Regulation of Molecular Weight of Styrene–Butadiene Rubber. II. Influence of Variation of Polymerization Recipe on the Regulating Efficiency of Diisopropyl Xanthogen Disulfide

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Synopsis

The influence of kind and amount of an anionic emulsifier, pH of water phase, addition of free rosin, and content of conjugated structures in rosin on the regulation efficiency of diisopropyl xanthogen disulfide in emulsion copolymerization of butadiene with styrene at +5°C. was studied. The apparent chain transfer constant C decreased in the order: $Li^+ > Na^+ > K^+$, for the cations with the hydrolysis of rosin soap. This soap is replaceable with other anionic emulsifiers, C being dependent on the absorption area of one soap molecule. With increasing amount of soap the value of C decreased. With the decreasing pH of the water phase, the value of C increases. This fact can be explained by the increase in hydrolysis of carboxylic groups of rosin and oleate soaps and an increase in the permeability of the monomer–polymer particle surface to molecules of regulator. This tendency does not exist in the case of sulfonate-type soaps. After addition of free rosin to the monomer phase, a similar increase in C is noted. The value of C increased also with an increase in the content of conjugated structures characterized by a value δ, which is related to the retardation of polymerization. The standard polymerization recipe at pH 10.8 is suitable from the point of view of using diisopropyl xanthogen disulfide as a molecular weight regulator.

INTRODUCTION

In the previous paper[1] of this series, as result of investigation of regulation efficiency of some compounds of the homologous series of dialkyl xanthogen disulfides, diisopropyl xanthogen disulfide was chosen as the most convenient molecular weight regular for emulsion copolymerization of butadiene with styrene at +5°C. The purpose of the present paper is to explain the influence of some components of polymerization recipe on the regulation efficiency of the chosen compound.

THEORETICAL

As stated previously,[1] the process of regulation of molecular weight in emulsion polymerization consists of four steps: (*1*) 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 in particles.

The first step can be controlled by speed and kind of mixing. By more intensive mixing the diameter of monomer droplets is reduced, their surface area is increased, and the passage of monomer and regulator molecules through the phase boundary takes place more quickly; as a consequence some increase of regulation efficiency of regulator can be observed without any change in polymerization recipe. On the other hand, with less intensive mixing there is observed some decline in regulation efficiency. This is noted with slow mixing only; under the usual conditions of polymerization in an ampule or flask it cannot be observed.

The influence of diffusion of regulator through the water phase for xanthogen disulfides has been examined previously.[1,2] It was found that the solubility in water is a limiting factor for formation of a concentration gradient. An interesting observation on the influence of the pH on the regulation efficiency of mercaptans was reported by Smith,[3] who found that *n*-dodecyl mercaptan consumption in emulsion polymerization of styrene in the presence of fatty acid soaps was faster with an excess of sodium hydroxide than in cases in which the neutralization was made by exact equivalent amount of NaOH. In a strongly alkaline medium the mercaptans are neutralized to mercaptides. The RS^- anions are more hydrated than the RSH molecules and therefore they diffuse more quickly. As the dissociation constants of mercaptans are very small, the effect takes place at very large pH values only.

The third step is passage of regulator through the monomer–polymer particles phase boundary. It can be controlled by changing the surface area or the surface structure of the particles and by varying the degree of covering of the particles by the soap.

The total area of the surface of the particles increases with a decrease in their diameter. In the past it was assumed that change in diameter of the particles would not influence the ratio passage rates of monomer and regulator; probably this is not correct. According to the kinetic theory formulated by Smith and Ewart,[4] the total rate of polymerization is a function of the number of particles N defined as:

$$v = k_2(N/2)[M] \tag{1}$$

where k_2 is an absolute rate constant of propagation and [M] is the concentration of monomer in particles. Dvořák[5] studied the connection between the regulation efficiency and total rate of polymerization. He found that the apparent chain transfer constant C of diisopropyl xanthogen disulfide (in the same polymerization recipe as in present paper) decreased with increasing total rate of polymerization ($v \equiv$ total rate of polymerization), and wrote for it the empirical relation:

$$C = kv^{-\alpha} \tag{2}$$

where $\alpha = 0.9$. The k value varied with the kind of soap used, the ex-

ponent α being constant. By using these results and considerations on ratio of monomer and regulator concentrations in particles and in whole emulsion system, Dvořák and Hrabák[6] derived an equation:

$$1/C' = (1 + K)/C \qquad (3)$$

where C' is the relative chain transfer constant for a homogeneous system and K is proportionality factor. This equation coincides with eq. (2) when $\alpha = 1$. It follows that by extrapolation to zero polymerization rate it is possible to find the relative chain transfer constant. This constant refers to the actual reactivity of regulator and monomer molecules in relation with polymer radicals only.

