

Flammability and Thermal Properties of Rigid Polyurethane Foams with Additionally Introduced Cyclic Structures

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Synopsis

Flammability, smoke evolution, thermal, and thermomechanical properties of low-density rigid polyurethane foams obtained from different aromatic polyols were investigated. The foams were prepared according to a standard formulation ensuring the same foam phosphorus content. Cellular polyurethanes with the best fire resistance were obtained from polyols containing disubstituted naphthalene and biphenyl rings. A linear equation was proposed to describe the influence of various structural units of the polyurethane (the content of cyclic structures C_c , nitrogen content C_N , and crosslinking equivalent M_c) upon its flammability, expressed in terms of its oxygen index (OI)

$$OI = B_0 + B_1C_c + B_2C_N + B_3(1/M_c)$$

Thermal stability of crosslinked polyurethanes was not found to influence significantly their thermomechanical properties, while crosslink density and the type and quantity of cyclic structures additionally introduced did have a pronounced effect upon these properties.

INTRODUCTION

Cellular polyurethanes (PU) in the form of low-density rigid polyurethane foams are particularly inflammable because of their highly developed surface.^{1,2} Owing to their unusually low thermal conductivity and high strength-to-weight ratio, rigid PU foams are increasingly used as thermal insulation materials.^{3,4}

Rigid PU foams have been used extensively in the construction field, and the potential for future growth in this market is considered to be great.⁵ Applications have increased because of needs to reduce construction costs and provide more effective thermal insulation materials for air-conditioned and electrically heated buildings. The oil embargo imposed by the OPEC nations has prompted various governments to propose far-reaching energy conservation programs. Rigid PU foams have been given an important and significant role in these programs.

Rigid PU foams may cause serious hazard in some applications, e.g., if they do not possess a sufficient degree of fire resistance. In the last decade, a large number of articles dealing with the improvement of the fire performance of polyurethane foams were published.⁶⁻¹⁰ Many new fire-retardant compounds and methods of their application were developed in order to obtain rigid PU foams with a maximum fire resistance. The emphasis of research efforts has shifted to flame-resistant composition of PU foams which are integral parts of the polyurethane chemical structure.^{8,10} Rigid PU foams prepared with reactive-type flame retardants comprise roughly 75% of total sales of flame-retardant

rigid foams.¹⁰ The best flame retardants are known to produce char on polymer combustion.^{2,11} The char acts as a mechanical barrier, so that the physical compactness of the material is preserved by preventing the access of oxygen to the material. Thus, the char at least partially eliminates the exothermic oxidation reactions. The char also makes more difficult the evolution of gaseous and often toxic combustion products.^{2,11}

Phosphorus compounds that fulfil all the above-mentioned requirements are regarded to be the best flame retardants.^{2,6,12} The introduction of phosphorus into the rigid PU foams, however, results in a considerable decrease of their thermal stability,¹²⁻¹⁴ thermomechanical properties, and, in many cases, hydrolytic stability.¹⁰ In practice, in order to obtain a polyurethane foam with acceptable physical properties, its phosphorus content should not exceed 1%.^{14,15} On the other hand, this amount of phosphorus does not always provide a satisfactorily high flame retardance of the rigid PU foam. Thus, the effectiveness of the phosphorus can be greatly increased by the incorporation of a halogen.^{2,6,10} Unfortunately, halogens were found to deactivate the amine catalysts commonly used in the technology of rigid PU foams.¹⁰ Polyols containing halogens bromine or chlorine also offer a suitable means of flameproofing the PU foams.^{6,10}

The presence of cyclic structures in polymers is known to improve their fire performance and increase the char formation tendency during the combustion of these polymers.^{6,8,10,16} An example of such a modification is provided by foams containing thermally stable groups, such as isocyanurates, carbodiimides, imides, formed as a result of respective reactions of polyisocyanates.^{10,17} These foams, however, were found to have some obvious shortcomings, such as a considerable friability, complicated production technology, and relatively higher prices, in comparison with conventional polyurethane foams.^{10,18,19} In recent years, polyols containing cyclic structures^{3,8,20,21} have assumed growing importance in the technology of fire-retardant rigid PU foams. Polyols containing glucoside rings, for example, sucrose, α -methylglucoside-based polyols³ are the best known members of this group of compounds and for a long time applied. Interest in the use of aromatic-based polyols is on the increase. Included in this group are products obtained by alkoxyating phenol-formaldehyde, aniline-formaldehyde resins, Mannich condensation products of phenol, etc.^{8,22-25}

It was the purpose of our work to examine and compare the flammability and thermal properties of rigid PU foams modified by the introduction of additional aromatic rings, in addition to the phosphorus, to the chemical structure of the polyurethane. The modification was made using a phosphonate diol and suitable aromatic-based polyols. In our investigations we used some commercial products and some new synthesized polyols (Table 1).

EXPERIMENTAL

Polyols

Properties of the polyols used are summarized in Table 1. The polyol I used as a standard was a polyoxypropylenated sorbitol with a hydroxyl number of 492 mg KOH/g. The following aliphatic polyether polyols were used for preparation of standard series of cellular polyurethanes: Diol, Triol, and N-Triol with the same hydroxyl group content (Table I). These polyols were obtained by the

polyoxypropylenation of ethylene glycol, glycerol, and isopropanolamine, respectively.

Polyols III–VII contained different types of aromatic rings. Polyols III and IV were industrial products, other having been specially synthesized. The naphthalene rings containing polyols VI and VII had the highest content of aromatic rings of all the polyols studied (Table I). Owing to the different hydroxyl numbers of the cyclic polyols studied, a suitable amount of glycerol was added to obtain a hydroxyl number of 492 mg KOH/g, corresponding to that of the standard polyol I. In the case of the sucrose-based polyol II having a functionality of 8, a pentaerythriol polyol was added to obtain a functionality of 6, corresponding to the functionality of the standard polyol I. The phosphonate diol (P-Diol)—diethyl-*N,N*-bis(2-hydroxyethyl) aminomethylphosphonate—was used as the reactive fire retardant in all formulations.

Foam Preparation

The foams were prepared by a hand-mix technique using a conventional “one-shot” process based on 200 g polyol. The polyols, the fire retardant, blowing agent, a surfactant, and a catalyst were mixed; then they were combined with a polyisocyanate and vigorously stirred with a mechanical blender. The blend was then rapidly poured into a 27 × 27 × 20-cm wooden box and allowed to rise and gel. The buns were allowed to cure and age at ambient temperature for at least 2 weeks and then for 24 hr at 60°C before being sectioned into appropriately sized blocks for testing.

