

Reactions of Phenolic Ester Alcohol with Aliphatic Isocyanates—Transcarbamylation of Phenolic to Aliphatic Urethane: A ^{13}C -NMR Study

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ABSTRACT: Reactions of aliphatic isocyanates with a phenolic ester alcohol (PHEA) were investigated using ^{13}C -NMR spectroscopy. PHEA has two reactive sites: a phenolic —OH group and a secondary aliphatic —OH group. Both —OH groups react with the isocyanate groups. With an organotin catalyst, dibutyltin dilaurate (DBTDL), the aliphatic —OH group reacts first. With a tertiary amine catalyst, 1,4-diazabicyclo[2.2.2]octane (DABCO), or triphenylphosphine (Ph_3P) or even in the absence of a catalyst at room temperature (RT) the phenolic —OH group reacts first. With the organotin catalyst, the reactions are generally complete in a day at RT. With DABCO or triphenylphosphine or DNDSA catalysts, the reactions are almost complete only in 3–4 days at RT in ethyl acetate or acetonitrile. Uncatalyzed reactions are slower. With an acid catalyst such as dinonylnaphthalenedisulfonic acid (DNDSA), both —OH groups react with the isocyanate. When equimolar quantities of PHEA and hexamethylenediisocyanate (HDI) polymerize at RT or reflux in the presence of a catalyst, both —OH groups react, with the phenol reacting slowly. Upon refluxing, the phenolic —OH-based urethane slowly rearranges (transcarbamylation) to the aliphatic —OH-based urethane. DABCO and Ph_3P catalysts effect this rearrangement at a much slower rate than does the acid catalyst. In the presence of a catalytic amount of DBTDL in a refluxing solvent, this rearrangement is complete in 2 h. By refluxing the phenolic—OH-based urethane in isopropanol, the mechanism of transcarbamylation was found to be intermolecular. The mechanism is likely to involve deblocking of the phenolic urethane and subsequent reaction of the isocyanate generated, with the aliphatic —OH group. This conclusion was confirmed by differential scanning calorimetry (DSC) experiments. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2212–2228, 2000

Key words: phenolic; alcohol; isocyanate; urethane; ^{13}C -NMR

INTRODUCTION

In industrial coatings, it is very common to combine aliphatic polyols with aminoplast or polyisocyanate crosslinkers. There is growing interest in the use of polyols that contain phenolic hydroxyl groups instead of, or in addition to, aliphatic hy-

droxyl groups in coatings.^{1–3} Most of this interest has centered on coatings that are crosslinked with aminoplast resins such as melamine–formaldehyde resins.^{2,3} An obvious question concerns how phenolic polyols might react with other classes of crosslinkers that are used in coatings, notably with di- and triisocyanates. This study addresses that question.

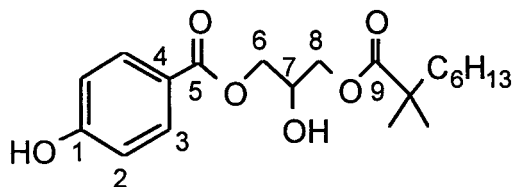
We investigated the reactions of an aliphatic/phenolic diol with di- and triisocyanate crosslinkers commonly used in coatings. The diol is designated “PHEA” for “phenolic ester alcohol.”^{2f} It

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was recently introduced for use in a variety of industrial coatings. Its structure is



PHEA

There are many compounds containing both phenol and aliphatic alcohol groups. These include naturally occurring flavonoids,⁴ tetralin-1,5-diol,⁵ and hydroxymethylphenols.⁶ The last are intermediates in the condensation products of phenol and formaldehyde. Keck and Kline⁷ reported the syntheses of new phenolic alcohols such as 2-(3,5-bis(*tert*-butyl)-4-hydroxybenzyl)-1,3-propanediol for synthesizing thermooxidatively stable polyesters. Recently, Francis and Mitra⁸ reported 4-hydroxyphenyl-substituted mono-carbamates of glycerol. Hinney et al.⁹ obtained a patent for the syntheses of stabilized polyurethane foams containing *N,N*-bis(2-hydroxyethyl)-4-hydroxybenzamide. Phenolic alcohols may also be obtained by the reaction of an epoxy resin with 1 mol equivalent of bisphenol-A, which finds application in water-reducible coatings.¹⁰ Perhaps, PHEA is the first phenolic alcohol reported having ester linkages and a long aliphatic chain.

Di- and triisocyanate crosslinkers¹¹ are generally used in coatings with aliphatic polyols. Several patents disclosed their use in crosslinking phenolic resins, for example, in vapor permeation coatings.¹ However, there have been few reports bearing directly on how materials with both aliphatic and phenolic hydroxyl groups, such as PHEA, might react with commonly used isocyanate crosslinkers. Several research groups have reported the use of trichloroacetyl isocyanate (TAI), an especially reactive monoisocyanate, for derivatization of alcohols, phenols, and amines without any catalyst added.¹² To probe the reactivities of phenolic and benzylic —OH groups in tetralin-1,5-diol, Agrawal⁵ studied the ¹³C-nuclear magnetic resonance (NMR) spectra of its TAI-based carbamate derivatives *in situ* in the NMR tube and confirmed that the phenolic group reacts with the isocyanate and that the benzylic

—OH group reacts thereafter. On the other hand, the report by Francis and Mitra⁸ suggested that aliphatic hydroxyl groups react preferentially with various diisocyanates in the presence of the dibutyltin dilaurate (DBTDL) catalyst, leaving the phenolic groups unreacted.

In this article, we describe the reactions of PHEA with two aliphatic isocyanates, hexamethylene diisocyanate (HDI) and its trimer, HDI-isocyanurate,* with different catalysts: DBTDL, 1,4-diaza[2.2.2]bicyclooctane (DABCO), triphenylphosphine (Ph₃P), and dinonylnaphthalenedisulfonic acid (DNNSA). Ph₃P was used as a weaker base catalyst than is DABCO. Besides, phosphines have been used in the reactions involving isocyanates.¹⁴ The use of acids to catalyze in isocyanate reactions was recently reported by Nordstrom et al.¹⁵ DNNSA is a commonly used acid catalyst in the coatings. Both amine and tin catalysts are widely used in isocyanate-based crosslinked coatings. We also report the reactions with no added catalyst. The reactions were performed in acetonitrile or in an ethyl acetate solution. The reaction products were analyzed by ¹³C-NMR spectroscopy. We show that the reactivities of the two —OH groups are different, and different products may be obtained depending on the catalyst used. Also, discrete adducts, linear polymers, or gels can be formed depending on the reactant functionalities and proportions.

EXPERIMENTAL

PHEA was obtained from Exxon Chemical Co. (Baytown, TX) as Exx-RD™ 100 Reactive Diluent. HDI (Desmodur® H) and its isocyanurate (Desmodur® N3300) were obtained from Bayer Corp. (Desmodur® N3300 is a mixture of polyisocyanate isocyanurate species). DBTDL, DABCO, Ph₃P, and all the solvents were purchased from Aldrich Chemical Co. (Milwaukee, WI) DNNSA was obtained from King Industries (Norwalk, CT) as a 55 wt % solution in isobutanol under the trade name Nacure® 155. Solvents were purified by distillation before use or dried using molecular sieves (4 Å). Selected physical properties of these solvents are listed in Table I.

Melting points were determined using a Thomas Hoover capillary melting-point appara-

* For the reactivities of different polyisocyanates from HDI, see ref. 13.

Table I Selected Physical Properties of Solvents Used

Solvent	Boiling Point (°C)	Dipole Moment (μ/D)	Dielectric Constant
Acetonitrile	81.6	3.92	38.8
Ethyl acetate	77.1	1.78	6.02
Cyclohexane	80.7	0.00	2.02
Diethyl ether	34.6	1.15	4.24
Isopropanol	82	—	19.9

tus and are uncorrected. IR spectra were recorded on a Nicolet 5DX spectrometer using KBr plates or in the form of KBr pellets. NMR spectra were recorded using a Bruker AC-250 spectrometer. Chemical shifts are reported relative to tetramethylsilane (TMS) in $CDCl_3$. Each spectrum was recorded using a solution of about 0.08 g of the sample in 1 mL $CDCl_3$ containing 5 wt % TMS. Differential scanning calorimetry (DSC) was performed on a TA 2920 modulated differential scanning calorimeter at a heating rate was $5^\circ C/min$ under nitrogen.

