# Synthesis of poly(t-butyl acrylate) macromonomers

**Katherine Antolin, Jean-Philippe Lamps, Paul Rempp and Yves Gnanou***

*Institut Charles Sadron (CRM-EAHP) (CNRS-ULP), 6 rue Boussingault, 67083 Strasbourg, France*

*(Received 10 April 1989; revised 8 August 1989; accepted 14 August 1989)*

Teyssié *et al.* have recently shown that anionic polymerization of hindered acrylates exhibits the characteristic features of 'living' systems, provided LiCl is used in order to decrease the nucleophilicity of the growing carbanion. This paper extends Teyssié's method to the synthesis of various model poly(t-butyl acrylate)s, emphasis being put on the macromolecular engineering aspect. We have synthesized linear poly(t-butyl acrylate) over a broad range of molecular weights (3000–200 000), using successively monofunctional and difunctional initiators. Tailor-made poly(t-butyl acrylate) macromonomers were also obtained by deactivation of the living sites with an electrophilic unsaturation either styrenic or methacrylic. Accurate characterization of the various model polymers (gel permeation chromatography, light scattering, end-group analysis) was performed.

**(Keywords: synthesis; poly(t-butyl acrylate); macromonomers)**

## INTRODUCTION

It is well known that methacrylic esters can be polymerized anionically to linear polymer species of known molecular weight and low polydispersity[1]. It has also been established that functionalizations at chain end are possible under specific conditions[2]. Macromonomers of various poly(alkyl methacrylate)s, fitted at chain end with either a styrene or a methacrylic ester function have been obtained and characterized[3].

The case for acrylic esters is quite different. The existence of side reactions prevents the anionic polymerization of such monomers from yielding well-defined polymer species, even under rigorous conditions, such as highly purified monomer and solvent and very low temperatures. The occurrence of transfer reactions accounts for the low values of the molecular weight, and for the width of the molecular weight distribution (MWD)[4].

Group transfer polymerization[5,6] has been shown to provide a pathway for controlled polymerization of several acrylic monomers, if Lewis acids are used to catalyse the process. Functionalizations at chain end are also possible, though not always quantitative. The occurrence of side reactions cannot be entirely disregarded, contrary to what is observed in the case of methacrylic esters.

In recent publications[7,8], Teyssié *et al.* have claimed that t-butylacrylate can be polymerized anionically to quantitative yields by using an initiator system of butyllithium and lithium chloride in tetrahydrofuran (THF) solution. Control of the molecular weight and of the polydispersity of the samples is possible, which implies that neither termination nor transfer reactions occur. The presence of lithium chloride presumably modifies the environment of the growing ionic sites. The side reactions which were known to occur on the carbonyl groups, and on the acidic α-hydrogen atoms of the monomer units are drastically reduced. Teyssié's method is a vast improvement over previous attempts to anionically polymerize this acrylic monomer.

The first objective of the present work was to synthesize poly(t-butyl acrylate) macromonomers, i.e. low molecular weight poly(tBuA), end-capped with a polymerizable unsaturation. Macromonomers are useful intermediates in graft copolymer synthesis, upon free radical copolymerization with a vinylic or acrylic monomer. Poly(tBuA) exhibits a low glass transition temperature, and a low surface energy. The synthesis of graft copolymers constituted of a vitrous backbone chain fitted with poly(tBuA) grafts should be of interest for their potential applications as surface modifiers or as adhesives.

Our second objective was to apply Teyssié's method to a wider domain of molecular weights than that investigated so far. It is of interest to check whether the side reactions shown to be ineffective in the range of moderate molecular weights remain negligible while extending the method to samples of higher molecular weight.

A specific advantage of poly(tBuA) is the ease of the ester hydrolysis, yielding poly(acrylic acid). This ionogenic polymer exhibits in alkaline media the typical behaviour of a polyelectrolyte. The preparation of poly(tBuA) macromonomers is therefore a step towards the synthesis of amphiphilic graft copolymers exhibiting polyelectrolytic grafts, a type of polymer that has not been subject to detailed investigations yet.