The foams with an increased content of cyclic structures were prepared according to the standard formulation given in Table II. Two standard series of cellular polyurethanes, i.e., with a variable nitrogen content ($C_c = \text{const}$, $M_c = \text{const}$) and with a variable crosslink density ($C_c = \text{const}$, $C_N = \text{const}$), were prepared according to formulations listed in Tables III and IV, respectively. Regression equations obtained for these formulations were as follows:

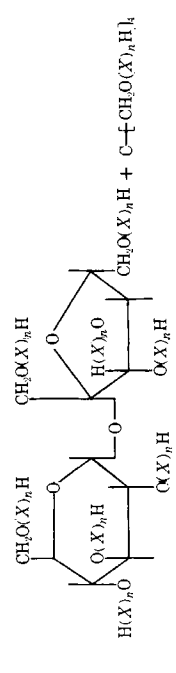
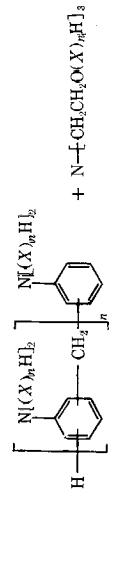
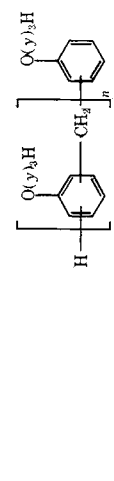
$$\begin{aligned} \text{OI} &= 19.4533 + 0.3575 C_N \quad \text{for } C_c = 30.94 \text{ wt } \% \\ &M_c = 462.2 \text{ wt } \% \end{aligned} \quad (1)$$

$$\begin{aligned} \text{OI} &= 20.1007 + 763.4 (1/M_c) \quad \text{for } C_c = 30.94 \text{ wt } \% \\ &C_N = 6.21 \text{ wt } \% \end{aligned} \quad (2)$$

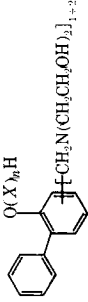
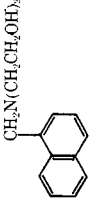

where OI is the oxygen index, % O₂; C_c is the cyclic structures content in polyurethane, wt %; C_N is the nitrogen content in polyurethane, wt %; and M_c is the molecular weight per crosslink (weight crosslinking equivalent). All quantities, i.e., C_c , C_N , C_P (phosphorus content in polyurethane), and crosslinking equivalent M_c were calculated only from the polyol and polyisocyanate contributions.

The isocyanate component used was polymethylene polyphenyleneisocyanate PAPI having an average functionality of 2.74, a weight equivalent of 134.5, a

TABLE I
Properties of Polyols

Polyol symbol	Chemical formulas ^a	OH No. (mg KOH/g)	Viscosity at 25°C (cP)	Polyol functionality	Nitrogen content (wt %)	Cyclic structure content (wt %)
P-Diol	$(C_2H_5O)_2P(O)CH_2N(CH_2CH_2OH)_2$	445	180	2	5.49	—
I	$H(X)_hOCH_2 \left[\begin{array}{c} CH_2 \\ \\ O(X)_hH \end{array} \right]_n$	492	5500	6	—	—
II	 $CH_2O(X)_hH + C \left[\begin{array}{c} CH_2O(X)_hH \\ \\ O(X)_hH \end{array} \right]_n$	490	22000	6	—	12.08
III	 $N(X)_hH + N \left[\begin{array}{c} CH_2 \\ \\ O(X)_hH \end{array} \right]_n$	490	6200	3.65	4.87	13.43
IV		250	3700	2.38	—	31.2

Fyrol 6
(Stauffer
Chemical Co.)
Propylan RF55
(Lankro
Chemicals Ltd.)
Propylan RF33
-67 wt %
(Lankro
Chemicals Ltd.)
Bypolet 45 - 33
wt % (Poland)
Propylan RF66
(Lankro
Chemicals Ltd.)
Isopol K1
(Poland)

V	 $\text{O}(X)_n\text{H}$ $\text{---}[\text{---}\text{C}_6\text{H}_4\text{---}\text{C}(\text{OH})\text{---}\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2]_{1+2}\text{---}$	390	250,000	4.38	3.76	24.2	(Institute of Polymer Chemistry, Zabrze, Poland)
VI	 $\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$ $\text{H}(X)_n\text{---O---CH}_2\text{CH}_2\text{---O}(X)_n\text{H}$	458	26,000	2	5.72	51.84	(University of Lublin and Institute of Polymer Chemistry, Poland)
VII	 $\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$ $\text{H}(X)_n\text{---O---CH}_2\text{CH}_2\text{---O}(X)_n\text{H}$	492	45,000	3.44	6.64	41.3	
Diol	$\text{H}(X)_n\text{---O---CH}_2\text{CH}_2\text{---O}(X)_n\text{H}$	492	300	2	—	—	(Institute of Polymer Chemistry, Zabrze, Poland)
Triol	$\text{H}(X)_n\text{---O---CH}_2\text{---CH---CH}_2\text{---O}(X)_n\text{H---O}(X)_n\text{H}$ $\text{O}(X)_n\text{H}$	492	480	3	—	—	
N-Triol	$\text{N}[(X)_n\text{H}]_3$	493	600	3	4.16	—	Propylan A350 (Lankro Chemicals Ltd.)


^a X = $\text{---CH}_2\text{---CH---O---}$; Y = $\text{---CH}_2\text{CH}_2\text{---O---}$.


TABLE II
Standard Formulation Used for Foams Preparation

Foam ingredient	Parts by weight
Cyclic polyol + glycerol (av. OH No. 492)	X
P-Diol (OH No. 445)	20
Standard polyol I (OH No. 492)	80-X
CFCl ₃ (Arcton 11) ^a	30
Silicone L 5340 ^b	1.5
DABCO R8020 ^c	0÷2
Polymeric polyisocyanate PAPI ^d ($k = 1.05$)	122

^a ICI.

^b Union Carbide Corp.

^c Air Products and Chemicals.

^d Upjohn Polymer Chemicals.

nitrogen content of 10.409 wt %, and an aromatic rings content of 56.305 wt %.

TABLE III
Formulation Used in Investigations of Nitrogen Content Influence upon Flammability of Rigid Polyurethane Foams Containing the Same Amount of Phosphorus

Foam ingredient	Parts by weight
P-Diol (OH No. 445)	20
N-Triol (OH No. 492)	X ^a
Triol (OH No. 492)	80 - X
CFCl ₃ (Arcton 11)	30
Silicone L5340	1.5
DABCO R8020	0.5-2.0
Polymeric polyisocyanate PAPI ($k = 1.05$)	122

^a X = 0, 10, 25, 40, 55, 70, 80.