In the following reactions, we will examine the ^{13}C -NMR spectra of the products for any changes in the chemical shifts of the carbons to which the —OH groups are attached and also to their neighboring carbons. In these experiments, the —OH groups were allowed to react with isocyanate groups in order to synthesize urethane linkages.¹⁶ This reaction was controlled by varying the ratio of diisocyanate to the diol. The experimental details are described below.

DBTDL-Catalyzed Reactions

Reaction of PHEA with HDI (2 : 1 Molar Ratio) (1)

Into a 25-mL round-bottomed flask equipped with a magnetic stirrer was placed PHEA (1.90 g, 5.21 mmol) dissolved in 5 mL acetonitrile. A solution of HDI (0.44 g, 2.62 mmol) in 5 mL acetonitrile was added, followed by DBTDL (0.06 g, 2.5 wt % total) as the catalyst. The solution was stirred at RT for 24 h. The solution remained clear and transparent. The IR spectrum of the solution showed weak to no ν_{NCO} band between 2260 and 2280 cm^{-1} . Acetonitrile was removed under aspirator pressure to give a sticky, resinous material (**1**) which was transferred to an aluminum pan. Any remaining solvent was removed using a stream of air overnight, at room temperature (RT).

Reaction of PHEA with HDI (1 : 1 Molar Ratio) (2)

The procedure was similar to the reaction discussed above. The quantities of the reagents were as follows: PHEA (2.71 g, 7.42 mmol), HDI (1.26 g, 7.50 mmol), and DBTDL (0.06 g, 2 wt % total). Unlike the previous experiment, a white solid precipitated in 4 h, which, with the precipitation of more product (**2**), became a sticky, transparent, and colorless mass in about 12 h.

Reaction of PHEA with HDI Isocyanurate (3 : 1 Molar Ratio) (3)

The experimental procedure and workup was similar to those described above. The quantities of the reagents used were PHEA, 2.01 g, 5.51 mmol, HDI isocyanurate, 0.96 g, 1.64 mmol, and DBTDL, 0.06 g, 2 wt % total. An oily, transparent product (**3**) was separated at the bottom of the flask within 24 h.

This experiment was also performed using ethyl acetate as the solvent. The product, however, did not separate in this experiment. Instead, the solution became quite viscous.

DABCO-Catalyzed Reactions

Reaction of PHEA with HDI (2 : 1 Molar Ratio)—RT Reaction (4)

Into a 25-mL round-bottomed flask equipped with a magnetic stirrer was placed a solution of PHEA (5.03 g, 0.014 mol) and DABCO (0.03 g, 0.5 wt % total) in 5 mL ethyl acetate. A solution of HDI (1.14 g, 6.79 mmol) in 5 mL ethyl acetate was also added. The flask was stoppered using a rubber septum and the solution was stirred at RT for 4–5 days until the isocyanate band at 2256 cm^{-1} in the IR spectrum disappeared or considerably weakened. Ethyl acetate was removed from the solution in a vacuum using a rotary evaporator and the resin was transferred into an aluminum pan. Any remaining solvent was removed in a stream of air at RT, overnight. A colorless resinous residue (**4**) was obtained.

Reaction of PHEA with HDI (2 : 1 Molar Ratio)—Reflux-Temperature Reaction (4')

Into a 25-mL round-bottomed flask equipped with a magnetic stirrer and a reflux condenser was placed a solution of PHEA (2.58 g, 7.05 mmol) and DABCO (0.03 g, 0.96 wt % total) in 5 mL ethyl acetate. A solution of HDI (0.55 g, 3.27 mmol) in 5 mL ethyl acetate was also added and the solution

was refluxed for 4 h until the isocyanate band at 2256 cm^{-1} in the IR spectrum disappeared. Ethyl acetate was removed from the solution in a vacuum using a rotary evaporator and the resin was transferred into an aluminum pan. Any remaining solvent was removed in a stream of air at RT, overnight. A colorless resinous residue (**4'**) was obtained.

Reaction of PHEA with HDI (1 : 1 Molar Ratio)—RT Reaction (5)

The procedure was similar to the synthesis of **4**. The quantities of the reagents were PHEA, 5.05 g, 0.014 mol, DABCO, 0.04 g, 0.5 wt % total, and HDI, 2.32 g, 0.014 mol. Ethyl acetate was used as the solvent. The isocyanate band at 2256 cm^{-1} was diminished considerably but was still present even after stirring at RT for 4 days. A colorless resinous residue (**5**) was obtained after the workup as described above.

Reaction of PHEA with HDI Isocyanurate (3 : 1 Molar Ratio)—RT Reaction (6)

The procedure was similar to the synthesis of **4**. The quantities of the reagents were PHEA, 5.02 g, 0.014 mol, DABCO, 0.03 g, 0.4 wt % total, and HDI isocyanurate, 2.31 g, 4.62 mmol. Acetonitrile was used as the solvent. A colorless, resinous product (**6**) was obtained after the workup as described above.

Triphenylphosphine-Catalyzed Reactions

Reaction of PHEA with HDI (2 : 1 Molar Ratio)—RT Reaction (7)

The procedure was similar to the synthesis of **4**. The quantities of the reagents were PHEA, 3.36 g, 9.21 mmol, HDI, 0.76 g, 4.52 mmol, and triphenylphosphine, 0.02 g, 0.49 wt % total. The solution remained clear and transparent. A sticky, resinous material (**7**) was obtained after the workup.

Reaction of PHEA with HDI (2 : 1 Molar Ratio)—Reflux-Temperature Reaction (7')

The procedure was similar to the synthesis of **4'**. The quantities of the reagents were PHEA, 2.43 g, 6.64 mmol, HDI, 0.54 g, 3.21 mmol, and triphenylphosphine, 0.02 g, 0.67 wt % total. The solution remained clear and transparent. A colorless resinous residue (**7'**) was obtained after the workup.

Reaction of PHEA with HDI (1 : 1 Molar Ratio)—Reflux-Temperature Reaction (8)

The procedure was similar to the synthesis of **4'**. The quantities of the reagents were PHEA, 2.11 g, 5.78 mmol, HDI, 1.00 g, 5.95 mmol, and triphenylphosphine, 0.02 g, 0.64 wt % total. The solution remained clear and transparent. A sticky, resinous material (**8**) was isolated after the workup.

DNNSA-catalyzed Reactions

Reaction of PHEA with HDI (2 : 1 Molar Ratio)—RT Reaction (9)

The procedure was similar to the synthesis of **4**. The quantities of the reagents were PHEA, 4.33 g, 11.86 mmol, HDI, 1.06 g, 6.31 mmol, and DNNSA, 0.06 g, 0.33 wt % total. The solution turned translucent during the reaction. A colorless, sticky, resinous material (**9**) was obtained after the workup.

Reaction of PHEA with HDI (2 : 1 Molar Ratio)—Reflux-Temperature Reaction (9')

The procedure was similar to the synthesis of **4'**. The quantities of the reagents were PHEA, 4.04 g, 11.07 mmol, HDI, 0.94 g, 5.60 mmol, and DNNSA, 0.06 g, 1.20 wt % total. The solution remained clear and transparent. A sticky product (**9'**) was isolated after the workup.

Reaction of PHEA with HDI (1 : 1 Molar Ratio)—RT Reaction (10)

The procedure was similar to the synthesis of **4'**. The quantities of the reagents were PHEA, 3.43 g, 9.40 mmol, HDI, 1.59 g, 9.46 mmol, and DNNSA, 0.09 g, 1.79 wt % total. The experiment was carried out at RT for 2 days and in a refluxing ethyl acetate solution for an additional 24 h. A white solid precipitated after 3–4 h of reflux, and the originally clear solution turned cloudy. The ν_{NCO} band was still present even after 24 h of reflux. The solution was worked up as described above to give a sticky product (**10**).

