Macromolecules 1989, *22*, 1530–1533

Radical Polymerization of Vinyl Monomers Containing Cyclotriphosphazene and Thermal Behavior of Their Polymers

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ABSTRACT: Polymerization of novel monomers, 2-(4′-vinyl-4-biphenylyloxy)pentachlorocyclotriphosphazene (2; 2,4,4,6,6-pentachloro-2-(4′-vinyl-4-biphenylyloxy)-1,3,5,2λ^5,4λ^5,6λ^5-triazatriphosphorine) and 2-(4′-vinyl-4-biphenylyloxy)pentafluorocyclotriphosphazene (3; 2,4,4,6,6-pentafluoro-2-(4′-vinyl-4-biphenylyloxy)-1,3,5,2λ^5,4λ^5,6λ^5-triazatriphosphorine) and the thermal behavior of their polymers were examined. The polymerizations of 2 and 3 occurred smoothly and gave white polymers. The rate of polymerization of 2 with AIBN in 1,2-dichloroethane was identical with that of 3, indicating the substituent at the phosphazene ring did not affect the polymerization processes. The bulk polymerization of 3 without initiators at 115 °C gave soluble and high molecular weight polymers ($M_n > 10^6$). The thermogravimetric analysis (TGA) of poly(2) has shown thermal stability up to 300–400 °C, depending on the molecular weights of the polymers. The char yields of poly(2) were 59–65% in nitrogen at 800 °C and 55–63% in air. The result of isothermal gravimetric analysis indicates that 55% residue remains after heating at 700 °C for 3 h in air.

Introduction

Poly(organophosphazenes) have attracted much attention in both basic and applied research.[1] A number of them have been prepared by the ring-opening polymerization/substitution method.[2] In contrast, few attempts to prepare polymers with pendant cyclotriphosphazene groups by radical polymerization have been demonstrated.[3-7] Allcock et al.[3] have showed that the polymerization of allylaminocyclotriphosphazene occurs but yields insoluble material. Allen et al.[4-7] have developed the syntheses of the olefins attached to cyclotriphosphazenes and examined the homo- and copolymerizations of monomers such as 2-(α-ethoxyvinyl)- and 2-(2-propenyl)-pentafluorocyclotriphosphazenes. From the failure of homopolymerization, they pointed out that the olefin polarity induced by the highly electron-withdrawing phosphazene substituent causes difficulty in the formation of polymer and favors termination in copolymerization. On the basis of these results, they found that the polymerization of (vinyloxy)pentachlorocyclotriphosphazene occurred smoothly when AIBN was used.[7]

Several high-temperature polymers based on cyclotriphosphazenes have appeared,[1b,11,12] but there are few reports of the preparations of such polymers by radical polymerization due to the difficulty of the formation of polymer as described above.

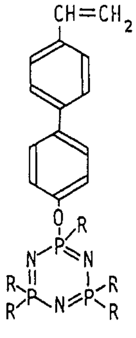
Recently, we examined the homo- and copolymerizations of 4′-hydroxy-4-vinylbiphenyl (1) and demonstrated that 1 is an electron-rich monomer.[8] Therefore, one would expect that 2-(4-vinyl-4′-biphenylyloxy)pentachlorocyclotriphosphazene (2; Chart I) prepared from 1 and $(NPCl_2)_3$ has sufficient electron density at the double bond to polymerize with a radical initiator. Furthermore, the presence of an oxygen atom between the phosphazene ring and the biphenyl moiety probably reduces the influence of electron-withdrawing substituents at the phosphazene ring on the vinyl group. As expected, 2 and 2-(4′-vinyl-4-biphenylyloxy)pentafluorocyclotriphosphazene (3) underwent the polymerizations with AIBN activation, as described in the previous paper.[9] The most important feature of the polymer of 2 is its excellent thermal behavior; i.e., the char yield at 800 °C is high even in air atmosphere.

In this article, we report in detail the polymerization of the interesting monomers 2 and 3 and the thermal behavior of their polymers.

