



Acyloxyimide derivatives as efficient promoters of polyolefin C–H functionalization: application in the melt grafting of maleic anhydride onto polyethylene

Mamy Daniel Rakotonirina, Marc Baron, Didier Siri, Anouk Gaudel-Siri, Sébastien Quinebeche, Jean-Jacques Flat, Didier Gigmes, Philippe Cassagnau, Emmanuel Beyou, Yohann Guillaneuf

► To cite this version:

Mamy Daniel Rakotonirina, Marc Baron, Didier Siri, Anouk Gaudel-Siri, Sébastien Quinebeche, et al.. Acyloxyimide derivatives as efficient promoters of polyolefin C–H functionalization: application in the melt grafting of maleic anhydride onto polyethylene. *Polymer Chemistry*, 2019, 10 (31), pp.4336-4345. <10.1039/C9PY00672A>. <hal-02360910>

HAL Id: hal-02360910

<https://hal.science/hal-02360910v1>

Submitted on 3 Feb 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

Acyloxyimide Derivatives as Efficient Promoters of Polyolefins C-H Functionalization: Application in the Melt Grafting of Maleic Anhydride onto Polyethylene

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Mamy Daniel Rakotonirina,^{a,†} Marc Baron,^{b,†} Didier Siri,^a Anouk Gaudel-Siri,^a Sébastien Quinebeche,^c Jean-Jacques Flat,^c Didier Gigmes,^a Philippe Cassagnau,^b Emmanuel Beyou,^{b,*} Yohann Guillauneuf^{a,*}

Acyloxyimides as new H-abstracting agent have been developed for the radical grafting of maleic anhydride (MA) onto polyethylene in the melt state. Their model decomposition in DMSO-*d*₆ as well as in tetradecane that mimic polyolefins were performed. These studies confirmed first the complete decomposition of N-acetoxypthalimide (NAPI) in 1 hour at 180°C by a N-O bond dissociation mechanism and also the patching of the produced macroradicals by the phthalimide group. The reaction was then performed in a mini-extruder at 190 - 250°C and the hydrogen abstraction ability of N-acyloxyphthalimide (NAP)-, N-acyloxynaphthalimide (NANP)- and N-acyloxysuccinimide (NAS)-based derivatives was demonstrated. Optimal experimental conditions were determined by varying the initial MA content and the degree of grafting of MA was quantified by infra-red spectroscopy. The MA grafting degree was as high as 2.98 wt% when using tBu-NAP as H-abstracting agent at 230°C with only a slight modification of the PE chains structures as proved by rheological experiments while the use of a peroxide (L101) lead to a lower grafting degree (1.9 wt%) and a cross-linking of the polymer chains confirmed by the three – five fold higher complex viscosity.

Introduction

Millions tons of polyolefins (mainly polyethylene (PE) and polypropylene (PP)) are produced each year. Although they are interesting inert and non-polar materials, some adhesion on their surfaces or their blending with other polar matrixes are desired.¹⁻⁶ Post-functionalization of polyolefins through C-H functionalization⁷ has received considerable attention in recent years either via metal catalyzed methods⁸⁻¹² or via organic reagents¹³⁻¹⁷. Industrially, polyolefins modified with maleic anhydride (MA) as polar co-monomer is a commercially-available product that exhibit enhanced adhesion to polar materials such as polyamides, metals, and glass. They are also used as compatibilizing agents that lead to an improvement of impact properties.¹⁸⁻²¹ These products are classically produced by the melt extrusion of the polyolefin and MA in presence of alkyl peroxides as radical initiators (Figure

1).^{14, 22-30} This process creates reactive radical sites that may initiate the graft modification of polymers in presence of a vinyl monomer. The main drawback of the grafting by a radical pathway is the low selectivity of the alkoxyl radicals generated from the dissociation of peroxides, leading to side reactions such as coupling, chain scission and homopolymer formation.^{23, 31} Nevertheless, until now, peroxides remain the conventional radical initiators used in all of the reactive extrusion systems. Ideally, the melt modification of a polyolefin should be performed without any drastic modification of the polymer backbone.

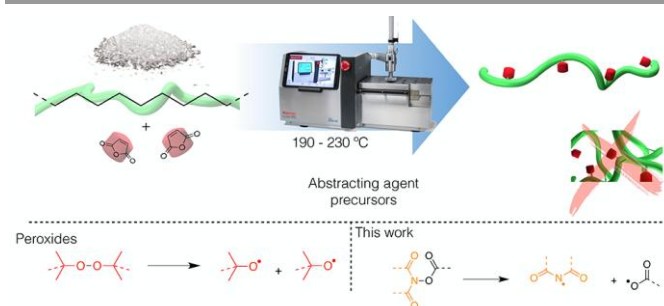


Figure 1. Melt grafting of maleic anhydride (MA) onto polyolefins by a radical pathway.

To achieve this objective, hydrogen abstraction onto the polymer backbone has to be done at high temperature ($T > 160^\circ\text{C}$) to reach convenient viscosity without any degradation of the polymer under shearing while creating radical sites on

^a Aix-Marseille-Univ, CNRS, Institut de Chimie Radicalaire, UMR 7273, F-13397 Marseille, France, Email: yohann.quillauneuf@univ-amu.fr

^b Université de Lyon 1, CNRS, UMR5627 IMP/LMPB, Villeurbanne, France, Email : emmanuel.beyou@univ-lyon1.fr

^c ARKEMA, Centre d'Etude de Recherche et de Développement, 27470, Serquigny, France.

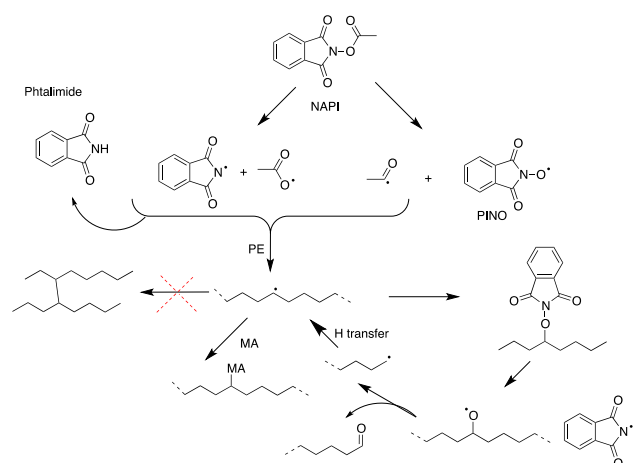
† These authors contributed equally.

