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Synthesis of telechelic polyacrylates with unsaturated end-groups

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Abstract

A convenient, one-pot synthesis of telechelic and semi-telechelic polyacrylates with unsaturated end-groups has been developed. Atom transfer radical polymerization of methyl or *n*-butyl acrylate was initiated with either ethyl α-bromomethylacrylate or methyl dichloroacetate, as a monofunctional or difunctional initiator, respectively, and mediated with various Cu/amine complexes. Addition of excess ethyl 2-bromomethylacrylate was found to not only immediately quench the polymerization but also installed 2-carbethoxyallyl moieties on the ends of the polymer chains. The telechelic polymers were found to undergo thermally or photochemically induced crosslinking reactions.

Keywords: Atom transfer radical polymerization; Telechelic polymers; Macromonomers

1. Introduction

Historically, polyacrylates have found extensive use as adhesives, coatings, and sealants [1]. They generally have low glass transition temperatures (T_g) which makes them convenient to handle, process, and purify. Furthermore, the large and diverse pool of available monomers allows the physical properties of the resultant polymeric material to be tailored. However, a common drawback of these polymers is that their flexible backbones impart limited thermal stability and mechanical strength. Thus, a number of techniques have been developed to enhance their properties by crosslinking the polymer chains [2]. The most common approach involves incorporation of an acrylic monomer with pendant hydroxy moieties followed by reaction with a multifunctional isocyanate substrate. Unfortunately, the distance between crosslinked points is often difficult to control or measure and often undesirable degrees of crosslinking are obtained. This restricts applications that require ample diffusion rates (i.e. hydrogels) or cases where only minimal perturbations in the polymer's mechanical properties are desired. Furthermore, the use of isocyanates introduces foreign functionality into the material, which may also affect the material's physical properties (e.g. density, refractive index, etc.).

Circumvention to this drawback is to selectively place crosslinkable groups at both ends of the polymer chains. Such polymers are often referred to as telechelic polymers [3]. In addition to being used to fabricate materials with enhanced thermal and chemical resistance, they have been successfully employed in the preparation of interpenetrating polymer networks and as intermediates in the synthesis of block copolymers [4–6]. The most commonly employed synthetic route to telechelic polymers involves the use of functionalized initiators and terminating agents in conjunction with a living polymerization method (e.g. anionic based polymerizations). Unfortunately, this approach has not been successful when applied toward the synthesis of telechelic polyacrylates. The presence of two sites of high reactivity (i.e. the olefin and the ester group) within the acrylic monomer creates additional synthetic challenges as a variety of side reactions can occur. Thus, the preparation of well-defined telechelic polyacrylates with tunable molecular weights would require a polymerization technique that is milder than anionic methods, yet still provide an adequate level of control over the polymerization. Furthermore, the introduction of functional groups with high reactivity on both ends of the polymer chain must be feasible and preferably not interfere with the polymerization process.

Atom transfer radical polymerization (ATRP) has

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emerged as a highly efficient procedure for controlling free-radical polymerizations [7,8]. By establishing a fast and dynamic equilibrium between active (i.e. propagating and free radical based) and dormant (i.e. terminated) polymer chains, the concentration of free radicals can be effectively minimized by shifting the equilibrium toward the dormant state. Ultimately, this prevents bimolecular termination, a major source for the lack of control found in typical free-radical polymerizations. The technique requires an initiator, a mediating metal catalyst, and monomer. A wide range of initiators exists and all essentially contains a relatively weak C–X (X = Cl or Br) bond. Furthermore, a large number of organometallic complexes have been employed including Cu/amines [9], Ru/phosphines [10], Ni/amines or phosphines [11], and Fe/imidazoles [12]. Most monomers that can be polymerized using free-radical methods have been shown to be polymerizable using ATRP.

