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Studies on Phosphorus-Containing Polymers. VII. Synthesis of Chain End-Functional Linear Phosphonitrilic Chlorides and Their Stability

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Studies on Phosphorus-Containing Polymers. VII. Synthesis of Chain End-Functional Linear Phosphonitrilic Chlorides and Their Stability

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ABSTRACT

It is well known that linear phosphonitrilic chloride (LPNC) is formed by reacting cyclic phosphonitrilic chloride with phosphorus pentachloride. From the point of view that this oligomerization is a kind of telomerization, we synthesized another LPNC by the use of phosphorus pentabromide, as a telogen, in place of phosphorus pentachloride, and treated the new LPNC with a nucleophilic reagent such as diethylamine or aniline to displace both chain ends and attained considerable improvement of its thermal and hydrolytic stabilities.

INTRODUCTION

Linear phosphonitrilic chlorides (LPNC) are greatly reactive with nucleophilic reagents and accordingly readily undergo hydrolysis.

We previously reported [1] that a substitution product having a

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remarkably improved hydrolytic resistance was obtained by subjecting the LPNC to the substitution permitting its terminal anion complex to disappear. However, it has been found that the substitution caused its original heat resistance to lower.

Therefore we have now investigated the influence of displacements of the ionic chain-end and other nonionic chain-end halogens on the thermal and hydrolytic stabilities.

In view of the fact that LPNC can generally be synthesized by the reaction of cyclic phosphonitrilic chloride (CPNC) with phosphorus pentachloride, the reaction being regarded as a kind of telomerization using CPNC as a taxogen and phosphorus pentachloride as a telogen, this time we have attempted to synthesize LPNC of which both chain ends have bromines [abbreviated LPNC(Br)] by the use of phosphorus pentabromide in place of phosphorus pentachloride, and have then attempted to introduce a nucleophilic reagent selectively into both chain end parts of the new LPNC by utilizing the reactivity of bromine. We report herein the results obtained that the substitution products of the new LPNC have improved their stabilities.

EXPERIMENTAL

Synthesis of Triphosponitrilic Chloride (CPNC)

According to the method of Lund et al. [2], triphosponitrilic chloride (PNCI_2)₃ can be synthesized by reacting phosphorus pentachloride with ammonium chloride in sym-tetrachlorethane. The melting point of the product is 112 to 113°C when recrystallized from petroleum ether. (The value described in the literature [2] is 112.8°C.)

Synthesis of LPNC(Br)

CPNC and phosphorus pentabromide are placed at a ratio of one to one under dry nitrogen gas into a tube for polymerization. After degassing, the tube is sealed and then heated at 300°C for 7 h. After completion of the reaction, the reaction mixture is extracted with benzene and the extract is dropped into petroleum ether to separate. The oily product obtained is reextracted with benzene and filtered. Finally the filtrate is subjected to freeze-drying with benzene.

Synthesis of Derivatives of LPNC(Br)

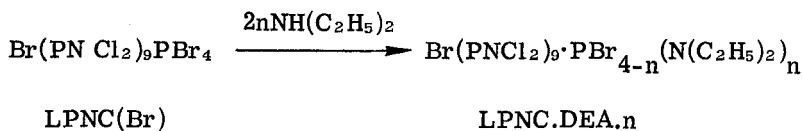
Commercial diethylamine (DEA) of special grade is purified by the ordinary method. Commercial aniline, benzene, petroleum ether, etc. of first-class grade are purified before use.

Using benzene as a solvent, LPNC(Br) is treated with diethylamine

TABLE 1. The Analysis [found (calculated)] of LPNC(Br), Reddish Viscous Oil, Soluble in Benzene

P (%)	\bar{M}_n
20.8	1430
(21.0)	(1475)

TABLE 2. The Reaction of LPNC(Br) with DEA

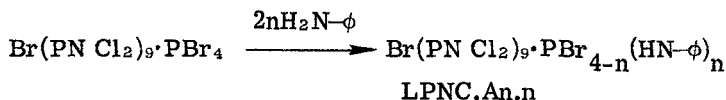


Solvent: benzene

Reaction temperature: room temperature

Reaction time: 4-5 h

The reaction of LPNC(Br) with aniline

 ϕ : C₆H₅ (phenyl group)

