Reactivity of 'living' t-butyl acrylic anions towards aldehydes: application to the synthesis of hydroxyl-terminated polyacrylates and their related copolymers

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The reaction between 'living' t-butyl acrylic anions and benzaldehyde (BZA) is shown to be highly selective. Advantage is taken of this fact in order to prepare well defined hydroxyl-terminated poly(t-butyl acrylate) (tBuA) samples. When a dialdehyde such as terephthalaldehyde (TAP) is used in place of BZA, both aldehyde functions of the electrophilic reagent participate in the deactivating reaction of the acrylic anions. Multiblock copolymers consisting of polyvinylic and poly(t-butyl acrylate) sequences can therefore be obtained by stoichiometric coupling reactions between the 'living' triblock copolymer and terephthalaldehyde.

(Keywords: living character; t-butyl acrylate; block copolymer)

INTRODUCTION

In recent years, several new polymerization techniques, which are neither purely anionic nor cationic processes, have been developed with the objective of fulfilling the essential features of living polymerizations.

Group transfer polymerization (GTP)[1] is one of these new processes which offers remarkable possibilities, particularly in the area of acrylic and methacrylic polymers. Polymers with controlled structures, e.g. telechelics, star-shaped forms, etc. have been obtained as a result of the living character of GTP processes. It is undisputed that this latter technique offers several advantages over the classical anionic polymerization process, such as reaction temperature, efficiency of functionalizations, etc. However, some limitations are associated with the use of GTP: it requires the preliminary synthesis of silyl ketene acetal as an initiator and it cannot be applied to the synthesis of block copolymers which contain non-acrylic sequences. As an extension of our long term interest in the functionalization of living polymers[2], we report in this paper the synthesis of novel hydroxyl-terminated poly(t-butyl acrylate) (PtBuA). In the course of this study we have also examined the reaction of living poly(t-butyl acrylate) with a difunctional electrophilic agent, such as terephthalaldehyde. When it is applied to living triblock copolymers, this reaction leads to well defined multiblock copolymers. The possibility is thus presented to synthesize multiblock copolymers consisting of alternating poly(t-butyl acrylate) and polyvinylic sequences.

EXPERIMENTAL

Materials

Solvents. Tetrahydrofuran (THF) was purified according to standard procedures.

Monomers. t-Butyl acrylate (tBuA) (Aldrich) was first vacuum distilled, and was then treated with a sufficient amount of a 10% solution of triethylaluminium in hexane at room temperature to give a coloured end-point, according to McGrath's procedure[3]. The monomer was then immediately vacuum distilled into a chilled Schlenk-type burette and used within 1–2 h. Methyl methacrylate (Aldrich) was also purified according to this same procedure.

Styrene (Aldrich) and 1,1-diphenylethylene (Aldrich) were distilled twice under vacuum in the presence of Na wire.

Functionalization reagents. Benzaldehyde (BZA) (Aldrich) was distilled from calcium, while terephthalaldehyde (terephthaldicarboxaldehyde) (TAP) (Aldrich) was recrystallized from water and was then extensively dried before use. Samples of pure 4,4′-diphenylmethane diisocyanate were generously supplied by Dow Chemicals.

Initiators. s-Butyllithium was made in the usual way, from Li metal pieces and 2-chlorobutane, in benzene solution, under an inert atmosphere. 1,1-Diphenylhexyllithium (DPHLi) was obtained *in situ* from the reaction of s-butyllithium with 1,1-diphenylethylene in THF, while

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1,1,4,4-tetraphenyl dilithiobutane (TPDLB) is formed in THF solution upon reaction of 1,1-diphenylethylene with pieces of Li metal. Lithium dihydronaphthalide (Li-naphthalene) was obtained by the reaction of lithium metal with naphthalene in THF, under an inert atmosphere.

Synthesis of poly(tBuA) and of copolymers containing poly(tBuA) sequences

The initiator used for the synthesis of monofunctional poly(tBuA) was DPHLi, while the synthesis of difunctional poly(tBuA) and of triblock copolymers containing two poly(tBuA) external sequences and a central poly(methyl methacrylate) (PMMA) sequence required the use of TPDLB. When the central sequence is made of polystyrene (PS), the initiator chosen was Li-naphthalene. The detailed procedures for the syntheses of these polymers are described in our previous papers[2,4].

Functionalization

After completion of the polymerization of tBuA, benzaldehyde was introduced into the reaction medium in order to end-cap the polymer with a benzyl alcoholate function. The alkoxide sites were protonated upon addition of a few drops of acetic acid, giving rise to the expected ω-benzyl hydroxyl polymer.

