Blocked Polyisocyanates Containing Fluorine Atoms as Crosslinking Agents for Polyurethane Powder Coatings

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ABSTRACT: Using alicyclic diisocyanates (HDI, TMDI, IPDI, H_{12}MDI), aliphatic unfluorinated and fluorinated alcohols, dibutyltin dilaurate as well as triethylamine as catalysts, blocked polyisocyanate crosslinkers for powder lacquers were synthesized. The chemical structure of these compounds was characterized by means of IR, ^{1}H-NMR, ^{13}C-NMR, and ^{19}F-NMR spectroscopy. Their molecular weight distribution parameters were determined by gel permeation chromatography. These blocked polyisocyanates were used for the production of powder lacquer compositions and coatings. The three-dimensional surface topography and surface chemical structure of the resulting powder lacquers were investigated by means of confocal microscope and ATR FT-IR. The values of surface roughness parameters were calculated. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 3302–3311, 2012

Key words: fluoropolymers; polyurethanes; coatings

INTRODUCTION

The continuing success of powder coatings results not only from their known ecological and economical advantages, but also from their improved performance and the variety of substrates on which they can be applied.[1] The properties of the coatings are determined by the chemical structures of the resin, the curing agent as well as the improved additives. The presence of fluorine offers a wide range of interesting properties, such as low wettability (water/oil repellency) and low coefficients of friction. The good water/oil repellency is especially due to the low surface energy of the fluorinated films, and there has been a considerable amount of interest to prepare fluorinated coatings. In such an approach, only a very small quantity of fluorinated species (at fluorine concentration of only 0.5 wt %) is needed to provide a surface with low surface energy.[2–8] The fluorinated species would migrate toward the air/film interface to minimize the interfacial energy.[2]

A blocked polyisocyanate is an adduct containing a comparatively weak bond formed by the reaction between a polyisocyanate and a compound containing an active hydrogen atom. At elevated temperatures, the reaction tends to proceed in such a way as to regenerate the isocyanate and the blocking agent. The regenerated polyisocyanate could react with a coreactant containing the hydroxyl functional groups to form urethane with thermally stable bonds (addition–elimination mechanism S_N2).[9]

Recently, I have presented a method of synthesizing polyisocyanates, which were internally blocked by allophanate bonds.[10] The synthesis of these polyisocyanates covered three stages: the synthesis of urethane polyisocyanate, the synthesis of allophanate, and the blocking reaction. In this article, I would like to report a convenient way of synthesizing fluorinated blocked polyisocyanate, which allows for an easy and accurate approach to prepare polyurethane powder lacquer systems. Replacing monohydric alcohol at an initial stage with fluorinated alcohol leads to urethane isocyanate containing fluorine atoms. The following stages involved an addition of the second molecule of diisocyanate to form allophanate, as well as the process of blocking the free (unreacted) —NCO groups. The principal purpose of this work was to determine the optimal reaction conditions, that is, molar ratio of diisocyanate and alcohol, temperature, time, catalysts, and atmosphere. It was also necessary to limit the formation of by-products. Special attention was paid to the contents of isocyanate groups at individual stages of the synthesis process, and to the distribution of molecular weight (MWD) in the produced polyisocyanates. The MWD of these polyisocyanates was investigated by means of gel permeation chromatography (GPC). Spectroscopic techniques such as Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance spectroscopy (^{1}H-NMR, ^{13}C-NMR, and ^{19}F-NMR) were used to characterize the chemical

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structure of these polyisocyanates. The surface topography analyses of the obtained polyurethane powder coating containing fluorinated polyisocyanates were performed and compared. In addition to the surface topography measurements, ATR FT-IR was used to reveal chemical structure at the surface.

EXPERIMENTAL

Raw materials and reagents

1,6-Hexamethylene diisocyanate (HDI)-Desmodur H, isophorone diisocyanate (IPDI)-Desmodur I, 4,4′-dicyclohexylmethane diisocyanate (H_{12}MDI)-Desmodur W from Bayer A.G. (Leverkusen, Germany). 2,2′,4- and 2,4,4′-Trimethyl-1,6-hexamethylene diisocyanate (TMDI)-Vestanat TMDI, from Evonik Degussa G.m.b.H. (Marl, Germany). 2,2,2-Trifluoroethanol (TFE) from Aldrich (Buchs, Switzerland). 2,2,3,3-tetrafluoropropanol (TFP) from Apollo Scientific (Stockport, England). Ethanol (ET), 1-propanol (PR) and *t*-butanol (*t*-BU) from POCH (Gliwice, Poland). Imidazol (I) and benzoin from Aldrich (Buchs, Switzerland). Rucote 102-polyester resin based on isophthalic acid and neopentyl glycol, acid value: 11–14 mg KOH/g, hydroxyl value: 35–45 mg KOH/g, T_g: 59°C, from Bayer A. G. (Leverkusen, Germany). WorleeAdd 902 (acrylate resin) and WorléeAdd ST-70 (stannous octoate (II)) from Worlée-Chemie G.m.b. H (Lauenburg, Germany). Byk 361*N* (acrylate copolymer) from BYK-Chemie G.m.b.H. (Wesel, Germany).

Synthesis of blocked polyisocyanates

The synthesis covered three stages: the synthesis of urethaneisocyanate, the synthesis of allophanate, and the blocking reaction.