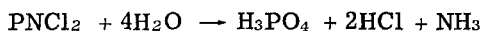
and aniline at various molar ratios in a nitrogen atmosphere. The reaction with diethylamine is carried out according to the following procedure: Exactly weighed (~0.5 g) LPNC(Br) is placed into a four-necked 100-cc flask fitted with a stirrer. Then 50 cc of benzene is poured into the flask to dissolve LPNC(Br). Into the solution is gradually added dropwise a fixed volume of diethylamine solution diluted 100-fold with benzene. Mixture ratios (mol/mol) of diethylamine to LPNC(Br) are equivalent to the numbers of terminal halogens to be displaced: 2, 3, 5, and 8. Accordingly, diethylamine are 4, 6, 10, and 16 times (in moles) as much as LPNC(Br). The conditions of the reactions are given in Table 2. The reactions with aniline are made under much the same conditions. All the reactions are carried out at room temperature, under stirring during the first period—4 to 5 h for the reactions with dimethylamine and 6 to 7 h for the reactions with aniline—and then allowed to stand overnight. Each reaction mixture is filtered to remove the salts produced. The filtrate is subjected to lyophilization. (If the products obtained are soluble in ether, the filtrate is poured into a large quantity of ether, after the

precipitate produced is filtered off, and the filtrate is again subjected to freeze-drying with benzene.)

Hydrolysis of the Derivatives

To 0.1 g of a sample, 50 cc of distilled water is added. The reaction is carried out under stirring. During the reaction, 2 cc of the reaction mixture is collected at fixed time intervals. The solution is titrated with sodium hydroxide solution of known concentration. The degree of hydrolysis is calculated from the titrated value.

It is conceivable that LPNC(Br), its rational formula being $(\text{PNCl}_2)_n \cdot \text{PBr}_5$, is hydrolyzed as follows: In the main part of the chain,



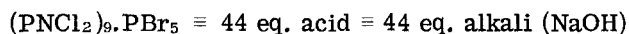
and in the end part,



Therefore, if y^* cc of alkali is required for complete decomposition of a sample of x g, and the titrated value is z cc, then the degree of hydrolysis D (%) is given by the following formula:

$$D = Z/y \times 100$$

*Hydrolysis of $(\text{PNCl}_2)_n \cdot \text{PBr}_5$ (case of $n = 9$):



therefore

$$y = \frac{44 \times 40 x}{1475 N} = 1.193 \frac{x}{N}$$

where N is the normality of the NaOH solution and 1475 is the molecular weight of $(\text{PNCl}_2)_9 \cdot \text{PBr}_5$.

Measurements

For the examination of thermal properties of the various derivatives, thermogravimetric and differential thermal analyses are carried out by an automatic recording differential thermobalance (manufactured by the Rigaku Electric Mfg. Co.). Molecular weights are measured according to the vapor pressure method, and phosphorus contents according to the molybdenum blue method [3]. IR absorption spectra are obtained by IR-S type IR spectrophotometer (manufactured by the Nippon Bunko Co.) and NMR absorption spectra by a R22 type High Resolution Nuclear Magnetic Spectrometer (manufactured by the Hitachi Co., standard substance: H_3PO_4).

RESULTS AND DISCUSSION

CPNC-PBr₅ Reaction Product and Its Chemical Structure

The IR spectrum of the reddish brown oily product together with that of the PCl_5-NH_4Cl reaction product are shown in Fig. 1. Both

