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Decarboxylation of Poly[*N*-(acryloyloxy)phthalimide] as a Versatile Tool for Postpolymerization Modification

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Herein the decarboxylation of poly[*N*-(acryloyloxy)phthalimide] (PAP) for the synthesis of functionalized polymers is reported. PAP homopolymer and block copolymers are used as precursor polymers for the straightforward functionalization via decarboxylation and subsequent Michael-type addition or nitroxide radical coupling (NRC).

1. Introduction

Functional polymers are of great interest for academical research as well as industrial production since they offer unique properties and applications, based on the presence of functional groups in the polymeric structure.[1]

The synthesis of functional polymers can be achieved by two different methods: Either by the direct polymerization of a functional monomer or by chemically modifying a precursor polymer after polymerization, so-called postpolymerization modification (PPM).[2] While the polymerization of functional monomers can be challenging due to intolerances of reactants with functional groups or to the inaccessibility of such functional monomers,[3] functionalization via PPM requires quantitative reactions, since nonfunctionalized units in the polymer chain cannot be removed by purification, very much in contrast to organic chemistry. Despite this challenge, PPM experienced a growing interest in the last decades and opened the way to new polymeric materials and architectures.[2] In the scope of PPM activated esters should be mentioned. As a special group of esters, they bear electron-withdrawing groups resulting in a drastically increased reactivity of the ester. This activation leads to their high versatility and popularity and makes them especially prone to nucleophilic reactions, in particular with amines. Well-known activated ester species are based on pentafluorophenyl-[4] or phthalimide[5] structural motifs. The combination of activated ester chemistry with polymer chemistry opens a wide field of PPM.[6]

The simple synthesis of activated ester monomers makes them easily accessible and the high tolerance of reversible-deactivation radical polymerization (RDRP) techniques towards activated esters allows for a straightforward and controlled polymerization of activated ester monomers leading to an additional architectural control.

Especially the already mentioned phthalimide structural motif deserves special attention since it cannot only undergo nucleophilic reactions, but is also prone to single-electron transfer (SET) to the imide unit of the phthalimide with subsequent reactions.[7,8] The SET, which can be performed employing different catalytic systems, is typically followed by expulsion of carbon dioxide leading to the formation of a secondary radical at the neighboring carbon atom (**Scheme 1**). In two former studies we used this secondary radical at the backbone in combination with a hydrogen donor for the synthesis of polyethylene homopolymers, copolymers and block copolymers.[9,10] More recently, Sumerlin and co-workers published a similar method to synthesize polyolefins based on a different catalytic system.[11] But the scope of decarboxylation of polymeric materials is by far not only limited to the synthesis of polyolefins.

Noteworthy, the decarboxylation of phthalimide-based activated esters is widely used for functionalization reactions in organic synthetic chemistry,[7,8] yet has not been explored much in polymer chemistry. In synthetic organic chemistry, one of the most studied reactions in the context of decarboxylation of phthalimide-based activate esters is the subsequent Michael-type addition of α,β-unsaturated carbonyl compound using various types of catalytic systems and reactants.[12–19] Michael-type additions then not only lead to the formation of a new C–C bond, but also allow for the introduction of new functionalities in a straightforward fashion. Another way of functionalizing employs stable radicals via the so-called nitroxide radical coupling (NRC).[20–22] NRC is based on the coupling of a persistent radical, e.g., 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO)-based persistent radicals, with the secondary radical formed at the polymer backbone during decarboxylation. This coupling method is widely known and used for different types of polymeric materials. However, most of those methods lack control and require harsh conditions like laser-based etching or the employment of peroxides.[23] An advantage of NRC is its high efficiency and the

