Mechanism of Phosphor Ylide-Mediated Living Polymerizations of MMA. Nature of Side Reactions in the Formation of Initiators

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Introduction

The anionic polymerization of methacrylates at ambient temperatures typically involves inter- and intramolecular Claisen-like side reactions.[1−4] Group transfer polymerization and other strategies have been developed to suppress these reactions.[2,5−8] We have reported that tetraphenylphosphonium triphenyl-methanide (TPP,TPM) prepared by the metathesis reaction of triphenylmethylpotassium (TPM,K) and tetraphenylphosphonium bromide (TPP,Br) initiates the living polymerization of alkyl (meth)acrylates at or below room temperature, giving narrow molecular weight distributions.[9−11] These polymerizations proceed in seconds.[12] The 1-naphthyltriphenylphosphonium triphenylmethanide (NTPP,TPM) turned out to be an even more useful initiator, giving slower and better controlled polymerizations (several hours at 25 °C) with narrower molecular weight distributions at temperatures between 25 and 76 °C (Scheme 1).[13] However, both of these polymerizations, thus far, gave less than quantitative initiator efficiencies (less than 68%). Polymerizations of methyl methacrylate (MMA) using the corresponding tetraoctylphosphonium carbanions as initiators also gave narrow distribution poly(methyl methacrylate) (PMMA) but with consistently low (~16%) initiator efficiencies.[14]

Here we report that the formation of the NTPP,TPM and TPP,TPM initiators are accompanied by deprotonation by TPM,K at the *o*-phenyl and 2-naphthyl position of the TPP and NTPP cations, respectively. Furthermore, for both systems MMA polymerizations with quantitative initiator efficiencies can be achieved by carrying out the initiator metathesis reaction below ambient temperatures. Upon warming to ambient temperatures, the corresponding MMA polymerizations show no evidence of side reactions.

Experimental Section

Materials. Tetrahydrofuran (THF) (HPLC grade, >99.99%) was stirred over potassium/sodium alloy until a sky-blue color was observed and distilled in vacuo before use. $NiBr_2$ (Fluka, 97%), Ph_3P (Aldrich, 99%), and 1-bromonaphthalene (Aldrich, 98%) were used as received. Triphenylmethane (TPM) (Aldrich, 97%) was dried under high vacuum at 60 °C for 3 h. MMA was stirred over CaH_2 for 24 h, distilled in vacuo, and then distilled twice over triethylaluminum. 1-Naphthyltriphenylphosphonium bromide (NTPP,Br, **1**) was prepared by stirring $NiBr_2$, Ph_3P, and 1-bromonaphthalene mixture at 200 °C for 3 h.[15] The NTPP,Br was of high purity based on proton and ^{31}P NMR: δ_H (400 MHz; $CDCl_3$) 8.42 (H^a, 1H, d, *J* 8.4), 8.12 (H^b, 1H, d, *J* 7.6), 7.87 (H^j, 3H, t, *J* 7.4), 7.77−7.72 (H^i + H^g, 7H, m), 7.66−7.60 (H^h + H^c, 7H, m), 7.53−7.46 (H^f, 1H, m), 7.40−7.36 (H^d + H^e, 2H, m) with the structure and assignment in Figure 2A and Figure SI-2 (Supporting Information); δ_P (162 MHz; $CDCl_3$): 22.2. TPP,Br (Aldrich, 97%) and

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Scheme 1. Mechanism of Initiation/Propagation of Methyl Methacrylate (MMA) Using the 1-Naphthyltriphenylphosphonium Triphenylmethanide Initiator
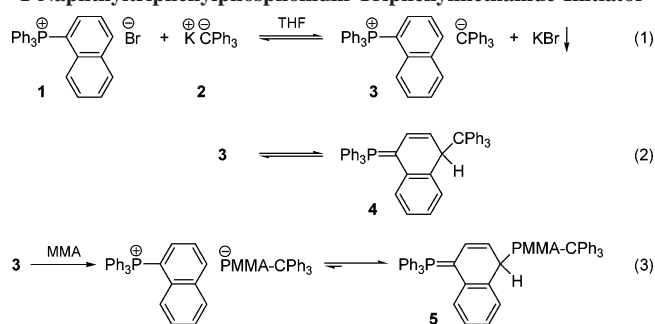
NTPP,Br were dried under high vacuum at 190 °C for 3 h before use. TPM,K (**2**) was prepared from TPM using a potassium mirror in THF.

