Regulation of Molecular Weight of Styrene–Butadiene Rubber. I. Choice of Regulator from the Homologous Series of Xanthogen Disulfides

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Synopsis

The regulating efficiency of 14 dialkyl xanthogen disulfides in emulsion copolymerization of butadiene with styrene at +5°C. with the use of a diisopropylbenzene hydroperoxide–complexed ferrous iron–sodium formaldehyde sulfoxylate redox system in the presence of sodium soap of disproportionated rosin as an emulsifier, was evaluated. The apparent chain transfer constants of n-alkyl and isoalkyl derivatives decreased logarithmically with increasing length of the alkyl group, which seems to be related to the analogous dependency of their solubilities in water. The dialkyl xanthogen disulfides, especially the lower homologs, acted as retarders of polymerization. The retardation did not affect their regulation efficiency. On the basis of values of the apparent chain transfer constants it is possible to predict the molecular weight of polymers, except for the region where the regulation is poor and where the deteriorative influence of termination and crosslinking reactions takes place. The diisopropyl xanthogen disulfide has been selected as the most convenient of the compounds studied for molecular weight regulation of emulsion copolymerization of butadiene with styrene in the system mentioned.

INTRODUCTION

As a part of a study in our laboratory on the development of a polymerization recipe for emulsion copolymerization of butadiene with styrene the choice of the molecular weight regulator was also investigated. The most advantageous polymerization recipe developed[1] was one in which the redox system consisting of diisopropylbenzene hydroperoxide, ethylenediaminetetraacetate complex of ferrous iron, and sodium formaldehyde sulfoxylate was used as initiator, the sodium soap of disproportionated rosin was used as an emulsifier; the reaction was carried out at +5°C.

The aliphatic mercaptans or xanthogen disulfides are known to be regulators of molecular weight in the emulsion copolymerization of butadiene with styrene. The present paper deals with the behavior of the homologous series in the system mentioned. The purpose of the work is to give some data for the choice of a convenient regulator and to elucidate some questions connected with the mechanism of molecular weight regulation in emulsion polymerization.

The first part of this work was the evaluation of the regulation efficiency of xanthogen disulfides. It was possible to link up with several early studies by different authors[2-6] of the behavior of compounds mentioned in emulsion copolymerization of butadiene with styrene in the polymerization recipes for Buna S-3, SKS-30-A, and a "sulfide redox." These results are presented in Table I.

From the values given in Table I the following conclusions may be drawn: (1) the regulation efficiency of xanthogen disulfides decreases with increasing chain length; (2) the regulation efficiency of the same compound for the cold polymerization is lower than for reaction at elevated temperatures; (3) the regulation efficiency compared at the same temperature is dependent on the polymerization recipe.

From the standpoint of the uniformity of regulation it is necessary that the regulator should disappear at the same rate with increasing conversion, i.e., that the apparent chain transfer constant C should be approximately equal to 1.   Such conditions lead to polymer with a narrow molecular weight distribution.   On the other hand, the value of C must not be too low; at the usual concentrations of regulator the polymer produced would be of such a high molecular weight that partial crosslinking could be expected.

THEORETICAL

In radical polymerization, the number-average degree of polymerization $\bar{P}_n$ of the polymer formed is defined as the ratio of the rate of the reaction maintaining the growth of polymeric chain (propagation, rate constant k_2) to the sum of the rates of the reactions interrupting the growth of polymeric chain (termination and chain transfer, rate constants k_3 and k_4, respectively):

$$\bar{P}_n = k_2[R\cdot][M]/(k_3[R\cdot]^2 + k_4[R\cdot][S]) \tag{1}$$

where $[R\cdot]$, $[M]$, and $[S]$ are the molar concentrations of polymeric radicals, monomer, and regulator, respectively. By neglecting termination it is possible to simplify eq. (1) into the relation derived by Mayo:[7]

$$1/\bar{P}_n = k_4[S]/k_2[M] = C[S]/[M] \tag{2}$$

This relation is valid provided that the ratio of the molar concentrations of monomer to regulator remains constant during the reaction, i.e., generally at low conversion.

