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Dibenzyl Structures in Macromolecular Chains

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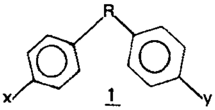
ABSTRACT

The dibenzyl system represents the simplest biaromatic system able for rotational isomerism which allows multiple spatial arrangements, with different reciprocal influences of the functional groups situated in the two rings. The possibility of introducing this system to a macromolecular chain and its influence on some properties of the polymer obtained was studied of the cases of polyurethanes, polyureas, poly(parabanic acids), and polyimides. In the case of copolyurethanes, made using 4,4'-dibenzyldiisocyanate, an unexpected phenomenon was the possibility of disproportionation of some homogeneous systems by two parallel polyaddition processes which progress in parallel in two places, i.e., solution and suspension, leading to different polymers. The process is probably governed by the lower entropy of the crystalline polymer which appears in suspension. Some practical applications of polymers with dibenzyl structures are presented.

Among the multitude of macromolecular structures there is a series which starts from biaromatic intermediates of type 1.



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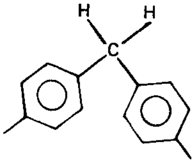

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$a^1 = 1.32$ $a^4 = 1.35$

$a^2 = 1.37$ $a^5 = 1.38$

$a^3 = 1.37$ $a^6 = 1.33$

$\measuredangle\ a^7 a^7 = 119°$

Crystal C_2 group symmetry

FIG. 1. The geometry of the diphenylmethane derivatives.

It has been reported that such macromolecular compounds contain radicals R = $-CH_2-$, $-O-$, $-S-$, $-SO_2-$, and $-C(CH_3)_2-$.

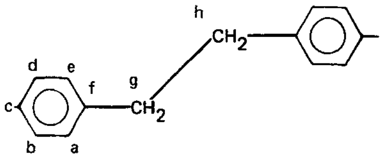
In all these cases the phenyl radicals are spaced only one atom apart. Each half of the molecule is planar with the benzene ring rotated around the C–C para position axis by an angle in an opposite sense from a hypothetical planar configuration.

In diphenylmethane derivatives, for example, the geometry of the molecule is as shown in Fig. 1 [1].

The introduction of these structures on the main backbone of a long chain molecule compels the chains to adopt a special conformation.

The data presented in this paper deal with a less studied system—dibenzyl—in which the two phenyl rings are separated by an ethylenic bridge. This represents the simplest biaromatic system that is able to have rotational isomerism.

It is known [2] that in the solid state, in the absence of substituents, the two aromatic rings of dibenzyl are in parallel planes. The angle between the plane and the $-CH_2-CH_2-$ linkage is 70.5°. The interatomic distances are given in Fig. 2.



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a = 1.37 e = 1.39

b = 1.38 f = 1.37

c = 1.38 g = 1.52

d = 1.37 h = 1.51

$\measuredangle$ gh = 112° 4″

Crystal C_i group symmetry

FIG. 2. The geometry of the dibenzyl derivatives.

To particularize this situation, a series of intermediates with two identical functional groups situated in different rings were synthesized: 2,2'-, 2,4'-, and 4,4'-diaminodibenzyl as well as 2,2'-, 2,4'-, and 4,4'-dibenzyldiisocyanate.

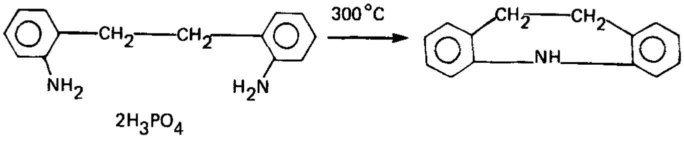
The behavior and some properties of these compounds for the synthesis of different classes of polymers, polyureas, poly(parabanic acid)s, polyimides, and polyurethanes, were studied.

Although these investigations are only beginning, and we have not been able to use many modern techniques of investigation, it is possible to draw some conclusions that illustrate the uniqueness of the dibenzyl system.

REACTIVITY OF THE FUNCTIONAL GROUPS

Theoretically, it is expected that the reactivity of the functional groups situated in different rings will not be influenced to the same degree due to the fact that the ethylenic bridge interrupts the electronic effects between the two aromatic rings. On the other hand, this does not exclude a possible spatial interaction due to the possible proximity of the two functional groups through rotation of the ethylenic bridge, especially in the case of 2,2'-disubstituted derivatives.

In this case the influence can be so great theoretically as to lead to a specific reaction similar to the case of thermal cyclization of the 2,2'-diaminodibenzyl derivatives to dihydroazepine (iminodibenzyl) [3]



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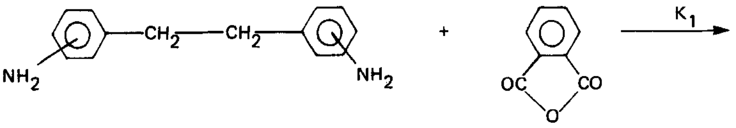
In order to estimate the reactivity of the amino groups from diaminodibenzyl (DAB) isomers, their capacity to react with both phthalic anhydride and pyromellitic dianhydride was investigated.

Taking into account the increased reaction speed, we used a technique which follows the results of the competitive reactions between DAB and phthalic anhydride (mol/mol).



