3992 *Macromolecules* **1997,** *30,* 3992−3998

Identifying the Nature of the Active Species in the Polymerization of Methacrylates: Inhibition of Methyl Methacrylate Homopolymerizations and Reactivity Ratios for Copolymerization of Methyl Methacrylate/*n*-Butyl Methacrylate in Classical Anionic, Alkyllithium/Trialkylaluminum-Initiated, Group Transfer Polymerization, Atom Transfer Radical Polymerization, Catalytic Chain Transfer, and Classical Free Radical Polymerization

David M. Haddleton,* Martin C. Crossman, Kirsty H. Hunt,
Clare Topping, Carl Waterson, and Kevin G. Suddaby

Department of Chemistry, University of Warwick, Coventry, CV4 7AL, U.K.

Received March 5, 1997; Revised Manuscript Received May 5, 1997[⊗]

ABSTRACT: Reactivity ratios have been determined for the monomer pair methyl methacrylate and *n*-butyl methacrylate under a range of polymerization conditions. The value of using reactivity ratios as a mechanistic probe is discussed. Reactivity ratios determined where M1 = MMA and M2 = *n*-BMA are 1.04, 0.81, classical anionic; 1.10, 0.72 , alkyllithium/trialkylaluminum initiated; 1.76, 0.67, group transfer polymerization; 0.98, 1.26, atom transfer radical polymerization; 0.75, 0.98, catalytic chain transfer; and 0.93, 1.22, classical free radical polymerization. The data suggest ATRP and CCTP proceed via radical type propagation. Li/Al-initiated polymerization undergoes an anionic mechanism, while strong evidence is found for an associative, catalyst dependent mechanism for GTP. Galvinoxyl is demonstrated to inhibit GTP as well as free radical polymerization, and it is suggested that neither the use of inhibition nor polymer stereochemistry can be used to distinguish between anionic and radical processes.

Introduction

The mechanism of addition polymerization of methacrylates is often the subject of intense speculation.[1] The ester substituent on the vinyl polymerizable group is an effective electron-withdrawing group activating the bond toward both anionic and radical initiation as well as promoting coordination polymerization. For example, there has been much debate concerning the mechanism of group transfer polymerization (GTP) regarding associative[2−4] or dissociative[5] (anionic) pathways. Indeed, although there remains an active debate concerning the mechanism, it has been firmly accepted that free radical propagation is not occurring. One of the test methods to distinguish between free radical and anionic, or anionic type, polymerizations has been the ability to obtain polymers with narrow molecular mass distributions and controlled number average molecular mass, M_n, so-called living polymerization, as is the case with GTP.[6]

Recently, certain transition metals have been used to promote atom transfer radical polymerization (ATRP).[7−13] ATRP involves abstraction of a halogen atom from a suitable initiating alkyl halide by the transition metal in a reversible reaction that maintains the propagating polymer radical end capped with the halogen, thus greatly reducing the amount of termination. ATRP results in narrow molecular weight distribution polymers, often with polydispersity index, PDI, less than 1.20, with controlled M_n. Thus, "living" polymerization can no longer be considered as a suitable mechanistic test to distinguish between radical and anionic propagation pathways. A suitable mechanistic test for ATRP so as to demonstrate the involvement of homolytic as opposed to heterolytic bond cleavage is not as obvious as it may first seem. Sawamoto uses two tests to demonstrate the involvement of free radicals in the ATRP of MMA as mediated by $Ru_2Cl_2(PPh_3)_3$: (1) the addition of radical inhibitors such as galvinoxyl, **2**, or DPPH immediately stops or prevents polymerization from occurring, and (2) ^{13}C NMR indicates the stereochemistry of the PMMA product to be consistent with a Bernoullian process with stereochemistry similar to PMMA prepared from AIBN in toluene at 60 °C.[7] Matyjaszewski also reports that the stereochemistry of PMMA as prepared from $Cu^{I}X/RX$/bipyiridine (X = Cl, Br) is similar to that from classical free radical initiators and that galvinoxyl acts as an efficient inhibitor.[9] Again these two pieces of evidence are used as evidence for a free radical process. Teyssie has demonstrated the use of $Ni[\{o,o'\text{-}(CH_2NMe_2)_2C_6H_3\}Br]$ as being an extremely effective ATRP catalyst; again inhibition by galvinoxyl and a persistence ratio, ρ (where $\rho = 2(m)(r)/(mr)$; m and r refer to meso and racaemic placement of monomer units along the polymer backbone), of close to unity are used as evidence for a free radical mechanism.[12] It is noted that only in this last example are the radicals discussed as *being temporarily confined within the coordination sphere of the metal.*

Group transfer polymerization has been established as proceeding via heterolytic bond cleavage, leading to nucleophilic attack of either a carbon-based anion or a carbon with δ^- charge on the vinyl group of the incoming monomer.[1] The stereochemistry of poly-

---

* Tel: 01203 523256. Fax: 01203 524112. E-mail: msrgs@csv.warwick.ac.uk.

[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1997.

S0024-9297(97)00303-3 CCC: $14.00

(methyl methacrylate) from GTP is similar to free radically produced PMMA, with a persistence ratio close to unity. No stereochemical effects have been observed by changing the nature of the SiR_3 protecting group.[14] This is consistent with free radical propagation. As it is firmly established that GTP does not proceed via a free radical process, proposed mechanisms based on stereochemical evidence must be open to question. We were thus interested to examine whether GTP is inhibited by certain free radical inhibitors. The use of *tert*-butyllithium in conjunction with stereochemically hindered aluminum alkyls and phenoxides to mediate the polymerization of methacrylates also proceeds via an undetermined mechanism.[1,15,16] If this mixed metal alkyl system is analogous to immortal polymerization, aluminum porphyrin-initiated polymerization, then the involvement of homolytic bond cleavage has been suggested as a possible step in the polymerization mechanism.[17] Many inhibitors of one type of polymerization may also inhibit others as well, albeit for different reasons. A definitive mechanistic test is required that can be applied to the range of new methacrylate polymerization types.

