

Butadiene/Styrene/2-Methyl-5-vinylpyridine Terpolymer. Composition-Conversion Data in Comparison with Calculated Values

L. CRESCENTINI, G. B. GECELE, and A. ZANELLA, *Soc. Edison, Research Center, Bollate, and Technical Division Milano, CNR Research Center for the Macromolecules Physics, Section I, University of Bologna, Italy*

Synopsis

Terpolymers from 1,3-butadiene, styrene, and vinylpyridine are important as rubbers, and, in latex form, as components of rubber-to-fabric adhesives. Three monomer mixtures having the approximate weight composition butadiene/styrene/2-methyl-5-vinylpyridine 70/15/15, 25/48/27, and 38.5/49/12.5 have been emulsion-polymerized at 30°C., and the terpolymer composition as a function of the conversion has been studied. The six monomer reactivity ratios have been determined by binary copolymerizations at 30°C. and checked by low conversion bulk terpolymerizations. Average and instantaneous composition-conversion curves have been calculated, on the assumption of a constant reaction volume, by numerical integration of the terpolymerization equations on electronic computer. Details, of general applicability, for calculations are given. The experimental results of the emulsion terpolymerizations fit satisfactorily the calculated curves over a wide range of conversions.

INTRODUCTION

Elastomers from butadiene, vinylpyridine, and in some cases styrene, in latex form, have found widespread application as rubber-to-fabric adhesives in tire manufacturing.¹⁻⁶ These elastomers show better elastic and fatigue properties, lower heat build-up, and considerably higher abrasion resistance than the conventional SB-R copolymers.⁷⁻¹²

In the present work we study the composition of the terpolymer butadiene/styrene/2-methyl-5-vinylpyridine as a function of the conversion for three monomer feed compositions. This was done also in order to follow the difference in composition of molecules formed at various conversions, taking into account the possible negative influence of the molecular heterogeneity on the final properties of the product.

In particular, terpolymers prepared in emulsion at 30°C. starting with three monomer charges with approximate butadiene/styrene/2-methyl-5-vinylpyridine compositions (by weight) of 70/15/15, 25/48/27, or 38.5/49/12.5 were considered.

The average and instantaneous composition curves were calculated for each charge by integration on electronic digital computer of the Alfrey-Goldfinger equations¹³ that relate, through the reactivity ratios, the terpolymer composition to the feed composition. The reactivity ratios at 30°C. were determined by us for the different combinations of the three monomers in binary systems.

The integral curves were compared with the experimental results of polymer composition at different conversions, which were obtained by analysis of the bound vinylpyridine by perchloric acid titration and of the bound styrene by a quantitative infrared technique.

INTEGRATION OF THE ALFREY-GOLDFINGER EQUATIONS

The theory of copolymerization of vinyl monomers developed by Alfrey and Goldfinger¹⁴ and by Mayo and Lewis¹⁵ was subsequently extended to a three-component system by Alfrey and Goldfinger¹³ and to n -component systems by Walling and Briggs.¹⁶

Some methods of approximating the integral of the differential terpolymerization equations were proposed by Walling and Briggs¹⁶ and by Skeist¹⁷ which allow the calculation of the composition-conversion curves.

Experimental verifications for low conversion three-component systems were also reported.^{16, 18-20} However, data which show the variation of the composition of high conversion terpolymers as a function of the conversion were obtained only recently by Kahn and Horowitz.²¹ These data concern the vinyl acetate *N*-vinylpyrrolidone dioctyl fumarate system at 76°C. They fit satisfactorily the predicted average composition-conversion curves which were calculated through numerical integration by means of a digital computer.²¹

We detail here the procedure of the numerical integration. The Alfrey and Goldfinger equations were put in the following form:

$$\frac{dM_1}{dM_3} = \frac{M_1(M_{123}r_{32} + M_{231}r_{23} + M_{321}r_{21})(M_{12}r_{13} + M_{21}r_{13} + M_{31}r_{12})}{M_3(M_{12}r_{23} + M_{21}r_{23} + M_{31}r_{21})(M_{31}r_{32} + M_{11}r_{32} + M_{21}r_{31})} \quad (1)$$

$$\frac{dM_2}{dM_3} = \frac{M_2(M_{12}r_{13} + M_{21}r_{13} + M_{31}r_{12})(M_{21}r_{23} + M_{11}r_{23} + M_{31}r_{21})}{M_3(M_{12}r_{23} + M_{21}r_{23} + M_{31}r_{21})(M_{31}r_{32} + M_{11}r_{32} + M_{21}r_{31})}$$

Here r_{ij} ($i \neq j$; $i, j = 1, 2, 3$) are appropriate reactivity ratios; $M_i = N_i/V$, where N_i ($i = 1, 2, 3$) are the numbers of moles of the monomers, and V is the volume of the system, considered homogeneous, and defined as follows:

$$V = \sum_1^3 (W_i/\rho_i) + (W/\rho) + (W_s/\rho_s) \quad (2)$$

W_i and ρ_i ($i = 1, 2, 3$) being respectively the weights and densities of each monomer, W , W_s , ρ , ρ_s respectively the weights and densities of the poly-

mer which is being formed and of the solvent. In order to simplify the theoretical development, terpolymerization processes conducted at constant volume were studied.

