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The synthesis and characterization of monodisperse poly(acrylic acid) and poly(methacrylic acid)

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Abstract: A number of polyacrylic (PAA) and polymethacrylic (PMAA) acids have been synthesized by living anionic polymerization of the monomeric tert-butyl esters followed by subsequent hydrolysis of the corresponding polyesters. The necessary precautions were taken in order to assure good molecular weight control, as well as high yields in the polymerization reactions. The intermediate and final polymers were characterized by gel permeation chromatography and NMR-H^1 spectrometry.

Key words: Poly(acrylic acid) – poly(methacrylic acid) – monodisperse polyelectrolytes – anionic polymerization

Introduction

Poly(acrylic acid) and poly(methacrylic acid) may be easily prepared by free-radical polymerization of their monomers using a conventional initiator [1]. However, when *monodisperse* samples are required, this method is unsuitable. The advent of "living" anionic polymerization [2] allowed the control of many reaction parameters which cannot be achieved by other polymerization routes. Anionic polymerization, in principle, allows control of parameters such as molecular weight, molecular weight distribution, stereochemistry, and end functional groups. It has been widely used in the preparation of number of vinyl addition polymers, especially acrylates and methacrylates [3, 4]. Anionic polymerization of tert-butyl acrylates has been widely reported since the late 1950s [2, 3]. In 1977 [5], the first attempts were made to perform a "living" anionic polymerization in order to obtain monodisperse PTBA that could be subsequently hydrolyzed to give the corresponding monodisperse PAA.

In spite of all its advantages, the living anionic polymerization technique does have severe limitations, mostly imposed by the necessity of high-purity reagents and the occurrence of some secondary transfer and termination reactions [4]. In recent years, efforts have been made to improve purification procedures for the reagents and to minimize the importance of undesired side-reactions [6, 7]. Major advances in the living polymerization technique have been recently reported, with respect to the purification of monomers by means of TEA [8] and to the use of lithium salts [6, 9] to tailor the environment of the propagating ion pair, reducing its nucleophilicity which inhibits the attachment to the monomer carbonyl group.

In the present paper, we report the preparation, using living anionic polymerization, of some poly(tert-butylacrylates) and poly(tert-butyl methacrylates), and their subsequent hydrolysis to give the corresponding poly(acrylic acid) and poly(methacrylic acid).

Experimental

Materials

Tert-butyl acrylate (TBA) was obtained from Aldrich. Tert-butyl methacrylate (TBMA) was purchased from TCI-Japan. All solvents were obtained from BDH. Diphenylethylene (DPE), tert-butyl lithium (Solution 1.2 M in pentane), sodium and calcium hydride, lithium chloride, triethylaluminium (TEA) were all obtained from Aldrich. Naphtalene was obtained from Fluka.

Solvent purification

Glassware was carefully cleaned before using. All the purification operations were carried out using a high vacuum frame. Tetrahydrofuran, used as the polymerization solvent, was purified using the following procedure: it was stirred over CaH_2 for 48 h, distilled over fresh CaH_2, and then degassed by three freeze-thaw cycles, before being distilled again, this time over a small amount of Na/naphtalene mixture; an intense dark-green color is indicative of complete dryness. (In the presence of moisture, a brown coloration is observed). Pure, dry THF was then distilled into the reaction vessel, as required.

Monomer purification

TBA was purified according to the method described by Allen et al. [8]: it was stirred over CaH_2 for 48 h, and transferred into a clean vessel containing fresh CaH_2. It was then attached to the high-vacuum frame and degassed by three freeze-thaw cycles. Two clean reaction vessels were then attached to the manifold, adjacent to the monomer flask, and baked out overnight at 10^{-5} torr and 120 °C. TBA was then distilled into one of these flasks, and then titrated with a 25% (w/v) solution of TEA in hexane (injected slowly through the rubber septum with vigorous stirring), until a persistent pale yellow color was observed. The monomer was then distilled into the other vessel, and kept frozen until required (1–2 h). A similar procedure was used for TBMA, but this monomer, being less hygroscopic than TBA, was not titrated with TEA.

Polymerization procedure

A 500 ml round-bottomed flask, containing a weighed amount of LiCl, was attached to the vacuum-frame and baked out overnight at 120 °C and 10^{-5} torr. 300 mL of pure, dry THF was then distilled from the Na/naphtalene mixture into the reaction vessel.

In those cases where the initiator was an adduct of tert-butyl lithium and DPE, the following procedure was adopted. An excess (3x) of DPE was added to the LiCl/THF mixture using a syringe. The mixture was then titrated with tert-butyl lithium until a persistent red color was observed. The required volume of tert-butyl lithium was then added, forming a deep red colored solution, which was cooled to -78 °C in an acetone/solid CO_2 bath. The solution was then stirred vigorously and the pre-cooled monomer was added using a double-tipped needle. The reaction vessel was kept at -78 °C and stirred for at least 1 h. The reaction was then terminated by addition of a large excess of methanol. The polyesters obtained, poly(tert-butyl acrylate) (PTBA) and poly(tert-butyl methacrylate) (PTBMA) were purified by precipitation from methanol. They were freeze-dried from dioxane and left overnight in a vacuum oven at 80 °C.

