Macromolecules **1999,** *32,* 1297−1300

Communications to the Editor

End-Active Phosphorus Initiator System for Polymerization of (Meth)acrylates Even in Water Medium

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Received April 23, 1998
Revised Manuscript Received November 23, 1998

Since Szwarc first established the concept of "living" polymers[1] 40 years ago, many unique anionic initiator systems such as organometallic compounds (alkyl- and/or aryllithium,[2] alkylmagnesium bromide,[3] organolanthanide complexes, [4] aluminum porphyrin complexes[5]), carbanion onium salts,[6] and silyl enolates[7] have been developed to perform the living polymerization of methacrylates. However to date, no commercial poly(meth)acrylates formed by living polymerization of (meth)acrylates have been established.[8] As an easily controllable technique, the "living" radical polymerization[9] of methacrylates, in which some organic halogens and simple metal complexes act as initiators, has attracted a significant amount of attention due to its applicability in industrial chemistry. During the polymerization of methacrylic ester systems, however, many "living" polymers die, simply because no true end-living polymer can exist in polymerization vessel in the presence of trace water, air, or active proton species. For this reason, applications involving the living polymerization of methacrylic esters have been limited. Subsequently, the establishment of "living" polymerization of methacrylates remains a formidable challenge.

In nature, a biopolymer such as rubber has simple propagating structure possesing the activated phosphates.[10] It is well-known that alkyl phosphates and phosphinates are robust to water; a property which is expected to play an important role in the formation of biopolymers. We recently found that chlorodiphenylphosphine (CDP), in the presence of a catalytic amount of epoxide, acts as a viable initiator[11] for the polymerization of (meth)acrylates. In this polymerization system, the active propagating site is believed to be a phosphorus enolate, one that favors the formation of high molecular weight polymers[12] and block copolymers.[3] Unfortunately, CDP should only be used as an initiator in the dehydrated state as it is rapidly hydrolyzed (e.g., killed) in the presence of trace water. We have, however, observed that the growing polymer chain initiated by CDP/epoxide continues to polymerize a second monomer, added at a later stage, even with the simultaneous addition of a small amount of water.[14] This has motivated us to explore the possibility of developing a useful end-active and water-robust phosphorus initiator system.

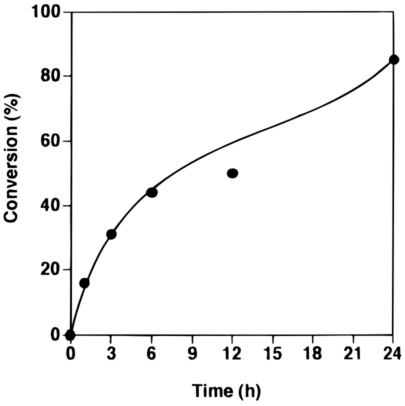
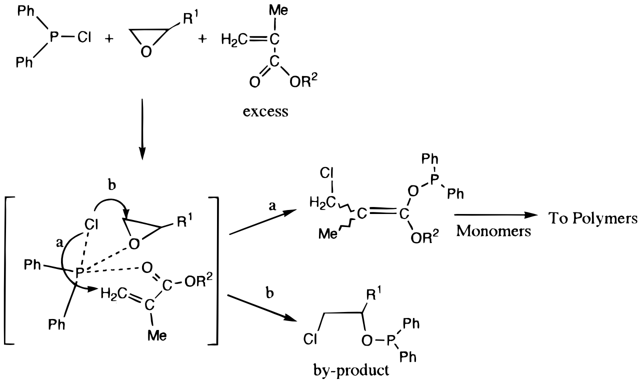


Figure 1. Relations between conversions of DMAEMA and reaction time: DMAEMA (14.5 mmol), DMF (3 mL), [DMAEMA]/[CDP] = 160/1; at 70 °C under Ar.