Electronic Supplementary Information (ESI) available: [Experimental details and NMR analyses of the acyloxyimides. FT-IR analyses of the MA-g-PE polymers and the calibration curve used for the grafting degree measurement]. See DOI: 10.1039/x0xx00000x

the polymer backbone which may only initiate the graft copolymerization of a second monomer without formation of both homopolymer or cross-linked materials (Figure 1).^{29, 32}

Therefore, the reaction parameters, such as the amount of peroxide,³³⁻³⁶ the monomer concentration^{19, 35} and PE structure,²⁴ have been modified to find the optimal parameters to get the best materials. Bhattacharya et al.³⁷ showed that the use of styrene as comonomer during the grafting reaction of maleic anhydride onto PE lead to a higher degree of grafting and less crosslinking. In a similar manner, Chaudhary et al.³⁸ showed that the scavenging of carbon-centered radicals by nitroxides and its derivatives is able to control the crosslinking of polyethylene chains initiated with peroxides. Passaglia and coworkers³⁹ as well as Beyou and coworkers^{29, 30} used nitroxides to prepare functionalized polyolefins either by using functionalized nitroxides or by performing a further nitroxide mediated polymerization to obtain comb-like polymer chains.

Recently, nitroxyl ethers (NORs) based radical generators (Irgatec 76, CIBA) were developed for efficient radical modification of polyolefins by maleic anhydride at temperatures above 250°C.⁴⁰ In the search for viable alternatives to peroxides, we have recently shown that *N*-acetoxy-phthalimide (NAPI) was efficient in the graft modification of low-density polyethylene (LDPE) at temperatures above 190°C.⁴¹ Based on DFT calculations, we designed such compound that is supposed to cleave homolytically into acyloxyl and amidinyl radicals at 190-230°C (Scheme 1).⁴¹ A MA grafting degree of 2.4 wt% was thus obtained. For comparison, the use of the L101 peroxide yields a PE grafting degree in the range 0 wt% to 1.4 wt% depending on the experimental parameters. The use of peroxides also leads to an important increase of the complex viscosity due to unwanted crosslinking reactions contrary to the case of NAPI.⁴¹ Recently we extend the scope of polymers that could be functionalized using NAPI to polyesters^{42, 43} and polyamides⁴⁴.

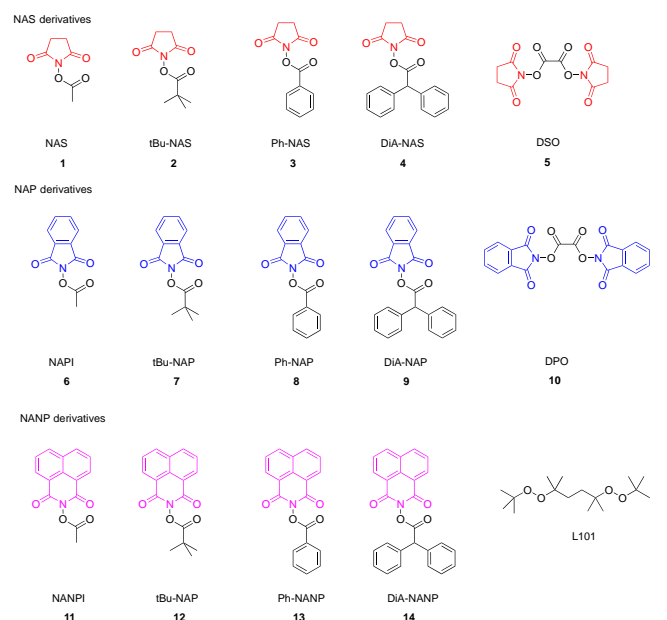


Scheme 1. Mechanism of MA grafting onto PE using NAPI as H-abstractor.

Since this pioneering study, Leibfarth and coworkers¹⁶ developed another amidinyl type precursor and showed that

xanthylation of polyolefins was possible using a specific *N*-xanthylamide. In this work either light irradiation or peroxide initiation were required to perform the functionalization. The cross-linking was not monitored and the functionalization was performed under inert conditions and in a halogenated solvent. Moreover, Chen and coworkers used also *N*-hydroxyphthalimide (NHPI) to aminate polyethylene.¹⁷ They extended the work of Inoue *et al.*⁴⁵ on the radical amination of C(sp³)-H bond to linear low *M_n* polyethylene. The reaction was thus performed at 110 °C in tetrachloroethane, conditions that are hardly compatible with an industrial process.

As we are more interested in industrial-related processes, we still focused on the grafting of the maleic anhydride monomer onto LDPE by reactive extrusion and thus to get further insights in the mechanism of the reaction and to still optimize the grafting, novel NAPI-derivatives were designed (Scheme 2). They were tested at 190°C and 230°C. The nature of the alkyl and the amidinyl moieties were tuned to enhance/avoid their ability to abstract hydrogen atoms and to avoid the side-reactions such as crosslinking that modified the rheology of the PE derivative.



Scheme 2. New acyloxyimide H-abstracting agent precursors based on the *N*-acetoxyphthalimide (NAPI) structure.

Experimental Section

Materials

All reagents and solvents were purchased from Aldrich or Alfa Aesar and used as received without further purification. All the products were prepared with analytical purity up to accepted standards for new organic compounds (> 98 %). All the new H-abstracting agents are described in ESI.

Grafting of Maleic Anhydride (MA) onto PE in presence of Acyloxyimides or L101.

In a typical process, 5 g of LDPE, MA (4 wt% or 2 wt%), NAP- or NNP- or NAS-derivatives (0.35–0.87 wt%) or L101 (0.18 wt%) were added in the preheated mini-extruder (Thermo Scientific HAAKE™ MiniCTW micro-conical twin screw compounder, 7 ml) simultaneously at a rotor speed of 60 rpm and a temperature of 110°C. This type of extruder allowed us to control the processing residence time from the recirculation of the molten polymer in the chamber. After 20 min, the temperature was increased to 190°C for 60 min (or 230°C for 7.5 min) to ensure fully decomposition of NAP-, NNP- and NAS-derivatives, and 160°C for 7.5 min in presence of L101 (8 half-time life of L101). After that, the products were recovered and extensively washed (4 days) with a purifying solvent such as THF (9 g) and dried at 100°C under vacuum for 24h to remove the residual MAH.

¹H NMR NAPI decomposition

A solution of NAPI in DMSO-*d*₆ (100 mg in 5 mL) was prepared and then poured in various NMR tubes (500 µL per tube). The various tubes were then heated up to 180°C for different times. After cooling, 100 µL of a isopropanol solution (5.23 10⁻² mol.L⁻¹) was added as an external standard. The tubes were then analyzed by ¹H NMR.

Model NAPI decomposition in tetradecane

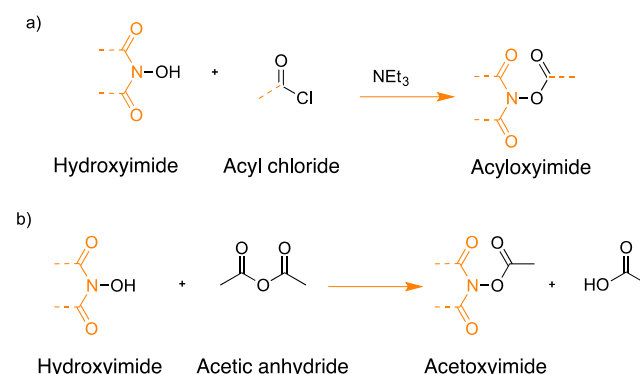
A solution of NAPI in tetradecane (1.95 10⁻² mol.L⁻¹) was prepared and then heated up to 190°C for two hours to ensure complete decomposition. After cooling the crude medium was filtered to remove any remaining NAPI and/or NAPI decomposition products and then analyzed by FTIR.