Uncatalyzed Reactions

Reaction of PHEA with HDI (2 : 1 Molar Ratio)—RT Reaction (11)

Into a solution of PHEA (2.03 g, 5.56 mmol) in 5 mL acetonitrile was added HDI (0.48 g, 2.86 mmol) and the solution was stirred at RT for 7

days. The IR spectrum of the solution still showed a weak ν_{NCO} band at 2256 cm^{-1} . The solvent was removed from the solution in a vacuum using a rotary evaporator. The remaining contents of the flask were transferred to an aluminum pan and traces of the remaining solvent were removed overnight using a stream of air at RT. A colorless, resinous product (**11**) was obtained.

**Reaction of PHEA with HDI (2 : 1 Molar Ratio)—
Reflux-Temperature Reaction (11')**

The procedure is similar to the synthesis of **4'**. Ethyl acetate was the solvent used (10 mL). The quantities of the reagents were PHEA, 2.80 g, 7.65 mmol, and HDI, 0.65 g, 3.87 mmol. The solution was refluxed for 24 h. The IR spectrum of the solution still showed a medium-intensity ν_{NCO} band. A light yellow, resinous product (**11'**) was obtained after the workup.

**Reaction of PHEA with HDI (1 : 1 Molar Ratio)—
RT Reaction (12)**

The procedure is similar to the synthesis of **11**. The quantities of the reagents were PHEA, 2.06 g, 5.56 mmol, and HDI, 0.99 g, 5.56 mmol, and the solution was stirred at RT for 3 days and subsequently refluxed for 4 days. A light yellow, resinous product (**12**) was obtained after the workup.

Transcarbamylation Reactions

These reactions were generally carried out according to the following procedure: Approximately 0.25 g of **4** was dissolved in 5 mL of the solvent and DBTDL (0.01 g) was added to this solution. The solution was heated for 2–12 h under the desired temperature conditions. The solution was cooled to RT and the solvent was removed in a vacuum using a rotary evaporator. The contents of the flask were transferred to an aluminum pan and the remaining solvent was removed using a stream of air at RT for 4–6 h.

Isopropanol-Blocked HDI (13)

HDI (0.1 g, 3.04 mmol) was added to isopropanol (2.36 g, 0.04 mol) followed by the DBTDL catalyst (0.02 g) and the solution was stirred for 12 h at RT. The solution was warmed up to 60°C . A white solid precipitated after 6 h. The solid was filtered and dried in a stream of air at RT.

Yield: 0.77 g (88%). Mp: $96\text{--}98^\circ\text{C}$. IR(KBr): 3342, 2987, 2940, 2868, 1697, 1552, 1368, 1282, 1229, 1137, 1065,

992, 788, 644 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3): δ 4.89 (m, 2 H), 4.67 (br, 2H), 3.14 (m, 4H), 1.49 (m, 4H), 1.33 (m, 4H), 1.22 (d, 12H). $^{13}\text{C-NMR}$ (CDCl_3): δ 156.20, 67.58, 40.59, 29.84, 26.20, 22.07.

RESULTS AND DISCUSSION

The $^{13}\text{C-NMR}$ spectrum of PHEA was recorded to compare its spectrum with those of the reaction products. The carbon atoms of PHEA and of the products (**1**, **2**, and **3**) are arbitrarily numbered as shown. The chemical shifts of various carbons in PHEA and the products are listed in Table II. The peaks were assigned by distortionless enhancement by polarization transfer (DEPT) $^{13}\text{C-NMR}$ and also by comparing the literature data.^{5,12d,17} Generally, the intensity of quaternary carbons is much weaker than that of the other carbons due to long relaxation times. Numerous peaks below 50 ppm are not shown in Table II and in subsequent tables; they are assigned to the aliphatic group of PHEA and to the $-(\text{CH}_2)_6-$ residues from the isocyanates.

Depending on the batch used, the $^{13}\text{C-NMR}$ of PHEA may have additional peaks between 62–69 ppm. This may be because in the synthesis of PHEA by the reaction of *p*-hydroxybenzoic acid glycidyl neodecanoate the reaction could give rise to two isomeric PHEA derivatives resulting from the opening of the epoxy group on its either sides and/or because of intramolecular transesterification of the isomer containing the secondary aliphatic alcohol to give a primary aliphatic alcohol-based PHEA.¹⁸

DBTDL-Catalyzed Reactions

In the reaction product (**1**) of PHEA with HDI in a 2 : 1 molar ratio, the chemical shift of carbon 7 changed upfield relative to PHEA, whereas the chemical shifts of the two methylene carbons (6 and 8) changed downfield. This product appeared light yellow and was quite viscous. The chemical-shift difference between carbons 6 and 8 in **1** decrease and, therefore, the two peaks appear as a single broad peak. Other peaks between 62 and 69 ppm, if any, overlap with these peaks upon reaction with HDI. There are also upfield shifts in the chemical shifts of the ester carbons 5 and 9. The urethane carbon (10) appeared at 156.24 ppm. The chemical shifts of the phenolic carbons did not change appreciably, indicating that no reaction took place at the phenolic hydroxyl group. Based on this analysis, the product (**1**), which will

Table II ^{13}C -NMR Chemical Shifts for DBTDL-Catalyzed Reaction Products

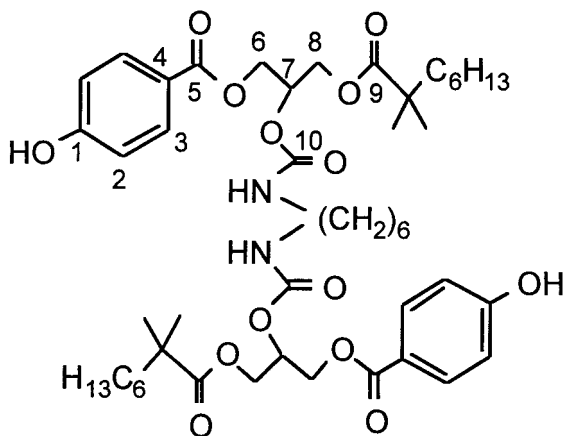
Carbon No.	PHEA	2 PHEA + 1 HDI, RT (1)	1 PHEA + 1 HDI, RT (2)	3 PHEA + 1 HDI Isocyanurate (3)
1	161.30	161.42	153.88	161.48
2	115.41	115.40	121.42, 115.36 ^a	115.36
3	132.09	131.99	131.15, 131.94 ^a	131.96
4	120.99	121.06	126.21	121.05
5 (>C=O) (benzoate ester)	166.80	166.13	165.43	166.05
6 (—CH ₂ —)	62.73	63.21	63.17	63.08
7 (—CH—)	72.26	69.24	69.20	69.28
8 (—CH ₂ —)	61.47	62.69	62.85	62.67
9 (>C=O) (neodecanoate ester)	177.98 ^b	176.96 ^b	176.66 ^b	176.86 ^b
10 (HNCO) (aliphatic urethane)	—	156.24	155.94	156.15
11 (HNCO) (phenolic urethane)	—	—	155.19	—
12 (isocyanurate carbon)	—	—	—	149.06

Numerous carbons below 50.00 ppm are not listed and are assigned to the aliphatic carbons of the HDI and PHEA moiety.

^a Several smaller peaks between 177.4 and 178.0 were noticed.

^b Peaks due to unreacted starting material.

be hereafter referred as aliphatic urethane, is assigned the following idealized structure:

**1** (aliphatic urethane)

When the above reaction was carried out in a refluxing solvent, the ^{13}C -NMR spectrum of the

product obtained was identical to that of **1**, suggesting that, irrespective of the reaction temperature, DBTDL always catalyzes the reaction of the aliphatic —OH group with the isocyanate.

