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YLIDE MEDIATED POLYMERIZATION OF METHACRYLATES AND ACRYLATES IN THE PRESENCE OF TETRAPHENYLPHOSPHONIUM CATION 3

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Abstract: Triphenylmethide tetraphenylphosphonium (TPM,TPP) or methylisobutyrate tetraphenylphosphonium (MIB,TPP) formed by ion exchange reactions of TPP chloride(TPPCl) with the TPM or MIB potassium salts in THF, initiate the living polymerization of MMA producing PMMA's with narrow MW distributions (below 1.3) at ambient temperatures.

In the presence of small amounts (10 mole% or less) of water, that is often present in the TPPCl, this water, under the polymerization conditions, participates in side reactions giving rise to the formation of triphenylphosphine and of a potassium PMMA enolate that causes chain termination giving incomplete MMA conversions and much wider PMMA distributions.

The corresponding polymerizations of acrylates can also produce relatively narrow MWD (<2.00) poly(n-butylacrylate)s and PMMA-b-polybutylacrylate block copolymers but these acrylate polymerizations are not living on the polymerization time scale and can be demonstrated by NMR and other techniques to undergo Claisen type side reactions followed by highly efficient proton transfers from the formed cyclic (-keto esters to the active acrylate chain end anions.

Both UV/Visible spectroscopy of this model (maximum at 415 nm) and 1H, 13C and 31P NMR studies of the MIB,TPP model of the propagating PMMA chains show the presence of a 2,5-cyclohexadienyl phosphor ylide formed by addition of the MIB enolate anion to the para position of one of the four phenyls of the TPP.

These and other data seem to be consistent with an equilibrium between the ylide and a small fraction of the MIB,TPP ion pair that may be partially dissociated

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into free ions. Thus the equilibrium is consistent with the kinetics of polymerization that indicates a propagation rate constant that is about two orders of magnitude lower than expected for the PPh4 enolate ion pair as the sole propagating species.

An alternative mechanistic model involving a PMMA ylide that propagates directly to give either TPP ion pairs or another ylide can not be ruled out at this stage but it would appear that such a model may be tested with means of polymerization kinetics.

Introduction

The synthetic importance of ester enolates and related compounds is reflected in numerous studies studies of their structures and their stereochemistry (Refs. 1-5). Enolate anions are also of great interest in the anionic polymerization of acrylates and methacrylates. Thus the synthesis of block copolymers consisting of PMMA ("hard") and poly(butylacrylate) or poly(2-ethylhexylacrylate) elastomeric ("soft") blocks requiring living polymerization of these monomers is of industrial interest as well.

Several groups have reported on the living anionic polymerization of (meth)acrylates at ambient or higher temperatures (Refs. 6-15). Several of these studies have employed "metal-free" systems, involving organic counterions that were demonstrated to be effective in minimizing the Claisen type side reactions of the enolate anion with the antepenultimate ester group of the PMMA (Refs. 7-8). An apparently closely related system is the so called group-transfer polymerization of (meth)acrylates where silylketene acetals are intermediates (Ref. 15) and where an ion pair of an organic cation and the ester enolate anion has been postulated as the reactive intermediate (Ref. 9).

A more recent development in this area is the polymerization of methacrylates in the presence of tetraphenylphosphonium (TPP) ion, that appears to have pronounced living character at ambient temperatures (Ref. 16). Thus, for the case of MMA, at ambient or lower temperatures, number average molecular weights increase linearly with conversion and MW distributions are narrow (<1.30) (Refs. 17-19). Molecular weights in excess of 50,000 are routinely achievable. The polymerizations of MMA in the presence of the TPP cation are quite rapid having MMA half lives in the order of .3-.5 seconds at 0°C (Ref. 18).

. In the following we review briefly some of the most important aspects of the living polymerization of both MMA and that of t-Bu acrylate (TBA) and report recent results on the initiation, polymerization and polymerization side reactions in these novel systems.

Results

Our interest in these systems was prompted by the fact that the livingness of the anionic polymerizations of MMA and acrylates is improved by the use of non metal cations such as NBu_4^{n+} (Ref. 8). Apparently the presence of small cations catalyzes the Claisen type side reactions documented for the reactions of ester enolates including anionic polymerizations. However, the presence of the NBu_4 cation in the anionic polymerization of MMA does not give narrow distribution PMMA's possibly due to the occurrence of Hoffman side reactions of the propagating PMMA ester enolate anion with the β proton of the NBu_4 cation or may be caused by a slow rate of initiation by some relatively stable initiators such as the $(Bu^n)_4N$ salt of 9-ethylfluorene (Tab 1, run 12).

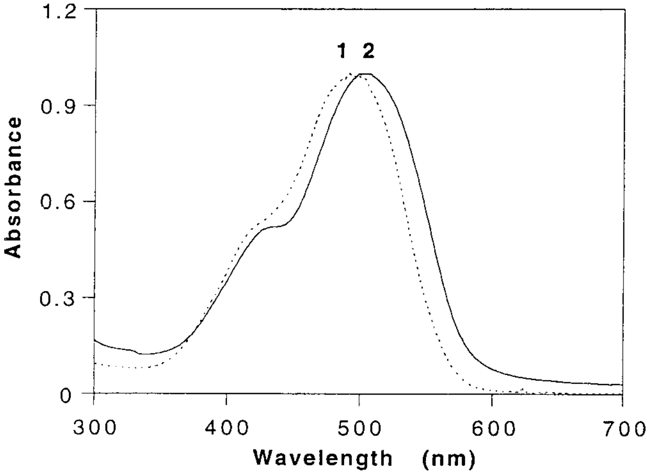
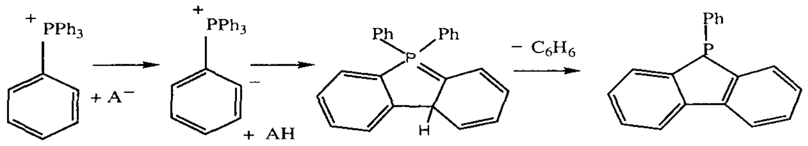


Fig. 1: UV-visible Spectrum of Triphenylmethyl Potassium and Triphenylmethyl Tetraphenylphosphonium in THF at -5°C.

