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Copolymerization of 2-(4′-vinyl-4-biphenylyloxy) pentachlorocyclotriphosphazene with acrylate and methacrylate monomers

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A cyclophosphazene substituted organic monomer, 2-(4′-vinyl-4-biphenylyloxy) pentachlorocyclotriphosphazene (CPHVB), has been copolymerized with methyl acrylate (MA), ethyl acrylate (EA) and methyl methacrylate (MMA) using free radical methods. Flame retardant thermally stable copolymers with up to a maximum of 90% phosphazene content were obtained. Reactivity ratios and Alfrey–Price parameters suggest that the biphenylyloxy unit successfully insulates the vinyl moiety from the σ-electron withdrawing effect of the cyclophosphazene ring. © 1997 Elsevier Science Ltd.

(Keywords: cyclophosphazene; copolymer; pendant polymer; flame retardant polymer)

INTRODUCTION

Linear polyphosphazenes containing a P–N backbone in the polymer chain are now quite well known and form one of the most important classes of inorganic polymers[1–6]. However, in contrast, studies on polymers containing a cyclophosphazene ring as part of the polymer chain or as a pendant group in a polymer are relatively few. The latter class of polymers are especially interesting as these can be viewed as organic polymers with unusual side chain substituents, where the substituents can be expected to render the polymer with unique properties. The development of this area of polyphosphazenes requires the synthesis of suitable cyclophosphazene monomers that contain a polymerizable functionality. Allen and coworkers have previously studied a few cyclophosphazene monomers towards this purpose (*Scheme 1*)[7–9]. They have found that the monomers **1–3** cannot be homopolymerized; however these could be incorporated into other organic polymeric frameworks by copolymerization thereby generating hybrid ‘organic–inorganic polymers’. More recently, Inoue and coworkers have been able to synthesize cyclophosphazenes **4–6** that can be homopolymerized (*Scheme 1*)[10–14]. Some of these polymers with modified etheroxy substituents have shown promising potential as polymer electrolytes[15–17] while the polymer obtained from 2-(4′-vinyl-4-biphenyloxy) pentachlorocyclotriphosphazene (CPHVB) (**5**), was found to possess excellent thermal properties. We thought that it would be rewarding to study the copolymerization behaviour of CPHVB (**5**) towards simple organic monomers. Firstly, as discussed above, there are only three examples (**1–3**) of well-studied copolymers involving cyclophosphazene containing organic monomers[7–9]. Secondly, all of these monomers are 1,1′-disubstituted olefins and consequently are sterically encumbered. Besides in **1** and **2** the cyclophosphazene ring, which is a σ-electron withdrawing group, is directly attached to the olefin. In contrast, in CPHVB (**5**) the vinyl group has only one substituent, and is also well insulated from the inorganic heterocyclic ring. Finally it is also of interest to study the effect of incorporating the monomer CPHVB into organic polymers in view of the excellent thermal properties of the homopolymer generated from this monomer[11]. Herein we report our findings on the copolymerization of CPHVB with methyl acrylate, ethyl acrylate, and methyl methacrylate.

EXPERIMENTAL

Materials

Hexachlorocyclotriphosphazene (Nippon Soda, Japan), was recrystallized from hexane (m.p. 114°C) prior to use. 4-Hydroxybiphenyl (Aldrich, USA and LOBA Chemicals, India), aluminium chloride, sodium borohydride, zinc chloride (anhydrous) (S.D. Fine Chemicals, India), trichloroacetic acid (Qualigens, India) were used without any further purification. Acetyl chloride (Qualigens, India) was distilled before use. The organic monomers, methyl acrylate, methyl methacrylate, and ethyl acrylate (Fluka, Switzerland) were washed twice with 0.1 N NaOH solution followed by distilled water to remove the *t*-butyl catechol inhibitor. The dried monomers were then distilled at reduced pressure and stored in a refrigerator. The monomers were added to excess methanol or hexane in drops to detect the presence of any polymer prior to use. The organic solvents were dried and purified according to standard literature procedures[18]. The