Results and Discussion

Synthesis of NAPI derivatives

The homolytic decomposition of the NAPI should mainly lead to the amidinyl and acetoxyl radical as described in Scheme 1. The behavior of such acyloxyl radical is not clearly stated in the mechanism and it could produce a methyl radical by decarboxylation and/or a hydrogen abstraction reaction to generate acetic acid. If decarboxylation occurs, a methyl radical is generated that could participate to H-abstraction. The generation of such methyl radicals by β-scission of alkoxy radicals is a well known side-reaction that occurred during the radical grafting or cross-linking in presence of peroxides. Consequently, we were interested in changing the alkyl part of the acyloxyl radical and replacing the methyl moiety by other moieties that are more or less prone to decarboxylation and whose released alkyl radicals should have different reaction paths. Herein, five acyloxyphthalimide derivatives were synthesized: (a) acetoxypthalimide (NAPI, **6**), (b) phthalimido benzoate (Ph-NAP, **7**), (c) phthalimido pivalate (tBu-NAP, **8**) (d) Phthalimido diphenylacetate (DiA-NAP, **9**) and (e) diphthalimido oxalate (DPO, **10**). Each targeted phthalimide derivative was readily prepared through a single synthetic step in high yield (60 - 90%). The general procedure was inspired by Hamaker et al.⁴⁶ and Dalal et al.⁴⁷ wherein an activated

hydroxyphthalimide reacted with a corresponding acyl chloride at room temperature in dry dichloromethane or dry tetrahydrofuran (Scheme 3a). For the acetoxyl derivative, the acetic anhydride was used instead of acyl chloride following the method described by Saha⁴⁸ (Scheme 3b).



Scheme 3. General synthetic pathway to prepare acyloxyimides.

The purification of the crude products consisted in either simple precipitations or washings with water. In particular, DPO (**10**) is a very interesting compound since upon dissociation only CO₂ and amidinyl type radicals should be produced.

Mechanistic investigation

In order to shed some light on the grafting mechanism, model experiments were performed. First the decomposition of NAPI at 180°C was monitored by ¹H NMR. Deuterated dimethylsulfoxide (DMSO-*d*₆) was chosen to ensure a good solubility of both the reactants and products. Before heating, only peaks attributable to the hydrogen atoms of NAPI were observed (i. e. 8.00 – 7.93 ppm (dd, 4H) corresponding to the aromatic hydrogen atoms and 2.45 ppm (s, 3H) corresponding to hydrogen atoms of the acetoxyl group). After heating at 180°C, for one hour (Figure 2a), additional peaks were present in the ¹H NMR spectrum.

In particular, a peak at 1.91 ppm was observed and was ascribed to the formation of acetic acid. Furthermore, the appearance of peaks around 7.83 ppm could be ascribed to the combination of phthalimide and N-hydroxyphthalimide (NHPI) that have similar chemical shifts in DMSO. Integration of the ¹H NMR spectrum via an external standard (isopropanol) led to the determination of the molar balance and also to the rate of both disappearance and formation of the various components. Decomposition of NAPI was monitored by following the signals corresponding to hydrogen atoms of the acyloxy moiety (2.45 ppm) as well as hydrogen atoms of the phenyl ring of the phthalimide moiety (8–7.93 ppm).

These analyses indicated a complete decomposition of NAPI after 1 hour at 180°C. In the same time, integration of the peak attributed to acetic acid increased and led to a concentration that is roughly the one of the initial NAPI.

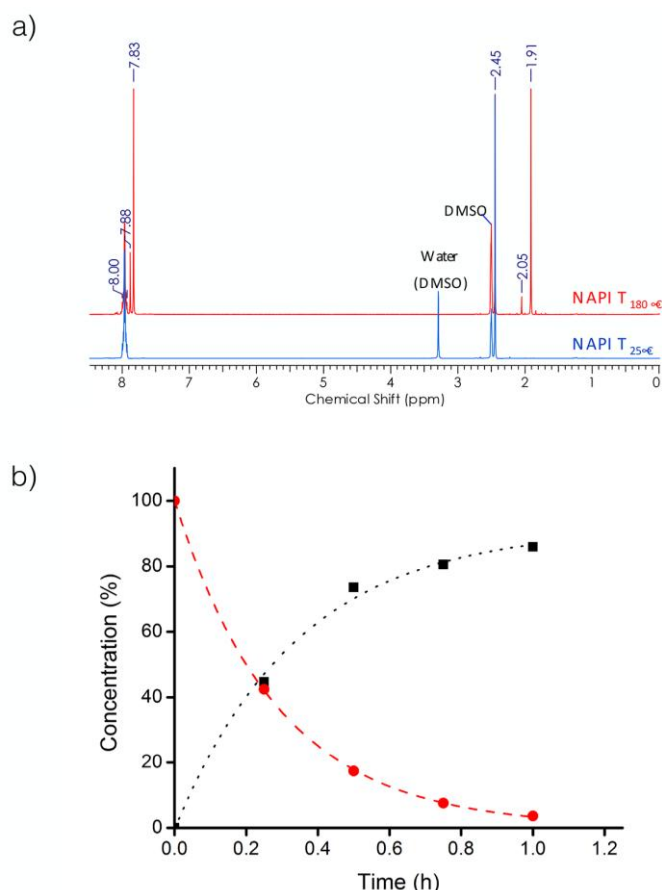


Figure 2. a) ¹H NMR spectra of NAPI in DMSO-*d*₆ at 25 °C and after one hour at 180 °C. b) Evolution of the relative concentration of both NAPI and acetic acid versus time during the decomposition of NAPI ($9.75 \times 10^{-2} \text{ mol.L}^{-1}$) in DMSO-*d*₆ at 180 °C

According to this result, we can conclude that NAPI decomposed mainly by the N-O dissociation while the released acyloxy radicals abstract hydrogen atoms rather than undergo a decarboxylation reaction. This result is surprising considering the extensive literature data about the fast decarboxylation reaction of aliphatic acyloxy radicals.^{49–52} Nevertheless the high temperature used in this study and the H-abstraction ability of DMSO⁵³ could explain that H-abstraction competes favorably in that case with the decarboxylation reaction and thus acetic acid was observed. The decomposition of other acyloxyimides also presented acid production (benzoic, pivalic acid, etc.). The complete kinetic analysis of these decompositions will be reported in a forthcoming study.