Polymerizations. Polymerizations were carried out in THF at 25 °C in vacuo using break-seal techniques. In a typical procedure (Table 1, no. 4), compounds **1** (0.118 g, 0.250 mmol) and **2** (8.40 mL, 0.0173 mol/L in THF) were mixed in THF and stirred for various periods (Scheme 1, eq 1) before addition of an MMA/THF solution (5.10 mL, 1.43 mol/L). The NTPP ylide-mediated polymerizations were terminated by 1 mL acetic acid/methanol (1/3 V/V). Methanol (1 mL) was used to terminate the TPP,TPM-initiated polymerizations. The PMMA solutions were precipitated in hexanes, filtered, and dried in vacuo to constant weight.

Characterization. NMR spectra were recorded in $CDCl_3$ on a Varian Mercury-400 ([1]H: 400 MHz; [13]C: 100 MHz; [31]P: 162 MHz) or a Bruker AMX-500 ([1]H: 500 MHz; [2]H: 77 MHz) instrument. $CDCl_3$ was used as an external standard for the ^{2}H NMR measurements. Size exclusion chromatography (SEC) analyses were carried out at 25 °C on a Waters-510 instrument using three "Polymer Laboratories" (10 μm 10⁴ Å (10K−600K), 5 μm 10³ Å (0.5K−60K), and 5 μm 50 Å (up to 2K) columns and equipped with UV and RI detectors in THF at a flow rate of 1.0 mL/min using PMMA standards. Molecular weights were also determined by proton NMR. UV−vis spectra were recorded on an HP 8453 UV−vis spectrophotometer.

Results and Discussion

NTPP,TPM is an excellent initiator for the living MMA polymerization at room temperature (polymerization time of several hours), giving narrow molecular weight (MW) distributions.[13] These living polymerizations occur up to 76 °C and plausibly at even higher temperatures. At room temperature the NTPP,TPM-initiated polymerization is much slower than that initiated by TPP,TPM which occurs in seconds.[12] This is consistent with the greater thermodynamic stability of the NTPP,PMMA-ylide which recaptures full aromaticity in the naphthyl group of the ylide. This greater stability is also indicated by density functional calculations.[16] Scheme 1 illustrates the synthesis of NTPP,TPM from NTPP,Br and K,TPM via a metathesis reaction that should also be driven, in part, by the lattice energy of KBr. The course of the reaction is followed by a 10 nm UV−vis red shift as the color changes from the deep-red of **1** (λ_{max} = 486 nm) to a dark purplish red of the NTPP,TPM ion pair (**3**) (λ_{max} = 496 nm).

Upon addition of MMA at ambient temperature the color immediately turns to a deep tomato-red color of the NTPP,PMMA ylide (**5**) (Scheme 1). In contrast to the NTPP,TPM (see below), this ylide is extremely stable as the red color remains virtually unchanged for several hours even after addition of methanol or water or exposure to air. The

Table 1. Polymerization of Methyl Methacrylate (MMA) Using 1-Naphthyltriphenylphosphonium Triphenylmethanide (NTPP,TPM) Initiator[a]

run	t^b (h)	T^c (°C)	yield (%)	$M_{n,calc}^d \times 10^{-3}$	$M_{n,NMR}^e \times 10^{-3}$	$M_{n,SEC} \times 10^{-3}$	M_w/M_n	f^f (%)	triad[g]		
									mm	mr	rr
1	0.25	25	>95	4.63	6.26	7.51	1.15	62	0.07	0.46	0.47
2	0.75	−30	>95	7.91		19.6	5.90	40	0.12	0.56	0.32
3	1	−30	85	5.48	4.84	4.58	1.17	>95	0.03	0.38	0.59
4	1	−30	>95	5.28	4.52	5.04	1.12	>95	0.05	0.42	0.53
5	47	−30	>95	7.82		43.6	2.84	18	0.11	0.54	0.35