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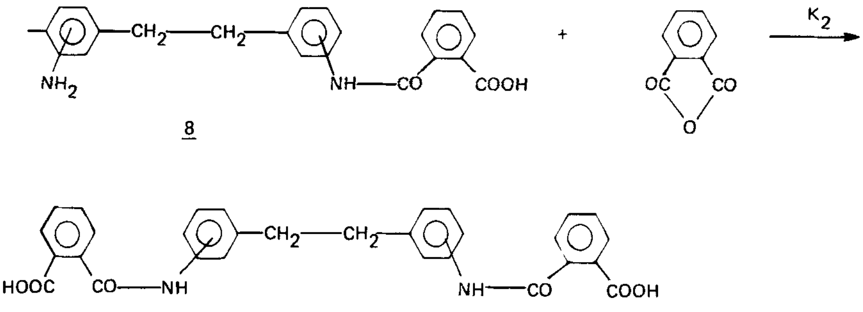

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Under the hypothesis that the two aromatic rings do not interact, $K_1 = 2K_2$ (because in Compound 8 the number of aminic group is half compared with 6).

Note for simplification the Product 6 with A and 7 with B:

$$A + B \xrightarrow{K} AB$$

$$AB + B \xrightarrow{\frac{1}{2}K} BAB$$

When we start from the initial molar ratio A/B = 1, as a result of these reactions we obtain three species of products, A, AB, and BAB, in the final mixture.

In the final situation the following equalities between molar concentrations are evident:

$$[A]_{final} = [BAB]_{final}$$

$$2[BAB]_{final} + [AB]_{final} = 1$$

From these relations it is concluded that it is sufficient to establish the final molar concentration of the unreacted diamine $[A]_{final}$ to know the composition of the entire system.

To establish the final calculated composition under the above mentioned conditions by using a calculus of probability for the case of equal reactivity of the aminic groups, we determined a theoretical final composition of 0.25 mol DAB, 0.5 mol Product 8, and 0.25 mol Product 9.

By analyzing the real final composition of the system with the aid of high pressure liquid chromatography (HPLC), we succeeded in determining the unreacted DAB concentration.

TABLE 1. Final Molar DAB Concentrations (% from initial concentrations)

Diamine	DMF	NMP
4,4'-DAB	0.27	0.23
2,4'-DAB	0.16	0.18
2,2'-DAB	0.306	0.31

Synthesis occurs in the usual solvents for polyimide synthesis, dimethylformamide (DMF) and N-methyl-2-pyrrolidone (NMP). The results are summarized in Table 1.

The 4,4'-DAB situation is normal. There is some solvent influence: DMF is favorable for the second step reaction and NMP for the first one.

The lower values found in the case of 2,4'-DAB show that the basicity of the amine group from the para position is greater than that from the ortho position. This fact is favorable for monoreacted compound formation.

The larger values obtained in the case of 2,2'-DAB compared to the calculated ones show a deviation from the initial supposition of $K_1 = 2K_2$. The reaction of the second aminic groups with phthalic anhydride takes place faster than that of the first one.

In this case there are intense solvatation effects. When 2,2'-DAB is dissolved with gentle heating in NMP, an insoluble complex is formed at room temperature. ATG analyses of these crystalline products show an NMP content of 68% (Fig. 3).

As seen from Table 1, although DMF does not separate the insoluble complex, it probably does exist in solution, leading to a course of reaction similar to the case of NMP solvent.

The higher reaction speed of the second amine group of 2,2'-DAB can be explained by the supposition that in the monoreactioned Compound 8 the amine group is not as strongly engaged in the solvent complex as in the case of pure DAB.

In a second series of investigations [4] we studied the reactivity of the functional groups of another valuable compound: 4,4'-dibenzyldiisocyanate (4,4'-DBDI).

The rate constants of the reactions of diisocyanates with n-butanol were determined by using the IR spectrophotometric method of Bailey [5] (Table 2).

The rate constant of the consecutive reactions K_1 and K_2 were determined by the time ratio method developed by Frost and Pearson [6].

The kinetic data indicate that the overall reactivity of a diisocyanate, and its decrease as the reaction progresses, are determined by two

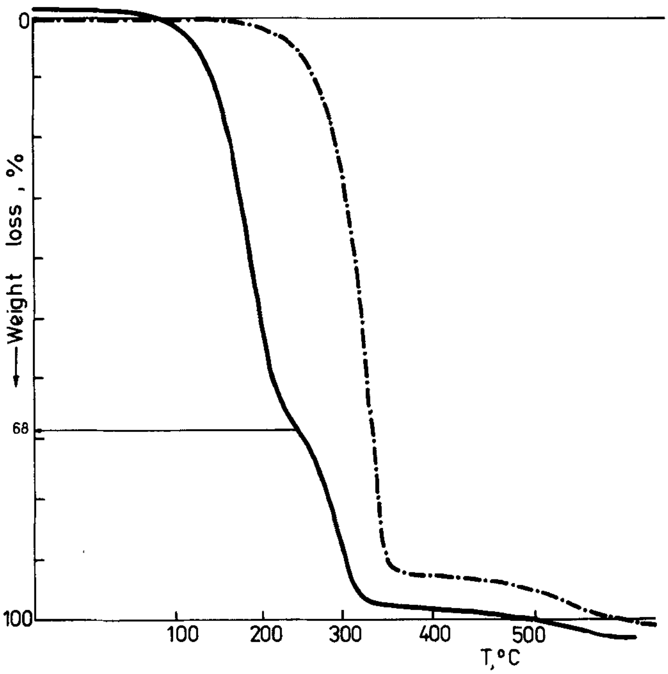


FIG. 3. Thermogravimetrical analysis of the 2,2'-diaminodibenzyl (-·-) and 2,2'-diaminodibenzyl-N-methyl-2-pyrrolidone complex (—).

