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Photoinduced Conjugation of Aldehyde Functional Polymers with Olefins via [2 + 2]-Cycloaddition

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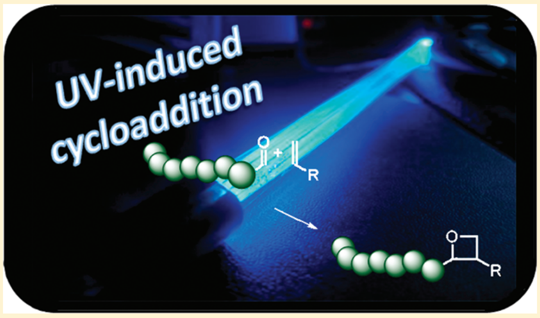
Supporting Information



ABSTRACT: Polymer end group modifications via [2 + 2] Paterno–Büchi reactions were carried out. Polyisobornyl acrylate (PiBoA, 3100 g·mol^{-1}) and polystyrene (PS, 2800 g·mol^{-1}) was synthesized by atom transfer radical polymerization (ATRP) employing an aldehyde functional initiator. Good control over the polymerizations was achieved, and material with high aldehyde functionality was obtained. The terminal aldehyde was then reacted with alkenes under UV irradiation in [2 + 2] cycloaddition reactions. Good yields of the modification reaction was confirmed via NMR and by electrospray ionization mass spectrometry (ESI–MS) analysis and generally conversion of the aldehyde function into the respective oxetanes of 90% or higher was observed. With the oxetane, a variety of functional groups were introduced to the polymer chain ranging from multifunctional allyl-compounds to disubstituted alkenes and amino- or hydroxyl-functional alkenes. In the photoreaction, the integrity of the bromine end group of the ATRP polymers is retained. ATRP chain extensions can be performed after the cycloaddition, demonstrating the versatility of this newly introduced polymer modification reaction.

INTRODUCTION

Not only since the introduction of the *click* concept,[1,2] a significant number of studies has been devoted to polymer conjugation and polymer end group modifications. On the basis of (hetero)telechelic polymers,[3] a broad variety of efficient chemistries were developed[4−7] that allow for conversion of materials for an even broader range of applications. The most prominent reactions in use are the copper catalyzed azid alkyne cycloaddition (CuAAC),[8] thiol–ene and thiol–yne[9] or (hetero) Diels–Alder[10] reactions to name the most prominent examples. Most of these reactions have, however, in common that they are triggered via thermal activation. Thus, end group conjugations proceed either upon heating or when the reactive compounds are mixed. A control over the reaction in the time domain is hence not given. To date, only few reactions can also be triggered by a light stimulus. The radical chemistry variant of thiol–ene is based on conventional radical initiators.[11] Thus, these reactions can be also started via UV-light or proceed under sunlight even when no dedicated initiator is added via a self-initiation mechanism.[12] Another example for a conjugation reaction started by light was recently introduced by Bowman and co-workers, who used the CuAAC reaction, but generated the active copper catalyst in situ.[13] Also, Barner-Kowollik showed that the light-induced formation of *o*-quinodimethanes can be used to generate a polymeric enophiles that can undergo a classical Diels–Alder conjugation.[14] The above approaches are indeed UV-triggered reactions and the first even allows for a "switch-off" after the light was turned off (with the CuAAC method this can only be achieved by addition of oxidizing agents), the conjugation reaction itself is in those cases, however, not driven by light.

It is evident from the criteria for efficient *click* reactions that cycloadditions (CA) are generally good candidates to perform conjugation reactions; they proceed in high yields on a single reaction trajectory and – in most cases – form stable C–C bonds. While the thermally allowed [2 + 3] and [2 + 4] cycloaddition reactions are already largely exploited, almost no example in the polymer field is so far found for photochemically allowed [2 + 2] CA reactions.[15] Only the team of Barner-Kowollik recently demonstrated that a [2 + 2]-like reaction can in principle be performed using the dithioester thiocarbonyl bond on a polymer derived by the reversible addition–fragmentation transfer polymerization (RAFT) technique.[16] In their study, these authors demonstrated that conjugation of an ene can be achieved under UV-irradiation even though the ene was—due to a rearrangement reaction—not conjugated in the form of a four-membered ring, but rather inserted into the bond. So far and to the best of our knowledge, this reaction is the only example of a polymer modification/conjugation reaction where the reaction itself is triggered by light and can thus be turned on and off by will without delay and without use of additional reagents to start or stop the reaction.

