

Anionic Polymerization

Synthesis and Characterization of Polyalkylmethacrylate Macromonomers

Pierre Lutz, Patrick Masson, Gérard Beinert, Paul Rempp

Centre de Recherches sur les Macromolécules (CNRS) 6, rue Boussingault -
67083 Strasbourg - France

SUMMARY

The synthesis of polyalkylmethacrylate macromonomers has been performed anionically by direct deactivation of the carbanionic sites with p-vinyl- or p-isopropenylbenzyl bromide. The characterization of the samples proved that the yields are close to quantitative, and that no side reactions are involved. The method also applies to hydroxyethylmethacrylate and to glycerylmethacrylate, provided the monomers are made aprotic by reversible silylation or acetalization.

INTRODUCTION

Several recent publications deal with the synthesis and characterization of polymethylmethacrylate macromonomers (1-4). In most cases two step methods are used: the free radical polymerization of the methacrylic ester is carried out in the presence of an efficient transfer agent that possesses an alcohol or a carboxylic function. The ω -functional polymer chains are then reacted with methacryloyl chloride, or with glycidyl methacrylate to yield the polymerizable unsaturation at chain end. These ω -methacryloyl polyalkylmethacrylates have not always been characterized very adequately; still, the method can be considered satisfactory.

However methods based on free radical polymerization exhibit some disadvantages: first the molecular weight of the macromonomers cannot be chosen at will. A rough control can be achieved by a proper choice of the mole ratio of transfer agent to monomer, but since this ratio varies with conversion, the molecular weight distribution broadens. Secondly macromolecules initiated by primary radicals do not carry the function required at chain end unless the initiator is fitted with the same function (1). Thirdly it is not very easy to carry out the reaction of the ω -functional polymer with the unsaturated reagent to completion.

We have attempted the synthesis of polyalkylmethacrylate macromonomers by anionic deactivation. To our knowledge, only one previous work (4) dealt with this matter. This synthesis involves two difficulties:

- . Anionic polymerization of methacrylic esters to low molecular weight polymers of low polydispersity is not very easy, owing to the fact that initiation either is slow or involves side reactions.
- . The nucleophilicity of the carbanions of "living" polymethacrylic esters towards unsaturated electrophilic deactivators can be questioned.

The purpose of this paper is to report on the synthesis of polymethacrylic macromonomers by means of anionic deactivation and on the characterization of the samples obtained. As starting monomers we have considered methyl-, n-butyl- and t-butyl methacrylates, and hydroxyethyl methacrylate (HEMA) and glycerylmethacrylate as well. Of course, the two latter monomers require efficient but reversible blocking of the protonic functions in order for the monomers to be able to undergo anionic polymerization.

EXPERIMENTAL PART

Monomers

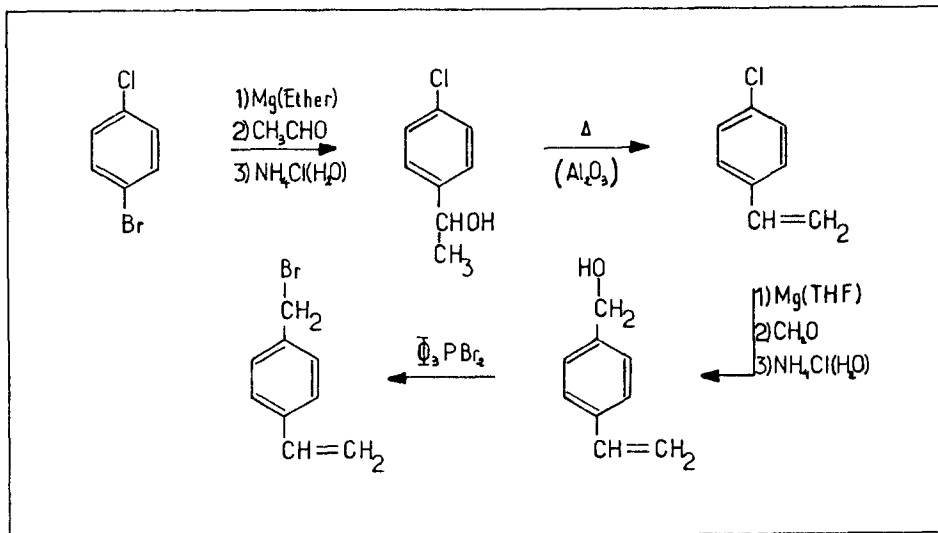
Methyl-, n-butyl- and t-butyl methacrylates are commercial products (Fluka, Prolabo), and they have been distilled twice over sodium wire or over calcium hydride, under vacuum, just before use.

2-hydroxyethyl methacrylate (HEMA) has been treated with trimethylchlorosilane (in ether, in the presence of pyridine) to make it aprotic. The trimethylsiloxyethylmethacrylate is then recovered and vacuum distilled over sodium wire.