To date, inhibition and stereochemistry have been the most widely used mechanistic probes for addition polymerization. Free radical inhibitors also invariably interfere with ionic and GTP polymerizations, making their use as mechanistic probes ineffective. Furthermore, the effectiveness of stereochemistry is also questionable as, for example, both GTP and free radical polymerization of methyl methacrylate give very similar polymer microstructures. At the outset of this work, we were interested in investigating if reactivity ratios would clearly distinguish between a range of polymerization processes. Reactivity ratios were considered as a possible mechanistic probe, as they express the effects of at least four rate constants. It is reasonable to assume that the relative changes in the rate constants of propagation and cross propagation for two monomers will not necessarily be exactly the same for different mechanisms. Even when similar monomers such as BMA and MMA are copolymerized, steric, electronic, and relative hydrophobicity will clearly have different effects with either anionic or radical propagation.

Statistical or random copolymerization is important from a scientific viewpoint for examining the reactivities of monomers and propagating centers, and from a technical perspective for the flexibility it offers in polymer synthesis. Reactivity ratios play a central role in the study of copolymerization and are obtained by establishing the relationship between the composition of the monomer feed and the composition of the copolymer produced from that feed. This can be achieved by measuring the concentrations of unreacted monomer (e.g., by GC) or by measuring the composition of the resultant copolymer (e.g., by NMR or IR). Some polymerization mechanisms are specific to monomer types, for example, GTP is extremely effective for methacrylates but inert toward styrene.[18] Catalytic chain transfer polymerization is very effective in reducing the molecular weight of methacrylates but ineffective with acrylates and less active for styrene, than for methacrylates, by 1 order of magnitude.[19,20] If care is used to choose appropriate monomers, which can be copolymerized with similar polymerization behaviours, then a consideration of reactivity ratios might be used as such a mechanistic probe. Reactivity ratios are defined as in eqs 1 and 2, where the symbols have their usual

$$r_1 = k_{11}/k_{12} \tag{1}$$

$$r_2 = k_{22}/k_{21} \tag{2}$$

meanings when applied to copolymerization.[21] These reactivity ratios give a measure of the relative rates of reaction of a polymer radical toward two different monomers. It is expected that if the two monomers have similar reactivities towards a propagating active polymer center, then values should be approximately unity. MMA and BMA provide such a monomer pair, with similar activities with regard to classical anionic polymerization, alkyllithium/trialkylaluminum-initiated polymerization, group transfer polymerization, atom transfer radical polymerization, catalytic chain transfer polymerization, and classical free radical polymerization. This paper describes a study of the reactivity ratios for MMA and *n*-BMA for a range of polymerization types in an attempt to classify new polymerization processes. Monomer 1 is defined as MMA and monomer 2 as *n*-BMA. The effect of certain radical inhibitors on the polymerization of MMA under a range of polymerization types is also discussed.

Measurement of Reactivity Ratios. Experimentally determined average copolymer composition data are related to the composition of the feed through the well-known differential form of the terminal (Mayo–Lewis) model copolymer composition[22],[23] equation given by eq 3. The terms F_1 and f_1 represent the mole fraction

$$F_1 = \frac{r_1 f_1^{\,2} + f_1(1 - f_1)}{r_1 f_1^{\,2} + 2f_1(1 - f_1) + r_2(1 - f_1)^2} \tag{3}$$

of monomer 1 in the polymer and monomer feed, respectively. As eq 3 is the differential form of the copolymerization equation, its use is limited to low-conversion copolymerizations (typically <5%), where the symbols have their usual meanings when applied to copolymerization.

A number of assumptions are used in the derivation of eq 3.[22] One of these is the long chain assumption, which states that the monomer incorporated into the chain by initiation, transfer, and termination reactions is negligible compared to the monomer incorporated by propagation. Clearly, this assumption is violated in copolymerizations where short chains are produced, such as those from CCTP. A second assumption is the equal reactivity assumption, which assumes that the relative rates of all the propagation reactions are independent of chain length and depend on the composition of the macroradical only through the terminal unit. Significant violation of these assumptions should show up as trends in the copolymer composition with chain length. This should be examined when reactivity ratios are being determined from relatively short polymer chains.

A number of procedures have been developed for the estimation of r_1 and r_2 based on the Mayo–Lewis model. Most of these procedures have involved the linearization of eq 3 and are statistically unsound.[24] The popularity of these methods has contributed to the large variation in reactivity ratios reported in the literature. It has also resulted in poor estimates of reactivity ratios with misleading confidence intervals. Better estimates are obtained by the use of the error-in-variables-model (EVM) approach. This work used an implementation of the error-in-variables-model approach for estimating reactivity ratios from the differential form of the Mayo–

Lewis equation.[24] The EVM approach is a more satisfactory method of analyzing copolymerization data, since it is statistically sound, allows for the major sources of experimental error to be properly accounted for, has thus been used in the present study.

