lent. It strongly supports the idea that an interface can be modeled as discrete fractions with T_g values between those of the pure components, contributing independently to the excess enthalpy.

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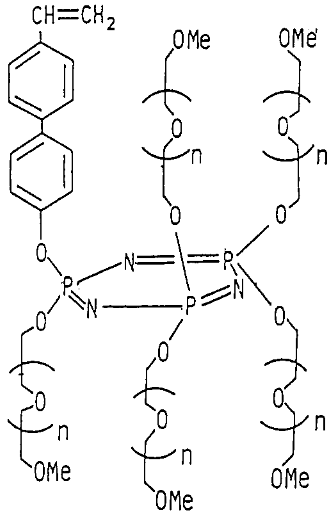
Polymerization of Vinyl Monomers Containing Oligo(oxyethylene)cyclotriphosphazene Derivatives and Binding of a Fluorescent Probe by Their Polymers

In previous papers,[1,2] we described the polymerization of vinyl monomers with pendant phosphazene groups such as 2-[(4′-vinyl-4-biphenylyl)oxy]pentachlorocyclotriphosphazene (**1**). Monomer **1** or its polymers can be modified by introducing functional groups by employing well-known phosphazene chemistry.[3] Cyclotriphosphazenes or phosphazene polymers with oligo(oxyethylenes) have been reported to be useful catalysts as phase-transfer reagents[4,5] or as ion-conducting solids.[6] These polymers have been prepared by the ring-opening/substitution method. We now report the polymerization of new multiarmed monomers, **2** and **3**, which have five oligo(oxyethylene) chains on the phosphazene ring. The polymers would be expected to exhibit unique properties due to the large number of donor atoms. We also demonstrate preliminary results of the binding of a fluorescent probe by poly(**2**) and poly(**3**) (Chart I).

Chart I



	n
2;	1
3;	2

A typical procedure for the preparation of **2** is as follows. A solution of **1**[1] (5.1 g, 10 mmol) in THF was added slowly to a solution of sodium 2-(2-methoxyethoxy)ethoxide, prepared from 2-(2-methoxyethoxy)ethanol (12 g, 0.1 mol) and NaH (2.4 g, 0.1 mol) in THF. The mixture was stirred for 10 h at room tempprature. After the usual workup, the reaction mixture was separated by column chromatography (silica gel, 1:9 methanol–chloroform) to give 4.0 g (43%) of **2**. Monomer **3** was prepared by a similar procedure (yield 37%).

The radical polymerization of **2** or **3** with AIBN in various solvents at 70 °C gave polymers as shown in Table I. The polymers are highly viscous and soluble in common organic solvents and water. The IR data showed the presence of $-N{=}POCH_2-$ at 1220 cm^{-1}, and the elemental analysis supports poly(**2**) and poly(**3**). Separation of poly(**2**) and poly(**3**) from the monomers by a reprecipitation method is rather difficult. Therefore, the conversion was determined by the disappearance of vinylic protons using benzaldehyde as an internal standard.[7] The conversion was little affected by the length of oxyethylene chain. However, the conversion was strongly influenced by the solvent and correlated with the Taft and Kamlet β-value, for hydrogen bond acceptor basicities.[8] This indicates that hydrogen-bond formation is the most important factor in polymerization of **2** and **3**. Number-average molecular weights (M_n) of the polymers obtained in ethanol and 2-propanol are higher than those in benzene and 1,2-dichloroethane (DCE). The results are opposite to those predicted from chain-transfer constants of the solvents. Hydrogen-bond interaction would lead to a change in both the polymerizability of the monomers and the propagation rate due to a change in concentration of monomer around the propagating polymer radical.[9] In DCE, the propagating polymer radical would interact more strongly with the monomer than with the solvent. This implies that increasing monomer concentration around the growing polymer radical increases the propagating rate. However, this was not the case. In order to clarify the solvent effect on monomer reactivity, ^{13}C NMR spectra were measured. The β-carbon peak of the vinyl group of **2** in DCE and in ethanol appeared at 113.5 and 114.8 ppm (from TMS), respectively. For **1**, neither the chemical shift nor the conversion was affected by solvents. From these results, the change in reactivity due to interaction between monomer and solvent is likely to be one of the important factors for the acceleration of polymerization in ethanol. Furthermore, the fact that the intrinsic viscosity of poly(**3**) (M_n = 50 000) in ethanol ($[\eta]_0$ = 0.10 at 30 °C) is lower than that in ben-

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Table I
Solvent Effects on the Polymerization of 1-3 at 70 °C[a]

monomer	solvent	β-value	time, h	conversion, %	$10^{-4} \times \bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$
1	dioxane	0.37	4	30.6	0.9	1.6
	DCE[c]	NHBA[d]	4	31.3	1.4	1.5
2	2-propanol	0.80	5	38.1	8.1	1.5
	ethanol	0.77	5	40.1	5.0	1.7
	dioxane	0.37	5	25.6	5.0	1.5
	benzene	0.10	5	23.4	3.9	1.6
	chlorobenzene	0.07	5	21.7	4.6	2.0
	DCE	NHBA	5	17.1	4.0	1.4
3	2-propanol	0.80	4.5	36.0	4.3	1.2
	ethanol	0.77	4.5	35.9	4.1	1.3
	dioxane	0.37	4.5	27.0	4.8	1.2
	benzene	0.10	4.5	22.8	3.6	1.2
	chlorobenzene	0.07	4.5	19.3	2.0	1.4
	DCE	NHBA	4.5	17.3	2.8	1.3

[a] [monomer] = 0.16 mol/L; [AIBN] = 1.4×10^{-3} mol/L; solvent, 2 mL. [b] Determined by GPC. [c] 1,2-Dichloroethane. [d] Nonhydrogen bond acceptor solvent.