The nature of ATRP places a halogen group at the terminus of the polymer chain. Recent attention in ATRP has been directed toward converting this end-group to various functionalities (e.g. amino and hydroxy groups) either in situ or in a post-polymerization modification step [13–15]. Addition-fragmentation agents have also been used to transform this terminus into other functionalities as well. For example, Sawamoto and co-workers employed a silyl enol ether agent to prepare keto end-functionalized polymers [16]. Haddleton and co-workers reported the use of methyl 2-bromomethylacrylate as means of installing methacrylate end-groups on poly(methyl methacrylate) [17]. In both of these cases, the agent is added at the conclusion of the polymerization. These reports prompted us to disclose our findings on preparing telechelic polyacrylates with unsaturated moieties on both ends of the polymer chains using a similar approach. A difunctional ATRP initiator is used in conjunction with various Cu/amine complexes to grow a polyacrylate chain in opposite directions. At the conclusion of the polymerization, ethyl 2-bromomethylacrylate, a commercially available addition-fragmentation agent, is added which not only quenches the ATRP but also installs a 2-carbethoxyallyl functional group on the ends of the polymer chains. The polymerizations are operationally very simple: they can conveniently be performed in a single pot, set-up under ambient conditions, and do not require any special equipment. Furthermore, the utility of these telechelic polymers is demonstrated in thermally and photochemically induced crosslinking reactions which greatly enhanced their thermal and mechanical stability.

2. Experimental

2.1. Materials and characterization methods

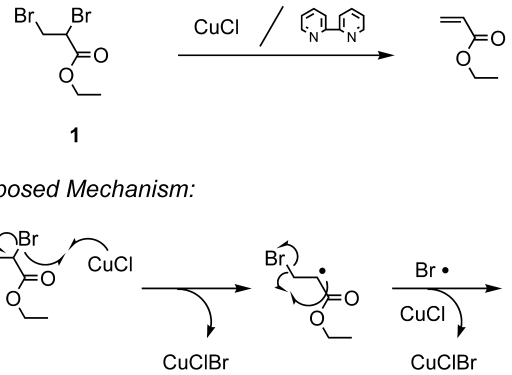
CuCl, 2,2′-bipyridine, ethyl 2-bromopropionate, methyl dichloroacetate, and ethyl 2,3-dibromopropionate were purchased from Aldrich and used without further purification. Except for the 'one-pot' synthesis described in the text, methyl acrylate and *n*-butyl acrylate (Aldrich) were purified by passing through an inhibitor removal column (Aldrich) followed by distillation. Ethyl 2-bromomethylacrylate was synthesized as previously reported [18], however, it is commercially available from Aldrich. Gel permeation chromatography (GPC) measurements were carried out using an Alltech HPLC pump equipped with a refractometer using THF as the eluent. The GPC columns (10 μm linear mixed bed, American Polymer Standards Corp.) were calibrated against monodispersed polystyrene standards (Shodex). All ^{1}H and ^{13}C NMR spectra were recorded on a Varian spectrometer (300 MHz, ^{1}H; 75 MHz, ^{13}C). Chemical shifts (δ) are given in ppm and were referenced to residual protio solvent. Spectra were obtained in the solvent indicated at 25 °C unless otherwise noted. Spectra notation is as follows: bs, broad singlet; bt, broad triplet; bm, broad multiplet. Infrared spectra were recorded on a Perkin–Elmer Paragon 1000 FT-IR spectrometer. Differential scanning calorimetry (DSC) was performed on a Perkin–Elmer Pyris-7 DSC using a scan rate of 10 °C/min under an atmosphere of nitrogen. Thermogravimetric analysis (TGA) was performed on a Perkin–Elmer TGA-7, using a scan rate of 10 °C/min under an atmosphere of nitrogen.

