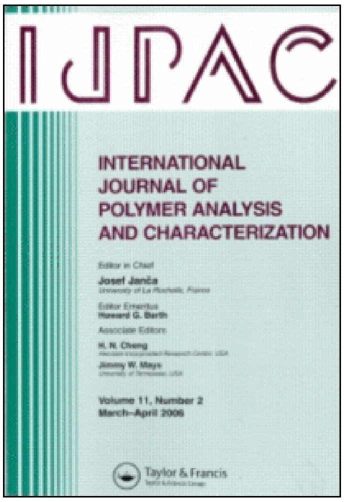

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SYNTHESIS OF SOME POLYISOCYANATE COMPOUNDS BASED ON DIBENZYL STRUCTURE

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The goal of this work is the synthesis of some polyfunctional isocyanate compounds. The comparative study of two methods of preparation of polyisocyanates containing dibenzyl structures is presented. The first method deals with the synthesis of the triisocyanate containing dibenzyl by the addition reaction between 2-ethyl-2-(hydroxymethyl)-1,3-propanediol(trimethylolpropane, TMP) and 2,4′-dibenzyl diisocyanate(2,4′-DBDI). The second method consists in the polyaddition reaction between a polyisocyanate 2,2′,4,4′-dibenzyl tetraisocyanate(2,2′,4,4′-DBTI) and a polyester diol in order to obtain a linear polyurethane that contains pendant-free isocyanate groups. Such a polymer can be used as a support polymer able to subsequently react with different compounds containing active hydrogen groups such as drugs and dyes.

Keywords: Dibenzyl diisocyanate; Dibenzyl tetraisocyanate; Polyisocyanates

INTRODUCTION

Polyurethanes (PU) are commercially available both as relatively rigid plastomers and as flexible elastomers with compact or foamed structures. PU plastics belong now to the group of important materials applicable in diverse fields of engineering, such as lacquers, coatings, adhesives, and resins.[1] The wide applicability of PU coatings is due to the versatility in selection of raw materials from a long list of macrodiols, diisocyanates, and chain extenders. The PU synthesis is centered on the isocyanate polyaddition reactions. The commercial manufacture of PU is based on the polyaddition reactions of diisocyanates and bi- or multifunctional polyols. The synthesis of PU involves a simple reaction of a di- or polyisocyanate with a di- and/or polyol.[2] The presence of multifunctional components, e.g., triisocyanates (obtained from the trimerization of isocyanate monomers), or the use of branched polyols can produce cross-linking PU.[3] Polyisocyanates were used as cross-linking agents, for example, for the manufacture of magnetic tape consisting of a coating of magnetic particles embedded in a matrix of organic polymer on a plastic film; the major binder is Mondur R (also known as Desmodur L), which is a polyurethane/

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polyisocyanate derived from TMP and 2,4–2,6-toluene diisocyanate (TDI).[4] Another example was published in a study dealing with the high-optical-quality PU films containing a high load of 60 fullerene (C_{60}) prepared with triisocyanate derived from trimethylolpropane (TMP) and xylylene diisocyanate or polyphenyl isocyanate-co-formaldehyde.[5]

There are many known kinds of polyisocyanates, aromatic or/and aliphatic,[6] used for the thermoset PU, coatings, high solid coatings, adhesives, and so on. For example, in the case of the production of polyurethane coatings, varnishes, adhesives, and resins, polyfunctional reactants are used, such as hydroxyl compounds like trimethylolpropane (TMP), pentaerythritol, and glycerol, as well as polyisocyanates like 4,4′,4″-methane tri(phenyl isocyanate) (Dermodur R), or the addition product of TMP and 2,4-tolylene diisocyanate (TDI) (Desmodur L).[7] In this work we present the synthesis of dibenzyl triisocyanate by the polyaddition reaction between TMP and 2,4′-dibenzyl diisocyanate (DBDI).[8] The second part of this work deals with a study of the preparation of a polyurethane bearing free NCO pendant groups based on 2,2′,4,4′-DBDI.[9]

EXPERIMENTAL SECTION

Materials

2,4′-Dibenzyldiisocyanate was obtained by a published method,[8] purified by physical and chemical methods, and its purity verified by high-performance liquid chromatography (HPLC).

