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Regulation of Molecular Weight of Styrene–Butadiene Rubber. III. Choice of Regulator from the Homologous Series of Aliphatic Mercaptans

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Synopsis

The regulating efficiency of four aliphatic mercaptans was studied in emulsion copolymerization of butadiene with styrene, at +5°C. with the use of the redox system, diisopropylbenzene hydroperoxide–complexed ferrous iron–sodium formaldehyde sulfoxylate as an initiator and the sodium soap of disproportionated rosin as an emulsifier. The apparent transfer constants *C* of tertiary mercaptans decreased logarithmically with increasing length of molecule. This tendency is connected with the analogous dependency of solubilities of these compounds in water. The mercaptans did not affect the rate of polymerization. The value of *C* is independent of the amount of regulator used. With the value of *C*, the amount of regulator, and the conversion known, it is possible to predict the molecular weight of the polymers, except for the region of poor regulation, where the deteriorative influence of termination and crosslinking reactions takes place. The apparent transfer constant of tertiary dodecyl mercaptan decreased with increasing rate of polymerization. After elimination of diffuse processes, the value of the actual relative transfer constant was calculated. The tertiary dodecyl mercaptan has been selected as the most convenient molecular weight regulator for emulsion copolymerization of butadiene with styrene of all compounds studied for the system mentioned.

INTRODUCTION

In the preceding papers of the present series,[1,2] the 14 dialkyl xanthogen disulfides were evaluated as molecular weight regulators in emulsion copolymerization of butadiene with styrene at +5°C. The regulation efficiency of the isopropyl derivative was found to be influenced by some components of the polymerization recipe. In view of the raw material situation it was not possible to use this compound for large-scale processes; it was therefore necessary to take the mercaptans. For this reason the aim of the present paper is to evaluate the regulating efficiency of the four most accessible aliphatic mercaptans.

THEORETICAL

Many authors have studied the regulation of molecular weight of styrene–butadiene rubber by means of mercaptans. The most important work in this field was done by Kolthoff and Harris,[3–6] who studied the behavior of aliphatic mercaptans in a standard GR-S recipe at +50°C. From their results it follows that the lower mercaptans diffuse more quickly than the higher ones, as quantitatively described by apparent chain transfer constants C. In the case of n-alkyl mercaptans up to C_{10}, C has approximately the same value; the diffusion is not a rate-controlling factor here. In the case of higher n-alkyl mercaptans, however, C decreases logarithmically with increasing length of the chain. Smith[7] and Meehan[8] interpreted this tendency by means of fact that the solubility of mercaptans in water also decreases logarithmically with increasing length of molecule.

On comparing the behavior of branched-chain mercaptans it is necessary to take into account the degree of branching. Frank et al.[9] studied the diffusion velocity of dodecyl mercaptan isomers and found that any new branch in the chain and the shortening of the largest dimension of the molecule both result in acceleration of diffusion and an increase in the C.

The apparent chain transfer value depends on the polymerization recipe and on conditions of polymerization. In the second paper of this series[2] the influence of pH value on the regulation efficiency has been discussed. In the case of mercaptans, the influence is of opposite sense than for the case of xanthogen disulfides. The amount of soap influences the regulation in two opposite ways. According to Kolthoff and Harris,[4] in the range of low conversions the number of micelles is reduced by lowering the amount of soap, which results in faster establishment of solubilization equilibrium and an increase in mercaptan consumption. In the range of higher conversion, with lowering of the amount of soap and the number of particles, the opposite effect is noted: particles of greater total surface area form, and the diffusion of mercaptan into the particles is sometimes hindered.

Kolthoff and Harris[4] found also that the method of emulsifier addition influences the rate of consumption of mercaptan. When an aqueous solution of sodium hydroxide was mixed with a monomer phase containing dissolved fatty acid, the rate of mercaptan consumption was greater than when the same amount of preformed soap was used. The neutralization of fatty acid at the phase boundary results in an emulsion with smaller droplets having a substantially greater surface area, and the diffusion rate of mercaptan is increased. This effect was especially marked for the higher mercaptans.

The influence of kind and speed of mixing were studied, too.[4] With more intensive mixing, small monomer droplets having a greater surface area are formed; the diffusion is accelerated, and the regulation efficiency is increased. This tendency is in accord with the observation that the same recipe gives a more regulated polymer in large-scale reactors than in laboratory-scale runs.