This condition can be experimentally approached by solution polymerization. In particular the hypothesis of a constant volume allowed us to substitute in the system (1) N_i in place of M_i .

Let $f_1(M_1, M_2, M_3)$ and $f_2(M_1, M_2, M_3)$ be the right-hand sides of eqs. (1); then we have approximately:

$$\begin{aligned}\delta M_1 &= f_1(M_1, M_2, M_3)\delta M_3 \\ \delta M_2 &= f_2(M_1, M_2, M_3)\delta M_3\end{aligned}\quad (1')$$

where the δ are small finite increments.

Given a feed composition M_{01}, M_{02}, M_{03} and an increment δM_3 , eqs. (1') allow us to ascertain the corresponding variations $\delta M_1, \delta M_2$. Obviously the correctness of eqs. (1') increases as δM_3 decreases. Let us now define

$$\begin{aligned}M_1' &= M_{01} - \delta M_1 \\ M_2' &= M_{02} - \delta M_2 \\ M_3' &= M_{03} - \delta M_3\end{aligned}\quad (3)$$

Putting M_i' ($i = 1, 2, 3$) and another δM_3 into eqs. (1') we obtain the new increments $\delta M_1', \delta M_2'$ corresponding to the feed composition M_1' ($i = 1, 2, 3$); thus by iterative use of eqs. (1'), as many values as desired of M_1 and M_2 , considered as functions of M_3 , can be calculated on the basis of their initial values M_{01}, M_{02} .

This numerical integration of eqs. (1') was programmed on a high speed digital computer (IBM 1620).

The program foresees the use of the same increment δM_3 at every step; the main input and output elements are as follows. Input elements are initial molar concentrations M_{0i} ($i = 1, 2, 3$) (or number of moles as V is assumed to be constant); molecular weights P_1, P_2, P_3 ; monomer reactivity ratios r_{ij} ($i \neq j$; $i, j = 1, 2, 3$).

Output elements are $M_{i,t}, C_{i,t}, \bar{C}_{i,t}$, and $P_{i,t}$, these being defined as follows. Numerical values of the integral of system (1):

$$M_{i,t} = M_{0i} - \sum_1^t \delta M_{i,p} \quad \begin{array}{l} t = 1, 2, \dots, T \\ i = 1, 2, 3 \end{array} \quad (4)$$

where $M_{i,t}$ are the unconverted molar concentrations (or moles accepting the hypothesis of a constant volume V) at the t th step of the iterative calculations; $\delta M_{i,p}$ ($i = 1, 2$) are the variations at the p th step of the molar concentrations (moles) M_i , for the independent variable M_3 varying from $M_{3,p-1} = M_{03} - (p-1)\delta M_3$ to $M_{3,p} = M_{3,p-1} - p\delta M_3$; the last term ($t = T$) of the above succession corresponds to $M_{03} - T\delta M_3 = 0$, that is, to the exhaustion of the independent monomer.

The instantaneous composition $C_{i,t}$ of the polymer being formed with respect to each monomer, expressed as a weight percentage is

$$C_{i,t} = 100 P_i \delta M_{i,t} / \sum_1^3 P_i \delta M_{i,t} \quad \begin{array}{l} i = 1, 2, 3 \\ t = 1, 2, \dots, T \end{array} \quad (5)$$

The corresponding polymer average composition (as weight percentage) is:

$$\bar{C}_{i,t} = 100 P_i \sum_1^t \delta M_{i,p} / P_i \sum_1^t \delta M_{i,p} \quad \begin{array}{l} i = 1, 2, 3 \\ t = 1, 2, \dots, T \end{array} \quad (6)$$

The conversion for each monomer (in per cent) is then:

$$P_{i,t} = 100 \sum_1^t \delta M_{i,p} / M_{0i} \quad i = 1, 2, 3 \quad (7)$$

Only one out of K values calculated ($K \geq 1$ being an integer given in input) may be actually punched.

Incidentally we remark that $C_{i,1} = \bar{C}_{i,1}$ ($i = 1, 2, 3$) are independent from the chosen increment δM_3 . These values give the initial polymer composition for $\delta M_3 \rightarrow 0$.

To attain a prefixed approximation a repetition of the stepwise integration was foreseen. Subsequent integrations with increments $\delta M_3/nR$ where R is a given reduction factor, $n = 1, 2, \dots$, are carried out.