[a] Polymerization conditions: 18 h at 25 °C in tetrahydrofuran, [MMA] is ca. 0.5 mol/L. [b] Time for the salt exchange reaction. [c] Temperature for the salt exchange reaction. [d] $M_{n,calc}$ = [MMA]/[K,TPM] × yield (%) × $M_{w,MMA}$ + $M_{w,TPM}$. [e] Determined by ^{1}H NMR integration of Ph_3C against the $COOCH_3$ groups. [f] Initiator efficiency (f) = $M_{n,calc}/M_{n,SEC}$. [g] By ^{1}H NMR integration of the PMMA α-methyl resonances, δ_H in ppm (triad): 1.19 (mm), 1.00 (mr), 0.81 (rr).[18,19]

Table 2. Polymerization of Methyl Methacrylate (MMA) Initiated by Tetraphenylphosphonium Triphenylmethanide (TPP,TPM)[a]

run	T^b (°C)	yield (%)	$M_{n,calc} \times 10^{-3}$	$M_{n,NMR}^c \times 10^{-3}$	$M_{n,SEC} \times 10^{-3}$	M_w/M_n	f^d (%)	triad[e]		
								mm	mr	rr
1	0	>95	3.96	5.00	5.45	1.15	73	0.05	0.38	0.57
2	−30	>95	5.90	5.20	5.69	1.09	>95	0.04	0.38	0.58

[a] Polymerization conditions: 10 min at 0 °C in tetrahydrofuran; [MMA] is ca. 0.5 mol/L. [b] Temperature for the salt exchange reaction. [c] Determined by ^{1}H NMR integration of Ph_3C against the $COOCH_3$ groups. [d] Initiator efficiency (f) = $M_{n(calc)}/M_{n(SEC)}$. [e] By ^{1}H NMR integration of the PMMA α-methyl resonances, δ_H in ppm (triad): 1.19 (mm), 1.00 (mr), 0.81 (rr).[18,19]

Scheme 2. Proposed Mechanism of the 1-Naphthyltriphenylphosphonium Triphenylmethanide Decomposition
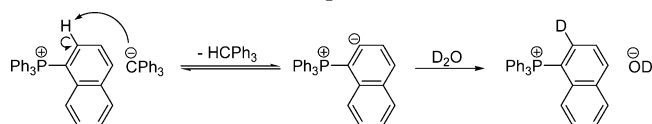
addition of 1 mL acetic acid/methanol (1/3 v/v) using an AcOH/anion molar ratio of about 30 was necessary to terminate the polymerization over a period of several minutes.

PMMA with very narrow molecular weight distributions can be synthesized using NTPP,TPM.[13] However, when this initiator is synthesized at room temperature, initiator efficiencies tend to be less than quantitative (Table 1, no. 1). Given the rigorous conditions we employ, this is unlikely to be due to adventitious impurities in NTPP,Br, MMA or to other sources. We have suspected for some time that this may be due to deprotonation of **3** by **1** (Scheme 2).[9,10,17] Presumably this reaction is also responsible for the less than quantitative initiator efficiencies in the case of the TPP initiators.

However, quantitative initiator efficiencies of both NTPP and TPP ylides can be achieved by performing the metathesis reaction at moderately low temperature (−30 °C; Table 1, no. 3 and 4; Table 2, no. 2) for about 1 h, indicating the elimination of the side reactions. Longer salt exchange times (47 h) at −30 °C gave very low initiator efficiencies (18%) and a broad MW distribution (PDI = 2.84, Table 1, no. 5). These observations are consistent with significant deprotonation of the *o*-phenyl or 2-naphthyl protons of NTPP,Br by K,TPM (Scheme 2).

A shorter metathesis reaction time at −30 °C gave a broad MW distribution polymer consistent with the room temperature polymerization conditions and the PMMA having a very high mr triad stereochemistry indicating that the polymerization proceeds virtually *only* through the potassium PMMA enolate (Table 1, no. 2). As the K,TPM gives much faster polymerizations than the NTPP ylide (hours at room temperature), very small amounts of residual K,TPM are likely to dominate the initiation/polymerization process, giving elevated heterotactic (mr) triads.

