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Polymerization of Methacrylates in the Presence of Tetraphenylphosphonium Cation. 2. Evidence for Phosphorylide-Mediated Polymerizations

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The synthetic importance of ester enolates and related compounds is reflected in numerous studies of their structures and their stereochemistry.[1−5] Enolate anions are also of great interest in the polymerization of acrylates and methacrylates. Thus the synthesis of block copolymers consisting of poly(methyl methacrylate) ("hard") and poly(butyl acrylate) or poly(2-ethylhexyl acrylate) 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.[6−13] Several of these studies have employed "metal-free" systems,[7,8] involving organic counterions that were demonstrated to be effective in minimizing side reactions of the enolate anion with the antepenultimate ester group of the PMMA resulting in the formation of cyclic β-ketoesters. An apparently closely related system is the group-transfer polymerization of (meth)acrylates where silylketene acetals are intermediates.[14]

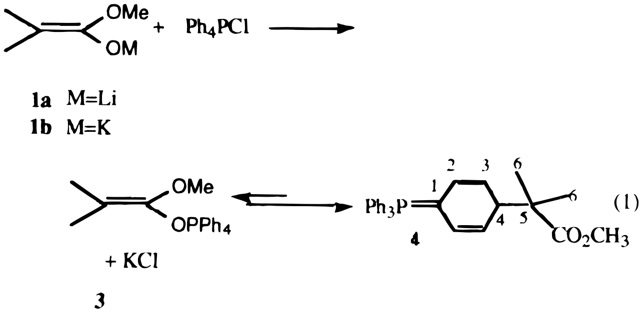
A more recent development is the polymerization of methacrylates in the presence of tetraphenylphosphonium (TPP) ion, which appears to have pronounced living character.[15] Thus, for the case of MMA, at ambient or lower temperatures, number average molecular weights increase linearly with conversion and MW distributions are narrow (<1.30). Molecular weights in excess of 50 000 are routinely achievable.[16] The polymerizations of MMA in the presence of the TPP cation are quite rapid, having MMA half-lives on the order of 0.3−0.5 s at 0 °C.[16] 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 the triphenylmethyl anion, an orange-red solution is formed ($\lambda_{max} = 415$ nm) unlike that of enolate anions that are colorless or slightly yellow. This color disappears upon addition of water or methanol.

We now wish to report the results of ^{1}H, ^{13}C, and ^{31}P NMR studies of a model of the active PMMA chain end, formed by reaction of potassium enolate, **1b**, with PPh_4-Cl (eq 1) indicating the presence in these polymerizations of phosphorylides formed by the addition of the PMMA enolate anion to one of the phenyls of the TPP cation. The model, which, unlike the corresponding tetrabutyl salt, is stable for hours at ambient temperatures, has the color and UV−visible spectrum ($\lambda_{max} =$ 415 nm) identical to that produced by addition of MMA to the Ph_3CPPh_4 salt.

Table 1. 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 °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)
$J_{^1H-^1H}$ (Hz)[d]			(9.4)	(9.4) (4.1) (4.1)	(4.1)
$J_{^1H-^{31}P}$ (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 ^{1}H NMR spectrum of $MIBPPh_4$ in THF-d_8 shows the presence of three equivalent phenyls and a set of three absorptions corresponding to five 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 phosphorylide, **4**, formed by addition of the enolate anion to the para position of one of the phenyl rings (Table 1). This structure is further supported by the geminal methyls now being equivalent, in contrast to that of the corresponding alkali metal enolates.[7,8,17] The ^{1}H NMR spectrum also indicates a very slow protonation (days) of the enolate, resulting in the parent ester, indicating the considerable kinetic stability of this compound.

The ^{13}C NMR of **4** shows resonances at 50.7, 21.4, 178.2, and 50.9 ppm of carbons 5−8, respectively, which are compared to those of (MIB)Li (**1a**) in Table 2.[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 1−4 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 phosphorus in good general agreement with ^{13}C chemical shifts and ^{13}C−^{31}P coupling constants of ylides **5**−**7**.[18,19]

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,[20,21] indicating a correlation with electron density.[22,23] The ^{13}C NMR assignments of carbons 1−4 in **4** are consistent with that of the 4,4-dimethylcyclohexadienyl anion, **8**,[21] 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.

The formation of phosphorylides by nucleophilic addition of nucleophiles to the Ph_4P^4 phenyl has been demonstrated for the reaction product, **9**, of *n*-BuLi and PPh_4Cl.[24] A similar reaction for the case of the far less basic and sterically hindered isobutyrate anion is un-

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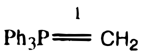
Table 2. Carbon-13 and ^{31}P NMR Chemical Shifts and ^{13}C−^{31}P Coupling Constants of 4 and Related Compounds in THF-d_8 at 25 °C[a,b]

	C_1	C_2	C_3	C_4	C_5	CH_3	OCH_3	CO	^{31}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
1a[c]					72.0	17.5, 18.3	56.4	161.0	
5[e]	−4.1 (51.9)								19.6
6[d]	53.3 (128.7)	131.3 (14.0)	142.1 (14.8)						
7[d]	78.3 (113.1)	117.2 (15.7)	114.6 (18.0)						12.9
8[f]	78.1	127.9	91.7	30.8					

[a] Carbon-13 spectra taken at 100 MHz; ^{31}P NMR at 202.4 MHz. [b] Values in parentheses are ^{13}C−^{31}P coupling constants in Hz. [c] From refs 16 and 17. [d] From ref 22. [e] From ref 18. [f] From ref 23.

expected especially since no such reaction is detected for the somewhat more basic Ph_3C anion.[25] Thus, equilibration with the tetraphenylphosphonium−isobutyrate enolate ion pair, **3**, by retroaddition of **4**, restoring the aromaticity of the phenyl ring, is not unexpected.