The iterative process stops at the $(n - 1)$ th iteration if, for every i and t , the corresponding values $C_{it}^{(n-1)}$, $C_{it}^{(n)}$ are such that

$$\Delta_{it} = |C_{it}^{(n)} - C_{it}^{(n-1)}| \leq \alpha \quad (8)$$

where α is a given tolerance. The tolerance was imposed on the instantaneous composition being the latter of course the most sensitive.

The theoretical values used in drawing Figures 2-7 were obtained for $\delta M_3 = 10^{-3} M_{03}$; a further reduction of this increment to the value of $\delta M_3 = 0.5 \times 10^{-3} M_{03}$ did not lead to any actual improvement. Table I shows

TABLE I
Maximum Absolute Values of Δ_{it} for $\delta M_3 = 10^{-3} M_{03}$ and $0.5 \times 10^{-3} M_{03}$

Charge ^a	Butadiene, %	Styrene, %	2-Methyl-5- vinylpyridine, %
A	3.89	3.17	0.73
B	0.46	2.51	2.05
C	1.07	1.95	0.88

^a See Table V.

the maximum absolute differences between the two cases.

It can be noted that in our average composition diagrams, the abscissas represent the overall conversion. This was done as the experimental re-

sults furnish with greater accuracy the overall conversion instead of a single partial conversion.

Moreover in the particular case of our terpolymer it was seen from the results of the numerical calculations that total conversion is reached approximately at the same time for all monomers; under such a condition these plots effectively represent the whole picture of the polymerization.

EXPERIMENTAL

Monomers

Styrene (Soc. Edison) was distilled under reduced pressure (20 mm. Hg) in order to free it from inhibitor and was stored at 0°C.

2-Methyl-5-vinylpyridine (MVP) (Soc. Edison) was distilled under reduced pressure (20 mm. Hg) and purified by fractional crystallization (m.p. -12.4°C.), the main impurity being 2-methyl-5-ethylpyridine (m.p. -70.3°C.). In this way the purity (analyzed by gas chromatography) rose to 98.8-99% starting from about 95%. The monomer could be stored as a solid for several days at -20°C.

1,3-Butadiene (Soc. Edison) was distilled from the container at the moment of the utilization. The purity (gas chromatography) was 99.0%.

MVP-Styrene Copolymers

Mixtures of styrene and MVP of different compositions were introduced into glass ampules and 1% (based on the monomer mixture) of methyl isobutyl ketone peroxide (MIBKP) was added.

The ampules were sealed under slight nitrogen pressure after several washings with vacuum and nitrogen. They were then kept in a water bath thermostatted at $30 \pm 0.1^\circ\text{C}$. and rotated end over end for the time necessary to obtain a conversion of a few per cent; the time required increased as the MVP content in the monomer mixture decreased. The purification of the copolymers caused many troubles, as poly-MVP is soluble in almost all of the most usual organic solvents but the low-boiling paraffins (petroleum ether, *n*-hexane). Unfortunately the most common peroxides in the latter products show limited solubility. On the other hand, as the conversion is only a few per cent, the peroxide is usually present in the reaction mixtures in amounts which are of the same order of magnitude of the copolymer, causing in this way a troublesome purification.

As an example, with the pair benzoyl peroxide-dimethylaniline as initiator, also after several purifications from chloroform-*n*-hexane, the sum of the analyzed MVP and styrene was in general not greater than 90% of the isolated product.

In conclusion, MIBKP was selected as initiator in view of its fair solubility in *n*-hexane, and the following purification method was adopted. The contents of the ampules were poured dropwise in *n*-hexane which contained a few crystals of hydroquinone, under strong stirring. The copolymers

were collected upon filtration, purified by dissolving them in chloroform, precipitating in *n*-hexane and filtering. This operation was repeated five times.

The copolymers were then dried at 50°C. under high vacuum for 24 hr. over phosphoric anhydride; under these conditions the water contents (Fisher method) amounted to a few tenths of one per cent.

The conversion was calculated from the weight of polymer obtained by a known amount of reaction mixture.

The bound MVP content was determined by potentiometric titration²²⁻²⁴ with perchloric acid (0.1*N* in dioxane) of the copolymer dissolved in acetic acid-acetonitrile (20/80). The errors of the results were estimated to be $\pm 1\%$.

In a few cases the above analysis was checked for the bound styrene content by spectrophotometric infrared technique as follows: copolymer solutions in carbon disulfide were prepared at a concentration of 0.5-2% according to the bound styrene content. They were examined in a Perkin-Elmer Model 21 spectrophotometer; the absorbancy at 688 cm.^{-1} was compared with that of a polystyrene solution of known concentration. The errors of the results may be estimated to be $\pm 2\%$ or lower.

MVP-Butadiene Copolymers

Cyclohexanone peroxide (CEP) was used as initiator at a level of 1% (based on the monomer mixture).

Initiator and MVP were introduced into a glass ampule, the neck of which was firmly fitted with a PVC tube extending a few millimeters over the end of the neck. The ampule was washed with nitrogen and subsequently its contents were solidified at -30°C .