As a result we chose the tetraphenyl phosphonium (PPh_4) cation that does not have highly acidic β protons (Ref. 16). Because the trityl anion is a well known initiator for the polymerization of MMA we synthesized the corresponding Ph_3C,PPh_4 salt that is conveniently prepared by the metathesis reaction of the potassium salt of the trityl anion with tetraphenylphosphoniumchloride (PPh_4Cl) in THF (Eq. (1)) (Ref. 16).

$$Ph_3C,K + Ph_4PCl \longrightarrow Ph_3C, PPh_4 + KCl \downarrow \qquad (1)$$

Interestingly, the reaction is fast at either -78°C or at ambient temperature although the PPh_4Cl is rather insoluble in THF under these conditions. The occurrence of the reaction is evident by the immediate change of color of the deep red solution of Ph_3C,K (λ_{max} = 486 nm) into the deep purple of the Ph_3C,PPh_4. Apparently the formation of the highly insoluble KCl drives the reaction. The UV-visible spectrum of the Ph_3C,PPh_4 salt shows an approximately 10 nm red shift that is consistent with the increased radius of the counter ion (Fig. 1) (Refs. 20,21). Thus the smaller K cation stabilizes the ground state of the anion relative to that of its more delocalized excited state thus increasing the excitation energy of the anion. A similar initiator system may be generated by a similar reaction of the K salt of methylisobutyrate (MIB,K) with PPh_4Cl (see below).



Scheme 1. Side reactions of tetraphenyl phosphonium ions with bases.

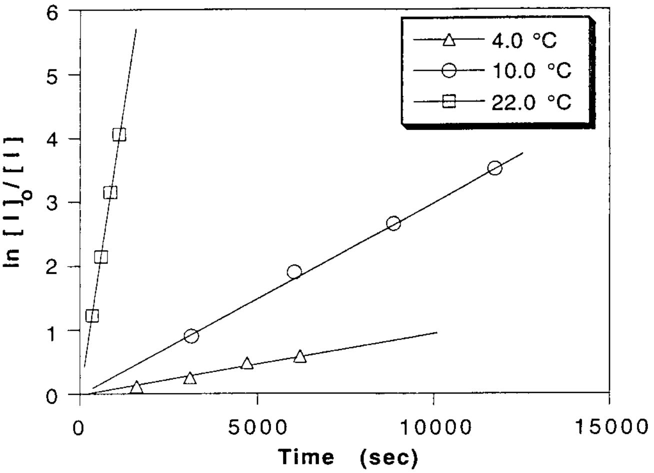


Fig. 2: Decomposition of Triphenylmethyl Tetraphenylphosphonium in THF-d8 at 4°, 10° and 22°C.

In contrast with the analogous tetrabutyl ammonium salt of the triphenylmethyl anion that has a half life time in the order of seconds, the resulting triphenylmethyl phosphonium salt (TPM,TPP) is relatively stable at ambient temperatures with a half life time in the order of about 30 minutes (Refs. 16,19).

The decomposition of the TPM,TPP is kinetically first -order and is readily followed by UV-visible spectroscopy (Fig. 2). The reaction of the TPM,TPP appears to occur not with THF but by an intramolecular abstraction of one of the phenyl ortho protons of the PPh_4 cation by the Ph_3C anion as reported for similar systems by others (Scheme 1) (Ref. 22). Because of the limited stability of the TPM,TPP initiator at ambient temperatures it is advisable to start the polymerization immediately following the metathesis reaction.

Polymerization of MMA. The polymerizations of MMA initiated by TPM,TPP and similar initiators were carried out under high vacuum conditions by the usual breakseal techniques but may be also conducted under inert gas (Ref. 16). The polymerization may be carried out by the slow addition of a MMA/THF solution or by vacuum distillation of MMA into the rapidly stirred reaction solution. The presence of KCl is of no consequence to the polymerization and need not be removed prior to monomer addition. The polymerizations of MMA are of considerable interest resulting in quantitative conversions and narrow PMMA distributions at ambient temperatures or lower (Tab. 1). At 0°C distributions typically are at or below 1.1 and are somewhat broader at ambient conditions (Tab 1). Number average molecular weights increase linearly with conversion and the polymerization kinetics are first order in monomer (Ref. 18).

Tab. 1. Polymerization of Methylmethacrylate in THF by Tetraphenylphosphonium Initiators at 0°C

Initiator	pK$_a$[a)]	T(°C)	Yield[b)]	Mn[c)]	MWD[d)]	f[e)]	mm	mr	rr[f)]
1. TPM	30.6[g)]	0	>95	16 900	1.06	.50	.06	. 37	57
2. TPM	-	0	85	15 500	3.45	.70	.09	.56	.35
3. TPM	-	0	>95	15 000	1.10	.60	.05	.37	.57
4. TPM	-	0	>95	54 000	1.22	.47	-	-	-
5. TPM		20	>95	13 200	1.18	.68	-	-	-
6. MIB	ca. 32[h)]	0	>95	25 000	1.12	.50	.06	.37	.57
7. MAP	22.6[i)]	0	>95	37 000	1.36	.20	.06	.37	.57
8. DEM	16.4[j)]	0	>95	45 000	2.80	.15	.05	.36	.59
9. EMO	14.4k[k)]	0	<14	oligoms	10	.05	.06	.42	.52
10. KAP		0	>95	21 500	1.50	.65	.04	.35	.61
11. MeO	29.0	0	<5	oligoms	-		-	-	-
12. 9-EF[l]	23	20	>95	12 500	3.80	.90	.18	.30	.52

a) For structures see Scheme-2. b) Polymer yield (%) determined gravimetrically. c) Number average MW by SEC. d) Molecular weight distribution by SEC using PS standards. e) Initiator efficiency, $f = M_n(\text{calc})/M_n(\text{SEC})$. f) ^{1}H NMR of α-methyl signals. g) from ref. 32c. h) From Hsieh, H. L.; Quirk, R. P. "Anionic Polymerization. Principles and Practical Applications" Marcel Dekker, New York, 1996, p40. i) Ethyl-3-oxobutanoate. j) Tetrabutylammonium salt of 9-ethyl fluorene.

However the nature of this polymerization appears to be different from that observed in the presence of other organic cations. For instance upon addition of MMA to the deep purple TPP salt of triphenylmethyl anion an orange-red solution is formed (λ_{max} =415 nm) unlike that of the MIB enolate anion that is colorless or slightly yellow (Ref. 7). The orange red color disappears upon addition of water or methanol and further addition of MMA then does not give polymerization. This pattern appears to be consistent with the colored species corresponding to the propagating species (see below).

