

Anionic Block Copolymerization of Methyl Methacrylate in the Presence of Alkali and Alkali-Earth Metal Salts

INTRODUCTION

Many studies have been devoted to the anionic polymerization of methyl methacrylate (MMA).^{1,2} It is well known indeed that this polymerization is complicated by side and termination reactions due to the possible attack of carbonyl groups by the carbanions and also by internal cyclizations in apolar solvents.^{3,4} Therefore, in contrast to the situation with styrene and dienes, the anionic polymerization of MMA proceeds predictably only with careful selection of solvent, temperature, and initiator. Moreover, block copolymers of hydrocarbons (e.g., styrene) and MMA can only be prepared by first forming the nonpolar segment and utilizing the resulting polymeric anion to initiate the polymerization of the methacrylic monomer. Due to the high reactivity of polystyryl or polydienyl anions towards the carbonyl groups, partial deactivation of the chains occurs during this initiation step. This side reaction can be avoided by addition of 1,1-diphenylethylene prior to the methacrylate polymerization⁵ or by using a mixture of butyllithium and α -methylstyrene as initiator for the hydrocarbon polymerization.⁶ In apolar solvents, dormant species are formed by internal cyclizations during propagation, leading to broad and, in some cases, multimodal molecular weight distributions.⁷ The use of alkali metal alkoxides and also borate derivatives has been proposed to prevent that situation as well as the carbonyl attack by carbanions.⁸⁻¹⁰ There is some evidence that such additives can act as stabilizers for the active centers and control the dissociation of ion pairs; however, their real efficiency has not been quantitatively ascertained.

Following the same concept, we have investigated the behavior of alkali and alkali-earth metal halides in the anionic (co)polymerization of alkyl(meth)acrylates.^{11,12} We report here some results obtained by using LiCl, BaCl₂, and BaBr₂ as complexing agents in the block copolymerization of MMA with styrene and isoprene, in pure THF as well as in THF-toluene and THF-benzene mixtures.

RESULTS AND DISCUSSION

The anionic copolymerization of styrene and MMA was performed under nitrogen atmosphere; monomers and solvents were carefully purified according to usual methods. The alkali(earth)metal salt (in a 10:1 stoichiometry versus *sec*-butyllithium) is first introduced in the reactor with toluene; it is dried by azeotropic distillation of the toluene and further heating under vacuum at 150°C for 3 h. The solvent(s) and initiator (*sec*-butyllithium) are then added. Styrene is polymerized first at -78°C for 1 h; MMA is then added to the reaction medium and allowed to polymerize for 3 h at -78°C. Anions are then deactivated by methanol and the polymer is recovered by precipitation into methanol.

Whatever the salt used, the conversion of monomers to polymers is quantitative, in all cases. Furthermore, the copolymerization products contain no homo-PMMA as confirmed by acetonitrile extraction whereas rather small amounts of homopolystyrene are recovered by cyclohexane extraction. The purity of the copolymers is particularly high when LiCl or BaCl₂ is used, as illustrated in Table I. That means that the presence of the salt efficiently prevents the attack of carbonyl groups by polystyryl carbanions during the initiation step of the MMA polymerization. GPC traces (Fig. 1) indicate unimodal and narrow molecular weight distributions. As observed in Table I, these low polydispersities are obtained in pure THF as well as in THF-toluene and THF-benzene mixtures. It is, however, to be noted that LiCl gives rise to the lowest polydispersity (M_w/M_n less than 1.1 in pure THF and 1.1-1.2 in solvent mixtures). In other words, alkali(earth)metal salts, particularly LiCl, are able to control very efficiently the propagation of the MMA chain by preventing side reactions and internal cyclizations which generally occur in pure hydrocarbon solvents as well as in THF-hydrocarbon mixtures.^{3,4,7}

TABLE I
Block Copolymerization of Styrene
and MMA in the Presence of Metal Halides^a

Solvent (v/v)	Salt	Homo-PS (%)	Polydispersity (\bar{M}_w/\bar{M}_n)	\bar{M}_n
THF	LiCl	2	< 1.1	140,000
THF-Tol 80/20	LiCl	2	1.10	125,000
THF-B _z 75/25	LiCl	3	1.12	100,000
THF-Tol 80/20	BaCl ₂	2	1.20	145,000
THF-Tol 80:20	BaBr ₂	11	1.25	120,000

^a[Sty] = 50 g/L; Sty/MMA (wt ratio) = 1; salt/s.BuLi (mole ratio) = 10.