Recent work has suggested that the EVM approach gives confidence intervals of only approximate shape. One alternate approach is to use nonlinear least squares (NLLS) data evaluation in conjunction with Tidwell−Mortimer criteria.[25] However, NLLS requires some prior knowledge of r_1 and r_2 and narrows confidence intervals quickly through an iterative process. Two experimental compositions are used, corresponding to a high mole fraction and a low mole fraction. In this current work, reliable r_1 and r_2 values were not available in all cases and only one set of experiments was carried out for each type of polymerization. The goal of the current work was to examine the nature of the chain carriers as opposed to determining the definitive set of reactivity ratios.

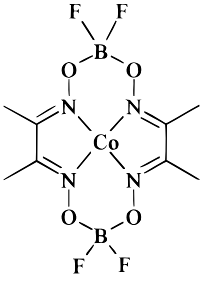
It is noted that we have recently reported the results of a determination of reactivity ratios for MMA and n-BMA by catalytic chain transfer polymerization.[26] The previous study was designed to compare the use of MALDI-TOF and NMR in reactivity ratio determination. The results from the NMR study of CCTP reported previously are included in the present work so as to allow a complete comparison.

Experimental Section

General Information. All reactions were carried out using standard Schlenk line techniques under a nitrogen atmosphere. Methyl methacrylate and *n*-butyl methacrylate were obtained from ICI Acrylics, stabilized with 5 ppm Topanol. Monomers were weighed and mixed prior to being stored under nitrogen over a mixture of 4 Å and 13X molecular sieves and activated basic alumina so as to remove inhibitor, water, and other protic impurities. Triisobutylaluminum (1.0 M solution in toluene) and diphenylethene (Aldrich) were used as received; *tert*-butyllithium (Aldrich) supplied as a 1.7 M solution in pentane and *n*-butyllithium (Aldrich) supplied as a 1.6 M solution in hexanes were stored in glass ampules and titrated against diphenylacetic acid in tetrahydrofuran (THF) before use. Methyl trimethylsilyl dimethylketene acetal (MTS) (Aldrich) was stored over 4 Å molecular sieves in the bottle supplied and used without further purification. Bis(dimethylamino)methylsilane was obtained from Fluorochem Ltd., stored in an ampule under N_2 and used as supplied. Tetrabutylammonium *m*-chlorobenzoate (TBA*m*CB) prepared by the method of Dicker and Sogah[27] was stored in a Schlenk tube under N_2 and prior to being used as a $\sim 8 \times 10^{-3}$ molar stock solution in THF. Tetrabutylammonium acetate (TBAAc) (Aldrich) was dried under vacuum and was stored in a Schlenk tube under an N_2 atmosphere and used as an $\sim 8 \times 10^{-3}$ solution in THF. Ethyl 2-bromoisobutyrate (Aldrich) (98+%) and copper(I)bromide (Aldrich) (99.9+%) were used as received without further purification. 2-Pyridinecabaldehyde *n*-propylimine was prepared as previously reported[13] and stored in a Schlenk tube under N_2 over 3 Å molecular sieves prior to use. Solvents, toluene and THF, were dried over sodium and distilled immediately prior to use. Galvinoxyl (Aldrich) was dried under vacuum and dissolved in THF or toluene as required. AIBN (2,2′ azobis(isobutyronitrile), BDH GPR grade, was used as received.

Three monomer mixtures were prepared with the following [MMA]/[BMA] ratios: 75/25 (563.05 g of MMA, 265.57 g of BMA, [MMA]/[BMA] = 3.011), 50/50 (374.90 g of MMA, 533.89 g of BMA, [MMA]/[BMA] = 0.9973), and 25/75 (188.72 g of MMA, and 799.28 g of BMA, [MMA]/[BMA] = 0.3353).

[Bis[*μ*-[(2,3-butanedione dioximato)(2−)-O:O′]] tetrafluorodiborato(2−)-N,N′,N″,N‴]cobalt, COBF, **1**, was used as the catalytic chain transfer agent. COBF was prepared according to the procedure of Espenson[28] and was assumed to be the bis(methanol) adduct. COBF was added from a stock solution prepared by dissolving COBF (0.0104 g, 2.32×10^{-5} mol) in toluene (50 mL).



1

Polymerizations to Investigate the Effect of Inhibitor. Group Transfer Polymerization. To a 100 mL flask equipped with a nitrogen inlet were added THF (30 mL), MTS (0.057 mL, 2.8×10^{-4} mol), and TBAAc (0.137 mL of a 8×10^{-3} M solution, 2.8×0^{-6} mol) at room temperature. MMA (3 mL, 0.028 mol) was added dropwise to the stirred solution over 90 s. Galvinoxyl (0.401 g, 9.51×10^{-4} mol in 5 mL of THF) was added 45 s after addition of MMA. The reaction was stirred for a further 10 min to allow complete reaction. NMR analysis of the reaction mixture showed polymer and unreacted monomer. SEC analysis of the polymer precipitated from 60−80 petroleum ether, $M_n = 2450$, PDI = 1.91.

