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ORGANOCUPRATES AS INITIATORS FOR METHYL METHACRYLATE POLYMERIZATION†

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ABSTRACT

Polymerizations of methyl methacrylate initiated by organocuprates in tetrahydrofuran solution have been investigated. The heterocuprate lithium *n*-butylcyanocuprate was found to be an effective initiator at -78°C , and lithium di-*n*-butylcuprate was confirmed as an effective initiator; both species give rapid polymerization to virtually complete conversion of monomer. Polydispersities (M_w/M_n) are about 1.5. Polymerizations have an inherent termination reaction and a low initiator efficiency. Polymerization of methyl vinyl ketone is virtually uncontrollable, and polymerizations of methyl methacrylate are inhibited by styrene.

INTRODUCTION

Enhanced control over polymerization processes, in terms of polymer microstructure and molecular weight distribution, is a continuing goal. Considerable success in the synthesis of polymers with narrow molecular weight distribution

†Dedicated to Professor Otto Vogl on the occasion of his 65th birthday.

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($M_w/M_n \approx 1.02$) has been achieved by living anionic polymerizations of styrene, α -methylstyrene, butadiene, or isoprene initiated by alkyllithium reagents or sodium naphthalenide [1]. Success in this sense requires rapid initiation with respect to propagation and a lack of termination or chain transfer. An absence of inherent chain termination reactions allows termination by reagents of choice to produce well-defined telechelics [2]. Similar levels of control over M_w/M_n can be achieved in cationic polymerizations of tetrahydrofuran initiated by silver hexafluorophosphate or hexafluoroantimonate [3] and for polymerizations of vinyl ethers [4], styrene, and isobutylene [5].

Anionic and cationic systems have very limited success when applied in general. Anionic polymerization of polar monomers almost invariably generates polymers with broad molecular weight distributions because of inherent chain termination reactions [1, 6]. For example, in the polymerization of α,β -unsaturated esters, such as methyl methacrylate (MMA), both 1,2- and 1,4-additions may compete with the required net 3,4-addition. The primary, inherent chain termination is an intramolecular back-biting reaction which generates a terminal cyclic β -keto-ester unit [7] (a similar termination occurs in the polymerization of acrylates [8]); gradual destruction of growing chains broadens the molecular-weight distribution of the final polymer. It is possible to minimize side reactions and produce poly(methyl methacrylate) (PMMA) with a narrow molecular weight distribution by performing anionic polymerizations at -78°C [9].

Considerable interest, therefore, was created by the announcement of group transfer polymerization (GTP) as a new living polymerization process [10]. The overall process, based on highly regioselective reactions of silyl ketene acetals with α,β -unsaturated esters, results exclusively in 3,4-addition in polymerizations of acrylates and methacrylates. GTP can be used to prepare methacrylate polymers with narrow molecular weight distributions. It does not provide such good control over acrylate polymerizations, and even the polymerizations of methacrylates are not truly living [11]. Its use in preparing terminally functionalized polymers is thereby restricted.

In synthetic organic chemistry, organocuprates are widely used because of their ability to give very high regioselectivity in conjugate addition reactions to various compound types, including α,β -unsaturated esters and ketones [12]. For example, dialkyl lithium cuprates undergo almost exclusive conjugate addition to α,β -unsaturated ketones with the new carbon-carbon bond formed at the β -position of the ketone; addition of lithium bis(allyl)cuprate to cyclohexenone is 94% conjugate addition [13] while no conjugate addition occurs if a copper-catalyzed Grignard reagent is used [14]. Subsequent workup with enolate protonation results in net addition across the C—C double bond. Since cuprates act like weak alkylmetal species and their addition reactions to α,β -unsaturated esters can result exclusively in conjugate addition giving a reactive nucleophilic enolate, the possibility exists that they might lead to well-controlled living polymerizations of vinyl esters or ketones if the intermediate enolate formed by conjugate addition adds further monomer with net 3,4-addition and if there is no inherent termination reaction.