In the second reaction product (**2**) of PHEA with HDI in a 1 : 1 molar ratio, in addition to the chemical-shift changes for carbons 5–10, there were also chemical-shift variations in the phenolic moiety. These changes in the chemical-shift data are attributed to the changes in the electron density in the phenol ring due to reaction with the isocyanate group and also due to the *ortho*- and *para*-directing effect of the phenolic oxygen. These changes are also consistent with the reported changes in the chemical shifts when phenols react with TAI.^{5,12d} A second urethane carbonyl carbon peak (11) due to the phenol-based urethane was observed at 155.19 ppm. These data show that phenolic hydroxyl groups will also react with isocyanates at ambient temperatures in presence of the DBTDL catalyst. However, the reaction will occur only after essentially all aliphatic —OH groups have reacted. These results indicate that this product (**2**) has a polymeric

Table III ^{13}C -NMR Chemical Shifts for DABCO-Catalyzed Reaction Products

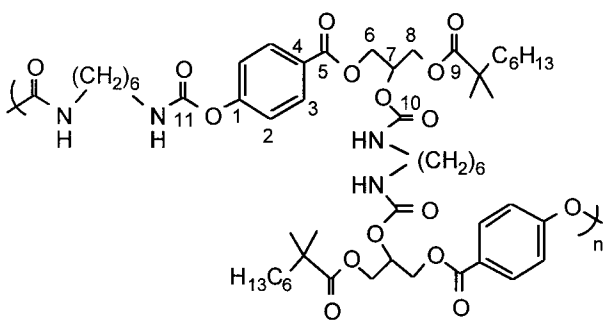
Carbon No.	PHEA	2 PHEA + 1 HDI RT (4)	1 PHEA + 1 HDI (5)	3 PHEA + 1 HDI Isocyanurate (6)	2 PHEA + 1 HDI, Δ (4')
1	161.23	153.86	153.81	153.70	153.97, 161.41 ^a
2	115.28	121.37, 115.31 ^a	121.35, 115.31 ^a	121.30, 115.24 ^a	121.25, 115.15 ^a
3	131.95	131.15, 131.98 ^a	131.10, 131.86 ^a	131.06, 131.83 ^a	130.96, 131.75 ^a
4	120.77	126.27	126.29	126.20	126.17, 120.71 ^a
5 (>C=O) (benzoate ester)	166.93	165.77	165.35	165.82	166.46, 165.93, 165.25
6 (—CH ₂ —)	62.64	62.99	62.86	62.97	62.88
7 (—CH—)	72.12	72.22	69.05	72.17	69.08
8 (—CH ₂ —)	61.26	61.48	62.79	61.35	62.45
9 (>C=O) (neodecanoate ester)	177.92 ^b	177.28 ^b	177.19 ^b	177.06 ^b	177.66, 177.26
10 (HNCO) (aliphatic urethane)	—	—	155.88	—	156.02
11 (HNCO) (phenolic urethane)	—	155.03	155.10	155.04	154.92
12 (isocyanurate carbon)	—	—	—	148.94	—

Numerous carbons below 50.00 ppm are not listed and are assigned to the aliphatic carbons of the HDI and PHEA moiety.

^a Several smaller peaks between 177.4 and 178.5 ppm were observed.

^b Peaks due to unreacted starting material.

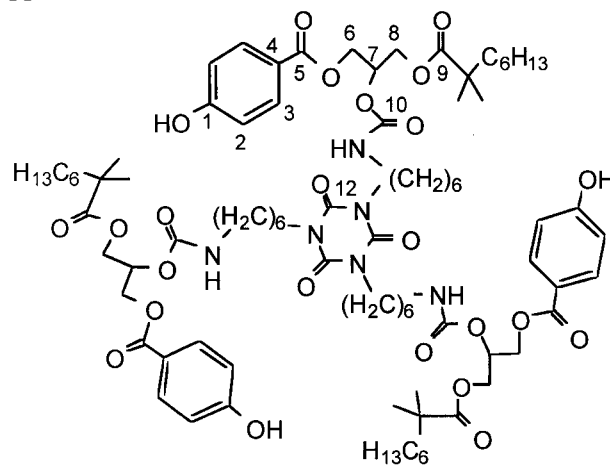
structure as shown below. This product continued to increase in viscosity for 4–5 days after the workup, perhaps due to further polymerization:



2 (and 5)

In the reaction product (3) of PHEA with HDI isocyanurate, the chemical shifts of carbons 1–10 in the product are closely similar to those of the aliphatic urethane 1, demonstrating that the aliphatic hydroxyl groups reacted under these conditions and the phenolic hydroxyl groups did not. The peak due

to the isocyanurate carbon (12) appeared at 149.06 ppm. An idealized structure of 3 is shown below:



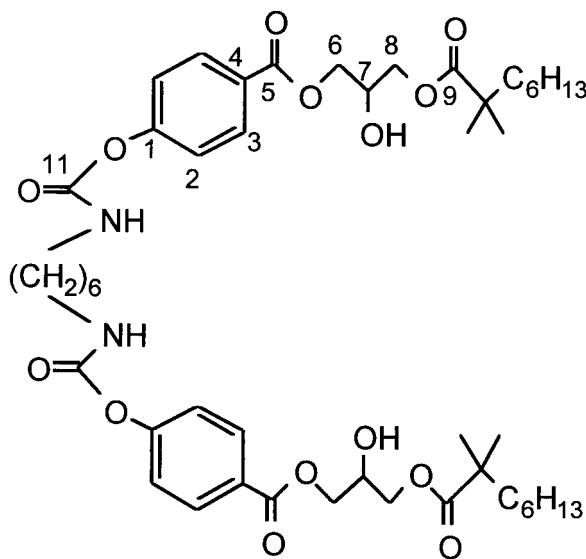
3

DABCO-Catalyzed Reactions

The chemical shifts of selected carbons in PHEA and the products 4, 5, 6, and 4' are shown in Table III. Unlike the DBTDL-catalyzed reactions,

DABCO-catalyzed reactions at RT did not go to completion. The reaction solutions were, however, worked up after 4–5 days for the RT reactions except for 4'. Therefore, the NMR spectra also showed the carbons due to the unreacted PHEA. Assignments of the peaks were carried out by the comparison of the chemical shifts of the products listed in Table II.

In the reaction product (4) of PHEA with HDI in a 2 : 1 molar ratio at RT, the chemical shifts of the aliphatic carbons 5–9 did not change significantly, compared to that of PHEA. However, the phenolic carbons have different chemical shifts, indicating that the reaction took place predominantly at the phenolic —OH group, as described in the case of the polymeric product 2. The urethane carbon (11) appeared at 155.03 ppm compared to that of the aliphatic urethane carbon (10) in 1 at 156.24 ppm. Based on these analyses, product (4), which will be hereafter referred as phenolic urethane, is assigned the following idealized structure. Compared to 1, product 4 was colorless and slightly less viscous.

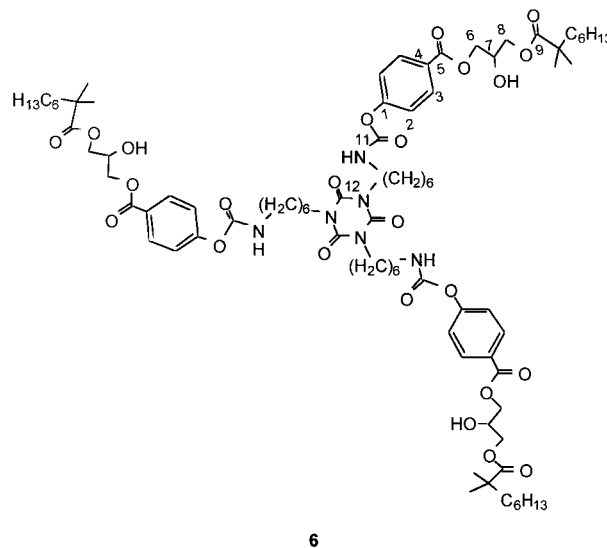


4 (phenolic urethane)

When PHEA was allowed to react with HDI in a 1 : 1 molar ratio using the DABCO catalyst at RT or reflux temperature, the ^{13}C -NMR spectrum of the product obtained (5) showed chemical-shift changes for both the phenolic carbons 1–4 and the aliphatic and ester carbons (5–9). The aliphatic

urethane carbonyl carbon peak (10) was observed at 155.88 ppm. These data show that aliphatic —OH groups will also react with isocyanates in presence of the DABCO catalyst. However, the reaction occurs at a much slower rate than does the DBTDL-catalyzed reaction; it was incomplete after 4 days. Based on the NMR data, the idealized structure of 5 could be similar to that of the linear polymer 2.

