SOLVAY
CAPROLACTONES

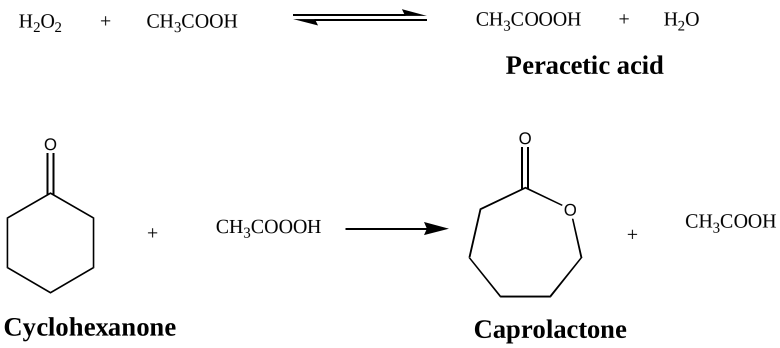
A20L-022

CAPA® POLYCAPROLACTONES, VERSATILE RAW MATERIALS FOR COATINGS

∊-Caprolactone monomer has been produced by Solvay at its facility in Warrington, England since 1974. The monomer is used to produce speciality polyester polyols which are sold under the CAPA® trade name. These products are used in a variety of demanding applications, particularly in performance polyurethane markets, including surface coatings where CAPA® Monomer is used to modify hydroxy acrylates, epoxy resins and as a component in copolyesters.

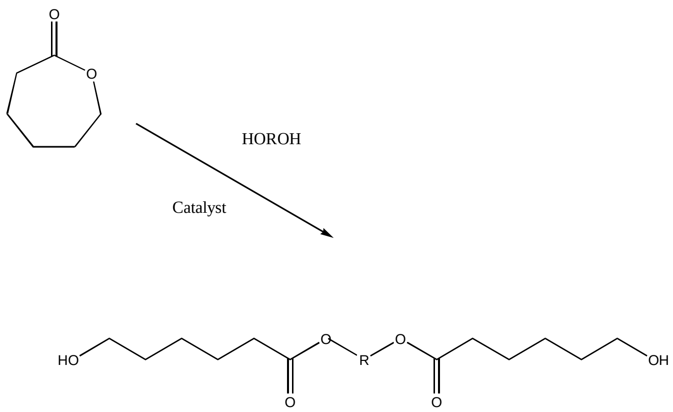
CAPA® monomer is made by the Bayer-Villager oxidation of cyclohexanone with peracetic acid (Figure 1).

Figure 1



The single grade of high purity monomer produced will react with a range of active hydrogen compounds in a ring opening reaction. Typically this function is carried out by a hydroxyl containing group, although other functional groups such as amino, thiol and carboxyl could be used. The reaction with the hydroxyl group initiates a ring opening addition polymerisation of the CAPA® monomer to produce a linear ester of hydroxy caproic acid with no by-products. The new primary hydroxyl function so formed can react further with other molecules of CAPA® monomer to build up polymer chains (Figure 2).

Figure 2



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In the schematic representation above a difunctional alcohol is shown, and in practice this would normally be the case. However one of the characteristics of caprolactone polymerisation is that the functionality of the initiator is repeated exactly in the resultant polyol. So for example, if we use trimethylol propane (TMP) we get a trifunctional polyol, if we use pentaerythritol we get a tetrol and so on. In some cases the initiating glycol can itself be polymeric, for example PTMEG giving rise to a block ether/ester copolymer.

The reaction is a ring opening addition polymerisation in contrast with the condensation reaction used to make conventional adipate polyesters. This means that the reaction temperatures used are lower, as no water needs to be eliminated and less catalyst is used. This results in a clean reaction giving a narrower molecular weight distribution, lower viscosity with a well defined functionality, as there are no side reactions.

One of the major advantages of the use of CAPA® in surface coatings has been their use to produce higher solids coating formulations whilst maintaining or improving performance, particularly low temperature flexibility of the coating. One of the early applications of CAPA® was in the modification of epoxy resins either by monomer or by polyols, and this is used extensively today in electrocoat primers.

