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Stereochemistry of Polymerization of Triphenylmethyl and Diphenylmethyl Methacrylate under Group-Transfer Conditions

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ABSTRACT: The polymerization of triphenylmethyl and diphenylmethyl methacrylate (TrMA and DMA, respectively) was investigated using group-transfer polymerization (GTP) initiators and various catalysts at temperatures varying from +50 to −97 °C. The catalysts found to be effective were tris(dimethylamino)-sulfonium trimethyldifluorosiliconate ((TAS)Me$_3$SiF$_2$) and the bifluoride TAS catalyst ((TAS)HF$_2$). Furthermore, the polymerizations required relatively large quantities of catalyst. The fluoride and acetate catalysts were found to be ineffective. The molecular weight control is relatively poor, presumably as a result of side reactions involving the GTP initiator. The stereochemistry of the PTrMA was highly isotactic (70–90%), the isotactic content increasing at higher temperatures. Furthermore, a plot of the log (k_r/k_m) vs $1/T$ where k_r and k_m denote the rate constants for racemic and meso placements shows a pronounced curvature. These and other observations suggest a mechanism of TrMA polymerization involving TAS enolates that equilibrate with other species. In contrast, the stereochemistry of polymerization of DMA resembles that of MMA in that mostly syndiotactic polymers are formed. In this case, the stereoregularity decreases with increasing temperature and Bernoullian statistics prevails, suggesting the intermediacy of a single propagating species. This is supported by a linear plot of log(r/m) vs $1/T$.

Introduction

The stereoregular polymerization of various methacrylate monomers has been studied extensively.[1] Among these, the polymerization of triphenylmethyl methacrylate (TrMA) initiated by alkyllithiums and similar initiators is of special interest. At −78 °C, highly isotactic polymers (>90%) are formed, not only in toluene but also in tetrahydrofuran (THF).[2-4] Even the radical polymerization of this monomer at 60 °C gives an isotactic (≈60%) polymer.[2,3,5,6] The unique nature of this polymerization has been ascribed to the bulky trityl group and its interaction with the polymer backbone. Okamoto and co-workers have reported that polymerization of TrMA with chiral anionic initiators results in optically active polymers, the chirality of which is caused by the helical conformation of the chain.[7]

In contrast to TrMA, the anionic polymerization of diphenylmethyl methacrylate (DMA) and benzyl methacrylate (BMA) in THf using butyllithium (BuLi) yields predominantly syndiotactic polymer.[3] In this case, the stereochemistry of polymerization is generally very similar to methyl methacrylate (MMA). The polymerization of acrylates and methacrylates by group-transfer polymerization (GTP) has been studied extensively both by the Du Pont group[8-16] and by others.[17-25] In order to understand more fully the stereoregulation mechanism of the GTP process, it was of interest to us to examine the tacticity of poly(TrMA) (PTMA) and poly(DMA) (PDMA) prepared by GTP and compare the results with those obtained from anionic and radical polymerizations.

Experimental Section

The initiator, [(1-methoxy-2-methyl-1-propenyl)oxy]trimethylsilane (Aldrich), was distilled from calcium hydride under high vacuum and stored as THF solutions in ampules equipped with break-seals at room temperature. Tris(dimethylamino)-sulfonium bifluoride ((TAS)HF$_2$) was prepared according to the literature procedure[8,10] and stored as an acetonitrile solution under argon. Tetrahydrofuran (THF) was refluxed over sodium and potassium metal, distilled onto fresh alloy, degassed, and stored with stirring under high vacuum with benzophenone. It was distilled through the vacuum line into the reaction flask. Tris-(dimethylamino)sulfonium trimethyldifluorosiliconate ((TAS)-SiMe$_3$Fe$_2$; Aldrich technical grade) was used without further purification. It was stored under dry argon and added as an acetonitrile solution prior to use. *n*-Tetrabutylammonium acetate (Alfa) and *n*-tetrabutylammonium fluoride (Aldrich; 1.0 M solution in THF, containing less than 5 wt % water) were used without further purification and were added as a THF solution into the reaction flask.

Silver methacrylate (AgMA) was prepared according to literature procedures.[26,27] Methacrylic acid was first distilled in vacuo over CaH$_2$ to remove the hydroquinone monomethyl ether inhibitor. A total of 50 mL (50.75 g, 590 mmol) was placed in a 500-mL three-neck, round-bottomed flask equipped with a mechanical stirrer and two additional funnels. At room temperature, 35.82 mL (590 mmol) of an aqueous 28% ammonium hydroxide solution was added dropwise. The 100.2 g (590 mmol) of silver nitrate (dissolved in 200 mL of deionized water) was added dropwise to the ammonium methacrylate. The silver methacrylate (AgMA) precipitated as a gray solid.

The reaction was stirred for an additional 2 h. The AgMA was separated by filtration and recrystallized from boiling water. The final product was either grayish or slightly purple. It was first dried in the vacuum oven overnight at room temperature and then further dried on the vacuum line (10^{-6} Torr) for 48 h. It was stored under high vacuum in flasks equipped with high-vacuum stopcocks. The yield after recrystallization was about 70%.

Triphenylmethyl methacrylate (TrMA) was prepared according to literature procedures.[7,26,27] AgMA (10.56 g, 54.7 mmol) suspended in dry ether was placed in a 500-mL three-neck, round-bottomed flask equipped with an additional funnel, a reflux condenser (with a calcium sulfate drying tube), a magnetic stirrer, and an oil bath.

