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Reactions in Surfactant Solutions(V): Dephosphorylation of *p*-Nitrophenyldiphenylphosphinate by Benzimidazole Catalyzed with Ethyltri-*n*-octylammonium Bromide

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The phase-transfer reagent (PTC), ethyl tri-*n*-octylammonium bromide (ETABr), strongly catalyzes the reaction of *p*-nitrophenyldiphenylphosphinate (*p*-NPDPI) with benzimidazole (BI) and its anion (BI⁻). In ETABr solutions, the dephosphorylation reactions exhibit higher than first order kinetics with respect to the nucleophile, BI, and ETABr, suggesting that reactions are occurring in small aggregates of the three species including the substrate, whereas the reaction of *p*-NPDPI with OH⁻ is not catalyzed by ETABr. This behavior for the drastic rate-enhancement of the dephosphorylation is referred as 'aggregation complex model' for reactions of hydrophobic organic phosphinates with benzimidazole in hydrophobic quaternary ammonium salt solutions.

Introduction

We have reported a series of papers¹ for reactions in surfactant solutions of cetyltrimethylammonium halides (CTAX) with respect to micellar catalysis. This work deals with dephosphorylation of an organic phosphinate, *p*-nitrophenyldiphenylphosphinate (*p*-NPDPI), catalyzed by a phase transfer catalyst, ethyltri-*n*-octylammonium bromide (ETABr) in aqueous solutions.

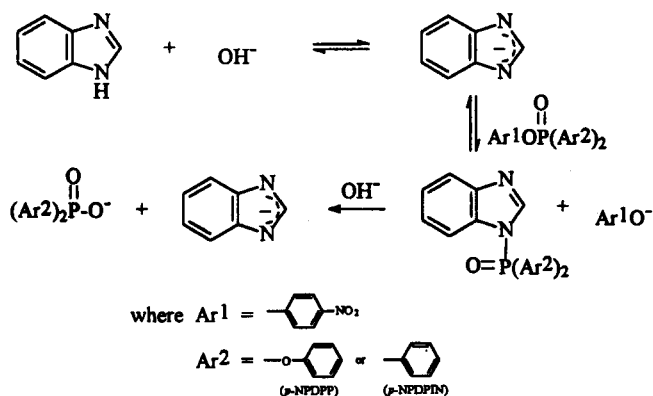
Micellar effects upon reaction rates in aqueous solutions have generally been analyzed in terms of a pseudophase model,²⁻⁴ assuming reactants are distributed between the aqueous solvent and micelles, with reaction occurring in either pseudophase. It was first applied to micellar inhibited bimolecular reactions⁵ and then to micellar catalyzed unimolecular reactions⁶ and has been extended to bimolecular micellar catalyzed reactions.^{3,4,7-9} It is implicit in this treatments that reactants do not perturb micellar structure and do not bind cooperatively to the micelle. These assumptions are reasonable, provided that surfactant is in large excess over reactants. However the quantitative treatments sometimes fail for [surfactant] near the critical micellar concentration (cmc), especially with hydrophobic reactants which may interact strongly with micelles or premicelles.^{10,11}

Pskiewicz has developed an alternative model in which rate-surfactant profiles are explained by an equation similar to the Hill equation for enzyme kinetics,¹¹ which stresses cooperative binding. Kunitake and co-workers found that the phase-transfer catalyst, tri-*n*-octylmethylammonium chloride (TMAC), strongly accelerates deacylation of *p*-nitrophenyl acetate by hydrophobic hydroxamates or imidazoles in water.¹² The reactions in TMAC were faster than in micellized cetyltrimethylammonium bromide (CTABr), show-

ing that nonmicellar aggregates could be catalytically active and that rate effects in very dilute surfactant might also be due to the formation of submicellar aggregates. The rate enhancements by micellized surfactants and nonmicellized quaternary ammonium ions were ascribed to the formation of 'hydrophobic ion pairs' which were considered to be more nucleophilic than the free ions.¹² These observations were especially interesting because phase-transfer catalysis typically applied to biphasic reactions in which transport of ionic reactant across a phase boundary is of key importance.¹³

