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POLYMERIZATION BY ALKALINE EARTH METAL COMPOUNDS—I

STUDIES ON THE POLYMERIZATION OF METHYLMETHACRYLATE BY TRIPHENYLMETHYL METAL DERIVATIVES AND RELATED COMPOUNDS OF CALCIUM, STRONTIUM AND BARIUM

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Abstract—A series of related organo-alkaline earth metal compounds of formula $(Ph_3C)MX(THF)_n$, (M = Ca, Sr, Ba; X = Cl; M = Ca, Sr; X = Br; M = Ba; X = CPh_3), has been isolated and characterized using analytical and spectroscopic techniques. The polymerization of methylmethacrylate (MMA) has been studied using these organometallic compounds as initiators. Investigations of the tacticity variations of polymethylmethacrylate (PMMA) produced in 1,2-dimethoxyethane or tetrahydrofuran (THF) at 210 K have shown that the syndiotacticity is higher in the former solvent, decreases with the following changes in initiator composition: Ca > Sr $\geqslant$ Ba; Cl > Br; in THF, it is dependent on the monomer concentration. The molecular weight distributions of the PMMA samples are broad and have distinct bi- or poly-modal features. The polymerization process appears to be anionic in nature but the evidence suggests that more than one type of propagation occurs and mechanistic aspects are discussed. Polymerization of bulk MMA by these same initiators is also reported. The initiators $RMX(THF)_n$ (M = Sr, R = Me, $n = 3$ or R = Et, $n = 2$) and $(C_3H_5)SrBr(THF)_2$ are shown to be inefficient for polymerization of MMA. The glass transition temperatures of a range of PMMA samples of differing tacticity are presented and discussed.

INTRODUCTION

Organometallic compounds of the alkaline earth elements, Ca, Sr and Ba, have not been extensively investigated as initiators for polymerizations. One reason for this lack of attention has been the relative difficulty in preparation of well characterized organometallic species of these elements when compared to analogous derivatives of the much studied alkali metals or magnesium [1]. The compounds of larger, dipositive group II metals, however, may exhibit significant differences in initiation and propagation stages of polymerizations and a detailed comparative investigation of such systems should prove to be of interest.

There have been several reports that calcium, strontium and barium compounds will cause polymerization of vinyl or diene monomers in ethereal or hydrocarbon solvents. Arest-Yakubovich and coworkers have described mechanistic studies of polymerization of styrene, butadiene and isoprene by adducts of 1,1-diphenylethylene with barium [2] or strontium [3] and also by dibenzyl-barium [4] or -strontium [5] and by ditriphenylmethylbarium [6]. Mathis and François *et al.* have used characterized barium and strontium [7] compounds in studies of styrene polymerization [8] and related work employing a barium initiator has also been reported by Szwarc [9]. These results have demonstrated differences from normal organo-alkali metal polymerizations.

Ate complexes produced from dialkylzinc compounds and alkaline earth metals were early shown to be effective initiators for polymerization of vinyl monomers, including acrylic esters [10], but the mode of polymerization by these bimetallic species is not clear. Work in this laboratory has identified several well characterized organocalcium compounds as initiators for homogeneous polymerization of methylmethacrylate (MMA) and an anionic type mechanism was postulated [11]. A brief note on the polymerization of MMA by the barium adduct of 1,1-diphenylethylene has appeared and a copolymerization study also supports an anionic propagation for this system [12]. Polymerizations by finely divided metals have been studied by François *et al.* and heterogeneous initiation of MMA by calcium, strontium or barium provides evidence for the occurrence of both anionic and radical pathways [13].

Many studies of magnesium compounds as polymerization initiators have been carried out (see [14] for earlier work). MMA polymerizations by organo-magnesium compounds have proved to have complex features and recently it has been proposed that several distinct polymerization processes may occur with eneidic pseudo-anionic mechanisms [15].

In this work we report a study of the polymerization of MMA in ethereal solvents by a series of closely related, characterized alkaline-earth metal compounds, Ph_3CMX (M = Ca, Sr, Ba, X = Cl;

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M = Ca, Sr, X = Br; M = Ba, X = Ph_3C) and other compounds RMX, (M = Sr, R = Me, Et, X = I; M = Sr, R = allyl, X = Br). These compounds were isolated as solid tetrahydrofuran (THF) adducts, $RMX(THF)_n$, (n = 1–5).