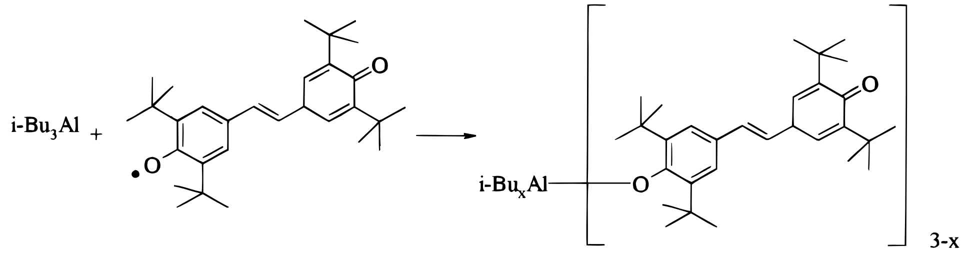
Lithium Alkyl/Aluminum Alkyl-Initiated Polymerization. Toluene (30 mL) followed by *i*-Bu_3Al (1.12 mL of a 1.0 M solution in toluene, 1.12×10^{-3} mol) and *t*-BuLi (0.33 mL of 1.7 M solution in pentane, 5.61×10^{-4} mol) were added to a 100 mL flask equipped with a nitrogen inlet. The flask was subsequently cooled in an ice/salt bath to −5 °C. MMA (3 mL, 0.028 mol) was added rapidly in one continuous addition. Galvinoxyl (0.3318 g, 7.87×10^{-4} mol in 5 mL of toluene) was added 60 s after addition of MMA. The reaction was stirred for a further 15 min. ^1H NMR analysis of the reaction mixture showed both poly(methyl methacrylate) and unreacted monomer. SEC analysis of the polymer precipitated from 60−80 petroleum ether, $M_n = 4120$, PDI = 3.71.

Reactivity Ratio Investigation. Group Transfer Polymerization. A 50 mL aliquot of THF was placed in a 250 mL flask equipped with a nitrogen inlet. Then 0.1 mL of bis(dimethylamino)methylsilane, 10 mL of MMA/*n*-BMA (50/50 mixture, 0.078 mol), 0.2 mL of TBA*m*CB of a 8×10^{-3} M solution in THF (1.56×10^{-6} mol), and 0.032 mL of MTS (1.58×10^{-4} mol) were added with stirring at ambient temperature. The reaction was allowed to proceed for 10 min, when it was terminated by the addition of 2 mL of methanol. Diphenylpicrylhydrazyl (DPPH, 0.01 g) was added prior to volatiles being removed from the reaction mixture under vacuum. The polymer product was isolated from the reaction vessel by extraction with a small quantity of dichloromethane and removal of solvent under vacuum at 60 °C until a constant weight was obtained.

Lithium Alkyl/Aluminum Alkyl Initiated Polymerization. In a typical synthesis, a solution of *i*-Bu_3Al in toluene (1.0 mL, 0.001 mol) was added to 100 mL of toluene under an atmosphere of nitrogen and cooled to −10 °C. *t*-BuLi solution (0.29 mL, 4.93×10^{-4} mol) was added to the reaction vessel and stirred for several minutes. The monomer mixture (75/25 MMA/BMA 12.0 mL, 50/50 MMA/BMA 13.3 mL, 25/75 MMA/BMA 14.6 mL) was added quickly in a single addition. Polymerization was terminated after 2 min by the addition of dilute HCl (1.0 mL) and left to stir vigorously for 15 min at room temperature. DPPH was added to the reaction mixture prior to removal of solvent, so as to inhibit further radical polymerization, under vacuum at 60 °C for 2 days.

Classical Anionic Polymerization. 1,1-Diphenylethene (0.74 mL, 4×10^{-3} mol) was dissolved in 20 mL of dry THF freshly distilled from purple sodium/benzophenone under an atmosphere of nitrogen. The solution was titrated by dropwise addition of *n*-butyllithium until a slight red coloration was

Scheme 1



observed; then a stoichiometric quantity of *n*-butyllithium (1.6 mL, 4 × 10^{-3} mol) was added with stirring over several minutes so as to maintain the reaction temperature below 40 °C. The reaction mixture was then left to stir at room temperature under nitrogen for 24 h. Freshly distilled THF (150 mL) was cooled to −78 °C in a dry ice/acetone bath and titrated under nitrogen with DPHLi until a faint red color persisted. DPHLi (0.63 mL) was added to the reaction vessel followed by addition of the monomer in a single aliquot (75/25 MMA/BMA 12.0 mL, 50/50 MMA/BMA 13.3 mL, 25/75 MMA/BMA 14.6 mL). The reaction was terminated immediately after monomer addition by injection of methanol (1 mL) into the reaction flask. 4-Methoxyphenol (0.2 g) was added to the solution as an inhibitor, and the solvent was removed under vacuum.

Conventional Free Radical Polymerization. In a typical reaction, 10 mL of each MMA/BMA mixture was degassed by three freeze−pump thaw cycles in a Schlenk tube. A 1 mL aliquot of AIBN stock solution (0.0467 g, 0.284 mmol of AIBN in 10 mL of toluene) was added. The solution was frozen, closed under vacuum, thawed to room temperature and heated to 60 °C for 60 min, after which the reaction was quenched by rapid cooling to 0 °C. Duplicate experiments were carried out in each case. The sample was dried to a constant weight *in vacuo*.

Catalytic Chain Transfer Polymerization. A 20 mL aliquot of monomer mixture and 0.03 g of AIBN (1.82 × 10^{-4} mol) were added to a Schlenk tube. COBF was added as a stock solution in toluene (0.0104 g of **1** (2.32 × 10^{-5} mol) in 50 mL of toluene). As **1** has a higher C_s for MMA than BMA,[29] more **1** was added as the proportion of *n*-BMA increased. The reaction mixture was heated at 60 °C in a constant temperature water bath for 45 min prior to being quenched by rapidly cooling to 0 °C. The sample was allowed to evaporate overnight and then placed in a vacuum oven at 60 °C until it reached a constant weight (≈3 days).

