 mmol of MA) with TMP-NH₂ 4 and estimated MA functionalization (%) for each macromolecular light stabilizer PP@NHTMP 13.

Entry	Sample	4 ^[a] (eq.)	min	(%) MA functionalization
1	DG69	1	15	2.0
2	MDM15	1	60	6.2
3	MDM16	2	120	20
4	MDM65	4	120	40

[a] Equivalents considering 0.6 mmol of MA.

2.3. Determination of ASM content - construction of calibration curves

Compounds 6–10 were used as standards to identify and quantify the products formed by reacting PP-g-MA 1 with derivatives 2–4 via ball milling process. Relative IR peaks correlated to ester, amide, or cyclic imide groups in compounds 6–10 provide a qualitative indication about the chemical nature of the bond to the polymer portion. Additionally, they were used to quantify the amount of active functionality effectively bonded to the polymer structure by implementation of ATR-FTIR

calibration curves. To this purpose, mixtures of 100 mg of PP-g-MA 1 (10 wt% of MA, 10 mg, 0.1 mmol) were formulated at known concentration of 6–8 (from 3×10^{-3} to 55×10^{-3} mmol), using the micro ball mill to ensure excellent mixing, and their ATR-FTIR spectra were subsequently recorded (Fig. 5SI-10SI). Neat PP-g-MA 1 (Fig. 4SI) shows the characteristic peaks of polypropylene at 2951 and 2917 cm^{-1} (asymmetrical stretching CH₃ and CH₂ respectively), 2868 and 2838 cm^{-1} (symmetrical stretching CH₃ and CH₂ respectively), and the methyl group umbrella mode at 1376 cm^{-1} . Additional bands at 1167, 973 and 841 cm^{-1} are related to the rocking deformations [66–69]. Given the presence of the succinic group, the peaks at 1777 cm^{-1} (symmetric) and 1857 cm^{-1} (asymmetric) related to the stretching of C=O of anhydride are also observable, instead the strong peak at 1712 cm^{-1} is related to the carboxylic C=O stretching of the (major) hydrolyzed portion. As expected, the prepared mixtures show the peaks of the PP-g-MA 1 and the distinctive absorptions related to the compounds 6–8, increasing with the increment of concentration in the polymer matrix.

The relative intensity of the model compounds 6–8 in the mixtures was used for the construction of the IR calibration curves to find out the exact concentration of the related active stabilizer moiety in a given samples by comparison with the set of samples of known concentration (Fig. 5SI-10SI).

3. Results and discussion

3.1. Synthesis of model systems

The macromolecular stabilizers bearing antioxidant or anti-UV moiety were prepared by performing a mechanochemically promoted reactive blending (Scheme 2). To identify and, possibly, quantify the functionalization achieved by reaction of derivatives 2–4 with the anhydride residues of PP-g-MA 1 we studied the reactivity of these three nucleophiles with succinic anhydride 5 under ball milling conditions as reported in Scheme 3.

The reaction of succinic anhydride 5 with alcohol 2 to afford ester 6 required the use of 4-dimethylaminopyridine (DMAP) as catalyst [70]. We performed this reaction both ‘classically’ in solution and under ball milling, obtaining 6 with a comparable yield (see ESI). After several experiments to set-up the optimized ball milling conditions, the best results were achieved using a 5 mL stainless steel jar equipped with six balls of 5 mm in diameter, obtaining 6 in 64% of yield (Scheme 3). The reaction of succinic anhydride 5 with amines 3 and 4 gives amides 7 and 8. Cyclization of 7 and 8 to form imides 9 and 10 required more drastic in solution conditions [71], such as working at 80 °C in acetic anhydride/sodium acetate (Scheme 3).

Ester 6, amides 7 and 8 and imides 9 and 10 reported in Scheme 3 were carefully characterized (see ESI) to have model systems for infrared spectra.

These compounds were, in fact, used as standards to identify the nature of products formed by reacting 1 with 2–4 in the ball milling system and to quantify the amount of active functionality effectively

bonded to the polymer structure by quantitative analysis using Fourier Transform Infrared spectroscopy in Attenuated Total Reflection mode (ATR-FTIR) for fast and objective determination of functionalization degree. The representative functional groups for products 6–10 were investigated by ATR-FTIR spectroscopy, compared with literature data [72–73], and used to prepare calibration curves (see Experimental Section 2.3).