In discussing possible influences on regulation efficiency it is necessary to consider also the dependency of apparent chain transfer constant on the overall rate of polymerization found by Dvořák[10,11] for diisopropyl xanthogen disulfide. This dependency, also discussed in the second paper of this series,[2] has not been described in current literature for mercaptans, although it is possible to expect it with great probability in this case, too.

A survey of published values of the apparent chain transfer constant of mercaptans is given in Table I.

The values of apparent chain transfer constant can be verified by comparison of measured values of intrinsic viscosity of polymers prepared in the presence of regulator with values calculated by the method used in the first paper of the present series.[1]

EXPERIMENTAL

Materials

Butadiene, styrene, water, sodium formaldehyde sulfoxylate, disproportionated rosin, and diisopropylbenzene hydroperoxide were as described in Part I of the present series.[1]

n-Dodecyl mercaptan was supplied by Glynn Brothers Chem. Ltd., (London, England). It was characterized by values $d^{20} = 0.8454$ g./cm.^{3}, $n_D^{20} = 1.4592$ and contained 15.9% mercaptan sulfur (theory = 15.82%).

tert-Dodecyl mercaptan was supplied by Light & Co. (Colbrook, England). It was characterized by values $d^{20} = 0.8487$ g./cm.^{3}, $n_D^{20} = 1.4613$, and contained 15.7% mercaptan sulfur (theory = 15.82%).

tert-Tetradecyl mercaptan was supplied by Phillips Petroleum Co. (Bartlesville, Okla., USA). It was characterized by values $d^{20} = 0.8625$ g./cm.^{3}, $n_D^{20} = 1.4622$ and contained 13.4% mercaptan sulfur (theory = 13.68%).

tert-Hexadecyl mercaptan was supplied by Phillips Petroleum Co. (Bartlesville, Okla., USA). It was characterized by values $d^{20} = 0.8654$ g./cm.^{3}, $n_D^{20} = 1.4362$ and contained 12.2% mercaptan sulfur (theory = 12.4%).

The other chemicals, of Czechoslovakian origin, were reagent grade.

Technique

Emulsion polymerization was performed in the same manner as described previously.[1] The polymerization recipe (in parts by weight) was as follows: butadiene, 70.0; styrene, 30.0; *tert*-dodecyl mercaptan, 0.0748; diisopropylbenzene hydroperoxide, 0.1; sodium soap of disproportionated rosin, 4.3; Disodium phosphate dodecahydrate, 1.15; Ferrous sulfate heptahydrate, 0.020; disodium ethylenediaminetetraacetate, 0.0333; sodium formaldehyde sulfoxylate dihydrate, 0.1; water phase to 200.0. Individual changes in recipe are mentioned at described experiments. Before addition of monomers the pH value of water phase was adjusted to 10.8. Polymerization was carried out at 5.0 ± 0.1°C. Reaction was stopped short by addition of: (*a*) 0.1 part by weight of dinitrochlorobenzene (experiments followed by consumption of mercaptans), or (*b*) 0.2

TABLE I
Comparison of Regulating Efficiency of Some Aliphatic Mercaptans for Emulsion Copolymerization at Butadiene and Styrene

Polymerization recipe				*C* value			
Polymer	Initiator	Emulsifier	Temp., °C.	*n*-Dodecyl mercaptan	*tert*-Dodecyl mercaptan	*tert*-Tetradecyl mercaptan	*tert*-Hexadecyl mercaptan
Hot GR-S[a]	$K_2S_2O_8$	Na^+ soap of fatty acid	50	2.07	2.78	1.2	0.27
SBR 1502[b]	ROOH–sulfoxylate–Fe^{++} pyrophosphate	Na^+ soap of fatty and rosin acid	5		4.1		

[a] Data of Kolthoff and Harris.[4]

[b] Data of Booth et al.[12]

part by weight of sodium dimethyldithiocarbamate (experiments followed by intrinsic viscosity).