Atom Transfer Radical Polymerization. A 20 mL aliquot of monomer mixture was placed into a Schlenk tube. Copper(I) bromide (0.1391 g , 9.7 × 10^{-4} mol) and 2-pyridinecabaldehyde *n*-propylimine (0.4296 g , 2.9 × 10^{-3} mol) were added with stirring at ambient temperature. Ethyl 2-bromoisobutyrate (0.1898 g , 9.73 × 10^{-4} mol) was added, and the reactions were then placed in an oil bath (90 °C for 50 min) under N_2 prior to being quenched to 0 °C. After quenching, 1 cm^3 of 50% aqueous hydrochloric acid was added to terminate the reaction. A sample was removed and allowed to evaporate overnight and then placed in a vacuum oven at 60 °C until it reached constant weight (∼3 days).

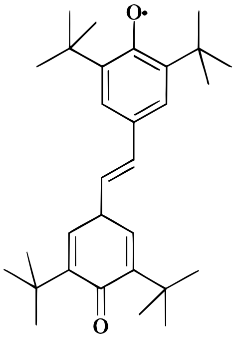
Analysis Methods. SEC was carried out using a Polymer Laboratories (PL) guard column (50 × 7.5 mm), and either one PL Mixed-E column (300 × 7.5 mm), two Mixed-D columns (300 × 7.5 mm), or two Mixed-C columns (300 × 7.5 mm). THF was used as the eluent at a flow rate of 1 mL/min, and data were collected at 1 point/s from a DRI detector. The system was calibrated with log molecular weight expressed as a third-order polynomial of elution volume based on Polymer Laboratories PMMA standards and pure samples of MMA dimer and trimer. No account was taken of the samples being copolymers, and the SEC data are presented as "PMMA equivalent" molecular weights.

Copolymer compositions were ascertained using ^{1}H NMR in $CDCl_3$ at 250 MHz by integration. These data were used in the EVM program, assuming a 1% uncertainty in the feed and a 5% uncertainty in the copolymer composition.

Results and Discussion

Effect of Galvinoxyl on Group Transfer Polymerization and *tert*-Butyllithium/Triisobutylaluminum-Initiated Polymerization of Methyl Methacrylate. The attempted polymerization of MMA using MTS initiator and TBAAc catalyst in THF at room temperature in the presence of galvinoxyl resulted in no detectable polymerization, reaction A. Addition of galvinoxyl, **2**, to a similar polymerization shortly after initiation, reaction B, results in termination of the reaction and the PMMA has a much broader molecular weight distribution than would have otherwise been expected. Thus galvinoxyl acts as an effective inhibitor for GTP of MMA.

Addition of triisobutylaluminum to a dark solution of **2** in toluene produces a red solution that immediately turns yellow on addition of *tert*-butyllithium. In contrast to the above observations with GTP, this solution polymerises methyl methacrylate to give a polymer of reasonably narrow MWD, *C*, and close to the expected M_n, assuming approximately 50% initiator efficiency,[15] M_n(theo) = 10 000 M_n(obs) = 11 600. Addition of **2** shortly after initiation, D, gives a much lower M_n with broader MWD. Addition of galvinoxyl after propagation has been completed, E, again gives a broad MWD polymer that does not reinitiate polymerization on addition of more methyl methacrylate. It appears that if **2** is added at the beginning of the reaction, then it reacts with the metal alkyls to form a new, as yet unassigned, metal-containing species that is active toward polymerization. The new species presumably contains a new aluminum−oxygen bond such as that shown in Scheme 1.



2

The reaction shown in Scheme 1 is plausible and produces a sterically hindered aluminum phenoxide species that has characteristics similar to those of previously reported aluminum species that are active in methacrylate polymerization.[15,17] Addition of **2** part

Table 1. Experimental Details and Molecular Weight Data for Inhibition with Galvinoxyl Studies

exp	polym type	galvinoxyl ($\times 10^{-4}$ mol)	addition time of galvinoxyl (min)	M_n	PDI
A	GTP	6.16[a]	0		
B	GTP	9.51[c]	2.25	2 450	1.91
C	Li/Al	5.55[a]	0	11 600	1.35
D	Li/Al	5.93[b]	1	4 120	3.71
E	Li/Al	7.87[b]	15	11 480	1.78

[a] Added as a solid at the start of the reaction. [b] Added as a solution in toluene. [c] Added as a solution in thf.

Table 2. Molecular Weight Data and Details of Experiments Carried out To Determine Reactivity Ratios

exp	polym type	composition MMA/BMA	M_n	PDI	% conversion
F	CFR	75/25	487 900	2.07	4.65
G	CFR	75/25	458 700	2.07	6.19
H	CFR	50/50	544 500	1.80	4.69
I	CFR	50/50	535 600	1.75	6.40
J	CFR	25/75	515 800	1.96	7.82
K	CFR	25/75	457 900	2.01	7.83
L	anionic	75/25	12 730	5.65	1.71
M	anionic	50/50	11 790	4.56	2.24
N	anionic	25/75	21 620	3.95	1.71
O	Li/Al	75/25	2 690	6.72	1.25
P	Li/Al	50/50	1 380	3.56	1.83
Q	Li/Al	25/75	2 790	6.96	1.13
R	GTP	75/25			2.41
S	GTP	50/50			2.18
T	GTP	25/75			3.51
U	CCTP	75/25	2 020	2.14	5.29
V	CCTP	50/50	1 610	2.14	4.43
W	CCTP	25/75	2 370	1.87	4.11
X	CCTP	25/75	2 270	1.84	4.17
Y	ATRP	75/25			4.5
Z	ATRP	50/50			5.5
AA	ATRP	25/75			0.88

way through the reaction gives rise to competition between reaction with aluminum alkyl and polymerization termination.

