

Technical Bulletin

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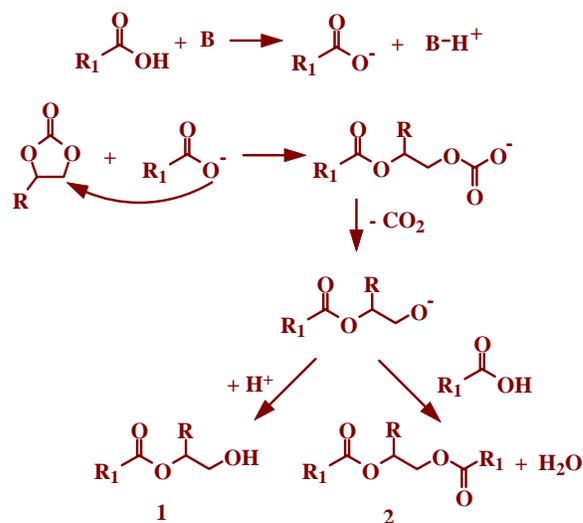
JEFFSOL® ALKYLENE CARBONATES ALKOXYLATION OF CARBOXYLIC ACIDS

As chemical intermediates, JEFFSOL® alkylene carbonates are quite versatile. Huntsman brand **JEFFSOL® ethylene carbonate** (EC), **JEFFSOL® propylene carbonate** (PC) and **JEFFSOL® butylene carbonate** (BC) undergo reaction with aliphatic and aromatic hydroxyl, amine, thiol and carboxylic acid functional groups. In general, alkylene carbonates react with aromatic hydroxyl, amine and thiol groups via an alkoxylation mechanism, yielding the corresponding hydroxyalkyl derivative and carbon dioxide byproduct, e.g. the reaction product of EC with phenol is phenoxyethanol and carbon dioxide. In contrast, alkylene carbonates react via a transesterification mechanism with the corresponding aliphatic functional groups, yielding a glycol byproduct, e.g. the reaction product of EC with n-hexanol is dihexyl carbonate and ethylene glycol. The reaction of alkylene carbonates with carboxylic acids represents a special case in which reaction proceeds via an alkoxylation route for both aromatic and aliphatic species.

In general, the reactivity of the JEFFSOL® alkylene carbonates follows the order EC > PC > BC. Temperatures in the range 140-200°C are typically required, depending on the particular alkylene carbonate employed. In addition, a base catalyst is often required. A survey of issued U.S. Patents shows that suitable catalysts include weakly basic species such as tertiary amines¹, triphenylphosphine² and phosphonium halides³, or more strongly basic species such as alkali metals, alkoxides, hydroxides⁴ and carbonates.⁵

During the course of the reaction, which can be performed neat or with the aid of an inert solvent, carbon dioxide is evolved. By monitoring the release of carbon dioxide visually or with the appropriate analysis equipment, the progress of the reaction can be monitored. During the initial phase of reaction, very little carbon dioxide generation is observed until the gas reaches its solubility limit in the reaction mixture. The time required for this to occur can vary widely depending on the nature of the specific reactants involved but is generally within a range of 5-30 minutes. Once saturation is achieved, the generation of carbon dioxide bubbles is observed.

The general reaction scheme is given as follows:



where **R**₁ may be either aromatic or aliphatic and **B** represents any number of base catalysts mentioned above. Note that a mixture of

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hydroxyalkyl (**1**), and diester (**2**) products is obtained in addition to two isomers of **1** should $R \neq H$. By employing an excess of one reactant over the other, the ratio of products **1** and **2** obtained can be affected. For instance, the literature shows the use of a 260% excess of EC to obtain **1** as the predominant product.⁶ The literature also shows that a mere 10% excess could be effective using a triethylammonium iodide catalyst in combination with a shorter reaction time⁷. In this manner, reacting EC with benzoic acid at 140-145°C for 0.7 hours resulted in an 86.5% yield of **1**.⁷

Although production of multiple species such as **1** and **2** may represent a drawback to the pure synthetic chemist, it has been exploited to synthesize prepolymers. EC and PC have been reacted with multi-functional carboxylic acids such as terephthalic acid to synthesize polyester oligomers (See U.S. Patents 5,714,568 and 5,969,056).⁸ These hydroxy-functional oligomers were then reacted with simple diols and unsaturated anhydrides to give unsaturated polyesters useful in composites for the aerospace industry.