Trityl chloride (Aldrich; 11.70 g, 42.0 mmol) was dissolved in 150 mL of dry ether and added to the AgMA–ether suspension. The reaction was refluxed overnight. The slightly yellowish AgCl was collected by vacuum filtrations, and the ether filtrate was concentrated on a rotary evaporator. It was purified by a hot filtration using Celite and dry ether and then a simple recrys-

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tallization using ether. Final product yields were 50% or less. The TrMA was ground to a fine powder and stored under high vacuum. It was characterized by melting point, elemental analysis, and ^{1}H and ^{13}C NMR. The melting point was 99–101 °C (lit. mp 101–103 °C).[3,26,27]

Elem anal. Calcd for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14. Found: C, 84.08; H, 6.15. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.35 (m, 15 aromatic H's); 6.30 (s, 1 vinyl H); 5.60 (s, 1 vinyl H), 2.0 (s, CCH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 18.5 (CCH_3), 90.0 ($OCPh_3$), 125.5, 137.5 (vinyl C's); 127.3, 127.6, 128.2 (para, meta, and ortho aromatic C's); 143.5 (ipso aromatic C); 165.0 (C=O).

Diphenylmethyl methacrylate (DMA) was prepared according to literature procedures.[3] Silver methacrylate (17.26 g, 89.4 mmol) and dry ether were placed in a 500-mL three-neck, round-bottomed flask equipped with a reflux condenser, a magnetic stirrer, an addition funnel, and an oil bath. Diphenylmethyl chloride (Aldrich; 15.0 g, 0.074 mol) was added to the flask at room temperature. The reaction mixture was refluxed overnight with stirring. AgCl was separated by vacuum filtration, and the ether filtrate was concentrated to yield crude diphenylmethyl methacrylate (DMA). A fraction of the crude product was kept for analysis by melting point, elemental composition, and NMR. The rest of the DMA was recrystallized by one hot filtration using Celite and ether and a simple recrystallization from ether. The mother liquors were kept and concentrated to give additional DMA. The crude yield was 76% and the recrystallized yield was about 40%, but elemental analysis and NMR spectra showed no difference in purity between the crude and recrystallized product, although the latter looked somewhat whiter. Therefore, the DMA obtained from concentration of the mother liquor filtrate from the recrystallization was kept and used for subsequent polymerizations. The melting point was 78–79 °C (lit. mp 79 °C).[3,26]

Elem anal. Calcd for $C_{17}H_{16}O_2$: C, 80.95; H, 6.35. Found: C, 80.86; H, 6.39. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.30 (m, 10 aromatic H's), 6.95 (s, Ph_2CH), 6.25 (s, 1 vinyl H), 5.60 (s, 1 vinyl H), 2.00 (s, CCH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 18.3 (CCH_3), 126–128.8 (3 aromatic C's and $-CHPh_2$), 136.6, 140.5 (vinyl C's), 166.5 (C=O).

Group-Transfer Polymerization of DMA and TrMA. The polymerization was carried out on the vacuum line under high-purity argon. After evacuation and flame drying of the polymerization flask, argon was introduced into the flask. The monomer was then added to the flask, and the flask was reevacuated. Tetrahydrofuran was distilled into the flask through the vacuum line. After dissolution of the monomer, the initiator was added to the flask from an ampule. Argon was against introduced into the flask, and the catalyst dissolved in CH_3CN was injected into the stirred monomer solution through a septum. Aliquots of samples were removed periodically by a long syringe to monitor the conversion with time by ^{1}H NMR examination of residual monomer (vinyl absorption). The polymerization was complete in less than 1 min at −78 °C. MeOH was finally introduced into the flask either by distillation through the vacuum line or under argon to terminate the polymerization.

PDMA was found to be soluble in THF and chloroform. Some of the PTMA samples were insoluble in common organic solvents on account of their high molecular weight in accordance with literature reports.[28] Polymers soluble in THF or $CHCl_3$ were precipitated in a 10-fold excess of methanol to remove the GTP catalysts and unreacted monomer (if any), and the polymer was collected by vacuum filtration. Samples insoluble in the above solvents were collected by either filtration or centrifugation, and the filtrate from the centrifugation was further concentrated and added to methanol in order to recover additional polymer. The polymer samples were then dried in a vacuum oven at 50 °C for at least 2 days.

Transesterification of PTMA and PDMA to PMMA. The hydrolysis of PTMA and PDMA to poly(methacrylic acid) (PMA) was performed using acidified methanol according to literature procedures.[3] The PMA samples were then methylated using diazomethane according to standard literature procedures.[26] The samples were then dissolved in chloroform and precipitated in a 10-fold excess of hexane or cyclohexane. NMR spectra of the PMMA samples indicated quantitative hydrolysis and methylation.

Polymer Characterization. NMR (^{1}H and ^{13}C) measurements on the PMMA samples were carried out using a Varian XL-200 spectrometer in either $CDCl_3$ (50 °C) or tetrachloroethane (TCE-d_2) at 90 °C at concentrations of about 200 mg/mL. The triad tacticities of the chain were determined both by integration of the α-methyl protons (0.7–1.3 ppm) and by integration of the α-methyl carbon signals (17–23 ppm).