These results demonstrate that **2** can inhibit and terminate polymerizations occurring via an anionic *and/or* anionic type polymerization process. The mode of action of **2** can also be complicated by possible reaction to form new active *or* dormant species. The way in which **2** inhibits either of these types of MMA polymerization is as yet not fully elucidated. However, we may conclude that inhibition by **2** cannot be used as evidence to support a free radical polymerization mechanism.

Reactivity Ratios of MMA and *n*-BMA. The copolymer composition was determined in each case from ^{1}H NMR. The areas from the alkoxy region of the spectrum were used, $\delta(-OCH_3$, MMA$)$ = approximately 3.50−3.65 ppm and $\delta(-OCH_2$, BMA$)$ = approximately 3.80−4.00 ppm. These data were used in the EVM program, assuming a 1% uncertainty in the monomer feed composition and a 5% uncertainty in the copolymer composition. All reactions were carried out to low conversion, Table 2. The resultant point estimates for the reactivity ratios and 95% confidence contours are shown in Table 3 and Figure 1, respectively.

Conventional Free Radical and Anionic Polymerization. The reactivity ratios obtained for conventional free radical polymerization, reactions F−K, of $r_1 = 0.93$ and $r_2 = 1.22$ compare very favorably with those reported by Manders using a nonlinear least squares analysis with NMR data with reactions taken to approximately 0.5% conversion.[30] Surprisingly, we have been unable to find literature values for the reactivity ratios of MMA and BMA in conventional anionic polymerization in any solvent. Our values, reactions L−N, of $r_1 = 1.04$ and $r_2 = 0.81$ indicate that normal anionic polymerization in thf at −78 °C is relatively unselective toward both MMA and BMA, as would be expected. It is useful that the values are significantly different for conventional free radical polymerization and that the 95% confidence intervals do not overlap, Figure 1. This difference in reactivity ratio between classical anionic and free radical polymerization of MMA and BMA allows measuring the reactivity ratio to be used as a probe of the reaction mechanism.

Table 3. Reactivity Ratios from This Work and the Literature

	r_1 (MMA)	r_2 (*n*-BMA)	
CFR	0.93	1.22	this work
CFR	0.91	1.09	ref 30
CFR	0.79	1.27	ref 37
CFR	1.27	1.20	ref 38
ATRP	0.98	1.26	this work
CCTP	0.75	0.98	this work
anionic	1.04	0.81	this work
Li/Al	1.10	0.72	this work
GTP	1.76	0.67	this work
GTP	0.44	0.26	ref 31
GTP	0.52	0.34	ref 31[a]

[a] Data taken from ref 31 reanalyzed using the EVM program.

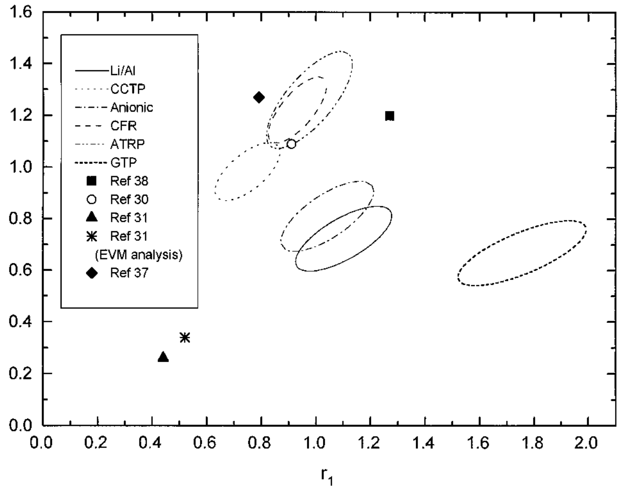


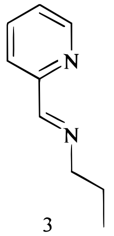
Figure 1. Plot of the reactivity ratio data from this work and literature values.

***tert*-Butyllithium/Triisobutylaluminum-Initiated Polymerization.** Reactions were carried out at −10 °C so as to slow the rate of propagation so that less than 10% conversion was reached after 2 min, prior to termination by the addition of acid, reactions O−Q. The molecular weight distributions from these experiments are broader than would be expected in this type of "*living*" polymerization due to the constraints on the experimental procedure from the speed of the reaction. However, this increased MWD is not expected to affect the reactivity ratios appreciably. Both r_1 and r_2 are similar to those for conventional anionic polymerization, 1.10 and 0.72, respectively. The 95% confidence level overlaps with conventional anionic polymerization but not with free radical polymerization, Figure 1. As anionic polymerization is well-known to exhibit strong solvent and temperature effects, this is a striking similarity. Again, this polymerization shows little selectivity between the two monomers and it is concluded that *tert*-butyllithium/triisobutylaluminum initiated-polymerization proceeds via an enol anion in an anionic type polymerization.