In the reaction product (6) of PHEA with HDI isocyanurate at RT, the chemical shifts of carbons 1–9 and 11 in the product are closely similar to those of 4, demonstrating that the phenolic hydroxyl groups reacted under these conditions and the aliphatic hydroxyl groups did not. The peak due to the isocyanurate carbon (12) appeared at 148.94 ppm. The idealized structure of 6 is shown below:



In the reaction product (4') of PHEA with HDI in a 2 : 1 molar ratio at refluxing ethyl acetate, there were peaks due to the unreacted moieties as well as new peaks due to the reaction with the isocyanate groups. The IR spectrum of the product did not show any ν_{NCO} band, showing that all the isocyanate groups reacted. In addition, there were also peaks due to the phenolic urethane (11) carbon at 154.92 ppm and the aliphatic urethane carbon (10) at 156.02 ppm. Thus, product (4') appears to be a mixture of the phenolic urethane and aliphatic urethane derivatives. The relative intensity of the aliphatic urethane carbon is higher than that of the phenolic urethane carbon. Correspondingly, the intensities of the unreacted phenol carbons are higher those of the reacted

Table IV ^{13}C NMR Chemical Shifts for Triphenylphosphine-Catalyzed Reaction Products in Ethyl Acetate

Carbon No.	PHEA	2 PHEA + 1 HDI RT (7)	2 PHEA + 1 HDI Δ (7')	1 PHEA + 1 HDI (8)
1	161.23	153.92, 161.32 ^a	153.96, 161.32 ^a	153.80, 161.54 ^a
2	115.28	121.37, 115.16 ^a	121.26, 115.16 ^a	121.25, 115.19 ^a
3	131.95	131.04, 131.79 ^a	130.99, 131.79 ^a	130.96, 131.72 ^a
4	120.77	126.17, 120.85 ^a	126.17, 120.74 ^a	125.89, 120.65 ^a
5 (>C=O) (benzoate ester)	166.93	165.66, 165.33	166.49, 165.94, 165.29	165.88, 165.25
6 (—CH ₂ —)	62.64	62.96	62.92	62.74
7 (—CH—)	72.12	72.04	72.08, 69.12	69.13
8 (—CH ₂ —)	61.26	61.17	62.54, 61.15	62.74
9 (>C=O) (neodecanoate ester)	177.92 ^b	177.28, 177.72, 178.22	177.73 ^b	177.12, 176.57
10 (HNCO) (aliphatic urethane)	—	—	156.03	155.90
11 (HNCO) (phenolic urethane)	—	154.95	154.92	154.99

Numerous carbons below 50.00 ppm are not listed and are assigned to the aliphatic carbons of the HDI and PHEA moiety.

^a Several smaller peaks between 177.4 and 178.5 ppm were observed.

^b Peaks due to unreacted starting material.

phenol moiety. Also, it appears that the urethane formation directly influences the chemical shifts of the benzoate ester carbons (5) at about 165 ppm as there were at least three benzoate ester carbon peaks. Perhaps, in this reaction, the phenolic urethane might have formed first and a subsequent rearrangement to the aliphatic urethane might have followed. This suggests that phenolic urethane is formed as a result of kinetic control, whereas the formation of aliphatic urethane is of thermodynamic control. These rearrangement reactions will be discussed in detail later.

Compounds **4** and **6** are di- and triisocyanates, respectively, blocked with the phenolic hydroxyl group of PHEA. PHEA is an ester derivative of 4-hydroxybenzoic acid.^{2f} There are reports of several blocked isocyanates[†] of 4-hydroxybenzoate esters which find applications in powder coatings,²⁰ plastisols,²¹ and radiation-curable coatings.²²

Triphenylphosphine-Catalyzed Reaction

The ^{13}C -NMR chemical shifts of various carbons in PHEA and the products (**7**, **7'**, and **8**) are listed

in Table IV. The procedure for atom numbering used is the same as in DBTDL- and DABCO-catalyzed reactions.

Similar to the DABCO-catalyzed reactions of PHEA with isocyanate, triphenylphosphine-catalyzed reactions also did not go to completion except for **7'**. The reaction solutions were, however, worked up after 3–4 days at RT. Therefore, the NMR spectra also showed the carbons due to the unreacted PHEA. Assignments of the peaks were carried out by comparison of the chemical shifts of the products listed in Tables II and III.

In the reaction product (**7**) of PHEA with HDI in a 2 : 1 molar ratio at RT, the chemical shift of carbons 5–9 did not change significantly, compared to that of PHEA. However, the phenolic carbons have different chemical shifts, indicating that the reaction took place predominantly at the phenolic hydroxyl group, as described for **2** or **5**. The phenolic urethane carbon (11) appeared at 154.95 ppm. Based on these analyses, product **7** has the same structure as that of the phenolic urethane, **4**.

When PHEA with HDI were allowed to react in a 1 : 1 molar ratio using the triphenylphosphine catalyst in a refluxing ethyl acetate solution, the

[†] For extensive reviews on blocked isocyanates, see ref. 19.

Table V ^{13}C NMR Chemical Shifts for DNNSA-Catalyzed Reaction Products in Ethyl Acetate

Carbon No.	PHEA	2 PHEA + 1 HDI RT (9)	2 PHEA + 1 HDI Δ (9')	1 PHEA + 1 HDI (10)
1	161.30	153.86, 161.62 ^a	161.33	153.74, 161.58 ^a
2	115.41	121.24, 115.18 ^a	114.95	121.12, 115.06 ^a
3	132.09	130.95, 131.71 ^a	131.51	130.79, 131.85 ^a
4	120.99	125.92, 120.61 ^a	120.28	125.82, 120.35 ^a
5 (>C=O) (benzoate ester)	166.80	165.92, 166.29	165.77	165.77, 165.08, 164.96
6 (—CH ₂ —)	62.73	62.54	62.50	62.54
7 (—CH—)	72.26	69.14, 72.03 ^a	69.04	69.05
8 (—CH ₂ —)	61.47	62.54	62.50	62.52
9 (>C=O) (neodecanoate ester)	177.98 ^b	177.12 ^b	176.52, 176.91, 178.76	176.94, 176.40
10 (HNCO) (aliphatic urethane)	—	156.00	155.97	155.82
11 (HNCO) (phenolic urethane)	—	154.95	—	154.89

Numerous carbons below 50.00 ppm are not listed and are assigned to the aliphatic carbons of the HDI and PHEA moiety.

^a Several smaller peaks between 177.4 and 178.5 ppm were observed.

^b Peaks due to unreacted starting material.

^{13}C -NMR spectrum of the product obtained (**8**) showed chemical-shift changes for the phenolic carbons 1–4 and also for the aliphatic and ester carbons (5–9). The aliphatic urethane carbonyl carbon peak (10) was observed at 155.90 ppm, besides the phenolic urethane at 154.99 ppm. These data show that aliphatic hydroxyl groups will also react with isocyanates in the presence of the triphenylphosphine catalyst. Based on the NMR data, the idealized structure of **8** is similar to that of linear polymer, **2**.