Carboxylic acid and ester have distinctive absorption frequencies, relatively to the C=O stretching, in the range 1700–1730 cm^{-1} and 1715–1750 cm^{-1} respectively. The diagnostic peak pattern for linear chain amides is a C=O stretching in the range 1620–1680 cm^{-1} combined with a strong N–H bending at 1555–1640 cm^{-1} . Cyclic imides have a double carbonyl stretching (1790–1735 and 1750–1680 cm^{-1}). This means that linear chain amides 7 and 8 and cyclic imides 9 and 10 can be distinguished based on their infrared spectra [72–73].

ATR-FTIR spectrum of 6 shows two C=O stretching bands with the characteristic absorption frequencies of carboxylic acid (1712 cm^{-1}) and ester (1724 cm^{-1}) moieties and two peaks at 3590 and 3647 cm^{-1} related to the OH stretching of the carboxylic group and the hindered phenol, respectively (Fig. 2 SI).

Products 7 and 8 (Fig. 2 SI) have the typical peaks associated to the C=O stretching and N–H bending of amide groups (7: 1643 cm^{-1} and 1550 cm^{-1} , 8: 1623 cm^{-1} and 1550 cm^{-1}). Compounds 9 and 10 show two peaks at 1698 cm^{-1} and 1773 cm^{-1} correlated to the symmetric and asymmetric stretching of the imide C=O (Fig. 3SI).

The NMR spectroscopy was also crucial to confirm the structures 6–10, in particular, ^{13}C NMR spectra of the linear chain 6–8 derivatives show asymmetric structures with two resonances assigned to the two different C=O present in the open structures (Fig. 26SI, Fig. 27SI and Fig. 28SI). The cyclic symmetric structure of 9 and 10 was confirmed by NMR analysis with a single C=O signal in the related ^{13}C NMR spectra (Fig. 29SI and Fig. 30SI respectively), proving the intramolecular nucleophilic addition with cyclization. All structures were confirmed also by ESI-MS spectrometry.

Two calibration curves were prepared for ester 6, related to the ester C=O and to the phenolic OH stretching peaks, at 1727 cm^{-1} or 3647 cm^{-1} respectively (Fig. 6SI). Two calibration curves for 7, related to the amidic C=O stretching peak at 1643 cm^{-1} and the phenolic OH stretching peak at 3643 cm^{-1} , are shown in Fig. 8SI. The calibration curve for 8 is related to the amidic C=O stretching peak at 1620 cm^{-1} (Fig. 10SI).

3.2. Synthesis of macromolecules stabilizers 11–13

A solvent-free ball milling mechanochemistry approach, with a smart and easy washing and filtering system (Fig. 1, see details in Experimental Section 2.2), allowed us to isolate the desired macromolecular stabilizers 11–13. Specifically, functionalization of PP-g-MA 1 with derivatives 2, 3 and 4 gave polymeric materials PP@OBHT 11, PP@NHBHT 12 and PP@NHTMP 13 respectively, as reported in Scheme 4. The modifications of the distinctive succinic group in the grafted macromolecular products were evaluated by ATR-FTIR by comparing their spectra with those obtained for the model systems 6–10 and with literature data [72–73]. To set up the method, we prepared a series of polymeric materials PP@OBHT 11 obtained at different reaction conditions (Table 1).

Corresponding ATR-FTIR spectra (Fig. 11SI) show all the typical peaks of the PP-g-MA, included the strong peak at 1710 cm^{-1} related to the carboxylic C=O stretching of the hydrolyzed portion of anhydride. On the left side of this peak, the unresolved characteristic peak at 1730 cm^{-1} related to the formation of an ester bond between BHT-OH and anhydride residue was observed. However, the absorbance value of this signal is not reliable as the peak is not well resolved, hence useless for quantification by the related calibration curve.