In some cases, α-methyl styrene was used instead of DPE. The experimental procedure was the same in both cases.

Hydrolysis of the polyesters

About 15 g of the polymer (PTBA or PTBMA) were dissolved in 300 mL of 1,4 dioxane and refluxed for 1 h. 25 mL of concentrated HCl and 40 mL of water were then added, and the mixture refluxed for 24 h. In the case of PTBA, the solution was then exhaustively dialyzed against water; the poly(acrylic acid) (PAA) is obtained by freeze drying and then vacuum dried at 80 °C in an oven. No dialysis is needed in the case of PTBMA, but instead the poly(methacrylic acid) (PMAA) is precipitated in acetone, redissolved in 1,4 dioxane, freeze-dried and vacuum dried at 80 °C.

Characterization

Gel-permeation chromatography was carried out using a Waters Analytical GPC apparatus fitted with a refractive index detector. Polystyrene samples were used for calibrations. NMR spectra were recorded in a Bruker 200 MHz Spectrometer. Conductimetric titrations were performed using a Wayne Kerr Bridge and platinum electrodes to measure the conductivity of the solutions.

Table 1. Polymerization conditions, yields, and GPC results for some selected PTBA and PTBMA samples

Polymer code	Initiator system	LiCl/initiator ratio	Yield %	GPC M_n	M_w/M_n
PTBA 7	DPE:*t*-BuLi	4.8:1.0	84	19800	1.27
PTBA 10	α-MeSty:*t*-BuLi	5.9:1.0	80	20610	1.15
PTBA 14	DPE:*t*-BuLi	1.0:26*	80	162600	1.12
PTBA 15	DPE:*t*-BuLi	1.0:34*	67	107800	1.15
PTBMA 1	DPE:*t*-BuLi	1.0:44*	84	19000	1.14
PTBMA 2	DPE:*t*-BuLi	1.0:44*	82	61000	1.02

* LiCl:monomer ratio

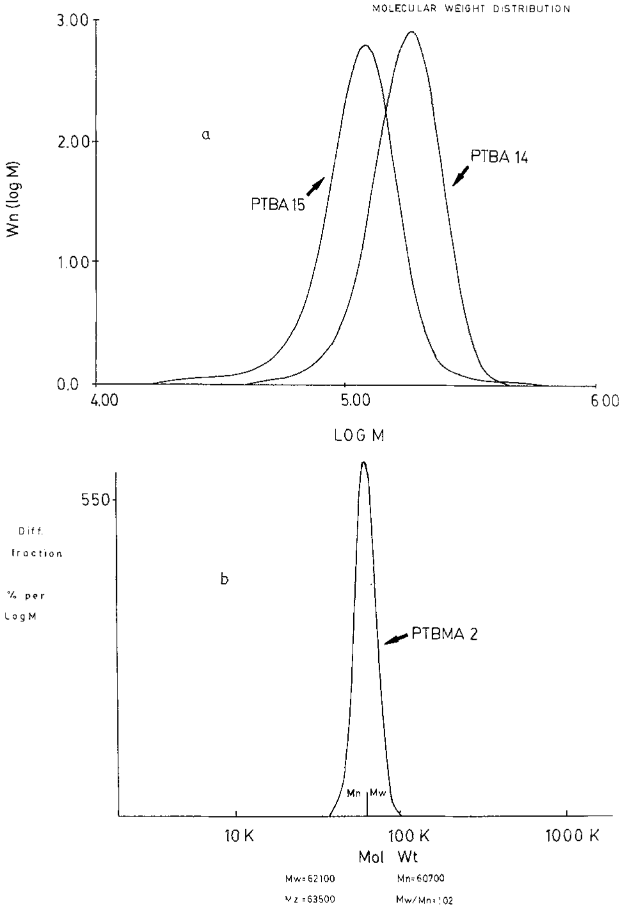

Fig. 1. GPC curves for some poly(tert-butyl esters) taken on chloroform at 25 °C. a) Poly(tert-butyl acrylates), Samples 14 and 15. b) Poly(tert-butyl methacrylate), Sample 2

Results and discussion

Table 1 summarizes some selected conditions and results, obtained for a number of PTBA and two PTBMA samples, as well as the GPC results for the same polymer samples. Figure 1 displays some GPC traces for two PTBA and one PTBMA samples.

