Comparative Study on Post-Polymerization Modification of C1 Poly(benzyl 2-ylidene-acetate) and Its C2 Analog Poly(benzyl acrylate)

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ABSTRACT: The present study investigates the challenging approach of post-polymerization modification on polymers with a sterically demanding reaction center. Therefore, the general possibility to functionalize polymethylene moieties was investigated. Poly(benzyl 2-ylidene-acetate) was synthesized by polymerization of benzyl 2-diazoacetate utilizing [(*L*-prolinate)Rh¹(1,5-dimethyl-1,5-cyclooctadiene)] as a catalyst. Subsequently, the modification of C1 polymerized poly(benzyl 2-ylidene-acetate) with amines was analyzed and the obtained

data set was compared with experimental data derived for the C2 analog poly(benzyl acrylate). This is the first study on postpolymerization modification utilizing densely functionalized polymethylenes as starting materials. © 2015 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2016**, *54*, 686–691

KEYWORDS: amidation; C1 polymerization; functionalization of polymers; post-polymerization modification; polymethylenes; syndiotactic; synthesis

INTRODUCTION Ever since Staudinger¹ devised the term polymer analogues reaction in 1939, post-polymerization modification got recognized as a powerful synthetic toolbox in polymer science and developed into a widely used approach to vary the functionalities of polymeric materials.² However, up to date, little to no research has been conducted on polymethylenes with densely packed side chain functionalities. This is mainly attributed to difficulties in conventional polymerization techniques to synthesize the appropriate polymethylenes. Conventional polymerization techniques usually suffer from limitations arising from higher functionalities on monomers, for example, due to catalyst poisoning.³ Various approaches were tested to synthesize polyolefins functionalized with an ester- or acid group attached to every main chain carbon atom. However, facile radical homopolymerization, for example, of maleic anhydride is not suitable, and hence numerous attempts following classic approaches were made.⁴ There is one exception, a recent example of Müllen et al. shows the feasibility of this route to synthesize poly(methylene amine), utilizing 1,3-diacetyl-4-imidazolin-2one as a monomer.⁵ For the first time, they succeeded in the synthesis of a polymer containing an amino group at each carbon atom of the polymer backbone. Recently, densely functionalized polymethylenes got accessible via novel C1 polymerization techniques, such as trialkylborane-mediated living polyhomologation of sulfoxide ylides, which was

invented by *Shea* et al. in 1997.⁶ This technique is highly interesting with respect to the living polymerization character and the variability of end groups. However, the synthetic access toward functional sulfoxide ylides remains highly challenging. Many other ylide structures have either not yet been investigated or did not lead to polymeric materials and remained unpublished.^{7,8} Another approach is based on transition metal catalyzed polymerization of α -diazocarbonyl compounds as monomers, which was mainly influenced by the research groups of *Liu*, *Ihara*, and *de Bruin* (Scheme 1).⁹⁻¹¹

While, all research groups make use of α -diazocarbonyl compounds as monomers, the investigated catalytic systems, based on copper, palladium, and rhodium perform tremendously different. Many of the investigated catalysts result in a lack of control of the resulting polymethylene backbones and their molecular weight. Palladium catalysts often result in polymers containing azo-groups in their backbone besides the desired polymethylene repeating unit.¹² In 2006, *de Bruin* et al. developed a polymerization technique of α diazocarbonyl compounds via rhodium catalyst mediation.¹¹ This approach results in well defined syndiotactic polymethylenes, marking a turn in carbene polymerization as it is the first example of stereoregular carbene polymerization.¹³ Furthermore, no ill-defined repeating units were noticed, that is, no presence of azo-groups. By far, this

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SCHEME 1 Illustrating the general approach of C1 polymerization utilizing α -diazocarbonyl compounds as monomers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].

