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Synthesis of a Polyamine Macromer by Cationic Polymerization

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Summary

Desactivation of the active species (aziridinium ion) of living poly(1-tert.butyl aziridine) by methacrylic acid leads to the corresponding polyamine-methacrylate ester macromer. Macromers of different molecular weights were characterized by gel permeation chromatography and by 360 MHz ^{1}H NMR spectroscopy.

Introduction

Macromolecules with polymerizable vinyl-end-groups, commonly called macromers, are receiving considerable interest since the last five years. Such compounds can provide a new method for the preparation of graft copolymers by copolymerization with usual vinyl monomers.

Macromers have been synthesized by poly-addition reaction of divinyl compounds (TSURUTA, 1980) by transformation of reactive polymer end groups (HUDECEK et al. 1980) or, most frequently, by reacting anionic living polymers with electrophiles containing unsaturated functions (MILKOVICH 1980, MILKOVICH et al. 1970, 1975, 1978). Recently, also cationic techniques have been successfully applied for the preparation of macromers (KENNEDY 1980, SIERRA VARGAS et al. 1980). Kennedy used vinylbenzylchloride as co-initiator for the preparation of polyisobutylene macromer and the Strasbourg-group (SIERRA VARGAS et al. 1980) produced a polytetrahydrofurane macromer by using a combination of methacryloyl chloride and silver hexafluoroantimonate as initiating system followed by desactivation of the active species with sodium phenolate. In both cationic systems, the insaturation was introduced in the polymer chain via the initiator. Theoretically the unsaturated group could also be introduced by the desactivator, as was already pointed out by the last authors. However this approach necessitates the occurrence of typical "living" conditions which is a rather exceptional feature in cationic polymerizations. The cationic polymerization of THF is one of these systems although at high conversions transfer to polymer becomes important, leading to a broadening in molecular weight distribution and to the presence of "dead" and bifunctional polymers (PENCZEK et al. 1980).

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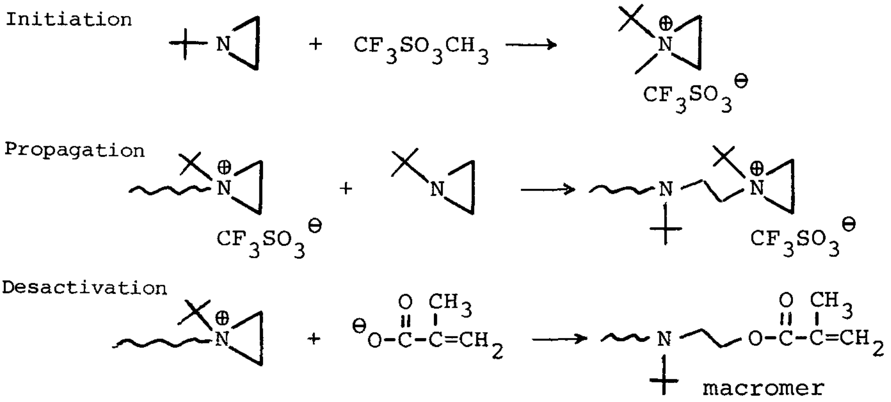
In previous papers (GOETHALS et al. 1980) we have reported that cationic polymerization of N-tert.butylaziridine (TBA) can lead to the corresponding temporarely living polymers with predictable molecular weight and narrow molecular weight distribution. The active species of these polymers are aziridinium salts which were found to react very readily with nucleophiles leading to polyamines with well defined end-groups. If the nucleophile contains a polymerizable functional group, this should lead to the polyamine macromer. These experiments are the subject of the present paper.

Results and Discussion

Synthesis of the macromers.

In order to obtain macromers with a well defined structure by the desactivation method, the polymerization must meet the following requirements: (i) initiation must be quantitative and fast compared with propagation, (ii) transfer reactions and termination reactions must be absent or be slow compared with the propagation reaction, (iii) the desactivation reaction must be quantitative and fast compared with other possible reactions of the active species (e.g. a slow termination). The first two requirements are fulfilled in the polymerization of TBA when methyl triflate is used as initiator in a 9/1 mixture of THF/HMPT as solvent, at temperatures between 0° and 20°C. At this temperature range, the reaction of an aziridinium ion with a carboxylate anion is almost instantaneous as was proved by reactions of a low molecular model compound for the active species. Thus, it was expected that addition of a 10-fold excess (based on the active species concentration) of methacrylic acid to the living poly-TBA would lead to the corresponding methacrylate macromer, since the acid should be transformed into the carboxylate ion by the large excess of amino functions of the polymer.

The reaction scheme is as follows :



The macromer is isolated by precipitation in methanol/water containing enough sodium hydroxide to remove the excess methacrylic acid bound to the polymer by ammonium salt formation.

Characterization of the macromers.

Fig. 1 shows the GPC analysis of three macromers obtained with different monomer/initiator ratios. As expected from the living character of the polymerization the $\overline{DP}$'s are equal to m_o/c_o and the molecular weight distributions are narrow.