We have compared catalysis by a micellar forming surfactant, CTABr, with that by a phase-transfer catalyst, ethyl tri-*n*-octylammonium bromide (ETABr).^{1a,1c,14} In the dephosphorylation reactions of *p*-nitrophenyldiphenylphosphate (*p*-NPDPP) and *p*-nitrophenyldiphenylphosphinate (*p*-NPDPI) by benzimidazole (BI) or its anion. The anion of BI is an effective dephosphorylating agents in solutions of micellized CTABr^{1a,1c} (Scheme 1). Except in very dilute CTABr, the rate enhancements are due wholly to the concentration of reactants in the micelles, and second-order rate constants in the micellar pseudophase are similar to those in water and are independent of the total concentrations of the reactants. Reactions of benzimidazole ion (BI⁻) with *p*-NPDPP and *p*-NPDPI are reversible (Scheme 1),^{1a-1c} but the reverse reaction is unimportant in very dilute *p*-nitrophenoxide ion, return of the phosphorylated intermediate to reactants can be neglected when the concentration of *p*-nitrophenoxide ion is less than 10⁻⁵ M.^{1a,1c}

There is extensive catalysis for the dephosphorylations of *p*-NPDPP and *p*-NPDPI at [CTABr] below the cmc in water,^{1a-1c} which could be due to induced formation of normal micelles in the presence of the hydrophobic reactants, or the reactants might combine with surfactant to form



Scheme 1. Dephosphorylations of *p*-nitrophenyldiphenylphosphate (*p*-NPDPP) and *p*-nitrophenyldiphenylphosphinate (*p*-NPDPIN) mediated by benzimidazole ion in water and CTABr solutions.

small, submicellar, aggregates which are catalytically effective (cf. ref. 11). One might expect CTABr at submicellar concentrations to behave similarly to the phase-transfer catalysts (PTC) in its catalytic effectiveness.

Experimental

Materials. The preparation and properties of most of the reagents have been described earlier.^{1a-1f} The phase-transfer catalyst, ethyltri-*n*-octylammonium bromide (ETABr) were prepared by alkylation of tri-*n*-octylamine with ethyl bromide.¹²

Kinetics. Formation of *p*-nitrophenoxide ion was measured spectrophotometrically at 25.0 °C, generally at pH 10.7 (10^{-2} M carbonate buffer). A few experiments were run in dilute NaOH. The nucleophile was in large excess over substrate, and reactions were first order in the range of 0.30×10^{-6} – 2.00×10^{-5} M of substrate concentrations. Initial values (over 4 half lives) of the first-order rate constants, k_w (s^{-1}), are quoted for these reactions.

The phase-transfer catalyst, ETABr, is sparingly soluble in water,¹² and its solubility was decreased by buffer. Due to the reproducibility problem in the kinetic data obtained from very turbid solution, we used sufficiently low concentrations of reagents so that kinetic solutions were no more than faintly turbid.

Deprotonation of Benzimidazole (BI). The concentrations of BI⁻ in the reaction solutions were measured at 283 nm following methods already described.^{1a,15}

Results and Discussion

Reactions in the Absence of the Quarternary Ammonium Salt (ETABr)

The rate constant (k_w) of dephosphorylation mediated by OH⁻ in 10^{-2} M carbonate buffer (pH 10.7) was 4.30×10^{-3} s⁻¹ (Table 1). And the benzimidazolide ion, BI⁻, make a small contribution to reaction of *p*-NPDPIN in water at pH 10.7, 10^{-2} M carbonate buffer, largely because benzimidazole (BI) are very weak acid.^{1a,15} At 25.0 °C under this condition (pH 10.7, 10^{-2} M carbonate buffer) 10^{-3} k_w was 5.02 s⁻¹ and 6.29 s⁻¹ respectively in 1 and 2×10^{-2} M

Table 1. Effect of ETABr on dephosphorylation of *p*-NPDPIN mediated by BI

10^2 [BI], M	10^3 [ETABr], M					
	0.00	0.25	0.50	1.00	1.50	2.00
0.00	4.30	4.53	4.51	4.67	–	4.50
0.25	–	6.82	7.42	8.92	12.0	15.3
0.50	–	7.17	8.04	11.2	16.8	26.2
1.00	5.02	7.54	9.68	18.5	30.0	74.0
1.50	–	8.42	12.2	30.3	65.0	116
2.00	6.29	10.2	14.5	47.0	120	271

$10^3 k_w$ (sec⁻¹), 25 °C, 10^{-2} M carbonate buffer (pH 10.7), 3×10^{-6} M substrate.