Tobolsky[8] took into account the change of the concentrations of monomer and regulator and derived eqs. (3) for the dependence of the average degree of polymerization on the ratio of initial concentrations of monomer and regulator ($[M]$ and $[S_0]$, respectively) and on the conversion:

$$\bar{P}_n = \frac{[M_0]x}{[S_0][1 - (1 - x)^C]} \tag{3a}$$

TABLE I

Comparison of Regulating Efficiency of Xanthogen Disulfides in Emulsion Copolymerizations of Butadiene with Styrene

	Polymerization recipe			Apparent chain transfer constant for various xanthogen disulfides													
Polymer	Initiating system	Emulsifier	Temp., °C.	Methyl	Ethyl	n-Propyl	n-Butyl	n-Amyl	n-Hexyl	n-Heptyl	n-Octyl	Iso-propyl	Iso-butyl	Iso-amyl	sec-Butyl	Neo-pentyl	Cyclo-hexyl
Buna S-3[a]	$K_2S_2O_8$	Neokal[b]	50	27.04	16.04	9.20	5.34	3.20	1.78	1.12	0.64	9.78	6.43	4.38		3.40	3.71
SKS-30-A[c]	Cumene hydroperoxide-hydroquinone-Na sulfide	Neokal[b]	5		7.0							3.4					
Sulfide[d]	Cumene hydroperoxide-FeS	K myristate	5	15.86	4.23	1.815	1.75	1.70				1.185	1.573	1.85	1.565		

[a] Data of Václavek.[2]
[b] Sodium salt of dibutylnaphthalenesulfonic acid.
[c] Data of Škrabal and Rosík.[4]
[d] Data of Kamenár.[6]

$$\bar{P}_w = \frac{2[M_0][1 - (1 - x)^{2-C}]}{C[S_0](2 - C)x} \tag{3b}$$

where x is conversion. On the basis of eqs. (3) it is possible to predict the molecular weight of polymer prepared under conditions of efficient regulation when the termination reaction is negligible compared to the chain transfer reaction.

The value of the relative chain transfer constant can be determined by using the relation derived by Smith[9] from equations for the rate of chain transfer and growth reactions:

$$- \ln ([S]/[S_0]) = -C \ln ([M]/[M_0]) \tag{4}$$

To determine the relative chain transfer constant it is necessary to follow the disappearance of regulator during polymerization as a function of conversion.

In case of copolymerization of two monomers it is possible to use the same equations, where values [M] and [M_0] are replaced by the sum of the molar concentrations of the two monomers and where the degree of polymerization is multiplied by the average molecular weight of the monomer unit, which is related to the change of average composition of copolymer with conversion. These values may be calculated from the known monomer reactivity ratios by Skeist's method.[10]

These considerations pertain to radical polymerization in homogeneous systems where the concentrations of monomer and regulator are the same in the whole system. In this case the observed value of the relative chain transfer constant exactly corresponds to the actual reactivity of monomer and regulator molecules with the polymer radicals. In case of emulsion polymerization the situation is much more complicated. The monomer and regulator molecules participate in several steps: (1) the passage through the phase boundary of monomer droplets; (2) diffusion through the water phase; (3) passage through the phase boundary of monomer-polymer particles; (4) chain transfer and growth reactions which take place in the particles.

Usually steps (1)–(3) are concerned entirely with diffusion of monomer and regulator molecules from droplets into particles. In the case of polymerization of monomers giving sufficiently reactive polymer radicals, the diffusion takes place more slowly than the chain transfer reaction. The regulator molecule reacts in a very short time after entering the particles.