The surface layer of the particles consists of partly dissociated anionic soap molecules, which gives the particles negative charge. This charge prevents the coalescence of particles when they collide, forms a diffusion ionic atmosphere around particles, and forms a hydrated film upon their surface. The rigidity of the film is to some extent a barrier for the passage of regulator molecule. If now the degree of hydrolysis of the adsorbed soap increases, the regulation efficiency of the regulator can be increased. This behavior has been observed by Dvořák[5] in some polymerization experiments with lauric acid neutralized to the various degrees. With an increase in amount of free acid the apparent chain transfer constant of diisopropyl xanthogen disulfide increases.

The fourth step, the chain transfer reaction itself, takes place in particles after the same kinetics as in bulk or solution polymerization. From the preceding considerations it follows that this step should be faster than the preceding three steps, i.e., as soon as the regulator molecule enters the particle, it will react in a very short time. In connection with this fact it should be very interesting to determine how the C' value obtained by extrapolation of C to $v = 0$ coincides with the k_4/k_2 ratio found in homogeneous systems.

In order to explain the role of the various factors on the regulation process, the influence of kind and amount of anionic soap, cation of rosin soap, pH value of water phase, addition of free rosin, and δ value of rosin used on the apparent chain transfer constant of diisopropyl xanthogen disulfide has been studied.

EXPERIMENTAL

Materials

Butadiene, styrene, water, diisopropyl xanthogen disulfide, sodium formaldehyde sulfoxylate, disproportionated rosin, diisopropylbenzene hydroperoxide were described previously.[1] For the experiments on the influence of the δ value, special samples of disproportionated rosin supplied by Organic Syntheses Research Institute, Pardubice-Rybitví (Czechoslovakia), were used. These are characterized in Table I.

TABLE I

Designation	δ	Saponification number, mg. KOH/g.	Acidity number, mg. KOH/g.	Content of unsaponified material, % (by wt.)
6051-ID	1.06	182.3	181.8	0.53
6048-IID	3.13	177.3	175.8	0.77
6039-VID	5.1	178.8	178.0	0.42
6056-52D	6.7	171.7	170.0	0.87
6056/20D	8.67	171.7	170.0	0.87
		171.0	167.3	1.48
6056/36D	10.47	178.0	170.8	1.35

Neokal was a technical product of local origin. Its essential component is sodium dibutylnaphthalene sulfonate. It was purified from inorganic salts by extraction with anhydrous methanol. After this treatment it contained 99.96% active component and 0.04% Na_2SO_4.

Oleic acid supplied by E. Merck, (Darmstadt, Germany) in purity defined by *Deutsches Arzneibuch*, 6th Ed., was used to the preparation of soap without further purification.

Mersolate was an anionic emulsifier of German origin, sodium alkyl sulfonate C_{14}–C_{20}, containing 90% of active component, was purified by the same way as Neokal.

The other chemicals of Czechoslovakian origin were reagent grade.

Technique

Emulsion polymerization, determination of conversion, and determination of diisopropyl xanthogen disulfide were described in the first paper of this series.[1]

RESULTS AND DISCUSSION

At first the behavior of diisopropyl xanthogen disulfide was examined by replacing the rosin soap with another anionic emulsifier. Results are listed in Table II and plotted in Figure 1.

The apparent chain transfer constant of diisopropyl xanthogen disulfide as a function of adsorption area per soap molecule is plotted in Figure 2.

The observed tendency can be explained by the more negative character per unit surface area of particles stabilized by Mersolate than those stabilized by sodium oleate or resin soap. As a consequence, the surface layer of the hydrated soap molecules is less permeable to regulator molecules. The emulsifier Neokal does not follow this tendency due to its high solubility in water.