Liquid butadiene in slight excess was then introduced into the ampule; part of it was subsequently allowed to evaporate, in order to help to deoxygenate the system. The ampule was then closed with a rubber stopcock which was firmly fixed in the PVC tube with the help of a needle which crossed both. The ampule was then weighed to determine exactly the amount of butadiene introduced and subsequently put in a water bath at $30 \pm 0.1^{\circ}\text{C}$. and rotated end over end.

Even in this case the length of time required to obtain a few per cent conversion decreased with increasing percentage of MVP in the charge. The contents of the ampule were then poured dropwise with stirring into *n*-hexane containing traces of hydroquinone. The copolymer was then collected, dissolved in chloroform, and precipitated in *n*-hexane to remove the unreacted monomers.

In order to free it from the peroxide it was then dissolved in 5% sulfuric acid; the solution was filtered and poured dropwise in an aqueous solution which contained sufficient KOH to maintain an alkaline pH value. The commercial CEP is actually a mixture of peroxides and hydroperoxides which can easily mutually transform.²⁵ It is known that, in the presence

of acids or bases, this equilibrium shifts toward the formation of hydrosoluble compounds.

After prolonged water washing, the copolymer was dissolved in 95% ethanol and precipitated with water (in order to eliminate the inorganic salt). Finally it was twice precipitated from chloroform/*n*-hexane. The MVP content was detected as in the former case, the copolymer being dissolved in chloroform-acetonitrile (1/1).

The concentration of the latter solution was determined by drying a known weight of it in a high purity aluminum vessel at 50°C. at first at normal pressure and then under vacuum.

Butadiene-Styrene Copolymers

CEP (1%) was used as initiator; the ampule and the charging operations were as detailed above for MVP-butadiene copolymers.

The reaction mixture was poured in methanol containing hydroquinone. The copolymer was then purified three times by pouring its chloroform solutions in methanol, where CEP is very soluble.

The product was then dried at 50°C. under vacuum, dissolved in carbon disulfide, and analyzed for bound styrene content via infrared spectroscopy, as described above.

Terpolymers in Bulk

Mixtures of styrene and MVP of different compositions were introduced into glass ampules, and 1% of CEP was then added. The procedure of charging butadiene, washing, and sealing was the same as described for MVP-butadiene copolymers.

The ampule was then kept in a water bath thermostatted at $30 \pm 0.1^\circ\text{C}$. and rotated end over end. After a sufficient length of time to get a few per cent conversion, the ampule was cooled at -20°C ., then opened and the terpolymer recovered and purified according to its composition as above detailed for the three types of copolymers.

The polymer was finally dried under vacuum over phosphoric anhydride at 50°C. for 24 hr. and the composition was then determined as above.

Terpolymers in Emulsion

The emulsion terpolymerizations were carried out according to the recipe indicated in Table II in beverage bottles.

An aqueous solution containing soap, glucose, and sodium pyrophosphate was prepared; to this, ferrous sulfate was added under stirring in very diluted aqueous solution in order to avoid precipitation (solution A).

Another solution, containing MVP, styrene, and *tert*-dodecyl mercaptan (solution B) was then prepared.

The required amount of solution A was charged in the bottle, which was over a balance and subsequently, solution B was charged; cumene hydroperoxide was then added, followed by slight excess of liquid butadiene.

TABLE II
Emulsion Terpolymerization Recipe

Component	Parts
Monomers	100.00
Potassium salt of disproportionated rosin	5.30
Sodium pyrophosphate decahydrate	0.95
Glucose	0.95
Ferrous sulfate heptahydrate	0.10
<i>tert</i> -Dodecyl mercaptan	0.50
Cumene hydroperoxide	0.17
Water	155.00

After evaporation of part of the butadiene, as soon as its weight corresponded to the desired amount, the bottle was rapidly closed with a crown cap. It was then introduced in a water bath at $30 \pm 1^\circ\text{C}$. and rotated end over end at 72 rpm.

After the required length of time the bottles were extracted from the bath, opened, and 2 ml. of about 3% sodium diethyldithiocarbamate aqueous solution were added.

The bottles were then shaken in order to remove most of the unreacted butadiene; the resulting latex was weighed and coagulated by pouring it in methanol; the terpolymer was three times purified by chloroform-methanol. Part of it was dissolved in chloroform-ethanol (10/1) in order to analyze the bound MVP, as described above. Another sample was dissolved in carbon disulfide and analyzed for bound styrene by infrared spectroscopy as described above.

The concentrations of the solutions were determined by drying part of them at 50°C . under vacuum, a known weight for the chloroform-ethanol solution and a known volume for the carbon disulfide solution. To determine the conversion, about 2 g. of the latex was introduced in a very pure aluminum vessel and a few drops of a dilute alcoholic solution of phenol red were added; the vessel was heated at 110°C . at normal pressure till dryness and for additional 20 min. under vacuum.