Then, the decomposition of NAPI was performed at 190 °C for 2 hours in tetradecane that is used to mimic the polyolefin. In this solvent, it should be mentioned that NAPI as well as NHPI and phthalimide are not soluble at room temperature. At the end of the reaction, the medium was thus cooled and filtered to remove any remaining NAPI and reaction products and the tetradecane liquid phase was analyzed by FTIR (Figure 3). We can observe the appearance of a new peak located at 1738 cm^{-1} that could be ascribed to the grafting of an imide group onto the polymer backbone coming from the decomposition of NAPI (scheme 1). This experiment confirmed

both the production of alkyl macroradicals by H-abstraction onto the tetradecane and the patching of macroradicals either by the amidinyl radical or by the PINO nitroxide. The PINO could be produced either by a minor C-O decomposition of the NAPI or by the reaction of the amidinyl radical with oxygen. Once these mechanistic considerations investigated, we focused on structure-reactivity relationships using the various alkyl groups and also succinimide (**1-5**) and naphthalimide (**11-14**) amidyl-based radicals to test the influence of the aromatic ring and the cycle size on the efficiency of the MA grafting at 190 and 230 °C.

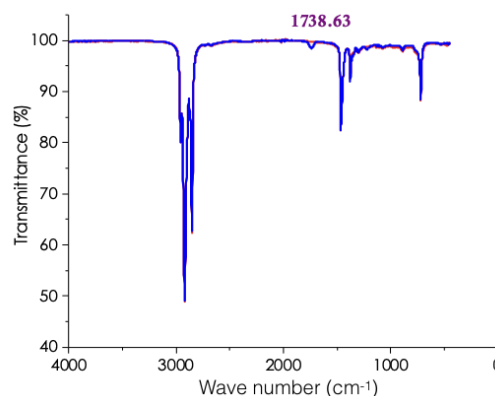


Figure 3. FTIR spectra of the pristine tetradecane and the tetradecane that was reacted with $1.95 \times 10^{-2} \text{ mol.L}^{-1}$ of NAPI at 19 °C for 2 hrs.

Indeed, we previously showed⁴¹ that the optimal experimental conditions obtained in presence of NAPI were based on the use of 2 wt% of MA and 0.5 wt% of NAPI, at 190 °C for 1 h or at 230 °C for 7.5 minutes, giving respectively a MA grafting degree of 1 wt% and 1.1 wt%. Moreover, their viscoelastic behavior showed only a slight change in the molecular structure of PE chains after the chemical modification.

H-abstraction ability of the acyloxyimides

At first, the reactivity of the hydrogen scavengers was studied on LDPE without MA in the reaction media in order to check the presence of undesired crosslinking reactions between the formed PE macroradicals. A common method to follow the crosslinking process is to measure the dynamic storage modulus (G') at a fixed temperature. The covalent polymer network that is created by recombination restricts polymer segment mobility, thereby raising the compound's G' in a manner that correlates with the crosslink network density. As a typical example, Figure 4 depicts the viscoelastic behavior of the neat LDPE and the LDPE after reaction with NAPI. The classic viscoelastic liquid behavior of LDPE molten polymers^{54, 55} was observed suggesting that there is no modification of the PE chain when the reaction is performed in presence of NAPI at 190 °C. Qualitatively, the mean relaxation time (λ) obtained from the crossover $G'-G''$ frequency ($\omega\lambda=1$), and the complex viscosity at 0.01 rad.s^{-1} of all the samples remain close to the neat LDPE (e.g. 0.2 s and $2.6 \times 10^4 \text{ Pa.s}$ at 190 °C) (Table 1).

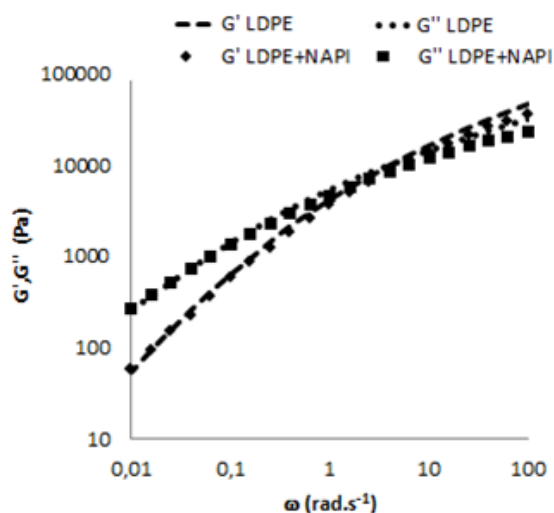


Figure 4. Variation of the complex shear modulus $G^*(\omega)$ versus frequency measured at 160 °C for neat LDPE after 1 h at 190 °C and LDPE/NAPI (0.5 wt%) after 1 h at 190 °C

Considering these results it can be concluded that no crosslinking reactions are evidenced whatever the reaction temperature (presence of a $G'-G''$ crossover frequency and consequently of a finite relaxation time) and no appearance of a secondary plateau at low frequencies on the storage modulus. However, the complex viscosity slightly increases for most samples by increasing the reaction temperature from 190 °C to 230 °C suggesting some branching reactions.

Table 1. Relaxation time λ and absolute complex viscosity η_{01} at 10^{-2} rad/s as a function of the H-abstracting agent and the reaction temperature

H-abstracting agent	Temperature (°C)	Relaxation Time (λ) (s)	η_{01} at 0.01 rad.s^{-1} (10^4 Pa.s)
NAS	190	0.2	3.2
1	230	0.5	3.0
tBu-NAS	190	0.2	2.4
2	230	0.4	3.9
Ph-NAS	190	0.2	1.0
3	230	0.6	5.0
NAPI	190	0.3	.72
6	230	0.6	3.9
tBu-NAP	190	0.3	2.6
7	230	0.5	4.4
Ph-NAP	190	0.2	2.5
8	230	0.8	4.7
NANPI	190	0.1	1.1
11	230	0.2	2.2
tBu-NANP	190	0.2	2.5
12	230	0.4	6.2
Ph-NANP	190	0.2	1.8
13	230	0.4	5.7

Herein, it is suggested that the H-abstracting agents also act as radical scavengers preventing the formed PE macroradicals

(thermooxidative degradation of the PE under melt extrusion) from too much branching reactions leading to cross-linking.

Grafting of MA onto PE in presence of H-abstractors

As discussed before, it is expected that the thermolysis of the H-abstracting agent will lead to the formation of radicals that are more efficient for hydrogen abstraction from polyethylene than the usual peroxides.^{31, 56} Then, the polyethylene radicals that are created through hydrogen abstraction are able to react with MA by radical addition and with other radical species via the classic radical coupling reactions or by recombining with stable free radicals such as PINO radicals (Scheme 1). The latter combination reactions may create a labile bond at high temperature that may favor the addition of polyethylene radicals to MA and may limit branching and crosslinking reactions leading to a higher MA grafting density. The first experiments were performed at 190 °C. The MA grafting degree was determined using FTIR data because it was not possible to quantify it through the ^1H NMR analysis. The FTIR spectrum of PE after MA grafting shows carbonyl absorption bands due to the presence of anhydride ($1830\text{--}1750\text{ cm}^{-1}$) and carboxylic acid groups ($1750\text{--}1660\text{ cm}^{-1}$) as well as the absorption band of CH_2 sequences of PE at $760\text{--}680\text{ cm}^{-1}$ (Figure S1) so that the MA grafting degree was measured using a calibration curve (Figure S2) according to the Samay method⁵⁷ and already used in our previous study.⁴¹

The use of Luperox 101 as H-abstracting agent in presence of LDPE and MA led to a MA grafting degree of 1.91 wt%. However no $G'-G''$ crossover frequency was observed (Figure 5), meaning a relaxation time $\lambda \rightarrow \infty$ when analyzing the viscoelastic behavior of the resulting MA-g-LDPE. This solid elastic-like behavior (appearance of a secondary plateau modulus at low frequencies) suggests the formation of 3D chemical network and consequently a high degree of branching and/or crosslinking, as shown in Figure 2. The complex viscosity that is measured at 0.01 rad.s^{-1} is thus very high, reaching $1.65 \times 10^6\text{ Pa.s}$.

