ORGANIC CHEMICALS

Product Information

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MERCAPTANS AS CHAIN TRANSFER AGENTS IN POLYMERIZATION

ARKEMA

INTRODUCTION

Mercaptans have long been used as chain transfer agents to modify free radical polymerizations in the production of polystyrene, styrene-butadiene rubber (SBR), ABS terpolymers, poly-acrylates and methacrylates as well as other vinyl type polymers.

Modification to control the molecular size and the molecular weight distribution is necessary so that the resulting polymers have good processability and other properties required for their intended application.

The literature provides an abundance of information on mercaptans as chain transfer agents or polymerization modifiers, as they are sometimes called. However, this information is widely scattered. For convenience of researchers and others in the field this bulletin has been compiled to abstract and bring together information in the following categories:

I. Chain Transfer Constants of Mercaptans
II. Representative Polymerization Recipes Using Mercaptan Modifiers
III. Literature and Patent References on the Use of Mercaptans as Modifiers.

Although many different types of aliphatic mercaptans have been and are being used as modifiers, this bulletin is limited primarily to the normal and tertiary alkyl mercaptans of the type produced by ATOFINA Chemicals, INC.

In addition to the standard mercaptan modifiers, such as normal dodecyl, normal octyl and tertiary dodecyl mercaptans, ATOFINA offers a line of mercaptans ranging from C_1-C_{18}.

I. CHAIN TRANSFER CONSTANTS OF MERCAPTANS

Chain transfer constants are an index to the efficiency of chain transfer agents in certain free radical polymerization systems. The chain transfer constant, C, is defined as:

$$C = \frac{\textit{reaction rate constant of the transfer reaction}}{\textit{reaction rate constant of the propagation reaction}}$$

Mayo[1] has developed the following equation relating the chain transfer constant to the degree of polymerization:

$$\frac{1}{\overline{P}} = C\,\frac{(S)}{(M)} + \frac{1}{\overline{P}_\bullet}$$

where $\overline{P}$ = Degree of polymerization in the presence of a chain transfer agent

$\overline{P}_\bullet$ = Degree of polymerization in the absence of a chain transfer agent

(S) = Concentration of chain transfer agent

(M) = Concentration of monomer

The above relationship was derived for low conversions.

When (S) = (M), the chain transfer constant represents the ratio of free radicals that will undergo transfer with the chain transfer agent to those that will grow by addition of monomer. The validity of these relationships is based on the assumption that both the propagation and transfer reactions are of the same kinetic order. Experimental confirmation has been achieved at low orders of monomer conversion. Pryor[2] has outlined the mechanism of these reactions.

Since the propagation and transfer reactions show similar temperature dependence, chain transfer constants are only slightly temperature dependent. The listing in Table I, compiled from the literature, illustrates this point. This listing also provides a tabulation of values for ATOFINA mercaptans in various systems.