The MIB,PPh_4 initiator generated by the reaction of MIB,K with PPh_4Cl has a color and UV/visible spectrum similar to that of the polymerizing system and thus would appear to have a similar structure as well (see below). This initiator is an equally effective initiator as TPM,TPP (Tab. 1, run 6) but is more stable (several hours at ambient temperatures) (Ref. 19).

Initiator efficiencies of Ph_3C,PPh_4 and MIB,PPh_4, calculated on the basis of the known concentration of the K salt precursors, are generally high if proper precautions are taken in the handling of the initiator. The relatively low values reported in Tab. 1 are all based upon the concentration of the TPM,K and are mostly caused by inadvertent protonation of these precursors and their TPP products during handling and the decomposition of the TPM,TPP prior to initiation.

Another source of a lower initiator efficiency is water that is often contained in the PPh_4Cl salt. The removal of this water is more difficult than it would appear and it is difficult to dry this salt by conventional means such as drying under high vauum at temperatures at or below 100°C.

Occasionally we observed that the polymerizations gave poor results (poor distributions incomplete conversions etc.) with some commercially available sources of PPh_4C, indicating premature termination (Tab. 1, run 2). The occurrence of terminations was also indicated by the gradual disappearance during the polymerization of the typical orange-red color characteristic of the propagating PMMA chains (see below).

We suspected that these difficulties could be related to the presence of water in the PPh_4Cl. Accordingly we prepared samples of solid PPh_4Cl that were first "titrated" with

Ph_3C,K/THF solutions until a faint reddish color developed of the Ph_3C,PPh_4 initiator. However, if these samples were subsequently used as initiators without further purification the difficulties, particularly the poor MW distributions, still persisted.

$$\mathrm{TPM,K} + H_2O \longrightarrow \mathrm{TPMH} + \mathrm{KOH} \qquad (2)$$

$$\mathrm{PMMA,TPP} + \mathrm{KOH} \longrightarrow \mathrm{PMMA,K} + Ph_3PO + PhH \qquad (3)$$

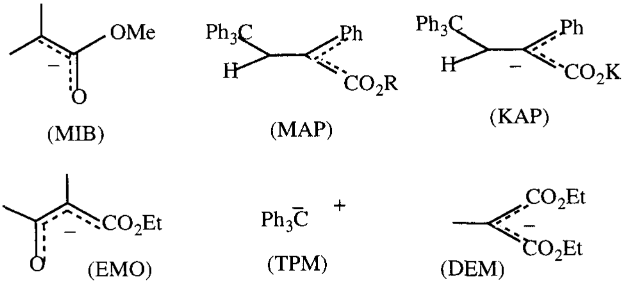
$$\mathrm{PMMA,K} \longrightarrow \mathrm{PMMA} + CH_3OK \qquad (4)$$

$$\mathrm{PMMA,TPP} + CH_3OK \rightleftarrows \mathrm{PMMA,K} + CH_3OTPP \qquad (5)$$

We then reasoned that these latter difficulties could be caused by the presence of KOH generated by the reaction of TPM,K with the water in the PPh_4Cl salts. Thus, the KOH could be expected to exchange with the propagating PMMA,PPh_4 chains (Eq. (2)), producing PMMA,K and PPh_4,OH that subsequenly decomposes into triphenylphosphineoxide and benzene thus driving the reaction forward (Eq. (3)). The PMMA,K would give the well documented intramolecular Claisen type side reactions (Eq. (4)) resulting in the formation of potassium methoxide that could undergo exchange reactions with PMMA,TPP, thus "recycling" the K ions (Eq. (5)) (Ref. 23). Accordingly when the KOH was removed from the "titrated" PPh_4Cl salts by repeatedly washing with THF there were no further problems and the corresponding PPh_4Cl salts could then be used successfully without further purification.

Further evidence for this course of events was provided by the stereochemistry of the PMMA produced (Ref. 23). In the absence of water in the PPh_4Cl, the stereochemistry of the PMMA was found to resemble that of the Li ion - and GTP mediated MMA polymerizations in THF at ambient conditions consistent with the presence of the large PPh_4 cation (Tab. 1) (Ref. 15).

The stereochemistry of the PMMA produced using the "wet" PPh_4Cl salts (containing as little as 5 mole % water) was found to have an unusually high heterotactic (mr) content of 56% (Tab. 1, run 2) closely resembling the PMMA stereochemistry produced by the anionic polymerization of MMA in the presence of K ion. It is clear therefore that in the presence of even small amounts of water the exchange processes shown in in Eqs. (2)-(5) satisfactorily account for the wider MW distributions, the incomplete monomer conversions and the heterotactic stereochemistry all of these effects being attributable to the presence of small amounts of water.



Scheme 2. Initiators for the TPP cation mediated polymerization of MMA.

Initiator Basicity. In order to better understand the role of the initiator reactivity in molecular weight broadening and initiator efficiency, the effect of initiator basicity was explored by carrying out the TPP-mediated polymerizations of MMA using the initiators shown in Scheme 2.

These salts, as was the case for the Ph_3C,PPh_4 and the MIB,PPh_4 initiators, were prepared by reaction of the K salts of the corresponding anions in THF at -78°C with TPPCl that was first dried overnight under high vacuum (10^{-6} Torr) at 100°C followed by titration with Ph_3C,K and extensive rinsing of the PPh_4Cl salt with THF.

As expected the MW distributions were broader and initiator efficiencies were reduced with decreasing initiator basicity as measured by the acidity of their parent esters (Tab. 1, runs

6-11). Interestingly, the enolates derived from the K salt of KAP (Tab. 1, run 10) although inferior to the MIB (run 3) and TPM (runs 1 and 2) initiators still produce relatively narrow MW distributions (M_w/M_n of about 1.5) and give a relatively good initiator efficiency. This is attributable to the reduced stabilization-of the carbanion (by the carboxyl anion) and hence greater basicity of the enolate that is expected to be more basic than the MAP anion that is stabilized by the ester and phenyl groups and that gives a lower intitiator efficiency of about 20% (Tab. 1, run 7).

The highly resonance stabilized DEM and EMO anions in the presence of TPP cation are largely ineffective initiators and this is probably attributable to their low basicity (Tab. 1, runs 8 and 9). The greater effectiveness of the DEM initiator in the tetrabutyl ammonium mediated polymerization of acrylates is plausibly due to the greater electrophilicity of butyl acrylate - compared with MMA (Ref. 8). Surprisingly the methoxide anion TPP system, notwithstanding the considerable basicity of the methoxide anion, proved to be a poor initiator giving very low yields of oligomers (Tab. 1, run 11).