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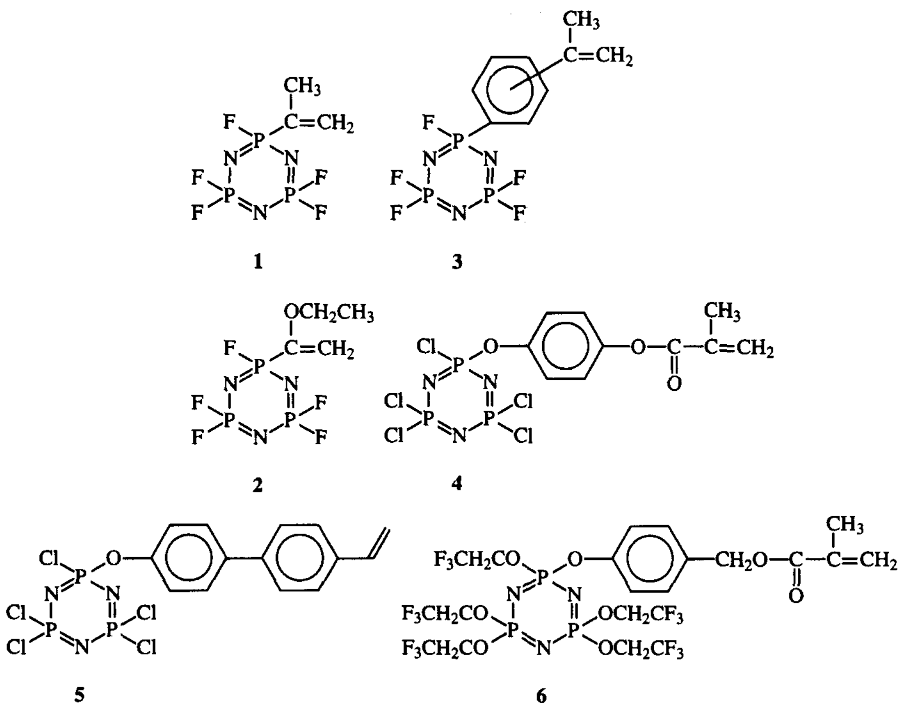
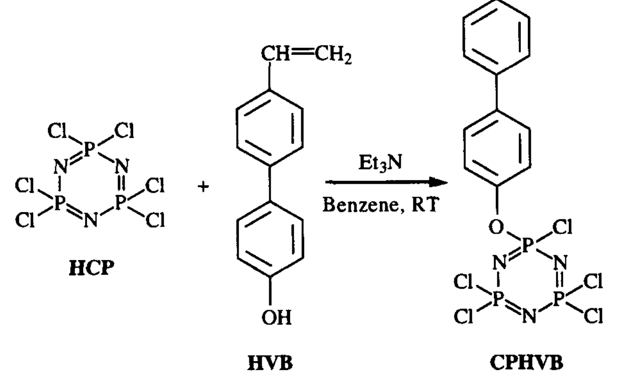


Scheme 1

Table 1 Experimental details of the copolymerization of CPHVB with methyl acrylate including composition and conversion data for CPHVB-MA copolymers used for reactivity ratio calculations

Copolymer code	CPHVB (g)	MA (g)	Amount of polymer (g)	CPHVB (mol) % Feed	CPHVB (mol) % Polymer	wt% conversion
CPHVB-MA(1)	1.00	0.20	0.12	45.72	70.80	10.13
CPHVB-MA(2)	0.99	0.54	0.37	23.80	55.56	24.33
CPHVB-MA(3)	1.53	0.22	0.24	53.76	78.48	13.47
CPHVB-MA(4)	1.16	0.08	0.04	70.92	82.53	3.46
CPHVB-MA(5)	1.00	0.50	0.30	25.84	57.00	16.99
CPHVB-MA(6)	1.00	1.32	0.83	11.38	32.85	35.97
CPHVB-MA(7)	0.12	0.20	0.15	48.29	79.83	11.31
CPHVB-MA(8)	1.11	1.46	0.21	11.41	39.78	8.07
CPHVB-MA(9)	1.03	0.57	0.07	23.57	40.24	4.54
CPHVB-MA(10)	1.59	0.27	0.13	49.83	78.95	6.78



Scheme 2

initiator, α,α'-azoisobutyronitrile (AIBN), was recrystallized from methanol and vacuum dried before use. CPHVB has been synthesized as reported earlier (*Scheme 2*)[10].