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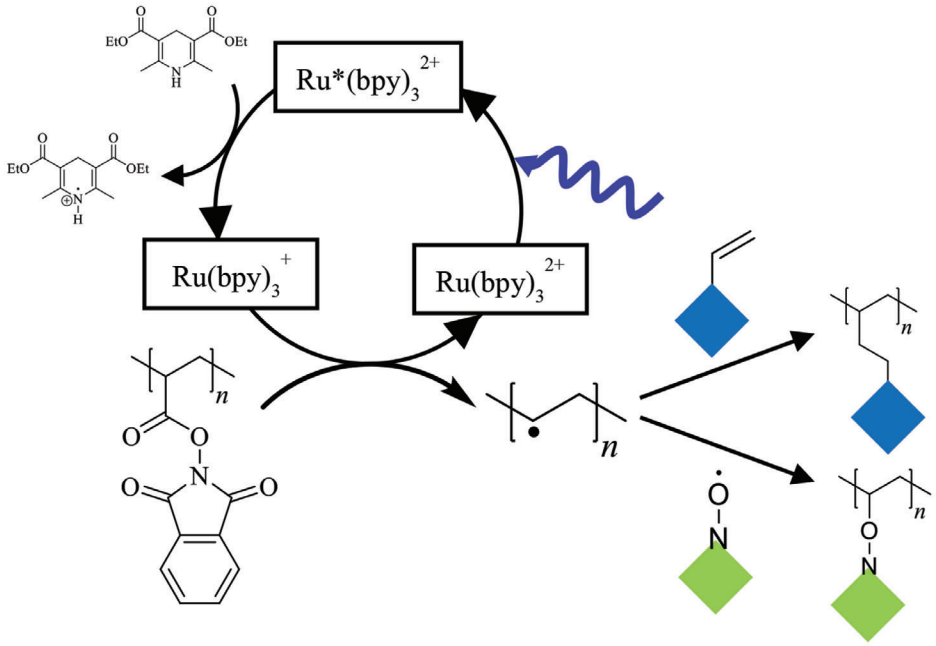

Scheme 1. Reaction mechanism of the decarboxylation of poly[*N*-(acryloyloxy)phthalimide] by a single-electron transfer from $Ru(bpy)_3Cl_2$ to the respective imide and further functionalization of the formed secondary radical.