The corresponding polyacids were obtained by hydrolysis of the polymers listed above. Figures 2 and 3 show the NMR-H^1 spectra for two poly(tert-butyl esters) and their corresponding poly(acids) obtained by hydrolysis with HCl solution, as detailed before. In both cases, it can be seen that after hydrolysis, the distinctive tert-butyl peak at 1.3 ppm has almost totally disappeared, assuring that complete hydrolysis has taken place. The small remaining peak at 1.3 ppm can be attributed to traces of unhydrolyzed polyester, and to tert-butyl groups inserted in the macromolecular backbone due to the initiator system (t-BuLi:DPE).

Some hydrolyzed polymer samples were also titrated with standard NaOH solution and the titration was followed conductimetrically. A typical result is shown in Fig. 4. In all cases the end point corresponded to 98% or better of the theoretical number of moles of polyacid monomer present in solution.

Some GPC analysis in water was performed in order to determine the molecular weight of the poly(acrylic acid) and poly(methacrylic acid) (PAA and PMAA) obtained by hydrolysis of the corresponding parent PTBA and PTBMA samples but, unfortunately, there was no agreement observed between the expected results from the non-aqueous results and the actual GPC traces for the poly-(meth)acrylic acid in the water. Even so, this is not surprising since there are a number of problems associated with GPC analysis of polyelectrolytes [10], which are attributed mainly to their rather unpredictable interactions with the GPC columns. Nevertheless, there was little difference observed in the overall "shape" of the

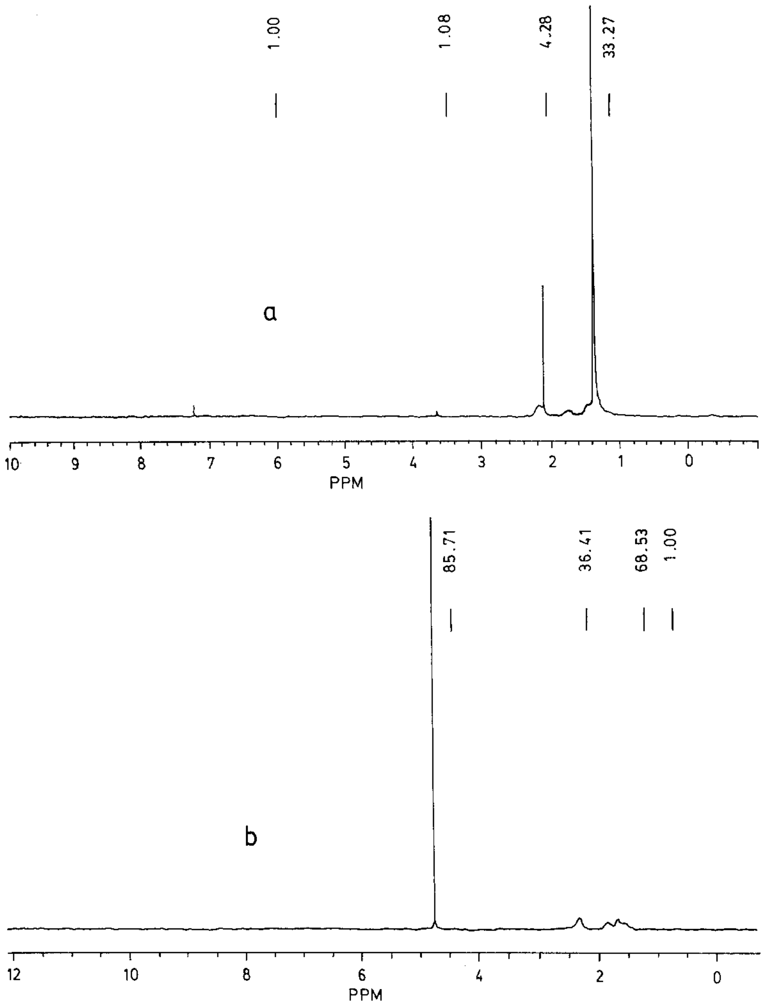

Fig. 2. NMR-H^1 spectra for one PTBA sample (a) and its corresponding PAA (b) obtained by hydrolysis. Solvents: $CDCl_3$ and D_2O, respectively. (Peak at 4.8 ppm in (b): H_2O as solvent impurity)