Measurements

^1H n.m.r. spectra were obtained on Bruker WP80 and Bruker WM400 spectrophotometers operating at 80 MHz and 400 MHz respectively, using $CDCl_3$ as solvent and TMS as internal reference. ^{31}P n.m.r. spectra were recorded on a Bruker WM400 spectrophotometer functioning at 135 MHz using $CDCl_3$ as solvent and 85% H_3PO_4 as external reference. I.r. spectra were obtained on a Perkin–Elmer FTIR 1600 series spectrophotometer using KBr pellets. Thermogravimetric analysis (t.g.a.) was obtained on a Shimadzu thermal analyser and a Cahn 2000 thermal analyser in N_2 atmosphere at a heating rate of $10°C\,min^{-1}$. Gel

Table 2 Experimental details of the copolymerization of CPHVB with ethyl acrylate including composition and conversion data for CPHVB-EA copolymers used for reactivity ratio calculations

Copolymer code	CPHVB (g)	EA (g)	Amount of polymer (g)	CPHVB (mol) % Feed	CPHVB (mol) % Polymer	wt% conversion
CPHVB-EA-(1)	1.01	0.21	0.01	49.33	70.09	0.87
CPHVB-EA-(2)	1.00	0.42	0.03	32.48	64.52	2.14
CPHVB-EA-(3)	1.00	0.79	0.63	19.94	50.17	36.31
CPHVB-EA-(4)	1.00	0.10	0.10	66.16	81.18	9.28
CPHVB-EA-(5)	0.89	0.73	0.36	19.45	51.56	22.11
CPHVB-EA-(6)	0.94	0.05	0.12	80.58	88.89	11.66
CPHVB-EA-(7)	0.82	0.41	0.01	41.80	49.56	0.98
CPHVB-EA-(8)	0.84	0.37	0.08	28.30	55.93	6.97
CPHVB-EA-(9)	0.59	0.22	0.07	34.71	38.84	8.78
CPHVB-EA-(10)	0.55	0.41	0.08	21.14	56.41	7.99

Table 3 Experimental details of the copolymerization of CPHVB with methyl methacrylate including composition and conversion data for CPHVB-MMA copolymers used for reactivity ratio calculations

Copolymer code	CPHVB (g)	MA (g)	Amount of polymer (g)	CPHVB (mol) % Feed	CPHVB (mol) % Polymer	wt% conversion
CPHVB-MMA(1)	1.01	0.22	0.22	48.22	74.82	18.09
CPHVB-MMA(2)	1.02	0.12	0.04	63.44	88.13	3.53
CPHVB-MMA(3)[a]	1.52	0.11	0.09	-	-	5.43
CPHVB-MMA(4)	0.51	0.30	0.07	24.70	55.52	8.55
CPHVB-MMA(5)[a]	0.51	0.50	0.32	-	-	31.45
CPHVB-MMA(6)	0.51	0.23	0.04	30.17	59.97	4.94
CPHVB-MMA(7)	0.50	0.51	0.13	16.26	42.06	12.65
CPHVB-MMA(8)	0.52	0.12	0.18	46.56	93.16	28.87
CPHVB-MMA(9)	0.80	0.28	0.07	35.82	72.46	6.70
CPHVB-MMA(10)	0.82	0.15	0.09	51.24	84.16	9.52
CPHVB-MMA(11)	0.82	0.31	0.09	34.22	70.91	7.51

[a] It was not possible to determine the CPHVB content in the polymer in these experiments

Table 4 Characteristic i.r. stretching frequencies of CPHVB and some representative copolymers of CPHVB

Copolymer	$\nu_{P=N}$ (cm^{-1})	$\nu_{C=O}$ (cm^{-1})
CPHVB	1212.7 (vs)	-
CPHVB-MA(7)	1184.8 (vs)	1732.4 (s)
CPHVB-EA(8)	1209.2 (vs)	1729.0 (s)
CPHVB-MMA(8)	1210.7 (vs)	1728.1 (m)

Table 5 ^{31}P n.m.r. data of CPHVB and representative copolymers of CPHVB

Copolymer	Chemical shift values AB$_2$2 type	(ppm)
CPHVB	20.8 (d),	10.6 (t)
CPHVB-MA(1)	22.8 (d),	12.5 (t)
CPHVB-EA(4)	22.8 (d),	12.5 (t)
CPHVB-MMA(8)	22.9 (d),	12.5 (t)

permeation chromatography (g.p.c.) was carried out with a maxima 800 instrument using THF as solvent and polystyrene as the standard. Dilute solution viscosity studies were done on a Schott–Gerate viscometer using a Ubbelohde viscometer with a capillary pore size of 0.645 mm. The experiment was carried out at 26°C in dry benzene. The elemental analyses were done using a Carl Erba 1108 elemental analyser.