The NTPP,TPM initiator at ambient temperatures is relatively unstable at least as judged by the fairly rapid (half-lives of less than 5 min) disappearance of its typical purple color. We have reported much slower decomposition rates for the TPP,TPM
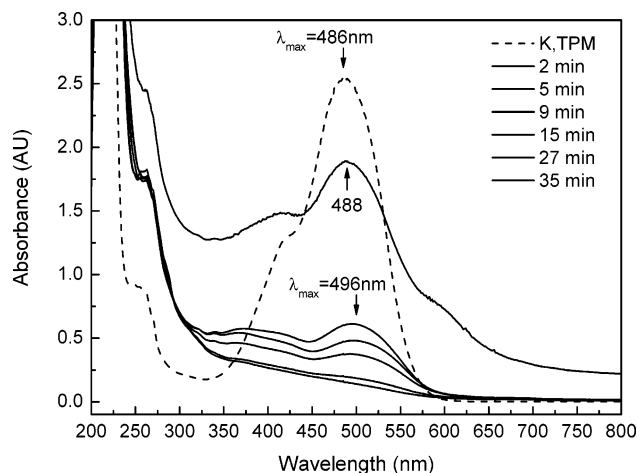
Figure 1. Formation and decomposition of the 1-naphthyltriphenylphosphonium triphenylmethanide (NTPP,TPM) by UV−vis analysis in tetrahydrofuran at 25 °C. From top to bottom at 500 nm, the spectra represent triphenylmethylpotassium (K,TPM, 0.0173 mol/L) and that of the product, at 2, 5, 9, 15, 27, and 35 min after the addition of 1-naphthyltriphenylphosphonium bromide (NTPP,Br).

ylides that have an apparent activation energy of 32.5 kcal/mol in the 4−22 °C range.[17] However, at or below −30 °C the TPP,TPM initiating systems showed no color change on standing for several hours. An essentially quantitative formation of the initiator is observed so that the apparent initiator efficiency is quantitative as well. The MMA polymerization products all have narrow MW distributions as shown in Table 2, confirming these observations.

In order to investigate the nature of the spontaneous NTPP,TPM decomposition reaction(s), the exchange reaction of K,TPM (λ_{max} = 486 nm) and NTPP,Br was monitored by UV−vis analysis. The addition of **2** into **1** at 25 °C gives ion pair **3** in about 5 min (Figure 1), showing a 10 nm red shift (λ_{max} = 496 nm), as documented for the TPP,TPM system.[17] At 2 min at room temperature the reaction is still incomplete with an absorption maximum at about 488 nm. The NTPP,TPM peak maximum of the ion pair seen after about 5 min at 496 nm nearly completely disappears in about 27 min, indicating virtually complete degradation. Along with the formation of the ion pair, a new band at 350−450 nm emerges and then disappears at nearly the same rate. This band is assignable to the NTPP,TPM ylide since the (much more stable)

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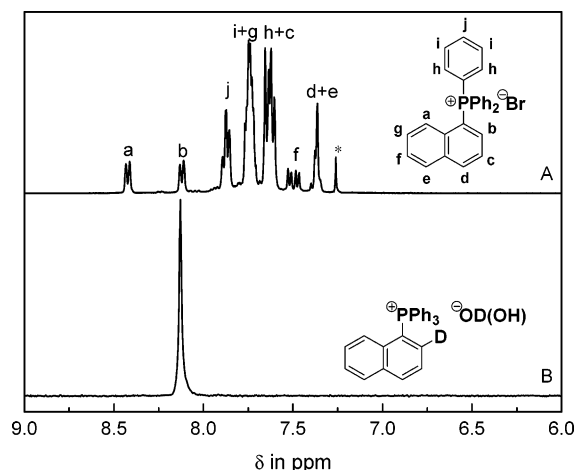
Figure 2. Proton NMR spectrum of 1-naphthyltriphenylphosphonium bromide (NTPP,Br) in CDCl$_3$ (A) and the ^{2}H NMR of the 1-naphthyltriphenylphosphonium triphenylmethanide (NTPP,TPM) in tetrahydrofuran terminated with D$_2$O (B). The signal signed with an asterisk is the residue of CHCl$_3$.
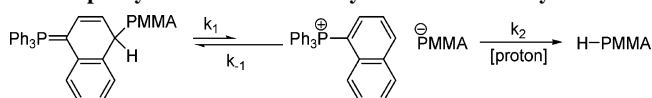
NTPP,PMMA ylide gives a similar UV−vis spectrum that vanishes after protonation. The NTPP,TPM ion pair/ylide disappearance occurs at a rate that is slower but roughly comparable to that of the metathesis reaction (Figure 1).

