Synthesis and characterization of block copolymers containing poly(tert.butyl acrylate) blocks

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Block copolymers constituted of one polyvinylic block (polystyrene, poly(methyl methacrylate) or poly(vinylpyridine)) and one or two poly(tert.butyl acrylate) blocks have been synthesized by sequential anionic polymerization of the two monomers, using a lithium organic initiator, in the presence of lithium chloride, as an extension of Teyssié's method. The living character of these polymerizations was established. Characterization measurements showed that the copolymers obtained exhibit molecular weights and compositions close to those expected, narrow molecular weight distributions and low compositional heterogeneity. Interest in these species arises from the ease of ester hydrolysis of the tert.butyl acrylate units. The block copolymers described in this paper can thus be considered as promising precursors for amphiphilic species, and even for ampholytic polymeric materials if the other sequence is of poly(vinylpyridine).

(Keywords: block copolymers; anionic polymerization; poly(tert.butyl acrylate)

INTRODUCTION

In some recent publications, Teyssié *et al.*[1,2] demonstrated that the anionic polymerization of tert.butyl acrylate (t.BuA), initiated with an adequate lithium organic compound in the presence of lithium chloride, produces polymers with narrow molecular weight distribution and with the desired degree of polymerization. No spontaneous transfer or termination reactions seem to be involved. We have recently confirmed and extended Teyssié's results. Low polydispersity samples of poly(tert.butyl acrylate) were obtained by this method over a broad range of molecular weights[3].

The living character of the anionic polymerization of tert.butyl acrylate does not arise only from the molecular weight control. It is also evidenced by quantitative functionalizations at chain ends, obtained upon reacting the living sites with functional deactivators (usually added in excess). The synthesis of poly(tert.butyl acrylate) macromonomers[4] is an example of a successful functionalization at chain end.

Interest in poly(tert.butyl acrylate) arises from the relative ease of hydrolysis of its ester functions: this smooth reaction can be performed in various ways and yields poly-(acrylic acid), a hydrophilic ionogenic polymer with numerous potential applications.

The present paper is devoted to the synthesis of various A–B diblock or B–A–B triblock copolymers containing poly(tert.butyl acrylate) (B) blocks, by sequential addition of the two monomers A and B to an initiator solution. A prerequisite to the formation of well defined copolymers is that the polymerization of monomer B is initiated fast and quantitatively by the living sites A^- of the precursor. The ease of this reaction is determined by the nucleophilicity of the monomer. The reverse reaction (attack of monomer A by the B^- sites) is consequently either impossible or extremely slow.

Teyssié[1,2] stipulated that the absence of spontaneous termination in anionic tert.butyl acrylate polymerization – when LiCl is added to the system – is due to formation of a complex between the carbanionic sites and the lithium salt. As a consequence, the nucleophilicity of the B^- carbanions derived from the acrylic monomer is lowered sufficiently to avoid side reactions. Yet these sites are still able to add tert.butyl acrylate monomer, yielding polymers of molecular weight and molecular weight distribution indicative of a living polymerization.

A prerequisite to these block copolymer syntheses is the ability of the comonomers A to undergo polymerization in the presence of lithium chloride. The resulting living poly-A precursor can then serve as a polymeric initiator for the polymerization of tert.butyl acrylate (B). The incorporation of well defined sequences of poly(tert.butyl acrylate) to form di-, tri- or multiblock copolymers is of great interest for a plethora of applications. Under relatively mild conditions, ester hydrolysis should subsequently produce poly(acrylic acid) sequences at desired locations, with no polymer degradation.

EXPERIMENTAL

Materials

The monomers (styrene, 1,1-diphenylethylene, methyl methacrylate, tert.butyl acrylate and 2-vinyl pyridine) were made free of their inhibitors, washed, dried and vacuum distilled several times over sodium wire (or calcium hydride), to make them anhydrous. They were

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kept in Schlenk vessels to prevent access of air or moisture.

The solvents (tetrahydrofuran (THF) and benzene) were purified and carefully dried according to classical procedures.

Sec.butyllithium was prepared under inert atmosphere, in benzene solution, from pieces of lithium metal (120% excess) and 2-chlorobutane. The reaction requires 72 h to reach 70% yield at room temperature.