In this way the total solid content is obtained, from which the conversion is calculated if the weight of the latex after venting of the butadiene is known.

Repeated solids determinations showed reproducibility of about 0.1% absolute.

RESULTS AND DISCUSSION

In Table III data for styrene-MVP, MVP-butadiene and butadiene-styrene copolymers prepared at 30°C . in bulk in order to determine the monomer reactivity ratios, are given.

The conversion was generally kept below 3%, in a few cases below 4%. The data have been plotted according to Fineman and Ross²⁶ and Mayo and Lewis¹⁵ with almost identical results.

TABLE III
Determination of the Reactivity Ratios. Molar Ratio of the Two Monomers in the Feed (F) and in the Copolymer (f)

Styrene-butadiene		MVP-butadiene		Styrene-NVP	
F	f	F	f	F	f
0.685	0.519	0.742	0.478	0.269	0.306
1.33	1.05	1.41	0.817	1.60	1.45
1.36	1.01	1.42	0.825	2.87	2.41
1.97	1.56	1.79	1.03	3.70	3.09
		1.81	0.992		
		2.20	1.21		

In Figure 1 (F/f) ($f - 1$) is plotted against F^2/f , where F is the molar ratio of the two monomers in the feed, f is the same ratio in the copolymer. Least squares straight lines have been drawn. The numerical values of the monomer reactivity ratios are shown in Table IV; errors were calculated by regression analysis.

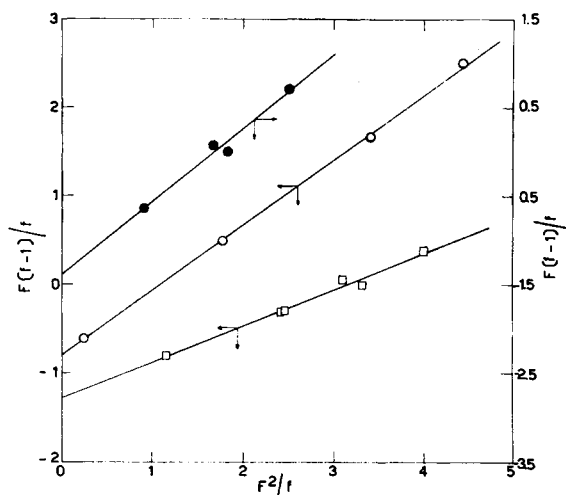


Fig. 1. Fineman-Ross plots for monomer reactivity ratios: (●) styrene-butadiene; (○) styrene-MVP; (□) MVP-butadiene.

The range of feed composition is not so wide in the case of styrene-butadiene and MVP-butadiene copolymers as for styrene-MVP copolymers, owing to the experimental difficulties met in obtaining polymers from

TABLE IV
Monomer Reactivity Ratios and Associated Standard Deviations for Butadiene (M_1), Styrene (M_2), and MVP (M_3)

$r_{12} = 1.39 \pm 0.15$	$r_{13} = 1.30 \pm 0.07$	$r_{23} = 0.738 \pm 0.010$
$r_{21} = 0.825 \pm 0.086$	$r_{31} = 0.412 \pm 0.026$	$r_{32} = 0.801 \pm 0.030$

butadiene-rich monomer feeds. However the extrapolation is satisfactory even in these cases, as can be seen from Figure 1.

Both r_{12} and r_{21} are almost identical to those determined at 60°C. by Lewis and co-workers²⁷ ($r_{12} = 1.39$, $r_{21} = 0.78$). This is not very surprising, in view of the slight sensitivity of the monomer reactivity ratios to changes in temperatures, especially when they are not very different from unity.²⁸

In the case of styrene-MVP, experiments have been carried out over a relatively broad feed composition range (F between 0.27 and 3.70). The values we obtained for our reactivity ratios are slightly lower than those obtained at 60°C. by Tamikado²⁴ ($r_{23} = 0.812$, $r_{32} = 0.91$) who also determined the bound MVP by perchloric acid titration.

In the MVP-butadiene case the value of r_{31} is different from the one determined at 70°C. by Tsailingol'd and co-workers²⁹ ($r_{31} = 0.72$, $r_{13} = 1.32$). A critical examination of the six reactivity ratios shows for binary copolymers an almost random distribution of the units in the polymer chain. An azeotropic composition exists only for the pair MVP-styrene for MVP molar fraction equal to 0.568.

We tried to determine if the three-component system had an azeotropic composition, by numerical calculation according to Walling and Briggs.¹⁶ However, within the limit of the experimental errors in the determination of the reactivity ratios it was found that the sign of the determinants \bar{D} , \bar{D}_a , \bar{D}_b , and \bar{D}_c cannot be unambiguously determined, thus preventing correct calculations.