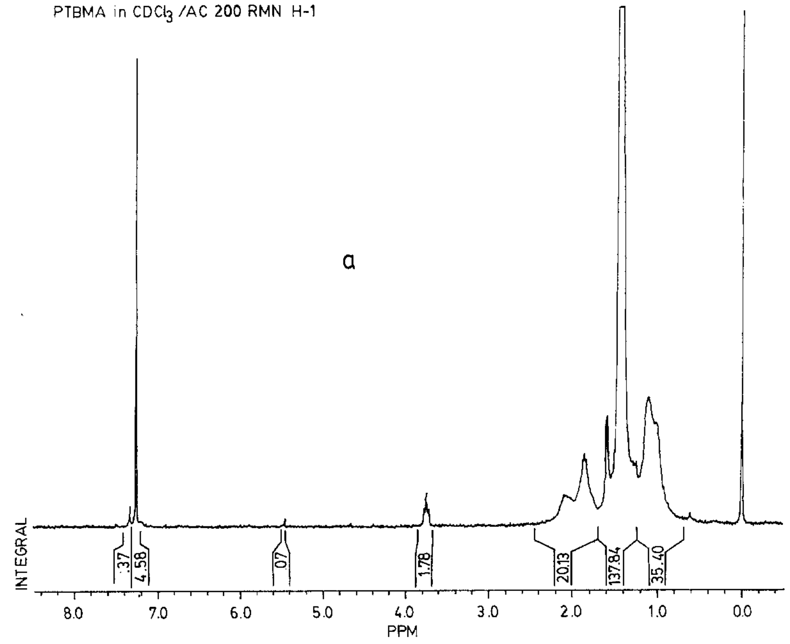

Fig. 3a

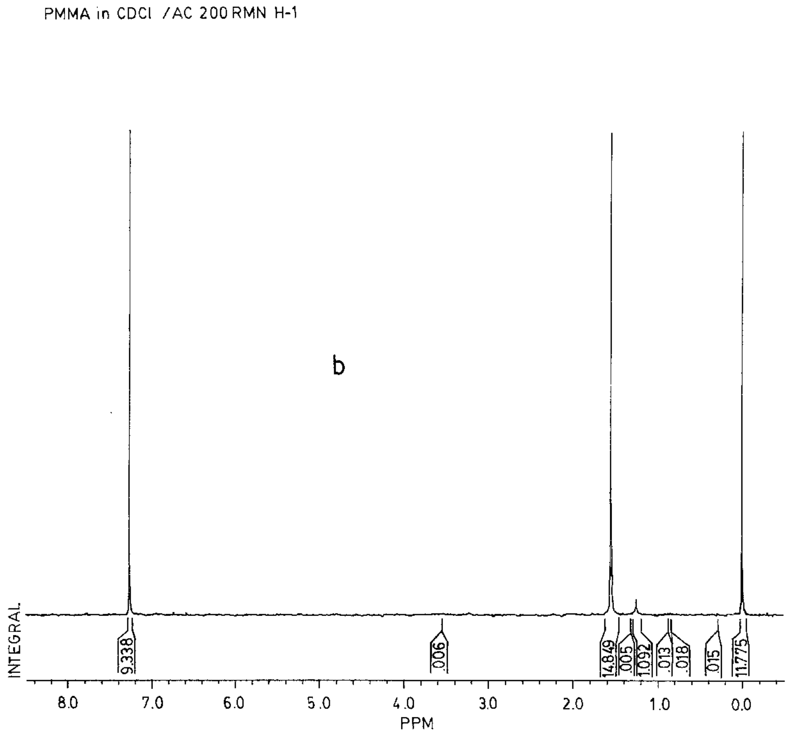

Fig. 3. NMR-H^1 spectra for one PTBMA sample (a) and its corresponding PMAA (b), obtained by hydrolysis. Solvent: $CDCl_3$. [Peak at 7.2 ppm: $CHCl_3$ as solvent impurity]

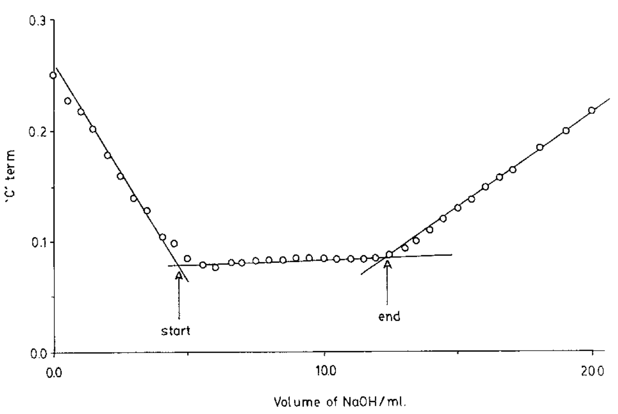

Fig. 4. Conductimetric titration plot for one PAA sample, obtained with NaOH standard solution

GPC traces obtained for the PTBA and PTMA samples and the aqueous GPC traces performed in water, which is indicative of the absence of chain degradation due to the hydrolysis reaction.

Conclusions

Several low dispersity PAA and PMAA have been prepared by hydrolysis of their corresponding poly(tert-butyl esters), obtained via living anionic polymerisation. Special care has been taken in the use of high purity reagents and the evidence of unwanted traces of water. The results, with respect to polymer yields and polydispersity, are remarkably good. No differences were observed if α-methylstyrene was used instead of diphenylethylene in the initiator system.

Acknowledgments

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