On the other hand, the peak at 3647 cm^{-1} related to the phenolic OH stretching is visible and well resolved, significant is the absence of the

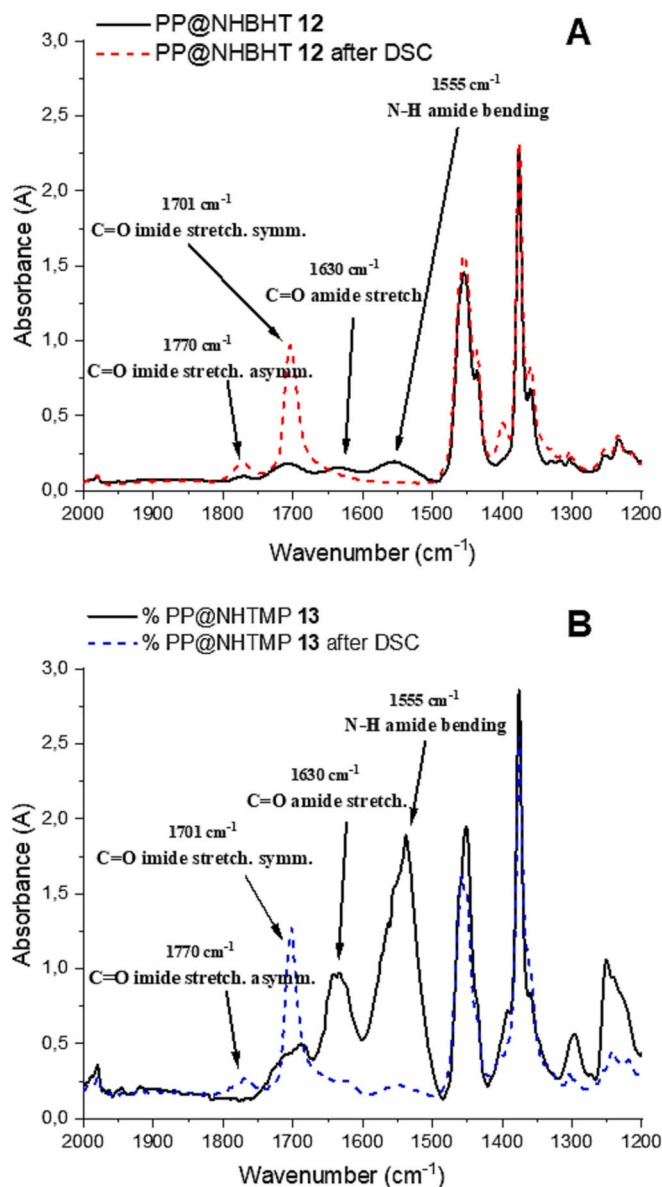


Fig. 2. ATR-FTIR spectra of A) PP@NHBHT 12 (MDM71) and B) PP@TMP 13 (MDM 65), before (full black line) and after (dotted red and blue line respectively) DSC experiments under N_2 . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3427 cm^{-1} FTIR peak related to the OH stretching of the alcohol 2 used in the reaction. It was therefore possible to evaluate the concentration of BHT-OH bonded to the polymer using the calibration curve prepared by exploiting this peak for quantification (Fig. 12SI).

The analysis of data reported in Table 1 shows that employing the same reaction conditions adopted for the synthesis of 6, by reacting PP-g-MA 1 with 2 and DMAP as activation agent after 180 min a very low macromolecular functionalization was obtained (entry 1).

Carbodiimides are commonly used as coupling reagent to prepare amides, esters, and anhydrides from carboxylic acids. In particular, *N,N*-diisopropylcarbodiimide (DIC) is used in solid phase synthesis since the urea byproduct is more soluble and remains in solution. Despite the use of 1 eq. of DIC as coupling agent, the (%) MA functionalization had a small increase from 2 to 5% (Table 1 entry 2). Instead, employing the Steglich esterification conditions, with DIC as coupling reagent and DMAP as activation agent (Table 1 entry 3–7), resulted in a good increment of functionalization (11–17%) corresponding to a

macromolecular PP@OBHT **11** with $0.11\text{--}0.17 \times 10^{-3}$ mol/g of active stabilizing moiety. Variations on stoichiometry or reaction time did not have relevant impact on the % of functionalization.