Similar to the DABCO-catalyzed reactions, in the reaction product (**7'**) of PHEA with HDI in a 2 : 1 molar ratio at refluxing ethyl acetate, there were peaks due to the unreacted moieties as well as new peaks due to the reaction with the isocyanate groups. The IR spectrum of the product did not show any ν_{NCO} band, suggesting that all the isocyanate groups have been reacted. There were also peaks due to the phenolic urethane (11) carbon at 154.92 ppm as well as aliphatic urethane carbon (10) at 156.02 ppm. The intensity of the latter is higher than that of the former. Based on these analyses, product (**7'**) appears to be a mixture of the phenolic urethane and aliphatic urethane derivatives. There are also three benzoate

ester carbons around 165 ppm for **7'**, suggesting it to be a mixture. As mentioned in the case of **4'**, a partial rearrangement from the phenolic to aliphatic urethane might have taken place upon reflux.

DNNSA-Catalyzed Reactions

Key peaks in the ^{13}C -NMR spectra of the products **9**, **9'**, and **10** are shown in Table V. The procedure for atom numbering is the same as those of the previous structures.

Analogous to the DABCO or the Ph_3P -catalyzed reactions, the acid-catalyzed reactions also proceeded very slowly at RT, according to IR spectroscopy. In the reaction product (**9**) of PHEA with HDI in a 2 : 1 molar ratio in ethyl acetate at RT, peaks due to the unreacted carbons were observed both in the aliphatic and phenolic moiety. There were also peaks due to the reactions on both —OH groups, suggesting that the reaction takes place at both —OH groups, perhaps at different rates. Phenolic urethane carbon (11) was observed at 154.95 ppm, and the aliphatic urethane carbon, at 156.00 ppm. These data show that both phenolic and aliphatic —OH groups

Table VI ^{13}C -NMR Chemical Shifts for Uncatalyzed Reaction Products

Carbon No.	PHEA	2 PHEA + 1 HDI, RT, (11)	2 PHEA + 1 HDI Δ (11')	1 PHEA + 1 HDI (12)
1	161.23	153.87, 161.34 ^a	154.07, 161.35 ^a	153.74, 161.34 ^a
2	115.28	121.34, 115.07 ^a	121.27, 115.16 ^a	121.25, 115.14 ^a
3	131.95	130.89, 131.65 ^a	130.97, 131.76 ^a	130.94, 131.71 ^a
4	120.77	126.05, 120.72 ^a	125.99, 120.60 ^a	126.42, 120.85 ^a
5	166.93	165.53, 165.19	166.55, 166.37, 166.02, 165.29	165.77, 165.22
6	62.64	62.94	62.88	62.99
7	72.12	71.77	71.97, 69.15	69.24
8	61.26	61.31	62.49	62.50
9	177.92 ^b	178.05, 177.55, 176.96	177.83, 177.31, 176.78	176.44 ^b
10	—	—	156.11	155.78
11	—	154.98	154.82	155.04

Numerous carbons below 50.00 ppm are not listed and are assigned to the aliphatic carbons of the HDI and PHEA moiety.

^a Several smaller peaks between 177.4 and 178.5 ppm were observed.

^b Peaks due to unreacted starting material.

react at ambient temperatures with aliphatic isocyanates in presence of an acid catalyst. These results indicate that product **9** may be a mixture of the aliphatic and phenolic urethane similar to **4'** or **7'**. Analogous to the NMR spectra of **4'** and **7'**, the presence of several benzoate carbon peaks (5) in the NMR spectrum also suggests that **9** is a mixture.

The ^{13}C -NMR spectrum of **9'**, obtained by the reaction of PHEA and HDI (2 : 1) in refluxing ethyl acetate, was comparable to the ^{13}C -NMR spectrum of **1**. Therefore, **9'** is thought to have the structure of the aliphatic urethane **1**. As noted earlier, it is likely that a phenolic urethane might have formed first, which rearranged to the aliphatic urethane upon refluxing. This will be discussed later.

When PHEA was allowed to react with HDI at a 1 : 1 molar ratio in a refluxing ethyl acetate solution, the ^{13}C -NMR spectrum of the reaction product (**10**) showed the peaks where the aliphatic —OH groups completely reacted but the phenolic —OH groups were only partially reacted. This suggests that the phenolic —OH group reacts with the isocyanate functionality at a slower rate compared to the aliphatic —OH group. Therefore, an idealized structure of **10** is likely to be that of the polymeric product **2**.

Uncatalyzed Reactions

Chemical shifts of the carbons in the uncatalyzed products are listed in Table VI. Like the the DABCO and triphenylphosphine catalyzed reactions, the uncatalyzed reactions also did not go to completion even after stirring at RT for 1 week or at reflux for 24 h. Therefore, the NMR spectra also showed the carbons due to unreacted starting material (PHEA).

The ^{13}C -NMR analyses of the products from the uncatalyzed reactions of PHEA with HDI suggest that these reactions proceeded similarly to the reaction using the DABCO catalyst. Thus, a 2 : 1 ratio of PHEA and HDI at RT gives product **11** mainly through reaction with the phenolic —OH group; its idealized structure is similar to that of **4**. When the above reaction was performed in refluxing ethyl acetate, the ^{13}C -NMR spectrum of the product (**11'**) suggested it to be a mixture of phenolic and aliphatic urethanes, besides unreacted starting materials, analogous to **4'** or **7'** or **9**. Also, when a 1 : 1 mol ratio of PHEA and HDI are refluxed in acetonitrile, the ^{13}C -NMR of product (**12**) confirmed that the urethane formation proceeds through both —OH groups with an idealized structure similar to that of **2**.

Transcarbamylation Reactions

From the above reactions, it was found in the case of **4'**, **7'**, **9'**, and **11'** that the more aliphatic urethane derivative was obtained when the reactions were performed in refluxing solutions than at RT. This may be attributed to kinetically controlled formation of a phenolic urethane, whereas aliphatic urethane formation is thermodynamically controlled. It may be noticed that compounds **1** and **3** are di- and triisocyanates blocked with the aliphatic hydroxy group of PHEA and compounds **4** and **6** are di- and triisocyanates blocked with the phenolic hydroxy group of PHEA. These observations show that free isocyanate is generated more readily from a phenol-blocked isocyanate than from an aliphatic alcohol-blocked isocyanate.

In the literature, there are several reports of deblocking reactions of aliphatic alcohol-blocked urethanes²³ and phenol-blocked urethanes.²⁴ For example, Muramatsu et al.²⁵ reported that the deblocking reactions are related to the electron densities of these compounds and, therefore, can be predicted using computer-based simulation. Endo and co-workers²⁶ reported the transesterification of poly(*N*-acylurethanes) using various diols and triols at ambient temperatures. They also reported that phenyl esters in toluene solution undergo transesterification at temperatures as low as 75°C.

There are also reports of the deblocking reactions in the presence of reactants containing active hydrogens. Thus, Yang and Lee²⁷ studied phenol-blocked urethane from triisocyanates in the presence of glycerin-terminated urethane prepolymers, using IR spectroscopy. They found that the phenol-blocked urethanes deblock above 120°C and the isocyanate generated reacts with hydroxyl groups of urethane prepolymers. More recently, Ma and co-workers²⁸ studied the copolymerization of phenolic resin with blocked polyurethane along with the *p*-toluenesulfonic acid catalyst using IR spectroscopy and dynamic mechanical analysis (DMA). The IR spectra of the copolymerization products were recorded at 170°C at various times. They reported the appearance of the ν_{NCO} band at 2270 cm⁻¹ after heating for 30 s due to the deblocking reaction. The isocyanate band disappeared in 1.5 min due to the fast reaction of the isocyanate group with the hydroxyl groups of the phenolic resins. Carlson et al.²⁹ reported the deblocking reactions in a blend of methyl ethyl ketoxime (MEKO)-blocked

trimerized isophoronediiisocyanate (IPDI) and acrylic copolymers, using IR spectroscopy and DMA. The experiments were performed in the presence of DBTDL and DABCO catalysts. They found that DABCO catalyzes the deblocking reaction, whereas DBTDL significantly favors the curing reaction between the free isocyanate and hydroxyl functionalities. Katsamberis and Pappas³⁰ studied the reactions of MEKO-blocked HDI isocyanurate and 4,4'-methylenediphenyldiisocyanate (MDI) with polyester polyol, using various amine catalysts. They monitored the progress of the reaction by the gelation time. They found that the extent of reaction was dependent on the basicity of the amine and its steric hindrance. Boutevin et al.^{31a,‡} reported that the deblocking reactions of phenol-blocked aliphatic urethanes can be effected at lower temperatures (<100°C) using amine catalysts. Generally, electron-withdrawing groups, such as —CO₂R, —NO₂, and —CN groups, at the *para* position of the phenol group lower the temperature of the deblocking reactions.^{19a}