BI solutions (Table 1), whereas 10^{-3} k_w in the aqueous buffer solution (without ETABr) was 4.30 s⁻¹ as mentioned above.

Reaction with Hydroxide Ion in ETABr

The phase-transfer catalyst, ETABr, did not catalyze the reaction of *p*-NPDPIN with OH⁻ as shown in Table 2. However concentration of OH⁻ had quantitative effect on rate constants. It means that the insoluble substrate in water can not react within the solution, but reacts only at the surface of the two phases.

Reactions with the Areneimidazoles in ETABr

The pseudo first-order rate constants for dephosphorylation with BI, k_{BI} , at pH 10.7, are shown in Table 1. (These rate constants are corrected for small contribution of reaction with OH⁻).

(1) Effect of substrate concentration. Although dephosphorylations with 3×10^{-6} M *p*-NPDPIN in ETABr solutions are first order at a given BI concentration, the rate constants do not depend on initial [*p*-NPDPIN] (Table 3). This effect is especially large for reactions in NaOH concentrations larger than 0.01 M where BI are extensively deprotonated.^{15,16}

(2) Effect of BI concentration on dephosphorylation of *p*-NPDPIN in ETABr solution. Although reaction kinetics is approximately first order at low concentrations of ETABr, there are the variations of the kinetics at higher [BI], which does not fit for no simple kinetic equation as shown in Figure 1 and 2 for plots of k_{BI} against [ETABr] and for plots of log k_{BI} against [ETABr]. For example, in higher concentrations than 10^{-3} M ETABr solution, increase of [BI] gave rise to drastic increase of rate constants at a given [ETABr].

Table 2. First Order Rate Constants of Dephosphorylation of *p*-NPDPIN mediated by OH⁻ in ETABr Solutions

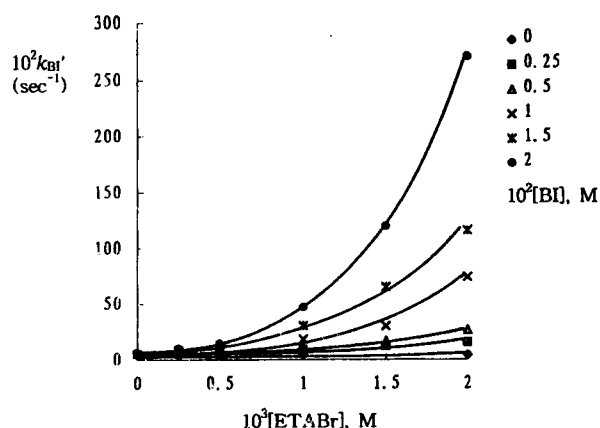
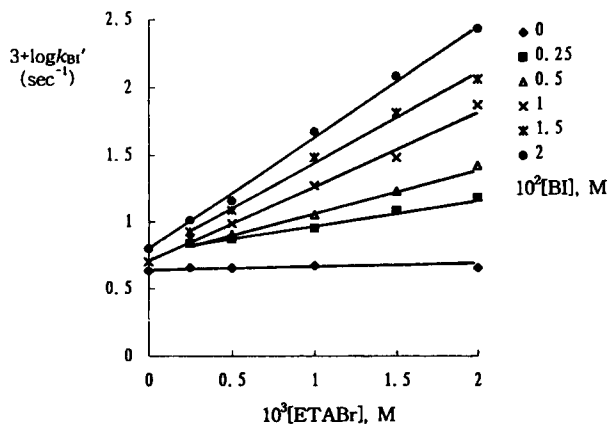
10^3 [OH ⁻], M	10^4 [ETABr], M			
	0.00	1.00	2.50	5.00
0.00	4.52	4.61	4.49	4.53
1.00	5.01	5.19	5.14	5.08
2.00	9.48	10.1	9.29	9.02
4.00	18.1	18.3	19.1	18.3

$10^3 k_p$ (sec⁻¹), 25 °C, 3×10^{-6} M substrate.