Experimental Section

Materials. Hexachlorocyclotriphosphazene, $(NPCl_2)_3$, was purchased from Tokyo Kasei and used without further purification. Hexafluorocyclotriphosphazene was synthesized from $(NPCl_2)_3$ and NaF.[10] 4-Hydroxy-4′-vinylbiphenyl (1) was prepared by the procedure described previously (Scheme I).[8] Monomer 2 was prepared from 1 and $(NPCl_2)_3$ in the presence of triethylamine in dry benzene at room temperature. Monomer 3 was synthesized from $(NPF_2)_3$ and sodium 4′-vinylbiphenyl-4-olate prepared from 1 and NaH. Details of preparation and characterization of 2 and 3 have been described in the previous paper.[9] Other chemicals and solvents were purified by known procedures.

Chart I



2, R = Cl
3, R = F

Polymerization. Polymerizations were performed in Pyrex glass ampules. A typical procedure was as follows. Solutions containing 2 (0.51 g, 1 M) and AIBN (2.5 × 10^{-3} M) in 1,2-dichloroethane were placed in the ampules. The ampules were degassed by a freeze–thaw procedure and sealed off. The polymerization was carried out in a bath maintained at 70 °C. The polymers were obtained by pouring the reaction mixture into large amounts of hexane. A similar procedure was used for the bulk polymerization of 3 without an initiator.

Measurements. ^{1}H NMR spectra were obtained on a JEOL-FX 100 spectrophotometer. Infrared spectra were recorded on a Shimadzu IR-420 spectrophotometer. Gel permeation chromatography (GPC) was performed on a Shimadzu LC-3A instrument equipped with a UV detector (254 nm), using THF as eluent. The column consisted of Shimadzu HSG 60 and 30. The columns were calibrated with polystyrene standards. Number average and weight average molecular weight were calculated with a Shimadzu CR-4A. Thermogravimetry (TG) was performed on a Shimadzu T-30 thermal analyzer system. Measurements were done in an atmosphere of nitrogen or air (50 mL/min) at a heating rate of 20 °C/min. Elemental analysis was performed in the center for chemical analysis, Ehime University.

Results and Discussion

Solution Polymerization of 2 and 3 with AIBN. Novel monomers 2 and 3 were synthesized starting with