In urethane coatings use is made of the ability to produce highly functional polyols with low viscosity and high reactivity. Some typical examples are listed in Table 1.

Table 1

Grade	MW	OH (mg KOH/g)	Acid (mg KOH/g)	Viscosity	Melting Point (ºC)
CAPA® 3031	300	560	< 1.0	171	0-10°C
CAPA® 3041	400	560	< 1.0	162	0-10°C
CAPA® 3050	540	310	< 1.0	157	0-10°C
CAPA® 3091	900	183	< 1.0	164	0-10°C
CAPA® 4101	1000	218	< 1.0	258	10-20°C

The use of CAPA® polyesters as soft segment components in speciality cast elastomer, adhesives and thermoplastic urethane systems are well established using linear diols. For surface coating applications, higher functionality and liquid systems are required. As shown earlier, the versatile nature of caprolactone chemistry means that manufacture of liquid with functionality of three, four or higher can readily be achieved.

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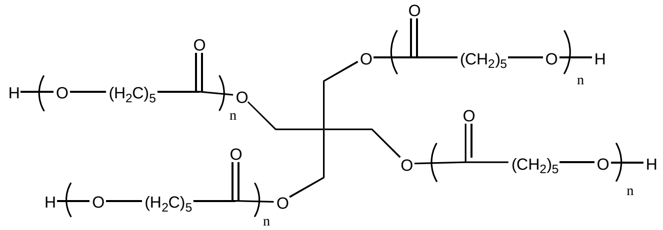
Solvay Caprolactones have utilised this innovative approach to design polyols with unique properties. These products are aimed at the highly demanding requirement of today's coatings, particularly where high cross link density high solids and water borne systems are needed.

One of these materials is a product called CAPA® 4101. This material is a tetra functional polycaprolactone with a molecular weight of 1000. It is a clear free flowing liquid with all hydroxyl groups being primary (Figure 3). It is a 100% polycaprolactone material, has no ether functionality, so gives excellent UV stability and is used to formulate coatings with high cross link density and high solids.

Figure 3

CAPA® 4101



CAPA® 4101 is extensively used in highly demanding applications for both OEM and refinish in the aerospace and automotive markets.

With the current trends in major solvent borne applications such as coatings and adhesives coming under increasing environmental pressure, there is a move within these industries to look at lowering solvent levels or removing them altogether, in either solvent free or water borne systems.

One of the major areas of interest is in the development of water based polyurethane dispersions (PUD's). One of the raw materials used in this application is DMPA[i] this has the advantage of having two primary hydroxyl groups and one free tertiary carboxylic group. This means that it is possible to do conventional urethane chemistry on the two hydroxyl groups. The hindered nature of the carboxylic function means that the competing carboxyl isocyanate reaction is quite slow and is incorporated as a pendant group in the urethane backbone and can be then dispersed in water with the appropriate base. The DMPA however is a crystalline solid with a melting point of 189-191ºC which is quite high when compared with other urethane raw materials.

We have utilised our innovative technology to graft caprolactone onto the hydroxyl groups of the DMPA, leaving the carboxylic group unchanged. This converts the DMPA, a hard segment, into a polycaprolactone polyol with a pendant carboxyl group for water dispersability. This has the added advantage of translating the crystalline DMPA into a low viscosity, low melting wax which can now act as a soft segment. These materials are called CAPA® HC grades and the typical properties are described below (Table 2).

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Table 2

Grade	MW	OH (mg KOH/g)	AV (mg KOH/g)	Viscosity [ii]	Melting Point (ºC)
CAPA® HC1060	600	180	90	545	35-40°C
CAPA® HC1100	1000	112	60	610	45-50°C
CAPA® HC1200	2000	56	30	940	45-50°C

i DMPA is a trademark of Geo Specialties

ii Shear rate = 500 sec^{-1}, temperature = 60°C

Solvay has an active development programme looking at introducing new products. Currently the range of CAPA® polyols stands in excess of 30 commercial grades, with numerous new grades under development to meet customers needs. Caprolactone chemistry combined with the production facilities operated by Solvay enables the production of polymers with many different combinations of functionality and molecular weight. We actively seek to work with customers' R&D groups to develop new products, to meet defined performance requirements for specific applications.

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