Lithium dihydronaphthylide (Li-naphthalene) was obtained upon reaction of lithium metal with naphthalene in tetrahydrofuran, under inert atmosphere at room temperature. Since this initiator lacks stability in THF, it is necessary to have it freshly made for each experiment.

1,1,4,4-Tetraphenyl-1,4-dilithiobutane ($TPBLi_2$) was obtained from lithium dihydronaphthylide and 1,1-diphenylethylene in stoichiometric amounts. The reaction was carried out at room temperature, under argon atmosphere, and was considered to be complete within 2 h.

1,1-Diphenyl-3-methylpertyllithium (DPHLi) was prepared under inert atmosphere, by stoichiometric reaction of 1,1-diphenylethylene onto butyl lithium, in tetrahydrofuran, at −30°C, to avoid side reactions involving BuLi and THF. The reaction was usually carried out in the reactor used subsequently for the polymerization process.

All the initiator solutions were titrated by the acetamide method to determine their molarity.

Procedure

Polymerizations were carried out in a tight reactor equipped with magnetic stirring, temperature control, argon inlet, sampling device and burettes meant to introduce solvent, initiator and monomers. The entire experiment was conducted under a slight argon overpressure. The required amount of dry lithium chloride (1 mol for ≈50 mol of monomer is the best choice, as established earlier[3]) was introduced first. The reactor was then heated to 120°C and submitted to several vacuum–argon cycles. After cooling, the chosen amount of solvent was introduced into the reactor, and 'neutralized' with a few drops of initiator. The calculated volume of initiator solution was then introduced and the mixture was cooled to −30°C (or even −60°C). The first monomer was added dropwise, under efficient stirring. After a given time (10–60 min, depending upon the monomer) part of the solution was sampled out, deactivated protonically and used to characterize the precursor.

To the rest of the precursor solution the chosen amount of tert.butyl acrylate (second monomer) was added dropwise, at the same temperature. Time was allotted to allow the polymerization to attain completion. The deactivation of the carbanionic sites was achieved protonically. The copolymers were precipitated from their solutions, preferably into a non-solvent of both types of block. Cold heptane, or mixtures of methanol and water (90/10 or 80/20 v/v at room temperature), were the systems most commonly used. The raw polymers and block copolymers were redissolved in benzene, filtered to remove the salt (LiCl) and recovered by freeze-drying.

The composition of the samples was determined from elemental analysis, and from refractometric measurements (Brice Phoenix differential refractometer). Size exclusion chromatography (Waters) was used merely to check the width of the molecular weight distribution, and light scattering (laser equipped Fica apparatus, $\lambda = 632$ nm) to measure the molecular weights. Owing to the low compositional heterogeneity of the samples the values of M_w arising from light scattering can be considered a good approximation to their true weight average molecular weight.

RESULTS AND DISCUSSION

Homopolymerization in the presence of lithium chloride

Anionic homopolymerization experiments have been run with various monomers to establish whether the presence of LiCl in the reaction medium influences the process. All polymerizations were conducted in tight reactors, under a slight argon overpressure, at temperatures around −30°C (or lower), in tetrahydrofuran (THF) solution, using lithium organic initiators. Most of the polymers formed exhibited molecular weights close to those expected from the mole ratio of monomer consumed to initiator used and narrow molecular weight distributions. Some results are shown in *Table 1*.

The living character of the tert.butyl acrylate polymerization has been established[1,4], as mentioned above, and no further comments are necessary.