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Scheme I

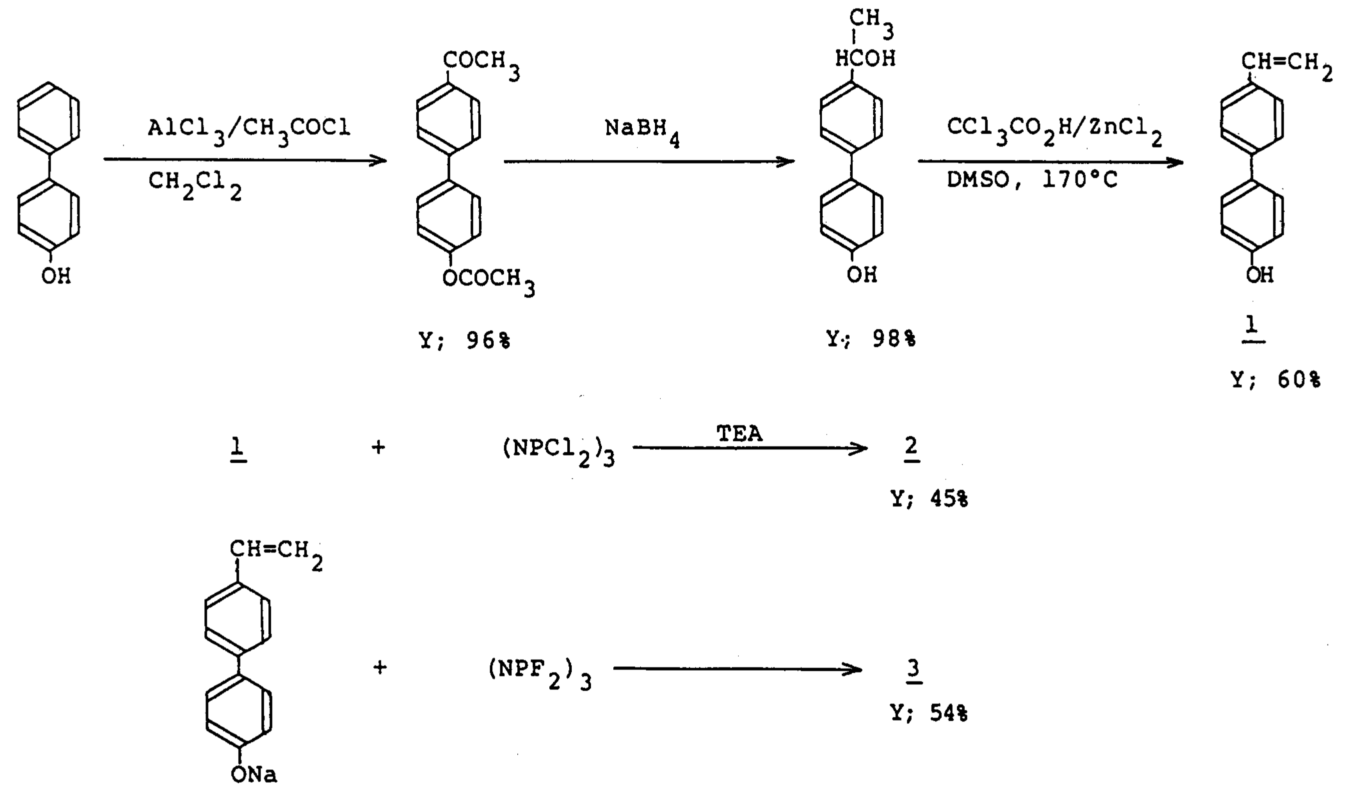

Table I
Results of Polymerizations of 2 and 3 with AIBN at 70 °C[a]

monomer	[M], mol/L	solvent	time, h	convrsn, %	$10^{-5}M_n$	$10^{-5}M_w$	M_w/M_n
2	0.5	DCE[b]	3	31.9	0.76	2.7	3.6
	1.0	DCE	0.5	7.0	0.96	2.0	2.1
		DCE	1	14.2	1.0	2.1	2.0
		DCE	1.5	22.8	1.2	2.3	1.9
		DCE	2	30.2	1.1	2.1	1.9
		benzene	2	28.7	1.1	3.4	3.2
		p-xylene	2	29.0	1.1	3.8	3.5
		THF	2	31.3	1.2	9.6	7.8
3	1.0	DCE	0.5	7.3			
		DCE	1	15.5	0.94	2.0	2.2
		DCE	1.5	21.5	0.89	2.1	2.3
		DCE	2	30.6	0.84	1.8	2.2

[a] [AIBN] = 2.5 × 10^{-3} M. [b] 1,2-Dichloroethane.

p-hydroxybiphenyl as shown in Scheme I.[8,9] The monomers obtained are stable, insensitive to moisture, and soluble in a wide variety of solvents. The polymerization of 2 in 1,2-dichloroethane (DCE) was initiated with AIBN at 70 °C. The time–conversion curve was linear and without an induction period. The polymerization gave a white polymer (poly(2-I)) with M_n = 110 000. The polymers are also soluble in a number of solvents, and their appearance does not appreciably change for a long period. The ^{1}H NMR spectrum of poly(2-I) obtained showed the disappearance of olefinic protons. The P–N stretching mode (1200 cm^{-1}) was observed in the IR spectrum. The significant broadening of this region was not observed, suggesting retention of the phosphazene ring.[5] Similar results were obtained for the polymer of 3.

From the plots of conversion vs time (Table I), the rate of polymerization (R_p) of 2 and 3 was determined to be 4.19 × 10^{-5} and 4.14 × 10^{-5} (mol/L·s), respectively. The rate of polymerization of 2 is proportional to $[\mathrm{AIBN}]^{1/2}$ and the first order of the monomer concentration as shown in Figure 1. As expected, the line obtained from the plots of R_p vs [3] is in agreement with that of R_p vs [2]. The degree of polymerization of poly(2) is also identical with that of poly(3). These results indicate that the polymerization of 2 and 3 proceeds by a normal radical mechanism and that the substituent at the phosphazene ring did not