Organocopper compounds (RCu) have been reported as polymerization initiators [15]. Lithium organocuprates (R_2CuLi) are normally used in stoichiometric amounts in addition reactions, but polymeric products from side reactions have

been reported [16]. While low-molecular-weight oligomers (dimers, trimers) have been found as by-products in stoichiometric reactions of cuprates and some substrates [17], there are few reports where cuprates have been consciously used as polymerization initiators [18, 19]. Han et al. [19] found lithium di-*n*-butylcuprate to be an effective initiator for the α,β -unsaturated monomers MMA, acrylonitrile, acrolein, and *N*-acryloylpyrrolidone; the same reagent was ineffective with methyl acrylate and other monomers.

Although the mechanism of organocuprate reactions is not yet established, Han et al. proposed a mechanism involving Cu(III) intermediates which have been invoked elsewhere [12a]. It has also been shown that in polymerizations of hydroxyethyl methacrylate in toluene solution the product is highly isotactic poly(hydroxyethyl methacrylate), while in tetrahydrofuran solution the product is mainly syndiotactic [18]. Similar results were obtained for methyl methacrylate polymerizations [19].

Han et al. [19] reported 99% conversion of MMA and acrylonitrile to polymer at -10°C . They reported on the influence of solvent on the tacticity of the PMMA formed and the influence of additives on the polymerization, but they did not report any evidence relating to the molecular weight distribution of the polymers or to the possibility that the reaction is a living polymerization. Here we report the results of a short study performed to examine whether or not the reaction is a living polymerization. In addition to the homocuprate lithium di-*n*-butylcuprate, we have also investigated the heterocuprate lithium *n*-butylcyanocuprate as an initiator.

EXPERIMENTAL

Materials

Hydroquinone inhibitor was removed from MMA (Aldrich Chemical Co.) by passing through a column of neutral activated alumina (Brockman No. 1); the monomer was further dried with calcium hydride. Some samples of MMA were purified by the traditional washing with alkali and subsequently drying and distilling. In all cases MMA was distilled from calcium hydride under reduced pressure (40°C , 70 torr) immediately prior to use.

Methyl vinyl ketone (Aldrich Chemical Co.), inhibited by acetic acid and hydroquinone, was purified by washing with sodium carbonate and subsequently distilling twice (35°C , 125 torr) immediately prior to use.

Tetrahydrofuran (THF), AR grade (Aldrich Chemical Co.), was dried over anhydrous calcium sulfate, then over sodium wire. Prior to use, the stabilizer was removed by passing the THF through a column of neutral activated alumina (Brockman No. 1) and then distilling it from sodium benzophenone solution. Copper(I) iodide (Aldrich Chemical Co.) was washed with freshly distilled tetrahydrofuran prior to drying (50°C) and storing under vacuum. Copper(I) cyanide (Aldrich Chemical Co.), the tan-colored form [20], was also dried at 50°C and stored under vacuum.

Hexane solutions of *n*-butyllithium (1.6 *M*) (Aldrich Chemical Co.) were standardized by titrating with acid before and after reaction with 1,2-dibromoethane [21]. Solutions were stored at -30°C in bottles sealed with septa.

Procedures

Standard techniques for handling air-sensitive compounds were adopted for all reactions [22].

Synthesis of Lithium Di-*n*-butylcuprate (Bu_2CuLi)

Two equivalents of precooled butyllithium in hexane solution were added slowly to a 0.64 *M* solution of copper(I) iodide in tetrahydrofuran at -12°C . The mixture, containing a fine black precipitate, was maintained at -12°C for 45 min, cooled to -78°C , and used immediately.

Synthesis of Lithium *n*-Butylcyanocuprate

Butyllithium (5.6 mmol) in hexane solution was added to 6.0 mmol of copper(I) cyanide in tetrahydrofuran at -78°C . The temperature of the reaction mixture was allowed to rise to -30°C over 30 min during which period the color of the reaction mixture changed from a turbid beige mixture, through tan, to a clear dark brown solution. The mixture was cooled to -78°C and used immediately.