Copolymerization of CPHVB with methyl acrylate

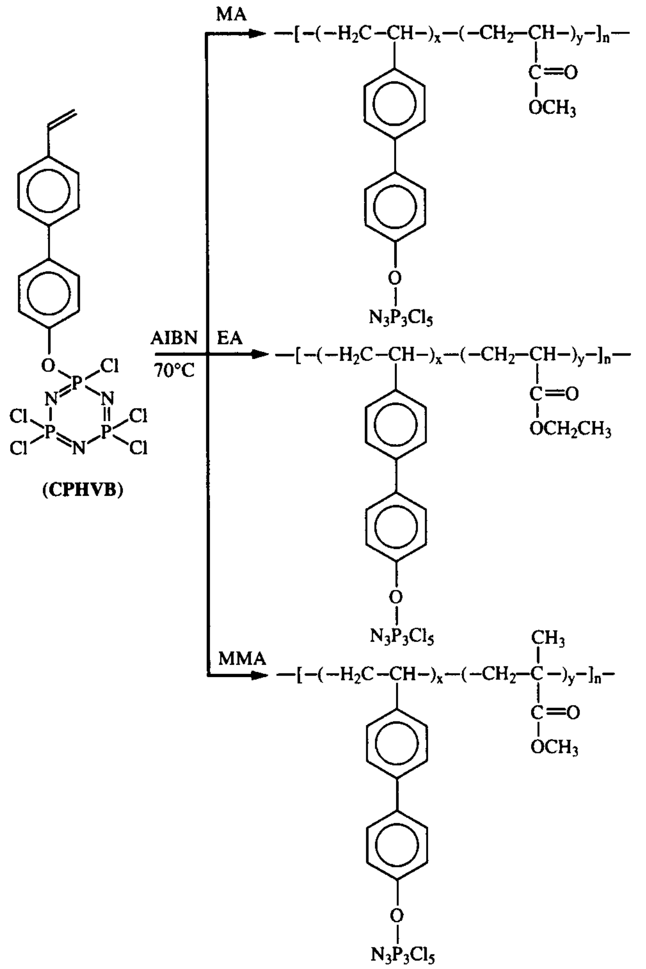
The monomers CPHVB (1.0 g, 1.97 mmol) and methyl acrylate (0.2 g, 2.30 mmol) in 20 ml of the solvent dichloroethane were placed in a polymerization tube along with 2% AIBN. The tube was fitted with a reflux condenser and nitrogen was bubbled through the solution for 45 min. The tube was then kept in an oil bath which was maintained at 70 ± 0.1°C for 3 h. The polymerization tube was kept under a positive pressure of N_2 throughout. After cooling to room temperature the reaction mixture was poured into an excess of hexane. The precipitated residue was filtered and reprecipitated twice using dichloromethane as solvent and hexane as nonsolvent. Finally, the solid material was dried in vacuum to afford 0.12 g (10.1%) of the copolymer (CPHVB-MA-1).

Different initial feeds of the two monomers were used to get different copolymers. The data are given in *Table 1*. Using a similar procedure as above, the copolymers of CPHVB with ethyl acrylate and methyl methacrylate have been synthesized[19]. The detailed experimental conditions are given in *Tables 2* and *3* respectively.

RESULTS AND DISCUSSION

Synthesis of copolymers

CPHVB could be copolymerized readily with acrylates such as methyl acrylate (MA), ethyl acrylate (EA) and methyl methacrylate (MMA) at 70°C in dichloroethane in a nitrogen atmosphere (*Scheme 3*). *Tables 1*, *2* and *3* summarize the details of the experimental conditions and give the composition and conversion data. High field proton n.m.r. recorded at 400 MHz has been used to find out about the extent of incorporation of the monomer CPHVB in the copolymers. No cross-linked products were obtained in any experiment. Attempts were made such that low copolymer conversions were obtained so that the data could be used in the evaluation of reactivity ratios. All the copolymers obtained were isolated as white powders and were found to be soluble in a variety of organic solvents such as benzene, dichloromethane, THF, etc. but were found to be insoluble in solvents like hexane, water and methanol. The copolymers are quite stable to moisture and have long shelf lives. The maximum incorporation of CPHVB in the copolymer was found to be 93%. To the best of our knowledge this represents the maximum incorporation of any cyclophosphazene monomer in a copolymer.