EXPERIMENTAL

1. *Preparation of initiators*

All manipulations were carried out under vacuum or an atmosphere of dry nitrogen. Solvents were purified and dried by previously described techniques [16].

(a) *$Ph_3CCaCl(THF)_2$*. This was prepared as a red crystalline solid by the method described by Masthoff [17].

(b) *$Ph_3CSrCl(THF)_4$*. Prepared by a similar method to above by stirring excess strontium amalgam (10%) with triphenylmethylchloride (4 g) in THF (75 ml) for 16 hr at room temperature. The red suspension was decanted from excess amalgam, the solid product collected by filtration, washed and dried under vacuum at room temperature. Yield 64%. Found Sr: 13.85%, Cl: 5.5%, Base: 35.2%; Calculated for $C_{35}H_{47}ClO_4Sr$, Sr: 13.4%, Cl: 5.4%; Base: 37.1%. Ratio THF:Ph_3C (from ^1H NMR) 3.8:1.

(c) *$Ph_3CBaCl(THF)_2$*. Prepared as in (b) using barium amalgam at room temperature, 48 hr. Yield 17%. Found Ba: 25.1% Cl: 6.6%. Calculated for $C_{27}H_{31}ClO_2Ba$, Ba: 24.4%; Cl: 6.3%. Ratio THF:Ph_3C (from ^1H NMR) 1.8:1. The solvent was removed from the filtrate of this reaction under vacuum to yield a dark red oil which, after recrystallization from toluene, formed a red solid shown to be $(Ph_3C)_2Ba(THF)_2$. Found Ba: 16.6%; Cl: 0%. Calculated for $C_{46}H_{48}O_2Ba$, Ba: 17.8%. Ratio THF:Ph_3C (from ^1H NMR) 1:1.

(d) *$Ph_3CCaBr(THF)_4$*. Prepared by a similar method to (b) using Ph_3CBr (purified by reprecipitation from dry hexane/acetylbromide, 100/20), 48 hr. Yield 70–80%. Found, Ca: 6.2%; Br: 12.1%. Calculated for $C_{35}H_{47}BrO_4Ca$, Ca: 5.9%; Br: 11.8%. Ratio THF:Ph_3C (from ^1H NMR) 4.1:1.

(e) *$Ph_3CSrBr(THF)_5$*. Prepared as above. Yield 70–80%. Found, Sr: 10.9%; Br: 10.1%. Calculated for $C_{39}H_{55}BrO_5Sr$, Sr: 10.9%; Br: 10.0%. Ratio THF:Ph_3C (from ^1H NMR) 5.2:1.

(f) *$C_3H_5SrBr(THF)_2$*. Redistilled, dried allyl bromide was distilled into a suspension of strontium amalgam (10%) in THF (75 ml). The reaction was stirred at room temperature for 48 hr; during this time, a white precipitate was produced. It was collected, washed well with THF and dried under vacuum. Found, Sr: 24.6%; Br: 22.3%. Calculated for $C_{11}H_{21}BrO_2Sr$, Sr: 24.8%; Br: 22.4%. Qualitative gas chromatographic analysis of hydrolysis products showed the major hydrocarbons present to be propene and propane (1:0.84).

(g) *$CH_3SrI(THF)_3$ and $C_2H_5SrI(THF)_2$*. These were prepared as previously reported [16].

2. *Polymerization reactions*

Solvents, THF and 1,2-dimethoxyethane(DME), were predried over sodium and distilled twice from naphthalene–sodium before use. MMA and styrene were purified by standard techniques and distilled at least six times under vacuum over 72 hr from stirred samples containing freshly powdered CaH_2. Polymerizations were carried out in sealed tubes under vacuum under conditions given in Tables 1–5 after distilling monomer(s) into a solution of initiator ($4–8 \times 10^{-3}$ mol l^{-1}) in THF or DME (*c*. 25 ml) at 77 K. Polymerizations were terminated by addition to methanol and the methanol insoluble products purified by reprecipitation from benzene solution by dropwise addition to methanol at *c*. −30°C.