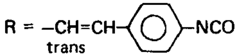
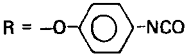
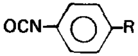
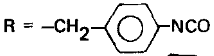
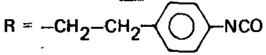
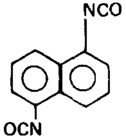
factors: (a) the electron attracting power (electrophilicity) of the radical attached to the isocyanate groups and (b) the interaction between the two functional groups.

The initial reactivity of a diisocyanate is similar to that of a monoisocyanate substituted by an activating group. As soon as one isocyanate group has reacted, the remaining isocyanate group has a reactivity similar to that of a monoisocyanate substituted by a urethane group. The urethane group has only a very mild activating effect, much less than that of the isocyanate group.

For 4,4'-stilbene diisocyanate (I) and for 4,4'-diisocyanatodiphenyl ether (II), the extended conjugated systems through the stilbene C=C double bond and through the unshared electron pairs of the oxygen atom, respectively, have an activating effect on the reaction center. The rate constants are subsequently greater than that of phenylisocyanate. On the other hand, the opposite influence of the substituent groups is possible, so that the rate constants decrease as the reaction passes approximately 50% completion.

In the case of methylene-bis-(4-phenylisocyanate) (III) and of 4,4'-dibenzyl diisocyanate (IV), the activating influence of the isocyanate

TABLE 2. *Effects of Substituents on the Reactivities of Diisocyanates with n-Butanol*

No.	Isocyanates	Substituent	$K_1 \times 10^2$ min^{-1}	$K_2 \times 10^2$ min^{-1}	K_1/K_2	$K_1{}^*$ relative	$K_2{}^*$ relative
I			7.34	3.64	2.01	3.65	1.81
II			5.47	2.43	2.24	2.72	1.20
III			4.56	4.51	3.02	2.22	0.75
IV			3.72	1.31	2.67	1.85	0.69
V		R = H	2.01	-	-	1	
VI		—	3.54	1.15	3.06	1.76	0.5

and urethane groups, respectively, is transmitted by an inductive mechanism through the methylene and ethylene groups, respectively. Simultaneously, the methylene and ethylene groups have a deactivating influence. The balance among these opposing effects during the process is illustrated by the decrease of the rate constants.

The smaller electron attracting power of the naphthalene ring, compared with the benzene ring, is indicated by the smaller reactivity for 1,5-naphthalene diisocyanate (V). The influence of the urethane groups on the second isocyanate group is very pronounced, and the rate constant decreases significantly as the reaction proceeds.

STERIC CONFORMATION

The introduction of a rotary ethylenic bridge between the phenyl rings of a macromolecular chain entails a series of specific phenomena.

In previous investigations we found that 4,4'-DBDI reacts with glycols, leading to insoluble products which exhibit a higher melting point temperature and high crystallinity in contrast with such other common diisocyanates as diphenyl methane diisocyanate [8-10].

4,4'-DBDI and ethylene glycol (EG) based polyurethane, after being dissolved in DMF, precipitate from solution. This powder could not be redissolved in DMF even by heating due to high association in the crystalline lattice [8].

The x-ray diffraction spectrum of this product shows a periodicity of 19.7 ± 0.2 Å and is similar to that of the triclinic form of the nylon 66 [11], nylon 6, and nylon 8 [12]. This suggests a transformation of polymer conformation in solution from the disordered form into the extended form. This is due to the lower entropy level of the crystalline structure and to maximum hydrogen bridge formation (Fig. 4).

The melting point of the polymer is 312°C and the initial decomposition temperature of the polymer is 220°C (Fig. 5).

In the case of polyurethane based on MDI and EG, x-ray determination shows a periodicity of 15.7 ± 0.1 Å with a qualitatively similar arrangement (Fig. 6) but belonging to the hexagonal lattice crystalline system.

This polymer has a melting point temperature of 73°C, below that of the above-mentioned one. It also has good solubility, which shows that even if the ordering phenomena are similar, quantitatively it is lower.

We later studied how to utilize the orientation effects which are produced by the introduction of hard segment derivatives from 4,4'-DBDI and EG into polyesterurethane elastomers.

We investigated the copolyaddition of 3 mol 4,4'-DBDI and a mixture of 1 mol poly(ethylene adipate) (PEA), M ± 2000 with OH terminal groups, and 2 mol EG in DMF at 60°C. In this case we observed an unexpected phenomenon: although at the beginning the mixture was

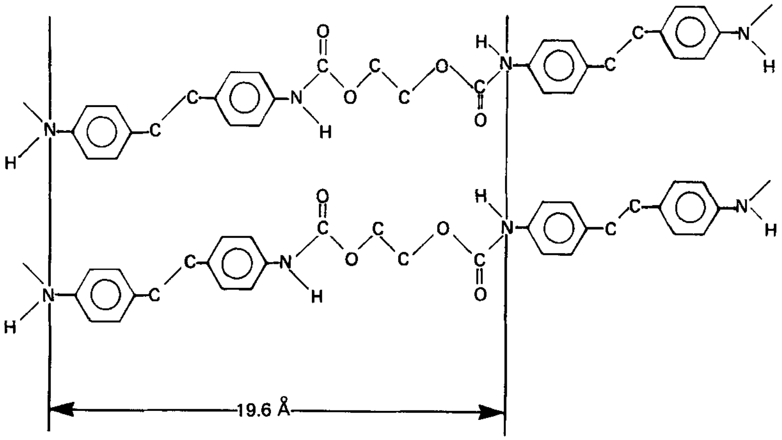


FIG. 4. Extended chain conformation of polyurethane based on ethylene glycol and 4,4'-dibenzyl diisocyanate.