2,2′,4,4′-Dibenzyltetraisocyanate (DBTI) was synthesized by a new method derived from a known method[9] and was purified by vacuum distillation. Commercial 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (trimethylolpropane) (TMP) p.a. was dried under vacuum for 3–4 days. Polyethylene adipate (PEA-2000) was from commercial sources and was used as received. Commercial ethyl acetate (EtOAc) p.a. and technical purity was dehydrated before use by different drying agents like calcium hydride (CaH_2) p.a., siccative calcium chloride ($CaCl_2$) p.a., anhydrous sodium carbonate (Na_2CO_3) p.a., and anhydrous sodium sulfate (Na_2SO_4) p.a. The solvents were kept on the drying agents of different concentrations for different durations and were freshly distilled before use (Table I). Commercial N-methyl-2-pyrrolidone (NMP) p.a. was dehydrated on isocyanate and freshly distilled; *ortho*-dichlorobenzene was distilled as well. Commercial methanol (MeOH) p.a. was used as received.

Methods

IR spectra were recorded on a PerkinElmer 577 spectrometer (KBr pellets). UV spectra were recorded on a Specord M42 spectrophotometer. Thermogravimetric analysis was determined on a MOM (Budapest) derivatograph in air at 12°C/min rate. Inherent viscosity measurements were determined for 0.5 g/dL polyurethane solutions in NMP at 20°C by using an Ubbelohde viscometer. Dynamic viscosity was performed on samples of triisocyanate solutions in EtOAc by using a Brookfield viscometer. The water content of dried ethyl acetate samples was tested by the Karl

Table I. Solvent drying methods

Sample	Solvent	Drying agent	Quantity (%)	Humidity[a] (%)	Drying time (days)
1	Ethyl acetate p.a.	CaH_2	3	<0.1	3
2	Ethyl acetate p.a.	$CaCl_2$ sicc.	5	<0.1	3
3	Technical ethyl acetate	—	—	0.09	—
4	Technical ethyl acetate	$CaCl_2$ sicc.	5	0.017	3
5	Technical ethyl acetate	$CaCl_2$ sicc.	7.5	0.019	3
6	Technical ethyl acetate	$CaCl_2$ sicc.	10	0.017	3
7	Technical ethyl acetate	$CaCl_2$ sicc.	15	0.05	3
8	Technical ethyl acetate	$CaCl_2$ sicc.	20	0.063	3
9	Technical ethyl acetate	Na_2SO_4 anh.	10	0.06	3
10	Technical ethyl acetate	Na_2CO_3 sicc.	10	0.07	3

[a] The maximum limit of water is 0.1%, corresponding to ASTM E 203-08.

Fischer method, ASTM E203-08. A few samples were tested for isocyanate content by reaction with piperidine and titration of the excess of piperidine with hydrogen chloride solution.

Synthesis of Dibenzyltriisocyanate (Ti)

A 15.8388 g (0.06 mole) amount of 2,4′-DBDI was added to a solution of 2.6783 g (0.02 mole) TMP in 6.85 mL ethyl acetate freshly distilled. The reaction mixture was stirred at room temperature for one hour, then was heated up to the reflux temperature for 10 min when the reaction became exothermic (rapid reflux). The reaction mixture became viscous and was stirred for other 3 h without supplementary heating. The product appearance was a yellow viscous liquid. The details of the synthesis and the characteristics of reaction products are presented in Table II.

