Cyclotrimerization of Isocyanate Groups. II. Catalyzed Reactions of Phenyl Isocyanate in the Presence of 1-Butanol or Butyl-N-Phenylurethane

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SYNOPSIS

Cyclotrimerization of phenyl isocyanate at 30–50°C in the presence of 1-butanol or butyl-N-phenylurethane and catalysts of tertiary amine, quaternary ammonium salt, or carboxylate types in 1,4-dioxane was studied by reverse-phase liquid chromatography. Urethane, allophanate, urea, biuret, isocyanurate, and isocyanate model compounds were found in the system. Stability of all reaction products was also examined. The time dependence of evolution of various products depends on the catalyst type and temperature. The overall reaction scheme was proposed. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polyurethanes often contain in addition to urethane also other groups, such as hydroxy (carboxy), isocyanate, urea, allophanate, biuret, isocyanurate, carbodiimide, or oxazolidone groups (cf., e.g., Scheme 1 in Ref. 1). Their type and amount depend on the reaction conditions.

Isocyanurate (i.e., hexahydro-1,3,5-triazine-2,4,6-trione) groups are formed by cyclotrimerization of isocyanates. The thermal and hydrolytic stabilities of isocyanurate cross-links are high, unlike the allophanate or biuret cross-links. In systems of practical importance, cyclotrimerization is combined with other reactions of isocyanate groups, e.g., the isocyanate-endcapped diols are cyclotrimerized. The combination of urethane and isocyanurate linkages in poly(urethane–isocyanurate)s is used, e.g., in the manufacture of rigid foams, coatings, and elastomers.

Cyclotrimerization of isocyanate groups in model systems with alcohols and various catalysts was studied by several authors: Bechara et al.[2-4] studied reactions of phenyl isocyanate with alcohols (1-pro-

panol, methoxy-2-propanol) and water in the presence of two types of catalysts, either DABCO* TMR (quaternary ammonium carboxylate) or DABCO* T (tertiary amine with hydroxy groups), and in various solvents (toluene, acetonitrile, and diglyme) at 30–50°C. The trimer and urethane compounds were formed simultaneously, when DABCO* TMR was used. At low catalyst concentrations, only urethane groups were observed. At higher catalyst concentrations, the trimer was formed and the ratio urethane/trimer increased with increasing catalyst concentration. However, this ratio passed through a maximum with increasing temperature. When isocyanate reacted with water, the ratio trimer/urea decreased with increasing catalyst concentration and temperature.[2,3]

When DABCO* T was used, no trimer was formed at the equimolar ratio of isocyanate and alcohol groups. At an excess of isocyanate, the mixture of urethane and trimer was formed. The rates of water–isocyanate and methoxy-2-propanol–isocyanate reactions were almost the same in the presence of DABCO* T.[4]

Kresta and Hsieh[5,6] discovered a co-catalytic effect of urethane groups in the cyclotrimerization of isocyanates (40 and 50°C, dimethylformamide, sodium ethoxide as catalyst). This effect was found to be valid for aromatic as well as for aliphatic is-

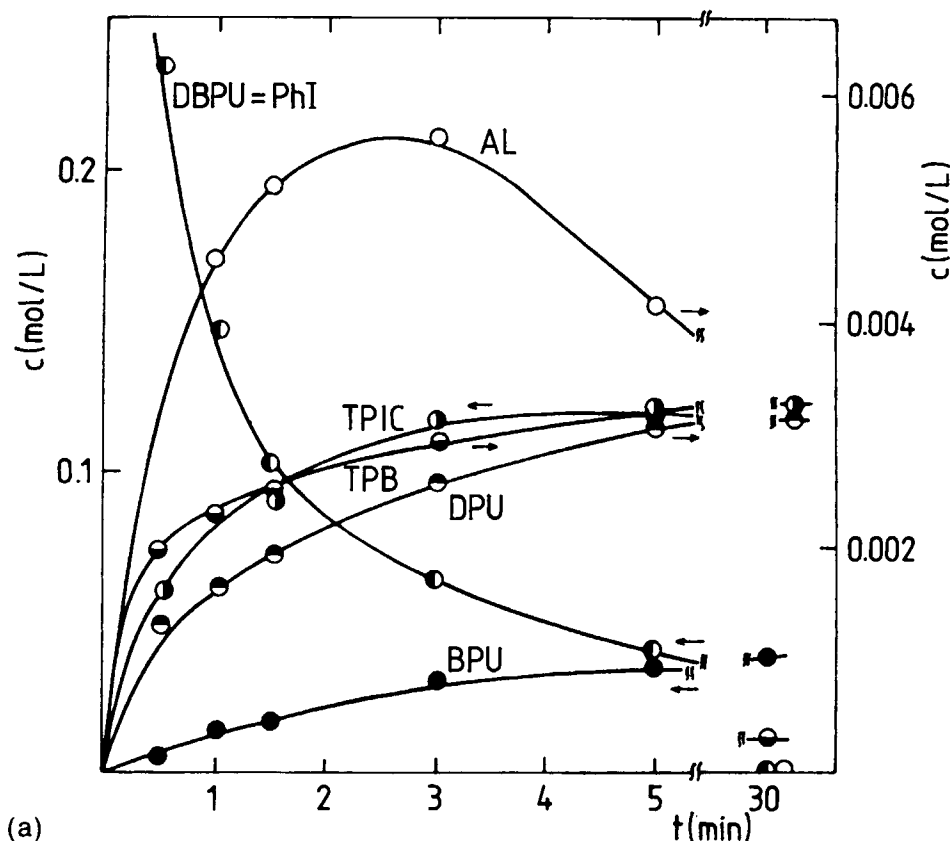**Figure 1** (a) Reaction of phenyl isocyanate in the presence of 1-butanol and DABCO* TMR catalyst. $(c_{PhI})_0 = 0.436$ mol/L; $(c_{BuOH})_0 = 0.104$ mol/L; $c_{TMR} = 8.26 \times 10^{-4}$ g/mL; 50°C (Series 1). Reaction products denoted as (◑) TPIC, (◓) DPU, (●) BPU, (◐) PhI determined as DBPU, (◒) TPB, and (○) AL. (b) Reaction of phenyl isocyanate in the presence of butyl-N-phenylurethane and DABCO* TMR catalyst. $(c_{PhI})_0 = 0.431$ mol/L; $(c_{BPU})_0 = 0.096$ mol/L; $c_{TMR} = 7.78 \times 10^{-4}$ g/mL; 50°C (Series 2). Symbols as in (a).

ocyanates. The co-catalytic effect was explained by induced polarization of isocyanate groups by urethanes through hydrogen bonding.