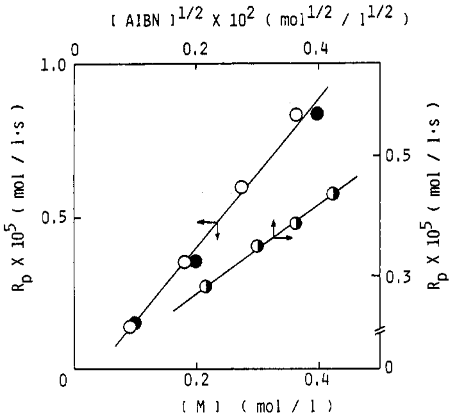

Figure 1. Relationship between R_p and the concentration of AIBN or the monomer 2 and 3: (○) [AIBN] = 9 × 10^{-4}, [2] = 0.09–0.36 mol/L; (●) [AIBN] = 9 × 10^{-4} mol/L, [3] = 0.1–0.4 mol/L; (◑) [2] = 0.18 mol/L, [AIBN] = 0.45–1.8 × 10^{-3} mol/L.

Table II
Bulk Polymerization of 2

poly(2)	temp, °C	convrsn, %/0.5 h
-II	115	16.1
-III	130	42.5
-IV	170	61.9
-V	210	66.2
-VI	250	78.1 (73.7)[a]

[a] Value in parentheses is for 5 min.

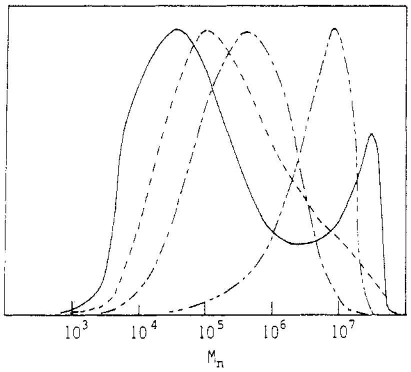

Figure 2. Molecular weight distribution curves of polymer obtained from bulk polymerization of **2**: (– - - –) at 115 °C; (– - –) at 170 °C; (- - -) at 210 °C; (—) at 250 °C. The distribution curve of the polymer obtained at 130 °C overlapped with the one obtained at 115 °C.

affect the polymerization processes, as suggested in the previous paper.[9]

There are many reports on the electronic interaction between a phosphazene ring and aryl substituents. In contrast to the establishment of the inductive effect of chloro- or fluorocyclotriphosphazene, the mesomeric interaction has been the subject of much controversy and evidence has been reported for and against this effect.[13-17] The fact that no dependence of the substituents at the phosphazene ring on the rate of polymerization is observed suggests no mesomeric interaction between the phosphazene ring and the biphenyl moiety. The strong electron-withdrawing effect of the phosphazene ring on the vinylbiphenyl moiety is probably reduced due to insulation by an oxygen atom.[4,6,7,17] Therefore, it seems that the difference of substituent results in no influence on the electron density of vinyl group. Consistent with this argument, ^{1}H NMR spectra showed that the chemical shifts of vinyl protons of **2** are the same as those of **3**.[9] The role of the oxygen atom in suppressing the influence of phosphazene ring was observed for the polymerization of (vinyloxy)pentachlorocyclotriphosphazene.[7]

Bulk Polymerization of 2. The bulk polymerizations of **2** without an initiator were carried out in evacuated sealed tubes at 115, 130, 170, 210, and 250 °C. As shown in Table II, the polymerization rapidly proceeded at 170 °C and above. Appreciable decomposition of the monomer was not observed. Even the polymer obtained from polymerization at 250 °C for 0.5 h is a white solid and soluble in a number of solvents. ^{1}H NMR and IR spectra of the poly(**2**-II) are the same as those of poly(**2**-I) obtained from AIBN initiation. Recently, Allcock et al.[18-20] have shown that phenyl- and alkyl-substituted cyclotriphosphazenes undergo a ring-opening polymerization at 250 °C, although this process requires long reaction times. In order to clarify whether a ring-opening process is involved or not in the polymerization of **2**, the polymerization of 2-(2-phenylphenoxy)pentachlorocyclotriphosphazene (**4**) was examined at 250 °C for 0.5 h. However, **4** was recovered unchanged. These results indicate that poly(**2**-II) is formed by polymerization through the $CH_2{=}CH-$ group without participation of the phosphazene ring.