2.2. General procedure for synthesizing telechelic polyacrylates

A 100 ml round-bottomed flask was charged with 5.0 ml (56 mmol) of *n*-butyl acrylate, 0.3 g (3 mmol) of CuCl, 0.93 g (6.0 mmol) of 2,2′-bipyridine, 0.31 ml (3.0 mmol) of methyl dichloroacetate, 0.25 ml of 1,3,5-trimethylbenzene (as an internal standard) and a stir bar. The flask was then sealed and heated to 75 °C. Monomer consumption was monitored over time using gas chromatography and compared against the internal standard. After 80–90% of the monomer was consumed, ethyl 2-bromomethylacrylate (4.6 g, 24 mmol) and either CuCl (9.5 g, 96 mmol) or Cu^{0} (6.0 g, 9.5 mmol) were added. After 3 h at 75 °C, the reaction vessel was cooled to ambient temperature. The polymer was dissolved in CH_2Cl_2 or diethyl ether and extracted with a saturated disodium ethylenediaminetetraacetate (EDTA) solution to remove residual Cu salts. The polymer solution was concentrated under dynamic vacuum and then poured into excess water, which caused the polymer to precipitate. The polymer was then collected, dried under high vacuum, and analyzed. Yield: 3.8 g (85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.1 (bs, terminal CH_2), 5.5 (bs, terminal CH_2), 4.4–4.1 (bm, terminal alkyl CH_2's), 4.0 (bs, OCH_2 butyl group), 3.6 (bs, CH_3 from initiator), 2.4 (bs, butyl CH_2), 1.9 (bs, butyl CH_2), 1.6 (bs, butyl CH_2), 1.4 (bs, butyl CH_2), 1.3 (bt, terminal alkyl CH_3), 1.0 (bt, butyl CH_3). GPC (THF, relative to polystyrene standards): M_n = 2400, PDI = 1.3.

2.3. General procedure for crosslinking the telechelic polyacrylates

In a 5 ml glass vial, polyacrylate (1 g) was dissolved in toluene (1 ml) with either benzoyl peroxide or 2,2-dimethoxy-2-phenylacetophenone (5 mg). This solution was then either heated in an oil bath at 90 °C (benzoyl peroxide-initiated) or photolyzed using a 450 watt medium pressure mercury Hanovia lamp (benzoyl peroxide- or 2,2-dimethoxy-2-phenylacetophenone-initiated). An insoluble, tacky material was formed within 15 min under these conditions and was insoluble in common organic solvents. The resulting material was characterized by IR spectroscopy, DSC, and TGA.



Scheme 1. Copper catalyzed atom transfer radical elimination of ethyl 2,3-dibromopropionate (**1**) to form ethyl acrylate. A proposed mechanism is also illustrated.

3. Results and discussion

During our investigation of whether ethyl 2,3-dibromopropionate (**1**) could be used as a difunctional ATRP initiator, an unexpected result was observed. As shown in Scheme 1, upon introduction of CuCl (or CuBr) (as well as an excess of 2,2′-bipyridine to solubilize and activate the Cu) to **1**, ethyl acrylate was obtained as the exclusive product. We believe that after a Cu atom abstracted the relatively weak secondary bromide from **1**, the resultant radical quickly eliminated the primary bromide, forming a Br radical and ethyl acrylate.[1] The Br radical later added to Cu(I)Cl to form Cu(II)ClBr.[2] Under typical ATRP conditions, a stoichiometric amount of metal catalyst is added relative to the initiator. Under these conditions, approximately 50% conversion of **1** to ethyl acrylate was observed as well as an equal amount of Cu(II) species. As shown in Table 1, increased amounts of CuCl furnished higher yields of ethyl acrylate. Under optimized conditions, the addition of at least 4 equiv. of CuCl (see Table 1) afforded a quantitative yield. These results poised us with the opportunity of preparing polyacrylates with unsaturated end-groups (i.e. 2-carbethoxyallyl moieties) in one pot through the use of an addition-fragmentation reagent with an analogous structure to **1**: ethyl 2-bromomethylacrylate (**2**). Thus, upon the conclusion of the polymerization, the addition of **2** which, like **1**, contains an eliminable primary bromide, would subsequently afford a polyacrylate with an unsaturated end-group.

Using ethyl 2-bromopropionate as a monofunctional initiator and CuCl/bipy (bipy = 2,2′-bipyridine) as the mediating catalyst, methyl acrylate was polymerized using standard ATRP conditions (temp = 75 °C, $[M/I]_0 = 25$). At the conclusion of the polymerization, excess ethyl 2-bromomethylacrylate (**2**) (5 equiv.) and CuCl (5 equiv.) were added affording poly(methyl acrylate) with a 2-carbethoxyallyl end-group (see Eq. (1)). The extra CuCl was necessary to sequester the Br radical and prevent a build up of Cu(II) species, which was found to greatly slow down the reaction. The polymer was isolated using multi-step purification process to ensure purity. First, upon conclusion of the termination reaction, the mixture was dissolved in excess CH_2Cl_2 or diethyl ether and extracted with a saturated aqueous solution of disodium EDTA. The solvent was concentrated and then poured into excess water, which caused the polymer to precipitate. The water was then decanted and the polymer was collected and dried to a constant weight. GPC analysis of the polymer indicated that the molecular weight (MW = 1900 Da, relative to PS standards) was close to the expected value (MW = 1500 Da) and the PDI was 1.4. End-group analysis using ^{1}H NMR spectroscopy (by comparing signals from the methyl group on the initiator with the terminal olefin) indicated that the average