The efficiency of LiCl was also evaluated in the block copolymerization of MMA with isoprene. Polymerization conditions were the same as above, except that isoprene was first polymerized in pure benzene or pure toluene for 12 h at 35°C. After that, THF was introduced in the reaction medium, progressively cooled to -78°C before MMA addition. Conversion to polymer was 100% but, as indicated in Table II, significant amounts of homopolyisoprene were recovered by hexane extraction. That situation was assumed to result from the poor stability of the polyisoprenyl anion in THF at room temperature. Isomerizations are believed to take place.¹³ In order to prevent that phenomenon, a small amount of styrene was introduced in the reaction medium after isoprene polymerization but before THF addition. Results summarized in Table II demonstrate that, under these modified conditions, the amount of recovered homopolyisoprene is

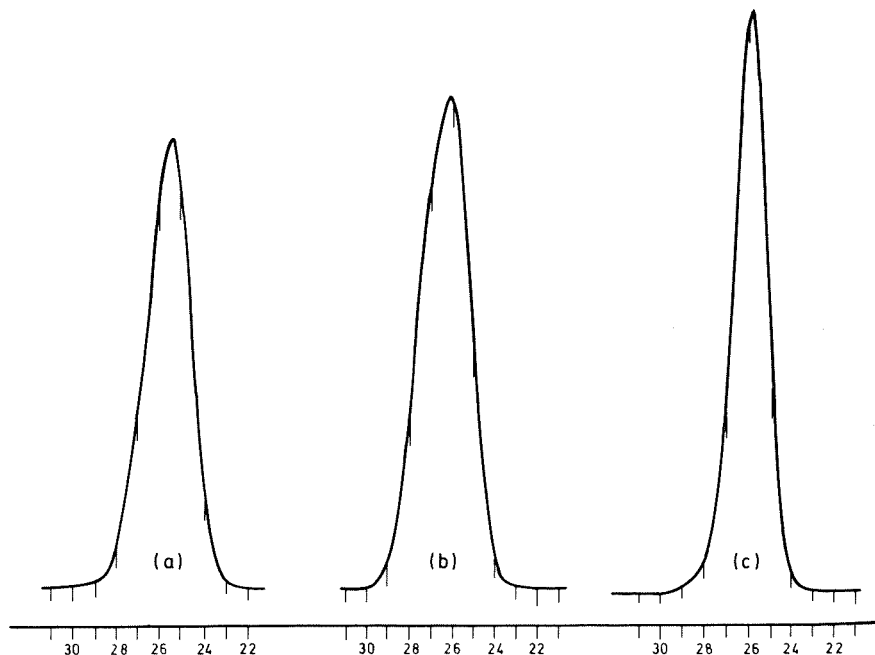


Fig. 1. GPC traces of PS-*b*-PMMA copolymers (crude products) synthesized in a THF/Toluene (80/20) mixture in the presence of: (a) BaCl₂; (b) BaBr₂; (c) LiCl.

TABLE II
Block Copolymerization of Isoprene
and MMA in the Presence of LiCl^a

Solvent ^b	Homo-PIP	Polydispersity (\bar{M}_w/\bar{M}_n)	\bar{M}_n
THF-Tol 75:25	35	1.40	110,000
THF-B _z 80:20	30	1.35	95,000
THF-B _z ^c (2) 80:20	12	1.25	60,000

^a[Isoprene] = 150 g/L in hydrocarbon solvent; Is/MMA (wt ratio) = 1; salt/s.BuLi (mole ratio) = 10.

^bFinal composition for MMA copolymerization.

^cStyrene (6 wt %) added after isoprene polymerization.

significantly reduced; also a narrow molecular weight distribution is obtained as illustrated in Figure 2.

Although additional experiments should be performed to adjust the optimum conditions of this copolymerization, we can conclude from these first investigations that the block copolymerization of MMA with styrene and also with isoprene, in THF/hydrocarbon solvent mixtures, proceeds by a well-"living" mechanism: Neither significant side reactions during the initiation step nor termination or cyclization during the propagation of the PMMA chain are observed, when it is performed in the presence of catalytic quantities of alkali(earth)metal halides, in particular LiCl. The salt seems indeed to control very efficiently the stability of the active species and the dissociation of the ion pairs, either by a complexation mechanism or by a simple salt effect. Further investigations are certainly in order to fully understand the real mechanism of this polymerization. The specificity of salts with respect to the nature of the metal counter-anion as well as the relative quantities of salt and initiator are important parameters which must be

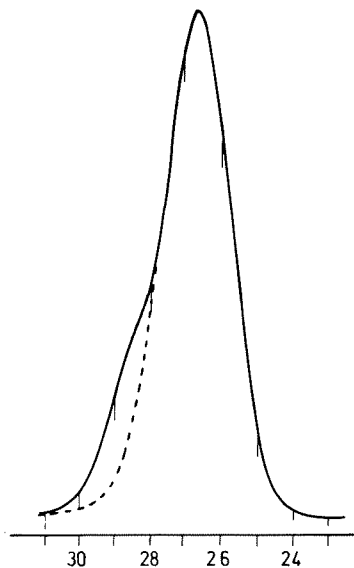


Fig. 2. GPC trace of PIP-*b*-(PS)-*b*-PMMA copolymer (crude product) synthesized in the presence of LiCl in a THF/benzene (80/20) mixture.

investigated more deeply and more systematically in order to optimize that (co)polymerization process.

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