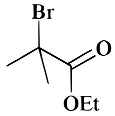
Group Transfer Polymerization. The reactivity ratios determined are $r_1 = 1.76$ and $r_2 = 0.67$, reactions R−T. The 95% confidence ellipse does not overlap with values for either anionic or free radical polymerization. This is strong evidence to suggest that GTP is neither radical or anionic. The differences in GTP with anionic polymerization are also good evidence for a coordinative associative mechanism as opposed to a dissociative mechanism, in accordance with Webster.[2] GTP is significantly more selective than either anionic or *tert*-butyllithium/triisobutylaluminum-initiated polymerization. If low concentrations of enol propagating centers are responsible for propagation, a dissociative mechanism, we would expect reactivity ratios similar to those of anionic polymerization. It is also interesting to compare our values with those reported by Jenkins.[31] It is noted that in this previous study polymerizations were taken to 20% conversion using tris(dimethyl)sulfonium biflouride/acetonitrile as catalyst. The data were analyzed using the unreliable Kelen−Tudos methodology.[32] Even when the data are reanalyzed with the EVM program, Table 3, the values determined in the present work are significantly different from those reported by Jenkins. These literature values are also significantly different from those for conventional anionic polymerization. The literature values are consistent with each propagating polymer preferring to cross propagate as opposed to undergoing homopolymerization. Our data show that the rate of reaction of MMA is faster than that of BMA with both propagating poly(methyl methacrylate) and poly(butyl methacrylate). This is what might be expected on the basis of steric considerations. Indeed, the observation by Jenkins that *both* reactivity ratios are less than unity is somewhat surprising. All other studies of GTP reactivity ratios in the literature give two values that are either side of unity. Catalgilgiz reports[33−35] $r_{\mathrm{MMA}} = 1.24{-}1.25$ and $r_{\mathrm{EMA}} = 0.30{-}0.34$ for the GTP of EMA and MMA; these values were calculated using statistically sound linearized semiintegral and nonlinear fully integrated methods.[35] This study supports our observations with the BMA/MMA system. The catalysts used by Jenkins and in the present work are different, Jenkins used bifluoride as opposed to an oxygen-centered TBA*m*CB. The bifluoride is a harder nucleophile and might be expected to promote a more dissociative mechanism; also the formation of trimethylsilyl fluoride from dissociation might be expected to be favored. Clearly, the nature of the catalyst plays an important role in determining the extent of dissociation in GTP. Nevertheless, these two sets of results indicate that the mechanism of GTP under these conditions is not by a purely dissociative mechanism. In addition to this, the mechanism of GTP seems to be dependent upon the exact reaction conditions, especially on the nature of the catalyst used.

Catalytic Chain Transfer Polymerization. As we have previously reported,[26] CCTP gives reactivity ratios that are consistent with a free radical polymerization mechanism. The data are consistent with results reported by Manders,[30] reactions U−X. The mechanism of CCTP is seen to proceed via a free radical mechanism. The relatively poor overlap between conventional free radical and CCTP might be due to the low molecular weight polymers produced by CCTP, which possibly lead to a violation of the long chain assumption used in the analysis.

Atom Transfer Radical Polymerization. ATRP using the Schiff base complex **3** as ligand in conjunction with Cu$^{\mathrm{I}}$Br and ethyl 2-bromoisobutyrate, **4**, give reactivity ratios of $r_1 = 0.98$ and $r_2 = 1.26$, Table 3, reactions Y−AA, and Figure 1. The 95% confidence limit completely encompasses that obtained from conventional free radical polymerization, indicating a similar mechanism. Thus, reactivity ratios show ATRP is consistent with a free radical mechanism. It is noted that addition of radical inhibitors to ATRP reactions have been reported to inhibit polymerization. However, work by the current authors has shown that this is not necessarily the case.[36]



3



4

General Discussion. The r_1r_2 products for our point estimates for classical radical polymerization and GTP are 1.13 and 1.18, respectively. It is generally believed that $r_1r_2 = 1$ represents the upper limit for proper copolymerization. Recent work aimed at precise estimation of the classical free radical reactivity ratios indicates that for radical copolymerization the product lies within these limits.[30] Similar data are not available for GTP. As alluded to earlier, a value of $r_1r_2 > 1$ may be plausible for steric reasons in GTP. However, the confidence ellipse for GTP does contain a region where $r_1r_2 < 1$. Therefore, the product of the ratios for GTP and classical radical polymerization cannot be distinguished from unity within experimental error. It is worth noting that there are many systems in the literature, even free radical copolymerizations, which contradict the belief that $r_1r_2 = 1$ represents the upper limit for proper copolymerization. For example the table of free radical reactivity ratios in the popular text book Cowie lists reactivity ratios where unity is exceeded for the products of 5 of the 19 monomer pairs listed.[39] Analysis for sequence distribution has not been carried out and thus we cannot comment on copolymer homogeneity, although we have no reason to believe that there is marked inhomogeneity. It is also noted that solvent effects tend to be small or negligible in free radical polymerizations. However, this will not necessarily be the case for nonradical polymerization.

Conclusions

The reactivity ratios for the MMA/BMA monomer pair differ for anionic and free radical polymerization. A measure of these values for new polymerization mechanisms gives an indication of how the propagation in each system proceeds. *tert*-Butyllithium/triisobutylaluminum-initiated polymerization proceeds via a classical anionic mechanism and a stabilized enol anion. GTP differs from this and other reactivity ratios, favoring an associative mechanism. However, the mechanism of GTP does seem to be highly dependent upon the reaction conditions, when literature values for reactivity ratios are considered along with the current data. Both CCTP and ATRP are consistent with a free radical propagation step. Galvinoxyl has been demonstrated to inhibit GTP and also play a role in metal alkyl initiated anionic polymerization, the mechanism of this inhibition is as yet undetermined. As such the effects of radical inhibitors on a polymerization cannot be used as a definitive mechanistic test. This coupled with the stereochemistry of poly(methacrylates) being similar in GTP and conventional free radical polymerization results in a new more reliable indication of the polymerization mechanism being required. Reactivity ratios have been demonstrated to give such an indication. The use of a reliable statistical interpretation of suitably resolved ^{1}H NMR spectra is an excellent mechanistic probe. It is apparent that the differences in polymerization mechanism highlighted by reactivity ratios were anticipated, as discussed earlier. This approach is, however, limited to polymerization processes with an appropriate monomer set.