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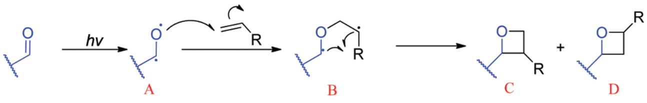
Scheme 1. Mechanism of the Paterno−Büchi Reaction



As a starting point in this research project, the alkene-enone and the Paterno−Büchi reaction seem to be the best choice as most data is available on these reactions in literature.[15,17] Generally, the reaction can proceed via two distinct pathways that lead to cyclization. No cyclization can occur from the ground state because of a phase mismatch of the frontier molecular orbitals. If the ground state of the activated compound is promoted to the S_1 state via a photon, then cycloaddition is allowed and can occur in a concerted mechanism. Via intersystem crossing, also a T_1 level can be reached, which is then followed by cycloaddition via a biradical intermediate (see Scheme 1A). Which pathway is predominant is dependent on substituents, solvent and concentration of the reaction partners. The exact influence of substituents on the regio- and stereoselectivity of the cycloaddition is hard to predict, but olefins with electron withdrawing substituent generally proceed via a concerted mechanism, while a donor-substituent preferentially leads to a radical pathway. The radical intermediate pathway (B) is most commonly observed, which leads to less predictable regio- and stereoselectivity; a stable C−C bond is however reached in any case. Thus, both reaction pathways are viable routes toward stable conjugations (C + D).

Many high-yield Paterno−Büchi reactions are found in literature, where ethyl-phenylgloxylate,[18] benzaldehyde, acetophenone, or benzophenone have been used as the carbonyl group source to name some prominent examples. Generally, substrates that are electron rich and stabilized via aromatic rings are good choices for such reactions. The part of the alkene quencher can be taken for example by allylic alcohol,[19] oxazole,[20] methyl vinyl ketone,[21] isobutene,[22] 1,2-dicyanoethane,[23] furan (-derivatives),[24] and octene,[25] for which yields in the range >70−92% were reported.

In here, we want to report on the conjugation of a variety of alkene compounds onto aldehyde-functional polymers that were synthesized via atom transfer radical polymerization (ATRP) by employing a ATRP initiator bearing a benzaldehyde-type functional group.[26] Examples for polystyrene (PS) and polyisobornyl acrylate (PiBoA) are given and the conjugation products carefully analyzed using NMR spectroscopy as well as electrospray ionization mass spectrometry (ESI−MS).

EXPERIMENTAL SECTION

Materials. Isobornyl acrylate (iBoA, Aldrich, tech.), styrene (Sty, Aldrich, 99%), and methyl methacrylate (MMA, Aldrich, 99%) monomers were deinhibited over a column of activated basic alumina. Copper(I) bromide (Cu^IBr, Sigma-Aldrich, 98%) was washed with acetic acid at 80 °C for 18 h to remove any soluble oxidized species before being filtered, washed with absolute ethanol, to pH 7, then washed with ethyl ether, and then dried under vacuum. 4-Hydroxybenzaldehyde (Aldrich, 98%), 2-bromopropanoyl bromide (Aldrich, 97%), triethylamine (TEA, Sigma-Aldrich, 99%), 1-octene (Aldrich, 98%), 2-methylpentene (Aldrich, 98%), allylamine (Aldrich, 98%), 3-buten-1-ol (Aldrich, 96%), trimethylolpropane allyl ether (Aldrich, 98%), and triallyl cyanurate (Aldrich, 97%) were used as received.

Synthesis of 4-Formylphenyl 2-bromopropanoate (FPBP). The compound 4-hydroxybenzaldehyde (9.327 g, 0.076 mol), 200 mL of THF and TEA (9.754 g, 0.096 mol) were placed into a 250 mL three-necked round-bottom flask fitted with a condenser, a magnetic stirrer, a nitrogen inlet−outlet, and an addition funnel containing a mixture of 2-bromopropinoyl bromide (20 g, 0.096 mol) and 50 mL THF. The flask was placed into an ice−water bath. The solution of 2-bromopropionyl bromide was added dropwise over a period of 0.5 h under inert conditions. Subsequently the mixture was allowed to reach room temperature and left stirring overnight. A white precipitate was filtered off. The solvent was removed and the crude product was dissolved in dichloromethane. The solution was washed three times with 1 M HCl and twice with water. Finally, the solution was dried with $MgSO_4$, and the solvent was removed in vacuo. Further purification by column chromatography, using hexane and ethyl acetate (hex:EtOAc = 5:1 → 3:1) as eluents, yielded 15.16 g (77.3%) yellowish liquid product.

^1H NMR (300 MHz, $CDCl_3$): δ = 9.96 (s, 1H, CHO), 7.92−7.88 (m, 2H, ortho to CHO), 7.30−7.23 (m, 2H, meta to CHO), 4.61−4.54 (q, 1H, CHBr, J = 6.86 Hz) and 1.92 (d, 3H, CH_3, J = 6.86 Hz).