The cyclotrimerization of phenyl isocyanate in the presence of 1-butanol or water and two types of catalysts (an organotin and four tertiary amines) was studied by Wong and Frisch.[7,8] Three amine catalysts, i.e., N,N,N',N',N''-pentamethyldipropylenetriamine (PMPT), tris(3-dimethylaminopropyl)hexahydro-s-triazine (TDHT), and N,N,N'-trimethyl-N'-(2-hydroxyethyl)ethanediamine (TMEE) support the cyclotrimerization. The organotin catalyst did not. Reactions catalyzed by PMPT, TDHT, and TMEE could be described by the first-order kinetics up to almost 90% conversion. Whereas in the case of catalysis by PMPT and TDHT the formation of urethane and trimer proceeded simultaneously, with TMEE, urethane was formed first followed by the trimer.[7]

Studies of isocyanate–alcohol and isocyanate–

water reactions in the presence of PMPT have revealed that allophanate is an intermediate product. When water was added, biuret and, later, urea were formed. Whereas alcohol accelerated the trimerization reaction, water had an opposite effect.[8]

The main objective of our investigations has been the study of network buildup in polyurethane systems catalyzed by conventional catalysts and at different regimes. The results obtained with model systems serve as the main input information for the theoretical treatment of network formation.[9] The buildup by cyclotrimerization in combination with other reactions has not been studied yet from this point of view.

The first part[1] of our studies was concerned with the reaction products of phenyl isocyanate and the overall kinetics. It was found[1] that the activity of catalysts for cyclotrimerization decreased in the following order: quaternary ammonium salts > organic acid salt ≫ tertiary amines. Besides isocyanurate,
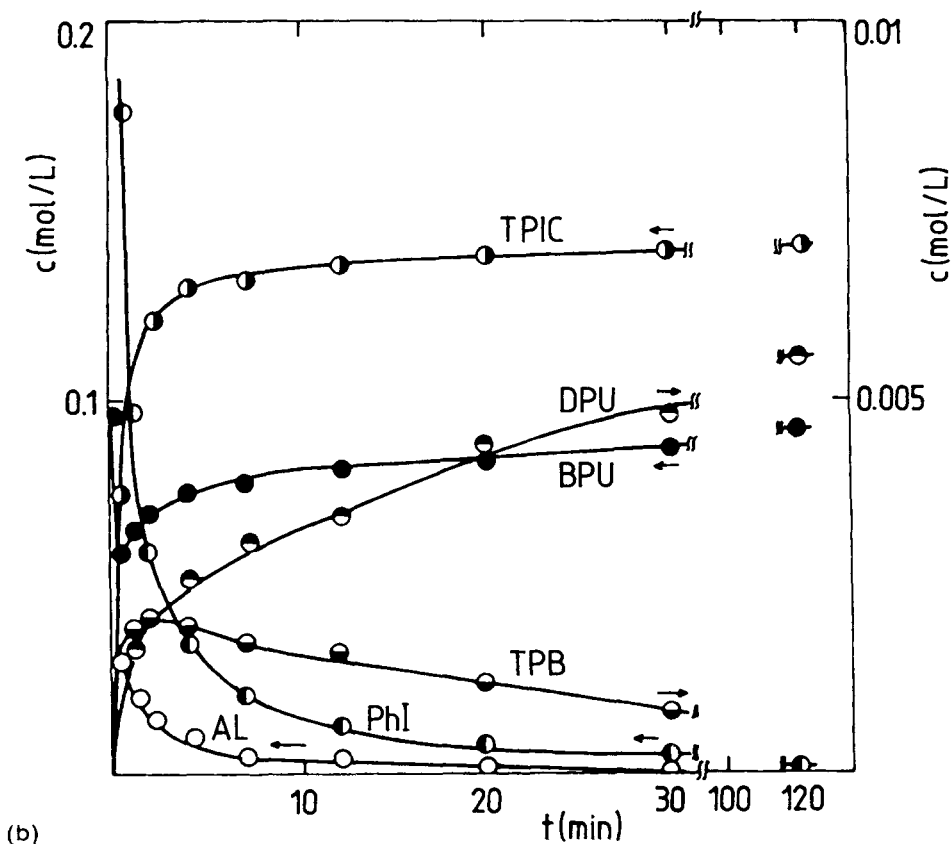
Figure 1   (*Continued from the previous page*)

traces of biuret and urea were found, but cyclic dimer or higher oligomers of isocyanate were not detected by HPLC at all. The order of the kinetics of cyclotrimerization with respect to isocyanate concentration was dependent on the catalyst used; it appeared to be either second-order for quaternary ammonium salts or its order varied from the first (lower isocyanate conversions) to the second (higher isocyanate conversion) for organic acid salts and tertiary amines. The kinetics order aspect has been discussed elsewhere.[10]

This article (Part II) deals with catalyzed cyclotrimerization of phenyl isocyanate in the presence of 1-butanol (modeling the one-shot preparation of polyurethanes) or butyl-N-phenylurethane (modeling the prepolymer technique).

EXPERIMENTAL

The preparation and characterization of initial materials, standard compounds, and procedures used for preparation of samples and characterization of reaction products were the same as before.[1,11,12]

Three types of catalysts (Air Products) were used: *quaternary ammonium salt* (DABCO* TMR and DABCO* TMR-4), *organic acid salt* (DABCO* K-15), and *tertiary amine* (POLYCAT* 41 and DABCO*). These catalysts are marked as TMR, TMR4, K15, P41, and DABCO, respectively. For the reader's convenience, the trademarks, codes, and compositions are summarized in Table I.