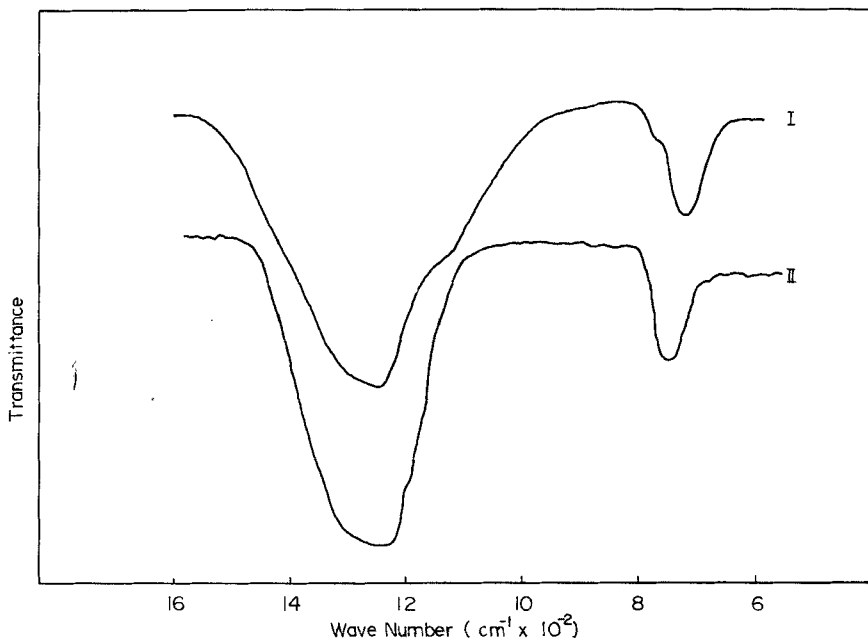


FIG. 1. Infrared spectra of LPNC (I) and LPNC(Br) (II).

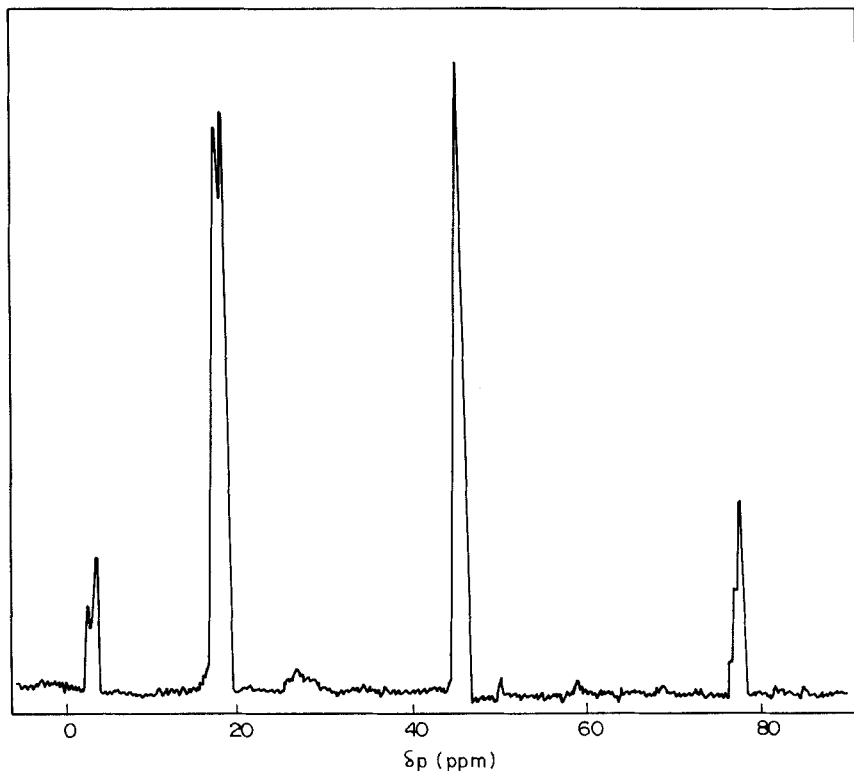


FIG. 2. ^{31}P -NMR spectrum of LPNC(Br).

products have a maximum absorption peak due to the stretching vibration of $-(\text{P}=\text{N})$ [4] at about 1230 cm^{-1} and another specific absorption peak due to LPNC [4] at about 750 cm^{-1} . Table 1 shows the determined phosphorus content and molecular weight of LPNC(Br). Under the presumption that LPNC(Br) would be represented as $(\text{PNCI}_2)_n \cdot \text{PBr}_5$, in conformity to the CPNC- PCl_5 reaction product, both determined values correspond approximately to the calculated values if $n = 9$, i.e., LPNC(Br) is a nonamer.

Figure 2 shows the NMR absorption spectrum of LPNC(Br). The spectrum has four sharp absorption peaks at 3, 18, 46, and 77 ppm from its lower magnetic field. The ratio of these areas of these absorption peaks is 1:4:4:1. Comparing the spectrum with the afore-said assumed structure, the two small absorption peaks at the left hand and right hand positions can be regarded as being due to phosphorus at both ends of the chain, and the central two absorption peaks

to phosphorus in the main part of the chain. The area ratio is consistent with the determined value of molecular weight when a nonamer is assumed.

