

Applications: Free Radical Initiators

Thermal Initiators: Decomposition Rate and Half-Life

Ideally, a thermal free radical initiator should be relatively stable at room temperature but should decompose rapidly enough at the polymer-processing temperature to ensure a practical reaction rate. In addition to temperature, the decomposition rate (k_d) of the initiator will depend on the solvent/monomer system used. The confining effect of solvent molecules (the cage effect) causes secondary "wastage" reactions including recombination of radicals to regenerate the initiator. The cage effect becomes more significant as viscosity increases.

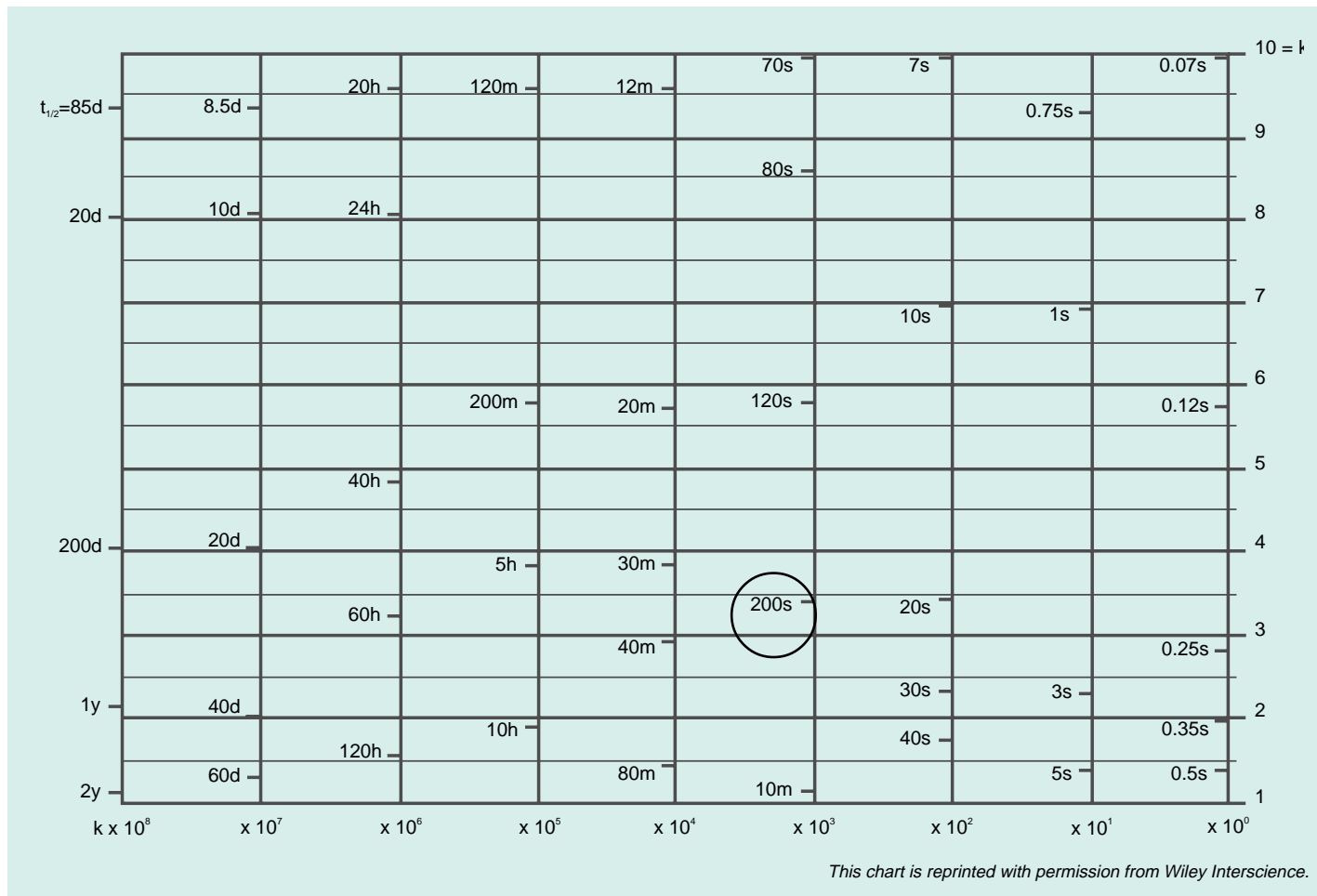
The most important indicator of activity of an initiator is its half-life ($t_{1/2}$). It is the time required to reduce the original initiator content of a solution by 50%, at a given temperature.