Following the reaction of PP-g-MA **1** with BHT-NH₂ **3**, two signals appeared at 1630 cm^{-1} and 1555 cm^{-1} related respectively to the C=O stretching and N—H bending of the amidic group (Fig. 13SI), suggesting that the reaction leads to the formation of the secondary amide PP@NHBHT **12**. Moreover, it was possible to evaluate the concentration of **3** bonded to the polymer using the calibration curve built-up with the peak at 3643 cm^{-1} (Fig. 8SI C) related to the phenolic OH stretching (Fig. 14SI A). Increasing equivalents and reaction time we achieved an increase in the MA functionalization (Table 2 entry 2). The excess and unreacted molecular stabilizers were recovered unchanged by evaporation of the solvents used for polymer washing (see Experimental Section 2.2). In the case of MDM27 (Table 2 entry 2) the recovered reagent was reprocessed in MDM28 (Table 2 entry 3) proving the high sustainability of the process.

In addition, to verify the reproducibility, the reaction was conducted with 600 mg of PP-g-MA (Table 2 entry 5) confirming that the use of 2 equivalents of **3** (considering 0.2 mmol of MA) for 2 h represent the best compromise to attain a 15.5% of MA functionalization, corresponding to a macromolecular PP@NHBHT **12** with 0.15×10^{-3} mol/g of ASM.

To prepare macromolecular light stabilizer PP@NHTMP **13** all the reactions were carried out using 600 mg of PP-g-MA **1** (Table 3). The infrared spectra compared with those of **8** and **10** confirmed the formation of the amide bond with the C=O stretching at 1620 cm^{-1} and N—H amidic bending at 1555 cm^{-1} (Fig. 15SI).

The absorbance value at 1620 cm^{-1} of the prepared macromolecular HALS PP@NHTMP **13** was fitted with the calibration curve prepared with **8** (Fig. 10SI) to estimate the concentration of stabilizers bonded to the polymer (Fig. 16SI).

Varying reaction time or stoichiometry (Tables 3), we observed that the number of equivalents of **4** (considering the mmol of MA) strongly influences the amount of active stabilizing moiety bonded to the polymer.

Overall, it was evidenced that working in excess of TMP-NH₂ leads to an increase in the amount of stabilizer grafted onto the polymer. Higher value of MA functionalization (40%), corresponding to a macromolecular PP@NHTMP **13** with 0.4×10^{-3} mol/g of HALS active moiety, resulted when 4 eq. of TMP-NH₂ **4** was used (Table 3 entry 4).

In summary, using ASM decorated with a primary amine as nucleophile a very efficient mechanochemical MA functionalization with a total recovery of the unreacted starting materials (>98% conversion) was achieved.

Together with FTIR, macromolecular stabilizers **11–13** were characterized by solid-state NMR spectroscopy (See Fig. 32SI–34SI) which is widely used to obtain structural information on non-crystalline heterogeneous materials [53,74–76].

The new signals observed in the $\{^1\text{H}\}\text{-}^{13}\text{C}$ cross-polarization SSNMR spectra of macromolecular BHT **11** and **12** support the occurrence of polymer functionalization. Specifically, the new signals in the aromatic (120–155 ppm) and aliphatic carbon region (29–34 ppm, Fig. 32SI–33SI) are consistent with the presence of a butylated hydroxytoluene moiety. New signals were observed also in the Csp³ region of the spectrum of the macromolecular HALS **13** (Fig. 34SI), confirming PP-g-MA **1** functionalization.

3.3. Thermal behavior of macromolecular stabilizers 11–13

The thermal behavior of macromolecular BHT **11** and **12** and HALS **13** stabilizers with the highest % of MA functionalization (MDM46, $0.17 \cdot 10^{-3}$, MDM71, $0.15 \cdot 10^{-3}$ and MDM65, $0.4 \cdot 10^{-3}$ mol/g respectively) was studied through thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) experiments (Fig. 17SI–19SI). Table 4 shows the thermal stability parameters obtained by dynamic TGA measurements carried out in N₂ and O₂ atmosphere: the

Table 4

Thermal stability parameters of PP-g-MA **1** and macromolecular PP@OBHT **11**, PP@NHBHT **12**, PP@NHTMP **13** with the highest % of MA functionalization.

