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Anionic synthesis of cyclic anhydride end-capped poly(methyl methacrylate)

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Abstract

This paper reports on the anionic synthesis of poly(methyl methacrylate) chains end-capped by cyclic anhydride. The method is based on the chemical derivatization of a precursor *tert*-butyl diester end-group. Compared to the thermal modification, which was previously used, this method allows intermolecular coupling and polymer degradation to be avoided. But up to now, the final anhydride content remains moderate and has still to be improved.

Keywords: Anionic synthesis; End-capped; Poly(methyl methacrylate)

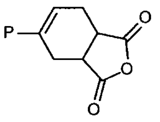
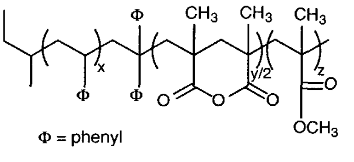
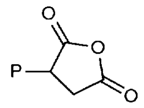
1. Introduction

The end-capping of synthetic polymers is of great interest since end-reactive polymers are highly valuable intermediates for the synthesis of macromolecules of more complex molecular architecture, either in solution or in the bulk by reactive processing. Anionic polymerization is a key technique for the controlled end-capping of polymers. Indeed, in addition to predictable molecular weight and narrow molecular weight distribution, well-defined end-groups can be attached to the chains by the appropriate choice of either the initiator or the terminating agent or both.

To the best of our knowledge, few examples of polymer end-capping by cyclic anhydride have been reported in the scientific literature [1-4]. Takaneka et al. [1] reported a method for the synthesis of anhydride terminal polystyrene and polyisoprene based on the Diels–Alder addition of maleic anhydride to a diene end-group (Table 1, entry 1). Cernohous and coworkers [2-4] published the synthesis of several anhydride containing polymers based on the thermal treatment of *tert*-butyl ester groups close enough to each other to allow cyclic anhydride formation (Table 1, entries 2, 3). For this purpose, *tert*-butyl ester containing chains were synthesized by anionic polymerization. On the one hand [2], ABC triblock copolymer of polystyrene-*b*-poly(*tert*-butyl methacrylate)-*b*-poly(methyl methacrylate) was synthesized by anionic polymerization and on the other hand [3-4polystyrene, poly(methyl methacrylate), poly(vinyl pyridine) and polyisoprene end-capped by di-*tert*-butyl maleate were synthesized. The thermal treatment led to high anhydride yields even though polymer degradation was observed in some cases [4].

This communication reports on an alternative method for the derivatization of the *tert*-butyl diester end-group of poly(methyl methacrylate) (PMMA) into cyclic anhydride. Diester ended PMMA will be first prepared by end-capping the living chains by di-*tert*-butyl fumarate according to Cernohous et al. [4]. The chemical derivatization of the end-group will be investigated as a possible substitute for the thermal treatment. Indeed, preliminary experiments of thermal modification of diester ended PMMA in the melt led to some polymer degradation, to conversion yields lower than expected and to the occurrence of a significant amount of intermolecular reaction responsible for chain extension [5]. The chemical derivatization of the diester end-group into cyclic anhydride conducted in dilute solution and at moderate temperature could prevent polymer degradation and intermolecular coupling from occurring.

Table 1
Literature survey of the anionic synthesis of cyclic anhydride containing polymers

Entry	Polymer	Functionality (%)	Reference
1	 P = polystyrene polyisoprene	100	[1]
2	 Φ = phenyl	/	[2]
3	 P = polystyrene poly(methyl methacrylate) poly(vinyl pyridine) polyisoprene	≥ 72 ≥ 81 20 /	[3,4]