TABLE IV
Formulation Used in Investigations of Influence of Rigid PU Foams Crosslink Density upon Their Flammability and Thermomechanical Properties

Foam ingredient	Parts by weight		
	A	B	C
P-Diol (OH No. 445)	20	20	20
Poliol I (OH No. 492)	80-X	—	80-Z
Triol (OH No. 492)	X ^a	80-Y	—
Diol (OH No. 492)	—	Y ^b	Z ^c
CFCl ₃ (Arcton 11)	30	30	30
Silicone L 5340	1.5	1.5	1.5
DABCO R 8020	2.0	2.0	2.0
Polymeric polyisocyanate PAPI ($k = 1.05$)	122	122	122

^a X = 0, 8, 16, 24, 40, 56, 80.

^b Y = 0, 20, 40, 60, 80.

^c Z = 0, 20, 40, 60, 80.

The cellular polyurethanes obtained had an apparent density of $31 \pm 2 \text{ kg/m}^3$ and all contained 1.1 wt % of phosphorus.

Description of Crosslinking

The mathematical description of crosslinking used was the average molecular weight per crosslink M_c .²⁶ M_c was calculated according to the formula

$$M_c = \sum W_i / \sum \frac{W_i(f_i - 2)}{E_i \cdot f_i} \quad (3)$$

where W_i is the the weight of the "ith" ingredient in the formulation, f_i is the functionality of the "ith" ingredient, and E_i is the weight equivalent of the "ith" ingredient (for polyols, $E = 56100/\text{OH No.}$; for polyisocyanates, $E = 4200/\% \text{ NCO}$).

Obviously, not all the functional groups may react in highly crosslinked systems of PU foams owing to the presence of unreacted ends, so that such descriptions are only valid for completely crosslinked networks.

Test Methods

Thermal Analysis

All thermogravimetric analyses were made using a Derivatograph MOM (Hungary). The following conditions were employed for each sample: sample weight, 100 mg; temperature range, 25–900°C; heating rate, 9 K/min; sample atmosphere, air. The thermal stability of rigid PU foams was characterized by the values T_{10} and T_{50} . T_{10} was the temperature of the 10% weight loss and T_{50} was the temperature of the 50% weight loss. The kinetic information on the decomposition of polyurethanes were obtained using the maximum point method developed by Fuoss²⁷ and illustrated by the equation

$$E_a = RT_{\max}^2 \left(\frac{dC}{dT} \right)_{\max} \left(\frac{1}{1 - C} \right)_{\max} \quad (4)$$

where E_a is the activation energy, kcal/mole; R is the gas constant, kcal/mole; T_{\max} is the temperature of maximum rate of weight loss, K; C is the degree of decomposition at the point T_{\max} ; and $(dC/dT)_{\max}$ is the rate of weight loss at the point T_{\max} , mg/K.

Thermomechanical Properties

The softening points of rigid PU foams were determined from thermomechanical measurements carried out according to the DIN 53424-1964 Standard.²⁸ Softening points T_s determined by that was the temperature corresponding to a 10% compression of the foam under a load of 0.0245 MPa (0.25 kg/cm²). The

specimens of $4.0 \times 4.0 \times 2.0$ cm were heated at a rate of 50 K/hr. The reported results are the average value from a total of six determinations for each formulation.

Flammability Tests

The foam samples were tested for flammability by the oxygen index method (according to ASTM D-2863) and for flame propagation by ASTM D-1692.²⁹ The oxygen index measurements were carried out on $15.0 \times 1.3 \times 1.3$ cm specimens using the Stanton Redcroft's FTA Flammability Unit. The flame propagation measurements used $15.0 \times 5.0 \times 1.3$ -cm specimens, as prescribed by the ASTM D-1692-68. The burned distances reported in this study were the average values from a total of ten determinations carried out for each formulation.

Smoke Test

Smoke measurements were carried out using the Stanton Redcroft smoke chamber (FTB Unit) in conjunction with the oxygen index apparatus (FTA Unit). The conditions were the same as those for the oxygen index test, except that the level of oxygen was set at a level higher by 1% than the critical oxygen index value for the sample concerned, in order to ensure a continuous burning. Five specimens, $15.0 \times 1.3 \times 1.3$ cm, were used for each foam. The percentage obscuration of the total light in the smoke chamber, $0.6 \times 0.6 \times 1.2$ m, was recorded continuously. The maximum optical density (OD_m) per gram of the material burned was measured³⁰

$$OD_m = \log_{10}(100/T_m)/(w_0 - w_r) \quad (5)$$

where w_0 is the initial weight of specimen, g; w_r is the final weight retention of specimen, g; and T_m is the minimum transmission, i.e., 100 minus percentage of maximum obscuration, %. The char residue (in wt %) of specimens burned during the smoke measurements was also noted.

Calculation of Regression Coefficients

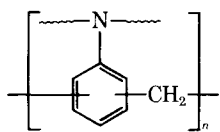
The regression coefficients were calculated using the Wang minicomputer. The calculations were carried out by the least-squares method employing programs from the Wang Library.

RESULTS AND DISCUSSION

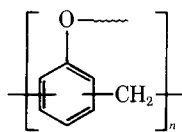
Changes in the Chemical Structure

The aromatic polyols used in our investigations differed in the type of aromatic rings in the way the hydroxyl groups were linked with the ring and also in their functionality, i.e., in the content of hydroxyl groups in a polyol molecule. The polyols used contained the following aromatic rings:

substituted benzene rings in the form of poly(phenylenemethylene) structures:

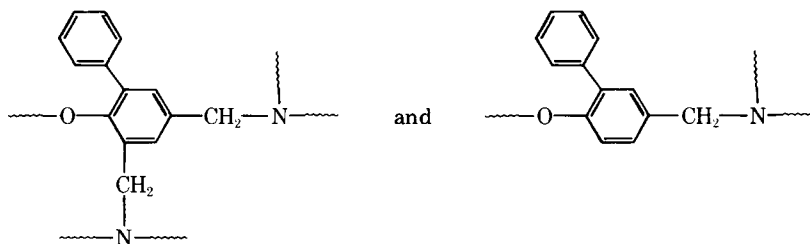


Polyol III



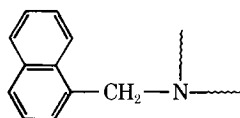
Polyol IV

substituted biphenyl rings (a mixture):



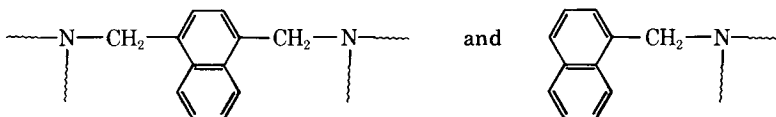
Polyol V

naphthalene mono-substituted rings:



Polyol VI

a mixture of mono- and di-substituted naphthalene rings:



Polyol VII

For the sake of comparison, the cyclic polyol II containing glucoside rings (polyoxypropylenated sucrose) was included in this study (Table I). Each cyclic polyol was used for obtaining a series of rigid PU foams, differing in the content of that particular cyclic polyol in an initial polyhydroxyl mixture (Table II). In this way some quantitative information about the influence of the content of cyclic structures in polyurethane foams on their properties was obtained.