Table 1 Data on homopolymers prepared in the presence of lithium chloride

			Polymer characteristics			
Ref.	Monomer[a]	Initiator	M^b_{TH}	M_{gpc} (peak)	M_{LS}	I^c
43	Styrene	Li Naphth.		14000	14500	1.18
45	Styrene	BuLi	10000	14000	13600	1.18
47	Styrene	Li Naphth.	40000	65000	71000	
48	Styrene	Li Naphth.	40000	44000	47000	1.32
50	Styrene	BuLi		89000	94000	1.10
52	MMA	$TPBLi_2$		35000	43800	1.17
54	MMA	$TPBLi_2$	20000	21000	25000	1.11
55	MMA	$TPBLi_2$		17000		1.02
56	MMA	$TPBLi_2$		34200	35700	1.04
90	2-ViPyridine	$TPBLi_2$	19000	20000	21900	1.07
08	2-ViPyridine	DPHLi	15000	12600	20500	1.07

[a] Mole ratio of LiCl to monomer is steadily equal to 1/44
[b] Calculated from the monomer to initiator mole ratio
[c] I, polydispersity index $= M_w/M_n$

The case of styrene polymerization is straightforward: it is unaffected by the presence of LiCl, although the polymerization rate is definitely lower than that in the absence of LiCl.

It has been confirmed that methyl methacrylate can be polymerized readily in the presence of LiCl. The polymers obtained exhibit the expected molecular weight and are of low polydispersity. Again, the polymerization rate is significantly lower than that in the absence of LiCl.

The case of 2-vinylpyridine is remarkable. In the absence of lithium chloride polymerization is very fast, even at −80°C. Special experimental conditions have to be selected[5], such as using diluted monomer along with efficient stirring, if samples exhibiting low polydispersity are to be obtained. In the presence of LiCl the polymerization rate is decreased markedly, yet it can proceed smoothly to completion. Undiluted vinylpyridine is introduced dropwise into the reaction medium, maintained at −60°C. This has the salient advantage of avoiding parasitic deactivations due to residual protonic impurities contained in the diluting solvent. Furthermore, the final concentration of polymer in the reaction medium can reach 10%, whereas in the absence of LiCl it is advisable to stay below 5%.

Block copolymer synthesis

The presence of LiCl in the reaction medium is a requirement for the living character of anionic tert.butyl acrylate polymerization. Since it does not affect the anionic polymerization of monomers such as styrene, 2-vinylpyridine and methyl methacrylate, except to slow down rates, the synthesis of block copolymers containing the aforementioned monomers was attempted, by sequential addition of monomers A and B to a solution of a lithium organic initiator in THF, containing a predetermined amount of LiCl. As the acrylic ester exhibits the highest electron affinity among the monomers selected, monomer B was always added last.

Several di- and triblock copolymers have been synthesized by this lithium chloride-assisted polymerization technique. Results are presented on *Table 2* and commented on below.

Polystyrene–poly(tert.butyl acrylate) blocks copolymers. The block copolymer synthesis proceeds in three steps:

(1) The polymerization of styrene is carried out in THF solution, with a lithium organic initiator, in the presence of the quantity of LiCl considered necessary for the subsequent tert.butyl acrylate polymerization. Well defined living polystyrene precursor chains result.

(2) The second step aims at lowering the nucleophilicity of the active sites and warrants additional explanation. The styryl carbanions are highly nucleophilic and addition of a methacrylic ester results in competing reactions: with the unsaturation (initiation) and with the ester carbonyl[6]. The latter reaction is undesirable. To prevent its occurrence, some 1,1-diphenyl-ethylene (DPE) is added, resulting in the formation, at chain end, of diphenylmethyl anions of lower nucleophilicity. These sites still initiate the polymerization of methacrylic esters, but they are unable to attack the ester carbonyls.

The same considerations prevail for the system styrene–tert.butyl acrylate. It had been anticipated that complexation of the active sites with LiCl would reduce their nucleophilicity enough to prevent this side reaction. This is not the case. A single experiment carried out without the intermediate addition of DPE failed to give the expected molecular weight.

(3) Tert.butyl acrylate is polymerized from the end-standing diphenylmethyl carbanions to build the block copolymer.

Diblock A–B copolymers and triblock B–A–B copolymers, the latter consisting of a central polystyrene (A) block surrounded by two poly(tBuA) (B) blocks, have been synthesized and characterized. Butyllithium served as the monofunctional initiator for the polystyrene precursor, while lithium dihydronaphthylide was used as an electron transfer initiator when a bifunctional precursor was needed.

