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Direct Access to Functional (Meth)acrylate Copolymers through Transesterification with Lithium Alkoxides

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Abstract

A straightforward and efficient synthetic method that transforms poly(methyl methacrylate) (PMMA) into value-added materials is presented. Specifically, PMMA is modified by transesterification to produce a variety of functional copolymers from a single starting material. Key to the reaction is the use of lithium alkoxides, prepared by treatment of primary alcohols with LDA, to displace the methyl esters. Under optimized conditions, up to 65% functionalization was achieved and copolymers containing alkyl, alkene, alkyne, benzyl, and (poly)ether side groups could be prepared. The versatility of this protocol was further demonstrated through the functionalization of both PMMA homo and block copolymers obtained through either radical polymerization (traditional and controlled) or anionic procedures. The scope of this strategy was illustrated by extension to a range of architectures and polymer backbones.

GRAPHICAL ABSTRACT

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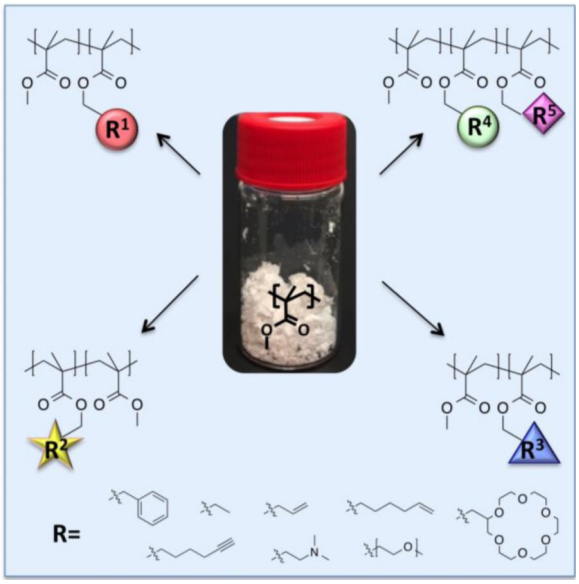
Additional Supporting Information may be found in the online version of this article.



A straightforward transesterification protocol that transforms poly(methyl methacrylate) (PMMA) into value-added materials is presented. The efficiency of this approach is demonstrated with a variety of alcohols, introducing alkyl, alkene, alkyne, benzyl, and (poly)ether side groups. In addition to PMMA homopolymers, a rage of other polymer backbones and architectures is functionalized following this transesterification protocol.

Keywords

transesterification; poly(methyl methacrylate); radical polymerization; graft copolymers; functionalization of polymers

INTRODUCTION

Polymers containing two or more different monomers, so-called copolymers, are valuable for various applications and often show superior performance to their homopolymer counterparts. Traditionally, copolymers are prepared through the combination of different monomers and can be tailored depending on the intended application.[1–4] For example, by employing copolymerization, researchers have been able to fine tune mechanical, thermal, or optical properties.[5–7] In fact, even small amounts of suitable comonomers can significantly influence certain properties, e.g. the material's impact resistance or crystallinity.[8–11] In this context, a prominent example is the incorporation of small amounts of isophthalic acid into poly(ethylene terephthalate) which lowers the material's crystallinity and increases its transparency.[12]

The classical strategy for preparing copolymers involves the copolymerization of different monomers[13] and while many different materials are accessible, the preparation of copolymers with different composition or functional groups requires multiple polymerization reactions. In addition, the relative arrangement of the monomer units in the polymer chain is influenced by the reactivity ratios of the monomers; this arrangement may

have a significant impact on the properties and performance of the final copolymer.[14] In contrast, post-polymerization functionalization introduces different functionalities directly along the backbone of a common starting material, which enables the efficient synthesis of a library of functional copolymers. By virtue of a common precursor, these materials have the added advantage of the same degree of polymerization, polydispersity and macromolecular architecture. Key to this strategy are reactive monomers, such as pentafluorophenyl acrylates, which can be secondarily functionalized by amidation or esterification but suffer from cost and the presence of unreacted groups and lower material stability if the reactions do not proceed to completion.[15]

Ideally, the direct transformation of commodity homopolymers into functional copolymers would overcome these challenges and provide an efficient platform for material development.[16, 17] To demonstrate the potential of this approach, PMMA was selected a candidate material due to the high availability from commercial sources or synthesis using anionic or radical polymerization processes. In addition, PMMA is widely used for various applications, including shatter-resistant alternatives to glass, additives for inks and coatings,[18] intraocular lenses,[19] and bone cement.[20] With these applications in mind, purposeful post-polymerization functionalization of PMMA has the potential to enhance performance and extend the range of applications.

Transesterification is a powerful and widely applied strategy in organic chemistry and materials synthesis.[21–24] As just one illustrative example, it is used as the key reaction step for the production of biodiesel.[25–28] To optimize and increase the efficiency of transesterification reactions a variety of suitable catalysts, ranging from organic and inorganic bases,[29–33] to Lewis acids,[34, 35] and *N*-heterocyclic carbenes, have been developed.[36, 37] For polymer chemists, transesterification is a useful tool for the synthesis of polyesters, e.g. poly(ethylene terephthalate) through transesterification of dimethyl terephthalate with ethylene glycol[37] or for reactive compatibilization of polymer blends by the in-situ formation of copolymers in the presence of transesterification catalysts.[38–44]