2. Experimental

2.1. Materials

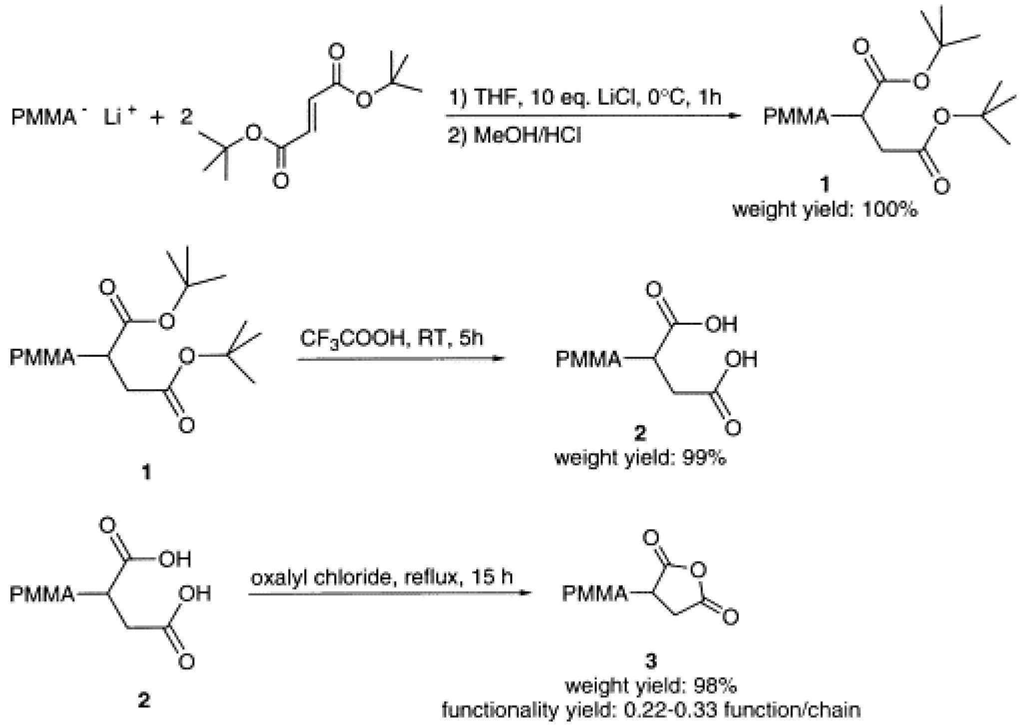
Lithium chloride, diphenylethylene and methyl methacrylate were purified as reported elsewhere [6-8]. Di-*tert*-butyl fumarate was synthesized as described by Pantoustier and coworkers [9], and dried by azeotropic distillation of toluene. Diethyl ether and tetrahydrofuran (THF) were refluxed over sodium-benzophenone complex, hexane used for precipitation of cyclic anhydride end-functional PMMA and triethylamine were dried over sodium and calcium hydride, respectively, and distilled prior to use. Methylene chloride, trifluoroacetic acid and oxalyl chloride were used as received.

2.2. Synthesis of diester end-capped poly(methyl methacrylate) (polymer **1**, Scheme 1)

Methyl methacrylate was polymerized in tetrahydrofuran (THF) at −78°C using 1,1-diphenyl-4 methylpentyllithium as initiator and lithium chloride as a ligand as detailed elsewhere [6-8]. One hour later, di-*tert*-butyl fumarate (2 equiv. with respect to the living chains) in solution in a 3:1 (v/v) THF/toluene mixture at −78°C was added to the reaction medium. The temperature was raised to 0°C, and the solution was stirred for 1 h at this temperature before adding acidified methanol. Polymer **1** (see Scheme 1) was recovered by precipitation in hexane for molecular weight lower than 10,000 and in methanol for higher molecular weight. It was purified by repeated precipitations and dried under vacuum at room temperature. Finally, the weight of polymer recovered represented 100% of the initial monomer weight introduced in the synthesis (weight yield: 100%).

2.3. Synthesis of diacid end-capped poly(methyl methacrylate) (polymer **2**, Scheme 1)

Polymer **1** was dissolved in trifluoroacetic acid, the concentration being 5% (wt/v). The solution was stirred at room temperature for 5 h under argon before the solvent was eliminated under reduced pressure. The polymer was dissolved in methylene chloride and washed three times with water. The organic layer was dried over magnesium sulfate and concentrated under reduced pressure. Polymer **2** was finally recovered by precipitation in hexane or methanol depending on its molecular weight and dried under vacuum at room temperature. The total weight yield of the reaction was 99%.



Scheme 1.

2.4. Synthesis of cyclic anhydride end-capped poly(methyl methacrylate) (polymer **3**, Scheme 1)

Polymer **2** was dissolved at a concentration of 5% (wt/v) in oxalyl chloride, and the solution was refluxed overnight under argon. For PMMA of molecular weight lower than 10,000, the oxalyl chloride was eliminated under reduced pressure. The polymer was dissolved in dry THF and precipitated in dry hexane under argon. For higher molecular weight samples, the solution was concentrated under reduced pressure and poured in dry diethyl ether under argon. After filtration, polymer **3** was dried under vacuum at room temperature and stored in a dessicator. The total weight yield of the reaction was 98%.

3. Results and discussion

Anionic polymerization of methyl methacrylate was initiated by 1,1-diphenyl-4 methylpentyllithium in THF at low temperature with lithium chloride as a ligand. Polymer **1** was prepared by reaction of living PMMA chains with di-*tert*-butyl fumarate followed by protonation (Scheme 1). The diester reacts with the living chains in a 1,4-fashion as the maleate isomer does [4]. Three samples of diester end-capped PMMA of different molecular weights were synthesized (Table 2, entries 1–3). A low molecular weight sample (entry 1) was first synthesized in order to optimize each step of the end-capping of PMMA by cyclic anhydride. Low molecular weight is indeed a requirement for the end-groups analysis by traditional spectroscopic techniques. Once optimized, the recipe can be extended to polymers of higher molecular weight.