The conversion was determined by the same method as described in the first paper of the series.[1]

Determination of mercaptans was performed by amperometric titration with silver nitrate according to the method developed by Kolthoff and Harris.[13] At a given time the ampule was removed, opened, and the content quantitatively transferred into beaker with 130 ml. acetone and dinitrobenzene in an amount corresponding to 0.1 part by weight. The ampule was rinsed twice with 10 ml. water. The coagulated rubber was filtered off on a Büchner funnel with weighed filter, the solute squeezed out, solute; the rubber was washed with acetone and extracted with ethanol in a Soxhlet apparatus for 24 hr. at atmospheric pressure. To the acetone filtrate were added 10 ml. 2N NH_4NO_3 and 10 ml. 5N NH_4OH. The mercaptan content was determined by amperometric titration with 0.005N $AgNO_3$ (measuring electrode: rotated platinum wire, reference electrode: Hg/K_2HgI_4, indication: Interflex galvanometer with sensitivity of 1.6×10^{-2} amp. and sensitivity reductor). At the same time the mercaptan content of the ethanolic extract was determined, the two values were totaled, and the ratio $[S]/[S_0]$ was calculated. The extracted rubber was used for determination of conversion.

The determination of intrinsic viscosity in toluene solution at 30°C. was carried out in an Ubbelohde viscometer by the method described by Škrabal and Rosík.[14] The same relation for theoretical $[\eta]$ and $\bar{M}_n$ (number-average molecular weight) values calculation was used as in the first paper.[1]

RESULTS AND DISCUSSION

The results of determination of apparent chain transfer constants of various mercaptans are given in Table II and plotted in Figure 1. The total polymerization rates observed are also given.

From these results it follows that the apparent chain transfer constants of tertiary mercaptans decrease logarithmically with increasing length of the alkyl group. This can be written as an empirical equation:

$$\log C = 1.747 - 0.138n \qquad (1)$$

TABLE II
Apparent Chain Transfer Constants for the Mercaptans and the Observed Total Polymerization Rates

Mercaptan	Amount mercaptan, parts by weight	Apparent chain transfer constant C	Total rate of polymerization, % conversion/hr.
n-Dodecyl	0.0748	0.66	10.9
tert-Dodecyl	0.0748	1.22	11.7
tert-Tetradecyl	0.0852	0.64	11.25
tert-Hexadecyl	0.0955	0.34	12.05

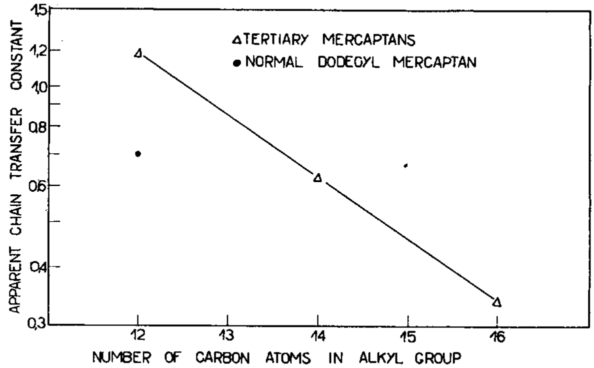

Fig. 1. Apparent chain transfer constants of mercaptans.

where n is number of carbon atoms in the alkyl group. Since the mercaptans used had the same degree of branching (one tertiary carbon atom only, regardless of the position in the molecule) it held as a rule that elongation of molecule by two carbon atoms results in a 2.74-fold decrease of the C value. This result is in agreement with the suggestion of Smith[7] and Meehan[8] that the solubility of mercaptans in water limits the maximal reachable concentration gradient which controls the diffusion rate of regulator through the aqueous phase.

Of some interest is also the fact that n-dodecyl mercaptan has a substantially lower C value than the tertiary dodecyl mercaptan and that the value is lower by approximately the same factor as in the case of elongation of the molecule of two carbon atoms. This agrees with the conclusions of Frank et al.[9]

The mercaptans cause no retardation. Polymerization takes place at the same rate regardless of the regulator used. Evidently the RS· radicals formed by chain transfer are at least equal in reactivity to the hydrocarbon polymeric radicals.

The values of apparent chain transfer constant can be used for the calculation of molecular weight of polymer if there are three assumptions made: (*1*) C is independent of amount of regulator used; (*2*) the regulator is not consumed by any side reaction; (*3*) the chain transfer reaction takes place much more frequently than the termination reaction.

