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Effect of ethyl aluminium sesquichloride on the specificity of the reactions of 1-methyl-1-methoxycarbonylethyl radical

Implications as to the mechanism of alternating copolymerization

Julia Krstina, Graeme Moad*, and David H. Solomon**

CSIRO, Division of Chemicals and Polymers, Private Bag 10, Clayton, Victoria 3168, Australia

Summary

Copolymerizations of styrene and methyl methacrylate (MMA) have been carried out with azo-bis-(methyl isobutyrate-α-^{13}C) (AIBMe-α-^{13}C) as initiator and in the presence of ethyl aluminium sesquichloride (EASC). The specificity of the 1-methyl-1-(methoxycarbonyl)ethyl radical (**I**) for reaction with styrene over MMA is substantially enhanced by the presence of very low concentrations of EASC. This behaviour is consistent with the involvement of a complexed radical and suggests that such species may play an important role in Lewis acid induced alternating copolymerization.

Introduction

It has been established that the structure of copolymers can be markedly influenced by Lewis acids. Most notably, Lewis acids are effective in enhancing the tendency towards alternation in the copolymerization of certain monomer pairs (1-3).

Three basic mechanisms have been proposed to account for the influence of Lewis acids on copolymerization:

(a) that involving a binary complex between the Lewis acid and the acceptor monomer. The electrophilicity of the double bond is enhanced by complexation with the Lewis acid and their reactivity towards nucleophilic radicals is therefore increased.

(b) that involving a ternary complex between the Lewis acid and acceptor and donor monomers. An alternating polymer may be formed by 'homopolymerization' of such a complex.

(c) that involving a complex between the Lewis acid and the propagating radical to create a species with selectivity different to that of the normal propagating species.

It should be noted that these mechanisms are not mutually exclusive and that the mechanism may vary according to the particular monomer pair and Lewis acid involved. One of the most widely studied alternating copolymerizations is that of styrene and methyl methacrylate (MMA) in the presence of ethyl aluminium sesquichloride (EASC) (4-9).

In this paper we provide preliminary results from a study of end groups formed in MMA-styrene copolymerizations initiated by AIBMe-α-^{13}C in the presence of EASC. The initiator-derived radical **I** is a model for the MMA propagating species.

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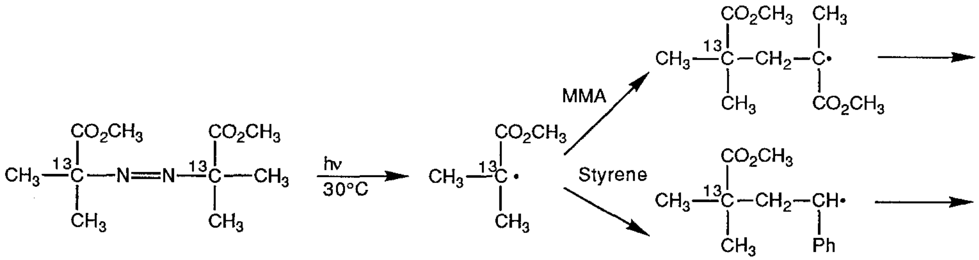
*To whom offprint requests should be sent