Table 3. Effect of Substrate Concentration on De-phosphorylation of *p*-NPDPIN in ETABr Solution

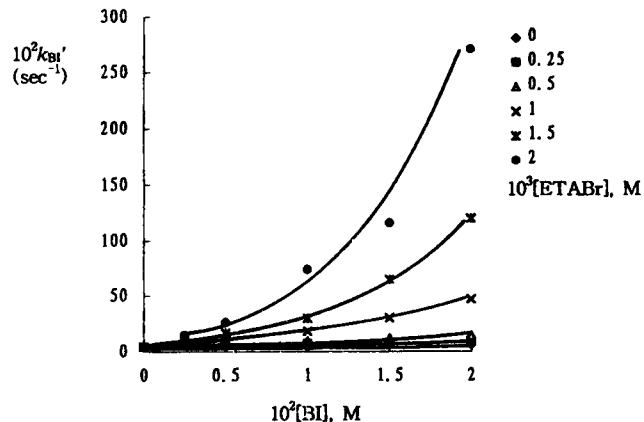
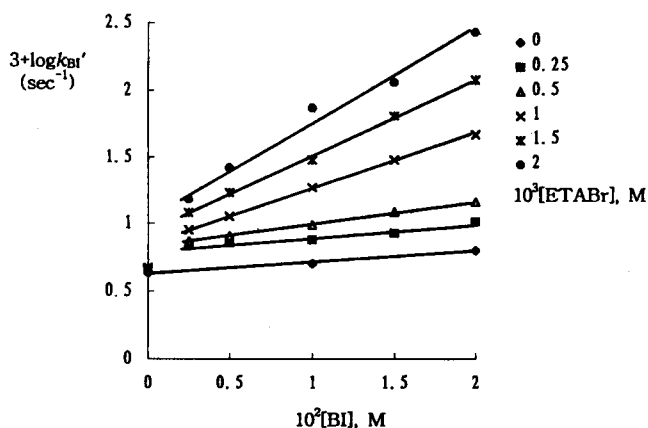
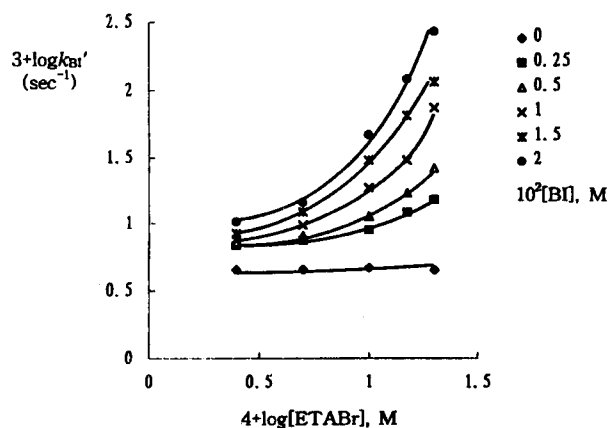
10^5 [DPNPIN], M	10^2 [ETABr], M	
	2.50	5.00
0.30	6.80	7.44
0.50	6.93	7.67
0.75	7.35	8.07
1.00	7.68	8.04
1.25	7.65	7.99
1.50	7.57	7.66
2.00	7.02	7.23

$10^3 k_p$ (sec^{-1}), 25 °C, 10^{-2} M carbonate buffer (pH 10.7), 2.5×10^{-3} M BI.

**Figure 1.** Effect of ETABr on dephosphorylation of *p*-NPDPIN mediated by BI. (Plots of k_{BI} against [ETABr])**Figure 2.** Effect of ETABr on dephosphorylation of *p*-NPDPIN mediated by BI. (Plots of $\log k_{BI}$ against [ETABr])

(3) Effect of ETABr concentration on reaction of *p*-NPDPIN with BI. As shown in Figure 3 and 4 for plots of k_{BI} against [BI] and for $\log k_{BI}$ against [BI], in higher concentrations than 10^{-2} M BI solution, increase of [ETABr] lead to rapid increase of rate constants at a given [BI], and the reaction do not follow the first order kinetics (*vide infra*).

