PERGAN
The Peroxide Company

Technical Bulletin

Polymerization of monomers

with Organic Peroxides for the High Polymer Industry

Introduction

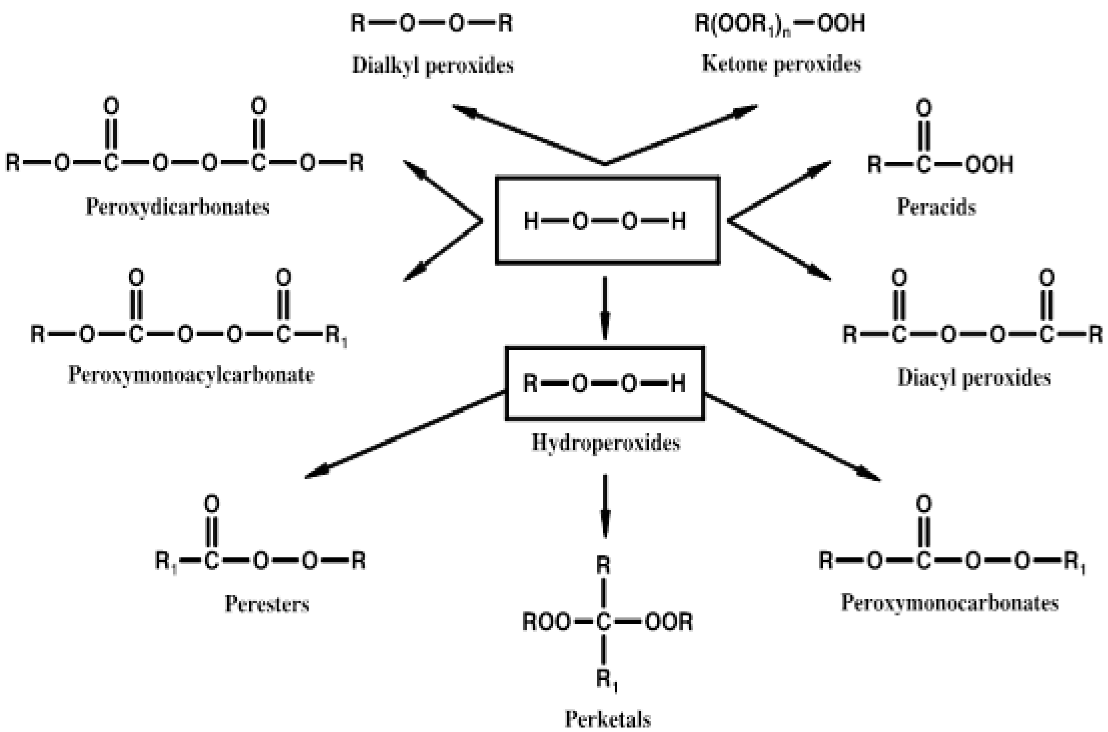
The polymerization of monomers is one of the main fields of application for organic peroxides. In this bulletin we would like to give you a rough overview on the use of organic peroxides for the free-radical polymerization. We will start off with a look at what qualifies organic peroxides for the polymerization of monomers followed by a look on the mechanism of the free radical polymerization. Next will be a short overview on the different types of polymerization processes for monomers. Finally we will take a closer look on the characteristics of the different organic peroxides which can be used for the free radical polymerization.

Initiators for high polymers

A wide range of organic peroxides and azo compounds are used as initiators for the radical polymerization of monomers. The reason for this is that organic peroxides are able to form radicals very easily by decaying of the O-O bond, induced by heat or by UV-radiation. This qualifies organic peroxides for a controllable trigger of the reaction and thus as an initiator for the free-radical polymerization. There are various types of organic peroxides available, which mainly differ in their thermal decomposition behavior. For this reason you can find organic peroxides for a broad temperature range.

Organic peroxides can be divided into diacylperoxides, hydroperoxides, dialkylperoxides, peroxyesters, peroxyketals and peroxy(di)carbonates (see Figure 1). The main areas of application for these initiators are the production of low density polyethylene (LDPE), polyvinylchloride (PVC), styrenics (PS/EPS), acrylics (PMMA) and other polymers. The polymerization of monomers takes place under varying controlled conditions, to which the properties of the initiator have to be adapted. Certain types of organic peroxides are also used for the chain degradation of polypropylene.