General ATRP Polymerization. The purified Cu^IBr (0.75 mmol, 108 mg, 1.5 equiv) was added under inert atmosphere into a sealed Schlenk tube. A mixture of 0.076 mol (16 mL, 150 equiv) of the monomer iBoA and 1.13 mmol (235 μL, 2.2 equiv) of PMDETA was purged with nitrogen for 1 h to remove residual oxygen followed by addition to the reaction flask via a degassed syringe. The EtOAc solution (25 vol %) was degassed likewise and the reaction mixture was heated up to 75 °C in an oil bath. Subsequently, the polymerization is started by adding 0.5 mmol (128 mg, 1 equiv) of degassed initiator. After the desired reaction time was reached, polymerization was stopped by cooling in liquid nitrogen and a NMR sample was taken for conversion determination. The polymer/monomer mixture was dissolved in THF and the copper catalyst was removed by passing the diluted reaction mixture over silica. After evaporating of the excess solvent, the polymer was precipitated into a mixture of ice cold methanol:water (4:1; 10-fold excess) yielding 5.32 g of polymer with M_n = 3200 g mol^{-1} and PDI = 1.16 (by THF−SEC).

Procedure for [2 + 2]-Cycloaddition. A typical procedure is given: 55 mg (0.02 mmol, 1 equiv) of aldehyde functional polymer (M_n = 3200 g mol^{-1}, PDI = 1.16) was mixed with 140 μL of 1-octene (0.885 mmol, 50 equiv) and dissolved in 1.25 mL toluene. The flask was sealed and flushed for 10 min with N_2 and later stirred for 48 h at room temperature while irradiated with UV-light using a Multilamp Reactor MLU 18 from Photochemical Reactor Ltd. The reactor consists of 12 × 15 W lamps with a peak emission of 254 nm and a distance of 12 cm to reaction flask. After reaction the solvent and remaining olefin was removed in vacuo.

Electro Spray Ionization Mass Spectrometry (ESI−MS). The Spectra were recorded on an LCQ mass spectrometer (Finigian MAT) equipped with an atmospheric pressure ionization source operating in the nebulizer assisted electro spray mode. The instrument was calibrated in the m/z range 220−2000 using a standard solution containing caffeine, MRFA and Ultramark 1621. A constant spray voltage of 4.5 kV was used and nitrogen at a dimensionless auxiliary gas flow-rate of 10 and a dimensionless sheath gas flow-rate of 60 were applied. The capillary voltage, the tube lens offset voltage and the capillary temperature were set to 34 V, 10 V, and 270 °C respectively. A 250 μL aliquot of a polymer solution with concentration of 1 mg mL^{-1} was injected. A mixture of dichloromethane and methanol (DCM:MeOH = 1:3), all HPLC grade, were used as solvent.

THF Size Exclusion Chromatography (THF−SEC). Analysis of the MWDs of the polymer samples were performed on a Polymer Laboratories Spectra Series (P100, AS100, Shodex RI-71), comprising an autosampler, a PLgel 5.0 μm guard column (50 × 7.5 mm), followed by three PLgel 5 μm Mixed-C columns (300 × 7.5 mm) and a differential refractive index detector using THF as the eluent at 40 °C with a flow rate of 1 mL min^{-1}. The SEC system was calibrated using linear narrow polystyrene standards ranging from 474 to 7.5 × 10^6 g mol^{-1} (PS (K = 14.1 × 10^{-5} dL g^{-1} and α = 0.70), PiBoA (K = 5.0 × 10^{-5} dL g^{-1}

and $\alpha = 0.745$) and PMMA ($K = 9.44 \times 10^{-5}$ dL g^{-1} and $\alpha = 0.719$)) and toluene as a flow marker.

Nuclear Magnetic Resonance Spectroscopy. ^{1}H NMR spectra were recorded in deuterated chloroform applying a pulse delay of 12 s with two NMR spectrometer (300 and 400 MHz) from Oxford Instruments Ltd. using a Varian probe (9 mm-4-nucleus AutoSWPFG).

■ RESULTS AND DISCUSSION

To find suitable reaction conditions, first model studies using low-molecular weight compounds were carried out. As expected from theory, best results were obtained with terminal olefins in presence of benzaldehyde. When activated alkenes were used, e.g., an acrylate, homocyclization was observed, however the alkene showed a high propensity to react with itself. Ketones, as described in the literature as suitable reagents in Paterno—Büchi reactions[15] underwent the desired reactions, with however very slow reaction rates. Figure 1 depicts the proton NMR spectrum of the cycloaddition product from benzaldehyde and 1-octene. Despite the simple starting materials, a complex spectrum is obtained, which is due to the large number of stereo- and regioisomers that are formed in the reaction. As in the depicted case an excess of octene was used (removed in vacuo after reaction) an almost complete disappearance of the characteristic aldehyde peak close to 10 ppm is observed. Even though a clear assignment is not easily done, the peak region between 2 and 2.5 ppm can be assigned to the protons at the carbon atom opposite to the oxygen in the four-membered ring, the proton region 4—5 ppm to the protons close to the oxygen and the region of 5—6 ppm to the protons adjacent to the aromatic ring (a zoom into this region of the spectrum can be found in the Supporting Information). For the formation of the two different regioisomers (see Scheme 1, parts C + D), indication is given that the 1,2 disubstituted oxetane is preferentially formed compared to the 1,3-substituted product. An abundant doublet at 5.91 ppm is observed, which can only be assigned to the 1,2-substituted product.[27,28] Despite the large number of isomers, it can be concluded that the oxetane formation out of the aldehyde is almost quantitative, therefore demonstrating that the Paterno—Büchi reaction can serve as a conjugation tool for two individual building blocks.

