**Journal of Macromolecular Science, Part A**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

# The Reaction between Diaminotetraalkoxycyclotriphosphazene Compounds and Toluene Diisocyanate and the Adhesive Property of the Products

Meisetsu Kajiwara[a]
[a] Department of Applied Chemistry Faculty of Engineering, Nagoya University, Nagoya, Japan

**To cite this Article** Kajiwara, Meisetsu(1981) 'The Reaction between Diaminotetraalkoxycyclotriphosphazene Compounds and Toluene Diisocyanate and the Adhesive Property of the Products', Journal of Macromolecular Science, Part A, 16: 2, 587 — 594

**To link to this Article: DOI:** 10.1080/00222338108058495

**URL:** http://dx.doi.org/10.1080/00222338108058495

J. MACROMOL. SCI.–CHEM., A16(2), pp. 587-594 (1981)

# The Reaction between Diaminotetraalkoxycyclotriphosphazene Compounds and Toluene Diisocyanate and the Adhesive Property of the Products

MEISETSU KAJIWARA

Department of Applied Chemistry
Faculty of Engineering
Nagoya University
Nagoya, Japan

## ABSTRACT

The reaction of diaminotetraalkoxycyclotriphosphazene compounds with toluene diisocyanate using the mole ratio 1:1 were carried out in benzene for 24 h. The products having the highest average molecular weight was prepared when dimethylaminotetraethoxycyclotriphosphazene was reacted with toluene diisocyanate. It was found from H-NMR, infrared absorption spectra, and chemical analysis that the products were cyclolinearphosphazene oligomers. The products dissolved in DMF were coated on polyvinyl chloride laminate and a test of adhesive bonding strength was made. However, it was difficult to obtain satisfactory results for the adhesives although the products were nonflammable materials.

## INTRODUCTION

Tesi [1] reported that diaminotetrakis(dimethylamino)cyclotriphosphazene reacted with phenylisothiocyanate to yield a monothiourea derivative and with toluene-2,4-diisocyanate in boiling benzene. Korshak [2, 3] reported that the product prepared from poly(phenylquinoxaline) and cyclotriphosphazehexaisothiocyanate was of interest as a vibration absorption material for use at elevated temperatures, and the polymer prepared from 1,4-butanediol and tetraphenoxydiisthiocyanocyclotriphosphazene was thermally stable at 400 °C or a self-extinguishing solid with a softening temperature of 50-80° C, soluble in most organic solvents except petroleum ether. The present work describes the reaction of diaminotetraalkoxycyclotriphosphazene compounds with toluene diisocyanate (TDI), and the adhesive property of the products to hard laminated polyvinyl chloride.

## EXPERIMENTAL

### Preparation of $(NPCl_2)_3$ and $N_3P_3(NHR)_2Cl_4$

#### $(NPCl_2)_3$

Hexachlorocyclotriphosphazene $(NPCl_2)_3$ was prepared from the reaction with phosphorus pentachloride ($PCl_5$) and ammonium chloride ($NH_4Cl$) by the method of Kajiwara [4]. The melting point of the purified trimer was about 112° C.

#### $N_3P_3(NHR)_2Cl_4$

Dianilinotetrachlorocyclotriphosphazene, [$N_3P_3(NHC_6H_5)_2Cl_4$], dibutylaminotetrachlorocyclotriphosphazene [$N_3P_3(NHBu^n)_2Cl_4$], and dimethylaminotetrachlorocyclotriphosphazene [$N_3P_3(NHMe)_2Cl_4$ (geminal or nongeminal)] were prepared by the methods of Ledale [5], Shaw [6], and Ford [7], respectively. The products were used as the starting materials because they could be easily synthesized and occurred in good yield among the aminocyclotriphosphazene compounds. Furthermore, when the reaction of $N_3P_3(NHR^1)_2Cl_4$ with $NaOR^2$ ($R^2$ = Me, Et, $Pr^i$, $Pr^n$) as carried out in THF solvent was over, the THF solvent was distilled under vacuum. The residue was extracted with ether or water. Ether was dried with anhydrous sulfate. The crude product formed was evaporated with ether and was purified with an $\alpha$-$Al_2O_3$ column. Yields of the products are summarized in Table 1.