3. *Instrumentation*

GPC measurements were carried out by RAPRA, Shrewsbury, England, using THF solvent at ambient temperature with a 4 column set (1×10^6, 1×10^5, 1×10^4 and 1×10^3 Å). ^1H NMR spectra of polymethylmethacrylate were recorded in bromobenzene at 120°C using a 100 MHz JEOL MH100 spectrometer. Glass transition temperatures (T_g) were measured using a Dupoint 900 Differential Thermal Analyser with Differential Scanning Calorimeter attachment.

RESULTS

1. *Polymerization by triphenylmethyl derivatives*

(i) *In 1,2-Dimethoxyethane (DME)*. Initiation of polymerization of MMA by triphenylmethyl derivatives of Ca, Sr and Ba occurred readily in DME at 210 K giving high conversion to polymethylmethacrylate (PMMA) within 15–30 min. Data for some representative polymers produced from reactions using a range of initiators are given in Table 1. These samples were reprecipitated from benzene by methanol and there was no evidence for methanol soluble polymeric products. The initial stages of these polymerizations were completely homogeneous but after approximately 30 min it was usually found that the polymer solutions formed a gel (see below for further discussion).

The fraction of triad stereochemical configurations (*S*, *H*, *I*) obtained by analysis of the ^1H NMR reso-

Table 1. Data for polymethylmethacrylate produced in 1,2-dimethoxyethane at 210 K

	Initial monomer concentration (mol l^{-1})	Conversion (%)	Triad fractions*							Molecular weights†	
			S	*H*	*I*	α_i‡	α_s‡	μ_i§	μ_s§	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
$Ph_3CCaCl(THF)_2$	2.9	60	0.88	0.12				1.0	15.7	12.8	5.2∥
$Ph_3CCaCl(THF)_2$	0.40	91	0.785	0.18	0.04	0.32	0.76	1.4	9.7	9.1	2.3
$Ph_3CSrCl(THF)_4$	1.9	100	0.535	0.33	0.14	0.52	0.71	1.8	4.2	4.7	4.0
$Ph_3CBaCl(THF)_2$	3.0	80	0.39	0.35	0.25	0.52	0.59	2.4	3.2	2.35	13.8
$Ph_3CCaBr(THF)_4$	2.0	64	0.66	0.24	0.115	0.31	0.61	2.0	6.5	4.0	3.8
$Ph_3CSrBr(THF)_5$	1.6	52	0.58	0.32	0.10	0.58	0.80	1.6	4.6	8.8	5.4
$(Ph_3C)_2Ba(THF)_2$	1.8	54	0.49	0.30	0.21	0.40	0.54	2.4	4.3	6.4	11.2

* ±5%.

† Overall average molecular weight data obtained from GPC traces.

‡ $\alpha_i = P_{si}/P_{ii}$, $\alpha_s = P_{is}/P_{ss}$; see Ref. [18].

§ Number average isotactic (μ_i) and syndiotactic (μ_s) block lengths.

∥ Separable into two components (i) $\bar{M}_n = 1.1 \times 10^5$, $\bar{M}_w/\bar{M}_n = 1.7$, (ii) $\bar{M}_n = 1.6 \times 10^6$, $\bar{M}_w/\bar{M}_n = 2.2$.

nances of α-methyl hydrogens shows these polymers to be prevalently syndiotactic. The influence of initial monomer concentration on the resulting triad structure was shown to be relatively small; thus a change from 2.9 to 0.40 mol l^{-1} resulted in a decrease in the racemic dyad fraction ($s = S + H/2$) from 0.94 to 0.875 (see Table 1). On changing the metal, M, in initiators $Ph_3CMX\ (THF)_n$, the syndiotactic content falls markedly in the order M = Ca > Sr > Ba (X = Cl or Br). If X is varied from Cl to Br the fraction of syndiotactic triads is reduced appreciably when M = Ca but is little changed when M = Sr. The triad analyses show divergence from a Bernoullian distribution. Calculating the relative probabilities for formation of the various triads from racemic (*s*) or meso (*i*) dyads, $P_{ii} = I/i$, $P_{is} = 1 - P_{ii}$, $P_{ss} = S/s$, $P_{si} = 1 - P_{ss}$, gives the ratios $\alpha_i = P_{si}/P_{ii}$ and $\alpha_s = P_{is}/P_{ss}$ [18]. The divergence of α values from unity are marked and may indicate the dependence of the polymer structure on penultimate effects [18]. Such values for α_i and α_s are not found in polymerizations of MMA by butyllithium in THF under similar conditions [19]. The number-average length of isotactic and syndiotactic blocks $\mu_i = 2i/H$ and $\mu_s = 2s/H$ are also given in Table 1.

