

Technical Bulletin

HUNTSMAN

JEFFSOL® ALKYLENE CARBONATES SYNTHESIS OF HYDROXYALKYL URETHANES

Alkylene carbonates such as Huntsman brand **JEFFSOL® ethylene carbonate** (EC), **JEFFSOL® propylene carbonate** (PC) and **JEFFSOL® butylene carbonate** (BC) readily react with primary and secondary aliphatic amines to yield β -hydroxyalkyl urethanes as shown below:

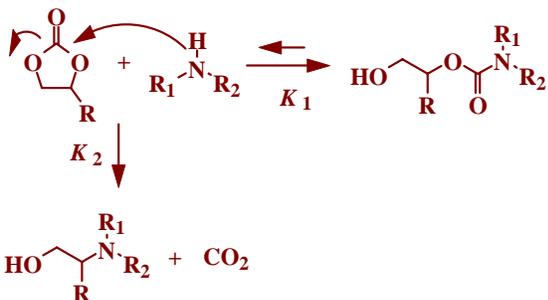


Note that two possible isomers of the hydroxyalkyl urethane product are possible should $R \neq H$. As can be seen, nucleophilic attack occurs at the carbonyl carbon of the cyclic carbonate, followed by ring opening to yield the β -hydroxyalkyl urethane. This reaction mechanism is in contrast to that observed when reacting aromatic amines with alkylene carbonates. In such cases, nucleophilic attack occurs at one of the alkylene carbons of the cyclic carbonate, followed by ring opening and loss of carbon dioxide to give a hydroxyalkyl amine alkoxylation product (See U.S. Patent 6,046,326).¹

In general, JEFFSOL® alkylene carbonates will react with primary and some secondary aliphatic amines with only mild heating. While most reactions require temperatures in the range of 30-50°C, some will proceed even at ambient temperature. Furthermore, these reactions may be accomplished without the aid of a catalyst. That said, alkali or other caustic substances may

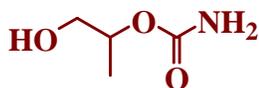
be employed to increase the reaction rate (See U.S. Patent 5,977,262).² Because these reactions are exothermic, they must be controlled by monitoring the addition rate of one component into the other. Once both components have been allowed to mix, a digestion temperature of 50-80°C over a period of 1-4 hours is recommended to achieve maximum conversion.

The consumption of amine may be monitored by amine number analysis. In this way, side reactions may also be monitored. For instance, by analyzing for primary and secondary amine number, the progress of the reaction between PC and 2-ethylhexyl amine may be quantified. As the reaction proceeds, the primary amine number decreases. However, a rise in the secondary amine number, which should theoretically equal zero throughout the course of the reaction, indicates the formation of side product. To elaborate, the reaction of alkylene carbonates with amines to form urethane linkages is reversible. For this reason, a small concentration of primary amine is always present. As was previously stated, aliphatic amines predominately undergo urethane synthesis when contacted with alkylene carbonates. However, they may also undergo alkoxylation in certain instances. Typically, the rate of urethane formation is approximately two orders of magnitude faster than the competing alkoxylation process but because alkoxylation is an irreversible process, the concentration of alkoxylation side products increases with time as illustrated below:

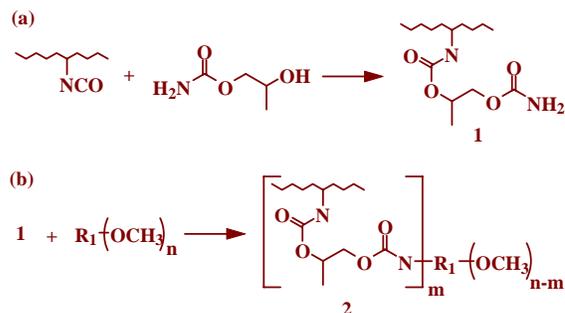


where K_1 and K_2 are the rate constants for urethane synthesis and alkoxylation, respectively ($K_1/K_2 \cong 100$). In the above example, alkoxylation yields 2-ethylhexyl propylamine; a secondary amine. If such side reactions are undesired, care should be taken to employ digestion temperatures no higher than is necessary. The concentration of alkoxylation side products increases significantly if digestion temperatures $> 80^\circ C$, and especially $> 100^\circ C$, are used.

A well known example of urethane formation via amine reactions with alkylene carbonates is the reaction of PC with ammonia to prepare hydroxypropyl carbamate, shown below (See U.S. Patent Nos. 2,627,524 and 4,883,854):³



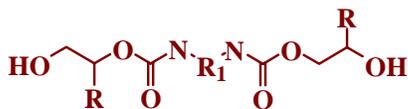
Hydroxypropyl carbamate (HPC) is commercially available from Huntsman under the trade name **CARBALINK[®] HPC hydroxypropyl carbamate**. The material is a somewhat viscous low-color liquid at slightly elevated temperatures (freezing range $30-40^\circ C$) that is a mixture of two isomers in a 50/50 +/- 10% ratio. A survey of issued U.S. patents shows that this material has found utility in the automotive coatings industry in methods for preparing novel polyurethane resins.⁴ For instance, reactions of HPC with isocyanate-functional polyacrylates to prepare carbamate-functional polymers have been discussed in the patent literature, as illustrated below:^{4d}



The resulting products of general structure **1** were then mixed with a crosslinking agent bearing methoxy substituents such as hexamethoxymethyl melamine ($n = 6$) during spray application to a surface. Subsequent baking or curing of the mixture gave urethane-crosslinked coatings, **2** in which $m = 3-4$. Although similar coatings can be obtained simply by mixing a polyisocyanate with a polyol in a spray applicator, the polyisocyanate fumes generated under such conditions can be dangerous and difficult to contain. In the above example, however, the isocyanate has been converted to a much less hazardous material, **1**, under controlled laboratory conditions prior to application, eliminating the dangers previously associated with this industry. The resulting coating has been shown to have excellent resistance to environmental etch (acid rain), scratch and mar, salt corrosion, and hydrolysis,⁵ all necessary of coatings in the automotive industry.