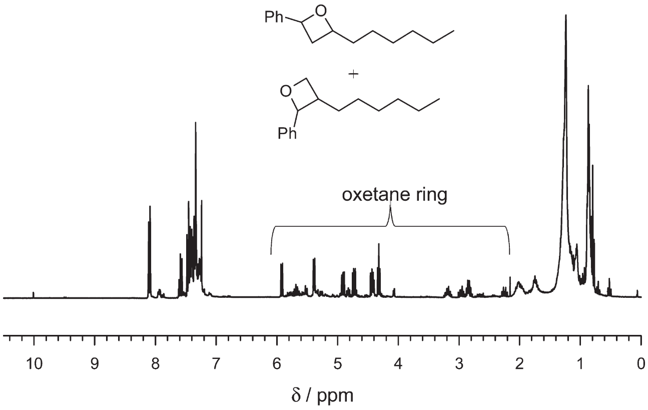


Figure 1. NMR spectrum from model studies with benzaldehyde and 1-octene (1:50) after 48 h UV irradiation.

In order to transfer the results from small organic compounds to a polymeric system, several design criteria need to be considered. Generally, high fidelity (hetero) telechelic polymers are required to ensure a complete conjugation of substrates onto polymer chains. Since the carbonyl function is the moiety that is activated by UV light, higher reaction efficiencies are obtained when the alkene is employed in excess. Hence, for purification reasons, polymers carrying a terminal aldehyde moiety needed to be synthesized to allow for an excess of alkene that can be removed after reaction. A facile route to reach such structures is given via the ATRP process employing an aldehyde-functional initiator (see Scheme 2). A suitable initiator, 4-formylphenyl-2-bromopropanoate (FPBP), carrying a benzaldehyde moiety has been synthesized before by Yagci and his team and no interference of the aldehyde group with the ATRP process was observed.[29]

Two polymers were synthesized employing the FPBP. To cover different materials, a polystyrene and a polyisobornyl acrylate was targeted as starting materials for later conjugation reactions. The molecular weights and polydispersities of the residual polymers are collated in Table 1. Low conversions were chosen to prevent chain termination via chain transfer-to-polymer, [33] which would result in a lower end group fidelity. The molecular weight distributions of the polymers are given in the Supporting Information. In both cases, a successful ATRP could be carried out. Also MMA was tested with FPBP, however, significant amounts of dead polymer material was observed repeatedly, giving rise to broad molecular weight distributions with low-molecular weight shoulders. It should be noted that NMR analysis revealed a relatively high aldehyde functionality, indicating that the initiator was effective and that by changing the reaction conditions, i.e., the ligand, well-controlled PMMA should be obtainable with FPBP.

Scheme 2. Synthesis of the Aldehyde Functional ATRP Initiator Followed by Polymerization of Styrene

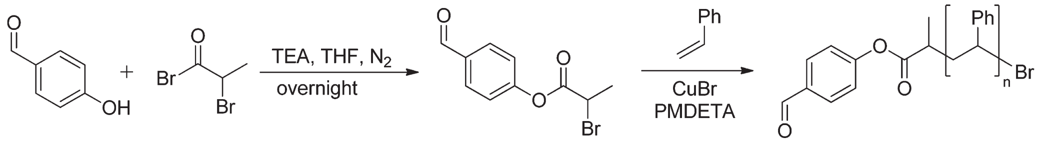


Table 1. Average Molecular Weights and Functional Fidelity of the Aldehyde-Functional Polymers

	polymer	M_n/ g·mol^{-1}	M_w/ g·mol^{-1}	*PDI*	conv, %	$M_{n,NMR}$/ g·mol^{-1}	$M_{n,theo}$/ g·mol^{-1}	end group funct,[a] %
I	PiBoA	3100	3600	1.16	13.4	2700	2705	97
II	PS	2770	3080	1.11	20	3380	2930	91

[a] Calculated by comparing peak integrals of the polymer end groups.

Also for the other two polymers, PMMA and PiBoA, high end group functionalities were obtained. Also, a good match between expected average molecular weight, measured M_n from SEC analysis and from NMR analysis was found. Molecular weights from NMR were deduced via comparison of the characteristic peak of the proton adjacent to the bromine at 4.1−4.25 ppm. Functional fidelity was obtained by comparing the peaks of both end groups. A representative NMR spectrum of the polystyrene sample **II** is shown in Figure 2.