Coupling reactions

A stoichiometric amount of terephthalaldehyde (based on the concentration of living sites) was slowly introduced into the reaction medium containing the living polymer. A physical gel rapidly formed, but this vanished upon acidification.

Characterization

After protonation of the reaction medium, the poly(tBuA) samples were precipitated into a cold methanol–water mixture and recovered by subsequent centrifugation. The polymer was redissolved in benzene, filtered to remove any residual LiCl and then freeze-dried prior to its characterization.

U.v. spectroscopy was used to determine the number-average molecular weight of the samples, since the groups contained in the initiators have a specific absorption. (This is the case with both DPHLi and TPDLB.) Their extinction coefficient was assumed to be identical to that of 2,2-diphenylbutane ($\varepsilon = 11\,430\,\mathrm{mol}^{-1}\,\mathrm{cm}^{-1}$ at 254 nm in THF).

The characterization was carried out on unfunctionalized aliquots, as the terminal benzyl alcohol which is present in functionalized samples could interfere with the absorption of the diphenylbutane moiety. Polymers containining a PS sequence were not characterized by u.v. spectroscopy for the obvious reason that the phenyl ring absorbs in the same spectral region.

Gel permeation chromatography (g.p.c.) has also been used for molecular weight determination; the $\bar{M}_n$ values of the samples obtained after initiation by either DPHLi or TPDLB (calculated by the use of a PS standard calibration curve) were found to be in good agreement with the data obtained from the u.v. measurements.

The functionalization yield of benzyl-alcohol-terminated samples was evaluated in two distinct ways. When the polymer did not contain poly(tBuA), the hydroxyl content was determined by chemical analysis[5], using phosgene as a reactant. This latter method was not applied to those samples containing poly(tBuA), owing to the possible hydrolysis of the t-butyl ester functions by the HCl that is formed. To check the functionality of these polymers, we resorted to an indirect method, in which ω – hydroxyl-terminated poly(tBuA)s were reacted with stoichiometric amounts of 4,4′-diphenylmethane diisocyanate (MDI) (based on the $\bar{M}_n$ value determined by u.v.) at 60°C for 2 days. Quantitative coupling was systematically obtained by using this method (*Figure 1*).

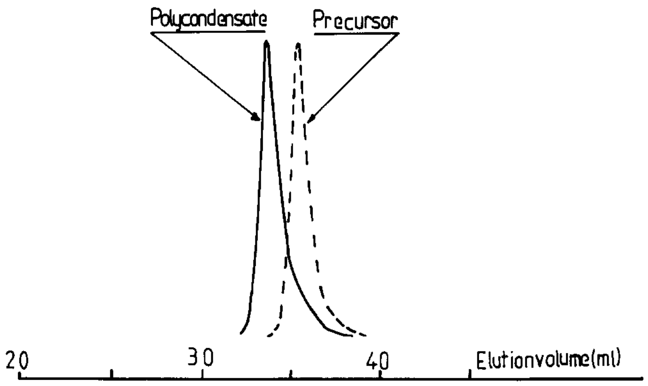

Figure 1 Gel permeation chromatography chart of the polycondensate obtained upon reacting α,ω-dihydroxyl poly(tBuA) with a stoichiometric amount of 4,4′-diphenylmethyl diisocyanate

RESULTS AND DISCUSSION

Synthesis of hydroxyl-terminated poly(t-butyl acrylate)s

ω-Hydroxyl polyacrylates, or even polymethacrylates, are not easily accessible by anionic methods. Addition of ethylene oxide to living poly(methyl methacrylate) (PMMA), for example, does not lead to the ring opening of the latter electrophilic reagent; hydroxyl-functionalized polymethacrylates have, however, been obtained by Sharkey and coworkers[6], who used a complicated initiator, which carried a protected hydroxyl function.

More recently, Smith[7] took advantage of the ability of aldehydes to react with organometallic compounds to prepare PMMA which was fitted at the chain end with a benzyl alcohol function. Since we have recently come to work on the anionic polymerization of t-butyl acrylate, we therefore thought of applying Smith's method to prepare hydroxyl-terminated poly(t-butyl acrylate).

The anionic polymerization of t-butyl acrylate is a truly living polymerization reaction[8], provided that a sufficient amount of LiCl is present in the reaction medium. The introduction of this salt results in a decrease of the overall nucleophilicity of the t-butyl acrylic anions and it allows a perfectly controlled process, which is free of termination and transfer reactions. However, the reduced nucleophilicity of the living site has some disadvantages: the t-butyl acrylic anion does, in fact, fail to react with most electrophilic compounds such as ethylene oxide or dibromo-*p*-xylene. Bromomethylstyrene is the only successful reagent that we know of[2]. It is therefore of great interest to establish whether the complex formed by t-butyl acrylic anions and LiCl does react with benzaldehyde.