The lower functionality of the aromatic polyols in comparison with that of the standard polyol I resulted of course in a decrease of the crosslink density in the cellular polyurethane obtained (Fig. 1). Polyols IV and VI were obviously found to give the highest decrease of crosslinking, i.e., the highest values of M_c were obtained (Fig. 1). The highest increase in the content of cyclic groups (about 48 wt %) was obtained for PU foams based on the polyol VI. The content of aromatic rings in the latter foams was about 56% higher than that of the standard polyurethane prepared from the aliphatic polyol I and from the aromatic polyisocyanate PAPI. The aromatic polyols III and V–VII resulted in an increase of the nitrogen content in the polyurethanes.

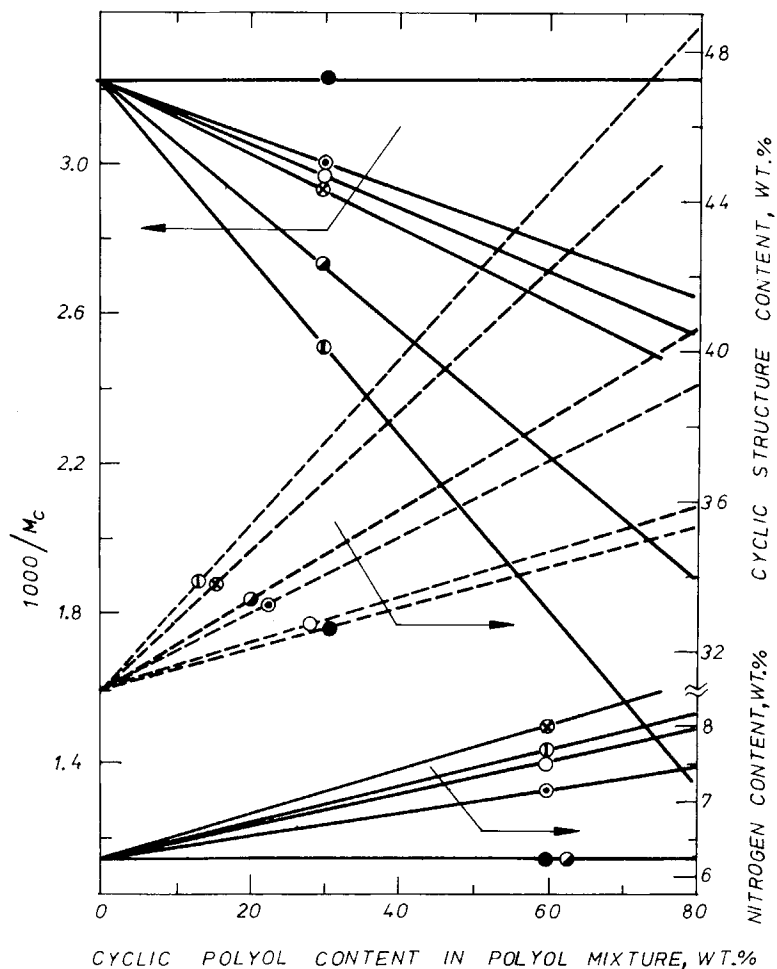


Fig. 1. Effect of II-VII [polyol (●) II, (○) III, (⊙) IV, (⊕) V, (⊖) VI, (⊗) VII] cyclic polyol content in polyol mixtures on degree of crosslinking ($1000/M_c$) of rigid PU foams and on nitrogen and cyclic structures content in PU foams.

Thermal Decomposition

The course of thermal decomposition in air of the investigated rigid PU foams was typical.^{31,32} With increasing temperature the PU foams decomposed in two stages into volatile products (Fig. 2). The first occurred at 230–380°C and accounted for the loss of approximately 40% of the polymer weight. The remainder of the foam decomposed in the second stage at 400–700°C. The presence of C—N bonds of low thermal stability in some aromatic polyols suggested the possibility of considerably decreasing the initial decomposition temperature (T_{10}) of rigid PU foams obtained therefrom. However, it was found that cellular polyurethanes obtained from these polyols began to decompose at temperature only slightly below that of the standard polyurethane from the polyol I (Fig. 3). It was observed that the lowest decomposition temperatures (T_{10}) were obtained for polyurethanes with the highest nitrogen content (Fig. 3). The polyurethanes obtained from the sucrose-based polyol II and the nitrogen-free, phenol-form-

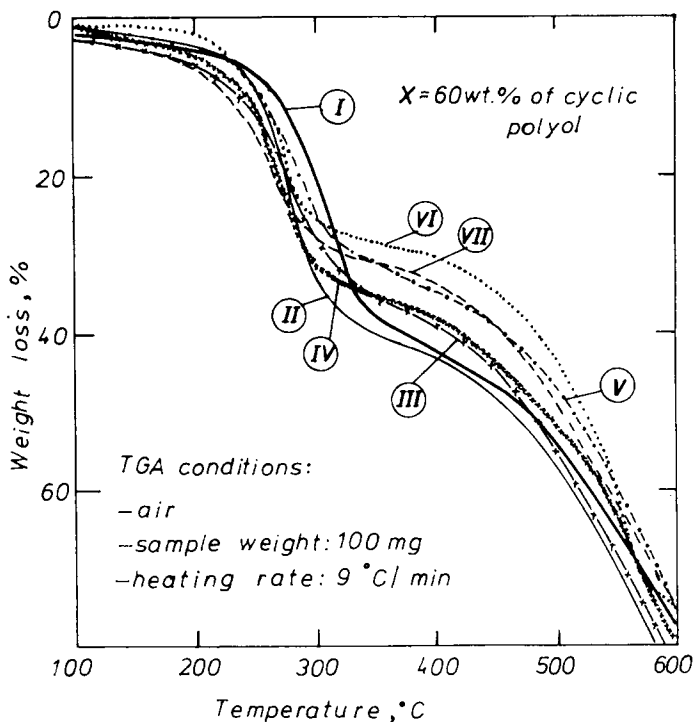


Fig. 2. Comparison of the course of rigid PU foams thermal decomposition in air. The foams were obtained from polyols I-VII according to the standard formulation given in Table II. TGA conditions: air; sample weight, 100 mg; heating rate, 9°C/min.

aldehyde resin-based polyol IV were found to undergo the smallest change in the first stage of decomposition.