Scheme 3 depicts the Paterno−Büchi [2 + 2] reaction of the polymeric substrate. In the scheme, R is a representative for the different polymer types, PS or PiBoA. In a first step, the polymers were all conjugated with 1-octene (**a**). To test for the conjugation efficiency, trials were carried out with varying contents of **a** whereby all other reaction conditions were kept constant, that is reaction at room temperature for 2 days under constant UV irradiation in a degassed toluene solution. The yield of the photoreaction was determined by two different techniques after isolation of the polymer by precipitation. NMR analysis was carried out on all polymers to test for complete disappearance of the aldehyde peak. It should thereby be noted that to stay on the side of caution, a prolonged pulse delay time (12 s) and a larger than normal number of scans was applied in the proton peak acquisition to ensure that a reliable quantitative analysis of the polymer end group could be performed. An example for a NMR spectrum of a completely converted aldehyde-functional polymer is also given in the lower part of Figure 2. Integration of the aldehyde peak region reveals complete disappearance of the aldehyde signal. At the same time, peaks according to the oxetane appear, which are, however, not abundant enough to allow for accurate integration.

To allow for a better assignment of the products, the polymers obtained from the cycloadditions were subjected to ESI−MS mass analysis to further test the conjugation efficiency. The advantage of a mass spectrometric analysis over the NMR characterization is that both the disappearance of the starting material and emergence of the products can be traced in higher detail and with a largely increased accuracy. Also, all of the different stereoisomers of the formed oxetane are isobaric and hence appear as only one apparent species in the mass spectrum. In view of the present study this is an advantage since the exact configuration of the conjugated moiety is not of relevance. In the upper part of Figure 3, a representative section of the full mass spectrum is depicted. The peak assignment alongside experimental and theoretical m/z can be found in Table 2. Several peaks are seen which may practically all be assigned according to the expectations of an ATRP polymerization. The most abundant peak in each monomer repeat unit (i.e., 1735.7 m/z) can be assigned to

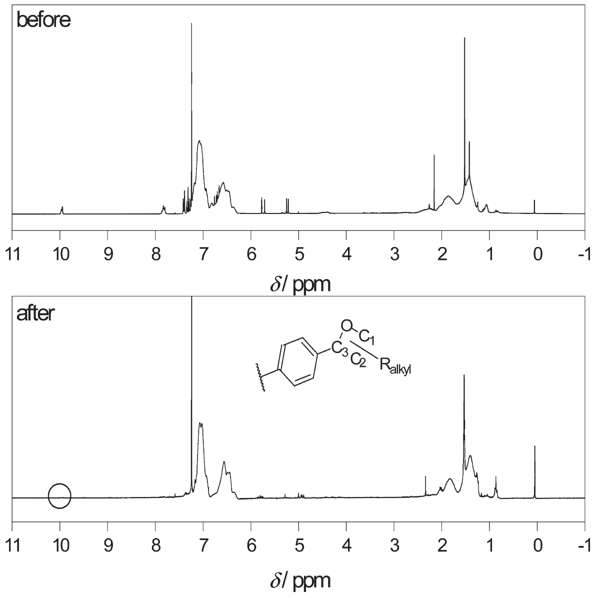


Figure 2. NMR spectra of polystyrene **II** before (upper part) and after cycloaddition with 1-octene at room temperature (**II** to octene = 1:50).

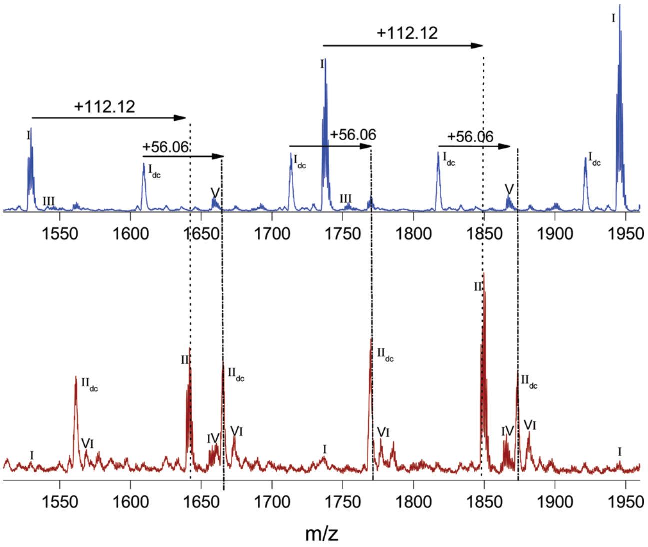


Figure 3. ESI−MS spectrum of polyisobornyl acrylate sample **I** before (top) and after (bottom) conjugation with 1-octene.