By using of various amounts of the same emulsifier the C value decreases with increasing soap concentration. For a quantitative evaluation it should be necessary to know the number of particles and the degree of their

TABLE II
Influence of Rosin Sodium Soap, Sodium Oleate, Mersolate, and Neokal on the
Regulation Efficiency of Diisopropyl Xanthogen Disulfide

Emulsifier used		Apparent chain transfer constant	Total rate of polymerization. % conversion/hr.
Type	Amount, parts by wt.[a]		
Na$^+$ soap of	2.15	3.02	3.9
disproportionation	4.30	2.74	5.5
rosin	6.45	2.55	6.5
	8.60	2.40	7.0
Sodium	1.0	2.58	7.0
oleate	2.0	2.41	9.6
	3.0	2.29	11.8
	4.0	2.17	14.4
Mersolate	2.0	1.91	8.3
	4.0	1.67	13.3
	6.0	1.61	20.8
	8.0	1.41	27.0
Neokal	2.0	3.55	5.9
	4.0	3.40	8.7
	6.0	3.20	11.7
	8.0	2.85	14.8

[a] Amount replacing 4.3 parts by weight of sodium soap of disproportionated rosin in standard polymerization recipe.

covering by soap.   Qualitatively it may be stated that also in this case there appears an analogous influence of increasing polymerization rate as found by Dvořák.[5]

As a next factor there was examined the influence of the cation of the rosin soap.   The disproportionated rosin was neutralized by an equivalent
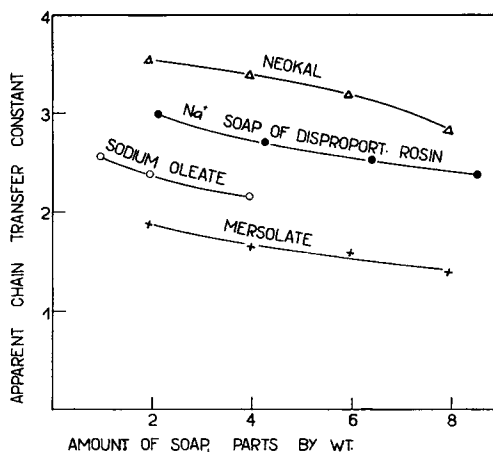

Fig. 1. Influence of various anionic soaps on the regulation efficiency of diisopropyl xanthogen disulfide.

TABLE III
Influence of Cation of Disproportionated Rosin Soap on the Regulation Efficiency of
Diisopropyl Xanthogen Disulfide

Type	Soap, Amount, parts by weight	Type	Electrolyte, Amount, parts by weight	Apparent chain transfer constant	Total rate of polymerization, % conversion/hr.
Li rosinate	4.08	LiCl	0.284	3.20	5.4
Na rosinate	4.30	NaCl	0.387	2.74	5.5
K rosinate	4.50	KCl	0.500	2.39	5.5

amount of lithium hydroxide, sodium hydroxide, or potassium hydroxide. The prepared soap was used in the polymerization recipe in amount equivalent to 4.3 parts by weight of sodium soap. Lithium chloride, sodium chloride, or potassium chloride, in amount equivalent to 0.387 parts by weight of NaCl was used as electrolyte. The results are summarized in Table III.

The value of C depends markedly on the kind of cation of rosin soap. The lithium soap is probably most hydrolyzed and forms more permeable film on the surface of particles which provide the least barrier for the passage of regulator molecules through the phase boundary of the particle surface. The situation is different for potassium soap.
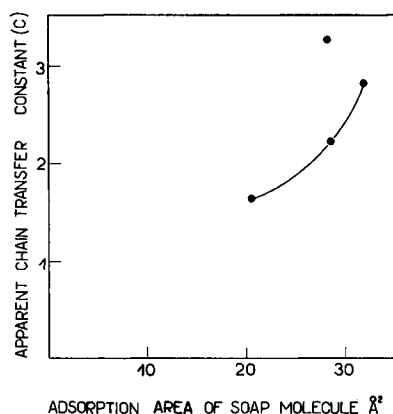

Fig. 2. Apparent chain transfer constant of diisopropyl xanthogen disulfide as a function of adsorption area per soap molecule. Values of C from Fig. 1 for amounts equivalent to 4.0 parts of Mersolate.
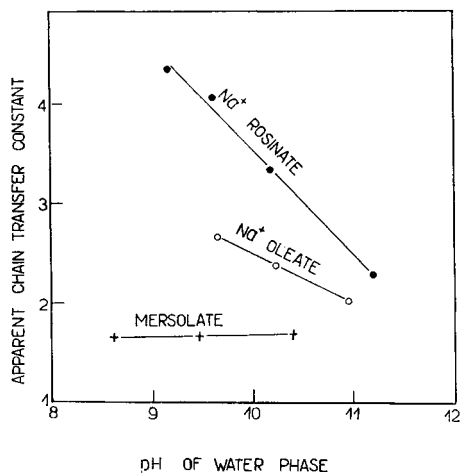
Fig. 3. Influence of pH of water phase on the apparent chain transfer constant of diisopropyl xanthogen disulfide.