## EXPERIMENTAL

*Solvents.* THF was purified and made free of protonic impurities following classical procedures.

* To whom correspondence should be addressed

0032-3861/90/050967-04

*Monomers.* t-Butyl acrylate (Fluka, Switzerland) was distilled twice under vacuum in the presence of either Na wire or $CaH_2$ powder. It was recovered in a Schlenck vessel to avoid any contact with air or moisture.

*Initiators.* s-Butyllithium was made in the usual way, from Li metal pieces and 2-chlorobutane, in benzene solution, under inert atmosphere. The molarity of the initiator solution was determined by titration with acetanilide.

1,1-Diphenyl,3-methylpentyllithium (DPHLi) was made from s-butyllithium and 1,1-diphenylethylene. In polar solvents (THF) the reaction is almost instantaneous. The solution is dark red.

1,1,4,4-Tetraphenyl dilithiobutane (TPDLB) is formed in THF solution upon reaction of 1,1-diphenylethylene with pieces of Li.

Lithium chloride was used as received.

*Functionalization reagents.* *p*-Vinyl benzyl bromide was made in the laboratory according to a method already described[3].

Chlorodimethylsilylpropyl methacrylate was obtained by hydrosilylation involving dimethylchlorosilane and allylmethacrylate. The reaction procedure has been described elsewhere[9]. The raw compound is purified by distillation under reduced pressure, and kept under vacuum in a graduated cylinder fitted at both ends with stopcocks.

*Synthesis of poly(tBuA)*

*General procedure and application to the synthesis of macromonomers.* The reactor was fitted with an argon inlet, thermometer, magnetic stirring device, and with specific entries for the solvent, the initiator, the monomer and the functionalization reagent.

The necessary amount of LiCl was introduced first, and the reactor was heated to about 120°C, and subjected to several vacuum–argon cycles. Then the chosen volume of solvent (THF) was introduced, and 'neutralized' with a few drops of initiator. (If BuLi is the initiator a few drops of styrene are added to serve as coloured indicator.) Subsequently, the calculated amount of initiator solution was introduced and the solution cooled to −70°C (sometimes to −30°C). The monomer was then added slowly, under permanent temperature control. A few minutes after the addition of the monomer had been completed, part of the solution was sampled and deactivated protonically.

To the rest of the solution, maintained at low temperature, the functional deactivator (in benzene solution) was added at once, under efficient stirring. The reaction was allowed to proceed for 1 h. The polymer was recovered by precipitation into cold methanol containing 10–20% of water. Alternatively, the polymer can be precipitated into cold hexane (at −60°C), redissolved in benzene, to allow separation of the LiCl, and recovered by freeze-drying.

*Synthesis of high molecular weight poly(tBuA).* The experimental procedure differs slightly in this case. The monomer was introduced into the reaction medium before addition of the metal organic initiator. Deactivation of the living sites upon addition of the monomer can thus be prevented, avoiding any broadening of the molecular weight distribution.

*Synthesis of difunctional poly(tBuA).* It has also been attempted to use a bifunctional initiator in order to get poly(tBuA) chains fitted at both ends with carbanionic sites. The initiator chosen was 1,1,4,4-tetraphenyl dilithiobutane, again with lithium chloride in excess. After addition of a few drops of monomer, the red colour of the medium vanished, indicating that initiation is rapid and quantitative.

*Synthesis of ω-hydroxy poly(tBuA).* After completion of the tBuA polymerization—conducted under the same conditions as those described above—oxirane was introduced into the reaction medium. A nucleophilic attack was expected to occur, giving rise to a non-propagating ring-opening reaction. One oxirane unit should be attached to the chain end, the lithium alkoxide site being unable to further propagate. Protonation was expected to lead to ω-hydroxy poly(tBuA).