TABLE III
Apparent Chain Transfer Constant for Various Amounts of Tertiary Dodecyl Mercaptan

tert-$C_{12}H_{25}SH$, parts by weight	Apparent chain transfer constant C	Total rate of polymerization, % conversion/hr.
0.1496	1.22	11.5
0.2992	1.21	12.6

Correctness of the first assumption was proved by control experiments in which the chain transfer constant of *tert*-dodecyl mercaptan was determined by using two- and fourfold amounts of mercaptan. The results are summarized in Table III. It is apparent from Table III that the first assumption is fulfilled.

In order to verify the second assumption, the concentration of *tert*-dodecyl mercaptan was determined as a function of time for a blank experiment, in which the monomers were replaced by an equal weight of benzene. The results are given in Table IV. No side reaction took place, and the assumption that regulator is consumed by chain transfer only is also verified.

Now it was possible to prove the third assumption. Several series of SBR samples containing known amounts of regulator were prepared, and their intrinsic viscosities were measured. In Table V are given the results of determinations of intrinsic viscosity as a function of conversion for *tert*-dodecyl, *tert*-tetradecyl, *tert*-hexadecyl, and *n*-dodecyl mercaptans and theoretical values of intrinsic viscosity (calculated on the basis of the apparent chain transfer constants listed in Table II and ratio of initial molar concentrations of monomer and regulator taken from polymerization recipe by the procedure described previously[1]). The calculations account for the influence of copolymer composition change with conversion.

The intrinsic viscosities as a function of conversion are plotted in Figure 2.

The measured values of intrinsic viscosity are generally in good agreement with predicted values, except for the region of very high molecular weights. In this region the measured $[\eta]$ values are always lower than calculated ones. The difference between them increases with conversion.

The obtained results lead to the following conclusions.

(*1*) Under conditions of effective regulation with, e.g., *tert*-dodecyl mercaptan, especially in higher amounts, the termination reaction is negligible compared to chain transfer. The molecular weight of the polymer depends on the rates of chain transfer and growth reactions, and it is possible to predict it on the basis of kinetic data.

(*2*) All other mercaptans studied were not very effective. Termination is not negligible compared to chain transfer, and the molecular weight

TABLE IV
Determination of Side Reactions of *tert*-Dodecyl Mercaptan

Reaction time, hr.	$[S]/[S_0]$, % by weight
0	100.0
1	97.6
2	100.0
3	99.0
4	101.0
5	98.3
6	99.0

TABLE V. Intrinsic Viscosities of Styrene–Butadiene Copolymers Prepared in the Presence of Various Mercaptans

Mercaptan	Amount of mercaptan, parts by weight	Conversion, % by weight	$\bar{M}_n$ (theor.)	$[\eta]$, dl./g.		Solubility, % by weight
				Theoretical	Measured	
t-$C_{12}H_{25}SH$	0.0748	15.3	235,000	3.15	3.07	100
		22.3	237,000	3.18	3.04	100
		30.4	240,000	3.21	3.15	99
		41.3	245,000	3.26	3.13	99
		51.6	247,000	3.31	3.22	100
t-$C_{12}H_{25}SH$	0.1496	28.4	120,000	1.89	1.90	100
		35.4	122,000	1.92	1.98	100
		42.5	127,000	1.95	2.03	99
		62.5	130,000	2.00	2.26	100
t-$C_{12}H_{25}SH$	0.2992	15.3	57,000	1.09	1.21	100
		21.5	59,000	1.11	1.26	99
		30.0	60,000	1.13	1.22	100
		40.3	61,000	1.15	1.29	100
		50.0	62,000	1.16	1.35	100
t-$C_{14}H_{29}SH$	0.0852	19.2	429,000	4.94	4.60	99
		32.4	416,000	4.83	4.54	100
		41.5	405,000	4.75	4.36	95
		56.8	390,000	4.60	4.03	90
t-$C_{16}H_{33}SH$	0.0955	19.5	776,000	7.75	6.11	99
		29.4	748,000	7.51	6.04	97
		39.4	719,000	7.28	5.72	90
		55.9	656,000	6.81	5.25	83
n-$C_{12}H_{25}SH$	0.0748	15.5	414,000	4.80	4.50	99
		26.1	405,000	4.74	4.38	100
		33.2	400,000	4.69	4.35	99
		44.5	391,000	4.60	4.19	96
		55.3	381,000	4.51	3.84	92