Because the whole process is diffusion-controlled, the relative chain transfer value for a given monomer and regulator observed in emulsion polymerization must be lower than the same values observed for the polymerization carried out in bulk or solution systems. The relative chain transfer value observed in the given emulsion polymerization recipe is called the apparent chain transfer constant.

A discussion of the influence of step (3) on the apparent chain transfer

constant will be given in the second paper of this series.[11]   In the present paper we shall deal only with the influence of diffusion factors.

All the cited authors[2,4,6] observed a decrease in the apparent chain transfer constant of xanthogen disulfides with increasing chain length, but their interpretations of this phenomenon were different.   Kamenár[6] has explained it by inductive action of various substituents on the central S—S linkage which is connected with the actual reactivity of regulators. Contrary to this opinion, Václavek found[2] a definite parallel between the effect of the length of the molecule on the C value of the regulator and its solubility in water.   This fact would indicate that the slowest step of the whole process is diffusion through the water phase.   Because this observation has been made for in the polymerization at elevated temperatures (50°C.) it should be interesting to examine behavior of the same homologous series in "cold" polymerization.

EXPERIMENTAL

Materials

Butadiene of U.S.S.R. manufacture was stabilized by a mixture of biphenols.   After purification in an ammonia solution of cuprous acetate with subsequent desorption the product had the composition (determined by gas chromatography): 1,3-butadiene, 98.9%; butane, 0.22%; 1-butene, 0.45%; 2-butene, 0.35%.   Before use the monomer vapor was bubbled through 2% aqueous sulfuric acid, 30% aqueous sodium hydroxide, passed through a tower with solid NaOH, and condensed at −15°C.

Styrene obtained from Belgium was stabilized by hydroquinone.   The inhibitor was removed by shaking with 2% aqueous sodium hydroxide. The monomer was stabilized again by copper powder and stored at −10°C. in the dark.   Immediately before use it was rectified in a nitrogen atmosphere at 55°C. at reduced pressure on a column with 6 theoretical plates.   The rectified styrene was characterized by values of $d^{20} = 0.906$ g./cm.^{3} and $n_D^{20} = 1.5461$.

Water was distilled.

The disproportionated rosin, Rosin 731-D, a product of Hercules Powder Co. (U.S.A.), was purified according to Hays.[12]   The purified rosin was characterized by following values: acidity number, 179.65 mg. KOH/g.; saponification number, 182.65 mg. KOH/g.; δ value (degree of decomposition of conjugated structures) 3.0;   it contained 1.09% nonsaponified fractions and 0.07% phenols.

The methyl, ethyl, n-heptyl, n-octyl, neopentyl, and cyclohexyl xanthogen disulfide were prepared by the author.   The isopropyl derivatives was supplied by VEB Chemische Werke Buna (Schkopau, German Democratic Republic).   The n-propyl, n-butyl, isobutyl, sec-butyl, n-amyl, and isoamyl derivatives were prepared by S. Kamenár (Slovak Technical University Bratislava, Czechoslovakia).   The constants of the all xanthogen disulfides used have been described in previous papers.[2,13]

Sodium formaldehyde sulfoxylate was a technical grade product of Czechoslovakian origin; it was twice crystallized from water. After this step it contained 98.5% of sodium formaldehyde sulfoxylate dihydrate and melted at 65.5°C.

Diisopropylbenzene hydroperoxide was prepared by oxidation of diiso-propylbenzene (mixture of *o*, *m*, and *p* isomers) by air at 115°C. and by concentration *in vacuo*. It contained 83.5% of active component, the remainder being the original hydrocarbon.

The other chemicals of local origin were reagent grade.

Technique

Emulsion polymerization was carried out in 50-ml. glass ampules and in thick-walled glass flasks of 1000 ml. capacity by the technique previously described. The polymerization recipe (in parts by weight) was as follows: butadiene, 70.0 parts; styrene, 30.0 parts; diisopropylbenzene hydro-peroxide, 0.1 part; diisopropyl xanthogen disulfide, 0.1 part; sodium soap of disproportionated rosin, 4.3 parts; sodium chloride, 0.387 part; sodium ethylenediaminetetraacetate, 0.025 part; ferrous sulfate heptahydrate, 0.015 part; sodium formaldehyde sulfoxylate dihydrate, 0.1 part; water phase to 200.0 parts.