Table I CHAIN TRANSFER CONSTANTS OF ALKYL MERCAPTANS

Chain Transfer Agent	Temperature(°C)	Constant	Reference
	BUTADIENE MONOMER		
n-Octyl Mercaptan	5	21.8	3,18
	50	16.0	3,18
	50	18	4
	50	19	5
t-Octyl Mercaptan	5	5.3	3
	50	3.7	3
n-Decyl Mercaptan	50	18.2	4
n-Tetradecyl Mercaptan	50	19.4	3
	ETHYLENE MONOMER		
n-Butyl Mercaptan	130	5.8	6,18
n-Butyl Mercaptan	130	15	6,18
	METHYL ACRYLATE MONOMER		
Ethyl Mercaptan	50	1.57	7,18
n-Butyl Mercaptan	30	1.53 ± 0.04	8,18
	60	1.69 ± 0.17	8,18
	METHYL METHACRYLATE MONOMER		
Isopropyl Mercaptan	60	0.38	9,18
n-Butyl Mercaptan	60	0.67 ± .03	8,18
	60	0.66	9,18
	100	0.92	10
t-Butyl Mercaptan	60	0.18	9,18
n-Amyl Mercaptan	50	0.72	10
	50	0.8	18
	STYRENE MONOMER		
Ethyl Mercaptan	50	17.1	11,18
n-Butyl Mercaptan	60	21	12,18
	60	22 ± 3	8,18
	70	15	12,18
	80	17	12,18
	99	15.4	13,18
t-Butyl Mercaptan	50	4.0	10,18
	60	3.1	14,18
	60	3.6 ± 0.3	15
	100	1.8	14,18
		3.2 ± 0.3	15
n-Amyl Mercaptan	40	21	10
	62.5	17.8	3
n-Hexyl Mercaptan	99	15.3	13,18
n-Octyl Mercaptan	5	23	3,18
	50	19	3,18
sec-Octyl Mercaptan	99	3.2	13,18
t-Octyl Mercaptan	5	5.5	3
	50	4.3	3
n-Dodecyl Mercaptan	60	18.7 ± 1	3
	100	13	16,18
	110	26	16,18
t-Dodecyl Mercaptan	25	3.2	17
	50	2.9	17
	75	2.4	17
n-Tetradecyl Mercaptan	50	19	3,18
	100	3.2	10
n-Octadecyl Mercaptan	99	14.7	13,18
	VINYL ACETATE MONOMER		
n-Butyl Mercaptan	60	48 ± 14	8,18

References for Part I

1. F. R. Mayo, *J. Am. Chem. Soc., 65,* 2324 (1943).
2. W. A. Pryor, *Mechanisms of Sulfur Reactions,* 82-88, McGraw-Hill, NY (1962).
3. E. J. Meehan, I. M. Kolthoff, and P. R. Sinha, *J. Polymer Sci., 16,* 471 (1955)
4. W. V. Smith, *J. Am. Chem. Soc., 68,* 2064 (1946)
5. E. J. Meehan, I. M. Kolthoff, and P. R. Sinha, *J. Polymer Sci A., 2,* 4911 (1964).
6. G. A. Mortimer, *J. Polymer Sci. A-1, 10,* 163 (1972)
7. G. P. Scott, C. C. Soong, W. S. Huang, and J. L. Reynolds, *J. Org. Chem., 29,* 83 (1964).
8. C. Walling, *J. Am. Chem. Soc., 70,* 2561 (1948).
9. J. L. O'Brien and F. Gornick, *J. Am. Chem. Soc.,77,* 4757 (1955).
10. W. V. Smith, *J. Am. Chem. Soc., 68,* 2059 (1946).
11. G. P. Scott and J. C. Wang, *J. Org. Chem., 28,* 1314 (1963).
12. L. A. Wall and D. W. Brown, *J. Polymer Sci., 14,* 513 (1954).
13. V. A. Dinaburg and A. A. Vansheidt, *J. Gen. Chem. USSR (Eng. Trans.), 24,* 839 (1954).
14. M. Morton, J. A. Cala, and I. Piirma, *J. Am. Chem. Soc., 80,* 5596 (1958).
15. R. A. Gregg, D. M. Alderman, and F. R. Mayo, *J. Am. Chem. Soc., 70,* 3740 (1948).
16. T. Huff and E. Perry, *J. Polymer Sci. A, 1,* 1553 (1963).
17. R. Pierson, A. Costanza, and A. Weinstein, *J. Polymer Sci., 17,* 221 (1955).
18. J. Brandrup and E. H. Immergut, *Polymer Handbook,* Second Edition, Wiley-Interscience, NY (1975).

II. REPRESENTATIVE POLYMERIZATION RECIPES USING MERCAPTAN MODIFIERS

A. High Styrene-Butadiene Latex for Emulsion Paints.
Reference:
T. T. Serafini and E. G. Bobalek, *Official Digest, Federation of Societies for Paint Technology, 32,* 1259-1288 (1960).

