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(21) Average number of end groups = 1.9 (±10%).
(22) 29 monomer units of oxy-2,6-dimethyl-1,4-phenylene.
(23) *n* repeat units (2.7) + 2.

Heat-Resistant Polymers Prepared from [(4′-(2-Vinyl)-4-biphenylyl)oxy]pentachlorocyclotriphosphazene

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ABSTRACT: The radical-initiated copolymerization of [(4′-(2-vinyl)-4-biphenylyl)oxy]pentachlorocyclotriphosphazene (**2**) with styrene or methyl methacrylate in 1,2-dichloroethane and the thermal behavior of their copolymers were investigated. The copolymers, poly(**2**-*co*-St) and poly(**2**-*co*-MMA), were found to be enriched in **2** with respect to the monomer feed. The comparison of Alfrey–Price parameters of **2** with those of 4-hydroxy-4′-vinylbiphenyl (**1**) suggests that the phosphazene ring in **2** acts only as an electron-withdrawing group. The thermogravimetric analysis indicates that incorporation of **2** in the copolymers leads to increased thermal stability. The copolymers containing more than 50 mol % of **2** afford 56–65% char yields at 800 °C in air or nitrogen atmosphere.

Introduction

There has been considerable interest in poly(organophosphazenes).[1-7] These polymers often exhibit useful, interesting properties, such as flame retardency, high thermal stability, and resistance to chemicals. Attempts to improve the thermal stability and flame retardency of polymers by incorporation of a cyclotriphosphazene moiety have been demonstrated.[8-13] For example, the polymer obtained from maleimide-substituted aromatic cyclotriphosphazene has good thermal stability and affords a residue with high yield at 800 °C.[8,9] Furthermore, Allen et al.[10-13] have examined the thermal behavior of the copolymers with the pendant pentafluorocyclotriphosphazene unit, which were prepared by a conventional radical copolymerization. Although the incorporation of the phosphazene moiety imparts flame-retardant properties to the copolymers, significant improvement in the thermal stability of these copolymers over that of the organic homopolymer was not observed.

In the previous papers,[14,15] we reported that the radical polymerization of [(4′-(2-vinyl)-4-biphenylyl)oxy]pentachlorocyclotriphosphazene (**2**; Scheme I) and the thermal behavior of its polymer showed that **2** has a high-radical polymerizability and that poly(**2**) is thermally stable up to 300–400 °C, depending on the molecular weight. Of particular interest is the fact that the polymer gives a residue with high yield (60%) at 800 °C in both air and nitrogen atmospheres. From these results one would expect that the copolymers containing the desired content of **2** could be prepared and show improved thermal stability relative to the organic homopolymer.

In this paper, we describe the copolymerization of **2** with styrene or methyl methacrylate with AIBN initiation and the thermal behavior of their copolymers. Furthermore, the thermal stability of blend polymer of poly(**2**) and polystyrene is also described.

Table I
Conditions and Results of Copolymerization of 2 with Styrene in 1,2-Dichloroethane at 70 °C[a]

mol % of 2 in monomer feed	mol % of 2 in copolymer	conversion for 6 h, %	$10^{-4}\bar{M}_n$[b]	$10^{-4}\bar{M}_w$[b]	$\bar{M}_w/\bar{M}_n$
5	11.5	12.2	1.0	1.4	1.4
10	20.7	12.0	1.1	1.6	1.4
15	29.6	14.0	1.3	1.9	1.5
20	37.2	14.6	1.5	2.2	1.5
30	49.8	16.2	1.9	5.5	2.9
40	59.9	20.6	2.5	4.3	1.7
50	68.8	23.5	2.8	5.8	2.1
60	76.4	28.8	3.6	8.0	2.2
70	82.9	36.1	4.4	9.4	2.1
90	94.6	50.7	6.5	16.7	2.6

[a] [2] + [St] = 0.4 M, [AIBN] = 2 mM. [b] Determined by GPC.

Experimental Section

Materials. Hexachlorocyclotriphosphazene was kindly provided by Nippon Soda Co. and used without further purification. [(4′-(2-Vinyl)-4-biphenylyl)oxy]pentachlorocyclotriphosphazene (**2**) was prepared from 4-hydroxy-4′-vinylbiphenyl (**1**)[16] and hexachlorocyclotriphosphazene. Details of preparation and characterization of **2** were described in the previous paper.[14] AIBN was recrystallized from methanol. Styrene and methyl methacrylate were distilled before use. Other chemicals were purified by known procedures.