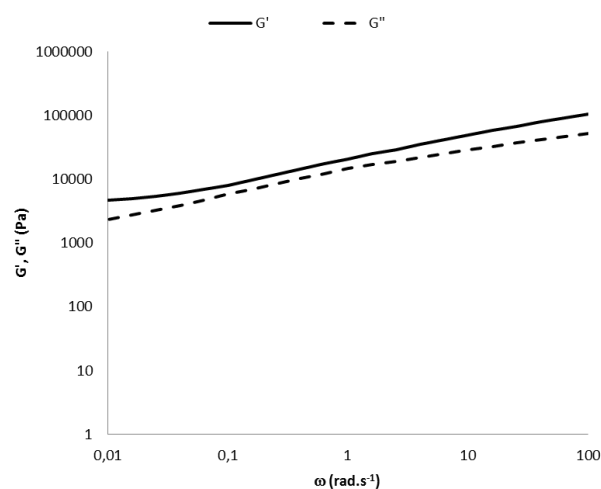
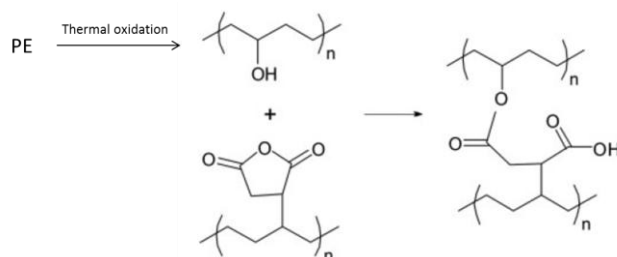


Figure 5. Typical variation of complex shear modulus $G^*(\omega)$ versus frequency determined at 160 °C for the reaction of LDPE with 2 wt% of MA in presence of L101.

It has to be noted that the grafting mechanism using alkoxyl radical is a chain mechanism since only a small amount (0.18 wt%) of peroxide led to a quantitative grafting of MA (1.91 wt% from an initial amount of 2 wt% that is 95% yield). When an equimolar ratio of acyloxyimide is used with a residence time of 60 min, the grafting degree is ranging between 1.0 and 1.5 wt%, showing a rather good grafting efficiency. The rheological profile of such MA-g-LDPE is also a solid elastic-like behavior but with complex viscosities at 0.01 rad.s⁻¹ that are in the range $1.5 \times 10^5 - 6.0 \times 10^5$ Pa.s, that is a two or a three fold lower than the L101 peroxide one (Table 2).

The solid-like behavior that is observed for all the new H-abstracting agents could be due to the long reaction time that is required at 190°C. As discussed by Huang et al.⁵⁸, prolonged heating of MA-g-PE at high temperatures may favorably oxidized PE units to form hydroxyl groups followed by the

formation of a crosslinked structure by further reacting them with the maleic anhydride containing PE units (Scheme 4).



Scheme 4. Reaction between hydroxyl groups of thermo-oxidized PE units and maleic anhydride group of MA-g-PE.

Table 2. Influence of the grafting agent on the melt extrusion of LDPE in the presence of 2 wt% of MA.

Temperature		190 °C (60 min)			230 °C (7.5 min)			
H-abstracting agent	Grafting degree (wt%)	Grafting yield (%)	ω (rad.s ⁻¹)	η_{01} at 0.01 rad/s (10 ⁴ Pa.s)	Grafting degree (wt%)	Grafting yield (%)	ω (rad.s ⁻¹)	η_{01} at 0.01 rad/s (10 ⁴ Pa.s)
-	-	-	7.62	1.2	-	-	3.06	4.0
L101 0.18wt%	1.91	95	-	165.0	1.6	80	-	84.0
NAS 0.38 wt%	1.5	75	-	41.0	1.24	62	0.29	19.0
tBu-NAS 0.49 wt%	0.99	49	-	24.0	1.07	53.5	0.4	12.5
Ph-NAS 0.53 wt%	1.22	61	-	44.0	1.06	53	0.1	18.5
DiA-NAS 0.75 wt%	1.47	73	-	27.5	1.28	64	0.4	16.0
DSO 0.35 wt%	1.3	65	-	32.0	1.05	52.5	0.07	26.0
NAPI 0.5 wt%	1.11	55	-	52.5	1.11	55.5	0.22	22.0
tBu-NAP 0.6 wt%	1.16	58	-	67.0	1.31	65.5	0.07	27.0
Ph-NAP 0.65 wt%	1.13	56	-	61.5	1.11	55.5	-	6.0
DiA-NAP 0.87 wt%	1.08	54	0.16	15.5	1.08	54	0.4	6.0
DPO 0.44 wt%	1.51	75	-	115.0	1.87	75	-	31.0
NANPI 0.62 wt%	0.61	30	-	16.5	0.31	15.5	0.36	12.2
tBu-NANP 0.72 wt%	0.91	45	-	51.0	0.96	47	0.08	24.0
Ph-NANP 0.77 wt%	0.96	48	-	20.0	0.79	37	0.31	12.5

In order to confirm the latter reaction, MA was mixed with PE at 190°C for 1 hour without any H-abstractor agent and a

similar viscoelastic behavior was obtained (no G' - G'' crossover frequency).

The use of a higher temperature (e.g. 230°C) and thus a lower residence time (e.g. 7.5 min.) for the new H-abstracting agents permitted to recover finite relaxation time as confirmed by the presence of a G' - G'' crossover frequency on the viscoelastic analysis spectrum for all the samples (Table 2). In a similar experiment, the L101 modified PE still lead to cross-linking without any G' - G'' crossover frequency and with a complex viscosity of 8.4×10^5 Pa.s. These results thus confirmed the mechanism that is a lowering of side-reaction by scavenging a part of the formed macroradical species by the PINO nitroxide or the amidinyl radical. The PINO nitroxide could be produced by the C-O decomposition of the starting reagent or by the reaction of the amidinyl radical with O_2 . Nevertheless whatever the radical species that lower the macroradical side-reactions, the chain reaction that is usually occurring during the melt grafting is less efficient and thus the grafting yield cannot be as high as with peroxide and experimentally such value are ranging between 50 and 70 %.