Synthesis of Polymer-Support-Containing Pendant-Free Isocyanate Groups (PUI_{1-3})

Three polymers were obtained in slightly different conditions of reaction, as presented in Table III. A 4 g (0.002 mole) amount of PEA dehydrated under vacuum

Table II. Synthesis and characterization of triisocyanates (Ti) with dibenzyl structure

					Dynamic viscosity (cp)		
Sample	TMP (g)	2,4′-DBDI (g)	Solvent (mL)	Drying solvent methods[a]	After 1 day	After 7 days	After 6 months
T_1	2.68	15.84	6.17	1	38000	40000	—
T_2	2.678	15.838	6.85	2	9900	12000	52600
T_3	2.705	15.99	6.85	3	19100	43500	100000
T_4	4.04	23.77	10.5	7	24000	30000	96800
T_5	4.16	23.76	10.2	5	42000	gel	—
T_6	4.02	23.76	10.2	7	22000	—	—
T_7	4.01	23.75	10.2	10	14500		82500

[a] Corresponding to Table I.

Table III. Synthesis and characterization of polyurethane with free NCO groups

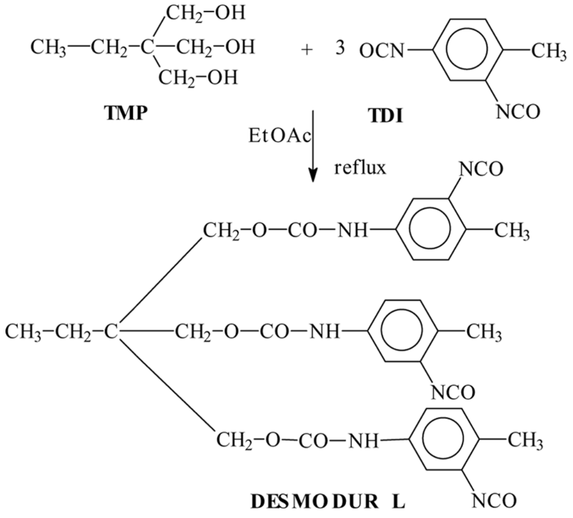
PU	Polyol	Isocyanate	Quantity of PEGA/DBTI (g)	Solvent	Temperature (°C)	η_{inh} (dL/g)	N% Calcd.	N% Found
PUI_1	PEGA	DBTI	4/0.696	NMP	60	gel	—	—
PUI_2	PEGA	DBTI	4/0.696	NMP	20	0.61	2.4	3.04
PUI_3	PEGA	DBTI	4/0.696	1,2-dichloro benzene	20	0.17	2.4	3.11

for 2 h and 0.696 g (0.002 mole) of DBTI freshly distilled were mixed with stirring in NMP (20% concentration) ($PUI_{1,2}$). The third polymer was synthesized in *ortho*-dichlorobenzene. The reaction mixture was stirred at room temperature for 2–3 h until it became viscous. The polyurethane solution was poured into methanol p.a. and the rubbery precipitate was filtered, washed with methanol, and dried. The polymers were characterized by IR spectra, elemental and thermogravimetric analyses, and inherent viscosity measurements (Table III).

RESULTS AND DISCUSSION

Study of the Triisocyanate with Dibenzyl Structure

The successful commercial Desmodur L (also named Mondur R[4] or Imprafix TH[6]) is manufactured by the addition reaction of TDI with TMP (Scheme 1). The product consists of a mixture of triisocyanate (75%) and ethyl acetate (EtOAc) containing approximately 13–14% isocyanic groups (NCO) and dynamic viscosity of 2000–2500 cp; it is relatively stable for storage for a few months, due to TDI's properties. TDI's isocyanic groups have different reactivities because of the steric hindrance exerted by CH_3 group on the NCO from the 2 positions.