Scheme 1



It is presumed that the catalytic role of the epoxide is attributed to its ability to coordinate the phosphorus atom of CDP to form an intermediate. This intermediate is known to react with (meth)acrylates to initiate the growth of a chain possessing a terminal phosphorus group (Scheme 1). However, this intermediate is also able to form adducts, e.g., chloroalkyldiphenylphosphinite, a competitive reaction that effectively reduces the initiating efficiency of CDP. In light of this, it is feasible to suggest that a suitable candidate for catalyzing the initiation reaction between CDP and (meth)acrylates might be a base that coordinates to the acidic electrophile of CDP, resulting in the chlorine on CDP to become a nucleophile. On the basis of such opinions, we have elected to use (*N*,*N*-dimethylamino)ethyl methacrylate (DMAEMA) as the catalytic monomer, where the tertiary amine bound in ester substituent may behave as the Lewis base. This paper reports on the development of an end-active phosphorus initiator system, generated by the products obtained from the reaction between CDP

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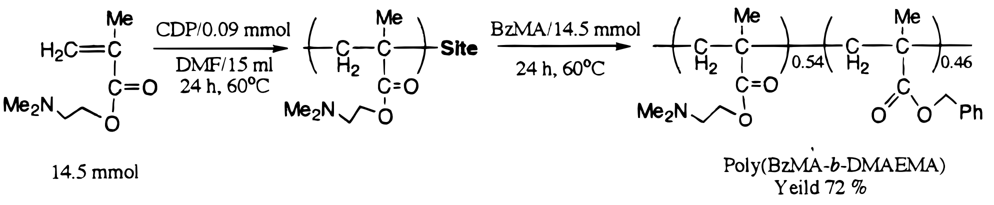
10.1021/ma980662x CCC: $18.00

Scheme 2



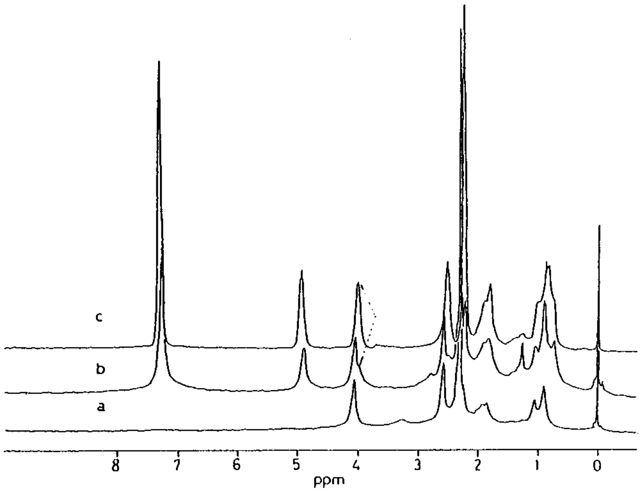


Figure 2. Representation of ^{1}H NMR spectra for poly(DMAEMA) (a), poly(DMAEMA-*b*-BzMA) (b), and poly(DMAEMA-*co*-BzMA) (c) in CDCl$_3$.

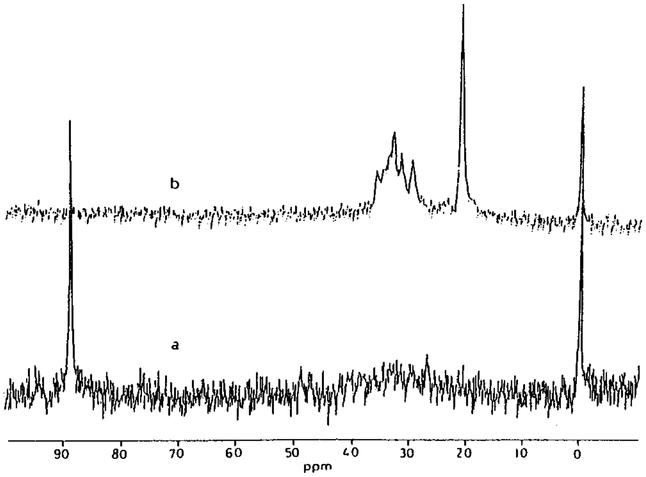


Figure 3. Representation of ^{31}P NMR spectra for CDP (a) and **PN-Ini** (b) in DMF related to Ph$_3$P as an external standard at 0 ppm.

and DMAEMA.