Synthesis of urethaneisocyanate

Diisocyanate and dibutyltin dilaurate as well as triethylamine as catalysts (both at 0.1 wt % with respect to diisocyanate) were placed in a three-necked flask equipped with a reflux condenser, thermometer, glass stirrer, nitrogen inlet, and dropping funnel. A calculated amount of alcohol (to keep the molar ratio of diisocyanate to alcohol at 2 : 1) was introduced drop-wise to diisocyanate. The time of introduction was adjusted to about 30 min. The reaction mixture was then maintained at the temperature of 60–110°C, stirred and refluxed for 3 up to 33 h, depending on the kind of diisocyanate and alcohol. The end point of the reaction was controlled by the content of —NCO groups.

Allophanate synthesis

The reaction mixture was heated up to 80–150°C, stirred and refluxed for 3 up to 66 h, depending on the kind of diisocyanate and urethaneisocyanate. The reaction progress was controlled by the content of —NCO groups.

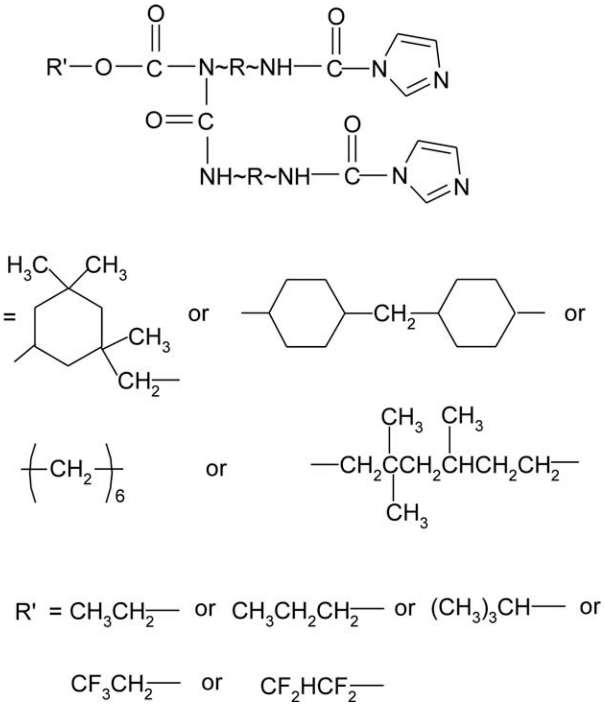


Figure 1 The molecular structure of the obtained blocked polyisocyanates.

Blocking reaction

A calculated amount of the blocking agent was added to reaction mixture in each case (the molar ratio of —NCO group to blocking agent at 1 : 1). The reactions were carried out in THF at the temperature of 55–70°C for 3 up to 6 h. After the completion of the reaction, the levelling agent Byk 361*N* (3 wt %) was added. The products were evaporated under vacuum and dried at the temperature of 100 ± 1°C to remove the solvent. The molecular structure of obtained blocked polyisocyanates was presented in Figure 1 and the compilation of the synthesis parameters (reaction temperature and reaction time) was presented in Table I. The obtained products were marked with symbols, for example, IPDI-TFP-I, where individual segments stand for the names of the feeds used.

Preparing lacquer compositions and coatings

The blocked polyisocyanate was mixed with polyester resin RUCOTE 102 (NCO:OH molar ratio = 1 : 1) as well as the catalyst WorleeAdd ST-70 (stannous octoate (II) (3 wt %) and degassing agents: WorleeAdd 902 (acrylate resin) (1.5 wt %) and benzoin (1 wt %). The mixture was grinded, melted, and

TABLE I
Comparison of Synthesis Parameters

Sample no.	Symbol of sample	Time/temp. stage I	Time/temp. stage II	Time/temp. stage III	Total time of synthesis
1	HDI/TFE/I	3 h, 60°C	5 h, 105°C	3 h, 65°C	11 h
2	HDI/n-PR/I	6 h 30 min, 60°C	6 h 30 min, 80°C	3 h 30 min, 60°C	16 h 30 min
3	TMDI/TFE/I	3 h 30 min, 60°C	13 h, 115°C	5 h, 55°C	21 h 30 min
4	TMDI/E/I	4 h, 60°C	3 h, 150°C	4 h, 60°C	11 h
5	TMDI/n-PR/I	7 h 30 min, 60°C	9 h, 130°C	4 h 30 min, 60°C	21 h
6	H_{12}MDI/TFE/I	5 h, 60°C	66 h 30 min, 105°C	6 h 30 min, 60°C	78 h
7	H_{12}MDI/E/I	6 h, 60°C	6 h, 150°C	6 h, 60°C	18 h
8	H_{12}MDI/n-PR/I	15 h, 110°C	43 h, 116°C	5 h, 70°C	63 h
9	H_{12}MDI/t-BU/I	33 h 30 min, 110°C	47 h, 110°C	5 h, 70°C	85 h 30 min
10	IPDI/TFE/I	4 h, 60°C	19 h, 100°C	6 h, 50°C	29 h
11	IPDI/E/I	5 h, 60°C	4 h, 150°C	5 h, 60°C	14 h
12	IPDI/TFP/I	4 h, 60°C	12 h, 120°C	5 h, 60°C	21 h
13	IPDI/n-PR/I	12 h, 95°C	10 h, 130°C	4 h, 70°C	26 h

pulverized to the average particle size of 60 μm. The final powder coating was applied manually to steel panels and cured at 150°C for 30 min. The obtained lacquer compositions were marked with symbols: for example, H_{12}MDI/TFE/RU, where individual segments stand for the names of the feeds used.