Reaction conditions were as follows: phenyl isocyanate (PhI) concentration up to 0.5 mol/L, 1-butanol (BuOH) concentration approximately 0.1 mol/L, butyl-N-phenylurethane (BPU) concentration 0.08–0.30 mol/L, and catalyst concentration ca. 8×10^{-4} g/mL. All reactions were studied in 1,4-dioxane at 30–50°C. Unreacted PhI was determined (after reaction with dibutylamine) in the form of 1,1-dibutyl-3-phenylurea (DBPU). Some reaction conditions, e.g., temperature, PhI, and catalyst concentrations were the same as in our preceding paper.[1]

Retention times of individual standard compounds were about 3.5 min for 1,3,5-triphenyl isocyanurate (TPIC), 6 min for 1,3-diphenylurea (DPU), 9.5 min for BPU; 12 min for DBPU, 13 min for 1,3,5-triphenylbiuret (TPB), and 14.5 min for butyl-2,4-diphenylallophanate (AL).
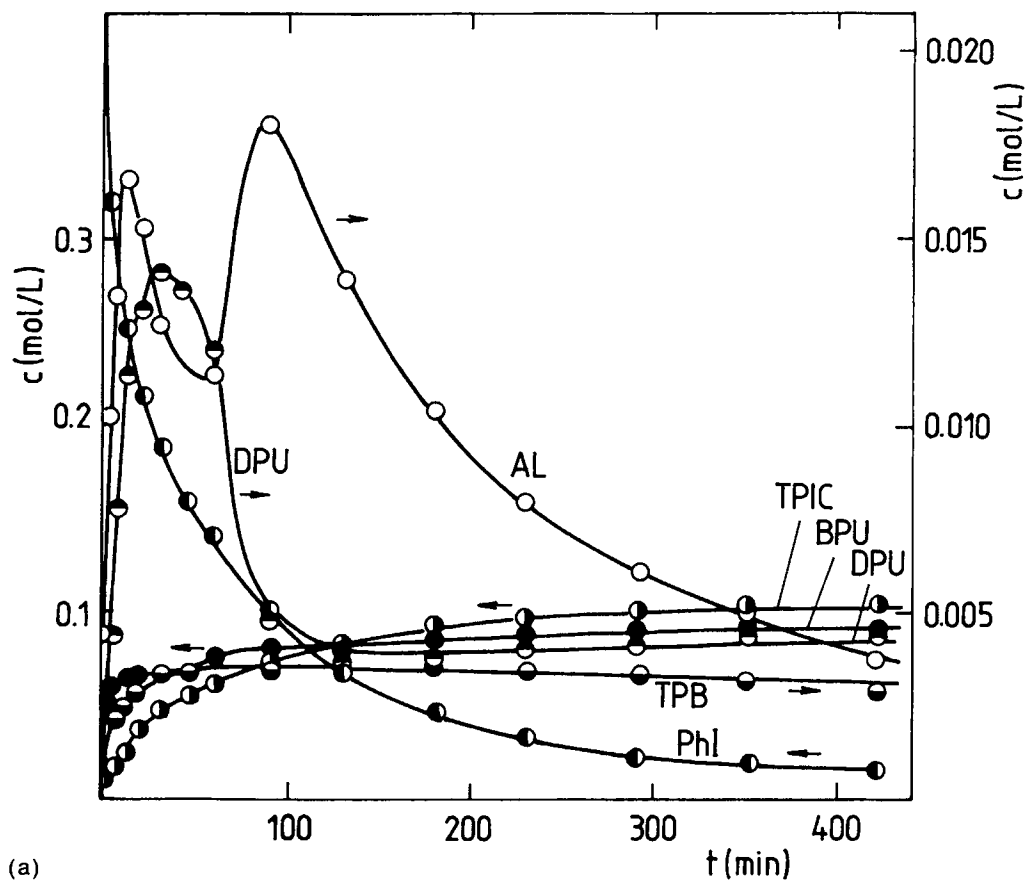
Figure 2   (a) Reaction of phenyl isocyanate in the presence of 1-butanol and DABCO* K-15 catalyst. $(c_{PhI})_0 = 0.457$ mol/L; $(c_{BuOH})_0 = 0.097$ mol/L; $c_{K15} = 8.08 \times 10^{-4}$ g/mL; 50°C (Series 3). Symbols as in Figure 1(a). (b) Reaction of phenyl isocyanate in the presence of butyl-N-phenylurethane and DABCO* K-15 catalyst. $(c_{PhI})_0 = 0.459$ mol/L; $(c_{BPU})_0 = 0.088$ mol/L; $c_{K15} = 7.89 \times 10^{-4}$ g/mL, 50°C (Series 4). Symbols as in Figure 1(a).

RESULTS AND DISCUSSION

Time dependencies of the concentrations of the reaction products of PhI at 50°C in the presence of (a) *catalyst and BuOH* and (b) *catalyst and BPU* for all types of catalysts are illustrated in Figures 1(a)-3(b). Figure 4 shows the time dependence of catalyzed allophanate decomposition at 50°C.

From the preceding studies, it was concluded that the organic-acid salt catalyst DABCO* K-15 was placed in the middle of the activity scale of the used catalysts.[1] That is why this catalyst has been chosen for the more detailed studies—the determination of the dependencies of changes in concentrations of reaction products on temperature, initial concentrations, ratios of reaction components, and presence of all possible reaction products.

The study of the systems (a) *PhI-BuOH-catalyst*

and (b) *PhI-BPU-catalyst* at 50°C for all catalysts can be summarized as follows: Urea and biuret are formed from traces of water simultaneously when TMR, TMR4, or K15 catalysts are used in both studied systems. In the case of P41 and DABCO, urea is formed first and biuret considerable later. When the most effective catalysts TMR and TMR4 are used, there exists a maximum in the time dependence of biuret concentration.