One of the most important effects of polymerization recipe composition on the regulation efficiency of diisopropyl xanthogen disulfide is the influence of the pH of the water phase. This was studied in the presence of rosin soap, sodium oleate, and Mersolate as emulsifiers; Na_2HPO_4 was used as the electrolyte. The pH value was adjusted by replacing a little part of water by an equal amount of $0.1N$ NaOH. The results are listed in Table IV and plotted in Figure 3.

With both soaps of carboxylate type the apparent chain transfer constant decreases with increasing pH value. This is related to the decreasing degree

TABLE IV
Influence of pH of the Water Phase on the Apparent Chain
Transfer Constant of Diisopropyl Xanthogen Disulfide

Emulsifier		Electrolyte			Apparent chain transfer constant	Total rate of polymerization, % conversion/hr.
Type	Amount, parts by weight	Type	Amount, parts by weight	pH		
Na rosinate	4.3	Na_2HPO_4	0.939	9.15	4.39	4.5
				9.6	4.09	5.7
				10.2	3.36	5.8
				11.25	2.31	5.7
Na oleate	2.0	NaCl	0.387	9.65	2.71	9.5
				10.25	2.41	9.6
				11.0	2.05	9.5
Mersolate	4.0	Na_2HPO_4	0.939	8.65	1.67	13.3
				9.5	1.72	12.4
				10.45	1.71	11.2

TABLE V
Influence of Addition of Free Rosin on the Apparent Chain
Transfer Constant of Diisopropyl Xanthogen Disulfide

Free rosin added, parts by weight	Apparent chain transfer constant	Total rate of polymerization, % conversion/hr.
—	2.74	5.5
1.0	3.24	6.0
2.0	3.86	6.5

of hydrolysis of anionic carboxylic groups.   For this reason the degree of hydratation of the surface film increases.   The film is thus more rigid and less permeable for regulator molecules.   In case of rosin having a large great adsorption area this influence is more definite than in the case of oleate, with less adsorption area.   On the other hand, with Mersolate, the sulfonate group of which does not hydrolyze regardless of pH, there was observed no dependency.

The correctness of this interpretation was verified by experiments in which an initial polymerization emulsion was prepared with the standard recipe previously described[1] with 4.3 parts by weight of sodium soap of disproportionated rosin and 0.387 parts NaCl, the pH of the water phase being adjusted at 10.8.   In addition there was added various amounts of free rosin.   The results are given in Table V.

Evidently through addition of free rosin has the same effect as lowering of the pH value of the water phase.   The molecules of rosin acids are also adsorbed on the surface of the particles but as they do not carry negative charge, they decrease the degree of hydratation of the surface layer and they increase the surface permeability of the particles to the regulator molecules.

The wood rosin represents a complicated mixture of rosin acids of miscellaneous structure.   For the purpose of using it in form of soap as a com-
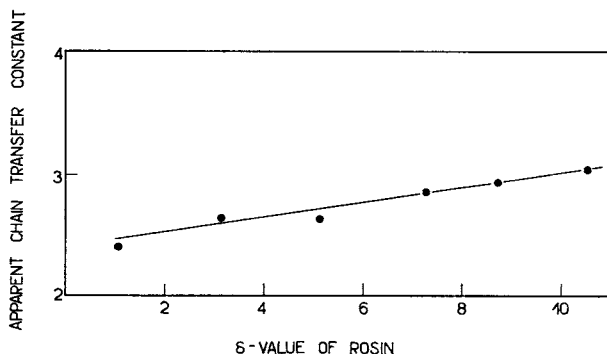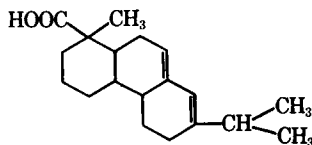

Fig. 4. Influence of δ value of rosin used on the apparent chain transfer constant of diisopropyl xanthogen disulfide.

TABLE VI
Influence of δ Value of Rosin Used on the Apparent Chain
Transfer Constant of Diisopropyl Xanthogen Disulfide

δ	Apparent chain transfer constant	Total rate of polymerization, % conversion/hr.
1.06	2.40	8.4
3.13	2.64	7.2
5.10	2.64	6.1
6.7	2.86	5.9
8.67	2.94	5.0
10.47	3.10	4.5

ponent of initial polymerization emulsion it was modified by dispropor-
tionation in order to destroy the conjugated double bonds, e.g., in the

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abietic acid (I), which act as polymerization retarders. The degree of
destruction of conjugated structures is characterized by the so-called
δ value, defined as the extinction at $\lambda = 2420$ A. divided by weight of sample
in milligrams and multiplied by 100. Nonmodified natural rosin has
$\delta = 40$, and for production of SBR there a rosin with $\delta = 3$ is suitable. In
order to prove the connection of retardation influence of conjugated struc-
tures with the molecular weight regulation, the apparent chain transfer
constant of diisopropyl xanthogen disulfide was studied as a function of
δ value of rosin used. The experiments were performed on a standard recipe
with 4.3 parts sodium rosinate and 0.387 parts NaCl at pH = 10.8. The
results are listed in Table VI and plotted in Figure 4.