Size-exclusion chromatographic (SEC) analyses were carried out at room temperature using a Waters 6000 liquid chromatograph. The columns used were Phenomenex TSK G3000 (7.8 mm × 30 cm; 10^3 Å) and TSK gel type G500 HXL (10^5 Å) columns placed in series. THF was the eluent in all cases, and the flow rates used were typically 0.7–1.5 mL/min. Both refractive index and UV (222-nm) detectors were used. The column set was calibrated with PMMA standards (Polymer Standards Services, Mainz, West Germany). In all analyses, corrections were made for column band broadening.

Results and Discussion

Group-Transfer Polymerization of TrMA. Previously, satisfactory results on the GTP of MMA at 25 °C were obtained by us[29,30] and by others[17] by adding a mixture of monomer and initiator to the catalyst. Therefore, initially the GTP of TrMA was attempted under similar conditions, i.e., slow addition of a monomer and initiator mixture into the catalyst suspension in THF at −70 °C. At initiator to catalyst concentration ratios of about 78, virtually no polymer formed and all of the unreacted monomer was recovered, as seen by ^{1}H NMR. This indicated that conditions different from the GTP of MMA had to be employed. This was done by using a molar ratio of initiator to catalyst of about 1. Under these conditions, complete monomer conversion was observed in less than 1 in at −70 °C. Since the initial failure of polymerization could have been due to insufficient catalyst concentration in the reaction mixture, a variety of catalyst concentrations were used in order to see what conditions would bring about quantitative conversion of TrMA into polymer. The results of these experiments are summarized in Table I.

It is apparent from this table that much higher levels of catalyst are required (i.e., higher values of catalyst to initiator ratios) for quantitative polymerization of TrMA than for the MMA polymerizations, where catalyst levels as low as 0.1 mol % with respect to initiator (methyltrimethylsilyl dimethyl ketene acetal) had been found to yield narrow MW distribution PMMA in quantitative yield.[8,12]

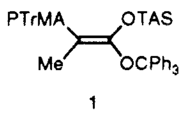
Thus, all of the polymerizations in Table I (except run no. 17 where a mixture of monomer and initiator was added to the catalyst) were batch polymerizations in which the catalyst was added at one time as an acetonitrile solution (0.1–1.0 M depending on the amount of initiator) to a mixture of monomer and initiator in THF. Several conclusions can be drawn from the data in Table I. The molecular weight control appears very poor in that it far exceeds the expected molecular weight, indicating poor initiator efficiency which varies from 11 to 53%. There does appear to be some internal consistency, however, in that agreement between expected and actual MW becomes poorer with increasing degrees of polymerization. This indicates that not all of the initiator is used to initiate polymerization. It is somewhat surprising, however, that the MW distributions are fairly narrow despite the poor initiator efficiencies. This means that initiation is reasonably fast compared to propagation but that some initiator is destroyed before initiation. This is most likely due to side reactions involving the initiator and catalyst. The rates of these side reactions apparently are more competitive with initiation in this case compared to the MMA polymerization where there usually was good

Table I
Effects of Temperature and Relative Proportions of Initiator and Catalyst on the Polymerization of TrMA

run no.	temp (°C)	catalyst	mol of init. × 10^{-3}	[init.]/[cat.]	yield (%)	M_w[e]	M_n[e]	M_w/M_n	M_n (calcd)[f]
1	–97	*a*	0.25	1.0	>95	4100	3210	1.28	1340
2	–95	*a*	0.70	1.0	>95	3030	2690	1.12	1440
3	–82	*a*	0.46	1.0	>95	4440	3640	1.21	1870
4	–70	*a*	0.29	1.0	>95	39560	26870	1.47	2930
5	–70	*a*	0.31	1.0	>95	3390	3090	1.11	1310
6	–70	*a*	0.21	2.6	>95	14100	11230	1.26	3030
7	–70	*a*	0.27	93.0	~30	31790	21590	1.47	2880
8	–42	*a*	0.49	1.0	>95	4220	3460	1.22	1440
9	–21	*a*	0.37	1.0	>95	3220	2770	1.16	680
10	0	*a*	1.39	1.0	>95	8650	6950	1.24	850
11	0	*a*	0.57	1.0	>95	8090	4950	1.63	1130
12	25	*a*	0.32	1.0	>95	28420	15130	1.88	2720
13	25	*a*	0.69	1.0	70	9840	5850	1.68	970
14	35	*a*	0.49	1.0	<5	32320	11310	2.86	1000
15	50	*a*	0.98	1.0	<5	25700	8140	3.16	640
16	–70	*b*	0.55	1.0	>95	10910	8550	1.28	1230
17	–70	*b*	0.73	78.0	<5				
18	–70	*c*	0.61	1.0	≈10	ND[g]	ND	ND	ND
19	–70	*d*	0.18	1.0	≈15	ND[h]	ND	ND	ND

[a] (TAS)SiMe$_3$F$_2$. [b] (TAS)HF$_2$. [c] *n*-Bu$_4$NF. [d] *h*-Bu$_4$OAc. [e] Molecular weight of the transesterified PMMA samples. [f] Calculated from the mole ratio of monomer to initiator. [g] Sample not transesterified, but the elution volume of the poly(TrMA) corresponded to an approximate molecular weight of 199 000 based on a PMMA calibration curve; $M_w/M_n > 2.0$. [h] Sample not transesterified, but the elution volume of the poly(TrMA) corresponded to a molecular weight of approximately 126 000 based on a PMMA calibration curve; $M_w/M_n \approx 1.5$.