Nature of the propagation sites. As indicated above, the propagating PMMA,TPP chains and the corresponding MIB,TPP model appeared to have a typical orange-red color that is quite a typical of the PMMA anion alkali cation ion pairs. Because of the excellent stability of the MIB,TPP model system we decided to investigate its structure using ^1H, ^{13}C, and ^{31}P NMR (Ref. 17).

As shown in Fig. 3, the proton spectrum of MIB,PPh_4 in THF-d_8 is inconsistent with a simple ion MIB^-,TPP^+ ion pair, **3**, showing the presence of three equivalent phenyls and a set of three absorptions corresponding to 5 protons at 5.72, 4.35 and 3.70 ppm in the ratio of 2:2:1 consistent with the presence of a 2,5-cyclohexadienyl ring of a phosphor ylide, **4**, formed by addition of the MIB enolate anion to the para position of one of the phenyl rings (Tab 2).

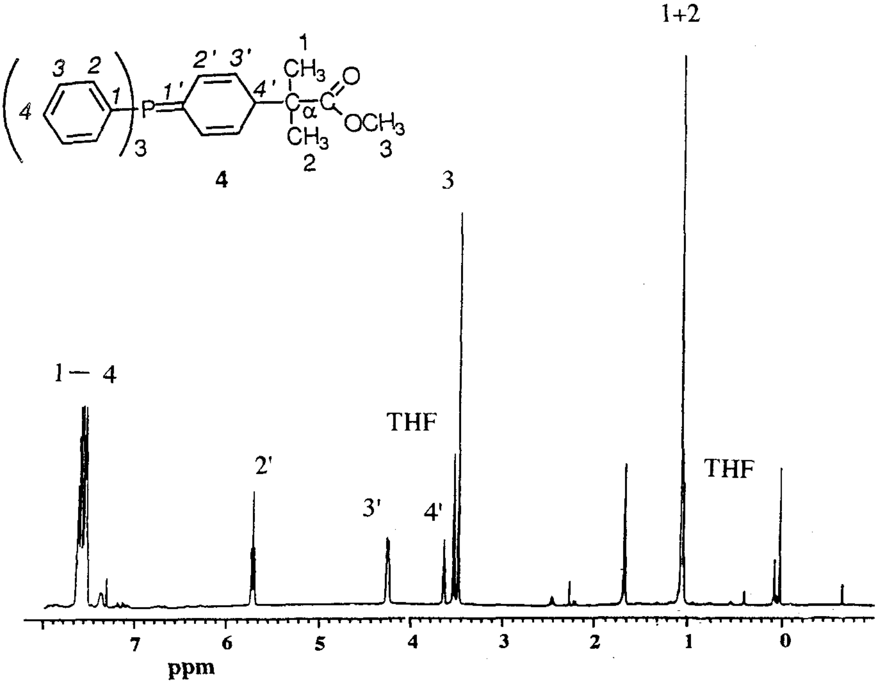
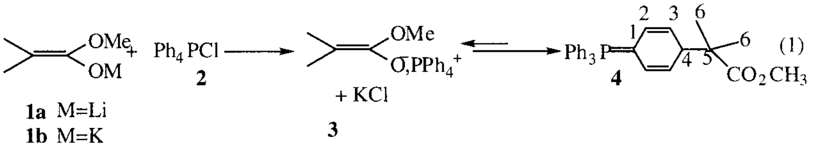


Fig. 3: Proton NMR of Methylisobutyrate Tetraphenylphosphonium in THF-d8 (250 MHz).

This structure is further supported by the geminal methyls now being equivalent in contrast to that of the corresponding alkali enolates (Refs. 7,24). The ^{1}H NMR spectrum also indicates a very slow protonation (days) of the enolate resulting in the parent ester, confirming the considerable kinetic stability of this compound. The MIB,TPP has the color and UV-visible spectrum (λ_{Max} =415 nm), identical to that produced by addition of MMA to the Ph_3C,PPh_4 salt.



Scheme 3. Possible PMMA Propagation sites and their Interconversion

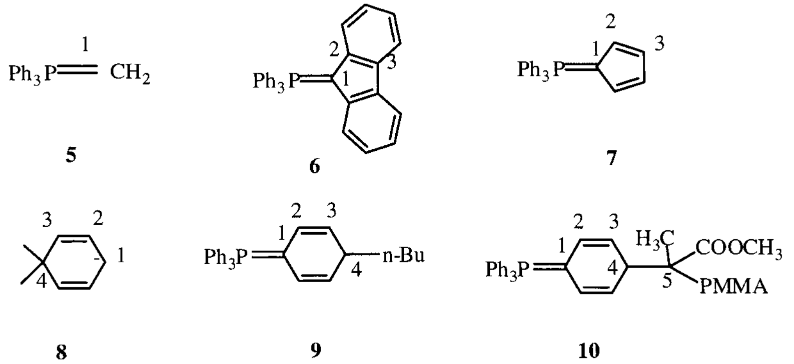
Tab. 2. Proton NMR chemical shifts of **1a**, **3** and **4** and ^{1}H-^{1}H and ^{1}H-^{31}P coupling constants of **4** in THF-d_8 at 25^{0}C $^{(a)}$

	Me	OMe	H-2	H-3	H-4
1a$^{b)}$	1.45/1.46	3.53	—	—	—
3$^{c)}$	1.58	3.65	—	—	—
4	1.15	3.55	5.72(t)	4.35(m)	3.70(t)
$J_{1H\text{-}1H}$(Hz)$^{d)}$	—	—	(9.4)	(9.4)(4.1) (4.1)	(4.1)
$J_{1H\text{-}31P}$(Hz)$^{d)}$	—	—	(10.3)	(4.1)	(1.2)

a) Chemical shifts (ppm) downfield from TMS. b) From ref. 1.
c) Small broad signals. d) Coupling constants of **4.**

The ^{13}C NMR of **4** shows resonances at 50.7, 21.4, 178.2, and 50.9 ppm of carbons 5,6,7 and 8, respectively, which are compared to those of MIB,Li (**1a**) in Tab. 3 (Ref. 17). The presence of a single α-methyl resonance at 21.40 ppm, slightly downfield from that of the parent ester at 21.1 ppm, is again consistent with structure **4**. The upfield shift of carbon 5 compared with that of the lithium enolate (**1a**) is consistent with the change in hybridization

(sp^2 to sp^3). The cyclohexadienyl carbons 1, 2, 3 and 4 resonate at 48.6, (134.5 Hz), 130.0, (12.5 Hz), 104.2 (15.1 Hz), and 47.8 ppm showing expected strong couplings to phosphorous in good general agreement with ^{13}C chemical shifts and ^{13}C-^{31}P coupling constants of the related ylides **5** – **7** (Refs. 25-27).