All aromatic polyols were found to bring about a considerable decrease of the activation energy (E_a) of the decomposition process of cellular polyurethanes obtained from them (Fig. 4). Especially low values of E_a were found for the PU foams obtained from polyols V-VII. In extreme cases, the activation energy E_a reached a value of about 20 kcal/mole (Fig. 4). The activation energy of decomposition of polyurethanes prepared from the sucrose-based polyol II was on the same level as that of the standard polyurethane (Fig. 4).

Although polyurethanes obtained from the aromatic polyols were less thermally stable at temperatures below 350°C than the standard foam, at temperatures above 350-500°C these PU foams were found to form a higher weight fraction of char (Figs. 2 and 3). The extent of this effect was mainly influenced by the quantity of aromatic rings introduced into the polyurethane macromolecules. A high degree of crosslinking was also found to have a favorable influence on increasing the weight residues in the second stage of decomposition to be observed on the TGA curves. Thus, for example, the polyurethanes obtained from polyol IV had temperatures of the 50% weight loss identical to those of polyurethanes obtained from polyol III which had a lower degree of aromaticity and a higher degree of crosslinking owing to the higher functionality of polyol III (Table I, Fig. 3). At temperatures above 600°C the TGA curves were almost identical for all investigated cellular polyurethanes (Fig. 2).

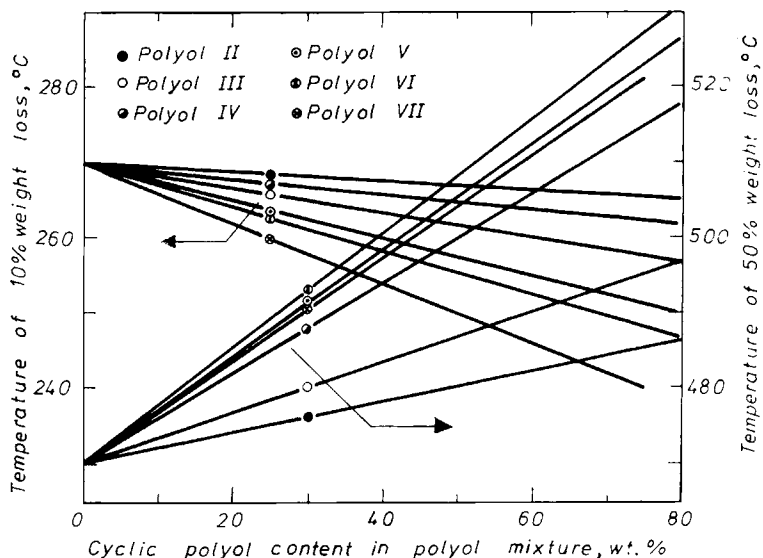


Fig. 3. Effect of II-VII cyclic polyol content in polyol mixtures on temperature of 10 and 50% weight loss during the rigid PU foams thermal decomposition in air. Symbols as in Fig. 1.

Thermomechanical Properties

Changes of thermomechanical properties (indicated by the T_s values) of the investigated rigid PU foams were not consistent with the observed changes of their thermal stability and degree of crosslinking. Although a majority of the investigated cellular polyurethanes exhibited lower decomposition temperatures (Fig. 3) and lower degrees of crosslinking (Fig. 1) than the standard polyurethane obtained from polyol I, the softening temperatures of these polyurethanes were

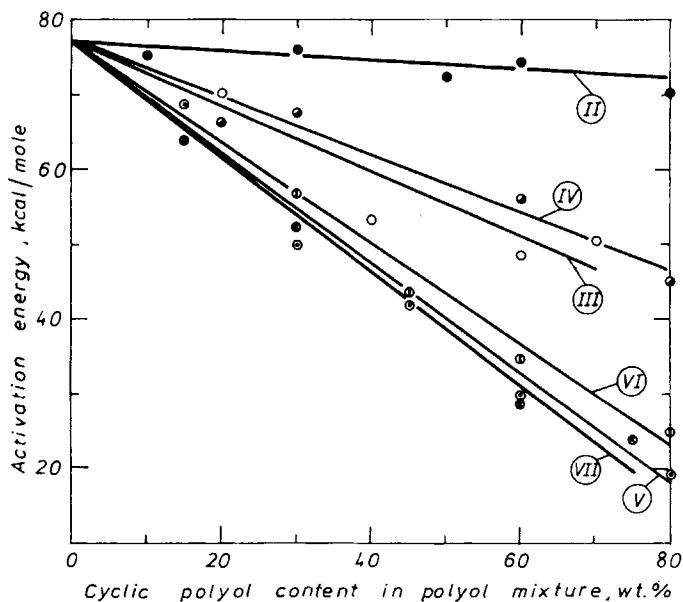


Fig. 4. Dependence of the activation energy of the rigid PU foams thermal decomposition process in air on the II-VII cyclic polyol content in polyol mixtures.

not found to have been decreased in all cases (Fig. 5). Apart from the degree of crosslinking, the type and quantity of aromatic rings, as well as the way they were built into the polyurethane backbone, were found to influence the thermomechanical properties of the rigid PU foams investigated.

The use of polyol II containing glucoside rings with a functionality corresponding to the standard polyol I did not bring an evident improvement of the thermomechanical properties of PU foams. This may be thought to indicate that glucoside rings have only a very small stiffening effect. The constant density of crosslinking of these polymers (Fig. 1) was hence concluded to be the decisive factor affecting the practical invariability of the softening points of the foams obtained from polyol II.