approach results in the highest molecular weights published on C1 polymers via transition metal catalysis. With respect to the investigated monomer scope of C1 polymerization techniques, benzyl 2-diazoacetate and ethyl 2-diazoacetate have been most frequently used and polymers were obtained in good yields and high molecular weights, that is, 85% yield and 590000 g/mol (M_w) for poly(ethyl 2-ylidene-acetate).¹⁴ Polyolefins and their structural analogues polymethylenes, originating from carbene precursors as monomers, are highly important polymeric materials. However, up to now it still remains an elusive goal to account for the need of various densely packed side chain functionalities by classic approaches and even by C1 polymerization as their monomer scope is not yet fully explored. Consequently, postpolymerization modification might help to solve the current limitation for monomer functionalities, simply by applying click chemistry modification tools to C1 polymers and/or their respective monomers. However, up to now, the investigated polymethylene side chains are inherently non-reactive, for example, common esters, and do not feature any side groups suitable for click modifications. In 2014 the group of Theato transferred the synthetic approach of Yang and Birman,¹⁵ utilizing 1,2,4-triazole (Tz) and 1,8-diazabicyclo[5.4.0]undece-7-ene (DBU) as organo activators, to polyacrylates opening up a new pathway for post-polymerization modification of non-activated ester side chains.¹⁶

In this study, we describe the evaluation of functional polymethlyenes in view of their accessibility to postpolymerization modification using amines as substituents. To the best of our knowledge, this is the first time that functionalized polymethylenes have been investigated in a postpolymerization modification approach. Scheme 2 shows the concept of post-polymerization modification of poly(benzyl 2-ylidene-acetate) using amines as substituents. Furthermore, we will compare the resulting products to the products obtained from polyacrylates and highlight the observed differences.

EXPERIMENTAL

Materials and Methods

All chemicals were commercially available and used as received without further purification. Stated yields refer to the purified and isolated products. [(*L*-prolinate)Rh¹(1,5-dimethyl-1,5-cyclooctadiene)] was prepared as described in literature.¹⁷



Fourier transform infrared (FT-IR) spectroscopy was measured on a Thermo Scientific Nicolet iS10. Measurements were conducted with an attenuated total reflectance (ATR) attachment. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 300 MHz FT-NMR spectrometer in deutorated solvents. Size exclusion chromatography (SEC) data were obtained from two setups: (1) Intelligent pump JASCO PU-980, RI detector SFD RI 2000, Linear 5 μ m column MZ-Gel SDplus calibrated with polystyrene standards. Chloroform was used as eluent. (2) SEC setup using tetrahydrofurane as eluent consisted of FLOM Intelligent Pump Al-12-13, SFD RI 2000 detector, one guard column PLgel 10 μ m and two PLgel 10 μ m MIXED-B columns. For calibration linear polystyrene standards with various molecular weights were used. Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA 1 Star System under air. Differential scanning calorimetry was done on a DSC 1 Star System. For static light scattering (SLS) analysis an ALV/CSG-3 Compact Goniometer was used together with an ALV/LSE-5003 Multiple Tau Digital correlator. Measurements of the refractive index increments were conducted on a DnDc-2010 differential refractometer.

Benzyl 2-diazoacetate¹⁸

Benzyl alcohol (21.73 g, 2.0 mmol, 1.0 equiv.) and 2,2,6-trimethyl-4H-1,3-dioxin-4-one (28.59 g, 2.0 mmol, 1.0 equiv.) were heated at reflux in 50 mL toluene. After 20 hours, the solvent was removed and the residue was used in the next step without further purification. The residue containing benzyl acetoacetate (37.20 g, 1.9 mmol, 1.0 equiv.) was dissolved in 100 mL acetonitrile and triethylamine (29 mL, 2.1 mmol, 1.1 equiv.) was added. Next, a solution of tosylazide (35.77 g, 2.5 mmol, 1.3 equiv.) in 150 mL acetonitrile was added dropwise. The resulting reaction mixture was stirred for 16 hours, followed by addition of lithium hydroxide (9.27 g, 3.9 mmol, 2 equiv.) in 170 mL distilled water. The mixture was finally stirred for 4 hours, filtrated, and extracted three times with diethylether. The combined organic phases were washed with brine and dried with magnesium sulfate, followed by solvent removal. The obtained residue was purified by column chromatography [petrol ether/ethyl acetate (4:1)@SiO₂; $R_f = 0.8$]. Yield: 15.34 g yellow liquid (0.87 mmol, 45%). ¹H NMR (300 MHz, CDCl₃, δ): 7.37 (s, 5H, CH_{ar}), 5.22 (s, 2H, CH_2), 4.81 (br. s, 1H, CH); ¹³C NMR (75 MHz, CDCl₃, δ): 135.9 (C_{ar}), 128.6 (CH_{ar}),128.3