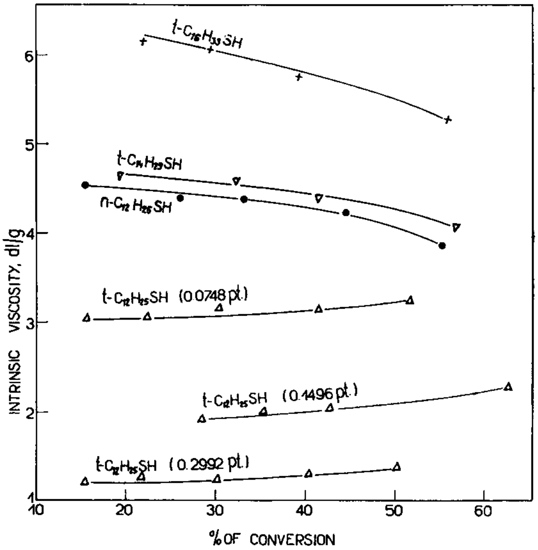

Fig. 2. Intrinsic viscosities as a function of conversion for styrene–butadiene copolymers prepared in the presence of various mercaptans.

prediction became inaccurate. In any case it is impossible to get a polymer with intrinsic viscosity exceeding 6.0–6.5. This limiting value is somewhat higher than that obtained in the case of polymer regulation by xanthogen disulfides.

(*3*) There is a much greater decrease of intrinsic viscosity with conversion in the region of poor regulation, as expected from theory. At the same time, there is some decrease of solubility of polymers prepared. The reason for this is formation of crosslinks by the reactions of the polymer molecule with growing polymer radicals or with radicals formed by the decomposition of initiator. If the mercaptans do not retard, these reactions take place to somewhat less degree than in the case of xanthogen disulfides, i.e., the crosslinking reaction takes place at higher conversions.

As it has been pointed out above, one of the most important factors influencing regulation efficiency is the total rate of polymerization. This influence was studied by using *tert*-dodecyl mercaptan. The total polymerization rate was varied by using various amounts of complexed ferrous iron, the molar ratio $FeSO_4 \cdot 7H_2O$/complex being held constant at the same value as in the standard polymerization recipe. The results of these experiments are given in Table VI.

The apparent chain transfer constant of *tert*-dodecyl mercaptan decreases with increasing total rate of polymerization. The obtained results can be evaluated in two different ways;[10,11] such evaluations are carried out in the Figures 3 and 4.

In the first methods we write an empirical equation relating apparent chain constant C and polymerization rate v:

TABLE VI
Influence of Total Polymerization Rate on the Apparent Chain Transfer Constant of Tertiary Dodecyl Mercaptan

Amount of t-$C_{12}H_{25}SH$, parts by weight	Amount of $FeSO_4 \cdot 7H_2O$, parts by weight	Apparent chain transfer constant			Total rate of polymerization, % conversion/hr.
		C	log C	$1/C$	
0.0748	0.010	2.02	0.306	0.496	7.0
0.0748	0.020	1.22	0.086	0.820	11.7
0.0748	0.030	0.94	−0.027	1.063	16.0

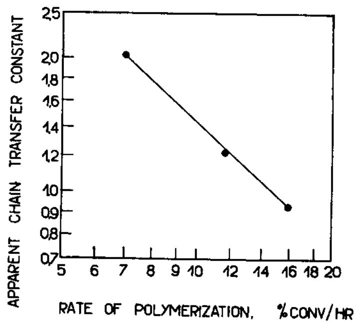

Fig. 3. Apparent chain transfer constant of *tert*-dodecyl mercaptan as a function of total rate of polymerization.

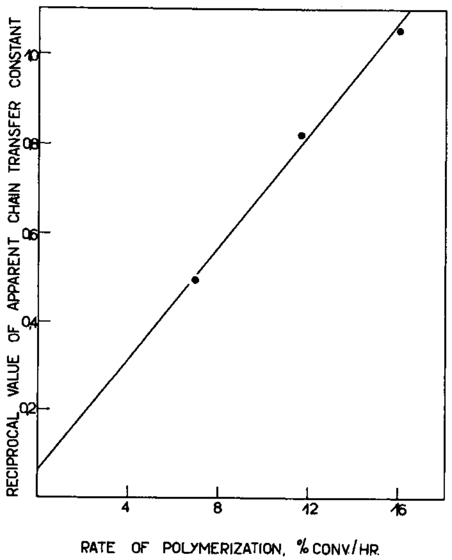

Fig. 4. Extrapolation of reciprocal values of chain transfer constant of *tert*-dodecyl mercaptan to zero polymerization rate.

