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Photocurable System of Polythiol and Polyphosphazene-Containing Allyl Groups

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ABSTRACT

To investigate their applicabilities as photocurable formulations, photochemical reactions of poly(allylaminophosphazenes) with polythiols of ethylene glycol dimercaptoacetate or trimethylolpropane tri(3-mercaptopropionate) were carried out in the presence of photoinitiators. As a model reaction, hexaallylaminocyclotriphosphazene(II) was reacted with polythiols, and the thermal properties were investigated. Benzoin alkyl ethers were employed as photoinitiators; in particular, benzoin methyl ether (BME) gave better results in photoreactions. Trimethylolpropane tri(3-mercaptopropionate) was more effective than ethylene glycol dimercaptoacetate in photocrosslinking. The photoreactive system of polyphosphazene containing allyl groups/BME photoinitiator/polythiol was found to be an efficient photocurable system.

INTRODUCTION

The hydrolytic instability of poly(dichlorophosphazene), which is prepared by thermal polymerization of hexachlorocyclotriphosphazene, can be overcome by substitution of chlorine by various nucleophiles. Such poly(organophosphazenes) show a number of unusual properties

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lacking in common organic polymers [1-4], such as low-temperature flexibility, high stability to visible and ultraviolet radiation, resistance to solvents, and thermal stability. The properties of poly(organophosphazenes) can be modified by changing substituents. Thus, photosensitive phosphazene polymers can be prepared by the incorporation of photosensitive substituents on the phosphorous-nitrogen backbone.

The polythiol-polyene photocurable system is known to be industrially applicable for its ability to give excellent physical properties when cured together with extremely fast cure rates. Usually, the polyenes used contained allylic groups, and the polythiols were esters of thiol-containing acids. It was claimed that the significant advantage of the thiol-allylic photopolymer systems is that the presence of air has little effect on cure rates and the surface cure shows no tackiness due to oxygen inhibition at the surface [5]. The addition of thiols to carbon-carbon double bonds to form thioethers can occur through a free-radical mechanism, and eventually it crosslinks the polymer system by ultraviolet irradiation [6]. The free-radical process can be initiated by various photoinitiators. In that system, benzoin ether compounds were known to be more efficient than aromatic carbonyl compounds, such as benzophenone derivatives.

In the present study we have tried to prepare photocurable polythiol-allylphosphazene polymer systems. Allylamino groups were attached to the phosphazene backbone to make the allylphosphazene polymers in which n-butylamino or piperidino substituents were also incorporated to improve flexibility and solubility. Hexaallylaminocyclotriphosphazene was also prepared for the model reaction study. The photochemical reaction and the thermal degradation of the model compound and copolymer systems were studied.

EXPERIMENTAL

Materials and Instrumentation

Reagent-grade chemicals were purified by conventional methods. Hexachlorocyclotriphosphazene (phosphonitric chloride trimer) was purchased from Aldrich Chemical Co. and Tokyo Kasei (Japan) and was purified by sublimation, followed by recrystallization in n-heptane, to give a melting point of 113°C. Tokyo Kasei's reagent usually gave a better yield in preparation of the precursor polydichlorophosphazene. Two polythiol compounds, ethylene glycol dimercaptoacetate (DSH) and trimethylolpropane tri(3-mercaptopropionate) (TSH), were kindly donated by Evans Chemetics, W. R. Grace & Co., and used without further purification.

Infrared spectra were taken on a JASCO Model A-102 spectrophotometer. Proton NMR spectra were recorded on a Varian Model T-60A referenced to TMS, and ^{31}P-NMR spectra were obtained on a Varian Model FT-80A spectrometer in ppm with 85% H_3PO_4 as reference.

Solution viscosities of polymers were measured at 25 ± 0.1°C with a Cannon-Ubbelohde capillary viscometer. Thermogravimetric analysis of polymer samples was carried out on a Du Pont Model 951 TGA at a heating rate of 10°C/min under nitrogen flow. Melting temperatures of polymer samples were measured with a Du Pont Model 951 DSC at a heating rate of 10°C/min. All measured temperatures were uncorrected, and melting points were measured with an electrothermal capillary melting point apparatus of Electrothermal Engineering Ltd.