### The Reaction of $N_3P_3(NHR^1)_2(OR^2)_4$ with Toluene Diisocyanate (TDI)

The reaction of $N_3P_3(NHR^1)_2(OR^2)_4$ with TDI was carried out in benzene solvent with refluxing for 24 h. The mole ratio of the phosphazene compound to TDI was 1:1. When the reaction was over, the

TABLE 1. Yield of $N_3P_3(NHR^1)_2(OR^2)_4$ Prepared from the Reaction of $N_3P_3(NHR^1)_2Cl_4$ with $R^2ONa$

| $R^1$ | $R^2$ | $N_3P_3(NHR^1)_2Cl_4$ (g) | Yield Calcd (g) | Yield Found (g) | Yield (%) |
|---|---|---|---|---|---|
| gem-Me | Me | 3.63 | 3.44 | 2.90 | 84.45 |
|  | Et | 3.60 | 4.04 | 3.00 | 74.17 |
|  | $Pr^n$ | 1.93 | 2.47 | 1.27 | 51.46 |
|  | $Pr^i$ | 2.36 | 3.02 | 0.42 | 14.01 |
| Nongeminal | Me | 3.60 | 3.44 | 3.27 | 95.20 |
|  | Et | 3.60 | 4.07 | 3.69 | 87.76 |
|  | $Pr^n$ | 5.91 | 4.61 | 3.74 | 81.08 |
|  | $Pr^i$ | 5.91 | 4.61 | 3.99 | 86.52 |
| gem-$Bu^t$ | Me | 0.96 | 0.91 | 0.75 | 82.80 |
|  | Et | 0.95 | 1.03 | 0.66 | 64.0 |
|  | $Pr^n$ | 1.82 | 2.26 | 2.25 | 99.40 |
|  | $Pr^i$ | 1.81 | 2.25 | 2.12 | 94.25 |
| gem-$C_6H_5$ | Me | 1.49 | 1.43 | 0.80 | 55.74 |
|  | Et | 3.20 | 3.19 | 2.36 | 73.94 |
|  | $Pr^n$ | 2.83 | 2.54 | 0.96 | 37.79 |
|  | $pr^i$ | 1.76 | 1.58 | 1.74 | 100 |

reaction mixture was filtered and the filtrate was evaporated under vacuum.

### Analysis of the Products and Application of the Products as Adhesive Agent to Hard Laminated Polyvinyl Chloride

The molecular weight of the products were determined by gel permeation chromatography. H-NMR and IR spectra were recorded on a Nihon Denshi Model-100 type spectrometer and a Shimazu Model-450 type spectrometer (4000-200 $cm^{-1}$), respectively. Adhesive agents were made by dissolving the products in DMF to make up a 30% solution. Then 0.5 g of the solution was coated between polyvinyl chloride test pieces with a load of 500 g for 48 h. The size of the hard polyvinyl chloride laminate used was 25 × 25 × 3 mm, and the adhesive test was carried out by JIS-K 6850. Test pieces were examined with a tensile tester.

## RESULTS AND DISCUSSION

### Effects of Side Groups Owing to the Molecular Weight of the Products

The molecular weight of the purified product from the reaction of $N_3P_3(NHMe)_2(OPr^1)_4$ with TDI was determined by GPC. The distribution curve is shown in Fig. 1.

It was found that the product consists of multiple layers. Also, the molecular weight distribution of other products were determined by GPC. The calculated weight-average molecular weights from the data are summarized in Table 2.

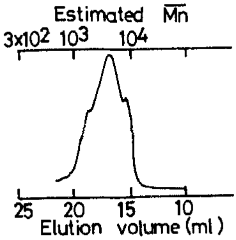


FIG. 1. Gel permeation chromatogram of the product formed from the reaction of TDI with $N_3P_3(OPr^1)_4(NHMe)_2$.