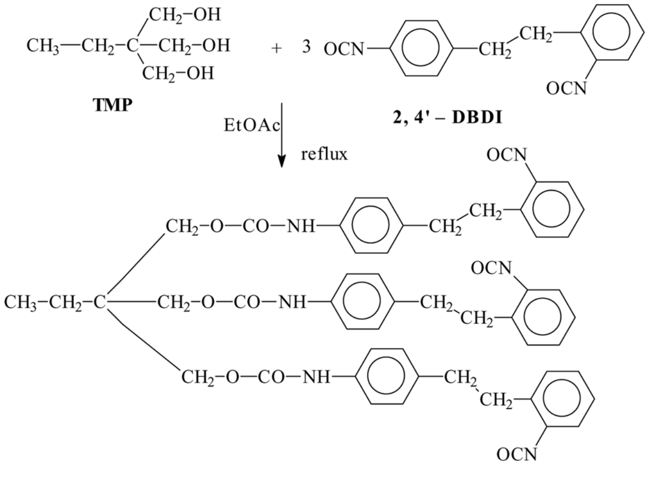


Scheme 1. The synthesis of triisocyanate by the addition reaction of 2,4′-DBDI and TMP.

At the same time, the urethane group formed first in the 4 position can induce the inactivation of the NCO group from the 2 position, as reported elsewhere.[10,11] The nonsymmetrical molecules of 2,4′-DBDI that show reactivity differences of NCO groups were used for the synthesis of many kinds of polymers (polyamides,[12] polyimides,[13] polyurethanes,[13] polyureas,[14] poly(parabanic acids),[15] and so on) because of the amorphous character of polymers containing 2,4′-DBDI. Its properties recommend it for the preparation of a new triisocyanate based on 2,4′-DBDI and TMP by using a modified method (Scheme 2). Thus, in the case of this diisocyanate, the NCO group of 2 positions suffers a similar steric hindrance exerted from the ethylene bridge between the two aromatic rings. As concerns the two NCO groups situated in two different aromatic rings, the influence of the first NCO (or urethane) group on the second NCO function, if any, is certainly smaller than that of the TDI molecule.[11,12] The synthesis of dibenzyl triisocyanate required highly purified raw materials as shown in the Experimental Part. A very important material is the solvent, ethyl acetate (EtOAc) p.a. or technical, which must be dried by different dehydration agents presented in Table I. The quantity of water in the solvent was tested by the Karl Fischer method (ASTM E203-08)[16] and by UV spectra also.

The most effective drying agent was the siccative $CaCl_2$ (5–10%), water content of the solvent being 0.017–0.019%. Seven samples of triisocyanate were prepared as described in the Experimental Part. The triisocyanate content in the reaction mixture is approximately 75.16% at the end of synthesis. Details of synthesis and characterization of reaction products are presented in Table II.

Two samples (T_1 and T_2) were tested for the content of isocyanic groups by the reaction with piperidine and titration of the excess of piperidine with hydrogen chloride solution. We found for $T_1 = 10.27\%$ NCO groups after synthesis, 8.76% after two weeks, and for $T_2 = 10.23\%$ and 8.275%. Dynamic viscosity was tested immediately after synthesis, then at different times in order to verify stability to storage. Even if the tests were made one day after synthesis, the values of dynamic viscosity were different, probably due to traces of water, which can react with the



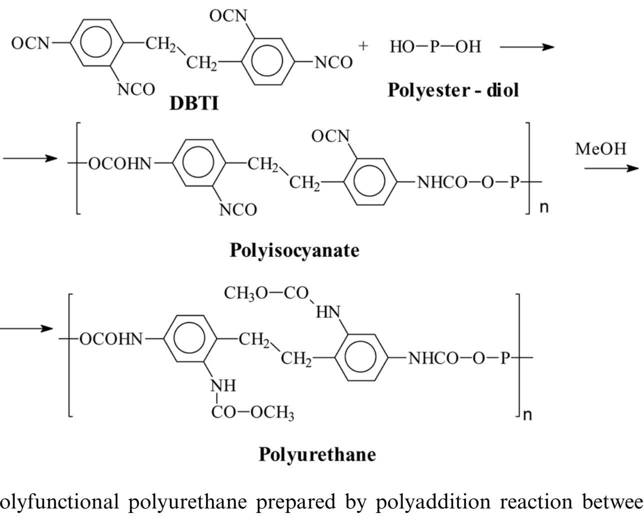
Scheme 2. The triisocyanate obtained by the addition reaction of 2,4′-DBDI and TMP.