$$\log C = 1.091 - 0.933 \log v \tag{2a}$$

$$C = 15.5v^{-0.933} \tag{2b}$$

The second method is based on the assumption that an exponent for v of unity yields the relation:

$$1/C = 0.0631v + 0.0632 \tag{3}$$

from which after extrapolation to zero polymerization rate a value of $C = 15.8$ may be obtained. As Dvořák[11] showed, this value represents the actual relative chain transfer constant of *tert*-dodecyl mercaptan which is not dependent on diffusion during emulsion polymerization.

Of the compounds studied, only *tert*-dodecyl mercaptan is a sufficiently effective regulator. The apparent chain transfer constant is so near unity that it is possible to reach nearly ideal uniform regulation and narrow molecular weight distribution. For that reason it may be preferred as a molecular weight regulator for emulsion copolymerization of butadiene with styrene in the investigated recipe.

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Résumé

On a étudié l'efficacité régulatrice de quatre mercaptans aliphatiques pour la copolymérisation en émulsion du butadiène et du styrène à +5°C, en utilisant comme système initiateur oxydo-réducteur, le diisopropylbenzène hydroperoxyde–fer-ferreux complexé–sulfoxylate de formaldéhyde sodium et comme émulsifiant le savon sodé de la colophane disproportionnée. Les constantes de transfert de chaîne apparentes C des mercaptans tertiaires décroissaient logarithmiquement avec l'augmentation de la longueur de la molécule. Cette tendance était liée à la dépendance analogue de la solubilité de ces composés dans l'eau. Les mercaptans n'affectent pas la vitesse de polymérisation. La valeur de C est dépendante de la quantité de régulateur utilisé. Avec une valeur connue de C, et une valeur connue de la quantité de régulateur et du taux de conversion, il est possible de prédire le poids moléculaire de polymères sauf dans la région de pauvre régulation où une influence néfaste de terminaison et des réactions de pontage ont lieu. La constante apparente de transfert du mercaptan tertiaire dodécylique décroissait avec une augmentation de vitesse de polymérisation. Après élimination du processus de diffusion, la valeur de la constante de transfert relative a été calculée. Comme régulateur de poids moléculaire le plus adapté à la copolymérisation en émulsion du butadiène et du styrène, dans les systèmes sus-mentionnés, c'est le mercaptan tertiaire dodécylique qui a été choisi parmi les composés étudiés.

Zusammenfassung

Die Regulatorwirksamkeit von vier aliphatischen Merkaptanen bei der Emulsionscopolymerisation von Butadien und Styrol bei +5° mit dem Redoxsystem Diisopropylbenzolhydroperoxyd–Ferroeisenkomplex–Natriumformaldehydsulfoxylat als Initiator und der Natriumseife von disproportioniertem Kolophonium als Emulgator wurde bestimmt. Die scheinbare Übertragungskonstante (*C*) tertiärer Merkaptane nahm logarithmisch mit steigender Moleküllänge ab. Diese Tendenz ist mit der analogen Tendenz der Löslichkeit dieser Verbindungen in Wasser verknüpft. Die Merkaptane hatten keinen Einfluss auf die Polymerisationsgeschwindigkeit. Ihr *C*-Wert hängt von der verwendeten Regulatormenge ab. Mit dem bekannten *C*-Wert, der Regulatormenge und dem Umsatz ist eine Voraussage des Molekulargewichts der Polymeren möglich, mit Ausnahme des Bereiches schlechter, durch den störenden Einfluss von Abbruchs- und Vernetzungsreaktionen bedingter Regulation. Die scheinbare Übertragungskonstante des tertiären Dodecylmerkaptans nahm mit steigender Polymerisationsgeschwindigkeit ab. Nach Eliminierung der Diffusionsprozesse wurde der Wert der wirklichen relativen Übertragungskonstanten berechnet. Als brauchbarster Molekulargewichtsregler bei der Emulsionscopolymerisation von Butadien und Styrol in dem angegebenen System wurde unter den untersuchten Verbindungen das tertiäre Dodecylmerkaptan ausgewählt.

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