It is also interesting to compare the evolution of BPU and AL in the PhI-BuOH-catalyst systems. Although a large excess of isocyanate over butanol (4 : 1) was chosen in all cases, the amount of urethane ($c_{AL} = 0$) reached only 35% of the starting BuOH concentration for the TMR catalyst [Fig. 1(a)]; for the TMR4 catalyst, this figure was 78% at the end of reaction (i.e., when c_{PhI} had fallen below 0.5% of its initial value). The conversion of BuOH
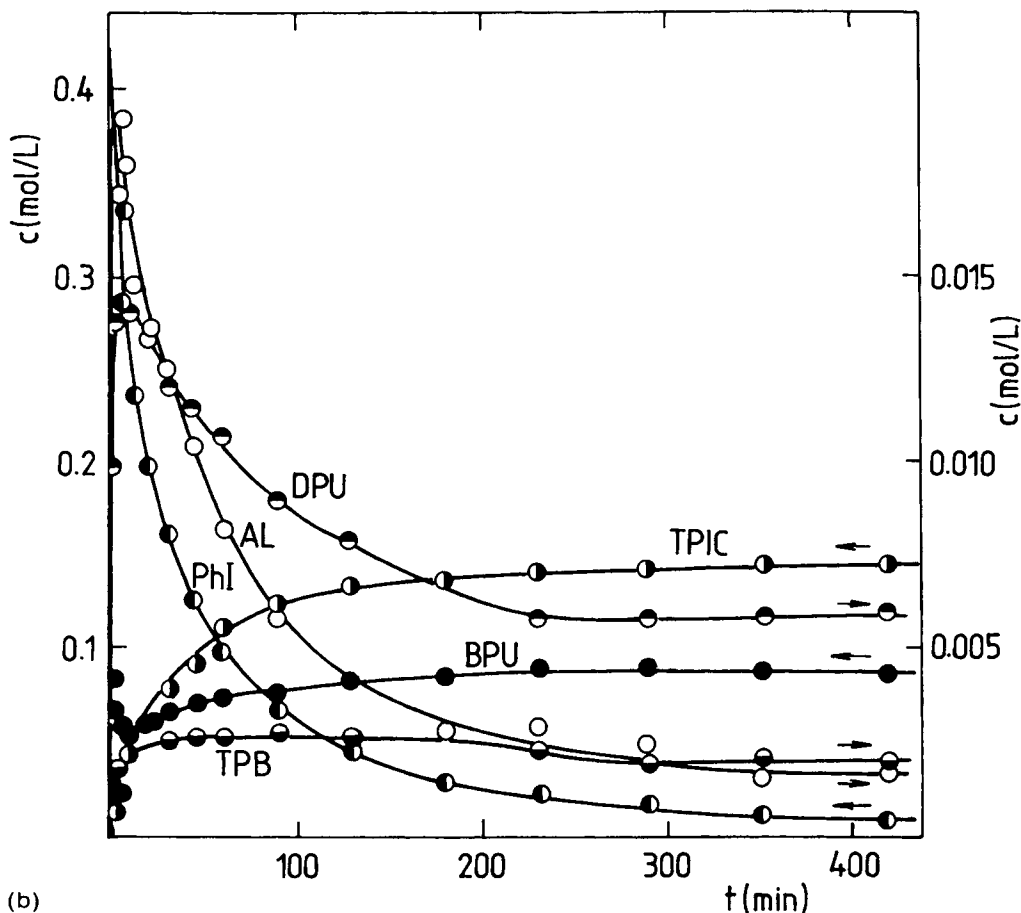
(b)

Figure 2 (*Continued from the previous page*)

is complete for K15, P41, and DABCO [Figs. 2(a) and 3(a)].

When TMR and TMR4 are used, the formation of urethane and allophanate proceeds simultaneously and their amounts are comparable at the beginning of reaction. However, the allophanate concentration passes through a maximum very soon (t < 3–7 min) and then decreases very quickly, so that c_{AL} = 0 for t > 20 min in the case of TMR [Fig. 2(a)] and for t > 100 min in the case of TMR4. By using the K15 catalyst, allophanate is also formed very quickly, but allophanate decomposition is slower than with TMR and TMR4. That is why there still remain traces of allophanate (several mmol/L) after 7 h [Fig. 2(a)]. (The complicated course of time dependence of allophanate concentration is discussed below in connection with allophanate decomposition.) In the case of P41, urethane is formed first, and when most butanol (ca. 85%) has been converted into urethane, the formation of allophanate starts. Later, it reaches a constant value. Allophanate concentration is con-

stant in the interval between 4 and 8 h. At a higher temperature (80°C), however, the allophanate concentration in this time region also passes through a maximum (cf. Fig. 3 in Ref. 15). By using DABCO, allophanate was not found at all for t < 10 h. Allophanate and biuret are converted into the stable products—urethane, urea, or isocyanurate (cf. Scheme 1)—faster the more effective a catalyst is used.

The cyclic dimer or higher oligomers of PhI have not been found. Traces of aniline have been observed (retention time at about 1.5 min). The mass balance over all isocyanate-containing compounds gives a value equal to the initial isocyanate concentration, which means that no material has been lost or remained undetected.

The time dependencies of concentrations of all reaction products for systems (a) and (b) for individual catalysts are similar, with the exception of that for urethane. This means that the same substances (groups) are formed irrespective of whether the one-shot and prepolymer preparation techniques
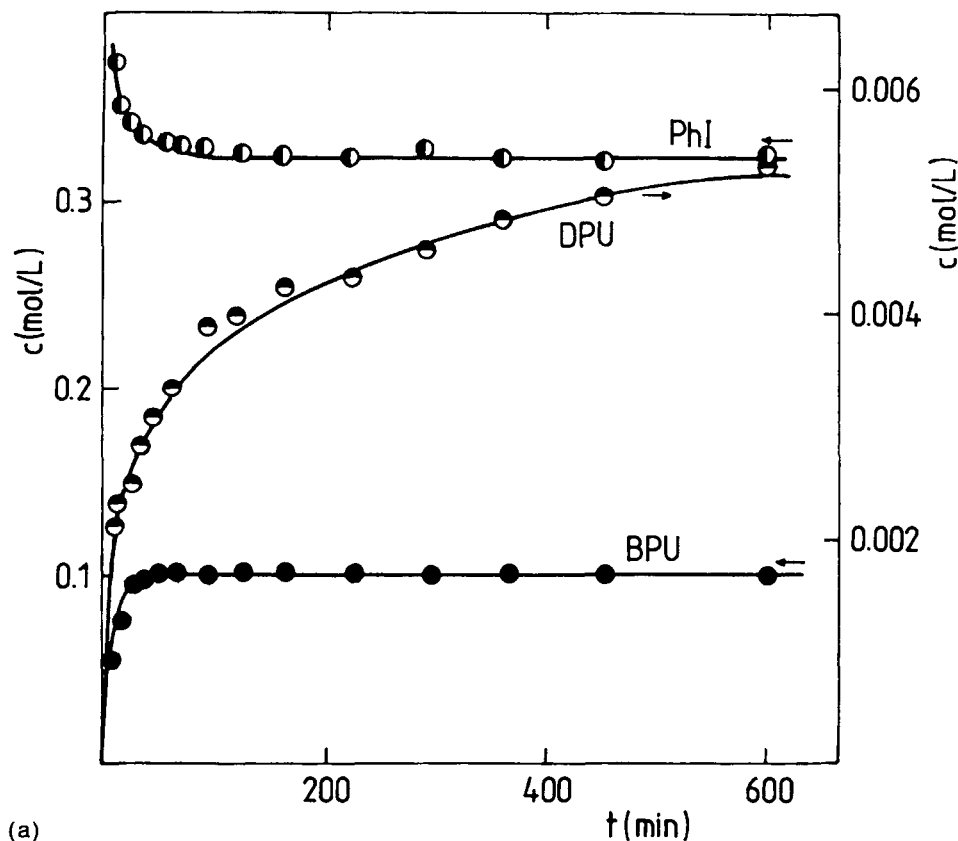
Figure 3   (a) Reaction of phenyl isocyanate in the presence of 1-butanol and DABCO* catalyst. $(c_{PhI})_0$ = 0.435 mol/L; $(c_{BuOH})_0$ = 0.106 mol/L; c_{DABCO} = 8.34 × 10^{-4} g/mL; 50°C (Series 5). Symbols as in Figure 1(a). (b) Reaction of phenyl isocyanate in the presence of butyl-N-phenylurethane and DABCO* catalyst. $(c_{PhI})_0$ = 0.459 mol/L; $(c_{BPU})_0$ = 0.099 mol/L; c_{DABCO} = 8.45 × 10^{-4} g/mL; 50°C (Series 6). Symbols as in Figure 1(a).

are used, but their time evolution can be very different.