agreement between expected and actual M_n.[8,12] In that case, it is reported18 that it is desirable to use the minimum amount of catalyst in order to avoid side reactions and to obtain polymers of lowest polydispersity, particulary when preparing polymers of M_n above about 20 000. However, in the presence of high levels of catalyst, it was found that addition of monomer after 30 min gave no polymerization, indicating initiator destruction. Since a high level of catalyst is necessary to obtain complete conversion of monomer to polymer in the case of TrMA, it is not surprising that the polymerization is self-terminating. This was demonstrated by the addition of monomer (TrMA) 30 min after an initial polymerization of TrMA at –70 °C. A second batch of monomer failed to polymerize. If the propagating species is a silyl ketene acetal activated with a nucleophile as in the GTP of MMA, then this self-termination is most likely due to the destruction of the silyl ketene acetal end group by its side reaction with the catalyst. This is corroborated by our inability to methylate the chain end of PTrMA prepared by GTP. In a first attempt, $^{13}CH_3I$ (99% enriched) was added after a GTP of TrMA at –70 °C. The resulting polymer had no methyl end group signal as determined by ^{13}C NMR analysis. In a second attempt, the methylation of the PTrMA chain end at –70 °C was attempted by the addition of $^{13}CH_3I$, followed immediately by the addition of 1 equiv of (TAS)-SiMe$_3$F$_2$ (with respect to initiator). Again, no methyl end group was observed in the PTrMA. Under similar conditions ($^{13}CH_3I$ addition followed by (TAS)Me$_3$SiF$_2$) methylation of the PMMA chain end after a HF_2^--catalyzed GTP of MMA proceeded in high yield.[30] In this case, the reaction presumably proceeded by way of a PMMA TAS ion pair which rapidly underwent methylation. Reversing the order of addition of the CH$_3$I and the (TAS)SiMe$_3$F$_2$ resulted in PMMA with no detectable ^{13}C-labeled methyl end group. In contrast, the methylation of the PMMA lithio enolate in THF at –78 °C proceeds slowly but in high yield.[31]



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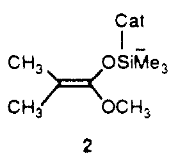

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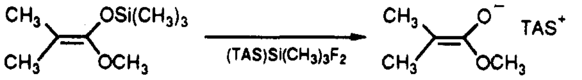
The above supports the high reactivity and transient nature of the TAS enolate in the TrMA polymerization. Presumably, the TAS anion (1) or a similar species rapidly underwent side reactions with the catalyst.

The relative rates of side reactions competing with initiation and polymerization of TrMA increase with temperature, as was demonstrated during attempted polymerizations at temperatures higher than 25 °C. Thus, attempted polymerizations at 35 and 50 °C resulted in complete failure with virtually all the TrMA recovered. This is apparently due to a lack of initiation caused by the rapid destruction of the silyl ketene acetal initiator or propagating oligomeric species.

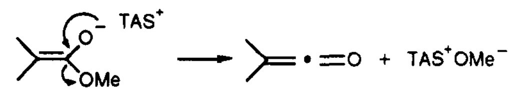
This was demonstrated by cooling the reaction mixture after a GTP polymerization of TrMA at 50 °C down to 0 °C and adding an additional amount of initiator. In this case, all of the monomer polymerized immediately. Thus, it appears that, although at higher temperatures, initiation is inhibited due to destruction of the initiator, there is still sufficient active catalyst left capable of catalyzing the polymerization upon the addition of additional initiator at lower temperature. This indicates that the destruction of the initiator or propagating oligomer is not due to a 1:1 equimolar reaction between the initiating or propagating species and the catalyst and is completely consistent with our earlier investigations into the side reactions involving the initiator and (TAS)HF$_2$ catalyst in CD$_3$CN at room temperature without the presence of monomer.[29] In this case, all of the initiator disappeared in approximately 2 h after the start of reaction even though a large excess of initiator over catalyst (11:1 mole ratio) was present. These results are in good general agreement with those of Bandermann and co-workers, who studied the nature of side reactions between GTP initiators and anion catalysts.[21-24]

Various color changes were seen in the case when the initiator was added at 0 °C to the reaction mixture following an unsuccessful 50 °C attempted polymerization of TrMA. As more initiator was added, the color changed from slight yellow to orange to dark brown to red and finally to green. These color changes could be due to reactions involving the catalyst complex (2) or the TAS enolate ion pair (eq 1). Such an enolate could eliminate a methoxide ion to yield a ketene that is expected to react further (eq 2). It



(1)

is to be noted, however, that no direct evidence was found for the presence of the ketene; such reactions, however, have been reported[32] in addition to other well-known side reactions such as cyclization and O to C silyl migration.[16] However, there is no evidence for any of these reactions in the ^{13}C NMR spectra.



(2)

Good catalytic activity was expected from NBu_4F on account of it being a highly efficient source of nucleophilic fluoride ion and due to its use in the GTP of MMA. However, even 1 equiv of NBu_4F with respect to initiator was incapable of catalyzing the polymerization of TrMA to complete monomer conversion (run no. 18, Table I).