To confirm the self-catalytic power of the monomer DMAEMA, we performed the polymerization of DMAEMA using CDP as the preinitiator, in the absence of epoxy compounds. The relationship between the conversion of DMAEMA and reaction time, as plotted in Figure 1, shows that DMAEMA converts from its initial reaction state and increases steadily over time. The polymerization of DMAEMA with CDP even proceeds at ambient temperature (30 °C), the conversion of DMAEMA being 32% and 40% after 24 and 48 h, respectively. The copolymerization reaction involving DMAEMA and BzMA monomers (1:1 feeding in the presence of 1/160 eq CDP at 60 °C for 24 h) was also performed and found to form the corresponding copolymer, poly(DMAEMA-*co*-BzMA) in 62% yield (precipitated in MeOH). The mole composition of the copolymer was calculated to be 50/50 (DMAEMA/BzMA) by analysis of the signal intensities in the ^{1}H NMR spectrum. From these results, it can be assumed that CDP reacts with DMAEMA to produce an end-active, phosphorus-containing species, which continues to polymerize in the presence of additional DMAEMA and BzMA. For the case where poly(DMAEMA) was formed, by consuming 90% DMAEMA at 60 °C over a period of 24 h (see Scheme 2), the second monomer BzMA was added, and the mixture was stirred continuously for 24 h at the same temperature. This reaction resulted in the formation of the corresponding block copolymer, poly(DMAEMA-*b*-BzMA) containing 46% (in mole) BzMA units,[15] in 72% yield (precipitated in MeOH). Figure 2 shows a comparison of the ^{1}H NMR spectra for polymers poly(DMAEMA) (a), poly(DAEMAE-*b*-BzMA) (b), and poly(DMAEAMA-*co*-BzMA) (c), where distinguishable signals appeared between poly(DMAEMA-*co*-BzMA) and poly(DMAEMA-*b*-BzMA).[16] The signals corresponding to the DMAEMA units (OCH$_2$CH$_2$NMe$_2$) in poly(DMAEMA-*co*-BzMA) were found slightly higher upfield (ca. 0.06−0.1 ppm) from those in poly(DMAEMA-*b*-BzMA). Furthermore, the chemical shifts for OCH$_2$CH$_2$NMe$_2$ (4.0, 2.51, and 2.24 ppm) in poly(DMAEMA-*b*-BzMA) were nearly identical to those in poly(DMAEMA), while the smaller shoulders, upfield from the OCH$_2$, NCH$_2$, and N(CH$_3$)$_2$ signals, appeared at chemical shifts similar to those in the random copolymer poly(DMAEMA-*co*-BzMA). From these comparisons, we can assume that the DMAEMA block is connected to the BzMA/DMAEMA block (a small amount of residues DMAEAMA in the first stage was taken into the second stage) in poly(DMAEMA-*b*-BzMA).

On the basis of the above results, it was concluded that DMAEMA self-catalyzed the initiation reaction between itself and CDP, from which polymerization continued. As such, we then attempted to prepare a phosphorus initiator system derived from both CDP and DMAEMA. For example, CDP (1 mmol, 0.185 mL) and DMAEMA (3 mmol, 0.51 mL) were mixed together and stirred under an atmosphere of argon for 3 h at room temperature. Dry DMF (3 mL) was then added, and the mixture was stirred continually overnight. (This solution is noted by **PN-Ini** and stocked for using as an initiator.) The ^{31}P NMR (in DMF) of **PN-Ini**, shown in Figure 3, displays a sharp singlet peak at 22 ppm and a broad, complex set of signals in the 30−38 ppm region. The absence of a signal at 88 ppm confirms the loss of CDP. Interestingly, we also observed that all the signals in the ^{31}P NMR spectrum of **PN-Ini** were shifted downfield by ca. 3 ppm, maintaining their original splitting pattern, even after the addition of water (0.1 mL). In comparison, when water (2 drops) was added to CDP (in DMF), a sharp doublet appeared in the region 25−29 ppm corresponding to the formation of Ph$_2$P(O)H. This replaces the signal at 88 ppm associated with CDP. The following key reaction, as shown in