With the K15 catalyst, the relative time dependencies of concentrations of individual reaction products are little dependent on temperature, catalyst concentrations, and initial ratio of reaction components. If the systems isocyanate–catalyst, isocyanate–butanol–catalyst, and isocyanate–urethane–catalyst are compared, it is clear that the concentration of unreacted isocyanate during the reaction is higher in the presence of urethane (alcohol) than in its absence [cf., e.g., Fig. 2(a) and (b) along with Fig. 3 in Ref. 1).

The reaction products (urethane, urea, isocyanurate) are stable at 50°C with the exception of TPB and AL in the presence of a catalyst. Although biuret decomposition proceeds without any side reactions, giving an equivalent amount of urea, the decomposition of allophanate is more complicated (cf. Fig. 4). The amounts of formed urethane and

urea are equal approximately to one-half of the amount of the decomposed allophanate at the beginning of the reaction (for c_{AL} > ca. 0.5 $(c_{AL})_0$), but at the end of allophanate decomposition, the concentration of urethane corresponds to the starting concentration of allophanate. This observation is explained by allophanate decomposition with water in the presence of a catalyst yielding urea and butanol (cf. Scheme 1). The same interpretation can be used for explanation of the complicated changes of allophanate concentration illustrated in Figure 2(a).

A deficit in the material balance of the sum of the number of moles of urethane and allophanate in the system of type (b), i.e., isocyanate–urethane–catalyst, was found when TMR, TMR4, and K15 were used, but not for DABCO or for P41 at times < 200 min (Fig. 5). A similar deficit was also found for the K15 catalyst. These results are summarized in Figure 6. As has been already mentioned, any
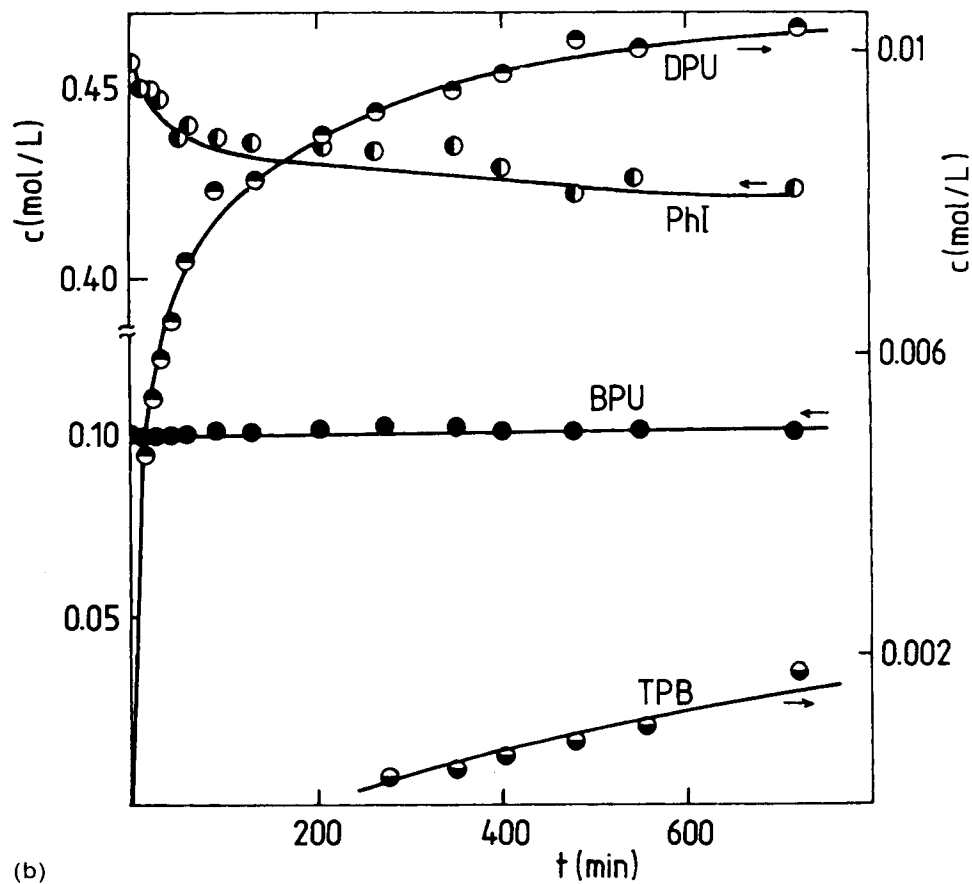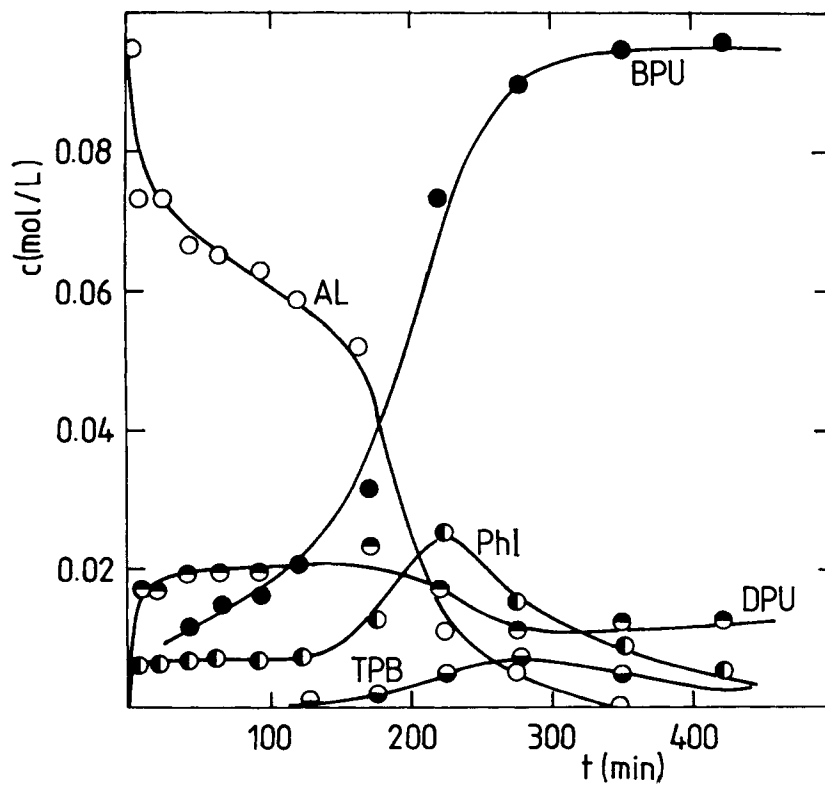
(b)