The acetal derived from glycerylmethacrylate was synthesized from isopropylidene glycerol and methacryloyl chloride, in the presence of triethylamine (5). It was purified by vacuum distillation in the presence of sodium, to remove all protonic impurities.

Unsaturated electrophilic reagents

- Methacryloyl chloride, commercial pure grade (Fluka) was made free of traces of acid by vacuum distillation over calcium hydride.
- Commercial vinylbenzylchloride (VBC) was found unsuitable. Pure p-vinylbenzylbromide (VBB) was synthesized according to the following scheme:



The overall yield of this four-step preparation method is 25%. The VBB thus obtained was found to be of excellent purity, and it was used as an unsaturated electrophilic deactivator.

Characterization data

- . Elemental analysis : calc. (%) H 4,60 Br 40,55 C 54,85
 found (%) H 4,68 Br 42,27 C 53,08
- . NMR ^1H : CH : 6,3/6,45/6,6/6,75 ppm
 CH₂(Br) : 4,2 ppm
 = CH₂ : 4,9/5,1/5,3/5,6 ppm
 ArH : 7,0 ppm
- . p-isopropenylbenzyl bromide was made according to a procedure described earlier (6).

Initiators

The anionic polymerization initiators were made in THF solution by methods that are widely known:

- . diphenylmethyl sodium (or potassium) by reacting the corresponding naphthenide onto diphenylmethane (7).
- . 1,1-diphenyl-3 methylpentyllithium, obtained from sec-butyllithium and 1,1-diphenylethylene (8).
- . 1,1,4,4-tetraphenyl-1,4 disodiobutane, which is the dimerization product of 1,1-diphenylethylene in the presence of sodium in THF, at room temperature.

Apparatus and procedure

The macromonomer synthesis are carried out in tight reactors fitted with magnetic stirring and temperature control, under a slight argon overpressure. All reagents are added from graduated ampoules fitted with stopcocks at both ends to prevent any contact with air. The solvents used - THF and benzene - were purified and dried thoroughly.

The experimental procedure that was found best suited involves slow addition of the monomer - sometimes diluted with the same volume of THF - into the initiator solution, at temperatures between -60 and -80°C.

A typical example would involve 20 g (0.2 mol.) of methylmethacrylate, slowly added to 4×10^{-3} mol. of initiator dissolved in 400 ml of THF, at -70°C, to yield a "living" PMMA of theoretical molecular weight $\bar{M}_n = 5\ 000$. Thereafter a fraction of the solution (1/10) is sampled out, deactivated protonically, and the polymer is recovered by precipitation into a methanol/water (9/1 v/v) mixture or into heptane, for purpose of characterization. The rest of the reaction medium still kept at -70°C is treated with 0,8 g (4×10^{-3} mol.) of vinylbenzyl bromide dissolved in 10 ml of dry THF. An hour is allowed for the reaction to be completed. Thereafter the KBr formed is filtered off, and the macromonomer is recovered by precipitation into cold methanol (at -40°C); it is redissolved in benzene, filtered once more, and freeze dried.

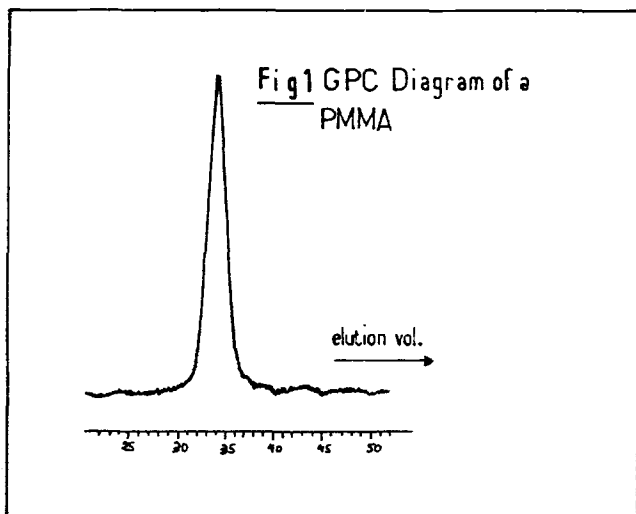
RESULTS AND DISCUSSION

The most appropriate initiators are those which are sufficiently nucleophilic to efficiently initiate the polymerization of the alkylmethacrylate but which do not give yield to side reactions with the ester carbonyl. That is why we have deliberately chosen initiators exhibiting diphenylmethyl carbanions. The draw-back involved is that initiation is relatively slow, which may have consequences on the width of the molecular weight distribution, when low molecular weights are wanted. We have established that the best fit between calculated and measured degrees of polymerization - and also the smallest polydispersity indices - are obtained upon using the procedure described in the experimental section.

Below -60°C the alkylmethacrylate carbanions are quite stable, and no spontaneous deactivation does occur; it is therefore essential to carry out the whole procedure at very low temperature.