Scheme 3. End Group Modification of the Aldehyde-Terminal Polymers via [2 + 2] Cycloaddition

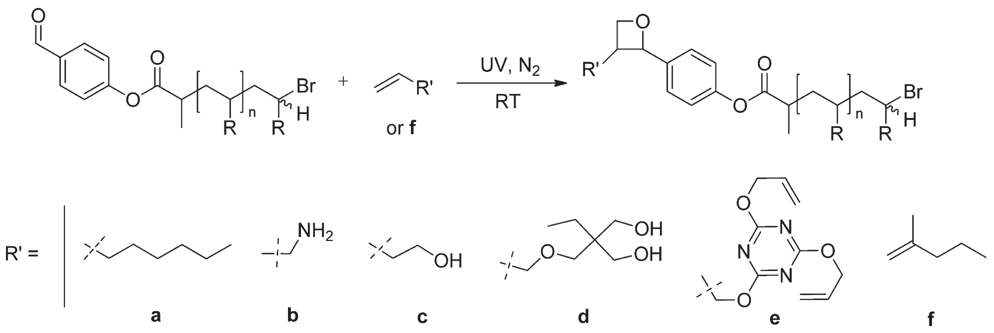


Table 2. Species Identified in the Mass Spectra As Shown in Figure 3

number	name	formula	experiment/ (m/z)	theory/ (m/z)	δ
		Na^+ Adducts			
II	Br-M_7-oxe	$C_{109}H_{165}BrO_{17}Na^+$	1847.80	1848.11	0.3
I	Br-M_7-CHO	$C_{101}H_{149}BrO_{17}Na^+$	1735.67	1735.99	0.3
V	H-M_7-CHO	$C_{101}H_{150}O_{17}Na^+$	1658.73	1658.08	0.6
		K^+ Adducts			
IV	Br-M_7-oxe	$C_{109}H_{165}BrO_{17}K^+$	1863.80	1864.09	0.3
III	Br-M_7-CHO	$C_{101}H_{149}BrO_{17}K^+$	1751.73	1751.96	0.2
VI	H-M_7-CHO	$C_{101}H_{150}O_{17}K^+$	1673.73[a]	1674.05	
VI	=-M_7-CHO	$C_{101}H_{149}O_{17}K^+$	1673.73[a]	1672.04	
		${Na_2}^{2+}$ Adducts			
$\mathbf{I}_{dc}$	Br-M_{15}-CHO	$C_{205}H_{309}BrO_{33}{Na_2}^{2+}$	1711.93	1712.07	0.1
$\mathbf{II}_{dc}$	Br-M_{15}-oxe	$C_{213}H_{325}BrO_{33}{Na_2}^{2+}$	1767.93	1768.14	0.2
VI	H-M_{15}-CHO	$C_{205}H_{310}O_{33}{Na_2}^{2+}$	1673.73[a]	1673.12	
VI	=-M_{15}-CHO	$C_{205}H_{309}O_{33}{Na_2}^{2+}$	1673.73[a]	1672.11	

[a] The monoisotopic peak of the species is overlapped, m/z 1673.73 is the maximum of the full peak.

species **I** (Br-M_7-CHO) (see Table 2), which is a polymer species consisting of seven monomer units, the aldehyde-functional initiator on one side and a bromine end group on the other side. A relatively good match (0.3 Da) between theoretical and experimental mass is found considering the mass spectrometer type used and mass range under observation. The peak pattern of the main peak (and all others) can be adequately simulated when taking the natural abundances of isotopes into account. Other peaks in the spectrum represent double-charged products which can be also assigned to the main ATRP product. Low abundant single-charged species (**III** and **V**) also appear in the spectrum, which can be assigned to potassium adducts of the main product (**III**) and disproportionation products stemming from conventional termination during polymerization (**V**). Occurrence of such termination product is not uncommon for ATRP polymerizations in the observed amounts.[30] Regardless, even though species **V** cannot be reactivated in further ATRP polymerization, it nevertheless carries the desired aldehyde end group and can hence be functionalized. Satisfyingly, no side products resulting from transfer to polymer reactions, which are often observed in acrylate polymerizations, are observed in significant concentrations. Thus, all species present in the mass spectrum can in principle be conjugated with alkenes and a complete shift of all peaks should be observable after a successful Paterno—Büchi reaction. Indeed, when inspecting the ESI—MS spectrum of the polymer after conjugation, a more or less complete shift is observed, as indicated in Figure 3. The main product, both the single charged as well as the double charged species are shifted according to the mass of octene (112.12 and 56.06 Da for the double charged chains, respectively). Only few, very low abundant species are seen in the depicted case. Success of the reaction can thus also be confirmed from the side of the product, where the NMR only confirmed the conversion of the starting material. For the analysis of the product mass spectra, it is important to note that Barner-Kowollik and co-workers, when trying the cycloaddition of RAFT C=S bonds with alkenes obtained products where an insertion rather than a cycloaddition had taken place.[16] Such product is isobaric and can, at least in principle, also contribute to the spectrum in the present case. Via MS/MS experiments it can, however, be shown that no analogue species as in the RAFT reaction is present.