According to Hayashi [5] and Moran et al. [6], the NMR absorption spectrum of the CPNC- PCl_5 reaction product has absorption peaks due to phosphorus at both ends of the chain at -12 and +16 ppm and one due to phosphorus in the main part of the chain at 18 ppm. Accordingly, in the spectrum of LPNC(Br) the two absorption peaks at 3 and 77 ppm can be attributed to the terminal phosphorus, and the shift toward a higher magnetic field would be caused by bromine taking the place of chlorine. The absorption peak at 18 ppm can be attributed to phosphorus in the main part of the chain. The remaining absorption peak at 46 ppm appears because some absorptions due to phosphorus in the main part of the chain are shifted toward a higher magnetic field under the influence of the terminal bromines.

If the structure of the product was not in the form of linear chain but rather in a large cyclic form, the positions of the absorption peak in the IR absorption spectrum and the four positions of the absorption peak in the NMR absorption spectrum could not be explained. Moreover, the absorption peaks [2, 5] due to CPNC at -20 ppm and phosphorus pentabromide, which would appear in a higher magnetic field than 80 ppm, are not found in the spectrum having the four absorption peaks. Accordingly, it may be concluded that LPNC(Br) does not contain these unreacted substances as an impurity. It is also conceivable that LPNC(Br) has no counteranion in its complex because the spectrum has no absorption [7] peak due to PBr_6^- in the magnetic field higher than 300 ppm.

Therefore, from the data of the IR absorption spectrum, the NMR spectrum, the molecular weight, and the phosphorus content, LPNC(Br) can be represented by the following rational formula: $\text{Br} \cdot (\text{PNCI}_2)_n \cdot \text{PBr}_4$, $n = 9$.

In an attempt to make LPNC having a higher molecular weight, we examined how long the length of the chain can be extended by changing the molar ratio of PBr_5 to CPNC. For example, the reddish-brown viscous liquid obtained by the reaction of CPNC with PBr_5 in the molar ratio (PNC unit/ PBr_5) of 1 to 0.3 at 300°C for 7 h has a molecular weight of 6320 (conversion yield 33.4%), which corresponds approximately to a degree of polymerization of 50 and more. This proves that polymers of fairly high molecular weight can be obtained by selecting the molar ratio of PBr_5 to CPNC.

Derivatives of LPNC(Br)

Referring to the diethylamine derivatives of LPNC (LPNC.DEA. n , where $n = 2, 3, 5$, and 8), their IR absorption spectra are in Fig. 3 and their NMR absorption spectra in Fig. 4. The IR absorption spectra have two absorption peaks due to the stretching vibration [4]

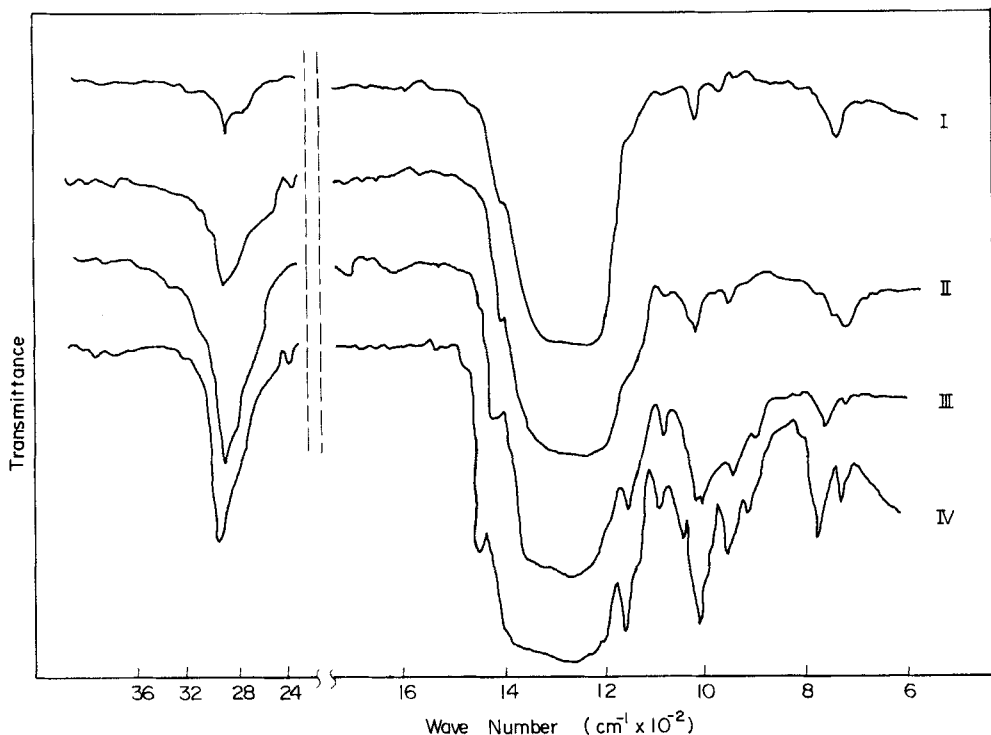


FIG. 3. Infrared spectra of LPNC.DEA.*n*, where *n* = 2 (I), *n* = 3 (II), *n* = 5 (III), and *n* = 8 (IV).