To compare the different H-abstracting agents, the results are summarized in Figure 6 where the grafting degree is depicted as a function of the complex viscosity. According to these results, it is clear that an increase in temperature from 190 to 230°C leads to similar or increased grafting degree combined with a drastic decrease of the complex viscosity for all the new grafting agents. Indeed, all the absolute complex viscosities are below 5×10^5 Pa.s and are thus at least 3 to 5 fold lower than the ones obtained with the L101 peroxide. Moreover, it is observed that the NANP-derivatives with a naphthalimide moiety are the least efficient agents with grafting degrees below 1 wt% whatever the alkyl structure. Concerning NAP- and NAS derivatives, the grafting degree are roughly similar with values ranging mainly from 1 to 1.5 wt%, not showing a huge influence of the amidinyl structure. The nature of the alkyl moiety of the acyloxy group also modify slightly the grafting degree and among the various structure, the *tert*-butyl alkyl group seemed to be the most promising one in terms of grafting efficiency and rheology behavior.

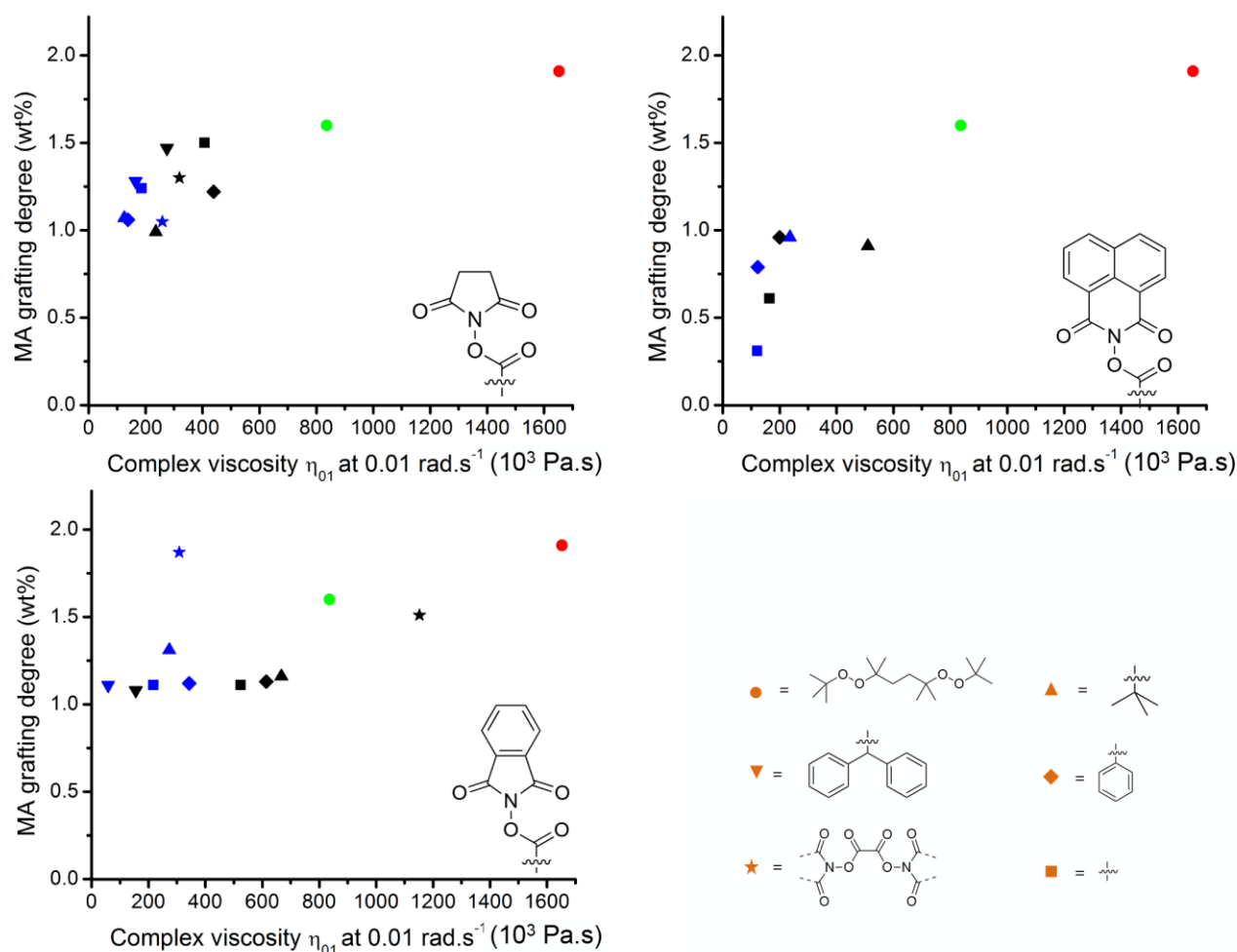


Figure 6. Maleic anhydride (MA) grafting degree obtained at 190°C (60 min, black and red symbols) and 230 °C (7.5 min, blue and green symbol) as a function of the absolute complex viscosity at 10⁻² rad.s⁻¹ for NAP-based derivatives NAS-based derivatives and NANP-based derivatives.

These results also confirmed that the H-abstracting efficiency of acyloxyimides is mainly related to the amidinyl radicals and that the

impact of the released alkyl radical is rather low. The diphenylacetyl moiety (**4** - **9**) is another alkyl moiety of interest since

it is possible to reach various MA grafting degree with the lowest modification of the polymer rheological behavior. The dimer of phthalimidy radical (DPO **10**) is also very promising showing the highest efficiency with a grafting degree of 1.87 wt% and a complex viscosity of 3.1×10^5 Pa.s at 0.01 rad.s^{-1} .

Optimization of the MA grafting efficiency

The grafting of MA onto PE chains is very well performed with L101 peroxide since a grafting yield of 95 % is obtained with 0.18 wt% at 190°C . The influence of the peroxide amount on both the grafting degree and the complex viscosity is described in Figure 7. It can be seen that decreasing the amount of peroxide led to a slightly decrease of both the grafting degree and viscosity.

A L101 weight content of 0.18 % is the optimized value to reach 95% grafting yield, nevertheless the obtained complex viscosity cannot envision to increase both the amount of MA and/or peroxide content to reach higher MA grafting degree. In contrary, the lower values of complex viscosities that are observed with the use of the new grafting agents let us investigate if it is possible to increase the MA grafting degree by increasing the initial MA content by a factor 2 when using NAPI as reference and tBu-NAP as the best alkyl fragment (Table 2). The results are summarized in Figure 7.

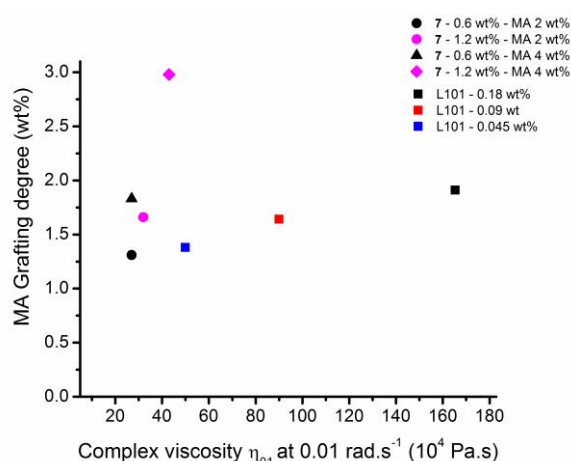


Figure 7. Influence of the concentration of the H-abstrating agent precursor on the maleic anhydride (MA) grafting degree as a function of the absolute complex viscosity at $10^{-2} \text{ rad.s}^{-1}$ for L101 (MA 2 wt% - 60 min at 190°C) and tBu-NAP (7.5 min at 230°C).