Table 1
Optimization of the atom transfer radical elimination reaction

Entry	CuCl (equiv.)[a]	Time (h)	Yield (%)[b]
1	1.0	1	40
2	1.0	3	47
3	1.0	5	54
4	1.0	1	74
5	2.0	3	85
6	4.0	1	100

Conversion of ethyl 2,3-dibromopropionate (**1**) to ethyl acrylate, as shown in Scheme 1. All reactions were performed in benzene at 90 °C. CuCl/2,2′-bipyridine (1:2) was used as catalyst.

[a] Number of equivalents of CuCl relative to ethyl 2,3-dibromopropionate (**1**).

[b] Yield of ethyl acrylate as determined by GC.

[1] The mechanism is formally an atom transfer radical elimination (ATRE) reaction and effectively the reverse of ATRP.

[2] The Br radical appears to kinetically favor adding to the Cu(I)X species over the unsaturated ester (e.g. ethyl acrylate) since primary C–Br bonds were not observed in the resultant polymers (see text). The reaction is thermodynamically favored as well, compare: ΔH_f(Cu–Br) ~ 79 kcal/mol; ΔH_f(C–Br) ~ 67 kcal/mol.

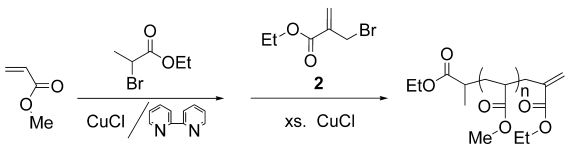
Table 2
Synthesis of telechelic polyacrylates with unsaturated end-groups

Entry	$[M]_0/[I]_0$[a]	$M_{n,theo}$[b]	$M_{n,gpc}$[c]	$M_{n,nmr}$[d]	PDI	% Conv.[e]	Yield[f]	F_n[g]
1	10	1250	1600	1500	1.5	90	80	1.94
2	20	2500	3100	2900	1.4	93	79	2.03
3	50	5750	7100	6000	1.3	88	82	2.04
4[h]	20	2500	2900	2800	1.2	94	85	2.02
5[i]	20	2500	3300	2900	1.3	93	83	1.96

Synthesis was accomplished using a two-step, one-pot approach. (1) ATRP of *n*-butyl acrylate:methyl dichloroacetate (initiator)/CuCl/bipy = 1/2/4, 75 °C, nitrogen atmosphere; polymerizations were performed in bulk monomer. (2) Upon the conclusion of the polymerization, excess ethyl 2-bromomethylacrylate and CuCl or Cu^0 were added.

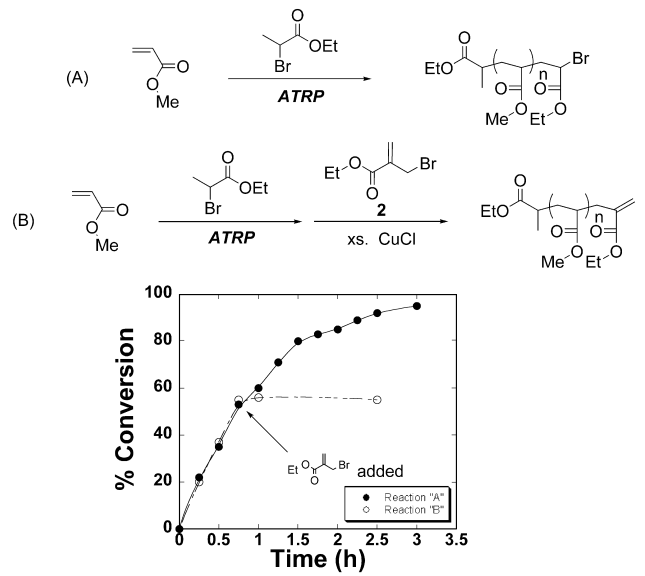
[a] Initial monomer/initiator ratio.
[b] Calculated based on monomer conversion.
[c] Relative to PS standards in THF.
[d] Determined by ^{1}H NMR spectroscopy using end-group analysis.
[e] Monomer conversion as determined by GC.
[f] Isolated yield.
[g] Average number of terminal 2-carbethoxyallyl groups per polymer chain, as determined by end-group analysis using ^{1}H NMR spectroscopy.
[h] Me_6TREN was used in lieu of bipy (CuCl/Me_6TREN = 1). Polymerization temp. = 40 °C.
[i] One-pot synthesis as described in the text. ATRP was performed under a closed system of air. The radical inhibitor was not removed from the monomer.