Component	Parts by Weight
Water	180
Styrene	60
Butadiene	40
Stearic Acid	4.6
Lithium Hydroxide	0.39
n-Dodecyl Mercaptan	0.10
Potassium Persulfate	0.50

B. Acrylic Terpolymer Intermediate for Thermosetting Acrylic Baking Enamels
Reference:
P. M. Christenson and D. P. Hart, *Official Digest, Federation of Societies for Paint Technolgy, 33,* 684-698 (1961).

Component	Parts by Weight
Acrylamide	150
Styrene	400
Ethyl Acrylate	450
n-Butanol	1000
Cumene Hydroperoxide	10
Tertiary Dodecyl Mercaptan	10

C. Sol Chloroprene Polymer (Emulsion Polymerization)
Reference:
U. S. Patent 3,929,752 issued December 30, 1975 to T. A. Cooper and A. A. Khan, assigned to E. I. duPont deNemours and Co.
Polymerization Temperature: 40˚C

Component	Parts by Weight
Chloroprene	100
Disproportioned Rosin	4
n-Dodecyl Mercaptan	1.5
Dodecyl di(isopropanol)amine	0.5
Water	99.4
NaOH	0.24
"Lomar" PW (Napco Chemical)	0.10
Sodium Sulfite	0.15
Ammonium Hydroxide	4

Catalyst: Aqueous 0.15% solution of ammonium persulfate containing a trace of 2-anthroquinonesulfonate.

D. Acrylonitrile - Butadiene - Styrene (ABS) (Graft Polymer)
Reference:
U. S. Patent 2,820,773 issued January 21, 1958 to C. W. Childress et al.

Component	Parts by Weight
Polybutadiene	58
Styrene	70
Acrylonitrile	48
Sodium Stearate	1.7
Potassium Persulfate	0.4
tert-Octyl Mercaptan	0.8

E. Polystyrene (bulk polymerization)
Reference:
H. R. Snyder, J. M. Stewart, R. E. Allen and R. J. Dearborn, *J. Am. Chem. Soc., 68*, 1422 (1946).

Component	**Parts by Weight**
Styrene	20
Benzoyl Peroxide	0.5
n-Dodecyl Mercaptan	0.1 to 5.0
Hydroquinone	0.5

F. Polybutadiene (emulsion polymerization)
Reference:
W. V. Smith, *J. Am. Chem. Soc., 68*, 2064 (1946).

Component	**Parts by Weight**
Butadiene	70
n-C_5, n-C_6, n-C_8, n-C_{12}, or n-C_{14} Mercaptan	0.8 to 1.7
Soap	3.5
Potassium Persulfate	0.21
Distilled Water	120

G. Vinyl Toluene - Butyl Methacrylate copolymers for a pigmentation base.
Reference:
Belgian Patent 611,218, June 6, 1962 to Imperial Chemical Industries.

Component	**Parts by Weight**
Stearic Acid	25
Vinyl Toluene	350
n-Butyl Methacrylate	150
Water	1860
9.1% Aqueous K_2CO_3	94
Potassium Persulfate	5
Tertiary Amyl or Tertiary Dodecyl Mercaptan	21.1

H. Acrylic Molding and Laminating Syrup
Reference:
U. S. Patent 3,153,022 issued October 13, 1964 to W. H. Calkins and W. M. Edwards.

Component	**Parts by Weight**
Methyl Methacrylate	2478
Ethylene Dimethacrylate	12.5
Alpha, Alpha'-Azobisisobutyronitrile	0.75
n-Dodecyl Mercaptan	9
Hydroquinone	0.088

I. SBR"Cold" Rubber (Styrene-Butadiene Copolymer)
Reference:
ATOFINA "cold" rubber test recipe based upon sodium formaldehyde sulfoxylate (SFS) recipe for SBR from G. S. Whitby, *Synthetic Rubber*, 217, Wiley, New York (1954).
Polymerization Temperature: 5˚ C.

