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Tailor-made Crosslinkers for High Performance PUR Coatings - Hyperbranched Polyisocyanates

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Summary: The introduction of Self-Crosslinking Isocyanates (SCI) as AB_2-building blocks makes it possible to synthesize hydroxyl- or isocyanate-group terminated dendrimers. Furthermore, inherent reactivity differences of non equivalent NCO-groups of specific diisocyanates (such as isophorone diisocyanate [IPDI] or toluylene diisocyanate [TDI]) can be used to build up hyperbranched polyurethane structures in a one pot synthesis without the need of arduous protection/deprotection steps. This synthetic approach allows the construction of tailor-made hyperbranched molecular architectures which are end-functionalized with either hydroxyl or isocyanate groups. These products were then tested as crosslinkers in 2-component coating formulations where they displayed better hardness than any other aliphatic isocyanate raw material.

Keywords: coatings; crosslinking; dendrimers; hyperbranched; isocyanates; polyurethanes; synthesis

Introduction

The development of Self-Crosslinking Isocyanates (SCI)[1] provided suitable molecules and functionalities for the synthesis of dendritic and hyperbranched structures based on polyurethane chemistry. SCI combine at least one isocyanate functionality with multiple hydroxyl or amine functional groups in one molecule. To obtain stable products, the hydroxyl or amine functionalities need to be capped with suitable protecting groups. These protecting groups are designed to react immediately with water to liberate the corresponding active hydrogen functionality which then can react with isocyanates (Figure 1). Originally, these SCI-systems were developed as reactive diluents for super high solids 2-component polyurethane coating systems. However, it quickly became apparent that SCI, which contain one isocyanate and two active hydrogen groups, have great potential to be used as building blocks for dendrimers and hyperbranched structures. SCI molecules can be regarded as capped AB_2-building blocks (Figure 1) which are necessary for the synthesis of dendrimers or hyperbranched polymers.

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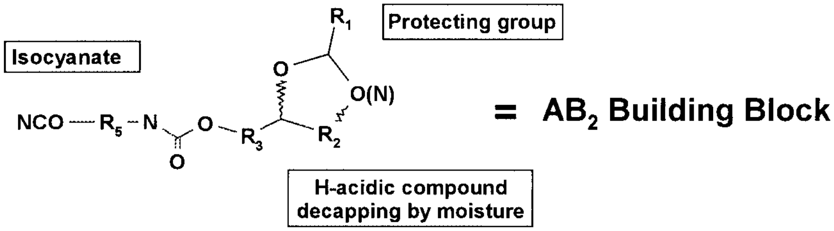


Figure 1. Schematic Representation of Self-Crosslinking Isocyanates (SCI)

Results and Discussion

Although a wide range of synthetic strategies have been developed for the construction of dendrimers[2] there are only few reports existing on the synthesis of dendrimers or hyperbranched polymers using isocyanate or urethane chemistry.[3-10] Now SCIs open up new routes to simple, divergent syntheses of a variety of dendrimers.