The results shown in *Table 2* indicate that the sequential addition of styrene, diphenylethylene (1 mole per site, as this monomer does not homopolymerize), and tert.butyl acrylate yields the expected block copolymers. The molecular weights found for the block copolymers are in satisfactory agreement with those arising from the molecular weight of the polystyrene precursor and the final polystyrene content of the copolymer. It can be concluded that the living precursor molecules efficiently initiate the subsequent tert.butyl acrylate polymerization. The molecular weight distribution of the copolymers is usually rather narrow, similar to that of the precursor from which they originate. Consequently, fluctuations in

Table 2 Characteristics of block copolymers containing poly(tert.butyl acrylate) blocks

	Precursor		Block copolymer				
Ref.	Polymer	M_w	Type[a]	PtBuA (%)	M_{gpc}	M_{LS}	M_{calc}[b]
43	PStyrene	14 500	T	63	41 700	38 000	39 200
45	PStyrene	13 600	D	41	26 800	21 300	23 000
47	PStyrene	71 000	T	67	141 000	177 000	215 000
48	PStyrene	47 000	T	59	71 000	98 000	115 000
50	PStyrene	90 000	D	58	172 000		214 000
52	PMMA	43 100	T	55.4	90 000	115 000	97 000
54	PMMA	25 100	T	74.8	53 000	123 000	100 000
55	PMMA	15 000	T	63.5	38 200	42 000	41 100
56	PMMA	35 000	T	61.6	70 000	86 200	91 000
90	P2VP	19 000	T	81[c]	71 000	110 000	100 000
08	P2VP	22 000	D	56.7	33 000	60 000	51 000

[a] T, triblock; D, diblock copolymer

[b] $M_{calc} = M_{precursor}/(1-x)$, x being the weight fraction of tBuA

[c] Vinylpyridine polymerization was not complete when BuA was added

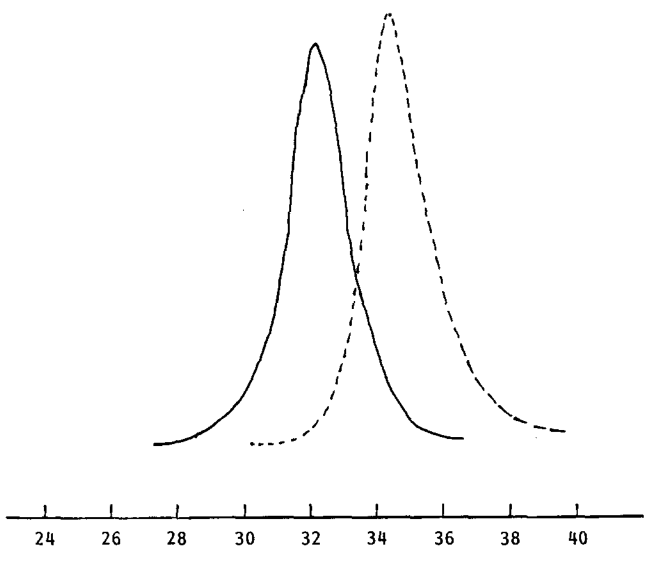

Figure 1 Size exclusion chromatograms (SEC) of a polystyrene precursor (----) and of the corresponding polystyrene–poly(tert.butyl acrylate) triblock copolymer (——); sample 43

composition within a block copolymer sample are of low amplitude. When lithium dihydronaphthylide is used as initiator the molecular weight distributions are unimodal, indicating that accidental deactivations during the process can be disregarded. The gel permeation chromatography (g.p.c.) chromatograms shown in *Figure 1* confirm that the sequential polymerization of these two monomers involves neither side reactions nor accidental deactivations, as the amount of homopolymer left is negligible.

The molecular weights of the copolymers arising from the g.p.c. analysis are apparent values, given in terms of polystyrene equivalents. It is well known that the hydrodynamic volume of the block copolymer, which is the parameter determining the g.p.c. retention[7], is influenced by the interactions between chemically unlike blocks. In the present case, however, the two constituting homopolymers exhibit similar affinities for the solvent (THF) and similar g.p.c. calibration curves, at least in the range of small molecular weights. Nevertheless, the values of the molecular weights derived from the g.p.c. calibration differ substantially from those measured by light scattering.