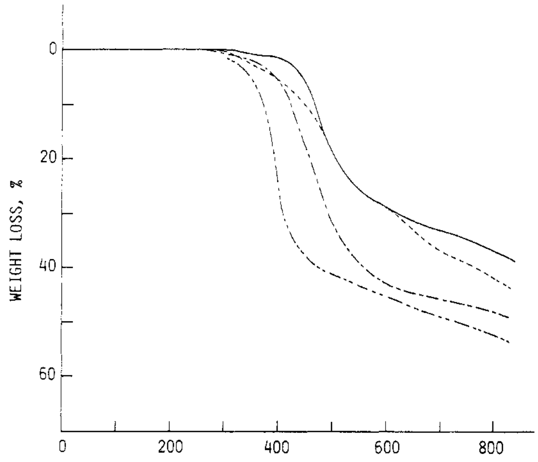

Figure 3. Thermogravimetric analysis of (—) poly(**2**-I) in N_2, (- - -) poly(**2**-I) in air, (– - –) poly(**3**) in N_2, and (– - - –) poly(**3**) in air. Conditions: heating rate, 20 °C/min; gas flow rate, 50 mL/min.

Table III
Decomposition Temperatures and Char Yields of Poly(2) and Poly(3)

			char yield, %			
	PDT, °C		700 °C		800 °C	
polymer	N_2	air	N_2	air	N_2	air
poly(2-I)	300	280	67	64	63	60
poly(2-II)	400	310	66	67	64	64
poly(2-III)	380	310	67	63	65	57
poly(2-IV)	350	300	62	62	60	55
poly(2-V)	350	295	64	62	63	57
poly(2-VI)	340	290	61	64	59	59
poly(3)	270	250	54	51	52	48

Figure 2 shows the molecular weight distributions, measured by gel permeation chromatography (GPC). A large portion of the polymer molecules obtained at 115 and 130 °C apparently had molecular weights above the exclusion limit of the columns ($M_n = 2 \times 10^6$). At 170 °C mainly medium molecular weight polymer was formed. At 250 °C marked changes were observed; i.e., the GPC spectra showed the formation of low and extremely high molecular weight polymers (poly(**2**-VI)). In order to investigate this behavior, the change of molecular weight distribution with polymerization time was examined. With respect to polymerization time, a movement of the center of the distribution curves from $M_n = 1 \times 10^5$ to $M_n = 4 \times 10^4$ was observed. This was accompanied by the formation of a high molecular weight polymer ($M_n > 10^6$). This result suggests the coincidence of depolymerization and cross-linking reactions. On long term heating (6 h) at 250 °C, an insoluble, glassy material was obtained.

Thus, the polymer with pentachloro- or pentafluorocyclotriphosphazene can be prepared by a convenient radical polymerization. The polymer having a reactive P–Cl or P–F group can easily be modified by introducing various functional groups. The modifications are in progress in our laboratory.

Thermal Behavior of Polymer. The thermal stability and degradation behavior of poly(**2**) were investigated by TG in air and nitrogen atmospheres. Typical TGA curves are shown in Figure 3, and the polymer decomposition temperatures (PDT) and the char yields are summarized in Table III. The decomposition of poly(**2**-I) with $M_n = 1.1 \times 10^5$ in nitrogen occurred at 300 °C. The maximum weight loss was observed at 435–510 °C, and 63% residue

Table IV
Results of Isothermal Gravimetric Analyses of Poly(2-I)

	residue, %			residue, %	
temp, °C	N_2	air	temp, °C	N_2	air
300	94 (99)[a]	93 (99)	600	65	64
400	78	77	700	60	55
500	72	70			

[a] Value in parentheses is for poly(2-II).