Table 3. Conjugation Efficiencies for Aldehyde Functional PiBoA I with 1-Octene

[**a**]/[polymer]	$yield_{MS}$/%	$yield_{NMR}$/%
1000	90	100
100	90	100
50	85	100
40	44	75
30	32	75
25	29	63
20	33	75
15	25	55

Both NMR and ESI—MS are suitable to determine the yield of the reaction. A series of experiments was carried out at constant reaction time with varying amounts of alkene. The results from these experiments are collated in Table 3. In this table, yields based on NMR, that is disappearance of aldehyde in the product spectrum, and yields based on ESI—MS are given. ESI—MS yields were obtained by integration of all single charged species within a representative monomer repeat unit in the mass spectra that are unambiguously assignable to a polymeric species (that are peaks that show a typical isotopic pattern). Such an approach can be taken for acrylates to obtain relative concentrations of all polymer species with different end groups.[31] As one can see from the table, NMR predicts higher yields for the reaction that is observable with ESI—MS. This may have two reasons: (i) occurrence of side products, which are too low in concentration to be detectable in NMR, and (ii) peaks that represent the desired product but have been degraded (e.g., ring-opened) during the ESI process are falsely accounted for. Regardless, the ESI-based yields represent a lower limit and the true yields may lay between both numbers obtained.

Overall, with decreasing equivalents of alkene present in the reaction mixture a decreasing yield is observed. Close to quantitative conversion of the aldehyde is only seen when at least 50 equiv are employed at the chosen reaction time of 2 days.

Table 4. Yields of Reaction of Polyisobornyl Acrylate I with Various Alkenes

alkene	$C_{C=O}/C_{C=C}$	$yield_{MS}$, %
1-octene (**a**)	1:40	95
allylamine (**b**)	1:50	60
3-buten-1-ol (**c**)	1:50	34
trimethylolpropane allyl ether (**d**)	1:50	88
triallyl cyanurate (**e**)	1:50	86
2-methylpentene (**f**)	1:50	90

It should be noted that in order to avoid side-reactions, relatively low intensity UV light was used and therefore long reactions times were chosen to compensate. Higher amounts of alkene in the reaction mixture or higher light intensities will lead to an increase in reaction rate and further refinement of the exact conditions will be required.

After a relatively good correlation between NMR analysis and ESI–MS is established, estimates on the overall quality of the reaction can be made based on NMR analysis alone. This is important to allow for an easy screening of reaction conditions. Also, an even more important, NMR also allows for reaction control in case where no mass spectra can be obtained. ESI–MS is in most cases limited to low molecular weight compounds and polymers with sufficient polarity in order to ionize. Thus, unpolar polymers such as polystyrene can only be analyzed via mass spectrometry with comparatively high effort.[32] In the case of the polystyrene (**II**) that was prepared via ATRP with the aldehyde functional polymer, no mass analysis could be carried out. With identical reaction conditions and 50 equiv of 1-octene, however, were quantitative yields indicated by NMR, thus allowing for the conclusion that also for these type of polymers successfully end group modifications via the [2 + 2] cycloaddition could be carried out.

In the subsequent step, different alkenes carrying various functional groups were subjected to Paterno–Büchi end group modifications. Largely successful modifications were achieved in case of the functional alkenes depicted in Scheme 3 as well as 2-methylpentene to also test a 1,1-disubstituted alkene. In all cases, complete conversion of the terminal aldehyde was observed by NMR. Yields based on ESI–MS are given in Table 4. Satisfying results were obtained in most cases. Somewhat surprisingly, even the disubstituted methylpentene exhibited very high yields, demonstrating that steric hindrance might not be too high. It may be assumed that with a disubstituted compound, a higher regioselectivity was potentially achieved; however, no further characterization was carried out to test for this hypothesis.

It should be noted again that the MS technique most likely leads to an underestimation of the true yield of the reaction. For example, in case of the alcohol **c**, the expected oxetane product peak is clearly the most abundant. However, due to unfavorable signal-to-noise and presence of many small background peaks, a low yield was numerically deduced. Regardless, yields close to or higher than 90% are observed (with the exception of **b** and **c**), indicating good success of the end group modifications and demonstrating that the [2 + 2] photoreaction is relatively tolerant toward other functional groups. This is a very important observation, since only with a high functional tolerance, applicability of the method to a large number of polymers consisting of functional monomers is given. In particular, the cyanurate **e** is therefore of high interest, since it introduces two alkenes to the polymer chain, hence allowing for branch point for further modification reactions. An interesting effect is seen with the analysis of the conjugation product with trimethylolpropane allyl ether **d**. In the mass spectra, peaks according to an internal cyclization of the conjugated molecule appear as the most abundant species in the mass spectrum. Since such cyclization was not observed when irradiating **d** alone by UV light (as confirmed by NMR), it can be concluded that this specific peak is a result of a condensation reaction occurring during the ESI process. Thus, both the product peak as well as the cyclized product together were counted to calculate the yield. All mass spectra and assignment of peaks can be found in the Supporting Information.