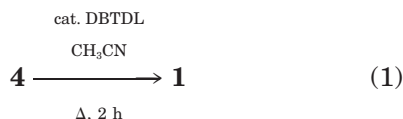
Most of these deblocking reactions are performed in the melt phase even though a few are reported in the solution phase. The reaction conditions in the solution phase will also be dependent on solvent polarity. Thus, Thames and Boyer³² described an inverse relationship, for various blocked isocyanates, between the deblocking temperature and solvent polarity. Contrary to this, Lucas and Wu,³³ who studied the deblocking of MEKO-blocked dimethyl *m*-isoprenyl benzyl isocyanate, reported that the deblocking of blocked isocyanates is favored in nonpolar solvents. Generally, the solution-phase deblocking reactions take place at a faster rate or at lower temperatures. For example, Shimizu et al.³⁴ studied the kinetics of deblocking reactions of phenol-blocked MDI at 110°C in DMSO or diglyme solutions containing an alcohol (diethylene glycol monomethyl ether) and an amine catalyst (DABCO). The reaction in DMSO was found to be 10 times faster than in diglyme.

Among the compounds synthesized in this study, the phenolic urethanes were obtained by the DABCO (**4**), Ph₃P (**7**), or uncatalyzed (**11**) reactions between PHEA and HDI (2 : 1 mol ratio)

‡ Alternately, Burton and Doorkian^{31b} reported the use of phosphines or organophosphorus-containing catalysts, such as tetrabutylphosphonium bicarbonate, for deblocking reactions that occur at lower temperatures or in a shorter time compared to the DBTDL-catalyzed reactions.

at RT. Since tin catalysts always favored the formation of aliphatic urethane first, these phenolic urethanes may be rearranged to the aliphatic urethane upon heating with the DBTDL catalyst.

The rearrangement reactions, discussed below, were studied where DABCO and DBTDL catalysts are involved since they are widely used in isocyanate reactions. Compound **4** has an active hydrogen in the form of an aliphatic alcohol functionality. Based on the above literature reports, it seems likely that if the phenolic urethane is deblocked the isocyanate generated might react with the aliphatic hydroxyl group. Thus, when the acetonitrile solution of **4** (containing the residual DABCO catalyst) was refluxed for 2 days, the ^{13}C -NMR of the product was comparable to that of **4'**, which is a mixture of the phenol and aliphatic —OH-based urethanes. This reaffirms our earlier assertion that the initially formed phenolic urethane could undergo rearrangement to the aliphatic urethane (**1**). When the DBTDL catalyst was added to the refluxing acetonitrile solution, this rearrangement, known as transcarbamylation,[§] was complete in approximately 2 h:



This result is consistent with the observations of Carlson et al.²⁹ However, transcarbamylation was found to be temperature dependent according to the ^{13}C -NMR of the product obtained by stirring the acetonitrile solution of **4** with DBTDL at RT for 2 days.

Refluxing the acetonitrile solution of the aliphatic urethane (**1**) containing a residual amount of DBTDL, along with a catalytic amount of DABCO, did not give rise to any transcarbamylation to the phenolic urethane, according to the ^{13}C -NMR spectrum. This confirms that **1** is thermodynamically more stable than is **4**. There are precedents for such NMR studies for the thermal deblocking of MEKO-blocked MDI and 2,4- and 2,6-toluenediisocyanates (TDI)³⁶ and also the de-

blocking of acetone oxime-blocked MDI in the presence of active hydrogen-containing polymers such as poly(vinyl alcohol), polyacrylamide, and poly(acrylic acid).³⁷

Amine and tin catalysts reportedly bring about synergistic effects in the deblocking reactions of phenol-blocked isocyanates.²⁴ Perhaps, the transcarbamylation reaction of **4** using DBTDL and residual DABCO catalysts may be accelerated by such synergistic effects. This could be confirmed by allowing the transcarbamylation reaction of **11**, which has a similar structure but no residual catalyst present. Thus, **11** was refluxed in acetonitrile for 12 h in the presence or absence of the DBTDL catalyst. The relative intensities of the peaks in the ^{13}C -NMR spectra of the products suggested that in the absence of a catalyst the transcarbamylation reaction is slower than when the DABCO catalyst was present and that the addition of the DBTDL catalyst increases the rate. Therefore, the synergistic effects of the amine and tin catalysts significantly influence the rate of transcarbamylation.

To examine the effect of solvent polarity on the transcarbamylation reaction of **4**, it was mixed with catalytic amount of DBTDL and was refluxed in cyclohexane or ethyl acetate. These solvents have lower polarity (see Table I) but similar boiling points. The phenolic urethane **4** was not quite soluble in cyclohexane and formed an oily bottom layer. The ^{13}C -NMR spectra of the products from these solvents was similar to that of **1**, suggesting that the transcarbamylation is independent of the solvent polarity. This is contrary to the observations by Thames and Boyer,³² who described an inverse relationship between the deblocking temperature and solvent polarity, and by Lucas and Wu,³³ who concluded that less polar solvents favor the deblocking reaction.

When **4**, mixed with a catalytic amount of DBTDL, was refluxed in anhydrous ether for 12 h, the ^{13}C -NMR data indicated only partial rearrangement, suggesting that the rearrangement is temperature-dependent. Further, when this reaction was performed at 60–65°C in acetonitrile and cyclohexane for 12 h, only partial rearrangement occurred, reaffirming the temperature dependence for the rearrangement.

Two mechanisms have been proposed for the reactions involving blocked isocyanates.^{23,24,32} They are (1) an elimination–addition mechanism and (2) a substitution-type mechanism. Most of the deblocking reactions reported in the literature are thought to involve the elimination–addition

[§] Many transcarbamylation reactions are enzyme catalyzed. For recent reports, see ref. 35a–d. A nonenzymatic transcarbamylation was reported by Al-Rawi et al.,^{35e} wherein the histamine and histidine are carbamoylated on the heterocyclic ring nitrogen in aqueous solutions of isocyanic acid (HNCO) at pH 3–11. Upon further reaction, the carbamoyl group is transferred to the amino nitrogen to form a urea via an elimination–addition mechanism.

mechanism. De Aguirre and Collot³⁸ studied the mechanism of dissociation of blocked urethanes, derived from several phenolic and aliphatic alcohols, using kinetic and thermodynamic equilibrium states and concluded that deblocking occurs via an elimination–addition mechanism.

To examine whether the rearrangement of **4** is intermolecular, approximately 0.20 g of **4**, mixed with DBTDL (0.01 g), was refluxed (A) in acetonitrile, along with stoichiometric amount of isopropanol (IPA), and (B) in IPA as solvent. IPA was chosen since it is a secondary alcohol as is the aliphatic alcohol in PHEA. IPA-blocked-HDI (**13**) was independently synthesized.[#] Its ¹³C-NMR spectrum showed its urethane carbon at 156.20 ppm and the 2-carbon of the IPA moiety appeared at 67.58 ppm. ¹³C-NMR spectra of the products of reaction (A) showed **1** along with the reaction product of IPA with HDI. Three different blocked isocyanates can result from these reactions: IPA-blocked-HDI-blocked-IPA, IPA-blocked-HDI-blocked-PHEA, and PHEA-blocked-HDI-blocked-PHEA. However, because of peak overlap, only two chemical shifts were observed for the urethane carbons, at 156.22 and 155.88 ppm, and for the carbons bonded to the alkoxy groups at 67.54 and 69.10 ppm.