Measurements

Characterizations of polyisocyanates

Concentration of —NCO groups. The typical dibutylamine method was employed. Excess of unreacted dibutylamine was titrated with aqueous HCl against bromophenol blue.[11]

Structural analysis

FT-IR spectroscopy. The IR spectra were taken by means of Thermo Scientific Nicolet 6700 FT-IR spectrophotometer in KBr pellets.

^{1}H-NMR, ^{13}C-NMR, and ^{19}F-NMR spectroscopy. The NMR spectra were recorded using a Bruker AvanceII 500 MHz unit. Deuterated chloroform, $CDCl_3$, or dimethylsulfoxide DMSO-d_6, were used as solvents. The chemical shifts values are given in ppm with reference to internal tetramethylsilane.

Gel permeation chromatography

The GPC apparatus used was a Viscotec T60A equipped with a triple detector: RI, light scattering (LS), and viscosity (DV) detector. Separations were made at 30 ± 0.1°C on two SDV columns (size 7.8 × 300 mm^2) packed with gel of pore diameter 100, 1000, and 10,000 Å from Polymer Standards Service. The eluent (THF) flow rate was 1 cm^3/min, with volume of inflow circuit—20 μdm.^{3} Operation of the chromatograph was controlled by the original computer software TRISEC Data Acquisition System by Viscotec; deconvolution was possible for individual peaks which corresponded to nonhomogeneous oligomers. The interpretation of the results was based on the conventional calibration of columns with polystyrene standards. The chromatographic analysis of standards yielded the calibration relation for logarithm of mass versus retention volume. The differential curves for distribution of molecular weights, as obtained from the sample elution curves and from the calibration equation, were presented in the form of standardized charts: detector signal divided by the total area below the chromatogram—logarithm of the molecular weight of components.

Characterizations of powder coatings

Surface topography measurements. The surface topography of the powder lacquers was investigated with the use of a NanoFocus Confocal Microscope (CM) μsurf explorer with a capability to perform an accurate three-dimensional measurement and submicron imaging, with outstanding 2 nm resolution. The 505-nm diode combined with optics, specifically enables resolution in *z*-direction 2–20 nm as well as in *x*, *y*-direction 500–3100 nm.

The values of R_a, R_z, R_t, R_q, $R_{\max}$, R_{mss}, and R_{pc} were used to characterize the coating roughness parameter. These symbols are defined as follow:

- R_a, arithmetic mean deviation of the assessed profile.
- R_z, max. height of the profile within a sampling length.
- R_t, total height of the profile on the evaluation length.
- R_q, root mean square deviation of the assessed profile.
- $R_{\max}$, max. profile peak height within a sampling length.
- R_{mss}, root-mean-square slope of the profile within a sampling length and the result is expressed in degrees.

- R_{pc}, peak count, number of peaks per centimeter. Each peak being higher than the upper threshold and falling under the lower threshold. The threshold is defined by a band, symmetrically separated (Sep) around the mean line [if Sep = 0.5 (μm), then the size of side of the mean is ± 0.25 (μm)]. The result is expressed in peaks/cm.

ATR FT-IR spectroscopy

Attenuated total reflection (ATR) spectra were recorded by reflection technique with a Thermo Scientific Nicolet 6700 FTIR instrument, equipped with a diamond crystal. The ATR experiment consists of placing the sample to be analyzed in contact with a high refractive index material (diamond, $n = 2.3$) through which the infrared beam is confirmed.

RESULTS AND DISCUSSION

Using alicyclic and aliphatic diisocyanates, aliphatic monohydric fluorinated and unfluorinated alcohols as well as the blocking compound, it was possible to obtain blocked polyisocyanates which were stable in the room temperature. Aliphatic (HDI, TMDI) and alicyclic diisocyanates (IPDI, H_{12}MDI) were employed in the syntheses because the coatings produced therefrom offer high resistance to yellowing. The synthesis itself involved three stages. The first stage was to form the urethane bond. Monohydric fluorinated alcohols like 2,2,2-trifluoroethanol (TFE) and 2,2,3,3-tetrafluoropropanol (TFP) or unfluorinated alcohols like: ethanol (ET), 1-propanol (PR), and *t*-butanol (*t*-BU) were used for that purpose. The use of dihydric alcohols would produce a mixture of urethane oligomers, while trihydric alcohols would yield branched structures, which would make it hard to identify the products. The reactions were conducted in bulk, at the alcohol-to-diisocyanate molar ratio equal to 1 : 2. Nitrogen blanketing was employed for the whole process to prevent side reactions. Since the allophanate bond is not a fast-forming one, two catalysts were used simultaneously: dibutyltin dilaurate and triethylamine. The combined use of two catalysts: organometallic and amine has been described in subject literature,[12] whereas their quantities were determined experimentally.