Preparation of Phosphazene Polymers

Hexaallylaminocyclotriphosphazene, II. The compound was prepared following the modified method of Allcock [7]. A solution of 2.00 g (5.8 mmol) hexachlorocyclotriphosphazene, I, in 20 mL THF was added to a solution of 3.90 g (68.0 mmol) allylamine and 7.00 g (69.0 mmol) triethylamine in 50 mL THF. The mixture was reacted at 40°C for 24 h. Filtration of triethylamine hydrochloride was followed by the evaporation of the solvent. The crude product was recrystallized from ethyl acetate to yield 1.77 g (65.0%) of colorless crystals II, mp 94-95°C (Ref. 7: 90-91°C); ^{1}H-NMR ($CDCl_3$), 5.90 (m, 1H), 5.13 (m, 2H), 3.56 (broad s, 2H, $-CH_2-$), 2.46 (broad s, 1H, –NH–) ^{31}P-NMR ($CDCl_3$) (85% H_3PO_4 solution as reference), 17.65 ppm (only one peak).

Poly(dichlorophosphazene), III. Soluble poly(dichlorophosphazene), the precursor polymer, was prepared by thermal reaction in bulk according to a known procedure [8]. In an ampule, 6.00 g of purified hexachlorocyclotriphosphazene (mp 113°C) was placed. Then it was degassed by a repeated freeze-thaw technique under nitrogen and evacuation. The ampule was sealed and heated to 250°C for 24 h to give a transparent immobile product. Uncrosslinked, soluble poly(dichlorophosphazene) was obtained in a yield of 2.70 g (45%) by precipitating a benzene solution of the product into excess n-heptane.

Poly[bis(allylamino)phosphazene], IV. A solution of 2.50 g (equivalent to 21.6 mmol of $-N=PCl_2-$ unit) poly(dichlorophosphazene) in 60 mL benzene was added dropwise to a solution of 4.92 g (86.2 mmol) allylamine and 8.72 g (86.2 mmol) triethylamine in 60 mL benzene. The mixture was reacted at 40°C for 48 h and the resulting triethylamine hydrochloride was filtered off. After precipitation of the polymer solution into ethanol-water (1:1 by volume), the product was washed with ethanol and dried. White fibrous polymer IV was obtained in a yield of 2.21 g (65.2%), and the polymer was soluble only in 2,2,2-trifluoroethanol. A characteristic absorption band due to P=N stretching appeared between 1300 and 1100 cm^{-1}. Absorption bands of the allylamino group were noted at 910, 990, 1190, 1640, 3080, and 3250 cm^{-1}.

Poly(allylaminopiperidinophosphazene), V. A solution of 2.32 g (equivalent to 20.0 mmol of $-N=PCl_2-$ unit) poly(dichlorophosphazene) in 60 mL benzene was added to a solution of 0.91 g (16.0 mmol) allylamine, 2.04 g (24.0 mmol) piperidine, and 4.05 g (40.0 mmol) triethylamine in 40 mL benzene. The solution was reacted at 60°C for 48 h. After filtration of triethylamine hydrochloride, polymer V was precipitated into ethanol-water (1:1 by volume) and washed with ethanol. The yield was 2.08 g (62.5%). Polymer V was a film-forming material, soluble in toluene, benzene, and tetrahydrofuran. IR absorption bands appeared at 910, 990, 1640, 3080, and 3250 cm^{-1} due to the allylamino groups, and at 950, 1060, 1120, and 1180 cm^{-1} for the piperidino groups. The composition of allylamino side chains was determined by an NMR spectrum in $CDCl_3$: δ (ppm) 5.0-6.2 (broad m, $CH_2{=}CH-$), 2.8-4.0 (broad m, $-CH_2-NH-$, $-CH_2-\underset{|}{N}-CH_2-$ in piperidine) 1.7 (broad m, 6 methylene protons of piperidino group).