Component	**Parts by Weight**
Butadiene	72
Styrene	28
Water	200
t-Dodecyl Mercaptan (ELF ATOCHEM)	0.232
Dresinate 515 (Emulsifier: Hercules, Inc.)	4.50
Daxad 11 (Dispersant: Dewey & Almy Chemicals, Div. of W. R. Grace Co.)	0.152
Versene 100 (Chelating agent: Dow Chemical Co.)	0.032
p-Menthane Hydroperoxide	0.044
$FeSO_4 \cdot 7H_2O$	0.0224
$Na_3PO_4 \cdot 12H_2O$	0.80
(SFS) Sodium Formaldehyde Sulfoxylate	0.0676
Shortstoppers:	
Diethylhydroxyl Amine: Pennstop® 1866	0.02 - 0.06
or Sodium Dimethyldithiocarbamate	0.15

J. SBR "Hot" Rubber (Styrene-Butadiene Copolymer), SBR 1000
Reference:
ATOFINA "hot" rubber test recipe based upon the standard U. S. Government synthetic rubber recipe used in World War II as described in Whitby, *Synthetic Rubber*, pp 228 and 243, Wiley, New York (1954).
Polymerization Temperature: 50˚ C

Component	**Parts by Weight**
Butadiene	72
Styrene	28
Water	180
n-Dodecyl Mercaptan (ELF ATOCHEM)	0.30
*NaORR Soap Flakes	4.72
Potassium Persulfate	0.252
Short Stoppers:	
Diethylhydroxyl Amine; Pennstop 1866	0.15
or Hydroquinone	0.15

*Sodium Office of Rubber Reserve Soap Flakes

K. NBR (Nitrile-Butadiene Rubber)
Reference:
ATOFINA NBR test recipe based upon one cited by Whitby, *"Synthetic Rubber"*, 802, Wiley, NY (1954).
Polymerization Temperature: 40˚ C.

Component	**Parts by Weight**
Butadiene	72
Acrylonitrile	28
Water	180
NaORR Soap Flakes (see recipe "J" above)	4.5
Stearic Acid	0.6
t-Dodecyl Mercaptan (ATOFINA)	0.4
KCl	0.3
$K_4P_2O_7$	0.1
$Fe_2(SO_4)_3$ (anhydrous basis)	0.02
$K_2S_2O_8$	0.10
Hydroquinone Shortstopper	0.15

III. LITERATURE AND PATENT REFERENCES ON THE USE OF MERCAPTANS AS MODIFIERS

The following list should not be considered comprehensive. Only references believed to be of greatest value and interest are included.

Acrylic Polymers

Acrylics - General	W. H. Brown and T. J. Miranda, *Official Digest, Federation of Societies for Paint Technology, 36,* NO. 475, Part II, 92-134 (August, 1964).
Acrylics - General	E. H. Riddle, *Monomeric Acrylic Esters*, Reinhold, New York, (1954).
Acrylics	D. D. Hicks, U.S. 3,960,824 issued June 1, 1976 assigned to Celanese Coatings and Specialty Co.
Acrylamide-Ethyl Acrylate	R. M. Christenson and D. A. Hart, *Official Digest, Federation of Societies for Paint Technology, Vol. 33*, 684-698 (June 1961) cited in Recipe "B" above.
Methyl Methacrylate	S. Basu, J. N. Sen and S. R. Palit, *Proc. Royal Society* (London), *214 A*, 247 (1952).
n-Butyl Methacrylate-Vinyl Toulene	Belgian Patent 611,218 cited in Recipe "G" above.
Methyl Methacrylate	British Pat. 582,010.
Methyl Methacrylate	W. H. Calkins and W. M. Edwards, U. S. 3,153,022
Ethylene Dimethacrylate	issued October 13, 1964, assigned to duPont cited in Recipe "H" above.
Methyl Methacrylate	S. G. Cohen and D. B. Sparrow, *J. Polymer Sci., 3*, 693 (1948).
(also Allyl Meth.)	
Methyl Methacrylate	E. Teupel, British Pat. 907,406, Oct. 3, 1962; *C. A., 58*, 11535c.
	See also references 7-10 in Part I above.