The results of the experiments and the characterization data are gathered on Tab.1.

The molecular weight distributions of the precursors deactivated protonically are pretty narrow (Fig.1), though they are broader than those of polystyrenes obtained anionically in the same molecular weight range.



The functionalizations obtained with vinylbenzyl bromide and with isopropenylbenzyl bromide are quite satisfactory. No side reaction involving the double bond is observed, and the agreement between the molecular weight of the precursor and that of the macromonomer is good. The functionalization yield is close to quantitative, thus confirming earlier results (4): alkylmethacrylate carbanions do react with benzylic halides; since they are unable to attack styrene type double bonds, no side reaction can be expected.

Tab. 1 - Characterization of poly-alkylmethacrylate macromonomers

Ref.	Init.	Deactivation	\bar{M}_n^* th.	\bar{M}_n^* /	\bar{M}_n^* UV	\bar{M}_n^* GPC	\bar{M}_w^* GPC	\bar{M}_w^* LS
<u>Methyl</u>								
2578	DMK	EO + MACl	2 000	14 100	-	13 700	-	-
2636	DMNa	IBBr	3 000	3 500	3 160	3 700	5 300	-
2687	DHLi	"	3 000	3 900	3 900	3 600	4 000	-
2689	"	VBC	3 000	30 000	-	-	-	-
2699	"	IBBr	1 000	2 000	1 800	1 900	2 600	5 400
2697	"	"	2 000	2 700	2 100	2 500	3 000	4 300
2701	"	"	2 000	3 000	2 200	2 900	3 150	3 800
2696	"	"	4 000	5 200	3 100	4 800	5 250	5 600
2698	"	"	6 000	6 700	5 800	5 800	7 000	7 500
2830	"	VBBr	6 000	6 300	5 800	6 200	6 900	8 300
<u>Butyl</u>								
2633	DMNa	IBBr	3 000	3 100	2 700	3 100	4 800	-
2634	"	"	7 000	7 500	5 800	6 300	7 600	-
<u>t.butyl</u>								
2712	DMK	IBBr	3 000	3 400	3 000	-	-	-
<u>Isopropylidene-glyceryl</u>								
2719	DMK	IBBr	5 500	20 000	23 600	5 300	9 300	15 000
<u>Trimethylsilylethyl</u>								
2720	DMK	IBBr	3 000	2 700	-	-	-	-
Initiators : DMK, DMNa : diphenylmethyl-K or Na DHLi : 1,1-diphenyl-3 methylpentyllithium End capping agents : EO : oxirane VBC ... : vinylbenzyl chloride IBBr .. : p.isopropenyl (or p.vinyl) benzyl VBBr bromide								
\bar{M}_n : chemical titration * \bar{M} : expressed in g/mole 								

In contrast, the results of the functionalizations carried out with methacryloyl chloride are not satisfactory. A sharp increase of the molecular weight is observed, and the functionalization yield is not quantitative: the attack of the carbanion onto the double bond of the deactivating agent competes with the expected reaction onto the acid chloride function.

It has been established earlier (9) that the trimethylsilyl derivative of HEMA can be polymerized anionically and that the process does not involve spontaneous deactivation. This implies that functionalization by means of an unsaturated electrophile such as isopropenylbenzyl bromide should be possible, yielding the corresponding macromonomer. Our experiments have checked this assumption. However when the polymer is precipitated in excess methanol, part of the protecting functions are hydrolyzed, where upon the polymer redissolves. The hydrolysis can be made quantitative by adding a few drops of acid into the methanolic solution. The ω -isopropenylphenyl poly(HEMA) can then be recovered by precipitation in excess THF, or by freeze drying from its dioxane solution.

We have also attempted to make macromonomers of polyglycerylmethacrylate. The starting material was the acetalized monomer, which polymerizes anionically under conditions similar to those employed for butyl-methacrylate (5). After polymerization and subsequent functionalization by means of isopropenylbenzyl bromide the hydrolysis of the acetal functions requires a few drops of hydrochloric acid, and it is rather slow. The functionalization yield is poor as shown from the double bond analysis.

CONCLUSION

It is now confirmed that the carbanionic sites of "living" polyalkyl-methacrylates are still sufficiently nucleophilic to react quantitatively with an unsaturated benzylic halide, thus yielding ω -styryl polyalkyl-methacrylate macromonomers (or the corresponding α -methylstyrene derivatives), almost quantitatively, and without side reactions. The experimental conditions had to be chosen such as to get narrow molecular weight distributions, in the range of molecular weights required for macromonomers.

The alkylmethacrylate macromonomers described here are of interest for the synthesis of graft copolymers exhibiting hydrophilicity (poly-HEMA or polyglycerylmethacrylate grafts) or adhesive properties (poly-butyl-methacrylate grafts). This will be studied in a forthcoming paper.

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