Scheme 3

Characterization of CPHVB copolymers

Table 4 summarizes the i.r. spectral data for representative copolymers of CPHVB along with CPHVB. In

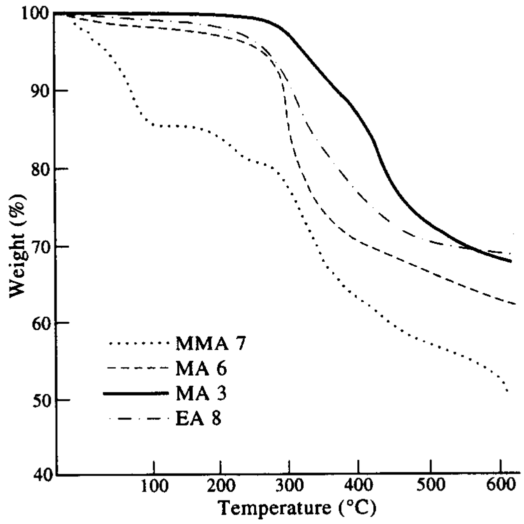


Figure 1 Thermal analysis curves for selected copolymers of CPHUB

Table 6 Thermal data of CPHVB and representative copolymers of CPHVB and some other cyclophosphazene copolymers

Copolymer	Cyclophosphazene content in copolymer (wt%)	Char yield % (600°C)	T_g (°C)	Ref.
CPHVB-MA(3)	78.5	68	91.3	Present work
CPHVB-MA(5)	57.0	69	92.4	Present work
CPHVB-MA-6	32.9	62	86.0	Present work
CPHVB-EA-8	35.9	68	103.5	Present work
CPHVB-EA-4	81.2	70	-	Present work
CPHVB-MMA-7	61.5	65	85.2	Present work
CPHVB-MMA-8	87.8	67	-	Present work
CPHVB (homopolymer)	100	65	-	11
1-STY	31.9	50[b]	93.0	7
2-STY	42.5	50[a]	-	8

[a] 50% weight loss by 355°C and nearly 100% weight loss by 400°C

[b] 50% weight loss by 425°C

Table 7 Intrinsic viscosity data of representative copolymers of CPHVB

Copolymer	Intrinsic viscosity (g cm^{-2})	CPHVB in copolymer (%)
CPHVB-MA-4	6.93	82.53
CPHVB-MA-1	4.43	70.80
CPHVB-MA-5	2.12	57.00
CPHVB-EA-3	1.20	50.17
CPHVB-EA-4	7.75	81.18
CPHVB-EA-6	8.45	88.90
CPHVB-MMA-10	6.45	72.46
CPHVB-MMA-9	4.80	69.62
CPHVB-MMA-4	4.15	55.52

Table 8 Molecular weight data of representative copolymers

Copolymer	$\bar{M}_w$	Polydispersity	CPHVB in copolymer (%)
CPHVB-MA-6	11 995	1.88	32.85
CPHVB-EA-8	10 450	1.61	55.93
CPHVB-MMA-7	3 406	6.28	42.06

CPHVB as well as in the copolymers the (P=N) stretching frequency is retained and is found within a narrow range (1185–1213 cm^{-1}) indicating that the cyclophosphazene ring is intact and is retained in the copolymers. This has been confirmed by ^{31}P n.m.r. studies on the copolymers (*vide infra*). Strong peaks due to C=O stretch are also seen in the copolymers (*Table 4*).

The comparison of ^{1}H n.m.r. of CPHVB and the copolymers clearly reveals the disappearance of the olefinic multiplet in the copolymers and the appearance of new signals due to alkyl groups. The ^{31}P n.m.r. spectral data of selected copolymers are listed in *Table 5*. The chemical shift values observed for the copolymers clearly and unambiguously prove that the original cyclophosphazene moiety is retained in the copolymers without any modification. It is to be noted that linear polyphosphazenes containing the $+\overset{\vee}{\mathrm{P}}=\mathrm{N}+$ backbone generally show chemical shift values which are up-field to 85% H_3PO_4[20]. Secondly, in all the cases the ^{31}P n.m.r. spectrum is of AB_2 type indicating that the cyclophosphazene ring does not suffer any change in the copolymers.