It is well-known that polymers containing urethane linkages in their backbones exhibit increased chemical-, thermal-, and hydrolytic stability as well as superior physical and mechanical properties. For these reasons, polyurethanes are widely used in the manufacture of paints, adhesives, footwear, structural components, furniture, and coatings for wood, metal, concrete, plastic, and other surfaces. Unfortunately, the most industrially viable method of obtaining the valuable urethane linkage has traditionally involved reaction with toxic isocyanates. Recognizing that the reaction of alkylene carbonates with aliphatic amines is a convenient method of introducing the urethane linkage into polymer systems without the need for isocyanates, interest in these materials has increased considerably in recent years. For example, alkylene carbonates have been reacted

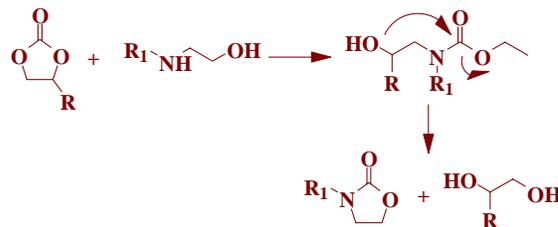
with aliphatic diamines to give difunctional hydroxyalkyl urethanes, as shown below (See U.S. Patent 4,820,830):⁶



The resulting urethane diols can be considered “blocked isocyanates”. By reacting these materials with polyester polyols in the presence of a transesterification catalyst, polyurethanes may be synthesized by removing the glycol byproduct by distillation. Polyurethanes may also be synthesized by more conventional means simply by reaction of the urethane diol with a di- or polyisocyanate. In such cases reliance on isocyanates, although not eliminated, may be significantly reduced.

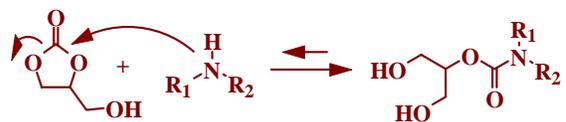
In addition to polyurethanes, the above technology has also been applied to the modification of amino acids for the production of bio-compatible polymers,⁷ and dispersants for use in lubricating oils and gasoline. For instance, polyisobutylene has been capped with maleic anhydride followed by reaction with ethylene amines such as triethylene tetraamine (TETA) to form polyalkylene succinimides (See U.S. Patent 5,716,912). Reaction of EC with the resulting secondary and primary amines yields hydroxyalkylurethane adducts with superior dispersant characteristics.⁸ These adducts are useful in reducing engine deposits such as sludge and ash resulting from incomplete combustion. Modification via ethylene carbonate also improves the compatibility of the polyalkylene succinimide dispersant with other components of the formulation.

Alkylene carbonates may also be reacted with amines that possess hydroxyl groups to give added functionality to the urethane product. However, reactions with β -hydroxyalkylamines such as ethanolamine are often accompanied by cyclization and loss of glycol to give oxazolidinones under mild heating as shown below:⁹



The patent literature contains reference to the fact that oxazolidin-2-one ($R_1 = H$), in particular, may also be prepared by the reaction of EC with urea.¹⁰ Such materials and their derivatives find use as medicinal actives for the treatment of bacterial infections, arthritis, and toxicity caused by chemotherapy (See U.S. Patent Nos. 6,194,441 and 6,277,868).¹¹

In addition to EC, PC and BC, **JEFFSOL[®] glycerine carbonate** (GC), a recent addition to the JEFFSOL[®] carbonate family, may also be reacted with aliphatic primary and secondary amines. The result is a urethane with dihydroxy or diol functionality as shown below:



References to patent documents herein are provided as background information only, and should not be construed as a suggestion to make, use, or sell any invention claimed without authorization from the patent owner.

REFERENCES

- 1) U.S. Patent 6,046,326.
- 2) U.S. Patent 5,977,262.
- 3) (a) U.S. Patent 2,627,524. (b) U.S. Patent 4,883,854.
- 4) (a) U.S. Patent 4,708,984. (b) U.S. Patent 5,089,617. (c) U.S. Patent 5,175,231. (d) U.S. Patent 5,336,566. (e) U.S. Patent 6,103,816.
- 5) Green, M; Low VOC Carbamate Functional Coatings Compositions for Automotive Topcoats. In *International Waterborne, High-Solids, and Powder Coatings Symposium*; School of Polymers and High Performance Materials, The University of Southern Mississippi, Hattiesburg, MS, 2000, 224.
- 6) U.S. Patent 4,820,830.
- 7) Kihara, N. et al.; Polycondensation of ω -Hydroxy Carboxylic Acid Derived from L-Phenylalanine and Ethylene Carbonate. *J. Poly. Sci. A*, **1996**, 34, 1819.
- 8) (a) U.S. Patent 4,612,132. (b) U.S. Patent 5,716,912.
- 9) Dyer, E. et al.; The Preparation of Polymeric and Cyclic Urethanes and Ureas from Ethylene Carbonate and Amines. *J. Amer. Chem. Soc.*, **1956**, 79, 672.
- 10) European Patent 1,069,115.
- 11) (a) U.S. Patent 6,194,441. (b) U.S. Patent 6,277,868.