In addition to pre-polymer synthesis, the above chemistry also finds use in polymer modification. EC has been reacted with polyethylene terephthalate (PET) polyesters in an effort to reduce the acid number of the material. PET polyesters are excellent materials for industrial conveyor belts that operate under heavy loads and at high speeds. However, degradation of the polymer can occur over time, resulting in reduced tensile strength and even visible cracking. It was discovered that a more chemically resistant material could be obtained simply by reacting the polymer with EC, thereby reducing the number of carboxylic acid end-groups at which degradation typically occurs (See U.S. Patent 4,348,314).⁹ The modification procedure follows the polycondensation of dimethyl terephthalate or terephthalic acid with ethylene glycol and involves the addition of an alkali metal salt such as potassium iodide. Typically, 0.5-1.0% by weight EC is added and allowed to react at 280°C for 5-15 minutes. The result is a material with an acid number < 3 (mg KOH/g) as compared to approximately 20 for the untreated polymer. PC has been employed in a similar application. In that case, the low-acid-number PET material reacted much more

quickly with isocyanates to produce polyurethane foams (See U.S. Patent 4,897,429).¹⁰ The foams produced exhibited the improved surface adhesion necessary for the production of laminate foam board.

Yet another useful example of polymer modification by reaction with 5-membered alkylene carbonates takes advantage of the diester product **2** as a crosslink site. Lightly crosslinked sodium polyacrylate is a hydrophilic material that absorbs many times its weight in water yet will not dissolve. This property makes the material useful as a super-absorbing media for sanitary articles such as diapers and feminine hygiene products.¹¹ However, the liquid-filled material is easily deformed by an external pressure such as the sitting action of a child, resulting in unwanted discharge of the absorbed liquid. Traditionally researchers have modified super-absorbent polymers (SAPs) of this type by further reacting them with simple, non-toxic diols or triols such as propylene glycol or glycerine (See U.S. Patent 6,150,582).¹² However, researchers at Stockhausen have found that alkylene carbonates may also be used in this application (See U.S. Patent 5,409,771).¹³

Table 2 shows the performance of a typical super-absorbing polymer (SAP) before and after modification with EC, PC, and BC.¹³

Carbonate Employed	Time at 215°C	FSC (g/g)	AAP (g/g)
---	---	39	11
EC	15	37	30
PC	20	37	31
PC	30	36	33
BC	20	37	30

In each case, alkylene carbonate, water, and ethanol (2.0g each) were mixed with 100g of the polymer to be modified. The mixture was then placed in an oven preheated to 215°C and allowed to react for 15-30 minutes. The performance of the resulting powder was quantified by the following tests: 1) free swell capacity (FSC) -the amount of saline solution (0.9% NaCl) retained by the polymer upon immersion said liquid for 30 minutes, 2) absorbency against pressure (AAP) - the amount of saline solution retained by the polymer upon immersion in said liquid for 1 hour while under

a weight exerting a force of 20 g/cm².¹⁴ In both tests, the results were given in units of grams of liquid absorbed per gram of polymer. Note that before modification the AAP of the polymer was significantly lower than the FSC indicating that the force of the weight squeezed out much of the absorbed liquid. However, after modification

the AAP was nearly equal to the FSC, indicating that the alkylene carbonate had reacted to create a high density of diester crosslinks on the surface of the powder. These crosslinks act as a hard shell, reducing the tendency of the liquid-swollen material to deform under an applied weight

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.

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