Gel permeation chromatography (GPC) on these polymers in all cases revealed a broad molecular weight distribution (MWD) with $\bar{M}_w/\bar{M}_n \gg 1$ (Table 1) and generally showed more than one distinct peak or inflection, indicative of a bi- or poly-modal nature. A typical GPC trace for these polymers is shown in Fig. 1(A), overall average molecular weights $\bar{M}_n = 1.3 \times 10^5$, $\bar{M}_w/\bar{M}_n = 5.2$. A relatively broad low molecular weight peak ($\bar{M}_n = 1.1 \times 10^5$) can be separated from an accompanying broader high molecular weight fraction ($\bar{M}_n = 1.6 \times 10^6$). This component analysis of the GPC trace gives more realistic values for the polydispersity ratios, $\bar{M}_w/\bar{M}_n = 1.7$ and 2.2, respectively. Similar fractional analyses can be made, with varying degrees of precision, for the other GPC traces.

(ii) *In Tetrahydrofuran (THF).* Polymerization of MMA also occurs readily in THF at 210 K and again high conversion to PMMA can be obtained. The product is methanol insoluble and there is no evidence for significant amounts of low molecular weight polymers. Data for some representative examples are given in Table 2. As in DME, most reactions, including those producing polymers listed in Table 2, formed a gel after approx. 30–60 min but some reactions were deliberately terminated before the onset of gelation and results for polymers produced under these conditions are presented in Table 3.

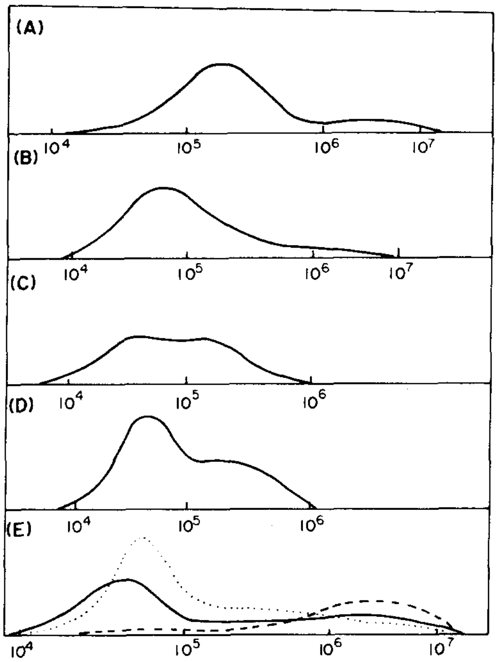

Fig. 1. GPC traces for PMMA initiated by $Ph_3CCaCl(THF)_2$ at 210 K. (A) In DME, initial monomer concentration $[M_0] = 2.9$ mol l^{-1}; (B) In THF, $[M_0] = 0.26$ mol l^{-1}; (C) In THF, $[M_0] = 0.41$ mol l^{-1}; (D) In THF, without gel formation, $[M_0] = 0.62$ mol l^{-1}, (E) In THF, without gel formation, $[M_0] = 1.33$ mol l^{-1}, (——) overall GPC, (- - - -) high MW fraction, (· · · · · ·) low MW fraction (see text).

The polymer triad fractions produced in THF and DME under similar reaction conditions differ considerably. In THF the syndiotactic content is invariably lower and in some samples isotactic content predominates.

In samples of similar reactant concentrations in THF, the syndiotactic content of PMMA decreases with variation of initiator $Ph_3CMX(THF)_n$ in the orders Ca > Sr ~ Ba (X constant) and Cl > Br (M constant). The initial monomer concentration was found to have an important effect on the sterochemistry of the resulting polymer, in contrast to results obtained in DME solutions. Results obtained from varying concentrations of MMA are presented in Table 4, Table 3 (no gel formation) and illustrated