Thermal analysis

T.g.a. of the copolymers reveal that CPHVB containing polymers are extremely stable. *Table 6* summarizes the thermal data of selected copolymers. *Figure 1* gives the thermal analysis curves for selected samples. The salient features of the t.g.a. studies can be summarized as follows:

(a) all the thermal decompositions of the CPHVB copolymers reveal that in general there is no change or decomposition up to 300°C and beyond that they show a single or two step decomposition (*Figure 1*);
(b) in comparison with the homopolymer derived from CPHVB, CPHVB containing copolymers are less stable thermally; the former has a char yield of 67% at 800°C whereas the latter in various compositions show a char yield of at least 54–70% at 600°C (*Table 9*);
(c) all the copolymers containing CPHVB (CPHVB-MA, CPHVB-EA, and CPHVB-MMA) are more stable than any previous organic polymers containing cyclophosphazene pendant groups. Thus, for example, styrene copolymers containing **2** and **3** are much less stable (char yields, <10% at around 450°C);
(d) only small amounts of CPHVB incorporation in the organic polymers can lead to dramatic thermal stabilities. Thus, CPHVB-MA-6, which has only 32.9% of CPHVB, has a char residue of 62% at 600°C. However, there is no linear relationship between the thermal stability imparted and the extent of CPHVB incorporation. I.r. spectra of chars obtained from the copolymers show the complete absence of C=O along with P=N stretching frequencies.

In addition to t.g.a. studies simple flame tests were conducted on all the copolymers containing CPHVB. All of these are flame retardant. When soaked in a flammable solvent such as petroleum ether and burned against a spirit lamp blue flame the copolymers act as self extinguishers.

It is clear that the incorporation of the hydroxy vinylbiphenyl on the cyclophosphazene moiety imparts excellent thermal stabilities to the resulting polymers. It is to be noted that the homopolymer derived from hydroxy vinyl biphenyl (HVB) itself or copolymers of HVB are not that thermally stable[21]. Evidently, the char contains highly stable aromatic rings containing P and N. The insolubility of these residues in common organic solvents precluded attempts at their characterization.

Molecular weight measurements

Dilute solution viscosity measurements were carried out on all the copolymer samples. These data which give an indication of the relative molecular weights of the copolymers are summarized in *Table 7*.

For selected samples g.p.c. measurements were also carried out. The molecular weights obtained along with the polydispersity values are given in *Table 8*. These data suggest that the molecular weights involved are in the order of 10^4. However, it is likely that the actual molecular weights are much higher than indicated by g.p.c. in view of previous studies by Allen and coworkers[7–9]. These researchers have found that in their hybrid copolymers, molecular weights obtained by absolute methods such as membrane osmometry and vapour phase osmometry were higher than those obtained from g.p.c. This was attributed to the non-suitability of polystyrene as a calibrant for cyclophosphazene derived polymers. From an inspection of *Table 7*, it can be clearly seen that the intrinsic viscosities of the copolymers increase with increased cyclophosphazene content. This is in keeping with the high reactivity ratios (r_2) obtained for CPHVB in its copolymerization with MA, EA, and MMA (*vide infra*). Previously, Allen and coworkers have studied the copolymerization of styrene with cyclophosphazene monomers **1**, **2** and **3**, and have found that increased amounts of cyclophosphazene in the copolymers leads to a decrease in molecular weights[7–9]. It was proposed that high reactivity of the cyclophosphazene radical and a low homopropagation rate leads to increased occurrence of termination steps in the copolymerization. In the present system, since CPHVB has a high propensity to

Table 9 r_1 and r_2 values of the monomers in the copolymerization of CPHVB, HVB and other cyclophosphazenes

Copolymer system	Finemann–Ross method	Mortimer–Tidwell method	Reference
CPHVB-MA	r_1 (MA) = 0.04	r_1 (MA) = 0.21	Present work
	r_2 (CPHVB) = 1.55	r_2 (CPHVB) = 2.63	
CPHVB-EA	r_1 (EA) = 0.05	r_1 (EA) = 0.09	Present work
	r_2 (CPHVB) = 1.71	r_2 (CPHVB) = 1.11	
CPHVB-MMA	r_1 (MMA) = 0.03	r_1 (MMA) = 0.11	Present work
	r_2 (CPHVB) = 2.48	r_2 (CPHVB) = 3.41	
1-STY	r_1 (STY) = 1.35[a]	-	7
	r_2 (1) = 2.20		
2-STY	r_1 (STY) = 3.40[a]	r_1 (STY) = 3.04	8
	r_2 (2) = 0.30	r_2 = 0.19	
3-STY	-	r_1 (STY) = 0.41	9
		r_2 (3) = 0.28	
4-STY	r_1 (STY) = 0.33[a]	-	13
	r_2 (4) = 0.26		
4-MMA	r_1 (MMA) = 0.49[a]	-	13
	r_2 (4) = 1.17		
HVB-STY	r_1 (STY) = 0.54[a]	-	21
	r_2 (HVB) = 0.53		
HVB-MMA	r_1 (MMA) = 0.21[a]	-	21
	r_2 (HVB) = 0.61		
HVB-MA	r_1 (MA) = 0.17[a]	-	21
	r_2 (HVB) = 0.34		