Although this reagent may still contain moisture which could terminate the polymerization, it is unlikely that the presence of water was the primary reason for the low level of activity of NBu_4F. It would be difficult to understand how a higher catalyst concentration involving a proportionately higher H_2O concentration would be effective in polymerization of TrMA. It is therefore not clear why this catalyst failed to give a good yield of poly(TrMA) based on the conventional associative mechanism of GTP. Another catalyst, NBu_4OAc, known to catalyze the GTP of MMA also failed to effectively catalyze the polymerization of TrMA in good yield at −70 °C (run no. 19, Table I). These findings hint at the possibility of a mechanism for the GTP of TrMA different from that postulated by the Du Pont group for the GTP of MMA. The intermediacy of a highly reactive TAS enolate would seem most plausible.[33]

Stereochemistry of GTP of TrMA. Representative PTMA samples from the runs in Table I were transesterified to PMMA, and the stereochemistry was determined by ^{13}C and ^{1}H NMR of the α-methyl groups. The agreement between ^{1}H and ^{13}C NMR was excellent in all cases, the difference between them never exceeding 3%; however, the tacticity determination by ^{13}C NMR was preferred, owing to the somewhat better resolution of the spectra. The tacticity data and several stereochemical parameters are shown in Table II. The literature tacticity results for the anionic and free-radical polymerization of TrMA are shown in Table III for comparison purposes.

Examination of Tables II and III reveals that the polymers obtained are predominantly isotactic for all temperatures and all methods of polymerization whether anionic, radical, or GTP. However, in contrast to the anionic and radical polymerization of TrMA, the group-transfer polymerization appears to produce more highly isotactic polymers as the temperature increases. Thus, about a 90% isotactic polymer is obtained at room temperature as compared to a 70% isotactic content at −78 °C. At −97 °C, the tacticity data for GTP appear to be similar to those for the free-radical polymerization at 30 °C, while for the GTP of TrMA at ambient temperatures, the results resemble that for the anionic polymerization at −78 °C. Figure 1 shows tactic content versus temperature for the GTP of TrMA.

The increase in stereoregularity with increasing temperature as found in the group-transfer polymerizations of TrMA is rather unusual and contrasts with the normally observed decreases at higher temperature seen in typical radical and anionic polymerizations of vinyl monomers and in the GTP of MMA. For example, inspection of Table III reveals that the isotactic content decreases with increasing temperature in the n-BuLi-initiated anionic polymerization of TrMA in THF. Also, in both anionic and group-transfer polymerization of MMA, the syndiotactic content decreases with increasing temperature.[8,30,34] The same general trend is seen in the radical polymerization of MMA.

The degree of stereoregularity of a vinyl polymer is specifically determined by the k_r/k_m ratio, where k_r and k_m are the rate constants for syndiotactic (racemic) and isotactic (meso) placement of monomer, respectively. For k_r/k_m values between zero and infinity, one obtains a distribution of isotactic and syndiotactic placements, respectively. The ratio of rate constants for racemic and meso placements is given by

$$k_r/k_m = \exp(-\Delta\Delta G^{\ddagger}/RT) = \exp(\Delta\Delta S/R^{\ddagger})\exp(-\Delta\Delta H^{\ddagger}/RT) \quad (3)$$

where subscripts r and m refer to the racemic and meso

Table II
Tacticity of PMMA Derived from PTMA by GTP in THF

run no.	temp (°C)	f_{mm}[a]	f_{mr}[a]	f_{rr}[a]	f_m[b]	ρ[c]	$\sum P$[d]	$\Delta(\rho)$[e]	$\Delta(\sum P)$[f]
1	−97	0.67	0.23	0.10	0.78	1.47	0.79	0.13	0.04
	−70	0.70	0.23	0.07	0.81	1.31	0.76	0.15	0.06
8	−42	0.77	0.18	0.05	0.86	1.34	0.74	0.18	0.08
9	−21	0.83	0.12	0.05	0.89	1.63	0.62	0.23	0.07
10, 11	0	0.89	0.08	0.03	0.93	1.63	0.61	0.34	0.10
12, 13	25	0.91	0.07	0.02	0.94	1.48	0.68	0.38	0.17

[a] Determined directly from ^{13}C NMR; uncertainty in measurement is ±0.02. [b] Calculated from $f_m = f_{mm} + 0.5f_{mr}$. [c] Persistence ratio calculated from $\rho = 2f_m f_r/f_{mr}$. [d] Sum of first Markoff parameters P_{rm} and P_{mr} calculated from triads. [e] Uncertainty in ρ. [f] Uncertainty in $\sum$P. Uncertainties determined from the analysis of the propagation of error.

Table III
Tacticity of PMMA Derived from PTrMA by Anionic and Radical Polymerization[a,b]

initiator	temp (°C)	f_{mm}	f_{mr}	f_{rr}	f_m	ρ	$\sum P$
BuLi[c]	−78	0.96	0.03	0.01	0.975	1.63	0.62
DPML[d]	−78	0.91	0.08	0.01	0.95	1.19	0.84
BuLi[c]	0	0.81	0.13	0.06	0.875	1.68	0.59
AIBN[e]	30	0.63	0.23	0.14	0.74	1.65	0.60
AIBN[e]	60	0.64	0.22	0.14	0.75	1.70	0.59

[a] Determined by ^{1}H NMR. [b] Anionic polymerizations in THF. Radical polymerizations in toluene. [c] Reference 3. [d] Diphenylmethyllithium. Tacticity data from ref 27. [e] Triad tacticity data taken from ref 3.