We checked the correctness of the monomer reactivity ratios determined by us by synthesizing a few bulk terpolymers at low conversions; this was done as we could not, in principle, consider a possible coincidence between calculated composition and experimental results of emulsion terpolymerizations as a definite conclusion. There are in fact important differences in the latter case from the assumptions involved in the integration of the eqs. (1) i.e., (1) one of the three comonomers, MVP, is partially soluble in water (about 1% at 30°C.); (2) the condition of the constancy of the volume (see above) is not *a priori* fulfilled in an emulsion polymerization carried out at high conversions. This owing to the facts that the picture of an emulsion polymerization is not the one of a polymerization performed under conditions of constant volume³⁰⁻³² and also that, in general, the density of the polymer formed is different (greater) from the density of the monomer mixture.

The results of the bulk terpolymerizations are reported in Table V. We give in column 7 the solvent-nonsolvent purification pair and in column 8 the titration solvent.

The agreement between found and calculated data is satisfactory. It can be seen that in our experiments monomer feeds with high butadiene content were not considered. This was due to the fact that starting from such monomer feeds only extremely small amounts of polymer were obtained in reasonable short time. These quantities were not sufficient for the analytical determinations.

TABLE V
 Bulk Terpolymerizations^a

No.	Monomer	Feed composition		Polymer composition		Purification pair	Titration solvent
		Wt.-%	Mole-%	Calcd.			
				for zero conversion, wt.-%	Found, wt.-%		
1	MVP	14.90	12.64	17.50	16.8	Chloroform-ethanol (10/1)	Chloroform-ethanol (10/1)
	Styrene	79.84	77.53	75.80	75		
2	MVP	14.72	12.49	17.31	16.9	Chloroform-methanol ^b	Chloroform-ethanol (10/1)
	Styrene	79.99	77.64	75.96	77		
3	MVP	79.50	74.03	75.46	74.8	Chloroform-acetonitrile (1/1)	Chloroform-ethanol (10/1)
	Styrene	15.18	16.18	15.79	9		
4	MVP	23.81	19.74	26.03	25.6	Chloroform-methanol	Chloroform-ethanol (10/1)
	Styrene	67.09	63.64	62.04	62		
5	MVP	26.73	21.08	27.79	26.1	Benzene-methanol	Chloroform-ethanol (10/1)
	Styrene	57.96	52.31	52.51	52		
6	MVP	59.64	46.92	53.64	52.1	Methyl ethyl ketone- <i>n</i> -hexane	Chloroform-acetonitrile (1/1)
	Styrene	20.25	18.22	18.08	15.5		

^a Conversions lower than 4%.^b Purification as for MVP-butadiene copolymers.^c Polymer not soluble in carbon disulfide.

TABLE VI
Monomer Feeds for Emulsion Terpolymerizations

Charge	Monomer	Wt.-%
Charge A	Butadiene	70.2
	Styrene	14.9
	MVP	14.9
Charge B	Butadiene	24.8
	Styrene	47.9
	MVP	27.3
Charge C	Butadiene	38.3
	Styrene	49.2
	MVP	12.5

However the monomer reactivity ratios can be considered as satisfactorily confirmed taking into account the emulsion polymerizations of feeds A and C, butadiene-rich, MVP-poor, stopped at relatively low conversions. Monomer feeds having the composition shown in Table VI were used for the emulsion polymerizations. The relatively low MVP content was selected for the fact that the practical interest of these terpolymers is mainly directed toward low vinylpyridine percentages.

With our polymerization recipe (Table II) we obtained satisfactorily high reaction rates and very stable latexes even at relatively low conversions, i.e., in the presence of large amounts of unreacted monomers. Moreover the terpolymers prepared in this way show absence of microgel up to high conversions. It is well known that the presence of microgel can be detected in SB-R copolymers by observing the plot of Vistex³³ intrinsic viscosity versus conversion.^{34,35} In our case it was observed³⁶ that the curve was always rising at least up to about 90% conversion for charge A,

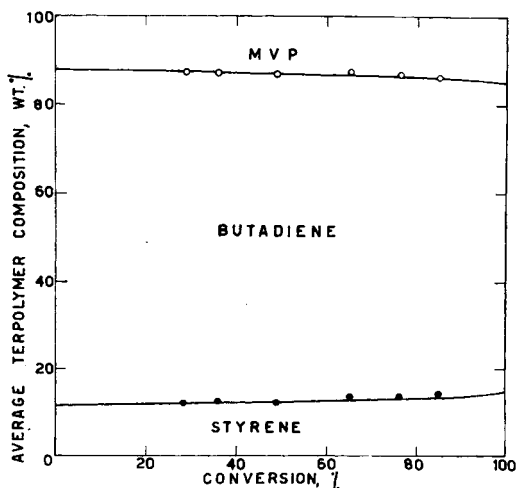


Fig. 2. Average terpolymer composition as a function of overall conversion with monomer charge A: (O, ●) experimental points; (—) calculated from eqs. (1).