SCHEME 2 Post-polymerization modification of functionalized polymethylenes, containing ester-groups, with amines as substituents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



SCHEME 3 C2 polymerization of benzyl acrylate and C1 polymerization of benzyl 2-diazoacetate as well as their reaction with primary amines leading to amides or imides as main products.

 (CH_{ar}) , 128.2 (CH_{ar}) , 66.5 (CH_2) , 46.4 (CH); FTIR (ATR) \tilde{v} $(cm^{-1}) = 2106$, 1683, 1386, 1351, 1171, 1003, 737, 696.

Poly(benzyl 2-ylidene-acetate) (C1)

Benzyl 2-diazoacetate (2.48 g, 14.10 mmol, 50 equiv.) and [(*L*-prolinate)Rh¹(1,5-dimethyl-1,5-cyclooctadiene)] (0.10 g, 0.28 mmol, 1.0 equiv.) were separately dissolved in 7.5 mL chloroform each.¹⁹ The catalyst solution was rapidly added to the monomer solution and the resulting reaction solution was stirred for 22 hours at room temperature. Yield: 1.22 g colorless solid (8.24 mmol, 58%). ¹H NMR (300 MHz, CDCl₃, δ): 6.92–7.25 (m, 5H, *CH*_{ar}), 4.73 (br. s, 2H, *CH*₂), 3.60 (br. s, 1H, *CH*); ¹³C NMR (75 MHz, CDCl₃, δ): 170.9 (*C*OO), 135.7 (*C*_{ar}), 128.1 (*C*H_{ar}), 66.8 (*C*H₂), 45.1 (*C*H); FTIR (ATR) \tilde{v} (cm⁻¹) = 1727, 1155, 981, 733, 694.

Poly(benzyl acrylate) (C2)

Polymerization was conducted by free radical polymerization of benzyl acrylate (3.51 g, 21.6 mmol, 1.0 equiv.) with azobisisobutyronitrile (0.03 g, 0.21 mmol, 0.01 equiv.) (AIBN) as the initiator in 20 mL 1,4-dioxane at 95 °C. The polymer was purified by repeated precipitation into methanol. Yield: 2.42 g colorless solid (14.92 mmol, 69%) ¹H NMR (300 MHz, CDCl₃, δ): 7.25 (br. d, *J* = 4.6 Hz, 5H, *CH*_{ar}), 4.96 (s, 2H, *CH*₂), 2.36 (s, 1H,*CH*), 1.24–2.02 (m, 2H, *CH*₂CH); ¹³C NMR (75 MHz, CDCl₃, δ): 174.2 (COO), 135.8 (*C*_{ar}), 128.5 (*C*H_{ar}), 128.1 (*C*H_{ar}), 66.4 (*C*H₂), 41.3 (*C*H), 35.0 (*C*H₂CH); FTIR (ATR) \tilde{v} (cm⁻¹) = 1727, 1455, 1151, 735, 695.

Post-Polymerization Modifications

All post-polymerization modifications were conducted for a reaction time of 17 hours at 120 °C. Purification was done by dialysis against methanol/dichloromethane (1:1, v/v).

General Procedure Using Acyl Transfer Reagents

A round bottom flask was charged with 1.0 equiv. of polymer **C1** or **C2** dissolved in anisole, 1.0 equiv. 1,2,4-triazole (Tz), 3.0 equiv. 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and 3.0 equiv. of amine.

