ABSTRACT

A screening of catalysts for the group transfer polymerization (GTP) of methyl methacrylate (MMA) with (1-methoxy-2-methyl-1-propenyl)oxy trimethylsilane (MTS) as initiator (I) was performed. The use of tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF₂SiMe₃), one of the most preferred catalysts of Du Pont, needs the addition of acetonitrile as solvent, which unfortunately reacts with the active centres in the presence of the catalyst under termination. This difficulty can be overcome using tris(piperidino)sulfonium bifluoride (TPSF₂H) as catalyst. It is soluble in pure tetrahydrofuran and only traces are sufficient for the catalysis of a very rapid GTP of MMA. But it catalyses a rapid oligomerization of the initiator, too. So, tetrabutylammonium cyanide (Bu₄N·CN) is recommended as catalyst. It is soluble in tetrahydrofuran, an as powerful catalyst as TPSF₂H, but less active in the oligomerization reaction of MTS. Its initiation of an anionic polymerization of MMA can be neglected under the reaction conditions of the GTP.

INTRODUCTION

In 1983 Du Pont claimed a new type of living polymerization, termed group transfer polymerization (GTP) (1). Especially derivatives of acrylic and methacrylic acid may be polymerized. Besides a silicon containing initiator (I), a catalyst (C) is necessary. As catalysing agents, Du Pont proposed a number of basic compounds, tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF₂SiMe₃) and tris(dimethylamino)sulfonium bifluoride (TASF₂H) being the most preferred ones.

In this paper we would like to compare some catalysts with concern to their catalytic activity in the GTP of methyl methacrylate (MMA) with (1-methoxy-2-methyl-1-propenyl)oxytrimethylsilane (MTS) as initiator.
MATERIALS AND METHODS

MTS was prepared according to Ainsworth et al. (2), TASF$_2$SiMe$_3$ and tris(piperidino)sulfonium bifluoride (TPSF$_2$H) according to Middleton (3). Tetrabutylammonium cyanide (Bu$_4$NCN) was purchased from Fluka AG, FRG. Tetrahydrofuran was treated with CuCl, then dried over KOH and sodium wire, distilled under Argon and condensed from n-Butyllithium before use. The purification of MMA and acetonitrile and the measuring of time conversion curves and of average molecular weights are described elsewhere (4).

RESULTS AND DISCUSSION

TASF$_2$SiMe$_3$ is insoluble in THF. Therefore, small amounts of acetonitrile about 3 - 5% by volume have got to be added to the system, to obtain a homogeneous solution. Recently, we reported (5), that in the presence of the catalyst, acetonitrile can react with MTS and, as we assume, also with the growing chains under formation of trimethylsilyl acetonitrile (Me$_3$SiCH$_2$CN). These reactions reduce the concentration of the active centres, so that complete conversions cannot be obtained at all experimental conditions.

Fig. 1 shows time conversion curves for different MTS concentrations in a THF/acetonitrile mixture in dependence on the catalyst concentration. The numbers at the curves give the ratio of the initiator to the catalyst concentration.

![Figure 1. Time conversion curves for the polymerization of MMA with MTS (I) and TASF$_2$SiMe$_3$ (C) in a THF/acetonitrile mixture.](image)

Figure 1. Time conversion curves for the polymerization of MMA with MTS (I) and TASF$_2$SiMe$_3$ (C) in a THF/acetonitrile mixture. (MMA)$_0$ = 1.58 mol/1; (I)$_0$ = 0.008 mol/1; (C)$_0$ (mol/1) : (ø) 0.00073; (■) 0.0024; (o) 0.004; (•) 0.008; (+) 0.016;