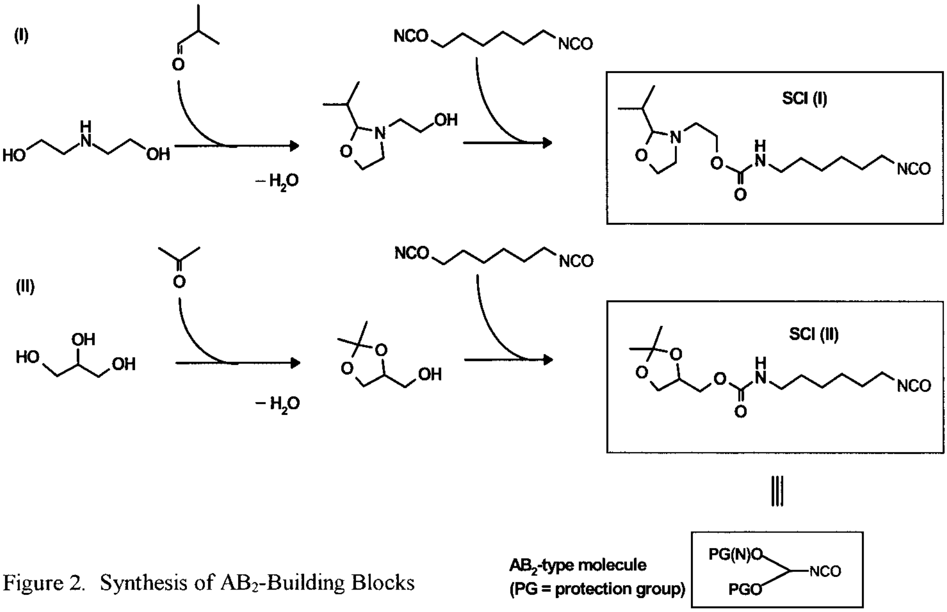


Figure 2. Synthesis of AB2-Building Blocks

Two types of SCI were studied: (I) a 1:1 reaction product of hexamethylene diisocyanate with a hydroxyl functional oxazolidine and (II) a 1:1 reaction product of hexamethylene diisocyanate with a hydroxyl functional 1,3-dioxolane. Both, the oxazolidine and the dioxolane, are easily accessible by reaction of an aldehyde or ketone with diethanolamine or glycerol, respectively (Figure 2).

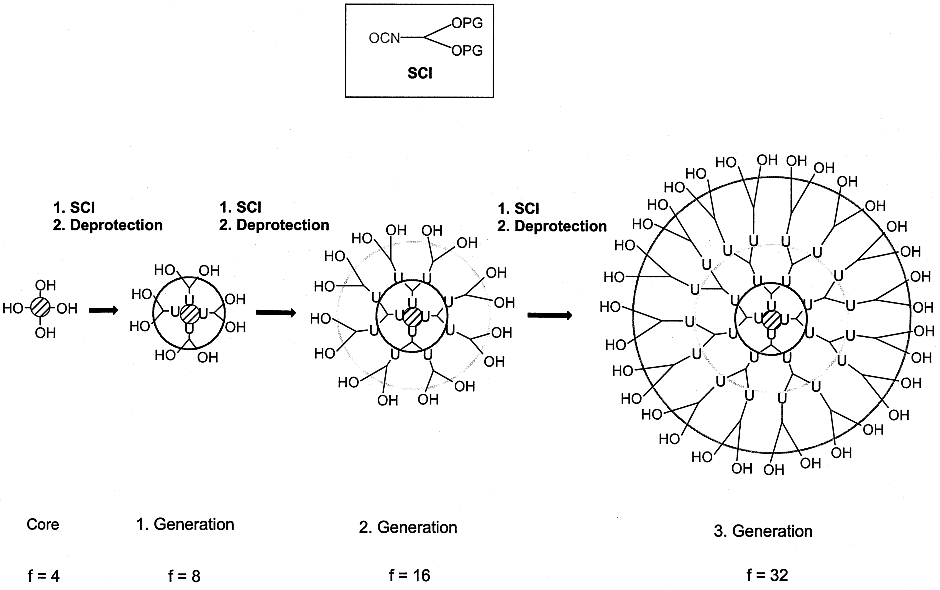


Figure 3. Synthesis of a Urethane Dendrimer

Starting from a multifunctional amine or alcohol as a core molecule the addition of e.g. SCI (II) will form the first generation dendrimer with a doubled functionality. Addition of water to deprotect and release the OH-groups sets the molecule up for the formation of the second generation dendrimer by adding again SCI. The repetition of these reaction steps allows the controlled synthesis of higher dendrimer generations (Figure 3).