Polymerizations

Aliquots of precooled monomer were added by syringe to solutions of the cuprate initiators as required. Reactions were quenched by addition of a little precooled methanol which caused precipitation of oxidation products. This mixture was centrifuged and the precipitate was filtered off. Polymers were isolated from the solutions by precipitation into a large excess of petroleum spirit.

Gel Permeation Chromatography

Molecular weights and molecular weight distributions of the polymeric products were determined by gel permeation chromatography (GPC) using a system having columns packed with 10 μm PL-gel (Polymer Laboratories) and a Knauer refractive index detector. The solvent was tetrahydrofuran (1 cm^3/min) and the system was calibrated with poly(methyl methacrylate) standards (Polymer Laboratories).

RESULTS

Homocuprates

Organocuprate reagents are generally much less reactive than their organolithium counterparts, but the homocuprate lithium di-*n*-butylcuprate (Bu_2CuLi) is more effective than butyllithium as an initiator for polymerization of MMA at -10°C , Table 1, in that polymer yields are higher. Initiator efficiencies in Table 1 are calculated from polymer yields and molecular weights, and represent the moles of polymer formed per mole of initiator. The calculated efficiency for the cuprate is probably too high as a cuprate concentration of 1.6 *mM* is assumed, based on reagents used in its synthesis. Cuprates are susceptible to decomposition at -10°C , and the true concentration may have been less than that calculated. Also, quoted

TABLE 1. Comparison of BuLi and Bu₂CuLi as Initiators for the Polymerization of Methyl Methacrylate at -10°C; Reaction Mixtures Consisted of 0.027 M Initiator in Tetrahydrofuran and Methyl Methacrylate (1.5 M); Reaction Times Were 15 min

Initiator	Conversion of monomer, %	M_n , kg/mol	M_w/M_n	Initiator efficiency, %
BuLi	13	16.35	3.48	5.2
Bu ₂ CuLi	>95	10.35	1.79	57.5

concentrations are based on monomeric species, but the cuprate exists as a dimeric tetrahedral, but difunctional, complex in solution [16b]. From gel permeation chromatography data, from polymers prepared using the same initiator concentrations, it is clear that while the peak and number-average molecular weights are similar, the molecular weight distribution of the polymer prepared using butyllithium as initiator is much broader than that initiated by the cuprate.

The polydispersity of the PMMA formed from initiation by Bu₂CuLi is greater than that from ideal living polymerizations ($M_w/M_n < 1.03$) but is less than that for conventional anionic polymerization. The lower polydispersity is indicative of reduced termination which may arise because of reduced nucleophilicity of the propagation species, possibly through coordination to a bulky complexed counterion. The high conversion of monomer and these results leave open the possibility that the cuprate-initiated polymerization is living. To test this possibility, we performed experiments using successive monomer additions.

Precooled MMA (2 cm³) was added to Bu₂CuLi (0.057 M) in 28 cm³ tetrahydrofuran at -78°C (the Bu₂CuLi was prepared at -12°C). After 15 min, one-half of the reaction mixture was removed by syringe and added to cold methanol; Polymer A (Table 2) was extracted from this sample by precipitation. Precooled tetrahydrofuran (55 cm³) and MMA (5 cm³) were added to the residual reaction mixture; the ratio of monomer:solvent after addition was approximately that used for the initial reaction mixture. After a further 15 min the reaction mixture was quenched with methanol and the polymer extracted was Polymer B.