Poly(methyl methacrylate) poly(tert.butyl acrylate) block copolymers. The potential interest in this system arises from the fact that tert.butyl ester functions are easily hydrolysed to acid, whereas under the same mild conditions the methyl ester groups are not. Block copolymers containing both poly(methyl methacrylate) and poly(tert.butyl acrylate) sequences are thus good starting products for amphiphilic materials containing hydrophobic poly(methyl methacrylate) blocks and hydrophilic ionogenic poly(acrylic acid) blocks, the latter being soluble in slightly alkaline aqueous media.

Both monomers considered here contain strongly electron withdrawing ester substituents. It was anticipated that these monomers would have similar electron affinities, making anionic cross-initiation possible both ways: A^- initiating the polymerization of B and B^- being able to attack A. Methacrylic esters, methyl, butyl, hexyl, stearyl, are examples of systems allowing two-way cross-initiation[8,9]. Multiblock copolymers have thus been synthesized by alternating additions of monomers A and B to an adequate metal organic initiator solution.

The system investigated here, involving a methacrylic ester and an acrylic ester, is different. The carbanions derived from MMA (A^-) do initiate the polymerization of the acrylic ester (B), but the reverse reaction is not possible, as demonstrated conclusively by two different experiments.

First an attempt was made to use a living poly(tert.butyl acrylate) solution, maintained at low temperature (−55°C), to initiate the polymerization of methyl methacrylate. One hour later the sites were deactivated protonically. The resulting polymer was found to be identical to the initial precursor, indicating that the living poly(tert.butyl acrylate) sites had been unable to initiate the polymerization of the methacrylic ester.

In the second experiment, an equimolar mixture of the same two monomers was added slowly, at low temperature, into a solution of 1,1-diphenyl-3-methyl-pentyllithium (DPHLi) in THF containing the required amount of LiCl and it was allowed to polymerize for an hour. The resulting polymer was almost pure (>95%) poly(tert.butyl acrylate). This confirms that tBuA-carbanions fail to initiate the polymerizations of MMA. The difference in electroaffinity probably arises from the electron donating effect of the α-methyl group in the methacrylic monomer, which makes the unsaturation less electrophilic.

As a consequence, the synthesis of PMMA (A)–poly(tBuA) (B) block copolymers is limited to A–B diblock and B–A–B triblock copolymers, as methyl methacrylate must be the first monomer to be polymerized. The initiators were chosen to avoid undesirable side reactions with the ester carbonyl of MMA. 1,1-Diphenyl 3-methylpentyllithium (DPHLi) served as the monofunctional initiator for the synthesis of diblock copolymers, and 1,1,4,4-tetraphenyl 1,4-dilithiobutane ($TPBLi_2$, obtained *in situ* upon reaction of DPE and lithium dihydronaphthylide) was the difunctional initiator selected for the synthesis of triblock copolymers.

Results presented in *Table 2* show that the synthesis of poly(methyl methacrylate)–poly(tert.butyl acrylate) block copolymers is possible, in the presence of lithium chloride, provided the monomers are added in the proper order. The time interval between the two monomer additions should be sufficient to allow completion of the first step. This condition is not critical, however, as unconsumed methyl methacrylate would not interfere with the tert.butyl acrylate polymerization. Account must merely be taken of the polymerization yields when calculating the molecular weights.

Poly(2-vinylpyridine)–poly(tert.butyl acrylate) block copolymers. The initiators used were the same as in the preceding case: DPHLi or $TPBLi_2$, depending upon whether diblock or triblock copolymers were desired. Initiation was fast and free of side reactions. The syntheses were conducted in THF at low temperature (−60°C). Vinylpyridine was introduced first into the initiator solution, as its electrophilicity is lower than that of the acrylic ester. Once the polymerization of vinylpyridine was completed, the desired amount of tert.butyl acrylate was introduced dropwise at the same temperature (−60°C).