A considerable stiffening effect resulting from the introduction of aromatic rings into the polyurethane backbone was found to exist (Fig. 5). This effect may readily be seen in Figure 6, where the changes of softening points (T_s) of PU foams are presented as a function of the degree of crosslinking ($1000/M_c$). Curve I represents the change of the T_s of a series of rigid PU foams obtained from mixtures of aliphatic polyether polyols having different functionalities and the same hydroxyl number. These foams were prepared according to the formulation given in Table IV and possessed the same phosphorus content ($C_p = 1.1$ wt %) as all investigated polyurethanes. For the same crosslink density ($M_c = \text{const}$), PU foams obtained from aromatic polyols had higher softening points than foams obtained from aliphatic polyols, as shown by curve I in Figure 6. The biphenyl rings from polyol V and substituted benzene rings in the form of poly(phenylenemethylene) structures from polyol III introduced into the polyurethane backbone were found to most advantageously increase the softening

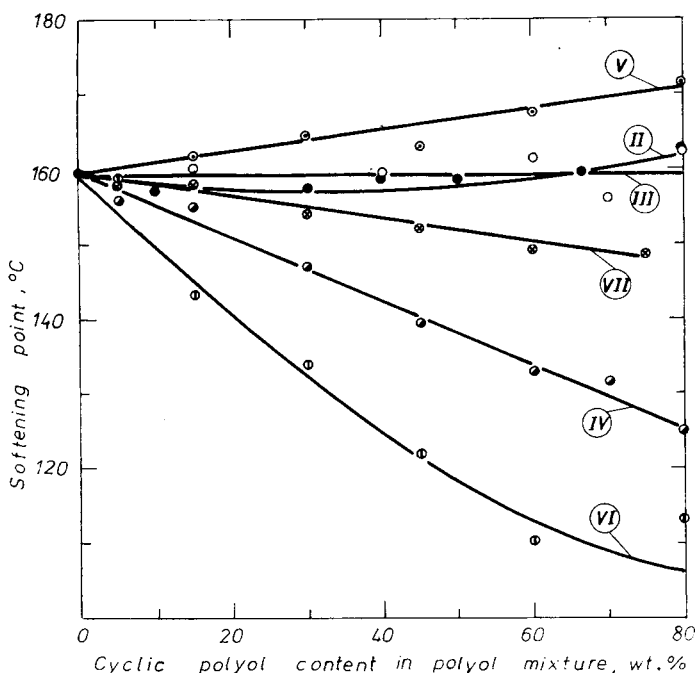


Fig. 5. Relationship between softening points of the rigid PU foams and the II-VII cyclic polyol content in polyol mixtures.

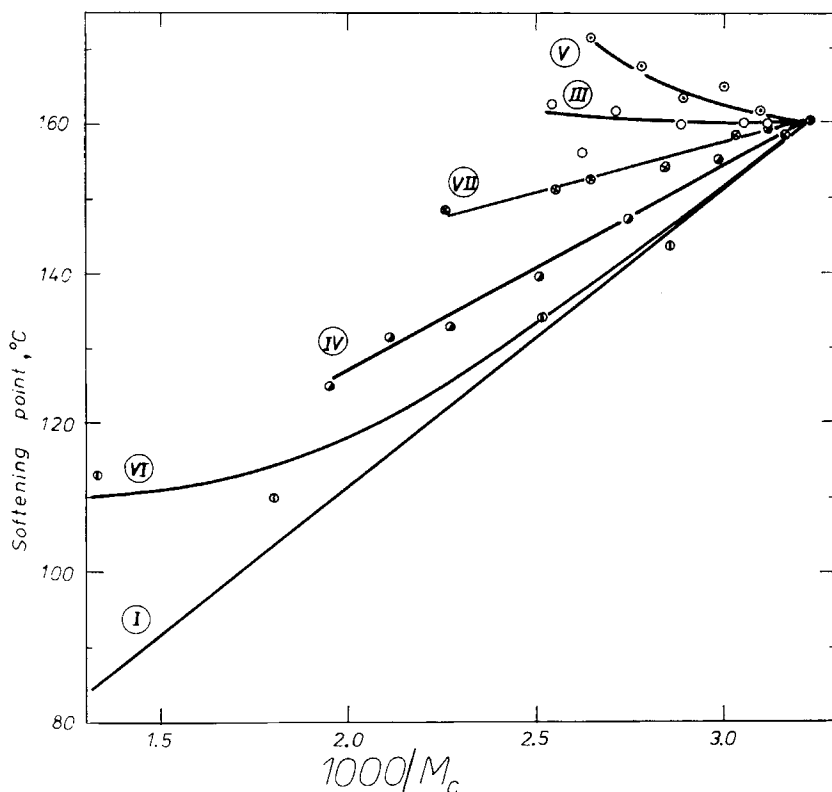


Fig. 6. Relationship between degree of crosslinking ($1000/M_c$) and softening points of rigid PU foams obtained from polyols I and III-VII.

points. An abnormal decrease of the softening points of PU foams obtained from compositions containing polyol IV was observed. This was probably due to the presence of mono-functional compounds in that polyol.

A relatively small stiffening effect was produced by the introduction of naphthalene rings into a polyurethane "molecule" in a pendent position (from polyol VI). A more pronounced stiffening effect owing to the presence of these rings was observed for polyurethanes with a very low degree of crosslinking (Fig. 6). When introduced into the polyurethane backbone (PU from polyol VII), the naphthalene rings, similar to biphenyl and benzene rings in the form of poly(phenylenemethylene) structures, were found to produce a considerable stiffening effect and increase of the softening points of PU foams, as compared with the softening points of foams prepared from aliphatic polyols and having the same crosslink density (Fig. 6).

Flammability

Flame Propagation

Flammability characteristics of the PU foams, as evaluated by the ASTM D-1692-68 test method, are given in Figure 7. The burned length was considered to provide a measure of changes in the performance of PU foams. All the foams investigated were classified on the basis of that test as self-extinguishing (SE)

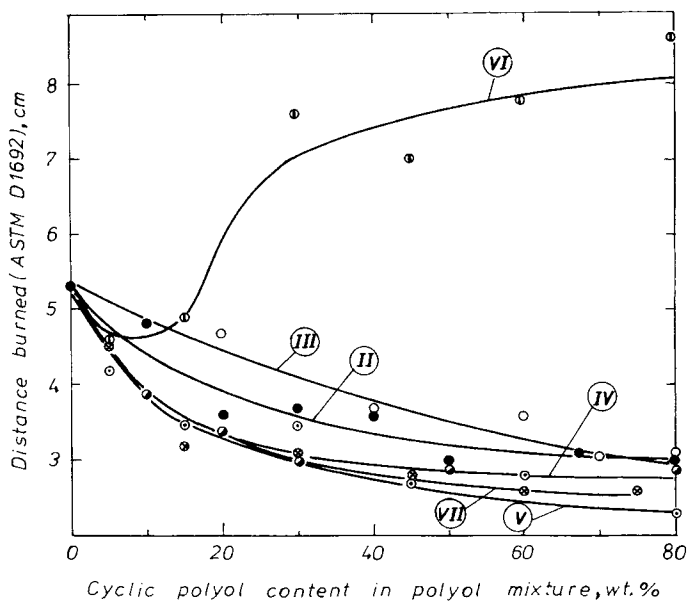


Fig. 7. Effect of II-VII cyclic polyol content in polyol mixtures on surface flammability of the rigid PU foams.

foams. These measurements revealed that an increase of the content of a cyclic polyol in the polyol mixture resulted in a decrease of the burned distance of the PU foams, except for the foams obtained from polyol VI. The influence of the cyclic polyols IV, V, and VII on the surface flammability (ASTM D-1692) was essentially the same if their content in the polyol mixture had not exceeded the level of 40 wt % (Fig. 7). Differences in the effect of individual polyols on the flame propagation became pronounced at higher concentrations of cyclic polyol in the mixture used.