degree of end-functionality was close to one ($F_n = 0.97$), as desired.



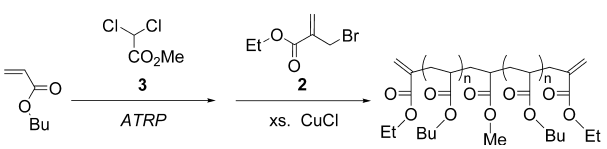
(1)

To gain an understanding of the reaction, two identical 'side-by-side' polymerizations were set-up as described earlier and monitored by GC. As shown in Scheme 2, in addition to providing a polyacrylate with an unsaturated end-group, the addition of **2** immediately quenched the reaction. Thus, the substrate served a dual purpose and proved to be an effective means of terminating the polymerization as well. This is an important feature since the resultant end-functionalized terminated polymer contains a functional group capable of further reaction (see later). However, fast quenching ensures the newly formed 'macromonomer' does not experience an appreciable degree of polymerization.



Scheme 2. Side-by-side reactions (A and B) to aid in understanding the effect of adding 2-bromomethylacrylate to an ATRP. As shown in the graph (open circles), the polymerization is immediately terminated upon addition of the reagent.

While this provided an efficient method for preparing monofunctionalized end-terminated polyacrylates, we next focused our attention on preparing the analogous difunctional telechelic polyacrylates. As shown in Eq. (2), the ATRP of *n*-butyl acrylate was initiated with a commercially available difunctional initiator, methyl dichloroacetate (**3**), affording the corresponding difunctional poly(*n*-butyl acrylate). At the conclusion of the polymerization, excess ethyl 2-bromomethylacrylate (**2**) (10 equiv.) and CuCl (10 equiv.) were added which afforded end-functionalized poly(*n*-butyl acrylate)s. As shown in Table 2, a variety of telechelic polymers were prepared with molecular weights ranging from 1500 to 5000 with PDIs < 1.4. Furthermore, we found that lower temperatures as well as lower amounts of catalyst could be used by employing a more active ligand, tris [2-(dimethylamino)ethyl]amine (Me_6TREN), in lieu of 2,2′-bipyridine [19]. In all cases, end-group analysis using ^{1}H NMR spectroscopy (by comparing the methyl group on the initiator with the terminal olefins) indicated that the average degree of end-functionality (F_n) was near 2.0, as desired.



(2)

To prevent reaction of oxygen with free radicals and catalyst, inert atmospheres must be used with ATRP. However, Matyjaszewski et al. reported a simple procedure for performing ATRP under atmospheres of air [20]. When the

polymerization is carried out in a closed system with Cu^0 (and small amounts of CuX_2) in lieu of Cu^I halide salts, the Cu^0 sequesters free radicals (from O_2 and impurities) and converts to Cu^I, the active catalyst in ATRP. The application of this technique toward our system permitted a one-pot synthesis of telechelic polyacrylates. The ATRP was set-up under ambient conditions using Cu^0 and a small amount of $CuBr_2$ ($Cu^0/CuBr_2 = 20$) as the mediating catalyst. Upon the conclusion of the polymerization, excess **2** and Cu^0 were added and heated to 75 °C for 6 h. After isolating and purifying the polymer, telechelic polyacrylates were obtained in yields and F_n's that were similar to the two-step approach described earlier.