of ν_{CH} at about 2950 and 1450 cm^{-1} , two absorption peaks due to the stretching vibration [4] of $-\text{P}-\text{N}-(\text{C}_2\text{H}_5)_2$ at 920 and 960 cm^{-1} , and two absorption peaks due to the symmetric or antisymmetric vibration of $-\text{N}-(\text{Me})_2$ at 1060 and 1180 cm^{-1} . These absorption peaks become broader with a rise of the molar ratio of the mixture. Moreover, the absorption peak which should appear at about 3300 cm^{-1} due to secondary amines is not found.

Referring to Fig. 4, LPNC.DEA.2 shows an NMR absorption in which the absorption peak at the lowest magnetic field shifts to a higher magnetic field up to 9 ppm compared with that of LPNC(Br). It is probable that this shift is caused by the disappearance of the ionic property due to the action of a reagent on the ionic ends. Also, the absorption peak at the highest magnetic field shifts toward lower a magnetic field: from 77 to 74 ppm. This seems to show that when the reactivity of the ionic ends is lost, the reactivity of the nonionic ends rises.

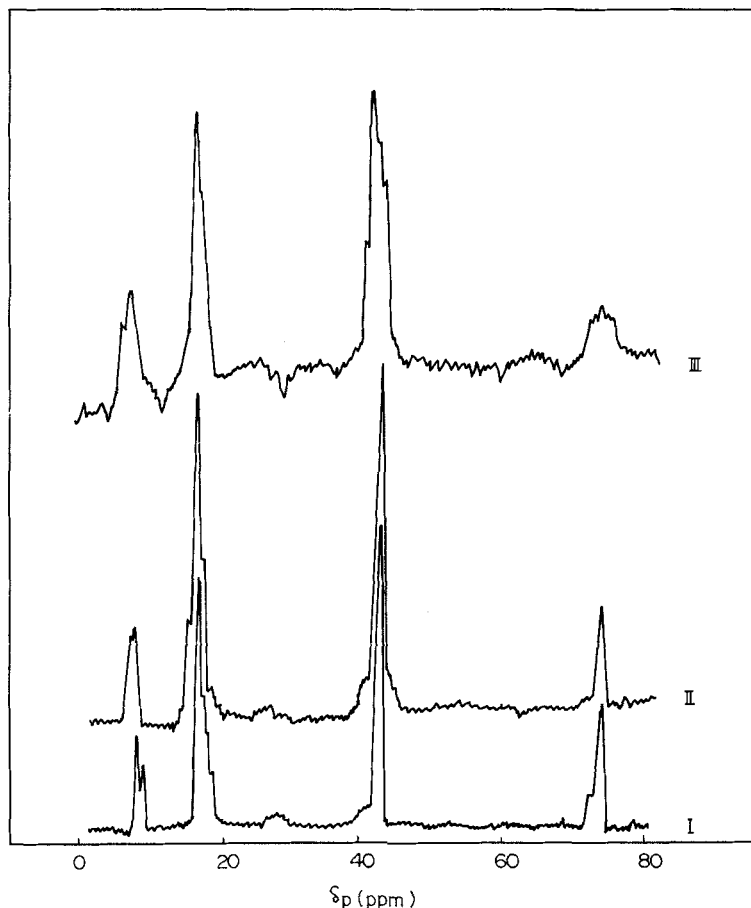


FIG. 4. ^{31}P -NMR spectra of LPNC.DEA. n , where $n = 2$ (I), $n = 3$ (II) and $n = 5$ (III).