Scheme 3. Proposed Key Reaction to PN-Ini from DMAEMA and CDP

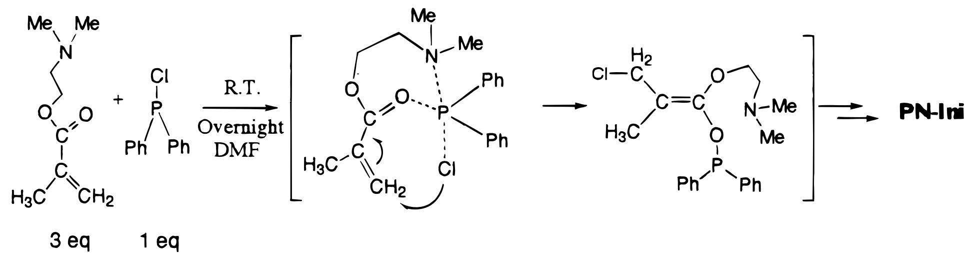


Table 1. Polymerization of (Meth)acrylates with PN-Ini[a]

entry	monomer[b]	DMF (mL)	yield (%)	$M_n/10^{-3}$	$M_w/10^{-3}$	M_w/M_n
1	MMA	3	51	73	125	1.71
2	*n*-BMA	3	61	133	227	1.71
3	*t*-BMA	3	23	123	332	2.7
4	BzMA	3	62	220	312	1.42
5	c-HMA	3	78	71	507	7.14
6	c-HMA	3[d]	90	295	903	3.06
7	EA	3	62	49	101	2.06
8	c-HA	3	46	89	167	1.88
9	*n*-BMA	0	26	565	2405	4.26
10	*t*-BMA	0	60	110	1760	16.33
11	c-HMA	0	96			
12	BzMA	0	43	70	1100	15.67
13	HEMA	3	82	120	188	1.57
14[c]	HEMA/BzMA	3	93	269	654	2.43

[a] Monomer = 5.12 mmol; **PN-Ini** = 0.1 mL; 60 °C, 24 h. [b] MMA = methyl methacrylate; *n*-BMA = *n*-butyl methacrylate; *t*-BMA = *t*-butyl methacrylate; BzMA = benzyl methacrylate; c-HMA = cyclohexyl methacrylate; EA = ethyl acrylate; c-HA = cyclohexyl acrylate; HEMA = 2-hydroxyethyl methacrylate. [c] HEMA = BzMA = 2.56 mmol. [d] A 0.1 mL aliquot of H_2O was added.

Scheme 3, has been proposed to account for the formation of **PN-Ini**.[17]

The polymerization of several (meth)acrylates, in DMF and/or by bulk feeding 5.12 mmol of the monomer to 0.1 mL of **PN-Ini** (containing ca. 0.03 mmol of phosphorus atoms), at 60 °C was carried out. The polymerization results given in Table 1 show that all the polymers obtained have high number- and/or weight-average molecular weights (over 10^5). Furthermore, poly(MMA), poly(BzMA), poly(*n*-BMA), and poly(HEMA) were all found to possess molecular weight distributions (MWD) below 1.71. It should be noted that even for cases where polymers have high molecular weight and large MWD values, no multimodal GPC traces were recorded. When c-HMA was polymerized in DMF, the solution became opaque due to the reduced solubility of the growing polymer. This would explain why the MWD for poly(c-HMA) was found to be so large. Surprisingly, the polymerization of c-HMA conducted in a mixture containing 3 mL of DMF and 0.1 mL of water (see entry 6 in Table 1) gave poly(c-HMA) in 90% yield, a value greater than that obtained when no water was present. Moreover, the M_n value for poly(c-HMA) was increased significantly (295 × 10^3), while its MWD value decreased. This result strongly suggests that not only the initiator **PN-Ini** but also the propagating site in poly(c-HMA) initiated from **PN-Ini** is not destroyed in the presence of water. Bulk polymerization of *n*-BMA, *t*-BMA, c-HMA, and BzMA, under the same conditions, also gave the corresponding polymers, with M_w values in excess of 1 million. Indeed, the corresponding MWD values for these polymers are equally significant. In bulk conditions, c-HMA polymerized quickly, forming a white solid in just 3 h. The yield of poly(c-HMA) obtained after 24 h (reprecipitation incurred by pouring the polymer solution (in $CHCl_3$) into excess hexane) was 96%.[18]