The other regulators were used in amounts equimolar to the isopropyl derivative. Before addition of monomers the pH of the water phase was adjusted at 10.8. Polymerization was carried out at 5.0 ± 0.1°C. The reaction was shortstopped by adding of 0.2 parts by weight of sodium dimethyldithiocarbamate.

Determination of conversion was carried out by weighing copolymer, as described previously.[2]

Determination of xanthogen disulfides was performed by a modification[2] of the polarographic method developed by May and Kolthoff.[14] It has been shown that in case of higher derivatives (butyl to octyl) the correct results can be obtained using extraction of rubber by ethanol in a Soxhlet apparatus for 16 hr. at 200 mm. It is possible by this step to overcome the troublesome influence of poor separation of the regulator from polymer in course of rubber precipitation, which takes place in case of the higher homologs.

Determination of intrinsic viscosity in toluene solution at 30°C. was performed in an Ubbelohde recording viscometer to the method described previously.[2] For calculation of the theoretical $[\eta]$ and $\bar{M}_n$ values eq. (5)

$$[\eta] = 2.95 \times 10^{-4}\bar{M}_n^{0.75} \tag{5}$$

which was found by Chinese authors[15,16] for butadiene–styrene rubber (70:30) prepared by emulsion polymerization at +5°C., was used.

TABLE II
Apparent Chain Transfer Constants of Xanthogen Disulfides
and Polymerization Rates Observed

Xanthogen disulfide	Apparent chain transfer constant	Rate of polymerization, % conversion/hr.
Methyl	16.43	2.1
Ethyl	8.43	3.8
n-Propyl	4.42	5.1
n-Butyl	2.42	5.9
n-Amyl	1.45	6.1
n-Hexyl	0.74	6.4
n-Heptyl	0.41	6.5
o-Octyl	0.23	6.6
Isopropyl	2.83	5.9
Isobutyl	1.87	6.2
Isoamyl	1.21	6.3
sec-Butyl	1.65	6.2
Neopentyl	1.01	4.8
Cyclohexyl	1.78	5.6
No regulator	—	6.7

RESULTS AND DISCUSSION

The results of apparent chain transfer constant determination and observed polymerization rates are listed in Table II and plotted in Figures 1 and 2.

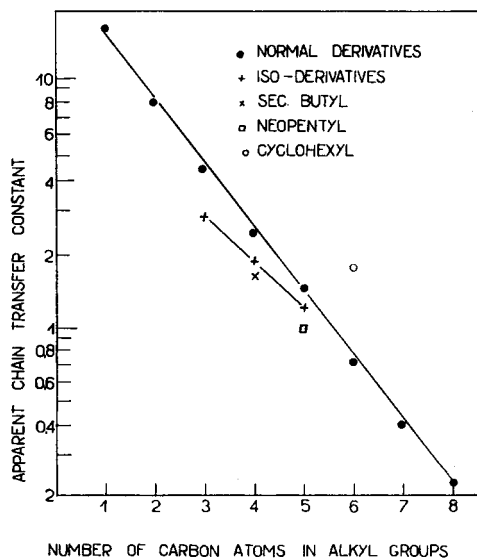As can be seen from Figure 1, the apparent chain transfer constants C

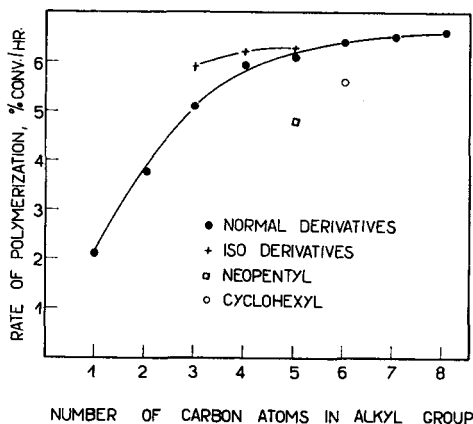Fig. 1. Apparent chain transfer constants C of xanthogen disulfides.