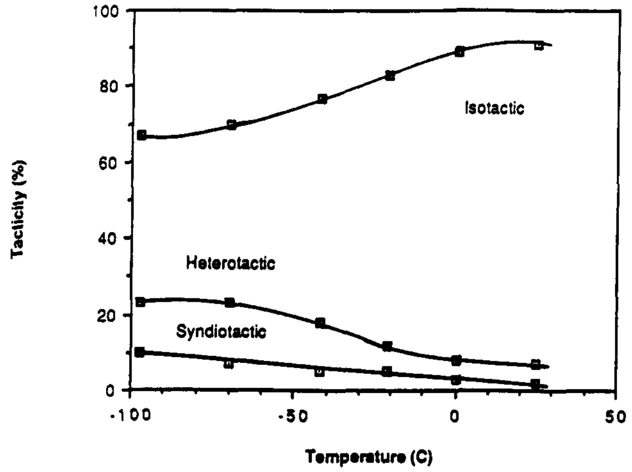


Figure 1. Dependence of triad tacticity upon temperature for the polymerization of TrMA under GTP conditions.

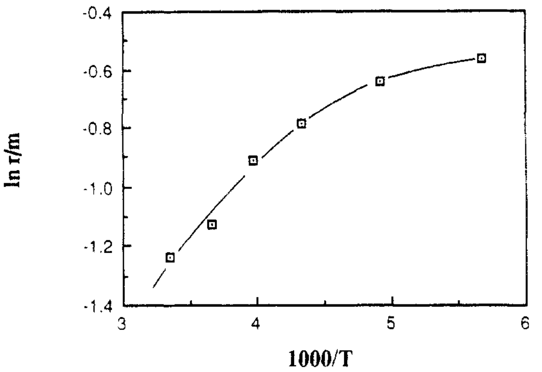


Figure 2. ln(r/m) as a function of $1/T$ (K^{-1}) for the polymerization of TrMA under GTP conditions.

Table IV
Calculated Values of $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ (from Figure 2)

temp range (°C)	$\Delta\Delta H^{\ddagger}$ (kcal/mol)	$\Delta\Delta S^{\ddagger}$ (eu)
−100 to −70	−0.76	−6.7
−21 to +25	−2.46	−14.0

placements, respectively, and where $\Delta\Delta G^{\ddagger}$ is the difference in free energies of activation for syndiotactic and isotactic placements and is given by

$$\Delta\Delta G^{\ddagger} = \Delta\Delta H^{\ddagger} - T\Delta\Delta S^{\ddagger} \quad (4)$$

where

$$\Delta\Delta H^{\ddagger} = \Delta H_{r}^{\ddagger} - \Delta H_{m}^{\ddagger} \text{ and } \Delta\Delta S^{\ddagger} = \Delta S_{r}^{\ddagger} - \Delta S^{\pm} \quad (5)$$

Taking the log of both sides of eq 3 yields

$$\ln(k_r/k_m) = (\Delta\Delta G^{\ddagger}/RT) = \Delta\Delta S^{\ddagger}/R - \Delta\Delta H^{\ddagger}/RT \quad (6)$$

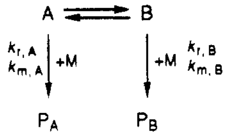
Thus, a plot of $\ln(k_r/k_m)$ vs $1/T$ should yield a straight line with slope $\Delta\Delta H^{\ddagger}/R$ and intercept $\Delta\Delta S^{\ddagger}/R$. The data for the polymerization of TrMA under GTP conditions are plotted in Figure 2. The values of $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ were calculated from the slopes and intercepts of the tangents at low and high temperatures. The values are listed in Table IV.

Thus, $\Delta\Delta H^{\ddagger}$ favors the formation of r diads by 0.76–2.46 kcal/mol, while $\Delta\Delta S^{\ddagger}$ favors the formation of m diads by about 6.7–14 entropy units.

The unusual effect of temperature on the tacticity of poly(TrMA) is consistent with the participation of two active species in the group-transfer polymerization of TrMA. Somewhat analogous behavior is observed for the kinetics of polymerization of polystyrene in the presence of alkali counterions in THF which involved the simultaneous participation of solvent-separated and contact ion pairs.[35-37] In that case, the ln k vs $1/T$ curve had two linear regions where either the contact or the solvent-separated ion pairs existed. Since TrMA could not be polymerized by GTP at temperatures above 25 °C, evidence for linearity above that temperature could not be found.

However, in the above cases involving different types of ion pairs, the interconversion between two species is rapid compared to polymerization. Hence, only a unimodal distribution is expected. In such a case it would be impossible to fractionate the sample to demonstrate different tacticities arising from each active species since the different tacticities are now present in a single chain. Since there should be some differences in the tacticities produced by the two species, their presence may be indicated by an anomalous dependence of stereoselectivity on temperature for example. This may be a likely explanation in the case of GTP of TrMA where fairly narrow unimodal distributions are obtained at all temperatures. Thus, in Figure 2, the portions of the curve at high and low temperatures may represent conditions where essentially only one of the two species exists.