It can be observed that the use of an initial MA amount 4 wt% in presence of tBu-NAP (**7**) leads to approximately the same absolute complex viscosity at 0.01 rad.s^{-1} as with the use of a MA weight content of 2 % while the grafting degree increases to 1.8 wt%, even if the grafting yield decreases to 45%.

Moreover, by increasing the tBu-NAP weight content from 0.6 % to 1.2 % in order to reach the same MA/tBu-NAP weight ratio as the experiment using 2 wt% of MA, we obtained the highest MA grafting degree (2.98 wt%) with a grafting yield of 75%, while keeping an absolute complex viscosity to 4.3×10^5 Pa.s.

Since the increase of the reaction temperature from 190°C to 230°C led to improved results in terms of both grafting efficiency and polymer rheological behavior we have also increased the temperature to 250°C with a residence time of 2 minutes in presence of NAPI as a reference and DPO. The results are gathered in Table 3 and it is observed a slightly higher grafting degree combined with a similar complex viscosity by using NAPI. In presence of DPO, the effect was not identical with a slightly lower grafting degree at a temperature of 250°C . This result showed that each new acyloxyimide compound required finding specific optimized conditions that could be related to their rate of decomposition.

Conclusion

The melt grafting of maleic anhydride onto low-density polyethylene has been performed in presence of acyloxyimides as new H-abstrating agents to be used as an alternative to the use of peroxides. In preliminary experiments, mechanistic investigations were carried out and showed that the decomposition of NAPI was complete in 1 hour at 180°C and lead exclusively to the formation of acetic acid confirming the N-O dissociation. Moreover, decompositions performed in tetradecane as model for polyolefin confirmed the patching behavior of this system since imidyl groups were grafting onto the tetradecane backbone. Secondly, optimal conditions for MA grafting were obtained by using various H-abstrating agents at 190°C for 1 hour and at 230°C for 7.5 min.

These molecules differ either by the alkyl group of the acyloxy moiety or by the nature of the imidiny moiety (succinimide NAS, phthalimide NAP, naphthalimide NAMP). It was found that NAP-, NAMP- and NAS-based derivatives are efficient for H-abstraction combined with a lower rheological modification than peroxides.

Table 3. Relaxation time λ and absolute complex viscosity η_{01} at 10^{-2} rad/s as a function of the H-abstrating agent and the reaction temperature

Temperature ($^\circ\text{C}$)	H-abstrating agent	Grafting degree (wt%)	η_{01} at 0.01 rad.s^{-1} (10^4 Pa.s)
190	NAPI	1.11	52.5
230		1.11	22.0
250		1.52	34.0
190	DPO	1.51	115.0
230		1.83	31.0
250		1.72	55.0

The addition of MA in the reaction mixture led to the grafting of MA monomer and the macroradical formed by H-abstraction onto the polyethylene backbone. The MA grafting degree was higher in

presence of NAP- and NAS-based derivatives than in presence of NNP-based derivatives. However, crosslinking reactions were observed at 190 °C with a residence time of 1 hour which was attributed to a reaction between thermo-oxidized PE and MA-g-PE.

In contrary, the use of a higher temperature (230 °C) prevented PE from crosslinking since low residence time was required (7.5 min.). The tBu-NAP, the DPO and the DiA-NAP/DiA-NAS were particularly efficient. First the DiA-NAP/DiA-NAS allowed obtaining moderate grafting but very low rheological modification. Secondly, tBu-NAP and DPO presented the best compromise between MA grafting degree and rheological modification. The highest grafting degree was obtained when using tBu-NAP as hydrogen abstracting agent with a MA grafting degree of 2.98% combined with an absolute complex viscosity of 4.3×10^5 Pa.s. In that case 4 wt% of MA and 1 wt% of tBu-NAP was used.

These results showed the interest of these new structures to modify polyolefins by melt extrusion with little change of their rheological properties. The extension of these results to others commodities polymers such as polycondensates will be reported in due course.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

The financial supports from the French National Agency for Research (ANR-14-CE07-0015) and the competitiveness cluster Plastipolis are acknowledged.