Copolymerization. Copolymerization of **2** with St or MMA in 1,2-dichloroethane was run at 70 °C in tubes sealed under vacuum, with AIBN as initiator (Tables I and II). The copolymer was obtained by precipitation from hexane.

Measurements. Infrared spectra were recorded on a Shimadzu IR-420 spectrophotometer. UV spectra were obtained on a Shimadzu UV-260 spectrophotometer. Gel permeation chromatography was performed on a Shimadzu LC-3A instrument equipped with UV and RI detectors, using THF as eluent. The columns consisted of Shimadzu HSG 60 and 30 (MW range, 1×10^3–1×10^6). The columns were calibrated with polystyrene

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Scheme I

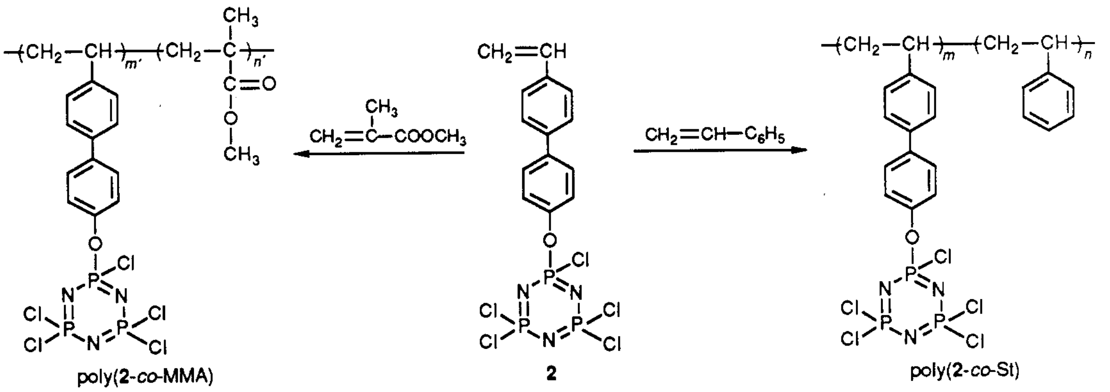

Table II
Conditions and Results of Copolymerization of 2 with MMA in 1,2-Dichloroethane at 70 °C[a]

mol % of 2 in monomer feed	mol % of 2 in copolymer	time, h	conversion, %	$10^{-4}\bar{M}_n$[b]	$10^{-4}\bar{M}_w$[b]	$\bar{M}_w/\bar{M}_n$
10	24.9	4	19.4	2.1	3.7	1.8
20	42.2	4	17.1	2.2	3.8	1.7
30	52.7	4	16.2	2.5	4.4	1.8
40	54.0	3.5	16.9	2.6	4.7	1.8
50	69.6	3.5	16.2	3.0	5.6	1.9
70	83.4	3.5	15.7	4.1	8.5	2.1
80	92.8	3	18.4	4.9	10.9	2.2

[a] [2] + [MMA] = 0.4 M, [AIBN] = 2 mM. [b] Determined by GPC.

standards. Number average and weight average molecular weight were calculated with a Shimadzu CR-4A. Thermogravimetric analyses were carried out using a Shimadzu T-30 system, and glass transition temperatures were measured on a Shimadzu DSC-50 differential scanning calorimeter. Measurements were made in an atmosphere of nitrogen or air (50 mL/min) at a heating rate of 20 °C/min (TGA) and 10 °C/min (DSC). Copolymer compositions of poly(2-*co*-MMA) and poly(2-*co*-St) were determined from absorbance at 260.5 nm using a Shimadzu UV 260 and elemental analysis, respectively. The elemental analysis was performed in the center for chemical analysis, Ehime University. Reactivity ratios were calculated by the Mayo–Lewis integral method. The copolymers up to 25% conversion were used for the calculation.

Results and Discussion

The conditions and the results of copolymerization of 2 with styrene or MMA in 1,2-dichloroethane are listed in Tables I and II. The polymer obtained from the copolymerization of 2 with MMA exhibited a characteristic –P=N– stretching absorption between 1240 and 1160 cm^{-1} and a –COO– group at 1720 cm^{-1}. The gel permeation chromatography (GPC) trace showed a symmetrical and relatively narrow peak. These results apparently indicate the formation of the copolymer, poly(2-*co*-MMA). Similarly, the involvement of 2 in the styrene copolymer was confirmed.