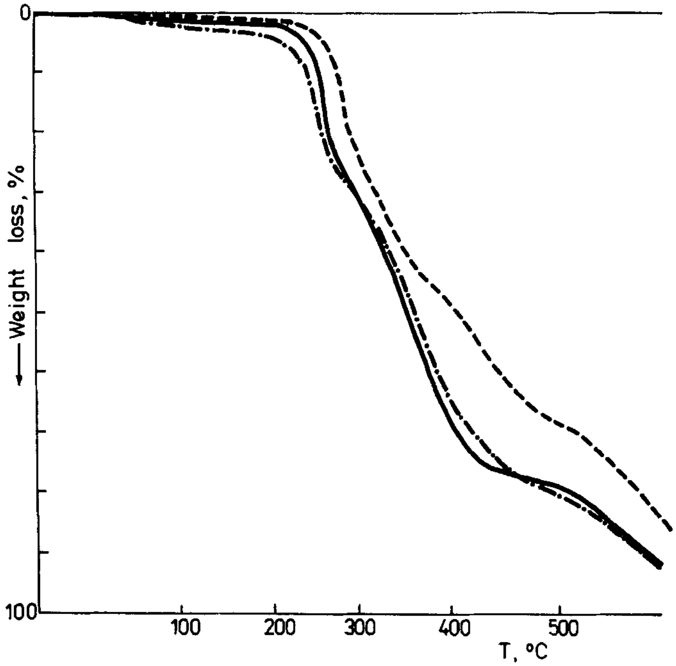


FIG. 5. Thermogravimetrical analysis of the polyurethane based on ethylene glycol and 2,2'-dibenzyl diisocyanate (—), 2,4'-dibenzyl diisocyanate (-·-), and 4,4'-dibenzyldiisocyanate (- -).

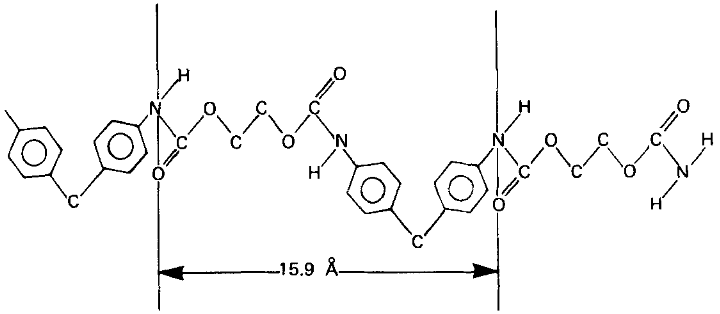


FIG. 6. Extended chain conformation of polyurethane based on ethylene glycol and 4,4'-diphenylmethane diisocyanate.

homogeneous (as a result of the initial reaction between 4,4'-DBDI and EG), even in the incipient first phase oligomers result which, due to association and crystallization, separate from solution as a very fine suspension. The reaction progresses in two phases: solution and suspension.

The mixture is disproportionate, probably due to the steric necessity of crystallization, resulting in a white, viscous, and stable solution-suspension. By intense centrifugation a precipitate can be separated. By precipitation in water of the remaining clear solution a second polymer with a different structure (PUB) can be separated.

Their compositions were easily determined quantitatively with the aid of NMR spectra by using aromatic proton integrals as well as the proton integrals of the CH_2 group from the polyester (Fig. 7 and Table 3).

If the suspension is diluted with 4 times the volume of DMF and heated at 60-70°C, it becomes clear. The crystalline structure is probably destroyed, and it does not precipitate by cooling or standing at room temperature. These facts, and the apparent constant composition of the polymers obtained when starting from different molar ratios of the reactants, suggest that in copolyaddition the growth of the macromolecules in suspension is governed by the formation of crystalline structure.

This behavior was used (see the section on applications) for the processing of artificial leather.

In the case of 4,4'-disubstituted isomers of dibenzyl, if the main characteristic of the polymers is the capacity to self-orientate in crystalline structures, the problem of the specific behavior of 2,2'-disubstituted isomers is raised.

We first studied the hypothetical concurrent reaction in the polyimide polymer class which can lead to the formation of small rings in the reaction for the preparation of polyamic acids, starting from 2,2'-DAB and pyrromellitic anhydride (AP).