Scheme 4. Structure of PMMA Ylide 10 and Comparable Ylide Structures

Thus the ^{13}C chemical shifts of the ylide carbon-1 are arranged as **5**> **4**> **6**> **7** in order of decreasing field whereas the ^{31}P chemical shifts are arranged in opposite order (Refs. 27,28) indicating a correlation with electron density.(Refs. 29,30). The ^{13}C NMR assignments of carbons 1-4 in **4** are consistent with that of 4,4-dimethyl-cyclohexadienyl anion, **8**, the C-1 carbon of which is shifted downfield compared to the corresponding carbon in **4** while carbons -2 ,-3 and -4 are shifted upfield.

Tab. 3. Carbon-13 and ^{31}P NMR chemical shifts and ^{13}C-^{31}P coupling constants of **4** and related compounds in THF-d$_8$ at 25°C.a,b)

	C_1	C_2	C_3	C_4	C_5	CH_3	OCH_3	CO	^{1}P
4	48.6 (134.5)	130.0 (12.5)	104.2 (15.1)	47.8	50.7	21.4	50.9	178.2	14.4
1ac)	___	___	___	___	72.0	17.5 18.3	56.4	161.0	
5e)	-4.1 (51.9)	___	___	___	___	___	___	___	19.6
6d)	53.3 (128.7)	131.3 (14.0)	142.1 (14.8)	___	___	___	___	___	
7d)	78.3 (113.1)	117.2 (15.7)	114.6 (18.0)	___	___	___	___	___	12.9
8g)	78.1	127.9	91.7	30.8	___	___	___	___	___

a) Carbon-13 spectra taken at 100 MHz; ^{31}P NMR at 202.4 MHz. b) Bracketed values are ^{13}C-^{31}P coupling constants in Hz. c) From ref. 35. d) From ref. 29. e) From Albright,T.; Freeman,W. ; Schweizer, E. *J. Am. Chem. Soc.* **1975**, *97*, 940. f) From ref. 30.

The formation of phosphor ylides by a similar nucleophilic addition to one of the Ph$_4$P phenyls has been demonstrated by Cristau and coworkers for the reaction product, **9**, of n-BuLi and PPh$_4$Cl (Ref. 31). A similar reaction for the case of the far less basic and sterically hindered isobutyrate anion is unexpected especially since no such reaction has been detected thus far for the somewhat more basic Ph$_3$C anion (Ref. 32). Thus, equilibration with the tetraphenylphosphonium - isobutyrate enolate ion pair, **3**, by retroaddition of **4**, restoring the aromaticity of the phenyl ring would seem possible.

Although the conversion of ylides into anions have been implicated in the initiation step of anionic polymerizations, (Refs. 33,34) to our knowledge the above TPP mediated polymerizations of MMA appear to be the first example where a vinyl polymerization involves *ylides* as intermediates.

Polymerization of Acrylates. It is clear that the TPM,TPP- and MIB,TPP- initiated polymerizations of MMA are capable of producing well defined narrow distribution PMMA at ambient temperatures in high yield. Given the commercially attractive potential of block copolymers of PMMA and poly(2-ethylhexylacrylate) (PMMA-b-PEHA) or of PMMA and polybutylacrylate (PNBA-b-PMMA), the potential of these interesting new initiators with regard to the polymerization of acrylates seemed worth exploring.

Addition of THF solutions of n-butylacrylate (NBA) to the above TPM, TPP or MIB,TPP initiators appears to result in rapid polymerization . Thus upon addition of NBA there is a rapid disappearance of the purple color of TPM,TPP and an orange color is observed that is similar to that seen for the case of MMA. However in this case the orange color disappears during the polymerization and the MW distributions of the PNBA's are wider (Tab. 4). Moreover the polymerization yields of PNBA are reduced and the MW's generally do not exceed about 10,000.

Tab. 4. Polymerization and Block Copolymerization of Meth(acrylate) Initiated with TPM,TPP

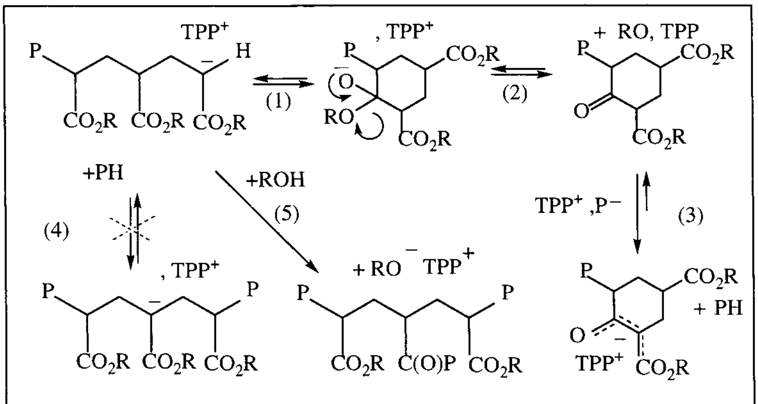
	Initiator	T(^{0}C)	Mon.	Yield a)	Mn b)	MWD c)	f d)
1.	TPM	0	NBA	85	4 200	1.31	1.20
2.	TPM	0	NBA	80	8 300	1.60	1.10
3.	TPM	0	NBA	70	7 200	1.24	1.30
4.	TPM	-78	NBA	42	1 600	4.70	2.20
6.	TPM	23	NBA	88	9 100	1.43	1.70
7.	TPM	23	NBA	86	9 100	1.23	1.40
8.	TPM	23	NBA	88	5 200	1.43	1.70
9.	MIB	0	TBA	65	4 200	1.25	2.00
10.	PMMA e)	0	NBA	88	9 100	1.17	1.10
11.	PMMA f)	0	NBA	88	8 700	1.23	-
12.	PMMA g)	0	NBA	71	7 200	1.19	-
13.	TPM h)	0	MMA	95	18 100	4.20	.60
14.	TPM i)	0	MMA	95	3 900	14.80	.45

a) Polymer yield (%) determined gravimetrically. b) Number average MW by SEC using universal calibration method. c) Molecular weight distribution by SEC. d) Initiator efficiency, $f = M_n(calc)/M_n(SEC)$. e) Initiation with TPM, TPP. f) Mn of PMMA is 1300. Mn of PMMA precursor is 840. g) Mn of PMMA precursor is 720. h) Presence of 20 fold excess of MIB with respect to initiator. i) Presence of one equivalent of EMO with respect to initiator.