Sample	Dynamic TGA in N ₂			Dynamic TGA in O ₂			OIT 230 °C in O ₂ min
	T ₉₀ (°C)	T ₅₀ (°C)	T _{max} (°C)	T ₉₀ (°C)	T ₅₀ (°C)	T _{max} (°C)	
PP-g-MA 1	358	450	466	259	310	312	1,2
PP@OBHT 11 MDM46	379	451	468	301	349	361	>30
PP@NHBHT 12 MDM71	399	452	465	310	378	390	>30
PP@NHTMP 13 MDM65	382	450	465	281	332	324	3,8

temperatures corresponding to 10% (T₉₀), 50% (T₅₀) weight loss and to the maximum of the dTG derivative curves (T_{max}).

No significant variations are observed in T₅₀ and T_{max} values obtained from the TGA experiments under N₂ atmosphere, confirming that the presence of the radical scavenger portion does not modify the thermal properties of the polypropylene bulk.

Conversely, the presence of the stabilizer moieties bonded to the PP-g-MA strongly influences the value of T₉₀. In particular, PP@OBHT **11**, PP@NHBHT **12** and PP@NHTMP **13** show a T₉₀ from 20 up to ca. 45 °C higher than that recorded for the PP-g-MA **1** blank.

The increase in polymer stability, as expected, is more evident during the measurements carried out under O₂, that is under thermo-oxidative conditions. The oxygen presence causes a more rapid degradation of PP-g-MA **1** that shows a T₉₀ and T₅₀ corresponding to 259 °C (358 °C in N₂) and 310 °C (450 °C in N₂), respectively. In a similar way to what occurred in N₂ atmosphere, the presence of the antioxidant functionalities bonded to PP-g-MA causes an increase in the thermal stability of the polymers **11–13** showing a T₉₀ of about 20–50 °C higher than that recorded for the PP-g-MA **1** blank. Under O₂ atmosphere, also the T₅₀ and T_{max} values remarkably increase, especially for the polymers **11** and **12**, containing the BHT moiety.

These results are not surprising, in fact, hindered phenolic antioxidants, also known as primary antioxidants, are used to protect the polyolefin materials from thermal-oxidative degradation by blocking the reactions of free radical with molecular oxygen. Conversely, HALS are extensively used to inhibit the photo-oxidation of polymeric materials [77].

The determination of the Oxidative Induction Time (OIT) is a widely used method in the thermal analysis of polymers. This relative measure of the resistance to oxidative decomposition of the polymer materials was here determined by means of TGA measurements carried out at 230 °C (Fig. 18SI). For PP@NHTMP **13** (MDM65) we obtain an OIT three times higher than for PP-g-MA **1**. While for PP@OBHT **11** (MDM46) and PP@NHBHT **12** (MDM71) the OIT values are at least 25 times higher than that of the PP-g-MA blank (see Table 4 and Fig. 18SI).

Differential scanning calorimetry (DSC) allowed us to investigate the thermal behaviour of the additives and to verify their stability under the conditions occurring during the polypropylene melt blending extrusion process. The DSC melting endotherm and crystallization exotherm of the polymeric samples (Fig. 19SI) showed that the T_g values of the PP samples are almost constant.

As discussed previously, the macromolecular materials **12** and **13** exhibiting the amide bond can undergo cyclization with formation of the corresponding cyclic imide. As widely documented by the literature, cyclization of the β-carboxamide to the cyclic imide requires heat and is accelerated by the presence of an acid catalyst [56,71,78–81]. These

circumstances did not occur during the synthesis of the additives *via* ball milling, however the temperatures reached during the DSC and TGA experiments caused the cyclization and the consequent water release. This result can be explained by analyzing the ATR-FTIR spectra recorded on the macromolecular stabilizers **12** and **13** soon after the DSC analysis (Fig. 2). The infrared spectra of both PP@NHBHT **12** and PP@NHTMP **13**, recovered after DSC assay, show a changing in the characteristic peaks of the amide bond (1630 and 1555 cm^{-1}) which disappear to give rise to two new peaks at 1701 and 1770 cm^{-1} , assigned to the imide formation.