Table III
Reactivity Ratios and Alfrey–Price Parameters

M_1	M_2	r_1	r_2	R[a]	Q_1	e_1
2	St	2.4	0.36	0.997	2.0	–0.39
2	MMA	2.1	0.23	0.978	2.3	–0.44
1[b]	MMA	0.61	0.21		1.98	–1.03

[a] Correlation coefficient. [b] Reference 16.

Both poly(2-*co*-St) and poly(2-*co*-MMA) obtained are soluble in a number of solvents. From Tables I and II it can be seen that the copolymers are more rapidly formed as the content of 2 in the monomer feed increased. The molecular weights of poly(2-*co*-St), determined by GPC, increase with an increase in the content of 2 in the monomer feed. Interestingly, the copolymers have a fairly low degree of polydispersity at higher concentrations of St. Similar results were obtained for poly(2-*co*-MMA). Such low polydispersity was observed for the copolymerization of 2-(2-propenyl)pentafluorocyclotriphosphazene (3) with styrene, although low polydispersity was observed at high content of the phosphazene monomer in the copolymer.[10] The opposite results may be interpreted by the difference of polymerizability of the phosphazene monomers; i.e., 2 has a high radical polymerizability whereas 3 does not undergo the homopolymerization. Independent experiments of the polymerization of St in the presence of 2-(4-phenylphenoxy)pentachlorocyclotriphosphazene (4) show that 4 does not affect the yield of polystyrene, the molecular weight of the polymer, and polydispersity, suggesting no specific interaction between 2 and St.

The copolymer compositions of poly(2-*co*-St) and poly(2-*co*-MMA) were determined by elemental analysis and UV technique, respectively. The analyses were performed in duplicate. As shown in Tables I and II, both copolymers were found to be enriched in 2 with respect to the monomer feed. The monomer reactivity ratios (r_1 and r_2) were calculated from the Mayo–Lewis integral equation, using the data up to 25% conversion (most of data used are in the range of 11–20% conversion). The r_1 and r_2 values are listed in Table III, together with those obtained from copolymerization of 4-vinyl-4′-hydroxybiphenyl (1) with MMA.[16] From the values, it is apparent that the propagating radical of 2 preferentially adds to 2 and the cross-propagation is roughly 3 times faster than homopropagation of St or MMA. The Alfrey–Price parameters, Q and e, calculated from poly(2-*co*-St) are slightly different from those of poly(2-*co*-MMA). The correlation coefficient (R) for the calculation of r_1 and r_2 indicates that the data obtained from poly(2-*co*-St) are more reliable than those of poly(2-*co*-MMA). Thus, it seems reasonable to assume that Q and e values of 2 are 2.0 and –0.39, respectively. Recent studies have demonstrated the importance of the penultimate model.[17] In fact, Allen et al.[13] have pointed out that the penultimate effect is operative for the co-

Table IV
Thermal Analysis Data for Poly(1), Poly(2), and Poly(2-*co*-St)

mol % of 2 in copolymer	T_g, °C	PDT, °C		T_{10}, °C		char yield, %			
						500 °C		800 °C	
		N_2	air	N_2	air	N_2	air	N_2	air
[a]	209	250	220	393	330	20	62	13	0
11.5	88	237	220	407	335	32	44	29	8
20.7		245	230	414	355	48	48	43	28
37.2		250	235	427	365	63	63	56	43
49.8	84	252	225	437	385	72	71	64, 68[d]	60, 68[d]
59.9	81	250	235	446	405	74	75	66	65
68.8		235	225	448	430	75	75	65	65
82.9	80	230	235	458	420	76	77	65	60
100[b]	76	300	280	465	450	78	78	63	60
50.0[c]		275	260	442	405	84	70	60[d]	58[d]

[a] Poly(1) with $\bar{M}_n = 4 \times 10^4$. [b] Poly(2) with $\bar{M}_n = 1.1 \times 10^5$. [c] Blend polymer of poly(2) with $\bar{M}_n = 1.1 \times 10^5$ and polystyrene with $\bar{M}_n = 1 \times 10^5$. [d] Char yield at 700 °C.