remained at 800 °C. In air, the decomposition started at 280 °C and the maximum weight loss occurred at 425–510 °C, and surprisingly 60% residue was observed at 800 °C. Thus, the presence of oxygen had little affect on the maximum weight loss temperatures and the char yields, although the polymer decomposition temperature (PDT) in air is 20 °C below that in nitrogen. The char yields were comparable to those of the polymers of maleimido-substituted aromatic cyclotriphosphazenes reported by Parker et al.[11] For the poly(2-II) obtained from bulk polymerization, the thermal stability was considerably improved. Decomposition in nitrogen started at 400 °C, indicating that the thermal stability depends on the molecular weight. The dependence of thermal stability on the molecular weight was also observed in an air atmosphere, but the degree of increase in thermal stability was small. Furthermore, it was found that the insoluble poly(**2**) obtained at 250 °C for 2 h is thermally stable up to 410 °C. This may be explained in terms of the formation of the polymer with high molecular weight by cross-linking. No effect of the molecular weight on the char yield was observed.

It should be noted here that the results of TGA of **4** and poly(**1**) obtained by radical polymerization with AIBN initiator showed the formation of 100% volatile products and a residue of approximately 20% of the sample weight below 500 °C, respectively. This implies that the combination of phosphazene ring and poly(**1**) is necessary to produce a high yield of residue. Interestingly, the TGA curve of monomer **2** in nitrogen is almost the same as the one of poly(**2**-I) except for the weight loss (2%) in the temperature ranges from 200 to 300 °C. This is probably due to the volatility of **2**. This indicates that polymerization occurs during analysis, in agreement with a high radical polymerizability.

The result of TGA of poly(**3**) in nitrogen showed that the decomposition temperature is approximately 30 °C below that of poly(**2**-I). The maximum weight loss was observed at 400–515 °C, and the char yield at 700 °C was 50%. In air, a fast weight loss was observed; i.e., the decomposition of poly(**3**) is susceptible to the presence of oxygen.

Isothermal gravimetric analyses of poly(**2**) were carried out in both nitrogen and air at 300, 400, 500, 600, and 700 °C for 3 h. The results are shown in Figure 4 and Table IV. An interesting feature is that the behavior of the decomposition at a given temperature, except 700 °C, in air is the same as in nitrogen. This behavior is in contrast to the results on polymers reported by Parker et al.[11] For poly(**2**-I), a 6% weight loss was observed at 300 °C while for poly(**2**-III) having high molecular weight the weight loss was only 1%. This is an agreement with the fact that the thermal stability increases with increasing molecular weight as described earlier. Although a slightly faster weight loss for poly(**2**-I) occurred in air at 700 °C, 55% of its weight still remained. The formation of a high yield of residue in both air and nitrogen atmospheres may be explained by the presence of the thermally stable biphenyl unit and the high content of phosphorus, chlorine, and nitrogen in the polymer. A qualitative test of flame retardance of the polymer indicates that the polymer has self-extinguishing property, in agreement with the known flame retardency of phosphazene system.[4,7,11,21]

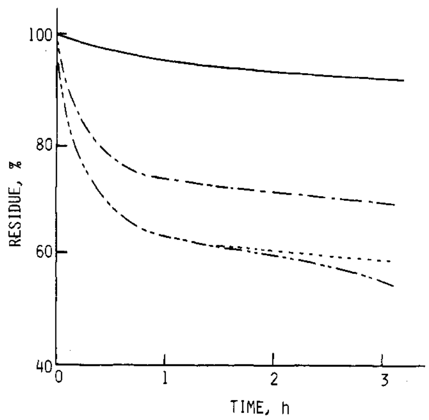

Figure 4. Isothermal gravimetric analysis of poly(**2**-I): (—) at 300 °C in air; (–-–) at 500 °C in air; (---) at 700 °C in N_2; (–--–) at 700 °C in air.

In summary, novel monomers **2** and **3** have high radical polymerizability. The poly(**2**) obtained is apparently superior in heat and fire resistance and gives the highest char yield at 800 °C in air of the polymers obtained by radical polymerizations. This indicates that poly(**2**) has a potential use as heat- and fire-resistant polymers.

Registry No. **2**, 115529-67-4; **2** (homopolymer), 115529-68-5; **3**, 115721-01-2; **3** (homopolymer), 115785-71-2; AIBN, 78-67-1.

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