By heating it was possible to convert the amide group into an imide group, which being chemically more stable than the amide, allowed to improve the stabilizing capacity of the additive. Although here the heat treatment was carried out by DSC and TGA, it is reasonable to assume that the cyclization of the amide to imide could also occur upon the addition of the macromolecular material as additive during the processing of the polymer, increasing the stabilizing ability of the macromolecular radical scavengers. Heat stabilizers are antioxidants that are used to protect polymers and biopolymers from the degrading effects of heat during processing or use [82].

Usually, for commercial low molecular weight stabilizers as Irganox 1076 (a butylated hydroxytoluene derivative) and Tinuvin 770 (a tetramethyl piperidine derivative) the recommended concentrations between 0.05 and 1.0 wt% provide long term thermal stability to the polyolefinic material.

These concentrations correspond to 0.01–0.02 mol of active stabilizing moiety (ASM) for 1 kg of polymer, therefore, considering the % MA functionalization of the macromolecular additives **12** and **13** ($0.15 \cdot 10^{-3}$ and $0.4 \cdot 10^{-3}$ mol/g respectively) it would be possible use 100 g of **12** or 25–50 g of **13** to stabilize 1 kg of polyolefinic material.

The use of these macromolecular stabilizers as additives could also improve the quality of the recycled material, limiting the thermal degradation that usually occurs during the mechanical recycling step [83–86] and reducing the total amount of additive to add to the polymer materials.

4. Conclusion

We developed a straightforward solvent-free mechanochemical synthesis of macromolecular stabilizers PP@OBHT **11**, PP@NHBHT **12** and PP@NHTMP **13**. This work is based on a careful molecular design and planning of chemical syntheses to reduce adverse consequences, as expected by Green Chemistry (GC12 Inherently Safer Chemistry for Accident Prevention).

In case of **12** and **13** the choice of the better nucleophile leads in increasing % of MA functionalization and the possibility to recover a clean unreacted starting material, with high yield conversion (>98%), and the possibility to reuse it; pursuing the incorporation of all starting materials used in the reaction into the final products, thereby reducing the depletion of raw materials and generation of waste (GC2 Atom economy).

Leaving out organic solvents contributed to meet GC1 (Pollution Prevention) and GC5 (Safer Solvents and Auxiliaries) facilitating the synthesis of products otherwise difficult to access.

The analytical ATR-FTIR technique allowed to control the reaction progress in accordance with the GC11 (Real-time analysis for pollution prevention).

This process provides alternative routes to a new class of BHT and HALS based macromolecular materials, opening the way to high value resources to face the challenges in recycling post-consumer polyolefins for a circular economy. Furthermore, these results provide a general solid-state method for post-functionalization of PP-g-MA and should stimulate further developments, as highlight the versatility and the enormous potential of reactive solid-phase chemistry.

Mechanochemistry offers an environmentally sustainable approach to prepare and process molecules and materials and offers a new

research space full of opportunities, however, its full industrial potential has not yet been realized. This work is a further row on the opportunities offered and challenges laying ahead for the adoption of mechanochemical manufacturing technologies into industry.

The potentiality of polypropylene, one of the most versatile polymers available on the market with countless applications, is well known and for this reason we believe in the impact of our research in the industrial sector. Our purpose is proof of concept to illustrate that this idea can be successful, and we hope this outlook will stimulate and accelerate such development.

CRedit authorship contribution statement

Mattia Di Maro: Investigation, Formal analysis, Data curation. **Domitilla Giraldi:** Investigation. **Stefano Menichetti:** Writing – review & editing, Funding acquisition, Conceptualization. **Simona Losio:** Writing – review & editing, Investigation, Formal analysis, Conceptualization. **Paola Stagnaro:** Writing – review & editing, Investigation, Formal analysis, Conceptualization. **Roberto Utzeri:** Writing – review & editing, Investigation, Formal analysis. **Linda Cerofolini:** Investigation, Formal analysis. **Marco Fragai:** Writing – review & editing, Investigation, Formal analysis. **Caterina Viglianisi:** Writing – review & editing, Writing – original draft, Supervision, Methodology, Funding acquisition, Conceptualization.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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