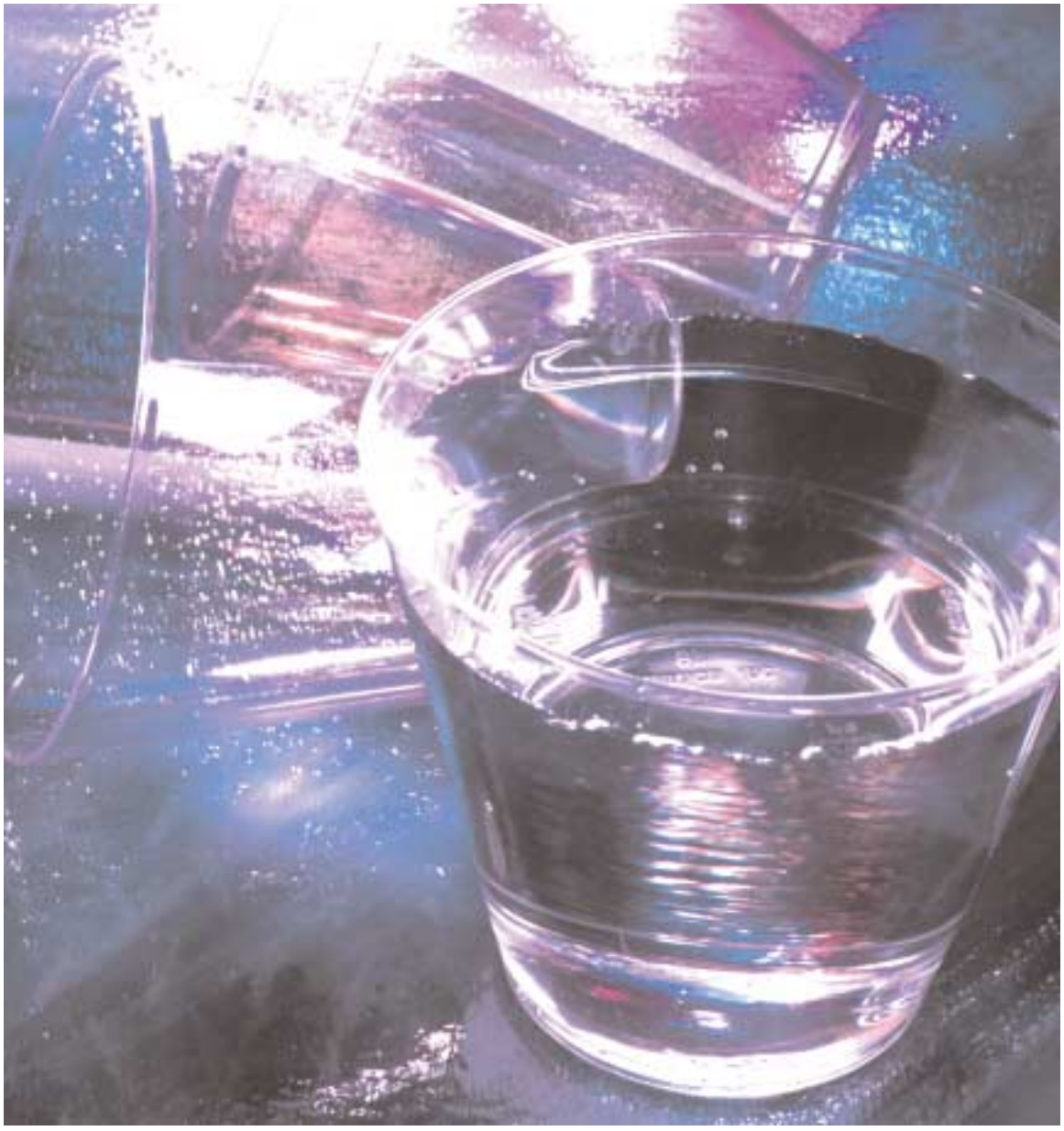


DIFUNCTIONAL PEROXIDES

Better Performance In Crystal Polystyrene

ARKEMA

DIFUNCTIONAL PEROXIDES FOR CRYSTAL POLYSTYRENES

Difunctional Peroxides for Crystal Polystyrene:

- **Narrow Molecular Weight Distribution**
- **Peroxide Mixtures for Higher Output**
- **Higher Molecular Weight**
- **Improved Productivity over Thermal**