General Procedure Using Bulk Conditions

A round bottom flask was charged with 1.0 equiv. of polymer **C1** or **C2** and 25 equiv. of amine.

RESULTS AND DISCUSSION

Synthesis and Characterization of C1 and C2 Polymers

Poly(benzyl acrylate) (**C2**) was obtained by free radical polymerization of benzyl acrylate with 1 mol% AIBN in dioxane (Scheme 3). Poly(benzyl 2-ylidene-acetate) (**C1**) was synthesized in chloroform according to known procedures.²⁰ In brief, the polymerization was conducted with benzyl 2diazoacetate as the monomer and 2 mol % (*L*-prolinate) Rh^I(1,5-dimethyl-1,5-cyclo-octadiene)] was utilized as the catalyst.

Both polymers were fully characterized by ¹H NMR, ¹³C NMR, IR spectroscopy, and SEC (see Supporting Information) and selected polymer data are listed in Table 1.

Both polymers showed a relatively broad molecular weight distribution and exhibited high molecular weights. Therefore, we anticipate similar and comparable polymer characteristics solely differing in density of the benzyl esters, which might affect reactivity. This functional density difference originates by the two different types of polymerization (**C1** and **C2** polymerization). With suitable starting materials in hand, we aimed in the next step for studying appropriate postpolymerization modification conditions.

Post-Polymerization Modification of C1 and C2 Polymers

In order to modify both polymers, we first investigated the use of 1 equiv. 1,2,4-triazole (Tz) and 3 equiv. 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as organo activators for acyl transfer reactions, following a recent publication that utilized polyacrylates as starting materials.¹⁶ This organo catalytic system successfully converts non-activated esters to amides in amidation reactions.¹⁵ As the solubility of both starting materials in dimethylsulfoxide is poor, we changed the solvent to anisole as a mid-range polar solvent.

Post-Polymerization Modification of C2 Polymer

First, we investigated the conversion of poly(benzyl acrylate) **C2** with 3 equiv. *n*-hexylamine in the presence of the Tz/DBU system and observed an ester conversion of 87.5% according to ¹H NMR (bottom spectrum Fig. 1). The ¹H NMR spectrum exhibited the expected alkyl chain signals, which were a direct result of the successful amidation reaction.

TABLE 1 Summarizing Characteristic Polymer Data of C1 and C2

Polymer	<i>M</i> n (g/mol)	<i>M</i> w (g/mol)	Dispersity (<i>M</i> _w / <i>M</i> _n)	Yield (%)
C2	25,000	96,900	3.9	69
C1	68,000	316,200	4.6	58



FIGURE 1 ¹H NMR spectra showing the successful amidation of poly(benzyl acrylate) **C2** with 3 equiv. *n*-hexylamine and Tz/DBU mediation (**C**). For comparison, the ¹H NMR spectra for poly(*n*-hexyl acrylamide) (**B**) and poly(benzyl acrylate) (**A**) are illustrated as well. All spectra were recorded in CDCl₃. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In the absence of the organo activators Tz/DBU, when solely heating **C2** dissolved in anisole with 3 equiv. *n*-hexylamine, we observed no conversion at all after the same reaction time. Hence, the clear difference in conversion highlights the importance of Tz/DBU in case of polyacrylates of non-activated esters. However, if we run the amidation under bulk reaction conditions (25 equiv. amine), a conversion of at least 74% was obtained without additional catalyst. The corresponding infrared spectrum presents the typical vibration modes for amides, including the NH-stretching and bending vibration modes at 3287 and 1543 cm⁻¹, respectively (Fig. 2).



FIGURE 2 Infrared spectra of C2 (*red solid line*) and C2 after reaction with 25 equiv. *n*-hexylamine at 100 °C (*black dashed line*) and 120 °C (*blue dotted line*) (C). Reactions were done in bulk for 17 hours. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE 2 Investigated Amines for Post-Polymerization Modification of Non-Activated Ester Polymer C1

Amine	Conversion in bulk reaction ^a (%)
Hexylamine	82 ^b
2-Ethylhexylamine	35
Piperidine	75 ^b
Dihexylamine	0
Benzyl amine	nd ^{bc}

^a Conversions calculated by ¹H NMR do not account for the proposed imide formation.