To limit the formation of by-products, which is promoted by high temperatures and a long time period, the reactions were conducted at the lowest possible temperatures. The first stage, that is, formation of the urethane bond for the samples 1–7 and 10–12, was reasonably easy under these conditions, that is, at the temperature as low as 60°C. The synthesis of samples H_{12}MDI/*n*-PR/I (8), H_{12}MDI/*t*-BU/I (9) and IPDI/*n*-PR/I (13) was conducted at higher temperatures, as the reaction did not progress at 60°C (Table I). The reaction progress was monitored by analyzing the content of free —NCO groups and by comparing the findings to those calculated theoretically. The reaction involving addition of fluorinated alcohols to diisocyanates was considerably easier than the addition of analogous alcohols which did not contain fluorine atoms. The presence of electronegative fluorine atoms in an alcohol molecule results in its increased polarity, which leads to an increase in —OH group reactivity. The rate of the reaction decreased simultaneously with an increase in the rank of alcohol. The addition reaction of secondary and tertiary alcohols to cycloaliphatic diisocyanates (H_{12}MDI and IPDI) was significantly more difficult. At stage II another molecule of diisocyanate was added into the urethane isocyanate created in stage I, thus creating an allophanate group. To optimize the temperature and the synthesis time at this stage, the process was conducted at temperatures of 80–150°C. Despite the respectively, severe process conditions, that stage took much longer. The rate of the addition reaction at this stage mostly depends on the diisocyanate structure and decreases in the following order: HDI, TMDI, IPDI, H_{12}MDI. The observed decrease in the rate of diisocyanate addition reaction is caused by the presence of deactivating alkyl substituents in TMDI, IPDI, and H_{12}MDI molecules. As the HDI reactivity is relatively high at the temperature of 80°C (the duration of stage II of the synthesis of sample HDI/*n*-PR/I was 6 h 30 min), the HDI addition reaction at this stage can be successfully conducted at this temperature. The analysis of the remaining data shows that the optimal temperature to conduct the bonding process of the remaining diisocyanates (TMDI, H_{12}MDI, IPDI) with appropriate urethane isocyanates should fall within the 130–150°C range.

The final stage was designed to block the remaining —NCO groups with the use of heterocyclic compound imidazole, which was nontoxic and which could be unblocked at relatively low temperature (about 140°C). The rate of this reaction depended on the structure of the blocked polyisocyanate. This process was already relatively easy at a temp. of 50–70°C. The influence of the structure of the diisocyanate used for the synthesis can be noted here, in a manner similar to stages I and II. The process of blocking the unreacted —NCO groups in polyisocyanate, which was obtained with the participation of HDI, occurred with the fastest rate, while in polyisocyanate which was obtained with the participation of H_{12}MDI the same process occurred with the slowest rate. The synthesis reactions allowed for obtaining products with solid consistency which could be easily powdered.

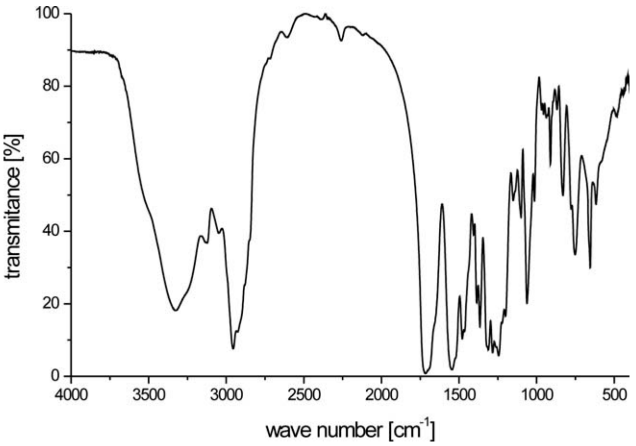


Figure 2 IR spectrum for sample IPDI/TFE/I.

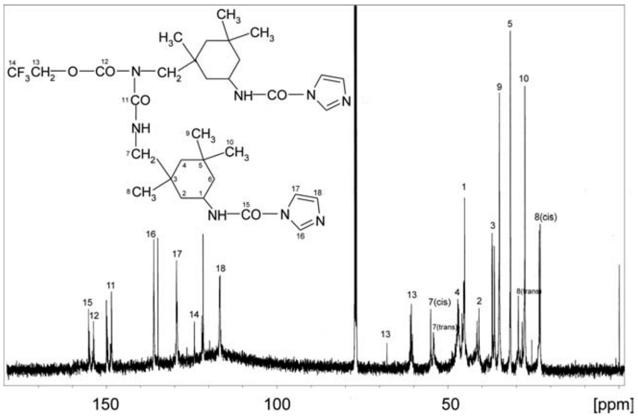


Figure 4 ^{13}C-NMR spectrum for sample IPDI/TFE/I.