Scheme I
Interconversion of Two Propagating Species in the GTP of TrMA



Scheme I is actually a case of Coleman–Fox statistics and has been worked out in detail.[38] Let K be the equilibrium constant for the interconversion of two propagating species, A and B, which is rapid compared to propagation so that

$$K = [B]/[A] \quad (7)$$

If $k_{r,A}$ and $k_{r,B}$ are the propagation rate constants for racemic monomer addition for species A and B, respectively, and $k_{m,A}$ and $k_{m,B}$ the corresponding rate constants for meso addition, it follows that

$$k_r/k_m = (k_{r,A}[A][M] + k_{r,B}K[A][M])/(k_{m,A}[A][M] + k_{m,B}K[A][M]) \quad (8)$$

so that

$$k_r/k_m = (k_{r,A} + k_{r,B}K)/(k_{m,A} + k_{m,B}K) \quad (9)$$

For $K \ll 1$ or $K \gg 1$ eq 9 reduces to $k_r/k_m = k_{r,A}/k_{m,A}$ or $k_r/k_m = k_{r,B}/k_{m,B}$, respectively. By differentiation of ln(r/m) with respect to $1/T$, it is readily shown that a curve is expected with $\Delta H_{A}^{\ddagger}/R$ and $\Delta H_{B}^{\ddagger}/R$ as slopes for the cases where only A or B is present, respectively.

The tacticity results for the TrMA polymerization suggest the possibility of two active species in dynamic equilibrium. Increasing the temperature would have the effect of increasing the proportion of the active chain ends responsible for an isotactic-like chain growth. There is a possibility of one of the species being the TAS enolate, while the other could be an activated (i.e., pentacoordinated) silyl ketene acetal as claimed for the case of MMA polymerizations with HF_2^- ion. However, a clear identification of the actual species involved is not possible on the basis of our data. Neither is it clear why the temperature-dependent stereochemistry is completely different from that of MMA and DMA (below) nor why the dependence of stereochemistry of TrMA polymerization on temperature is different under anionic and GTP conditions. It is of course possible that the unusual temperature dependence of the stereochemistry is attributable to the presence of the organic TAS counterion.

Examination of Table III reveals that the persistence ratios, ρ, and the ΣP values deviate considerably from unity, indicating non-Bernoullian behavior. The persistence of the isotactic sequence is consistent with the helical growth of poly(TrMA). Non-Bernoullian behavior would also be consistent with the presence of two or more propagating species as demonstrated by Coleman and Fox.[38] A comparison of main chain and chain end tacticity could have provided further evidence for the non-Bernoullian behavior in this system.[39] However, as already mentioned, several attempts to methylate the chain end with $^{13}CH_3I$ proved unsuccessful.

Group-Transfer Polymerization of DMA. The results of the polymerization of DMA under various GTP conditions are given in Table V. Once again, the molecular

Table V
Effect of Temperature on the Polymerization of DMA under GTP Conditions

run no.	temp (°C)	catalyst	[init.]/[cat.]	yield (%)	M_w[a]	M_n[a]	M_w/M_n	M_n (calcd)
1	−78	*b*	1.0	100	18403	17188	1.07	6600
2	−50	*b*	1.8	100	22318	14176	1.57	5420
3	−21	*b*	1.5	100	27113	16123	1.68	7400
4	0	*b*	1.5	100	4542	3967	1.14	1382
5	0	*c*	0.9	<5				
6	25	*b*	1.9	100	39102	20272	1.93	5120

[a] Molecular weight of transesterified PMMA. [b] (TAS)$SiMe_3F_2$. [c] *n*-Bu_4NOAc.

Table VI
Tacticity and Stereochemical Parameters for GTP of DMA in THF[a]

temp (°C)	run no.	f_{mm}	f_{mr}	f_{rr}	f_r	ρ	ΣP
−78	1	0.04	0.26	0.70	0.83	1.07	0.95
−50	2	0.05	0.34	0.61	0.78	1.08	0.99
−21	3	0.06	0.37	0.57	0.75	0.98	1.00
0	4	0.08	0.38	0.54	0.73	0.99	1.02
25	6	0.09	0.39	0.52	0.71	1.05	0.95

[a] Triad tacticity determined by ^{13}C NMR.

Table VII
Anionic and Radical Polymerization of Diphenylmethyl Methacrylate in THF[a]

initiator	temp (°C)	f_{mm}	f_{mr}	f_{rr}	f_r	ΣP	ρ
BuLi	−95	0.02	0.12	0.86	0.92	0.82	1.23
BuLi	−78	0.02	0.11	0.87	0.93	0.79	1.26
DPML[b]	−78	0.02	0.14	0.84	0.91	0.85	1.17
BuLi	−30	0.04	0.12	0.84	0.90	0.67	1.50
BuLi	0	0.02	0.31	0.67	0.83	1.08	0.93
BuLi	30	0.04	0.36	0.60	0.78	1.05	0.95
BuLi	60	0.05	0.44	0.51	0.73	1.11	0.90
AIBN[c]	30	0.02	0.36	0.62	0.20	1.12	0.89
AIBN[c]	60	0.02	0.41	0.57	0.225	1.17	0.85

[a] Triad tacticity determined by ^1H NMR.[3] [b] Reference 27. [c] Triad tacticity data taken from ref 3.