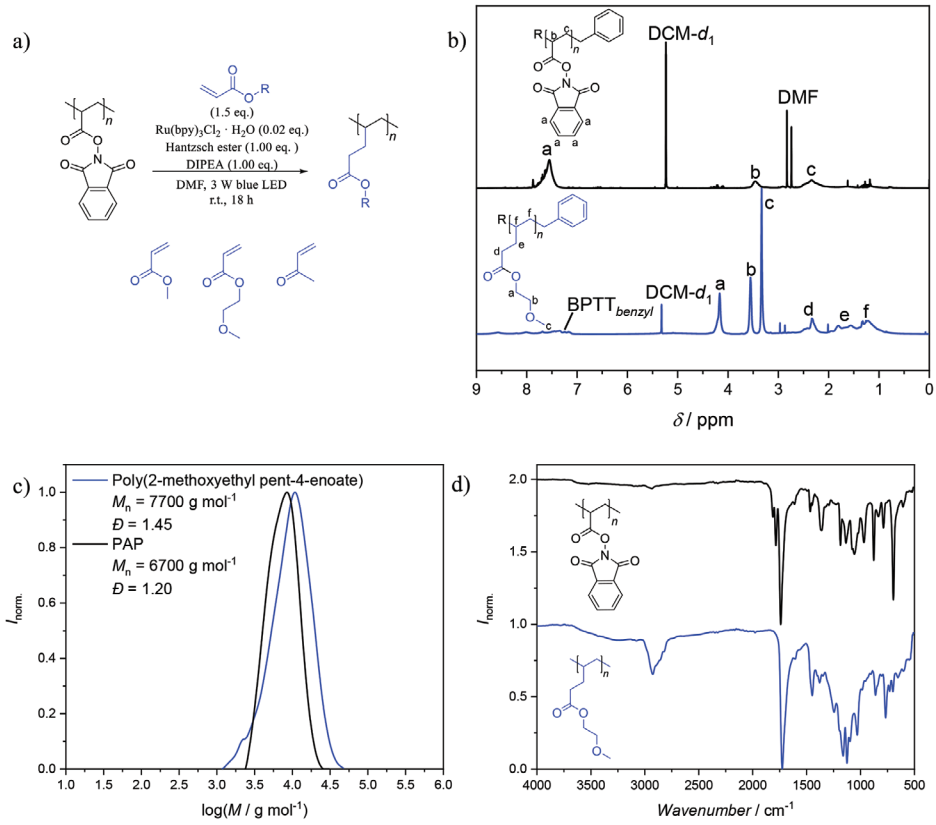

Figure 1. a) Schematic reaction equation of Michael-type addition on PAP, used Michael acceptors marked in blue. b) Comparison of ^{1}H NMR spectra of PAP (top, black) and after Michael-type addition of 2-methoxyethyl acrylate (MEA) (bottom, blue), BPTT is the signal of the benzyl group of the RAFT agent; solvent: DCM-d_2. c) SEC chromatogram of PAP (black) and after Michael-type addition of MEA (blue). d) Comparison of IR spectra of PAP (top, black) and after Michael-type addition of MEA (blue).