The spectra of LPNC.DEA.3 are much the same as those of LPNC.DEA.2. When $n = 5$, its solubility in CHCl_3 becomes lower, so that the spectra have slightly broader peaks. Another point of difference from the other spectra is that the absorption peak at the highest magnetic field ranges from 73 to 77 ppm. The absorption peak shifts toward a higher magnetic field compared with that of LPNC.DEA.2 and LPNC.DEA.3. It is conceivable that this shift is due to the action of the reagent on the nonionic ends, and in this step the substitution reaches the nonionic ends. In other words, it is probable that substitution of the added reagent is limited to the ionic ends of LPNC.DEA.2 and LPNC.DEA.3 but reaches the nonionic ends of LPNC.DEA.5.

TABLE 3. Analysis of LPNC(Br) Derivatives^a

Sample	P contents (%)	
	Found	Calculated
LPNC(Br)	20.7	21.0
LPNC.DEA.2	20.8	21.25
LPNC.DEA.3	20.9	21.4
LPNC.DEA.5	21.0	21.6
LPNC.DEA.8	19.9	21.0
LPNC.An.2	20.5	20.7
LPNC.An.3	20.2	20.5
LPNC.An.5	20.1	20.1
LPNC.An.8	15.2	18.7

^aLPNC.DEA.n: The substitution products of LPNC(Br) with diethylamine; 2, 3, 5, and 8 are the number of substitution groups. LPNC.An.n: The derivatives of LPNC(Br) with aniline.

The determined values of the phosphorus content in the derivatives, shown in Table 3, increase gradually as the mixture ratio of the reagent to LPNC.DEA rises in the order of $n = 2, 3, \text{ and } 5$, and decreases when $n = 8$. Since the molecular weight of diethylamine lies between those of chlorine and bromine, this result is consistent with the calculated phosphorus content values of the derivatives obtained by substitution for bromine.

Therefore, from the above-mentioned data of IR absorption spectra, NMR absorption spectra, and phosphorus contents, it is clear that the formation of diethylamine-substituted LPNC(Br) started with substitution of both terminal bromines, and the actual percentage of substitution of this halogen was nearly equal to the percentage of substitution assumed from the molar ratio of the mixture.

Similar results for the derivatives prepared by reactions with aniline (An) were obtained. The IR spectrum of the derivatives with An is shown in Fig. 5. From the determined values of the phosphorus content and the results of IR spectra, it is presumed that the same substitution occurs in this derivative as in the diethylamine derivatives.

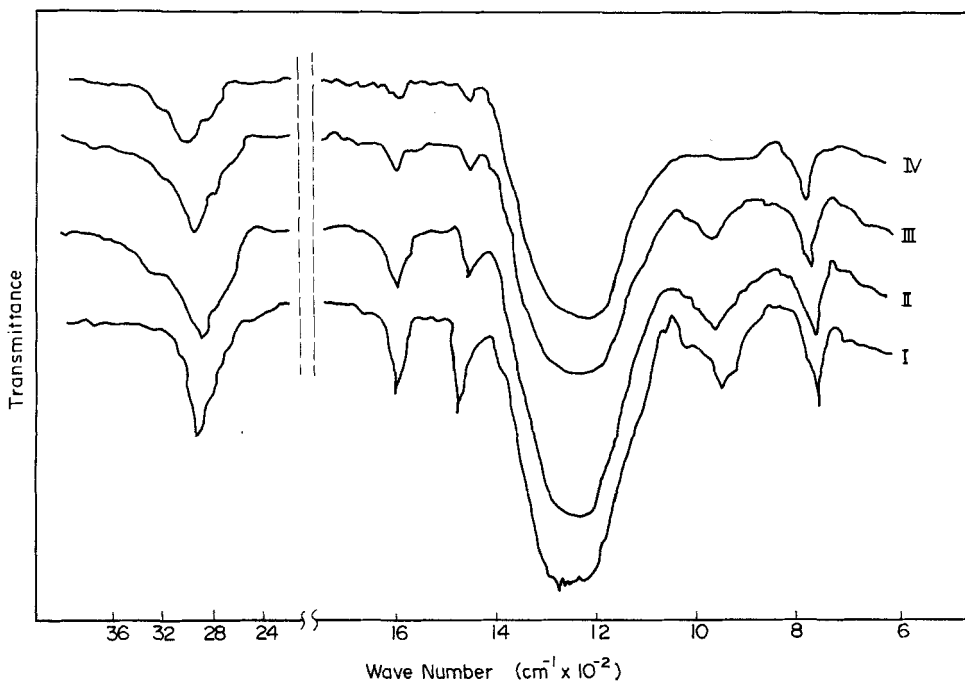


FIG. 5. Infrared spectra of LPNC.An.n, where $n = 2$ (I), $n = 3$ (II), $n = 5$ (III), and $n = 8$ (IV).