Notes and references

1. C. J. Zhou, K. Wang and Q. Fu, *Polymer International*, 2009, **58**, 538-544.
2. E. Passaglia, S. Coiai and S. Augier, *Progress in Polymer Science*, 2009, **34**, 911-947.
3. E. Passaglia, S. Coiai, M. Aglietto, G. Ruggeri, M. Ruberta and F. Ciardelli, *Macromolecular Symposia*, 2003, **198**, 147-159.
4. A. V. Machado and J. A. Covas, *Advances in Polymer Technology*, 2004, **23**, 196-210.
5. G. H. Hu, J. J. Flat and M. Lambla, *Makromolekulare Chemie-Macromolecular Symposia*, 1993, **75**, 137-157.
6. P. Cassagnau, V. Bounor-Legare and F. Fenouillot, *International Polymer Processing*, 2007, **22**, 218-258.
7. J. B. Williamson, S. E. Lewis, R. R. Johnson, 3rd, I. M. Manning and F. A. Leibfarth, *Angew Chem Int Ed Engl*, 2018.
8. C. Bae, J. F. Hartwig, N. K. B. Harris, R. O. Long, K. S. Anderson and M. A. Hillmyer, *Journal of the American Chemical Society*, 2005, **127**, 767-776.
9. C. S. Bae, J. F. Hartwig, H. Y. Chung, N. K. Harris, K. A. Switek and M. A. Hillmyer, *Angewandte Chemie-International Edition*, 2005, **44**, 6410-6413.
10. Y. Kondo, D. Garcia-Cuadrado, J. F. Hartwig, N. K. Boen, N. L. Wagner and M. A. Hillmyer, *Journal of the American Chemical Society*, 2002, **124**, 1164-1165.
11. A. Ray, K. M. Zhu, Y. V. Kissin, A. E. Cherian, G. W. Coates and A. S. Goldman, *Chemical Communications*, 2005, 3388-3390.
12. A. Bunescu, S. W. Lee, Q. Li and J. F. Hartwig, *Acs Central Science*, 2017, **3**, 895-903.
13. C. M. Plummer, H. B. Zhou, W. Zhu, H. H. Huang, L. X. Liu and Y. M. Chen, *Polymer Chemistry*, 2018, **9**, 1309-1317.
14. T. C. Chung, *Progress in Polymer Science*, 2002, **27**, 39-85.
15. M. Aglietto, R. Alterio, R. Bertani, F. Gallechi and G. Ruggeri, *Polymer*, 1989, **30**, 1133-1136.
16. J. B. Williamson, W. L. Czaplyski, E. J. Alexanian and F. A. Leibfarth, *Angewandte Chemie-International Edition*, 2018, **57**, 6261-6265.
17. H. B. Zhou, S. S. Wang, H. H. Huang, Z. Y. Li, C. M. Plummer, S. L. Wang, W. H. Sun and Y. M. Chen, *Macromolecules*, 2017, **50**, 3510-3515.
18. M. van Duin, A. V. Machado and J. Covas, *Macromolecular Symposia*, 2001, **170**, 29-39.
19. K. J. Ganzeveld and L. Janssen, *Polymer Engineering and Science*, 1992, **32**, 467-474.
20. F. Ciardelli, M. Aglietto, M. B. Coltelli, E. Passaglia, G. Ruggeri and S. Coiai, in *Modification and blending of synthetic and natural macromolecules.*, eds. F. Ciardelli and S. Penczek, Kluwer Academic Publishers, Dordrecht, 2004, p. 47.
21. T. Bray, S. Damiris, A. Grace, G. Moad, M. O'Shea, E. Rizzardo and G. Van Diepen, *Macromolecular Symposia*, 1998, **129**, 109-118.
22. M. Xanthos, *Reactive Extrusion*, Hanser Publishers, Oxford University Press 1992.
23. K. E. Russell, *Progress in Polymer Science*, 2002, **27**, 1007-1038.
24. A. V. Machado, J. A. Covas and M. van Duin, *Polymer*, 2001, **42**, 3649-3655.
25. A. H. Hought, J. Meijer and J. Jelenic, ed. S. Al-Malaika, 1997, p. 84 (and references cite herein).
26. M. Gaboyard, J. J. Robin, Y. Hervaud and B. Boutevin, *Journal of Applied Polymer Science*, 2002, **86**, 2011-2020.
27. D. Bertin, B. Boutevin and J. J. Robin, **1999**,
28. T. Badel, E. Beyou, V. Bounor-Legare, P. Chaumont, J. J. Flat and A. Michel, *Macromolecular Chemistry and Physics*, 2009, **210**, 1087-1095.
29. T. Badel, E. Beyou, V. Bounor-Legare, P. Chaumont, J. J. Flat and A. Michel, *Journal of Polymer Science Part a-Polymer Chemistry*, 2007, **45**, 5215-5226.
30. T. Badel, E. Beyou, V. Bounor-Legare, P. Chaumont, P. Cassagnau, J. J. Flat and A. Michel, *Macromolecular Materials and Engineering*, 2012, **297**, 702-710.
31. G. Moad, *Progress in Polymer Science*, 1999, **24**, 81-142.
32. J. H. Cha and J. L. White, *Polymer Engineering and Science*, 2003, **43**, 1830-1840.
33. H. R. Z. Sheshkali, H. Assempour and H. Nazockdast, *Journal of Applied Polymer Science*, 2007, **105**, 1869-1881.
34. N. G. Gaylord, R. Mehta, V. Kumar and M. Tazi, *Journal of Applied Polymer Science*, 1989, **38**, 359-371.
35. N. G. Gaylord and R. Mehta, *Journal of Polymer Science Part a-Polymer Chemistry*, 1988, **26**, 1189-1198.
36. M. K. R. Aghjeh, H. Nazockdast and H. Assempour, *Journal of Applied Polymer Science*, 2006, **99**, 141-149.
37. P. Chandranupap and S. N. Bhattacharya, *Journal of Applied Polymer Science*, 2000, **78**, 2405-2415.

38. B. I. Chaudhary, L. Chopin and J. Klier, *Polymer Engineering and Science*, 2007, **47**, 50-61.
39. F. Cicogna, S. Coiai, E. Passaglia, I. Tucci, L. Ricci, F. Ciardelli and A. Batistini, *Journal of Polymer Science Part a-Polymer Chemistry*, 2011, **49**, 781-795.
40. R. Pfaendner, *Comptes Rendus Chimie*, 2006, **9**, 1338-1344.
41. D. Belekian, P. Cassagnau, J. J. Flat, S. Quinebeche, L. Autissier, D. Bertin, D. Siri, D. Gigmes, Y. Guillaneuf, P. Chaumont and E. Beyou, *Polymer Chemistry*, 2013, **4**, 2676-2679.
42. S. Rolere, S. Monge, M. D. Rakotonirina, Y. Guillaneuf, D. Gigmes and J. J. Robin, *Journal of Polymer Science Part A: Polymer Chemistry*, 2018, **57**, 120-129.
43. S. Rolere, S. Monge, M. D. Rakotonirina, Y. Guillaneuf, D. Gigmes and J.-J. Robin, *Journal of Polymer Science Part A: Polymer Chemistry*, 2019, **57**, 917-928.
44. M. Baron, M.-D. Rakotonirina, M. I. El Assil, Y. Guillaneuf, D. Gigmes, D. Siri, A. Gaudel-Siri, J.-J. Flat, S. Quinebeche, P. Cassagnau and E. Beyou, *Materials Today Communications*, 2019, **19**, 271-276.
45. Y. Amaoka, S. Kamijo, T. Hoshikawa and M. Inoue, *J Org Chem*, 2012, **77**, 9959-9969.
46. C. A. Goodman, C. G. Hamaker and S. R. Hitchcock, *Tetrahedron Letters*, 2013, **54**, 6012-6014.
47. D. S. Dalal, N. S. Pawar and P. P. Mahulikar, *Organic Preparations and Procedures International*, 2007, **39**, 81-85.
48. B. Saha, N. Koshino and J. H. Espenson, *Journal of Physical Chemistry A*, 2004, **108**, 425-431.
49. G. Baquey, L. Moine, O. Babot, M. Degueil and B. Maillard, *Polymer*, 2005, **46**, 6283-6292.
50. M. Buback, H. Frauendorf, F. Gunzler and P. Vana, *Polymer*, 2007, **48**, 5590-5598.
51. T. Uchimaru, R. Hara, K. Tanabe and K. Fujimori, *Chem. Phys. Lett.*, 1997, **267**, 244-250.
52. G. Moad and D. H. Solomon, in *The chemistry of free radical polymerization*, 2nd edition, Elsevier, 2005.
53. B. A. Chalmers, J. C. Morris, K. E. Fairfull-Smith, R. S. Grainger and S. E. Bottle, *Chemical Communications*, 2013, **49**, 10382.
54. S. Mani, P. Cassagnau, M. Bousmina and P. Chaumont, *Polymer*, 2010, **51**, 3918-3925.
55. S. Mani, P. Cassagnau, M. Bousmina and P. Chaumont, *Macromolecules*, 2009, **42**, 8460-8467.
56. S. Akbar, E. Beyou, P. Cassagnau, P. Chaumont and G. Farzi, *Polymer*, 2009, **50**, 2535-2543.
57. G. Samay, T. Nagy and J. L. White, *Int Polym Sci Tech* 1995, **22**, 30.
58. J. W. Huang, W. C. Lu, M. Y. Yeh, C. H. Lin and I. S. Tsai, *Polymer Engineering and Science*, 2008, **48**, 1550-1554.