As pointed out above, the NTPP,TPM degradation rate is much more rapid than that observed for the TPP system and is likely to proceed through the ion pair (see below). The reason for this difference is not completely clear but is consistent with a higher acidity of the *o*-naphthyl compared to the corresponding phenyl proton. In order to clarify this further, the ion pair/ylide **3** was reacted with D$_2$O for several hours until the disappearance of color.

Deuterium NMR of the product shows only a *single* ^{2}H resonance at 8.1 ppm (Figure 2) that is assignable to the 2-position of the naphthyl group on the basis of the ^{1}H NMR spectrum of NTPP,Br (Figure 2). Significantly, the triphenylmethane isolated from the product does not contain *any* deuterium. This indicates that the deprotonation of the NTPP 1-naphthyl group by the TPM anion is responsible for the degradation reaction. Apparently, the 2-proton of the naphthyl group appears to have a far greater kinetic acidity than the three other phenyls and is solely responsible for the proton transfer (Scheme 2). This is also consistent with the greater stability of the TPP,TPM ylide. It is possible that, given the similar rates of the NTPP,TPM ion pair/ylide formation and the side reaction, the TPM anion may deprotonate the NTPP bromide as well. Given the lower initiator efficiencies at higher metathesis reaction temperatures, the aryl anion, assuming no further side reactions, does not appear to initiate polymerization. Hence, it is clear that the efficiency of the initiator formation and hence overall initiation efficiencies at −30 °C are now quantitative.

As stated earlier, the ion pair, perhaps along with free anion, is most likely the active species in the ylide-mediated polymerizations of methacrylates and in other reactions of these ylides.[12] This is based on the following four observations: First, the polymerization rates of the NTPP ylide are much slower than that of the TPP ylides as the ion pair−ylide equilibrium is displaced much further to the ylide.[13] Second, as pointed out above, DFT calculations indicate the greater stability of the ylide compared to the ion pair.[16] Third, the kinetics of the TPP ylide-mediated polymerization of MMA is consistent with the presence of about 1% ion pair.[12] Finally, as shown by Mayes and Bannerjee,[14] the tetraoctylphosphonium triphenylmethanide-initiated MMA polymerizations for which ylide formation is

impossible show a very similar PMMA stereochemistry with that obtained for both the TPP- and NTPP-ylide systems.

We have also tested the rates of protonation of the NTPP,PMMA-ylide in THF with methanol (1 mL), water (1 mL), and acetic acid (1 mL of AcOH/methanol = 1/3 v/v). The red color of the very stable NTPP,PMMA-ylide existed for hours after the addition of methanol or water but disappears in about 5 min after the addition of AcOH/methanol. This observation is inconsistent with the formation of the ion pair being rate determining as in that case the rates would be identical for all three proton donors assuming rapid protonation of the PMMA anion (Scheme 3, k_1). This assumption may or may not be accurate. For steady-state conditions the apparent rate constant of protonation of the ion pair would be given by eq 4.

Scheme 3. Protonation of the 1-Naphthyltriphenylphosphonium Triphenylmethanide Ion Pair/ylide and Similar Systems

$$k_{eff} = k_2/(k_{-1} + k_1) \tag{4}$$

Also, the collapse of the ion pair to the ylide occurring with rate constant, k_{-1}, could be fast enough to compete with the protonation of the ion pair. Given the much greater stability of the NTPP ylide compared to the ion pair, k_{-1} should be much larger than k_1 so that the effective rate constant would be $k_{eff} = k_2/k_{-1}$. Thus, the variation in apparent reaction rates could be consistent with this. To our knowledge, a direct reaction of ylides of this type with protic acids has not been reported, but this remains a possibility. Further studies on these and related issues are in progress.

Supporting Information Available: Full spectra of Figure 2 (Figure SI-1), ^{1}H−^{1}H COSY spectrum of NTPP,Br in CDCl$_3$ (Figure SI-2), and ^{1}H spectrum of NTPP,Br in CDCl$_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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