Table 2. Molecular weights and molecular weight distribution of the *ω*-functional PMMA

Entry	Polymer	M_n[a]	M_w[b]	MWD[c]
1	**1a**	2600	3200	1.23
2	**1b**	16, 700	17, 500	1.05
3	**1c**	63, 500	65, 200	1,03
4	**2a**	2400	3000	1.25
5	**2b**	16, 500	17, 300	1.05
6	**2c**	62, 100	64, 000	1.03
7	**3a**	2300	2900	1.26
8	**3b**	16, 500	17, 300	1,05
9	**3c**	61, 000	63, 100	1.03

[a] M_n: number average molecular weight.
[b] M_w: weight average molecular weight.
[c] MWD: molecular weight distribution.

Analysis of polymer **1** by FT-IR and ^{1}H NMR confirms the presence of the end-group. FT-IR spectroscopy shows the CH deformation of the *tert*-butyl group at 1368 cm^{-1} (Fig. 1a) [10]. The resonance of the *tert*-butyl ester protons is also clearly observed at 1.3–1.6 ppm on the ^{1}H NMR spectrum (Fig. 2a). The relative intensity of the protons of the α-end-group (aromatic protons of the initiator fragment at 7.0–7.2 ppm) and the *tert*-butyl ω-end-group agrees with the quantitative end-capping of the chains.

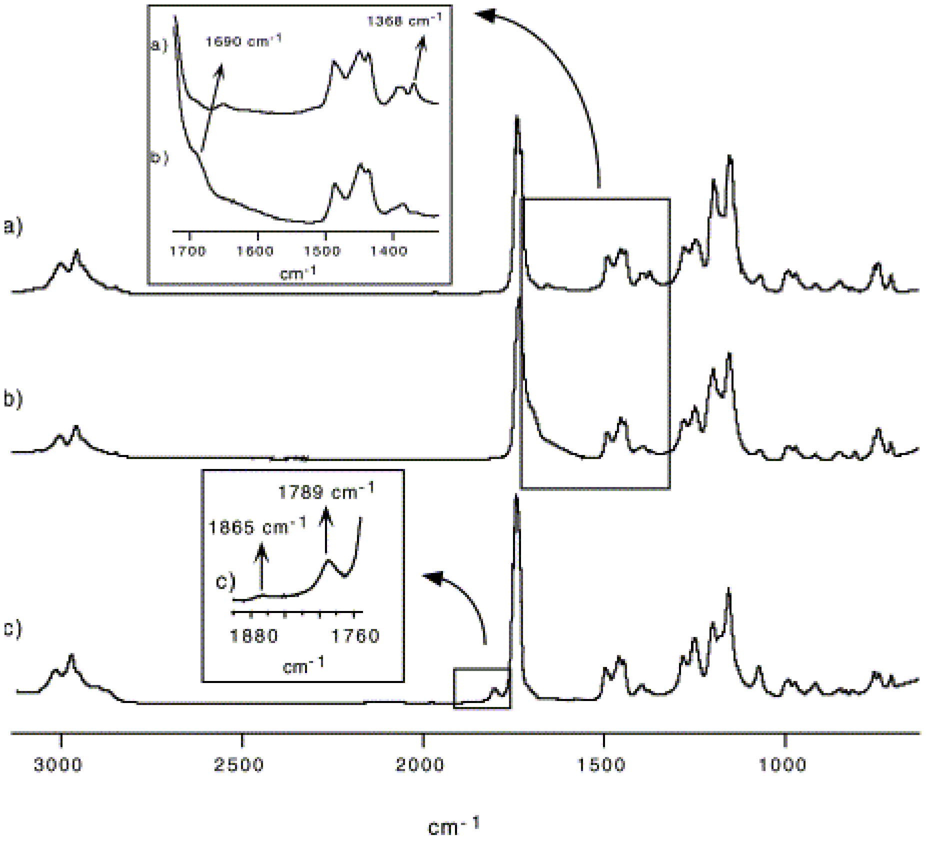


Fig. 1. FT-IR spectra of: (a) polymer **1a**; (b) polymer **2a**; (c) polymer **3a**.