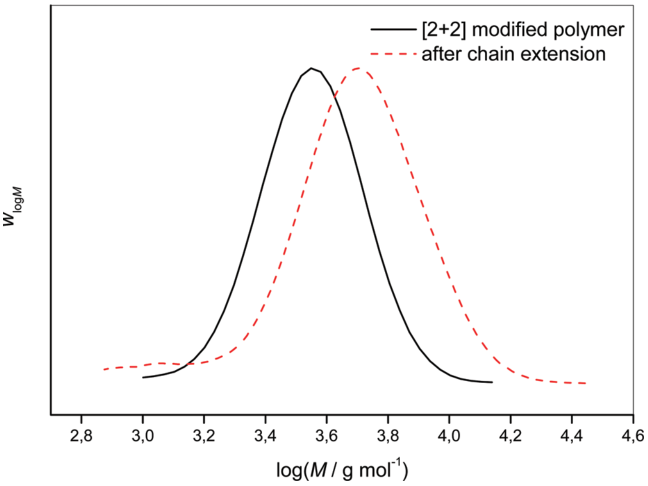


Figure 4. Molecular weight distributions of the chain-end modified polyisobornyl acrylate **I** (full line) and chain extended polymer via subsequent ATRP (dashed line).

Unsatisfying yields are determined for **b** and **c**. As noted above, for **c** this may be attributed to the appearance of many smaller product peaks that cannot be assigned unambiguously, thus reducing the calculated yield of the reaction. For the amine derivative **b**, less products are observed. In this case, the desired product is only low abundant in the spectrum. Therefore, a peak according to an oxidized version of the expected functional oxetane is seen. Since the reaction is carried out under inert conditions, it is therefore assumed that the oxidation to the substituted hydroxylamine occurs during mass analysis and the conversion of the reaction was calculated based on this peak. The overall yield is, however, still low (60%), and the reaction with the amine must be considered as unsuccessful at this point in time. It should, however, be stressed again that the presence of unassigned peaks in the spectrum does not necessarily mean that the reaction was unsuccessful. In this specific case, side reactions—before or after cycloaddition—may occur such as oxetane ring-opening, imine formation, or bromine substitution reactions or further oxidations during the ESI measurement. Further studies as well as analysis with higher resolution mass spectrometry may help to elucidate the exact situation.

The mass spectra described above indicated that the bromine end group is retained in the end groups modification and is not disturbed by the UV light. Therefore, it should be possible to carry out ATRP chain extensions after the photoreaction had taken place. Therefore, the chain-end modified **I** was subjected to further polymerization under ATRP conditions. Figure 4 depicts the molecular weight distributions before and after the ATRP reaction. The full line represents **I** after successful cycloaddition with 1-octene where all polymer characteristics such as average molecular weight and polydispersity of the original ATRP polymer was retained. The dashed line shows the polymer after chain extension. In the given example, the number-average molecular weight increased from 3100 to 4100 $g\cdot mol^{-1}$ and the PDI increased from 1.16 to 1.32. While the extended polymer is hence slightly broader in its distribution than usually achievable in ATRP block polymerizations, it still shows a complete shift of the whole distribution toward higher molecular weights, which is an independent proof for the retention of the active bromine functionality at the polymer chain end.

It must be noted that the experiments described herein resemble a fundamental study to resolve whether the Paterno—Büchi reaction is suitable as an efficient polymer modification reaction. Compared to typical *click*-reactions, the photocycloaddition may not fulfill the stringent criteria of the click concept[2] as reaction times are generally somewhat too high and also relatively large excesses of the alkene compound need to be employed in order to achieve complete conversions of the aldehyde compounds. Nevertheless, the required starting materials are easily obtained at low cost via the route described and reaction conditions may still be further refined to allow for faster reactions and lower excess amounts of alkene. Such investigations are currently underway in our laboratories. Overall, the Paterno—Büchi CA has a distinct synthetic potential: A relatively high tolerance toward other functional groups is achieved and thus secondary functionalities can be introduced at the chain end under relatively mild reaction conditions. Combinations of the CA with other efficient modification reactions or ATRP block polymerizations can be made, giving rise to interesting synthesis pathways toward more complex macromolecular architectures. It should hereby be also noted that the oxetane ring that is formed in the CA can potentially be ring-opened and hence serve as a secondary conjugation point in the polymer. Investigations into this particular feature are also currently underway in our laboratories.

CONCLUSION

The successful implementation of UV-induced Paterno—Büchi cycloaddition of alkenes onto aldehyde-functional polymers was demonstrated. A polyisobornyl acrylate as well as a polystyrene derivative, both carrying a terminal aldehyde end group were synthesized utilizing an aldehyde-functional ATRP initiator. The efficiency of the CA reaction was tested via NMR and ESI—MS analysis and for the conjugation of 1-octene, conversions of 90—100% were obtained after mild UV irradiation for 2 days at room temperature, when 50 equiv of the alkene were used. Via this modification reaction, different functional groups were introduced ranging from multifunctional allyl-compounds to disubstituted alkenes and amino or hydroxyl-functional alkenes. In the photoreaction, the integrity of the bromine end group of the ATRP polymers is unchanged and subsequent ATRP chain extensions can be performed after the cycloaddition, demonstrating the versatility of this newly introduced polymer modification reaction.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Detailed evaluation of NMR and ESI spectra of the discussed polymer samples and molecular weight distributions of the starting materials. This material is available free of charge via the Internet at http://pubs.acs.org/.

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