TABLE 2. Yield and Molecular Weight of the Products Formed from the Reaction of $N_3P_3(NHR^1)_2(OR^2)_4$ and Toluene Diisocyanate

| | | | Product | | |
|---|---|---|---|---|---|
| $R^1$ | $R^2$ | $N_3P_3(NHR^1)_2(OR^2)_4$ (g) | Yield (g) | $\overline{M}_w$ | $\overline{M}_n$ |
| gem-Me | Me | 3.27 | 4.20 | 852 | 766 |
| | Et | 3.69 | 4.75 | 1918 | 1292 |
| | $Pr^n$ | 4.61 | 4.61 | 1328 | 836 |
| | $Pr^i$ | 4.61 | 2.99 | 1397 | 810 |
| Nongeminal-Me | Me | 2.90 | 2.83 | 1087 | 658 |
| | Et | 3.00 | 3.47 | 1412 | 1129 |
| | $Pr^n$ | 1.27 | 1.47 | 1113 | 714 |
| | $Pr^i$ | 0.42 | 0.60 | 1207 | 831 |
| gem-$Bu^t$ | Me | 0.96 | 0.75 | 842 | 755 |
| | Et | 0.95 | 0.66 | 846 | 499 |
| | $Pr^n$ | 1.82 | 2.25 | 985 | 983 |
| | $Pr^i$ | 1.81 | 2.12 | 823 | 816 |
| gem-$C_6H_5$ | Me | 0.80 | 1.35 | 1015 | 843 |
| | Et | 2.36 | 1.89 | 1315 | 826 |
| | $Pr^n$ | 0.96 | 1.26 | 906 | 763 |
| | $Pr^i$ | 1.74 | 1.89 | 2212 | 789 |

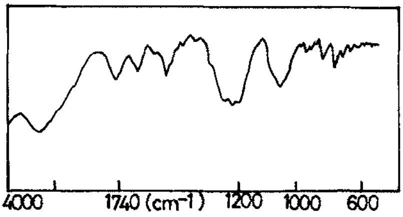
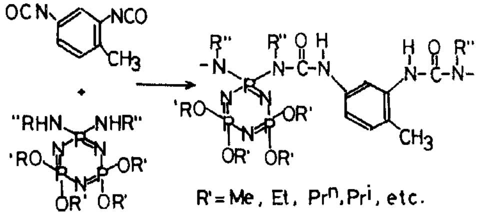


FIG. 2. Infrared absorption spectrum of the product prepared from $N_3P_3(NHMe)_2(OEt)_4$ and TDI.

It was found that the product having the highest molecular weight was prepared from the reaction of $N_3P_3(NHMe)_2(OEt)_4$-geminal type with TDI. The products are amorphous solids, soluble in most organic solvents. To learn the structure of the product, H-NMR was measured in CDCl using TMS. Two peaks appeared at 3.339 and 1.796 ppm, respectively. They can be assigned to –NH. The proton –NH disappears with $D_2O$. Also, $-NH_2$ in diaminotetrachlorocyclotriphosphazene $[N_3P_3(NH_2)_2Cl_4]$ or diaminotetrafluoroethoxycyclotriphosphazene $[N_3P_3(NH_2)_2(OCH_2CF_3)_4]$ appeared at 1.80 ppm. It is assumed that the peaks appearing at 1.796 ppm belong to –PNH and at 3.339 ppm to –NHC(O). Owing to the reaction of $-P(NHR^1)_2$ with –NC(O) groups, the product could have such bonds as –C(O)NH–. In order to investigate the bonding, the IR absorption spectrum of the reaction of $N_3P_3(NHMe)_2(OEt)_4$ with TDI was recorded using the KBr disk technique, and the result is shown in Fig. 2.