Fig. 2. Rate of polymerization in the presence of xanthogen disulfides.

in the homologous series of xanthogen disulfides decreased logarithmically with increasing length of alkyl group. It is possible to describe this fact by the empirical relations (6) and (7) for derivatives with unbranched and branched chains, respectively.

$$\log C = 1.454 - 0.263n \tag{6}$$

$$\log C = 1.007 - 0.184n \tag{7}$$

where n is the number of carbon atoms in the alkyl group.

From comparison of these results with the known values of C reviewed in Table I, it is obvious, that the values of C observed here are about half of those found for the polymerization of Buna S-3 at 50°C.;[2] also the slope of this line is approximately the same as there was found in recipe mentioned.

The explanation of logarithmical dependence of apparent chain transfer constants of xanthogen disulfides upon the length of the alkyl group is without doubt the same as for "hot" polymerization, i.e., that the solubility of the mentioned compounds in water limits the maximal concentration gradient possible in the water phase, which governs the rate of diffusion.

As can be seen from Table II and Figure 2, the process of regulation is accompanied by reduction of the polymerization rate, which is most outstanding for the lowest members of the homologous series. With increasing length of the alkyl group the rate of polymerization approaches the rate obtained without regulator.

According to the results obtained by Dvořák[17] the apparent chain transfer constant is inversely proportional to the rate of polymerization. He interpreted the observation of Kamenár[6] in terms of differences in retarding action of lower and higher xanthogen disulfides. If that hypothesis is correct, then an increase in amount of regulator should cause stronger retardation and increase the apparent chain transfer constant.

TABLE III
Determination of Apparent Chain Transfer Constant
with Different Amounts of Regulator

$(C_3H_7OCS_2)_2$, parts by wt.	Rate of polymerization, % conversion/hr.	C
0.17	4.0	2.84
0.25	3.2	2.76

In order to verify this, an experiment was carried out by measuring the consumption of diisopropyl xanthogen disulfide when this compound was used in greater amounts.   The results are given in Table III.

From the results and from the value of C in Table II for the isopropyl derivative it is seen that on increasing the amount of regulator there is a reduction of polymerization rate but the apparent chain transfer constant remains unchanged.

If the influence of polymerization rate upon the regulation efficiency is considered as to be proved[17] then the affection by means of the regulator only must be eliminated. It is highly probable that the influence of lowered reactivity of xanthogen radicals $ROCS_2\cdot$ in comparison with the hydrocarbon polymer radicals retards the chain growth regeneration and thus also polymerization. The strongest effect may be observed for the lowest homologs which, due to their high solubility, diffuse at high velocity and form a high concentration of xanthogen radicals in polymer particles.

This conclusion is confirmed by the finding[2] that in polymerization of elevated temperatures in the presence of various xanthogen disulfides the same number of particles formed in spite of the differences in regulation efficiency and retardation effect. It is probable that the apparent chain transfer constant can be changed only by changes in the polymerization rate which influence the number of particles or the concentration of the alkoxy radicals $(RO\cdot)$ in the particles.

The regulation efficiency of six xanthogen disulfides was tested by measuring the intrinsic viscosity of polymers prepared in the presence of these compounds In Table IV are listed results of experiments with determination of intrinsic viscosity as a function of conversion for the ethyl, n-propyl, isopropyl, n-butyl, n-hexyl, and n-octyl derivatives, and these values are compared with theoretical intrinsic viscosity values calculated on the basis of the apparent chain transfer constants listed in Table II and the ratio $[M_0]/[S_0] = 4279.2$ by means of eqs. (3a) and (5). In the calculation a correction was made for on the change of copolymer composition with conversion.