^b Greater than 50% according to IR spectrum (vide infra).

^c Not determined (nd) due to signal overlapping.

Furthermore, a shift of the original ester C=O stretch vibration mode at 1727 cm⁻¹ to smaller wave numbers upon amide formation (1640 cm⁻¹) was recorded. Higher reaction temperatures resulted in increased conversions, as can be seen in the IR spectra.

Next, we aimed for a comparison of these data with data obtained for modification reactions of the **C1** polymer poly (benzyl 2-ylidene-acetate).

Post-Polymerization Modification of C1 Polymer

Experimental details regarding post-polymerization modification with *n*-hexylamine, piperidine, and benzylamine will be discussed in the following as they show the most promising and interesting results regarding conversions, functionality, and size. Further analytic data are summarized and discussed in the Supporting Information (i.e., TGA, DSC, SLS). The investigated amidation reactions with various amines are listed in Table 2. Noteworthy, determination of the molecular weights by SEC was not successful using chloroform as eluent as for the starting material, but all polymers have been dialyzed with a membrane of MWCO = 6000 prior characterization, hence guaranteeing that only high molecular polymers have been obtained and analyzed. Analysis by SEC using tetrahydrofuran as eluent resulted in an $M_{\rm n}$ of 15000 g/mol and M_w of 34900 g/mol for functionalization using *n*-hexylamine utilizing bulk conditions with no additional catalyst and solvent. As comparative analysis via SEC was rather unsatisfactory due to different eluents, analysis via SLS has been performed and is depicted in the Supporting Information. These analytical data were measured from a different batch of polymer and therefore solely shown in the Supporting Information. They show the anticipated decrease in molecular weight upon functionalization.

Utilizing the same reaction conditions as for the functionalization of poly(benzyl acrylate) **C2** with *n*-hexylamine, involving the organo-activators Tz/DBU, on poly(benzyl 2-ylideneacetate) **C1** results in a conversion of roughly 60%, therefore being less effective as for polymer **C2**. However, in the absence of the organo activators Tz/DBU and solely heating the polymer with 3 equiv. *n*-hexylamine, led to a conversion of at least 30%, suggesting a sterical hindrance regarding ARTICLE



FIGURE 3 (A) ¹H NMR spectra in $CDCI_3$ of poly(benzyl 2-ylidene-acetate) **C1** before (**top**) and after (**bottom**) reaction with 25 equiv. *n*-hexylamine. (**B**) Proposed imide structure. (**C**) Infrared spectra of polymer **C1** before (*red solid line*) and after reaction with 25 equiv. *n*-hexylamine at 100 °C (*black dashed line*) and 120 °C (*blue dotted line*) All reactions were done in bulk for 17 hours. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the functional mechanism of Tz/DBU in case of the polymethylene polymer C1. At the same time, the successful partial conversion without organo activators suggests a certain tension of the C1 polymer backbone, resulting in an increased reactivity when compared with C2 (no conversion). Next, experiments to increase the conversion of C1 were conducted and we therefore investigated the overall conversion in absence of solvent. Bulk reaction with 25 equiv. n-hexylamine resulted in the highest conversion (82%) of C1, calculated for anticipated amidation of the polymer. The recorded data revealed an unexpected difference between the polymers C1 and C2. As illustrated in the IR spectra in Figure 3, the ester carbonyl stretch vibration mode at 1727 cm⁻¹ decreased upon conversion with *n*-hexylamine. Furthermore, a new band was observed at 1692 cm⁻¹. Comparison of these spectral data with the spectral data obtained for polymer C2, vide supra, depicts a tremendous difference. By examination of the recorded ¹H NMR spectrum, the attachment of alkyl chains can be observed. However, the IR spectrum of the obtained product revealed the absence of NH-stretching band as well as bending vibration modes. Besides, the C=O stretch vibration mode of the resulting product was only shifted from 1727 to 1692 cm^{-1} exhibiting a shorter wave number-shift as in case of polymer C2. Noteworthy, both starting polymers C1 and C2 were characterized by the same wavenumber 1727 cm⁻¹ for the C=O ester stretch vibration mode (see ESI for both complete IR spectra of C1 and C2). Hence, the same vibration mode would be expected for a potentially formed amide.