Since **PN-Ini** is stable in the presence of hydroxyl groups, we attempted the polymerization of the highly water-soluble monomer 2-hydroxyethyl methacrylate (HEMA) (entries 13 and 14 in Table 1). In DMF, polymerization proceeds smoothly at 60 °C, over a 24 h period, to give poly(HEMA) in 82% yield, with an M_n value of 120 × 10^3 and an MWD value of 1.57. Under the same reaction conditions, HEMA is copolymerized with BzMA in the presence of **PN-Ini** (0.1 mL in DMF) to afford poly(BzMA-*co*-HEMA) in 93% yield. The composition of BzMA in the copolymer was determined to be 50% (in mole), and the M_n was found to be 269 × 10^3 with 2.43 polydispersity. In an aqueous medium, the polymerization of HEMA resulted surprisingly in the formation of a hydrogel, after just 6 h at 60 °C. By comparison with the aforementioned reaction conditions for poly(c-HMA), it appears that water is not responsible for quashing the reaction when **PN-Ini** is used as the initiator. On the contrary, an aqueous medium appears to accelerate polymerization in the presence of **PN-Ini**. The poly(HEMA) hydrogel was found to be completely insoluble in DMF, 20% NaOH(aq), and 20% HCl(aq), a stark contrast to poly(HEMA) obtained from the reaction in DMF, which is readily soluble in MeOH, $CHCl_3$, DMF, and H_2O (>50 °C) but insoluble in acetone. The copolymer poly(BzMA-*co*-HEMA), on the other hand, is highly soluble in acetone, $CHCl_3$, and DMF but completely insoluble in MeOH and hot water. By comparison, poly(BzMA) was found to be insoluble in acetone. The high solubility of poly(BzMA-*co*-HEMA) in acetone indicates that there are no homopolymeric mixtures of poly(HEMA) and poly(BzMA) in the copolymer. It seems that the end-active **PN-Ini** has potential applications in the polymerization of those functional (meth)acrylates that cannot be afforded by traditional anionic and/or GTP living polymerization systems.

While the definite structure of **PN-Ini** is not well understood at present, we believe this simple initiating system is a valuable method by which to obtain metal-free, end-active poly(meth)acrylates. Indeed, the development of this system as a new controlled method for the polymerization of (meth)acrylates is underway. We are currently exploring the phosphorus initiators for controlling the polymeric sequence and molecular weights in the polymerization of (meth)acrylates.

Acknowledgment. We are extremely grateful to Kansai Polymer R & D Center and Dainippon Ink & Chemicals, Inc., for their financial support and the GPC measurements for this work. We also thank Mr. K. Kaikake (Miyazaki University) for his assistance in the measurement of the ^{31}P NMR spectroscopy.

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(15) CDP (0.09 mmol) was added to the mixture containing DMAEMA (14.5 mmol) and 10 mL of DMF (dry), and the mixture was stirred for 24 h at 60 °C under argon (within this period, 90% of DMAEMA consumed). Then, 5 mL of DMF (dry) and BzMA (14.5 mmol) was added, and the mixture was stirred further for 24 h.

(16) The GPC traces for the polymers containing the DMAEMA unit, unfortunately, could not be recorded precisely in both THF and DMF eluent systems due to strong adsorption of the polymers in column.

(17) We do not understand the bonding structure of phosphorous for **PN-Ini** from the ^{31}P NMR spectra at present. In our attempt to isolate the phosphorus mixture, it was observed that the ^{31}P NMR signals for a solid fraction obtained from **PN-Ini** appeared at −164 ppm. Further investigation is now underway.

(18) Poly(c-HMA) was reprecipitated by pouring the polymer solution in $CHCl_3$ into a large amount of hexane. However, the molecular weight of the polymer could not be determined by GPC because the solution of this poly(c-HMA) in THF did not pass the filter; nevertheless, the solution was purified by a centrifugal separator. Perhaps, the molecular weight of the polymer is too high to pass the filter.

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