*Characterization of the poly(tBuA) samples*

Light scattering was used to measure weight average molecular weights of the samples, either in ethyl acetate (refractive index increment, $dn/dc = 0.092$ at a wave length of 6320 Å) or in THF (0.056). In the case of high molecular weight samples, dissymmetry of the scattered light intensities has been observed, pointing to aggregate formation in ethyl acetate. This phenomenon was never observed in THF solution. However, measurements on low molecular weight samples are not very accurate in this solvent, because of the low value of the $dn/dc$.

Gel permeation chromatography (g.p.c.) has also been used for molecular weight determinations. The $M_w$ data arising from the calibration curve established with polystyrene standards were found to be in good agreement with the values arising from light scattering measurements. The polydispersity indices of the poly(tBuA) samples were also calculated from their g.p.c. diagrams.

Ultraviolet (u.v.) spectroscopy can be used to determine the number average molecular weight, provided the group arising from the initiator has a specific u.v. absorption. This is the case with DPHLi and with TPDLB. The extinction coefficient was assumed to be identical to that of 2,2-diphenylbutane ($\varepsilon = 1143\ l\ mol^{-1}\ cm^{-1}$ at 254 nm in THF).

The functionalization yield of the macromonomers was evaluated in several ways. In a first attempt, the method based on the use of mercurous acetate was selected, but it failed to give reliable results. Side reactions leading to the hydrolysis of t-butyl ester functions occur and the method was given up. The double bond content was then determined from u.v. spectroscopy for both ω-styryl- ($\varepsilon$ is that of *p*-methylstyrene in hexane, $15910\ l\ mol^{-1}\ cm^{-1}$ at 252 nm) and ω-methacryloyloxy- ($\varepsilon$ is assumed to be same as for n-butylmethacrylate, $7670\ l\ mol^{-1}\ cm^{-1}$ in hexane at 215 nm) macromonomers. The usual initiator DPHLi could not be used for the obvious reason that it absorbs in the same spectral region as the end-standing unsaturation. BuLi was thus preferred.

$^{19}F$ nuclear magnetic resonance (n.m.r.) spectroscopy was used to characterize the OH content of polymers that had been functionalized with oxirane. A stable adduct is formed upon treating the hydroxy-ended polymer with hexafluoroacetone. It is detectable by

**Table 1** Characterization of poly(t-butyl acrylate) samples by g.p.c. and light scattering

| Initiator | Temperature (°C) | $M_n$ (calculated) | $M_n$ (g.p.c.) | $M_w$ (g.p.c.) | $M_w$ (Light scattering) |
|---|---|---|---|---|---|
| DPHLi | −80 | 3000 | 3400 | 3700 | 4100 |
| DPHLi | −80 | 5000 | 4800 | 6000 | 5700 |
| DPHLi | −80 | 8000 | 9300 | 10900 | 9000 |
| DPHLi | −80 | 10000 | 10300 | 12000 | 13900 |
| DPHLi | −40 | 5000 | 5800 | 6800 | |
| DPHLi | 0 | 5500 | 6600 | 7600 | |
| BuLi | −80 | 60000 | 85000 | 109000 | |
| BuLi | −80 | 100000 | 140000 | 175000 | 160000 |
| TPDLB | −80 | 6000 | 7300 | 9500 | |
| TPDLB | −80 | 25000 | 30000 | 36000 | |

Conditions of polymerization: [LiCl]/[initiator] = 5; the concentration of initiator ranges from $1.5 \times 10^{-2}$ mol $l^{-1}$ for the low molecular weight samples to $1.5 \times 10^{-3}$ mol $l^{-1}$ for the highest ones

means of $^{19}F$ n.m.r. Quantitative measurements are however difficult because of the high volatility of hexafluoroacetone, which is used as the internal standard.

## RESULTS AND DISCUSSION

t-Butyl acrylate has been polymerized anionically with either butyllithium or DPHLi as initiators, provided LiCl is present to at least three times the mole amount of the initiator. This statement fully confirms the findings of Teyssié *et al.*[7,8]. The hindered DPHLi should be preferred, because side reactions with the ester carbonyl are still less likely to occur. The first experiments were run at −80°C, but it was established that the results are satisfactory at higher temperatures as well (up to −20°C).