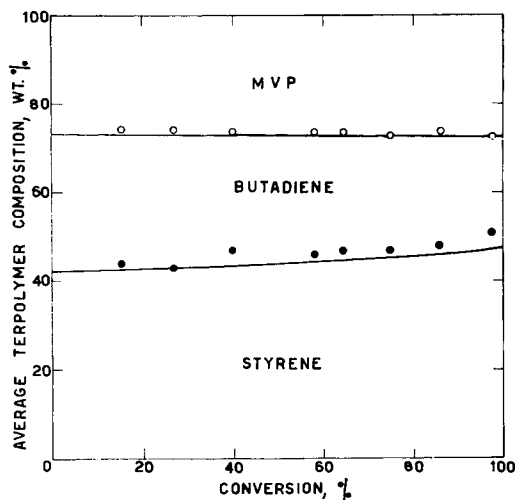


Fig. 3. Average terpolymer composition as a function of overall conversion with monomer charge B: (O, ●) experimental points; (—) calculated from eqs. (1).

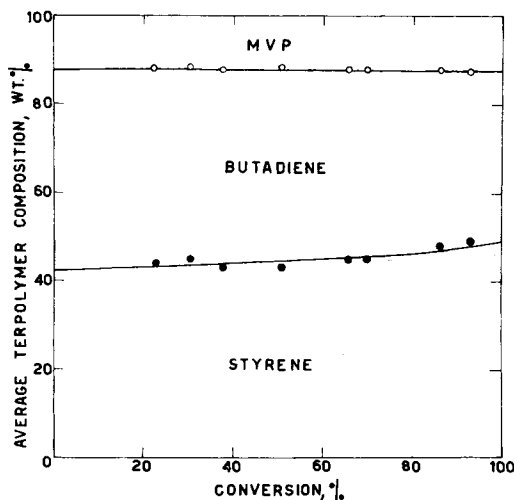


Fig. 4. Average terpolymer composition as a function of overall conversion with monomer charge C: (O, ●) experimental points; (—) calculated from eqs. (1).

the Vistex viscosity being taken in 80/20 benzene-isopropanol at 25°C. Hence we could easily dissolve even the terpolymers prepared at very high conversions.

In Table VII and Figures 2-4 the average composition of the terpolymers at various conversions are shown. Within the limits of the experimental error, the agreement between calculated and experimental curves is satisfactory. The MVP values show tendency to be low in the case of charge B for relatively low conversions. This can be possibly explained

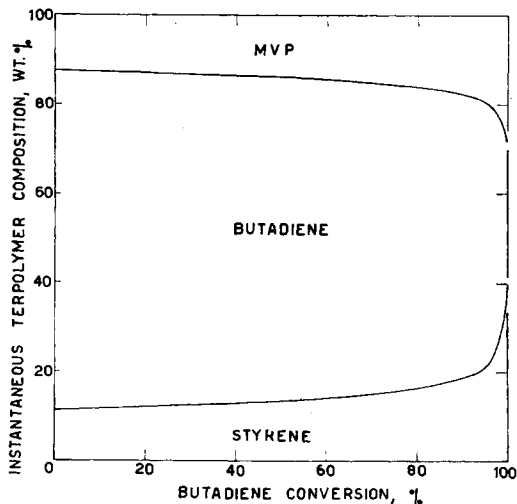


Fig. 5. Calculated instantaneous terpolymer composition as a function of butadiene conversion with monomer charge A.

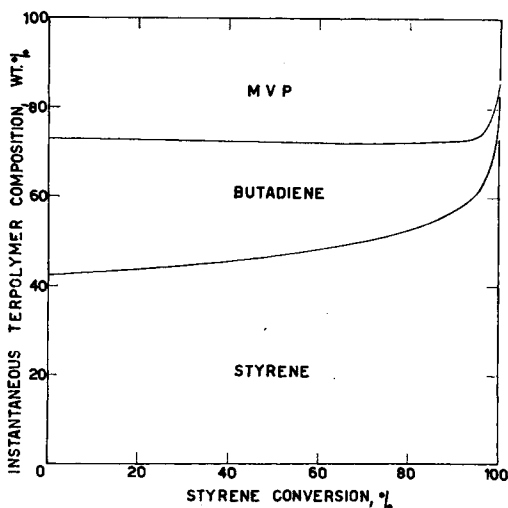


Fig. 6. Calculated instantaneous terpolymer composition as a function of styrene conversion with monomer charge B.

by the relatively high water solubility of MVP, which is in this case present in considerable amount in the monomer feed. With the aid of the differential curves (Figs. 5-7) the heterogeneity of the terpolymers formed at every stage of conversion can be easily obtained.

If uniformity of polymer composition is desired the reaction must, of course, be stopped at the conversion where the curves sensibly begin to deviate from horizontality; alternatively proper amounts of more reactive monomers must be continuously added.