Stability of the Derivatives

Hydrolytic Stability of the Derivatives

We examined how the initial displacement with halogens exerts influence on the hydrolytic stability of the derivatives of LPNC(Br). The results are given in Figs. 6 and 7. Figure 6 gives the hydrolysis curves of LPNC.DEA.n ($n = 2, 3, 5,$ and 8). LPNC(Br) is hydrolyzed to about 60% in several minutes. LPNC.DEA.2 shows a considerably improved stability, and the stability increases steeply with rise of n from 3 to 5. LPNC.DEA.8, however, is much the same in stability as LPNC.DEA.5. Figure 7 shows the hydrolysis curves of the aniline derivatives, any of which has the same patterns as those of diethylamine derivatives.

Thermal Stability of the Derivatives

Figure 8 shows TGA curves of the diethylamine derivatives. LPNC(Br) has fairly good heat resistance. All the various diethylamine

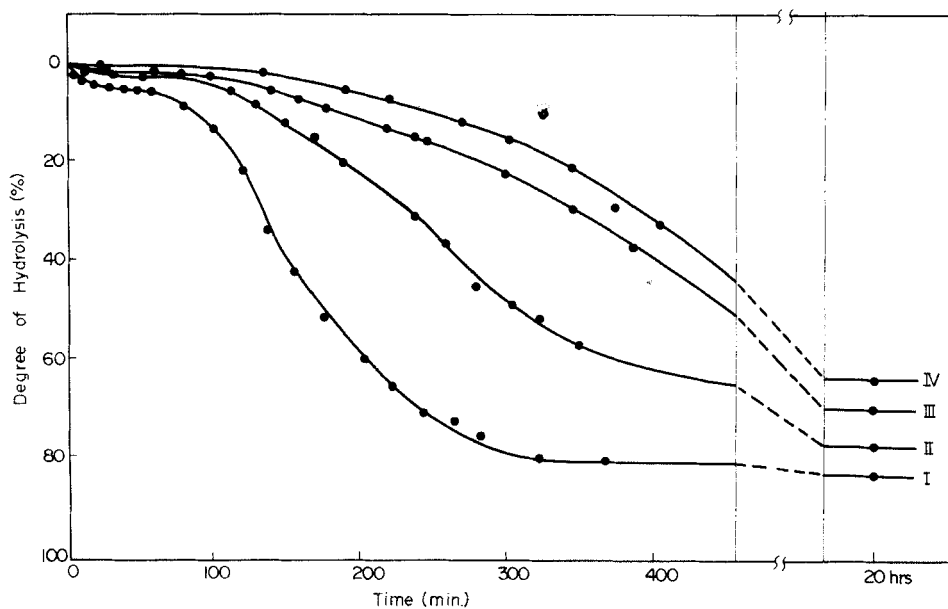


FIG. 6. Hydrolysis of LPNC.DEA. n , where $n = 2$ (I), $n = 3$ (II), $n = 5$ (III), and $n = 8$ (IV). Temperature of hydrolysis: 25°C.

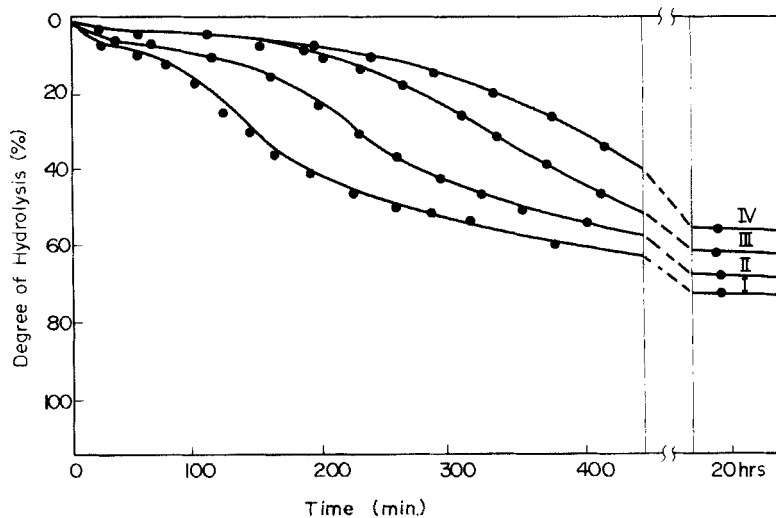


FIG. 7. Hydrolysis of LPNC.An. n , where $n = 2$ (I), $n = 3$ (II), $n = 5$ (III), and $n = 8$ (IV). Temperature of hydrolysis: 25°C.