Assuming first order decomposition kinetics, which is true for most free radical organic initiators, the half-life ($t_{1/2}$) is related to the initiator decomposition rate (k_d) as follows:

$$t_{1/2} = \ln 2 / k_d$$

Table I lists the decomposition rate (k_d) data¹ for several commonly used free radical initiators, at specific temperatures and solvents. To further assist you in your selection of a thermal initiator, the temperature corresponding to a 10 hour half-life in a specific solvent is also shown. Fig. 1 relates the initiator decomposition rate (k_d) in s^{-1} to the half-life for a broad range of k_d values, including those found in Table I.

Fig 1: Relationship of Half Life ($t_{1/2}$) to Decomposition Rate (k_d).



How to read the chart:

See circled example: Half lives are to the left of each vertical line.
A half life of 200s has a rate constant of 3.4×10^{-3}

Key:

- y = years
- d = days
- h = hours
- m = minutes
- s = seconds

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Thermal Initiators: Decomposition Rate and Half-Life (continued)

Table I: Decomposition Rates and 10-Hour Half-life Temperatures of Common Thermal Initiators (arranged alphabetically by initiator)

Aldrich Cat. No.	Initiator	Solvent	T(°C)	k_d (s ⁻¹)	10h Half-life °C (Solvent)
	<i>tert</i> -Amyl peroxybenzoate				99 (benzene)
11,816-8	4,4-Azobis(4-cyanovaleric acid)	Acetone	70	4.6×10^{-5}	69 (water)
			69	1.9×10^{-5}	
			80	9.0×10^{-5}	
38,021-0	1,1'-Azobis(cyclohexanecarbonitrile)	Toluene	80	6.5×10^{-6}	88 (toluene)
			95	5.4×10^{-5}	
			102	1.3×10^{-4}	
44,109-0	2,2'-Azobisisobutyronitrile (AIBN)	Benzene	50	2.2×10^{-6}	65 (toluene)
			70	3.2×10^{-5}	
			100	1.5×10^{-3}	
17,998-1	Benzoyl peroxide ²	Benzene	60	2.0×10^{-6}	70 (benzene)
			78	2.3×10^{-5}	
			100	5.0×10^{-4}	
44,169-4	2,2-Bis(<i>tert</i> -butylperoxy)butane				100 (benzene)
38,809-2	2,5-Bis(<i>tert</i> -butylperoxy)-2,5-dimethylhexane	Benzene	115	1.1×10^{-5}	120 (benzene)
			145	4.7×10^{-4}	
54,460-4	2,5-Bis(<i>tert</i> -Butylperoxy)-2,5-dimethyl-3-hexyne				125 (benzene)
44,171-6	Bis(1-(<i>tert</i> -butylperoxy)-1-methylethyl)benzene				115 (benzene)
41,666-5	<i>tert</i> -Butyl hydroperoxide	Benzene	130	3×10^{-7}	170 (benzene)
			160	6.6×10^{-6}	
			170	2.0×10^{-5}	
			183	3.1×10^{-5}	
38,807-6	<i>tert</i> -Butyl peracetate	Benzene	85	1.2×10^{-6}	100 (benzene)
			100	1.5×10^{-5}	
			130	5.7×10^{-4}	
16,852-1	<i>tert</i> -Butyl peroxide	Benzene	80	7.8×10^{-8}	125 (benzene)
		Benzene	100	8.8×10^{-7}	
		Benzene	130	3.0×10^{-5}	
15,904-2	<i>tert</i> -Butyl peroxybenzoate	Benzene	100	1.1×10^{-5}	103 (benzene)
			130	3.5×10^{-4}	
	<i>tert</i> -Butylperoxy isopropyl carbonate				98 (aliphatic hydrocarbons)
24,750-2	Cumene hydroperoxide	Benzene	115	4.0×10^{-7}	135 (toluene)
			145	6.6×10^{-6}	
	Cyclohexanone peroxide	Benzene			90 (benzene)
32,954-1	Dicumyl peroxide	Benzene			115 (benzene)
29,078-5	Lauroyl peroxide	Benzene	40	4.9×10^{-7}	65 (benzene)
			60	9.2×10^{-6}	
			85	3.8×10^{-4}	
51,355-5	2,4- Pentanedione peroxide				125 (triethyl phosphate)
26,933-6	Peracetic acid				135 (toluene)
21,622-4	Potassium persulfate ³	Water	80	6.9×10^{-5}	60 (H ₂ O) 70 (0.1M NaOH)
		0.1M NaOH	50	9.5×10^{-7}	
			60	3.2×10^{-6}	
			80	9.2×10^{-5}	
			90	3.5×10^{-4}	

¹"Polymer Handbook", Eds. Brandrup, J; Immergut, E.H.; Grulke, E.A., 4th Edition, John Wiley, New York, 1999, II/2-69; Aldrich Catalog No. Z41,247-3.

²Amines can significantly increase the decomposition rates of peroxides, e.g., addition of *N,N*-dimethyl aniline to benzoyl peroxide causes the latter to decompose rapidly at room temperature.

³Persulfate decomposition is pH dependent.