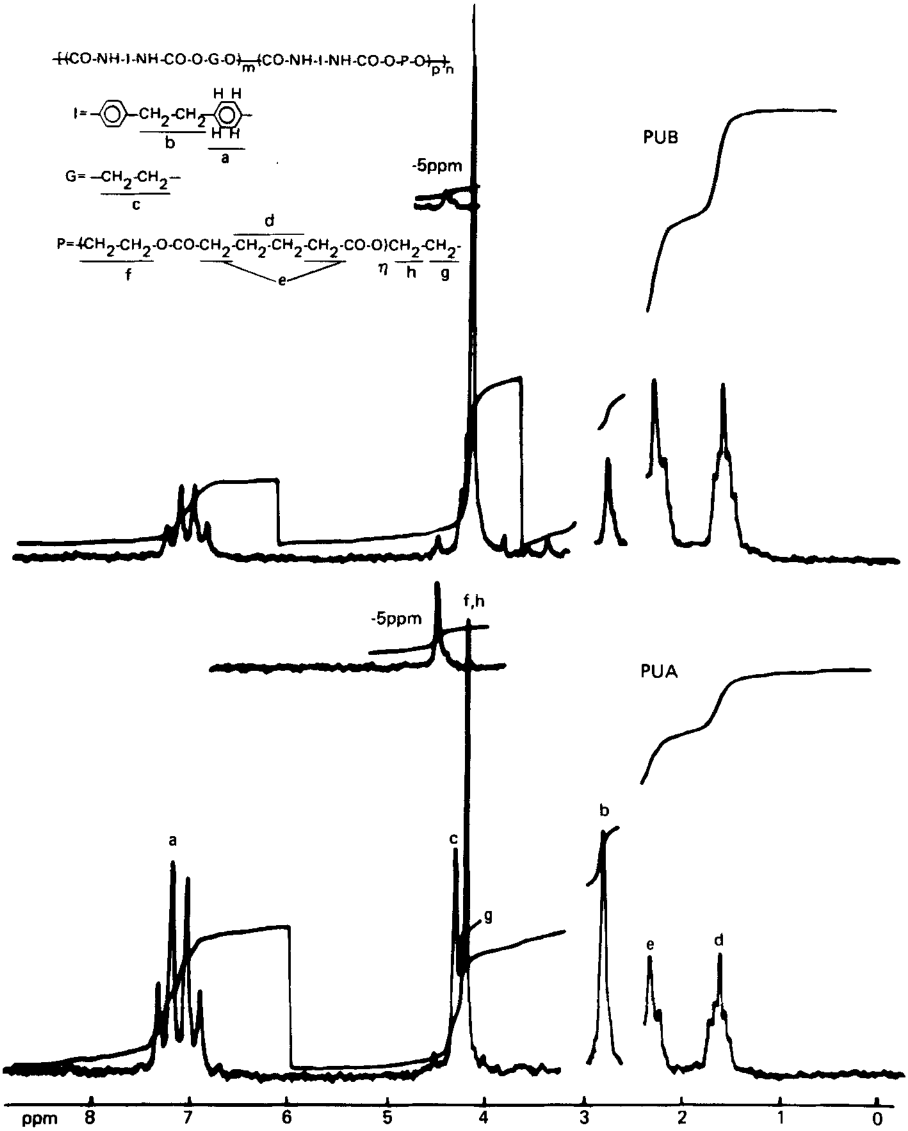


FIG. 7. The ^{1}H-NMR spectra of polyurethanes PUA_1 and PUB_1 in DMSO d_6 at 80°C.

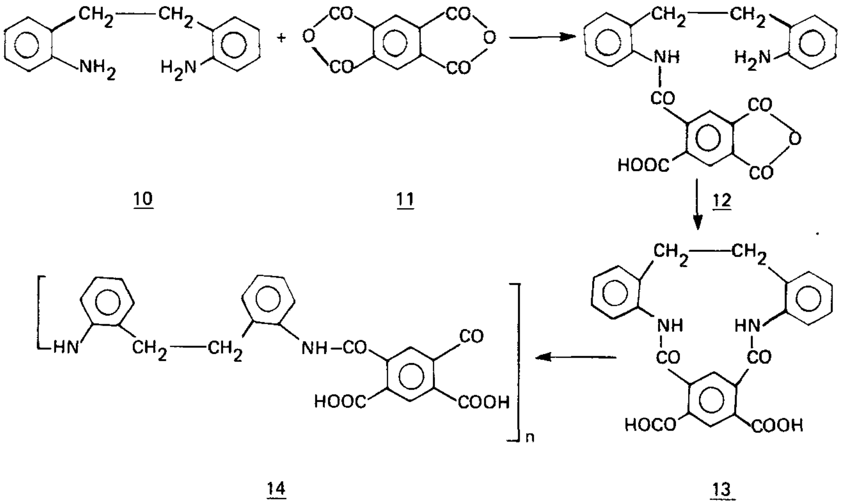
TABLE 3. The Composition of the Polymers Obtained by the Copolyaddition of 4,4'-DBDI and a Mixture of PEA with EG

No.	Starting composition (mol)		Separated polymers	Molar ratio determined			% Grav.	η_{inh}
				PEA	EG	4,4'-DBDI		
1	PEA	1	PUA_1	1	9.71	10.71	14.4	0.26
	EG	2						
	4,4'-DBDI	3	PUB_1	1	1.31	3.31	85.6	0.23
2	PEA	1	PUA_2	1	10.45	11.45	26.2	0.26
	EG	3						
	4,4'-DBDI	4	PUB_2	1	1.83	2.83	73.8	0.24

Studies on spatial models show that in this case (in contrast with derivatives of type 1) there is the possibility of creating small rings of 13 units without apparent tension.