(4) Cooperative Effect of BI and ETABr concentrations on dephosphorylations of *p*-NPDPIN. The variations of the rate constants with [BI] or [ETABr] do not

**Figure 3.** Effect of BI on dephosphorylation of *p*-NPDPIN in ETABr solution. (Plots of k_{BI} against [BI])**Figure 4.** Effect of BI on dephosphorylation of *p*-NPDPIN in ETABr solution. (Plots of $\log k_{BI}$ against [BI])**Figure 5.** Effect of ETABr on dephosphorylation of *p*-NPDPIN mediated by BI. (Plots of $\log k_{BI}$ against \log [ETABr])

fit simple kinetic equation. For example, as shown in Figure 5, plots of $\log k_{BI}$ against \log [ETABr] are linear with approximately unit slope for reactions below 0.75×10^{-3} M ETABr concentrations, but the slopes increase with increasing [ETABr]. And plots of $\log k_{BI}$ against \log [ETABr] are curved with slopes increasing from approximately 1 at low [BI] and [ETABr] to approximately 4-5 at higher [BI] and [ETABr] (Figure 5). Same situations are appeared in

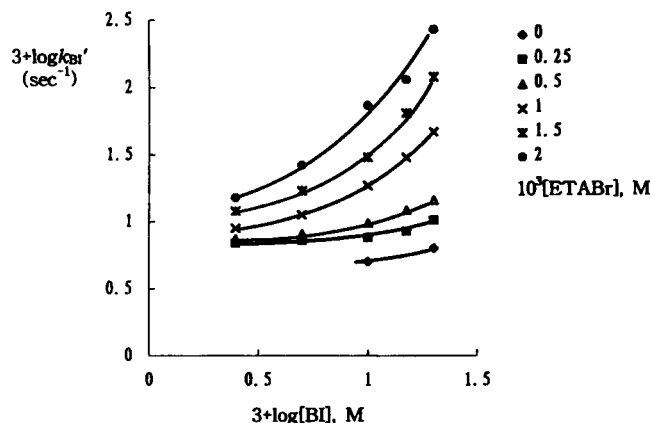
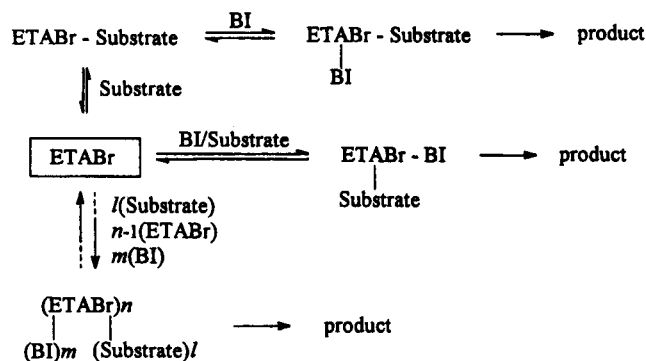


Figure 6. Effect of BI on dephosphorylation of *p*-NPDPIN in ETABr solution. (Plots of $\log k_{Br}$ against $\log [BI]$)

Figure 6, plots of k_{Br} against $\log [BI]$.

'Aggregation Model' for dephosphorylation with high concentrations of BI and ETABr. The observations for the reactions in high concentrations of BI and ETABr as shown in Figure 5 and 6 suggest that small aggregates of reactants (BI and *p*-NPDPIN) and ETABr are present in the solution, rather than 1:1 adducts of the substrate and nucleophile. In particular the curvature, and greater than unit slope, of the \log vs. \log plots of rate constants against [ETABr], it show that the monomeric ion of ETABr is not the most active form, and it appears that there is a cooperative interaction between catalyst (ETABr) and two reactants (cf. ref 11). However these aggregates do not build up in concentration because there is no saturation effect. It is assumed that formation of reactive aggregates depends upon both reactants, BI and *p*-NPDPIN, because for example ETABr does not catalyze the reaction of OH^- with *p*-NPDPIN (Table 2). We referred this behavior as 'aggregation complex model' for reactions of hydrophobic organophosphinates or phosphates with areneimidazoles in quarternary ammonium salt solutions, as shown in Scheme 2.

The rate enhancements for the dephosphorylations of the organophosphinates by ETABr are very large. For example, the first order rate constant of the reaction of *p*-NPDPIN



where l , m and n are integers

Scheme 2. 'Aggregation Complex Model' on hydrophobic phase-transfer catalysis of dephosphorylation of *p*-NPDPIN (substrate) mediated by BI.

with 2.00×10^{-2} M BI in 2.00×10^{-3} M ETABr solution is about 0.271 s^{-1} , whereas the rate constants of the reactions in water and in 2×10^{-2} M BI solution are about 4.30 and $6.29 \times 10^{-3} \text{ s}^{-1}$ respectively, which most of those reactions involve attack by H_2O and OH^- . On this basis 2.00×10^{-3} M ETABr in 2.00×10^{-2} M BI solution increases the rate constant by a factor *ca.* 43 (Table 1). Use of the higher concentrations than 2.00×10^{-3} M ETABr are not available to measure the rate constants spectrally, because of drastic rate-enhancements.