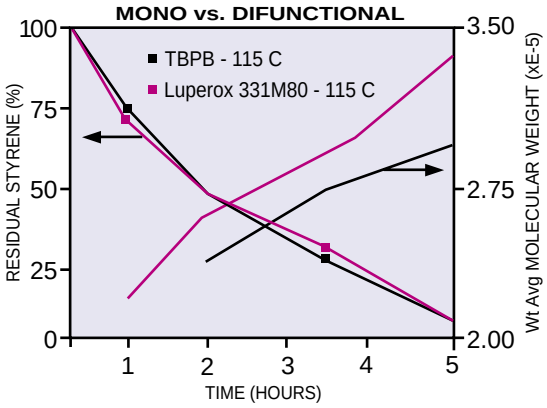
ATOFINA DIFUNCTIONAL PEROXIDES FOR CRYSTAL POLYSTYRENE

ATOFINA offers over 50 organic peroxides in over 150 formulations. Of these, one class of peroxides outperforms all others for making crystal polystyrene. That class consists of our difunctional peroxides.

ATOFINA offers a full range of difunctional peroxides spanning a broad spectrum of temperatures. This allows producers to optimize rates over the entire reaction temperature profile. Luperox® 256 is best in prepolys at temperatures below 110°C. Luperox® 231, 331M80 and 531M80 are best in initial reactors from 100 to 130°C. Luperox® 101 is best at temperatures above 130°C.

ONE HOUR HALF LIFE TEMPERATURES (C) OF DIFUNCTIONAL PEROXIDES

LUPEROX 256	91
LUPEROX 331M80	116
LUPEROX 531M80	112
LUPEROX 231	115
LUPEROX 101	140



DIFUNCTIONAL PEROXIDES PREFERRED OVER MONOFUNCTIONALS

Why are difunctional peroxides preferred over all of ATOFINA's other peroxides for crystal polystyrene? Just compare the polymerization of styrene using t-butyl perbenzoate (TBPB) to Luperox® 331M80. The monofunctional TBPB yields essentially the same conversion as Luperox® 331M80 but the difunctional gives superior molecular weight. Demonstrated here is a polymerization using 540 ppm TBPB or 450 ppm Luperox® 331M80 at 115°C containing 5% ethyl benzene.

DIFUNCTIONALS >> THERMAL

Luperox®331M80 (ppm)	Temp. (°C)	Conversion (%)	Weight Avg M.W.	P.D.I. (M_W/M_n)
Thermal	120-160	82	265,000	1.93
450	105-150	80	299,000	1.93
675	105-150	86	285,000	1.95

Higher molecular weights with the same residence time are readily obtained using Luperox® 331M80.

Demonstrated here is a 4 hour polymerization using a constant temperature ramp. The initial temperature is decreased to use the peroxide at its fullest potential while minimizing the occurrence of thermal polymerization. The end temperature approaches that of thermal, thus minimizing any problems with high viscosity materials. Here a 10% increase in molecular weight is obtained with no loss in productivity. Of course, if one can obtain higher molecular weight, it is also possible to obtain the same molecular weight with higher production rates. All of the samples in the table above contained 5% ethyl benzene.

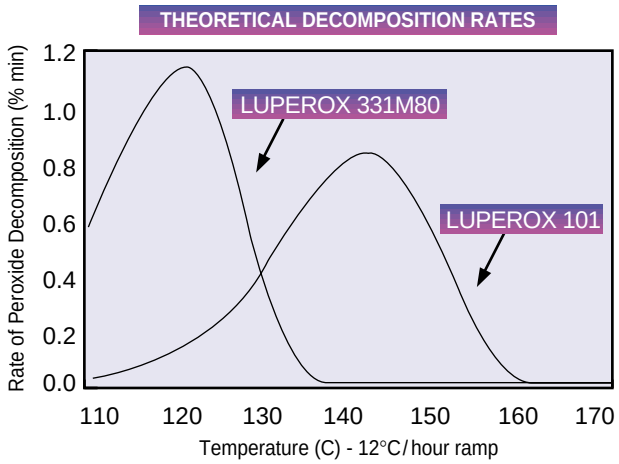
NARROW AND HIGH MOLECULAR WEIGHT USING LUPEROX®531M80

When compared to other cyclic perketals, Luperox® 531M80 gives a 7% higher M_n without significantly increasing the M_w. Thus, the molecular weight distribution narrows while simultaneously increasing molecular weight. In a 40 sample experimental design, the average values obtained were:

	Luperox® 231	Luperox® 531M80
Number Avg MW	138,000	149,000
Weight Avg MW	257,000	267,000
Polydispersity	1.86	1.79

COMBINATIONS OF DIFUNCTIONAL PEROXIDES

Because styrene polymerization occurs over a broad temperature range, peroxide combinations are necessary to optimize output. Luperox® 331M80 works only in the lower temperature ranges of a styrene polymerization. To complement this, Luperox® 101 can supply difunctional radicals for the higher temperatures. The curves demonstrate the number of radicals formed per minute using either Luperox® 331M80 or Luperox® 101 over a common temperature profile.