Acknowledgment. We would like to thank the EPSRC (K.G.S., ROPA:GR/K35952; M.C.C., GR/33538; C.W., ROPA:GR/K65652) and ICI (C.T.) for funding. We would also like to thank Andrew Shooter and Dr. Stuart Richards for invaluable discussions and ICI Acrylics for monomers.

References and Notes

(1) Davis, T. P.; Haddleton, D. M.; Richards, S. N. *J. Macromol. Sci., Rev. Chem. Phys.* **1994**, *C34*, 243.
(2) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; Rajan Babu, T. V. *J. Am. Chem. Soc.* **1983**, *105*, 5706.
(3) Eastmond, G. C.; Webster, O. In *New Methods for Polymer Synthesis*; Eastmond, G. C., Webster, O., Eds.; Blackie: Glasgow, 1991.
(4) Sogah, D. Y.; Farnham, W. B. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1982**, *27*, 167.
(5) Quirk, R. P.; Bidinger, G. P. *Polym. Bull.* **1989**, *22*, 63.
(6) Webster, O. W. *Science* **1991**, Feb. 887.
(7) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721.
(8) Kotani, Y.; Kato, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1996**, *29*, 6979.
(9) Matyjaszewski, K.; Wang, J.-S. *Macromolecules* **1995**, *28*, 7901.
(10) Wang, J.-S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614.
(11) Percec, V.; Barboiu, B.; Neumann, A.; Ronda, J. C.; Zhao, M. *Macromolecules* **1996**, *29*, 3665.
(12) Granel, C.; Teyssie, P.; DuBois, P.; Jerome, P. *Macromolecules* **1996**, *29*, 8576.
(13) Haddleton, D. M.; Jasieczek, C. B.; Hannon, M. J.; Shooter, A. J.; *Macromolecules* **1997**, *30*, 2190.
(14) Sogah, D. Y.; Hertler, W. R.; Webster, O.; Trost, B. M. *Macromolecules* **1988**, *21*, 1473.
(15) Ballard, D. G. H.; Bowles, R. J.; Haddleton, D. M.; Richards, S. N.; Sellens, R. J.; Twose, D. L. *Macromolecules* **1992**, *25*, 5907.
(16) Kitayama, T.; Shinozaki, T.; Sakamoto, T.; Yamamoto, M.; Hatada, K. *Macromol. Chem. Suppl.* **1989**, *15*, 167.
(17) Kuroki, M.; Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1987**, *109*, 4739.
(18) Webster, O.; Anderson, B. C. In *New Methods of Polymer Synthesis*; Mijs, W. J., Ed.; Plenum: New York, 1992; p 1.
(19) Davis, T. P.; Kukulj, D.; Haddleton, D. M.; Maloney, D. R. *Trends Polym. Sci.* **1995**, *3*, 365.
(20) Haddleton, D. M.; Maloney, D. R.; Suddaby, K. G. *Macromol. Chem. Phys., Macromol. Symp.* **1996,** *111*, 37.
(21) Moad, G.; Solomon, D. H. *The Chemistry of Free Radical Polymerization*; Pergamon: Bath, 1995.
(22) Rudin, A. *The Elements of Polymer Science and Engineering*; Academic Press: New York, 1982.
(23) Odian, G. *Principles of Polymerization*, 2nd ed.; John Wiley & Sons: New York, 1981.
(24) Dube, M.; Sanayei, R. A.; Penlidis, A.; O'Driscoll, K. F.; Reilly, P. M. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 703.
(25) Tidwell, P. W.; Mortimer, G. A. *J. Polym. Sci., Polym. Chem.* **1965**, *3*, 369.
(26) Suddaby, K. G.; Hunt, K. H.; Haddleton, D. M. *Macromolecules* **1996**, *29*, 8642.
(27) Dicker, I. B.; Cohen, G. M.; Farnham, W. B.; Hertler, W. R.; Laganis, E. D.; Sogah, D. Y. *Macromolecules* **1990**, *23*, 4034.
(28) Bakac, A.; Brynildson, M. E.; Espenson, J. H. *Inorg. Chem.* **1986**, *25*, 4108−4114.
(29) Haddleton, D. M.; Maloney, D. R. *Unpublished results.*
(30) Manders, B. G.; Smulders, W.; Aerdts, A. M.; van Herk, A. *Macromolecules* **1997**, *30*, 322.
(31) Jenkins, A. D.; Tsartolia, E.; Walton, D. R. M.; Stejskal, J.; Kratochvil, P. *Polym. Bull.* **1988**, *20*, 97.
(32) Kelen, T.; Tudos, F. *J. Macromol. Sci. (Chem.)* **1975**, *A9*, 1.
(33) Catalgilgiz, H.; Uyanik, N.; Erbil, C. *Polymer*, **1992**, *33*, 655.
(34) Onculkoc, A.; Catalgilgiz, H. *Macromol. Chem. Phys.* **1995**, *196*, 2475.
(35) Catalgilgiz, H. *Macromol. Chem. Phys.* **1996**, *197*, 2647.
(36) Shooter, A. J.; Haddleton, D. M. Unpublished work.
(37) Bevington, J. C.; Harris, D. O. *J. Polym. Sci., Part B: Polym. Lett.* **1967**, *5*, 799.
(38) Musha, Y.; Hori, Y.; Sato, Y., Katayama, M. *Nihon Daigaku Kogakubu Kiyo, Bunrui A* **1985**, *26*, 175.
(39) Cowie, J. M. G. *Polymers: Chemistry and Physics of Modern Materials*; Intext Educational Publishers: London, 1973.

MA970303M