PU foams with the lowest flame propagation were obtained from the biphenyl rings containing polyol V. In marked contrast to all other polyols studied, diol VI containing naphthalene rings in a pendent position was not found to decrease the surface flammability of the PU foams produced. Unexpectedly, in spite of the highest concentration of aromatic rings in these polyurethanes, their burned length was observed to have risen (Fig. 7). This effect may be due to the lowest degree of crosslinking of those foams and the low thermal stability of the aliphatic C—N bonds, which facilitates the evolution of inflammable aromatic fragments (a fuel) during polyurethane combustion. The smallest effect on the burned extent was found to exist for rigid PU foams prepared from polyol III and from the sucrose-based polyol II (Fig. 7). On the other hand, these polyols had the lowest concentration of cyclic structures (Table I).

In the Table V the surface flammabilities (according to ASTM D-1692) of rigid PU foams containing the same quantities (4.5 wt %) of additionally introduced cyclic structures are compared. Although the influence of the foam crosslink density and nitrogen on the surface flammability was not considered in Table V, it may be stated that the same cyclic structures responsible for the greatest stiffening effect in the previously mentioned thermomechanical measurements, i.e., biphenyl rings from the polyol V, resulted in the most advantageous decrease

TABLE V
Comparison of Surface Flammability (ASTM D1692) of Rigid Polyurethane Foams Containing the Same Amount of Additionally Introduced Cyclic Structures

Polyol symbol	X_E (wt %) ^a	Burn length (cm)
II	80	3.1
III	71.5	3.1
IV	35.5	3.0
V	41.5	2.7
VI	19	5.7
VII	23	3.2

^a X_E is the cyclic polyol content in polyol mixture (according to the standard formulation in Table II), equivalent to the same quantity of cyclic structures introduced into polyurethane.

of the flame propagation of rigid PU foams. Conversely, the smallest decrease of flame propagation was found for the mono-substituted naphthalene rings from polyol VI.

Ease of Ignition

The ease of ignition of PU foams was expressed in our investigations in terms of the oxygen index. It was found to change with the content of cyclic polyols in the polyol mixture (Fig. 8). A linear correlation between the foam oxygen index (OI, % O₂) and the cyclic polyol content of the polyol mixture (X , wt %) was obtained:

$$OI = A + B X \quad (6)$$

The regression coefficients A and B are given in Table VI. Polyol VII (a mixture of di- and mono-substituted naphthalene derivatives) and polyol V, containing the biphenyl rings, had the greatest effect on increasing the foam oxygen index. The smallest effect was found for the glucoside rings containing polyol II. Polyol

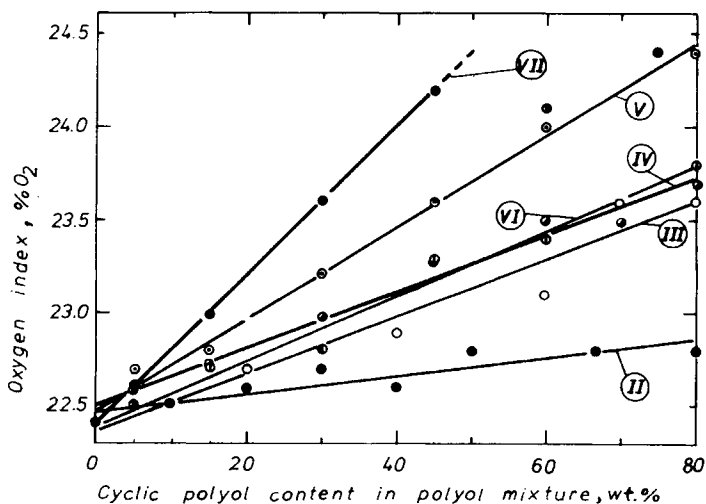


Fig. 8. Effect of II-VII cyclic polyol content in polyol mixtures on ease of ignition (OI) of the rigid PU foams.

TABLE VI
Regression Coefficients of the Equation $OI = A + BX^a$

Polyol symbol	A	$B \times 10^3$
II	22.47	4.95
III	22.36	15.3
IV	22.52	15.12
V	22.47	24.8
VI	22.4	17.4
VII	22.4	40.0

^a OI is the oxygen index, % O₂; X is the cyclic polyol content in polyol mixture (wt %) according to the standard formulation in Table II.

VI with the highest content of naphthalene rings and the lowest functionality was found to produce an increase of the oxygen index of PU foams almost the same as that produced by the polyol III containing nearly four times less cyclic structures but having a higher functionality (Fig. 8).

In order to describe the influence of various units of the polyurethane chemical structure in PU foam upon its flammability, expressed in terms of its oxygen index, the following linear equation was proposed:

$$OI = B_0 + B_1C_c + B_2C_N + B_3(1/M_c) \quad (7)$$

where OI is the PU foam oxygen index, % O₂; C_c is the content of cyclic structures in the polyurethane, wt %; C_N is the polyurethane nitrogen content, wt %; and M_c is the molecular weight per crosslink calculated according to eq. (3). The data obtained from testing two standard series of foams were used to calculate the regression coefficients, namely the results of tests of the influence of the polyurethane nitrogen content on its flammability (Table III) and that of the foam crosslink density on its flammability (Table IV). The values of regression coefficients in eq. (7), calculated by the least-squares method, are given in Table VII. A good correlation of the proposed equation with experimental data was obtained. The thus obtained values of regression coefficients $B_2 = 0.305$ – 0.323 and $B_3 = 708$ – 786 , characterizing, respectively, the influence of the nitrogen content and the crosslink density on the oxygen index of PU foams, did not virtually differ from the values of coefficients obtained from the investigations of the standard foam series: $B_2 = 0.357$ [eq. (1)] and $B_3 = 763$ [eq. (2)]. The values of coefficient B_1 indicated that biphenyl rings from polyol V had the greatest effect on the flammability of rigid PU foams (expressed in terms of the oxygen index), with the glucoside rings from polyol II (Table VII) having influenced the flammability of the PU foams to the smallest extent. Values of the coefficients B_1 obtained for aromatic rings are compared in Table IX with those found for the glucoside rings. The introduction of aromatic rings into the polyurethane backbone was found to increase the oxygen index of PU foams two times more than the glucoside rings introduced into PU structure. Naphthalene rings introduced into the polyurethane in a pendent position however, were found to decrease the PU foam flammability by only 30% more than did the glucoside rings.

