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Synthesis and characterization of high molecular weight poly(tert.butyl acrylate)

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ABSTRACT : High molecular weight poly(tert.butyl acrylate)s have been synthesized anionically using a technique derived from that of Teyssié et al. It was established that under proper conditions the sites remained living, allowing proper control of the molecular weight and yielding samples with narrow molecular weight distributions.

INTRODUCTION

The anionic polymerization of acrylic esters is known to involve side reactions, rendering impossible the synthesis of well-defined polymer samples of low polydispersity. Even when carried out at very low temperature, these polymerizations yield chiefly low molecular weight oligomers. Three kinds of side reactions may be involved : attack of the living sites onto the ester carbonyl of the monomer, or onto the α-protons of the monomer units of the polymer chain, or intramolecular Claisen type condensation (back-biting).

In recent papers, however, Teyssié [1,2] has reported a procedure which enabled him to polymerize tert.butyl acrylate (tBuA) anionically by a "living" mechanism, to form polymers with a narrow molecular weight distribution. The polymerization was initiated with lithium organic compounds, in tetrahydrofuran (THF), in the presence of added lithium chloride. LiCl is soluble in THF and, according to Teyssié, it lowers the nucleophilicity of the sites, preventing transfer and termination reactions. This LiCl-assisted tert.butyl acrylate polymerization is a special case, as the method is not satisfactory with other acrylic esters.

Poly(tert.butyl acrylate) is of great interest, since tert.butyl ester functions are easily hydrolyzable to the acid form. This method should allow, for the first time, the synthesis of well-defined poly(acrylic acid) samples of low polydispersity.

Teyssié carried out most of his experiments at very low temperature, and his objectives were polymers with rather low molecular weights. The experimental molecular weights were found in good agreement with those expected from the mole ratio of monomer to initiator, and the polydispersities testified to the living character of the polymerization.

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Methods of macromolecular engineering have already been applied to this system, in the low molecular weight range [3]. The synthesis of high molecular weight poly(tert.butyl acrylate) should establish the synthetic limits of the method : Deactivation or transfer reactions would cause unpredictable changes in the molecular weights and distributions of the products.

EXPERIMENTAL PART

Materials

Solvent : Tetrahydrofuran (THF) was purified by double distillation, first over sodium wire, and secondly from a benzophenone-sodium adduct solution, to remove protonic impurities.

Monomer : Tert.butyl acrylate (tBuA) was vacuum distilled, then treated with a 10% solution of triethylaluminum in hexane at 20°C to a colored end-point, according to a procedure of McGrath [4]. The highly purified monomer was then immediately vacuum distilled into a chilled Schlenk-type burette and used within 1 or 2 hours. This method of purification was found adequate.

Initiators : Sec.butyllithium was made from lithium metal and 2-chlorobutane, in benzene solution, under dry argon atmosphere. The initiator molarity was determined by acetamide titration before use. Lithium naphthylide was made in THF solution from naphthalene and lithium metal, under inert atmosphere. It has to be used within 48 hours, because of its rather low stability.

The effective initiators were then prepared *in situ* in the reactor: 1,1-Diphenyl-3-methylpentyllithium (DPHLi) from sec.butyllithium and 1,1,diphenylethylene (adduct formation), 1,1,4,4-tetraphenyl-1,4-dilithiobutane from lithium dihydronaphthylide and diphenylethylene by an electron transfer and radical dimerization reaction.

Polymerizations

A tight reactor was fitted with magnetic stirrer, temperature control, argon inlet, sampling device, burettes to introduce solvent, initator and monomer. The entire experiment was carried out in the absence of air, under a slight argon overpressure (about 70 mm Hg above atmospheric pressure). After the desired amount of LiCl had been introduced, the reactor was heated to 120°C, and submitted to several vacuum-argon cycles in order to eliminate residual moisture from both the apparatus and the salt.

After cooling to about - 30°C, the solvent (THF) was introduced first, followed by the required amount of diphenylethylene. Then a calculated volume of either BuLi or Lithium dihydronaphthylide solution was added (after neutralization of residual protonic impurities). This initiator solution was cooled to the temperature chosen and tBuA was added dropwise, at a rate such as to maintain the temperature inside the reactor within 5°C of its initial value. After completion of the monomer addition stirring was continued for a another 15 minutes before deactivation was carried out with methanol.