NCO group, leading to the increase of molar mass. The best results are observed for T_1, T_2, and T_4 samples made in solvent with smaller quantity of water. In time, viscosity values rose until thickening was reached in some cases. The triisocyanate based on TDI was stable enough in time due to the strong interactions between the two NCO groups, leading to a severe inactivity of NCO of 2 positions. In the case of 2,4′-DBDI, despite their different reactivities, the two NCO groups practically do not interact, being situated in two aromatic rings. It seems to need some protection during storage such as the reaction of the triisocyanate with blocking agents (small molecules with active hydrogen atoms and able to block the NCO group reactions during storage and for dissociation at reasonable temperatures (110–180°C) during coating preparation).[17]

Polymers Based on Dibenzyl Tetraisocyanate

As mentioned in the introduction, polyfunctional polymers are available as elastomers, foams, or compact structures and are used in numerous fields of engineering and biomedical applications. Based on earlier studies in the field of reactivity of NCO groups of 4,4′-, 2,4′-, and 2,2′-DBDI,[10,11] it can be concluded that the reactivity differences are important only when the NCO groups are situated in the same aromatic rest as in the case of TDI or dibenzyl tetraisocyanate (DBTI), but the differences are moderate for the three isomers of DBDI, although they are significant for the polymer synthesis.[12–15]

The 2,2′,4,4′-DBDI (DBTI) contains four NCO groups in 2,2′- and 4,4′-positions. Since DBTI has in each aromatic ring two NCO groups of 2 and 4 positions, the reactivity differences are similar to those of the NCO groups of the TDI molecule. In Scheme 3, we present the synthesis of the polyurethane with NCO pendant groups by the polyaddition reaction (molar ratio: PEA/DBTI = $100 \times (0.002/0.002) = 100\%$ isocyanic index), followed by the subsequent reaction of MeOH at NCO groups from 2 positions, leading to a branched polymer. Details



Scheme 3. The polyfunctional polyurethane prepared by polyaddition reaction between DBTI and the macrodiol PEA.

of syntheses are presented in the Experimental Part; some characterizations of reaction products are shown in Table III.

Three polymers have been synthesized in somewhat different conditions. The polymer main chain was built in the first step from NCO groups of 4,4′-positions as having better reactivity, while NCO groups from 2 positions remain free as pendant groups. In the second step, the free NCO can react with many different mono-functional reactants like alcohols, amines, and biological molecules such as enzymes and drugs. Interpenetrate polymer networks can also be built from this kind of reactive polymer. Polyurethane with pendant-free NCO can also be used as adhesive material that is cured by the reaction with atmospheric moisture. Although reactivity differences of 2 and 4 NCO groups exist, the reactive polyurethane can suffer in time a cross-link reaction between NCO free groups and urethane groups on the main chain by forming interchain allophanate groups (PUI_1). This reaction caused a viscosity increase, leading to a cross-linked product.

Table III summarizes reaction conditions, elemental analyses, and inherent viscosity measurements. The structure of the second polymer support that contains NCO free groups (PUI_2) and of the PU with pendant methyl-urethane groups derived from PUI_2 was confirmed by IR spectra (Figure 1). A sharp peak at 2300 cm^{-1} is attributed to NCO groups and other peaks at 1710 cm^{-1} to the urethane groups; a shoulder at 1760 cm^{-1} is attributed to the polyester blocks. In the case of PU treated with MeOH, the isocyanic peak at 2300 cm^{-1} disappeared. As concerns the viscosities of polymers, some differences between viscosity values of PUI_2 (0.61 dL/g) and PUI_3 (0.17 dL/g) can be observed because of the different polarities of solvents used for the PU synthesis. By using an appropriate solvent for polyurethanes (NMP), two samples were obtained: PUI_1, having a gel appearance due to the reaction temperature (60°C), and PUI_2, synthesized at 20°C, for 2–3 h to a moderate viscosity, followed by the treatment with MeOH. However, in some cases, at higher temperatures NMP can act as a catalyst for the side reactions leading to interchain bonds. That's why the last synthesis was carried out in *ortho*-dichlorobenzene, a less polar solvent, leading to a lower value of viscosity without side reactions. PUI_2 containing methylene-urethane groups was tested by thermogravimetric analysis (Figure 2), and it shows a good thermal stability (up to 250°C) followed by a slow degradation process when the MaxDTG was around 400°C.