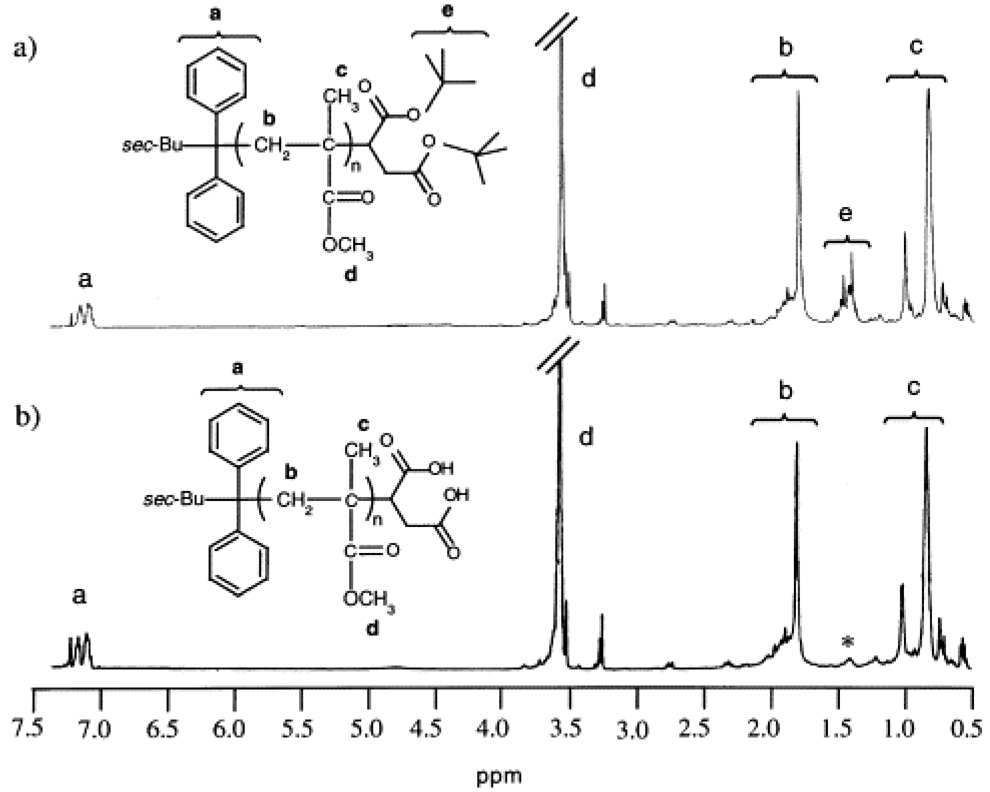


Fig. 2. ^{1}H NMR spectra of: (a) polymer **1a**; (b) polymer **2a**. (*Signal also observed on unfunctionalized PMMA and independent of the diester end-group.)

The derivatization of the diester end-group of PMMA into dicarboxylic acid has been achieved by reaction with pure trifluoroacetic acid at room temperature (Scheme 1) [11]. Within the limits of experimental errors, size exclusion chromatography (SEC) analysis of polymer **2** shows that the average molecular weights and the molecular weight distribution remain essentially unchanged (Table 2, entries 4–6). The characteristic signals of the *tert*-butyl group is no longer observed by FT-IR (Fig. 1b) and ^{1}H NMR (Fig. 2b). FT-IR spectrum also shows a shoulder around 1690 cm^{-1} more likely characteristic of the acid functions [10]. Moreover, ^{1}H NMR spectroscopy proves that the hydrolysis of the *tert*-butyl ester is selective since the integration ratio of the methyl protons c and d of the polymer backbone (Fig. 1a and b) is close to unity before and after deprotection.

The diacid end-group has been dehydrated into anhydride by heating at reflux temperature in oxalyl chloride (b.p. 63–64°C) [12]. Once PMMA is end-capped by anhydride, it has to be precipitated and dissolved in carefully dried solvents. The molecular weight and molecular weight distribution of PMMA remain unchanged (Table 2, entries 7–9) indicating the lack of intermolecular coupling reaction.

The observation of two carbonyl absorption bands at 1789 and 1865 cm^{-1} characteristic of the anhydride groups supports that the dehydration reaction has occurred. The higher intensity of the lower frequency band proves that intramolecular dehydration was dominant with formation of cyclic anhydride end-groups. The position of the bands is also consistent with those of succinic anhydride which is a good model for the chain end-group [10]. SEC and NMR data for polymers **2** and **3** support that PMMA chains are not degraded during the chemical modification of the end-groups.

Quantification of the anhydride end-groups based on the absorbance at 1789 cm^{-1} agrees with an anhydride content in the range of 0.22–0.33 group per chain whatever the PMMA molecular weight (from 2500 to 60,000).

4. Conclusion

This paper has reported on the end-capping of PMMA chains by cyclic anhydride, based on the chemical derivatization of a *tert*-butyl diester end-group. Compared to the thermal modification, which was previously used, this method allows intermolecular coupling and polymer degradation to be avoided. However, the anhydride content (0.22–0.33 group per chain) has to be optimized. It is not clear yet whether the diacid formation or the cyclization reaction is the limiting step. Would the cyclization reaction be incomplete, other dehydrating agents should be tested as a way of improving the method efficiency.

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