Table 2. Data for polymethylmethacrylate produced in tetrahydrofuran at 210 K*

Initiator	Initial monomer concentration (mol l^{-1})	Conversion (%)	Triad analysis S	H	I	α_i	α_s	μ_i	μ_s	Molecular weights $\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
$Ph_3CCaCl(THF)_2$	0.90	88	0.51	0.34	0.15	0.53	0.71	1.9	4.0	5.9	4.2
$Ph_3CSrCl(THF)_4$	0.98	100	0.25	0.30	0.45	0.50	0.40	4.0	2.7	5.7	2.5
$Ph_3CBaCl(THF)_2$	1.00	72	0.23	0.46	0.31	0.88	0.86	2.3	2.0	3.1	1.9
$Ph_3CCaBr(THF)_4$	0.98	100	0.26	0.30	0.44	0.49	0.40	3.9	2.8	4.1	2.8
$Ph_3CSrBr(THF)_5$	0.86	76	0.14	0.26	0.605	0.59	0.34	5.7	2.1	2.3	4.0
$(Ph_3C)_2Ba(THF)_2$	1.54	56	0.31	0.43	0.26	0.74	0.77	2.2	2.4	4.2	2.8

* See footnotes for Table 1.

Table 3. Data for polymethylmethacrylate produced in tetrahydrofuran at 210 K without formation of a gel*

Initial monomer concentration (mol l^{-1})	Conversion (%)	Triad fractions S	H	I	α_i	α_s	μ_i	μ_s	Molecular weights $\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
0.62	31	0.72	0.24	0.04	0.57	0.87	1.3	7.0	5.4	2.8
0.62	78	0.68	0.26	0.05	0.57	0.86	1.4	6.2	5.9	2.3
1.14	13	0.655	0.29	0.06	0.62	0.87	1.4	5.6	3.4	2.0
1.70	71	0.65	0.28	0.07	0.53	0.81	1.5	5.7	3.5	2.4
1.93	52	0.62	0.30	0.08	0.55	0.80	1.5	5.2	5.9	8.8

* See footnotes for Table 1.

Table 4. Data for polymethylmethacrylate produced in tetrahydrofuran at 210 K with varying initial monomer concentration*

	Initial monomer concentration (mol l^{-1})	Conversion (%)	Triad fractions S	H	I	α_i	α_s	μ_i	μ_s	Molecular weight $\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
$Ph_3CCaCl(THF)_2$	0.26	92	0.515	0.30	0.19	0.40	0.57	2.2	4.4	5.9	5.1
$Ph_3CCaCl(THF)_2$	0.73	99	0.66	0.25	0.09	0.39	0.69	1.7	6.3	6.8	5.0
$Ph_3CCaCl(THF)_2$	0.90	88	0.51	0.34	0.15	0.53	0.71	1.9	4.0	4.6	8.7
$Ph_3CCaCl(THF)_2$	2.11	62	0.515	0.35	0.14	0.56	0.74	1.8	4.3	4.3	3.8
$Ph_3CCaCl(THF)_2$	2.62	85	0.46	0.36	0.17	0.58	0.71	2.0	7.5	7.5	11.6
$Ph_3CCaCl(THF)_2$	3.61	63	0.38	0.31	0.31	0.43	0.46	3.0	7.8	7.8	3.0
$Ph_3CCaBr(THF)_4$	0.67	36	0.17	0.23	0.605	0.49	0.27	6.3	2.4	—	—
$Ph_3CCaBr(THF)_4$	0.98	100	0.26	0.30	0.44	0.49	0.40	4.0	2.8	4.1	2.8
$Ph_3CCaBr(THF)_4$	1.81	39	0.185	0.29	0.53	0.55	0.38	4.7	2.3	1.8	5.4
$Ph_3CCaBr(THF)_4$	3.34	85	0.11	0.28	0.615	0.69	0.42	5.4	1.8	1.65	3.1

* See footnotes for Table 1.

graphically in Fig. 2 with respect to syndiotactic dyad content. At high monomer concentration, the syndiotactic content decreases but when gels are produced there are notable variations in sterochemistry in polymers produced from intermediate concentrations. In experiments terminated before gel formation, the syndiotactic fraction is higher but variation in polymer stereochemistry with monomer concentration was still observed.