Table 2 presents monomer conversions achieved after each of the above 15

TABLE 2. Polymerizations of Methyl Methacrylate Initiated by Lithium Di-*n*-butylcuprate at -78°C with Successive Monomer Additions at 15 min Intervals

Sample	Monomer conversion, %	M_p , kg/mol	M_n , kg/mol	M_w/M_n	Initiator efficiency, %
A	77	6.83	4.86	1.51	18.6
B	96	104.39	26.6	3.26	25.0 ^a

^aOverall efficiency based on total cuprate added and final yield and molecular weight of poly(methyl methacrylate).

min periods (based on monomer added prior to that time); also included in Table 2 are molecular weight data for Polymers A and B and efficiencies of the initiator. From these data and the gel permeation chromatograms in Fig. 1 it is obvious that addition of the second aliquot of monomer caused a significant increase in molecular weight of the polymer formed. Although the increase in number-average molecular weight, by a factor of about 6, is comparable to that expected if the reaction was a true living polymerization, the peak molecular weight showed a much greater increase as a result of the formation of polymer with number-average molecular weight of about 50 kg/mol and the formation of a bimodal molecular weight distribution. It should also be noted that the chromatogram for Polymer B (Fig. 1) has a long low molecular weight tail which extends under the peak for Polymer A. At high detector sensitivity the chromatogram for Polymer B exhibits a shoulder corresponding closely with the chromatogram for Polymer A. The combined results are consistent with Polymer B containing a large proportion of Polymer A which did not initiate polymerization of the second aliquot of monomer but was initiated

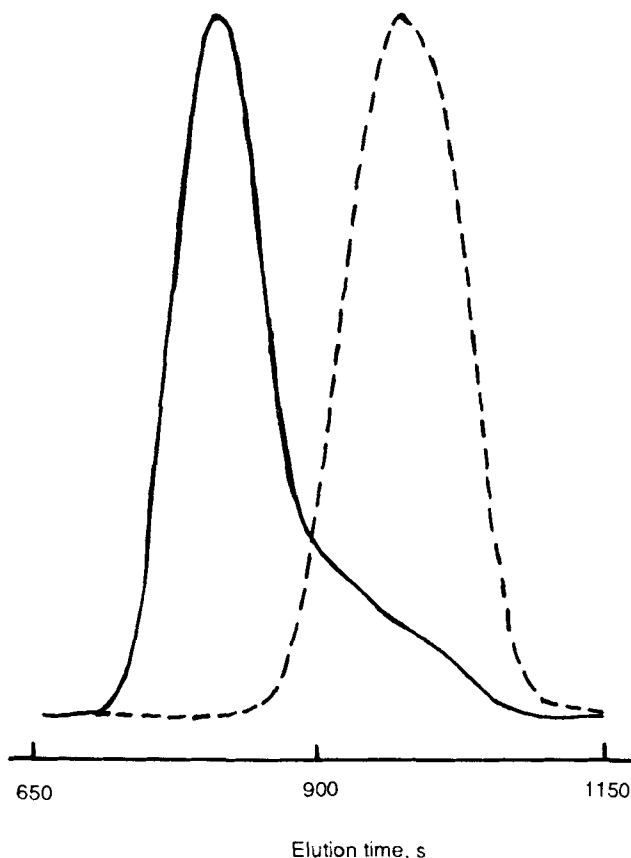


FIG. 1. Gel-permeation chromatograms of samples of poly(methyl methacrylate) produced at -78°C by polymerization of one (---) and two (—) aliquots of methyl methacrylate initiated by Bu_2CuLi (the second aliquot added 15 min after the first); polymers are designated as A and B, respectively, in Table 2.

by initiator not consumed in the first stage. Results suggest that, at the reaction temperature used, initiation by cuprate is slower than by butyllithium and that the cuprate-initiated polymerization has an inherent termination reaction which is slow compared to propagation. The termination reaction is slow enough to allow complete conversion of monomer to polymer, with a relatively narrow molecular weight distribution for the product, but is not negligible when compared with the time scale for further monomer addition and polymerization.