To facilitate the cyclization process, we worked at very low reactant concentrations, e.g., 2.5 × 10^{-3} mol 2,2'-DAB/L and the equivalent amount of AP using anhydrous acetone as solvent [13].

High pressure liquid chromatography (HPLC) of samples of the reaction mixture after 24 h at room temperature showed total consumption of amine 10.



The amorphous product obtained after vacuum distillation of the acetone was soluble in aprotic polar solvents as well as in alkaline water from which it precipitated by acidification.

The IR spectrum shows the disappearance of the maximum corresponding to the anhydride group at 1845 cm^{-1}.

Elemental analysis corresponds to products 13 and 14 with a small content of water (up to 5%, as determined by ATG). This trace of water is not removed by drying in high vacuum at room temperature. Heating did not produce transformation to the imide group.

To decide between possible structures 13 and 14, we determined the molecular mass by cryoscopy in dimethylsulfoxide. We found values between 360 and 400, which correspond quite well with the theoretical value of 430 for cyclic structure 13. (The somewhat lower values found may be explained by the presence of some impurity traces of low molecular weight, such as water or the solvents, which are not removed.)

If additional studies confirm the cyclic structure of this product, the way for the synthesis of polyamic acids of this type by ring-opening polymerization (similarly to lactam polymerization) is possible.

THERMAL STABILITY

The influence of dibenzyl structures on the thermal stability of polymers was studied by following the modification of this property on thermostable polymers containing such structures. In parallel, we studied their solubilities and properties.

With this aim in mind we studied the polyimides obtained by the usual reaction conditions in DMF, starting from the three DAB isomers [13]. 4,4'-DAB led to high molecular weight polymers ($\eta_{\text{inh}, c = 0.5\%\ \text{DMF}} > 4$ while 2,4'- and 2,2'-DAB isomers led to low molecular weight polymers ($\eta_{\text{inh}, c = 0.5\%\ \text{DMF}} = 0.36$). The lower molecular weight is probably due to interference in the cyclization reactions.

As TGA shows (Fig. 8), all the polyimides obtained by chemical

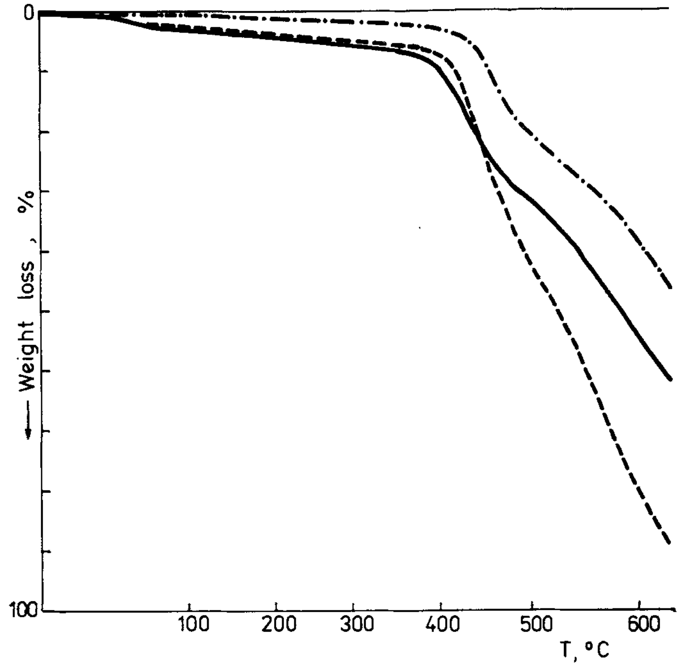


FIG. 8. Thermogravimetrical analysis of the polyimide based on pyrromellitic anhydride and 2,2'-diaminodibenzyl (—), 2,4'-diaminodibenzyl (-·-), and 4,4'-diaminodibenzyl (- -).

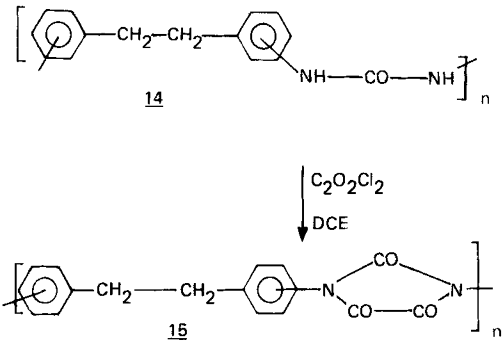
cyclization present about the same thermal stability. This fact demonstrates the independence of thermal stability toward position isomerism in the case of dibenzyl systems.

In contrast with this observation, the physical characteristics of the polymers are different. While 4,4'-DAB leads to high molecular polymers which form resistant and flexible films, 2,4'- and 2,2'-DAB lead to brittle polymers. The films cleave, even on coated surfaces.

The properties of polyurea class polymers obtained by reaction between DAB and the corresponding diisocyanate are shown in Table 4.

In the case of Polymer 2 (Table 4), the good solubility and the capacity to form flexible films with good thermal resistance is remarkable.

For this type of polymer we applied a polymer analogous transformation reaction with the aid of oxalyl chloride in 1,2-dichloroethane (DCE).



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The products obtained are presented in Table 5.

Dilute solutions of these polymers in a DMF-acetone mixture present a remarkable phenomenon. The solutions become turbid when heated but again become clear on cooling. This phenomenon can be attributed to the liquid-crystal character of the polymers obtained due to the change in the degree of association in the system DMF-acetone-polymer at different temperatures.