GPC studies show that all these polymers, as in related samples from DME, have very broad MWD and in many cases possess distinct bi- or poly-modal features. These poly-modal distributions occur for polymers produced both in the presence and absence of gel (see Fig. 1). Some polymer samples with distinct bi-modal distributions were fractionated into high and low MW fractions by controlled addition of methanol to a solution of PMMA in toluene at 0°C. GPC analyses of one set of products are illustrated in Fig. 1(E). Tacticity measurements showed distinct differences in stereochemistry between high and low MW fractions, e.g. triad analyses for the example presented were $S = 0.58$, $H = 0.28$; $I = 0.14$ and $S = 0.70$, $H = 0.24$, $I = 0.06$ respectively (original polymer $S = 0.61$, $H = 0.28$, $I = 0.11$). The results generally show a higher isotactic content in the high MW material and support the presence of more than one propagation mechanism in these systems.

An ESR study showed that low concentrations (<2%) of the triphenylmethyl radical, $Ph_3C^{\cdot}$, ($g_{iso} = 2.0026$ from Ph_3CCaBr in THF) were present in solutions of the free initiators in ethereal solvents but attempts to polymerize MMA by $Ph_3C^{\cdot}$ radicals (produced from Ph_3CCl and mercury) under conditions similar to the other experiments were unsuccessful. Furthermore, attempted copolymerization of MMA and styrene in varying initial concentrations using Ph_3CMX initiators in THF solutions afforded polymers which, from ^1H NMR evidence, contained no styrene units.

(iii) *In absence of solvent.* Initiation of polymerization of bulk MMA by $Ph_3CMX(THF)_n$ was slow and conversion to polymer, even after 12 hr, was low.

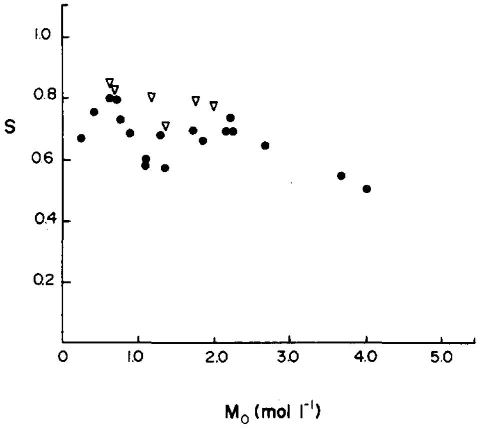

Fig. 2. Syndiotactic dyad content (S) in PMMA initiated in THF by $Ph_3CCaCl(THF)_2$ as a function of initial monomer concentration in solution, M_0 (●) with gel formation, (▽) without gel formation.

Table 5. Data for polymethylmethacrylate produced from undiluted monomer at 288 K

	Conversion	Triad fractions*			Molecular Weights†	
Initiator	(%)	*S*	*H*	*I*	$\bar{M} \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
$Ph_3CCaCl(THF)_2$	14	0.30	0.35	0.35	8.5	11.8
$Ph_3CSrCl(THF)_4$	10	0.25	0.34	0.42		
$Ph_3CCaBr(THF)_4$	59	0.42	0.34	0.25	2.0	16.6
$Ph_3CSrBr(THF)_5$	18	0.12	0.22	0.66	4.0	5.3

* ±5%.

† Overall molecular weight data from GPC distributions.

Results are shown in Table 5 for reactions carried out at 25 C. It must be noted that THF of solvation is present in 2–5 mol per mol of initiator so that this may influence the resulting polymerization.

2. *Polymerization by other initiators*

Although a preliminary study had previously suggested that alkyl strontium halides might act as polymerization initiators [16], $MeSrI(THF)_3$ and $EtSrI(THF)_2$ were found to be inefficient initiators for polymerization of MMA. In DME at 195 K over 36 hr neither initiator was active but after warming to ambient temperatures for a further 36 hr $EtSrI(THF)_2$ gave a 12% conversion to PMMA ($S = 0.675$, $H = 0.325$).

The allyl derivative (C_3H_5) $SrBr(THF)_2$, was also an inefficient initiator and only at ambient temperatures in DME was PMMA produced (8%). Polymer stereochemistry was predominantly syndiotactic ($S = 0.74$, $H = 0.26$) but a broad GPC trace ($\bar{M}_n = 19.8 \times 10^4$, $\bar{M}_w/\bar{M}_n = 20.8$) could be easily separated into two components ($\bar{M}_n = 1.85 \times 10^6$ $\bar{M}_w/\bar{M}_n = 2.7$; $\bar{M}_n = 2.3 \times 10^4$, $\bar{M}_w/\bar{M}_n = 1.3$).