Heterocuprates

As a possible means of varying the relative rates of initiation, propagation, and termination, we examined briefly the use of the heterocuprate *n*-butyl(cyano)-copperlithium (Bu(CN)CuLi) as an initiator. Marino and Floyd [23] reported greater regiospecificity in Bu(CN)CuLi addition, i.e., larger proportions of 1,4-addition, to the epoxide of 1,3-cycloheptadiene than for Bu₂CuLi. Various problems recognized in the synthesis of homocuprates, as a result of their inherent reactivity and sensitivity to oxidative and thermal decomposition [12a, 24], were found to be less serious in the preparation of the mixed cuprate, and clear beige solutions, with no evidence of complicating side reactions, were obtained at low temperatures (typically -78°C).

The results in Table 3 demonstrate that Bu(CN)CuLi is an effective initiator for the polymerization of MMA at -78°C in that complete conversion of monomer to polymer was achieved within 10 min, although very little of the cuprate was involved in forming polymer chains. Complete monomer conversion and the relatively narrow molecular weight distribution could indicate a living polymerization system. We tested for this possibility by performing a series of experiments, following the procedure described in the preceding section, using sequential aliquots of monomer. Ten minutes after each monomer addition, aliquots of reaction mixture were extracted and polymer yields and molecular weights were determined. Results are summarized in Table 4.

It is apparent from Table 4 that, although virtually 100% conversion of monomer was achieved within minutes after each addition, the polymer formed in the later stages was not derived by growth on living polymer formed in the first stage (A) of the reaction. Indeed, the molecular weights of polymer formed in successive stages were virtually identical, as if each polymerization were independent. A further characteristic feature of the polymerizations is that only a very small fraction of the cuprate was responsible for initiating chains at each stage, although the

TABLE 3. Polymerization of Methyl Methacrylate Initiated by Mixed Cuprate for a Reaction Time of 10 min; Reaction Temperature -78°C

[Bu(CN)CuLi], mol/L	MMA, cm ³	Conversion, %	M_n , kg/mol	M_p , kg/mol	M_w/M_n	Initiator efficiency, %
0.26	2	>95	42.7	66.0	1.37	0.54

TABLE 4. Polymerization of Methyl Methacrylate Initiated by Heterocuprate (0.26 *M*) with Sequential Additions of Monomer at 10 min Intervals; Reaction Temperature -78°C

Experiment	MMA added, cm^3	Time of addition, min	Conversion, %	M_n , kg/mol	M_w/M_n	Initiator efficiency, ^a %
1A	2	0	>95	20.9	1.74	0.90
1B	5	15	>95	34.7	1.52	3.24
2A	2	0	91	24.0	1.51	0.71
2B	5	15	>95	32.9	1.55	3.32

^aAs in previous cases, efficiencies were calculated from total amount of cuprate added, polymer yield, and molecular weight, making allowance for the aliquot removed where appropriate.

system remained active throughout the series of reactions and reagents were not destroyed by impurities, and residual initiator was responsible for initiation in subsequent stages.

In another series of experiments, summarized in Table 5, 1 cm^3 aliquots of MMA were added to a solution of $\text{Bu}(\text{CN})\text{CuLi}$ (0.085 *M*) in THF (60 cm^3) at -78°C at 2 min intervals. Two minutes after the last addition the reaction was quenched with cold methanol. The distributions in Fig. 2 and data in Table 5 indicate that continued addition of monomer causes continued growth of polymer molecules formed in the early stages of reaction, without termination on the time scale of this experiment (compare with results obtained for longer intervals between monomer additions). Polymer yields indicate that at no stage was the reaction mixture starved of monomer. Increases in monomer conversion and initiator efficiency between the series are consistent with slow initiation and rapid propagation.

Poor initiator efficiencies are not due to destruction of the initiator by impurities. Table 6 summarizes data from experiments in which the amount of initiator in polymerizations of MMA (0.6 *M*) in tetrahydrofuran was varied. Although the monomer conversions are high in all cases, the polymer molecular weights are insensitive to the concentration of initiator and the calculated initiator efficiency decreases with increasing [initiator]; concentrations of polymer chains formed in all experiments are similar.