Herein we report the combination of transesterification and side chain modification for the development of a robust and versatile strategy for PMMA modification. Unfortunately, previous attempts at PMMA functionalization have been problematic due to the steric hindrance surrounding the ester groups with only a limited number of examples being reported in the literature.[45, 46] For example, graft copolymers have been prepared through the transesterification of PMMA or similar poly(methacrylates) with poly(ethylene glycol); however, this procedure is not versatile and requires the use of potassium metal (as metallation reagent) and specialized glassware.[45, 47–52] In a recent study, selective transesterification of the terminal MMA repeat unit in ATRP derived PMMA was described. In this particular case, the authors attribute the differential and selective reactivity of the end group units to the lower steric hindrance and electron withdrawing character of the adjacent chlorine atom. Interestingly, the internal methacrylate repeat units did not participate in the transesterification reaction.[53]

Alternative strategies leading to functionalized poly(methacrylates) include the condensation of poly(methacrylic acid) with alcohols in the presence of coupling agents,[54] tandem

catalysis of monomer transesterification and living radical polymerization, [55–57] and utilization of polymeric active esters , such as poly(pentafluorophenyl methacrylate).[58] The drawbacks of these methods are the utilizations of costly reagents and the requirement of separate polymerization reactions for each desired material. Amidation is another alternative strategy for functionalization of PMMA and has been demonstrated with 2-ethylhexalamine in the presence of organocatalysts.[59, 60] However, the resulting poly(methacrylamides) exhibit significantly different material properties compared to their poly(methacrylate) analogs. A straightforward and versatile synthetic method to prepare functionalized methacrylate and acrylate copolymers from readily available starting materials would overcome many limitations and drawbacks of prior routes and provide access to a broad scope of functionalized materials.

EXPERIMENTAL

Instrumentation

^{1}H NMR spectra were recorded on a Varian 600 MHz instrument. All experiments are reported in δ units, parts per million (ppm), and were measured relative to the signal for residual chloroform (7.26 ppm) in the deuterated solvent. Gel permeation chromatography (GPC) was performed on a Waters 2695 separation module with a Waters 2414 refractive index detector in chloroform with 0.25% triethylamine. Number average molecular weights (M_n) and weight average molecular weights (M_w) were calculated relative to linear poly(methyl methacrylate) standards.

Materials

Poly(styrene-*block*-methyl methacrylate) block copolymer (P6, prepared via anionic polymerization) was obtained from Dow Chemical Company. All other reagents were obtained from Sigma Aldrich and used without further purification. Lithium diisopropylamide (LDA) was obtained as a 2 M solution in THF/heptane/ethylbenzene. Trimethylsilyldiazomethane was obtained as a 2 M solution in diethylether. Dimethylformamide (DMF) was obtained from a JC Meyer dry solvent system; all other solvents were purchased in analytical grade and used without further purification.

Syntheses

Synthesis of PMMA via free radical polymerization (P1)—Methyl methacrylate (MMA) (47 mmol, 5.0 mL) was dissolved in acetone (23.8 mL, 80 wt %) and purged with argon for 45 minutes. Azobisisobutyronitrile (AIBN) (0.24 mmol, 39 mg) was added and the solution purged for additional 10 minutes. The reaction vessel was then placed in an oil bath preheated to 55 °C and the reaction was allowed to run overnight. After cooling to room temperature the polymeric material was isolated through precipitation in hexanes. In order to remove unreacted monomer, the material was re-dissolved in dichloromethane and precipitated in hexanes. The polymer was dried in a vacuum oven at 50 °C for 24 hours.

Yield: 2.4 g

^{1}H NMR (600 MHz, $CDCl_3$, δ): 3.74-3.46 (OCH_3), 2.07-1.54 (CH_2 backbone), 1.10-0.74 (CCH_3); GPC ($CHCl_3$): M_n 92 kg/mol, Đ 1.8.

General procedure for the synthesis of poly(benzyl methacrylate) (P4, PBnMA), poly(tert-butyl methacrylate) (P5, PtBA), and poly(methyl acrylate) (P8, PMA) via free radical polymerization—The monomer (exact amounts are summarized in the Supporting Information) was dissolved in tetrahydrofuran (THF) (50 wt %) and purged with argon for 20 minutes. AIBN (0.5 mol-%) was added and the solution was purged for additional 10 minutes. The reaction vessel was then placed in an oil bath preheated to 60 °C and the reaction was allowed to run overnight. After cooling to room temperature the polymeric material was isolated through precipitation in hexanes. In order to remove unreacted monomer, the material was re-dissolved in dichloromethane and precipitated in hexanes. The polymer was dried in a vacuum oven at 50 °C for 24 hours.

PtBMA ^{1}H NMR (600 MHz, $CDCl_3$, δ): 2.16-1.57 (CH_2 backbone), 1.52-1.27 ($C(CH_3)_3$), 1.19-0.88 (CCH_3).

PBnMA ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.38-7.22 (Ar H), 5.00-4.81 (OCH_2Ph), 2.12-1.67 (CH_2 backbone), 1.03-0.65 (CCH_3).

PMA ^{1}H NMR (600 MHz, $CDCl_3$, δ): 3.85-3.35 (OH_3), 2.45-2.19 (CH backbone), 2.01-1.32 (CH_2 backbone).

Synthesis of PMMA via ATRP (P2 and P3)—The synthesis of PMMA via ATRP process was conducted following a modified literature procedure.[61]

MMA (4 mL, 50 equiv.), pre-activated copper wire (5 cm), α;-bromophenylacetate (0.119 mL, 1 equiv.), $CuBr_2$ (8.4 mg, 0.05 equiv.) and DMSO (4 mL) were added to a septum sealed vial. The copper wire was carefully wrapped around the stir bar and the mixture was subsequently degassed by bubbling with nitrogen for 15 min. *N,N,N′,N″″*-pentamethyldiethylenetriamine (0.057 mL, 0.36 equiv.) was then introduced to the vial via a gas-tight syringe and the polymerisation was allowed to commence at 40 °C. Samples were taken periodically under a nitrogen blanket and passed through a short column of neutral alumina to remove dissolved copper salts prior to analysis by ^{1}H NMR and GPC. The resulting materials were dialyzed against dichloromethane for 2 days. The polymer was dried in vacuum.