The polymer was recovered by precipitation into a cold methanol-water mixture (80/20 v/v, at - 15°C), recovered by subsequent centrifugation, and dried in a vacuum oven at room temperature for several days. The polymer was redissolved into high purity benzene, filtered through filter paper to remove any residual LiCl, and freeze-dried.

Characterization of the polymers obtained

The Size Exclusion Chromatography (GPC) measurements were utilized primarily for the determination of sample polydispersities. In the low molecular weight range, the retention volumes of polystyrene and of poly(tert.butyl acrylate) of same molecular weight are very similar. This is no longer true for molecular weights higher than 100 000. Consequently the values of the molecular weight averages arising from the GPC analysis - using polystyrene calibration - underestimate the true molecular weight of the polymer.

Light scattering measurements were concurrently carried out on the polymers either in THF or in ethyl acetate, in order to determine their true weight-average molecular weights and, whenever possible, their mean-square radii of gyration.

RESULTS AND DISCUSSION

A number of poly(tert.butyl acrylate) samples have been made following the principle of Teyssié's method, and characterized thoroughly. The results are displayed in table 1 and call for a few comments :

* Teyssié used the adduct of BuLi onto α-methylstyrene as the initiator. The high nucleophilicity of this initiator may give rise to undesirable side reactions making it a poor candidate for acrylate polymerization. Thus diphenylmethylpentyllithium (formed in situ) was chosen as the initiator. The nucleophilicity of the diphenylmethyl anion is far lower, preventing any attack onto the ester carbonyl of the monomer, but it is high enough to initiate rapidly and quantitatively the polymerization of this monomer (as it does for methacrylic esters). Similarly, 1,1,4,4-tetraphenyl-1,4-dilithiobutane (formed *in situ* upon reaction of lithium dihydronaphthylide and diphenylethylene) was used as an efficient bifunctional initiator whenever polymer chains carrying living sites at both ends were desired.

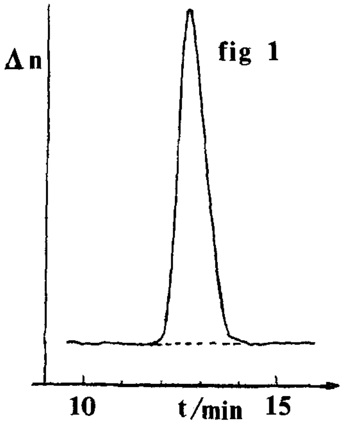
* The concentration of LiCl added plays an important role. The proportion used by Teyssié - i.e. a 5-fold molar excess of LiCl *per initiating site* - was sufficient in the low molecular weight range, when the initiator and LiCl concentrations were rather high. For the synthesis of high molecular weight samples (M_n > 60,000) this proportion was shown to be inadequate : If the mole ratio of LiCl added to initiator used is kept constant for the synthesis of high molecular weight samples, the polydispersity increases beyond desirable values (say 1.3).

For example, when tBuA was polymerized using Teyssié's mole ratio of LiCl to living sites with a desired molecular weight of less than 100 000, GPC results indicated polydispersities lower than 1.25. If the same ratio was kept when higher molecular weights were desired the resulting polydispersity became unacceptable. When a polymer with a desired molecular weight of 250 000 was attempted, using the same ratio of LiCl to carbanionic sites - the yield being close to 80% - the resulting polydispersity, from GPC analysis, indicated M_n = 108 000 and M_w = 183 000, the polydispersity index amounting to 1.71.