TABLE 5. Polymerization of Methyl Methacrylate Initiated by Heterocuprate (0.085 *M*) with Sequential Additions of Monomer at 2 min Intervals; Reaction Temperature -78°C

Experiment	Total reaction time, min	No. of MMA additions	Conversion of monomer, %	M_n , kg/mol	M_w/M_n	Initiator efficiency, %
3	2	1	38	6.8	1.5	1.01
4	6	3	83	24.3	1.66	1.85
5	10	5	92	25.7	1.76	3.24

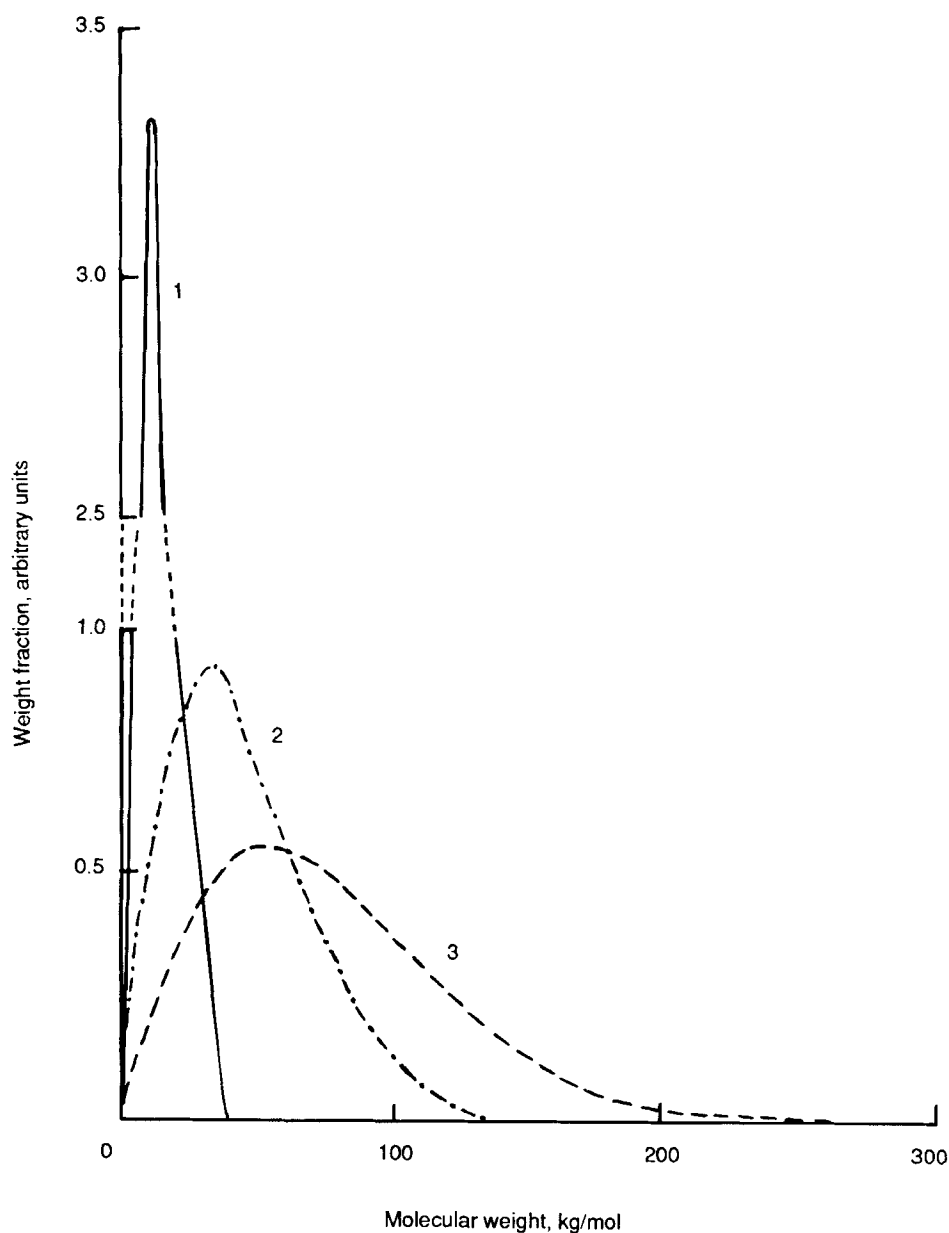


FIG. 2. Molecular-weight distributions of samples of poly(methyl methacrylate) produced by polymerization of methyl methacrylate initiated by $\text{Bu}(\text{CN})\text{CuLi}$ at -78°C by addition of aliquots of monomer at 2 min intervals; the order of samples produced is 1, 2, and 3. Samples are further described in Table 5.

TABLE 6. Polymerization of Methyl Methacrylate (0.6 *M*) Initiated by a Heterocuprate at Different Concentrations; Reaction Temperature -78°C

[Bu(CN)CuLi], mol/L	M_n , kg/mol	Monomer conversion, %	Initiator efficiency, %	Polymer yield, mol/L
0.026	61.8	>95	0.04	9.7×10^{-4}
0.26	55.5	>95	0.004	10.7×10^{-4}
0.50	74.7	>95	0.00015	7.8×10^{-4}

Polymerization of Methyl Vinyl Ketone

Data from synthetic organic chemistry indicate that, as expected from electronic considerations, unsaturated esters are less reactive toward cuprates than are unsaturated ketones [25]. At 25°C , conjugate addition of organocuprate reagents to methyl vinyl ketone derivatives is complete in less than 1 second [26]. In order to examine the possibility that complexities (low initiator efficiency) in the polymerization of MMA might, in part, be a result of slow initiation relative to propagation, we examined the polymerization of methyl vinyl ketone. Because of the low solubility of poly(methyl vinyl ketone) in tetrahydrofuran at -78°C , reactions were performed in a 50:50 (v/v) tetrahydrofuran:toluene mixture with [Bu(CN)CuLi] = 0.33 *M*. Reaction was so rapid that the monomer, added dropwise, almost instantly polymerized to solid particles without dissolution in the reaction mixture before the monomer (2–5 cm^3) could