^{1}H NMR (600 MHz, $CDCl_3$, δ): 3.74-3.46 (OCH_3), 2.07-1.54 (CH_2 backbone), 1.10-0.74 (CCH_3); GPC ($CHCl_3$): M_n 13.3 kDa, Đ 1.15; M_n 4.6 kDa, Đ 1.20

Synthesis of poly(styrene-block-methyl methacrylate) via RAFT process (P7)

Step 1: MMA (40 mmol, 4.26 mL, passed through a plug of basic alumina) and 2-cyano-2-propyl benzodithioate (0.12 mmol, 27 mg) were dissolved in THF (10.8 mL, 70 wt %, passed through a plug of basic alumina) and purged with argon for 30 minutes. AIBN (0.05 mmol, 8 mg) was added and the solution was purged for additional 10 minutes. The reaction vessel was then placed in an oil bath preheated to 60 °C and the reaction was allowed to run

for 24 hours. After cooling to room temperature, the polymeric material was isolated through precipitation in hexanes. The material was re-dissolved in dichloromethane and precipitated in hexanes to remove unreacted monomer. The polymer was dried in a vacuum oven for 24 hours at 50 °C.

Yield: 2.6 g macro-CTA

^{1}H NMR (600 MHz, $CDCl_3$, δ): 3.74-3.46 (OCH_3), 2.07-1.54 (CH_2 backbone), 1.10-0.74 (CCH_3); GPC ($CHCl_3$): M_n 26.7 kDa, Đ 1.09

Conversion: 65 %, M_n(theo) 21.7 kDa

Step2: Styrene (16.1 mmol, 1.79 mL), macro-CTA (0.01 mmol, 300 mg), and anisole (0.4 mL) were loaded into a screw cap septum reaction vial and the resulting solution was purged with argon for 15 minutes. The vial was then placed in a heating block pre-heated to 110 °C and the reaction was allowed to run for 48 hours. The reaction mixture was diluted with dichloromethane and precipitated in hexanes. The precipitate was re-dissolved in dichloromethane and precipitated in hexanes in order to remove unreacted monomer. The isolated polymer was dried in a vacuum oven for 24 hours at 50 °C.

Yield: 800 mg

^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.25-6.30 (Ar H), 3.74-3.48 (OCH_3), 2.28-1.20 (CH_2 and CH backbone), 1.08-0.77 (CCH_3); GPC ($CHCl_3$): M_n 84.7 kDa, Đ 1.39

Conversion: 45 %, M_n(theo) 100.6 kDA

General procedure for the transesterification of poly(methacrylates)—The polymeric material (exact amounts see Table S1 and S2, Supporting Information) was placed in a screw cap septum reaction vial, which was evacuated and purged with argon three times. The polymer was then dissolved in dry DMF (10 wt % solution).

A separate screw cap septum reaction vial was evacuated and purged with argon three times and subsequently loaded with DMF and the alcohol. The mixture was cooled in an ice bath and lithium diisopropylamide (LDA) (2 M solution in THF/heptane/ethylbenzene) was added via degassed syringe. The solution was stirred at 0 °C for 30 minutes until the DMF-polymer solution was added. The ice bath was removed and the mixture stirred for 10 minutes before the reaction vial was placed in a heating block preheated to 120 °C. After the appropriate reaction time, the reaction mixture was precipitated into an acidic water methanol mixture (e.g. 10 mL DI water + 10 mL methanol + 0.5 mL conc. HCl). The precipitate was washed with water and hexanes several times and dried in a vacuum oven for 24 hours at 50 °C after isolation.

For reactions that ran longer than 2 hours, the dried product was treated with trimethylsilyldiazomethane to re-methylate potentially hydrolyzed methyl ester groups.

Spectroscopic data can be found in the Supporting Information.

Transesterification of poly(methyl acrylate) (P8, PMA)—PMA (86 mg, 1 mmol methyl acrylate repeat units) was placed in a screw cap septum reaction vial, which was evacuated and purged with argon three times. The polymer was then dissolved in dry DMF (1 mL, 8 wt % solution).

A separate screw cap septum reaction vial was evacuated and purged with argon three times and subsequently loaded with 0.5 mL DMF and benzyl alcohol (0.104 mL, 1 mmol). The mixture was cooled in an ice bath and LDA (0.25 mL, 0.5 mmol, 2 M solution in THF/heptane/ethylbenzene) was added via syringe. The solution was stirred at 0 °C for 30 minutes until the DMF-polymer solution was added. The ice bath was removed and the mixture stirred for 10 minutes before the reaction vial was placed in a heating block preheated to 50 °C. After three hours reaction time, the reaction mixture was neutralized by the addition of dilute HCl and then dialyzed against methanol (2 days). The solvents were removed and the obtained polymeric material was dried in a vacuum oven for 24 hours at 50 °C. The dried product was treated with trimethylsilyldiazomethane to re-methylate potentially hydrolyzed methyl ester groups. The benzyl acrylate content was 30 %.

Spectroscopic data can be found in the Supporting Information.

General procedure for re-methylation of poly(meth)acrylates—The polymeric material was placed in a screw cap septum reaction vial and dissolved in a mixture of dichloromethane and methanol (9:1 vol:vol, 1 wt % polymer). A needle was inserted into the septum (reaction and quenching liberate N_2 gas, needle served as “outlet”) and the reaction mixture was cooled in an ice bath before trimethylsilyldiazomethane (1.0 equivalent per (meth)acrylate repeat unit) was slowly added via syringe. The mixture was stirred while still cooled in an ice bath and allowed to slowly warm to room temperature. After four hours, the reaction was quenched through the addition of acetic acid (2 M in methanol) and stirred for an additional hour. The solvents were removed and the polymeric material dissolved in a small amount of dichloromethane and precipitated in hexanes. The polymer was isolated and dried in a vacuum oven at 50 °C for 24 hours.