Furthermore, experimental DP_n values are *lower* than calculated and initiator efficiencies are as high as 200% or more indicating the presence of significant chain-transfer (Tab. 3). Thus, although the TPP-mediated NBA polymerizations give more control than what is typically observed for anionic polymerizations of acrylates, the above results indicate the occurrence of significant termination as also found for other anionic polymerizations of NBA (Ref. 8).

PMMA-PNBA Block Copolymers. Several PMMA-PNBA block copolymers were synthesized by initiation of NBA with PMMA,TPP (Tab. 4). As shown in the table the distribution of the block copolymers was reasonably narrow (MWD<1.5) but this is hardly surprising since the distribution of the PMMA precursors was quite narrow. Nevertheless, the results appear to be comparable to such block copolymers synthesized by other recent methods.

Nature of the PNBA Side Reactions. It is clear that the anionic polymerization of NBA in the presence of the TPP cation is inherently susceptible to side reactions that appear to be due to the nature of the propagating PNBA chain. For the anionic polymerization of MMA, some of these termination reactions are well documented to involve an intramolecular Claisen reaction between the reactive chain ends and the antepenultimate ester group resulting in the formation (with loss of alkoxide anion) of a biscarboxyalkyl substituted cyclohexanone moiety at the polymer chain end (Refs. 34,35). A similar reaction for the anionic polymerization of acrylates seems plausible. However in this case the initial cyclization generates a highly reactive β-keto ester proton that has the potential to cause additional problems (Scheme 5, Eq. (3)).



Scheme 5. Termination Reactions in the TPP mediated Polymerization of Acrylates

For the case of acrylates, there is an additional possibility of proton transfer to the active chain end of the backbone methine protons (Scheme 5, Eq. (4)). However, there has been a general lack of clarity concerning the importance of the presumed backbone methine proton transfer to the propagating site relative to that of the Claisen cyclization of the chain-end anion.

In order to distinguish between these two side reactions we carried out the TPP mediated anionic polymerization of MMA in the presence of MIB (20 fold excess) and EMO (Scheme 2) (1 mole equivalent) as models for the polyacrylate backbone and the β-ketoester fragment of the cyclohexanone end group, respectively. The additives were added along with the monomer in the course of the polymerization, the MIB and EMO as additives being present in 20 fold excess and equimolar amounts with respect to initiator respectively. As shown in Tab. 4 (runs 13 and 14), the MW distributions in both cases are broadened but the distribution is much wider for the case of EMO although it was present in far smaller amounts. Not surprisingly, the highly acidic betaketoester group of EMO (pKa= 14.4) is an unusually effective terminating agent and the same is undoubtedly the case for the cyclic beta keto ester formed in the chain end cyclization shown in Scheme 5.

Thus the abstraction of the methine protons of the poly (NBA) chain or the occurrence of other termination reactions with the methyl of MIB is far less significant than the proton transfer from EMO. This result is in agreement with the lack of proton transfer observed between lithio-t-butyl-isobutyrate and t-butylpropanoate in THF at ambient temperatures on the time scale of several hours (Ref. 36). Furthermore, proton-transfer from MIB to the PMMA anion is merely a transfer reaction and can not account for the incomplete NBA conversions (Tab. 4) and is inconsistent with the low initiator efficiency observed in this case (40%). The data are, however, consistent with nucleophilic attack by the PMMA anion on the MIB *ester group* accounting also for the lowered yield (75%) and the wide distribution (MWD= 4.2) as well as for the low initiator efficiency (about 40%). Thus, the above together with data on the polymerization of NBA seem to indicate the absence of direct protonation of the chain end by the PNBA methine protons.

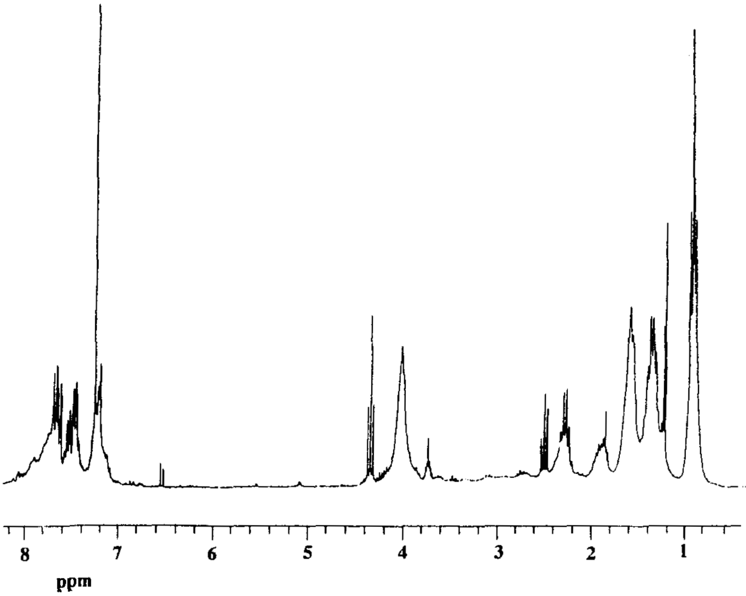


Fig. 4: Proton NMR of Spontaneously Terminated Poly (t-butylacrylate), Tetraphenylphosphonium in THF-d8 at 30°C (250 MHz).

Further independent evidence for the nature of the termination occurring for the case of these TPP-mediated NBA polymerizations is provided by the structure of the β-ketoester end groups generated in the MIB,TPP initiated polymerization of t-butylacrylate (TBA) (Tab. 4, run 9). In contrast to the case of NBA and similar acrylates the ^{1}H NMR signals from the methoxycarbonyl group of the MIB initiator fragment at 3.62 ppm and a methine triplet at 4.33 ppm from the cyclic β-ketoester end group are clearly visible (Fig. 4). Integration shows that ca. 55% of the chains contain a terminal cyclic β-ketoester group. This is consistent with Scheme 5 since formation of the cyclic β-ketoester would be expected to be followed by a rapid proton transfer to another polyacrylate chain end anion. If the protonation step is rapid compared to that of the cyclization one would expect to see one protonated chain for each cyclized chain end.