Figure 3 (*Continued from the previous page*)

Figure 4 Decomposition of butyl-2,4-diphenylallophanate by DABCO* K-15 catalyst. $(c_{AL})_0 = 0.096$ mol L^{-1}; $c_{K15} = 1.62 \times 10^{-3}$ g/mL; 50°C (Series 7). Symbols as in Figure 1(a).
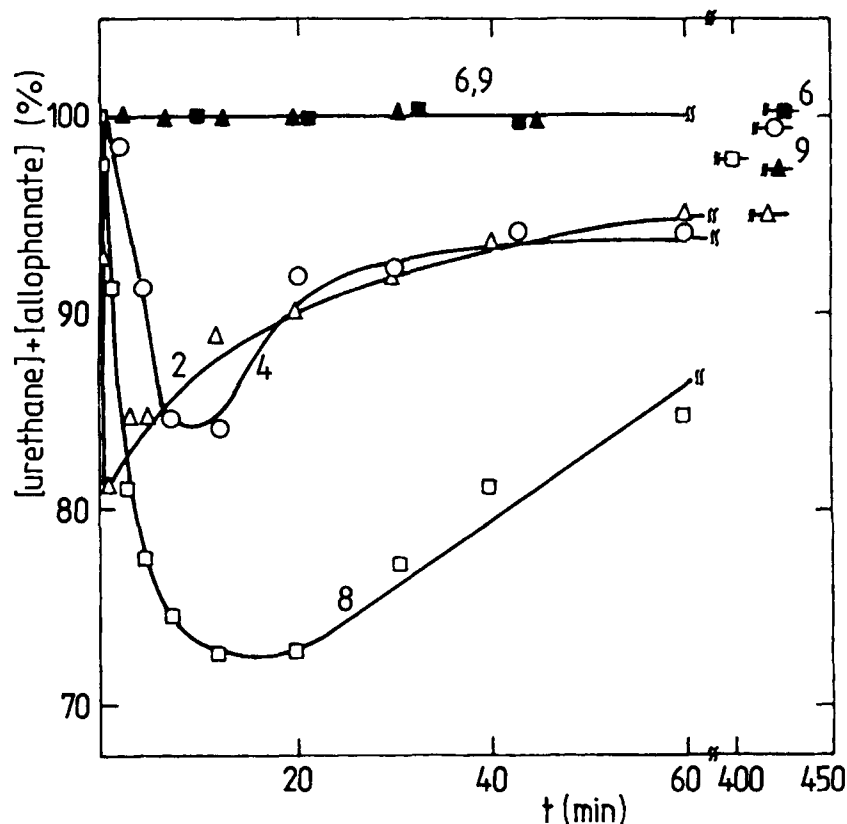
Figure 5 Time dependence of the sum of urethane and allophanate concentrations relative to starting urethane concentration. Symbols for individual series: ($\triangle$) 2 (TMR); ($\bigcirc$) 4 (K15); ($\blacksquare$) 6 (DABCO); ($\square$) 8 (TMR4); ($\blacktriangle$) 9 (P41).

Table I Basic Information About Catalysts Used

Trademark (Catalyst Type)	Code	Chemical Composition	Reference
DABCO* TMR catalyst (QAS)	TMR	Quaternary ammonium salt in ethylene glycol	13
		Quaternary ammonium carboxylate	14
DABCO* TMR-4 catalyst (QAS)	TMR4	Proprietary tertiary amine/glycol blend	13
		Quaternary ammonium carboxylate	14
DABCO* K-15 catalyst (OAS)	K15	Potassium 2-ethylhexanoate in diethylene glycol	13
POLYCAT* 41 catalyst (TA)	P41	Tertiary amine	13
		1,3,5-Tris(3-dimethylaminopropyl)-hexahydro-s-triazine	14
DABCO* catalyst (TA)	DABCO	1,4-diazabicyclo[2.2.2]octane	13

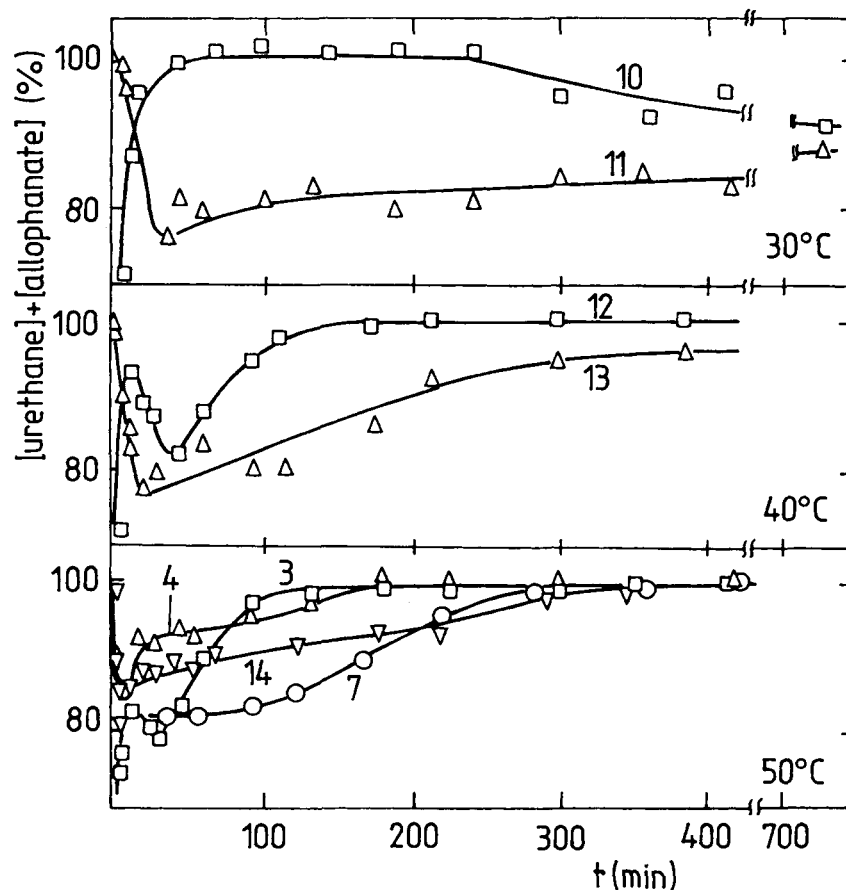QAS = quaternary ammonium salt; OAS = organic acid salt; TA = tertiary amine.