STABILITY TO OXIDATION PROCESS

It is well known that the methylenic group is activated in oxidative reactions by the presence of phenyl rings. This process is accelerated by the number of bonded phenyls and becomes maximum in the case of triphenyl methane derivatives.

The oxidative destruction mechanism of MDI-based polyurethanes suggested by Gardette is as follows [14]:

TABLE 4. The Properties of Polyureas with Dibenzyl Structures

No.	Type of isomer	η_{inh}[a]	mp, °C	Initial decomposition temperature, °C	Solubility[b]		Film property
					DMF	DMF + 2% LiCl	
1	2,2'-	-	350	280	-	-	Powder
2	2,4'-	0.61	240-290	240	+	+	Flexible
3	4,4'-	0.40	350	290	-	±	Powder

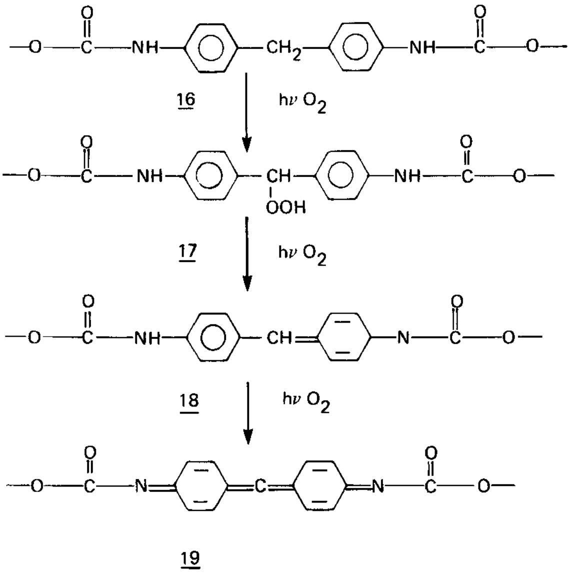
[a] C = 0.5% (DMF + 2% LiCl), Ubbelohde.
[b] - insoluble, ± soluble on heating, + soluble.

TABLE 5. The Properties of Poly(Parabanic Acid)s with Dibenzyl Structures

No.	Type of isomer	η_{inh} [a]	mp, °C	Initial decomposition temperature, °C	Solubility[b]		Film property
					DMF	DMF + 2% LiCl	
1	2,2'-	0.08	333	280	-	±	Powder
2	2,4'-	0.44	241-328	350	±	+	Flexible
3	4,4'-	0.38	350	290	±	±	Powder

[a] C = 0.5% (DMF + 2% LiCl) Ubbelohde.

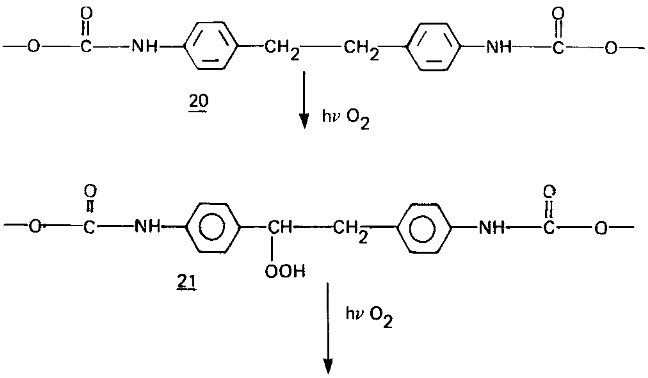
[b] - insoluble, ± soluble on heating, + soluble.

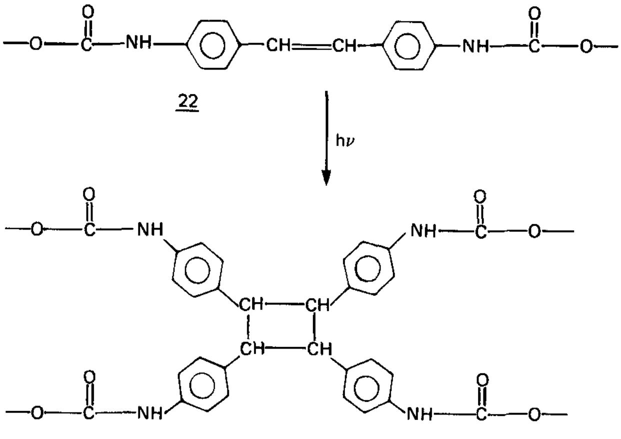


We expect the dibenzyl system to present higher oxidative stability than the diphenyl methane system. In dibenzyl systems every methylenic group is activated by only one phenyl group.

Indeed, all the DBDI-obtained polyurethanes are more light resistant than those based on MDI. The color of the products remains constant longer, even in the absence of stabilizers.

Once the oxidation process starts, it is to be expected to have a different course of reaction which perhaps involves stilbene structure formation and its dimerization to a cyclobutane structure (23) without the appearance of the quinoide conjugated system (19).





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PRACTICAL APPLICATIONS OF POLYMERS WITH DIBENZYL STRUCTURES

Based on previous observational findings related to the first part of this work, our laboratory had been making applicative investigations concerning the study of the dibenzyl structural polymers starting in 1959.

According to these studies, 4,4'-DBDI represents a potential valuable product. Starting from this diisocyanate, a series of polyurethane elastomers with remarkable properties has been synthesized.