TABLE VII
Emulsion Terpolymerization

Overall conversion, %	Charge A			Charge B			Charge C		
	Bound styrene, wt.-%	Bound MVP, wt.-%	Overall conversion, %	Bound styrene, wt.-%	Bound MVP, wt.-%	Overall conversion, %	Bound styrene, wt.-%	Bound MVP, wt.-%	Overall conversion, %
28.3	12.1	12.6	15.2	44	25.7	22.2	44	12.0	22.2
36.0	12.6	12.9	26.6	43	25.9	30.2	45	11.8	30.2
49.0	12.3	13.0	39.7	47	26.3	37.4	43	12.5	37.4
65.3	13.6	12.6	57.9	46	26.3	50.6	43	11.9	50.6
76.3	13.6	13.2	64.4	47	26.3	65.6	45	12.3	65.6
85.0	14.4	13.7	74.9	47	27.1	69.7	45	12.4	69.7
			85.8	48	26.0	86.1	48	12.4	86.1
			97.5	51	27.2	92.8	49	12.5	92.8

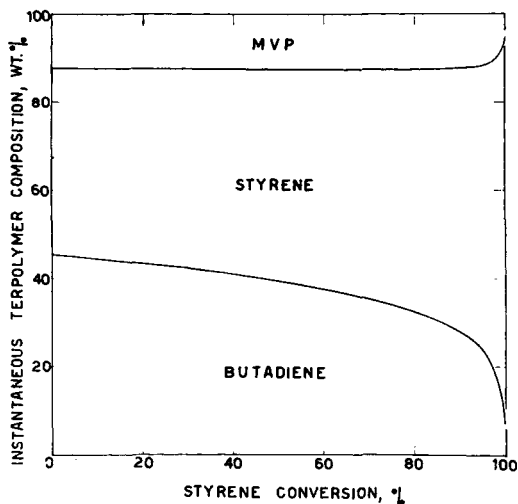


Fig. 7. Calculated instantaneous terpolymer composition as a function of styrene conversion with monomer charge C.

The good agreement between experimental results of emulsion polymerization and calculated data, although not predictable on theoretical basis, suggests the possibility of satisfactory predictions of the composition of these emulsion terpolymers, even for monomer feeds which are different from the ones studied by us.

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Résumé

Les terpolymères de 1,3-butadiène, styrène et vinylpyridine sont importants comme caoutchoucs synthétiques et, sous la forme de latex, comme composants de certains adhésifs caoutchouc-textiles. Nous avons polymérisé en émulsion à 30°C trois mélanges de monomères, dont la composition approximative en poids était: butadiène/styrène/2-méthyl-5-vinylpyridine 70/15/15, 25/48/27 et 38.5/49/12.5. La composition des terpolymères résultants a été étudiée en fonction du degré de conversion. Les six rapports de réactivité des monomères ont été déterminés au moyen de copolymérisations à 30°C des systèmes à deux composants et essayés par des expériences de terpolymérisation arrêtées à faible degré de conversion. Les courbes qui montrent la variation de composition instantanée et moyenne avec le degré de conversion ont été calculées, en admettant que la volume de réaction soit constant, en intégrant numériquement les équations de la terpolymérisation avec l'aide d'une machine à calculer électronique. La procédure d'intégration est décrite en détail. Les résultats expérimentaux des terpolymérisations en émulsion s'accordent d'une manière satisfaisante avec les courbes calculées dans un vaste domaine de degrés de conversion.

Zusammenfassung

Terpolymere aus 1,3-Butadien, Styrol und Vinylpyridin sind als Kautschuk wichtig, und, als Latex, werden für Kautschuk Gewebe-Klebstoffkomponenten benutzt. Es wurde die Emulsionspoly Emulsionspolymerisationen von drei Monomerenmischungen bei 30°C durchgeführt: Butadien/Styrol/2-Methyl-5-vinylpyridin mit einem Gewicht-prozentverhältnis von 70/15/15, 25/48/27, und 38,5/49/12,5. Die Zusammensetzung der Terpolymeren wurde als Funktion der Umsatzes untersucht. Die sechs möglichen Monomerreaktivitätsverhältnisse wurde bei 30°C. mittels Copolymerisationen der drei

binaren Systeme bestimmt und durch Blockterpolymerisation bei niedrigen überprüft. Kurven für die integrale und differentielle Zusammensetzung gegen dem Umsatz wurden unter der Annahme eines konstanten Reaktionsvolumens durch numerische Integration der Gleichungen der Terpolymerisation mit Hilfe einer elektronische Rechenmaschine berechnet. Hinweise auf die allgemeine Anwendung Berechnung werden gegeben. Die experimentellen Ergebnisse der Emulsionspolymerisation stimmen mit den berechneten Kurven in einem breiten Umsatzbereich gut überein.

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