Diene Polymers

Dienes - General	British Patent 625,647 to Sharples Chemical, now ELF ATOCHEM.
Dienes - General	H. W. Starkweather et al, *Ind. Eng. Chem. 39*, 210 (1947).
Dienes -Styrene	N. S. Kharash et al, *J. Org. Chem., 20*, 1550 (1955).
Butadiene	J. J. Drysdale and C. S. Marvel, *J. Polymer Sci., 13*, 513 (1954).
Butadiene	R. W. Laundrie and B. G. Labbe, *Rubber Age, 75*, 545 (1954).
Butadiene	H. R. Snyder et al, *J. Am. Chem. Soc., 68*, 1422 (1946) cited in Recipe "E" above.
Butadiene	P. Davis et al, U. S. 3,314,931 issued April 18, 1967, assigned to Continental Oil Co.
Butadiene - Acrylonitrile	Whitby, " Synthetic Rubber," 802, cited in Recipe "K" above.
Butadiene Vinyl Acetate	H. F. Park, U. S. 2,600,680 issued June 17, 1952.
Butadiene - Styrene	See "Styrene-Butadiene" in following section, "Styrene Polymers."
Chloroprene	J. W. McFarland and R. Pariser, *J. Appl. Polymer Sci., 7*, 675 (1963).
Chloroprene	T. A. Cooper et al, U. S. 3,929,752 issued December 30, 1975, cited in Recipe "C" above.
Isoprene	Y. Conwell et al, *J. Polymer Sci, 4*, 309 (1949).
Isoprene	M. Morton et al, *J. Polymer Sci., 15*, 167 (1955).
Isoprene - Styrene	A. J. Johansen and L. A. Goldblatt, *Ind. Eng. Chem., 40*, 2086 (1948).
	See also references 3-5 in Part I above.

Styrene Polymers

Styrene - General	R. H. Boundy and R. E. Boyer, *Styrene, Its Polymers, Copolymers and Derivatives*, Reinhold, New York (1955).
Vinyl Aromatics	D. D. Hicks, U. S. 3,960,824 issued June 1, 1976 assigned to Celanese Coating & Specialty Co.
Styrene	H. R. Snyder et al, *J. Am. Chem. Soc., 68*, 1422 (1946).
Styrene - Drying Oils	E. S. Bradshaw and E. M. Evans, British Pat. 674,155: *C.A., 46*, 11712g.

III. LITERATURE AND PATENT REFERENCES ON THE USE OF MERCAPTANS AS MODIFIERS

Styrene - Isoprene	See "Isoprene - Styrene" above under "Diene Polymers."
Styrene - Diene	See "Dienes - Styrene" above under "Diene Polymers."
Styrene - Butadiene	M. Morton et al, *Canadian J. Res., 25B,* 159 (1947); *C. A., 41,* 6758c.
Styrene - Butadiene	R. H. Boundy et al, cited above for "Styrene - General."
Styrene - Butadiene	F. L. Frank, P. V. Smith, F. E. Woodward, W. R. Reynolds and P. J. Caterino, *J. Polymer Sci., 3,* 50 (1948).
Styrene - Butadiene	T. T. Searfini et al, *Official Digest, Federation of Societies for Paint Technology, 32,* 1259-1288, October, 1960, cited above in Recipe "A."
Styrene - Butadiene	H. R. Snyder et al, *J. Am. Chem. Soc., 68,* 1422 (1946) cited in Recipe "E."
Styrene - Butadiene	G. S. Whitby, Synthetic Rubber, cited above for Recipe "I" and Recipe "J."
Styrene - Butadiene	C. A. Uraneck and J. E. Burleigh, *J. Appl. Polymer Sci., 9,* 1273 (1965).
Styrene - Butadiene	C. A. Uraneck, M. G. Barker and W. D. Johnson, *Rubber Chem. Tech., 38,* 802 (1965).
Styrene - Butadiene	C. A.Uraneck and J. E. Burleigh, *Rubber Chem. Tech, 43,* 1424 (1970).
Styrene	P. R. Sinha and K. L. Mallik, *J. Ind. Chem. Soc., 34,* 424 (1957) *C. A., 52,* 784h.
Styrene - Butadiene	C. A. Uraneck and W. M. St. John, Jr., U. S. 2,888,442 issued May 26, 1959.
Styrene - Butadiene	C. A. Uraneck and J. E. Burleigh, U. S. 3,855,188 issued December 17, 1974 assigned to Phillips Petroleum Company.
Styrene - Butadiene	C. A. Uraneck and J. E. Burleigh, U. S. 3,928,498 issued December 23, 1975 assigned to Phillips Petroleum Company.
	See also references 3, 8, 10 - 17 in Part I above.

