



# Study on the thermal behavior of new blocked polyisocyanates for polyurethane powder coatings



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## ABSTRACT

In this study, the thermal behavior of new blocked polyisocyanate crosslinkers for polyurethane powder coatings was investigated. Blocked polyisocyanates were synthesized on the basis of biuretization process using isophorone diisocyanate (IPDI) and formic acid as biuretizing agent.  $\epsilon$ -caprolactam was employed as blocking agent. Blocked polyisocyanates were additionally modified with  $\alpha,\omega$ -bis(hydroxyethyleneoxypropylene)-poly(dimethylsiloxane). The thermal behavior was investigated by means of coupled thermal analysis, differential scanning calorimetry and Fourier transform infrared spectroscopy (TG/DSC/FTIR). The TG analyses reveal that thermal decomposition of the blocked diisocyanate and blocked polyisocyanate comprising biuret moieties occurs in two main steps in the range of 120–275 °C and 310–375 °C, respectively. However, two additional stages in the range of 275–310 °C and 375–500 °C, for blocked polyisocyanate modified with polysiloxane, were observed.

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## 1. Introduction

Stability of the blocked isocyanate groups at room temperature to hydroxyl groups was used to develop a one-component coating systems. At elevated temperature, the isocyanate groups are deblocked and then they are ready to react with hydroxyl-terminated component which is present in the system. As a result of the above reaction the crosslinked polyurethane coatings are formed. Blocked diisocyanates and polyisocyanates (PIC) are widely used as crosslinking agents in heat-curable polyurethane coatings systems, such as coil coating, can coating, electrodeposition coating, wire coating, automotive and powder coating [1]. Blocking of isocyanate groups prevents the reaction between –NCO and –OH groups during extrusion and storage of powder coating. Study on the deblocking parameters of polyisocyanate is more important for processing and curing of powder coating. The powder coating extrusion temperature must be higher than the melting temperature of the system and less than the deblocking temperature of –NCO groups. If deblocking occurs partially in the extruder, the properties of the coating will be poor, especially the flow [2,3]. The coating curing temperature and curing time depend on the deblocking temperature and deblocking rate of the polyisocyanate

component. Too high curing temperature and too long curing time result in yellowing of the coating and poor coating properties.

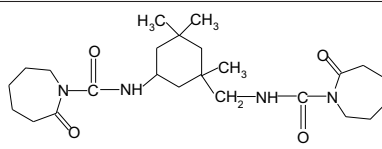
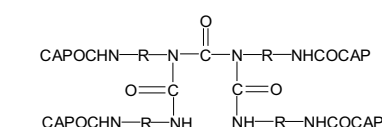
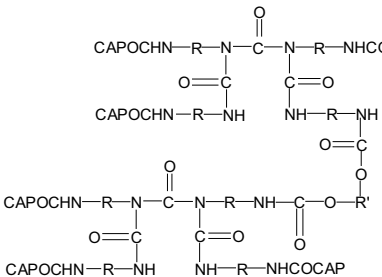
The commercial polyurethane powder coating systems were crosslinked by externally or internally blocked polyisocyanates. The most externally blocked polyisocyanates were blocked by means of  $\epsilon$ -caprolactam [4], methyl ethyl ketoxime (MEKO) [5], pyrazole [6] and diethyl malonate [7]. Internally blocked polyisocyanates contained uretdione, biuret or allophanate bonds. The residual –NCO groups of internally blocked polyisocyanates were blocked by means of blocking agent. These polyisocyanates contain less blocking agent and because of that they are more environmental friendly. The industrial importance of blocked isocyanates can be clearly seen from the number of patents. More than 90% references were found as patents [3].

There are a few reports in the literature concerning the research on the thermal decomposition mechanism of diisocyanate or polyisocyanate. Gedan-Smolka and co-workers investigated of model blocked aliphatic diisocyanate using STA/QMS system and temperature dependent FTIR [8]. The thermal decomposition of the reaction product of HDI trimer with functionalized urethanes was studied by Kozakiewicz et al. by means of TG coupled with FTIR [9]. Deblocking mechanism of N-methylaniline-blocked di- and polyisocyanates with the use of hot-stage FTIR was described by Sankar and Nasar [3,10]. The reaction products of deblocking of model pyrazole and oxime-blocked phenylisocyanate in the aque-

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**Table 1**  
Qualitative/quantitative components of the investigated blocked di- and polyisocyanates.