Hyperbranched structures may be obtained more easily by simply adding water as well as a small amount of an alcohol to the SCI-system. The water will open the oxazolidine or dioxolane ring to yield the partners for an intermolecular reaction with the isocyanate group, while the amount of alcohol will regulate the average molecular mass by terminating the polymer/oligomer chain (Figure 4). Unfortunately, in this approach it is unavoidable that a certain amount of water may also react with the isocyanate group leading to side reactions. The choice of protecting group and, consequently, the speed of deprotection need to be chosen carefully to minimize this side reaction.

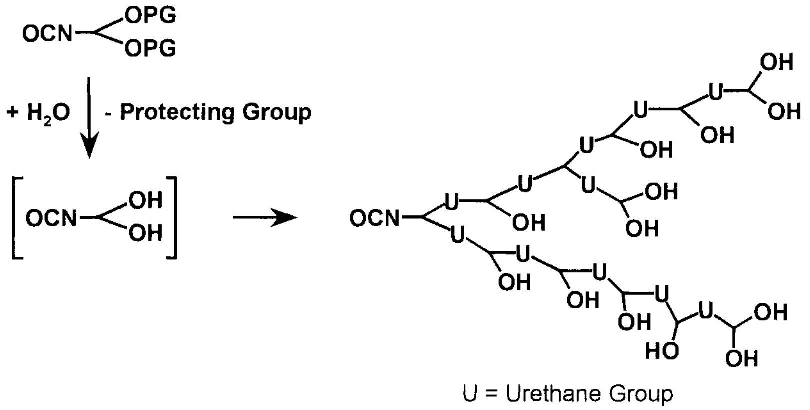


Figure 4. One-Step Synthesis of Hyperbranched Structures

By employing modified self-crosslinking isocyanates this side reaction can be avoided. While the isocyanate group is blocked with an isocyanate blocking agent, e.g. a ketoxime, it is possible to deprotect the alcohol functionalities completely without risking a side reaction between isocyanate and water. Upon heating, the isocyanate group is regenerated and reacts to yield a hyperbranched structure (Figure 5).

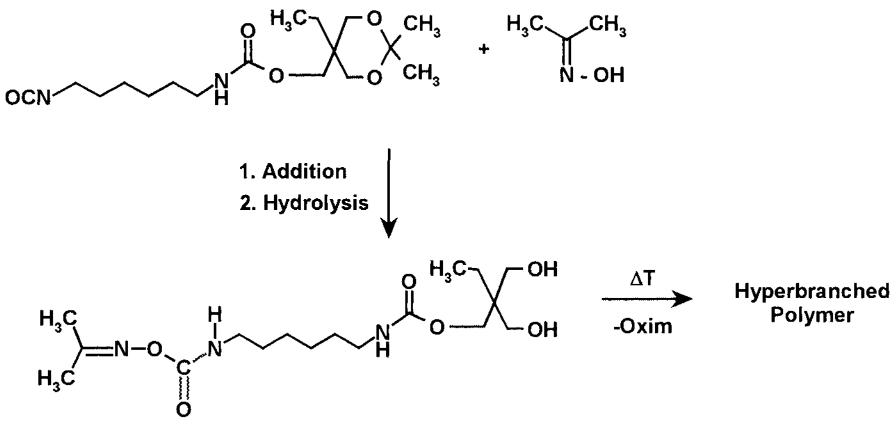


Figure 5. Blocked Isocyanates as Building Blocks for Hyperbranched Polymers

The syntheses described above for the production of hyperbranched structures have several attractive features such as the ready availability of the raw materials and the simplicity of the processes involved. However, protecting and deprotecting functional groups require additional process steps. Furthermore, the protecting groups which are employed require water for deprotection so that a rigorous drying step needs to follow every deprotection step in order to avoid side reactions. The deprotection, the removal of protecting group, and the removal of water limits the versatility of this approach. Consequently, a simpler process for the construction of hyperbranched structures was investigated.