The conditions used for polymerizing t-butyl acrylate, namely amount of LiCl, temperature, solvent, etc., were similar to those described in previous papers. The initiator was formed *in situ* by reacting 1,1-diphenylethylene with butyllithium (BuLi). The monomer was introduced dropwise into the solution containing the initiator, and benzaldehyde was added in slight excess after total consumption of the t-butyl acrylate had taken place. The medium is then acidified in order to transform the alkoxide which is possibly generated upon the previous step into secondary benzyl alcohol. Qualitative i.r. spectroscopic analysis of the polymer confirmed the presence of alcohol functions (strong band at 3400 cm^{-1}). Further evidence of the successful functionalization by benzaldehyde was obtained upon coupling this functional polymer with 4,4′-diphenylmethane diisocyanate (*Figure 1*). The absence of any residual precursor chain in the g.p.c. chart does confirm that each chain is end-fitted with the expected secondary benzyl alcohol function; functionalization of living poly(tBuA) anions by benzaldehyde was thus found to be quantitative (*Table 1*). Determination of the hydroxyl content by the phosgene method[5] was not attempted because of possible side reactions between the HCl that was formed and the t-butyl ester functions.

α,ω-Dihydroxyl-terminated poly(t-butyl acrylate)s were also prepared, with the only difference from the previous case arising from the use of a difunctional initiator, namely 1,1,4,4-tetraphenyl dilithiobutane. Again, the results obtained were in good agreement with those predicted (see *Table 1*).

Table 1 Functionalization of living methacrylic and t-butyl acrylic anions by reaction with benzaldehyde

Functional polymer					Condensation
Type of polymer	Initiator	$\bar{M}_n$ (u.v.)	$\bar{M}_n$ (g.p.c.)	$\bar{M}_n$ (chemical analysis)[a]	$\bar{M}$ (g.p.c)[b]
PMMA	DPHLi	6 000	6 200	6 100	
PMMA	DHPLi	3 500	3 600	3 400	
PtBuA	DPHLi	3 300	3 500	–	6 700[c]
PMMA-*b*-PtBuA (50/50 by wt)	DPHLi	7 200	7 000	–	13 500
PtBuA	TPDLB	20 500	21 000	–	220 000

[a] Determination of OH content by the phosgene method[5]
[b] Characterized after reaction of hydroxyl-terminated polymers with a stoichiometric amount of 4,4′-diphenylmethane diisocyanate
[c] See g.p.c. chart (*Figure 1*)

Table 2 Molecular weight data obtained for the coupling reactions between t-butyl acrylic anions and terephthalaldehyde

Precursor				Polycondensate
Type of polymer	Initiator	$\bar{M}_n$ (u.v.)	$\bar{M}_n$ (g.p.c.)	$\bar{M}_n$ (g.p.c.)
PtBuA	DPHLi	11 600	12 000	21 500
PtBuA	TPDLB	16 000	15 000	50 000[a]

[a] See g.p.c. chart (*Figure 2*)

Table 3 Molecular weight data obtained for (PS–PtBuA)$_n$ and (PMMA–PtBuA)$_n$ multiblock copolymers

Triblock copolymer				Multiblock copolymer
Type of polymer	Initiator	$\bar{M}_n$ (g.p.c.)	PtBuA (wt%)	$\bar{M}_n$ (g.p.c.)
PS–PtBuA	Li-naphthalene	34 000[a]	61	123 000[a]
PMMA–PtBuA	TPDLB	26 000[b]	70	107 000[b]

[a] See g.p.c. chart (*Figure 3*)
[b] Using PMMA calibration curve

We have recently synthesized well defined block copolymers, consisting of one polyvinylic sequence and one or two poly(t-butyl acrylate) blocks, by the sequential anionic polymerization of these two monomers in the presence of LiCl. It was shown that this salt does not affect the polymerization of vinylic monomer insofar as the molecular weight and the molecular-weight distribution (*MWD*) are concerned[4]. The possibility was thus offered to synthesize telechelic hydroxyl-ended di- and triblock copolymers through benzaldehyde functionalization. The interest in such materials arises from the fact that they can participate in further reactions. The results that were obtained do indeed confirm the selectivity of this functionalization reaction (see *Table 1*).