LUPEROX® 101 AND LUPEROX®331M80 COMBINATION FOR HIGH OUTPUT

Using a combination of Luperox® 101 and Luperox® 331M80 increases rates without losing molecular weight. Using 450 ppm of Luperox® 331M80 and 5% ethyl benzene, a styrene polymerization carried out from 100 to 150°C requires 5 hours to reach high conversion.

The same polymerization with just 100 ppm of Luperox® 101 gives an indentical product in only 4 hours.

	0 ppm Luperox 101		100 ppm Luperox 101	
Time (hrs)	Conversion (%)	Molecular Wt (Mw)	Conversion (%)	Molecular Wt (Mw)
4	76	316,000	81	311,000
5	84	312,000	94	299,000

LUPEROX® 256 FOR HIGH MOLECULAR WEIGHT

Using the difunctional Luperox® 256 gives molecular weight advantages over Benzoyl Peroxide (BPO) at low conversions. Thus, it is ideal for a low temperature prepoly reactor. However, only BPO is recommended for obtaining conversion above 50%. Shown here are polymerizations at 90°C comparing BPO to Luperox 256.

Time (min)	Concentration (MMDL/kg) BPO or Luperox 256	BPO % Styrene Converted	Luperox 256 % Styrene Converted	BPO Wt Avg Molecular Weight	Luperox 256 Wt Avg Molecular Weight
180	1700/1517	39	38	150,000	220,000
240	1700/1517	48	42	170,000	250,000
300	1700/1517	56	48	200,000	280,000
180	2300/2049.5	46	46	130,000	190,000
300	2300/2049.5	70	60	200,000	260,000

	2, 2-Di-(t-Butylperoxy) butane	Luperox TBPB	Luperox 7M75	Luperox TBEC	Luperox 555M60	Luperox TAEC	Luperox 331M80
Concentration (ppm)	325	539	913	683	677	722	451
One hour half life (°C)	127	125	123	121	120	117	116
115°C % Conversion 30 minutes	9	10	8	11	10	12	12
115°C % Conversion 60 minutes	16	15	19	18	22	23	22
115°C % Conversion 120 minutes	33	33	36	38	40	41	38
115°C % Conversion 300 minutes	-	82	83	83	-	-	74
125°C % Conversion 30 minutes	18	16	19	20	22	23	21
125°C % Conversion 60 minutes	32	31	33	36	36	37	34
125°C % Conversion 120 minutes	57	58	60	58	57	56	53

ISOTHERMAL CONVERSION RATES FOR INTERMEDIATE TEMPERATURE PEROXIDES

Conversion rates are closely tied to the rate of peroxide decomposition. Peroxides that decompose faster cause faster initial polymerization; however, at longer times they burn out. For example, Luperox® 331M80 converts faster than TBPB initially; however, Luperox® 331 burns out after several hours while Luperox® TBPB continues to perform. Thus, the proper peroxide choice requires consideration of both temperature and time.

ISOTHERMAL CONVERSION RATES FOR LOWER TEMPERATURE PEROXIDES

At low temperatures and high conversions, nothing is more efficient than BPO. Other peroxides, such as the difunctional Luperox® 256, are just as efficient as BPO at low conversions, but above 50% conversion, BPO is always the peroxide of choice.

	Luperox 80M75	Luperox 26	Luperox 575	BPO	Luperox 256	Luperox 665M50	Luperox DEC
Concentration (ppm)	1240	1339	1426	1500	1336	3224	2120
One hour half life (°C)	102	95	92	92	91	84	83
90°C % Conversion 60 minutes	13	16	19	19	18	23	20
90°C % Conversion 120 minutes	22	28	31	29	30	30	25
90°C % Conversion 240 minutes	39	43	45	50	45	36	27
95°C % Conversion 60 minutes	18	25	27	24	26	22	17
95°C % Conversion 120 minutes	33	35	34	35	33	24	22
95°C % Conversion 240 minutes	48	47	44	54	43	35	30