TABLE 1
Characteristics of Poly(tert.butyl acrylate) Homopolymers

Ref	$M_{n\ TH}$	GPC Data* M_w	GPC Data* M_n	$I^{b)}$	Light scattering data M_w	Light scattering data R_G
KA[a]	10 000	12 000	10 300	1.17	13 900[d]	
20[a]	250 000	183 000	108 000	1.71	138 000[d]	
21[a]	500 000	238 000	118 000	2.02	171 000[d]	
22[a]		475 000	78 000	6.1	346 000[d]	
37	150 000	73 000	67 000	1.09	59 000[c]	
					54 000[d]	
		175 000	140 000	1.25	160 000[d]	
30	200 000	143 000	127 000	1.12	107 000[c]	
					126 000[d]	
31		129 000	112 000	1.16	116 000[d]	
28	250 000	171 000	148 000	1.15	257 000[c]	
					252 000[d]	
33	250 000	161 000	121 000	1.35	230 000[c]	
34	500 000	420 000	334 000	1.26	571 000[c]	360
39		1 160 000	680 000	1.70	1 796 000[d]	730
38		1 370 000	546 000	2.50	2 200 000[d]	850
36		1 600 000	776 000	2.10	2 600 000[d]	890

*) calculated from polystyrene calibration
a) Mole Ratio LiCl to Initiator = 5 ; All other experiments, see text.
b) Polydispersity Index (M_w/M_n)
c) measured in tetrahydrofuran
d) measured in ethyl acetate



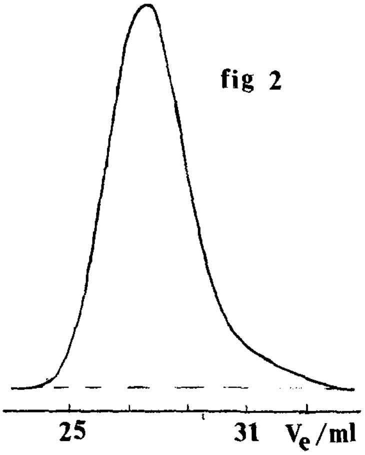


Figure 1. GPC chromatogram of sample 34, in THF. The peak is symmetric, showing no significant deactivation of living sites. The calculated polydispersity index for this sample is 1.26.

Figure 2. GPC Chromatogram of ref 38, a high molecular weight sample. Some protonic deactivation has occured here, broadening the curve to a polydispersity index of 2.5.

That is why higher concentrations of LiCl were used, based upon a *constant mole ratio between monomer and LiCl* (44:1) and the results were greatly improved as it can be seen from Table 1. It is difficult to account for this experimental observation as the effect of LiCl on the polymerization mechanism is only partially understood.

* As far as temperature is concerned, the stabilization of the active sites is such that it is possible to polymerize tBuA at temperatures as high as 0°C, in contrast to the requirement expressed by Teyssié. A check of livingness was made : A polymerization was run at - 70°C ; after half an hour the mixture was allowed to warm up to + 10°C. Then it was cooled again to - 30°C and further monomer was added. The final polymer sample had the expected molecular weight and a low polydispersity, demonstrating that the sites had remained living.

* A good test of the efficiency of the method is to use it for the synthesis of high molecular weight samples, as the concentration of the "living" sites is low and that of the monomer units is high. Partial deactivation would induce broadening of the molecular weight distribution. Accidental transfer reactions would result in molecular weights lower than expected. The results are presented in table 1, and GPC measurements shown in Figure 1 confirmed that in the presence of a sufficient amount of LiCl the sites remain living throughout the process.

* For molecular weights exceeding 200 000, under the experimental conditions chosen, the initiator volume required becomes so small that it is not possible to precisely control the molecular weight. However, it is important to establish that molecular weights in the million range could be synthesized, as this clearly demonstrates the livingness of the polymerization. Accidental deactivations due to unavoidable protonic impurities are responsible for the broadening of the molecular weight distribution for molecular weights above 500 000, but this is considered as a limitation of the experimental set-up involving inert atmosphere techniques instead of high vacuum methods. GPC chromatograms of references 34 and 38 from Table 1 are presented in Figures 1 and 2. These illustrate the success of the new polymerization conditions as well as the limitations of the inert atmosphere technique.

We can conclude that the anionic polymerization of tert.butyl acrylate carried out in the presence of lithium chloride is a truly living process, involving neither transfer nor termination reactions, and capable of yielding high molecular weight polymers of rather low polydispersity.

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