The measured values of intrinsic viscosity as a function of conversion are plotted in Figure 3.

The measured intrinsic viscosity values agree very well with the values of $[\eta]$ which have been predicted on the basis of kinetic relations, except for the region of very high polymers. The measured values of $[\eta]$ are

TABLE IV

Intrinsic Viscosity of Copolymers of Butadiene with Styrene Prepared in the Presence of Various Xanthogen Disulfides

Regulator	Amt. of regulator parts	Conversion, % (by wt.)	$\bar{M}_n$ (theor.)	$[\eta]$, dl./g. Theoretical	Measured	Solubility, % (by wt.)
$(C_2H_5OCS_2)_2$	0.0896	19.2	64,000	1.25	1.35	100
		25.1	80,000	1.43	1.50	99
		31.3	95,000	1.60	1.74	100
		38.2	112,000	1.82	1.90	100
$(n\text{-}C_3H_7OCS_2)_2$	0.1000	19.0	89,000	1.54	1.64	100
		27.0	101,000	1.72	1.77	99
		39.3	127,000	2.02	2.09	100
		44.8	141,000	2.16	2.22	100
$(i\text{-}C_3H_7OCS_2)_2$	0.1000	15.4	109,000	1.84	1.95	100
		26.4	127,000	2.05	2.07	99
		37.4	144,000	2.22	2.20	99
		47.8	164,000	2.42	2.45	100
$(n\text{-}C_4H_9OCS_2)_2$	0.1104	21.2	136,000	2.10	2.15	100
		34.2	155,000	2.30	2.33	99
		48.5	179,000	2.55	2.58	97
		59.5	196,000	2.79	2.62	90
$(n\text{-}C_6H_{13}OCS_2)_2$	0.1311	23.1	374,000	4.40	4.20	98
		35.8	361,000	4.35	4.02	93
		50.0	353,000	4.26	3.67	90
		62.4	346,000	4.18	2.95	81
$(n\text{-}C_8H_{17}OCS_2)_2$	0.1519	20.0	1,125,000	10.20	5.42	92
		34.7	1,050,000	9.66	4.68	85
		49.2	965,000	9.05	3.85	78
		61.1	886,000	8.50	3.24	68

always lower than the calculated ones. This discrepancy increases with conversion. From this the following conclusions were reached.

(1) In the presence of effective regulators (ethyl to butyl derivatives) termination is negligible compared to chain transfer. The molecular weight is controlled by chain transfer and growth reactions only and obeys the eqs. (3a) and (3b).

(2) In the presence of poor regulators (hexyl to octyl derivatives) the termination is not negligible compared to chain transfer, and eqs. (3a) and (3b) cannot be used for the molecular weight prediction. It seems that there exists some maximum value of intrinsic viscosity which cannot be exceeded, regardless of initiator and regulator concentrations in a given recipe.

(3) In the region of poor regulation the intrinsic viscosity decrease with conversion appears to be much faster than theoretically expected. At the same time there appears to be some decrease of solubility of the polymers prepared as a result of crosslink formation by reactions of poly-
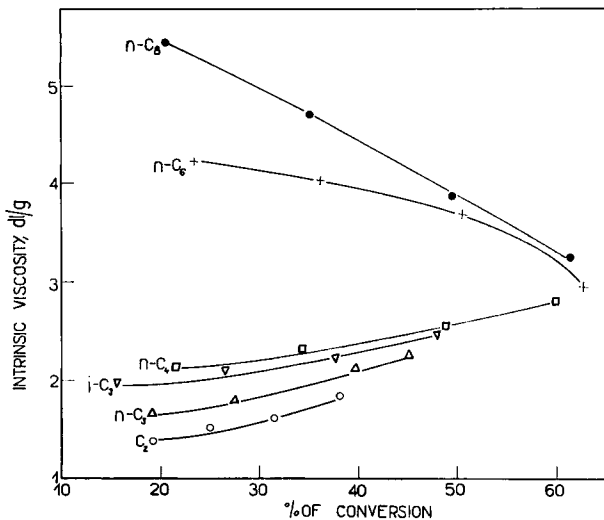
Fig. 3. Intrinsic viscosity of copolymers of butadiene with styrene prepared in the presence of various xanthogen disulfides.

mer molecules with growing polymer radicals or with radicals generated by decomposition of initiator.