Comparison of ^{1}H NMR spectra of the transesterified materials recorded before and after re-methylation indicated that the maximum degree of hydrolysis that occurred was 15 %, however in far most cases it remained below 10 %, two hour reaction times did not cause hydrolysis. For detailed information on percent hydrolysis over time, see SI, Figure S2B.

RESULTS AND DISCUSSION

General reaction conditions

Finding an efficient and simple synthetic method to transesterify PMMA is challenging due to the hindered nature of the methyl esters. A variety of different procedures were initially examined in which the temperature (ambient to 120 °C) and base or Lewis acid (e.g. sodium hydride, 1,8-diazabicycloundec-7-ene or scandium triflate, see Supporting Information) were varied. Unfortunately, in no case was high conversion to give the desired transesterified products observed. The general utility of lithium diisopropylamide (LDA) as a strong base has been widely accepted due to its good solubility in non-polar organic solvents and non-

nucleophilic nature, which suggested the use of LDA with various alcohols to quantitatively form lithium alkoxides. To examine this process, PMMA (**P1**, M_n 92 kg/mol, Đ 1.8) was treated with lithium benzyloxide at 120 °C and found to successfully result in the formation of benzyl methacrylate containing copolymers (see Scheme 1).

The influence of reaction time and molar ratio of MMA units to lithium alkoxide was then examined. It should be noted that all reactions were conducted in septa sealed reaction flasks or vials and did not require the use of specialized glassware, e.g. Dean-Stark apparatus, an advantage of this protocol when compared to more basic or harsh procedures. The reactions were monitored after two, five, and eight hours and analyzed via ^{1}H nuclear magnetic resonance (NMR) spectroscopy with the integration values for the methyl ester signals **a** (3.73 - 3.45 ppm) and the benzylic signals **b** (5.05 - 4.92 ppm) being used to calculate the final copolymer composition (see Figure 1).

After two hours, the reactions employing 0.5, 1.0, and 2.0 equivalents lithium benzyloxide yielded copolymers with benzyl methacrylate incorporation slightly below 20 mol% (see Figure S1, Supporting Information). Increasing the reaction time to five and eight hours resulted in higher conversions being observed (maximum of 30 mol% with 2.0 equivalents of lithium benzyloxide for eight hours). As expected, increasing the amount of lithium benzyloxide relative to MMA units and the reaction time both allowed for the extent of functional group incorporation to be tuned. In examining the limits of this transesterification process, PMMA was treated with 20.0 equivalents of benzyl alcohol (lithiated with 10.0 equivalents LDA) for 24 and 48 hours with both conditions resulting in 60 % and 65 % conversion respectively (see Table 1; Figure S2, Supporting Information).

The possibility of side reactions and chain-chain coupling during transesterification was examined by gel permeation chromatography (GPC). Comparison of the GPC traces for PMMA, before and after 48 hours reaction time with varying alkoxide ratio, revealed almost identical molecular weight distributions, indicating the absence of side reactions (see Figure 2, red line). In some cases, longer reaction times led to a small degree of methyl ester hydrolysis (due to traces of moisture), which can be addressed by treatment with trimethylsilyldiazomethane during the work-up procedure. This results in quantitative methylation of hydrolyzed methyl esters and does not change the ratio of benzyl to methyl groups in the polymer (see Supporting Information).

Since the degree of polymerization and number of backbone functional groups may influence the success of post-polymerization transformations, the transesterification reaction was repeated with PMMA samples of differing molecular weights. These materials were prepared by atom transfer radical polymerization (ATRP)[61] and had significantly lower molecular weights (**P2**, M_n 13.2 kg/mol, Đ 1.15 and **P3**, M_n 4.6 kg/mol, Đ 1.20) than the PMMA obtained by free radical polymerization (M_n 92 kg/mol). After treatment with lithium benzyloxide (1.0 equivalent) for two hours, the benzyl methacrylate content of both new polymers was determined to be 15 % (see Figures S3 and S4, Supporting Information), which was equal to the substitution level for the higher molecular weight PMMA derivative prepared by free radical polymerization. Accordingly, these results suggest that the degree of

polymerization for the polymer - at least up to 1000 repeat units - does not affect its reactivity towards the alkoxides investigated.

Introduction of functional alcohols

To explore the scope of functionalized PMMA-based materials, the transesterification protocol was applied to a variety of aliphatic and polyether-based alcohols (see Table 2). Initial focus was directed towards the introduction of alkene and alkyne containing alcohols as these moieties can be used in secondary, “click”, reactions (e.g. Diels-Alder, thiol-ene, thiol-yne, and copper (I)-catalyzed azide-alkyne cycloaddition).[62–65] Using transesterification to introduce alkenes and alkynes into polymers typically made by radical polymerization processes is especially advantageous because these groups can participate in radical reactions, resulting in cross-linking and a variety of unwanted side reactions. To demonstrate the transesterification of PMMA with alkene containing alcohols, reactions were conducted with allyl alcohol and 5-hexen-1-ol with conversions of 15 and 20 % being observed, respectively, after two hours (Table 2, Entries 3 and 4; Figures S6 and S7, Supporting Information). Similarly, the introduction of alkyne moieties was achieved by reaction of PMMA with 5-hexyn-1-ol, which leads to 15 mol-% of hexynyl methacrylate units along the polymer backbone (Table 2, Entry 5; Figure S8, Supporting Information).