Poly(allylaminobutylaminophosphazene), VI. Polymer VI was prepared by the same method as polymer V. Allylamine and butylamine were reacted in a molar ratio of 2:3. Polymer VI was obtained in 56.0% yield and was soluble only in 2,2,2-trifluoroethanol. IR absorption bands of allylic double bonds appeared at 910, 990, 1640, and 3080 cm^{-1}, and of n-butylamino at 1190, 1250, 2950, and 3300 cm^{-1}.

Poly[bis(piperidino)phosphazene], VII, and Poly[bis(n-butylamino)phosphazene], VIII. Polymer VII and VIII were obtained following the procedure of Allcock with 59.0 and 48.0% yield, respectively [9, 10]. Polymer VII was soluble in toluene, benzene, and THF, but polymer VIII was soluble only in 2,2,2-trifluoroethanol.

Photoreaction

Photochemical reactions were carried out by using a photochemical reaction apparatus of Ace Glass Inc. A Hanovia (high-pressure) mercury lamp (450 W) was employed as a light source, and the distance between the lamp and a reactant sample was 20 cm, where the light intensity was 5.0 mW/cm^2. The reactant was in the form of solution in a Pyrex test tube or a thin film coated on a glass plate.

Photoreaction of Hexaallylaminocyclotriphosphazene, II, with Polythiols. In the following photoreactions of phosphazene compounds and thiols, the concentrations of the thiol compounds were adjusted to be equivalent to those of the allylamino groups of the reacting phosphazene compounds. In a 10-mL Pyrex test tube, 200 mg (0.425 mmol) II, 340 mg (0.850 mmol) TSH, and 16 mg (3.0 wt% of other components) of benzoin methyl ether were dissolved in 5.0 mL toluene. The solution was irradiated with UV light for 15 min to give a white precipitate. The precipitate was extracted with methanol in a Soxhlet extractor for 15 h to yield insoluble crosslinked polymers (530 mg, 95%). Under the same conditions, the photoreaction of a solution of II, DSH, and benzoin methyl ether in toluene gave no appreciable precipitate.

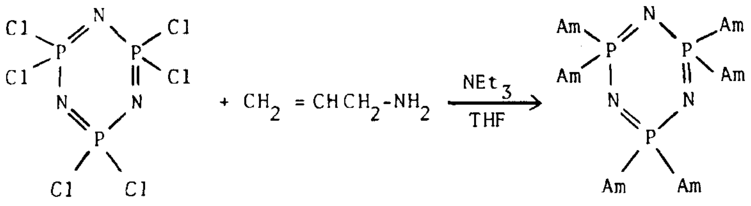
Photoreaction of Poly(allylaminopiperidinophosphazene), V, with Polythiols in Solution. In a Pyrex tube, a solution of 200 mg V, 112 mg (0.281 mmol) THS, and 9.3 mg (3.0 wt% of other components) of benzoin methyl ether in 5.0 mL toluene was irradiated for 20 min. The gel obtained was extracted with methanol in a Soxhlet extractor for 15 h to yield 257 mg (80%) of white crosslinked polymers. With DSH, under the same reaction conditions, insoluble polymers were obtained in somewhat lower yield (70%).

Photoreaction of Poly(allylaminopiperidinophosphazene), V, with Polythiols as Film. A film 5 μm thick was coated on a small glass slide plate from a solution of 300 mg V, 168 mg (0.422 mmol) TSH, and 56 mg (12.0 wt% of other components) of benzoin methyl ether in 3.0 mL toluene. The irradiation of the film for 30 min brought about complete disappearance of the IR-absorption bands of allylic double bonds at 910, 990, 1640, and 3080 cm^{-1}.

RESULTS AND DISCUSSION

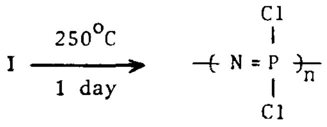
Preparation of Phosphazene Polymers

For the model photoreaction, hexaallylaminocyclotriphosphazene (II) was prepared from a reaction of hexachlorocyclotriphosphazene (I) and allylamine in a yield of 65% (Scheme 1). ^{31}P-NMR of II in deuterochloroform exhibited only one singlet peak at 17.65 ppm with 85% phosphoric acid as reference to confirm complete substitution. The soluble poly(dichlorophosphazene) (III), the precursor polymer of all the corresponding phosphazene polymers, was prepared by thermal reaction of the trimer I in a sealed ampule. The usual precautions were imposed for handling the halide precursor polymer III.