FT-IR and NMR spectra

The structures of the obtained products were confirmed by FT-IR (Fig. 2) and NMR spectra (Figs. 3–5). The stretching vibration of the C=O group at 1720 cm^{-1} (amide I band) and of the N—H group at 3360 cm^{-1} confirm the presence of the urethane, urea, and allophanate linkages for all the adducts. The amide II band originated from combined scissoring deformation vibrations of the —N—H group occurring at 1541 cm^{-1}. Other amide bands were visible at 1246 cm^{-1} (amide III band), 654 cm^{-1} (amide IV band), and 763 cm^{-1} (amide V band). The bands at 1164, 1214, and 1284 cm^{-1}, respectively, corroborate the occurrence of symmetrical and asymmetrical stretching vibrations coming from the carbon–fluorine bond.[13]

The absence of absorption at 2260–2270 cm^{-1} indicates that isocyanate groups have been completely blocked. In the spectra of samples: H_{12}MDI/TFE/I, H_{12}MDI/n-PR/I, H_{12}MDI/t-BU/I, the occurrence of a small band was observed at 2120 cm^{-1} confirming the formation of products containing carbodiimide bonds. Although the formation of these bonds is promoted only at temperatures above 450°C,[14] small amounts of those were formed here already under significantly milder conditions (temperatures of 105–116°C). Very long time periods of synthesis probably favored the formation of these products (78–85 h). There were no bands in the spectra of the studied compounds at about 1415 cm^{-1}, which are specific for the isocyanurate ring. The absence of these bands confirms the proposed route for the reaction.

Deuterated chloroform, CDCl$_3$, or dimethylsulfoxide DMSO-d_6, were used as solvents for NMR analysis. CDCl$_3$ is less polar. In this solvent, the NH proton signals were less attributable because their resonances were very close to those of aromatic protons. The most suitable method was then found to carry out ^{1}H-NMR analysis in DMSO-d_6 and to use CDCl$_3$ for ^{13}C-NMR analysis.

In ^{1}H-NMR spectra the signals coming from allophanate and urea bond protons were present at 12.0 and 5.5 ppm, respectively (Fig. 3).[15,16] Weak signals appear for urethane bond protons within 8.4 ppm, which suggests that not all urethane groups have reacted with diisocyanate to form allophanate structures. In the 8.3–7.0 ppm range, the signals from imidazole were present. The peak at 7.7 ppm

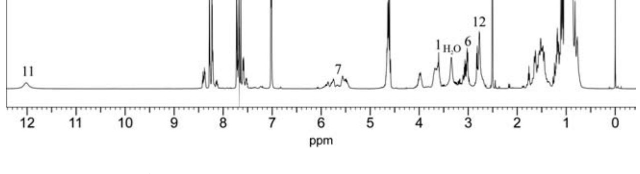


Figure 3 ^{1}H-NMR spectrum for sample HDI/TFE/I.

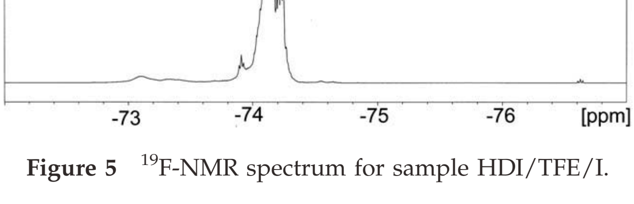


Figure 5 ^{19}F-NMR spectrum for sample HDI/TFE/I.

comes from the unreacted imidazole.[17] In the 2.8–4.6 ppm range, these signals are present from the $-CH_2-$ groups which are neighbors to urethane, allophanate or urea groups. The signal coming from alcohol methylene group protons adjacent to the allophanate group is visible at 4.6 ppm. The bands at 3.7 and 3.1 ppm come from hydrogen atoms of methylene group of diisocyanate adjacent to an allophante and urea bond, respectively. Two bands at 4.0 and 2.9 ppm probably come from other products present in the reaction mixture, for example, from hydrogen atoms of the methylene group of diisocyanate adjacent to a urethane and urea bond. Within the range of 0.7–1.7 ppm, signals of the methylene groups of diisocyanate were marked with numbers 2–5.

The ^{13}C-NMR spectrum (Fig. 4) reveals the presence of four main signals in the carbonyl region. According to literature,[15,18] the signals at 155.0 and 149.5 are attributed to the $C{=}O$ from allophanate. The signal at 150.1 ppm comes from the $C{=}O$ of primary type urethane. IPDI is the diisocyanate that contains primary and secondary isocyanate groups. The $C{=}O$ resonances from urea are found at 155.3 ppm. The chemical shift of this peak shows that the secondary type urea was formed. The possible dimer (uretidion), trimer (isocyanurate) and carbodiimide of isocyanate would have been present around 157.5, 148.0, and 140.0 ppm, respectively. Such functions, not observed in this case, are mostly present in aromatic diisocyanates. There were no peaks at 124 ppm, where a characteristic signal of the carbon atom forming an isocyanate group occurs, which shows that diisocyanate was completely reacted, something which is also confirmed by the IR analysis. Signals within the range of 115.6–136.2 ppm come from the imidazole blocking agent. Similarly as in ^{1}H-NMR spectra, peaks coming from unreacted imidazole were present here (peaks at 134.9 and 121.7 ppm).[17] However, it was not necessary to purify synthesized polyisocyanates, as imidazole evaporates during the coating hardening process. New bands at 67.9 and 61.1 ppm can be seen in the spectra. They originate from carbon atoms of alcohol methylene group adjacent to the allophanate and urethane bond. Within the 55.1–23.1 ppm range carbon atoms creating the IPDI skeleton generate their characteristic signals. IPDI exists as two isomers, *cis* (Z) and *trans* (E). Previous studies[18] showed that the *cis* form is the major isomer present at 75%, while the *trans* form is present at 25%. The polyisocyanate, the synthesis of which was performed by the addition of IPDI with TFE, shows peaks of *cis* and *trans*-isomers of the IPDI backbone.