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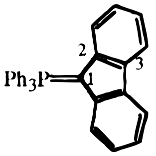

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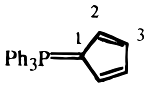

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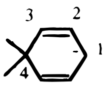

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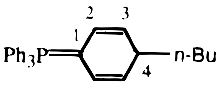

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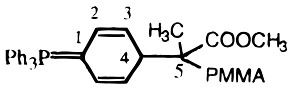

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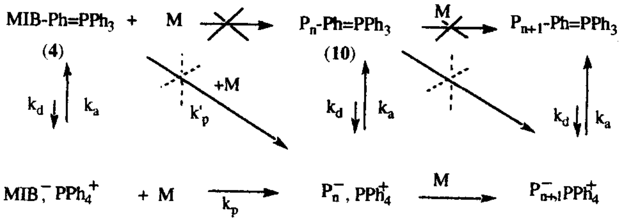
Some evidence suggesting the retroaddition of ylide **4**, leading to a very small fraction of enolate **3**, is provided by ^{1}H resonances at 1.58 and 3.65 ppm that may correspond to the methyl and methoxy protons of **3**. Further evidence for the coexistence of small amounts of **3** in equilibrium with **4** is provided by ^{1}H NMR and by NOE. At ambient temperature, irradiation of **4** at H-2 (5.7 ppm) gives a positive NOE at H-3, strong negative signals of the phenyl protons, and weak positive NOE signals at the phenyls of **3** at 7.8 ppm. Upon irradiation of H-4 at 3.7 ppm, there is a positive NOE at H-3 and a strong negative phenyl signal at 7.6 ppm with smaller negative signals at the phenyls of **3** at 7.8 ppm.

These strong NOE enhancements cannot be attributed to spatial proximity considering the internuclear distances. It could arise from the exchange of saturation of the cyclohexadiene ring protons with that of the other three phenyls as a result of inter- or intramolecular exchange of the MIB anion through the intermediacy of the phosphonium enolate, **3**. Thus, during the presaturation time (3 s), MIB anion exchange between the ylide phenyls results in pronounced saturation transfer and weaker phenyl transfer to **3**. Furthermore, irradiation of the phenyl signals of **3** at 7.8 ppm gives negative enhancements of H2- and H3-, of **4**, again consistent with the existence of an equilibrium between **3** and **4**.

The presence of such phosphorylides as polymerization intermediates is plausible because of the similarity of the PMMA and MIB ester enolates. This is also indicated by their very similar orange-red solutions having the same UV/visible spectra. Furthermore, both intermediates are characterized by their considerable kinetic stability at ambient temperatures.

Scheme 1. Proposed Mechanism for the Ylide-Mediated Polymerization of MMA



Although ylides have been implicated in the initiation step of anionic polymerizations,[26] to our knowledge these ylide-mediated polymerizations are unprecedented.

The presence of these PMMA ylides in these polymerizations raises several questions (Scheme 1).

The first of these involves the possible reaction of the PMMA chain-end ylide, **10**, with MMA at either carbon 1 or 5. Reaction at carbon 1 would lead to incorporation of a cyclohexadienyl moiety into the polymer. Since there is no ^{1}H or ^{13}C NMR evidence for such a structure in any of our PMMAs, 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. Second, since any reaction of ylide **10** with MMA requires the retroaddition of MIB from **4**, the reactivity of **4** toward MMA or other electrophiles is expected to be less than that of **3**. Furthermore, even if the direct reaction of the ylide with MMA were not negligible, such a reaction would have to result in the formation of a phosphonium enolate since the concerted addition of MMA to the chain-end ylide *giving another ylide* is quite unlikely, requiring a highly strained cyclic transition state. As a result, regardless of the precise mechanistic role of **4** in the polymerization, intermediates of type **3** are most probably involved.

The presence of a small fraction of (presumably highly reactive) enolate **3** is also consistent with the polymerization kinetics of MMA using Ph_4PCPh_3 as initiator in THF at temperatures between −20 and +20 °C.[16] The observed polymerization rate constants in the presence of PPh_4^+ would be expected to be of the same order of magnitude as that in the presence of the cryptated (Na,2,2,2) ion,[27] considering the similar cation sizes (about 5 Å), but were found to be about 2 orders of magnitude smaller. Thus the data again are consistent with the presence of a small fraction of a highly reactive phosphonium enolate 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 ($D \leq 1.20$) suggests that equilibration between **3** and **4** is rapid on the polymerization time scale.

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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