Figure 6 Time dependence of the sum urethane and allophanate concentrations relative to starting concentration. Symbols denoted as ($\triangle$) or (∇) for $(c_{BPU} + c_{AL})/(c_{BPU})_0$ in %; ($\square$) for $(c_{BPU} + c_{AL})/(c_{BuOH})_0$ in %; ($\bigcirc$) for $(c_{BPU} + c_{AL})/(c_{AL})_0$ in %; 50°C. The number of series is marked in Figure 6. (Starting conditions for Series 8–14 are summarized in Table II.)

deficit in the balance of isocyanate-based groups has not been observed.

The deficit in the urethane-based compounds

Table II Initial Conditions for Reaction Systems Given in Figures 5 and 6

Series No.	$(c_{PhI})_0$ (ml/L)	$(c_{BPU})_0$ (mol/L)	$c_{K15} \times 10^4$ (g/mL)	Temperature (°C)
8	0.446	0.095	8.18[a]	50
9	0.425	0.096	8.20[b]	50
10	0.440	0.096[c]	7.97	30
11	0.457	0.092	7.91	30
12	0.465	0.095[c]	7.97	40
13	0.463	0.094	7.96	40
14	0.318	0.304	26.1	50

[a] TMR4.
[b] P41.
[c] BuOH.

(urethane, allophanate) can be explained by the formation of 1-butanol (cf. Scheme 1). Butanol does not absorb in the UV region and thus it is invisible by HPLC detectors. The formed butanol reacts with free isocyanate (if present in the system), and urethane and/or allophanate results.

All these facts allow us to propose the overall reaction scheme given in the Appendix.

The activity of the catalysts in individual reaction steps may be different, which affects the relative concentrations of the reactive intermediates and products at a given reaction time.

CONCLUSIONS

The studied catalysts support the formation of urethane, urea, allophanate, biuret, and isocyanurate and the dissociation of allophanate and biuret. The

reactions of isocyanate groups in the presence of urethane (alcohol) and the catalyst is thus very complex.

The dimer or higher oligomers of phenyl isocyanate have not been detected by HPLC among the reaction products. They are apparently very unstable and/or are present in small quantities. The analysis of data has revealed that 1-butanol can be formed most likely from allophanate and traces of water yielding stable urea as well as by a reaction of active isocyanate (complexes) with allophanate to yield isocyanurate. Traces of aniline have been found.

In the presence of the catalyst, 1,3-diphenylurea can be formed in three ways: from water and isocyanate, by decomposition of biuret, or by decomposition of allophanate (in the presence of water). Butyl-2,4-diphenylallophanate is formed either from urethane and the isocyanate–catalyst complex or from butanol and another isocyanate–catalyst complex. Allophanate is not found at all in the reaction systems when DABCO is used. During the reaction of phenyl isocyanate with 1-butanol in the presence of TMR, urethane and isocyanurate formation proceeds simultaneously.

The co-catalytic effect of urethane groups on the cyclotrimerization of isocyanate has not been observed in the presence of the catalysts used. The deficit in the balance of urethane-based units has been explained by the formation of 1-butanol during the reaction.
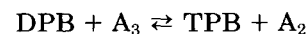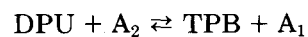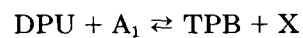
The data obtained make it possible to choose reaction conditions (catalyst type and concentration, reaction temperature and time) in which either certain products or only stable products prevail. Also, conditions can be chosen for having the majority of cross-links in the stable (isocyanurate) or less stable (allophanate, biuret) forms.

APPENDIX
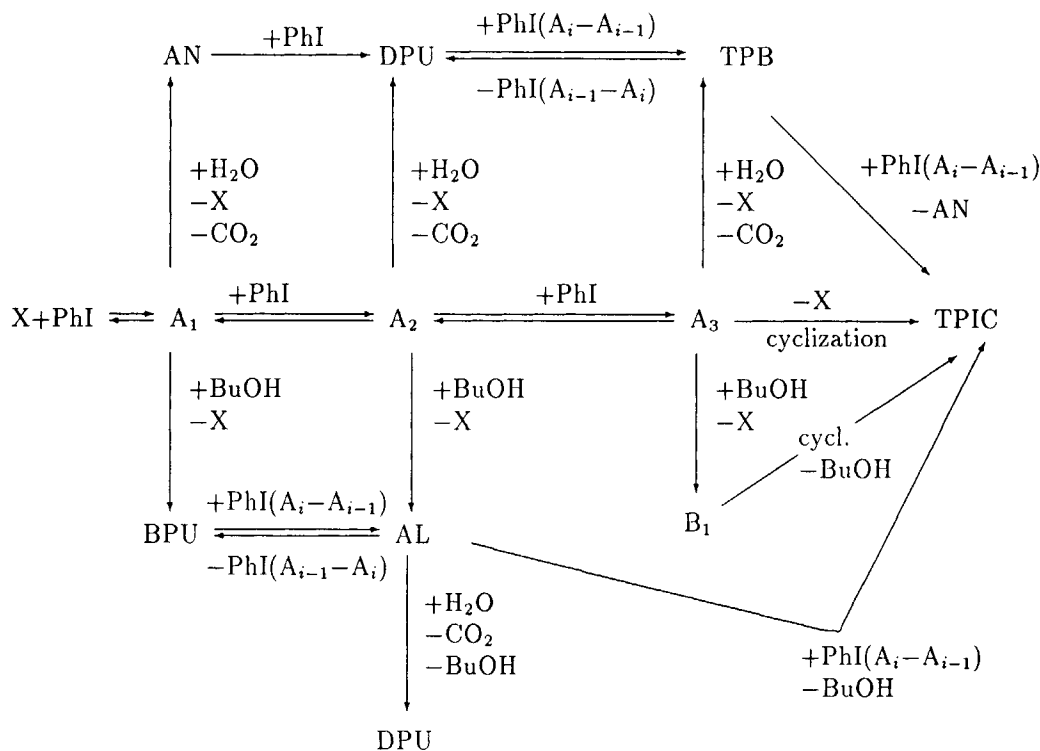
Scheme 1   The overall reaction scheme of phenyl isocyanate cyclotrimerization in the presence of 1-butanol (butyl-N-phenylurethane) and the catalyst.
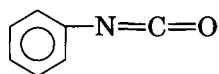
The notation $+\mathrm{PhI}(A_i - A_{i-1})$ or $-\mathrm{PhI}(A_{i-1} - A_i)$ means that the catalyzed addition or abstraction of a molecule of PhI can occur via the polyisocyanate–catalyst complexes. Thus, for instance, TPB can be formed from DPU in the following ways:
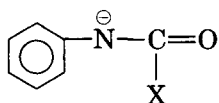
$$\mathrm{DPU} + A_1 \rightleftarrows \mathrm{TPB} + X$$