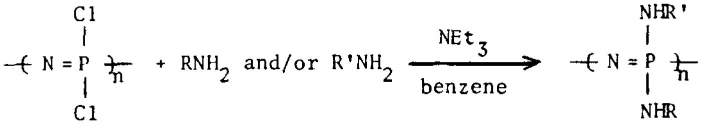
I II

SCHEME 1. Synthesis of hexaallylaminocyclotriphosphazene (II) (Am: $CH_2=CHCH_2NH-$).



$$\mathrm{I} \xrightarrow[\text{1 day}]{250^{\circ}\mathrm{C}} \left(N = \overset{\displaystyle Cl}{\underset{\displaystyle Cl}{P}} \right)_n$$

III



$$\left(N = \overset{\displaystyle Cl}{\underset{\displaystyle Cl}{P}} \right)_n + RNH_2 \text{ and/or } R'NH_2 \xrightarrow[\text{benzene}]{NEt_3} \left(N = \overset{\displaystyle NHR'}{\underset{\displaystyle NHR}{P}} \right)_n$$

Polyphosphazenes

III IV - VIII

IV, poly(bis(allyamino)phosphazene), R,R': $CH_2{=}CHCH-$

V, poly(allylaminopiperidinophosphazene), R: $CH_2{=}CHCH-$
R'NH: piperidino

VI, poly(allylaminobutylaminophosphazene), R: $CH_2{=}CHCH-$
R': n-Bu-

VII, poly(bis(piperidino)phosphazene), RNH,R'NH: piperidino

VIII, poly(bis(butylamino)phosphazene), R,R': n-Bu-

SCHEME 2. Syntheses of polyphosphazenes by substitution reactions.

Phosphazene polymers were synthesized by the substitution reactions of III with corresponding amines as shown in Scheme 2. The results of the substitution reactions are summarized in Table 1.

Polyphosphazenes of IV, VI, and VIII have very limited solubility and are soluble only in 2,2,2-trifluoroethanol (TFE). When piperidino groups instead of n-butylamino groups were substituted, the polymer V showed enhanced solubility in common solvents.

All the polyphosphazenes, IV to VIII, were obtained by substitution reactions in good yields with sufficiently high viscosity values compared to other published results [9, 10].

The composition of allylamino groups in the polymer V was determined by NMR spectra. The peaks of six methylene protons of piperi-

TABLE 1. Polyphosphazenes Prepared by Substitution Reactions of Poly(dichlorophosphazene)[a] with Various Amines

Polymer	Yield, %	η_{inh}, dL/g	T_m, °C	Remarks
IV	65.2	1.42[b]	137	Soluble in TFE
V	62.5	1.36[c]		Soluble in toluene, benzene, THF
				Allylamino:piperidino = 4:6 (mol)
VI	56.0	1.32[b]		Soluble in THF
				Allylamino:butylamino = 4:6 (mol)
VII	59.0	1.25[c]		Soluble in toluene, benzene, THF
VIII	48.0	2.02[b]	135[d]	Soluble in THF

[a] Concentration 0.5 g/dL, temperature 25 ± 1°C.
[b] In TFE solution.
[c] In toluene solution.
[d] 139°C in Ref. 10.

dino groups and three vinyl protons of allylamino groups in V appeared at 1.7 and 5.0-6.2 ppm in $CDCl_3$, respectively. By comparison of the integrated areas of those two peaks, the mole ratio of allylamino to piperidino groups was calculated to be about 4:6. By the same method, the mole ratio of allylamino to butylamino groups in the polymer VI was determined to be 4:6. The substitution reactions of polymers V and VI resulted in compositions of side chains that agreed well with the mole ratio of the fed amino compounds.