The molecular weights, $M_n$, obtained are usually in good agreement with the values expected from the mole ratio of monomer to initiator, regardless of the initiator used. The molecular weight distributions are rather narrow, with polydispersity indices close to 1.2 (*Table 1*). In a few cases however, $M_n$ values higher than those expected were obtained, which can be explained by the presence of residual impurities in the monomer.

It has been ascertained that the presence of LiCl is necessary. Polymerizations carried out under the same experimental conditions, but without LiCl, yield samples exhibiting a very broad molecular weight distribution. No control of the $M_n$ values is then possible.

The role of LiCl, which apparently prevents most of the side reactions is only schematically understood. According to Teyssié, LiCl coordinates with the cations of the 'living' sites and forms a ligand. The nucleophilicity of the resulting complex R–Li:ClLi is decreased, although not so much as to make it inactive towards acrylic unsaturations. The ionic equilibrium may also be affected by the presence of LiCl in the reaction medium, which changes the proportions of free ions and ion pairs. These two effects obviously contribute to lowering the polymerization rate.

The effect of temperature is apparently insignificant, as documented by the results obtained on samples prepared, respectively, at −80, −40 and 0°C (*Table 1*). Molecular weights and polydispersity indices are the same, within experimental accuracy. This implies the absence of transfer or termination reactions.

A further check of the 'living' character of tBuA polymerization is brought by experiments in which

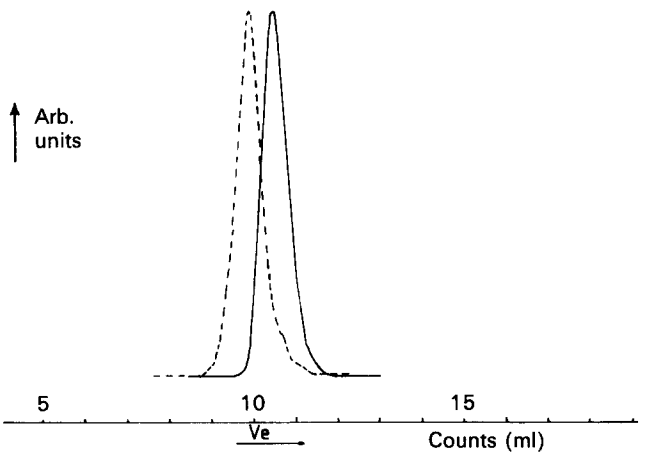


**Figure 1** Gel permeation chromatography charts of poly(t-butyl-acrylate) samples. The broken line displays the shift of molecular weight distribution after further addition of monomer

further monomer was added after the temperature had been raised to −20°C. The molecular weight $M_n$ increases correspondingly, and the molecular weight distribution remains as narrow as it was. The g.p.c. diagram shows the expected shift (*Figure 1*). It can be concluded that the number of active sites has remained constant.

Difunctional poly(tBuA)s have been characterized according to the procedure described above (*Table 1*). The g.p.c. diagrams were narrow and symmetric and the agreement between molecular weights measured and calculated was satisfactory, indicating that initiation is fast enough and that polymerization proceeds as expected.

### *Functionalization—synthesis of macromonomers*

The question now arises as to whether the 'living' sites of poly(tBuA) can be deactivated by means of an electrophilic reagent, to yield $\omega$-functional polymer chains. Macromonomers are usually made this way, upon reaction of a living $\omega$-carbanionic polymer with an unsaturated electrophile such as *p*-vinyl benzyl bromide or chlorodimethylsilylpropyl methacrylate. These reagents have been chosen because their reaction with anionic sites was found to be unambiguous and quantitative.