Symbol of PIC	Chemical structure of PIC	IPDI content, wt%	$\epsilon$ -caprolactam content, wt%	PDMS content, wt%
IPDI/CAP	 <p>CAPOCHN—R—NHCOCAP</p> <p>R=IPDI segment</p>	49.6	50.4	–
IPDI/B/CAP	 <p>CAPOCHN—R—NHCOCAP</p> <p>R=IPDI segment</p>	66.3	33.7	–
IPDI//PDMS/CAP	 <p>CAPOCHN—R—NHCOCAP</p> <p>R=IPDI segment, R'=PDMS segment</p>	51.2	26.1	22.7

ous media in the presence of amido- and hydroxyl-nucleophiles were investigated using HPLC [11].

The aim of this work was to investigate the mechanism of decomposition of a new, synthesized by us polyisocyanate, which was modified with polysiloxane and partially blocked with biuret moieties. Since there are no reports on the thermal behavior of this type of PIC, the purpose of our research was to evaluate if this new PIC can be employed as a curing agent for polyurethane powder coatings. We may expect that the deblocking ability of biuret moiety at curing temperature (170–220 °C) and decomposition to revert back to urea and isocyanate, as well as the stability of urethane bonds between isocyanate and polysiloxane under curing conditions, results in good crosslinking of powder coating with simultaneous incorporation of the polysiloxane in the coating structure. Polyurethane coatings modified with polysiloxane were characterized with increased hydrophobicity, thermal, chemical, scratch and abrasion resistance [12]. The simultaneous thermal analysis, differential scanning calorimetry and Fourier transform infrared spectroscopy (TG/DSC/FTIR) was employed for this purpose. In order to facilitate interpretation of the results, model compounds were additionally synthesized. One of model compounds (IPDI/CAP) was obtained as externally blocked IC with the use of isophorone diisocyanate and  $\epsilon$ -caprolactam and the second (IPDI/B/CAP) as partially internally blocked polyisocyanate through biuret bonds and partially externally blocked with  $\epsilon$ -caprolactam.

## 2. Experimental

### 2.1. Preparation of starting materials

#### 2.1.1. Raw materials and reagents

Desmodur I – isophorone diisocyanate (IPDI) from Bayer A.G. (Leverkusen, Germany).  $\epsilon$ -caprolactam (CAP) from Zakłady Azotowe in Tarnów-Mościce S.A. (Tarnów, Poland). Polydimethyl-

siloxane (PDMS) (X-22-160AS  $\alpha,\omega$ -bis(hydroxyethoxypropyl)-poly(dimethylsiloxane)),  $M_n = 1000$  g/mol from Shin Etsu Chemical Co. Ltd. (Tokyo, Japan).

#### 2.1.2. Synthesis of externally blocked diisocyanate

The synthesis was carried out according to known method in solution (THF) [11]. IPDI and dibutyltin dilaurate (catalyst 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 the blocking agent ( $\epsilon$ -caprolactam) was added to the reaction mixture (the molar ratio of –NCO groups to blocking agent was 1:1). The reaction mixture was then maintained at the temperature of 65 °C, stirred and refluxed. The end point of the reaction was controlled by the content of –NCO groups. The chemical structure of the obtained blocked diisocyanate (IPDI/CAP) was presented in Table 1.

#### 2.1.3. Synthesis of blocked polyisocyanate contained biuret moieties

The synthesis was carried out according to the method described in our earlier reports [13]. The synthesis comprises three stages: synthesis of ureaisocyanate, synthesis of biuret polyisocyanate, and blocking reaction.

**2.1.3.1. Synthesis of ureaisocyanate.** IPDI and dibutyltin dilaurate as well as triethylamine as a catalysts (both at 0.1 wt% with respect to diisocyanate) was placed in a three-necked flask equipped with a reflux condenser, thermometer, glass stirrer, nitrogen inlet and dropping funnel. A calculated amount of formic acid (to keep the molar ratio of IPDI to formic acid at 4:1) was introduced drop-wise to diisocyanate. The time of introduction was adjusted to 30 min. The reaction mixture was then maintained at the temperature of 75 °C, stirred and refluxed for 6 h. The end point of the reaction was controlled by the content of –NCO groups.

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