The ability to place discrete functional units along the polymer backbone then raises the possibility of introducing multiple orthogonal groups during a single reaction. This versatility was demonstrated by the treatment of PMMA with a 1:1 mixture of alkene and alkyne alkoxides derived from 5-hexen-1-ol and 5-hexyn-1-ol. This results in a PMMA backbone containing 10 mol-% of alkene and alkyne groups which could be independently functionalized using selective chemistries (Table 2, Entry 6; Figure S9, Supporting Information). As demonstrated above, GPC analysis of this material showed a distribution similar to the starting PMMA and is clearly absent of any high molecular weight side-products that could be the result of chain-chain coupling or other side reactions (see Figure 2, blue line).

To further illustrate the ability to introduce functional groups into PMMA, metal ion coordinating groups were examined, as the resulting materials are promising candidates for ion transport applications. Initially, we focused on the transesterification of PMMA with 2-hydroxymethyl-18-crown-6 and poly(ethylene glycol) methyl ether (mPEG). On reaction with 1.0 equivalent 2-hydroxymethyl-18-crown-6 (Table 2, Entry 9; Figure S12, Supporting Information) or 0.5 equivalents mPEG (Table 2, Entry 8; Figure S11, Supporting Information), PMMA copolymers containing 5 mol% pendant crown ether or mPEG units were obtained. In addition to polyether functionalization, transesterification with a tertiary amine, 2-dimethylaminoethanol, was carried out, resulting in a similar degree of functionalization (Table 2, Entry 7, Figure S12, Supporting Information). In this case, the lower reactivity of this alcohol compared to aliphatic ones may be due to the tertiary amines ability to form chelate complexes with lithium salts.

Scope of modifiable polymer backbones

After demonstrating the versatility of this transesterification approach for the preparation of a variety of functionalized PMMA copolymers, the extension to other polymer backbones, side chains and macromolecular architectures was studied (Figure 3). Changing the methyl ester of PMMA to poly(benzyl methacrylate) (**P4**, PBnMA) followed by reaction with lithium ethoxide yielded copolymers containing 35 mol% ethyl methacrylate (see Figure S13, Supporting Information), while treatment of poly (*tert*-butyl methacrylate) (**P5**, PtBMA) with either lithium ethoxide or lithium benzyloxide did not result in the formation of any transesterified material, which we attribute to the steric hindrance of the tert-butyl group.

In addition to transesterification of homopolymers, PMMA-based block copolymers, polymers are substrates with even greater potential given the added complexity in the synthesis of block copolymers. As an example, poly(styrene-*b*-MMA) block copolymers are widely used for lithographic applications and are readily available via commercial sources, whereas functional derivatives are not commercially available and are a challenge to prepare.[66, 67] For this reason, a block copolymer containing 27 wt% PMMA (**P6**, M_n 59000 g/mol, Đ 1.05) was prepared via anionic polymerization and transesterified with lithium benzyloxide to give a diblock copolymer containing 10 mol% benzyl methacrylate substitution with respect to the MMA repeat units (see Figure S15, Supporting Information). The slightly lower degree of modification compared to the transesterified PMMA homopolymers is likely due to the relatively lower concentration of PMMA in solution since all solutions were prepared at 10 wt % total polymer. Interestingly, GPC analysis of the product showed a small shoulder shifted towards higher molecular weight, which was not present in the starting material (see Figure S16A, Supporting Information). We hypothesize that the slightly acidic protons at the polymer chain ends could induce oxidative chain-chain coupling during the work up procedure or cross-linking reactions via intermolecular nucleophilic attacks of the ester groups. To support this hypothesis, the same reaction was repeated with a similar PS-PMMA block copolymer prepared via RAFT polymerization and subsequent removal of the dithioester end groups (**P7**). This yields the same degree of functionalization but does not result in any high molecular weight side products (see Figure S16B, Supporting Information).

Having demonstrated the applicability of this approach for the synthesis of poly(methacrylate) derivatives, our attention was drawn to poly(acrylates) as another class of industrially important polymeric materials that could be functionalized using this transesterification approach. The absence of quaternary carbons along the polymer backbone may lead to the ester groups being more accessible from a steric point of view, resulting in higher reactivity towards chemical modification.[68, 69] Considering the aforementioned aspects, transesterification of poly(methyl acrylate) (**P8**, PMA, M_n 18.3 kg/mol) was attempted under mild reaction conditions. The treatment with lithium benzyloxide at 50 °C yielded the resulting copolymer, which contained 25 % benzyl acrylate after only 3 hours (see Figure S14, Supporting Information), demonstrating the high reactivity of poly(acrylates).