It is shown that the retardation influence of conjugated structures in poly-
merization results in an increase of apparent chain transfer constant. This
corresponds with the connection between regulation efficiency and total
rate of polymerization found by Dvořák.[5] The value $\delta = 3$ recommended
above can be taken to be suitable also from the point of view of molecular
weight regulation.

On the basis of the results of studies of the influence of some components
on the regulation efficiency of diisopropyl xanthogen disulfide it can be
concluded that the standard polymerization recipe mentioned in the first
paper[1] at a pH of the water phase of 10.8 is convenient for use of this
compound as a molecular weight regulator.

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Résumé

L'influence de la nature et de la quantité d'émulsifiant anionique, du pH de la phase aqueuse, de l'addition de colophane libre, et de la teneur en structures conjuguées dans la colophane sur l'efficacité de régulation du disulfure de diisopropyle xanthogène dans la copolymérisation en émulsion du butadiène avec le styrène à +5°C a été étudiée. La constante de transfert de chaîne apparente (*C*) décroissait dans l'ordre des cations: $Li^+ > Na^+ > K^+$, ce qui était relié à l'hydrolyse du savon colophanique. Ce savon peut être remplacé par un autre émulsifiant anionique, *C* étant dépendant de la surface d'absorption d'une molécule de savon. Avec une quantité croissante de savon, la valeur de *C* décroît. Avec une diminution de la valeur du pH de la phase aqueuse, la valeur de *C* augmente. Ce fait peut être expliqué par une augmentation de l'hydrolyse des groupes carboxyliques de la colophane et des savons, oléiques et une augmentation de la perméabilité de la surface des particules monomère–polymère aux molécules de régulateur. Cette tendance n'existe pas dans le cas du type sulfonate. Un effet semblable à celui de la diminution de la valeur du pH a été observé après addition de colophane libre dans la phase monomérique. La valeur de *C* croît également avec une augmentation de la teneur en structures conjuguées caractérisées par une valeur δ, ce qui était relié au retard à la polymérisation. Le mode de polymérisation standard à un pH de 10.8 convenait du point de vue de l'utilisation de disulfure de diisopropyl xanthogène comme régulateur de poids moléculaire.

Zusammenfassung

Der Einfluss von Art und Menge eines anionischen Emulgators, des pH-Wertes der Wasserphase des Zusatzes von freiem Kolophonium und des Gehaltes an konjugierten Strukturen im Kolophonium auf die Regulatorwirksamkeit von Diisopropylxanthogendisulfid auf die Emulsionscopolymerisation von Butadien und Styrol bei +5°C wurde untersucht. Die scheinbare Kettenübertragungskonsante (*C*) in der Reihenfolge der Kationen $Li^+ > Na^+ > K^+$ nimmt ab, was mit einer Hydrolyse der Kolophoniumseife zusammenhängt. Diese Seife kann durch einen anderen anionischen Emulgator ersetzt werden und *C* hängt vom Adsorptionsflächenbedarf eines Seifenmoleküls ab. Mit steigender Seifenmenge nahm der Wert von *C* ab. Mit abnahme des pH-Wertes der Wasserphase nimmt der Wert von *C* zu. Dieser Umstand kann durch die Zunahme der Hydrolyse der Carboxylgruppen von Kolophonium- und Oleatseifen und durch die Erhöhung der Durchlässigkeit der Oberfläche der Monomer–Polymerteilchen für Regulatormoleküle erklärt werden. Im Falle der Seifen vom Sulfonattyp besteht keine solche Tendenz. Ein ähnlicher Effekt wie bei der Herabsetzung des pH-Wertes wurde nach Zusatz von freiem Kolophonium zur Monomerphase beobachtet. Der Wert von *C* stieg auch mit Erhöhung des Gehaltes an konjugierten Strukturen an, der durch einen mit der Polymerisationsverzögerung zusammenhängenden Wert δ charakterisiert wurde. Das Standardpolymerisationsrezept bei pH 10,8 ist für die Verwendung von Diisopropylxanthogendisulfid als Molekulargewichtsregulator geeignet.