**Current address: Chemistry Dept., University of Melbourne, Parkville, Victoria 3052, Australia



AIBMe-α-^{13}C **I**

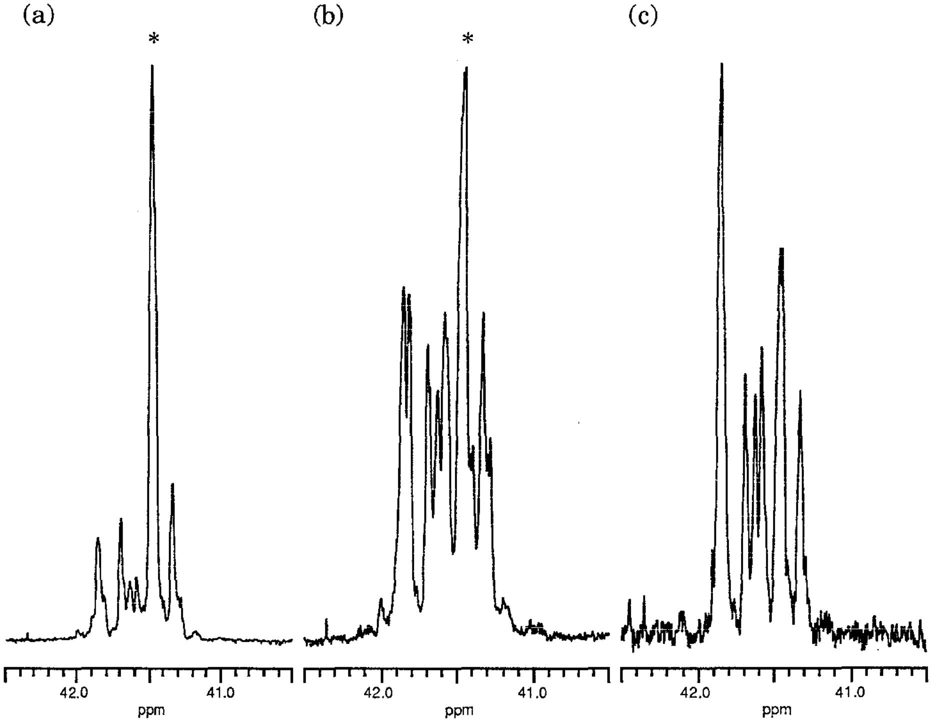


Fig. 1. Portions of 62.9 MHz ^{13}C NMR spectra of poly(methyl methacrylate-co-styrene) showing end group resonances. All copolymers were prepared with [total monomers] = 1.75 M and [AIBMe-α-^{13}C] 2x10^{-3} M. The copolymer (a) had MMA:styrene=4:1; (b) had MMA:styrene =1:1 and (c) had MMA:S=4:1 and [EASC] 4x10^{-3} M. The signal at 42.35 ppm is due to dimethyl tetramethylsuccinate. The group of signals indicated with an asterisk in (a) and (b) can be largely attributed to chains beginning in MMA (10).

Results and Discussion

Reactions were carried out at 30°C in benzene solvent. Polymerizations were initiated by irradiation at 360 nm in a Rayonette photoreactor, they were carried to ca. 3% conversion. The end groups were analysed by ^{13}C NMR spectroscopy.

It was found that large amounts of EASC [*i.e.* amounts needed to give alternating copolymerization (6,11)] lead to the formation of very high molecular weight copolymers and this prevented easy detection of the end groups by ^{13}C NMR spectroscopy.

Experiments were, therefore, attempted with very low concentrations of EASC (10^{-4} M). Under these conditions, the molecular weight of the copolymer formed, the conversion, and the overall polymer composition appeared the same, within experimental error, as for polymerizations carried out without added EASC. This indicates, the overall kinetics of copolymerization are unaffected by these low concentrations of EASC.

Representative ^{13}C NMR spectra of copolymers prepared with and without EASC at various monomer ratios are shown in Figs 1a-c. These spectra show that addition of EASC to the copolymerization reaction mixture has had a dramatic effect on the specificity of the reactions of radical **I**. Because of signal overlap, it is not possible at this stage to unambiguously assign all signals in these spectra to monomer sequences (10). However, it is clear that the intensity of signals marked with an asterisk in Fig 1a [largely attributable to chains beginning with MMA (10)] are substantially reduced relative to other end group signals (largely attributable to chains beginning with styrene) and we conclude from this that the specificity of the radical **I** for reaction with styrene has been significantly increased.

The amount of Lewis acid used in the experiment shown in Fig 1c is twice the initiator concentration. Use of higher concentrations (8×10^{-3}) of Lewis acid did not substantially enhance the specificity for addition to styrene. With lower Lewis acid concentrations (4×10^{-4}), no effect was evident.

The specificity shown by radical **I** for reaction with styrene is thus very much enhanced by EASC. Because of the very low concentration of EASC used in our experiments and because overall polymerization kinetics appear unaffected, a mechanism for this effect involving only monomer complexation seems unlikely. Given the very low concentration it also seems unlikely that preferential complexation of these species (**I**) could occur directly because of the short lifetime of these radicals under the reaction conditions. A possible explanation for our results is that the EASC preferentially forms a complex with the initiator, AIBMe. It is well known that Lewis acids form complexes with AIBMe and other azo-compounds and may significantly accelerate their *thermal* decomposition (12-14). We propose that such a complexed azo-compound undergoes photolysis to form a complexed, more electron deficient, radical which shows enhanced reactivity towards styrene and/or reduced reactivity towards MMA.

Further work needs to be done to confirm this mechanism, to establish the exact nature of any radical-Lewis acid complex, to quantify the effect, and to see if a similar effect can be observed with other radicals and monomer pairs.

Experimental

AIBMe-α-^{13}C (15) was prepared according to the established procedure (16). Monomers were purified by passage through basic alumina and fractional distillation under vacuum. Solvents were purified by standard procedures.

NMR spectra were obtained on a Bruker WM250 NMR. Deuterochloroform was used as NMR solvent and chemical shifts are reported relative to tetramethylsilane. GPC was conducted with a Waters 150C instrument equipped with 5 Waters Ultrastyragel columns (10^6, 10^5, 10^4, 10^3, 10^2 Å). Tetrahydrofuran was used as eluent.

For the copolymerization experiments, the required quantities of monomers were added to a 25 mL volumetric flask which was then made up to the mark with benzene to give a total monomer concentration of 1.75 M. This solution was then added to a pyrex reaction vessel containing the initiator (to give 0.002 M), the required amount of EASC (as a solution in toluene) was then added by syringe, and the resultant solution degassed under vacuum ($<10^{-3}$ mmHg) through three freeze-thaw cycles.

The reaction vessel was placed in a thermostatted (30±1°C) chamber inside a Rayonette photoreactor (2 x 8 watt 360 nm lamps) and irradiated for 162 min (this reaction time gave complete consumption of the initiator). The polymer was isolated by evaporation of the solvent and excess monomer and characterized by GPC and ^{13}C NMR.

Conversions were ca. 3% and the copolymer samples had $\bar{M}_n$ = ca. 5000 and polydispersities = 1.7±0.1.

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