Photoreaction of II as Model Reaction

The UV irradiation of a solution of hexaallylaminocyclotriphosphazene (II) and TSH in toluene gave insoluble white precipitates in high yield (95%) within 15 min in the presence of BME photoinitiator. With-

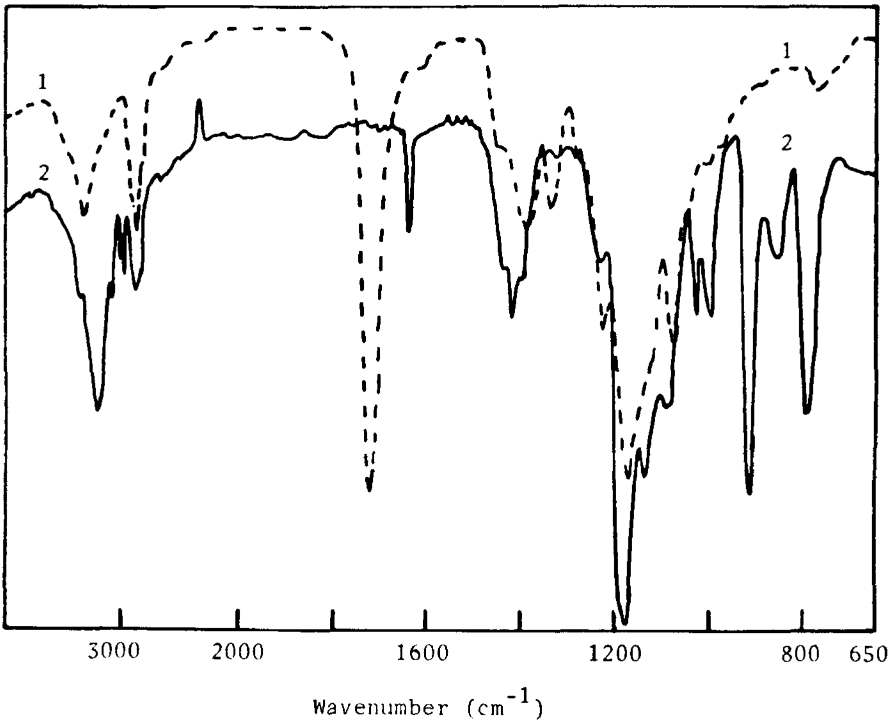


FIG. 1a. IR spectra of hexaallylaminocyclotriphosphazene, II (1), and UV-cured sample of II with TSH and BME for 15 min in toluene solution (2).

out BME, it gave no appreciable precipitates. The precipitates showed complete disappearance of carbon-carbon double bond absorption of allyl amino groups at 1640 cm^{-1} in IR spectra (Fig. 1a). When irradiated with DSH, only slightly viscous materials were formed in 15 min which still showed a weak absorption band at 1640 cm^{-1}, ascribable to an incomplete photoreaction. The explanation is that the higher activity of the trithiol compound TSH is due to weakening of the S–H bonds of the 3-mercaptopropionate moieties by forming a favorable cyclic six-membered hydrogen-bonded structure and also trifunctionality [6].

Photoreaction of Polymer V

In a photoreaction of V with TSH and BME in toluene solution for 20 min, a swollen gel was formed. After Soxhlet extraction of the gel, white crosslinked polymers were obtained in 80% yield. Insoluble gel in somewhat lower yield, 70%, was obtained in the case of DSH. The photoreactions of crosslinking of the polyphosphazene V with thiol compounds were confirmed by the disappearance of absorption bands of allylic double bonds at 910, 990, 1640, and 3080 cm^{-1} in IR spectra (Fig. 1b).

Polythiols were added to the double bonds of allyl groups in polyphosphazene V by UV irradiation. The addition reaction was verified by the appearance of carbonyl absorption at 1730 cm^{-1} and the disappearance of weak S–H stretching absorption at 2550 cm^{-1}. The spectral change of absorption of the curable systems of II and V with TSH by photoreactions is shown in Fig. 1. Photoreactions of the polymer VI also gave similar results, but the poor solubility of VI in common solvents raised some problems in handling.