CONCLUSIONS

An efficient and synthetically facile strategy for transforming commodity poly(methacrylates) and poly(acrylates) into value-added materials is presented. This protocol allows simple homopolymers to be employed as a platform for the preparation of libraries of functional copolymers with new properties and reactivity. Significantly, transesterification occurs in the absence of alkali metals, costly catalysts or activated monomers. The generation of copolymer libraries with the same degree of polymerization, dispersity and macromolecular architecture from a single starting material offers the potential for the fast and systematic evaluation of new materials, a screening process that is difficult to realize via traditional copolymerization techniques. The straightforward reaction set-up and the commercial availability of the starting polymers provide quick access to a broad scope of functionalized materials.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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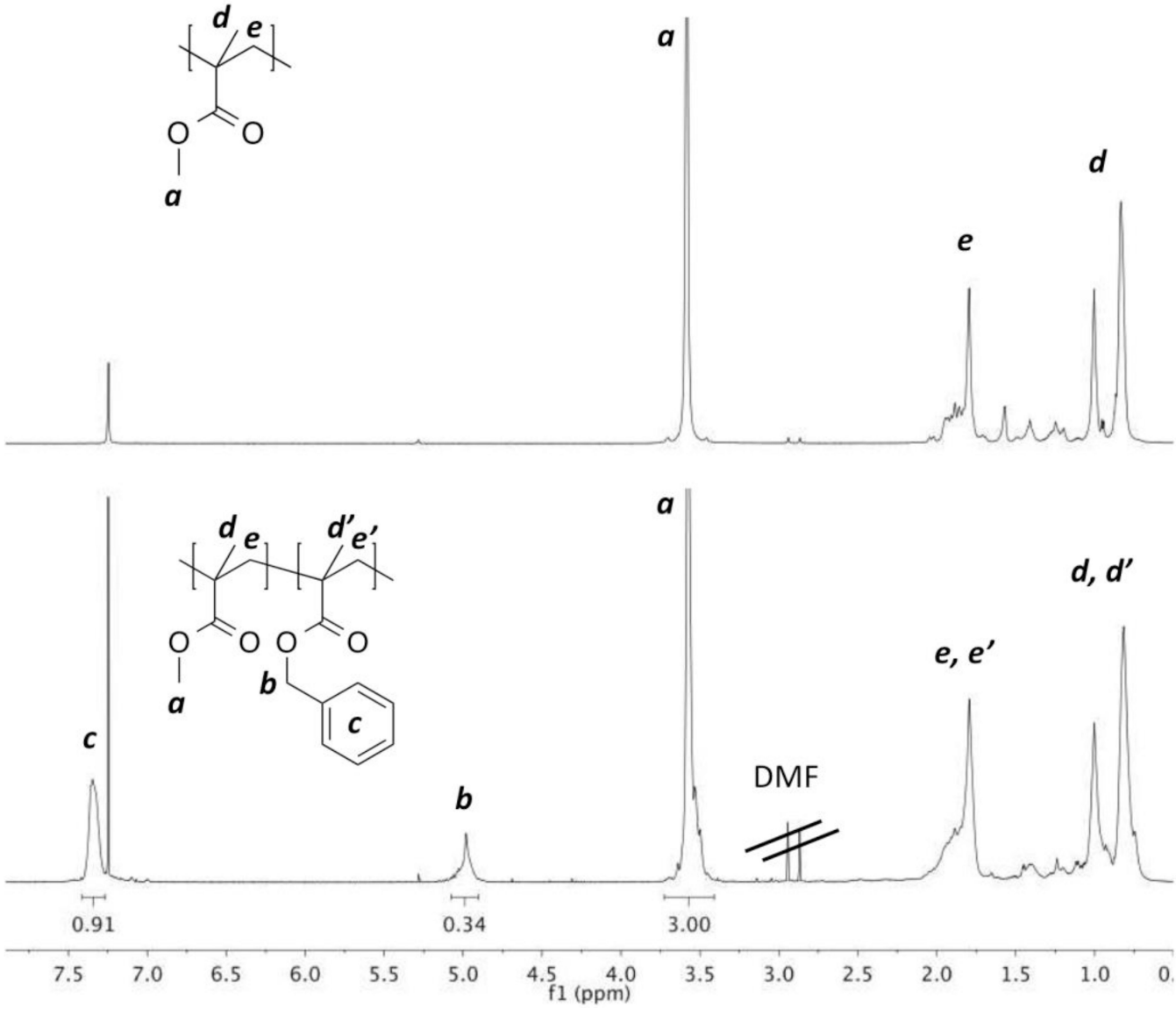


FIGURE 1.

^{1}H NMR spectra ($CDCl_3$, 600 MHz) of poly(methyl methacrylate) (top) and poly(methyl methacrylate-co-benzyl methacrylate) obtained from transesterification of PMMA with benzyl alcohol (bottom).