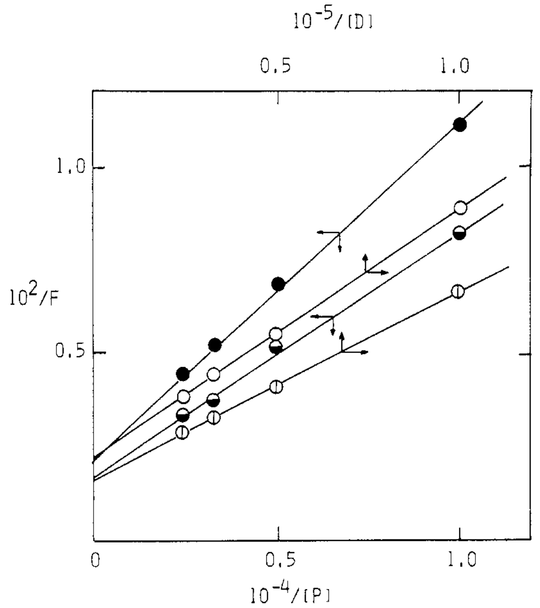

Figure 1. Plots of $1/F$ vs $1/[P]$ (●,◒) or $1/[D]$ (○,◑): (●,○) poly(2)–ANS system; (◒,◑) poly(3)–ANS system. [ANS] = 3×10^{-6} mol/L and [P] = 1×10^{-4} mol/L were used for the plots of eqs 1 and 2, respectively.

zene ($[\eta]_0 = 0.14$) suggests that the oligo(oxyethylene) chains aggregate in ethanol and disperse in benzene. This also suggests that steric crowding around the polymer radical is different; i.e., propagation is impeded in DCE because the polymer radical is surrounded by a oxyethylene moiety. Thus, solvent effects seem to be the origin of the change in monomer reactivity and steric crowding.

The copolymerization of **3** with styrene in DCE gave a viscous liquid. With 30 mol % of **3** in the monomer feed, a copolymer containing 37.8 mol % of these units was obtained (Table II).

Preliminary experiments concerning binding of a fluorescence probe, potassium 8-anilinonaphthalene-1-sulfonate (ANS), to poly(**2**) and poly(**3**) were carried out at 20 °C, according to the procedure described by Smid et al.[10,11] As expected, the fluorescence intensity of an aqueous solution of ANS was strongly enhanced by the addition of poly(**2**) and poly(**3**). An emission maximum was observed at 475 nm for both polymers. This value is higher than that obtianed from poly(vinylbenzo-18-crown-6) (P18C6; λ_{max} = 462 nm),[11] suggesting that the cavity formed by monomer units acting as a bound site has a highly hydrophilic character.

Table II
Copolymerization of 3 with Styrene in DCE at 70 °C[a]

mol % of 3			
in monomer feed	in copolymer	conversion, %	$10^4 \bar{M}_n$
10	14.9	5.4	4.9
30	37.8	18.7	8.7
50	54.0	24.3	10.3

[a] [3] + [St] = 1 mol/L; [AIBN] = 1.1×10^{-3} mol/L; DCE, 3 mL; time, 8 h.

The intrinsic binding constant (K) and the first binding constant (K_1) were determined from the equations[10]

$$1/F = 1/F_m + 1/KF_m[D] \qquad (1)$$

$$1/F = 1/F_m' + 1/K_1F_m'[P] \qquad (2)$$

where F, [D], and [P] are observed fluorescence intensity, dye concentration, and polymer concentration, respectively. Plots of $1/F$ vs $1/[P]$ and of $1/F$ vs $1/[D]$ gave straight lines (Figure 1). From the slope and the intercept, K and K_1 are calculated to be 3.2×10^4 and 2.5×10^3 M^{-1}, respectively, for poly(**2**) and 3.0×10^4 and 2.6×10^3 M^{-1} for poly(**3**). The value, K_1^*, which refers to the first binding constant expressed in 10^5 g of polymer, is 3.4×10^5 for poly(**2**) and 2.2×10^5 for poly(**3**). These K_1^* values are comparable to one of P18C6 ($K_1^* = 1.83 \times 10^5$ at 25 °C).[11] The monomer units, N needed to bind one dye molecule are calculated from $K = NK_1$ to be 13 and 12 for poly(**2**) and poly(**3**), respectively. The N value is smaller than that of the P18C6–ANS system (N = 80),[11] reflecting five oxyethylene chains on the phosphazene ring. Further studies on properties such as the binding of poly(**2**) and poly(**3**) are now in progress and will appear elsewhere.

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