In reaction (B), with excess IPA, the ¹³C-NMR spectra also showed a mixture of products, but the peaks at 156.2 and 67.5 were significantly stronger than in the product of reaction (A). This result excludes an intramolecular mechanism for the transcarbamoylation but does not confirm either of the two proposed mechanisms.

To examine whether the aliphatic urethane (**1**) will undergo a transcarbamoylation reaction with another aliphatic alcohol, it was refluxed with excess IPA for 12 h. The ¹³C-NMR spectrum of the product was similar to that of the starting material **1**, indicating the absence of any transcarbamoylation reaction. This experiment also reaffirms that an aliphatic urethane is thermodynamically more stable than is a phenolic urethane.

DSC Studies

The transcarbamoylation reaction of urethanes **4** (containing residual DABCO) and **11** (product of the uncatalyzed reaction) to give **1** were also studied by DSC, scanning at 5°C/min. The DSC trace

of **4** displayed an endotherm with the onset around 90°C and the maximum around 117°C, presumably due to the deblocking reactions. However, the DSC trace of **11** did not show an endotherm. Instead, the material started decomposing at temperatures greater than 170°C.^{||} These data confirm that deblocking of the phenolic urethane is catalyzed by the DABCO catalyst. The effect of different catalysts on the deblocking reactions of blocked isocyanates was discussed in the literature.^{19a,24}

It has been reported that the DSC scans of several phenol-blocked urethanes, derived from MDI, show endothermic transitions due to deblocking reactions.⁴¹ Anagnostou and Jaul⁴² also reported the deblocking reactions of several blocked isocyanates of MDI using different blocking groups, such as caprolactam, MEKO, and benzotriazole, using DSC and IR spectroscopy. They also observed endotherms at temperatures ranging from 40 to 200°C depending on the blocking group. Besides, they recorded the IR spectra of the deblocked products which showed the ν_{NCO} band at about 2256 cm⁻¹. However, when they heated these blocked isocyanates in the presence of a polyol, the DSC scans showed exotherms due to further reaction of the isocyanate with the —OH groups. Similarly, Pascault and coworkers⁴³ also reported the use of IR spectroscopy and DSC to study the deblocking of several aromatic and aliphatic diisocyanates using different blocking groups and reported that MEKO-blocked aromatic diisocyanates start decomposing at 80°C, whereas the corresponding aliphatic diisocyanates start deblocking at higher temperatures (ca. 120°C).

Since tin catalysts favor the formation of the aliphatic urethane (**1**) over the phenolic urethane (**4**), the latter was mixed with a catalytic amount of DBTDL by codissolving them in acetonitrile and subsequent evaporation of the solvent. The DSC scan of this mixture showed an initial endotherm of a lesser magnitude, followed by a major exothermic transition with onset around 120°C and the maximum around 135°C. This exotherm is probably due to the rearrangement of **4** to **1**, in line with the observations by ¹³C-NMR. Similarly, a mixture of **11** and a catalytic amount of

[#] Synthesis of isopropanol-blocked-HDI was previously reported for urethane-based waxy compositions for adhesives, sealants and binders. See ref. 39.

^{||} The decomposition of polyurethanes is expected to undergo three different routes: (1) endothermal depolymerization to the original monomers; (2) reactions involving a six-membered transition state; and (3) a rupture–recombination mechanism. The last two involve exothermal reactions.

DBTDL also showed an endotherm with the onset around 90°C and maximum around 120°C due to the deblocking reaction, followed by an exothermic reaction with a maximum around 140°C due to the reaction of the isocyanate liberated with the aliphatic alcohol group. The appearance of an endotherm followed by an exotherm in these DSC runs suggests that the mechanism of the transcarbamoylation reaction in the absence of a solvent involves deblocking of the phenolic urethane (**4** or **11**) and a subsequent reaction of the resulting free isocyanate with the aliphatic alcohol.

SUMMARY AND CONCLUSIONS

Reactions of a PHEA with HDI and its trimer and an organotin catalyst at RT give new urethane derivatives. The ¹³C-NMR spectra of the products clearly demonstrate that the two —OH groups react differently with the isocyanate functionality, depending on the reaction conditions. With the DBTDL catalyst at RT, the aliphatic —OH group reacts with the isocyanate group at a much faster rate than with the phenolic —OH group. With the DABCO or Ph₃P catalyst at RT, the relative reactivity is reversed. The differences in the reactivity are so great that different pairs of adducts (**1** and **4**, **3** and **6**) can be isolated in which different structures result from the same reactants. Uncatalyzed reactions at RT proceed similarly to the DABCO- or Ph₃P-catalyzed reactions but are much slower. These observations are similar to those of Agrawal⁵ where no catalyst was used and to those of Francis and Mitra⁸ using the DBTDL catalyst. Acid catalysts such as DNNSA favor the reaction at RT at both —OH groups, although at different rates.

However, in refluxing solutions, the structures of the reaction products for the DABCO, Ph₃P, or uncatalyzed reactions were different as they give a mixture of aliphatic urethanes along with the phenolic urethanes. The ¹³C-NMR data showed a higher intensity for the aliphatic urethane carbon than for the phenolic urethane carbon. Perhaps, the phenolic urethane might have formed first by kinetic control and then rearranged to the aliphatic urethane under these conditions. In the case of the DNNSA-catalyzed reactions, aliphatic urethane was the only product. It appears that the rearrangement, if any, is better catalyzed by the acid than by an amine or a phosphine catalyst.

When the phenolic urethane (**4**) was refluxed with the DBTDL catalyst in acetonitrile for 12 h, a rearrangement was observed to give the aliphatic urethane (**1**). This rearrangement, known as transcarbamoylation, was also noticed in refluxing cyclohexane or ethyl acetate, implying its indifference to solvent polarity. A slow transcarbamoylation reaction was also observed when **4** alone was refluxed in acetonitrile for 2 days or more, suggesting that transcarbamoylation may also be catalyzed by the residual DABCO catalyst present. This is in agreement with the observations in the synthesis of the products **4'**, **7'**, **9'**, and **11'**.

Slow transcarbamoylation of **4**, containing the DBTDL catalyst, was observed in refluxing ether or when heated at 60–65°C in acetonitrile or cyclohexane, confirming the absence of any solvent effect. Refluxing a solution of the uncatalyzed phenolic urethane **11** in acetonitrile with DBTDL for 12 h also gave rise to the transcarbamoylation. However, the reaction was not complete during this time period. Refluxing **11** without any added DBTDL catalyst in acetonitrile led to much slower transcarbamoylation. These observations suggest a synergistic effect due to the amine catalyst (DABCO) and tin catalyst (DBTDL). The aliphatic urethane (**1**) did not undergo a transcarbamoylation reaction with an external alcohol in the presence of DBTDL, suggesting that **1** is thermodynamically more stable than is **4**.

DSC studies showed an endotherm for **4** with the onset around 90°C and maximum around 117°C, due to deblocking reactions. However, a subsequent exotherm was noticed for **4** mixed with a catalytic amount of DBTDL, around 140°C, due to a transcarbamoylation reaction. The DSC trace of **11** did not show any endotherm between 90 and 120°C, suggesting the need of a catalyst for the deblocking reaction. However, when **11** was heated with the DBTDL catalyst, the DSC trace showed an endotherm with a maximum around 117°C due to the deblocking and subsequent exotherm with a maximum around 150°C due to the reaction of the isocyanate with the aliphatic alcohol.

These data give a clear indication of the sequence of reactions to be expected when PHEA is used as a component of isocyanate-crosslinked coatings along with reactive diluents such as diols and polyols: In coating formulations that contain excess isocyanate, both the aliphatic and the phenolic —OH groups will react at ambient temperatures, rapidly with organotin catalysts and more

slowly with amine, phosphine, or acid catalysts. In formulations with excess —OH groups at ambient temperatures, organotin catalysts strongly favor the reaction of the aliphatic —OH group and amine or phosphine catalysts strongly favor the reaction of the phenolic —OH group. Acid catalysts will give aliphatic urethane at higher temperatures.

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