be injected completely. The polymer gradually dissolved and although, under these conditions, no deductions can be drawn from the molecular weight of the product, it is worth noting that in all experiments, irrespective of the amount of monomer added, the polymer molecular weights were low and sequential monomer additions did not result in further polymerization.

Copolymerization

Compositions of copolymers formed in polymerizations are often used to indicate mechanisms of polymerization. We attempted to perform copolymerizations of styrene and MMA in which 5 cm^3 aliquots of each monomer were added sequentially to a solution of 6 mmol of Bu(CN)CuLi (0.1 *M*) in 60 cm^3 of tetrahydrofuran at -78°C . When styrene was added first, no polymer was formed. When MMA was added first, only 75% of the MMA polymerized and no styrene was incorporated into the copolymer; the latter observation was based on dual detection GPC and a lack of absorption in the chromatogram using UV detection. Thus, in some way the styrene quenches initiation and growth processes.

CONCLUSIONS

In this preliminary study of polymerizations initiated by organocuprates we have demonstrated that Bu(CN)CuLi is an effective initiator for the polymerization of MMA at -78°C and have confirmed that Bu_2CuLi is also. Polymer yields are almost quantitative and higher than when butyllithium is used as initiator.

The reaction kinetics appear complex with, probably, fast propagation and (relatively) slow initiation and very low effective use of initiator. Termination at -78°C occurs within a period of about half an hour so that, while polymerizations might appear living on a short time scale under the conditions we have explored, there are definite termination processes which prevent the effective use of the system to produce telechelics and block copolymers.

Polymerization of methyl vinyl ketone is extremely rapid at -78°C , and polymerization of MMA initiated by cuprates is inhibited by styrene.

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