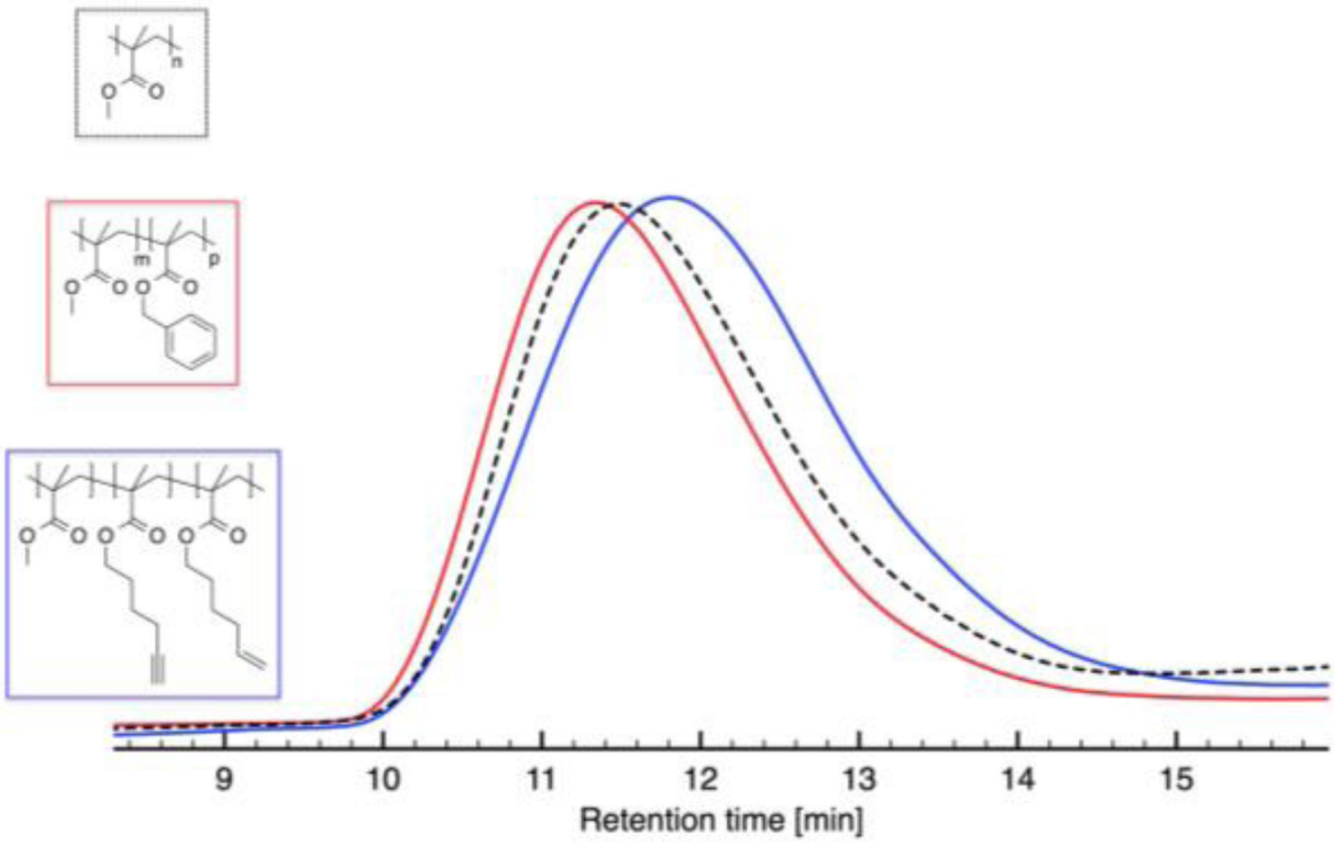


FIGURE 2.

GPC ($CHCl_3$) traces of PMMA (**P1**, black, dashed), P(MMA-*co*-BnMA) from transesterification of PMMA (**P1**) with 20 eq. benzyl alcohol (**I**) for 48 hours (red), and P(MMA-co-hexynyl methacrylate-*co*-hexenyl methacrylate) from transesterification of PMMA (**P1**) with 0.5 eq. 5-hexen-1-ol (**IV**) and 0.5 eq. 5-hexyn-1-ol (**V**) for 2 hours (blue)

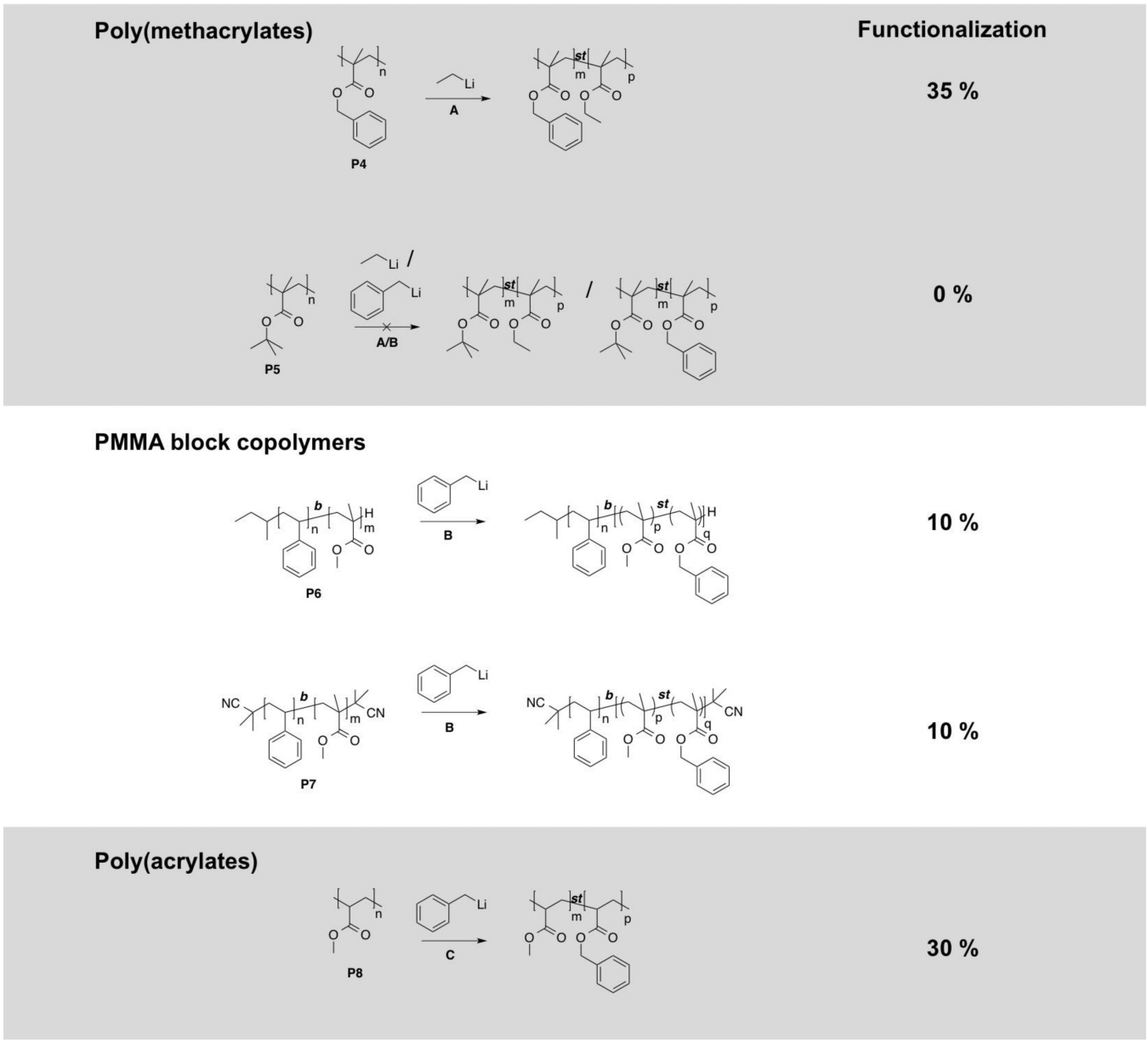
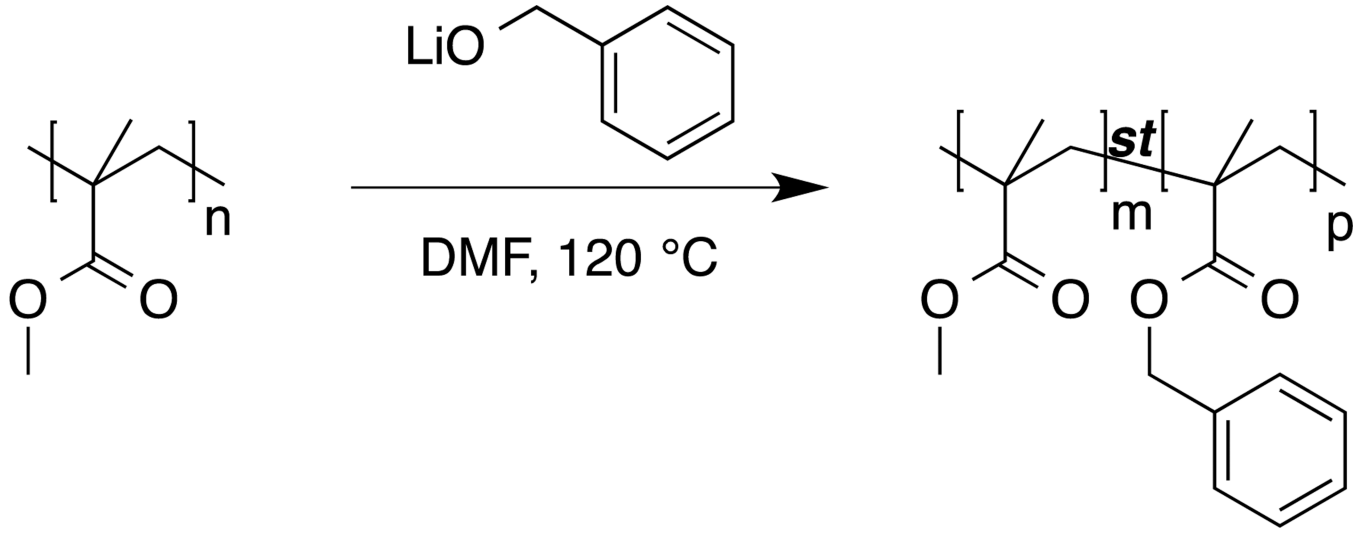