ISOTHERMAL POLYMERIZATIONS USING HIGHER TEMPERATURE PEROXIDES

	Luperox DTA	Luperox 101	Luperox 802	Luperox 500R	Thermal
Concentration (ppm)	483	403	469	750	N/A
135°C/60 min % Conversion	48	38	40	53	33
135°C/120 min % Conversion	75	70	72	79	49
135°C/210 min % Conversion	94	91	93	95	67
135°C/300 min % Conversion	98	97	98	98	78
135°C/60 min Wt Avg MW	200,000	230,000	220,000	180,000	250,000
135°C/120 min Wt Avg MW	220,000	250,000	240,000	200,000	250,000
135°C/210 min Wt Avg MW	230,000	260,000	250,000	200,000	260,000
135°C/300 min Wt Avg MW	220,000	260,000	240,000	200,000	270,000
140°C/60 min % Conversion	58	44	55	62	36
140°C/120 min % Conversion	85	83	84	85	58
140°C/210 min % Conversion	96	96	97	96	75
140°C/300 min % Conversion	99	98	99	98	84
140°C/60 min Wt Avg MW	190,000	220,000	190,000	170,000	220,000
140°C/120 min Wt Avg MW	200,000	240,000	210,000	180,000	240,000
140°C/210 min Wt Avg MW	200,000	230,000	200,000	180,000	240,000
140°C/300 min Wt Avg MW	200,000	230,000	200,000	180,000	240,000

Luperox® 101 is the peroxide of choice for polymerization at higher temperatures. Compared to thermal, Luperox® 101 yields faster conversion without loss in molecular weight. The other peroxides shown are all monofunctional and result in lower molecular weight than thermal polymerization.

LUPEROX® 331M80 ISOTHERMAL CONVERSION (450 PPM) NEAT

	60 min	120 mins	210 mins	300 mins
112°C % Conversion		36	52	68
115°C % Conversion	22	39	58	74
118°C % Conversion	31	46	64	81
121°C % Conversion	33	49	67	80
112°C Wt Avg MW	210,000	240,000	280,000	320,000
115°C Wt Avg MW	210,000	250,000	280,000	330,000
118°C Wt Avg MW	210,000	250,000	290,000	300,000
121°C Wt Avg MW	210,000	240,000	270,000	270,000
112°C Mw/Mn	1.65	1.73	1.84	1.99
115°C Mw/Mn	1.61	1.76	1.90	1.95
118°C Mw/Mn	1.69	1.81	1.94	2.02
121°C Mw/Mn	1.73	1.84	1.91	1.99

LUPEROX® 331M80 ISOTHERMAL CONVERSION (450 PPM) 5% ETHYL BENZENE

	60 mins	120 mins	210 mins	300 mins
112°C % Conversion		35	56	64
115°C % Conversion	27	42	58	70
118°C % Conversion	32	46	64	75
121°C % Conversion	34	52	66	76
112°C Wt Avg MW	200,000	240,000	260,000	300,000
115°C Wt Avg MW	200,000	230,000	260,000	290,000
118°C Wt Avg MW	200,000	230,000	270,000	270,000
121°C Wt Avg MW	200,000	230,000	260,000	260,000
112°C Mw/Mn	1.63	1.69	1.80	1.90
115°C Mw/Mn	1.69	1.73	1.84	1.92
118°C Mw/Mn	1.66	1.76	1.86	1.96
121°C Mw/Mn	1.68	1.79	1.87	1.91

GUIDE TO PRODUCT NAMES

PRODUCT NAME	CHEMICAL NAME
Luperox 7M75	t-Butyl Peroxyacetate
Luperox 80M75	t-Butyl Peroxyisobutyrate
Luperox 101	2, 5-Dimethyl-2, 5-di-(t-Butylperoxy) hexane
Luperox 231	1, 1-Di-(t-Butylperoxy)-3, 3, 5-trimethyl-cyclohexane
Luperox 256	2, 5-Dimethyl 2, 5-di (2-ethylhexanoyl peroxy) hexane
Luperox 331M80	1, 1-Di-(t-Butylperoxy) cyclohexane
Luperox 555M60	t-Amyl Peroxyacetate
Luperox 575	t-Amyl Peroxy-2-ethylhexanoate
Lupersox 665M50	1,1-Dimethyl-3-hydroxybutyl Peroxy-2-ethylhexanoate
Luperox 802	α-α'-bis (t-Butylperoxy) diisopropylbenzene
Luperox DTA	Di-t-amyl Peroxide
Luperox 26	t-butyl peroctoate
Luperox DEC	Decanoyl Peroxide

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