[a] By using the Mayo–Lewis method

Table 10 *e–Q* values of CPHVB and other cyclophosphazene monomers

Copolymer	*e*	*Q*	Ref.
CPHVB-MA	−0.16	1.25	Present work
CPHVB-EA	−1.30	4.17	Present work
CPHVB-MMA	−0.59	4.49	Present work
1-STY	0.18	0.21	7
2-STY	−0.06	0.18	8
3-STY	0.72	0.72	9
HVB-STY	−1.91	4.48	21
HVB-MMA	−1.03	1.98	21
HVB-MA	−1.05	2.59	21

add on to itself, it is not surprising to see increased molecular weights in the copolymers with increased cyclophosphazene content. Similar observations have also been made by Inoue and coworkers in the copolymerization studies of **4** with styrene[13,14].

Reactivity ratios

The reactivity ratios have been calculated for all the three copolymerization systems, viz. CPHVB-MA, CPHVB-EA, and CPHVB-MMA, using two different methods and summarized in *Table 9*[22,23]. It is to be noted that the input values for the more reliable Mortimer–Tidwell calculation were derived from the Finemann–Ross method. In all cases one can observe that r_2 (CPHVB) is much greater than one, indicating the large propensity for CPHVB to add to itself. In monomer **1** and **2** the vinylic functionality is attached directly to the phosphorus of the inorganic heterocycle and since the cyclophosphazene moiety has been shown to be σ-electron withdrawing in these two monomers the olefinic functionality suffers a depletion of electron density and hence reduced reactivities are observed. Surprisingly in **1**, although Allen observes an r_2 of 1.35 with styrene, no homopolymerization of **1** could be formed. Even in **3**, where the vinyl functionality is separated from the cyclophosphazene moiety by a phenyl substituent, r_2 is still low.

In comparison with the above cyclophosphazene monomers, it is seen in the present system that the biphenylyloxy substituent is very effective in insulating the vinyl functionality from the electron withdrawing effect of the cyclophosphazene ring. This accounts for the high r_2 values. Secondly, all Allen's monomers are α,α'-disubstituted olefins and are therefore sterically encumbered. In contrast, in CPHVB only one substituent is present on the olefinic group. Inoue and coworkers have recently reported the copolymerization studies of **4** with styrene[13,14]. It is clear that the reactivity ratios they have obtained (Mayo–Lewis method) are not very different from those seen in the present system. It is interesting to note that the copolymerization studies of HVB with styrene, methyl acrylate, methyl methacrylate and acrylonitrile (*Table 9*) show that r_2 (HVB) values are much higher than r_1 indicating that HVB prefers to add on to itself[21]. Thus the basic nature of the HVB monomer is not altered by substitution on the cyclophosphazene ring in CPHVB.

Q–e *scheme*

The r_1 and r_2 values obtained from the Mortimer–Tidwell method were used for calculating the Alfrey–Price parameters, Q and e[24,25]. The e and Q values are summarized for each system in *Table 10*. It can be seen from *Table 10* that the e values are negative for CPHVB and the Q values are positive and greater than unity. Comparison of the $Q-e$ values of CPHVB with that of HVB reveals that the nature of the olefin functionality remains unaltered[21]. High positive Q values indicate substantial mesomeric interaction of the olefin functionality with its substituent. It is difficult to comment whether the cyclophosphazene ring is also involved in any mesomeric interaction. However, in view of the similarity of the Q values of HVB and CPHVB, as well as the invariance of the phosphorus chemical shifts of cyclophosphazene in CPHVB and in the copolymers, it is reasonable to conclude that there is negligible electronic interaction between the cyclophosphazene ring and the olefinic centre. This reluctance of the phosphazene unit to enter into significant mesomeric interaction with unsaturated organic units has been pointed out earlier[7,26]. While comparing the $Q-e$ values of CPHVB with that of other cyclophosphazene monomers, it is quite clear that **1**, **2** and **3** have positive e values which reflect the reduction of the electron density of the olefin functionality by the strong σ-electron withdrawing effect of the cyclophosphazene moiety. The presence of an ethoxy substituent at α'-position in monomer **2**, to some extent counter-balances the electron withdrawing nature of the phosphazene ring.