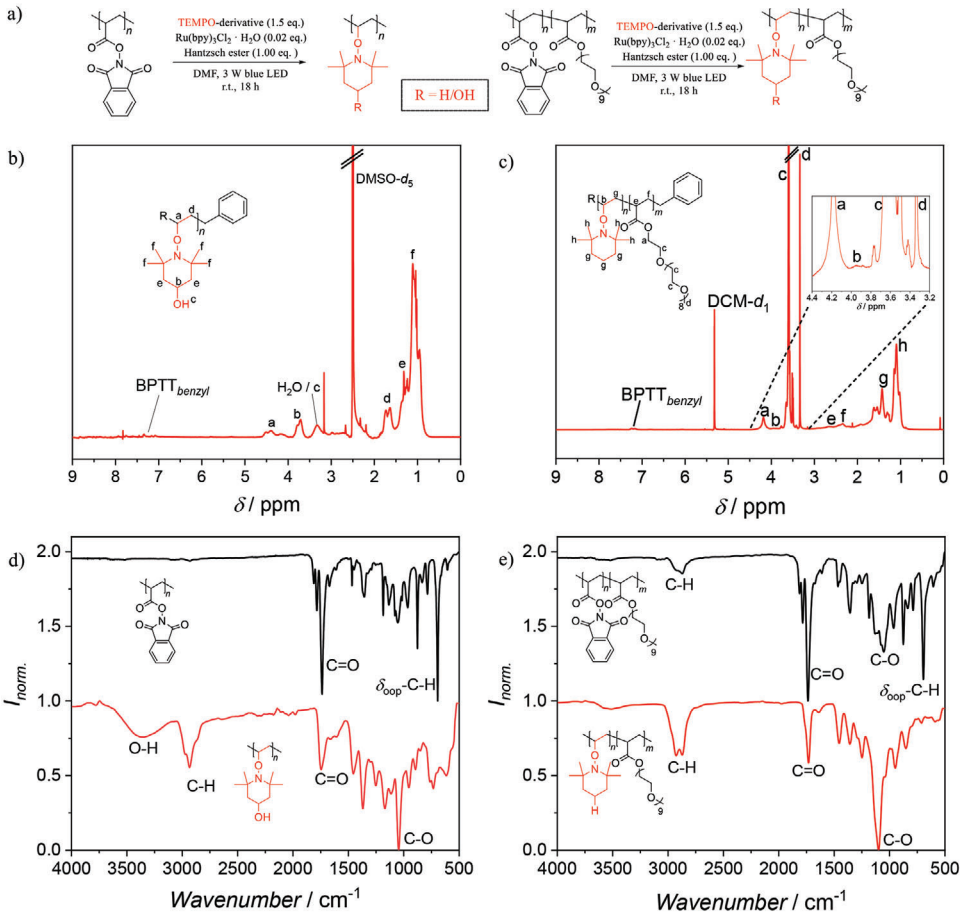

Figure 2. a) Schematic reaction equation of nitroxide-radical coupling on PAP (left) and PAP block copolymers (right) with TEMPO and TEMPO-OH; b) ^{1}H NMR spectrum of PTEMVPO after decarboxylation of PAP with 4-hydroxy TEMPO; solvent: DMSO-d_5; c) ^{1}H NMR spectrum of PTEMVP-*b*-POEGMEA after decarboxylation of PAP-*b*-POEGMEA with TEMPO; solvent: DCM-d_2; d) Comparison of IR spectra of PAP (top, black) and PTEMVPO (bottom, red; e) Comparison of IR spectra of PAP-*b*-POEGMEA (top, black) and PTEMVP-*b*-POEGMEA (bottom, red.

possibility to further employ the TEMPO functionality tethered to the polymer, for example to perform grafting reactions or realize more complex architectures such as brush polymers.

Hence, within this study we present synthetic routes that explore the decarboxylation of phthalimide-based activated esters of polyacrylates and their subsequent functionalization using Michael-type addition of α,β-unsaturated carbonyl compounds or NRC.

2. Results

PAP homopolymers and block copolymers used in the scope of the present study were synthesized by reversible addition–fragmentation chain-transfer (RAFT) polymerization employing *S´,S*-benzyl propyltrithiocarbonate (BPTT) as RAFT-agent. For the exploration of Michael-type addition experiments homopolymer **P1** featuring a molar mass of M_n = 6700 g mol^{-1} and a dispersity of $Đ$ = 1.20 was used (for detailed information see Table S1 in the Supporting Information). Following our previous study of decarboxylation reactions on PAP for the synthesis of PE and PE-block copolymers with a hydrogen-donor,[9,10] we utilize our optimized photochemical decarboxylation method employing $Ru(bpy)_3Cl_2$•$6H_2O$ as catalyst for the functionalization of PAP.

As Michael acceptor, methyl acrylate (MA), 2-methoxyethyl acrylate (MEA), and methyl vinyl ketone (MVK) were investigated. MA and MEA were chosen due to their acrylate-based structure and due to their prominent signals in ^{1}H NMR spectra at 3.0–4.2 ppm, which can be clearly distinguished from signals of PAP. MVK was chosen to widen the scope of usable reagents. Decarboxylation reactions were performed using $Ru(bpy)_3Cl_2$•$6H_2O$ (0.02 eq.), Hantzsch ester (1.00 eq.), Michael acceptor (1.50 eq.), and diisopropylethyl amine (DIPEA, 1.50 eq.) as reductive quencher[12,19] (**Figure 1**a). All Michael additions with the three acceptors MA, MEA, and MVK proceeded quantitatively judging from ^{1}H NMR and ATR-IR spectroscopy (see also Figures S1–S4 in the Supporting Information) and in high yields (>85%). Exemplarily the ^{1}H NMR spectrum before and after the decarboxylation and subsequent Michael-addition with MEA is presented in Figure 1b. The removal of the aromatic proton signal of the phthalimide as well as the arising signals of MEA (CH_3 at 4.1 ppm, CH_2O at 3.6 ppm, and $COOCH_2$ at 3.2 ppm) can be clearly identified. Additionally, SEC analysis (Figure 1c) revealed the intact structure of the polymer with a slight shift