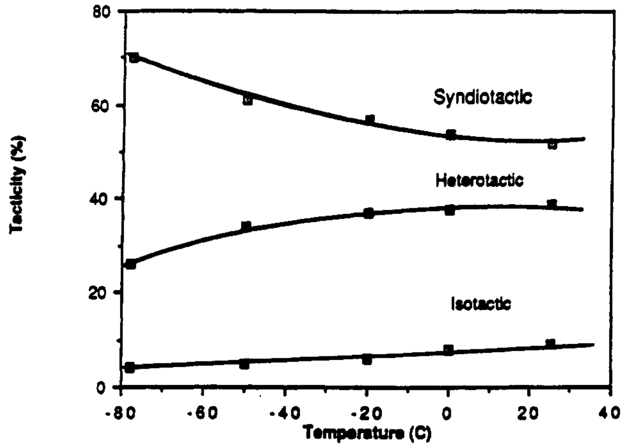


Figure 3. Dependence of triad tacticity upon temperature for the polymerization of DMA under GTP conditions.

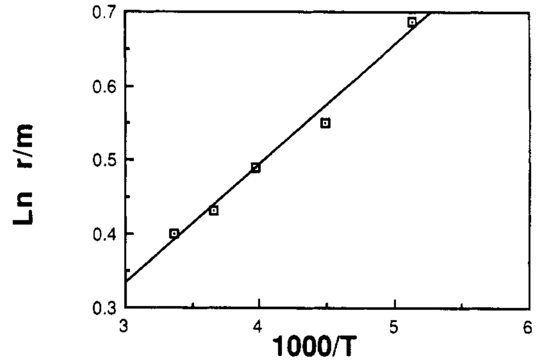


Figure 4. ln(r/m) as a function of $1/T$ (K^{-1}) for the polymerization of DMA under GTP conditions.

weight control is poor due to poor initiator efficiency resulting from side reactions. Unimodal MW distributions are obtained for all samples. With the exception of the 0 °C run (run no. 4, Table V, where the molecular weight is much lower than the rest of the samples) the width of the MW distribution appears to increase with temperature, indicating increases in rates of side reactions with temperature. When the polymerization of DMA was attempted using 1 equiv of NBu_4OAc catalyst at 0 °C, no polymerization resulted (run no. 5, Table V). That this failure was due to the destruction of the silyl ketene acetal initiator and not the catalyst was demonstrated by subsequent addition of 1 equiv of (TAS)$SiMe_3F_2$. This also failed to polymerize the DMA. However, when additional initiator was added to the above reaction mixture at 0 °C after the addition of (TAS)$SiMe_3F_2$ catalyst, all of the monomer polymerized instantaneously. Thus, the reason for the original unsuccessful polymerization of DMA with NBu_4OAc was probably due to destruction of the initiator as a result of a side reaction involving NBu_4OAc.

Stereochemistry of GTP of DMA. Although the α-methyl signals of PDMA samples themselves can be used to calculate triad tacticity fractions,[3] all of the samples prepared by GTP were transesterified to PMMA for better resolution of the α-methyl signals in both ^1H and ^{13}C NMR.

The tacticity results at various temperatures are shown in Table VI. For comparison purposes, the tacticity data for anionic and radical polymerization of DMA are included in Table VII. Examination of the data shows that, in contrast with the GTP of TrMA, the stereoregularity decreases with increasing temperature. The data for the temperature dependence of tacticity are plotted in Figure 3. The same trend is observed for both anionic and radical polymerizations, again in contrast to the case of the GTP polymerization of TrMA.

In the group-transfer polymerization of DMA, the persistence ratio (ρ) and the sum, ΣP, of the first-order Markov probabilities ($\Sigma P = P_{m/r} + P_{r/m}$) are both very close to unity, indicating consistency with a Bernoullian propagation process.

The above observations are consistent with the intermediacy of a single propagating species whether a silyl ketene acetal or enolate. In such a case, a plot of $\ln(k_r/k_m)$ vs $1/T$ is expected to be linear. Figure 4 shows that this is indeed the case.

Conclusions. It has been shown that TrMA and DMA can be polymerized successfully under GTP conditions at various temperatures. Only (TAS)Me_3SiF_2 and (TAS)HF_2 appear to be effective in these polymerizations and are required in much higher concentrations than in the GTP MMA polymerizations. This is consistent with TAS enolates as intermediates in the polymerizations. Both systems are severely affected by side reactions, competing with initiation, that result in the partial destruction of the silyl ketene acetal initiator and in poor control of molecular weight. This is also suggested by the fact that several attempts to methylate the chain end of poly(TrMA) prepared by GTP were unsuccessful.

In contrast to the corresponding anionic and radical polymerizations, the polymer stereoregularity in the GTP of TrMA increases with increasing temperature with a higher isotactic content at room temperature. A pronounced curve is obtained when the tactic content of poly(TrMA) is plotted as $\ln(k_r/k_m)$ vs $1/T$.

The results are consistent with the polymerization of TrMA proceeding through two active species such as an enolate and a silyl ketene acetal which are interconverting rapidly during the polymerization. On the other hand, the tacticity results for the polymerization of DMA in THF are similar to those of anionic polymerization of DMA in THF in that the stereoregularity decreases with increasing temperature. These tacticity results are also very similar to the GTP and anionic polymerization of MMA in THF. In contrast to TrMA, the polymerization of DMA is consistent with the participation of a single active species, presumably a TAS enolate, as indicated by the ρ and $\sum P$ values which are very close to unity in the entire temperature range from −78 to +25 °C. The participation of a single propagating species is also supported by a linear plot of ln (r/m) versus $1/T$.

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