The first industrialization of 4,4'-DBDI started from 4-nitrotoluene:

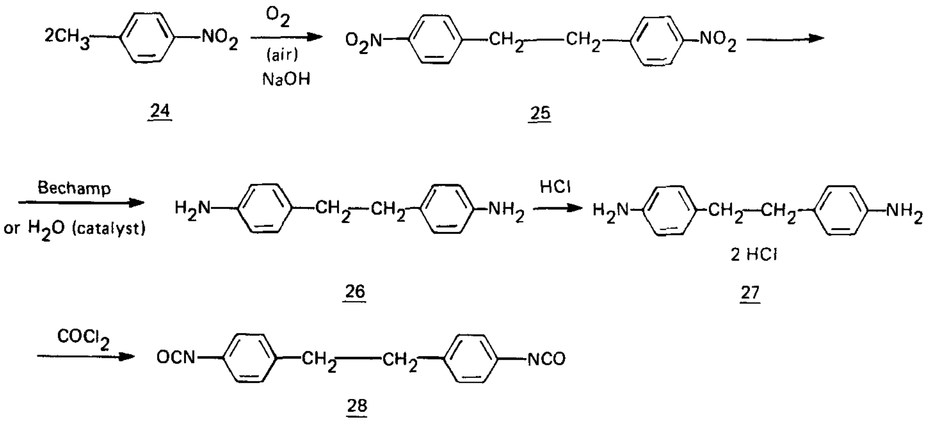

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TABLE 6. Mechanical Properties of Moldotan D Elastomers

					Modulus				
No.	Code[a]	Hardness, Shore A, degree	Specific gravity, g/cm^2	Tensile strength, kg/cm^2	100% kg/cm^2	300% kg/cm^2	Elongation to break, %	Residual elongation, %	Abrasion, mm^3/cm^2
					Reference				
1	25 NDI-BG	96	1.24	466	75	171	562	15	8
2	30 NDI-BG	95	1.24	449	80	192	483	20	44
					Moldotan D				
3	30 BG	92	1.24	377	76	125	650	35	5
4	40 BG	95	1.27	347	106	147	635	125	6
5	30 DEG	85	1.24	450	43	65	713	5	6
6	40 DEG	94	1.24	623	58	116	540	15	10
7	50 DEG	97	1.24	540	69	124	575	25	12
8	60 DEG	96	1.24	473	93	123	700	21	20
9	23 EG	80	1.23	520	31	69	680	20	11
10	40 EG	95	1.22	176	132	163	420	42	16
11	40 MOCA	98-99	1.26	561	113	352	388	40	43
12	40 DEG-PT	92	1.20	337	52	80	600	111	70

[a] NDI = 1,8-naphtylenediisocyanate, BG = 1,4-butylene glycol, DEG = diethylene glycol, EG = ethylene glycol, MOCA = 4,4'-methylene-bis(2-chloroaniline), PT = polytetrahydrofuran.

Using this diisocyanate, a series of industrial technologies for casting elastomers of the polyesterurethane type by prepolymer techniques and extended with different glycols or 4,4'-(methylene-bis-(2-chloroaniline)) (MOCA) were developed.

A series of polyurethanes with good possibilities for application was developed in Romania under the trade name Moldotan D. The properties of these polymers are shown in Table 6.

These polymers are utilized for the fabrication of such different technical articles as gaskets, elastic couplings, rubber-covered rolls, cog belts, rubber-covered pipes for the reduction of abrasion, metal piece substitutes for noise reduction, impeller coatings, and tires for low-speed vehicles.

Special attention has been given to research on microporous synthetic leather. It is well known that polymers used in synthetic leather fabrication must exhibit a series of properties difficult to put together, i.e., tensile strength, elongation at break, porosity (air and vapor permeability), and resistance at repeating flexing at low temperatures.

Many syntheses of polyurethanes were tried with the aim of obtaining materials for synthetic leather. The most reproducible was polyaddition in solution. Polyurethane-ureas, obtained by chain-extension of an isocyanate-terminated prepolymer with hydrazine hydrate (under the trade name Moldotan P-343), give a microporous sheet with excellent mechanical properties, but they are handicapped due to difficulties with the technology of transformation of microporous sheets due to coagulation with vapor water in the first phase. These polymers remain very valuable because of their formation to compact sheets with high mechanical resistance.

Modern techniques require polyurethane solutions which can be coagulated rapidly to elastic microporous sheet by direct immersion in water or water-solvent mixtures. To realize this, there is the need to treat the polyurethane solution so as to obtain a precoagulation state. Very good results were obtained by other producers by treating polyurethane solutions with variable ionomer polymers. This property was originally capitalized on in the case of coagulable polyurethanes by taking into account the great crystallization capacity of polyurethanes based on 4,4'-DBDI.

Some block copolymers with a polyester-DBDI-ethylene glycol-DBDI structure, created in a convenient ratio by parallel solution-suspension copolyaddition, led to colloidal stable solution-suspension. This system can be quickly transformed by immersion in water or a mixture of solvent-water into a microporous sheet.

These mixtures are industrially utilized for the fabrication of synthetic leather with the trade name Moldotan PR-100 or Nadolsin.

From the results presented we conclude that the introduction of dibenzyl structures to a macromolecular chain are interesting for both theoretical and practical studies. The results obtained justify the continuation of our studies.

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