Of the compounds studied, the requirement of uniform regulation is fulfilled by *n*-butyl, *n*-amyl, isopropyl, isobutyl, isoamyl, *sec*-butyl, neopentyl, and cyclohexyl derivatives. The neopentyl derivative has an apparent chain transfer constant approximately equal to unity. The requirement of sufficient regulating activity is fulfilled by all the derivatives mentioned. With regard to easy accessibility the diisopropyl xanthogen disulfide is preferred as a regulator of molecular weight for the polymerization recipe studied.

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Résumé

L'efficacité régulatrice de 14 disulfures dialkyl-xanthogéniques au cours de la copolymerization en émulsion de butadiène et de styrène à +5°C en présence d'un système oxydo-réducteur hydroperoxyde diisopropylbenzène–ion ferreux complexé–sulfoxylate de formaldéhyde sodium comme initiateur en présence de savon sodé de colophane dispro-portionnée comme émulsifiant a été évaluée. Les constantes de transfert de chaîne apparentes de dérivés *N*-alcoyle et iso-alcoyle décroissaient logarithmiquement avec une longueur croissante du groupe, alcoyle, ce qui semble être lié à la dépendance ana-logue de leur solubilité dans l'eau. Tous les disulfures de dialcoyle xanthogène et par-ticulièrement les homologues les plus bas agissent comme retardateurs de polymérisation. Leur retard n'affecte par leur efficacité de régulation. Sur la base de la valeur de la constante de transfert de chaîne apparente, il a été possible de prévoir le poids moléculaire des polymeres sauf pour la région où la régulation est pauvre et où une influence néfaste de la terminaison et de réactions de pontage a lieu. Comme régulateur de poids molécu-laire le plus adapté pour la copolymérisation en émulsion du butadiène avec le styrène dans le système ainsi mentionné, l'est le disulfure de diisopropylexanthogène qui a été choisi pour les composés étudiés.

Zusammenfassung

Die Regulatorwirksamkeit von 14 Dialkylxanthogendisulfiden bei der bei +5°C mit dem Redoxsystem Diisopropylbenzolhydroperoxyd–komplexiertes Ferroeisen–Natrium-formaldehydsulfoxylat als Starter in Gegenwart der Natriumseife von disproportionier-tem Kolophonium als Emulgator durchgeführten Emulsionscopolymerisation von Buta-dien und Styrol wurde bestimmt. Die scheinbare Kettenübertragungskonstante von *n*-Alkyl- und iso-Alkylderivaten nahm mit steigender Kettenlänge der Alkylgruppe logarithmisch ab, was mit der analogen Abhängigkeit der Löslichkeit in Wasser zusam-men zu hängen scheint. Alle Dialkylxanthogendisulfide, besonders die niedrigeren Homologen wirken als Polymerisationsverzögerer. Die Verzögerung beeinflusste die Regulatorwirksamkeit nicht. Mit den Werten der scheinbaren Kettenübertragungs-konstanten ist es möglich das Molekulargewicht der Polymeren zu berechnen, mit Aus-nahme der Bereiche schlechter Regulierung, wo der störende Einfluss von Abbruchs- und Vernetzungsreaktionen auftritt. Als am besten geeigneter Molekulargewichtsregulator für die Emulsionscopolymerisation von Butadien und Styrol unter den untersuchten Verbindungen wurde das Diisopropylxanthogendisulfid ausgewählt.