Derkach [7] stated that –NH stretching of compounds of the type –C(O)NH– occurred in the rather low range of 3160 to 3040 $cm^{-1}$ and appeared adjacent to the C=O group stretching. The band occurring at 1600 $cm^{-1}$ in Fig. 2 is assigned to –C(O)NH–. Consequently, the reaction between $N_3P_3(NHR^1)_2(OR^2)_4$ and TDI may be represented as follows:



R'=Me, Et, $Pr^n$, $Pr^i$, etc.
R"=H, Me, $Bu^t$, Ph.

TABLE 3. Bonding Strength and Failure of Molded Laminated Polyvinyl Chloride

| $N_3P_3(NHR^1)_2(OR^2)_4$ + toluene diisocyanate product | | | |
|---|---|---|---|
| $R^1$ | $R^2$ | Bonding strength (kg/cm$^2$) | Failure[a] |
| gem-Me | Me | 4.32 | C |
| | Et | 2.88 | C |
| | $Pr^n$ | 3.52 | C |
| | $Pr^i$ | 4.16 | C |
| Nongeminal-Me | Me | 4.48 | C |
| | Et | 4.96 | C |
| | $Pr^n$ | 1.12 | I |
| | $Pr^i$ | 3.04 | C |
| gem-$Bu^t$ | Me | 0 | |
| | Et | 0 | |
| | $Pr^n$ | 0 | |
| | $Pr^i$ | 0 | |
| gem-$C_6H_5$ | Me | 0 | |
| | Et | 0.16 | I |
| | $Pr^n$ | 0.16 | I |
| | $Pr^i$ | 0 | |

[a] I = interfacial; C = cohesive.

## Adhesive Test to Polyvinyl Chloride Laminates

After the products prepared from the reactions of the various phosphazene compounds with TDI were dissolved in DMF solvent and the solutions are coated on polyvinyl chloride laminates, the bonding strengths were measured. The results are summarized in Table 3.

As shown in the previous report [8], the products prepared from the reaction of $N_3P_3(NH_2)_2(OME)_4$ with TDI had a stronger bonding strength to hard polyvinyl chloride laminaters. However, the bonding strengths of the products prepared in the present work are very low. It was observed that bonding strength increased when the products were coated on glass. The relationship between bonding strength

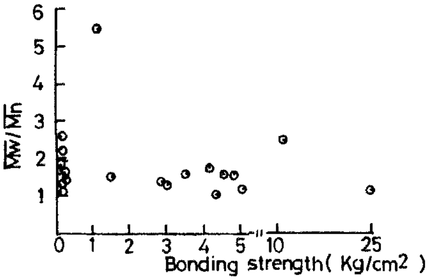


FIG. 3. The relation between bonding strength and $\overline{M}_w/\overline{M}_n$.

and $\overline{M}_w/\overline{M}_n$, together with the previous results [8] were determined, and the results are shown in Fig. 3. However, there are no correlation among them. It is difficult to find the factors concerned with bonding strength.

## REFERENCES

[1] G. Tesi, A. J. Matuzko, R. Zimmer-Galler, and M. S. Chang, Chem. Ind., p. 623 (1964).
[2] K. Bradt, V. V. Krieev, and V. V. Korshak, Vysokomol. Soedin., Ser. B, 20(3), 213 (1978).
[3] Yu. Kochingin, V. V. Krieev, and V. V. Korshak, Ibid., Ser. A, 20(4), 839 (1978).
[4] H. Saito and M. Kajiwara, J. Chem. Soc. Jpn., Ind. Chem. Sect., 66, 618 (1963).
[5] H. Lederle, G. Ottman, and E. Kober, Inorg. Chem., 5, 1818 (1966).
[6] S. K. Das, R. Keat, R. A. Shaw, and B. C. Smith, J. Chem. Soc., p. 5032 (1965).
[7] G. I. Derkach, Zh. Obshch. Khim., 34, 82 (1964).
[8] M. Kajiwara and H. Saito, J. Appl. Polym. Sci., In Press.

Accepted by editor April 7, 1980
Received for publication April 22, 1980