Figure 1: Types of Organic Peroxides



Free-Radical Polymerization

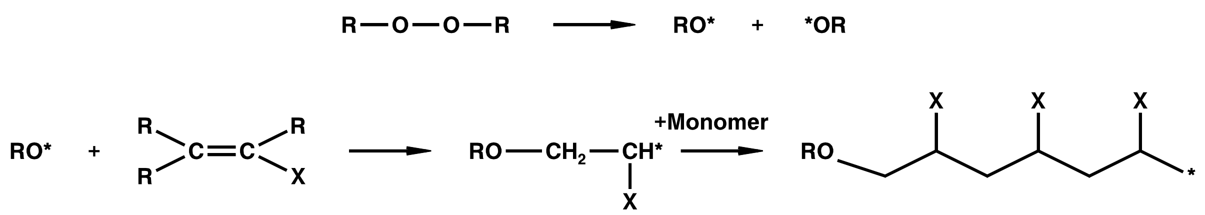
The synthesis of polymers is performed by linking of small molecules (*monomers*) in order to achieve macromolecules (*polymers*). Already during the 19th century this type of reaction was used in industrial scale, but only during the 20th century the researcher had understood the chemical background of this type of reaction and the age of the modern polymers was initiated.

The basic types of reaction are the polycondensation and the polyaddition.

The free-radical polymerization, which utilizes organic peroxides (Figure 1), but also Persulfates, compounds with an unstable C-C bond, Azo compounds and Hydrogen peroxide, is a polyaddition reaction, because the monomers react with each other without separation of byproducts.

A condition for this reaction will be that the reacting monomers are unsaturated compounds, i. e. compounds with a double bond between two C atoms, see reaction scheme in figure 2:

Figure 2: Reaction Scheme of the Free-Radical Polymerization



The physical properties of the polymers, for example the mean value of the molar mass and the molar mass distribution, are determined by the reaction temperature and the polymerization process. To ensure a sufficient amount of free-radicals at the chosen reaction temperature, one has to select a peroxide with a suitable thermal decomposition behavior (half life time).

Basic Types of Polymerization Processes

There exist four main processes, which are summarized in table 1:

Table 1: Basic Types of Polymerization Processes

Process	Medium
Bulk Polymerization	Monomer, only
Suspension Polymerization	Monomer / Water / Suspending Agent
Emulsion Polymerization	Monomer / Water / Emulsifier
Solution Polymerization	Monomer / Solvent

Compared with the bulk polymerization the remaining three processes do have the advantage that they ensure a better heat dissipation. The bulk polymerization does have the advantage that neither solvent nor water has to be removed from the final polymer. In case of bulk, solution and suspension polymerization (from the kinetics a bulk polymerization in the monomer droplets) monomer soluble initiators are common. Water soluble initiators, like Persulfates and Hydroperoxides are utilized for the emulsion Polymerization.

Organic Peroxides and their characteristics

Pergan is offering a wide rage of different peroxides. In Table 2 you will find a selection of peroxides, with their different characteristics. Some peroxides for example have to be stored and transported at temperature controlled conditions and at temperatures below 0 degrees Celsius. In Table 2 these can be easily identified. Important characteristics are stated hereafter.

Storage temperatures

Organic Peroxides are more or less stable products but will decompose under the influence of heat. To prevent a loss of quality during storage, it is important that the recommended maximum storage temperature is not exceeded and the minimum storage temperature not breached. In the table you will find the maximum storage temperature stated. Products that have a minimum storage temperature are marked.

SADT

The SADT (Self Accelerating Decomposition Temperature) is the lowest temperature at which a self accelerating decomposition may occur. The SADT is also depending on the packaging unit. Therefore you will find the SADT for the peroxide in an IBC stated separately.

Half life

An important factor for selecting an appropriate initiator is its decomposition rate, which is determined using its half life time. The half life is the time taken for half of the peroxide quantity to decompose in a specific solvent at a given temperature. With exception to the hydroperoxides, the half life times were determined in a solution of the initiator in 0.1 molar monochlorobenzene. Listed in table 2 is the temperature at which the half live is 1h.

Phlegmatization

Phlegmatization is an expression for desensitizing and stabilizing explosives, such as some peroxide grades, by adding an appropriate agent. In the right half of table 2 you will find information on the form the peroxide is available in as well as information on the phlegmatizing agent used.