FIGURE 3.

Polymeric materials subjected to transesterification with lithium benzyloxide. Reaction conditions: A: [monomer units]:[ethanol]:[LDA] 1:1:1, DMF, 120 °C, 2 hours. B: [monomer units]:[benzyl alcohol]:[LDA] 1:1:1, DMF, 120 °C, 2 hours. C: [Monomer units]:[benzyl alcohol]:[LDA] 1:1:1, DMF, 50 °C, 3 hours.



SCHEME 1.
Reaction conditions for the transesterification of PMMA

TABLE 1

Benzyl methacrylate content determined after transesterification with different PMMA-benzyl alcohol (BnOH)-Lithium diisopropylamide (LDA) ratios after different reaction times

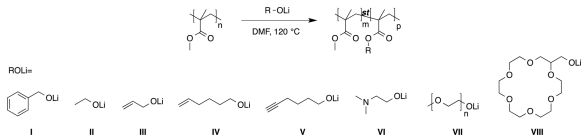
Entry	[MMA]/ [BnOH]/[LDA]	Reaction time (hours)	Conversion (%)[a]
1		2	15
2	1 / 0.5 / 0.5	5	20
3		8	20
4		2	15
5	1 / 1 / 1	5	25
6		8	25
7		2	20
8	1 / 2 / 2	5	30
9		8	30
10	1 / 20 / 10[b]	24	60
11		48	65

[a] Determined via ^{1}H NMR spectroscopy.

[b] Benzyl alcohol was treated with 0.5 equivalents LDA in order to minimize the amounts of THF/heptane/ethylbenzene introduced through the addition of the LDA solution.

TABLE 2

Summary of transesterification reactions performed with PMMA in DMF at 120 °C for two hours



Entry	Alcohol	[MMA]:[Li alkoxide]	Conversion (%)[a]
1	benzylalcohol (**I**)	1:1	15
2	ethanol (**II**)	1:1	20
3	allylalcohol (**III**)	1:1	15
4	5-hexen-1-ol (**IV**)	1:1	20
5	5-hexyn-1-ol (**V**)	1:1	15
6	5-hexen-1-ol + 5-hexyn-1-ol (**IV+V**)	1:0.5:0.5	10+10
7	*N,N*-dimethylaminoethanol (**VI**)	1:1	5
8	poly(ethylene glycol) methyl ether (**VII**)	1:0.5[b]	5
9	2-hydroxymethyl-18-crown-6 (**VIII**)	1:1	5

[a] Determined via ^{1}H NMR spectroscopy.

[b] Average MW 1 kg/mol. 0.5 eq. mPEG (500 mg) dissolved in 2.5 mL DMF. Lower feed ratio was applied in order to minimize decreasing the PMMA concentration.