In ^{19}F-NMR spectra a shift of the band of trifluoroethane coming from the $-CF_3$ towards higher values of the magnetic field is observed (from approximately −77.3 to −74.1 ppm) (by approximately 3.2 ppm) (Fig. 5). In the case of TFP, the signal coming from fluorine atoms of the tetrafluoropropanole $-CF_2-$ group is shifted from –126.9 to –124.2 ppm, while from fluorine atoms of the CF_2H- group the signal shifted from approximately –137.5 to –138.7 ppm and from –137.6 to –138.8 ppm compared to the TFP spectrum. This shows that these alcohols have reacted with the diisocyanate.

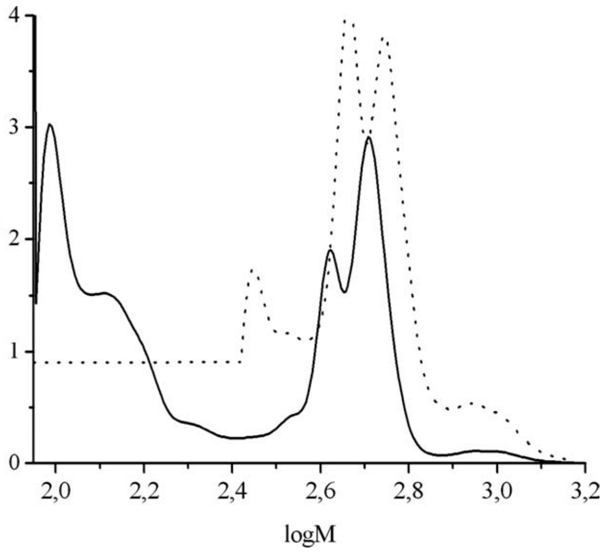


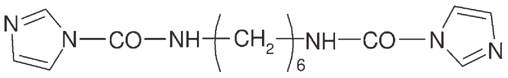
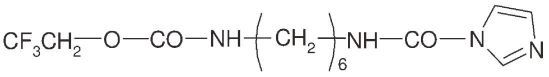
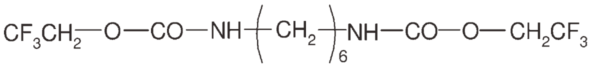
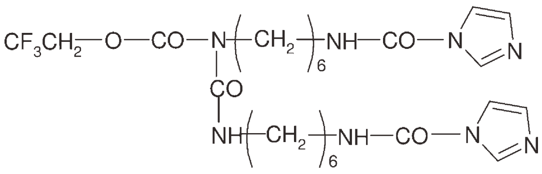
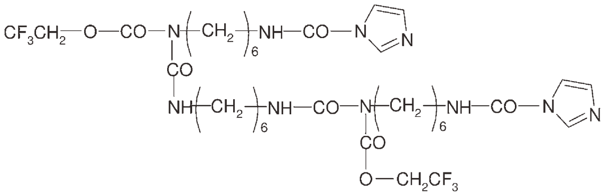
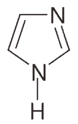
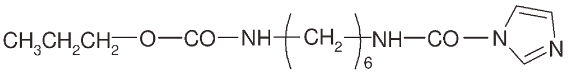
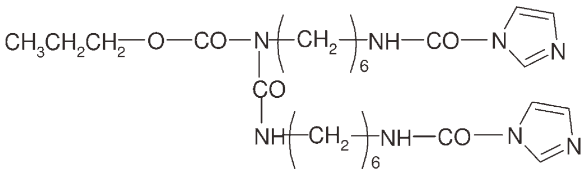
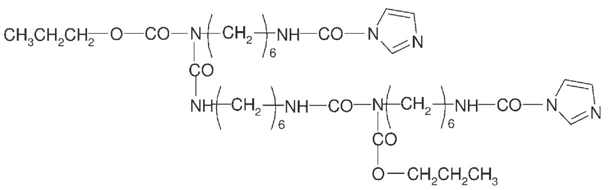
Figure 6 GPC chromatograms for sample HDI/TFE/I and HDI/*n*-PR/I.

Gel permeation chromatography

The principal task for the analysis of polyisocyanates is not only to confirm the expected chain structure but also to learn the complete distribution of molecular weights as well. Based on the GPC elution curves as recorded with the use of three detectors: RI, LS and DV, and based on the calibration curve, the molecular weight distribution (MWD) profiles were obtained (Fig. 6). The shape of the obtained MWD curves is very similar, which shows that the course of the reaction does not depend on the type of alcohol used for the synthesis. The shift of the sample $H_{12}MDI$/TFE/I chromatogram towards higher molecular masses results from the higher TFE molecular mass compared to *n*-propanol. It was concluded with the use of GPC that the composition of the obtained polyisocyanates is more complicated than it follows from the assumed stoichiometry.

Table II shows the most probable structures of compounds which were successfully attributed to the peaks registered by means of the GPC. The expected products were obtained besides other components, for example, oligomers with the gradually increasing molecular weights. The mixture contains diurethanes, diureas or urethane ureas, as well as

TABLE II
Interpretation for GPC Chromatograms

Symbol of sample	M_n as per MWD curves (g/mol)	Probable structure of compound	Theoretical molecular weight (g/mol)
HDI/TFE/I	292		304
	341		336
	467		368
	572		572
	880		840
HDI/n-PR/I	105		68
	420		295
	523		531
	860		758

small amounts of products created as a result of the reaction between urethane and allophanate. Small amounts of low molecular weight compounds were also present in the reaction mixture, and unconverted feedstocks were identified in some cases, as well.