Table 2: Choice of available Peroxides

PEROXAN…	Chemical name	max. storage temperature	SADT	IBC Volume [l] (SADT)	1h half life temperature	liquid	solid	Emulsion	Dispersion	Aliphats / Hydrocarbons	White Oil	thecnically pure	Water damped	Polypropylene
					Polym.T.			Konz.						
CND	Cumol-peroxyneodecanoate	-15°C	+10°C	1100 (+5°C)	56°C	X		50%		75%				
OPN	1,1,3,3-Tetramethylbutyl-peroxyneodecanoate	-15°C	+15°C	900 (+15°C)	57°C	X		50%		70%				
BCC	Di-(4-tert.-butyl-cyclohexyl)-peroxydicarbonate	+15°C	+40°C		64°C	X	P		40%			95%	75%	
EPS	Di-(2-ethylhexyl)-peroxydicarbonate	-20°C	0°C	1100 (0°C)	64°C	X		50%/60%		65%/75%		95%		
PND	tert.-Butyl-peroxyneodecanoate	-10°C	+15°C	900 (+15°C)	64°C	X		50%		30%/75%		95%		
NBC	Di-n-butyl-peroxydicarbonate	-15°C	+5°C		65°C	X				50%				
C124	Dicetyl-peroxydicarbonate	+15°C	+40°C	900 (+40°C)	65°C	X	P/G		40%			95%		
C126	Dimyristil-peroxidicarbonate	+15°C	+35°C	900 (+30°C)	65°C	X	P/G		40%			95%		
APV	tert.-Amyl-peroxypivalate	-10°C	25°C	850 (+25°C)	72°C	X				30%/75%				
PPV	tert.-Butyl-peroxypivalate	-5°C	+20°C	900 (+20°C)	75°C	X				40%/65%/75%				
NPO	Di-(3,5,5-trimetylhexanoyl)-peroxide	0°C	+20°C	900 (+20°C)	77°C	X		50%		50%/75%				
LP	Dilauroyl-peroxide	+30°C	+50°C	900 (+50°C)	79°C	X	F		25%/40%			98%		
APO	tert.-Amyl-peroxy-2-ethylhexanoate	+5°C	+35°C		91°C	X						95%		
BP	Dibenzoyl-peroxide	+30°C	+80°C		91°C		P						75%	
PO	tert.-Butyl-peroxy-2-ethylhexanoate	+15°C	+35°C	900 (+40°C)	91°C	X				32%/70%		98%		
PK295	1,1-Di-(tert.-butylperoxy)-3,3,5-trimethylcyclohexane	+30°C	+60°C		105°C	X				50%/75%/90%				
PK122	1,1-Di-(tert.-butylperoxy)-cyclohexane	+25°C	+60°C		113°C	X				50%/80%	50%			
AEC	tert.-Amyl-peroxy-2-ethylhexylcarbonate	+25°C	+55°C		113°C	X						95%		
PIN	tert.-Butyl-peroxy-3,5,5-trimethylhexanoate	+30°C	+60°C	900 (+55°C)	114°C	X				60%		98%		
PK234	2,2-Di-(tert.-butylperoxy)-butane	+30°C	+70°C		116°C	X				50%	50%			
BIC	tert.-Butyl-peroxyisopropylcarbonate	+25°C	+60°C		117°C	X				75%				
BEC	tert.-Butyl-peroxy-2-ethylhexylcarbonate	+30°C	+60°C		117°C	X						95%		
PA	tert.-Butyl-peroxyacetate	+10°C	+70°C		119°C	X				50%				
PB	tert.-Butyl-peroxybenzoate	+30°C	+60°C		122°C	X						98%		
DA	Di-tert.-amylperoxide	+30°C	+50°C		128°C	X						93%		
DC	Dicumyl-peroxide	+30°C	+80°C		132°C		G					98%		
BIB	Di-(2-tert.butyl-peroxyisopropyl)-benzene	+30°C	+80°C		134°C		P/G					95%		10%/20%/40%
HX	2,5-Dimethyl-2,5-di-(tert.-butylperoxy)-hexane	+30°C	+80°C		134°C	X	G			80%	50%/80%	92%		7,5%/10%/20%
BU	tert.-Butylcumyl-peroxide	+30°C	+90°C		136°C	X						94%		
HXY	2,5-Dimethyl-2,5-di(tert.-butylperoxy)-hexine-3	+30°C	+80°C		141°C	X					85%			
DB	Di-tert.-butyl-peroxide	+30°C	+80°C		141°C	X				50%/75%	50%	98%		
IHP	Di-isopropylbenzol-mono-hydroperoxide	+25°C	+80°C		154°C	X				50%				
PAM	p-Menthanhydroperoxide	+25°C	+80°C	925 (+80°C)	163°C	X				50%				
CU	Cumolhydroperoxide	+30°C	+80°C		166°C	X				80%/90%				
BHP	tert.-Butyl-hydroperoxide	+30°C	+90°C		185°C	X							70%	
AHP	tert.-Amyl-hydroperoxide	+30°C	+80°C		190°C	X							80%	

Legend for Table 2

Frozen
Cooled
Explosive law
Mind min. storage temp.
P=Powder/F=Flakes/G=Granules/K=Crystalline

With this legend you are able to determine which products have to be stored at temperatures below 0 degrees Celsius or refrigerated, as well as which products are subject to the explosives law. Furthermore it shows you which products are having a minimum storage temperature. The minimum storage temperatures are however not stated in table 2 and have to be taken from the technical data sheet of the product, which we can supply to you upon request. The last line of the legend is stating in which solid form the product is available. The four different forms are powder, flakes, granules or crystalline form.

PERGAN
PERGAN Marshall LLC

PERGAN Marshall LLC
710 Bussey Rd Marshall, TX 75670 USA
Tel.: +1 903-938-5141

info@perganmarshall.com

PERGAN
The Peroxide Company

PERGAN GmbH
Schlavenhorst 71 46395 Bocholt Deutschland
Tel.: + 49 (0) 2871 / 99 02-0
Fax: + 49 (0) 2871 / 99 02-50

info@pergan.com