Synthesis of multiblock copolymers involving poly(t-butyl acrylate) sequences

The good results that have been obtained with benzylaldehyde have prompted us to investigate the reactivity of living t-butyl acrylic anions towards dialdehydes, namely terephthalaldehyde (TAP). A stoichiometric amount of this latter dialdehyde was slowly added to the solution containing monofunctional living poly(tBuA). Before introduction of the coupling agent, an aliquot was taken from the reaction medium, deactivated protonically and then analysed by g.p.c. The same technique was used to characterize the product treated with terephthalaldehyde. Comparison of the g.p.c. traces of both products demonstrated that the coupling reaction had been successful. The number-average molecular weight of the final product is approximately twice that of the precursor (*Table 2*).

If terephthalaldehyde is added slowly to a solution containing difunctional anionic poly(tBuA), a physical gel is formed before the stoichiometry is reached, as a result of associations between the benzyl alcoholate functions that are generated. This behaviour indicates that each polymer chain of this 'polycondensate' carries more than two alcoholate anions, which thus shows that multiple coupling reactions have occurred (*Table 2*). The gel vanishes as soon as the medium is acidified. The isolated product is a 'clean' polycondensate, containing almost no detectable residual precursor (< 5%), as shown by the g.p.c. traces (*Figure 2*).

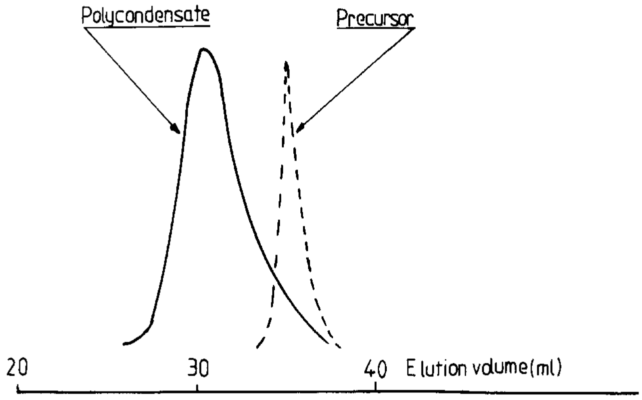

Figure 2 Gel permeation chromatography chart of the polycondensate obtained upon reacting difunctional living poly(tBuA) with a stoichiometric amount of terephthalaldehyde

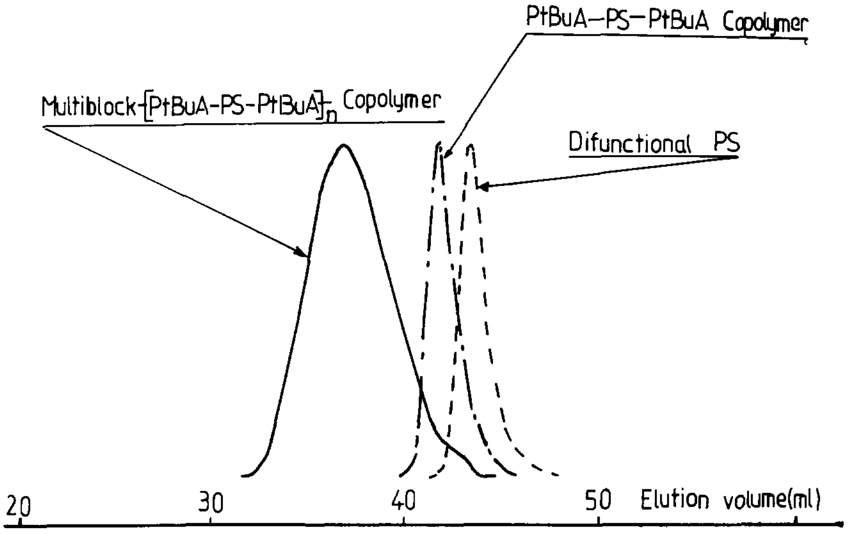

Figure 3 Gel permeation chromatography chart of a multiblock copolymer consisting of polystyrene and poly(t-butyl acrylate) sequences

In a similar way, living triblock copolymers, made up of two external poly(t-butyl acrylic) sequences and a central polyvinylic moiety (either PS or PMMA), give rise to multiblock copolymers upon reaction with TAP. A viscosity increase and gelation, as a result of physical association, are also observed in this case. The molecular weight of the multiblock 'polycondensate' that is obtained is five times that of the initial triblock copolymer (*Figure 3*), which further confirms the selectivity of the reaction between acrylic anions and phenylaldehydes (*Table 3*).

CONCLUSIONS

Hydroxyl-terminated poly(t-butyl acrylate)s are obtained upon treating living butyl acrylic anions with benzaldehyde. A dialdehyde, such as terephthalaldehyde, also reacts quantitatively with acrylic living ends, and addition of this dialdehyde to a difunctional living polymer results in a polycondensate. Multiblock copolymers, containing poly(t-butyl acrylic) and polyvinylic sequences, can be synthesized in this way.

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