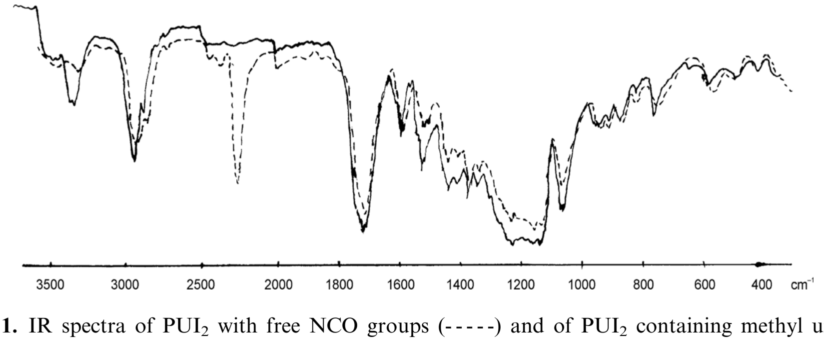


Figure 1. IR spectra of PUI_2 with free NCO groups (-----) and of PUI_2 containing methyl urethane groups (——).

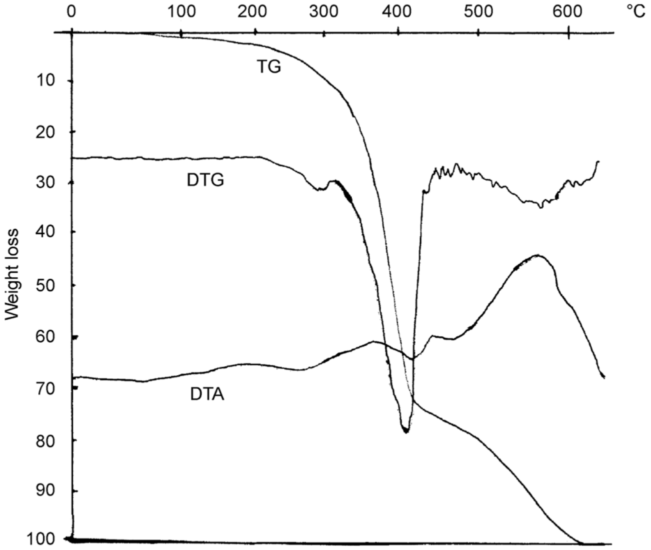


Figure 2. TGA curves of PUI_2 containing methyl urethane groups.

CONCLUSIONS

The present work deals with the synthesis of a triisocyanate with dibenzyl structure by the polyaddition reaction between TMP and 2,4′-DBDI. We used a modified method based on a well-known method.[7] Despite different reactivities of NCO groups from nonsymmetrical diisocyanate, the NCO groups situated in 2 positions can react with urethane groups of the triisocyanate product as well as with moisture traces. The product can be prepared before use, or it may be subjected to a method of protection of NCO groups such as the reaction with blocking agents. The second part of the article deals with the study of the preparation of polyurethanes bearing free NCO pendant groups based on 2,2′,4,4′-DBDI. Since DBTI has in each aromatic ring two NCO groups of 2 and 4 positions, the reactivity differences are similar with those of the NCO groups of the TDI molecule. Three polymers were obtained in somewhat different conditions of reaction as shown in the Experimental Part. PUI_2 was obtained as PU support of free NCO groups in the first step, which can subsequently react with different mono-functional molecules: alcohols, amines, and biological molecules such as enzymes and drugs.

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