polymerization of the phosphazene monomer with MMA. Therefore, one plausible explanation for the inconsistency of *Q* and *e* values is the involvement of the penultimate effects in the copolymerization of 2 with MMA. However, at the present time, it is unclear whether the penultimate effect exists in the copolymerization of 2 with MMA or not, because our conversion is too high to discuss about this effect. The *Q* value is similar to that determined from the copolymerization of 1 with MMA whereas the *e* value is apparently affected by the phosphazene ring. These results suggest no mesomeric interaction between the phosphazene ring and the vinylbiphenyl unit and that the difference of *e* value is ascribed to the decrease of electron density by the strong σ-electron-withdrawing effect of the phosphazene ring, as described in the previous papers.[10,13]

Thus, the copolymers with the desired content of cyclotriphosphazene moiety can be prepared in contrast to the previous studies.[10-13]

Thermal Behavior

Poly(2-*co*-St). Glass transition temperatures (T_g) of poly(1), poly(2), and poly(2-*co*-St) are listed in Table IV. The T_g of poly(1) was found to be 48 °C higher than that of poly(vinylbiphenyl) (T_g = 161 °C).[18] The increase in T_g is probably due to hydrogen bonding associated with the hydroxy group in 1. Presence of the bulky phosphazene moiety in poly(2) would be expected to restrict the conformational reorientation of the backbone and raise the T_g in comparison with those of polystyrene (T_g = 100 °C) or poly(vinylbiphenyl). However, the T_g's of poly(2) and poly(2-*co*-St) were in the range of 76–88 °C. Thus, presence of a phosphazene moiety lowers the T_g. A similar result has been reported for copolymers consisting of α-methylstyrene derivatives with a phosphazene moiety and St.[13] For poly(2-*co*-St), T_g values show the expected increase as the content of styrene monomer units in the copolymers increases. Current studies are in progress on phosphazene-containing (co)polymers in order to understand the relationship between structure and the glass transition temperature.

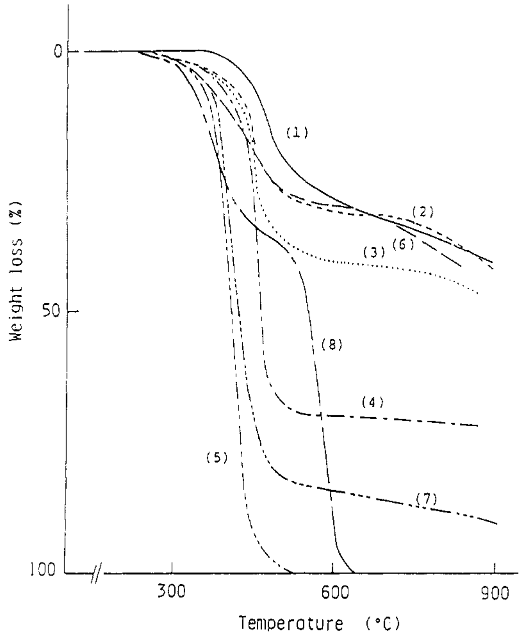

Figure 1. Thermogravimetric analysis of poly(2-*co*-St): (1) poly(2) in N_2; (2) copolymer with 49.8 mol % of 2 in N_2; (3) copolymer with 37.2 mol % of 2 in N_2; (4) copolymer with 11.5 mol % of 2 in N_2; (5) polystyrene in N_2; (6) copolymer with 49.8 mol % of 2 in air; (7) poly(1) in N_2; (8) poly(1) in air.

Typical TGA curves of poly(2-*co*-St) are shown in Figure 1. The polymer decomposition temperature (PDT), the temperature required for 10% weight loss (T_{10}), and the char yields are summarized in Table IV. Although the onset temperatures of decomposition of poly(2-*co*-St) (PDT) are not clearly related to the content of 2, there is a correlation between T_{10} and the content of 2 in the copolymer; i.e., T_{10} increases with an increase in the content of 2 in the copolymer. The fact that T_{10} of poly(2-*co*-St) is higher than that of poly(1) or poly(1-*co*-St)[19] indicates that incorporation of the phosphazene moiety rather than the 4-hydroxybiphenyl moiety is the reason for the increased value of T_{10} over that of the parent homopolymer (polystyrene). The amount of residue obtained from the thermal decomposition of poly(1) in the temperature range of 410–580 °C is greater in air than in nitrogen, even though decomposition in air begins at a lower temperature. Interestingly, the copolymers containing more than 50 mol % of 2 afford residues with high yields (60–66%) at 800 °C in nitrogen. These values correspond to the char yield of poly(2) at 800 °C. It is also a noteworthy feature that the copolymer containing 20.7 mol % of 2 units retains approximately half of its original weight at 800 °C, contrary to the complete decomposition of polystyrene below 500 °C. The lower onset temperature for decomposition observed in air versus nitrogen suggests the involvement of the oxidative decomposition. However, the contribution of this process seems to be small, judged from the decomposition pattern in Figure 1 and the fact that the ratio of the initial decomposition temperature in nitrogen to one in air exists in the range from 0.95 to 1.1. The char yields at 800 °C except for the copolymers with lower contents of 2 showed no influence of oxygen.