Taking these data into account, we propose the predominant formation of cyclic imides consisting of 5-membered rings in case of polymer C1, compared with the commonly observed amide formation in case of polymer C2 (Scheme 3). An exact conversion which counts for predominant imide formation and minor amidation was not calculated as the exact ratio between amide and predominant imide formation is impossible to calculate. However, according to the IR spectrum, more than 50% of the converted ester moieties were transformed to imides. Noteworthy, earlier studies by de Bruin et al. showed formation of similar 5-membered ring anhydrides upon ester cleavage.²⁰ While this cleavage at high temperatures leads to insoluble polymeric materials, apparently due to crosslinked materials, imide formation seems to occur predominantly within the chain and not between different chains. This supports the anticipated formation of 5-membered cyclic imides.

In order to proof the formation of imides, we investigated piperidine as a secondary amine in the amidation reaction. In case of secondary amines, no imide formation is possible and both vibration modes of the formed amides for polymer **C1** and **C2** are anticipated to be observed at the same wave number. That this expectation is indeed correct can be observed in Figure 4. The amides formed by substitution of benzyl ester side groups with piperidine resulted in a C=0 stretch vibration mode at 1626 cm⁻¹ for both polymers **C1** and **C2**. Consequently, this data can be seen as proof for a predominant imide formation in case of post-polymerization modification of poly(benzyl 2-ylidene-acetate) **C1** with primary amines.

Regarding the ratios of both C=O stretch vibration modes, resulting from the starting benzyl ester and the formed piperidyl amide, the reactivity of both polymers C1 and C2 can be estimated. Again, the C1 polymer showed significant higher conversion (>50%), possibly due to tension resulting from high functional side chain density. Besides, *n*-hexyl-amine and piperidine, we considered benzylamine as a third, very interesting substituent to gain deeper insight into the issue of steric hindrance regarding post-polymerization



FIGURE 4 IR spectra of poly(benzyl 2-ylidene-acetate) **C1** (*red solid line*) and poly(benzyl acrylate) **C2** (*black dotted line*) after reaction with 25 equiv. piperidine in bulk at 120 °C over night. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 5 ¹H NMR spectrum was recorded from polymer **C1** after reaction with 25 equiv. benzylamine. The corresponding IR spectrum (only carbonyl region shown) shows the expected C=O stretch vibration mode representative to a proposed imide formation.

modification of functional polymethylenes. Anticipating similar steric demands for the two functional groups benzyl alcohol and benzylamine a conversion would highlight the general feasibility of highly dense functional polymethylenes regarding their post-polymerization modification accessibility. Indeed we observed a conversion for benzylamine reacted with poly(benzyl 2-ylidene-acetate). Even though the conversion cannot be calculated by ¹H NMR in this case, due to signal overlapping and broadening, we can estimate a conversion higher than 50% by comparing the C=O stretch intensities of the ester and imide moieties (Fig. 5). We attribute this post-polymerization accessibility to a certain tension induced on C1 polymer chain.

CONCLUSIONS

To the best of our knowledge, this is the first time that the concept of post-polymerization modification using esteramine chemistry was transferred to functional polymethylenes. Amidation of non-activated esters by primary and secondary amines has been investigated, proving the general feasibility of post-polymerization modification in view of steric hindrance, resulting from high functional densities of ester groups on the polymethylene backbone. Furthermore, the differences in amidation reactions between C1 and C2 polymers were shown and we observed a predominant formation of cyclic imides consisting of 5-membered rings in our study on polymethylene functionalization when reacted with primary amines.

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