3. *Glass transition temperatures* (T_g)

The wide range of syndiotactic dyad contents of the polymers permitted the study of the dependence of T_g upon polymer tacticity. Figure 3 shows the variation in T_g with % syndiotactic dyad content. A general increase in T_g with increasing syndiotacticity is evident although wide deviations from a smooth trend are apparent. It is of interest that the general trend implies a T_g for 100% syndiotactic PMMA of *c*. 133°C. This value is in general agreement with that of *c*. 125°C currently in general favour and is considerably less than that of 160 C obtained by extrapolation of the early data of Thomson [20] and Wittman and Kovacs [21]. However, the T_g data appear to show a dependence upon thermal history of the sample; it is possible that such a dependence results from the formation of local order within the polymers. The phenomenon is subject to continued study in this laboratory.

DISCUSSION

Polymerization of MMA by monofunctional group 1A metal initiators at low temperatures in ethereal

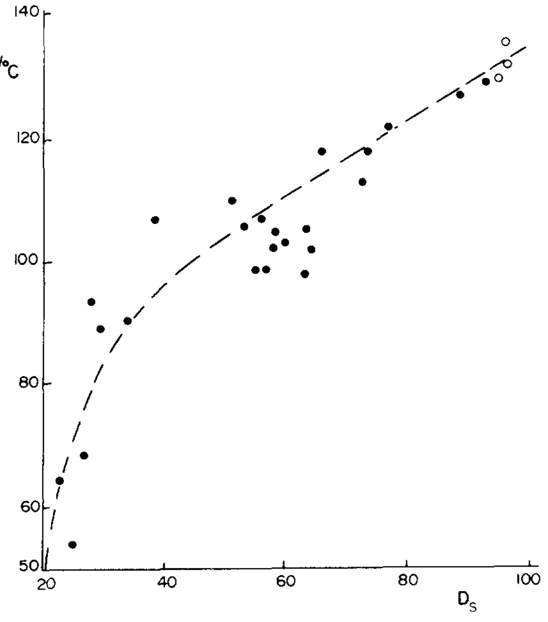

Fig. 3. Glass transition temp. as a function of % syndiotactic dyad content, D_s. {(●) This work; (○) from Ref. [11]}.

solvents gives predominantly syndiotactic polymers, resembling those obtained from free radical initiated reactions [22]. There are small changes if the initiator is present as ion-pairs or as solvent separated free ions and variation of metal has some influence on tacticity, syndiotactic content decreasing in the order $Li^+ > Na^+ > K^+$ [23]. The ratios α_i and α_s are close to unity and indicate the absence of a penultimate effect in the propagation mechanism [19]. The MWD's are monomodal and under ideal experimental conditions can be very narrow at *c.* 200 K ($\bar{M}_w/\bar{M}_n < 1.1$) [24]. However, because propagation rates are high, broader MWD may result if more inhomogeneous reaction conditions prevail. Also, at higher temperatures reaction with ester linkages may also cause broadness in MWD. Using bifunctional initiators in THF, it has been reported that polymer stereochemistry varies from mainly atactic to syndiotactic with the degree of conversion and bimodal MWD may arise at low conversions from the presence of both monofunctional and bifunctional initiation [25]. Organomagnesium initiators in toluene give PMMA with very broad MWD [26] and studies of these initiators in toluene–THF mixtures show polymers with multimodal distributions and polymerization mechanisms which are not simple and anionic [15].

The MMA polymers produced using Ph_3CMX (M = Ca, Sr, Ba) in DME and THF show significant differences from group 1A metal initiated polymers. The tacticity of the overall product shows a marked dependence on the metal and halide of the initiator with syndiotacticity generally falling in the sequences Ca > Sr > Ba and Cl > Br. The distribution of *I*, *H* and *S* triads is non-Bernoullian and α_i and α_s values deviate markedly from unity in both solvents. Assuming a single site scheme as the sole propagation mechanism these results indicate at least the presence of a penultimate effect on the stereochemistry of monomer addition. With the exception of highly syndiotactic polymers produced from $Ph_3CCaCl(THF)_2$ (cf. ref. [11]), the values for μ_i and μ_s are small and many of the polymers may be described as stereoblock macromolecules.