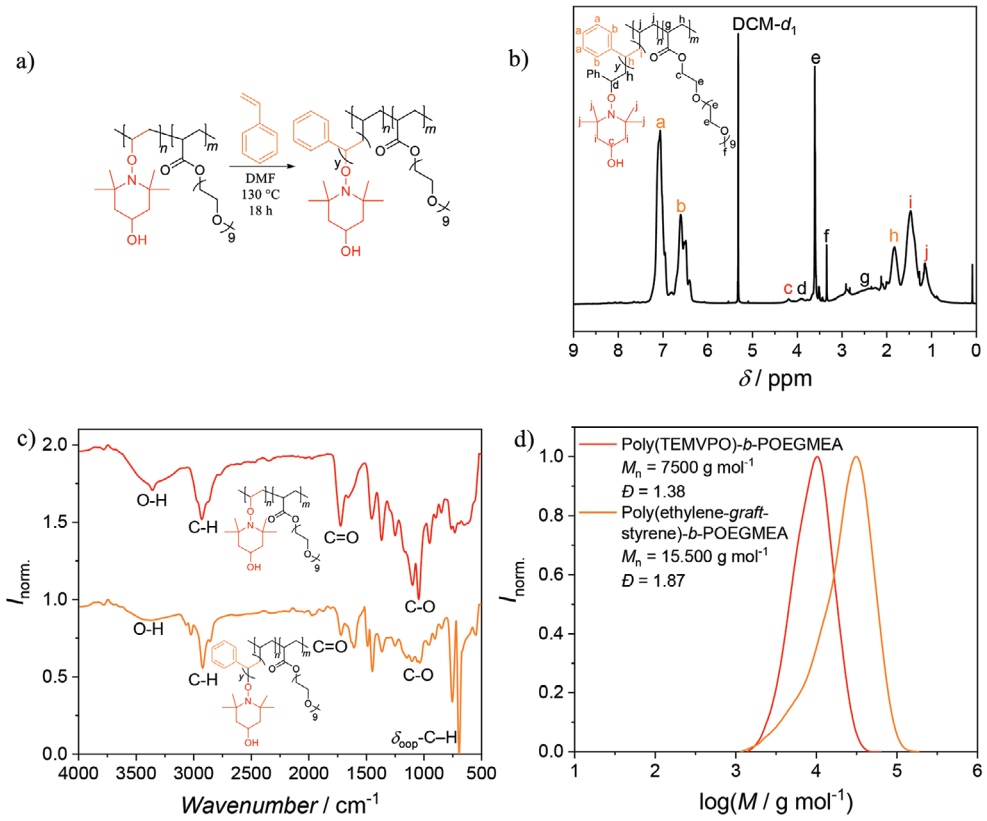

Figure 3. a) Schematic reaction equation of grafting styrene from PTEMVPO-*b*-POEGMEA; b) ^{1}H NMR spectrum of graft polymer poly(ethylene-graft-styrene)-*b*-POEGMEA; solvent: DCM-d_2; c) IR spectra of PTMVPO-b-POEGMEA (top, red) and graft polymer poly(ethylene-graft-styrene)-*b*-POEGMEA (bottom, orange); d) Comparison of SEC chromatogram of PTEMVPO-*b*-POEGMEA and graft polymer poly(ethylene-graft-styrene)-*b*-POEGMEA with PMMA calibration; eluent: DMAc.

towards higher molar masses, as expected. Yet, a slight broadening of the SEC curve as expressed by an increased dispersity of $Đ = 1.45$ was observed, likely due to minor radical polymer scission reactions.

It is important to note that the addition of a Michael-acceptor in absence of a reductive quencher (e.g., DIPEA) led to the formation of a cross-linked material. In an additional experiment we cross-linked the polymer during the decarboxylation by the addition of 30 equivalents of styrene in absence of DIPEA as reductive quencher (see also Figure S14 in the Supporting Information). Furthermore, this experiment demonstrated the necessity to employ a control agent for the synthesis of graft polymers, as discussed in the following.