With the successful syntheses of the methacrylate end-functionalized telechelic polyacrylates, focus shifted to examining their ability to be crosslinked. Crosslinking was accomplished both thermally and photochemically. Thermally induced crosslinking was initiated by adding benzoyl peroxide (1–2 wt%) to a concentrated solution of the polyacrylate (~1 g of polymer/1 ml toluene). After heating at 90 °C for 15 min, a tacky insoluble material was observed which was insoluble in common organic solvents. Crosslinking was photochemically induced by combining either benzoyl peroxide or 2,2-dimethoxy-2-phenylacetophenone (1–2 wt%) with a concentrated polymer solution and photolyzing using a mercury arc lamp. As in the thermally induced crosslinking reactions, a tacky, insoluble material was formed within 15 min. Spectroscopic evidence for the crosslinking reaction was obtained using infrared (IR) spectroscopy. The band between 1630 and 1640 cm^{-1} (characteristic of the methacrylate group) found in the IR spectrum of (uncrosslinked) polyacrylate was not observed in its crosslinked derivative [21].

Further evidence for the crosslinking reaction was provided through thermal analysis using DSC and TGA. As shown in Fig. 1, the glass transition temperature (T_g) of the telechelic poly(*n*-butyl acrylate)s was found to occur around −38 °C. However, upon crosslinking, this T_g

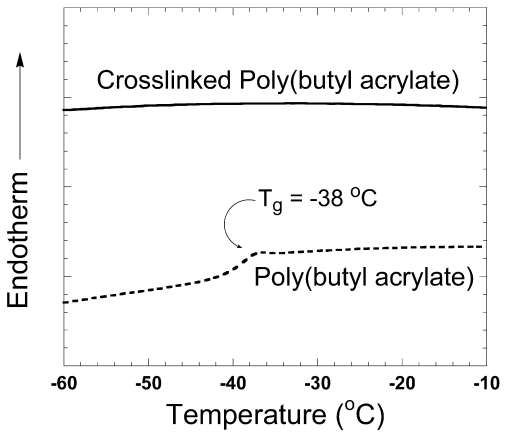


Fig. 1. Thermograph of a telechelic poly(*n*-butyl acrylate) and its crosslinked derivative. Data were obtained via DSC at a scan rate of 10 °C/min under an atmosphere of nitrogen.

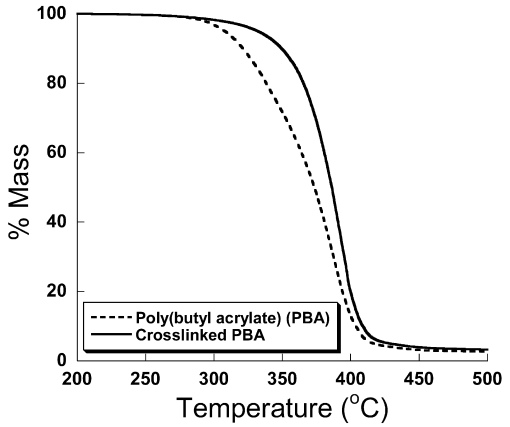


Fig. 2. Comparison of thermal stability between a telechelic poly(*n*-butyl acrylate) (dashed line) and its crosslinked derivative (solid line). Data were obtained via TGA at a scan rate of 10 °C/min under an atmosphere of nitrogen. See text for crosslinking procedures.

disappeared and no other distinctive transitions were observed. Since crosslinking generally enhances thermal stability, this should be reflected in the decomposition temperature (T_d), the temperature at which 10% weight loss occurs, as determined by TGA. As shown in Fig. 2, using TGA, the T_d of crosslinked poly(*n*-butyl acrylate) was found to increase by nearly 30 °C relative to its uncrosslinked form.

4. Conclusions

The synthesis of telechelic polyacrylates with unsaturated end-groups has been accomplished. Upon the conclusion of Cu mediated ATRP of methyl or *n*-butyl acrylate initiated with a difunctional initiator, ethyl 2-bromomethylacrylate was added which not only quenched the polymerization but installed 2-carbethoxyallyl moieties on both ends of the polymer chains. These polymers could be thermally or photochemically crosslinked to afford materials with an enhanced thermal stability relative to their parent uncrosslinked derivatives. These materials are expected to find use in high performance coating or adhesive applications.

Acknowledgements

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