In THF, unlike DME, polymer tacticity varies with the initial monomer concentration. This variation is somewhat irregular (Fig. 2) but may also depend on the formation of gel which occurred within 1 hr in most samples. It is of interest to note that addition of sufficient methanol to terminate polymerization did not destroy the constitution of these gels and hence they cannot arise solely from ion association effects. A possible cause of gelation is the presence of and association between PMMA molecules of differing tacticities produced in these systems [27]. The results obtained in experiments which were terminated before gelation (Table 3) showed that in THF a measurably higher syndiotactic fraction was present in these cases and that less variation of tacticity with monomer concentration occurred.

The bi- or poly-modal character of the GPC traces obtained from all polymers (with or without gel formation) suggested to us that at least two different polymerization processes were taking place. An obvious possibility, the presence of both an anionic and a radical process, has previously been proposed for polymerization initiated by bulk alkaline earth metals [13]. ESR spectroscopy detected small amounts of $Ph_3C^\cdot$ radicals in solutions of Ph_3CMX initiators but attempts to initiate MMA polymerization by $Ph_3C^\cdot$ radicals and to incorporate styrene into polymerizing MMA were unsuccessful. These experiments support the absence of radical initiation of propagation steps in these polymerizations. One other possible radical reaction is a chain transfer process of the type

$$\sim P^- + Ph_3C^\cdot \rightleftharpoons \sim P^\cdot + Ph_3C^-,$$

in which additional initiator is generated. Similar reactions have been suggested on kinetic evidence for polymerization of styrene by $Ba(CPh_3)_2$ in presence of excess hexaphenylethane [6] and also polymerization of MMA by benzophenone–magnesium [28]. Such a process will lead to broadening of the MWD but, in the absence of radical propagation, not to a bimodal distribution or tacticity variations.

The distribution of high molecular weight products can be explained by the occurrence of more than one anionic-type mechanism. In toluene–THF media it has been proposed for Grignard initiators that a pseudo-anionic, eneidic mechanism occurs involving prior coordination of MMA to magnesium before propagation [15]. The alkaline metals Ca, Sr and Ba form a range of coordination complexes with oxygen and other ligands and, because of their size and formal dipositive charge, coordination numbers greater than six are common [29]. Complexation (solvation) by THF and DME occurs. It is likely that free MMA and also growing polymer ends with several oxygen and alkene or carbanionic donor sites, respectively, will compete effectively with the ether molecules (especially monodentate THF) for coordination to these metals which can adopt several distorted coordination geometries. Propagation steps involving more than one of these coordination configurations of metal, monomer and growing chain could each generate polymers of differing tacticity at a different rate, providing the rate of exchange between propagating centres is slow. This hypothesis would explain the broad bi- or poly-modal MWD of these polymers and also the fact that fractionation experiments indicate significant tacticity differences for lower and higher MW fractions. Similar mechanistic suggestions have been made for organo-magnesium initiation in toluene-THF mixtures [15] but for magnesium only 4 or, at most, 6 ligands are to be expected thus limiting the stereochemical possibilities for a coordinative process.

The divalent metals exhibit one additional but related structural variation. Two formally uninegative groups will tend to be coordinated or, at least, ion-paired with each metal centre. In propagation the growing end (exluding other coordinated groups) will be either of type *A* or of type *B*, formed via a redistribution reaction analogous to the Schlenk equilibrium of Grignard reagents [30] or, when X = CPh_3, by double initiation.

$$\underset{A}{P^- \ldots M^{2+} \ldots X^-} \qquad \underset{B}{P^- \ldots M^{2+} \ldots P^-}$$

In some Grignard initiated polymerizations, it has been noted that the halide has no effect on the polymerization and consequently deduced that the active species is MgR_2, although in other cases when isotactic PMMA is produced the influence of halide in propagation is important [15]. In these polymerizations by alkaline earth metal species, Ph_3CMX, the facts that group X influences the reaction and that differences occur between initiators $Ba(CPh_3)_2$ and Ph_3CBaCl rule out propagation steps involving solely sites of type *A* where $X = CPh_3$ (formed by redistribution) or of type *B*. However, a coordinative anionic type mechanism involving various, relatively non-labile sites of types *A* (X = halide and/or CPh_3) and *B* would be consistent with the polymerizations observed.

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