In conclusion, it may be said that the reactivity ratios and the $Q-e$ values obtained for CPHVB in the various copolymerization studies indicate that the vinyl functionality of the monomer is electron rich and conjugatively stabilized. It is quite clear that the biphenylyloxy group is very effective in insulating the olefinic centre from the σ-electron withdrawing effect of the cyclophosphazene ring. These copolymers represent an interesting class of new hybrid polymers. Our studies show quite clearly that only small amounts of CPHVB are required in the copolymers to drastically affect the properties of the organic polymer. Further studies on copolymers containing substituted cyclophosphazenes are under investigation in our laboratory.

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REFERENCES

1. Mark, J. E., Allcock, H. R. and West, R., *Inorganic Polymers*, Polymer Science and Engineering Series, Prentice Hall, Englewood Cliffs, New Jersey, 1992.
2. Potin, Ph. and De Jaegar, R., *Eur. Polym. J.*, 1991, **27**, 341.
3. Allcock, H. R., Kuharcik, S. E., Morrissey, C. T. and Ngo, D. C., *Macromolecules*, 1994, **27**, 7556.
4. Wisian Neilson, P., Huang, L., Islam, M. Q. and Crane, R. A., *Polymer*, 1994, **35**, 4985.
5. Allock, H. R., *Chem. Eng.*, 1985, **63**, 22.
6. Wisian-Neilson, P. and Neilson, R. H., *Chem. Rev.*, 1988, **88**, 541.
7. Du pont, J. G. and Allen, C. W., *Macromolecules*, 1979, **12**, 169.
8. Allen, C. W. and Bright, R. P., *Macromolecules*, 1986, **19**, 571.
9. Allen, C. W., Shaw, J. C. and Brown, D. E., *Macromolecules*, 1988, **21**, 2653.
10. Inoue, K., Takagi, M., Nakano, M., Nakamura, H., Tanigaki, T., *Makromol. Chem., Rapid Commun.*, 1988, **9**, 345.
11. Inoue, K., Kaneyuki, S. and Tanigaki, T., *Macromolecules*, 1989, **22**, 1530.
12. Inoue, K., Kaneyuki, S. and Tanigaki, T., *Macromol. Chem. Rapid Commun.*, 1990, **11**, 467.
13. Inoue, K., Kaneyuki, S. and Tanigaki, T., *J. Polym. Sci. Part A: Polym. Chem.*, 1992, **30**, 144.
14. Inoue, K., Nakahara, H. and Tanigaki, T., *J. Polym. Sci. Part A, Polymer. Chem.*, 1993, **31**, 144.
15. Inoue, K., Nishikawa, Y. and Tanigaki, T., *Macromolecules*, 1991, **24**, 3464.
16. Inoue, K., Nishikawa, Y. and Tanigaki, T., *J. Am. Chem. Soc.*, 1991, **24**, 3464.
17. Inoue, K., Nishikawa, Y. and Tanigaki, T., *Solid State Ionics*, 1992, **58**, 217.
18. Vogel's *Textbook of Organic Chemistry*, 5th edn, ed. B. S. Furniss, A. J. Hannaford, P. W. Smith and A. R. Tatchell. ELBS/Longman, UK, 1989.
19. The yield is controlled by the polymerization time by trial and error.
20. Allcock, H. R., Connolly, M. S., Siski, J. T. and Alshali, S., *Macromolecules*, 1988, **21**, 323.
21. Tanigaki, T., Shirai, M. and Inoue, K., *Polymer J. Tokyo*, 1987, **19**, 881.
22. Finemann, M. and Ross, S. D., *J. Polymer Sci.*, 1950, **5**, 259.
23. Tidwell, P. W. and Mortimer, G. A., *J. Polym. Sci. Part A*, 1965, **3**, 369.
24. Alfrey, T. Jr. and Young, L. J., *Copolymerization*, 2nd edn, ed. G. E. Ham. Wiley, New York, 1971.
25. Young, L. J., *Polymer Handbook*, 2nd edn, ed. J. Brandrup and E. H. Immergut. Wiley, New York, 1975.
26. Allen, C. W., Toch, P. L., Perlman, M., Brunst, G. and Green, J. C., *Int. Conf. Chem. Inst. Can. Am. Chem. Soc., Abstr. Inorg.*, **63**, Montreal, 1977.