The thermal stability of several copolymers was also evaluated by isothermal thermogravimetric analysis as

Table V
Thermal Analysis Data for Poly(2-*co*-MMA)

mol % of 2 in copolymer	T_g, °C	PDT, °C		T_{10}, °C		char yield, % 500 °C		char yield, % 800 °C	
		N_2	air	N_2	air	N_2	air	N_2	air
22.3		249	252	348	314	49	55	32	6
42.5		251	260	377	337	58	62	54	48
57.8	80	263	265	369	344	64	67	57	54
79.6		300	278	415	368	72	70	62	58
83.7	79	287	295	423	423	72	74	60	62
97.5	77	281	293	415	420	70	75	56	60

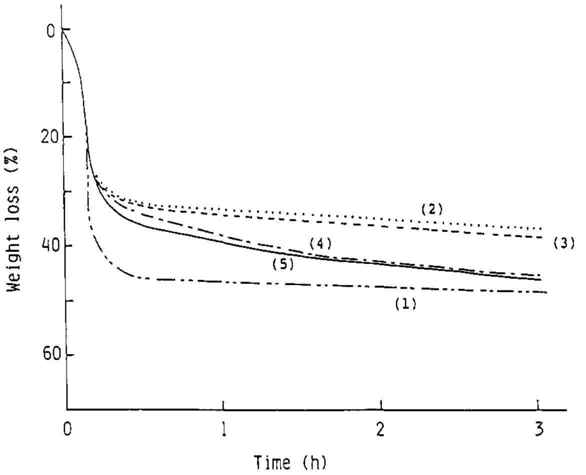

Figure 2. Isothermal gravimetric analysis of poly(2-*co*-St) at 700 °C in nitrogen. Mol % of 2: (1) 20.7; (2) 59.9; (3) 68.8; (4) 82.9; (5) 92.1.

shown in Figure 2. On heating at 700 °C, about 30–40% weight loss occurs within a short period but further heating results in extremely slow weight loss. The degree of weight loss is affected by the content of 2. The copolymer containing 59.9 mol % of 2 units affords the highest residue, and rather lower residue was observed for the copolymers with higher a content of 2. This suggests that the percentages of P, Cl, N, and C in the copolymer are important factors in retention of its original weight with high efficiency. Appreciable influence of oxygen on the residue was not observed.

The results of thermal behavior of the blend polymer (poly(2)/polystyrene = 1)) are also listed in Table IV. The PDT and T_{10} of the blend polymer are slightly higher than those of the component polymer whereas the char yield of the blend polymer at 700 °C is lower than that of poly(2-*co*-St).

These results described above could have been associated with other factors than chemical structure, such as molecular weight. In fact, the blend polymer of poly(2) with $M_n > 10^6$ and polystyrene with $M_n = 2 \times 10^4$ (poly(2)/polystyrene = 1) has scarcely suffered weight loss up to 400 °C in nitrogen and 390 °C in air.

Poly(2-*co*-MMA). The thermal behavior of poly(2-*co*-MMA) is similar to that of poly(2-*co*-St) (Table V). The PDT and T_{10} are considerably lower, reflecting the thermal properties of the comonomer. The increase of the phosphazene content in the copolymers results in increase of T_{10}. The residues at 800 °C were the same as those of poly(2-*co*-St), suggesting that the char yield is not affected by the type of comonomer.

As expected,[10,13,15] qualitative test of flame retardance of both poly(2-*co*-St) and poly(2-*co*-MMA) indicates that they have self-extinguishing property.

In summary, the copolymers with the desired content of the cyclotriphosphazene moiety can be prepared by a conventional radical polymerization. The incorporation of 2 improves thermal stability and the residue of the traditional polymers at higher temperatures.

Registry No. 2, 115529-67-4; (2)(ST) (copolymer), 122847-48-7; (2)(MMA) (copolymer), 122847-49-8; ST, 100-42-5; MMA, 80-62-6.

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