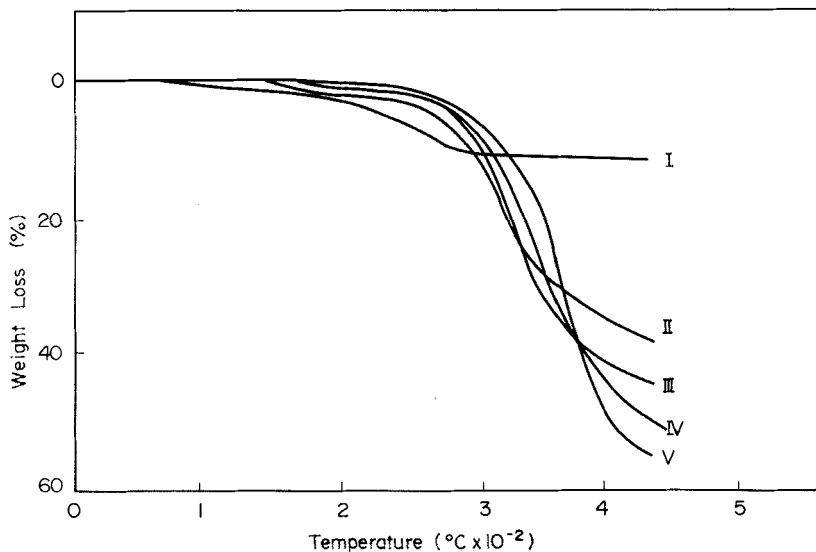


FIG. 8. The weight loss of LPNC(Br) and LPNC.DEA.*n* in N₂ at a rate of 5°C/min: (I) LPNC(Br), (II) LPNC.DEA.2, (III) LPNC.DEA.3, (IV) LPNC.DEA.5, (V) LPNC.DEA.8.

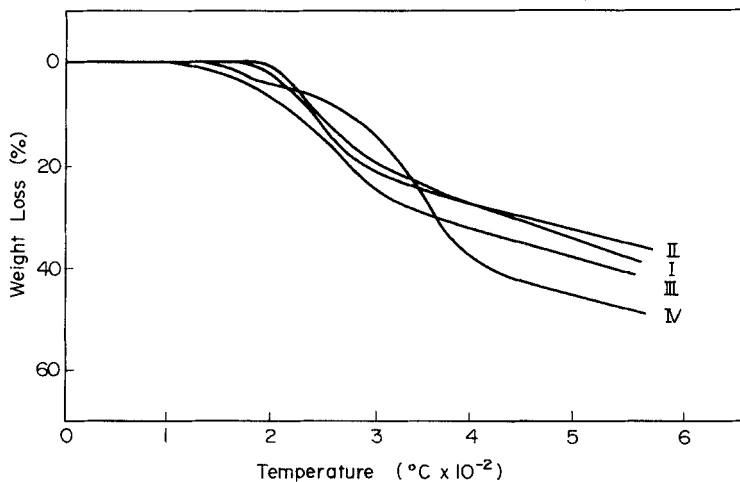


FIG. 9. The weight loss of LPNC.An.*n* in N₂ at a rate of 5°C/min: (I) LPNC.An.2, (II) LPNC.An.3, (III) LPNC.An.5, (IV) LPNC.An.8.

derivatives with displacement numbers 2, 3, 5, and 8 show a similar tendency in weight loss. The weight loss increases as the substitution number increases.

Figure 9 gives TGA curves of the derivatives of LPNC replaced by aniline. Tendencies similar to the dimethylamine derivatives are shown.

From the results on the physical properties of the various derivatives, their hydrolytic stability increases as the initial displacement of halogen increases, but there is not as great a change when the displacement numbers of halogens goes from 5 to 8.

The tendency for thermal weight loss increases with a rise in the substitution number.

The derivative prepared by reaction with the reagent at a mixture ratio corresponding to the displacement of five halogen atoms has a relatively greater thermal hydrolytic stability, and therefrom it can be regarded as contributing to the displacement of both chain ends.

It is probable that by utilizing the higher reactivity of bromine, the synthesis of a new polymer having a macromolecular weight may be achieved by use of a suitable reagent.

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