Independent studies by MALDI of poly(NBA) prepared by these methods indeed have shown that the chains are terminated roughly half by Claisen cyclization and half by protonation (Ref. 37). Thus our results provide ample support for the intramolecular Claisen reaction and subsequent proton transfer as the principal chain termination reactions in these anionic acrylate polymerizations. The highly effective acrylate anion termination reaction indicates that cyclization is likely to be further accelerated compared to the case of MMA due to the absence of the α-methyl groups in the cyclohexanone end group.

A similar course of events has been documented for the case of the crossover reaction from living poly(2-vinylpyridine) lithium to MMA in THF (Ref. 38) and for side reactions in the polymerization of N,N-dimethylacrylamide (DMA) (Ref. 39). For instance upon addition of MMA to the P2VP,Li in THF the anion attacks the MMA ester to give a highly acidic picolyl substituted vinylketone that quickly protonates the P2VP anion.

A similar scenario may hold for the termination observed in the anionic LiCl mediated copolymerization of MMA and t-butylacrylate in THF at -78°C (Ref. 40). In this case the intermediate postulated was the enol form of the cyclic β-ketoester formed by nucleophilic attack of the t-butylacrylate enolate on a penultimate MMA unit. However, considering the reaction conditions and the acidity of the β-ketoester it is more likely that the actual reaction intermediate is an enolate and that protonation of the chain end anion by β-ketoester is a significant pathway in the termination process.

Discussion

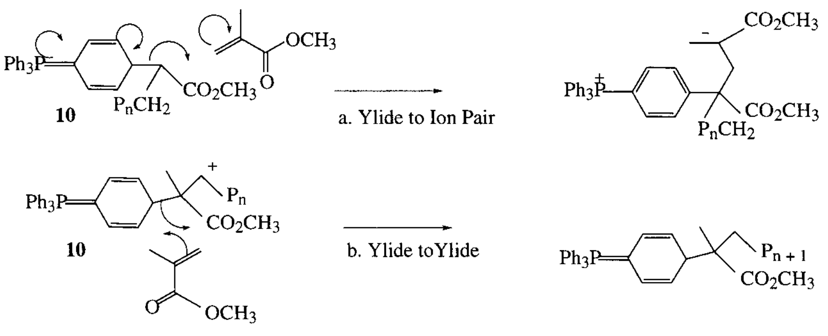
Mechanism of MMA Polymerization, Ylides or Ion Pairs? The presence of these PMMA ylides in these polymerizations raises several questions. The first of these involves the possible reaction of the PMMA chain-end ylide, **10**, with MMA at either carbons -1 or -5 (Scheme 6). Reaction at carbon -1 would lead to incorporation of a cyclohexadienyl moiety in the polymer. Since there is no ^{1}H or ^{13}C NMR evidence for such a structure in any of our PMMA's this possibility may be excluded.

Of course reaction of the ylide at carbon-5 with MMA would not show any structural irregularities in the PMMA consistent with our findings. Because the direct reaction of ylide, **10,** with MMA would be expected to require the retro-addition of MIB from **4** , the reactivity of **4** toward MMA or other electrophiles is expected to be less than that of ion pair **3**. We do not know how much less.

Our data appear to be consistent with several possibilities. The first of these involves the possible reaction of the PMMA chain-end ylide, **10**, with MMA at either carbons -1 or -5 (Scheme 3). Reaction at carbon -1 would lead to incorporation of a cyclohexadienyl moiety in the polymer. Since there is no ^{1}H or ^{13}C NMR evidence for such a structure in any of our PMMA's this possibility may be excluded. Of course reaction of the ylide at carbon-5 with MMA would not show any structural irregularities in the PMMA consistent with our findings.

The next important issue concerns the mechanism of the polymerization that may involve the exclusive polymerization through the ion pair or the ylide or both. The polymerization exclusively occurring through the ionic species is considered first. In this case the ylide is completely unreactive and the system would appear to resemble the postulated dissociative mechanism of GTP polymerization of MMA catalyzed by TAS fluorides and similar species in which a highly reactive propagating enolate TAS ion pair is in rapid equilibrium with an inactive silylketene acetal species (Refs. 14,15).

The presence of a small fraction of (presumably highly reactive) enolate ion pair, **3**, as the sole propagating species is consistent with the polymerization kinetics of MMA using Ph_3C,PPh_4 as initiator in THF at temperatures between -20 and +20^{0}C (Ref. 18). The observed polymerization rate constant in the presence of PPh_4^+ would be expected to be on the same order of magnitude as that in the presence of the cryptated (Na,2,2,2) ion (Ref. 26) considering the similar cation sizes (about 5Å) but was found to be about two orders of magnitude smaller (Ref. 18). Thus the data are consistent with the presence of a small fraction (<1%) of a highly reactive phosphonium enolate ion pair in equilibrium with an unreactive - or much less reactive - ylide. The fact that the molecular weight distributions of the PMMA prepared in the presence of PPh_4^+ are quite narrow (MWD ≤ 1.20) would be consistent with equilibration between **3** and **4** being rapid on the polymerization time scale.



Scheme 6. Possible Mechanisms of Direct Monomer Addition to Ylides

An example of a polymerization involving two active (propagating) species would be that demonstrated for the anionic polymerization of styrene in THF in the presence of alkali cations where the polymerization reaction was shown to proceed through reactive free anions in equilibrium with less reactive ion pairs (Ref. 21). An important distinction between the latter system and the current one (TPP) is that in the current system there is a predicted lack of a dependence on the concentration of active chain ends. Of course this would not be the case if the TPP ion pairs are present at concentrations where ionization into free anions could occur.