Photocuring of the Polythiol-Allyl Phosphazene Polymer System

It is well known that allylic functional groups do not effectively homopolymerize under free-radical conditions, but it has been reported that, when thiol compounds and polyenes, even containing allyl groups, were employed together as photocurable coatings, the coatings were crosslinked very effectively and even were curable in the presence of surface oxygen by the action of thiyl radicals and allylic functions [5].

In the absence of photoinitiators, the photocurable formulations comprising II or polymers V or VI, with or without polythiols, gave no appreciable precipitate on UV irradiation in solution. Without polythiol compounds, the formulations containing organophosphazenes II, V, or VI with photoinitiators also showed no appreciable photocrosslinking. On the basis of these results, the photoreactive system of polyphosphazenes containing allyl groups/BME photoinitiator/TSH polythiol is considered to be very effective in photocuring.

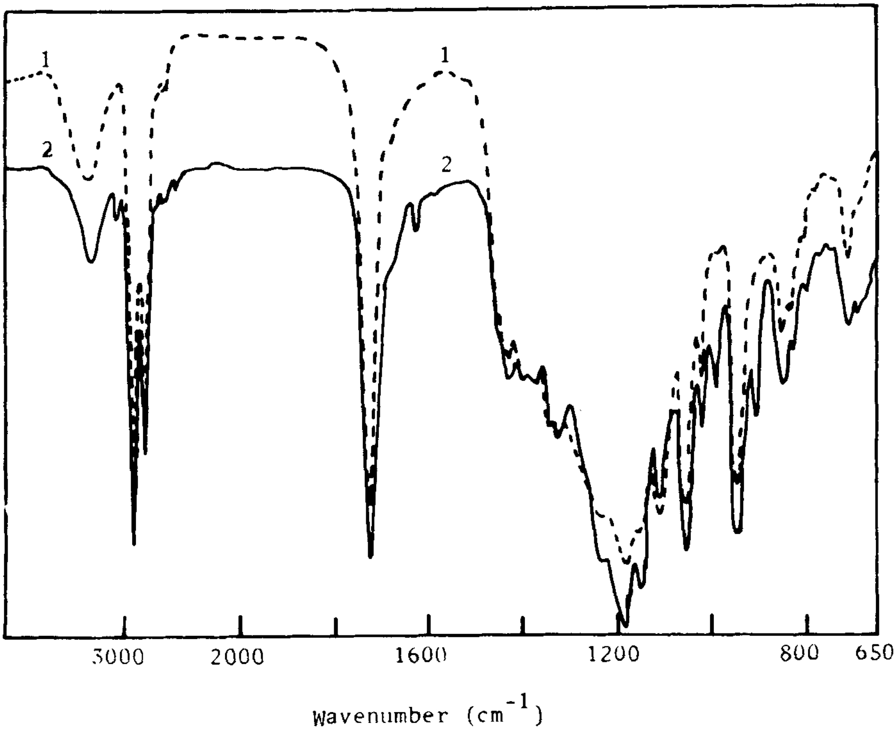


FIG. 1b. IR spectra of photocurable formulation, poly(allylaminopiperidinophosphazene), TSH, and BME. Before UV-irradiation (1) and after irradiation for 15 min in toluene solution (2).

Trimethylolpropane triacrylate, one of the multifunctional monomers widely used in commercial photocurable resin formulations, was employed instead of polythiols in the poly(allylaminophosphazene) systems to compare the photoreactivity. The photoreaction of trimethylolpropane triacrylate was confirmed by the disappearance of IR absorption of vinyl in-plane bending and C=C stretching at 1410 and 1620 cm^{-1}, respectively. However, the photoreaction of the system was not complete, because the C=C stretching band of allylamino groups in the polymer at 1640 cm^{-1} was nearly unchanged. It is supposed that only the trifunctional acrylate reacted in that photoreaction.

In film form, the photocrosslinking reactions were less sensitive than in solution because of the low mobility of reactants in the solid state. Increasing the amount of the photoinitiator BME up to 12% of other components brought about effective crosslinking, as estimated by the complete disappearance of the IR absorption bands of allylic double bonds.