$$\mathrm{DPU} + A_2 \rightleftarrows \mathrm{TPB} + A_1$$

$$\mathrm{DPB} + A_3 \rightleftarrows \mathrm{TPB} + A_2$$

Explanation of abbreviations used in Scheme 1:

$X^{\ominus}$	catalyst (in its active [anion] form)	
PhI	phenyl isocyanate	Ph—N=C=O
A_1	complex	Ph—N$^{\ominus}$—C=O with X
A_2	complex	Ph—N$^{\ominus}$—C(=O)—N(Ph)—C=O with X
A_3	complex	Ph—N$^{\ominus}$—C(=O)—N(Ph)—C(=O)—N(Ph)—C=O with X
AL	butyl 2,4-diphenylallophanate	Ph—NH—C(=O)—N(Ph)—C(=O)—OCH$_2$CH$_2$CH$_2$CH$_3$
AN	aniline	Ph—NH$_2$
BuOH	1-butanol	CH$_3$CH$_2$CH$_2$CH$_2$OH
BPU	butyl-N-phenylurethane	Ph—NH—C(=O)—OCH$_2$CH$_2$CH$_2$CH$_3$
B_1	1-(butoxycarbonyl)-1,3,5-triphenylbiuret	Ph—NH—C(=O)—N(Ph)—C(=O)—N(Ph)—C(=O)—OCH$_2$CH$_2$CH$_2$CH$_3$
DPU	1,3-diphenylurea	Ph—NH—C(=O)—NH—Ph
TPB	1,3,5-triphenylbiuret	Ph—NH—C(=O)—N(Ph)—C(=O)—NH—Ph
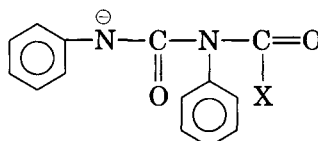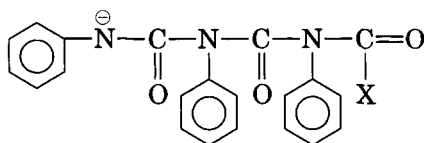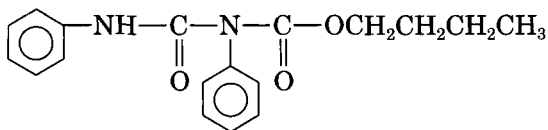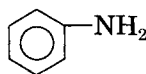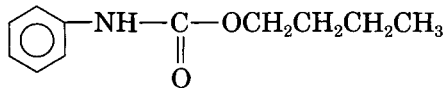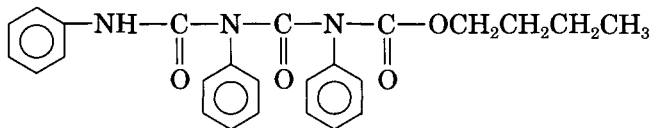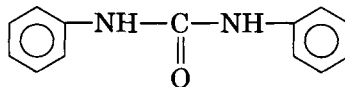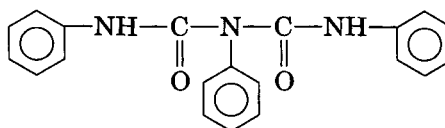
TPIC   1,3,5-triphenyl isocyanurate
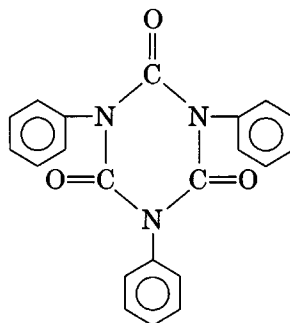
REFERENCES

1. M. Špírková, M. Kubín, P. Špaček, I. Krakovský, and K. Dušek, *J. Appl. Polym. Sci.,* to appear.
2. I. Bechara, *J. Cell. Plast.,* **15,** 102 (1979).
3. I. S. Bechara and R. L. Mascioli, *J. Cell. Plast.,* **15,** 321 (1979).
4. I. S. Bechara and F. P. Carroll, *J. Cell. Plast.,* **16,** 89 (1980).
5. J. E. Kresta and K. H. Hsieh, *Makromol. Chem.,* **179,** 2779 (1978).
6. J. E. Kresta and K. H. Hsieh, *Makromol. Chem.,* **180,** 793 (1979).
7. S. W. Wong and K. C. Frisch, *J. Polym. Sci. A24,* 2867 (1986).
8. S. W. Wong and K. C. Frisch, *J. Polym. Sci. A24,* 2877 (1986).
9. K. Dušek, M. Špírková, and I. Havlíček, *Macromolecules,* **23,** 1774 (1990).
10. I. Krakovský and M. Špírková, *Collect. Czech. Chem. Commun.,* **58,** 2663 (1993).
11. M. Špírková, M. Kubín, and K. Dušek, *J. Macromol. Sci.-Chem.,* **A24,** 1151 (1987).
12. M. Špírková, M. Kubín, and K. Dušek, *J. Macromol. Sci.-Chem.,* **A27,** 509 (1990).
13. Air Products Inc., Materials Safety Data Sheets.
14. K. C. Frisch and S. W. Wong, *Cell. Polym.,* **8,** 433 (1969).
15. M. Špírková, J. Budinski-Simendič, M. Ilavský, P. Špaček, and K. Dušek, *Polym. Bull.,* **31,** 83 (1993).