The calculated molecular mass of compounds associated with the individual peaks was sometimes different from the mass determined on the basis of chromatograms. This difference may result from the calibration of the chromatographic columns by means of polystyrene standards, as their chemical

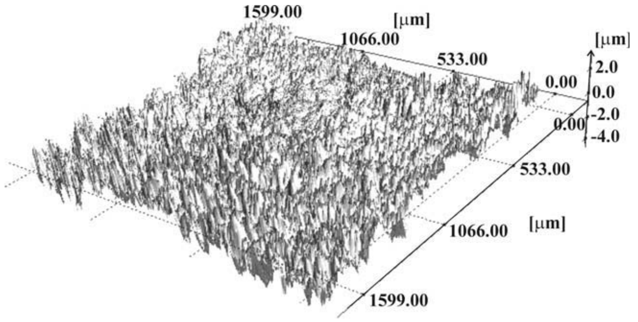


Figure 7 The confocal laser scanning microscope image of powder coating IPDI/*n*-PR/RU.

structure differs from the compounds under analysis. Therefore, they will act differently while penetrating a gel deposit.

Presentation of three-dimensional surface topography by confocal microscopy

This technique allowed for obtaining three-dimensional surface topographies of the powder coatings. This method is well-suited for investigating surface structures. The three-dimensional topographies of powder coatings were shown in Figures 7 and 8. The surface was smooth. The surfaces of the fluorine-containing powder coating exhibit a slightly larger irregularity and roughness (Fig. 9).

The values for surface roughness were calculated on the basis of confocal images. The obtained roughness parameters: R_a, R_z, R_t, R_q, $R_{\max}$, R_{mss}, and R_{pc} were somewhat higher in this case for the IPDDI/TFE/RU sample, than for the IPDI/*n*-PR/RU system (Table III).

ATR FT-IR spectroscopy

Reflection infrared spectra of HDI/TFE/RU and HDI/*n*-PR/RU coatings have been reported for comparison in Figure 10. The broad bands at 3360 cm^{-1} were assigned to NH stretching vibration of urethane, urea and allophanate groups (invisible in Fig. 10). The C=O stretching vibrations of urethane, urea, allophanate, and ester groups were responsible for the bands observed at 1715 cm^{-1}. Weak broad bands at 1580 and 1610 cm^{-1} were connected to C—C ring stretching vibration of polyester resin which included isophtalic acid. The band at 1372 cm^{-1} can be assigned to the so-called "umbrella" deformation of methyl groups from neopenthyl glycol and alcohol. The *N*—H scissors deformation vibration and C—N stretching vibration (amide II band) were split at 1536 cm^{-1}. In the spectra, the bands from C—F bond were visible. The bands at 1164, 1214, and 1284 cm^{-1} come from C—F symmetrical and asymmetrical stretching vibrations.[13] The 2365 cm^{-1} broad band was a combination overtone from the 1164 and 1220 cm^{-1}. In addition to the bands associated with the C—F vibration, in this region also reflectance of polyester resin and polyisocyanate was found (1070 cm^{-1} C—O—C stretching; 1230 cm^{-1} asymmetrical C=O and O—CH$_2$ stretching and 1245 cm^{-1} C—N stretching (amide III band)). These bands may have obscured bands associated with the C—F bond. The out-of-plane (rocking) weak band of —CH$_2$— linear structure from alcohol, HDI and resin was visible at 728 cm^{-1}.

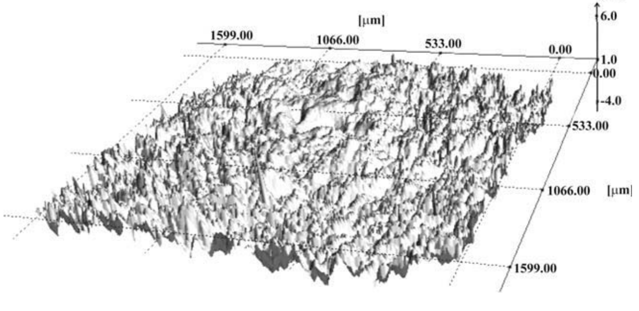


Figure 8 The confocal laser scanning microscope image of powder coating IPDI/TFE/RU.

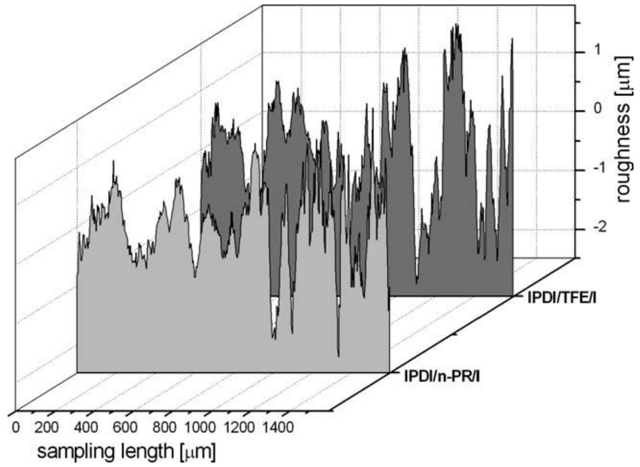


Figure 9 Comparison of the roughness profiles obtained on the basis of confocal images.