A B S Graft Polymers and the Like

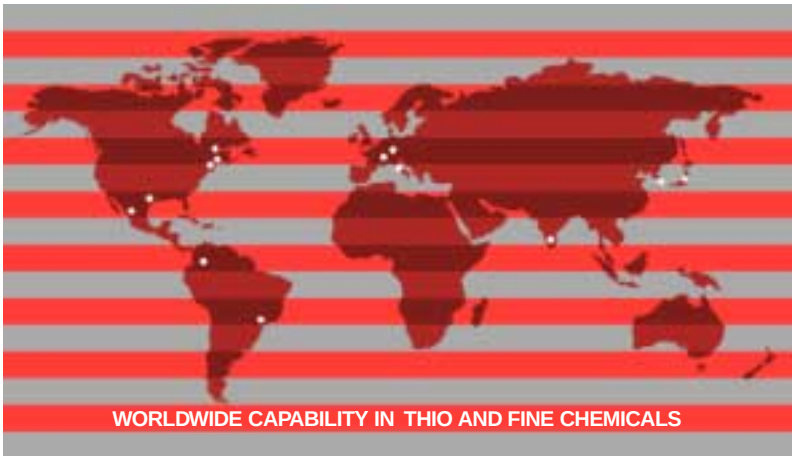
Acrylonitrile - Butadiene - Styrene	C. W. Childress et al U. S. 2,820,773 issued January 21, 1958,cited in Recipe "D" above.
Acrylonitrile - Butadiene - Styrene	G. H. Fremon et al, U. S. 3,168,593 issued February 2, 1965.
Acrylonitrile - Butadiene - Styrene	F. E. Carrock et al., U. S. 3,660,534 issued May 2, 1972, assigned to Dart Industries, Inc
Acrylonitrile - Auromatic Olefin-Terpene	E. Nield, U. S. 3,849,384 issued November 19, 1974, assigned to ICI.
Acrylonitrile - Butadiene - Styrene	G. P. Coffey, U. S. 3,951,932 issued April 20, 1976, assigned to Standard Oil Co., Ohio.

Other Polymers

Ethylene	A. E. Kober, U. S. 3,887,610 issued June 3, 1975 to Exxon Research & Engineering Company.
	See also references 6 and 8 in Part I above.

General Reference on Mercaptans as Polymerization Modifiers

F. Bovey et al, "Chain Transfer Agents," Chapter IV, *Emulsion Polymerization, High Polymers, Vol. IX,*" 95-139, Interscience, New York (1955).
J. W. Breitenback, O. F. Olaj & A. Schindlen, *Monatsh, 91,* 205 (1960); *C. A., 54,* 25961b.
R. J. Frank et al, *J. Polymer Sci., 3,* 354 (1948).
H. Merken and D. Phillips, *Rubber Age, 96,* 863 (1965).
N. Rabjohn et al, *J. Polymer Sci., 2,* 488 (1947); *C. A., 42,* 1443f.
W. V. Smith, *J. Am. Chem. Soc., 68,* 2069 (1946).



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