The structure of the macromers was proved by means of 360 MHz ^{1}H NMR spectroscopy. Fig. 2 shows the spectrum of a macromer with molecular weight 3000. Next to the large (off-scale) singlets at 1,0 and 2,5 ppm, which are due to the polymer protons, the signals of the methyl head-group (resulting from initiation) and those of the imino-methacrylate ester end-group are clearly visible. Integration of the head-or end-group peaks and the polymer peaks is another way to determine the molecular weight. However, due to the large difference in areas this method is not very accurate. The most important information obtained from the NMR spectra is that the concentration of the methyl head-groups is in all cases practically equal to the concentration of the methacrylate end-groups. The analytical results for a series of macromers with different molecular weights are summarized in Table 1.

TABLE 1.

Characteristics of poly-TBA methacrylate macromers.

m_o [mol.l^{-1}]	c_o [mol.l^{-1}]	M.W.$^{(a)}$ calcd.	M.W.$^{(b)}$ obsd.	$\overline{M}_w/\overline{M}_n$ (GPC)	$\frac{[\text{head}]}{[\text{end}]}$$^{(c)}$
0,33	0,0167	2081	2095	1,16	1,09
0,50	0,0167	3071	3140	1,08	0,97
0,50	0,0100	5051	4310	1,10	1,05

a) $\text{M.W.}_{\text{calcd.}} = 99\,\frac{m_o}{c_o} + 101$

b) Measured by vapor pressure osmometry in THF (at 40°C).

c) Ratio of methyl head group conc. over methacrylate ester conc. determined by integration of the corresponding peaks in the ^{1}H-NMR spectrum.

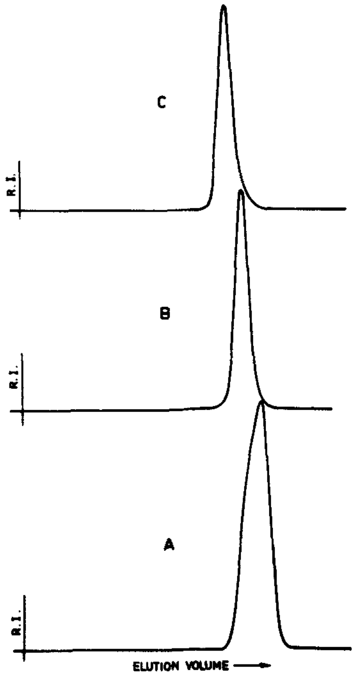


Fig. 1: GPC-analysis of poly-TBA methacrylate macromers of different mol.wt.
A : 2000, B : 3100
C : 4300. (T.S.K. column G3000H8, eluent THF).

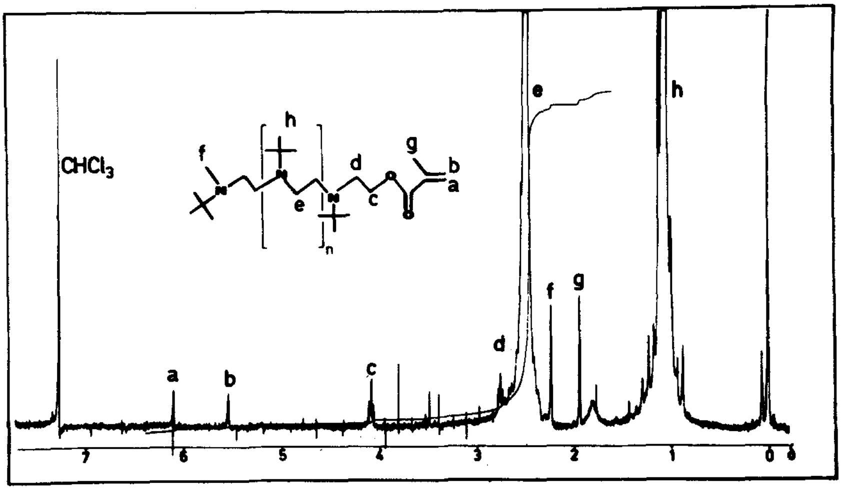


Fig. 2: 360 MHz ^{1}H-NMR spectrum of poly-TBA methacrylate macromer of mol.wt. 3000.

The macromers have the same physical properties as the normal poly-TBA. They are colourless, highly crystalline materials with a m.p. of 136° (DSC). They are soluble in chloroform, THF, ether, HMPT, DMSO, insoluble in water, alcohols, hydrocarbons. They become water-soluble when the pH is below 4.

Polyamine macromers (with different structure) have been described recently by TSURUTA (1980). These compounds can be useful to produce polymers with polyamine grafts which may possess a number of interesting properties.

At the present time, the synthesis of other poly-TBA macromers and their copolymerization with various vinyl monomers is investigated.

Experimental

Example for the synthesis of poly-TBA methacrylate macromer with molecular weight 5000.
A solution of 1,98 g of TBA in a mixture of 32 ml of dry THF and 5,6 ml of dry HMPT is cooled at 15 °C. Under vigorous stirring, 45 µl of methyltriflate is added. After 5 mins, 340 µl of methacrylic acid is added. The reaction mixture is allowed to warm up to room temperature and after 30 mins it is poured into 360 ml of methanol and 40 ml of 0,1-n.sodium hydroxide. The precipitate is isolated by filtration and is washed several times with methanol. After drying in a vacuum desiccator, 1,9 g of poly-TBA methacrylate macromer is obtained (96% yield).

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