The results presented in *Table 2* indicate that the block

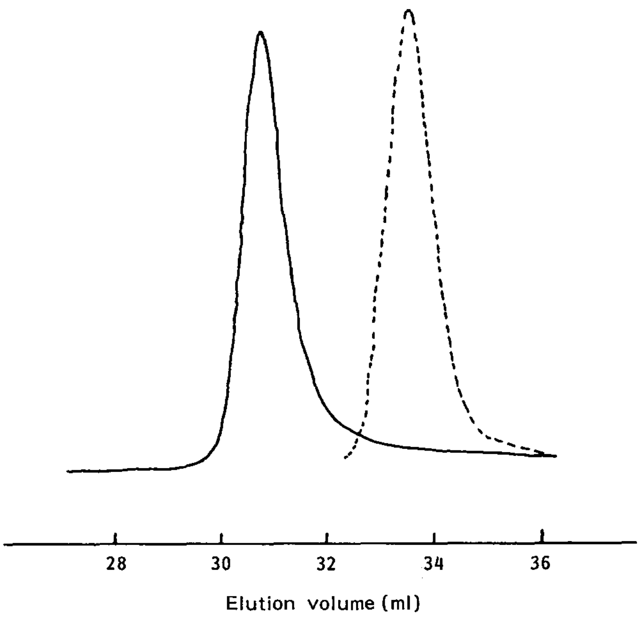

Figure 2 Size exclusion chromatograms (SEC) of a poly(vinylpyridine) precursor (----) and of the corresponding poly(vinylpyridine)–poly(tert.butyl acrylate) diblock copolymer (——); sample 08

copolymer formed meets satisfactorily with expectations. Its molecular weight is in fair agreement with the value calculated from the molecular weight of the precursor and its composition. The molecular weight distribution of the poly(vinylpyridine) precursor and of the final copolymer are relatively narrow, as can be seen from the g.p.c. traces shown in *Figure 2*. Consequently, the fluctuations in composition within a sample are also of low amplitude. It has thus been shown that, under adequate experimental conditions, this synthesis can be controlled easily and involves no spontaneous transfer or termination reactions.

In this paper we have considered exclusively the synthesis of the initial block copolymers. Their chemical modification and their behaviour will be discussed in a forthcoming paper.

The poly(vinylpyridine)–poly(tert.butyl acrylate) system is the most interesting of the block copolymers presented here. The potential of these species as precursors for tailor-made amphiphilic block copolymers of controlled molecular weight and composition, exhibiting narrow molecular weight distributions and low compositional heterogeneity, is great. If the ester functions of the poly(tert.butyl acrylate) blocks are hydrolysed, ampholytic poly(vinyl pyridine)–poly(acrylate) block copolymers result.

Such polymeric ampholytes are soluble in acidic aqueous media, as the result of protonation of the pyridine groups, and also in alkaline solution, because of the acrylate ions formed. There is an intermediate pH range in which the affinity of the polymer towards water is low, as neither of the two blocks is ionized to any large extent. If the poly(vinyl pyridine) blocks themselves undergo quaternization the situation should be different: water solubility should prevail, whatever the value of the pH may be.

Earlier attempts to make block copolymers that are precursors to polymeric ampholytes have to be acknowledged[9]. However, they usually refer to poly(tert.butyl methacrylate) blocks, associated with poly(vinyl pyridine) blocks. The poly(methacrylic acid) blocks arising from the ester hydrolysis reaction are known to be less hydrophilic than the poly(acrylic acid) blocks.

CONCLUSIONS

The synthesis of well defined block copolymers involving poly(tert.butyl acrylate) blocks is possible anionically, provided a lithium organic initiator is used, in the presence of added lithium chloride. Three comonomers have been selected: styrene, methyl methacrylate and 2-vinyl pyridine. The monomers are introduced sequentially, in the order of increasing electroaffinity. The purpose of the salt is to decrease the nucleophilicity of the sites, as shown by Teyssié[1,2], thus lowering the polymerization rates and drastically decreasing the probability of side reactions.

The block copolymers obtained are free of homopolymer: they exhibit molecular weights expected from the mole ratio of monomer consumed to initiator set in. Their polydispersity is low and their compositional heterogeneity is narrow. Copolymers containing poly(tert.butyl acrylate) sequences are interesting precursors of amphiphilic block copolymers, which can be obtained upon hydrolysis of the ester functions of the poly(tert.butyl acrylate) blocks.

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