By taking advantage of inherent reactivity differences in unsymmetrical isocyanates and in alcohols and aminoalcohols dendritic and hyperbranched structures may be assembled more satisfactorily. In the literature[10] the synthesis of 4-isocyanatomethyl-1-methyl-cyclohexyl-isocyanate has been reported. This diisocyanate displays large reactivity differences between its two isocyanate functionalities which allow an effective kinetic differentiation. However, more readily available diisocyanates are also useful building blocks, despite having slightly lower selectivities between their isocyanate groups (Figure 6). The addition of multifunctional alcohols or amino alcohols in which the reactive groups show differing reactivities towards isocyanate groups allows the in-situ formation of AB_2-building blocks using the A_2B_3 approach. This approach allows the construction of a wide range of tailor-made, functionalized hyperbranched systems. A few representative examples were synthesized.

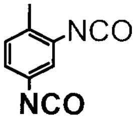
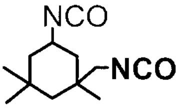
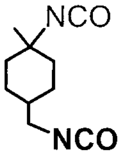
Reactivity differences	 **2,4-Toluylene-diisocyanate (TDI)**	 **Isophorone diisocyanate (IPDI)**	 **4-Isocyanatomethyl-1-methyl-cyclohexyl-isocyanate (IMCI)**
k_1/k_2	**10-70**	**3-10**	**100 (lit.[10])**

Figure 6. Diisocyanates with Kinetically Non-Equivalent Isocyanate Groups

Starting from isophorone diisocyanate and diethanolamine an isocyanate-dialcohol compound may be produced in the first reaction step which can react in an intermolecular polyaddition to yield a hyperbranched structure which contains urea and urethane groups in the backbone and hydroxyl groups on the molecular surface (Figure 7). As described in a previous example, the addition of alcohol allows the control of the molecular weight in this system. Once the desired hyperbranched structure has been synthesized it can be modified to a polyisocyanate by further reaction with an excess of diisocyanate such as isophorone diisocyanate. Care needs to be taken to avoid side reactions in which the diisocyanate bridges two hyperbranched molecules. Due to the high functionalities this side reaction can quickly lead to crosslinking and gelation.

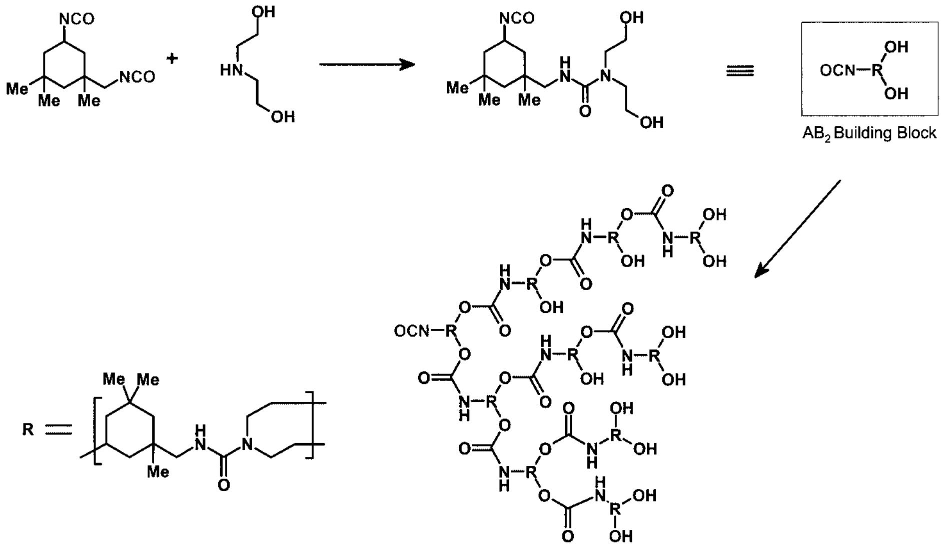


Figure 7. Synthesis of a Hyperbranched Polyalcohol

As an alternative to the NCO-functionalization of a polyol, a slightly different approach can be chosen to yield hyperbranched polyisocyanates. Starting from two molecules of diisocyanate and one molecule of a triol this $A_3(B_2)_2$-approach leads to an A_2B-type building block which bears two isocyanate and one hydroxyl group (Figure 8). In an intermolecular reaction this building block reacts to yield hyperbranched polyisocyanate structures. The addition of isocyanates allows an additional control of the molecular weight.