TABLE III
Specifications of the Coatings Roughness

Symbol of coating		IPDI/ n-PR/RU	IPDI/ TFE/RU
Fluorine content	(wt %)	–	2,6
Roughness parameters	R_a (μm)	0.511	0.731
	R_z (μm)	3.092	3.704
	R_t (μm)	4.216	4.406
	R_q (μm)	0.659	0.911
	$R_{\max}$ (μm)	4.216	4.406
	R_{mss} (degrees)	0.079	0.075
	Sep (μm)	0.5	0.5
	R_{pc} (peak/cm)	43.836	37.573

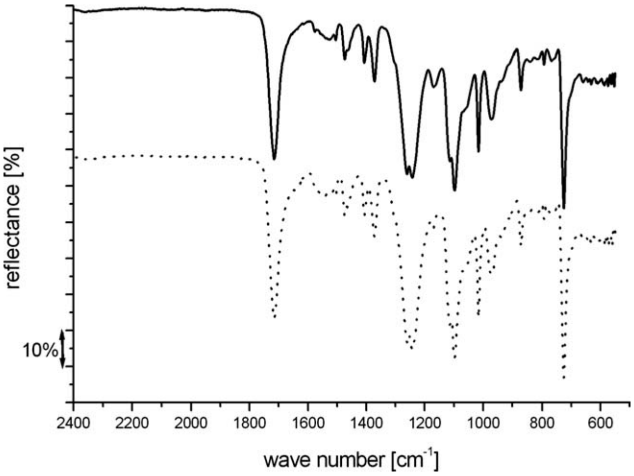


Figure 10 The ATR FT-IR spectra of the powder coating HDI/TFE/RU and HDI/*n*-PR/RU.

CONCLUSION

Using alicyclic diisocyanates, aliphatic fluorinated and unfluorinated alcohols and dibuthyltin dilaurate as well as triethylamine as catalysts, the experiment allowed for obtaining internally blocked polyisocyanates which, due to the allophanate linkages, were stable in the room temperature. On the basis of the synthesis reactions, it was concluded that the optimum conditions for obtaining blocked polyisocyanates containing fluorine atoms include a three-stage process carried out in the presence of two catalysts: dibuthyltin dilaurate and triethylamine, in a nitrogen atmosphere and an appropriate temperature (within a range from 60 to 110°C for stage I, 130°C for stage II, and 60–70°C for stage III). The duration of the synthesis of blocked polyisocyanates depends on the chemical structure of both diisocyanate and alcohol. It is shorter for aliphatic diisocyanates and primary alcohols, as well as for fluorinated alcohols.

Internal blocking of —NCO groups, through the formation of allophanate bonds which are unstable under curing conditions, made it possible to minimize the amount of the external blocking agent. Imidazol employed for additional external blocking of free —NCO groups was characterized by low toxicity and low unblocking temperature, which is of great importance in the modern powder coating technology.

An analysis of FT-IR spectra allowed for confirming the expected structure of the products and for demonstrating that during the process of long-term heating (63–85 h) at a temperature of 105–116°C, small amounts of by-products containing carbodiimide were produced. Further increase in the reaction temperature, up to 130–150°C, would have an adverse impact on the formation of compounds with carbodiimide groups. An analysis of magnetic nuclear resonance spectra allowed for the identification of the structure of the obtained compounds and made it possible to rule out the presence of by-products. The lack of bands from isocyanate groups in FT-IR and ^{13}C-NMR spectra (at 2264 and at 124 ppm) is an evidence for complete conversion of diisocyanates. The occurrence of three signals at the range 7.0–8.3 ppm (^{1}H-NMR) and 115.6–136.2 ppm (^{13}C-NMR) coming from *N*-substituted imidazole and signals at 5.5 ppm (^{1}H-NMR) coming from urea bond proton as well as at 155.3 ppm (^{13}C-NMR) from urea bond C=O is an evidence that the imidazole was reacted and the polyisocyanates were blocked.

The GPC analysis gave the qualitative and quantitative insight into the molecular weight distribution in the synthesized polyisocyanates. The obtained products were polydisperse, because of incomplete regioselectivity of diisocyanates used in this work (HDI, H_{12}MDI, and IPDI). Both HDI and H_{12}MDI have two equally reactive isocyanate groups. IPDI is much more selective. The primary isocyanate group of IPDI is more reactive to primary alcohols than the secondary isocyanate group. The difference in rate constants without catalysis at room temperature amounts to $k_{\mathrm{prim}}/k_{\mathrm{sec}} = 5$, whereas in the presence of most Levi's-acid catalysts, it is $k_{\mathrm{prim}}/k_{\mathrm{sec}} = 12$. Greater regioselectivity of diisocyanate correlates with lower polydispersity of the product.[19]

The modern confocal microscopy made it possible to obtain a 3-D visualization of the lacquer surfaces and to calculate the surface roughness parameters. Reflection infrared spectra confirmed the presence of bands from C—F bonds on the surface of the coating. It should be emphasized that these methods are sufficiently general to allow for applications while studying other polymer materials as well.

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