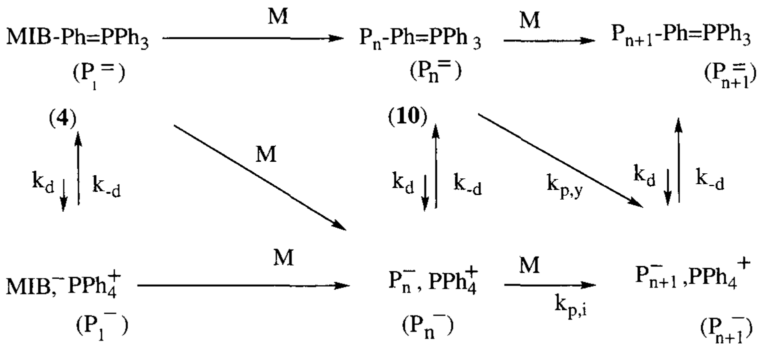
Given the low concentration of ion pairs in this system ($<10^{-5}$M) there would be the possibility for such a scenario that would predict increases in apparent rate constant with decreasing PMMA,TPP concentration.

Another possibility involves the participation in the polymerization of both the ionic and ylide species (Scheme 6). Because the direct reaction of the PMMA ylide, **10**, with MMA would be expected to require the retro-addition of the PMMA anion from **4**, the reactivity of the PMMA ylide toward MMA or other electrophiles is expected to be less than that of the corresponding ion pair. We do not know how much less.

For the direct reaction of **10** with MMA this would give either a PMMA phosphonium enolate ion pair (a) or producing another ylide (b) (Scheme 6). Both mechanisms would be unusual. The first mechanism would appear to be unique in the sense that the interconversion of one of the two active species into the other occurs directly through monomer addition.

The concerted addition of MMA to the chain-end ylide *giving another ylid* would involve the concerted addition of the MMA monomer with concurrent attachment of the new chain end to carbon -5 of the ylide (Scheme 6b). High level *ab initio* calculations (Ref. 41) appear to indicate that such a course of reaction is possible but a review of the literature to our knowledge indicates such a reaction to be without precedent.

Several of these scenarios may be probed by polymerization kinetics and a brief analysis of the polymerization kinetics, in particular the dependence of the apparent rate constant of polymerization on monomer concentration, is given below (Scheme 7).



Scheme 7. Survey of Polymerization Mechanisms of Ylide Mediated Polymerizations

We first consider the general case in which both ion pairs (P^-) and ylides ($P^=$), the sum of which equals the total concentration $[P]_T$, contribute toward the polymerization and where the ylides are converted into ion pairs through monomer addition but where the ylide to ylide propagation is absent. The ion pair collapse into the ylide and the ionization of the ylide into the ion pair is given by k_d and k_{-d} respectively and the rate constants of the ion pair propagation and the ylide to ion pair propagation are given as $k_{p,i}$ and $k_{p,y}$ respectively.

The application of steady state conditions of the ion pairs and ylides gives Eqs. (6), (7), (8) and (9) where $[P]_T = [P^-] + [P^=]$ is the total concentration of the propagating chains. The first and second terms of Eq. (9) represent the contribution of the ion pairs and the ylides to the apparent rate constant of polymerzation. Steady state conditions for both propagating species requires:

$$d[P^{-}]/dt = 0 = k_d[P^{=}] - k_{-d}[P^{-}] + k_{p,y}[P^{=}][M] \qquad \text{(eqn. 6)}$$

$$\text{so that: } [P^{-}] = [P^{=}](k_d + k_{p,y}[M])/k_{-d} \qquad \text{(eqn 7)}$$

$$\text{and since: } [P]_T = [P^{-}] + [P^{=}]$$

$$Rp = \frac{-d[M]}{dt} = (k_{p,i}[P^{-}] + k_{p,y}[P^{=}])[M] = k_{p,a}[P]_T[M] \qquad \text{(eqn 8)}$$

$$\text{leading to:} \quad k_{p,a} = \frac{k_{p,i} \cdot F + k_{p,y}}{1 + F} \qquad \text{(eqn 9)}$$

$$\text{Where } F = \frac{[P^{-}]}{[P^{=}]} = \frac{k_d + k_{p,y}[M]}{k_{-d}}$$

From Eq. (9) it is clear that the rate constant is monomer concentration dependent. For the case that F>>1, it is clear that the apparent rate constant of propagation decreases with the concentration of monomer whereas this rate constant increases with [M] when F<<1.

For the case (A) that association to the ylide is much faster than ion pair propagation or ion pair dissociation we have:

$$k_{-d} \gg k_{p,y}[M] \;;\; k_{-d} \gg k_d \;:$$

$$k_{p,a} = \underset{\text{ion pairs}}{\frac{k_{p,i}(k_d + k_{p,y}[M])}{k_{-d}}} + \underset{\text{ylides}}{k_{p,y}} \qquad \text{(eqn. 10)}$$

(i) $k_{p,y}[M] \gg k_d$ (high [M])

$$k_{p,a} = \frac{k_{p,i} \cdot k_{p,y}[M])}{k_{-d}} + k_{p,y} \qquad \text{(eqn. 11)}$$

(ii) $k_{p,y}[M] \ll k_d$ (low [M])

$$k_{p,a} = \frac{k_{p,i} \cdot k_d}{k_{-d}} + k_{p,y} \qquad \text{(eqn. 12)}$$

Depending on the relative magnitude of k_d and $k_{p,y}$ [M], the apparent rate constant of polymerization may be either linearly dependent on (i) or independent of (ii) monomer concentration giving Eqs. (11) and (12) respectively.

The special case (B) where the ylides do not propagate ($k_{p,y}=0$) leads to equation relating the equilibrium constant for ylide to ion pair interconversion, K_d, and the two rate constants for polymerization. In this case there is no predicted dependence of the rate constant upon the monomer concentration. For large values of K_d we obtain the intuitively obvious result that $k_{p,a}$, the apparent rate constant of polymerization, equals $k_{p,i}$. and for the case where K_d is small we find that $k_{p,a}= k_{p,i} .K_d$.

$$k_{p,a} = \frac{k_{p,i} \cdot k_d}{k_d + k_{-d}} = \frac{k_{p,i} \cdot K_d}{1 + K_d} \quad (K_d = k_d/k_{-d}) \qquad \text{(eqn.13)}$$

$$K_d >> 1 : \quad k_{p,a} = k_{p,i} \qquad K_d << 1 : \quad k_{p,a} = k_{p,i} \cdot K_d$$

As a result, regardless of the precise mechanistic role of **4** in the polymerization, intermediates of type **3** are most probably involved.

To our knowledge this is the first example of an ylide-mediated vinyl polymerization. The precise role of the ylides in these polymerizations remains to be elucidated. Further studies on this interesting new polymerization system are in progress.

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Keywords: Ester enolates, phosphorylides, anionic polymerization, living polymerization, methacrylates

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