After studying the decarboxylation and subsequent Michael-type additions, the resulting secondary radical at the polymer backbone was used for NRC with TEMPO-based persistent radicals. In this study, we employed both TEMPO and 4-hydroxy TEMPO for the NRC. The NRC with TEMPO-based radicals was first conducted on homopolymer PAP (**P1**). Photochemically-induced decarboxylation was performed (0.02 eq. $Ru(bpy)_3Cl_2$•$6H_2O$, 1.00 eq. Hantzsch ester) with the hydrogen-donor being exchanged by TEMPO or 1-hydroxy-2,2,6,6-tetramethylpiperidine (4-hydroxy TEMPO) (1.5 eq.) (**Figure 2**a). Both decarboxylation and subsequent TEMPO, or TEMPO-OH addition proceeded quantitatively and again with high yield (without further optimization of the reaction conditions. ^{1}H NMR and IR spectroscopy analyses of the homopolymer after functionalization with 4-hydroxy TEMPO are exemplarily shown in Figure 2b,d. While in the ^{1}H NMR spectrum the typical signal of the hydroxy-group and proton next to the hydroxy group as well as the intensive signals of the methyl groups of 4-hydroxy TEMPO can be identified, ATR-IR spectroscopy shows the vibration of O–H at 3370 cm^{-1} and intensive C–H vibration at 2931 cm^{-1} after decarboxylation on the one hand and a removal of the aromatic C–H (δ_{oop}) vibration at 695 cm^{-1} on the other hand. Additional experimental data supporting the successful attachment can be found in Figures S5–S7 in the Supporting Information.

Additionally, the NRC after decarboxylation was also investigated on block copolymers with OEGMEA (M_n = 480 g mol^{-1}) as comonomer (**P2** PAP-*b*-POEGMEA, see Table S2 in the Supporting Information). Again, the NRC after decarboxylation proceeded quantitatively with both TEMPO derivatives, without noticeable side reactions as proven by ^{1}H NMR and IR spectroscopy. In Figure 2 the ^{1}H NMR (Figure 2c) and IR spectrum (Figure 2e) of the TEMPO-functionalized block copolymer are exemplarily shown (see also Figures S8–S10 in the Supporting Information). Similar to the functionalization of the homopolymer, the disappearance of the aromatic proton signal of the phthalimide as well as appearance of the signals of the TEMPO methyl groups can be

clearly identified, indicating that the decarboxylation and subsequent NRC functionalization was successful on different polymer architectures.

To demonstrate the versatility and application of NRC with phthalimide-based precursor polymers for grafting reactions, experiments to graft styrene from PTEMVPO-*b*-POEGMEA were conducted (**Figure 3**a). Grafting polystyrene from a TEMPO-functionalized polymer backbone is mainly conducted with functionalized polyolefins and a common method to prove the successful functionalization.[23–27] To do so, 4-hydroxy TEMPO-functionalized block copolymer PTEMVPO-*b*-POEGMEA was dissolved in DMF and 150 eq. of styrene were added. After deoxygenation, the polymerization was conducted at 130 °C for 18 h and the polymer precipitated in cold diethyl ether and analyzed via ^{1}H NMR, ATR-IR spectroscopy and SEC in DMAc as eluent.

In Figure 3b the ^{1}H NMR spectrum of the graft polymer poly(ethylene-*graft*-styrene)-*b*-POEGMEA is presented and the characteristic aromatic proton signal of styrene can be identified. Furthermore, the signals of PEG and TEMPO clearly documented the successful graft polymerization. From the ^{1}H NMR spectrum a DP of 67 styrene units in the side chain was calculated. Additionally, SEC analysis (Figure 3c) proved the successful graft polymerization by revealing a unimodal distribution of the polymer and an increase of the molar mass. Based on the results of the SEC analysis a polystyrene side chain length of DP = 77 was calculated, fitting to the DP calculated from the ^{1}H NMR spectrum, resulting in a conversion of 50%, based on 150 equivalents of styrene added for the reaction.

3. Conclusion

In conclusion, the functionalization of a phthalimide-based precursor polymer by decarboxylation and subsequent Michael-type addition or subsequent NRC was successfully conducted. The versatility of Michael-type addition was demonstrated employing two different acrylates and a vinyl ketone as Michael-acceptors, proving the enormous variability of the decarboxylation-functionalization route. NRC was successfully performed on PAP homopolymers and block copolymers with two different TEMPO derivatives. Finally, the approach was also employed for the successful graft polymerization of styrene from PTEMVPO-*b*-POEGMEA. In summary, the developed synthetic method represents a highly versatile enrichment of synthetic methods suitable for the preparation of functional polymers by postpolymerization modification.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

decarboxylation, Michael-addition, nitroxide radical coupling, photochemistry, postpolymerization modification

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