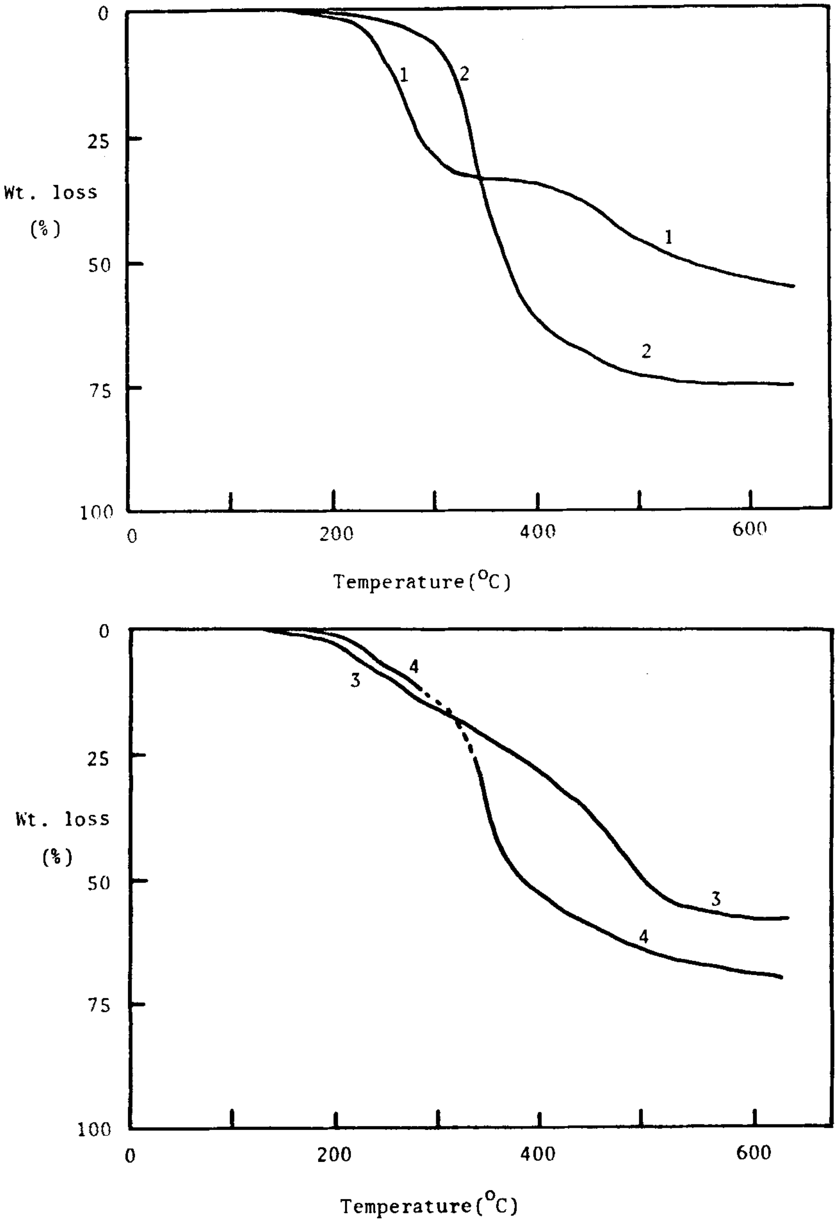


FIG. 2. TH thermograms of (1) hexaallylaminocyclotriphosphazene, II; (2) UV-cured sample of II with TSH and BME for 15 min in toluene; (3) poly(allylaminopiperidinophosphazene), V; (4) UV-cured sample of V with TSH and BME for 20 min in toluene.

Thermal Properties

Weight loss with increasing temperature was measured under nitrogen flow, and the thermograms are shown in Fig. 2.

The thermogram of II showed weight loss in two steps. At first, 35% weight loss occurred. The three allylamino groups amount to 35.6 wt% in HACPAZ. Thus, it is supposed that the degradation of the allylamino group is nongeminal because random degradation would not show such a TGA pattern. Upon crosslinking, the temperature at which weight loss began was somewhat higher, but the rate of weight loss was greatly increased by the breakdown of the sulfide bonds accompanied by the degradation of allylamino groups. In copolymer systems, it was less drastic because of the piperidino groups.

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