Conclusion

The phase-transfer reagent (PTC), ethyltri-*n*-octylammonium bromide (ETABr), strongly catalyzes the reactions of *p*-nitrophenyldiphenylphosphinate (*p*-NPDPIN) with benzimidazole (BI) and its anion (BI^-). For example, 2.00×10^{-3} M ETABr in 2.00×10^{-2} M BI solution increases the rate constant ($k_p=0.271 \text{ sec}^{-1}$) of the dephosphorylation by a factor *ca.* 43, when compared with the reaction ($k_p=0.006 \text{ sec}^{-1}$) in 2.00×10^{-2} M BI solution (without ETABr). In ETABr solutions, the kinetics of the dephosphorylations are greater than first order with respect to the nucleophile (BI) and ETABr, suggesting that reactions are occurring in small aggregates of the three species including the substrate (*p*-NPDPIN), whereas the reaction of *p*-NPDPIN with OH^- is not catalyzed by ETABr.

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Modification of Poly(methylsilene) Catalyzed by Group 4 and 6 Transition Metal Complexes and Its Pyrolysis

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The poly(methylsilene) (1) was modified with the group 4 metallocene $Cp_2MCl_2/Red-Al$ ($M = Ti, Zr, Hf$) combination catalyst and with the group 6 metal carbonyl $M(CO)_6$ ($M = Cr, Mo, W$) catalyst, producing the highly cross-linked insoluble polymer and the lowly cross-linked soluble polymer, respectively. An interrelationship between molecular weight and percent ceramic residue yield with metal within the respective group was not found. The polymers modified with the group 4 metallocene combination catalysts have higher molecular weight and lower percent ceramic residue yield than the polymers modified with the group 6 metal carbonyl catalysts do. The catalytic activity of group 4 metallocene combinations appears to be higher at ~ 100 °C, but to be lower at very high temperature than those of group 6 metal carbonyls. The pyrolysis of the modified 1 yielded SiC ceramic.

Introduction

There are two kinds of ceramics known: oxide type and non oxide type.¹ Silicon-containing ceramics have attracted a great deal of attention for many special applications. Silicon-containing non-oxide ceramics such as silicon carbide (SiC) and silicon nitride (Si_3N_4) have been known for some time.² In particular, silicon carbide ceramic has been widely used as a reinforcement in advanced ceramics and composites.³ A process of fabricating silicon carbide fiber was developed by Yajima *et al.*⁴. The process includes pyrolytic conversion (in the 400-470 °C temperature range) of polydimethylsilane into polycarbosilane (PCS), which is melt-spun into fiber form (trade name "Nicalon" manufactured by Nippon Carbon Co., Tokyo, Japan) and is then cross-linked under an air atmosphere (in the 300-350 °C temperature range), followed by its final pyrolysis (at 1200 °C or higher) under an inert atmosphere into SiC fiber. The cross-linking process by oxidative curing allows the con-

version of PCS fiber to SiC with minimal loss of organic constituent molecules without softening. However, the oxygen introduced during the oxidative curing process may cause fiber degradation at high temperature. In order to improve heat resistivity of PCS some doping agents (*e.g.*, BCl_3) or cross-linking agents (*e.g.*, vinyl derivatives) were added, resulting in the contamination of SiC ceramics and in the oversupply of carbon source to SiC ceramics, respectively.⁵ Another cross-linking method should be considered as an alternative of the disadvantageous curing processes by oxidation and hydrosilation.

The role of Si-H groups in PCS in the Yajima process is very important because Si-H groups permit cross-linking between PCS chains. Recently, Seyferth *et al.* described the preparation of near-stoichiometric silicon carbide by pyrolyzing a polymethylsilane modified by zirconocene-catalyzed dehydrocoupling of Si-H bonds.⁶ Harrod discovered an alternative group 4 metallocene-catalyzed dehydropolymerization leading to great progress in poly (organosilane) synthesis.⁷ Subsequently, Tilley *et al.* reported the catalytic dehydropolymerization of various silanes by

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