These hyperbranched polyisocyanates were tested as crosslinkers in conventional 2-component coating systems. A simple formulation containing isophorone diisocyanate trimeras crosslinker was employed; the isophorone diisocyanate trimer was then replaced by the hyperbranched polyisocyanate. The cured coatings containing these simple hyperbranched systems showed significant improvements regarding (pendulum) hardness, which were not achievable with any other known aliphatic isocyanate raw material.

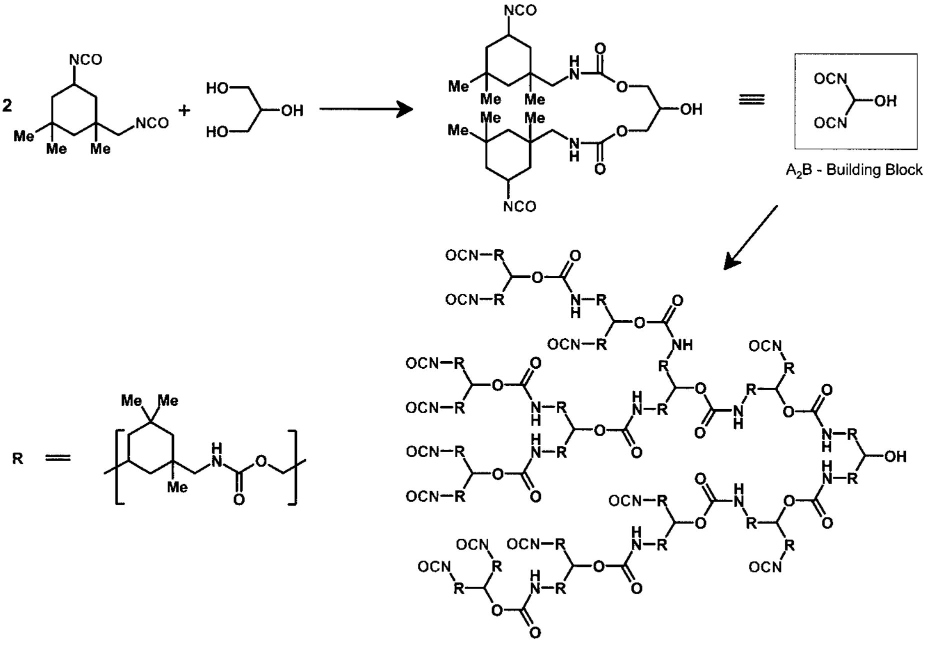


Figure 8. Synthesis of a Hyperbranched Polyisocyanate

Conclusion

Polyurethanes are an important polymer class for the coatings industry. Simple access to tailor-made, hyperbranched polyurethanes will open up new possibilities to improve properties of polyurethane coatings systems for matching customer demands. Hyperbranched polyisocyanates, for example, with their high NCO-functionality on the molecular surface represent a new class of crosslinkers for the formulation of coatings with improved properties. The synthetic approach exploits inherent reactivity differences of readily available, multifunctional raw materials to construct aliphatic as well as aromatic polymer backbones with isocyanate end-groups. Finally, all hyperbranched products are polymers according to the OECD and EU polymer definition.

Therefore, this new class of polyurethane polymers products fulfills the requirements for technical scale-up and commercialization. The unique properties of these products, especially with respect to the high hardness which they confer to a polymer film, may be of high interest to the coatings industry. Further studies on these hyperbranched polymers and their properties in coating systems are under investigation.

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