In the present case, the reaction of living poly(tBuA) with either of the two unsaturated electrophiles was carried out at −25°C, after it had been checked that the

**Table 2** Characterization of poly(t-butyl acrylate) macromonomers

| Type of unsaturation | $M_n$ (g.p.c.) | $M_w$ (g.p.c.) | $M_n$ (u.v.) |
|---|---|---|---|
| Styrene | 7 700 | 8 100 | 8 100 |
| Styrene | 9 600 | 10 500 | 11 000 |
| Methacrylic | 8 200 | 9 300 | 8 500 |
| Methacrylic | 15 300 | 17 500 | 15 000 |

sites are still active at that temperature. The mixtures were stirred for 2 h. In both cases, the living poly(tBuA) was end-capped with the unsaturated function. The resulting macromonomers were: $\omega$-styryl-poly(tBuA) and $\omega$-methacryloyl-oxy-poly(tBuA), respectively. The data shown in *Table 2* demonstrate that the end-capping reaction is close to quantitative. It can be concluded that in spite of their reduced nucleophilicity the sites are still efficient towards electrophilic compounds.

The attempts to fit poly(tBuA) chains with a terminal hydroxy group apparently failed. The polymer recovered after protonation was characterized by the hexafluoroacetone method. On the grounds of the results obtained, it can be stated that the functionalization is far from being quantitative. The same attempts were made using a difunctional initiator: 1,1,4,4-tetraphenyl dilithiobutane. The obtained polymer was subsequently protonated and submitted to chain extension using a diisocyanate. The molecular weight increases only slightly, which confirms the above statement.

## CONCLUSIONS

It is confirmed that Teyssié's method to carry out anionic polymerization of t-butyl acrylate is quite efficient, involving neither transfer nor termination, and yielding well-defined polymer samples of rather low polydispersity. This method is applicable to a wide range of molecular weights.

Poly(tBuA) macromonomers have been obtained by end-capping the 'living' sites with an unsaturated electrophile. These species have been characterized adequately. The interest of such polymers arises from the ease of the hydrolysis of their ester functions, providing access to poly(acrylic acid) macromonomers of known polymerization degree and of narrow molecular weight distribution, which cannot be obtained otherwise.

The drawback of Teyssié's procedure is that it does not apply to many other acrylic esters. Nevertheless, this method may find a number of applications: the synthesis of novel block copolymers (including amphiphilic ones) is currently being investigated.

## ACKNOWLEDGEMENTS

The authors wish to express their deep appreciation to Mrs Sabine Graff, and to Mr Maurice Keyser for their assistance in characterizations of the samples. One of us (K.A.) gratefully acknowledges the Rotary Club for providing financial support.

## REFERENCES

1 Freyss, D., Leng, M. and Rempp, P. *Bull. Soc. Chim. Fra.* 1964, 221
2 Anderson, B. C., Andrews, G. D., Arthur Jr, P., Jacobson, F. W., Melby, L. R., Playtis, A. J. and Sharkey, W. H. *Macromolecules* 1981, **14**, 1599
3 Lutz, P., Masson, P., Beinert, G. and Rempp, P. *Polym. Bull.* 1984, **12**, 79
4 Kitano, T., Fujimoto, T. and Nagasawa, M. *Polymer J.* 1977, **9**, 153
5 Hertler, W. R., Sogah, D. Y. and Webster, O. W. *Macromolecules* 1984, **17**, 1415
6 Sogah, D. Y., Hertler, W. R., Webster, O. W. and Cohen, G. M. *Macromolecules* 1987, **20**, 1473
7 Fayt, R., Forte, R., Jacobs, C., Jerome, R., Ouhadi, T., Teyssié, P. and Varshney, S. K. *Macromolecules* 1987, **20**, 1442
8 Teyssié, P., Fayt, R., Jacobs, C., Jérome, R., Leemans, L. and Varshney, S. K. *ACS Prepr.* 1988, **29**, 52
9 Gnanou, Y. and Rempp, P. *Makromol. Chem.* 1988, **189**, 1997