Smoke Evolution

Smoke-development properties of rigid PU foams obtained from the polyol compositions containing 60% of different cyclic polyols and of respective standard foams are compared in Table VIII. A considerable increase of smoke evolution during the combustion of PU foams with increased degree of aromaticity was expected. However, an increase of smoke evolution in relation to the standard foam from the aliphatic hexol I was observed only for foams obtained from polyols II, IV, and VII. In spite of the considerable content of aromatic rings in polyurethanes obtained from polyols III and V, these cellular polymers were found to evolve less smoke than the standard foam. The presence of naphthalene rings in the polyurethane backbone (from polyol VII) produced a considerable increase of smoke evolution during the burning process. On the contrary, polyurethanes containing naphthalene rings (from polyol VI) in the pendent position to the polyurethane backbone did not evolve so much smoke as did the polyurethanes obtained from the polyol VII.

Based on the results listed in Table VIII, there was every reason to believe that an increase of the nitrogen content in polyurethanes and a decrease of the degree of crosslinking would result in a reduction of smoke evolution, while an increase of the content of cyclic structures in polyurethanes would act in an opposite direction. Hence, the observed behavior of rigid PU foams in smoke evolution tests could be attributed to the interaction between these two opposite effects. The characteristic influence of the foam nitrogen content on decreasing the smoke evolution appeared to be related to the quantity of char remaining after combustion (with the exception of the polyurethane from naphthalene-based polyol VII). The foams evolving large amounts of smoke during combustion produced most frequently large amounts of char. An increase of the nitrogen content in polyurethane foams was found to decrease the amount of char formed.

CONCLUSIONS

The chemical modification of rigid polyurethane foams using the aromatic polyols with a phosphorus-containing polyol made it possible to obtain PU foams with considerably improved fire retardance and heat resistance properties, greatly exceeding those of the cellular PU based on aliphatic polyols of high functionality.

A distinct stiffening effect resulting from the addition of aromatic rings into the polyurethane backbone was found to exist. This effect was reflected by the improved thermomechanical properties of cellular polyurethanes with a higher content of aromatic structures, as compared with the thermomechanical properties of polyurethanes obtained from aliphatic polyols and having the same crosslink density. Moreover, thermal stability of crosslinked polyurethanes was not found to have a distinct influence on their thermomechanical properties. The following factors were found to have a pronounced effect upon the thermomechanical properties of the investigated PU foams: the crosslink density and the type and quantity of cyclic structures additionally introduced.

The factors mentioned above, and the PU foam nitrogen content, basically influenced the flammability characteristics of the rigid PU foams containing a constant amount of phosphorus (1.1 wt %). Cellular polyurethanes with the

TABLE VII
Regression Coefficients of Equation (7)

Polyol symbol	B_0	B_1	B_2	B_3	CD ^a	CMC ^b	SEE ^c
II	19.6953	0.08964	—	—	0.9993	0.9996	0.0039
III	11.7841	0.21038	0.30471	711.87	0.9896	0.9948	0.0668
IV	13.1294	0.22663	—	743.57	—	—	—
V	10.5302	0.24151	0.32293	783.71	0.9977	0.9987	0.0421
VI	14.6495	0.11510	0.31708	707.89	0.9965	0.9983	0.0500
VII	12.4298	0.18534	0.30884	757.25	0.9954	0.9977	0.0533
N-Triol	19.4533	—	0.3575	—	—	—	—
Triol	20.1007	—	—	763.4	—	—	—

^a Coefficient of determination.

^b Coefficient of multiple correlation.

^c Standard error of estimate.

$C_N = 6.21; M_c = 310.2$

$C_N = 6.21$

$C_c = 30.94; M_c = 462.2$

$C_c = 30.94; C_N = 6.21$

TABLE VIII
 Maximum Optical Density and Weight Retention after Burning of Rigid Polyurethane Foams Prepared from Polyol Mixtures Containing 60 wt % of Cyclic Polyols

Polyol symbol	Type of additionally introduced cyclic structure	C_c^a (wt %)	C_N^b (wt %)	M_c^c	OI (% O ₂)	OD _m ^d (g ⁻¹)	m_r^e (wt %)
I	—	30.94	6.21	312.3	22.5	1.15	12.8
II	glycoside	34.21	6.21	312.3	22.8	1.51	19.4
III	poly(phenylenemethylene)	34.57	7.53	368.8	23.1	0.84	13.2
IV	poly(phenylenemethylene)	38.10	6.21	446.4	23.5	1.42	29.5
V	biphenyl	37.01	7.16	359.6	24.0	1.03	17.0
VI	naphthalene	44.17	7.67	555.5	23.4	1.14	13.7
VII	naphthalene	42.11	8.01	407.7	24.1	2.12	26.9
N-Triol	—	30.94	7.71	462.2	21.9	1.04	10.5
Triol	—	30.94	6.21	462.2	21.3	1.08	12.9

^a Cyclic structures content in polyurethane, wt %.

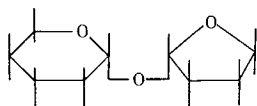
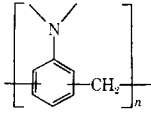
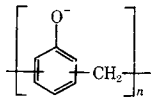
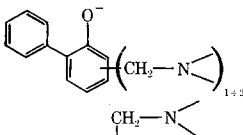

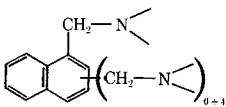
^b Nitrogen content in polyurethane, wt %.

^c Molecular weight per crosslink.

^d Maximum optical density.

^e Weight retention after burning.

TABLE IX
Relative Values of B_1 Coefficient Indicating Influence of Different Aromatic Rings upon the Flammability of Rigid PU Foams Measured by OI Method

i	Type of additionally introduced cyclic structure	$(B_1)_i/(B_1)_{II}$
II		1
III		2.35
IV		2.53
V		2.69
VI		1.28
VII		2.07

highest fire resistance were obtained from polyols containing disubstituted naphthalene rings (polyol VII) and biphenyl rings (polyol V). The improved fire performance of these polyurethanes was shown to be related directly to their thermal stability. The obtained regression equations showed the biphenyl rings to have the greatest effect on the increase of polyurethane fire resistance. An advantageous interaction between the foam nitrogen content and its aromatic rings content during the combustion of PU foams was observed to decrease evolution of smoke.

The most advantageous set of properties of rigid PU foams was obtained by introducing biphenyl rings into the polyurethane backbone using as a polyol component the polyoxypropylenated Mannich based obtained from *o*-phenylphenol.

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